

Solution Properties of Polymers

I. INTRODUCTION

In order to gain insight into the polymer dissolution process, let us briefly review the dissolution of low-molecular-weight (simple) substances. We know, for example, that while oil will not mix with water, an oil stain in clothing can be removed rather easily by using hydrocarbon solvents like naphtha. On the other hand, ordinary table salt, or sodium chloride, dissolves readily in water but not in gasoline. As will become evident presently, the physical phenomena associated with the solubilities of various substances in different solvents are intimately tied with the nature of the solutes and solvents. For example, in molecular crystals, the attractive forces are of the dipole–dipole or London dispersion type, which is relatively weak and therefore fairly easy to break apart. Consequently, this type of solid dissolves to an appreciable degree in nonpolar solvents, where the molecules are held together by London-type attractive forces also. However, crystals will not dissolve to any great extent in polar solvents since the strong attraction between the polar solvent molecules cannot be overcome by the much weaker solute–solvent interaction forces. By similar arguments, polar solutes and ionic solids are soluble only in polar solvents. They are insoluble in nonpolar solvents because the weak solute–solvent interaction is not strong enough to overcome the strong attractive forces between the solute molecules and hold them apart. In essence, therefore, when a solute dissolves in a solvent, solute–solute molecular contacts are replaced by solute–solvent contacts. Consequently, for solute particles to enter into solution, the solute–solvent forces of attraction must be sufficient to overcome the forces that hold the solid together.

It follows from the above discussion that polymers, by virtue of their macromolecular nature, will be soluble only in selected solvents. The polymer solution process is certainly more complex than that of simple compounds. The dissolution of both simple compounds and polymers depends on the nature of the solute and solvent, but in addition the dissolution of polymers is affected by the viscosity of the medium, polymer texture, and molecular weight. Dissolution of a polymer is necessarily slow and is a two-staged process: first, the solvent molecules diffuse into the polymer producing a swollen gel; second, the gel breaks down slowly forming a true solution. In some cases and depending on the nature of the polymer, only the first step occurs. However, if the polymer–polymer interaction forces can be overcome by polymer–solvent attraction, then the second stage will follow, albeit slowly. For example, unvulcanized rubber will dissolve in solvents in which vulcanized rubber will only swell. In other cases, materials with strong polymer–polymer intermolecular forces due to, say, cross-linking (phenolics), crystallinity (Teflon), or strong hydrogen bonding (native cellulose) will not dissolve in any solvent at ordinary temperatures and will exhibit only a limited degree of swelling.

II. SOLUBILITY PARAMETER (COHESIVE ENERGY DENSITY)

From thermodynamic considerations, it is possible to predict whether or not a given solute will be soluble in a given solvent using the relation:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (12.1)$$

where ΔG_m , ΔH_m , and ΔS_m are free energy, heat, and entropy of mixing, respectively. Solubility will occur if the free energy of mixing ΔG_m is negative. The entropy of mixing is believed to be always negative. Therefore, the sign and magnitude of ΔH_m determine the sign of ΔG_m . If we consider an ideal solution of two small spherical molecules with identical size and intermolecular forces, molecules of one type can replace neighbors with molecules of another type without changing the total energy of the system. This interchangeability of neighbors is the source of the configurational entropy term or the entropy of mixing ΔS_m . Since we are dealing with ideal conditions, the heat of mixing ΔH_m is zero

because the two types of molecules have the same force fields, and consequently, $\Delta G_m = -T\Delta S_m$. However, departure from ideality normally occurs because the intermolecular forces operative between similar and dissimilar molecules give rise to a finite heat of mixing. In this case, the energy of mixing associated with the formation of contact between two dissimilar molecules can be shown to be positive. Therefore, mixing is generally endothermic for nonpolar molecules in the absence of strong intermolecular attraction such as hydrogen bonding.

Using similar arguments, Hildebrand and Scott¹ showed that

$$\Delta H_m = V\phi_1\phi_2\left[\left(\frac{\Delta E_1^v}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2^v}{V_2}\right)^{1/2}\right]^2 \quad (12.2)$$

where V , V_1 , V_2 , are the volumes of the solution and components and the subscripts 1 and 2 denote the solvent and polymer, respectively. ΔE^v is the molar energy of vaporization and ϕ_1 and ϕ_2 are volume fractions. In terms of the heat of mixing per unit volume, Equation 12.2 becomes

$$\frac{\Delta H_m}{V} = \phi_1\phi_2\left[\left(\frac{\Delta E_1^v}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2^v}{V_2}\right)^{1/2}\right]^2 \quad (12.3)$$

The quantity $\Delta E/V$ is referred to as the cohesive energy density (CED): its square root is the solubility parameter (δ). Thus

$$\text{CED} = \frac{\Delta E}{V} = \delta^2 \quad (12.4)$$

Equation 12.3 may be rewritten:

$$\frac{\Delta H_m}{V} = \phi_1\phi_2[\delta_1 - \delta_2]^2 \quad (12.5)$$

To a first approximation and in the absence of strong intermolecular forces like hydrogen bonding, a polymer is expected to be soluble in a solvent if $\delta_1 - \delta_2$ is less than 1.7–2.0. Equation 12.5 is valid only when ΔH_m is zero or greater. It is invalid for exothermic mixing, that is, when ΔH_m is negative. Typical values of δ for various types of solvents are shown in Table 12.1. Values for some polymers were listed in Table 3.7. The magnitude of the enthalpy of mixing can be conveniently estimated from these tables.

Table 12.1 Values for Different Solvents

Solvent	δ	Solvent	δ	Solvent	δ
Poorly hydrogen bonded		Moderately hydrogen bonded		Strongly hydrogen bonded	
<i>n</i> -Pentane	7.0	Diethyl ether	7.4	2-Ethylhexanol	9.5
<i>n</i> -Heptane	7.4	Diisobutyl ketone	7.8	Methyl isobutyl carbinol	10.0
Apco thinner	7.8	<i>n</i> -Butyl acetate	8.5	2-Ethylbutanol	10.5
Solvesso 150	8.5	Methyl propionate	8.9	<i>n</i> -Pentanol	10.9
Toluene	8.9	Dibutyl phthalate	9.3	<i>n</i> -Butanol	11.4
Tetrahydronaphthalene	9.5	Dioxane	9.9	<i>n</i> -Propanol	11.9
<i>O</i> -Dichlorobenzene	10.0	Dimethyl phthalate	10.7	Ethanol	12.7
1-Bromonaphthalene	10.6	2,3-Butylene carbonate	12.1	Methanol	14.5
Nitroethane	11.1	Propylene carbonate	13.3		
Acetonitrile	11.8	Ethylene carbonate	14.7		
Nitromethane	12.7				

From Burrell, H. and Immergut B., in *Polymer Handbook*, Brandrup, J. and Immergut E.M., Eds., John Wiley & Sons, New York, 1967. With permission.

Table 12.2 Molar Attraction Constants, E (cal cm³)/mol

Group	E	Group	E
-CH ₃	148	NH ₂	226.5
-CH ₂ -	131.5	-NH-	180
>CH-	86	-N-	61
>C<	32	C> N	354.5
CH ₂ >	126.5	NCO	358.5
-CH<	121.5	-S-	209.5
>C<	84.5	Cl ₂	342.5
-CH< aromatic	117	Cl primary	205
-C< aromatic	98	Cl secondary	208
-O- ether, acetal	115	Cl aromatic	161
-O- epoxide	176	F	41
-COO-	326.5	Conjugation	23
>C-O	263	<i>cis</i>	-7
-CHO	293	<i>trans</i>	-13.5
(CO) ₂ O	567	six-membered ring	-23.5
-OH-	226	ortho	9.5
OH aromatic	171	meta	6.5
-H acidic dimer	-50.5	para	40

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In addition, the solubility parameter can be estimated from the molar attraction constants, E , using the structural formula of the compound and its density (Table 12.2). For a polymer:

$$\delta_2 = \frac{\rho \Sigma E}{M} \quad (12.6)$$

where ρ and M are the density and molecular weight, respectively, of the polymer repeating unit.

Example 12.1: Estimate the solubility parameters of the following polymers:

- Low-density polyethylene (LDPE)
- High-density polyethylene (HDPE)
- Polypropylene (PP)
- Polystyrene (PS)

Solution: From Equation 12.6,

Polymer	Repeating Unit	M	ρ	ΣE	δ
a. LDPE	-CH ₂ -CH ₂ -	28	0.92	$\frac{0.92[131.5 + 131.5]}{28}$	8.6
b. HDPE	-CH ₂ -CH ₂ -	28	0.95	$\frac{0.93[131.5 + 131.3]}{28}$	8.9
c. PP	-CH ₂ -CH- CH ₃	42	0.90	$\frac{0.90[131.5 + 86 + 148]}{42}$	7.8
d. PS	-CH ₂ -CH- Ⓢ	104	1.04	$\frac{1.04[131.5 + 86 + (5 \times 117) + 98]}{104}$	9.0

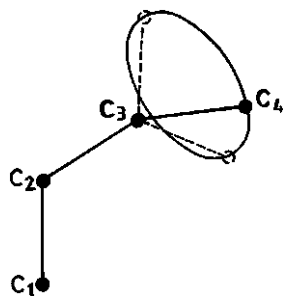


Figure 12.1 A segment of a polymer chain, showing four successive chain atoms. The first three of these define a plane, and the fourth can lie anywhere on the indicated circle perpendicular to and bisected by the plane.

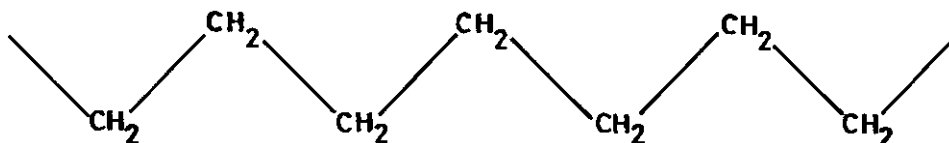


Figure 12.2 Fully extended chain with every carbon atom in *trans* location and in the same plane.

III. CONFORMATIONS OF POLYMER CHAINS IN SOLUTION

Molecules in the dissolved, molten, amorphous, and glassy states of macromolecules exist as random coils. This is a result of the relative freedom of rotation associated with the chain bonds of most polymers and the myriad number of conformations that a polymer molecule can adopt. As a consequence of the random coil conformation, the volume of a polymer molecule in solution is many times that of its segments alone. The size of the dissolved polymer molecule depends quite strongly on the degree of polymer-solvent contact. In a thermodynamically good solvent, a high degree of interaction exists between the polymer molecule and the solvent. Consequently, the molecular coils are relatively extended. On the other hand, in a poor solvent the coils are more contracted. Many properties of macromolecules are dictated by the random coil nature of the molecules. We now discuss briefly the conformational properties of polymer chains.

First, we need to develop a realistic physical picture of a polymer molecule. To do this, let us consider the properties of a single molecule in a dilute solution isolated from its neighbors by the molecules of the solvent. Let us consider initially a short segment of this molecule consisting only of four methylene groups, as shown in Figure 12.1. We define a plane by the first three carbon atoms C_1 to C_3 . Since there is free rotation about the C-C bond, the fourth carbon atom, C_4 , can be found in any position on the circle shown in the figure. Of course, some positions are more probable than others since absolutely free rotation about bonds is precluded by steric hindrance. Each successive atom on the chain can, in turn, occupy any random position on similar cycles based on the position of the preceding atom. It is easy to visualize, therefore, that for a molecule composed of thousands of atoms, the number of possible conformations is virtually limitless. One of these conformations is the fully extended chain, in which each successive carbon atom is coplanar and translocated with respect to the earlier atoms in the chain. The conventional formula for polymethylene expressed this configuration (Figure 12.2).

