Chapter 2
Physical Properties and Physical Chemistry of Polymers

2.1 Structure and Property Relationship in Organic Polymers

For a very large proportion of polymeric materials in commercial use, mechanical properties are of paramount importance, because they are used as structural materials, fibers, or coatings and these properties determine their usefulness. Properties that also determine their utilization are compressive, tensile, and flexural strength, and impact resistance. Hardness, tear, and abrasion resistance are also of concern. In addition, polymers may be shaped by extrusion in molten state into molds or by deposition from solutions on various surfaces. This makes the flow behaviors in the molten state or in solution, the melting temperatures, the amount of crystallization, as well as solubility parameters important.

The physical properties of polymer molecules are influenced not only by their composition, but also by their size and by the nature of their primary and secondary bond forces. They are also affected by the amount of symmetry, by the uniformity in their molecular structures, and by the arrangements of the macromolecules into amorphous or crystalline domains. This, in turn affects melting or softening temperatures, solubilities, melt and solution viscosities, and other physical properties [1].

Due to the large sizes of polymeric molecules, the secondary bond forces assume much greater roles in influencing physical properties than they do in small organic molecules. These secondary bond forces are van der Waal forces and hydrogen bonding. The van der Waal forces can be subdivided into three types: dipole–dipole interactions, induced dipoles, and time varying dipoles.

2.1.1 *Effects of Dipole Interactions*

Dipole interactions result from molecules carrying equal and opposite electrical charges. The amounts of these interactions depend upon the abilities of the dipoles to align with one another. Molecular orientations are subject to thermal agitation that tends to interfere with electrical fields. As a result, dipole forces are strongly temperature dependent. An example of dipole interaction is an illustration of two segments of the molecular chains of a linear polyester. Each carbonyl group in the ester linkages sets up a weak field through polarization. The field, though weak, interacts with another field of the same type on another chain. This results in the formation of forces of cohesion. Because polymeric molecules are large, there are many such fields in polyesters. While each field is weak, the net effect is strong cohesion between chains. The interactions are illustrated in Fig. 2.1.

A. Ravve, *Principles of Polymer Chemistry*, DOI 10.1007/978-1-4614-2212-9_2,

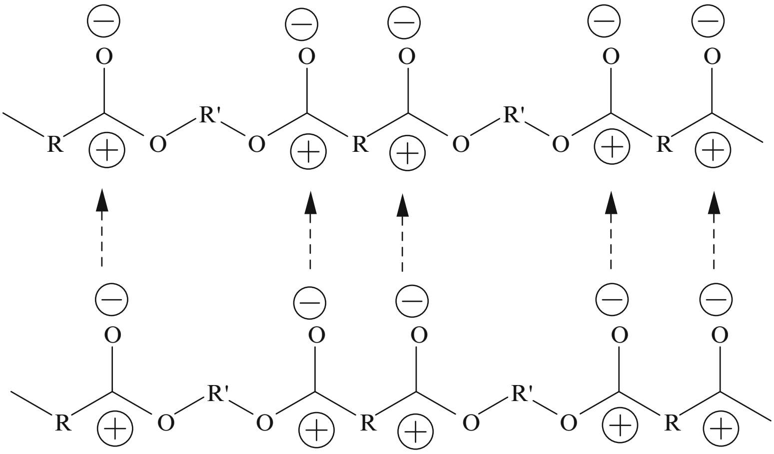


Fig. 2.1 Intramolecular forces

2.1.2 Induction Forces in Polymers

Electrostatic forces also result from slight displacement of electrons and nuclei in covalent molecules from proximity to electrostatic fields associated with the dipoles from other molecules. These are ***induced dipoles***. The displacements cause interactions between the ***induced dipoles*** and the ***permanent dipoles*** creating forces of attraction. The energy of the induction forces, however, is small and not temperature-dependent.

There are additional attraction forces that result from different instantaneous configurations of the electrons and nuclei about the bonds of the polymeric chains. These are time varying dipoles that average out to zero. They are polarizations arising from molecular motions. The total bond energy of all the secondary bond forces combined, including hydrogen bonding, ranges between 2 and 10 kcal/mole. Of these, however, hydrogen bonding takes up the greatest share of the bond strength. In Table 2.1 are listed the intramolecular forces of some linear polymers [2, 3].

As can be seen in Table 2.1., polyethylene possesses much less cohesive energy than does a polyamide. This difference is primarily due to hydrogen bonding. A good illustration is a comparison of molecules of a polyamide, like nylon 11, with linear polyethylene. Both have similar chemical structures, but the difference is that nylon 11 has in its structure periodic amide linkages after every tenth carbon, while such linkages are absent in polyethylene. The amide linkages participate in hydrogen bonding with neighboring chains. This is illustrated in Fig. 2.2.

Due to this hydrogen bonding, nylon 11 melts at 184–187°C and is soluble only in very strong solvents. Linear polyethylene, on the other hand, melts at 130–134°C and is soluble in hot aromatic solvents.

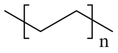
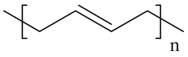
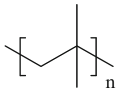
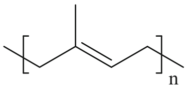
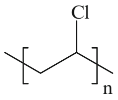
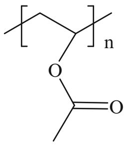
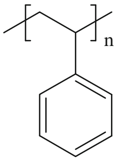
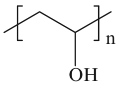
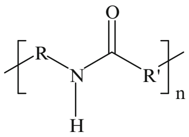
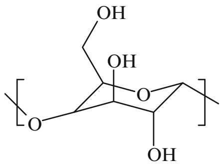
The energy of dipole interactions, (ϵ_k) can be calculated from the equation [1]:

$$\epsilon_k = -(2\mu^4/3RT)r^{-6}$$

where, μ represents the dipole moment of the polarized section of the molecule, r is the distance between the dipoles, T is the temperature in Kelvin, and R is the ideal gas constant.

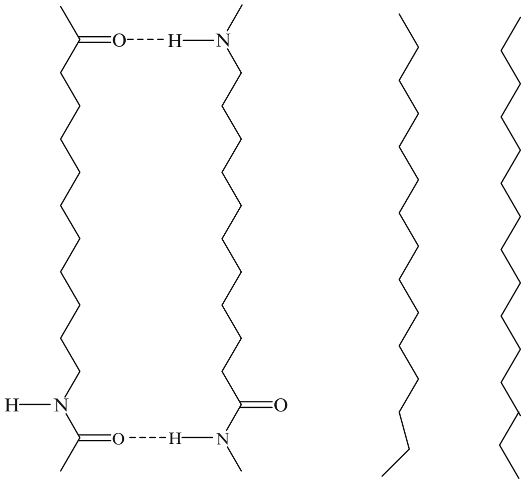
Intermolecular forces affect the rigidity of all polymers. Should these forces be weak, because the cohesive energy is low (1–2 kcal/mole), the polymeric chains tend to be flexible. Such chains respond readily to applied stresses and can exhibit typical properties of elastomers. High cohesive energy, on the other hand, (5 kcal/mole or higher) causes the materials to be strong and tough. These polymers exhibit resistance to applied stresses and usually possess good mechanical properties. The temperatures and the flexibility of polymeric molecules govern both the sizes of molecular segments,

Table 2.1 Molecular cohesion of some linear polymers[a]

Polymer	Cohesion/5 Å chain length	Polymer structure
Polyethylene	1.0	
Polybutadiene	1.1	
Polyisobutylene	1.2	
Polyisoprene (*cis*)	1.3	
Poly(vinyl chloride)	2.6	
Poly(vinyl acetate)	3.2	
Polystyrene	4.0	
Poly(vinyl alcohol)	4.2	
Polyamides	5.8	
Cellulose	6.2	

[a] From refs [2, 3], and other literature sources

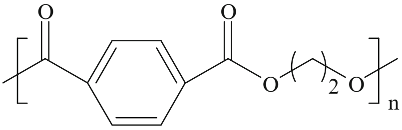
the motion, and the frequency at which that occurs. This in turn determines the rate at which the polymer molecules respond to molecular stresses. In flexible polymers, if the thermal energy is sufficiently high, large segments can disengage and slip past each other quite readily in response to applied stress. All elastomers possess such properties. Properties of polymers depend also upon ***morphology*** or upon the arrangement of their polymeric chains. This arrangement can be amorphous or crystalline. The term ***amorphous*** designates a lack of orderly arrangement. Crystalline



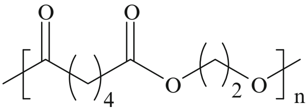
nylon 11 polyethylene

Fig. 2.2 Hydrogen bonding in (**a**) nylon 11, and absent in (**b**) polyethylene

morphology, on the other hand, means that the chains are aligned in some orderly fashion. Generally, the freedom of molecular motion along the backbones of polymeric chains contributes to lowering the melting temperature. Substituents that interfere with this motion tend to raise the melting point. For instance, isotactic polypropylene melts at a higher temperature than does linear polyethylene. If the substituent is bulky or rigid it raises the melting point because it interferes with molecular motion. Dipole interactions, as discussed above, have a similar effect [4]. A good illustration is a comparison of poly(ethylene terephthalate) that melts at 265°C with poly(ethylene adipate) that melts at only 50°C. In the first polyester, there is a rigid benzene ring between the ester groups while in the second one there is only a flexible chain of four carbons.



poly(ethylene terephthalate)

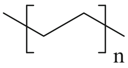


poly(ethylene adipate)

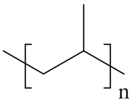
This flexibility of the four carbon segment in poly(ethylene adipate) contributes significantly to the lowering of the melting point.

Linear polymers that possess only single bonds between atoms in their backbones, C–C, or C–O, or C–N, can undergo rapid conformational changes [5]. Also ether, imine, or *cis*-double bonds reduce energy barriers and, as a result, "soften" the chains, causing the polymer to become more rubbery and more soluble in various solvents.

The opposite is true of cyclic structures in the backbones, as was shown in poly(ethylene terephthalate). Actually, cyclic structures not only inhibit conformational changes but can also make crystallization more difficult. Among the polymers of α-olefins the structures of the pendant groups can influence the melting point [6]. All linear polyethylene melts between 132 and 136°C [7]. Isotactic polypropylene, on the other hand melts at 168°C [8].



m.p. = 132-136 °C



m.p. = 168 °C

As the length of the side chain increase, however, melting points decrease and are accompanied by increases in flexibility [7] until the length of the side chains reached six carbons. At that point, the minimum takes an upturn and there is an increase in the melting points and decrease in flexibility. This phenomenon is believed to be due to crystallization of the side-chains [9].

Alkyl substituents on the polymers of α-olefins that are on the α-carbon yield polymers with the highest melting points. Isomers substituted on the β-carbon, however, if symmetrical, yield polymers with lower melting points. Unsymmetrical substitutions on the β-carbon, on the other hand, tend to lower the melting points further. Additional drop in the melting points result from substitutions on the γ-carbon or further out on the side-chains. Terminal branching yields rubbery polymers [10].

Copolymers melt at lower temperatures than do homopolymers of the individual monomers. By increasing the amount of a comonomer the melting point decreases down to a minimum (this could perhaps be compared to a eutectic) and then rises again.

The tightest internal arrangement of macromolecules is achieved by crystallinity. As a result, the density of a polymer is directly proportional to the degree of crystallinity, which leads to high tensile strength, and to stiff and hard materials that are poorly soluble in common solvents [11]. The solubility of any polymer, however, is not a function of crystallinity alone, but also of the internal structure and of the molecular weight. The solubility generally decreases with increases in the molecular weight. The fact that crystalline polymers are less soluble than amorphous ones can be attributed to the binding forces of the crystals. These binding forces must be overcome to achieve dissolution. Once in solution, however, crystalline polymers do not exhibit different properties from the amorphous ones. One should also keep in mind the fact that crosslinked polymers will not melt and will not dissolve in any solvent. This is due to the fact that the crosslinks prevent the chains from separating and slipping past each other.

2.2 The Amorphous State

A number of macromolecules show little tendency to crystallize or align the chains in some form of an order and remain disordered in solid form. This, of course, is also the condition of all molten polymers. Some of them, however, due to structural arrangement, remain completely amorphous upon cooling. The crystalline polymers, which crystallized from the melt, on the other hand, while containing areas of crystallinity, also contain some amorphous material. All crystalline polymers are also amorphous above their melting temperature. When sufficiently cooled, amorphous polymers can resemble glass. Above this glassy state, long-range segmented motions are possible and the molecular chains are free to move past each other. On the other hand, in the rigid, glass like state, only short-range vibrational and rotational motions of the segments are possible. At temperatures above the glassy state, amorphous polymers resemble rubbers, if crosslinked. If not crosslinked, amorphous polymers resemble very viscous liquids in their properties and there is molecular disorder. Tobolsky suggested [12] that polymer molecules in an amorphous state might be compared to a bowl of very long strands of cooked spaghetti. When molten, such molecules are in a state of wriggling motion, though the amplitude and speed depend very much on the temperature [13]. The important thing is to know that the chains possess random conformations. These conformations were characterized with the aid of statistical analysis [14].

2.2.1 The Glass Transition and the Glassy State

When the polymer cools and the temperature lowers, the mobility in the amorphous regions of the polymer decreases. The lower the temperature, the stiffer the polymer becomes until a point of transition is reached. This transition is called ***glass transition*** or ***second-order transition*** [15]. The temperature at that transition is called the ***glass transition temperature***, designated by T_g. Beyond stiffness, a change is manifested in specific volume, heat content, thermal conductivity, refractive index, and dielectric loss.

Bueche illustrated glass transition as follows [16]. In measuring the force necessary to force a needle into a polymer, like polystyrene, at various temperatures, there is a relationship between the force required to insert the needle and the temperature [16]. As the temperature is being lowered, maximum resistance to penetration is reached at T_g.

As stated, above T_g chains undergo cooperative localized motion. It is actually estimated that above T_g segmental motion of anywhere between 20 and 50 chain atoms is possible. Below the second-order transition temperature, however, there is insufficient energy available to enable whole segments of the polymeric chains to move. The structure is now stiff and brittle and resists deformation. When, however, sufficient amount of heat energy enters the material again and the temperature rises above T_g larger molecule motion involving coordinated movement returns. This requires more space, so the specific volume also increases and the polymer is in a rubbery or a plastic state. Above T_g, because large elastic deformations are possible, the polymer is actually both tougher and more pliable. Chemical structures of the polymers are the most important factors that affect the glass transition temperatures. Molecular weights also influence T_g, as it increases with the molecular weight. In addition, T_g also varies with the rate of cooling. Table 2.2. shows the structures of and lists relative T_g values of some common polymers.

One way to obtain T_g is by studying thermal expansion of polymers. It is generally observed that the thermal coefficient of expansion is greater above the glass transition temperature than below it, though the magnitude of the change differs from one polymer to another. By plotting volume vs. temperature for a polymer, one can obtain T_g as shown in Fig. 2.3, which illustrates obtaining T_g from specific volume-cooling temperature curves [17].

Polymers with bulky, tightly held side groups or stiff bulky components in the backbone have high T_g values. This is due to the fact that such side groups or bulky components interfere with segmental motion. Such polymers require higher temperatures to acquire sufficient free volume for segmental motion. This can be observed in Table 2.2. which shows that the glass temperature of polystyrene with stiff benzene ring side groups is much higher than that of polyethylene.

Also polymers with high attractive forces between chains will require more heat energy to go from a glassy to a rubbery or a plastic state. On the other hand, polymeric chains with loose hanging side chains that tend to loosen the polymer structure and increase the free volume for segmental movement will have lower T_g. For instance, the glass transition temperature of poly(methyl methacrylate) is higher than that of poly(*n*-butyl methacrylate) as can be seen from Table 2.2.

