means would afford fractionations of such a high accuracy and reliability which the present experimental facilities might not be able to warrant. Furthermore, any other side reaction or disturbing parameter not considered here might introduce further difficulties. As a result of this analysis, it seems to be extremely difficult to work out a successful experimental route of determining M_i. Nevertheless, this route invariably will have to make use of the differences in the molecular weight distribution of the dead polymer which would be caused by the different means.

VI. Final Remarks

The fundamental equations (eq 22 and 23) developed in this paper prove to be helpful in providing universal relationships between kinetic quantities. Their knowledge reduces the problem of solving the kinetic scheme for any form of chain length dependence of k_t to the evaluation (either by closed calculation, if possible, or numerically) of the expression $(\bar{k}_t/k_t^\circ)^{1/2}P^{b/2}$, which is fairly constant for moderate values of the parameter b and varies only by a few percent on passing from its limiting value for predominant termination by disproportionation to its limiting value for predominant chain transfer. If both these limiting values are accessible, as is the case with the geometric mean approximation in the long-chain approximation, a fully exact solution can be provided. In all other cases, the (exact) numeric data obtained by iterating the chain length distribution can be reproduced with fair accuracy. Furthermore, due to the factorizability connected with the geometric mean approximation, in addition an exact treatment of a kinetic scheme involving termination by recombination is possible in this case.

References and Notes

(1) Olaj, O. F.; Zifferer, G.; Gleixner, G. *Macromolecules*, preceding paper in this issue.
(2) Olaj, O. F.; Zifferer, G.; Gleixner, G. Preprints of "Makromolekulares Kolloquium", Freiburg/Brsg., Germany, March 4–6, 1982, pp 21–22.
(3) Zifferer, G. Doctoral Thesis, University of Vienna, 1982.
(4) Mahabadi, H. K. *Macromolecules* **1985**, *18*, 1319.
(5) Olaj, O. F.; Zifferer, G.; Gleixner, G. *Makromol. Chem.* **1986**, *187*, 977.
(6) Olaj, O. F.; Zifferer, G.; Gleixner, G. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 773, 851.
(7) Olaj, O. F.; Zifferer, G.; Gleixner, G.; Stickler, M. *Eur. Polym. J.* **1986**, *22*, 585.
(8) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions*; Dover: New York, 1972; Chapter 3, p 10.
(9) This name is inspired by the fact that the bimolecular rate constant of a diffusion-controlled reaction is proportional to the sum of the diffusion constants D_x and D_y of the two molecules involved. If these depend on chain length according to $D_x \sim x^{-t}$ and $D_y \sim y^{-t}$, respectively, neglecting any eventual chain length dependence of the collision diameter (which enters as another factor) would lead to a rate constant whose chain length dependence is characterized by an M_3-type of mean (see also ref 11). In addition, this type of mean is also presumed to apply to the reptation model of termination between large radicals at high conversions (Coyle, D. J.; Thulig, T. J.; Tirell, M. *Ind. Eng. Chem. Fundam.* **1985**, *24*, 343).
(10) Actually, for numerically solving the expression for the diffusion mean it is not necessary to evaluate the complete double sum in eq 10. S_1^2 in this case is obtained simply as the product of two single sums by an iteration process.
(11) Ito, K. *J. Polym. Sci., Part A-2* **1969**, *7*, 241; *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1991.
(12) Olaj, O. F.; Zifferer, G., in preparation.
(13) Actually, there are very small but noticeable deviations of the slopes from the theoretical value of $-b/2$ which are caused by the fact that the short-chain behavior is slightly dependent on the type of mean.

Lattice–Fluid Theory of Polymer Solutions

Constantinos G. Panayiotou

Department of Chemical Engineering, University of Thessaloniki, Thessaloniki, 54006, Greece.

Received May 2, 1986

ABSTRACT: A molecular theory of r-mer fluid mixtures is presented. It is based on the Sanchez–Lacombe lattice–fluid model for r-mer fluids and their mixtures. Each molecule is characterized by a constant number of segments in the pure state and in solution. A more general mixing rule is used for the close-packed volume per segment in the mixture and in the one-fluid approach. The number of contact sites is not considered constant for all types of segments, and, thus, surface area fractions are introduced in the formalism of the model. Experimental data on all basic thermodynamic quantities of mixing for poly(dimethylsiloxane), polyisobutylene, and natural rubber solutions are used to test the theory. Liquid–liquid phase equilibria are considered for polymer–polymer mixtures. For this case, the effect of the binary parameters is discussed. Extension of the theory to account for gas solubilities in polymeric liquids is also discussed. The theory is compared with the original Sanchez–Lacombe theory and Flory's equation-of-state theory of polymer solutions.

In recent years there has been a sustained interest toward the development and refinement of statisticomechanical theories of the liquid state.[1,2] The radial distribution function approach has proved a successful treatment of liquids formed by small molecules of nearly spherical force fields. For macromolecules, however, its applicability is limited and exact theoretical treatments remain elusive. Approximate treatments whose common starting point is the partition function formulation are commonly used as an alternative. In this respect, free-volume models for polymer solutions[3–7] have proved quite successful in explaining their thermodynamic behavior, including volume changes on mixing, the composition dependence of the Flory–Huggins χ interaction parameter, and the exhibition of lower critical solution temperatures by nonpolar polymer + nonpolar solvent mixtures as well as polymer + polymer mixtures. In these models the characteristics of the pure liquids, as manifested, for example, in their equations of state, are taken into account for the description of the thermodynamic behavior of their mixtures. From a quantitative standpoint, the success of these models is heavily based not only on the judicious choice of the binary parameters but also on the adequate description of pure component behavior.

The "cell" character of the so-called FPP (Flory–Patterson–Prigogine) theory[3–5] and the lack of any detailed

0024-9297/87/2220-0861$01.50/0

model for the dependence on external conditions of the total number of external degrees of freedom per molecular segment (parameter c) limit its range of applicability to the liquid state only. Coupling of the FPP approach for liquids with other models for the gaseous state cannot always be used in a thermodynamically consistent manner for the description of vapor–liquid equilibria. For instance, it cannot be used for external conditions approaching the critical state. Semiempirical modifications of Flory's equation-of-state theory[4] to make it applicable to the gaseous state have appeared in the literature.[8-10] The interesting combination of the "cell" and "hole" concepts in a single model[11,12] does not alleviate this problem due to the presence in the formalism of the imperfectly understood Prigogine parameter c.

