

Conformation, Solutions, and Molecular Weight

Solvents are frequently used during the polymerization process (Chapter 2), during fabrication (e.g., film casting, fiber formation, and coatings), and for determining molecular weights and molecular-weight distributions. Interactions between a polymer and solvent influence chain dimensions (i.e., conformations) and, more importantly, determine solvent activities. The measurement of osmotic pressure and scattered-light intensity from dilute polymer solutions—techniques based upon the principles of polymer-solution thermodynamics—are the primary methods used to determine number-average and weight-average molecular weights, respectively. Other solution-property techniques, such as the determination of intrinsic viscosity and gel-permeation chromatography (GPC), are widely used as rapid and convenient methods to determine polymer molecular weights and, in the case of GPC, molecular-weight distributions as described in this chapter.

3.1 POLYMER CONFORMATION AND CHAIN DIMENSIONS

As briefly discussed in Chapter 1, the *configuration* of a polymer chain refers to the stereochemical arrangement of atoms along that chain. Examples include tactic and geometric isomers, which are determined by the mechanism of the polymerization and, therefore, cannot be altered without breaking primary valence bonds. In contrast, polymer chains in solution are free to rotate around individual bonds, and almost a limitless number of *conformations* or chain orientations in three-dimensional space are possible for long, flexible macromolecules.

To describe the conformation of polymer molecules, a model of a *random-flight* or *freely jointed* and *volumeless* chain is often used as the starting point. Such a hypothetical chain is assigned n freely jointed links of equal length, ℓ . If one end of this hypothetical chain is fixed at the origin of a Cartesian coordinate-system, the other end of the chain has some finite probability of being at any other coordinate position, as illustrated by Figure 3-1. One of the many possible conformations, and the simplest, for this idealized chain is the fully extended (linear) chain where the end-to-end distance, r , is

$$r = n\ell. \quad (3.1)$$

Flory¹ was the first to derive an expression for the probability of finding one end of the freely jointed polymer chain in some infinitesimal volume ($dV = dx \cdot dy \cdot dz$) around a particular coordinate (x, y, z) point when one end of the chain is fixed at the origin of a Cartesian coordinate-system, as illustrated in Figure 3-1. The probability is given by a *Gaussian distribution* in the form

$$\omega(x, y, z) dx dy dz = \frac{b^3}{\sqrt{\pi}} \exp(-b^2 r^2) dx dy dz \quad (3.2)$$

where $\omega(x, y, z)$ is the Gaussian distribution function, r is the radius of a spherical shell centered at the origin

$$r^2 = x^2 + y^2 + z^2, \quad (3.3)$$

and

$$b^2 = \frac{3}{2n\ell^2}. \quad (3.4)$$

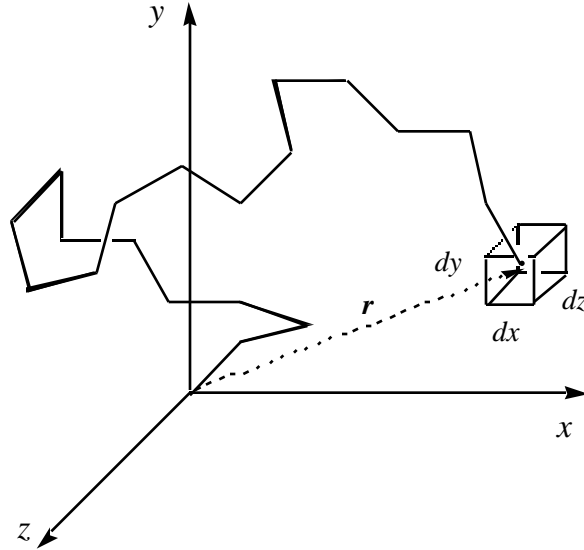


Figure 3-1 Illustration of a random conformation of an idealized freely jointed polymer chain having 20 segments of equal length. The end-to-end distance of this conformation is indicated as r . With one end of the chain fixed at the origin of the Cartesian coordinate system, the probability of finding the other end in some infinitesimal volume element ($dV = dx \cdot dy \cdot dz$) is expressed by a Gaussian distribution function (eq 3.2).

Alternately, the probability that a chain displacement length has a value in the range r to $r+dr$ is given as

$$\omega(r)dr = \frac{b^3}{\sqrt{2}} \exp(-b^2 r^2) 4 r^2 dr. \quad (3.5)$$

where $\omega(r)$ is the radial distribution function. The radial distribution function for a freely jointed polymer chain consisting of 10^4 freely jointed links each of length 2.5 \AA is plotted as a function of the radial distance, r , in Figure 3-2.

The mean-square end-to-end distance is obtained from the second moment of the radial distribution function as

$$\langle r^2 \rangle = \frac{\int_0^\infty r^2 \omega(r) dr}{\int_0^\infty \omega(r) dr}. \quad (3.6)$$

Substitution of the radial distribution function (eq. 3.5) into eq. 3.6 and evaluating the integral gives the mean-square end-to-end distance of the freely jointed and volumeless chain as

$$\langle r^2 \rangle = n\ell^2 \quad (3.7)$$

Alternately, the *root*-mean-square end-to-end distance, r^2 ^{1/2}, of the freely rotating chain is given as

$$\langle r^2 \rangle^{1/2} = n^{1/2} \ell \quad (3.8)$$

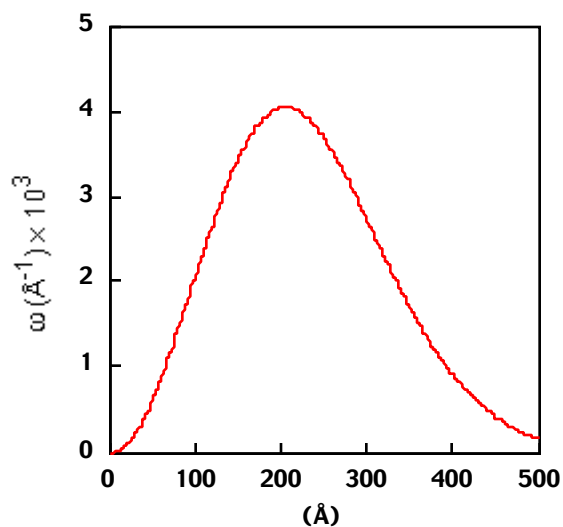


Figure 3-2 The radial-distribution function calculated (eq. 3.5) for a hypothetical polymer chain consisting of 10^4 freely jointed segments of length 2.5 Å.

Real polymer chains differ from the above idealized, freely jointed model in the following three significant ways:

- Valence angles of real bonds are fixed. For example, the tetrahedrally bonded C–C bond angle is 109.5° . Introducing fixed bond angles results in an expansion of the chain expressed by the mean-square end-to-end distance as (for large n)

$$\langle r^2 \rangle = n\ell^2 \frac{1 - \cos \theta}{1 + \cos \theta} \quad (3.9)$$

where θ is the valence bond angle, as illustrated for an extended chain conformation in Figure 3-3. For the tetrahedral angle, $\theta = 109.5^\circ$, $\cos \theta = -1/3$, and therefore

$$\langle r^2 \rangle = 2n\ell^2. \quad (3.10)$$

Comparison of this result with that of eq. 3.7 indicates that the fixed valence angle restriction results in a doubling of the mean-square end-to-end distance over that of a freely rotating chain.

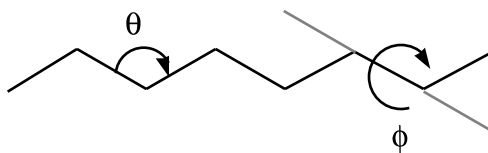


Figure 3-3 Illustration of an extended polymer chain showing the valence bond angle, θ , and bond-rotation angle, ϕ .

•Rotations of polymer chains may be restricted due to interference from bulky substituent groups. As illustrated by the potential-energy diagram shown in Figure 3-4, overlap of bulky substituent groups on adjacent carbon atoms results in a high-energy, unfavorable conformational state. The result of this steric interference is to further expand chain dimensions over the random-flight model. Equation 3.7 may be further modified to include the effects of both fixed bond angles and hindered rotations as

$$\langle r^2 \rangle = n\ell^2 \frac{1 - \cos \theta}{1 + \cos \theta} \frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \quad (3.11)$$

where $\langle \cos \phi \rangle$ represents the average cosine of the bond-rotation angle, ϕ , identified in Figure 3-3. This second contribution is much more difficult to evaluate but can be obtained by statistical-weighting methods, as discussed by Flory.²

•Real chain-bonds have a finite (van der Waals) volume and therefore some volume is *excluded*. This means that a real bond cannot occupy the same space of any other bond—a condition not imposed in the random-flight model. As in the case of restricted rotation, the effect of excluded volume is to increase the spatial dimensions of the polymer chain over that of the random-flight model.

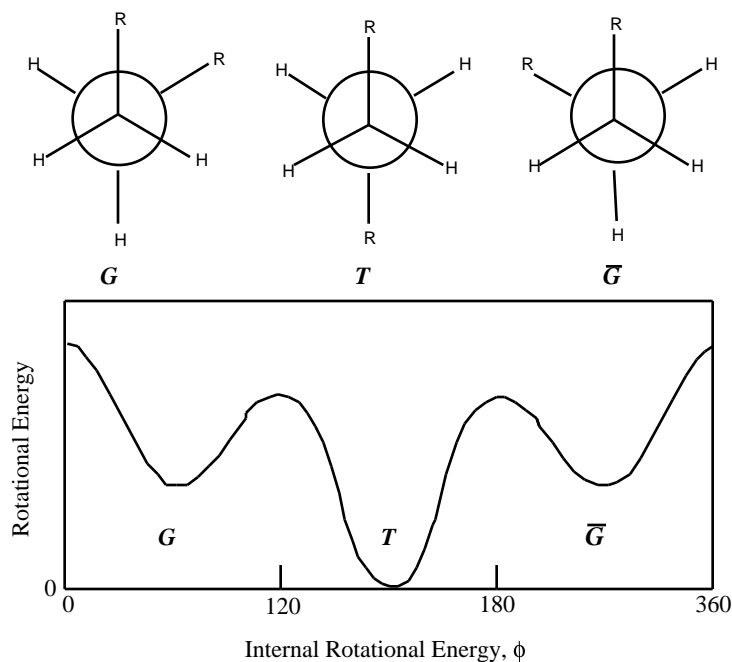


Figure 3-4 Newman projections (top) of three lowest energy projections of two adjacent bond atoms with substituent group, R. In the case of a polymer chain, R represents all chain segments before and after the bond in question. The potential-energy diagram (bottom) displays the three lowest energy rotational states — *trans* (*T*) and the two *gauche* forms, *G* and \bar{G} .

Beyond the calculation of mean-square end-to-end distances, the conformations of realistic polymer models can be simulated by computer. For example, Figure 3-5 shows the results of a Monte Carlo simulation of the conformation of a small polyethylene chain having 200 skeletal bonds using values of actual bond lengths, bond angles, and the known preference for *trans*-rotational states for this polymer.³

As a convenient way to express the size of a real polymer chain in terms of parameters that can be readily measured, the freely rotating chain model (eq. 3.7) may be modified to include the effects of fixed bond angles, restricted rotation, and excluded volume on the root-mean-square end-to-end distance in the following way:

$$\langle r^2 \rangle^{1/2} = \alpha (nC)^{1/2} \ell. \quad (3.12)$$

In this expression, α is called the *chain expansion factor* which is a measure of the effect of excluded volume, and C is called the *characteristic ratio*, which contains the contributions from both fixed valence angles and restricted chain rotation. For large polymer chains, typi-

cal values of C range from about 5 to 10. Another way to represent eq. 3.12 is by use of an *unperturbed* root-mean-square end-to-end distance, $r_o^{2,1/2}$, as

$$\langle r^2 \rangle^{1/2} = \alpha \langle r_o^2 \rangle^{1/2} \quad (3.13)$$

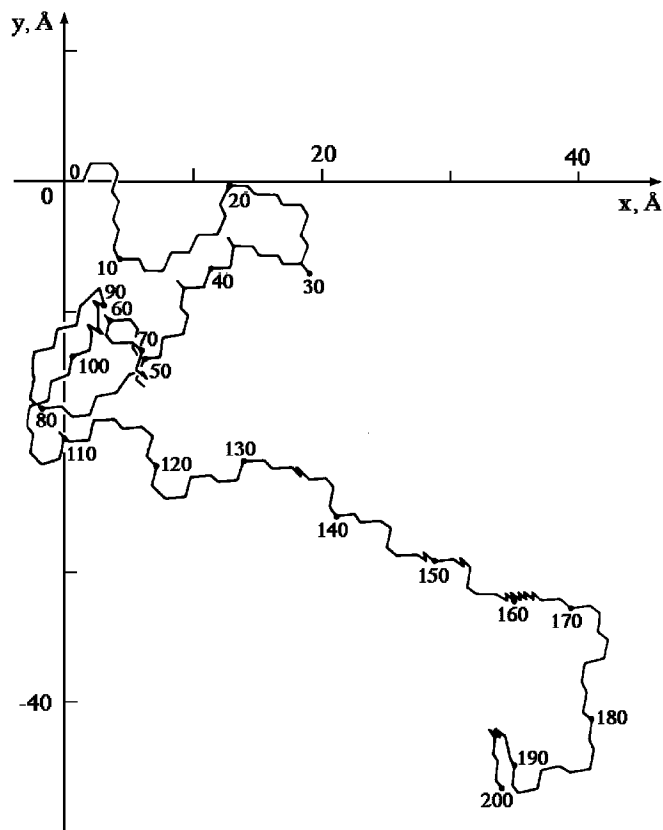


Figure 3-5 A three-dimensional computer simulation of a conformation of a small polyethylene chain (200 bonds) projected on the plane of the graph. (Reprinted with permission of the publisher from "Rubber Elasticity" by J. E. Mark. *Journal of Chemical Education*, 1981, **58**, pp. 2898–2903.)

Comparison of eqs. 3.12 and 3.13 indicates that *unperturbed* dimensions are those of a real polymer chain in the absence of excluded-volume effects (i.e., for $\alpha = 1$). By equating

eqs. 3.12 and 3.13, the characteristic ratio[†] is obtained as the ratio of the unperturbed mean-square end-to-end distance to the mean-square end-to-end distance of the freely jointed model (eq. 3.7)

$$C = \frac{\langle r^2 \rangle_0}{nl^2}. \quad (3.14)$$

Unperturbed dimensions are realized in the case of a polymer in solution with a thermodynamically-poor solvent at a temperature near incipient precipitation. This temperature is called the *theta* (θ) temperature. Experiments, using small-angle neutron scattering, have indicated that the dimensions of polymer chains in the amorphous solid-state are also unperturbed.⁴ In solution with a good solvent (i.e., $\alpha > 1$), where polymer-solvent interactions are stronger than polymer-polymer or solvent-solvent interactions, dimensions of the polymer chain are expanded over those in the unperturbed state ($\alpha = 1$).