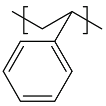
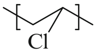
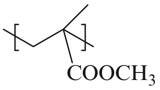
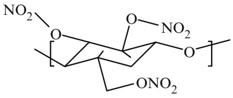
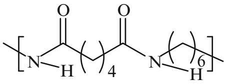
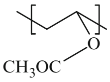
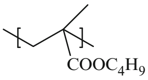
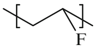
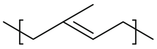
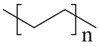
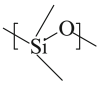
The transition to the glassy state from an equilibrium liquid results in changes in enthalpy, H, and volume, V. The specific heat is related to the enthalpy by definition:

$$C_p = (\partial H/\partial T)_p$$

The glassy state is nonequilibrium in nature and exhibits a tendency to undergo structural relaxation toward equilibrium. This tendency of the glassy state to relax structurally toward equilibrium is often referred to as ***structural recovery***. It was observed, however, that the progress towards structural recovery with time varies significantly between a down-quench and an up-quench. This is referred to as **asymmetry of structural recovery**. The nonlinearity of the process is described by the following equation [16]:

$$\mathrm{d}(\upsilon - \upsilon_0)/\mathrm{d}t = -(\upsilon - \upsilon_0)/\tau$$

Table 2.2 Glass transition temperatures, T_g, of some common polymers[a]

Repeat unit	Polymer	T_g (°C)
	Polystyrene	81; 90
	Poly(vinyl chloride)	75
	Poly(methyl methacrylate)	57–68
	Cellulose nitrate	53
	Nylon 6,6	47
	Poly(vinyl acetate)	30
	Poly(butyl methacrylate)	22
	Poly(ethyl acrylate)	−22
	Poly(vinyl fluoride)	−39
	Poly(butyl acrylate)	−56
	Polyisoprene	−70
	Polyethylene	−80; −90
	Silicone rubber	−123

[a] From ref [15] and other sources in the literature

where, τ is the relaxation time and υ is the specific volume. The value of T_g is also affected by other parameters, such as molecular weight, diluent concentration, tacticity, external pressure, crosslinking, chain stiffness, and mechanical deformation. For linear polymer, the ***Fox–Flory equation*** [18] described the relationship between T_g and the molecular weight:

$$T_g(M) = T_g(\infty) - K/\overline{M}$$

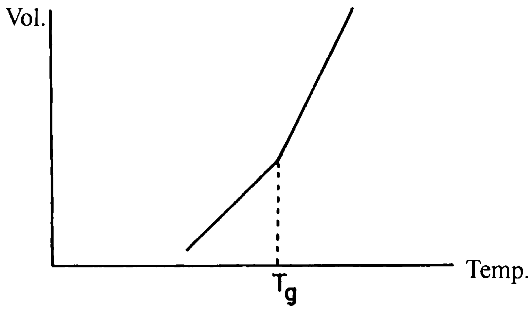


Fig. 2.3 The relationship of the specific volume of a polymer to the temperature

This equation, however, is limited in scope. It is actually neither valid for very high molecular weight polymers nor is it applicable to low molecular weight polymers.

The transition in a polymer from a molten state to a glassy one actually occurs over a temperature range. This range also includes T_g. At the glass transition temperature, however, the change in viscosity is rapid, from very viscous to a glassy one. Polymeric materials that undergo rearrangements in response to outside stimulus, like light, are becoming increasingly important in various industrial application (see Chap. 10). Urban and coworkers [19] studied stimuli-responsive (T_{SR}) transitions and correlated them to the glass transition temperatures (T_g). Based on their empirical data obtained from a copolymer, they concluded that the relationship between T_g and T_{SR} is

$$\log(V_1/V_2) = (P_1(T_{SR} - T_g))/(P_2(T_{SR} - T_g))$$

where the V_1 and V_2 are the copolymer's total volumes below and above the T_{SR}, respectively, T_g is the glass transition temperature of the copolymer, and P_1 and P_2 are the fraction of the free volume (f_{free}) at T_g (P_1) and $(T_{g,\ \mathrm{midpoint}} - T_{SR})_{50/50}$ for each random copolymer (P_2), respectively. They feel that this relationship can be utilized to predict the total volume changes as a function of $T_{SR} - T_g$ for different copolymer compositions.

2.2.2 *Elasticity*

The phenomenon of elasticity of rubber and other elastomers is a result of a tendency of large and very flexible amorphous polymeric chains to form random, thermodynamically favorable, conformations [18]. If a certain amount of crosslinking is also present, then these random conformations occur between the crosslinks. In a vulcanized (crosslinked) rubber elastomer, the crosslinks may occur at every five hundred to a thousand carbon atoms. The distance between the ends in such polymers is much shorter than when these elastomers are fully stretched. Deformation or stretching of rubber straightens out the various conformations in the molecules. They tend to return to the original state, however, when the forces of deformation are removed. So each segment behaves in a manner that resembles a spring. Some elastomeric materials are capable of high elongation and yet still capable of returning to the original conformation. Some soft rubbers, for instance, can be extended as high as 800% and even higher with full recovery. There is a preference for *trans* conformation, a planar zigzag at high extension. Rigidity of the chains, however, or crystallinity would hinder extension and, particularly, the recovery. High viscosity and a glassy state would do the same.

The high degree of elasticity of rubbers is due in part to the effects of thermal motions upon the long polymeric chains. These motions tend to restrict vibrational and rotational motions about the single bonds in the main chain. Such restrictive forces in the lateral direction, however, are much weaker than are the primary valence forces in the longitudinal direction. Greater amplitudes of motion also take place perpendicular to the chains rather than in the direction of the chains. These increased motions in the perpendicular direction result in repulsive forces between extended or parallel chains. Such forces cause them to draw together after stretching. So, the stretched rubber molecules retract due to longitudinal tension until the irregular arrangement of molecules is achieved again. This more random conformation is actually a higher entropy state.

When unstretched rubber is heated it increases in dimension with an increase in the temperature, as one might expect. At higher temperatures, however, rubbers, upon elongation, have a higher tendency to contract. This can be written as follows:

$$\text{retractive force, } f = -T(\partial \mathrm{S}/\partial L)_{\mathrm{Tv}}$$

$$(\partial f/\partial T)_{\mathrm{adiabatic}} = -(\partial L/\partial T)T/C_{\mathrm{p}}$$

In summary, polymeric materials exhibit rubber elasticity if they satisfy three requirements: (a) the polymer must be composed of long-chain molecules, (b) the secondary bond forces between molecules must be weak, and (c) there must be some occasional interlocking of the molecules along the chain lengths to form three-dimensional networks. Should the interlocking arrangements be absent, then elastomers lack memory, or have a fading memory and are not capable of completely reversible elastic deformations.

2.2.2.1 Thermodynamics of Elasticity

Stretching an elastomer reduces its entropy and changes its free energy. The retractive force in an elastomer is primarily the result of its tendency to increase the entropy towards the maximum value it had in the original deformed state Current explanations of rubber-like elasticity are based on several assumption [20]. The first one is that rubber-like elasticity is entirely intramolecular in origin. The second one is that the free energy of the network is separable into two parts, an elastic one and a liquid one. The liquid one is presumably not dependent on deformation. When an elastomer is stretched, the free energy is changed, because it is subjected to work. If we consider the stretching in one direction only, the work done W_{el} is equal to $f\partial l$, where f is the retractive force and ∂l is the change in length. The retractive force is then [19–21].

$$f = (\partial F/\partial L)_{\mathrm{T,p}} = (\partial H/\partial L)_{\mathrm{T,p}} - T(\partial S/\partial L)_{\mathrm{T,p}}$$

where F is the free energy, H is the enthalpy, and S is the entropy of the system. An ideal elastomer can be defined as one where $(\partial H/\partial L)_{\mathrm{T,p}} = 0$ and $f = -T(\partial S/\partial L)_{\mathrm{T,p}}$. The negative sign is due to the fact that work has to be done to stretch and increase the length of the elastomer. This description of an ideal elastomer is based, therefore, on the understanding that its retractive force is due to a decrease in entropy upon extension. In other words, the ***entropy of elasticity*** is the distortion of the polymer chains from their most probable random conformations in the unstretched condition. The probability that one chain end in a unit volume of space coordinates, x, y, z is at a distance r from the other end is [21, 22]:

$$W(x,y,z) = (b/\pi^{0.5})^3 e^{-b^2r^2}$$

where $b^2 = 3/2xL^2$. The number of links is x and the length is L. The entropy of the system is proportional to the logarithm of the number of configurations. Billmeyer expresses it as follows [7]:

$$S = (\text{constant}) - kb^2r^2$$

where k is the Boltzmann's constant. The retractive force for a single polymer chain, f' stretched to a length dr at a temperature T is, therefore,

$$f' = -T(\mathrm{d}S/\mathrm{d}r) = 2kTb^2r$$

It is generally assumed that the total retractive force of a given sample of an elastomer is the sum of all the f' forces for all the polymeric chains that it consists of. This is claimed to be justified in most cases, though inaccurate in detail [22].

Tobolsky wrote the equation for the entropy change of an unstretched to a stretched elastomer as depending upon the number of configurations in the two states [12]:

$$S - S_\mathrm{u} = k \ln \Omega/\Omega_\mathrm{u}$$

where Ω and Ω_u represent the number of configurations. The evaluation of these configurations by numerous methods allows one to write the equations for the change in entropy as:

$$S - S_\mathrm{u} = -\frac{1}{2}N_0k\left[(L/L_\mathrm{u})^2 + 2L/L_\mathrm{u} - 3\right]$$

where N_0 and L and L_u are the relative lengths of the unstretched and stretched elastomer. Tobolsky derived the tensile strength as being [12]:

$$X = (N_0kT/L_\mathrm{u})\left[(L/L_\mathrm{u}) - (L/L_\mathrm{u})^2\right]$$

By dividing both sides of the equation by the cross-sectional area of the sample, one can obtain the stress–strain curve for an ideal rubber.

The retractive force of an elastomer, as explained above, increases with the temperature. In other words, the temperature of elastomers increases with adiabatic stretching [21, 22]. The equation for the relationship was written by Kelvin back in 1857 [22]:

$$(\partial f/\partial T)_{\mathrm{p,l}} = (C_\mathrm{p}/T)(\partial T/\partial L)_{\mathrm{p,adiabatic}}$$

where C_p is specific heat and ∂l again is the change in length of the elastomer. Experimental evidence supports this, as the temperature of elastomers, like rubber, rises upon stretching. This equation can also be written in another form:

$$(\partial T/\partial f')_{\mathrm{p,adiabatic}} = T/C_\mathrm{p}(\partial l/\partial T)_{\mathrm{p},f'}$$

In actual dealing with polymers, stretching rubber and other elastomers requires overcoming the energy barriers of the polymeric chains with the internal energy of the material depending slightly on elongation, because

$$(\partial H/\partial L)_{\mathrm{T,p}} = (\partial E/\partial l)_{\mathrm{T,p}} + p(\partial V/\partial L)_{\mathrm{T,p}}$$

∂V is the change in volume. At normal pressures the second term on the right becomes negligible. It represents deviation from ideality. The contribution of the internal energy E to the force of retraction is

$$f = (\partial E/\partial L)_{\mathrm{T,p}} - T(\partial S/\partial L)_\mathrm{T}$$

Bueche [16] expressed differently the work done on stretching an elastic polymeric body. It describes deforming an elastomer of x length, stretched to an increase in length α in a polymeric chain composed of N freely oriented segments. The other dimensions of this polymeric chain are y and z. These are coordinates that become reduced as a result of stretching to $1/(\alpha)^{0.5}$.

$$\text{Work done per chain} = (3kT/2N\alpha^2)[(\alpha^2 - \alpha^{-1})x_0{}^2 + (\alpha^{-1} - 1)r_0{}^2]$$

where the chain ends are initially r_0 distance apart [16],

$$r_0{}^2 = x^2 + y^2 + z^2$$

Bueche [16] also described the average energy per chain as

$$\text{Ave. energy/chain} = (3kT/2)(1/3)[(\alpha^2 - \alpha^{-1}) + (\alpha^{-1} - 1)]$$

The modulus of elasticity, G, was shown to be related to strain in elongation of polymeric elastomers. For up to 300% elongation, or more, the following relationship [22] applies:

$$G = 2mkTb^2(1 + 2/\gamma^3)$$

Where k is Boltzmann's constant, m represents the number of polymeric chains in the sample, and γ is the strain. The relationship of stress to strain is:

$$\text{Stress} = 2mkTb^2(\gamma + 2/\gamma^3)$$

There are several molecular theories of rubber-like elasticity The simplest one is based on a Gaussian distribution function for the end to end separation of the network chains: [23] (the dimensions of the free chains as unperturbed by excluded volume effect are represented by $(r^2)_0$)

$$\omega(r) = (3/2\pi(r^2)_0)^{3/2} \exp(3r^2/2(r^2)_0)$$

Within this Gaussian distribution function $(r^2)_0$ applies to the network chains both in the unstretched and stretched state. The free energy of such a chain is described by a Boltzmann relationship [23]:

$$F(T) = -KT \ln \omega(r) = C(T) + (3kT/2(r^2)_0)r^2$$

$C(T)$ is a constant at a specified absolute temperature T. The change in free energy for a stretched elastomer can be expressed as follows:

$$\Delta F = [3kT/2(r^2)_0][(\alpha_x^2x^2 + \alpha_y^2y^2 + \alpha_z^2z^2) - (x^2 + y^2 + z^2)]$$

where α is the molecular deformation ratio of r components in x,y,z directions from the unstretched or elastomer to one that was stretched and deformed. Additional discussions of this theory and other theories of elasticity are not presented here because thorough discussions of this subject belong to books dedicated to physical properties of polymers.

2.2.3 Rheology and Viscoelasticity of Polymeric Materials

When an amorphous polymer possesses a certain amount of rotational freedom, it can be deformed by application of force. Application of force will cause the polymer to flow and the molecules will move past each other. The science of deformation and flow is called ***rheology***. In the event that the force is applied quickly, and then withdrawn rapidly, the polymer molecules will tend to revert back to their previous undisturbed configuration. This is called ***relaxation***. Thus, the amorphous polymers exhibit some ***elastic*** behavior due to disruption of thermodynamically favorable arrangements. If, however, the force is applied gradually and consistently, the molecules will flow irreversibly. Due to chain entanglement that increases with molecular weight and due to frictional effects, the viscosity of the flowing liquid will be high. Thus, molecular weight control is very important in polymer processing. In a way this is a paradoxical situation. Higher molecular weights usually yield better mechanical properties. On the other hand, higher molecular weight materials are harder to process. The molecular weight control, therefore, is quite critical. The combination of properties of polymeric liquids, elasticity, and viscous flow is referred to as ***viscoelasticity***. It means reversible uncoiling of the polymeric chains. By the same terminology, ***viscous flow*** means irreversible slipping of the chains past each other. Thus, viscoelastic materials exhibit simultaneously a combination of elastic and viscous behavior. This type of behavior is particularly prominent in polymeric materials. The flow behavior of polymeric liquids is also influenced by the molecular weight distribution.

At proper temperatures the mechanical properties of many amorphous polymers may approach the physical properties of three idealized materials individually. These are [20, 22, 24]:

1. *A* ***Hookian or an ideal elastic solid***, whose small reversible deformations are directly proportional to the applied force.
2. *A* ***Newtonian liquid*** that flows with a viscosity independent of the rate of shear.
3. *An* ***ideal elastomer*** that is capable of reversible extension of several hundred percent, with a much smaller stiffness than that of a Hookian solid.

In the elastic response for a Hookian liquid the stress–strain relationship is: $\sigma(t) = G\gamma(t)$. For the Newtonian liquid it is $\sigma(t) = \eta\gamma'(t)$. In these equations, $\gamma(t)$ and $\gamma'(t)$ represent shear strain and shear rate at time t, while $\sigma(t)$ is the shear stress.

Many forces can be applied to polymer deformation. The force that rheologists are particularly concerned with is ***tangential stress*** or ***shear***. This is due to the fact that many polymers are extruded and forced to flow into dies for shaping and commercial use. If a shearing force f is applied to a cube of molten polymer per unit area it causes the top layer of the liquid to move a distance x from a fixed point at the bottom of the material with a velocity v. Shear causes the molecules to move past each other. This is illustrated in Fig. 2.4.

The above assumes that the viscosity of the material is sufficiently small so that the cube is not very distorted during the process. The viscosity of the material, η is defined as the ratio between the applied force and the velocity gradient, $\partial v/\partial x$ or as the rate of shear γ, where

$$\text{free energy, } F = \eta(v/x)$$

The above equation can be rearranged into another form,

$$\eta = Fv/v^2$$

Fv is the energy used up per second on the cube.

The ***shear stress***, $\boldsymbol{\tau}$ is defined as

$$\tau = \eta\partial v/\partial x = \eta\gamma$$

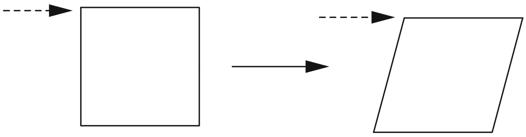


Fig. 2.4 Illustration of the movement of the upper layer due to applied force

where γ is the ***shear rate***. In this instance it should be equal to v. If the viscosity η is independent of the shear rate, the liquid exhibits ideal flow and is a ***Newtonian*** liquid. Tobolsky commented [12] that probably all Newtonian liquids, even those like water and benzene, that are very fluid, possess some elastic as well as viscous behavior. However, flow of most polymer liquids deviates strongly from an ideal behavior and either the viscosity decreases with the rate of shear, or no flow occurs until a certain minimum force is applied. The decrease of viscosity with the rate or shear is called ***shear thinning***. It is believed to be a result from the tendency of the applied forces to disturb the long chains from their favored equilibrium conformations. In this case, the polymer is at an ***yield point*** or at an ***yield value***. A liquid with an yield point is called a ***Bingham Newtonian fluid***, provided that it exhibits Newtonian behavior once it starts flowing. It is defined by

$$\tau = \tau_c + \eta\gamma$$

where τ_c is the critical shear stress, or threshold stress that is needed to initiate the flow. The Bingham fluid behavior might be attributed to structural arrangements of the molecules that give rise to conformational and secondary bonding forces. The **non-Newtonian** behavior occurs when shear stress does not increase in proportion to shear rate. In addition, there are ***thixotropic*** liquids that exhibit high viscosity or even resemble gelation at low shear rate but flow readily and exhibit low viscosity upon application of high shear. High shear rates can cause chain rupture and result in loss of molecular weight. In some cases, the shear rate may increase due to increase in molecular entanglement. In the case of flexible chain polymers, there is a critical molecular weight at which chain entanglement may show an increase. For most common polymers this may be in the molecular weight range of 4,000–15,000. Flow is also influenced by chain branching. The higher the degree of branching in a polymer, the lower will be the degree of entanglement at a given molecular weight. In general, the viscosity is higher with linear polymers than with branched ones at a given shear rate and molecular weight. Flow behavior is also influenced by molecular weight distribution (see Sect. 2.7.1). Usually, the broader the molecular weight distribution in polymers the lower is the shear rate that is needed to cause ***shear thinning***. On the other hand, for polymers with narrow molecular weight distribution, shear thinning, once it starts, is more pronounced. This is due to absence of chain entanglement of the higher molecular weight polymeric chains.