Lattice–fluid models,[6,7] on the other hand, are able to predict vapor–liquid transition in a fundamental manner. They can, for example, be used for the prediction and correlation of the solubilities of subcritical as well as supercritical gases in polymeric liquids.[13] They are also directly related to the classical Gibbs–DiMarzio[14] approach to glass transition.[15] Sanchez and Lacombe's model[6] is a remarkably simple model, but an extensive comparison of its performance with the performance of FPP models is still lacking. This may partly explain the fact that in spite of its shortcomings, the FPP approach is much more commonly used in the polymer solution literature than the lattice–fluid approach.

The purpose of this work is to present and test a modified lattice–fluid model of mixtures of r-mer fluids. It is based on Sanchez and Lacombe's model.[6] Seeking an improvement of the model, from the quantitative standpoint, without seriously sacrificing its simplicity, we will consider constant the number of segments per molecule in the pure state and in solution. Molecular shape differences will be taken into account, in direct analogy with Flory's equation-of-state theory,[4] through the characteristic surface-to-volume ratio, s, of each component. Aside from this latter feature, the theory for pure fluids is formally identical with the Sanchez–Lacombe theory of pure fluids.[16] Thus the characteristic equation-of-state or scaling parameters in the present model are the same as in the original Sanchez–Lacombe theory.[6,16]

The one-fluid approach is followed and a more general mixing rule is used for the close-packed volume per segment in the mixture.[17] The effect of incorporating an "entropic" binary parameter analogous to the Q_{12} parameter of Flory's theory[4] is discussed. Experimental data for a number of polymer–solvent systems extensively used to test Flory's theory[4] are used to test the present model.

This work is a direct continuation of our previous work[13] where we treated the simpler case of equal number of contact sites for all types of segments. However, no comparison of the theory with experimental data for the thermodynamic mixing quantities was done in that work.

Theory

Partition Function. Consider a mixture of N_1 molecules, each consisting of r_1 segments (r_1-mers) and N_2 r_2-mer molecules at temperature T and external pressure P. For an approximate description of our system, it is assumed that all molecules are arranged on a quasi-lattice of N_r sites, N_0 of which are empty (holes). Molecular segments and holes are assumed in the present work to be randomly mixed. We may then use Flory's combinatorial expression[18] for the number of configurations available to our system. In Sanchez–Lacombe[6,16,19] nomenclature, the pressure ensemble partition function in its maximum term approximation may be written as

$$Q(T,P) = \left(\frac{1}{f_0}\right)^{N_0}\left(\frac{\omega_1}{f_1}\right)^{N_1}\left(\frac{\omega_2}{f_2}\right)^{N_2} \exp\left[-\frac{E+PV}{RT}\right] \quad (1)$$

E and V are the potential (attractive) energy and the total volume of the system, respectively. The site fractions, f, are defined as

$$f_0 = N_0/N_r \quad (2)$$

and

$$f_i = r_i N_i/N_r, \qquad i = 1, 2 \quad (3)$$

On the basis of Flory's combinatorial expression[18] the parameter ω_i is given explicitly as

$$\omega_i = \frac{\delta_i r_i}{\sigma_i \exp(r_i - 1)}, \qquad i = 1, 2 \quad (4)$$

σ_i is a symmetry number and δ_i is a flexibility parameter characteristic of component i. ω_1 may be recognized to be the number of configurations available to an r_i-mer in the close-packed pure state;[18] it will be treated as a constant and terms containing it will cancel out in all expressions for the mixing quantities of our interest.

In order to proceed further we must evaluate V and E.

Volume of the Mixture. By adopting the one-fluid approach, we may attribute to each quasi-lattice site a volume v^*; it is the average close-packed volume per segment in the mixture. The total volume, V, of the system is then

$$V = N_r v^* \quad (5)$$

This volume must be distinguished from the total close-packed volume, V^*, of the mixture, which is

$$V^* = rNv^* = (r_1N_1 + r_2N_2)v^* \quad (6)$$

where

$$N = N_1 + N_2 \quad (7)$$

The reduced volume of the mixture is

$$\tilde{v} = \frac{V}{V^*} = \frac{N_r v^*}{rNv^*} = \frac{N_0 + rN}{rN} = \frac{1}{\tilde{\rho}} \quad (8)$$

$\tilde{\rho}$ being the reduced density.

The division of a molecule into segments is, in essence, arbitrary; a segment is simply considered to be an isometric portion of a chain molecule. As mentioned previously, our model in the case of pure components reduces to the theory of Sanchez and Lacombe for pure fluids.[16] This latter theory provides us with both a number of segments per molecule, r_i, and a close-packed volume per segment, v_i^*, for each pure fluid i. The characteristic volumes v_i^* are, generally, different for different fluids. We must then adopt an appropriate combining rule for the evaluation of mer volume, v^*, in the mixture. Following our previous work[13,17,20] we adopt for v^* the quadratic mixing rule

$$v^* = \varphi_1^2 v_1^* + 2\varphi_1\varphi_2 v_{12}^* + \varphi_2^2 v_2^* \quad (9)$$

where φ_i is the close-packed segment fraction for component i, given by

$$\varphi_i = \frac{r_i N_i}{rN} = \frac{r_i N_i}{N_r}\frac{N_r}{rN} = f_i\tilde{v} \quad (10)$$

v_{12}^* is given by

$$v_{12}^* = \xi_{12}\left(\frac{v_1^{*1/3} + v_2^{*1/3}}{2}\right)^3 \quad (11)$$

ξ_{12} is a dimensionless binary parameter (equal to one for

a mixture of hard spheres). For v_i^*'s not widely different, ξ_{12} is expected to have a value close to unity.

For simplicity and in accordance with our previous work,[13,17,20] we will consider the number of segments per molecule, r_i, to remain constant in the pure state and in solution. In general, then, the close-packed volume per r_i-mer is different in the pure state ($r_iv_i^*$) and in the mixture (r_iv^*). Lacombe and Sanchez's[19] mixing rule for v^* is recovered by equating v_{12}^* in eq 9 with the arithmetic mean of v_1^* and v_2^*. In this latter theory r_i is varying with composition in the mixture. Our assumption of constant r_i leads to a simpler formalism without worsening the quantitative character of the model.