A. END-TO-END DIMENSIONS

Any physical property of a polymer molecule that depends on its conformation can ordinarily be expressed as a function of some sort of average dimension. The polymer dimension that is most often used to describe its spatial character is the displacement length, which is the distance from one end of the molecule to the other. For the fully extended chain, this quantity is referred to as the contour length. Given the extremely large number of possible conformations and number of chains, a statistical average, such as the root-mean-square end-to-end distance, $(\bar{r}_2)^{1/2}$, is required to appropriately express this quantity.

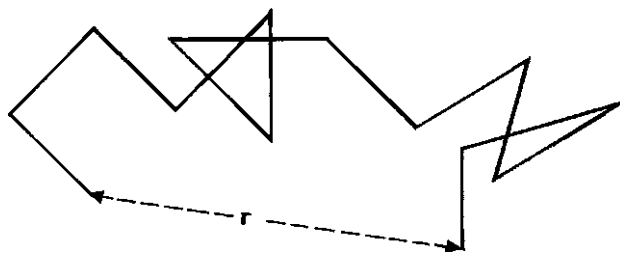


Figure 12.3 Freely jointed model of a polymer molecule with fixed and equal bond length and unrestricted value of bond angle.

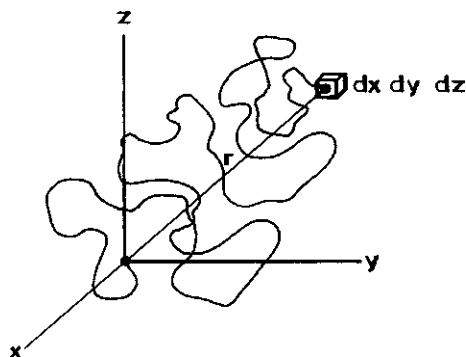


Figure 12.4 A highly schematic representation of a random-coil polymer chain, with one end at the origin of a coordinate system and the other in a volume element $dx dy dz$ at a distance $(x^2 + y^2 + z^2)^{1/2}$ from the origin.

Another way of expressing the effective size of a molecule is the radius of gyration, $(\bar{S}^2)^{1/2}$. This is the root-mean-square distance of the elements of the chain from its center of gravity. For linear polymers, the root-mean-square end-to-end distance has a simple relation with its radius of gyration $(S^2)^{1/2}$, given by Equation 12.7:

$$\bar{r}^2 = 6 \bar{s}^2 \quad (12.7)$$

B. THE FREELY JOINTED CHAIN

We begin by considering first a hypothetical freely jointed chain consisting of n bonds of fixed length l , jointed in a linear sequence without any restriction on the magnitude of the bond angles. Since the bond angles are free to assume all values with equal probability and rotations about bonds are similarly free, a given bond can assume all directions with equal probability regardless of the directions of its neighbors in the chain. Such a chain is illustrated in Figure 12.3. We are aware, however, that no real polymer approximates this model. The problem of determining the end-to-end distance, r , is reduced to that of random flight that occurs in diffusion theory. The question is determining the probability of finding one end of the chain in a volume element $dx dy dz$ at a distance r from the other end (Figure 12.4). It can be shown that the solution of this random flight problem, for a very long chain unperturbed by self-interactions of long-range and external constraints, the probability per unit volume $W(r)$, is a Gaussian distribution function shown in Figure 12.5. This shows that there is a much greater chance of finding the two ends close to each other and that as the two ends move farther apart, the probability decreases continuously. Another way of interpreting the curve is in terms of density distribution of chain ends. That is, if one end of the chain is located at the origin, the probability of finding the other end in a unit volume close to the origin is highest. On the other hand, granted that one end of the chain is at the origin, we want to find out the probability that the other end of the chain is in a spherical shell of thickness dr and at a distance r (Figure 12.6). This is given by Equation 12.8:

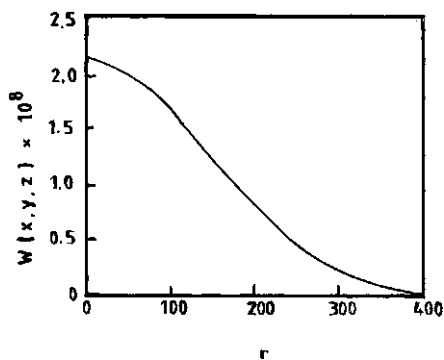


Figure 12.5 The probability $W(x, y, z)$ of finding the end of the chain of [Figure 12.4](#) in the volume element $dx dy dz$ as a function of r (in angstrom units) calculated for a chain of 10^4 links, each 2.5 \AA long.

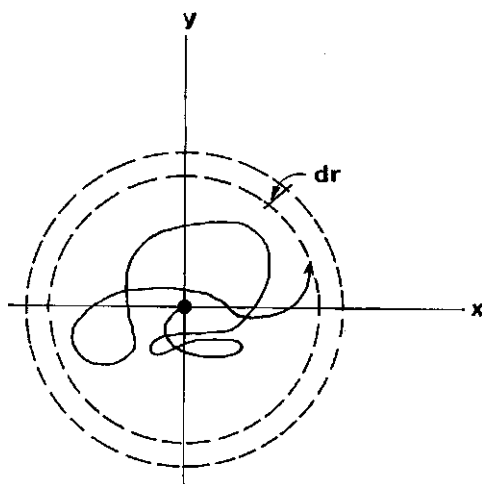


Figure 12.6 Spherical shell thickness dr at distance r from origin.

$$\int_0^{\infty} W(r) 4\pi r^2 dr = 1 \quad (12.8)$$

The integral is equal to one since there is a definite chance of finding the desired end in space. However, since the chain length has a finite value, the upper limit of the integral should appropriately be the contour length. That is,

$$\int_0^{\infty} W(r) 4\pi r^2 dr = \overline{r^2} \quad (12.9)$$

This is shown in [Figure 12.7](#), which demonstrates that the maximum probability corresponds to the most probable dimension for the chain. Assuming the root-mean-square end-to-end distance represents the most probable chain dimension, then, according to random flight theory,

$$\left(\overline{r^2}\right)^{1/2} = \ln^{1/2} \quad (12.10)$$

Here $\overline{r^2}$ is the square of the magnitude of the end-to-end distance averaged over all conformations, and f denotes the result of random flight calculation.

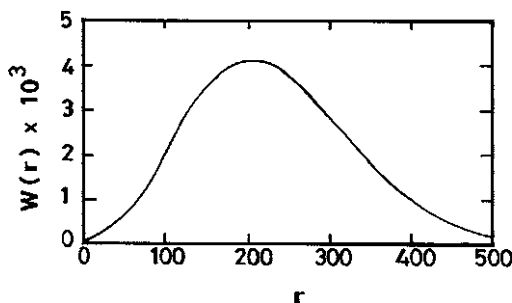


Figure 12.7 The probability of $W(r)$ of finding the end of the chain of [Figure 12.4](#) in a spherical shell of thickness dr at a distance r from the origin.

C. REAL POLYMER CHAINS

The freely jointed model discussed in the previous section grossly underestimates the true dimensions of real polymer molecules because it ignores restrictions to completely free rotation arising from fixed bond angles and steric effects (short-range interactions). Also, it fails to account for the effects of long-range interactions that result from the inability of two chain segments to physically occupy the same space at the same time.

1. Fixed Bond Angle (Freely Rotating)

In real polymer chains, the direction assumed by a given bond depends strongly on that of its immediate predecessor and to a smaller extent on the orientation of nearby bonds. While the structure of the chain unit determines the ultimate nature of the restrictions on given a bond, the overall effect of these short-range interactions is to expand the conformation of the real polymer chain relative to that obtained from the random flight model of the same contour length. The effect of fixed bond angles is a modification of the expression for the unrestricted bond angles from random flight (Equation 12.11):

$$\bar{r}^2 = nl^2 \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right) \quad (12.11)$$

where θ is the bond angle.

2. Fixed Bond Angles (Restricted Rotation)

Restriction to free rotation about bonds due to steric interferences between successive units of the chain leads to a further expansion of chain dimensions. Let us amplify this by considering [Figure 12.8](#). Here θ_i is the valence (bond) angle between bonds i and $i + 1$; α_i is its supplement (i.e., $\alpha_i = 180 - \theta_i$) and ϕ_i is the angle of rotation about i . It is a measurement of the dihedral angle between the planes defined by the two planes $i - 1, i$; and $i + 1$. The direction of bond $i + 1$ is, as we have seen from the above discussion, a function of bond angle θ_i . In addition, it also depends on the direction of bond $i - 1$ through the angle of rotation ϕ_i . However, as a result of hindrance to free rotation, ϕ_i cannot assume all values from 0 to 2π with equal probability; it is limited to certain preferred values. The same argument holds for each bond in relation to its predecessor. When some conformations are preferred over others as a result of restriction to free rotation, Equation 12.11 becomes

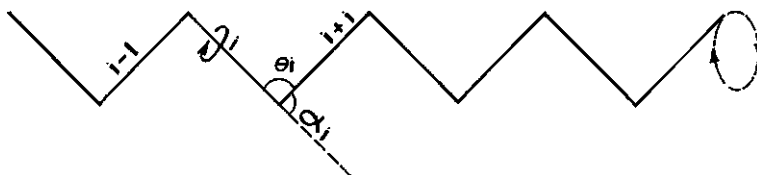


Figure 12.8 Rotation about bond i .

$$\overline{r^2} = nl^2 \left(\frac{1 - \cos\theta}{1 + \cos\theta} \right) \left(\frac{1 + \cos\phi}{1 - \cos\phi} \right) \quad (12.12)$$

The dimension obtained from random flight calculation, which includes the effects of bond angles and hindrances to rotation about bonds, is referred to as the unperturbed dimension of the polymer chain. It is represented by the symbol $(\overline{r_0^2})^{1/2}$. The subscript zero is used to emphasize the condition that the molecule is subject only to local constraints involving the geometrical character of the bond structure and restricted rotation.

3. Long-Range Interactions

The freely jointed model assumes implicitly that two elements of the same molecule, possibly remote along the chain, can occupy the same position in space at the same time. In real polymer chains conformations in which this exists are impossible. Each segment of a real polymer chain exists within a volume that excludes all other segments. The number of such forbidden conformations that must be excluded is greater for the more compact arrangements with smaller values of $\overline{r^2}$. The net effect of such long-range interaction is to expand the actual chain dimension $(\overline{r^2})^{1/2}$ over its unperturbed dimensions, $(r_0^2)^{1/2}$ by an expansion coefficient defined by Equation 12.13:

$$(\overline{r^2})^{1/2} = \alpha (\overline{r_0^2})^{1/2} \quad (12.13)$$

The magnitude of α depends on the environment of the polymer molecule. In a thermodynamically good solvent, where there is strong polymer–solvent interaction, α is large. By the same token, α is small in a poor solvent. The value of α is therefore an indirect measure of the magnitude of the polymer–solvent interaction forces, or the solvent power. When α is 1, these forces become zero and by definition the polymer assumes its unperturbed conformation. However, polymer–solvent interaction forces and, consequently α , depend on temperature. For a given solvent, the temperature at which $\alpha = 1$ is referred to as Flory temperature θ . When a solvent is used at $T = \theta$, it is called theta (θ) solvent. Alpha (α) increases with n (or M) with solvent power and with temperature. Other parameters for characterizing the dimensions of polymer molecules are summarized in Table 12.3. The physical significance of the parameters is illustrated by a brief discussion of the Flory characteristic ratio and the Stockmayer–Kurato ratio.

a. Flory's Characteristic Ratio (C_∞)

The quantity α represents the effect of “long-range interactions.” It describes the osmotic swelling of the chain due to polymer–solvent interaction. On the other hand, r_0^2 represents the effect of “short-range

Table 12.3 Parameters Characterizing Chain Dimensions

Parameter	Relation to Unperturbed Dimension
Flory's characteristic ratio (C_∞)	$C_\infty = \frac{\overline{r_0^2}}{nl^2}$
Stockmayer–Kurato ratio (σ)	$\sigma = \frac{(\overline{r_0^2})^{1/2}}{(\overline{r_{of}^2})^{1/2}}$
Characteristic length (a)	$a = C_\infty^{1/2} l j^{1/2}$ j = number of backbone bonds per monomer unit (usually 2)
Kratky–Porod persistence length (a_p)	$a_p = \frac{1}{2} (C_\infty + 1) l$

Table 12.4 C_∞ and σ for Some Polymers

Polymer	Solvent	Temperature (°C)	C_∞	σ
Polyethylene	Decalin	140	6.8	1.84
Polypropylene				
Isotactic	Tetralin	140	5.2	1.61
Syndiotactic	Heptane	30	6.1	1.75
Atactic	Decalin	135	5.3	1.63
Poly(methylmethacrylate)	Benzene	21	9.0	2.12
Polystyrene				
Isotactic	Benzene	30	10.5	2.30
Atactic	Cyclohexane	34	10.4	2.28

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interactions” induced by bond angle restrictions and steric hindrances to internal rotation. Flory’s characteristic ratio, C_∞ , is defined by

$$C_\infty = \frac{\overline{r_0^2}}{nl^2} \quad (12.14)$$

It is a measure of the effect of short-range interactions.