The viscosity of low molecular weight polymers is related to their temperature by an Arrhenius-type relationship [19, 22, 25]:

$$M_\eta = Ae^{-E/RT}$$

where E is the ***activation energy for viscous flow***, and A is a constant related to molecular motion, and M_η is the viscosity average molecular weight. For branched polymers, the larger or bulkier the side chains the greater is the activation energy, E. The same is true of polymers with large pendant groups. The activation energy of flow, E does not increase proportionately to the heat of vaporization for polymers but rather levels off to a value that is independent of molecular weight. This implies that for long chains the unit of flow is much smaller than the whole molecule. Instead, segments of the molecules, no larger than 50 carbon atoms move by successive jumps.

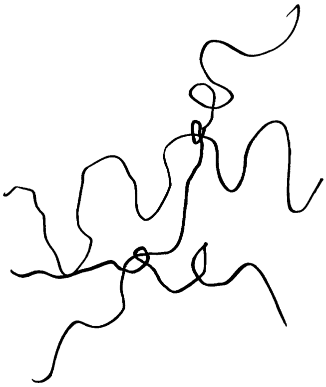


Fig. 2.5 Illustration of a physical crosslink in molten polymers

This is accomplished with some degree of coordination, but results in the whole chain shifting. Based on experimental evidence, the viscosity can be defined as,

$$\ln \eta = 3.4 \ln M_{\mathrm{w}} + C + E/RT$$

where C is a constant. M_{w} is weight average molecular weight (see Sect. 2.7) Chain length, Z, or the molecular weight of polymers is an important variable that influences flow properties of polymers. The relationship of a Newtonian viscosity of an amorphous polymer to the chain length when shear stress is low can be expressed as [19, 22, 25],

$$\log \eta = 3.4 \log Z_{\mathrm{w}} + k$$

where the constant k is temperature-dependent. By the same token, based on experimental evidence, the relationship of viscosity to temperature and to chain length at low shear rates, for many polymers can be expressed as follows:

$$\log \eta = 3.4 \log Z_{\mathrm{w}} - 17.44(T - T_{\mathrm{g}})/(51.6 + T - T_{\mathrm{g}}) + k'$$

where constant k' is specific for each polymer and T_{g} is the glass transition temperature (T_{g} is discussed in Sect. 2.2.3). Although linear molten polymers exhibit well-defined viscosities, they also exhibit elastic effects. These effects are present even in the absence of any crosslinks or a rubber network. It is referred to as ***creep***. This creep is attributed to entanglement of polymeric chain to form temporary physical crosslinks: This is illustrated in Fig. 2.5.

Deviations from Newtonian flow can occur when shear stress does not increase in direct proportion to shear rate. Such deviation may be in the direction of thickening (called **dilatent flow**) and in the direction of thinning (called **pseudo plastic**). Related to non-Newtonian flow is the behavior of thixotropic liquids when subjected to shear, as explained above. Flow behavior can be represented by the following equation:

$$\tau = A\gamma^{B}$$

where A is a constant and B is the index of flow. For Newtonian liquids $A = \eta$ and $B = 1$. All polymers tend to exhibit shear thinning at high shear rates. This is commonly explained by molecular entanglement, as mentioned above. Certainly, in the amorphous state there is considerable entanglement of the polymeric chains. Low shear rates may disrupt this to a certain degree, but the chains will still remain entangled. As the shear rates increases, disruption can occur at a faster rate than the chain

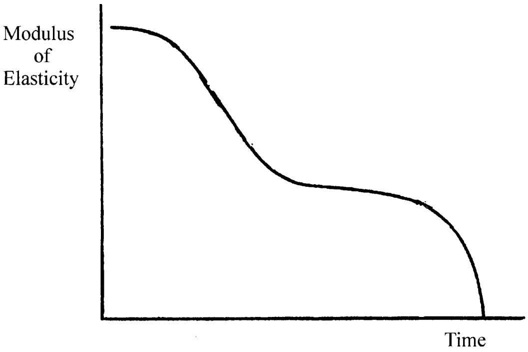


Fig. 2.6 Illustration of a plot of modulus of elasticity against time

can reentangle. The decreased amount of entanglement results in lower viscosity of the liquid, allowing the molecules to flow with less resistance. Actually, two factors can contribute to chain entanglement. These are high length of the chains for very large molecules and/or bulky substituents. Stress applied to a Newtonian liquid, outside of an initial spike, is zero. Stress, however applied to a viscoelastic fluid starts at some initial value. This value decreases with time until it reaches an equilibrium value due to the viscoelastic property of the material. Figure 2.6 illustrates what a plot of the modulus of elasticity $G(t)$, which depends on the temperature, when plotted against time, looks like:

The equation for ***shear–stress relaxation modulus*** that varies with temperature can be written as follows:

$$G(t) = \sigma(t)/\gamma_0$$

With constant stress, $\sigma(t) = G\gamma_0$, where creep strain $\gamma(t)$ is constant $[\gamma(t) = \sigma_0/G]$ for a Hookean solid. It would be directly proportional to time for a Newtonian liquid $[(\gamma(t) = \sigma_0/\eta)t]$. Here t is the initial time at which recovery of the viscoelastic material begins. For a viscoelastic fluid, when stress is applied, there is a period of creep that is followed by a period of recovery. For such liquids, strains return back toward zero and finally reach an equilibrium at some smaller total strain. For the viscoelastic liquid in the creep phase, the strain starts at some small value, but builds up rapidly at a decreasing rate until a steady state is reached. After that the strain simply increases linearly with time. During this linear range, the ratio of shear strain to shear stress is a function of time alone. This is ***shear creep compliance***, $J(t)$ The equation of shear creep compliance can be written as follows:

$$J(t) = \gamma(t)/\sigma_0$$

The stress relaxation modulus and the creep compliance are both manifestations of the same dynamic process at the molecular level and are closely related. This relationship, however, is not a simple reciprocal relations that would be expressed as $G(t) = 1/J(t)$, but rather in an integral equation that is derived from the Boltzman superposition principle. It relates recoverable compliance, J_s^0 to η_0, zero shear viscosity [22].

$$J_s^0 = \frac{1}{\eta_0^2}\int_0^{\infty} tG(t)\mathrm{d}t$$

$$\eta_0 = \int_0^{\infty} G(t)\mathrm{d}t$$

In relaxation back to equilibrium, the polymer assumes a new conformation. At first, the response is glassy. The modulus for such an organic glass is large, $G_g \sim 10^9$ Pa. This modulus decreases with

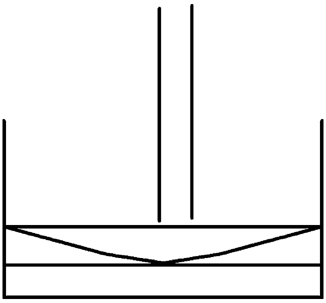


Fig. 2.7 Illustration of a cone and plate rheometer

time as the polymer begins to relax and continues along the whole length of the chain. For short chains this relaxation to zero takes place at a fairly constant rate. For very long chains, however, the relaxation rate tends to be in three stages. It starts at a certain rate at stage one, but after a while, noticeably slow down at some point, and at stage two the modulus remains relatively constant over some period of time. After that, at stage three, the relaxation is resumed again at a rapid rate until full equilibrium is reached. At stage two there is a period of relatively constant modulus that is not affected by the chain architecture and the material resembles a rubber network. The length of the third stage, however, is profoundly affected by the molecular weight, by the molecular weight distribution and by long-chain branching of the polymer.

Koga and Tanaka [23] studied the behavior of normal stresses in associated networks composed of telechelic polymers under steady shear flow. They showed numerically that the first and second normal stress coefficients reveal thickening as a function of shear rate and that the sign of the second normal stress coefficient changes depending on the nonlinearity in the chain tension, the dissociation rate of the associative groups from junctions and the shear rate by analytic calculation they showed that in the limit of small shear-rate, the sign inversion occurs by the competition between the nonlinear stretching and dissociation of associative groups. Thus, the molecular mechanism of the sign inversion is shown to be similar to that of thickening of the shear viscosity.

In the behavior of polymeric liquids two quantities are important. These are steady-state recoverable shear compliance, J_s^0 (as shown above) and steady-state viscosity at zero shear rate, η_0. These quantities are related:

$$\text{recoverable shear compliance } J_s^0 = \gamma_r/\sigma_0$$

$$\text{zero shear viscosity } \eta_0 = \sigma_0/\gamma'_{ss}$$

where γ'_{ss} is the shear rate and γ_r is the total recoil strain. Both shear compliance and shear viscosity can be obtained from creep studies. The product of the two, zero shear compliance and zero shear viscosity is the characteristic relaxation time of the polymer:

$$\tau_0 = J_s^0 \eta_0$$

There are various techniques for determining the viscosity of molten polymers. One commonly used piece of equipment is a cone and plate rotational viscometer. The equipment is illustrated in Fig. 2.7:

The molten polymer is placed between the bottom plate and the cone, and the cone is rotated at constant speed. Shear stress is obtained from the following relationship:

$$\tau = 3M/2\pi R$$

where M is the torque in dynes per centimeter, and R is the cone radius in centimeters (or meters). The shear rate can be obtained from the following equation

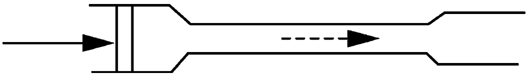


Fig. 2.8 Illustration of a capillary viscometer

$$\gamma' = \Omega/\alpha$$

where α is the cone angle in radians or in degrees, and Ω is the angular velocity in radians per second or in degrees per second. The viscosity is obtained from the following relationship [15, 16]:

$$\eta = \tau/\gamma' = 3\alpha M/2\pi R^3\Omega = kM/\Omega$$

k is a constant, specific for the viscometer used. It can be obtained from the relationship [7]:

$$k = 3\alpha/2\pi R^3$$

The cone and plate rheometers are useful at relatively low shear rates. For higher shear rates capillary rheometers are employed. They are usually constructed from metals. The molten polymer is forced through the capillary at a constant displacement rate. Also, they may be constructed to suit various specific shear stresses encountered in commercial operation. Their big disadvantage is that shear stress in the capillary tubes varies from maximum at the walls to zero at the center. On the other hand, stable operation at much higher shear rates is possible. Determination, however, of η_0 is usually not possible due to limitations of the instruments. At low shear rates. one can determine the steady-state viscosity from measurements of the volumetric flow rates, Q and the pressure drop:

$$\Delta P = P - P_0$$

where, P_0 is the ambient pressure. A capillary viscometer is illustrated in Fig. 2.8, where the diameter of the capillary can be designated as D. For Newtonian liquids the viscosity can be determined from the following equation:

$$\eta = \pi D^4 \Delta P/128LQ$$

where L represents the length of the capillary. The shear stress at the capillary wall can be calculated from the pressure drop:

$$\sigma_{\text{wall}} = D\Delta P/4L$$

Also, the shear rate at the walls of the capillary can be calculated from the flow rate [22]:

$$\gamma'_{\text{wall}} = 8Q\left(3 + \frac{\mathrm{d}\log Q}{\mathrm{d}\log \Delta P}\right)/\pi D^3$$

Wang et al. studied the homogeneous shear, wall slip, and shear banding of entangled polymeric liquids in simple-shear rheometry, such as in capillary viscometry, shown above [20]. They observed that recent particle-tracking velocimetric observations revealed that well-entangled polymer solutions and melts tend to either exhibit wall slip or assume an inhomogeneous state of deformation and flow during nonlinear rheological measurements in simple-shear rheometric setups.

It is important to control the viscoelastic properties of confined polymers for many applications. These applications are in both, microelectronics and in optics. The rheological properties of such films, however, are hard to measure. Recently, Chan et al. [27] reported that the viscoelasticity can be measured through thermal wrinkling. Thermally induced instability develops when polymer films are compressed between rigid, stiffer layers. This is due to differences in coefficients of thermal expansion between the polymer and the inorganic layers. A net compressive stress develops at the polymer–substrate interface when the composite layers are heated to temperatures that promote mobility of the polymer layer. Such wrinkling substrate surface is characterized by an isotropic morphology that can be approximated as a sinusoidal profile. Chan et al. utilized the thermal wrinkling to measure the rubbery modulus and shear viscosity of polystyrene thin films as a function of temperature. They used surface laser-light scattering to characterize the wrinkled surface in real-time in order to monitor the changes in morphology as a function of annealing time at fixed annealing temperatures. The results were compared with a theoretical model, from which the viscoelastic properties of the PS thin film are extracted.

2.3 The Crystalline State

Mendelkern [5] pointed out that essentially all properties of polymers are controlled by the molecular morphology. In contrast to the amorphous or liquid state, the crystalline state is relatively inelastic and rigid. In the crystalline state, the bonds adopt a set of successive preferred orientations, while in the liquid state the bond orientation is such that the chains adopt statistical conformations. In the crystalline state the properties of the polymers differ considerably. If a polymer molecule is coiled randomly, then it cannot fit readily into a geometrically arranged, regular crystalline lattice. So the molecules must change into a uniform shape to fit into a crystal pattern. In many cases they assume either a helix or a zigzag conformation. Such arrangements are more regular than in a random coil [29–40]. This can even be detected by spectral and thermodynamic studies. During crystallization, polymers with bulky substituents that are spaced close to each other on the polymeric chains tend to form helical conformations that remain in the crystalline phase. The arrangement allows close packing of the substituents without much distortion of the chain bonds. That is particularly true of many isotactic polymers that crystallize in helical conformations, taking on ***gauche*** and ***trans*** positions. For the *gauche* position steric hindrance always forces the rotation to be such as to place the substituents into a juxtaposition generating either a right-hand or a left-had helix. The helical conformations of isotactic vinyl polymers were illustrated by Gaylord and Mark [41] as shown in Fig. 2.9:

When macromolecules possess a certain amount of symmetry, then there is a strong accompanying tendency to form ordered domains, or crystalline regions. ***Crystallinity***, however, in polymers differs in nature from that of small molecules. When the small molecules crystallize, each crystal that forms is made up of molecules that totally participate in its makeup. But, when polymers crystallize from a melt, which means that certain elements of the polymeric system or segments of the polymeric chains have attained a form of a three-dimensional order. Complete crystallization, from the melt, however, is seldom if ever achieved The ordered conformations may be fully extended or may be in one of the helical forms as shown above. This resembles orderly arrangement of small molecules in crystals. The crystalline domains, however, are much smaller than the crystals of small molecules and possess many more imperfections.

2.3.1 Crystallization from the Melt

Certain basic information was established about the ***crystallization from the melt*** [5]: The process is a first-order phase transition and follows the general mathematical formulation for the kinetics of a

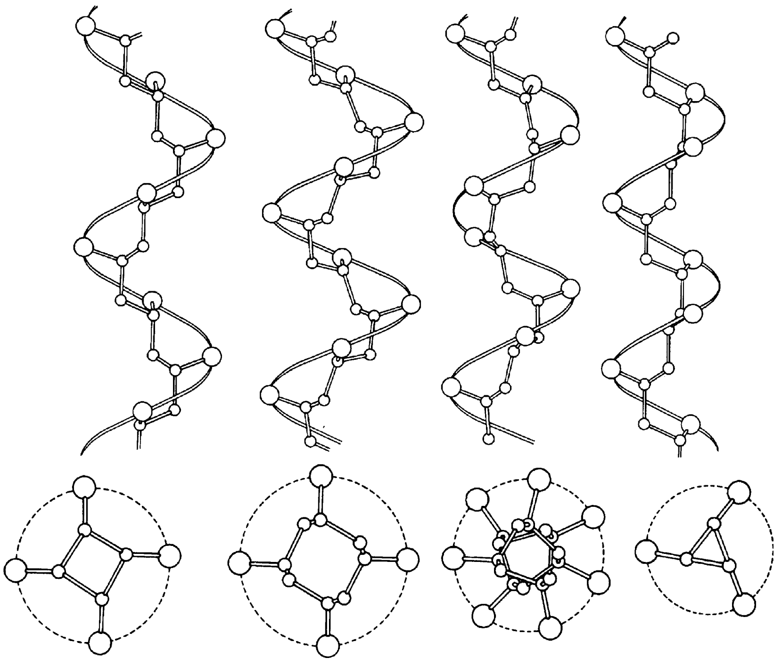


Fig. 2.9 Illustration of the helical conformation of isotactic vinyl polymers

phase change. Equilibrium conditions, however, are seldom if ever attained and as a result complete crystallinity, as stated above, is not reached. The tendency to crystallize depends upon the following:

1. Structural regularity of the chains that leads to establishment of identity periods.
2. Free rotational and vibrational motions in the chains that allow different conformations to be assumed.
3. Presence of structural groups that are capable of producing lateral intermolecular bonds (van der Wall forces) and regular, periodic arrangement of such bonds.
4. Absence of bulky substituents or space irregularity, which would prevent segments of the chains from fitting into crystal lattices or prevent laterally bonding groups from approaching each other close enough for best interaction.