Potential Energy of the Mixture. In the evaluation of the potential energy of the system, only nearest-neighbor interactions are taken into account. In addition, mer–hole and hole–hole interaction energies are assigned a zero value. We may then write for the potential energy

$$-E = N_{11}\epsilon_{11} + N_{12}\epsilon_{12} + N_{22}\epsilon_{22} \tag{12}$$

where N_{ij} is the number of i–j contacts, each contact being characterized by the interaction energy $-\epsilon_{ij}$. This number of contacts will certainly be influenced by the shape characteristics of the interacting molecules. The original Sanchez–Lacombe theory[6,19] as well as our previous work[13] does not take into account explicitly shape characteristics of the molecules in the mixture. Flory's theory[4,17] does take into account molecular shape, though in a crude manner, through the surface areas of contacts per segment, which are, in general, different for different components. By adopting then Flory's approach,[4] we may assign a value s_i to the number of contact sites per segment (proportional to the surface area per segment) of type i. In addition, we may introduce at this point, surface area fractions as

$$\Theta_i = \frac{N_i r_i s_i}{N_0 s_0 + N_1 r_1 s_1 + N_2 r_2 s_2}, \qquad i = 1, 2 \tag{13}$$

In the present treatment, holes are characterized not only by a varying size with composition (eq 9) but by a varying s_0 with composition as well. In order to keep unaffected the formalism of the Sanchez–Lacombe theory of pure fluids,[16] we have adopted the mixing rule

$$s_0 = s = \varphi_1 s_1 + \varphi_2 s_2 \tag{14}$$

in analogy with Flory's theory.[4]

The idea of introducing varying numbers of contact sites per segment in lattice theories is by no means a new one; it was already advanced in the thirties.[21] Kleintjens and Koningsveld[7] as well as Panayiotou and Vera[22] have incorporated this idea in lattice–fluid models. These treatments differ in the details from the present and lead to significantly different formalisms. Combination of eq 13, 14, and 8 gives

$$\Theta_i = \frac{rN\varphi_i s_i}{(N_0 + rN)s} = \frac{\vartheta_i}{\tilde{v}} \tag{15}$$

where the close-packed surface area fraction, ϑ_i, referred to as the surface fraction, is given by

$$\vartheta_i = \frac{N_i r_i s_i}{N_1 r_1 s_i + N_2 r_2 s_2} = \frac{\varphi_i s_i}{\varphi_1 s_1 + \varphi_2 s_2} = \frac{\varphi_i}{\varphi_i + \varphi_j(s_j/s_i)}, \qquad i \neq j \tag{16}$$

From the definitions of these fractions we obtain

$$\Theta_0 + \Theta_1 + \Theta_2 = 1 \tag{17}$$

and

$$\vartheta_1 + \vartheta_2 = 1 \tag{18}$$

We may now evaluate the number of contacts N_{ij}. In the random-mixing approximation pair and higher order probabilites may be evaluated in terms of singlet probabilities which are equal to the surface area fractions of each species in the system. Thus

$$N_{12} = N_1 r_1 s_1 \Theta_2 = N_2 r_2 s_2 \Theta_1 = \frac{rsN}{\tilde{v}}\vartheta_1\vartheta_2 \tag{19}$$

and

$$2N_{ii} = N_i r_i s_i \Theta_i = \frac{rsN}{\tilde{v}}\vartheta_i^2, \qquad i = 1, 2 \tag{20}$$

In order to proceed further we must relate the interaction energy ϵ_{ii} to the equation-of-state parameters of pure fluid i. In the case of pure fluids (superscript degree symbol), eq 12 for the potential energy reduces to the equation

$$-E_i^\circ = N_{ii}^\circ \epsilon_{ii} = \frac{N_i r_i}{\tilde{v}_i}\frac{s_i}{2}\epsilon_{ii} = \frac{N_i r_i}{\tilde{v}_i}\epsilon_i^* \tag{21}$$

The characteristic temperature T_i^* and pressure P_i^* are related to ϵ_i^* as follows:

$$\epsilon_i^* = RI_i^* = P_i^* v_i^* = P_i^* \frac{M_i}{r_i \rho_i^*} \tag{22}$$

where M_i is the molar mass and ρ_i^* is the characteristic density of pure fluid i. The three scaling parameters reported usually[6] are T_i^*, P_i^*, and ρ_i^*.

In analogy with eq 21 we may write for the mixture

$$-E = \frac{rN}{\tilde{v}}\epsilon^* \tag{23}$$

The composition dependence of ϵ^* may be obtained by substituting eq 19 and 20 in eq 12:

$$\epsilon^* = \frac{s}{2}(\vartheta_1^2\epsilon_{11} + 2\vartheta_1\vartheta_2\epsilon_{12} + \vartheta_2^2\epsilon_{22}) \tag{24}$$

By elementary algebra this equation may be cast in the more useful form

$$\epsilon^* = \varphi_1\epsilon_1^* + \varphi_2\epsilon_2^* - \varphi_1\vartheta_2 RTX_{12} \tag{25}$$

where

$$X_{12} = \frac{\epsilon_1^* + (s_1/s_2)\epsilon_2^* - 2(s_1/s_2)^{1/2}\epsilon_{12}^*}{RT} \tag{26}$$

and

$$\epsilon_{12}^* = \frac{(s_1 s_2)^{1/2}}{2}\epsilon_{12} = \zeta_{12}(\epsilon_1^*\epsilon_2^*)^{1/2} \tag{27}$$

The dimensionless binary parameter ζ_{12} is expected to take values close to unity (equal to one of Berthelot's rule). Equation 25 reduces, as it should, to the corresponding equations in simpler treatments[13,19] when $s_1/s_2 = 1$. It is important to notice that in this development of the theory the absolute values of s_1 and s_2 are not needed; only their ratio is needed.