3.2 THERMODYNAMICS OF POLYMER SOLUTIONS

It was recognized in the 1940s that the thermodynamics of polymeric systems needs to be treated in a special way. In 1942, Gee and Treloar⁵ reported that even dilute polymer solutions deviated strongly from ideal-solution behavior. In these early experiments, a high-molecular-weight rubber was equilibrated with benzene vapor in a closed system and the partial pressure of the benzene (the solvent), p_1 , was measured. The solvent activity, a_1 , was calculated as the ratio of p_1 to the saturated vapor pressure of pure benzene, p_1^0 , at the system temperature as[†]

[†] The characteristic ratio can be calculated from a knowledge of actual valence angles, θ , and the statistical weighting of torsional angles ϕ (see eq. 3.11), as²

$$C = \frac{1 - \cos\theta}{1 + \cos\theta} \frac{1 + \langle \cos\phi \rangle}{1 - \langle \cos\phi \rangle}.$$

[†] By definition, the activity of the i th component in a mixture is defined as

$$a_i = \frac{\hat{f}_i}{f_i^0}$$

where \hat{f}_i is the fugacity of that component in the mixture and f_i^0 is the standard-state fugacity, usually the fugacity of the pure liquid component at the system temperature. In the limit of low pressure at which the vapor mixture becomes ideal, the two fugacities may be replaced by the corresponding pressure terms (i.e., $\hat{f}_i = p_i = x_i p$ and $f_i^0 = p_i^0$). If the vapor phase is nonideal, the

$$a_1 = \frac{p_1}{p_1^0} \quad (3.15)$$

Experimental benzene activity is plotted as a function of the *volume fraction* of rubber, ϕ_2 , in Figure 3-6. These data are compared with predictions of *Raoult's law* for an ideal solution given as

$$p_1 = x_1 p_1^0 \quad (3.16)$$

where x_1 is the mole fraction of the solvent. Substitution of eq. 3.16 into eq. 3.15 yields the result that $a_1 = x_1$ for an ideal solution. As the experimental data (Figure 3-6) show, polymer-solution behavior follows a strong *negative deviation* from Raoult's ideal-solution law.

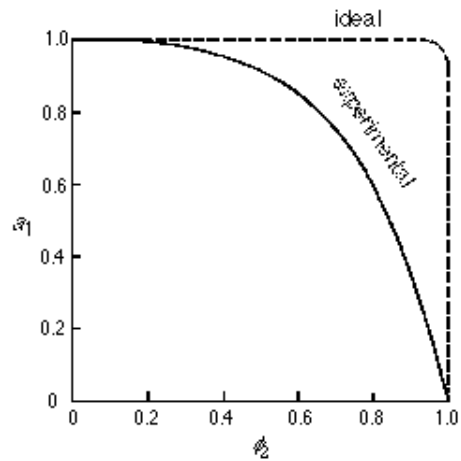


Figure 3-6 Plot of benzene activity, a_1 , versus volume fraction of rubber, ϕ_2 . Dashed line represents ideal-solution behavior. (Adapted from ref 1 by permission of the publisher.)

solvent activity can be obtained from the relationship⁶

$$a_1 = \frac{p_1}{p_1^0} \exp -\frac{B}{RT} (p_1^0 - p_1)$$

where B is the second virial coefficient of the pure vapor at the system temperature.

3.2.1 The Flory–Huggins Theory

In the early 1940s, Paul Flory⁷ and Maurice Huggins,⁸ working independently, developed a theory based upon a simple lattice model that could be used to understand the nonideal nature of polymer solutions. In the *Flory–Huggins model*, the lattice sites, or holes, are chosen to be the size of the solvent molecule. As the simplest example, consider the mixing of a low-molecular-weight solvent (component 1) with a low-molecular-weight solute (component 2). The solute molecule is assumed to have the same size as a solvent molecule, and therefore only one solute or one solvent molecule can occupy a single lattice site at a given time. A representation of the lattice model for this case is illustrated in Figure 3-7.

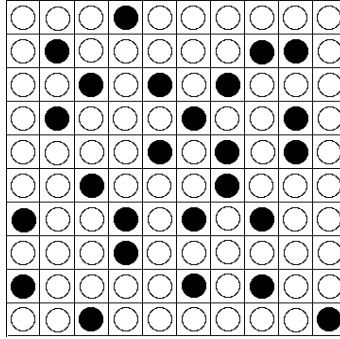


Figure 3-7 Representation of two-dimensional Flory–Huggins lattice containing solvent molecules (□) and a low-molecular-weight solute (■).

The increase in entropy due to mixing of a solvent and solute, S_m , may be obtained from the *Boltzmann relation*

$$S_m = k \ln \quad (3.17)$$

where k is Boltzmann's constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$) and gives the total number of ways of arranging n_1 indistinguishable solvent molecules and indistinguishable n_2 solute molecules, where $N = n_1 + n_2$ is the total number of lattice sites. The probability function is given as

$$= \frac{N!}{n_1! n_2!} \quad (3.18)$$

Use the Stirling approximation

$$\ln n! = n \ln n - n \quad (3.19)$$

leads to the expression for the entropy of mixing *per molecule* as

$$S_m = -k(n_1 \ln x_1 + n_2 \ln x_2). \quad (3.20a)$$

Alternately, the *molar* entropy of mixing can be written as

$$S_m = -R(x_1 \ln x_1 + x_2 \ln x_2) \quad (3.20b)$$

where R is the ideal gas constant[†] and x_1 is the mole fraction of the solvent given as

$$x_1 = \frac{n_1}{n_1 + n_2}. \quad (3.21)$$

Equation 3.20b is the well-known relation for the entropy change due to mixing of an *ideal* mixture, which can also be obtained from classical thermodynamics of an ideal solution following the Lewis–Randall law.[‡] Equation 3.20 can be written for a multicomponent system having N components as

[†] $R = N_A k$ where N_A is Avogadro's number.

[‡] The relationship between the partial-molar Gibbs free-energy and fugacity is given as

$$d\bar{G}_i = d\mu_i = RT d \ln \hat{f}_i.$$

Integration from the standard state to some arbitrary state gives

$$\bar{G}_i - G_i^\circ = RT \ln \frac{\hat{f}_i}{f_i^\circ}$$

where \hat{f}_i is the fugacity of component i in a mixture and f_i° is the standard-state fugacity. Substitution of the Lewis–Randall law

$$\hat{f}_i^{\text{id}} = x_i f_i^\circ$$

gives

$$\bar{G}_i^{\text{id}} = RT \ln x_i.$$

Since the thermodynamic properties of a solution are the sum of the product of the mole fraction and the partial-molar property of each of m components in the mixture, it follows that the molar change in Gibbs free energy of an ideal solution is then expressed as

$$S_m^{\text{id}} = -R \sum_{i=1}^N x_i \ln x_i. \quad (3.22)$$

The entropy of mixing a low-molecular-weight solvent with a *high*-molecular-weight *polymer* is smaller than given by eq. 3.20 for a low-molecular-weight mixture. This is due to the loss in conformational entropy resulting from the linkage of individual repeating units along a polymer chain compared to the less ordered case of unassociated low-molecular-weight solute-molecules dispersed in a low-molecular-weight solvent. In the development of an expression for S_m for a high-molecular-weight polymer in a solvent, the lattice is established by dividing the polymer chain into r segments, each the size of a solvent molecule, where r is the ratio of polymer volume to solvent volume (i.e., a lattice site). For n_2 polymer molecules, the total number of lattice sites is then $N = n_1 + rn_2$. A lattice containing low-molecular-weight solvent molecules and a single polymer-chain is illustrated in Figure 3-8.

$$G^{\text{id}} = \sum_{i=1}^m x_i \left(\overline{G}_i^{\text{id}} \right) = RT \sum_{i=1}^m x_i \ln x_i.$$

Since

$$\overline{G}_i^{\text{id}} = \overline{H}_i^{\text{id}} - T \overline{S}_i^{\text{id}}$$

and $\overline{H}_i^{\text{id}} = 0$ for an ideal solution, we have

$$\overline{S}_i^{\text{id}} = -\frac{1}{T} \overline{G}_i^{\text{id}} = -R \ln x_i$$

and

$$S^{\text{id}} = \sum_{i=1}^m x_i \left(\overline{S}_i^{\text{id}} \right) = -R \sum_{i=1}^m x_i \ln x_i.$$

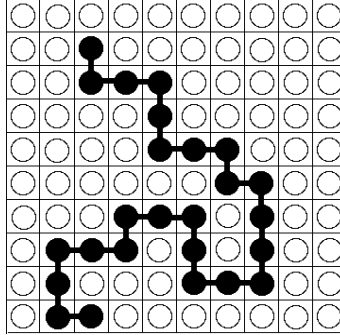


Figure 3-8 Lattice model for a polymer chain in solution. Symbols represent solvent molecules (○) and polymer-chain segments (●).

The expression for the entropy change due to mixing obtained by Flory and Huggins is given as[†]

$$S_m = -k(n_1 \ln \phi_1 + n_2 \ln \phi_2) \quad (3.23)$$

where ϕ_1 and ϕ_2 are the lattice *volume* fractions of solute (component 1) or polymer (component 2), respectively. These are given as

$$\phi_1 = \frac{n_1}{n_1 + m_2} \quad (3.24a)$$

and

$$\phi_2 = \frac{m_2}{n_1 + m_2} \quad (3.24b)$$

For a polydisperse polymer, eq. 3.23 can be modified as

$$S_m = -k \left[n_1 \ln \phi_1 + \sum_{i=2}^N n_i \ln \phi_i \right] \quad (3.25)$$

where the summation is over all polymer chains (N) in the molecular-weight distribution. For simplicity, the most commonly used form of the entropy expression, eq. 3.23, will be

[†] An excellent review of the development of the lattice model has been given by Flory.⁹

used in further discussion. Equation 3.23 provides the entropy term in the expression for the Gibbs free energy of mixing, G_m , of a polymer solution given as

$$G_m = H_m - T S_m. \quad (3.26)$$

Once an expression for the enthalpy of mixing, H_m , is known, expressions for the chemical potential and activity of the solvent can be obtained as

$$\mu_1 = \mu_1^\circ - \bar{G}_m = \frac{G_m}{n_1} \quad T, p \quad (3.27)$$

where \bar{G}_m is the partial-molar Gibbs free energy of mixing and the activity is related to the chemical potential as

$$\ln a_1 = \frac{\mu_1}{kT}. \quad (3.28)$$

For an ideal solution, $H_m = 0$. Solutions for which $H_m \neq 0$ but for which S_m is given by eq. 3.20 are termed *regular* solutions and are the subject of most thermodynamic models for polymer mixtures. The expression that Flory and Huggins gave for the enthalpy of mixing is

$$H_m = zn_1r_1\phi_2 \omega_{12} \quad (3.29)$$

where z is the lattice coordination number or number of cells that are first neighbors to a given cell, r_1 represents the number of "segments" in a solvent molecule for consideration of the most general case, and ω_{12} is the change in internal energy for formation of an unlike molecular pair (solvent-polymer or 1-2) contacts given by the *mean-field expression* as

$$\omega_{12} = \omega_{12} - \frac{1}{2} (\omega_{11} + \omega_{22}) \quad (3.30)$$

where ω_{ij} is the energy of i - j contacts. It is clear from eqs. 3.29 and 3.30 that an ideal solution ($H_m = 0$) is one for which the energies of 1-1, 1-2, and 2-2 molecular interactions are equal.

Since z and ω_{12} have the character of empirical parameters, it is useful to define a single energy parameter called the Flory *interaction parameter*, χ_{12} , given as

$$\chi_{12} = \frac{zr_1 \omega_{12}}{kT} . \quad (3.31)$$

The interaction parameter is a dimensionless quantity that characterizes the interaction energy per solvent molecule (having r_1 segments) divided by kT . As eq. 3.31 indicates, χ_{12} is inversely related to temperature but is independent of concentration.

The expression for the enthalpy of mixing may then be written by combining eqs. 3.29 and 3.31 as

$$H_m = kT\chi_{12}n_1\phi_2 . \quad (3.32)$$

Combining the expression for the entropy (eq. 3.23) and enthalpy (eq. 3.32) of mixing gives the well-known Flory–Huggins expression for the Gibbs free energy of mixing

$$G_m = kT \left(n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_{12} n_1 \phi_2 \right) . \quad (3.33)$$

From this relationship, the activity of the solvent (eq. 3.28) can be obtained from eq. 3.33 as

$$\ln a_1 = \ln (1 - \phi_2) + 1 - \frac{1}{r} \phi_2 + \chi_{12} \phi_2^2 . \quad (3.34)$$

In the case of high-molecular-weight polymers for which the number of solvent-equivalent segments, r ,[†] is large, the $1/r$ term within parentheses on the right-hand side of eq. 3.34 can be neglected to give

$$\ln a_1 = \ln (1 - \phi_2) + \phi_2 + \chi_{12} \phi_2^2 . \quad (3.35)$$

The Flory–Huggins equation is still widely used and has been largely successful in describing the thermodynamics of polymer solutions; however, there are a number of important limitations of the original expression that should be emphasized. The most important are the following:

- Applicability only to solutions that are sufficiently concentrated that they have uniform segment density.
- There is no volume change of mixing (whereas favorable interactions between polymer and solvent molecules should result in a *negative* volume change).

[†] For a polymer sample with a distribution of molecular weights, r may be taken to be the number-average degree of polymerization, \bar{X}_n .

- There are no energetically-preferred arrangements of polymer segments and solvent molecules in the lattice.
- The interaction parameter, χ_{12} , is independent of composition.

There have been a number of subsequent developments to extend the applicability of the original Flory–Huggins theory and to improve agreement between theoretical and experimental results. For example, Flory and Krigbaum have developed a thermodynamic theory for dilute polymer solutions, which was described in Flory's original text.¹ Koningsveld¹⁰ and others have improved the agreement of the original Flory–Huggins theory with experimental data by an empirical modification of χ_{12} to include a composition dependence and to account for polymer polydispersity. Both of these approaches are presented briefly in the following section. More recent approaches employ equation-of-state theories such as those developed by Flory⁹ and others for which a volume change of mixing can be incorporated. These are developed later in Section 3.2.3.

3.2.2 Flory–Krigbaum and Modified Flory–Huggins Theory

Flory–Krigbaum Theory. Flory and Krigbaum¹¹ have provided a model to describe the thermodynamics of a dilute polymer solution in which individual polymer chains are isolated and surrounded by regions of solvent molecules. In contrast to the case of a semidilute solution addressed by the Flory–Huggins theory, segmental density can no longer be considered to be uniform. In their development, Flory and Krigbaum viewed the dilute solution as a dispersion of clouds consisting of polymer segments surrounded by regions of pure solvent. For a dilute solution, the expression for solvent activity was given as

$$\ln a_1 = (\kappa_1 - \psi_1)\phi_2^2 \quad (3.36)$$

where κ_1 and ψ_1 are heat and entropy parameters,[†] respectively. They defined an "ideal" or *theta* (θ) temperature as

$$\theta = \frac{\kappa_1 T}{\psi_1} \quad (3.37)$$

from which eq. 3.36 can be written as

$$\ln a_1 = -\psi_1 \left(1 - \frac{\theta}{T}\right) \phi_2^2. \quad (3.38)$$

It follows from eq. 3.38 that solvent activity approaches unity as temperature approaches the θ temperature. At the θ temperature, the dimensions of a polymer chain collapse to unperturbed dimensions (i.e., in the absence of excluded-volume effects), as described in Section 3.1.

Modified Flory–Huggins. In the original lattice theory, χ_{12} was given an inverse dependence upon temperature (eq. 3.31) but there was no provision for a concentration dependence which experimental studies has shown to be important. Koningsveld¹⁰ and others have introduced an empirical dependence to improve the agreement with experimental data by casting the Flory–Huggins expression in the general form

$$G_m = RT(\phi_1 \ln \phi_1 + \phi_2 \ln \phi_2 + g\phi_1\phi_2). \quad (3.39)$$

In eq. 3.39, g is an interaction energy term for which the concentration dependence can be given as a power series in ϕ_2 as

$$g = g_0 + g_1\phi_2 + g_2\phi_2^2 + \dots \quad (3.40)$$

where each g term, g_k ($k = 0, 1, 2, \dots$), has a temperature dependence that can be expressed in the form

$$g_k = g_{k,1} + \frac{g_{k,2}}{T}. \quad (3.41)$$

3.2.3 Equation-of-State Theories

Although the Flory–Huggins theory is still useful as a starting point for describing polymer thermodynamics, there are a number of weaknesses. For example, the simple lattice model does not accommodate a volume change of mixing, which can be significant in the case of a thermodynamically good solution. Such an inability to incorporate a volume change of mixing can lead to particular weakness in the prediction of phase equilibria. Substantial improvement in the theoretical treatment of polymer thermodynamics has been obtained by adopting a statistical-thermodynamics approach based upon an equation of state (EOS) as first proposed by Flory.¹² Other successful EOS theories have been proposed by Sanchez¹³ and by Simha.¹⁴ For the purpose of providing an introduction to the use of EOS theories in the treatment of polymer thermodynamics, only the Flory EOS theory, which was the first and is still widely used, is described in this section.