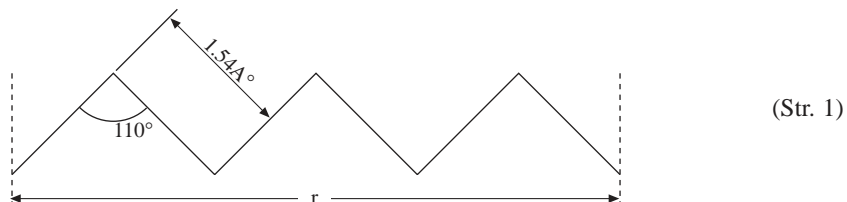
b. Stockmayer–Kurato Ratio (σ)

The freely rotating state is a hypothetical state of the chain in which the bond angle restrictions are operative but in which there are no steric hindrances to internal rotation. The Stockmayer–Kurato ratio, α , reflects such rotational isomerism preferences. That is, it is a measure of the effect of steric hindrance to the average chain dimension. It is given by

$$\sigma = \frac{(\overline{r_0^2})^{1/2}}{(\overline{r_{of}^2})^{1/2}} \quad (12.15)$$

Here $(r_{of}^2)^{1/2}$ is the root-mean-square end-to-end distance of the hypothetical chain with the same bond angles but with free rotation around valence cones. Table 12.4 lists the values of C_∞ and α for some polymers.

Example 12.2: A polyethylene molecule has a degree of polymerization of 2000. Calculate (a) the total length of the chain and (b) the contour length of the planar zigzag if the bond length and valence angle are 1.54 Å and 110°, respectively.



Solution:

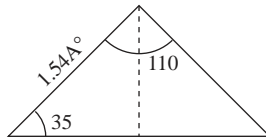
- The total length of the chain, L , is the sum of the length of each bond, l . It is the total distance traversed going from one end of the chain to the other following the bonds.

$$L = nl$$

where n = the number of bonds. Each monomer contributes the equivalent of 2 C–C bonds. Therefore,

$$\begin{aligned} n &= 2 \times \text{DP} \\ &= 2 \times 2000 = 4000 \\ L &= 1.54 \text{ \AA} \times 4000 = 6.16 \times 10^3 \text{ \AA} \end{aligned}$$

b. The contour length is that of the fully extended chain conformation.



(Str. 2)

$$\begin{aligned} r &= n (1.54 \cos 35) \\ &= 2 \times \text{DP} (1.54 \cos 35) \\ &= 2 \times 2000 \times 1.54 \cos 35 \\ &= 5.05 \times 10^3 \text{ \AA} \end{aligned}$$

IV. THERMODYNAMICS OF POLYMER SOLUTIONS

As may be expected, polymers behave differently toward solvents than do low-molecular-weight compounds. Studies of the solution properties of polymers provide useful information about the size and shape of polymer molecules. In this section we discuss how some of the molecular parameters discussed in the previous sections are related to and can be calculated from thermodynamic quantities. We start with a discussion of the simplest case of an ideal solution. This is followed by a treatment of deviations from ideal behavior.

A. IDEAL SOLUTION

Consider a binary mixture of two types of molecules that are roughly identical in size, shape, and external force field. Such a mixture constitutes an ideal solution. Thus, one of the components of an ideal solution may replace another without seriously disturbing the circumstances of immediate neighbors in the solution. Raoult's law provides an appropriate basis for the treatment of an ideal solution. Raoult's law states that the activity, a , of a solvent in the solution is equal to its mole fraction n_1 :

$$a_1 = \frac{N_1}{N_1 + N_2} = n_1 \quad (12.16)$$

where N_1 , N_2 are the number of solvent and solute molecules, respectively. The free energy of mixing ΔG_{mix} is given by Equation 12.17:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \quad (12.17)$$

For the ideal solution, since the intermolecular force fields around the two types of molecules are the same, $\Delta H_{\text{mix}} = 0$. Thus Equation 12.17 becomes

$$\Delta G_{\text{mix}} = -T \Delta S_{\text{mix}} \quad (12.18)$$

The entropy of an ideal solution is greater than that of the pure components because the number of possible arrangements of the molecules of the components of a solution is much greater than that for the molecules of a pure components. If N_0 is total number of molecules (i.e., $N_0 = N_1 + N_2$), then the total number of possible combinations of N_0 taken N_1 at a time is

$$W = \frac{N_0!}{N_1! N_2!} \quad (12.19)$$

From the Boltzmann relation,

$$\begin{aligned} \Delta S_{\text{mix}} &= k \ln W \\ &= k \ln \frac{N_0!}{N_1! N_2!} \end{aligned} \quad (12.20)$$

$$\Delta S_{\text{mix}} = k \ln (N_1 + N_2)! - k \ln N_1! - k \ln N_2! \quad (12.21)$$

Using Stirling's approximation, $\ln N! = N \ln N - N$, and rearranging in terms of mole fractions, Equation 12.20 becomes

$$\Delta S_{\text{mix}} = k [N_1 \ln n_1 + N_2 \ln n_2] \quad (12.22)$$

According to Raoult's law, the partial vapor pressure of each component in a mixture is proportional to its mole fraction. Thus for a binary solution consisting of solvent and a polymer, the partial pressure of the solvent in the solution, P_1 , is related to that of the pure solvent P_1^0 by

$$P_1 = n_1 P_1^0 \quad (12.23)$$

Since the molecular weight of a polymer is usually at least three orders of magnitude greater than that of the solvent, for a small weight fraction of the solvent $N_1 @ N_2$, consequently the mole fraction of the solvent approaches unity very rapidly. This, in effect, means that following Raoult's law, the partial pressure of the solvent in the solution should be virtually equal to that of the pure solvent over most of the composition range. Available experimental data do not confirm this expectation even if volume fraction is substituted for mole fraction. Polymer solutions exhibit large deviations from the ideal law except at extreme dilutions, where ideal behavior is approached as an asymptotic limit.

B. LIQUID LATTICE THEORY (FLORY–HUGGINS THEORY)

One of the reasons for the failure of the ideal solution law is the assumption that a large polymeric solute molecule is interchangeable with the smaller solvent molecule. The law also neglects intermolecular forces since the heat of mixing (ΔH_{mix}) is assumed to be zero. The Flory–Huggins theory attempted to remedy these shortcomings in the ideal solution law.^{5,6-8}

1. Entropy of Mixing

In order to calculate the entropy of mixing of a polymer solution, the polymer chain is assumed to be composed of x chain segments, where x is the ratio of the molar volumes of the solute polymer and the solvent. Each chain segment represents the portion of the polymer molecule equal in size to a solvent molecule. This means that a polymer chain segment can replace a solvent molecule in the liquid lattice and vice versa. However, unlike a solution containing an equal proportion of a monomeric solute, a polymer solution requires a set of x contiguous or consecutive lattice cells to accommodate the polymer molecule (Figure 12.9). A further assumption is that the solution is sufficiently concentrated that the occupied lattice sites are randomly distributed instead of being sparse and widely separated, which would exist in a very dilute solution.

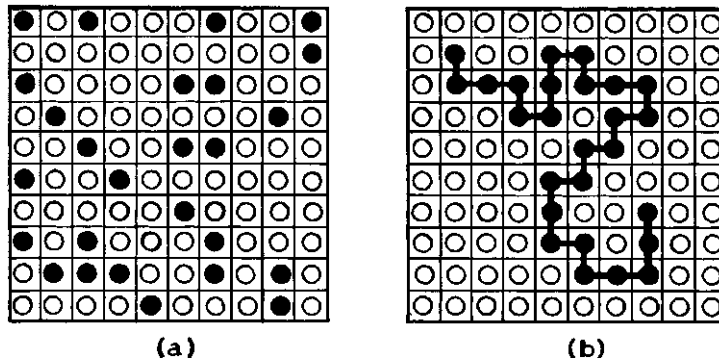


Figure 12.9 Binary solution of a monomer showing distribution of solute in lattice cells (a) compared with that of a polymer, which requires a set of contiguous cells to accommodate the solute (b).

The entropy of mixing of a polymer solution is relatively smaller than that of an equivalent proportion of a monomeric solute. This is because the macromolecular nature of the polymer molecule severely restricts the number of possible arrangements of polymer segments in the lattice sites. Once a given segment occupies a site, the number of sites available for adjacent segments becomes seriously limited. The dissolution of the polymer is conceived to occur in two consecutive steps: first, the polymer is disoriented, and then the disoriented polymer mixes with the solvent. The entropy of mixing of the disoriented polymer and solvent has been shown by Flory to be given by

$$\Delta S_{\text{mix}} = k [N_1 \ln v_1 + N_2 \ln v_2] \quad (12.24)$$

where the subscripts 1 and 2 denote the solvent and polymer, respectively, and v_1 and v_2 are their volume fractions defined as

$$v_1 = \frac{N_1}{N_1 + xN_2} \quad (12.25)$$

$$v_2 = \frac{xN_2}{N_1 + xN_2} \quad (12.26)$$

2. Heat and Free Energy of Mixing

To derive an expression for the heat of mixing of a polymer solution, the pure solvent and pure liquid polymer are taken as reference states. The heat of mixing is considered to be the difference between the total interaction energy in the solution relative to that of the pure components. It arises from the replacement of some of the solvent-solvent and polymer-polymer contacts in the pure components with solvent-polymer contacts in the solutions. As the distance between uncharged molecules increases, the forces between them decrease very rapidly. Consequently, interactions between elements that are not immediate neighbors can be safely neglected. If only the energies developed by first-neighbor elements are considered, then the heat of mixing of polymer solution, like that of ordinary solutions, is given by

$$\Delta H_{\text{mix}} = \chi_1 kTN_1 v_2 \quad (12.27)$$

where χ characterizes the interaction energy per solvent molecule divided by kT . Combining Equation 12.24 with that of the configurational entropy (Equation 12.27) gives the Flory-Huggins expression for the free energy of mixing of a polymer solution:

$$\Delta G_{\text{mix}} = kT(N_1 \ln v_1 + N_2 \ln v_2 + \chi_1 N_1 v_2) \quad (12.28)$$

Quantities that are determinable from experiments can be derived from Equation 12.28. For example, by differentiating the expression with respect to N_1 , the number of solvent molecules, and multiplying the result by Avogadro's number, the relative partial molar free energy $\overline{\Delta G}_1$ is obtained:

$$\overline{\Delta G}_1 = RT \left[\ln(1 - v_2) + (1 - 1/x)v_2 + \chi_1 v_2^2 \right] \quad (12.29)$$

We note that $\overline{\Delta G}_1$ is expressed on a per mole basis. The activity of the solvent, a_1 , and the osmotic pressure of the solution, π , are given by Equations 12.30 and 12.31, respectively:

$$\ln a_1 = \ln(1 - v_2) + (1 - 1/x)v_2 + \chi_1 v_2^2 \quad (12.30)$$

$$\pi = -\frac{RT}{V_1} \left[\ln(1 - v_2) + (1 - 1/x)v_2 + \chi_1 v_2^2 \right] \quad (12.31)$$

where V_1 is the molar volume of the solvent. Expanding the logarithmic term and neglecting higher order terms, the expression for the osmotic pressure becomes

$$\pi = \frac{RT}{V_1} \left[\frac{v_2}{x} + \left(\frac{1}{2} - \chi_1 \right) v_2^2 + \frac{1}{3} v_2^3 + L \right] \quad (12.32)$$

The above thermodynamic expressions for a binary solution of a polymer in a solvent include the dimensionless parameter χ_1 . Its value can be determined by measuring any of the experimentally obtainable quantities, like solvent activity or the osmotic pressure of the solution. The constancy of χ_1 over a wide composition range would be a confirmation of the validity of the Flory–Huggins theory. [Figure 12.10](#) represents such a plot obtained by the measurement of solvent activities for various systems. Only in the case of the nonpolar rubber–benzene system was the predicted constancy of χ_1 observed; other systems showed marked deviations from theory.