Equation of State. In analogy with eq 22 we may define the characteristic parameters T^* and P^* for the mixture as follows:

$$\epsilon^* = RT^* = P^* v^* \tag{28}$$

The corresponding reduced quantities are then

$$\tilde{T} = T/T^* \tag{29}$$

and

$$\tilde{P} = P/P^* \tag{30}$$

The free energy of the system may be obtained from eq 1 as

$$G = -RT \ln Q \tag{31}$$

Minimization of G with respect to N_0 leads to the equation of state

$$\frac{PV}{NRT} = r\frac{\tilde{P}\tilde{v}}{\tilde{T}} = 1 - r\left[1 + \frac{\ln(1-\tilde{\rho})}{\tilde{\rho}} + \frac{\tilde{\rho}}{\tilde{T}}\right] \tag{32}$$

which is formally identical with the equation of state derived by Sanchez and Lacombe[6,16,19] for both pure components and mixture. Notice that eq 32 gives the correct ideal gas limit ($P \to 0$, $T \to \infty$). In the case of high polymers ($r \to \infty$) and at negligible external pressure, eq 32 reduces to the equation

$$\tilde{\rho} = 1 - \exp[-\tilde{\rho} - (\tilde{\rho}/\tilde{T})^2] \tag{32a}$$

The thermal expansion coefficient, α, and the isothermal compressibility, β, obtained from eq 32 are given by

$$\alpha T = \frac{1 + \tilde{P}\tilde{v}^2}{\tilde{T}\tilde{v}[1/(\tilde{v}-1) + 1/r] - 2} \tag{33}$$

and

$$\beta P = \frac{\tilde{P}\tilde{v}^2}{\tilde{T}\tilde{v}[1/(\tilde{v}-1) + 1/r] - 2} \tag{34}$$

Basic Thermodynamic Quantities of Mixing. From classical thermodynamics, the chemical potential μ_i of component i in the mixture is given by

$$\mu_i = (\partial G/\partial N_i)_{T,P,N_{j\neq i}} \tag{35}$$

Using equation 31 and taking into account the minimization condition for G, which has led to the equation of state, eq 35 gives for the chemical potential of component 1

$$\frac{\mu_1}{RT} = \ln \varphi_1 + \left(1 - \frac{r_1}{r_2}\right)\varphi_2 + r_1\tilde{\rho}X_{12}\vartheta_2^2 + r_1(\tilde{v}-1)\ln(1-\tilde{\rho}) + \ln\frac{\tilde{\rho}}{\omega_1} - \frac{r_1\tilde{\rho}}{\tilde{T}_1} + r_1\frac{\tilde{P}\tilde{v}}{\tilde{T}}\left(2\frac{\varphi_1 v_1^* + \varphi_2 v_{12}^*}{v^*} - 1\right) \tag{36}$$

The chemical potential for component 2 is obtained from this equation by simple interchange of subscripts 1 and 2 ($v_{12}^* = v_{21}^*$, $s_2X_{12} = s_1X_{21}$). In the case of pure component 1 eq 36 gives for the chemical potential

$$\frac{\mu_1^\circ}{RT} = r_1(\tilde{v}_1 - 1)\ln(1-\tilde{\rho}_1) + \ln\frac{\tilde{\rho}_1}{\omega_1} - \frac{r_1\tilde{\rho}_1}{\tilde{T}_1} + r_1\frac{\tilde{P}_1\tilde{v}_1}{\tilde{T}_1} \tag{37}$$

In the close-packed limit (no allowance for empty sites) we obtain from eq 36 and 37 for liquids at low pressures the equation

$$\lim_{\tilde{\rho}_1,\tilde{\rho}\to 1}\left(\frac{\mu_1 - \mu_1^\circ}{RT}\right) = \ln\varphi_1 + \left(1 - \frac{r_1}{r_2}\right)\varphi_2 + r_1X_{12}\vartheta_2^2 \tag{38}$$

which is reminiscent of the familiar Flory–Huggins equation[4,17,18]

$$\frac{\mu_1 - \mu_1^\circ}{RT} = \ln\Phi_1 + \left(1 - \frac{r_1v_1^*}{r_2v_2^*}\right)\Phi_2 + \chi\Phi_2^2 \tag{39}$$

where the "volume" fraction Φ_i is defined as

$$\Phi_i = \frac{N_ir_iv_i^*}{N_1r_1v_1^* + N_2r_2v_2^*}, \qquad i = 1, 2 \tag{40}$$

It should be noted that there is a difference, though small, between this "volume" fraction and the true volume fraction in the mixture. Thus, for the system benzene (1)–poly(dimethylsiloxane) (2) at 25 °C ($\rho_1^* = 0.994$ g/cm^3, $v_1^* = 9.8$ cm^3/mol, $\rho_1 = 0.874$ g/cm^3, $\rho_2^* = 1.104$ g/cm^3, $v_2^* = 13.1$ cm^3/mol, $\rho_2 = 0.972$ g/cm^3) when $\varphi_1 = \varphi_2$, the value of Φ_1 is 0.428 while the corresponding true volume fraction is 0.429. On the other hand, for the system benzene (1)–polyisobutylene (2) at 25 °C ($\rho_2^* = 0.974$ g/cm^3, $v_2^* = 15.1$ cm^3/mol, $\rho_2 = 0.917$ g/cm^3) when $\varphi_1 = \varphi_2$, the value of Φ_1 is 0.395 while the corresponding true volume fraction is 0.410. Following common practice[4,6,17,23] we will use in this work Φ_i's instead of the true volume fractions. Combination of eq 36, 37, and 39 gives for the Flory–Huggins χ interaction parameter in solvent (1)–polymer (2) systems at low pressures.

$$\chi = \left\{\ln\frac{\varphi_1}{\Phi_1} + (\varphi_2 - \Phi_2) + r_1\tilde{\rho}X_{12}\vartheta_2^2 + \ln\frac{\tilde{\rho}}{\tilde{\rho}_1} - \frac{r_1}{\tilde{T}_1}(\tilde{\rho} - \tilde{\rho}_1) + r_1(\tilde{v}-1)\ln(1-\tilde{\rho}) - r_1(\tilde{v}_1 - 1)\ln(1-\tilde{\rho}_1)\right\} \Big/ \Phi_2^2 \tag{41}$$

The volume change upon mixing is

$$\Delta V^M = rNv^*\tilde{v} - r_1N_1v_1^*\tilde{v}_1 - r_2N_2v_2^*\tilde{v}_2 \tag{42}$$

or

$$\frac{\Delta V^M}{rNv^*} = \tilde{v} - \varphi_1\tilde{v}_1\frac{v_1^*}{v^*} - \varphi_2\tilde{v}_2\frac{v_2^*}{v^*} = \tilde{v} - \tilde{v}^\circ \tag{42a}$$