Natta and Carradini [30] postulated three principles for determining the crystal structures of polymers These are:

1. It is possible to assume that all mer units in a crystal occupy geometrically equivalent positions with respect to the chain axis. This is known as the ***Equivalence Postulate***.
2. The conformation of the chain in a crystal is assumed to approach the conformation of minimum potential energy for an isolated chain oriented along an axis. This is the ***Minimum Energy Postulate***.
3. As many elements of symmetry of isolated chain as possible are maintained in the lattice, so equivalent atoms of different mer units along an axis tend to assume equivalent positions with respect to atoms of neighboring chains. This is the ***Packing Postulate***.

X-ray diffraction studies of polymers crystallized from the melt show recognizable features in some of them. The Bragg reflections, however, appear more broad and diffuse than those obtained from well-developed single crystals. Such broadening could be the result of the crystals being small. It could also be the result lattice defects. Because diffraction patterns are too weak, it is impossible to reach a conclusion. The majority opinion, however, leans toward the small crystal size as being the

Fig. 2.10 Illustration of a fringed micelle

cause of the broadening [5]. The crystals from the melt are approximately 100 × 200 × 200 Å in size. Rough estimates from these diffraction studies indicate that the size of crystals, or crystallites, rarely exceeds a few hundred angstroms. The fact that there is a substantial background of diffuse scattering suggests that considerable amorphous areas are also present. Because the chains are very long, it has often been suggested that individual chains contribute to several different crystalline and amorphous domains. This resulted in a proposal of a composite single-phase structure [5], a ***fringed micelle*** or a ***fringed crystallite*** model. This is illustrated in Fig. 2.10. The fringes are transition phases between the crystalline and the amorphous regions. Some analytical studies, however, failed to support this concept.

The proportion of crystalline matter in a polymer is defined as the ***degree of crystallinity***. It can be expressed in volume or in mass. By expressing it in volume, it would be:

$$\text{degree of crystallinity}\, X_\text{v} = V_\text{c}/(V_\text{c} + V_\text{a}) = V_\text{c}/V$$

where, V_c, V_a, and V represent the respective volumes of the crystalline and amorphous regions and the total volume.

When expressed in terms of mass, the equation would be:

$$X_\text{m} = m_\text{c}/(m_\text{c} = m_\text{a}) = m_\text{c}/m$$

where, m_c, m_a, and m are the masses of crystalline, amorphous phases, and the total mass.

2.3.2 Crystallization from Solution

For many polymers, crystal growth can also take place from dilute solutions and from such solutions they yield **single crystals**. Crystal formations in polymers were studied intensively almost from the time of recognition of their existence in macromolecules. **Single crystals** of organic polymers were recognized as early as 1927 [26]. It became the subject of intensive investigations after observations that linear polyethylene can crystallize into single crystals. The observations made on polyethylene were followed by observations that it is possible to also grow single crystals of other polymers. Some of them are polyoxymethylene [30], polyamides [31], polypropylene [32], polyoxyethylene [33],

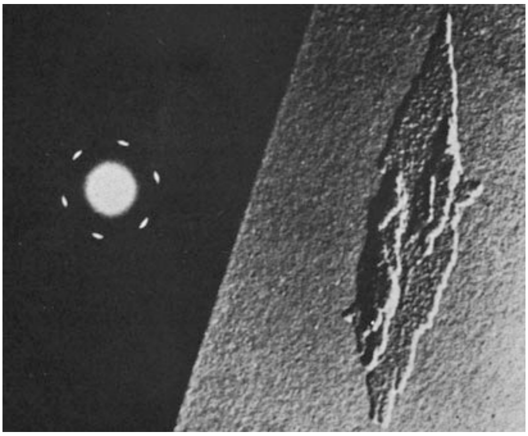


Fig. 2.11 Electron diffraction pattern and single crystal of polyacrylonitrile (from ref [50])

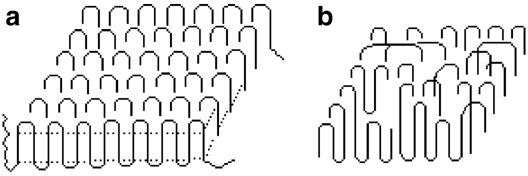


Fig. 2.12 Models of chain folding. (**a**) adjacent reentry model, and (**b**) nonadjacent reentry model

cellulose [34], and others [35]. The electron diffraction pattern and a single crystal of polyacrylonitrile are shown in Fig. 2.11.

There is good correlation between the structural regularity of a specific polymer and the appearance of its single crystals. Relatively larger single crystals with smooth, sharp edges, and little random growth are formed only from polymers that are known to have high regularity in their structures.

To explain the arrangement of the chains in the single crystals a theory of ***folded chain lamella*** was proposed in 1947 [36]. It states that the basic units in single crystals are ***lamellae*** about 100 Å thick. The evidence for the existence of lamellae-like crystallites comes from microscopic observations. Direct microscopic observations, however, do not yield information about chain structure on the molecular level. The thickness of the lamellae relative to the chain length led some to postulate that the molecules are arranged perpendicular or nearly so to the layers. Also that sharp, folded configurations form with the fold length corresponding to the layer thickness. In this view, one polymer molecule is essentially constrained to one lamellae and the interface is smooth and regularly structured with the chain folding back and forth on itself like an accordion during crystallization. Two models of chain folding are visualized. In one model, the chain folding is regular and sharp with a uniform fold period. This is called the ***adjacent-reentry model***. In the other one, the molecules wander through the irregular surface of a lamella before reentering it or a neighboring lamella. This mode is called ***switchboard*** or ***nonadjacent-reentry model***. The two are illustrated in Fig. 2.12. Some early experimental evidence failed to support the lamellae concept [37]. Since, much evidence was presented to support it, today it is accepted as an established fact [5]. Recently, Hosoda and coworkers [37] reported studies of the morphology of specially synthesized polyethylene with *n*-butyl branches precisely spaced on every 39th carbon. This was compared with a commercial ethylene/1-hexene copolymer possessing the same branching probability. The goal of their work was to elucidate the effect of the intramolecular sequence length heterogeneity on the lamella crystal thickness and its distribution. The commercial copolymer was found to have an orthorhombic crystalline polymorphism, which is normal for such polyethylenes and different from that of the specially synthesized material. The synthesized one exhibits a narrow lamella thickness distribution with the average thickness corresponding exactly to the space length between two consecutive branches. This suggests to them. complete exclusion of *n*-butyl branches from the crystal stem. On the other hand, the 1-hexene copolymer forms much thicker lamellae and a broader thickness distribution than the synthesized polyethylene with butyl branches. Here, the average thickness is 1.5 times larger than that calculated from the most probable ethylene sequence length obtained from NMR, or for a theoretical ethylene sequence Length distribution, indicating that the lamellae are composed predominantly of the sparsely branched longer ethylene sequences.

Linear polyethylene single crystals often exhibit secondary structural features that include corrugations and pleats. It was suggested that the crystals actually grow in form of pyramids, but that these pyramidal structures collapse when the solvent is removed during preparation for microscopy [42]. Various investigators described other complex structures besides pyramidal. Typical among these descriptions are sheaf-like arrays that would correspond to nuclei. Also there were observations of dendridic growths, of clusters of hollow pyramids, of spiral growths, of epitaxial growths, of moiré patterns, etc. [42, 43].

2.3.3 Spherulitic Growth

For polymers that **crystallize from the melt**, an important parameter in the characterization of the two-phase systems, is the weight fraction of the crystalline regions. The degree of crystallinity that can be reached is dependent on the temperature at which crystallization takes place. At low temperatures one attains a much lower degree of crystallization than at higher temperatures. This implies that crystallization remains incomplete for kinetic reasons [7].

Normal conditions of cooling of the molten polymer establish the crystalline texture of the polymer and usually result in formation of very tiny crystals. These crystals are part of a closely spaced cluster called ***spherulite***. The formation of a single nucleus in a polymer cooled below its melting point favors the formation of another nucleus in its vicinity due to creation of local stresses.

Microscopic examinations with polarized light of many polymeric materials that crystallized from the melt show the specimen packed with spherulites. Often these appear to be symmetrical structures with black crosses in the center [38]. It is believed [39] that these spherulites grow from individual nuclei. Ribbons of crystallites grow from one spherulitic center and fan out in all directions. Initially they are spherical but because of mutual interference irregular shapes develop. The diameters of spherulites range from 0.005 to 0.100 mm. This means that a spherulite consists of many crystalline and noncrystalline regions. The black crosses seen in the spherulites are explained [39] by assuming that the crystallites are arranged so that the chains are preferentially normal to the radii of the spherulites. Spherulitic morphology is not the universal mode of polymer crystallization. Spherulitic morphology occurs usually when nucleation is started in a molten polymer or in a concentrated solution of a polymer. Spherulitic growth is illustrated in Fig. 2.13.

The size and number of spherulites in the polymer tends to affects the physical properties. Thus, the impact strength of polymer films or their flex life usually increases as the spherulite size decreases. On the other hand, there does not appear to be any correlation between the yield stress and ultimate elongation and the size of the spherulites.

Rhythmic crystal growth is generally encountered in thin films of semicrystalline polymers. This is believed to be due to formation of ring-banded spherulites and attributed to the periodical lamellae twisting along the radial growth direction of the spherulites [42]. Recently, Gu and coworkers [43] reported that by using mild methylamine vapor etching method, the periodical cooperative twisting of lamellar crystals in ring-banded spherulites was clearly observed.

When the melt or the solutions are stirred ***epitaxial*** crystallinity is usually observed. One crystalline growth occurs right on top of another. This arrangement is often called **shish-kebab**

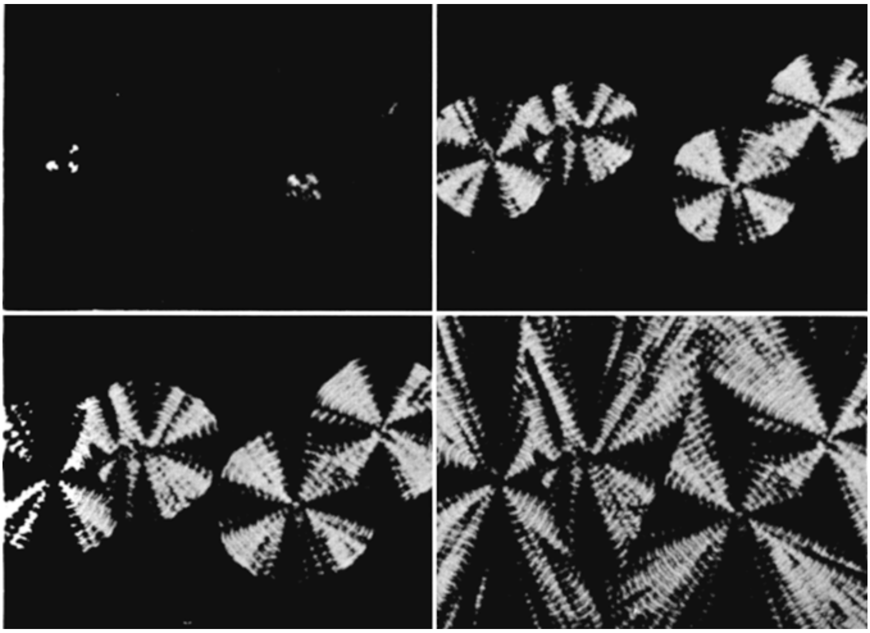


Fig. 2.13 Spherulitic growth (from ref [50])

morphology. It contains lamella growth on long fibrils. Drawing of a crystalline polymer forces the spherulites to rearrange into parallel arrangements known as ***drawn fibrilar morphology***.

In order for the ordered phase to crystallize from an amorphous melt a nucleation barrier must be overcome. This barrier is a result of interfacial energy between the ordered phase and the melt that causes super cooling. Sirota [44] suggested that in order for the nucleation barrier of the stable phase to be sufficiently high to form out of the melt, another phase with a lower nucleation barrier and a free energy intermediate between that of the stable phase and the melt must form. This, he points out, is implied by Oswald's rule [45] and evidence presented by Keller [35] that crystallization in semicrystalline polymer systems is mediated by a transient metastable phase [47, 48].

Stroble and coworkers demonstrated that lamellar thickness is determined by a transition between the metastable phase and the stable crystal phase [46–49]. In addition, by relating the crystallization temperature, melting temperature, and crystalline lamellar thickness, he suggested that lamellar growth fronts are thin layers of a mesomorphic phases. He feels that these phases thicken until such thickness is reached that stable crystal phases are favored. The conversion occurs in a block wise fashion but results in granular structures that were observed in many polymers [46–49]. This conversion is a stabilization process that lowers the free energy of the newly formed crystallites and prevents them from returning to the mesomorphic phase upon subsequent elevation of the temperature [46–49]. Such a concept of crystallization, however, is not universally accepted. Sirota [49], pointed out, however, that this picture and the thermodynamic framework are generally correct in many cases.

Sirota [49] believes that the origin of granular structures, mentioned above, can be understood in the following way. The initial nucleation and growth take place by stem addition. into mesophases. Lamellae thickness occurs while the chains are in the more mobile mesophase. When the thicknesses grow large enough to allow conversion from mesophases to crystals, the average densities in the lamellae have been set and the crystals break up into blocks. The transitions from mesophases to crystals also involves increases in lateral packing densities. In semicrystalline polymers, the entanglements in the amorphous regions, as well as the folding of the chains and the lamellar spanning the chains, will also have an effect. These effects limit the allowable lateral displacements of the crystalline stems during the rapid solid-state transformation from the mesophases to the crystal forms. As a result, over long distances, on molecular scale, and short times, the stems are kinetically constrained to be close to the lateral position that is maintained as they grew in the mesophase. At the same time, the local packing now favors the more stable crystal phase with a higher lateral density. The constraints on the chain ends favoring the lateral density of the mesophases, and forces competition with the density of the thermodynamically favored crystal structures. This causes the crystal to break up into domains. Sirota then suggests that the granular structures observed in many polymer crystals are fingerprints of the transitions from the transient intermediates from which the crystals have formed [49].

It was reported recently, that polymeric can also form quasicrystals. Hayashida et al. [50] demonstrated that certain blends of polyisoprene, polystyrene, and poly(2-vinylpyridine) form star-shaped copolymers that assemble into ***quasicrystals***. By probing the samples with transmission electron microscopy and X-ray diffraction methods, they conclude that the films are composed of periodic patterns of triangles and squares that exhibit 12-fold symmetry. These are signs of quasi-crystalline ordering. Such ordering differ from conventional crystals lack of periodic structures yet are well-ordered, as indicated by the sharp diffraction patterns they generate. Quasi-crystals also differ from ordinary crystals in another fundamental way. They exhibit rotational symmetries (often five or tenfold). There are still some basic questions about their structure.

2.3.3.1 Thermodynamics of Crystallization

The free energy change of a polymer from liquid to crystal is

$$\Delta F = \Delta H - T\Delta S$$

At the melting point T_m the crystals and the liquid polymer are at equilibrium. The change in free energy, therefore, $\Delta F = 0$. That means that at the melting point:

$$T_\mathrm{m} = \Delta H/\Delta S$$

If the heat of fusion is large, then the melting temperature of the polymer crystals will be high (due to high intermolecular attraction) or if the entropy of fusion is small.

Mendelkern [42] noted that there are three different interfacial free energies that are characteristic of crystallites. One, σ_e, is for the equilibrium extended chain crystallite, a second one σ_ec represents the mature, but non-equilibrium crystallite, and the third one is σ_en is the interfacial free energy involved in forming a nucleus. These quantities cannot be identified with one another. Because only portions of the polymeric chains participate in the formations of crystallites, the section or sections of the chains of x length that participate in crystallite formation can be designated as $\zeta_{\mathrm{e}'}$ and the sections of the chains that remain in disorder and amorphous, as $x - \zeta_{\mathrm{e}'}$.

The dependence of the melting temperature of such a system upon chain length is [42]:

$$1/T_\mathrm{m} - 1/T_\mathrm{m}^0 = (R/\Delta H_\mathrm{u})\{[(1/x) + (1/x - \zeta_{\mathrm{e}'} + 1)]\}$$

where, ΔH_u is the enthalpy of fusion per repeat unit and ζ_e is the equilibrium crystalline length. The effective interfacial free energy associated with the basal plane of an equilibrium crystalline length $\zeta_{\mathrm{e}''}$ designated as σ_e is [42]:

$$2\sigma_\mathrm{e} = RT_\mathrm{me}\{[\zeta_\mathrm{e}/(x - \zeta_\mathrm{e} + 1)] + \ln[(x - \zeta_\mathrm{e} + 1)x]\}$$

where T_m^0 is the equilibrium melting temperature for an infinite molecular weight chain and T_{me} is the corresponding melting temperature for a fraction that contains x repeat units. From the stand point of thermodynamics, T_{me} is a ***first-order transition temperature*** [15]. The melting points, when measured very carefully, can in many cases be sharp. On the other hand, melting points of ordinary crystals may melt over a range (Table 2.3). Table 1.2 shows some first-order transition temperatures, commonly designated as T_m.