[†] $\overline{H}_1 = RT\kappa_1\phi_2^2$; $\overline{S}_1 = R\psi_1\phi_2^2$.

Flory Equation of State. Thermodynamic variables in statistical thermodynamics are obtained from a suitable partition function which can be a simple or complex function depending upon the size and physical state of the molecule being considered. The simplest partition functions are obtained for monatomic and diatomic gases such as helium and nitrogen. The partition function chosen by Flory for the polymer was obtained from contributions by internal (i.e., intramolecular chemical-bond forces) and external (i.e., intermolecular forces) degrees of freedom. The internal contribution is dependent upon temperature, while the external contribution is dependent upon both temperature and volume. The Flory partition function can be given in reduced form as⁹

$$Z = Z_{\text{comb}} (g v^*)^{mc} (\tilde{v}^{1/3} - 1)^{3mc} \exp(rmc / \tilde{v} \tilde{T}). \quad (3.42)$$

Here, Z_{comb} is a combinatory factor, g is an inconsequential geometric factor, v^* is a characteristic (specific) volume per segment (usually called the hard-core or closed-packed volume), \tilde{v} is a reduced volume per segment defined in terms of the characteristic volume, r is the mean number of segments per molecule, n is the number of molecules (or mers), c is the mean number of external degrees of freedom per segment,[†] and \tilde{T} is a reduced temperature as defined later. The exponential term in eq. 3.42 is related to the configurational or mean potential energy (in van der Waals form), which is inversely proportional to volume.

Statistical thermodynamics provides the following equation to obtain an EOS from the partition function:

$$p = kT \frac{\partial \ln Z}{\partial V} \quad T. \quad (3.43)$$

The resulting EOS obtained from the partition function given by eq. 3.42 can be expressed in reduced form as

$$\boxed{\frac{\tilde{p}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{T}\tilde{v}}} \quad (3.44)$$

where \tilde{p} is the reduced pressure. The reduced parameters are defined in terms of the characteristic parameters (three EOS parameters, v^* , T^* , and p^* , for each of the pure components) as

[†] The total number of degrees of freedom in the system is $3mc$.

$$\tilde{v} = \frac{v}{v^*} \quad (3.45)$$

$$\tilde{T} = \frac{T}{T^*} = \frac{2v^* cRT}{s\eta} \quad (3.46)$$

and

$$\tilde{p} = \frac{p}{p^*} = \frac{2pv^{*2}}{s\eta}. \quad (3.47)$$

where c represents the mean number of external degrees of freedom per segment, s is the number of contact sites per segment, and η is an energy parameter characterizing a pair of sites in contact. The characteristic parameters can be obtained from experimental PVT data.[‡]

[‡] Differentiation of the EOS (eq. 3.44) with respect to temperature at constant pressure yields at zero pressure the characteristic hard-core volume as

$$v^* = v \frac{3 + 3\alpha T}{3 + 4\alpha T}.$$

Differentiation of the EOS with respect to temperature at constant volume yields at zero pressure the characteristic pressure

$$p^* = \gamma T \tilde{v}^2 = (\alpha/\beta) T \tilde{v}^2$$

where α is the *thermal-expansion coefficient*

$$\alpha = \frac{1}{V} \frac{\partial V}{\partial T}_p,$$

β is the *compressibility coefficient*

$$\beta = -\frac{1}{V} \frac{\partial V}{\partial p}_T,$$

and γ is the *thermal-pressure coefficient*

$$\gamma = \frac{\partial p}{\partial T}_v.$$

Representative values for Flory EOS-parameters evaluated at 25°C for four low-molecular-weight organic compounds and for four polymers are given in Table 3-1. In general, v^* and T^* increase with increasing temperature while p^* decreases.

Table 3-1 Flory Equation-of-State Parameters at 25°C

Polymer	v^* (cm ³ g ⁻¹)	T^* (K)	p^* (J cm ⁻³)
Toluene	0.9275	5197	547
Cyclohexane	1.0012	4721	530
Benzene	0.8860	4709	628
Methyl ethyl ketone	0.9561	4555	582
Polystyrene	0.8098	7420	547
Polydimethylsiloxane	0.8395	5530	241
Natural rubber	0.9432	6775	519
Polyisobutylene	0.9493	7580	448

Adaptation of the Flory EOS to *mixtures* is based upon the following two premises:

1. Core volumes of the solution components are additive.

$$v = \frac{n_1 v_1 + n_2 v_2}{n_1 + n_2} \quad (3.48)$$

2. The intermolecular energy depends on the *surface* area of contact between molecules and/or segments.

Since a segment is an arbitrary unit, the segment size can be chosen such that $v_1^* = v_2^* = v^*$. This gives the following mixing rules for the mixture:

$$\frac{1}{r} = \frac{\phi_1}{r_1} + \frac{\phi_2}{r_2} \quad (3.49)$$

where ϕ_1 and ϕ_2 are *segment (or core-volume) fractions* :

Finally, the characteristic temperature is obtained from the EOS by letting $\tilde{p} = 0$:

$$T^* = \frac{T\tilde{v}^{4/3}}{\tilde{v}^{1/3} - 1}$$

$$\phi_1 = 1 - \phi_2 = \frac{n_1 v_1^*}{n_1 v_1^* + n_2 v_2^*} . \quad (3.50)$$

The number of contact sites, s , for the mixture is given as

$$s = \phi_1 s_1 + \phi_2 s_2 \quad (3.51)$$

where s_i is the *surface area* of a segment of component i . In a similar manner, the mean number of external degrees of freedom for the mixture can be written as

$$c = \phi_1 c_1 + \phi_2 c_2 . \quad (3.52)$$

The *site fraction* is defined as

$$\theta_2 = 1 - \theta_1 = \frac{\phi_2 s_2}{s} . \quad (3.53)$$

The *characteristic pressure* for the mixture is given as

$$p = \phi_1 p_1 + \phi_2 p_2 - \phi_1 \theta_2 X_{12} \quad (3.54)$$

where X_{12} is called the *exchange interaction-parameter*, defined as

$$X_{12} = \frac{s_1 (\eta_{11} + \eta_{22} - 2\eta_{12})}{2v^{*2}} = \frac{s_1 \eta}{2v^{*2}} \quad (3.55)$$

where the η_{ij} terms are energy parameters for the i - j segment pairs and $\eta = \eta_{11} + \eta_{22} - 2\eta_{12}$. The exchange interaction-parameter is analogous to ω_{12} in the Flory–Huggins theory (i.e., eq. 3.30) but has the dimensions of energy density. Finally, the *characteristic temperature* for the mixture is given as

$$T^* = \frac{\phi_1 p_1 + \phi_2 p_2 - \phi_1 \theta_2 X_{12}}{\frac{\phi_1 p_1}{T_1} + \frac{\phi_2 p_2}{T_2}} . \quad (3.56)$$

The EOS of the mixture is given in the same form as that of the pure component (eq. 3.44) except that the reduced parameters refer to those of the mixture. The reduced volume of the mixture, \tilde{v} , may be obtained from the EOS with \tilde{p} set to zero for low pressures and \tilde{T} defined by use of the characteristic temperature given by eq. 3.56 for the mixture. Subsequently, other important quantities can be calculated such as the molar enthalpy of mixing as

$$H_m = \frac{\theta_2 x_1 v_1 X_{12}}{\tilde{v}} + x_1 v_1 p_1 \left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}} \right) + x_2 v_2 p_2 \left(\frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}} \right) \quad (3.57)$$

where

$$x_1 = \frac{n_1}{n_1 + n_2} . \quad (3.58)$$

An important relationship is the Flory-EOS expression for μ_1 given as

$$\begin{aligned} \mu_1 = RT \ln \phi_1 + \left(1 - \frac{v_1}{v_2} \right) \phi_2 + \frac{\theta_2^2 v_1 X_{12}}{\tilde{v}} \\ + v_1 p_1 \left[3\tilde{T}_1 \ln \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}} \right] . \end{aligned} \quad (3.59)$$

Alternately, eq. 3.59 has been given in the form

$$\begin{aligned} \mu_1 = RT \ln \phi_1 + \frac{1-r_1}{r_2} \phi_2 + p_1 v_1 \left[3\tilde{T}_1 \ln \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \tilde{v}_1^{-1} - \tilde{v}^{-1} + \tilde{p}_1 (\tilde{v} - \tilde{v}_1) \right] \\ + (X_{12} - TQ_{12}\tilde{v}) v_1 \frac{\theta_2^2}{\tilde{v}} \end{aligned} \quad (3.60)$$

A principal difference between eqs. 3.59 and 3.60 is the appearance of Q_{12} in the last term of eq. 3.60. This parameter is called the *noncombinational entropy correction* and generally is used as an adjustable parameter. Comparison of the standard Flory–Huggins relationship (eq. 3.34, where $\mu_1 = RT \ln a_1$ and $\phi_1 = 1 - \phi_2$) with the Flory EOS (eq. 3.59) shows that the first term within brackets in eq. 3.59 is simply a combinatorial term. Despite its cumbersome form, the Flory EOS theory provides substantial improvement over the earlier lattice theory. For example, the theory reasonably predicts an excess volume of mixing as

$$\frac{V^E}{V} = \frac{v^E}{\tilde{v}} = 1 - \frac{\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2}{\tilde{v}} . \quad (3.61)$$

Furthermore, it is capable of modeling the complete range of the observed phase-behavior of polymer solutions, as discussed in the next section.

3.2.4 Phase Equilibria

Whether or not a polymer and solvent are mutually soluble, or *miscible*, is governed by the sign of the Gibbs free energy of mixing, G_m , which is related to the enthalpy and entropy of mixing by eq. 3.26. Three different dependencies of G_m on solution composition (i.e., volume fraction of polymer) at constant temperature are illustrated in Figure 3-9. If G_m is positive over the entire composition range, as illustrated by curve I, the polymer and solvent are totally immiscible over the complete composition range and will coexist at equilibrium as two distinct phases. Two other possibilities are those of partial and total miscibility, as illustrated by curves II and III, respectively. For total miscibility, it is *necessary* that both

$$G_m < 0 \quad (3.62)$$

and that the second derivative of G_m with respect to the volume fraction of solvent (component 1) or polymer (component 2) be greater than zero over the entire composition range as formally expressed by eq. 3.63.

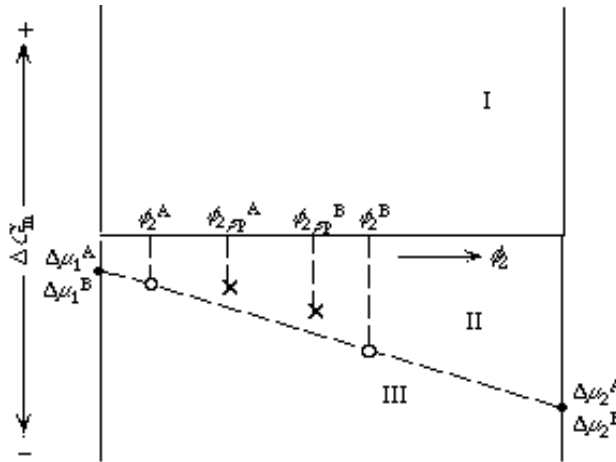


Figure 3-9 Dependence of the Gibbs free energy of mixing, G_m , of a binary mixture on volume fraction of polymer, ϕ_2 , at constant pressure and temperature. **I.** Total immiscibility. **II.** Partial miscibility. **III.** Total miscibility. In the case of partial miscibility (Curve II), the mixture will separate into two phases whose compositions (\square) are marked by the volume-fraction coordinates, ϕ_2^A and ϕ_2^B , corresponding to points of common tangent to the free-energy curve. Spinodal points, compositions $\phi_{2,sp}^A$ and $\phi_{2,sp}^B$, occur at the points of inflection (\times).

$$\frac{\partial^2 G_m}{\partial \phi_2^2} \Big|_{p,T} > 0 \quad (3.63)$$

Both conditions for miscibility are satisfied by curve III but not curve II, which exhibits two minima in G_m , and therefore the derivative criterion expressed by eq. 3.63 is not satisfied at all points along the G_m -composition curve. A solution that exhibits such minima will phase-separate at equilibrium into two phases containing different compositions of both components. The compositions of the two phases are given by the points of common tangent as illustrated in Figure 3-9, where the composition of the solvent-rich phase is identified as ϕ_2^A and that of the polymer-rich phase as ϕ_2^B .

Phase equilibrium is strongly affected by solution temperature. In fact, any of three types of phase behavior illustrated in Figure 3-9 may result by a change in the temperature (or pressure) of the system. Our usual experience with solutions of low-molecular-weight compounds is that solubility increases with an increase in temperature, as illustrated by the phase diagram shown in Figure 3-10. In this example, the solution is homogeneous (i.e., the two components are totally miscible) at temperatures above the point identified as UCST, which stands for the *upper critical solution temperature* as described below. At lower temperatures (i.e., below the UCST), phase separation may occur depending upon the overall composition of the mixture. At a given temperature below the UCST (e.g., T_1), compositions lying *outside* the curves are those constituting a homogeneous phase, while those lying *inside* the curves are thermodynamically unstable and therefore the solution will phase-separate at equilibrium. The compositions of the two phases, identified as phases A and B, are given by points lying along the curve called the *binodal*. The binodal is the loci of points that satisfy the conditions for thermodynamic equilibrium of a binary mixture given as

$$\mu_1^A = \mu_1^B \quad (3.64a)$$

and

$$\mu_2^A = \mu_2^B \quad (3.64b)$$

As the chemical potential is given by the derivative of the Gibbs free energy with respect to composition (eq. 3.27), the chemical potentials are obtained graphically from the intercepts of the common tangent drawn to curve II with the free energy axes as illustrated in Figure 3-9.

Between the binodal and the unstable region lies the *metastable* region, which is bounded by the *spinodal*. In the metastable region, the system can resist small concentration fluctuations but will eventually equilibrate to the stable two-phase state given by the binodal. Points lying along the spinodal correspond to the points of inflection identified in curve II of the free-energy diagram (Figure 3-9) and satisfy the relationship

$$\frac{\partial^2 G_m}{\partial \phi_2^2} \Big|_{p,T} = 0 \quad (3.65)$$

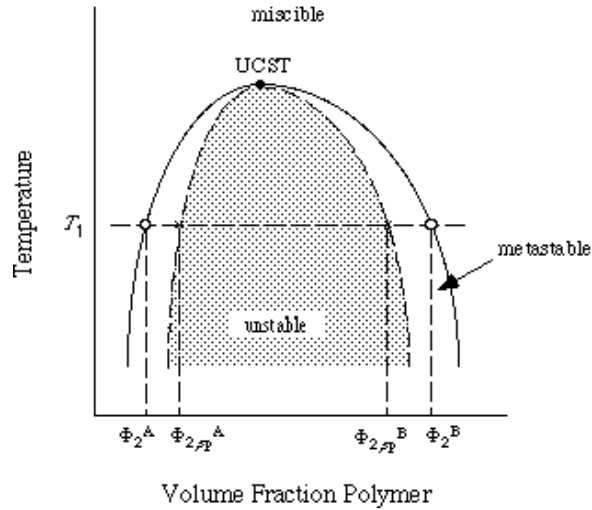


Figure 3-10 Representative phase diagrams for a polymer solution showing an upper critical solution temperature (UCST) (\bullet), spinodal curve (---), and binodal curve (—).