Equation 12.29 can be separated into contributions from the heat of dilution and configurational entropy, as shown in Equations 12.33 and 12.34, respectively:

$$\overline{\Delta H}_1 = RT \chi_1 v_2^2 \quad (12.33)$$

$$\overline{\Delta S}_1 = -R \left[\ln(1 - v_2) + (1 - 1/x)v_2 \right] \quad (12.34)$$

where $\overline{\Delta H}_1$ is the relative partial molar heat content while $\overline{\Delta S}_1$ is the relative partial molar configurational entropy of the solvent in solution. $\overline{\Delta H}_1$ was determined from the heat of mixing obtained from calorimetric methods. The predicted concentration dependence of $\overline{\Delta H}_1$ was also not observed.

C. DILUTE POLYMER SOLUTIONS (FLORY–KRIGBAUM THEORY)

The Flory–Huggins lattice model assumed a uniform density of lattice occupation. This assumption holds only for concentrated solutions; it is invalid for dilute polymer solutions. According to the Flory–Krigbaum model, a very dilute polymer solution consists of loose domains or clusters of polymer chain segments separated by intervening regions of pure solvent. Each such cloud is assumed to be approximately spherical with an average density that is maximum at the center and that decreases with increasing distance from the center in an approximately Gaussian function. Each molecule within a domain or occupied volume tends to exclude all other molecules. Long-range thermodynamic interactions

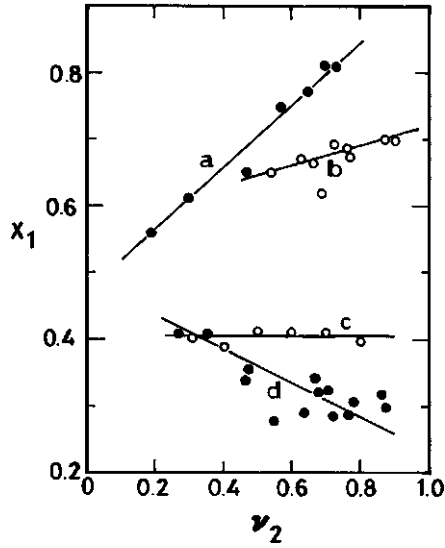


Figure 12.10 Experimentally observed variation of χ_1 with concentrations: (a) poly(dimethylsiloxane) in benzene; (b) polystyrene in benzene; (c) rubber in benzene; curve (d) polystyrene in toluene. [Curve (a) from Newing, M.J., *Trans. Faraday Soc.*, 46, 613, 1950; (b) and (d) from Bawn, C.E.H., Freeman, R.F.J., and Kamaliddin, A.R., *Trans. Faraday Soc.*, 46, 677, 1950; (c) from Gee, G. and Orr, W.J.C., *Trans. Faraday Soc.*, 42, 507, 1946; and Gee, G., *J. Chem. Soc.*, p. 280, 1947.]

occur between segments within such an excluded volume. The expression for the excess, relative, partial molar-free energy for these interaction is given by the relation:

$$\overline{\Delta G_1} = RT(\kappa_1 - \psi_1)v_2^2 \quad (12.35)$$

κ_1 and χ_1 are heat and entropy parameters also given by

$$\overline{\Delta H_1} = RT\kappa_1 v_2^2 \quad (12.36)$$

$$\overline{\Delta S_1} = R\psi_1 v_2^2 \quad (12.37)$$

If x is assumed to be infinite, Equation 12.29 reduces to

$$\overline{\Delta G_1} = RT[\ln(1 - v_2) + v_2 + \chi_1 v_2^2] \quad (12.38)$$

Expanding the logarithmic term and, as before, neglecting terms of order higher than 2 (i.e., $\ln(1 - v_2) = -v_2 - \frac{v_2^2}{2} - \dots$), Equation 12.38 becomes

$$\overline{\Delta G_1} = -RT\left[\left(\frac{1}{2} - \chi_1\right)v_2^2\right] \quad (12.39)$$

By comparing Equations 12.35 and 12.39, it is obvious that

$$\kappa_1 - \psi_1 = \frac{1}{2} - \chi_1 \quad (12.40)$$

Table 12.5 Behavior of Polymer Molecules with Change in Thermodynamic Parameters

Thermodynamic Parameter	Behavior of Polymer Molecules
$\kappa_1 = 0$ ($\theta = 0$)	A thermal solvent, $\delta\Delta G > 0$; increase in segment concentration within volume element causes a decrease in entropy; solution wants to dilute itself; polymer coils move apart
$\kappa_1 > 0$ ($T < \theta$)	Polymer–polymer contacts preferred to polymer–solvent contacts; spontaneous concentration
$\kappa_1 = \psi_1$ ($T = \theta$)	$\delta\Delta G = 0$; excluded volume effects eliminated; polymer in an unperturbed state
$\kappa_1 < 0$ ($T > \theta$)	Exothermic solution; $\delta\Delta G = 0$; spontaneous dilution; expansion of polymer coil occurs as a result of interaction with solvent

The deviations from ideality in a polymer solution can be eliminated by selecting a temperature where $\overline{\Delta H}_1 = T\overline{\Delta S}_1$ or when $\kappa_1 = \psi_1$. The temperature at which these conditions prevail is called the Flory or theta temperature, θ , and is defined by

$$\theta = \frac{\kappa_1 T}{\psi_1} \quad (12.41)$$

It follows that

$$\psi_1 - \kappa_1 = \psi_1(1 - \theta/T) \quad (12.42)$$

and

$$\overline{\Delta G}_1 = -RT\psi_1(1 - \theta/T)v_2^2 \quad (12.43)$$

We note for emphasis (also from Equation 12.43) that at the temperature $T = \theta$ the excess, relative, partial molar-free energy, ΔG_1 , due to polymer–solvent interactions is zero and deviations from ideality vanish.

The change in free energy δ (ΔG) in a volume element when two molecules are brought together depends algebraically on the magnitude of $\psi_1 - \kappa_1$ or $\psi_1(1 - \theta/T)$. Since the entropy of dilution is usually positive, the sign of the free energy change will depend on the relative magnitudes of ψ_1 and κ_1 or if θ/T is greater than unity. Table 12.5 summarizes the expected behavior of polymer molecules with thermodynamic parameters.

It follows from the above discussion that as the solvent is made poorer, i.e., as $\psi_1(1 - \theta/T)$ decreases, the excluded volume shrinks and at $T = \theta$ it disappears entirely. In other words, as the solvent becomes poorer, polymer–polymer repulsion diminishes and at the θ -point the net interaction becomes zero. Where $T < \theta$, polymer molecules attract each other and the excluded volume is negative. When the temperature is much lower than the θ -point, precipitation occurs.

D. OSMOTIC PRESSURE OF POLYMER SOLUTIONS

Osmotic pressure, as indicated earlier, is one of the quantities that can be obtained experimentally from the Flory–Huggins and Flory–Krigbaum theories. Before we illustrate how thermodynamic parameters characteristic of polymers can be derived from osmotic pressure measurements, let us first explain very briefly the basis of these measurements.¹³

Consider the apparatus shown schematically in Figure 12.11. The semipermeable membrane, represented by the dashed line, allows the passage of solvent but not the solute. Suppose in the first instance that both sides of the tube contain only the pure solvent. At equilibrium the levels of the liquid in both arms would be at the same height and the external pressure would be P_A . In this case, the chemical potential of the solvent on both sides would be the same. Suppose a solute is now added to the right-

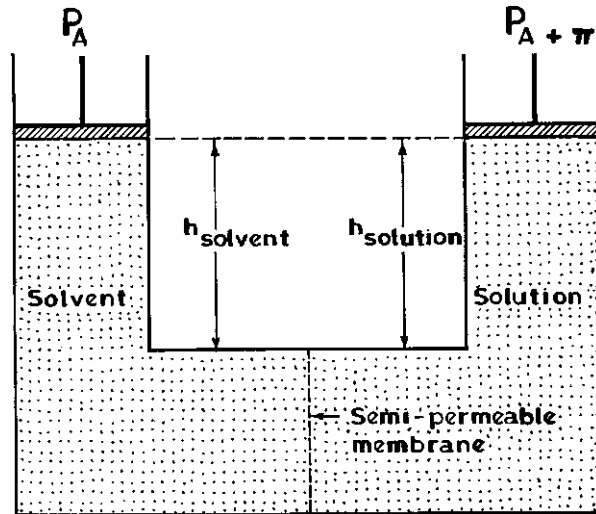


Figure 12.11 Schematic representation of an osmometer.

hand side. Since it cannot pass through the semipermeable membrane, it must remain on right-hand side. The chemical potential of the solvent on the right-hand side (solution) is now less than that of the solvent on the left-hand side (pure solvent). If the external pressure on the right-hand side is maintained at P_A , the liquid level on the right-hand side will rise as the solvent passes from the left (higher chemical potential) to the right (lower chemical potential) to equalize the chemical potential on both sides. However, this flow of solvent can be prevented if the external pressure on the solution is increased so as to keep the liquid levels the same on both sides. The additional pressure is the osmotic pressure, π , of the solution. It arises as the driving force for solvent flow in response to the reduction of the chemical potential of the solvent due to the addition of a solute.