For systems that are polydisperse, with a most probable chain-length distribution, the melting temperature molecular weight relation is expressed as [42]:

$$1/T_m^* - 1/T_m^0 = (R/\Delta H_u)(2/\overline{X}_n)$$

where $\overline{X}_n$ is the number average degree of polymerization. In this equation, the quantity $2/\overline{X}_n$ represents the mole fraction of non-crystallizing units. This equation is based on the stipulation for conditions for phase equilibrium. It is specific to and valid only for polymers that have a most probable molecular weight distribution. This relationship for the melting temperature of each polydisperse system has to be treated individually [42]. By applying the Clapeyron equation and from measurements of applied hydrostatic pressure the value of ΔH_u can be determined.

This equation, $T_m = \Delta H_m/\Delta S_m$ applies to very high molecular weight polymers. For polymers that are medium or low in molecular weight, the degree of polymerization (X) has to be included:

$$T_m = (\Delta H_0 + X\Delta H_1)/(\Delta S_0 + X\Delta S_1)$$

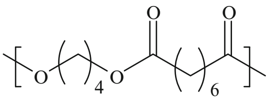
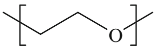
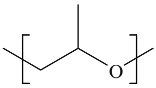
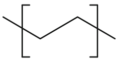
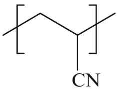
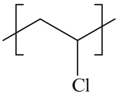
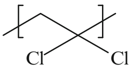
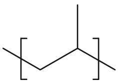
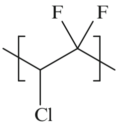
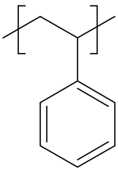
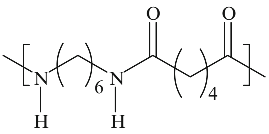
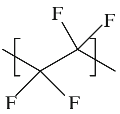
Mandelkern points out [38] that the experimental data shows that there is no correlation between the melting temperature of a polymeric crystal and the enthalpy of fusion, as is found in many small molecules. The ΔH values of polymers generally fall into two classes. They are ether within a few thousand calories per more or about 10,000 cal/mole. Polymers that fall into the category of elastomers have low melting temperatures and high entropies of fusion. This reflects the compacted highly flexible nature of the chains. At the other extreme are the rigid engineering plastics. These materials possess high melting points and correspondingly lower entropies of fusion [42].

2.3.3.2 Kinetics of Crystallization

The rate of crystallization in polymeric materials is of paramount importance. For some polymers, like atactic polystyrene or some rubbers, rapid cooling can lead to the glassy state without any formation of crystallites. The amount of crystallinity actually depends very much upon the thermal history of the material. The amount of crystallinity, in turn, influences the mechanical properties of the material. Microscopic observation of the growth of the spherulites as a function of time will yield information of the crystallization rate. The rate is a function of the temperature. As the temperature is lowered, the rate increases. This growth is usually observed as being linear with time. Presence of impurities will slow down the growth rate. When the growth rate is plotted against crystallization temperature, a maximum is observed. This is due to the fact that as the temperature is lowered the mobilities of the molecules decrease and the process eventually becomes diffusion-controlled. According to the Avrami equation, the fraction that crystallizes during the time t, and defined as $1 - \lambda(t)$, can be written as [42]:

$$1 - \lambda(t) = 1 - \exp\left(-\frac{\rho_c}{\rho_l}\int_0^t V(t,\tau)N(\tau)\mathrm{d}\tau\right)$$

Table 2.3 Melting points, T_m of some crystalline polymers[a]

Repeat unit	Polymer	Melting point (°C)
	Poly(tetramethylene suberate)	45
	Poly(ethylene oxide)	66
	Poly(propylene oxide)	70
	High-density polyethylene	132–138
	Polyacrylonitrile	317
	Poly(vinyl chloride)	212
	Poly(vinylidene chloride)	210
	Polypropylene	168
	Polychlorotrifluoroethylene	210
	Polystyrene	230–248
	Poly(hexamethylene adipamide)	250
	Polytetrafluoroethylene	327

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[a] From ref [15] and other sources in the literature

where, $N(\tau)$ is the nucleation frequency per untransformed volume, $V(t,\tau)$ is the corresponding volume of the growing center, and ρ_c and ρ_l represent the densities of crystalline and liquid phases. Based on that, the rate constant for crystallization kinetics can be described [42]:

$$\ln[(V_\infty - V_t)/(V_\infty - V_0)] = -(1/w_c)kt^n$$

where, V_∞, V_t, and V_0 are specific volumes at the times shown by the subscripts, and w_c is the weight fraction of the polymer crystallized. k is the rate constant for crystallization It was found, however, that crystallization continues in polymeric materials for much longer periods of time than the Avrami equation predicts.

For all homopolymers the rate of crystal growth increases linearly with time, or $G = \mathrm{d}r/\mathrm{d}t$. Mandelkern defines the steady-state nucleation rate, N as follows [42]:

$$N = N_0 \exp(-E_D T/RT - \Delta G^*/RT)$$

where E_D is the energy of activation for transporting the chain segments across the crystal–liquid interface.

If the crystallization takes place over an extended temperature range, most if not all homopolymers display a maxima in rates of spherulitic growth and in the overall crystallization. The equation for spherulitic growth is written as follows [42]:

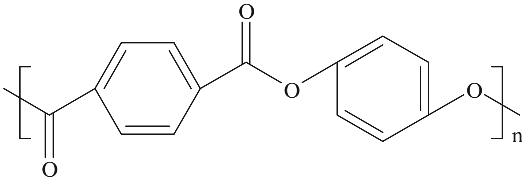
$$G = G^0 \exp(-U^*/(T - T_\infty) \exp(KT_m^0/T_c \Delta G_u T)$$

where T_∞ is the temperature at which all molecular and segmental motion stops.

2.4 The Mesomorphic State, Liquid Crystal Polymers

The state of mesomorphism is a spontaneously ordered liquid–fluid crystalline state. Liquid crystals were discovered as early as 1888. They are materials that exhibit order in one or two dimensions but not in all three. By comparison, the amorphous materials lack any order, while the crystalline ones exhibit order in three dimensions. All liquid crystalline polymers exhibit some degree of fluidity. They were investigated extensively in the 1900s and became commercially important in 1960s.

These are macromolecules that can align into crystalline arrays while they are in solution (***lyotropic***) or while in a molten state (***thermotropic***). Such liquids exhibit ***anisotropic*** behavior [51, 52]. The regions of orderliness in such liquids are called ***mesophases***. Molecular rigidity found in rigid rod-shaped polymers, for instance, is the chief cause of their liquid crystalline behavior. It excludes more than one molecule occupying a specific volume and it is not a result of intermolecular attractive forces. Some aromatic polyesters or polyamides are good examples, like polyphenylene terephthalate:



Because the molecules posses anisotropy, they are aligned while still in a fluid form. This differs from ordinary liquids, that are **isotropic**, where the molecules lack any kind of arrangement.

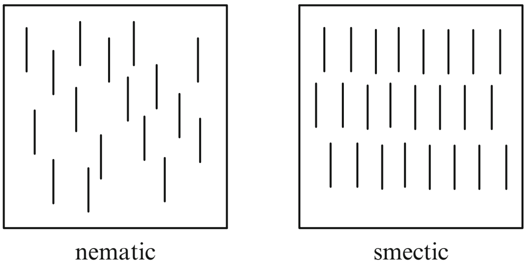


Fig. 2.14 Illustration of the arrangement of liquid crystal into nematic and smectic orders

Anisotropy is not affected by conformational changes. Generally, molecules that are rigid rod like and elongated or disc like in shape are the type that can form liquid crystal arrangements. Some biological polymers exhibit liquid crystalline behavior due to their rigid helical conformations. Among synthetic polymers, on the other hand, rigid rod structures, mentioned above are the ones that exhibit most of the liquid crystalline behavior. Polymers that form liquid crystals may exhibit multiple mesophases at different temperatures. Based on the arrangement of the liquid crystals in the mesophases, they are further classified as ***nematic, smectic,*** and ***cholesteric*** [51, 52].

Both, smectic and nematic are parallel arrangements along molecular axes. The smectic liquid crystals are more ordered, however, than the nematic ones. This is a result of differences in the orientations of the chain ends. In smectic liquid crystals the chain ends are lined up next to each other. In nematic ones, however, they lack any particular orientation. Also the smectic liquid crystals are layered while the nematic ones are not. Microscopic observations [51] can help distinguish between the two forms.

Smectic elastomers, due to their layered structure, exhibit distinct anisotropic mechanical properties and mechanical deformation processes that are parallel or perpendicular to the normal orientation of the smectic layer. Such elastomers are important due to their optical and ferroelectric properties. Networks with a macroscopic uniformly ordered direction and a conical distribution of the smectic layer normal with respect to the normal smetic direction are mechanically deformed by uniaxial and shear deformations. Under uniaxial deformations two processes were observed [53]: parallel to the direction of the mechanical field directly couples to the smectic tilt angle and perpendicular to the director while a reorientation process takes place. This process is reversible for shear deformation perpendicular and irreversible by applying the shear force parallel to the smetic direction. This is illustrated in Fig. 2.14.

If the mesogens are chiral, a twisted nematic, suprarmolecular, ***cholesteric*** (twisted) phase can form [51, 52]. The achiral nonlinear mesogens can also form chiral supramolecular arrangements in tilted smectic phases.

Recently, Tokita and coworkers [54] reported a direct transition from isotropic to smectic arrangement in a liquid crystalline polymer and determined experimentally the existence of metastable nematic orientational ordering that preceded the formation of translational smectic ordering. A polymeric material was used that exhibits very slow liquid crystalline transition dynamics [55]. This enabled use of conventional methods to study the transitions, such as of polarized light scattering and synchrotron wide-angle X-ray diffraction analyses. It was observed that at high quench rates or super cooling, metastable nematic (orientational) ordering occurs preceding full smectic (orientational and translational) order. Also, the occurrence of nematic preordering (high super cooling) resulted in morphological changes of growing liquid crystalline domains compared to solely smectic growth. Specifically, samples cooled at rates high enough to exhibit nematic preordering formed well-oriented or “neat” tactoidal smectic domains. Samples cooled at lower rates, where only smectic ordering was observed, formed radially oriented or textured spherulitic domains [55]. In commenting on this observation, Abukhdeir and Rey [56] point out that through a simulation model the isotropic to smectic liquid crystalline transition experimental observations of preordering of smectic liquid crystalline transitions can be studied. Phase transition kinetics results presented by them show that nematic preordering results from both thermodynamic potential and dynamic differences in phase-ordering time scales.

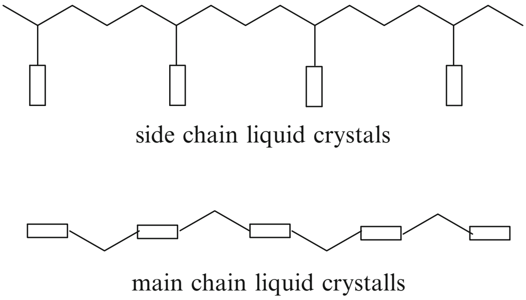


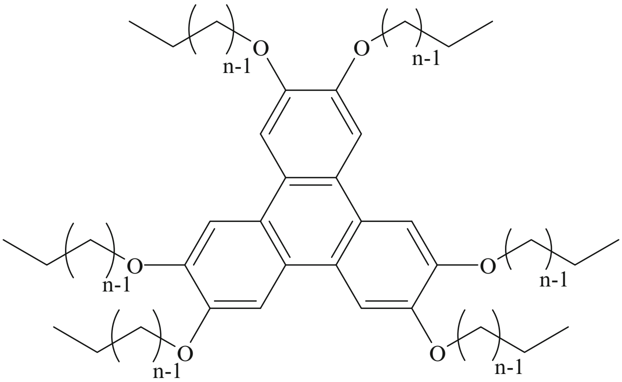
Fig. 2.15 Illustration of arrangements of liquid crystal structure

The chemical structure of the polymers determines whether the molecules can form rigid rods. If the backbone of the polymer is composed of rigid structures then it tends to form ***main chain*** liquid crystals. If, however, the side chains are rigid, then the polymer will tend to form ***side chain*** liquid crystals. From practical considerations, these two properties are of prime interest. The structures are illustrated in Fig. 2.15.

Liquid crystalline behavior affects the melt viscosity of the polymer and the ability of the polymer to retain the ordered arrangement in the solid state. Thus, liquid crystalline behavior during the melt results in lower viscosity because the rigid polymeric mesophases align themselves in the direction of the flow. As a result, the polymer is easier to process. Also, retention of the arrangement upon cooling yields a material with greatly improved mechanical properties. Several thermotropic liquid crystalline copolyesters and polyamides are available commercially.

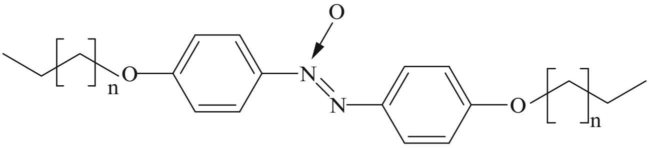
Samulski [57] gives examples of molecules that can typically form liquid crystals These are

1. A discotic liquid crystal



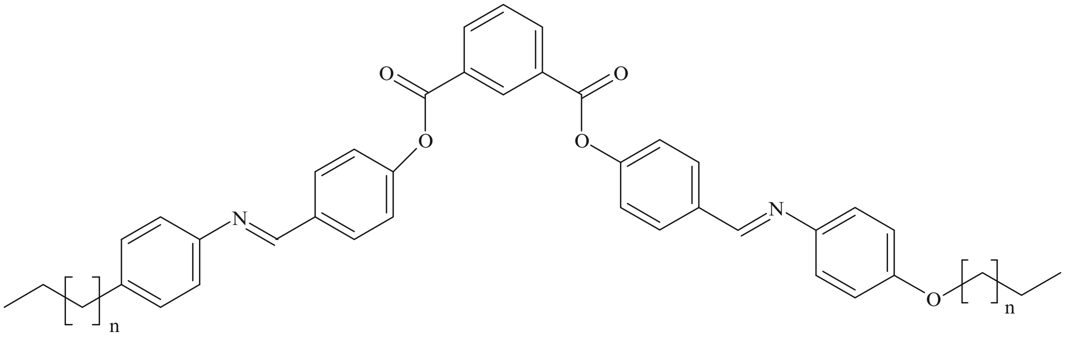
The above shown structure has a ***mesogenic core***, (hard central segment) correlated with dynamic packing of anisometric shapes. The flexible tales, often hydrocarbon chains, extend from the mesogenic core and facilitate the transformation from the solid state to the liquid crystalline phase.

2. A calamitic liquid crystal



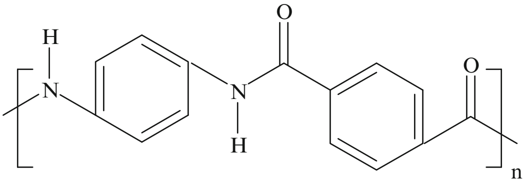
In this case there is a prolate mesogen axis and flexible hydrocarbon chains that extend from it.

3. A nonlinear liquid crystal



Many liquid crystal polymers tend to exhibit multiple mesophases at different pressures and temperatures [57]. When heated, these polymers will go through multiple first-order transitions. Such transitions are from more ordered to less ordered arrangements. This is referred to as the **clearing temperature** with the last one resulting in isotropic melts.

A lyotropic liquid crystalline aromatic polyamide, sold under the trade name of Kevlar, is an example of such a polymer that is available commercially:

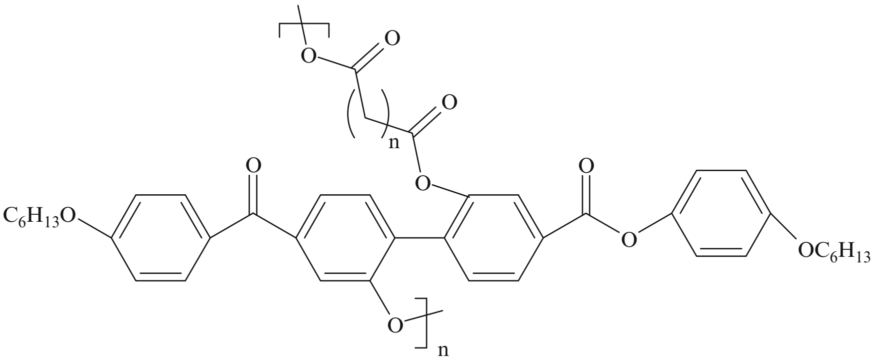


Kevlar

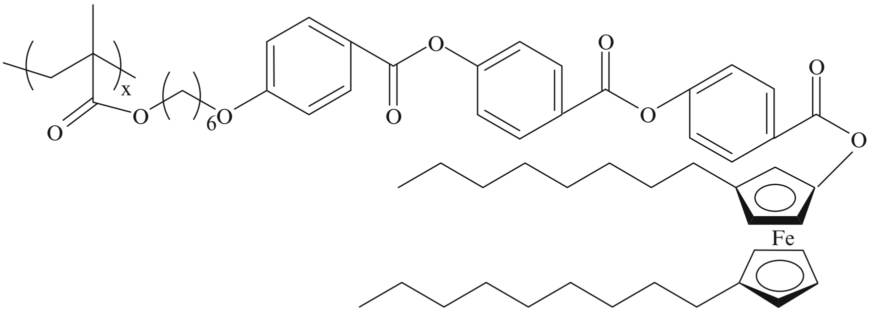
The polyamide forms liquid crystals in sulfuric acid solution from which it is extruded as a fiber. After the solvent is removed, the remaining fiber possesses greater uniform alignment than would be obtained by mere drawing. This results in superior mechanical properties.