The binodal and spinodal coincide at the *critical point*, which satisfies the following equality for the third derivative of the Gibbs free energy with respect to composition:

$$\frac{\partial^3 G_m}{\partial \phi_2^3} \Big|_{p,T} = 0 \quad (3.66)$$

In the case of the upper critical solution temperature (UCST), the critical point lies at the top of the phase diagram as shown in Figure 3-10.

Although the UCST behavior of dilute polymer solutions had been observed for many years, it was not until 1961 that phase separation of polymer solutions was first reported to occur with an *increase* in temperature.¹⁵ In this case, the binodal and spinodal curves coincide at a temperature and composition called the *lower critical solution temperature* or LCST. One serious limitation of the Flory–Huggins theory (Section 3.2.1) is that it fails to predict LCST behavior. The more recent equation-of-state theories (Section 3.2.3) are much more successful in predicting the entire range of phase behavior, as will be discussed in Section 7.2.1.

3.2.5 Determination of the Interaction Parameter

Experimentally, χ_{12} as well as the exchange interaction parameter, X_{12} , in the Flory EOS theory can be determined by a variety of techniques, including several scattering methods as discussed in the next section and from the melting-point depression of semicrystalline polymers (Section 4.2.2). By far the most commonly used method to determine polymer–solvent as well as polymer–polymer interaction parameters (Chapter 7) has been inverse gas chromatography or IGC.¹⁶

Inverse Gas Chromatography. The term "inverse" is used to indicate that the substance being characterized constitutes the stationary phase (i.e., the bed packing) rather than the mobile phase, as is the case in traditional gas chromatography. The stationary phase is prepared by coating a thin layer of a polymer or polymer blend from a dilute solution onto a commercial packing material in the form of small beads. A fluidized bed is sometimes used in the coating process. The coated packing is vacuum-dried to remove all residual solvent and then packed into a GC column which is heated to approximately 50°C above the glass-transition temperature (T_g). A solvent probe is then injected into the carrier gas (He or H₂), and the time for the probe to be eluted from the column is measured. During its passage, the probe is free to be sorbed into the liquid polymer coating of the packed bed. The extent of solubility (i.e., activity) is directly related to the retention time from which a *specific retention volume*, V_g , can be calculated. From this value, the infinite-dilution volume-fraction activity coefficient is then obtained as¹⁷

$$\ln \gamma_1 = \ln \frac{a_1}{\phi_1} = \lim_{\phi_1 \rightarrow 0} \frac{a_1}{\phi_1} = \ln \frac{273.16 R v_2}{V_g p_1^\circ} - \frac{p_1^\circ (B_{11} - V_1)}{RT} \quad (3.67)$$

where ϕ_1 is the volume fraction of solvent (probe), p_1° is the vapor pressure of the probe (solvent) in the carrier gas, v_2 is the specific volume of the polymer, V_1 is the molar volume of the probe, and B_{11} is the second virial coefficient of the pure probe vapor at the measurement temperature. From measurement of γ_1 at different temperatures, the heat of mixing can be determined as

$$H_m = R \frac{\partial \ln \gamma_1}{\partial (1/T)} \quad (3.68)$$

From eq. 3.67 and the Flory–Huggins equation (eq. 3.35), it is easily shown that the Flory interaction-parameter is obtained directly as

$$\chi_{12} = \ln \frac{273.16 R v_2}{V_g p_1^\circ V_1} - \frac{p_1^\circ (B_{11} - V_1)}{RT} - 1. \quad (3.69)$$

In a similar manner, the interaction energy, X_{12} , in the Flory equation of state also can be obtained.

3.2.6 Predictions of Solubilities

Solubility Parameters. As discussed in the previous section, there are a number of experimental methods by which approximate values of χ_{12} can be obtained; however, there is no theory by which values of χ_{12} can be *predicted* at the present time. One approach that can be used to estimate χ_{12} and predict solubility is based upon the concept of the *solubility parameter*, δ , which was originally developed to guide solvent selection in the paint and coatings industry. The solubility parameter is related to the cohesive energy-density, E^{coh} , or the molar energy of vaporization of a pure liquid, E^{v} , as

$$\delta_i = \sqrt{E_i^{\text{coh}}} = \sqrt{\frac{E_i^{\text{v}}}{V_i}} \quad (3.70)$$

where E^{v} is defined as the energy change upon isothermal vaporization of the saturated liquid to the ideal gas state at infinite dilution[†] and V_i is the molar volume of the liquid. Units of δ are $(\text{cal}/\text{cm}^3)^{1/2}$ or $(\text{MPa})^{1/2}$. Equation 3.70 can be used to calculate the solubility parameter of a pure solvent given values of E^{v} and V_i . Since it is not reasonable to talk about an energy of vaporization for solid polymers, the solubility parameter of a polymer has to be determined indirectly or calculated by group-contribution methods. Experimentally, the solubility parameter of a polymer can be estimated by comparing the swelling of a crosslinked polymer sample immersed in different solvents. The solubility parameter of the polymer is taken to be that of the solvent resulting in maximum swelling.

Alternately, the solubility parameter of a polymer can be estimated by use of one of several group-contribution methods, such as those given by Small¹⁸ and by Hoy.¹⁹ An extensive presentation of group-contribution methods for estimating polymer properties, including those for solubility parameters, is given by van Krevelen.²⁰ Calculation of δ by a group-contribution method requires the value of a molar attraction constant, F_i , for each chemical group in the polymer repeating-unit. Values of F_i have been obtained by regression analysis of physical property data for a large number of organic compounds (640 compounds in the case of Hoy¹⁹). In the case of Small, all compounds (e.g., hydroxyl compounds, amines, and carboxylic acids) in which hydrogen bonding occurs were excluded. A listing of some important molar attraction constants is given in Table 3-2.

[†] The energy of vaporization is approximately related to the enthalpy of vaporization as

$$E_i^{\text{v}} = H_i^{\text{v}} - RT$$

Table 3-2 Molar Attraction Constants at 25°C

Group	Molar Attraction Constant, F (MPa) ^{1/2} cm ³ mol ⁻¹		
	Small ¹⁸	Hoy ¹⁹	Van Krevelen ²⁰
-CH ₃	438	303	420
-CH ₂ -	272	269	280
>CH-	57	176	140
>C<	-190	65.5	0
-CH(CH ₃)-	495	(479)	560
-C(CH ₃) ₂ -	686	(672)	840
-CH=CH-	454	497	444
>C=CH-	266	422	304
Phenyl	1504	1398	1517
<i>p</i> -Phenylene	1346	1442	1377
-O- (ether)	143	235	256
-OH	—	462	754
-CO- (ketone)	563	538	685
-COO- (ester)	634	668	512
-OCOO- (carbonate)	—	(904)	767
-CN	839	726	982
-N=C=O	—	734	—
-NH-	—	368	—
-S- (sulfide)	460	428	460
-F	(250)	84.5	164
-Cl (primary)	552	420	471
-Br (primary)	696	528	614
-CF ₃ (<i>n</i> -fluorocarbon)	561	—	—
-Si-	-77	—	—

The solubility parameter of a polymer is then calculated from these molar attraction constants and the molar volume of the polymer, V (units of cm³ mol⁻¹), as

$$\delta = \frac{\sum_{i=1}^n F_i}{V}$$

(3.71)

where the summation is taken over all groups in the repeating unit. For this purpose, chemical groups are chosen to be the smallest uniquely identifiable groups in the polymer repeating unit such as methyl, methylene, phenyl, and halogen corresponding to those in Table 3-2. Calculated values of solubility parameters for some common solvents and polymers have been tabulated in a number of publications.²⁰⁻²² Some of these values are collected in Table 3-3. An example calculation is given next.

Table 3-3 Solubility Parameters of Some Common Solvents and Polymers

	Solubility Parameter, δ^*	
	(MPa) ^{1/2}	(cal cm ⁻³) ^{1/2}
Solvents		
<i>n</i> -Hexane	14.9	7.28
Carbon tetrachloride	17.8	8.70
Toluene	18.2	8.90
Benzene	18.6	9.09
Chloroform	19.0	9.29
Tetrahydrofuran	19.4	9.48
Chlorobenzene	19.6	9.58
Methylene chloride	20.3	9.92
1,4-Dioxane	20.5	10.0
<i>N</i> -Methyl-2-pyrrolidone	22.9	11.2
Dimethylformamide	24.8	12.1
Methanol	29.7	14.5
Water	47.9	23.4
Polymers		
Polysulfone	20.3	9.92
Poly(vinyl chloride)	21.5	10.5
Polystyrene	22.5	11.0
Poly(methyl methacrylate)	22.7	11.1
Polyacrylonitrile	25.3	12.4

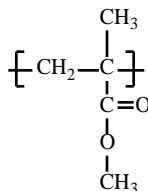
*Calculated from Hansen solubility parameters (eq. 3.77) at 25°C.

Example Problem 3.1

Estimate the solubility parameters, in units of $(\text{MPa})^{1/2}$, for poly(methyl methacrylate) (PMMA) by the method of Small. The density of PMMA is reported to be 1.188 g cm^{-3} at 25°C .

Solution

The structure of PMMA is



From the available chemical groups listed in Table 3-2, the molar-attraction constant for the repeating unit of PMMA can be obtained as follows:

Group	F	Number of Groups	F_i
-CH ₃	438	2	876
-CH ₂ -	272	1	272
>C<	-190	1	-190
-COO- (ester)	634	1	634
			1592

The formula weight of a PMMA repeating unit is calculated from atomic weights (Appendix F) as follows:

$$\begin{array}{rcl} \text{C:} & 5 \times 12.01115 & = & 60.06 \\ \text{O:} & 2 \times 15.9994 & = & 32.0 \\ \text{H:} & 8 \times 1.00797 & = & 8.06 \\ & & & \hline & & & 100.12 \end{array}$$

The molar volume, V , is then $100.12/1.188 = 84.28 \text{ cm}^3 \text{ mol}^{-1}$. The solubility parameter is then calculated as

$$\delta_i = \frac{F_i}{V_i} = \frac{1592}{84.28} = 18.9 \text{ MPa}^{1/2}$$

Another approach that can be used to calculate δ is based upon knowledge of the equation of state, $V(p,T)$, for the polymer:²³

$$\delta = \sqrt{\frac{T\alpha}{\beta}} \quad (3.72)$$

where α is the (isobaric) *thermal-expansion coefficient*,

$$\alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_p \quad (3.73)$$

and β is the (isothermal) compressibility coefficient,[†]

$$\beta = - \frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T \quad (3.74)$$

Equations of state are now available for most commercial polymers.^{22,24}

From values of the solubility parameters for the solvent and polymer, the heat of mixing can be *estimated* by the Scatchard²⁵–Hildebrand²⁶ equation as

$$H_m = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (3.75)$$

where V is the volume of the mixture. Making use of eq. 3.32, the interaction parameter can be estimated from this value of H_m as[†]

$$\chi_{12} = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (3.76)$$

[†] Since volume *decreases* with increasing pressure, the negative sign in eq. 3.74 provides a positive value for β .

[†] Sometimes, the Flory interaction parameter is considered to have both an enthalpic component, χ_H , and entropic (or residual) component, χ_S . In this case, we can write

$$\chi_{12} = \chi_S + \chi_H = \chi_S + \frac{V_1}{RT} (\delta_1 - \delta_2)^2 = 0.34 + \frac{V_1}{RT} (\delta_1 - \delta_2)^2 .$$

where V_1 is the molar volume of component 1. As the form of eq. 3.75 indicates, the solubility parameter approach can be used to estimate the heat of mixing when $H_m = 0$ but not when $H_m < 0$ (i.e., for exothermic heat of mixing).

The matching of polymer and solvent solubility parameters to minimize H_m is a useful approach for solvent selection in many cases but often fails when specific interactions such as hydrogen bonding occur. To improve the prediction, two- and three-dimensional solubility parameters, which give individual contributions for dispersive (i.e., van der Waals), polar, and hydrogen bonding interactions, are sometimes used. In the case of the three-dimensional model proposed by Hansen,²⁷ the overall solubility parameter can be obtained as

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \quad (3.77)$$

where δ_d , δ_p , and δ_h are the dispersive, polar, and hydrogen-bonding solubility parameters, respectively. Values of δ calculated from eq. 3.77 for common solvents and polymers were given in Table 3-3.

Activity Predictions. Once a value for the interaction parameter is known or can be estimated, the activity of a solvent in a polymer solution can be estimated by means of the Flory–Huggins equation (eq. 3.35). It is also possible to predict activity through a variety of chemical group-contribution methods.²⁸ The most fully developed of these methods is UNIFAC-FV.²⁹ The acronym UNIFAC stands for *UNIQUAC Functional-group Activity Coefficients*, which had been widely used for the prediction of vapor–liquid equilibria (VLE) for mixtures of low-molecular-weight components,³⁰ and FV represents a free-volume contribution originating from the Flory EOS theory. UNIQUAC, itself, is an acronym for *Universal Quasi-Chemical equations*, which provides good representation of both vapor–liquid equilibria (VLE) and liquid–liquid equilibria (LLE) for binary and multicomponent mixtures of nonelectrolytes using one or two adjustable (energy) parameters per binary pair.³¹ The difference between UNIQUAC and UNIFAC or UNIFAC-FV is that UNIFAC uses the solution-of-functional-groups (SOG) concept³² to obtain group-contribution parameters (the adjustable parameters in UNIQUAC) from knowledge of the chemical groups comprising the mixture components in a manner similar to the way that solubility parameters are calculated by the methods of Small or Hoy as discussed in the previous section.

According to UNIFAC-FV, solvent activities may be calculated as contributions from three sources—a combinatorial (entropy) term, a residual (enthalpic term), and a (Flory EOS) free-volume term as

$$\ln a_1 = \ln a_1^C + \ln a_1^R + \ln a_1^{FV}. \quad (3.78)$$

The combinatorial term is given as

$$\ln a_1^C = \ln \phi_1 + (1 - \phi_1) + \frac{z}{2} M_1 q_1 \ln \frac{\theta_1}{\phi_1} - 1 + \frac{\phi_1}{\theta_1} \quad (3.79)$$

where ϕ_1 is the segment volume fraction, θ_1 is the surface area fraction, z is the coordination number of the lattice (taken to be 10), and M_1 is the molecular weight of component 1 (i.e., the solvent). The parameter q_1 in eq. 3.79 is related to the van der Waals surface area as

$$q_1 = \frac{1}{M_1} \sum_{k=1}^N \nu_k^{(1)} Q_k \quad (3.80)$$

where $\nu_k^{(1)}$ is the number of functional groups of type k in the solvent and Q_k is a group area parameter obtained from the (Bondi) van der Waals group surface area, A_{wk} , and normalized to a methylene unit of polyethylene as

$$Q_k = \frac{A_{wk}}{2.5 \times 10^9} \cdot \quad (3.81)$$

The surface area fraction, θ_1 , is calculated from q_1 , as

$$\theta_1 = \frac{q_1 w_1}{\sum_{j=1}^N q_j w_j} \quad (3.82)$$

where the summation in the denominator of eq. 3.82 is taken over all N components of the mixture. Similarly, the segment volume fraction of the solvent, ϕ_1 , is calculated from the weight fractions and the group volume parameter of each component of the mixture, r_j , as

$$\phi_1 = \frac{r_1 w_1}{\sum_{j=1}^N r_j w_j} \quad (3.83)$$

where the relative van der Waals volume is given as

$$r_1 = \frac{1}{M_1} \sum_{k=1}^N \nu_k^{(1)} R_k \quad (3.84)$$

and $\nu_k^{(1)}$ is the number of groups (an integer) of type k in the solvent and R_k is the normalized van der Waals group volume, V_{wk} , evaluated as

$$R_k = \frac{V_{wk}}{15.17} \quad (3.85)$$

The molar group area parameter, Q_k (eq. 3.81), and the molar group volume parameter, R_k , are available for most structural groups as well as for some common solvents, such as water, carbon disulfide, and dimethylformamide. These group parameters are continuously updated and new ones added in the literature.³³ Some representative values of Q_k and R_k are given in Table 3-4.