From Equation 12.32, the osmotic pressure is given by

$$\pi = \frac{RT}{V_1} \left[\frac{v_2}{x} + \left(\frac{1}{2} - \chi_1 \right) v_2^2 + \frac{1}{3} v_2^3 + L \right] \quad (12.32)$$

It is generally more convenient to replace volume fraction with the concentration, C , of the solution expressed in weight per unit volume:

$$v_2 = C \bar{v}_2 \quad (12.44)$$

where v_2 is the (partial) specific volume of the polymer. Since $x = V_2/V_1$, then

$$\frac{v_2}{xV_1} = \frac{c \bar{v}_2}{xV_1} = \frac{C}{M_2} \quad (12.45)$$

where M_2 is the molecular weight of the polymer. For heterogeneous polymers, M_2 is replaced by the number-average molecular weight \bar{M}_n . From Equation 12.45

$$v_2 = \frac{c \times V_1}{M_2} \quad (12.46)$$

$$x = \frac{\bar{v}_2 M_2}{V_1} \quad (12.47)$$

Substituting Equations 12.46 and 12.47 successively in Equation 12.32 and rearranging terms yields

$$\frac{\pi}{c} = \frac{RT}{M_2} \left[1 + \left(\frac{1}{2} - \chi_1 \right) \frac{\bar{v}_2^2 M_2}{V_1} c + \frac{\bar{v}_2^3 M_2}{3 V_1} c^2 + L \right] \quad (12.48)$$

In applications to osmotic data, Equation 12.48 is most frequently preferred in the following forms:

$$\frac{\pi}{c} = RT [A_1 + A_2 c + A_3 c^2 + L] \quad (12.49)$$

$$\frac{\pi}{c} = \frac{RT}{M_2} [1 + \Gamma c + g \Gamma^2 c^2 + L] \quad (12.50)$$

where $A_1 = 1/M_2$ and A_2 and Γ are the second virial coefficients given by

$$\Gamma = \frac{\bar{v}_2^2}{V_1} \left(\frac{1}{2} - \chi_1 \right) \quad (12.51)$$

$$g \Gamma^2 = \frac{\bar{v}_2^3 M_2}{3 V_1} \quad (12.52)$$

Osmotic pressure data can, therefore, be used for the determination of the number-average molecular weight, M_n , or the solvent–polymer interaction parameter χ_1 . This depends, of course, on knowing the values of the densities and specific volumes of the polymer and the solvent. In good solvents, g is approximately 1/4 in which case Equation 12.50 becomes

$$\left(\frac{\pi}{c} \right)^{1/2} = \left(\frac{RT}{M_2} \right)^{1/2} \left[1 + \frac{1}{2} \Gamma c \right] \quad (12.53)$$

In poor solvents, $g \cong 0$. In either case, an appropriate plot of π/c vs. c gives $M_2(\bar{M}_n)$ and χ_1 .

Other thermodynamic parameters can be obtained from osmotic pressure. For example, the chemical potential of the solvent in the solution is given by $-\chi/\pi V_1$. From the foregoing discussion, it is evident that the thermodynamic behavior of the dilute polymer solution depends on the following factors:

1. Molecular weight
2. The interaction parameter ψ_1 and κ_1 or ψ_1 and θ , which characterize the segment–solvent interactions
3. The size or configuration of the molecules in solution

The first factor is usually determined from the coefficient A_1 . A_2 (or Γ_2) depends on all three factors. Therefore, to evaluate the thermodynamic functions that depend on A_2 , it is necessary to determine the size of the molecule in solution independently. The parameter α is related to the thermodynamic quantities according to Equation 12.54:

$$\alpha^5 - \alpha^3 = 4 C_M \psi_1 (1 - \theta/T) M^{1/2} \quad (12.54)$$

where C_M represents all the numerical and molecular constants. The expansion factor α^3 and \bar{r}_0^2/M may be determined from suitable measurements of intrinsic viscosities. The quantity $\psi_1(1 - \theta/T)$ may then

be deduced from the relevant equation. If measurements are made over a limited range of temperature in the vicinity of θ , $\psi_1(1 - \theta/T)$ may be resolved into its components θ and ψ_1 from a plot of A_2 against the reciprocal of the absolute temperature.

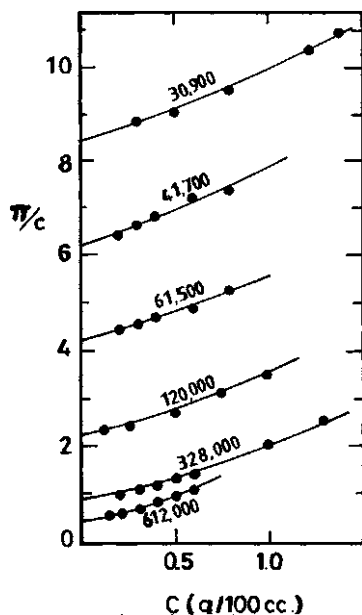


Figure 12.12 Concentration dependence of osmotic pressure of solutions of polystyrene in toluene at 30°C. Numbers on each curve denote polymer molecular weights. (From Flory, P.J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953. With permission.)

Typical results of osmotic pressure measurements are shown in Figure 12.12. The experimental data are in consonance with the predicted positive curvature in good solvents. However, these data also show that the quantity $\psi_1(1 - \theta/T)$ decreases with increasing molecular weight. This is contrary to theory, which predicts that these thermodynamic parameters should characterize the inherent segment-solvent interaction independent of the entire molecular structure. The theory predicts that α increases without limit with molecular weight and that χ_1 is constant over a wide range of polymer concentrations. However, experimental data show that χ_1 increases with increasing volume fraction v_2 . In spite of these shortcomings, the Flory-Huggins intermolecular interaction theory is in reasonably satisfactory agreement with experimental data within the approximations made in the theory. It provides a semiquantitative description of polymer solutions from which parameters characteristic of polymers may be derived. Table 12.6 gives values of χ_1 for some polymer-solvent systems.

Table 12.6 Polymer–solvent Interaction Parameter at 25°C

Polymer	Solvent	χ_1
Poly(dimethylsiloxane)	Cyclohexane	0.42
	Chlorobenzene	0.47
Polyisoprene (natural rubber)	Benzene	0.42
	Chloroform	0.377
Poly(methyl methacrylate)	Tetrahydrofuran	0.447
	Ethylbenzene	0.40
Polystyrene	Methyl ethyl ketone	0.47
	Cyclohexane	0.505

From Wolf, B.A., in *Polymer Handbook*, 2nd ed., Brandrup, J. and Immergut, E.M., Eds., John Wiley & Sons, New York, 1967. With permission.

Example 12.3: The data on the osmotic pressure of a sample of poly(vinyl acetate) in methyl ethyl ketone at 25°C are shown below:

Weight Fraction of Polymer	Pressure in cm of Solution
0.0021	0.40
0.0032	0.61
0.0057	1.23
0.0061	1.44
0.0082	2.10
0.0083	2.25
0.0093	2.52
0.0100	2.76
0.0114	3.54
0.0122	3.73

The densities of the polymer and solvent are 1.190 and 0.800, respectively; the solution densities can be calculated by assuming additivity of the volumes of the components. Using both linear and square-root plots, calculate the polymer molecular weight and the second virial coefficients, A_2 and Γ .

Solution: Basis: 1 g of solution:

$$\text{Vol of solution } V_s = \frac{\omega_2}{\rho_2} + \frac{1-\omega_2}{\rho_1} \text{ (in cm}^3\text{)}$$

where ω_2 = weight fraction of polymer; ρ_1 and ρ_2 are the densities of the solvent and polymer, respectively.

$$\text{Concentration of Solution, } C = \frac{\omega_2}{V_s} \text{ (g/cm}^3\text{)}$$

From these relations, data can be transformed into a [Figure E12.3A,B](#). Now

$$\frac{\pi}{c} = RT \left[\frac{1}{M_n} + A_2 c + A_3 c^2 + L \right]$$

$$\left(\frac{\pi}{c} \right)^{1/2} = \left(\frac{RT}{M_n} \right)^{1/2} [1 + 0.5 \Gamma c]$$

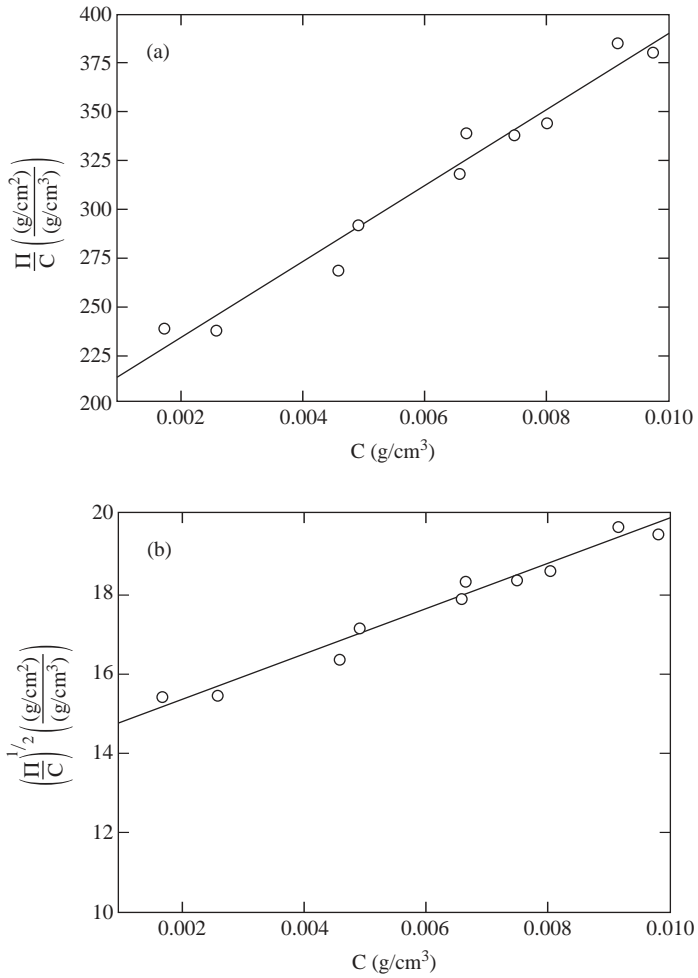


Figure E12.3

From Figure E12.3a,

$$\frac{RT}{M_n} = \text{intercept on } \pi/C \text{ as } c \rightarrow 0$$

$$\text{Intercept on } \pi/c = 194 \frac{\text{cm solution}}{\text{g/cm}^3}$$

$$\begin{aligned} \bar{M}_n &= \frac{RT}{\text{intercept}} = \left(82.06 \frac{\text{cm}^3 \text{ atm}}{\text{mol-K}}\right) (298 \text{ K}) \left(\frac{1}{194 \frac{\text{cm solution}}{\text{g/cm}^3}}\right) \\ &= \left(82.06 \frac{\text{cm}^3 - 1033 \text{ cm H}_2\text{O}}{\text{mol-K}}\right) (298 \text{ K}) \left(\frac{1}{194 \times 0.8 \frac{\text{cm H}_2\text{O}}{\text{g/cm}^3}}\right) \end{aligned}$$

Note: 1 atm = 1033 cm H₂O; cm solution $x\rho_s = \text{cm H}_2\text{O}$. Since the solution is dilute it is assumed that the density of solution is approximately that of the solvent.

$$\overline{M}_n = 1.63 \times 10^5 \text{ g/mol}$$

$$\text{Slope} = RTA_2$$

$$\begin{aligned} A_2 &= \frac{\text{slope}}{RT} = \frac{19648 \text{ cm solution}/(\text{g}/\text{cm}^3)^2}{82.06(\text{cm}^3 - \text{atm}/\text{mol-K})(298 \text{ K})} \\ &= \frac{19648 \times 0.8 \text{ cm H}_2\text{O}/(\text{g}/\text{cm}^3)^2}{82.06(\text{cm}^3 - \text{cm H}_2\text{O}/\text{mol-K} \times 1033)(298 \text{ K})} \\ &= 6.2 \times 10^{-4} \text{ mol} - \text{cm}^3/\text{g}^2 \end{aligned}$$

From Figure E12.3b,

$$\text{Slope} = 563 = 0.5 \Gamma \left(\frac{RT}{\overline{M}_n} \right)^{1/2}$$

$$\Gamma = \frac{563}{0.5} \left(\frac{RT}{\overline{M}_n} \right)^{-1/2}$$

$$\left(\frac{RT}{\overline{M}_n} \right)^{1/2} = \text{intercept at } \left(\frac{\pi}{c} \right)^{1/2} \text{ as } c \rightarrow 0$$

$$= 14.22$$

$$\Gamma = \frac{563}{0.5 \times 14.22} = 79.2 \text{ cm}^3/\text{g}$$

V. SOLUTION VISCOSITY

Rheology by definition is the science of deformation and flow of matter. Rheological measurements provide useful behavioral and predictive information for various products in addition to knowledge of the effects of processing, formulation changes, and aging phenomena. Material processability can also be determined through rheological studies. Rheology deals with those properties of materials that determine their response to mechanical force. For solids, as we shall see in subsequent chapters, this involves elasticity and plasticity. For fluids, on the other hand, rheological studies involve viscosity measurements. Viscosity is a measure of the internal friction of a fluid. For example, it has been observed that even at low concentrations of a dissolved polymer, the viscosity of a solution relative to that of the pure solvent is increased appreciably. This is due to the unusual size and shape of polymer molecules and the nature of their solutions. Thus measurements of the viscosity of polymer solutions can provide information about monomer molecular weight, molecular weight distribution, and other material characterization parameters. Before we deal with the relation between solution viscosity and polymer characterization parameters, we discuss briefly the various terms used to describe viscosity.