The relative volume change of mixing is

$$\frac{\Delta V^M}{V^\circ} = \frac{\tilde{v} - \tilde{v}^\circ}{\tilde{v}^\circ} \tag{42b}$$

V° being the sum of the volumes of the pure components. The enthalpy of mixing is given by

$$\Delta H^M = -rN\epsilon^*\tilde{\rho} + r_1N_1\epsilon_1^*\tilde{\rho}_1 + r_2N_2\epsilon_2^*\tilde{\rho}_2 + P\Delta V^M \tag{43}$$

or, in combination with eq 25

$$\frac{\Delta H^M}{rN} = RT\left\{\tilde{\rho}\varphi_1\vartheta_2X_{12} + \varphi_1\frac{\tilde{\rho}_1 - \tilde{\rho}}{\tilde{T}_1} + \varphi_2\frac{\tilde{\rho}_2 - \tilde{\rho}}{\tilde{T}_2}\right\} + \frac{P\Delta V^M}{rN} \tag{43a}$$

By series expansion of eq 43a in powers of φ_2, the enthalpy of mixing at infinite dilution, ΔH_∞, at low pressures is given by

$$\Delta H_\infty = \frac{RT}{\rho_2^*v_2^*}\left\{\frac{\tilde{\rho}_2 - \tilde{\rho}_1}{\tilde{T}_2} + \tilde{\rho}_1\frac{s_2}{s_1}X_{12} + \beta_1P_1^*\tilde{\rho}_1^2\psi_1\right\} \tag{44}$$

where

$$\psi_1 = \tilde{\rho}_1\left(\frac{1}{\tilde{T}_1} - \frac{1}{\tilde{T}_2} + \frac{s_2}{s_1}X_{12}\right) + \frac{1}{r_2} - \frac{1}{r_1} \tag{45}$$

Phase Stability. The stability with respect to diffusion of a homogeneous phase over the entire range of composition in a binary mixture at a given temperature and pressure requires the following

$$\frac{\partial\mu_1}{\partial x_1} > 0 \qquad \frac{\partial\mu_2}{\partial x_2} > 0 \qquad \frac{\partial\mu_1}{\partial x_2} = \frac{\partial\mu_2}{\partial x_1} < 0 \tag{46}$$

x_i being the mole fraction of component i. All these inequalities are simultaneously satisfied if

$$\partial^2 g/\partial\varphi_1^2 > 0 \tag{47}$$

where

$$g = G/(rN) \tag{48}$$

Using eq 1, 31, and 48, we obtain from inequality 47 the following condition for phase stability

$$\tilde{\rho}\left[2\frac{\vartheta_1}{\varphi_1}\left(\vartheta_1\frac{s_2}{s_1}+\vartheta_2\right)^2 X_{12}+\beta P^*\tilde{T}\psi^2\right] < \frac{1}{r_1\varphi_1}+\frac{1}{r_2\varphi_2}+2\frac{P\tilde{v}}{RT}(v_1^*+v_2^*-2v_{12}^*) \quad (49)$$

where

$$\psi = \tilde{\rho}\lambda_{12}+\frac{P\tilde{v}}{RT}(v_1^*-v_2^*)-\left(\frac{1}{r_1}-\frac{1}{r_2}\right)+\frac{P\tilde{v}}{RT}(\varphi_1-\varphi_2)(v_1^*+v_2^*-2v_{12}^*) \quad (50)$$

and

$$\lambda_{12}=\frac{1}{RT}\frac{\partial\epsilon^*}{\partial\varphi_1}=\frac{1}{\tilde{T}_1}-\frac{1}{\tilde{T}_2}\left(\vartheta_2^2-\vartheta_1^2\frac{s_2}{s_1}\right)X_{12} \quad (51)$$

Inequality 49 will be referred to as the spinodal inequality.

Gas Solubilities in Polymer Liquids. All equations in this work have been written in such a manner that a direct comparison is possible with corresponding equations in simpler treatments of the lattice-fluid theory.[4,13,19] Extension of the theory to account for gas solubilities in polymeric liquids can be done along the lines of our previous work.[13] The weight fraction Henry's law constant H_w at very low pressures is defined as

$$H_w=\lim_{y_1,w_1\to 0}(y_1P/w_1) \quad (52)$$

where y_1 is the mole fraction of the solute (gas) in the vapor phase and w_1 is its weight fraction in the liquid phase. In the present treatment H_w is given by

$$H_w=\frac{RT\rho_2^*}{M_1}\exp\left\{r_1\left[1+\tilde{\rho}_2X_{12}+(\tilde{v}_2-1)\ln(1-\tilde{\rho}_2)-\frac{\tilde{\rho}_2}{\tilde{T}_1}\right]+\ln\tilde{\rho}_2\right\} \quad (53)$$

M_1 is the molecular weight of the solute. Equation 53 is formally identical with eq 49 of ref 13; X_{12}, however, is given now by eq 26. Corrections for the effect of high pressures on H_w are given in ref 13.

Applications

Comparison of Theory and Experiment. Mixing Functions. In this section we test the lattice-fluid model presented in the previous section against experimental data for the basic thermodynamic quantities of mixing (volumes of mixing, heats of mixing, activities, and χ interaction parameters) for a number of representative polymer–solvent systems.

The test will be done in successive steps. First, we will consider the simple case of a one-parameter model (ξ_{12} = 1, s_1/s_2 = 1). Subsequently, we will introduce in the model values for s_1/s_2 obtained from the literature; the ratio s_1/s_2 will not be treated as an adjustable parameter in this test. In cases of discrepancies between theoretical and experimental volumes of mixing, agreement can be reached most effectively by considering ξ_{12} as an adjustable parameter. This test will make possible a direct comparison of the performances of the present model with existing similar theories.