It is noted that the first two terms on the RHS of eq. 3.79 are essentially the combinatorial terms of the Flory–Huggins (F–H) equation (eq. 3.35) with the exception that segment rather than volume fractions are used. The remaining two terms serve to correct for the effect of molecular shape. The difference between the combinatorial activity given by eq. 3.79 and that of the F–H expression is usually small when segment fractions are used in place of volume fractions in the F–H expression.

The residual contribution to the activity of the solvent in UNIQUAC is given as

$$\ln a_1^R = M_1 q_1 \left[1 - \ln \frac{\sum_{i=1}^N \theta_i \tau_{i1}}{\sum_{i=1}^N \theta_i \tau_{ii}} \right] - \sum_{j=1}^N \theta_j \tau_{ji} \quad (3.86)$$

where the two *adjustable* parameters, τ_{ij} and τ_{ji} , are given as

$$\tau_{ij} = \exp - \frac{u_{ij} - u_{jj}}{RT} \quad (3.87)$$

and

$$\tau_{ji} = \exp - \frac{u_{ji} - u_{ii}}{RT} \quad (3.88)$$

The parameter u_{ij} is the potential energy of an i – j pair.

Table 3-4 Molar Group Area (Q_k) and Volume (R_k) Parameters*

Main Group	Subgroup	R_k	Q_k	Sample Group Assignment
CH ₂	CH ₃	0.9011	0.848	Hexane
	CH ₂	0.6744	0.540	<i>n</i> -Butane
	CH	0.4469	0.228	2-Methylpropane
	C	0.2195	0.000	Neopentane
C=C	CH ₂ =CH	1.3454	1.176	Hexene-1
	CH=CH	1.1167	0.867	Hexene-2
	CH ₂ =C	1.1173	0.988	2-Methyl-1-butene
	CH=C	0.8886	0.676	2-Methyl-2-butene
	C=C	0.6605	0.485	2,3-Dimethylbutene
CH ₂ CO	CH ₃ CO	1.6724	1.448	Butanone
	CH ₂ CO	1.4457	1.180	Pentanone-3
ACH [†]	ACH	0.5313	0.400	Naphthalene
	AC	0.3652	0.120	Styrene
ACCH ₂	ACCH ₃	1.2663	0.968	Toluene
	ACCH ₂	1.0396	0.660	Ethylbenzene
	ACCH	0.8121	0.348	Cumene
SiO		1.1044	0.4660	Polysiloxane
OH		1.0000	1.200	Propanol-2
CH ₃ OH		1.4311	1.432	Methanol
H ₂ O		0.9200	1.400	Water
CHCl ₃		2.8700	2.410	Chloroform
HCON(CH ₃) ₂		3.0856	2.736	<i>N,N</i> -Dimethylformamide
SiO		1.1044	0.466	Octamethyl cyclotetrasilane

*Supplementary material to ref. 33.

†The prefix A indicates that the group is contained in an *aromatic* structure.In UNIFAC, the *residual* term is replaced by the SOG concept as

$$\ln a_1^R = \sum_{\text{all groups}} v_k^{(1)} \left[\ln v_k - \ln v_k^{(1)} \right] \quad (3.89)$$

where a_k is the group residual-activity (or activity coefficient) and $a_k^{(1)}$ is the group residual-activity (or activity coefficient) of group k in a reference solution containing only solvent molecules (for normalization so that $a_1 = 1$ as $w_1 = 1$). The group activation term, θ_k or $\theta_k^{(1)}$, is obtained from the expression

$$\ln \theta_k = M_k Q_k \left[1 - \ln \frac{\sum_{m \text{ all groups}} \theta_m \theta_{mk}}{\sum_{m \text{ all groups}} \theta_m} - \frac{\sum_{m \text{ all groups}} \theta_m \theta_{km}}{\sum_{n \text{ all groups}} \theta_n \theta_{nm}} \right] \quad (3.90)$$

where θ_m is the *area fraction* of group m , calculated in a similar way to that of θ_j :

$$\theta_m = \frac{Q_m W_m}{\sum_{n=1}^N Q_n W_n} \quad (3.91)$$

In eqs. 3.90 and 3.91, M_k is the molecular weight of the functional group k , Q_m is the group-area parameter per gram such that $Q_m = Q_m/M_m$, and W_m is the weight fraction of group m in the mixture. The *group interaction parameter*, Ψ_{mn} , is given by

$$\Psi_{mn} = \exp \left[- \frac{U_{mn} - U_{mm}}{RT} \right] = \exp \left[- \frac{a_{mn}}{T} \right] \quad (3.92)$$

where U_{mn} is a measure of the energy of interaction between groups m and n . The group-interaction parameters, a_{mn} and a_{nm} ($a_{mn} = a_{nm}$), for each pair of groups have been compiled and continuously revised, principally by fitting experimental VLE or LLE data for low-molecular-weight compounds. Representative values of the group-interaction parameters derived from VLE data are given in Table 3-5. In tables of group-interaction parameters, each major group contains several subgroups with their own R_k and Q_k values (Table 3-4), but *all subgroups have identical group-interaction parameters*.

Table 3-5 Representative Values of the Group-Interaction Parameters, a_{nm} and a_{mn} (K)*

	CH ₂	C=C	ACH	ACCH ₂	OH	CH ₂ CO	CH ₃ OH	SiO
CH ₂	0.0	86.02	61.13	76.50	986.5	476.4	697.2	252.7
C=C	-35.36	0.0	38.81	74.15	524.1	182.6	787.6	n.a.
ACH	-11.12	3.446	0.0	167.0	636.1	25.77	637.4	238.9
ACCH ₂	-69.70	-113.6	-146.8	0.0	803.2	-52.10	603.3	n.a.
OH	156.4	457.0	89.60	25.82	0.0	84.00	-137.1	n.a.
CH ₂ CO	26.76	42.92	140.1	365.8	164.5	0.0	108.7	n.a.
CH ₃ OH	16.51	-12.52	-50.00	-44.50	249.1	23.39	0.0	n.a.
SiO	110.2	n.a.	234.4	n.a.	n.a.	n.a.	n.a.	n.a.

*Supplementary material to ref. 33.

For polymer-solvent systems, Oishi and Prausnitz²⁹ have shown that the *free-volume* contribution appearing in eq. 3.78 can be a significant *positive* contribution to the total activity and used the Flory EOS (where $X_{12} = 0$) to obtain

$$\ln a_1^{\text{FV}} = 3c_1 \ln \frac{(\tilde{v}_1^{1/3} - 1)}{(\tilde{v}_M^{1/3} - 1)} - c_1 \frac{\tilde{v}_1}{\tilde{v}_M} - 1 - \frac{1}{\tilde{v}_1^{1/3}} \quad (3.93)$$

In this equation, $3c_1$ represents the number of external degrees of freedom per solvent (i.e., component 1) molecule (c_1 is usually set to 1.1), subscript M refers to the mixture, and \tilde{v} is the reduced volume as defined earlier (eq. 3.45). Oishi and Prausnitz have suggested calculating the reduced volume for the solvent as

$$\tilde{v}_1 = \frac{v_1}{15.17br_1} \quad (3.94)$$

where b is a proportionality factor of order unity (often taken as 1.28). The reduced volume of the mixture, \tilde{v}_M , is calculated by assuming that the volume of the liquid mixture is additive. For a binary mixture of solvent and polymer (component 2), \tilde{v}_M is given as

$$\tilde{v}_M = \frac{v_1 w_1 + v_2 w_2}{15.17b(r_1 w_1 + r_2 w_2)} \quad (3.95)$$

UNIFAC-FV has been very successful in the prediction of solvent activities for polymer solutions,²⁸ as illustrated for polyisobutylene/benzene in Figure 3-11. Although the

UNIFAC-FV approach was developed to improve predictions of activities or activity coefficients for polymeric systems, it also has been used for mixtures of low-molecular-weight compounds with reasonable success. Free-volume contributions can be important even for mixtures of low-molecular-weight components if the characteristic temperatures (T^*) differ significantly, as in the case of gas/hydrocarbon mixtures for example.

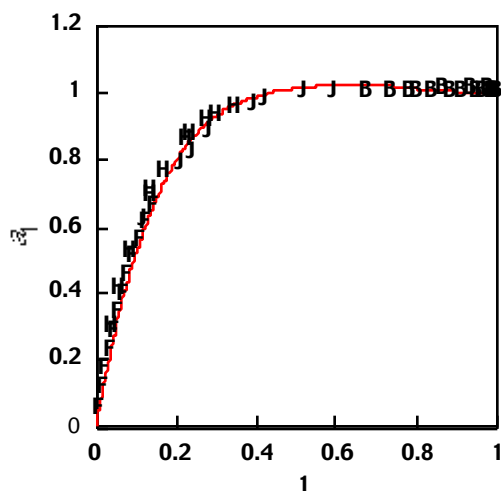
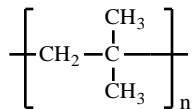


Figure 3-11 Comparison of experimental data (F,H,J,B) for the activity of benzene (a_1) as a function of its weight fraction (w_1) in polyisobutylene at 25°C with predictions (—) of UNIFAC-FV.²⁸

Example Problem 3.2

Using UNIFAC-FV, calculate the activity of benzene in polyisobutylene (PIB)



at 25°C when the weight fraction of benzene is 0.1.

Solution

Component	ρ g mL ⁻³	M	Main Group	Sub- Group	R_k	Q_k	No. Groups
Benzene	0.8736	78.11	ACH	ACH	0.5313	0.400	6
PIB	0.9169	56.07	CH ₂	C	0.2195	0.0	1
			CH ₂	CH ₂	0.6744	0.540	1
			CH ₂	CH ₃	0.9011	0.848	2

Combinatorial contribution:

$$q_1 = \frac{1}{78.11} 6(0.400) = 0.03073$$

$$r_1 = \frac{1}{78.11} 6(0.5313) = 0.04081$$

$$q_2 = \frac{1}{56.07} [1(0) + 1(0.540) + 2(0.848)] = 0.03987$$

$$r_2 = \frac{1}{56.07} [1(0.2195) + 1(0.6744) + 2(0.9011)] = 0.04808$$

$$\theta_1 = \frac{0.03073(0.1)}{0.0307(0.1) + 0.03987(0.9)} = 0.07888$$

$$\phi_1 = \frac{0.04081(0.1)}{0.04081(0.1) + 0.04808(0.9)} = 0.08618$$

$$\begin{aligned} \ln a_1^c &= \ln(0.08618) + (1 - 0.08618) + \frac{10}{2} (78.11)(0.03073) \ln \frac{0.07888}{0.08618} - 1 + \frac{0.08618}{0.07888} \\ &= -1.4831 \end{aligned}$$

Residual contribution:

$$W_{ACH} = 0.1$$

$$W_{\text{CH}_3} = 0.9 \frac{15.025(2)}{56.07} = 0.4823$$

$$W_{\text{CH}_2} = 0.9 \frac{14.0169}{56.07} = 0.2250$$

$$W_{\text{C}} = 0.9 \frac{12.001}{56.07} = 0.1926$$

$$Q_{\text{ACH}} = \frac{Q_{\text{ACH}}}{13.0089} = \frac{0.4}{13.0089} = 0.03075$$

$$Q_{\text{CH}_3} = \frac{Q_{\text{CH}_3}}{15.025} = \frac{0.848}{15.025} = 0.05644$$

$$Q_{\text{CH}_2} = \frac{Q_{\text{CH}_2}}{14.0169} = \frac{0.540}{14.0169} = 0.03853$$

$$Q_{\text{C}} = \frac{Q_{\text{C}}}{12.001} = \frac{0}{12.001} = 0$$

$$\Theta_{\text{ACH}} = \frac{Q_{\text{ACH}} W_{\text{ACH}}}{Q_{\text{ACH}} W_{\text{ACH}} + Q_{\text{CH}_3} W_{\text{CH}_3} + Q_{\text{CH}_2} W_{\text{CH}_2} + Q_{\text{C}} W_{\text{C}}} = \frac{0.003075}{0.03897} = 0.07892$$

$$\Theta_{\text{CH}_3} = \frac{Q_{\text{CH}_3} W_{\text{CH}_3}}{Q_{\text{ACH}} W_{\text{ACH}} + Q_{\text{CH}_3} W_{\text{CH}_3} + Q_{\text{CH}_2} W_{\text{CH}_2} + Q_{\text{C}} W_{\text{C}}} = \frac{0.02722}{0.03897} = 0.6986$$

$$\Theta_{\text{CH}_2} = \frac{Q_{\text{CH}_2} W_{\text{CH}_2}}{Q_{\text{ACH}} W_{\text{ACH}} + Q_{\text{CH}_3} W_{\text{CH}_3} + Q_{\text{CH}_2} W_{\text{CH}_2} + Q_{\text{C}} W_{\text{C}}} = \frac{0.008669}{0.03897} = 0.2225$$

$$\Theta_{\text{C}} = \frac{Q_{\text{C}} W_{\text{C}}}{Q_{\text{ACH}} W_{\text{ACH}} + Q_{\text{CH}_3} W_{\text{CH}_3} + Q_{\text{CH}_2} W_{\text{CH}_2} + Q_{\text{C}} W_{\text{C}}} = 0$$