A. NEWTON'S LAW OF VISCOSITY^{16,17}

Consider a fluid, which may be a gas or liquid, contained between two large parallel plates of area A and separated by the distance Y (Figure 12.13). The system is initially at rest. Now suppose the lower plate is set in motion in the x -direction at a constant velocity. The fluid gains momentum with time, and

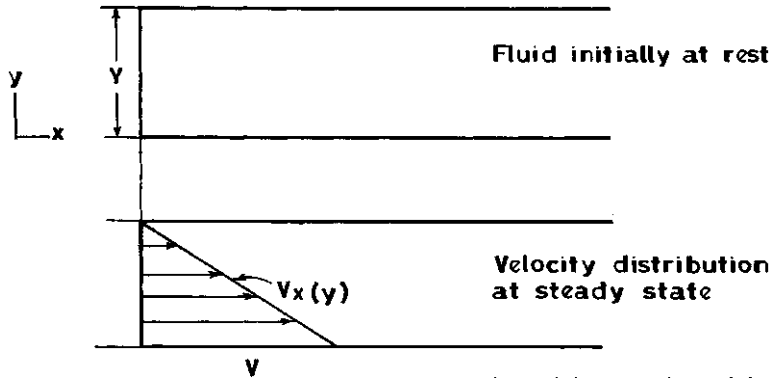


Figure 12.13 Laminar velocity profile for fluid between two plates.

at steady state a constant force, F , is required to maintain the motion of the lower plate. For laminar flow, this force is given by Equation 12.55:

$$\frac{F}{A} = \eta \frac{V}{Y} \quad (12.55)$$

According to this equation, the force per unit area is proportional to the velocity decrease in the distance Y . This constant of proportionality, η , is called the viscosity of the fluid. It is desirable and convenient to rewrite Equation 12.55 in a form that permits us to give a molecular interpretation to the meaning of viscosity (Equation 12.56):

$$\tau_{yx} = -\eta \frac{dV_x}{dy} \quad (12.56)$$

Equation 12.56 states that the shear stress is proportional to the negative of the local velocity gradient. This is Newton's law of viscosity, and fluids that exhibit this behavior are referred to as Newtonian fluids. According to this law, in the neighborhood of the surface of the moving plate (i.e., at $y = 0$), the fluid acquires a certain amount of x -momentum. This fluid, in turn, transmits some of its momentum to the adjacent layer of fluid causing it to remain in motion in the x -direction; in effect, the x -momentum is transmitted in the y -direction. The velocity gradient is a measure of the speed at which intermediate layers move with respect to each other. For a given stress, fluid viscosity determines the magnitude of the local velocity gradient. Fluid viscosity is due to molecular interaction; it is a measure of a fluid's tendency to resist flow, and hence it is usually referred to as the internal friction of a fluid.

Using the chain rule, the velocity gradient in Equation 12.56 can be interpreted differently:

$$\frac{dV}{dy} = \frac{d}{dy} \left(\frac{dx}{dt} \right) = \frac{d}{dt} \left(\frac{dx}{dy} \right) = \frac{d\gamma}{dt} = \dot{\gamma} \quad (12.57)$$

where $\dot{\gamma}$ is the strain rate. In a more general form, Equation 10.56 becomes

$$\tau = -\eta \dot{\gamma} \quad (12.58)$$

In this form, Newton's law simply states that for laminar flow, the shear stress needed to maintain the motion of a plane of fluid at a constant velocity is proportional to the strain rate. At a given temperature, the viscosity of a Newtonian fluid is independent of the strain rate (Figure 12.14). Fluids that do not obey Newton's law of viscosity are known as non-Newtonian fluids. For non-Newtonian

fluids, when the strain rate is varied, the shear stress does not vary in the same proportion, i.e., the

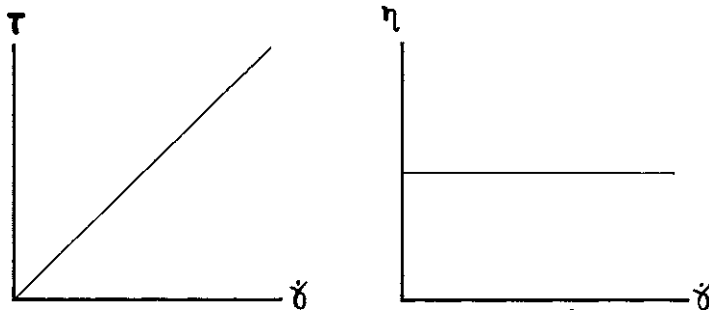


Figure 12.14 Behavior of Newtonian fluids.

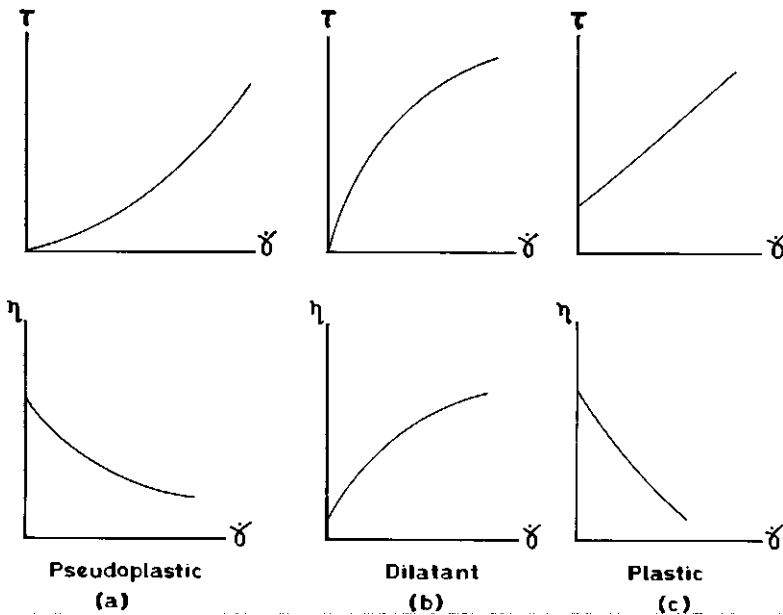


Figure 12.15 Some types of non-Newtonian behavior.

viscosity is not independent of the strain rate. In physical terms, non-Newtonian behavior means that as molecules pass each other, their size, shape, and cohesiveness determine how much force is required to maintain the movement. When the strain rate is changed, molecular alignment may change also as will the force required to maintain motion. There are several types of deviation from Newtonian behavior. Each is characterized by the way the fluid viscosity changes in response to variations in the strain rate (Figure 12.15). Pseudoplastic fluids display a decrease in viscosity with increasing strain rate, while a dilatant fluid is characterized by an increase in viscosity with increasing strain rate. For fluids that exhibit plastic behavior, a certain amount of stress is required to induce flow. The minimum stress necessary to induce flow is frequently referred to as the yield value. In addition, some fluids will show a change of viscosity with time at a constant strain rate and in the absence of a chemical reaction. Two categories of this behavior are encountered: thixotropy and rheopexy. A thixotropic fluid undergoes a decrease in viscosity, whereas a rheoplectic fluid displays an increase in viscosity with time under constant strain rate (Figure 12.16). Table 12.7 gives examples of fluids that display Newtonian and non-Newtonian behavior.

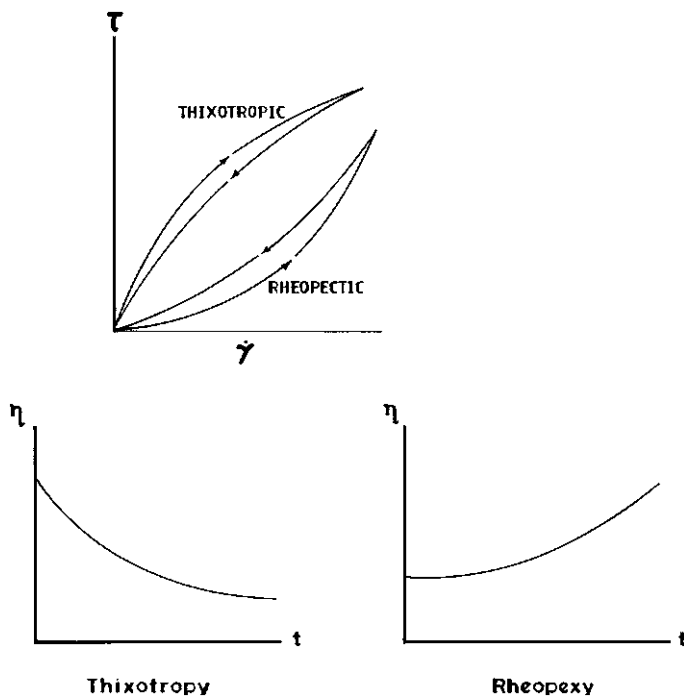


Figure 12.16 Change of viscosity with time under constant strain rate.

Table 12.7 Examples of Newtonian and Non-Newtonian Fluids

Viscosity Type	Example
Newtonian	All gases, water, thin motor oils
Non-Newtonian	
Pseudoplastic	Paints, emulsions, dispersions
Dilatant	In fluids containing high levels of deflocculated solids such as clay slurries, candy compounds, corn starch in water, sand/water mixtures
Plastic	Tomato catsup
Thixotropic	Greases, heavy printing inks, paints
Rheopectic	Rarely encountered

B. PARAMETERS FOR CHARACTERIZING POLYMER SOLUTION VISCOSITY¹²

The viscous flow of a polymer solution involves a shearing action in which different layers of the solution move with differing velocities. As we observed earlier, there is a pronounced increase in the viscosity of a polymer solution relative to that of the pure solvent even at low concentrations of the polymer. In this respect, the polymer solute behaves as a colloidal dispersion, which is known to retard the flow of adjacent layers of a liquid under shearing force. For spherical colloidal particles, the viscosity of the solution, η , relative to that of the pure solvent, η_0 , is referred to as the relative viscosity, given by

$$\eta_r = \eta/\eta_0 \quad (12.59)$$

The flow of fluids through a tube of uniform cross-section under an applied pressure is given by the Hagen–Poiseuille’s law:

$$Q = \frac{\pi R^4 \Delta P}{8\eta L} \quad (12.60)$$

where Q is the volume flow rate, ΔP is the pressure drop across the tube of length L and radius R . Some of the assumptions made in the derivation of this law include

1. The flow is laminar, which means that the dimensionless quantity called Reynold's number, R_e , < 2100 .
2. The fluid is incompressible, i.e., its density is constant.
3. The flow is independent of time, i.e., steady-state conditions prevail.
4. The fluid is Newtonian.