Poly(dimethylsiloxane) Solutions. PDMS solutions are a class of polymer solutions that have repeatedly been used in the past to test new theories.[23-29] Flory's equation-of-state theory[4] usually fails to reproduce the experimental data for this class of systems. Consideration of all three parameters X_{12}, Q_{12}, and s_1/s_2 of Flory's theory as adjustable does not always reproduce simultaneously the experimental data for all quantities of mixing; large contributions of the "entropic" term (containing Q_{12}) are often needed or the adjusted values of s_1/s_2 are meaningless.[23-25,27] Reformulation of Flory's theory by introducing a mixing rule analogous to eq 9 of the present work has led to considerable improvement of the theory.[17,20,28]

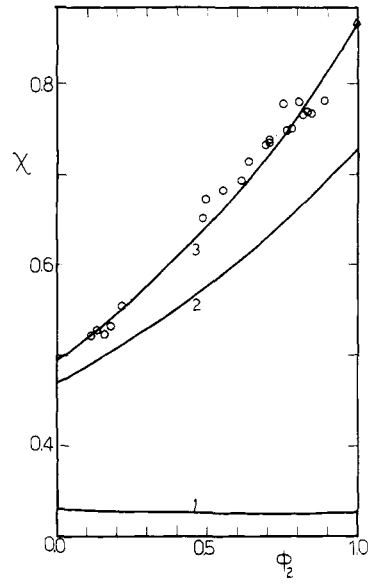

Figure 1. Comparison between experimental and calculated values of χ plotted against the "volume" fraction for the system benzene (1)–PDMS (2) at 25 °C. Circles represent experimental results of Flory and Shih[23] and the triangle represents the results of Summers et al.[32] Curve 1 was calculated by the Sanchez–Lacombe theory,[6] curve 2 was calculated by the present one-parameter model, and curve 3 was calculated by the present three-parameter model using the binary parameters in Table I.

The first system used to test the model is the mixture **benzene (1)–PDMS (2).** Experimental data for excess volumes at 25 °C were obtained from ref 23. The heats of mixing at infinite dilution at 25 °C reported in the literature are 14.2 J g^{-1} (Delmas et al.[30]) and 11 J g^{-1} (Morimoto[31]). The average value 12.6 J g^{-1} has been taken as a basis for all subsequent theoretical calculations. Data for χ interaction parameters have been obtained from ref 23 and 32.

On the basis of the average value 12.6 J g^{-1} for ΔH_∞, the estimated value of the binary parameter ζ_{12} for the original Sanchez–Lacombe theory[6] is 1.0027. With this value for ζ_{12} the Sanchez–Lacombe theory predicts for the ratio $\Delta V^M/V^\circ$ the value 0.00240 at Φ_2 = 0.5; the corresponding experimental value is[23] −0.00061. Curve 1 in Figure 1 for the χ interaction parameter was esimated by the Sanchez–Lacombe theory[6] with the above value for ζ_{12}.

Application of the one-parameter Flory theory for this system[23] (X_{12} determined from experimental ΔH_∞) gave the following: $\Delta V^M/V^\circ$ = 0.0121 at Φ_2 = 0.5, $\chi(\Phi_2 = 0)$ = 0.23, and $\chi(\Phi_2 = 1)$ = 0.66. In order to avoid confusion we have not plotted in Figures 1–9 the curves for χ calculated by Flory's theory.[4]

The simple version of the model presented in the previous section (ξ_{12} = 1, s_1/s_2 = 1) has one binary adjustable parameter, the parameter ζ_{12}. For the system benzene–PDMS with ΔH_∞ = 12.6 J g^{-1}, we obtain ζ_{12} = 0.9825. With this value for ζ_{12}, the calculated $\Delta V^M/V^\circ$ at Φ_2 = 0.5 is −0.00069, in fairly good agreement with the experimental value, and the calculated χ interaction parameters are

Table I
Binary Parameters of Lattice-Fluid Models

system	Sanchez-Lacombe theory[6] ζ_{12}	Present model ($\xi_{12} = s_1/s_2 = 1.0$, $q_{12} = 0$) ζ_{12}	present three-parameter model s_1/s_2	ζ_{12}	ξ_{12}	q_{12}
benzene–PDMS[a]	1.0027	0.9825	1.1[28]	0.9809	1.0000	0.015
chlorobenzene–PDMS	1.0082	0.9955	1.4[23]	0.9912	0.9967	0.060
cyclohexane–PDMS	0.9994	0.9918	1.2[23,28]	0.9936	1.0005	0.028
			1.0[e]	0.9920	1.0005	0.022
MEK[b]–PDMS	1.0013	0.9802	1.4[28]	0.9852	0.9990	0.039
benzene–PIB[c]	0.9824	0.9768	1.03[28]	0.9786	1.0187	−0.033
			1.72[36,e]	1.0367	1.0187	−0.049
cyclohexane–PIB	0.9932	0.9993	1.0	0.9993	1.0151	−0.027
			1.61[36,e]	1.0567	1.0151	−0.045
n-pentane–PIB	0.9865	1.0008	1.89[36]	1.1071	1.0163	−0.056
n-octane–PIB	0.9966	1.0014	1.47[28]	1.0429	1.0063	0.003
benzene–NR[d]	0.9901	0.9923	1.1[43]	0.9960	1.0070	0.0046
			1.0[e]	0.9924	1.0070	0.0046

[a] Poly(dimethylsiloxane). [b] Methyl ethyl ketone. [c] Polyisobutylene. [d] Natural rubber. [e] Alternative set of binary parameters.

Table II
Comparison between Calculated and Observed Values of $\Delta V^M/V^\circ$ ($\times 10^2$) at $\Phi_2 = 0.5$

system	exptl	calcd: Sanchez–Lacombe[6]	calcd: Flory[4]	calcd: present model ($\xi_{12} = 1.0$)
PDMS–benzene	−0.061	0.24	1.21	−0.069
PDMS–MEK	−0.030	0.36		−0.020
PDMS–cyclohexane	0.053	0.160	0.710	0.021
PDMS–chlorobenzene	−0.490	−0.220	0.250	−0.320
PIB–benzene	0.34	0.17	0.75	−0.54 (0.22)[a]
PIB–cyclohexane	−0.14	−0.44	−0.07	−0.88 (−0.42)
PIB–*n*–pentane	−1.28	−1.86	−1.55	−2.00 (−1.81)
PIB–*n*–octane	−0.48	−0.74		−0.78 (−0.72)
NR–benzene	0.09	−0.19	0.09	−0.27 (−0.18)

[a] Values in parentheses were calculated with the combining rule: $(2v_2^* = v_1^* + v_2^*)$.

shown by curve 2 in Figure 1. Although the model underestimates χ, it is in much better agreement with experiment than Sanchez and Lacombe's theory[6] and Flory's theory[23].