Note that interaction parameters are only between main groups, and in this case there are only two main groups — ACH (benzene) and CH₂ (C, CH₂, and CH₃ subgroups) in PIB. This greatly reduces the number of calculations for the residual contribution to the activity of benzene as follows:

$$\Psi_{\text{ACH,CH}_2} = \exp \left(-\frac{a_{\text{ACH,CH}_2}}{T} \right) = \exp \frac{11.12}{298} = 1.0380 = \Psi_{\text{ACH,CH}_3} = \Psi_{\text{ACH,C}}$$

$$\Psi_{\text{CH}_2,\text{ACH}} = \exp \left(-\frac{a_{\text{CH}_2,\text{ACH}}}{T} \right) = \exp \left(-\frac{61.13}{298} \right) = 0.8145 = \Psi_{\text{CH}_3,\text{ACH}} = \Psi_{\text{C,ACH}}$$

$$\begin{aligned} \ln \Gamma_{\text{ACH}} = & M_{\text{ACH}} Q_{\text{ACH}} \left[1 - \ln \left(\Theta_{\text{ACH}} \Psi_{\text{ACH,ACH}} + \Theta_{\text{CH}_3} \Psi_{\text{CH}_3,\text{ACH}} + \Theta_{\text{CH}_2} \Psi_{\text{CH}_2,\text{ACH}} + \right. \right. \\ & \left. \left. \Theta_{\text{C}} \Psi_{\text{C,ACH}} \right) - \frac{\Theta_{\text{ACH}} \Psi_{\text{ACH,ACH}}}{\Theta_{\text{ACH}} \Psi_{\text{ACH,ACH}} + \Theta_{\text{CH}_3} \Psi_{\text{CH}_3,\text{ACH}} + \Theta_{\text{CH}_2} \Psi_{\text{CH}_2,\text{ACH}} + \Theta_{\text{C}} \Psi_{\text{C,ACH}}} - \right. \\ & \frac{\Theta_{\text{CH}_3} \Psi_{\text{ACH,CH}_3}}{\Theta_{\text{ACH}} \Psi_{\text{ACH,CH}_3} + \Theta_{\text{CH}_3} \Psi_{\text{CH}_3,\text{CH}_3} + \Theta_{\text{CH}_2} \Psi_{\text{CH}_2,\text{CH}_3} + \Theta_{\text{C}} \Psi_{\text{C,CH}_3}} - \\ & \frac{\Theta_{\text{CH}_2} \Psi_{\text{ACH,CH}_2}}{\Theta_{\text{ACH}} \Psi_{\text{ACH,CH}_2} + \Theta_{\text{CH}_3} \Psi_{\text{CH}_3,\text{CH}_2} + \Theta_{\text{CH}_2} \Psi_{\text{CH}_2,\text{CH}_2} + \Theta_{\text{C}} \Psi_{\text{C,CH}_2}} - \\ & \left. \frac{\Theta_{\text{C}} \Psi_{\text{ACH,C}}}{\Theta_{\text{ACH}} \Psi_{\text{ACH,C}} + \Theta_{\text{CH}_3} \Psi_{\text{CH}_3,\text{C}} + \Theta_{\text{CH}_2} \Psi_{\text{CH}_2,\text{C}} + \Theta_{\text{C}} \Psi_{\text{C,C}}} \right] = \\ & 0.400 \left[1 - \ln \left(0 + 0.2225 \cdot 0.8145 + 0.6986 \cdot 0.8145 + 0.07892 \right) - \right. \\ & \frac{0.07892(1)}{0.07892(1) + 0.6986(0.8145) + 0.2225(0.8145) + 0} - \\ & \left. \frac{(0.6986 + 0.2225)(1.0380)}{0.0789(1.0380) + 0.6986(1) + 0.2225 + 0} \right] = 0.4 \left[1 - \ln(0.8292) - 1.0615 \right] = 0.05036 \end{aligned}$$

$$\ln \Gamma_{\text{ACH}}^{(1)} = 0$$

$$\ln a_1^{\text{R}} = 6(0.05036 - 0) = 0.3022$$

Free-volume contribution:

$$\tilde{v}_1 = \frac{1.145}{15.17(1.28)0.04081} = 1.445$$

$$\tilde{v}_M = \frac{1.1447(0.1) + 1.0906(0.9)}{15.17(1.28)[0.04081(0.1) + 0.04808(0.9)]} = 1.1920$$

$$\ln a_1^{\text{FV}} = 3(1.1) \ln \frac{1.445^{1/3} - 1}{1.1920^{1/3} - 1} - 1.1 \frac{1.445}{1.1920} - 1 \left(1 - \frac{1}{1.445^{1/3}} \right)^{-1} = 0.528$$

Total activity of benzene:

$$\ln a_1 = -1.483 + 0.302 + 0.528 = -0.653$$

$$a_1 = 0.520$$

These results indicate that the residual or enthalpic contribution to the activity is relatively small compared to the combinatorial contribution. This should be expected on the basis of the non-polar nature of PIB and benzene. As shown by a comparison of experimental activity data with calculated values in Figure 3-11, UNIFAC-FV very accurately predicts the activity of benzene in PIB. This extremely good agreement is due to extensive parameterization of UNIFAC for alkanes and aromatic compounds.

3.3 MEASUREMENT OF MOLECULAR WEIGHT

As discussed in Section 1.3, commercial synthetic polymers have broad distributions of molecular weight, and it is therefore necessary to report an average molecular weight when characterizing a sample. There are three important molecular-weight averages—number-average (M_n), weight-average (M_w), and z -average (M_z). Absolute values of M_n , M_w , and M_z can be obtained by the *primary* characterization methods of osmometry, scattering, and sedimentation, respectively. In addition to these accurate but time-consuming techniques, there are a number of *secondary* methods by which average molecular weights can be determined provided that polymer samples with narrow molecular-weight distributions are available for reference and calibration. The most important of these secondary methods is gel-permeation chromatography (GPC), sometimes called size-exclusion chromatography (SEC). This method is capable of determining the entire molecular-weight distribution of a polymer sample from which all molecular-weight averages can be determined. Another widely used secondary method is the determination of intrinsic viscosity from which the viscosity-average molecular weight can be determined. The viscosity-average molecular weight (M_v) normally

lies between M_n and M_w . The principles behind both primary and secondary methods for molecular-weight determination are discussed next.

3.3.1 Osmometry

Membrane Osmometry. The osmotic pressure, π , of a polymer solution may be obtained from the chemical potential, μ_1 , or equivalently from the activity, a_1 , of the solvent through the basic relationship

$$\mu_1 = RT \ln a_1 = - \pi V_1 \quad (3.96)$$

where V_1 is the molar volume of the solvent. Substitution of the Flory–Huggins expression for solvent activity (eq. 3.35) into eq. 3.96 and subsequent rearrangement gives

$$= -\frac{RT}{V_1} \left[\ln(1 - \phi_2) + \phi_2 + \chi_{12}\phi_2^2 \right]. \quad (3.97)$$

Simplification of this relation can be achieved by expansion of the logarithmic term in a Taylor series (see Appendix E) and the substitution of polymer concentration, c , for volume fraction, ϕ_2 , through the relationship

$$\phi_2 = cv \quad (3.98)$$

where v is the specific volume of the polymer. Substitution and rearrangement give the expression

$$\frac{\pi}{c} = \frac{RT}{M} \left[1 + \frac{Mv^2}{V_1} \frac{1}{2} - \chi_{12} c + \frac{1}{3} \frac{Mv^3}{V_1} c^2 + \dots \right]. \quad (3.99)$$

The classical van't Hoff equation for the osmotic pressure of an ideal, dilute solution

$$\frac{\pi}{c} = \frac{RT}{M}, \quad (3.100)$$

may be seen as a special or limiting case of eq. 3.99 obtained when $\chi_{12} = 1/2$ and second- and higher-order terms in c can be neglected (i.e., for dilute solution). For high-molecular-weight, polydisperse polymers, the appropriate molecular weight to use in eq. 3.99 is the number-average molecular weight, \bar{M}_n . Equation 3.99 can then be rearranged to give the widely used relation

$$\boxed{= RTc \frac{1}{\bar{M}_n} + A_2c + A_3c^2 + \dots} \quad (3.101)$$

where A_2 and A_3 are the second and third virial coefficients, respectively. Comparison of eqs. 3.99 and 3.101 reveals the following relations for the virial coefficients:

$$A_2 = \frac{v^2}{V_1} \left(\frac{1}{2} - \chi_{12} \right) \quad (3.102)$$

and

$$A_3 = \frac{1}{3} \frac{v^3}{V_1} \quad (3.103)$$

In the limit of dilute solution (typically less than 1 g dL⁻¹), terms containing second- and higher-order powers of c can be neglected, and therefore a plot of π/RTc versus c yields a straight line with an intercept, $1/\bar{M}_n$, and slope, A_2 . In Figure 3-12, plots of osmotic data for different molecular weight fractions of polyisobutylene in a good (cyclohexane) and poor (benzene) solvent are compared.

As shown by the relation between A_2 and χ_{12} given by eq. 3.102, the second virial coefficient is a convenient measure of the *quality* of polymer-solvent interactions. In good solvents in which the polymer chains are expanded (i.e., $\alpha > 1$, eq. 3.13), A_2 is large and, therefore, χ_{12} is small (e.g., < 0.5). At θ conditions (i.e., $\alpha = 1$), $A_2 = 0$ and $\chi_{12} = 0.5$.

Experimental procedures to determine osmotic pressure are relatively simple although often very time consuming. A basic osmometer design is illustrated in Figure 3-13. In operation, pure solvent and a dilute solution of the polymer in the same solvent are placed on opposite sides of a semipermeable membrane, typically prepared from cellulose or a cellulose derivative. Regenerated cellulose is an especially good membrane polymer because it is insoluble in most organic solvents. Normally, the membrane is first preconditioned in the solvent used in the measurements. An ideal membrane will allow the solvent to pass through the membrane but will retain the polymer molecules in solution. The resulting difference in chemical potential between solvent and the polymer solution causes solvent to pass through the membrane and raise the liquid head of the solution reservoir. The osmotic pressure is calculated from the height, h , of the equilibrium head representing the difference between the height of solvent in the solvent capillary and the height of solution in the opposite capillary at equilibrium as

$$\pi = \rho gh \quad (3.104)$$

where ρ is the solvent density.

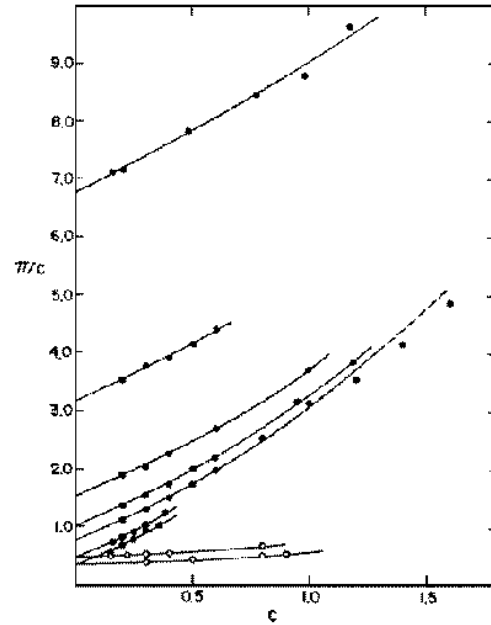


Figure 3-12 Plot of π/c versus c (g cm^{-3}) for polyisobutylene fractions (molecular weights between 38,000 and 720,000) in benzene (\square) and in cyclohexane (\bullet). (Adapted with permission from ref. 34. Copyright 1953 American Chemical Society.)

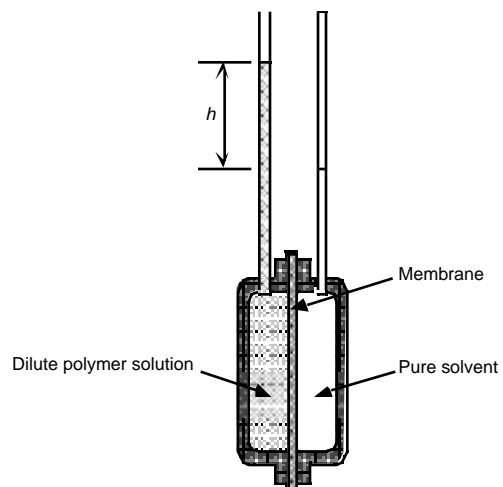


Figure 3-13 Schematic of a simple membrane osmometer.

One intrinsic problem with membrane osmometry is the performance of the membrane. No membrane is completely impervious to the passage of small molecules, and any migration of smaller polymer molecules across the membrane during measurement will not contribute to the osmotic pressure and, therefore, an artificially high value of M_n will be obtained. For this reason, membrane osmometry is considered to be accurate only for polymer samples with molecular weights above about 20,000. The upper limit for molecular weight is approximately 500,000 due to inaccuracy in measuring small osmotic pressures. For the characterization of low-molecular-weight (i.e., <20,000) oligomers and polymers, an alternative technique called vapor-pressure osmometry (VPO) is preferred, particularly when molecular weight is less than about 10,000. The basic principles of this technique are described next.

Vapor Pressure Osmometry. When a polymer is added to a solvent, the vapor pressure of the solvent will be lowered due to the decrease in solvent activity. The relation between the difference in vapor pressure between solvent and solution, p ($= p_1 - p_1^0$), and the number-average molecular weight, M_n , of the polymer is given as

$$\lim_{c \rightarrow 0} \frac{p}{c} = -\frac{p_1^0 V_1^0}{M_n} \quad (3.105)$$

where p_1^0 and V_1^0 are, respectively, the vapor pressure and molar volume of the pure solvent. Due to the inverse dependence of p on M_n given by eq. 3.105, the effect of even a low-molecular-weight polymer on the lowering of vapor pressure will be very small and, therefore, direct measurement of the vapor pressure is a very imprecise method of molecular-weight determination. For this reason, an indirect approach, based upon thermoelectric measurements, is used in commercial instrumentation as described below.

As shown by Figure 3-14, a commercial vapor pressure osmometer uses two matched thermistors that are placed in a closed, constant-temperature ($\pm 0.001^\circ\text{C}$) chamber containing saturated solvent vapor. A drop of solvent is placed by syringe on one thermistor and a drop of dilute polymer solution on the other. As a result of condensation of solvent vapor onto the solution, the temperature of the solution thermistor increases until the vapor pressure of the solution equals that of the solvent. The difference in temperature between the two thermistors is recorded in terms of a difference in resistance (R), which is calibrated by use of a standard low-molecular-weight sample. Extrapolation of R/c over a range of dilute-solution concentrations to zero concentration yields \bar{M}_n through

$$\frac{R}{c} \Big|_{c \rightarrow 0} = \frac{K_{\text{VPO}}}{M_n} \quad (3.106)$$

where K_{VPO} is the calibration constant obtained by measuring R for a low-molecular-weight standard whose molecular weight is precisely known. As in membrane osmometry,

the slope of the plot of R/c versus c is related to the second virial coefficient. Criteria for the selection of calibrants for VPO include high purity (>99.9%) and low vapor pressure (<0.1% of p_1°). Examples of calibrant include mannitol and sucrose for aqueous solution measurements and pentaerythryl tetrastearate, and low-polydispersity, low-molecular-weight polystyrene and polyisobutylene standards for organic-solution determinations. Since calibration by a low-molecular-weight standard is required to obtain K_{VPO} , VPO is considered a secondary method of molecular-weight determination, in contrast to membrane osmometry for which no calibrants are necessary.

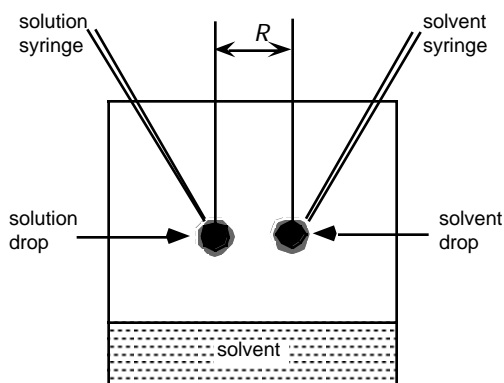


Figure 3-14 Illustration of basic instrumentation for vapor pressure osmometry.

3.3.2 Light-Scattering Methods

The weight-average molecular weight can be obtained directly only by scattering experiments. The most commonly used technique is light scattering from dilute polymer solution. It is also possible to determine M_w by small-angle neutron scattering of specially prepared solid samples. Although this technique has great current importance in polymer research, it is not routinely used for molecular-weight determination because of the difficulty and expense of sample preparation and the specialized facilities required. The basic principles of light-scattering measurements of dilute polymer solutions are described next.