There are polymers, however, that exhibit liquid crystalline behavior, but are very high melting and insoluble in most common organic solvents. This is a drawback, because such materials are hard to process.

A preparation of new liquid crystal polymers with bilaterally linked mesogens in main-chain was reported [57]. Such materials exhibit biaxial fluctuation in the nematic phase. This is interesting because most commonly encountered polymeric liquid crystals have mesogens linked at their ends to the polymer backbone by flexible spacers. On the other hand, liquid crystal polymers with mesogens linked bilaterally by flexible spacers are not common and only a few examples were reported [58]. One such material can be illustrated as follows:



It was also shown that it is possible to synthesize polymethacrylate liquid crystal polymers with mesomorphic properties that contain ferrocenes with two flexible chains at the 1,1′-positions [59]. Based on dilatometric measurements, a head-to-tail molecular arrangement of the monomeric units occurs within the smectic A phase. Because of special electrochemical properties of ferrocene, these materials are of interest for developing electroactive mesomorphic polymers. The structure of the polymer can be shown as follows [59]:



Finkelmann reported synthesis of a novel cross-linked smectic-C main-chain liquid-crystalline elastomer that was formed by polycondensation of vinyloxy-terminated mesogens, tetramethyldisiloxane, and pentamethyl-pentaoxapentasilicane. The introduction of the functional vinyloxy group allows the synthesis of well-defined networks with good mechanical properties due to elimination of side reactions as in the case of vinyl groups [60].

Large amplitude oscillatory shear is frequently capable of generating macroscopic alignment from an initially random orientation distribution in ordered polymer fluids. Berghardt and coworkers [61] reported that by combined rheological and in situ synchrotron X-ray scattering to investigate of such induced alignment in smectic side-groups *pf* liquid crystalline polymers. In all cases, they found that shear promotes anisotropic orientation states in which the lamellar normal tends to align along the vorticity direction of the shear flow (“perpendicular” alignment). Rheological measurements of the dynamic moduli by them revealed that large amplitude shearing in the smectic phase causes a notable decrease in the modulus. They also observed that increasing strain promotes higher degrees of orientation, while increasing molecular weight impedes development of smectic alignment.

Ahn et al. reported [62] preparation of a smetic liquid crystalline elastomer with shape memory properties. Shape memory polymeric materials can recover their equilibrium, permanent shapes from nonequilibrium, temporary shapes as a result of external stimuli, like heat or light. Such materials have application in medical practice. Main-chain polynorbornenes were linked with three different side-chains, cholesterol, poly(ethylene glycol), and butylacrylate.

2.5 Orientation of Polymers

There is no preferred direction or arrangement in the manner in which the macromolecules align themselves in a polymeric mass during crystallization. If, however, after crystallization an external stress is applied, the crystalline material undergoes a rearrangement. From the X-ray diffraction patter it is surmised that the chains realign themselves in the direction of the applied stress. Polymeric films and fibers usually show considerable increase in strength in the direction of that stress. Oriented fibers are considerably stronger along their length then perpendicularly to them. Generally, if the degree of crystallinity in crystalline polymers is well developed prior to the drawing, the process does not change the amount of crystallinity appreciably.

The orientation in the direction of applied stress occurs also in amorphous materials. The amorphous polymers, like the crystalline ones, also exhibit increased strength in the direction of orientation. If there is a small amount of crystallinity in polymers, the crystallinity often increases as a result of cold drawing.

Orientation of fibers and films is generally carried out above the glass transition temperature. At the same time, there usually is a desired limit on T_m. Thus it is preferred that the crystalline melting temperature does not exceed 300°C.

2.6 Solutions of Polymers

Polymers usually dissolve in two stages. First the materials tend to swell and form gels. The gels then tend to disintegrate into true solutions. Agitation only speeds up the process in the second stage. Chains held together by crosslinks will only swell. Crystallinity or strong hydrogen bonding might also keep some polymeric materials from dissolution and the materials only swell.

Some general rules about polymer solubility are:

(a) Solubility is favored by chemical and structural similarity between the solvent and the polymer.
(b) Solubility of the polymer tends to decrease with an increase in molecular weight.

When a polymer dissolves, the free energy of solution, ΔF is negative, while the entropy change, ΔS is positive, because of increased conformational mobility of the polymer. The magnitude of the enthalpy of solution determines whether ΔF is positive or negative. The heat of mixing, ΔH_{mix} for binary systems was suggested to be related to the concentration and energy parameters by the expression [7]:

$$\Delta H_{mix} = V_{mix}[(\Delta E_1/V_1)^{0.5} - (\Delta E_2/V_2)^{0.5}]^2\Phi_1\Phi_2$$

where V_{mix} is the total volume of the mixture, the molar volumes of the two components are, V_1 and V_2, respectively, and Φ_1 and Φ_2 are their volume fractions. The energies of vaporization are ΔE_1 and ΔE_2, while the ***cohesive densities*** (energy required to remove a molecule from its nearest neighbor) are $\Delta E_1/V_1$ and $\Delta E_2/V_2$.

2.6.1 Radius of Gyration

In solution, polymeric chains can form different conformations, depending upon the solvent. When the solvent is such that the chains are fully solvated, they are relatively extended and the molecules are randomly coiled. The polymer–solvent interaction forces determine the amount of space that the molecular coil of the polymer occupies in solution. While quite extended in a good solvent, if the solvent is a “poor” one, the chains are curled up. A measure of the size of the polymer molecule in solution, or the amount of space that a polymer molecule occupies in solution is determined as ***radius of gyration***., or ***root mean square radius of gyration***, S. Qualitatively, it is the average distance of the mass of the molecule from the center of its mass (from its center of gravity). The following equation

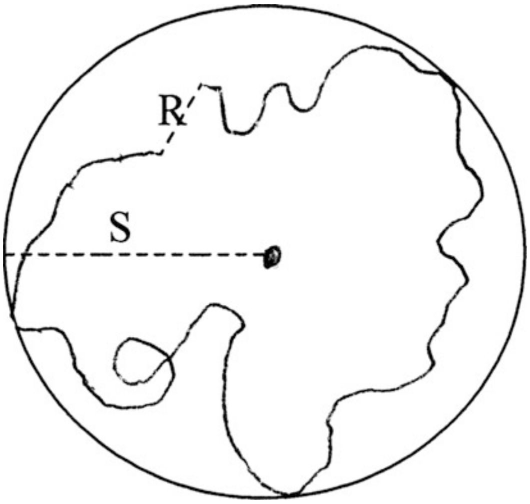


Fig. 2.16 Illustration of a molecular coil

defines this relationship [7]. To put it in other words, it is the square of the distances between various masses and the center of the mass:

$$S^2 = \sum_i m_i {s_i}^2 \Big/ \sum_i m_i$$

$$S^2 = \left\{ \sum ms^2 \right\}_{\text{av.}} (1/Nm)$$

where m is the mass associated with each of the N chain bonds, and S is the vector distance from the center of the mass to the terminal chain bond. The size of randomly coiled polymer molecules is commonly designated by the root-mean square distance between the ends, R^2. A molecular coil is illustrated in Fig. 2.16.

The distance between the chain ends is often expressed in terms of ***unperturbed dimensions*** (S_0 or R_0) and an ***expansion factor*** (α) that is the result of interaction between the solvent and the polymer

$$S^2 = {S_0}^2 \alpha^2 \quad \text{and} \quad R^2 = {R_0}^2 \alpha^2$$

The unperturbed dimensions refers to molecular size exclusive of solvent effects. It arises from intramolecular polar and steric interactions and free rotation. The expansion factor is the result of solvent and polymer molecule interaction. For linear polymers, the square of the radius of gyration is related to the mean-square end-to-end distance by the following relationship:

$$\overline{S}^2 = \overline{R}^2/6$$

This follows from the expansion factor, α is greater than unity in a good solvent where the actual "perturbed dimensions" exceed the unperturbed ones. The greater the value of the unperturbed dimensions the better is the solvent. The above relationship is an average derived at experimentally from numerous computations. Because branched chains have multiple ends it is simpler to describe them in terms of the radius of gyration. The volume that a branched polymer molecule occupies in solution is smaller than a linear one, which equals it in molecular weight and in number of segments.

The volume that these molecules occupy in solution is important in determinations of molecular weights It is referred to as the ***hydrodynamic volume***. This volume depends upon a variety of factors.

These are interactions between the polymer molecule and the solvent, chain branching, conformational factors arising from polarity, restricted rotation due to resonance, and the bulk of substituents. The above, of course, assumes that the polymer molecules are fully separated from each other.

2.6.2 The Thermodynamics of Polymer Solutions

Solutions of polymers deviate to a great extent from Raoult's law, except at extreme dilution. In extremely dilute solutions the ideal behavior is approached as an asymptotic limit. These deviations arise largely from small entropies of mixing. That is mostly due to the large difference in size between the solute and the solvent. The change in the ***entropy of mixing***, according to ***Flory–Huggins theory*** of polymer solutions [63] is:

$$\Delta S = -k(N_1 \ln v_1 + N_2 \ln v_2)$$

where subscript 1 denotes the solvent and subscript 2 the solute. v_1 and v_2 are ***volume fractions***. They are defined as follows

$$v_1 = N_1/(N_1 + xN_2)$$

$$v_2 = xN_2/(N_1 + xN_2)$$

where x is the heat of mixing. The change in the heat content of mixing of polymer solutions is similar to that of other solutions

$$\Delta H = x_1 kTN_1 v_2$$

where x_1 characterizes the internal energy per solvent molecule. The change in free energy of mixing, according to Flory–Huggins [63], is

$$\Delta F = kT(N_1 \ln v_1 + N_2 \ln v_2 + x_1 N_1 v_2)$$

The Flory–Huggins treatment overlooks the fact that dilute solutions of polymers consist of domains or clusters of polymeric chains that are separated by regions of pure solvent that is free from the solute. **Flory–Krigbaum** treatment assumes a model of dilute polymeric solutions where the polymeric clusters are approximately spherical and their density reaches a maximum at their centers and decreases in an approximately Gaussian function away from the center. The volume that is occupied by the segments of each molecule excludes the volumes of all other molecules. Long range intramolecular interactions take place within such excluded volumes. The thermodynamic functions of such interactions can be derived, such as the free energy change, the enthalpy change, and the entropy change:

$$\Delta F_1 = kT(k_1 - \Psi_1){v_2}^2$$

$$\Delta \overline{H}_1 = kTk_1{v_2}^2$$

$$\Delta S_1 = k\Psi_1{v_2}^2$$

where Ψ is an entropy parameter and can be expressed as,

$$k_1 - \Psi_1 = x_1 - 0.5$$

In addition, ***Flory temperature***, Θ is treated as a parameter, $\Theta = k_1T/\Psi_1$ At Θ temperature the partial molar free energy due to the solute–solvent interaction is assumed to be zero and deviations from ideality (ideal solution) become zero. What this means is that as the temperature of the solution of a polymer approaches Θ, the solvent becomes increasingly poorer and the excluded volume effect becomes smaller and approaches zero with the molecules interpenetrating one another with zero net interaction. The solvent is referred to as a Θ, solvent. Below Θ temperature the polymer molecules attract each other, the excluded volume is negative, and the polymer precipitates. This can be expressed as [63]:

$$\Psi_1 - k_1 = \Psi_1(1 - \Theta/T) = 0.5 - x_1$$

When the chains are extended, their conformations may be considered as being determined by equilibrium between the forces of expansion due to excluded volume and the forces of contraction due to chain segments expanding into less probable conformations. Based on random flight statistics, the chains are extended linearly by a factor α over their dimensions. The actual root-mean-square end-to-end distance is equal to $\alpha({R_0}^2)^{0.5}$. The change in the elastic part of free energy is

$$\Delta F_{\mathrm{el}} = kT[1.5(\alpha^2 - 1) - \ln \alpha^2]$$

where the parameter α can be expressed in terms of thermodynamic quantities:

$$\alpha^5 - \alpha^3 = 2C_{\mathrm{m}}\Psi_1(1 - \Theta/T)M^{0.5}$$

In the above equation, C_{m} represents a combination of molecular and numerical constants. Based on the above equation, at Θ temperature $\alpha = 1$. It has been stated that the Flory–Krigbaum treatment must be treated with some reservations, because it predicts that α increases without limit with increasing molecular weight [63].

2.7 Molecular Weights and Molecular Weight Determinations

The physical properties of polymers are also related to their molecular weights. Melt viscosity, hot strength, solvent resistance, and overall toughness increase with molecular size. Table 2.4 illustrates the effect of molecular weights (size) upon physical properties of polyethylene [64].

2.7.1 Molecular Weight Averages

Random events govern the process of synthetic polymer formation, whether it is by a chain propagating process or by a step-growth reaction. The result is that the chains vary in lengths. (There are special methods available, however, in chain-growth polymerizations that lead to formation of polymer molecules that are almost equal in length. This is discussed in subsequent chapters) As a result, most polymeric materials cannot be characterized by a single molecular weight, but instead must be represented by statistical averages [64]. These averages can be expressed in several ways. One way is to present an average as a ***number average*** molecular weight. It is the sum of all the molecular weights of the individual molecules present divided by their total number. Each molecule contributes equally to the average and can be obtained by averaging the measurements of all the colligative properties. If the total number of moles is N_i, the sum of these molecules present can be expressed as, ΣN_i. The total weight ω of a sample is similarly the sum of the weights of all the molecular species present

Table 2.4 Properties of low density polyethylene [48, 49]

DP	Molecular weight	Softening temperature (°C)	Physical state 25°C
1	28	−169 (mp)	Gas
6	170	−12 (mp)	Liquid
35	1,000	37	Grease
140	4,000	93	Wax
250	7,000	98	Hard wax
430	12,000	104	Plastic
750	21,000	110	Plastic
1,350	38,000	112	Plastic

$$\omega = \sum \omega_i = \sum M_i N_i$$

By dividing the total weight of the molecules by their total number we have the ***number average*** molecular weight,

$$\overline{M_\mathrm{n}} = \omega \Big/ \sum N_i = \sum M_i N_i \Big/ \sum N_i$$

Another way to express a molecular weight average is as a ***weight average***. Each molecule in such an average contributes according to the ratio of its particular weight to that of the total,

$$\overline{M_\mathrm{w}} = \sum M_i^2 N_i \Big/ \sum N_i$$

The above can be illustrated quite readily by imagining that a sample of a polymer consists of five molecules of molecular weights of 2,4,6,8, and 10, respectively. To calculate the number average molecular weight all the weights of the individual molecules are added. The sum is then divided by the total number of molecules in the sample (in this case 5):

$$\overline{M_\mathrm{n}} = 2/5 + 4/5 + 6/5 + 8/5 + 10/5 = 6$$

To calculate the weight average molecular weight of the above sample, the squares of each individual weight are divided by the total sum of their molecular weights, in this case it is 30:

$$\overline{M_\mathrm{w}} = 2^2/30 + 4^2/30 + 6^2/30 + 8^2/30 + 10^2/30 = 7.33$$

$\overline{M_\mathrm{w}}$ is more sensitive to the higher molecular weight species, while $\overline{M_\mathrm{n}}$ is sensitive to the lower ones. This can be seen by imagining that equal weights of two different sizes of molecules are combined, $M_1 = 10{,}000$ and $M_2 = 100{,}000$. The combination would consist of ten molecules of M_1 and one molecule of M_2. The weight average molecular weight of this mixture is ($10^8/2 \times 10^5 + 10^{10}/2 \times 10^5$) = 55,000 while the number average molecular weight is only 18,182. If, however, the mixture consists of an equal number of these molecules, then the weight average molecular weight is 92,000 and the number average molecular weight is 55,000.

The ratio of the weight average molecular weight to the number average molecular weight is important because it affects the properties of polymers. This ratio is called the ***molecular weight distribution***:

$$\text{Molecular weight distribution} = \overline{M_\mathrm{w}}/\overline{M_\mathrm{n}}$$

When all macromolecular species are of the same size, the number average molecular weight is equal to the weight average molecular weight. On the other hand, the greater the distribution of molecular sizes, the greater is the disparity between averages. The ratio of this disparity, M_w/M_n is a measure of ***polymeric dispersity***. A ***monodisperse*** polymer has a ratio of:

$$M_w/M_n = 1$$

In all synthetic polymers and in many naturally occurring ones the weight average molecular weight is greater than the number average molecular weight. Such polymers are ***polydisperse***.