Experimental χ parameters are best reproduced by using for s_1/s_2 the value 1.1 reported in the literature[28] and an "entropic" correction to X_{12}, analogous to the Q_{12} term in Flory's theory.[4] Following Flory's argument, we add to the expression for system's potential energy the "entropic" correction term $RTrN\varphi_1\vartheta_2 q_{12}$. The product of the dimensionless binary parameter q_{12} with R may be considered to represent the entropy of interaction between unlike segments. As in Flory's theory,[4] this correction term will affect only the expression for the chemical potential; thus, we must add to the right-hand side term of eq 36 the quantity $r_1\vartheta_2^2 q_{12}$.

Curve 3 in Figure 1 was obtained by setting $s_1/s_2 = 1.1$, $\zeta_{12} = 0.9809$, and $q_{12} = 0.0148$. With this set of parameters we obtain $\Delta H_\infty = 12.6$ J g^{-1} and $\Delta V^M/V^\circ = -0.00064$.

All subsequent systems are treated in the same manner. Values of the binary parameters of the lattice–fluid models considered are given in Table I. Volumes of mixing calculated with the three one-parameter models considered are summarized in Table II.

The second mixture used to test the lattice–fluid theory is **chlorobenzene (1)–PDMS (2)**. Excess volumes for this system were measured by Flory and Shih[23] at 25 °C. Delmas et al.[30] found for the same system $\Delta H_\infty = 7.53$ J g^{-1}. χ interaction parameters obtained from osmotic pressure measurements by Kuwahara et al.[33] at 20 °C are shown in Figure 2.

Flory's one-parameter theory for this system[23] gave $\chi(\Phi_2 = 0) = 0.15$ and $\chi(\Phi_2 = 1) = 0.2$.

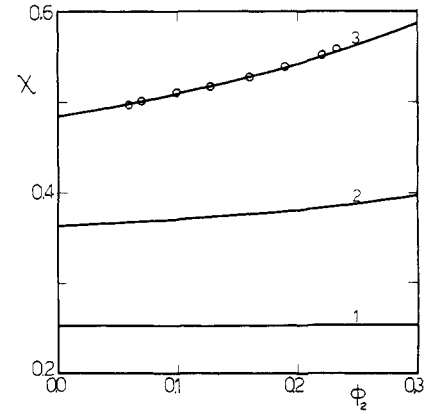

Figure 2. Comparison between experimental and calculated values of χ for the system chlorobenzene (1)–PDMS (2) at 25 °C. Circles represent osmotic pressure measurements of Kuwahara et al.[33] Curve 1 was calculated by the Sanchez–Lacombe theory,[6] curve 2 was calculated by the present one-parameter model, and curve 3 was calculated by the present three-parameter model using the binary parameters in Table I.

On the basis of the experimental ΔH_∞ we obtain for the simple version ($\xi_{12} = s_1/s_2 = 1.0$) of our model $\zeta_{12} = 0.9955$. With this value for ζ_{12} the calculated $\Delta V^M/V^\circ$ at $\Phi_2 = 0.5$ is −0.0032, while the calculated χ parameters are shown by curve 2 in Figure 2. In both respects this simple one-parameter model appears superior to the Sanchez–Lacombe theory[6] or the Flory theory.[4] Better agreement with experiment requires consideration of additional binary adjustable parameters.

The ratio s_1/s_2 for this system as calculated by Flory and Shih[23] is 1.4. The set of the parameters $\xi_{12} = 0.9967$, $\zeta_{12} = 0.9912$, and $q_{12} = 0.060$ reproduced the experimental values for ΔH_∞ and $\Delta V^M/V^\circ$, while the calculated χ parameters are shown by curve 3 in Figure 2.

The third system considered is **cyclohexane (1)–PDMS (2)**. Excess volumes for this system were measured by Flory and Shih[23] at 25 °C. Delmas et al.[30] found for the same system $\Delta H_\infty = 5.2$ J g^{-1}.

Experimental and calculated χ interaction parameters are shown in Figure 3. Flory's one-parameter theory for this system[23] gave $\chi(\Phi_2 = 0) = 0.13$ and $\chi(\Phi_2 = 1) = 0.24$.

The fourth system considered is **methyl ethyl ketone (MEK) (1)–PDMS (2)**. Experimental data for ΔH_∞, $\Delta V^M/V^\circ$, and χ parameters for this system were reported by Shiomi et al.;[35] they found $\Delta H_\infty = 14.3$ J g^{-1} and $\Delta V^M/V^\circ = -0.0003$ at $\Phi_2 = 0.5$. The observed χ parameters are represented by circles in Figure 4 along with the calculated ones.

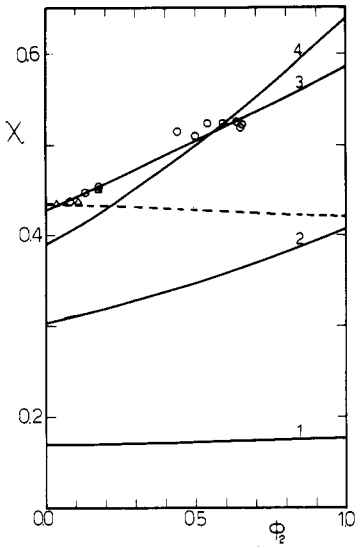

Figure 3. Comparison between experimental and calculated values for χ for the system cyclohexane (1)–PDMS (2) at 25 °C. Circles and triangles represent experimental results.[23,33] The dashed line is the least-squares experimental line of Brotzman and Eichinger.[34] Curve 1 was calculated by the Sanchez–Lacombe theory,[6] curve 2 was calculated by the present one-parameter model, and curves 3 and 4 were calculated by the present three-parameter model with $s_1/s_2 = 1.0$ and $s_1/s_2 = 1.2$, respectively, using the binary parameters in Table I.

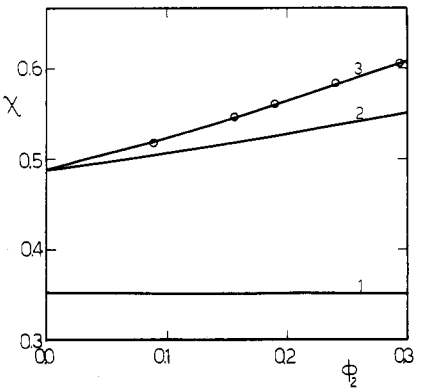

Figure 4. Comparison between experimental and calculated values of χ for the system MEK (1)–PDMS (2) at 35 °C. Circles represent experimental results.[35] Curves 1, 2, and 3 were calculated by the Sanchez–Lacombe theory,[6] the present one-parameter model, and the present three-parameter model, respectively, using the binary parameters in Table I.