The fundamental relationship for light scattering is given as[†]

$$R(\theta) = \frac{KcRTV_1(1 + \cos^2 \theta)}{-\partial\mu_1/\partial c} = \frac{KcRTV_1(1 + \cos^2 \theta)}{\partial \rho/\partial c}.$$

[†] It can be shown¹ from the thermodynamic theory of fluctuations that the relationship between scattered light intensity and chemical potential is given as

$$\boxed{\frac{Kc}{R(\theta)} = \frac{1}{\bar{M}_w P(\theta)} + 2A_2c + \dots} \quad (3.107)$$

In this equation, K is a function of the refractive index, n_o , of the pure solvent, the specific refractive increment, dn/dc , of the dilute polymer solution, and the wavelength, λ , of the incident light according to the relationship

$$K = \frac{2}{N_A} \frac{n_o^2}{\lambda^4} \left(\frac{dn}{dc} \right)^2 \quad (3.108)$$

where N_A is Avogadro's number (6.023×10^{23} molecules mol⁻¹). The specific refractive increment is the change in refraction index, n , of dilute polymer solutions with increasing polymer concentration. The term $R(\theta)$ appearing in eq. 3.107 is called the *Rayleigh ratio*, which is defined as

$$R(\theta) = \frac{i(\theta)r^2}{I_o V} \quad (3.109)$$

In this equation, I_o is the intensity of the incident light beam and $i(\theta)$ is the intensity of the *scattered* light measured at a distance of r from the scattering volume, V , and at an angle θ with respect to the incident beam. The parameter $P(\theta)$ appearing in eq. 3.107 is called the *particle scattering function*, which incorporates the effect of chain size and conformation on the angular dependence of scattered light intensity, as illustrated in Figure 3-15. Spherical particles smaller than the wavelength of light act as independent scattering centers generating a symmetrical envelope of scattered light intensity. In this case of small particles, $P(\theta)$ is unity, but in the case of polymer chains whose dimensions are $>\lambda/20$, scattering may occur from different points along the same chain and $P(\theta) < 1$. For this reason, diminution of scattered light intensity can occur due to interference, and the scattering envelope is no longer spherically symmetrical, as seen in Figure 3-15. In this case, the angular dependence of scattered light intensity is given by the particle scattering function, which, for a *monodisperse* system of randomly-coiling molecules in dilute solution, is given by the expression

$$P(\theta) = \frac{2}{v^2} [e^{-v} - (1 - v)] \quad (3.110)$$

where

$$v = 16 \frac{n^2}{\lambda^2} \langle s^2 \rangle \sin^2 \frac{\theta}{2} \quad (3.111)$$

and s^2 is called the mean-square radius of gyration. For linear-chain polymers, s^2 is related to the mean-square end-to-end distance as

$$\langle s^2 \rangle = \frac{\langle r^2 \rangle}{6}. \quad (3.112)$$

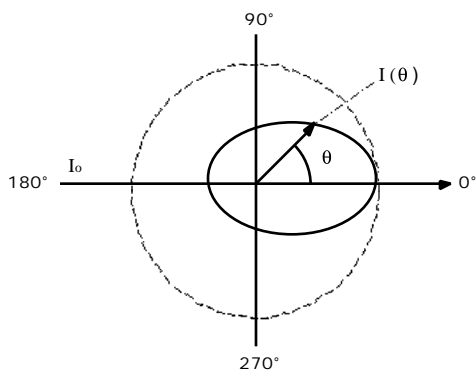


Figure 3-15 Intensity distribution of light scattering at various angles for a small particle (dashed circle) and a large polymer molecule (solid ellipse).

Basic instrumentation for light-scattering measurements is illustrated in Figure 3-16. Light from a high-intensity mercury lamp is polarized and filtered before passing through a glass cell that contains a filtered, dilute polymer solution. Scattered light intensity at an angle θ is recorded as a signal from a movable high-voltage photomultiplier tube.

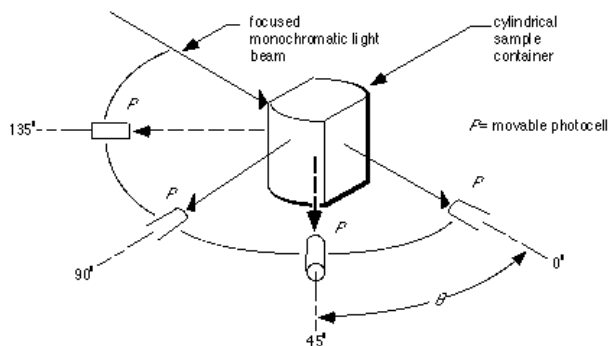


Figure 3-16 Conventional light-scattering instrumentation. (Copyright 1989 From *Principles of Polymer Systems*, 4th ed., by F. Rodriguez. Reproduced by permission of Routledge, Inc., part of The Taylor & Francis Group.)

To determine \bar{M}_w from eq. 3.107, it is necessary to know the value of $P(\theta)$ at each angle for which $R(\theta)$ has been measured. When the molecular-weight distribution of a polymer is polydisperse, as it usually is, $P(\theta)$ is not precisely given by eq. 3.110, but by a summation of similar equations for polymer chains of different sizes weighted by the amount of variously sized chains present in the polymer sample. Since this information is generally not known, it is customary to treat the data in a way that does not require explicit knowledge of $P(\theta)$. In practice, two approaches can be used. These are called the *Zimm* and *dissymmetry* methods which are discussed in the following sections.

Zimm Method. The most rigorous approach to determine M_w from light-scattering data is by means of a *Zimm plot*. This procedure has the advantage that chain conformation need not be known in advance; however, Zimm plots require tedious measurements of scattered light-intensity at many more angles than needed by the dissymmetry technique. A double extrapolation to both zero concentration and zero angle is used to obtain information concerning molecular weight, second-virial coefficient, and chain dimensions, as discussed next.

In the limit of small angles where $P(\theta)$ approaches unity, it can be shown by means of a series expansion of $1/P(\theta)$ that eq. 3.107 becomes[‡]

$$\frac{Kc}{R(\theta)} = \frac{1}{\bar{M}_w} \left[1 + \frac{16}{3} \frac{n}{\lambda} \langle s^2 \rangle \sin^2 \frac{\theta}{2} + 2A_2c \right]. \quad (3.113)$$

As illustrated in Figure 3-17, data is plotted in the form of $Kc/R(\theta)$ versus $\sin^2(\theta/2) + kc$ for different angles and concentrations (where k is an arbitrary constant added to provide spacing between curves). A *double* extrapolation to $\theta = 0^\circ$ and $c = 0$, for which the second and third terms on the right of eq. 3.113 become zero, yields M_w as the reciprocal of the intercept. As inspection of eq. 3.113 indicates, A_2 is then obtained as one-half of the slope of the extrapolated line at $\theta = 0$; the mean-square radius of gyration is obtained from the initial slope of the extrapolated line at $c = 0$ as

$$\langle s^2 \rangle = \frac{3\bar{M}_w}{16} \frac{\lambda}{n} \times \text{slope (at } c = 0). \quad (3.114)$$

One obvious difficulty with the Zimm method is that a large number of time-consuming measurements is required; however, the method provides a great deal of informa-

[‡] The Rayleigh ratio used in the scattering of dilute polymer solutions is the excess or reduced Rayleigh ratio,

$$\Delta R_\theta = R_\theta(\text{solution}) - R_\theta(\text{solvent}).$$

tion— \bar{M}_w , A_2 , and $\langle s^2 \rangle$. The number of experiments is greatly reduced by using the dissymmetry method; however, chain dimensions are less certain, as discussed next.

Dissymmetry Method. Molecular-weight determination by the *dissymmetry* method requires measurement of the scattered intensity at three angles—typically 45° , 90° , and 135° (see Figure 3-15)—and at several different (dilute) polymer concentrations. A dissymmetry ratio, z , is defined as

$$z = \frac{i(45^\circ)}{i(135^\circ)}. \quad (3.115)$$

Since z is normally concentration-dependent, a value at zero concentration is determined by plotting $(z - 1)^{-1}$ versus concentration. This value can then be used to obtain $P(90^\circ)$ and also r^2 from published values if the conformational state (e.g., rods, disks, spheres, or random coils) of the polymer in solution is known. In the absence of information to the contrary, a random-coil conformation, typical of flexible-chain polymers, is assumed. Once $P(90^\circ)$ is known, M_w can be obtained from the intercept and A_2 obtained from the slope of a plot of $Kc/R(90^\circ)$ versus concentration extrapolated to zero concentration.

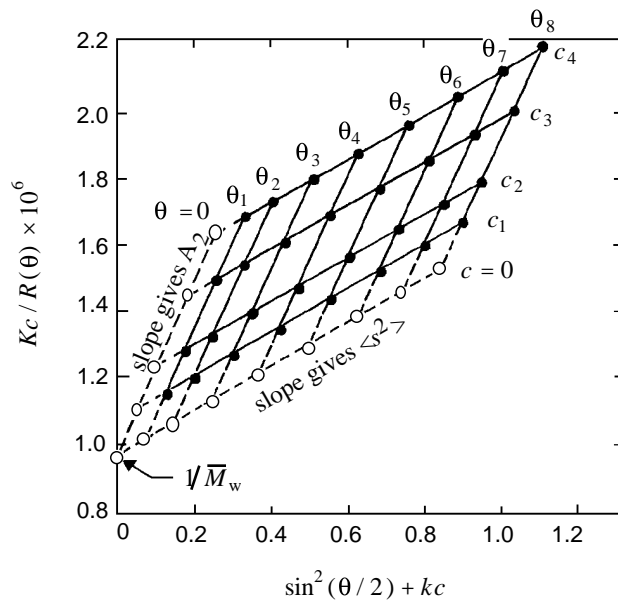


Figure 3-17 Idealized Zimm plot of light-scattering data (■) taken at different angles (θ) and solution concentrations (c). Double extrapolations to zero concentration and zero scattering-angle are represented by broken lines.

Low-Angle Laser Light-Scattering (LALLS). In recent years, helium–neon (He–Ne) lasers ($\lambda = 6328 \text{ \AA}$) have replaced conventional light sources in some commercial light-scattering instruments. The high intensity of these light sources permits scattering measurements at much smaller angles (2° to 10°) than possible with conventional light sources and for smaller samples at lower concentrations. Since at low angles the particle scattering-function, $P(\theta)$, approaches unity, eq. 3.107 reduces to the classical *Debye equation* for scattering by small spherical particles as

$$\frac{Kc}{R(\theta)} = \frac{1}{\bar{M}_w} + 2A_2c \quad (3.116)$$

Therefore, a plot of $Kc/R(\theta)$ versus c at a single angle gives \bar{M}_w as the inverse of the intercept and A_2 as one-half of the slope.

A representative LALLS plot of $Kc/R(\theta)$ versus c is shown for cellulose acetate (CA) in acetone at 25°C in Figure 3-18. From the intercept, a value of 150,000 is obtained for \bar{M}_w of the CA sample; the second virial coefficient, A_2 , is obtained from the slope as $7.53 \times 10^{-3} \text{ mL mol g}^{-2}$. One limitation of the LALLS method is that chain dimensions cannot be obtained since scattering is measured only at a single angle.

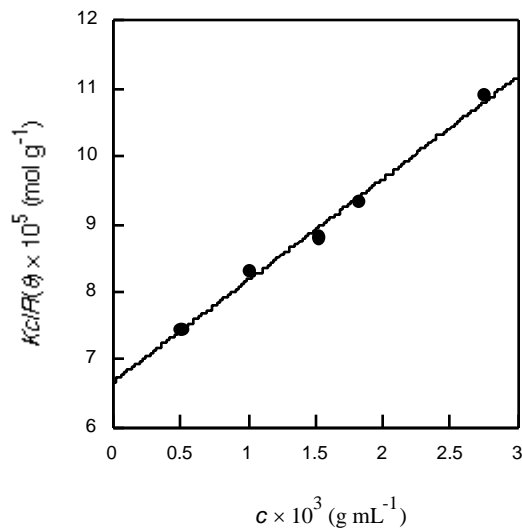


Figure 3-18. Plot of low-angle laser light-scattering data for cellulose acetate in acetone.³⁴

3.3.3 Intrinsic Viscosity Measurements

A method widely used for routine molecular-weight determination is based upon the determination of the intrinsic viscosity, $[\eta]$, of a polymer in solution through measurements of solution viscosity. Molecular weight is related to $[\eta]$ by the *Mark–Houwink–Sakurada equation* given as

$$[\eta] = K\bar{M}_v^a \quad (3.117)$$

where \bar{M}_v is the viscosity-average molecular weight defined for a discrete distribution of molecular weights (see Section 1.3) as

$$\bar{M}_v = \frac{\sum_{i=1}^N N_i M_i^{1+a}}{\sum_{i=1}^N N_i M_i^a} \quad (3.118)$$

Both K and a are empirical (Mark–Houwink) constants that are specific for a given polymer, solvent, and temperature. The exponent a normally lies between the values of 0.5 for a θ solvent and 1.0 for a thermodynamically good solvent. Extensive tables of Mark–Houwink parameters for most commercially important polymers are available.²² Some typical values for representative polymers are given in Table 3-6. The value of \bar{M}_v normally lies between the values of \bar{M}_n and \bar{M}_w obtained by osmometry and light-scattering measurements, respectively. As indicated by eq. 3.118, $\bar{M}_v = \bar{M}_w$ in the case of a thermodynamically good solvent when $a = 1$. The relationship between molecular weights is given by the expression

$$\bar{M}_n : \bar{M}_v : \bar{M}_w = 1 : [(1+a)^{-1} \Gamma(1+a)]^{1/a} : 2$$

where Γ is the gamma function (see Appendix E).

Intrinsic viscosity is implicitly expressed by the Huggins equation³⁶

$$\frac{\eta_i}{c} = [\eta] + k_H [\eta]^2 c \quad (3.119)$$

where k_H is a dimensionless parameter (the Huggins coefficient) whose value depends upon temperature as well as the specific polymer/solvent combination. The parameter η_i is called the *relative viscosity-increment*, which is defined as

$$\eta_i = \frac{\eta - \eta_s}{\eta_s} \quad (3.120)$$

where η and η_s are the viscosities of the dilute polymer solution and pure solvent, respectively. The ratio η_i/c is commonly called the reduced viscosity, η_{red} , or viscosity number according to recommended IUPAC[†] nomenclature.

Table 3-6 Mark-Houwink Parameters for Representative Polymers at 25°C*

Polymer	Solvent	$K \times 10^3$ (mL g ⁻¹)	a
Polystyrene	Tetrahydrofuran	14	0.70
	Toluene	7.5	0.75
	Benzene	9.2	0.74
Poly(methyl methacrylate)	Benzene	5.5	0.76
Cellulose acetate [†]	Tetrahydrofuran	51.3	0.69
Polycarbonate	Tetrahydrofuran	38.9	0.70
Polydimethylsiloxane	Toluene	2.4	0.84
Poly(2,6-dimethyl-1,4-phenylene oxide)	Toluene	28.5	0.68

* Values obtained from light-scattering data.

[†] 55.5 wt % acetal content.

As indicated by the form of eq. 3.119, $[\eta]$ can be obtained from the intercept of a plot of reduced viscosity versus c as shown for cellulose acetate in acetone at 25°C in Figure 3-19. In actual practice, reduced viscosity is obtained at different concentrations not by direct measurement of solution and solvent viscosities but by measurement of the time required for a dilute solution (t) and pure solvent (t_s) to fall from one fiducial mark to another in a small glass capillary. If these efflux times are sufficiently long (e.g., >100 s), the relative viscosity increment can be obtained as

$$\eta_i = \frac{t - t_s}{t_s} \quad (3.121)$$

Efflux times may be noted visually or more precisely by means of commercially available photocell devices.

[†] International Union of Pure and Applied Chemistry.

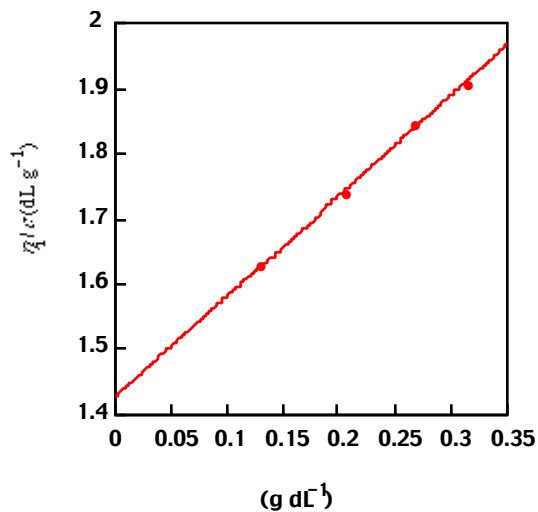


Figure 3-19 Plot of reduced viscosity of a cellulose acetate (intrinsic viscosity of 1.43 dL g⁻¹) in acetone at 25°C.³⁵

Capillary viscometers may be either Ostwald–Fenske or Ubbelohde types as illustrated in Figure 3-20. The latter have the advantage that different solution concentrations can be made directly in the viscometer by successive dilutions with pure solvent. During measurement, the viscometer is immersed in a constant temperature bath controlled to within 0.02°C of the set temperature, typically 25° or 30°C.