Two samples of the same polymer equal in weight average molecular weight may exhibit different physical properties, if they differ in the molecular weight distributions. Molecular weight distribution can affect elongation, relaxation modulus, tensile strength, and tenacity of the materials [65]. An additional average molecular weight that is obtained with the aid of ultracentrifugation is referred to as sedimentation average molecular weight, or Z-average molecular weight, M_z This was more often used in the past, particularly with naturally occurring polymeric materials. It is not used, however, as much today.

$$\overline{M_z} = \sum M_i{}^3 N_i \Big/ \sum M_i{}^2 N_i$$

In solutions of polymers the viscosities are more affected by the long chains than by the short ones. A correlation of the viscosity of the solution to the size of the chains or to molecular weight of the solute, allows an expression of a ***viscosity average*** molecular weight:

$$\overline{M_\eta} = \left(\sum M_i{}^{\beta+1} N_i \Big/ \sum M_i N_i\right)^{1/\beta}$$

where, β is a constant., usually less than unity. When $\beta = 1$, then M_η becomes equal to M_w. Actually, though, the values of M_η are usually within 20% of the weight average molecular weights. For polydisperse polymers M_w is larger than M_η and M_η in turn is larger than M_n.

Most of the methods for determining the molecular weights and sizes of polymers (with the exception of small-angle neutron scattering) require dissolving the polymers in proper solvents first. The measurements are then carried out on dilute solutions.

Solution viscosities of linear polymers relate empirically to their molecular weights. This is used in various ways in industry to designate the size of polymers. The values are obtained by measuring the efflux time t of a polymer solution through a capillary. It is then related to the efflux time t_o of pure solvent. Typical viscometers, like those designed by Ubbelohde, Cannon–Fenske, (shown in Fig. 1.3), and other similar ones are utilized and measurements are carried out in constant temperature baths. The viscosity is expressed in following ways:

Common name	Symbol	Definitions
1. Relative viscosity	η_{rel}	$\eta/\eta_o = t/t_o$
2. Specific viscosity	η_{sp}	$(\eta - \eta_o)/\eta_o = \eta_{rel} - 1 \propto (t - t_o)/t_o$
3. Reduced viscosity	η_{red}	$\eta_{sp}/C = \eta_{rel^{-1}}/CZ$
4. Inherent viscosity	η_i	$\ln \eta_{rel}/C$
5. Intrinsic viscosity	$[\eta]_{c\to 0}$	$(\eta_{sp}/C)_{c=0} = (\eta_i)_{c=0}$

2.7.2 Methods for Measuring Molecular Weights of Polymers

To determine the intrinsic viscosity, both inherent and reduced viscosities are plotted against concentration (C) on the same graph paper and extrapolated to zero. If the intercepts coincide then this is taken

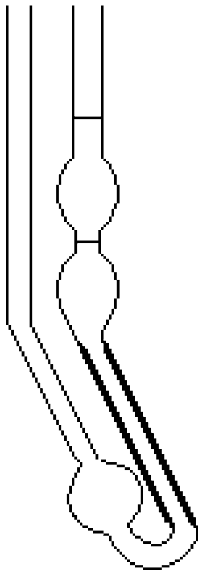


Fig. 2.17 Cannon–Fenske capillary viscometer

as the intrinsic viscosity. If they do not, then the two intercepts are averaged. The relationship of intrinsic viscosity to molecular weight is expressed by the Mark–Houwink–Sakurada equation [66]:

$$[\eta]_{c=0} = K\overline{M}_{\eta}^{\alpha}$$

where K and a are constants. Various capillary viscometers are available commercially. Figure 2.17 illustrates a typical capillary viscometer.

The logarithms of intrinsic viscosities of fractionated samples are plotted against log M_w or log M_n. The constants a and K of the Mark–Houwink–Sakurada equation are the intercept and the slope, respectively, of that plot. Except for the lower molecular weight samples, the plots are linear for linear polymers. Many values of K and a for different linear polymers can be found in the literature [66].

Actually, the Mark–Houwink–Sakurada equation applies only to narrow molecular weight distribution polymers. For low molecular weight polydisperse polymers this equation is useful, because the deviations due to chain entanglement are still negligible. On the other hand, chain entanglement in high molecular weight polydisperse polymers affects viscosity and this equation does not really apply.

The determinations of molecular weights of polymers rely, in most cases, upon physical methods. In some special ones, however, when the molecular weights are fairly low, chemical techniques can be used. Such determinations are limited to only those macromolecules that possess only one functional group that is located at the end of the chain ends. In place of the functional group, there may be a heteroatom. In that case, an elemental analysis might be sufficient to determine the molecular weight. If there is a functional group, however, a reaction of that group allows calculating the molecular weight. Molecular weights above 25,000 make chemical approaches impractical. In chemical determination each molecule contributes equally to the total. This determination, therefore, yields a number average molecular weight. With the development of gel permeation chromatography (discussed below), this method is hardly ever used today.

There are various physical methods available. The more prominent ones are ebullioscopy, cryoscopy, osmotic pressure measurements, light scattering, ultracentrifugation, and gel permeation chromatography (also called size exclusion chromatography). All these determinations are carried out on solutions of the polymers. Also, all, except gel permeation chromatography, require that the results

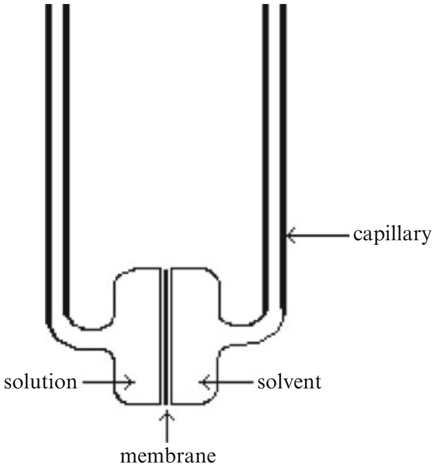


Fig. 2.18 Membrane osmometer

of the measurements be extrapolated to zero concentrations to fulfill the requirements of theory. The laws that govern the various relationships in these determinations apply only to ideal solutions. Only when there is a complete absence of chain entanglement and no interaction between solute and solvent is the ideality of such solutions approached. A brief discussion of some techniques used for molecular weight determination follows

Ebullioscopy, or boiling point elevation, as well as ***cryoscopy***, or freezing point depression, are well-known methods of organic chemistry They are the same as those used in determining molecular weights of small molecules. The limitation to using both of these methods to determine the molecular weight of macromolecules is that ΔT_b and ΔT_f become increasingly smaller as the molecular sizes increase. The methods are limited, therefore, to the capabilities of the temperature sensing devices to detect very small differences in temperature. This places the upper limits for such determinations to somewhere between 40,000 and 50,000. The thermodynamic relationships for these determinations are:

$$\begin{array}{ll} [\Delta T_{\mathrm{b/c}}]_{c\to 0} = RT^2/\rho\Delta H_{\mathrm{b}}M & [\Delta T_{\mathrm{f/c}}]_{c\to 0} = RT^2/\rho\Delta H_{\mathrm{f}}M \\ \text{boiling point rise elevation} & \text{freezing point depression} \end{array}$$

The above two determinations, because each molecule contributes equally to the properties of the solutions, yield number average molecular weights. How much this technique is used today is hard to tell.

A method that can be used for higher molecular weight polymers is based on ***osmotic pressure measurements***. It can be applied to polymers that range in molecular weights from 20,000 to 500,000 (some claim 1,000,000 and higher). The method is based on van't Hoff's law. When a pure solvent is placed on one side of a semi-permeable membrane and a solution on the other, pressure develops from the pure solvent side. This pressure is due to a tendency by the liquids to equilibrate the concentrations. It is inversely proportional to the size of the solute molecules. The relationship is as follow:

$$\overline{M}_{\mathrm{n}} = RT/(\pi/C)_{C=0} + A_2C$$

where π is the osmotic pressure, C is the concentration, T is temperature, and R is the gas constant, A_2 is a measure of interaction between the solvent and the polymer (second viral coefficient).

A *static* capillary osmometer is illustrated in Fig. 2.18. Rather than rely on the liquid to rise in the capillary on the side of the solution in response to osmotic pressure, as is done in the static method, a ***dynamic equilibrium*** method can be used. Here a counter pressure is applied to maintain equal levels of the liquid in both capillaries and prevents flow of the solvent. Different types of dynamic membrane osmometers are available commercially. The principle is illustrated in Fig. 2.19.

Fig. 2.19 Schematic of a high speed osmometer (from ref [68])

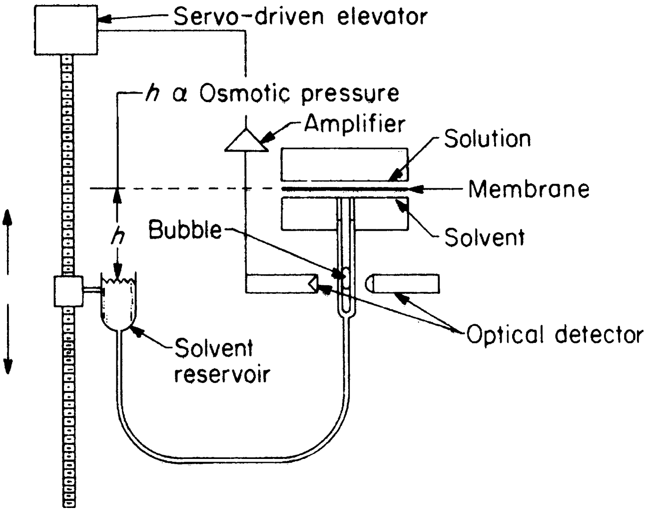
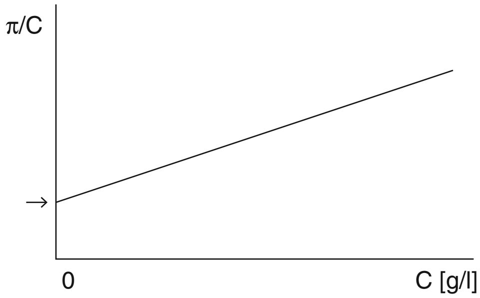


Fig. 2.20 Extrapolation to zero concentration



The results obtained from either method must still be extrapolated to zero concentration for van't Hoff's law to apply. Such extrapolation is illustrated in Fig. 2.20. Because all molecules contribute equally to the total pressure, osmotic pressure measurements yield a number average molecular weight.

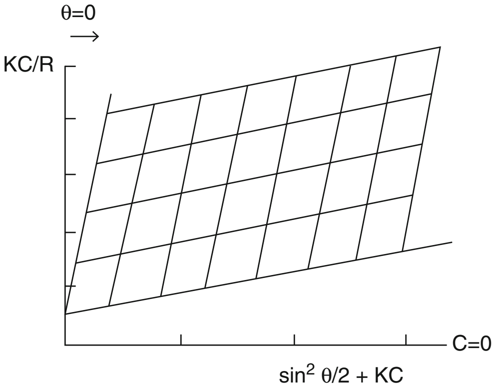
Light scattering measurement is a technique for determining the weight average molecular weight. When light passes through a solvent, a part of the energy of that light is lost due to absorption, conversion to heat, and scattering. The scattering in pure liquids is attributable to differences in densities that result from finite nonhomogenuities in the distribution of molecules within adjacent areas. Additional scattering results from a presence of a solute in the liquid. The intensity or amplitude of that additional scattering depends upon concentration, the size, and the polarizability of the solute plus some other factors. The refractive index of pure solvent and a solution is also dependent upon the amplitude of vibration. The turbidity that arises from scattering is related to concentration:

$$\text{turbidity}\ \tau = \sum \tau_1 - H \sum C_i M_i = H_c \overline{M_w}$$

$$H = 32\pi^3 n_o^{\,2} (\mathrm{d}n/\mathrm{d}c)^2 / 3\lambda^4 N_o$$

where n_o is the refractive index of the solvent, n is the refractive index of the solution, λ is the wavelength of the incident light, N_o is Avogadro's number, and c is the concentration. The $\mathrm{d}n/\mathrm{d}c$ relationship is obtained by measuring the slope of the refractive index as a function of concentration. It is constant for a given polymer, solvent, and temperature and is called the ***specific refractive increment***.

Fig. 2.21 A typical Zimm plot



Because scattering varies with different angles from the main beam of light, the results must be extrapolated to zero concentration and zero angle of scattering. This is done simultaneously by a method developed by Zimm. A typical Zimm plot is illustrated in Fig. 2.21.

A very popular technique for determining molecular weights and molecular weight distributions is ***gel permeation chromatography***. It is also called size exclusion chromatography [69, 70]. The procedure allows one to determine M_w and M_n, and the molecular weight distribution in one operation. The procedure resembles HPLC. It separates molecules according to their hydrodynamic volumes or their effective sizes in solutions. The separation takes place on one or more columns packed with small porous particles. As the solution travels down the columns, there is retention of the polymer molecules by the pores of the packing. It was postulated in the past that the separation that takes place by molecular sizes is due to smaller molecules diffusing into all the pores while the larger ones only into some of the pores. The largest molecules were thought to diffuse into none of the pores and pass only through the interstitial volumes. As a result, polymer molecules of different sizes travel different distances down the column. This means that the molecules of the largest size (highest molecular weight) are eluted first because they fit into the least number of pores. The smallest molecules, on the other hand, are eluted last because they enter the greatest number of pores and travel the longest path. The rest fall in between. The process, however, is more complex than the above postulated picture. It has not yet been fully explained. It was found, for instance, that different gels display an almost identical course in the relation of dependence of V_R (retention volume) to the molecular weight. Yet study of the pores of different gels show varying cumulative distributions of the inner volumes. This means that there is no simple function correlating the volume and/or the size of the separated molecules with the size and distribution of the pores [69]. Also, the shape of the pores that can be inferred from the ratio of the area and volume of the inner pores is very important [70]. Different models were proposed to explain the separation phenomenon. These were reviewed thoroughly in the literature. They are beyond the scope of this book.

As indicated above, the volume of the liquid that corresponds to a solute eluting from the columns is called the retention volume or elution volume (V_R). It is related to the physical parameters of the column as follows:

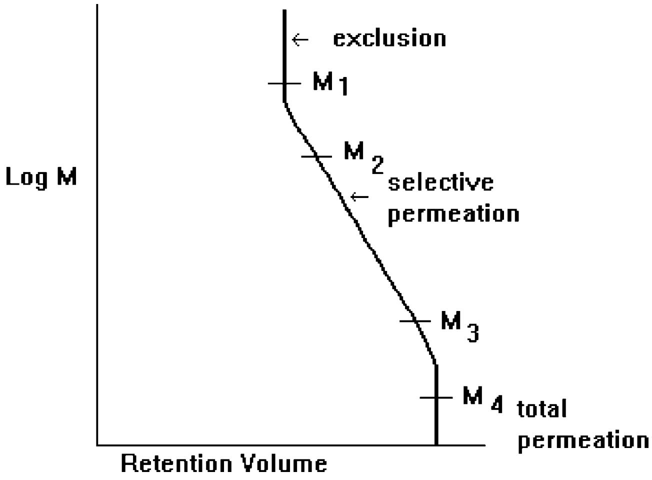
$$V_R = V_o + KV_1$$

where, V_o = the interstitial volume of the column(s)
K = the distribution coefficient
V_1 = the internal solvent volume inside the pores

The total volume of the columns is V_T that is equal to the sum of V_O and V_1. The retention volume can then be expressed as follows:

$$V_R = V_O(1 + K) + KV_T$$

Fig. 2.22 Molecular weight calibration curve for gel permeation chromatography



From the earlier statement it should be clear that polymer fractionation by gel permeation chromatography depends upon the spaces the polymer molecules occupy in solution. By measuring, experimentally, the molecular weights of polymer molecules as they are being eluted one obtains the molecular weight distribution. To accomplish this, however, one must have a chromatograph equipped with dual detectors. One must detect the presence of polymer molecules in the effluent. The other one must measure their molecular weights. Such detectors might be, for instance, a refractive index monitor and a low angle laser light scattering photogoniometer to find the absolute value of M.

Many molecular weight measurements, however, are done on chromatographs equipped with only one detector that monitors the presence of the solute in the effluent. The equipment must, therefore, be calibrated prior to use. The relationship of the ordinate of the chromatogram, commonly represented by $F(V)$, must be related to the molecular weight. This relationship varies with the polymer type and structure. There are three methods for calibrating the chromatograph. The first, and most popular one, makes use of narrow molecular weight distribution reference standards. The second one is based upon a polydisperse reference material. The third one assumes that the separation is determined by molecular size. All three methods require that an experimentally established calibration curve of the relationship between the molecular size of the polymer in solution and the molecular weight be developed. A chromatogram is obtained first from every standard sample. A plot is then prepared from the logarithms of the average weights against the peak retention volumes (V_R). The values of V_R are measured from the points of injection to the appearances of the maximum values of the chromatograms. Above M_1 and below M_4 there is no effective fractionation because of total exclusion in the first place and total permeation in the second case. These are the limits of separation by the packing material.

To date the standard samples of narrow molecular weight distribution polymers that are available commercially are mainly polystyrenes. These samples have polydispersity indexes that are close to unity and are available over a wide range of molecular weights. For determining molecular weights of polymers other than polystyrene, however, the molecular weights obtained from these samples would be only approximations. Sometimes they could be in error. To overcome this difficulty a ***universal calibration method*** is used. The basis for universal calibration is the observation [51] that the multiplication products of intrinsic viscosities and molecular weights are independent of the polymer types. Thus, $[\eta]M$ is the ***universal calibration parameter***. As a result, a plot of log $([\eta]M)$ vs. elution volume yields a curve that is applicable for many polymers. The log $([\eta]M)$ *for* ***a given column (or columns), temperature, and elution volume*** is assumed to be a constant for all polymers. This is illustrated in Fig. 2.22.