The viscosity of a liquid or solution can be measured by using a viscometer whose design is based on the Hagen–Poiseuille law. Essentially, this involves the measurement of the flow rate of the liquid through a capillary tube which is part of the viscometer. Consequently, by measuring the flow time of the solution, t , and that of the pure solvent, t_0 , the relative viscosity can be determined:

$$\eta_r = \eta/\eta_0 = t/t_0 \quad (12.61)$$

As indicated above, the viscosity of the polymer solution is always greater than that of the pure solvent. This fractional increase in the viscosity resulting from the dissolved polymer in the solvent is referred to as the specific viscosity η_{sp} , given by

Table 12.8 *Various Viscosity Terms*

Viscosity Term	Expression
Relative viscosity	$\eta_r = \eta/\eta_0 = t/t_0$
Specific viscosity	$\eta_{sp} = (\eta - \eta_0)/\eta_0 = \eta_r - 1$
Reduced viscosity	$\eta_{sp}/C = (\eta_r - 1)/C$
Intrinsic viscosity	$[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/C$

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1 \quad (12.62)$$

According to Einstein's viscosity relation for rigid spherical particles in solution,

$$\frac{\eta - \eta_0}{\eta_0} = 2.5 \left(\frac{n_2}{V} \right) V_e \quad (12.63)$$

where n_2/V is the number of polymer molecules per unit volume and $V_e = \frac{4\pi}{3} R_e^3$. R_e is the radius of an equivalent hydrodynamic sphere that would enhance the viscosity of the solvent medium to the same extent as would the actual polymer molecule. The quantity n_2/V may be written as

$$\frac{n_2}{V} = \frac{CN_A}{M} \quad (12.64)$$

where C and M are the concentration and molecular weight, respectively, of the polymer, and N_A is Avogadro's number. It is obvious from Equations 12.63 and 12.64 that both the relative viscosity and specific viscosity increase with increasing concentration of the polymer. The specific viscosity normalized with respect to the concentration, η_{sp}/C , is referred to as the reduced specific viscosity or, simply, reduced viscosity. It measures that capacity with which a given polymer enhances the specific viscosity. The intrinsic viscosity $[\eta]$ is the limiting value of the reduced viscosity at infinite dilution:

$$[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c \quad (12.65)$$

When $\eta_r < 2$, it has been found that a linear relation exists between the reduced viscosity and polymer concentration. For a given polymer–solvent system, this linear dependence is described adequately by the equation

$$\frac{\eta_{sp}}{c} = [\eta] + k^1 [\eta]^2 c \quad (12.66)$$

where k^1 is referred to as the Huggins constant, with a value usually in the range 0.35 to 0.40. Table 12.8 summarizes the various viscosity terms described above.

C. MOLECULAR SIZE AND INTRINSIC VISCOSITY

The Einstein viscosity relation given by Equation 12.62 may be written as

$$\frac{\eta - \eta_0}{\eta_0} = 2.5 \left(\frac{N_A C}{M} \right) V_e \quad (12.67)$$

or

$$[\eta] = \frac{\eta - \eta_0}{\eta_0 C} = 2.5 \frac{N_A}{M} V_e = 2.5 \frac{N_A}{M} \frac{4\pi}{3} R_e^3 \quad (12.68)$$

Equation 12.67 predicts that the specific viscosity is proportional to the volume of the equivalent hydrodynamic sphere. The Einstein viscosity relation was derived for rigid spherical particles in solution. However, real polymer molecules are neither rigid nor spherical. Instead the spatial form of the polymer molecule in solution is regarded as a random coil. Theories based on this characteristic form of polymer molecules have resulted in the expression

$$[\eta] = \Phi (\bar{r}^2)^{3/2} M \quad (12.69)$$

where Φ is considered to be a universal constant with a value of $2.1 (\pm 0.2) \times 10^{23}$, \bar{r}^2 is the mean-square end-to-end distance of the polymer coil expressed in cm, and $[\eta]$ is in cm^3/g . According to Equation 12.68, the intrinsic viscosity is proportional to the ratio of the effective hydrodynamic volume of the molecule to its molecular weight. Specifically, it states that the effective volume is proportional to the linear dimensions of the randomly coiled polymer chain. Therefore, to understand the factors that influence the intrinsic viscosity, the quantity in Equation 12.68 may be separated into its component parts. Recall from our discussion in Section III.B that the net effect of long-range interaction is to expand the actual chain dimension $(r_0^2)^{1/2}$ by an expansion factor α given by the relation:

$$(\bar{r}^2)^{1/2} = \alpha (\bar{r}_0^2)^{1/2} \quad (12.13)$$

Equation 12.69 may therefore be rewritten as

$$[\eta] = \Phi (\bar{r}_0^2 / M)^{3/2} M^{1/2} \alpha^3 \quad (12.70)$$

For a linear polymer of a given structural unit, the quantity \bar{r}_0^2 / M is independent of M . Consequently, Equation 12.70 becomes

$$[\eta] = K M^{1/2} \alpha^3 \quad (12.71)$$

where

$$K = \Phi \left(\overline{r_0^2} / M \right)^{3/2} \quad (12.72)$$

K is a constant independent of the polymer molecular weight and of the solvent.

From Equation 12.71, the intrinsic viscosity depends on the molecular weight as a result of the factor $M^{1/2}$ and also through the dependence of the expansion factor α^3 on molecular weight. By choosing a theta-solvent or θ temperature, the influence of the molecular expansion due to intramolecular interactions can be eliminated. Under these conditions, $\alpha = 1$, and the intrinsic viscosity depends only on the molecular weight. Thus Equation 12.71 is reduced to:

$$[\eta]_{\theta} = K M^{1/2} \quad (12.73)$$

This relation has been confirmed experimentally. It follows, therefore, that since Φ is regarded as a universal constant, the average dimensions of polymer molecules in solution can be estimated from knowledge of their intrinsic viscosities and molecular weight (Equation 12.71). Specifically, the unperturbed dimensions can be calculated from the value of K .

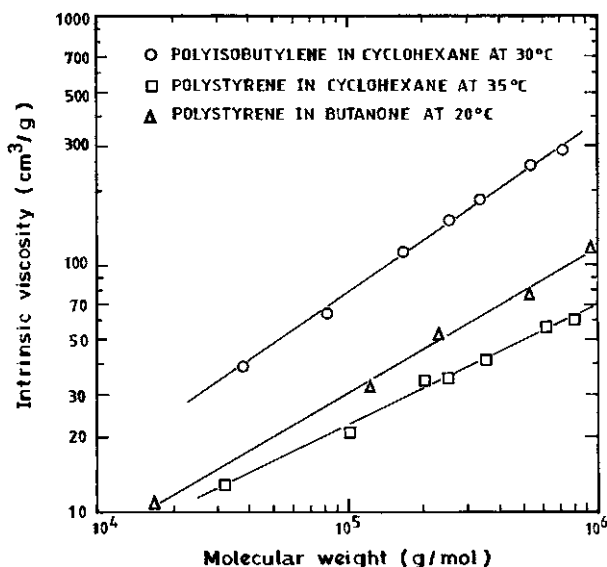


Figure 12.17 Intrinsic viscosity–molecular weight relationship. (From Alcock, H.R. and Lampe, F.W., *Contemporary Polymer Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1981. With permission.)

D. MOLECULAR WEIGHT FROM INTRINSIC VISCOSITY

Polymers possess the unique capacity to increase the viscosity of the solvent in which they are dissolved. Within a homologous series of linear polymers, the higher the molecular weight the greater the increase in viscosity for a given polymer concentration. In other words, this capacity to enhance viscosity or intrinsic viscosity is a reflection of the molecular weight of the dissolved polymer. Consequently, intrinsic viscosity measurements provide a tool for characterization of polymer molecular weight. However, since intrinsic viscosity does not provide absolute values of molecular weight, the relation between intrinsic viscosity and molecular weight has to be established empirically by comparison with molecular weights determined from absolute methods such as osmometry, light scattering, and ultracentrifugation. A linear relation has been found to exist between the logarithms of the intrinsic viscosities of different molecular weight fractions of a given polymer and the logarithms of the molecular weights of these fractions. This is illustrated for polyisobutylene in cyclohexane at 30°C and for polystyrene in cyclohexane at 35°C and in ethylethylketone at 25°C, as shown in Figure 12.17. The slopes of these curves for a given polymer depend on the solvent and, for a given polymer–solvent pair, on the temperature. It has also been

established that the slopes of such plots for all polymer–solvent systems fall within the range of 0.5 to 1.0. The linear relation between $\log[\eta]$ and $\log M$ may then be written as

$$[\eta] = K M^a \quad (12.74)$$

where K and a are constants determined from the intercept and slope of plots such as in [Figure 12.17](#).

The relation given in Equation 12.74 is referred to as the Mark–Houwink equation. Using the equation, it is possible to calculate the molecular weight from intrinsic viscosity measurements as long as K and a have been established for a particular temperature.

It must be reemphasized that the Mark–Houwink equation applies to fractionated samples of a given polymer. This means that, strictly speaking, it covers only a narrow molecular weight range. However, it is relatively easier in practice to use intrinsic viscosity measurements for the determination of the molecular weights even for unfractionated polymers. For such molecularly heterogeneous polymers, the appropriate relation becomes

$$[\eta] = K \bar{M}_v^a \quad (12.75)$$

where \bar{M}_v is the viscosity average molecular weight given by

$$\bar{M}_v = \left[\sum \omega_i M_i^a \right]^{1/a} = \left[\frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right]^{1/a} \quad (12.76)$$

Table 12.9 *Intrinsic Viscosity–Molecular Weight Relationship, $[\eta] = KM^a$*

Polymer	Solvent	Temperature (°C)	Mol-Wt Range $\times 10^{-4}$	$K \times 10^3$ (ml/g)	a
Polybutadiene	Cyclohexane	40	4–17	28.2	0.70
	Benzene	30	5–50	33.7	0.715
	Toluene	30	5–16	29.4	0.753
Natural rubber	Benzene	30	8–28	18.5	0.74
	Toluene	25	7–100	50.2	0.667
Polyethylene					
Low pressure	Decalin	135	3–100	67.7	0.67
High pressure	Decalin	70	0.2–3.5	38.73	0.738
Polyisobutylene	Benzene	25	0.05–126	83.0	0.53
	Cyclohexane	25	14–34	40.0	0.72
	Diisobutylene	25	0.4–2.5	130.0	0.50
	Toluene	25	14–34	87.0	0.56
Polypropylene (atactic)	Decalin	135	2–39	15.8	0.77
	Benzene	25	6–31	27.0	0.71
	Cyclohexane	25	6–31	16.0	0.80
Polypropylene (isotactic)	Decalin	135	2–62	11.0	0.80
Poly(methyl methacrylate)	Acetone	25	2–780	5.3	0.73
	Benzene	25	2–740	5.5	0.76
	Chloroform	25	40–330	3.4	0.83
	Benzene	20	0.6–520	12.3	0.72
Polystyrene (atactic)	Cyclohexane	34.5	14–200	84.6	0.50
	Benzene	30	4–37	10.6	0.735
Polystyrene (isotactic)	Toluene	30	15–71	9.3	0.72
	Chloroform	30	9–32	25.9	0.734

From Kurata, M., Tsunashima, Y., Iwama, M., and Kamada, K., in *Polymer Handbook*, 2nd ed., Brandrup, J. and Immergut, E.H., Eds., John Wiley & Sons, New York, 1975. With permission.

where $\omega_i = c_i/c =$ weight fraction of species i ; N_i , M_i , and C_i are the number of molecules, molecular weight, and concentration, respectively, of the same species; and $C = \sum c_i$ is the total concentration of all species. [Table 12.9](#) lists the values for K and θ for some selected polymer–solvent systems.

Example 12.4: Explain the variation in the value of K with temperature for polystyrene measured in different solvents.

Solvent	$\theta(K)$	$K \times 10^4$ (at $T = \theta$)
Cyclohexane	307	8.2
Methylcyclohexane	343.5	7.6
Ethylcyclohexane	343	7.5

Solution: K is a constant that is essentially independent of the molecular weight of the polymer and the character of the solvent medium, as amply demonstrated by the above data. However, K shows a decrease with increasing temperature. From Equation 12.72, K is proportional to the factor \bar{r}_0^2/M . We recall that the unperturbed root-mean-square end-to-end distance $(\bar{r}_0^2)^{1/2}$ is expanded invariably to greater dimensions relative to completely free rotation as a result of the effects of hindrances to free rotation. As the temperature is increased, the tendency to completely free rotation is enhanced as the effects of these hindrances are diminished. Consequently, K also decreases.