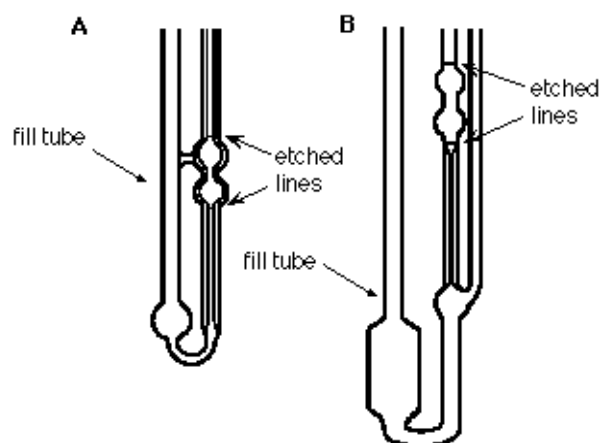


Figure 3-20 Ostwald–Fenske (A) and Ubbelohde (B) capillary viscometers.

In addition to determination of molecular weight, measurement of intrinsic viscosity can also be used to estimate chain dimensions in solution. The mean-square end-to-end distance is related to intrinsic viscosity through the relationship³⁷

$$\langle r^2 \rangle = \frac{M[\eta]}{K}^{2/3} \quad (3.122)$$

where K is considered to be a universal constant ($2.1 \times 10^{21} \text{ dL g}^{-1} \text{ cm}^{-3}$) known as the *Flory constant*.

3.3.4 Gel-Permeation Chromatography

One of the most widely used methods for the routine determination of molecular weight and molecular-weight distribution is gel-permeation chromatography (GPC), which employs the principle of size-exclusion chromatography (sometimes referred to as SEC) to separate samples of polydisperse polymers into fractions of narrower molecular-weight distribution. Basic instrumentation for GPC analysis is shown in Figure 3-21. Several small-diameter columns, typically 30 to 50 cm in length, are packed with small, highly porous beads. These are usually fabricated from polystyrene (crosslinked with a small fraction of divinylbenzene as a comonomer) or the packing may be porous glass beads that are usually modified with an ether or diol linkage. Pore diameters of the beads may range from 10 to 10^7 \AA , which approximate the dimensions of polymer molecules in solution. During GPC operation, pure prefiltered solvent is continuously pumped through the columns at a constant flow rate, usually 1 to 2 mL min^{-1} . Then, a small amount (1 to 5 mL) of a dilute polymer solution ($<0.2 \text{ g dL}^{-1}$) is injected by syringe into the solvent stream and carried through the columns. Polymer molecules can then diffuse from this mobile phase into the stationary phase composed of solvent molecules occupying the pore volumes. The smallest polymer molecules are able to penetrate deeply into the interior of the bead pores, but the largest molecules may be completely excluded by the smaller pores or only partially penetrate the larger ones. As pure solvent elutes the columns after injection, the largest polymer molecules pass through and finally out of the packed columns. These are followed by the next largest molecules, then the next largest, and so on, until all the polymer molecules have been eluted out of the column in descending order of molecular weight. Total sample elution in high-resolution columns may require several hours.

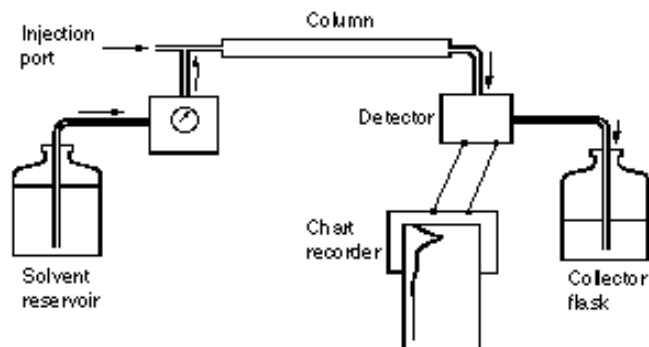


Figure 3-21 Gel-permeation chromatography (GPC). (Harry Allcock and Frederick W. Lampe, *Contemporary Polymer Chemistry*, 2nd ed., ©1990, p. 396. Reprinted by permission of Prentice Hall, Englewood Cliffs, NJ.)

The concentration of polymer molecules in each eluting fraction can be monitored by means of a polymer-sensitive detector, such as an infrared or ultraviolet device. Usually, the detector is a differential refractometer, which can detect small differences in refractive index between pure solvent and polymer solution. A signal from the detector is recorded (either by a chart recorder or digitally) as a function of time, which for a fixed flow rate is directly proportional to the elution volume, V_r . A representative GPC chromatogram for a commercial polystyrene sample is shown in Figure 3-22.

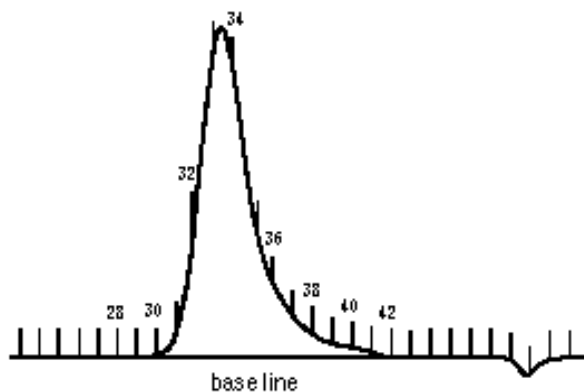


Figure 3-22 GPC chromatogram of polystyrene in tetrahydrofuran at 2.0 mL min^{-1} . Vertical marks represent elution counts. The negative peak at high counts may be due to a low-molecular-weight impurities, such as stabilizer, water, or dissolved air. (Adapted from *Introduction to Physical Polymer Science*, L. H. Sperling, Copyright ©1986 John Wiley & Sons. This material is used by permission of John Wiley & Sons, Inc.)

For a given polymer, solvent, temperature, pumping rate, and column packing and size, V_r is related to molecular weight. The form of this relation can be found only by comparing elution volumes with those of known molecular weight and narrow molecular-weight distribution, under identical conditions. Usually, only polymer standards of polystyrene and a few other polymers such as poly(methyl methacrylate) that can be prepared by anionic “living” polymerization (see Section 2.2.2) are available commercially for this purpose. Such standards are available with molecular weights ranging from about 500 to over 2 million with polydispersities as low as 1.06. Since different polymer molecules in the same solvent can have different dimensions, care must be exercised when using polystyrene standards to calibrate elution volumes of other polymers for which standards are not available. The most exact but demanding procedure is to use a universal calibration curve, as illustrated in Figure 3-23.

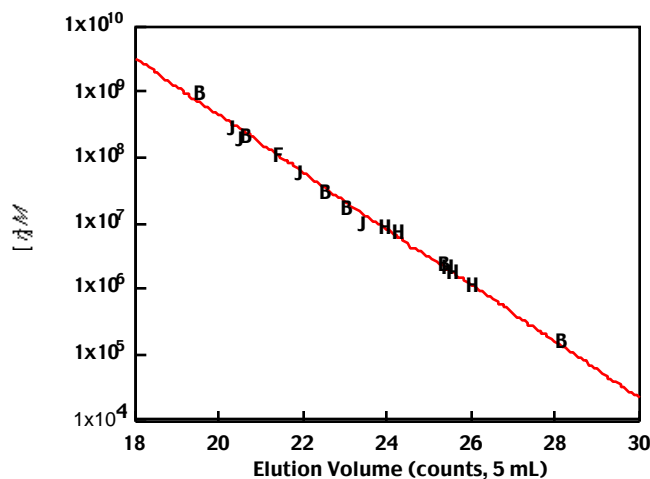


Figure 3-23 Universal GPC calibration curve showing data points for polystyrene (B), poly(vinyl chloride) (H), polybutadiene (F), and poly(methyl methacrylate) (J) standards in tetrahydrofuran. Line gives best fit of polystyrene data.³⁸

The universal calibration approach is based on the fact that the product $[\eta]M$ is proportional to the hydrodynamic volume of a polymer molecule in solution (see eq 3.122). This hydrodynamic volume is the effective molecular volume as seen by the pore sites. Universal calibration can be used if the Mark–Houwink constants (see eq. 3.117) are known for both the standard and unknown polymer samples in the same solvent and at the same temperature.

In the calculation of molecular-weight averages, the signal strength (i.e., peak height in Figure 3-21) is proportional to W_i (eq 1.2). Once a proper calibration curve is available to relate V_r to the molecular weight (M_i) of the calibration standard, direct calculation of all

molecular weights— \bar{M}_n , \bar{M}_w , \bar{M}_z , and even \bar{M}_{z+1} —and, therefore, polydispersities (\bar{M}_w/\bar{M}_n or \bar{M}_z/\bar{M}_n) is possible, typically by commercially available software. Recently, on-line coupling of GPC with low-angle light-scattering instrumentation (Section 3.3.2) has enabled rapid on-line computation of molecular weight without the need for separation calibration of the elution curve.

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Problems

3.1 Polyisobutylene (PIB) is equilibrated in propane vapor at 35°C. At this temperature, the saturated vapor pressure (p_1^0) of propane is 9050 mm Hg and its density is 0.490 g cm⁻³. Polyisobutylene has a molecular weight of approximately one million and its density is 0.915 g cm⁻³.

The concentration of propane, c , sorbed by PIB at different partial pressures of propane (p_1) is given in the following table. Using this information, determine an average value of the Flory interaction-parameter, χ_{12} , for the PIB–propane system.

p_1 (mm Hg)	c (g propane/g PIB)
496	0.0061
941	0.0116
1452	0.0183
1446	0.0185

3.2 The following osmotic pressure data are available for a polymer in solution:

c (g dL ⁻¹)	h (cm of solvent)
0.32	0.70
0.66	1.82
1.00	3.10
1.40	5.44
1.90	9.30

Given this information and assuming that the temperature is 25°C and the solvent density is 0.85 g cm⁻³

(a) Plot π/RTc versus concentration, c .

(b) Determine the molecular weight of the polymer and the second virial coefficient, A_2 , for the polymer solution.

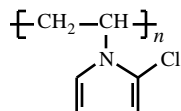
3.3 (a) What is the osmotic pressure (units of atm) of a 0.5 wt % solution of poly(methyl methacrylate) ($\bar{M}_w = 100,000$) in acetonitrile (density, 0.7857 g cm⁻³) at 45°C for which $[\eta] = 4.8 \times 10^{-3} \text{ M}^{0.5}$?

(b) What is the osmotic head in units of cm?

(c) Estimate the Flory interaction parameter for polysulfone in methylene chloride solution.

(d) Based upon your answer above, would you expect methylene chloride to be a good or poor solvent for polysulfone?

3.4 The osmotic pressure of two samples, A and B, of poly(vinyl pyridinium chloride)



were measured in different solvents, The following data were obtained:

Osmotic Pressure Data in Distilled Water

Sample	c (g mL ⁻¹)	Π (atm $\times 10^3$)
A	0.002	29
A	0.005	50
B	0.002	31
B	0.005	52

Osmotic Pressure Data in 0.01 N Aqueous NaCl

Sample	c (g mL ⁻¹)	Π (atm $\times 10^3$)
A	0.002	5
A	0.005	13
B	0.002	2
B	0.005	5.5

Discuss these results and account for any features that you consider anomalous.

3.5 The following viscosity data were obtained for solutions of polystyrene (PS) in toluene at 30°C:

c (g dL ⁻¹)	t (s)
0	65.8
0.54	101.2
1.08	144.3
1.62	194.6
2.16	257.0

Using this information:

- Plot the reduced viscosity as a function of concentration.
- Determine the intrinsic viscosity of this PS sample and the value of the Huggins constant, k_H .

(c) Calculate the molecular weight of PS using Mark–Houwink parameters of $a = 0.725$ and $K = 1.1 \times 10^{-4} \text{ dL g}^{-1}$.

3.6 Given that the molecular weight of a polystyrene (PS) repeating unit is 104 and that the carbon-carbon distance is 1.54 \AA , calculate the following:

(a) The mean-square end-to-end distance for a PS molecule of 1 million molecular weight assuming that the molecule behaves as a freely rotating, freely jointed, volumeless chain. Assume that each link is equivalent to a single repeating unit of PS.

(b) The unperturbed root-mean-square end-to-end distance, $r_o^{2/2}$, given the relationship for intrinsic viscosity, $[\eta]$, of PS in a θ solvent at 35°C as

$$[\eta] = 8 \times 10^{-4} M^{0.5}$$

where $[\eta]$ is in units of dL g^{-1} and the Flory constant () is $2.1 \times 10^{21} \text{ dL g}^{-1} \text{ cm}^{-3}$.

(c) The characteristic ratio, C_N , for PS.

3.7 The use of universal calibration curves in GPC is based upon the principle that the product $[\eta] M$, the hydrodynamic volume, is the same for all polymers at equal elution volumes. If the retention volume for a monodisperse polystyrene (PS) sample of 50,000 molecular weight is 100 mL in toluene at 25°C , what is the molecular weight of a fraction of poly(methyl methacrylate) (PMMA) at the same elution volume in toluene at 25°C ? The Mark–Houwink parameters, K and a , for PS are given as $7.54 \times 10^{-3} \text{ mL g}^{-1}$ and 0.783, respectively; the corresponding values for PMMA are $8.12 \times 10^{-3} \text{ mL g}^{-1}$ and 0.71.

3.8 Using the values of molar attraction constants given by van Krevelen in Table 3-2, calculate the solubility parameters, $(\text{MPa})^{1/2}$ at 25°C , for the following polymers:

(a) Polyisobutylene ($\rho = 0.924 \text{ g cm}^{-3}$)

(b) Polystyrene ($\rho = 1.04 \text{ g cm}^{-3}$)

(c) Polycarbonate ($\rho = 1.20 \text{ g cm}^{-3}$)

3.9 Show that the most probable end-to-end distance of a freely jointed polymer chain is given as $(2nl^2/3)^{1/2}$.

3.10 The (reduced or excess) Rayleigh ratio (R_θ) of cellulose acetate (CA) in dioxane was determined as a function of concentration by low-angle laser light-scattering measurements. Data are

given in the following table. If the refractive index (n_0) of dioxane is 1.4199, the refractive-index increment (dn/dc) for CA in dioxane is $6.297 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$, and the wavelength (λ) of the light is 6328 Å, calculate the weight-average molecular weight of CA and the second virial coefficient (A_2).

$c \times 10^3$ (g mL ⁻¹)	$R(\theta) \times 10^5$ (cm ⁻¹)
0.5034	0.239
1.0068	0.440
1.5102	0.606
2.0136	0.790
2.517	0.902

3.11 Using UNIFAC-FV, estimate the activity of toluene in a 50 wt % solution of polydimethylsiloxane in toluene at 298 K.

3.12 Chromosorb P was coated with a dilute solution of polystyrene in chloroform, thoroughly dried, and packed into a GC column. The column was then heated in a GC oven and maintained at different temperatures over a range from 200°C to 270°C under a helium purge. At each temperature, a small amount of toluene was injected and the time for the solute to elute the column was recorded and compared to that for air. From this information, the specific retention volume was calculated as given in the table below. Using this data, plot the apparent Flory interaction parameter as a function of temperature.

T °C	V_g mL/g-coating
200	6.55
210	5.58
220	4.66
230	4.07
240	3.38
250	2.87
260	2.88
270	2.38

3.13 Derive eq. 3.69 and develop an expression that can be used to obtain the exchange interaction parameter, X_{12} , appearing in the Flory equation of state from inverse gas chromatography measurements.