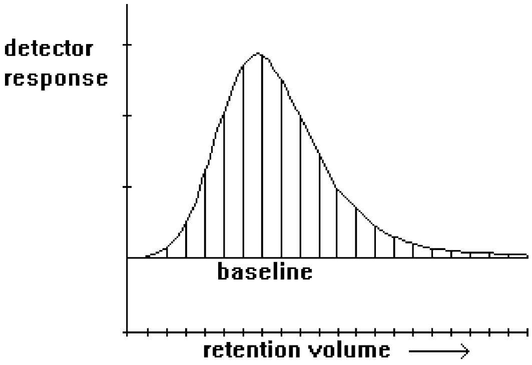


Fig. 2.23 A typical digitized gel permeation chromatogram

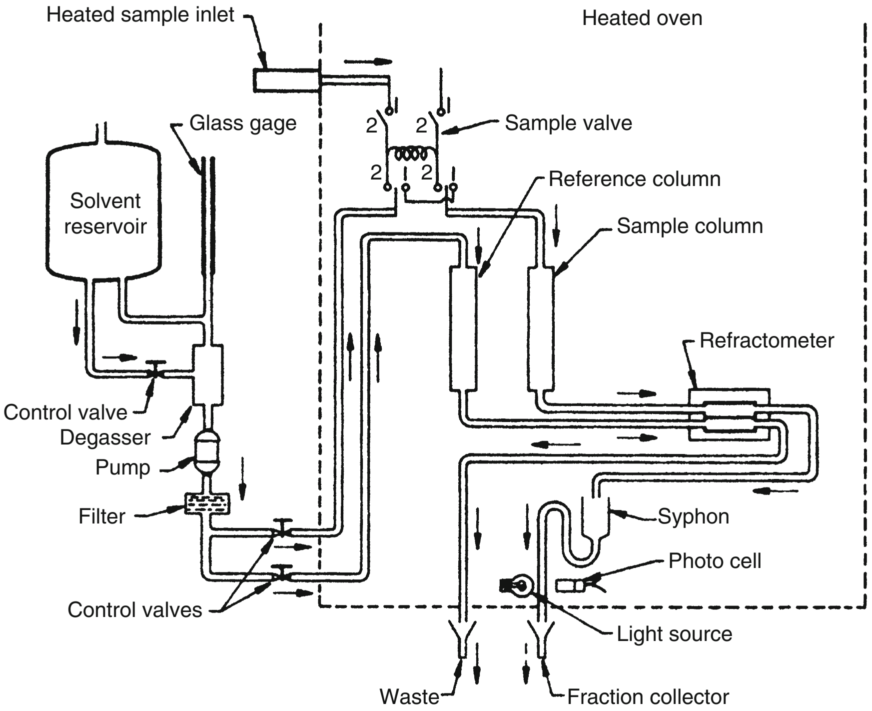


Fig. 2.24 Schematic illustration of gel permeation equipment (the illustration only shows one sample column. Several sample columns are often used) (from ref [68])

Numerous materials have been used for packing the columns. Semi rigid crosslinked polystyrene beads are available commercially. They are used quite frequently. Porous beads of glass or silica are also available. In addition, commercial gel permeation equipment is usually provided with automatic sample injection and fraction collection features. The favorite detectors are refractive index and ultraviolet light spectroscopic detectors. Some infrared spectroscopic detectors are also in use. Commercially available instruments also contain pumps for high-pressure rapid flow and are usually equipped with a microcomputer to assist in data treatment. Also, they come with a plotter in the equipment to plot the detector response as the samples are eluted through the column or columns. A typical chromatogram is illustrated in Fig. 2.23 and a schematic for the basic equipment is shown in Fig. 2.24. When polydisperse samples are analyzed, quantitative procedures consist of digitized chromatograms with indication of equally spaced retention volumes. These can be every 2.5 or 5.0 mL of volumes. The resultant artificial fractions are characterized by their heights h_i, their solute concentrations C_i, and by the area they occupy within the curve A_i. The cumulative polymer weight values is calculated according to:

$$I(V) = 1 \Big/ A_{\mathrm{T}} \sum A_i$$

After conversion of the retention volumes V_i into molecular weights (using the calibration curve), the molecular weights, M_{w}, M_{n}, and M_z can be calculated:

$$M_{\mathrm{n}} = \sum h_I \Big/ \left(\sum h_I / M_i \right); \quad M_{\mathrm{w}} = \sum h_i M_I \Big/ \sum h_i; \quad M_{\mathrm{z}} = \sum h_i M_i{}^2 \Big/ \sum h_i M_I$$

If the chromatogram is not equipped with a microcomputer for data treatment, one can easily determine results on any available PC. Programs for data treatment have been written in various computer languages. They are available from many sources.

Recently, there were several reports in the literature on combining size exclusion with high pressure liquid chromatography for more comprehensive characterization of polymers. Thus, Gray et al. reported that a combination of high pressure liquid chromatography with size exclusion chromatography allows comprehensive structural characterization of macromolecules [71].

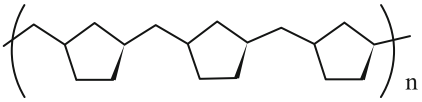
On the other hand, Chang et al. reported on using a modified form of high pressure liquid chromatography analysis, referred to as **interaction chromatography** for polymer characterization. The process utilizes enthalpic interaction of polymeric solutes with the stationary phase. Such interaction depends on both, the chemical composition and on molecular weight. It is claimed to be less sensitive to chain architecture and to offer superior resolution to SEC. The typical HPLC instrument is modified to precisely control the temperature of the column. The temperature of the column and the mobile phase is controlled by circulating a fluid through the column jacket from a programmable bath/circulator. The mobile and stationary phases require careful choices to adjust the interaction strength of the polymer solutes with the stationary phase so that the polymer solutes elute out in a reasonable elution time. The process depends upon variations of the column temperature for precise control of the solute retention in the isocratic elution mode. Mixed solvent system of a polar and a less polar solvent are often employed to adjust the interaction strength [72].

2.8 Optical Activity in Polymers

Optical activity in biopolymers has been known and studied well before this phenomenon was observed in synthetic polymers. Homopolymerization of vinyl monomers does not result in structures with asymmetric centers (The role of the end groups is generally negligible). Polymers can be formed and will exhibit optical activity, however, that will contain centers of asymmetry in the backbones [73]. This can be a result of optical activity in the monomers. This activity becomes incorporated into the polymer backbone in the process of chain growth. It can also be a result of polymerization that involves asymmetric induction [74, 75]. These processes in polymer formation are explained in subsequent chapters. An example of inclusion of an optically active monomer into the polymer chain is the polymerization of optically active propylene oxide. (See Chap. 5 for additional discussion). The process of chain growth is such that the monomer addition is sterically controlled by the asymmetric portion of the monomer. Several factors appear important in order to produce measurable optical activity in copolymers [76]. These are: (1) Selection of comonomer must be such that the induced asymmetric center in the polymer backbone remains a center of asymmetry. (2) The four substituents on the originally inducing center on the center portion must differ considerably in size. (3) The location of the inducing center must be close to the polymer backbone. (4) The polymerization reaction must be conducted at sufficiently low temperature to insure stereo chemical selectivity. An example is a copolymerization of maleic anhydride with optically active l-α-methylbenzyl vinyl ether. The copolymer exhibits optical activity after the removal of the original center of asymmetry [77].

An example of an asymmetric induction from optically inactive monomers is an anionic polymerization of esters of butadiene carboxylic acids with (*R*)-2-methylbutyllithium or with butyllithium complexed with (−)methyl ethyl ether as the catalyst. (This type of polymerization reaction is described in Chap. 4) The products, tritactic polymers exhibit small, but measurable optical rotations [78]. Also, when benzofuran, that exhibits no optical activity, is polymerized by cationic catalysts like aluminum chloride complexed with an optically active co catalyst, like phenylalanine, an optically active polymer is obtained [77].

By contrast, an example of formation of enantioselective polymer from achiral monomers, where the chirality is inherent in the main chain is polymerization of 1,5-hexadiene with an optically active catalyst [77]. The catalyst precursors are (*R*,*R*) or (*S*,*S*)-[ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)zirconium (1,1′-by-1-naphtholate). The product is an optically active version of poly(methylene-1,3-cyclopentane):



This polymer is highly isotactic and contains 72% *trans* rings.

It was also observed that conjugated polymers that are also electrical conductors (see Chap. 10) exhibit optical activity that depends critically on their structural organization [78]. Thus, strong chiroptical properties can be obtained from substituted polythiophene [79] (Chap. 10) with optically active side chains, especially when the monomers are coupled within the polymer in a regioregular head-to-tail fashion. Actually, optical activity of these materials is only found when the polymers are aggregated at low temperature, in poor solvent, or in solution cast films. This contrasts with other optically active polymers, like polypeptides, poly(l-alkynes) and polyisocyanates that show an optically active conformation of the main chain in the absence of supramolecular association.

In addition, it was shown that a repetitive inversion of optical activity in films can be obtained by warming and cooling cycles, where the cooling rate determines the handedness of the associates [78]. A similar result concerning inversion of chirality has been found in solution, depending on the composition of a binary solvent mixture.

Review Questions

Section 2.1

1. What are the secondary bond forces that influence the physical properties of macromolecules?

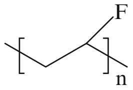
Section 2.1.1

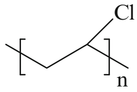
1. Explain and illustrate dipole–dipole interactions in polymers and how do they affect the properties of polymeric materials. Can you give other examples?

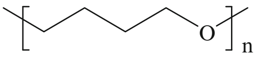
Section 2.1.2

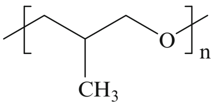
1. What are the induction forces?
2. Explain what type of chemical structures and chemical bonds in the backbones of the polymeric chains stiffen them and what type flexibilizes (or "softens") them.
3. How do the pendant groups affect the melting points of polymers?
4. Does copolymerization raise or lower the melting point of a polymer?
5. Which polymer, A or B, would have a higher melting point? Explain

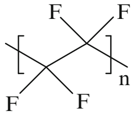
A B

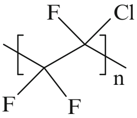












6. Explain what the induction forces of polymers and how they affect the physical properties of these materials?
7. Illustrate and explain why nylon 11 melts approximately 50°C higher than linear polyethylene
8. Why does poly(ethylene adipate) melt at a considerably lower temperature than does poly (ethylene terephthalate)?
9. What type of bonds in the polymeric chain tend to soften them?
10. Does copolymerization lower or raise the melting temperature of polymers? Explain

Section 2.2

1. Describe an amorphous state of polymers

Section 2.2.1

1. Describe the glassy state of polymers
2. What is the second order transition temperature? Are the send order transition temperatures of polymers absolute values or do they vary depending upon various conditions? Explain.
3. How can the transition to a glassy state be observed?
4. Explain structural recovery and the asymmetry of structural recovery.
5. What equation describes the asymmetry of structural recovery?
6. What is the Flory–Fox equation and what is it limited to?

Section 2.2.2

1. Explain the phenomenon of elasticity.
2. What natural structural arrangement of polymeric chains leads to rubber elasticity.
3. What is meant by the negative coefficient of expansion?

Section 2.2.2.1

1. Write the equation for the reactive force of an elastomer and explain what each term represents and define an ideal elastomer.
2. What is the entropy of elasticity? What is it proportional to?
3. What is the relationship between the retractive force of an elastomer and its temperature?
4. Write the equation for the work done in stretching a chain of an ideal elastomer and explain what each term represents.
5. Write the equation for a free energy change of a stretched elastomer.
6. Write the equation for the average energy per (stretched) chain
7. What is the free energy change for a stretched elastomer? Explain.

Section 2.2.2.2

1. Define a Newtonian liquid and a Hookian ideal elastic solid, and an ideal elastomer.
2. What is meant by viscoelasticity?
3. Explain what is meant by a yield point and a Bingham Newtonian fluid.
4. How is the viscosity of a molten polymer related to its temperature?
5. How is shear stress defined mathematically?
6. What is a thixotropic liquid?
7. What is the relationship Newtonian viscosity of amorphous polymers and their chain length?
8. What is shear creep compliance equal to ?
9. Why are shear thinning and thixotropy two different phenomena? Explain
10. What relationship describes flow behavior of liquids that deviate from Newtonian flow?
11. Write the equation for shear-stress-relaxation modulus for viscous fluids. Explain
12. What are the two important quantities in behavior of polymeric liquids?
13. Describe two techniques for measuring the viscosity of molten polymers.

Section 2.3

1. How does crystallinity of polymers that are formed from the melt differ from that of small molecules?
2. What are the two ways that crystal growth can take place in polymeric materials?
3. What type of polymers tend to crystallize?
4. What is the typical size of polymeric crystals formed from the melt?
5. What is a fringed micelle or a fringed crystallite model?
6. What is the folded chain lamella? An adjacent-reentry model? A switchboard or a nonadjacent-reentry model?
7. What is drawn fibrilar morphology? What is vitrification?

8. What are spherulites? How are they observed?
9. Explain the difference between a crystallite formed from the melt and a polymer crystal formed from a dilute solution

Section 2.3.1

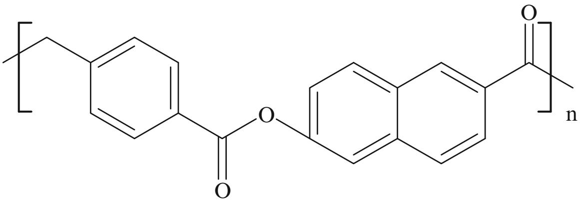
1. What are the three different interfacial free energies that are characteristics of crystals?
2. What equation described the dependence of the melting temperature of a polymer crystal upon its chain length? Explain and write the equation.
3. What is the first order transition temperature?

Section 2.3.2

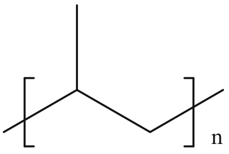
1. How can one obtain information on the kinetics of crystallization
2. What is the Avrami equation and what are its drawbacks?

Section 2.4

1. What are mesophases ?
2. What is anisotropic behavior?
3. What are lyotropic and thermotropic liquid crystals?
4. Explain nematic, smectic, and cholesteric liquid crystal arrangements.
5. Which of the two polymers would you expect to exhibit liquid crystalline behavior? Explain.



A



B

6. What is the difference between the main chain and side chain liquid crystals?

Section 2.5

1. What happens to the arrangement of the polymeric chains in films and fibers upon application of an external stress?
2. What is orientation and how does that benefit the properties of polymeric materials?

Section 2.6

1. What are the two stages of dissolution when a polymer dissolves in a solvent?
2. What is the heat of mixing of binary systems? Write equation.
3. What is the radius of gyration? Write equation
4. Define unperturbed dimensions and expansion factor

Section 2.6.1

1. What is the change in entropy of mixing, according to the Flory–Huggins theory? Explain and write the equation.
2. What is the change in the free energy of mixing according to the Flory–Huggings theory? Write equation.
3. What is the Flory temperature? write equation and explain what happens to a solution of a polymer below this temperature

Section 2.7

1. Define the degree of polymerization
2. What is the DP of polystyrene with molecular weight of 104,000 and poly(vinyl chloride) with molecular weight of 63,000?
3. What are the important features of chain-growth and step-growth polymerizations? Can you explain the difference between the two? Can you suggest an analytical procedure to determine by what mechanism a particular polymerization reaction takes place?
4. What is the DP of polystyrene with molecular weight of 104,000 and poly(vinyl chloride) with molecular weight of 630,000?
5. Explain the differences between thermosetting and thermoplastic polymers and define gel point.
6. Give the definitions of oligomer, telomer, and telechelic polymers
7. Why must statistical averages be used to express molecular weights of polymers?
8. What is number average molecular weight? What is the equation for number average molecular weight?
9. What is a weight average molecular weight? What is the equation for the weight average molecular weight?
10. In a mixture of two kinds of molecules there are ten of each in kind. The molecular weight of molecules A is 10,000 and the molecular weight of molecules B is 100,000. What is the number average molecular weight of the mixture and the weight average molecular weight?
11. What is the viscosity average molecular weight and how does it differ from the weight average molecular weight?
12. What is a molecular weight distribution? What is a monodisperse polymer and a polydisperse polymer?
13. What is the Mark–Houwink–Sakurada equation? Can you suggest a way to determine K and a constants experimentally for a given polymer?
14. Give the definitions and formulas for the relative viscosity, specific viscosity, reduced viscosity, inherent viscosity, and intrinsic viscosity.
15. Why is it necessary to extrapolate to zero (explain how this is done) in order to obtain intrinsic viscosity.
16. Discuss the various methods of molecular weight determination explain why a particular method yields a number of a weight average molecular weight, or, as in case of GPC, both.

Section 2.8

1. Discuss optical activity in polymers.

Recommended Reading

H. Sperling, *Introduction to Physical Polymer Science*, 2nd ed., Wiley, New York, 2006

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