Example 12.5: Given the following values of η_r for a polyisobutylene sample of molecular weight 1,500,000:

Solvent	Temp (°C)	C = 0.05	0.10	0.15	0.20g/dl
Cyclohexane	30	1.282	1.611	1.988	2.412
Diisobutylene	20	1.173	1.365	1.578	1.809
Benzene	25	1.066	1.136	1.209	1.287

- Determine $[\eta]$ and k' in each solvent.
- Calculate $(\bar{r}_0^2/M)^{1/2}$, C_∞ and the value α_n in each solvent. Note that 25°C is the θ -temperature in benzene and assume $\Phi = 2.6 \times 10^{21}$ in this case.

Solution:

$$\eta_{sp} = \eta_r - 1$$

From the plot of η_{sp}/C vs. C , i.e., [Figure E12.5](#)

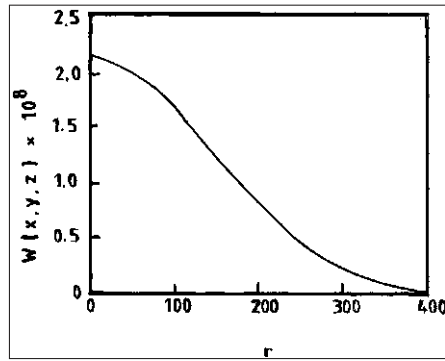


Figure E12.5

$$\text{Hexane: } [\eta] = 5.15 \text{ slope} = k'[\eta]^2 = 9.75$$

$$k' = 9.75 / (5.15)^2 = 0.368$$

	$[\eta]$	Slope	k'
Hexane	5.15	9.75	0.368
Diisobutylene	3.20	4.25	0.415
Benzene	1.28	0.8	0.488

b. Since 25°C θ is the temperature in benzene,

$$[\eta]_{\theta} = KM^{1/2} = 1.28$$

$$K = \frac{[\eta]_{\theta}}{M^{1/2}} = \frac{1.28}{(1.5 \times 10^6)^{1/2}} = 1.045 \times 10^{-3}$$

$$K = \Phi \left(\frac{\bar{r}_0^2}{M} \right)^{3/2}$$

or

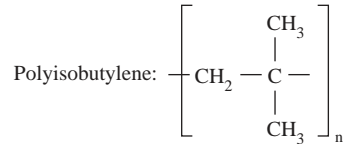
$$\left(\frac{\bar{r}_0^2}{M} \right)^{3/2} = \frac{K}{\Phi} = \frac{1.045 \times 10^{-3}}{2.6 \times 10^{21}}$$

$$= 0.402 \times 10^{-24}$$

$$\left(\frac{\bar{r}_0^2}{M} \right)^{1/2} = 0.738 \times 10^{-8}$$

$$C_{\infty} = \frac{\overline{r_0^2}}{nl^2}$$

$$\begin{aligned}\overline{r_0^2} &= (0.738 \times 10^{-8})^2 M \\ &= (0.738 \times 10^{-8})^2 (1.5 \times 10^6) \\ &= 0.817 \times 10^{-10}\end{aligned}$$



(Str. 3)

Molecular weight of monomer = 56 = M_o .

$$\begin{aligned}n = 2 \text{ DP} &= \frac{2 M}{M_o} = \frac{2 \times 1.5 \times 10^6}{56} \\ &= 5.357 \times 10^4\end{aligned}$$

$$l = 1.54 \times 10^{-8} \text{ cm}$$

$$\begin{aligned}C_{\infty} &= \frac{0.817 \times 10^{-10}}{5.357 \times 10^4 \times 2.372 \times 10^{-16}} \\ &= 6.43\end{aligned}$$

$$[\eta] = [\eta]_{\theta} \alpha_n^3$$

Cyclohexane:

$$\alpha_n = \left(\frac{[\eta]}{[\eta]_{\theta}} \right)^{1/3} = \left(\frac{5.15}{1.28} \right)^{1/3} = 1.59$$

Dilsobutylene:

$$\alpha_n = \left(\frac{3.20}{1.28} \right)^{1/3} = 1.36$$

Benzene:

$$\alpha_n = \left(\frac{1.28}{1.28} \right)^{1/3} = 1.0$$

VI. PROBLEMS

12.1. Which of the following is the most suitable solvent for (a) natural rubber and (b) polyacrylonitrile: *n*-pentane, toluene, *o*-dichlorobenzene, nitroethane, and nitromethane? The densities of natural rubber and polyacrylonitrile are 1.1 and 1.15, respectively.

12.2. Explain the following observations.

- a. An excellent example of a homogeneous polymerization is the bulk polymerization of methyl methacrylate, while heterogeneous polymerization is exemplified by bulk polymerization of vinyl chloride.

- b. Polyacrylonitrile is prepared industrially either by precipitation polymerization of acrylonitrile in water or its solution polymerization in dimethyl formamide.
- 12.3. Show that the end-to-end distance of the freely jointed chain is expanded by a factor of $\sqrt{2}$ when there is restriction to bond angles. Assume that the bond angle is tetrahedral.
- 12.4. The root-mean-square end-to-end distance of poly(acrylic acid) with molecular weight 1,000,000 in a θ solvent at 30°C is 670 Å. Taking the C–C bond length as 1.53 Å and all backbone bond angles as tetrahedral, calculate:
- Flory's characteristic ratio
 - The Stockmayer–Kurata ratio
 - The Kratky–Porod persistence length
 - The contour length of the planar zigzag
- 12.5. How does the root-mean-square end-to-end distance of a flexible polymer depend on:
- Molecular weight at the Flory temperature θ
 - Temperature at the Flory point
 - Molecular weight, well above the Flory temperature for a good solvent
- 12.6. Calculate the vapor pressure over a 50% solution (by volume) of poly(vinyl acetate) in methylethyl ketone at 25°C using the lattice theory and assuming that the value of χ_1 derived from the dilute solution data is valid in the concentrated solution. The vapor pressure of pure methylethyl ketone at 25°C is 100 mm Hg.
- 12.7. The size of a polyisobutylene molecule in the pure material is given experimentally as

$$\left(\frac{\overline{r_0^2}}{M} \right)^{1/2} = 0.795 \text{ at } 24^\circ\text{C}$$

$$= 0.757 \text{ at } 95^\circ\text{C}$$

where r_0 is in angstroms and M is molecular weight. Compare these results to those obtained by assuming free rotation about the valence bonds. Explain why the experimental values:

- Are higher than the calculated values
- Decrease with increasing temperature

If the root-mean-square end-to-end distance of the polymer molecule is 1000 Å, what is its molecular weight at 24°C?

- 12.8. Compute the root-mean-square end-to-end length for a polystyrene molecule having a molecular weight of 10^6 . Assume free rotation on the valence cone.
- 12.9. Polyisobutylene has a molecular weight of 885,000 and density 0.8 g/cm³. If

$$\left(\frac{\overline{r_0^2}}{M} \right)^{1/2} = 800 \times 10^{-11}$$

- What is the approximate contour length of this polymer molecule (length of the planar zigzag structure)?
- What is the approximate size of the molecule if a compact shape is assumed? Compact shape density is 0.8 g/cm³ (what is the radius of an equivalent sphere).
- What is the approximate size of the molecule if a hindered random coil is assumed?
- Discuss the relative magnitudes of parts b and c.

- 12.10. The ratios of the unperturbed end-to-end dimensions measured at 60°C to that calculated assuming completely free rotation $(\bar{r}_{00}^2/r_{0f}^2)^{1/2}$ for natural rubber and gutta-percha are 1.71 and 1.46, respectively. Explain.
- 12.11. The following data are for a narrow molecular weight fraction of poly(methyl methacrylate) in acetone at 30°C (density acetone = 0.780 g/cm³). Plot appropriately and estimate $[\eta]$, k' (Huggins constant), \bar{M}_n , and the second virial coefficient. Knowing that $[\eta]_0 = 4.8 \times 10^{-4} \text{ M}^{0.5}$ for this polymer in a theta solvent at 30°C, calculate from these data $(\bar{r}_0^2)^{1/2}$, $(\bar{r}_2^2)^{1/2}$ and α , the expansion factor.

Concentration C, (g/100 ml)	Osmotic Pressure (cm solvent)	η_r , Relative Viscosity
0.275	0.457	1.170
0.338	0.592	—
0.344	0.609	1.215
0.486	0.867	—
0.96	1.756	1.629
1.006	2.098	—
1.199	2.710	1.892
1.536	3.728	—
1.604	3.978	2.330
2.108	5.919	2.995
2.878	9.713	—

- 12.12. The following data are available for polymers A and B in the same solvent at 27°C.

Conc, C _A (g/dl)	Osmotic pressure, (cm of solvent)	Conc, C _B (g/dl)	Osmotic Pressure (cm of solvent)
0.320	0.70	0.400	1.60
0.660	1.82	0.900	4.44
1.000	3.10	1.400	8.95
1.900	9.30	1.800	13.0

Solvent density = 0.85 g/cm³; polymer density = 1.15 g/cm³.

- Estimate \bar{M}_n and the second virial coefficient for each polymer.
- Estimate M_n for a 25:75 mixture of A and B.
- If $\bar{M}_w/M_n = 2.00$ for A and for B, what is \bar{M}_w/M_n for the mixture in part b?

REFERENCES

- Hildebrand, J.H. and Scott, R.L., *The Solubility of Nonelectrolytes*, Van Nostrand-Reinhold, New York, 1950.
- Burrell, H. and Immergut, B., in *Polymer Handbook*, Brandrup, J. and Immergut, E.M., Eds., John Wiley & Sons, New York, 1967.
- Hoy, K.L., *J. Paint Technol.*, 42, 76, 1970.
- Kurata, M., Tsunashima, Y., Iwama, M., and Kamada, K., Viscosity molecular-weight relationships and unperturbed dimensions of linear chain molecules, in *Polymer Handbook*, 2nd ed., Brandrup, J. and Immergut, E.H., Eds., John Wiley & Sons, New York, 1975.
- Flory, P.J., *J. Chem. Phys.*, 10, 51, 1942.
- Huggins, M.L., *Ann. N.Y. Acad. Sci.*, 43, 1, 1942.
- Huggins, M.L., *J. Phys. Chem.*, 45, 151, 1942.
- Huggins, M.L., *J. Am. Chem. Soc.*, 64, 1712, 1942.
- Newing, M.J., *Trans. Faraday Soc.*, 46, 613, 1950.
- Bawn, C.E.H., Freeman, R.F.J., and Kamaliddin, A.R., *Trans. Faraday Soc.*, 46, 677, 1950.
- Gee, G. and Orr, W.J.C., *Trans. Faraday Soc.*, 42, 507, 1946.
- Gee, G., *J. Chem. Soc.*, p. 280, 1947.

13. Klotz, M., *Chemical Thermodynamics*, Prentice-Hall, Englewood Cliffs, NJ, 1950.
14. Flory, P.J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
15. Wolf, B.A. in *Polymer Handbook*, 2nd ed., Brandrup, J. and Immergut, E.M., Eds., John Wiley & Sons, New York, 1967.
16. Bird, R.B., Stewart, W.E., and Lightfoot, E.N., *Transport Phenomena*, John Wiley & Sons, New York, 1960.
17. Anon., *More Solutions to Sticky Problems*, Brookfield Engineering Laboratories, Stoughton, MA, 1985.
18. Alcock, H.R. and Lampe, F.W., *Contemporary Polymer Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1981.