In all four PDMS–solvent systems considered, the contribution of the q_{12} term to χ is significantly lower than the corresponding contribution of the Q_{12} term in Flory's theory.

Polyisobutylene (PIB) Solutions. PIB solutions are another class of polymer solutions that have also been repeatedly used in the past to test new theories.[6,7,28,36] Predictions of Flory's equation-of-state theory[4,36] and of Sanchez and Lacombe's theory[6] are in acceptable agreement with experiment for this class of solutions.

As a first example we will consider the mixture **benzene (1)–PIB (2)**. Excess volumes for this system were measured by Eichinger and Flory[36] at 24.5 °C. The integral heats of mixing at infinite dilution were measured by Delmas et al.[37] and by Cuniberti and Bianchi[38] at 25 °C. They have found $\Delta H_\infty = 17.8$ J g^{-1} and $\Delta H_\infty = 15.0$ J g^{-1}, respectively. χ interaction parameters determined by high-pressure osmometry[39] and vapor sorption measurements[36] are shown in Figure 5 by circles and squares, respectively.

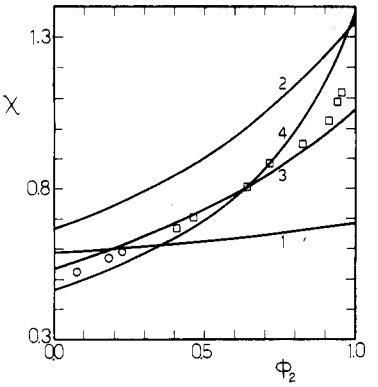

Figure 5. Comparison between experimental and calculated values of χ for the system benzene (1)–PIB (2) at 25 °C. Squares and circles represent experimental results.[36,39] Curves 1 and 2 were calculated by the Sanchez–Lacombe theory[6] and the present one-parameter model, respectively; curves 3 and 4 were calculated by the present three-parameter model with $s_1/s_2 = 1.03$ and $s_1/s_2 = 1.72$, respectively, using the binary parameters in Table I.

Flory's one-parameter theory for this system gave $\chi(\Phi_2 = 0) = 0.44$, $\chi(\Phi_2 = 1) = 1.42$, and $\Delta V^M/V^\circ = 0.0075$ at $\Phi_2 = 0.5$; the corresponding experimental value is $\Delta V^M/V^\circ = 0.0034$.[36]

On the basis of the average experimental value $\Delta H_\infty = 16.4$ J g^{-1} for this system, we obtained for the simple version ($\xi_{12} = s_1/s_2 = 1.0$) of our model $\zeta_{12} = 0.9768$. With this value of ζ_{12} the estimated volume of mixing at $\Phi_2 = 0.5$ is $\Delta V^M/V^\circ = -0.0054$, in remarkable disagreement with experiment. Analogous disagreement was observed by Hamada et al.[28] for this system when they used in their theory a combining rule analogous to eq 11; they observed that for PIB solutions the mean arithmetic combining rule ($2v_{12}^* = v_1^* - v_2^*$) gives much better results for the excess volumes. The calculated χ parameters with $\zeta_{12} = 0.9768$ are shown by curve 2 in Figure 5.

The ratio s_1/s_2 for this system was calculated to be equal to 1.03 by Hamada et al.[28] and to be equal to 1.72 by Eichinger and Flory.[36] The set of the parameters $\xi_{12} = 1.0187$, $s_1/s_2 = 1.03$, $\zeta_{12} = 0.9786$, and $q_{12} = -0.033$ reproduced the experimental values for ΔH_∞ and $\Delta V^M/V^\circ$, while the calculated χ parameters are shown by curve 3 in Figure 5.

It is worth observing the rather large value of ξ_{12} required to bring calculated volumes of mixing in agreement with experimental ones. Notice also that the value of v_{12}^* estimated by the combining rule of eq 11 with $\xi_{12} = 1.0$ is 12.26, while use of the mean arithmetic combining rule would give $v_{12}^* = 12.45$, a value that is close to the product $1.0187 \times 12.26 = 12.49$. Use of this latter combining rule would give $\Delta V^M/V^\circ = 0.0022$, much closer to the experimental value.

The second PIB–solvent system considered is **cyclohexane (1)–PIB (2)**. Excess volumes for this system were measured by Eichinger and Flory[36] at 25 °C. Delmas et al.[37] found for the same system $\Delta H_\infty = -0.61$ J g^{-1}. χ interaction parameters obtained from osmotic pressure measurements[39,40] at 30 °C and vapor sorption measurements[36] at 25 °C are shown in Figure 6.

Flory's one-parameter theory gave for this system[36] $\chi(\Phi_2 = 0) = 0.3$ and $\chi(\Phi_2 = 1) = 0.61$.

The third PIB–solvent system considered is ***n*-pentane (1)–PIB (2)**. Excess volumes for this system were measured by Baker et al.[41] at 25 °C. Delmas et al.[37] found for the same system $\Delta H_\infty = -3.6$ J g^{-1} at 25 °C. χ interaction parameters obtained from vapor sorption measurements[36,41] at 25 °C are shown in Figure 7.

Flory's one-parameter theory gave for this system[36] $\chi(\Phi_2$

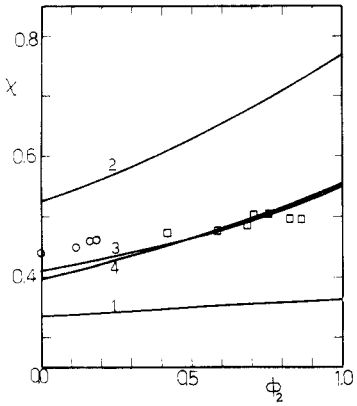

Figure 6. Comparison between experimental and calculated values of χ for the system cyclohexane (1)–PIB (2) at 25 °C. Squares and circles represent experimental results.[36,39,40] Curves 1, 2, and 3 were calculated by the Sanchez–Lacombe theory,[6] the present one-parameter model, and the present three-parameter model, respectively, using the binary parameters in Table I.

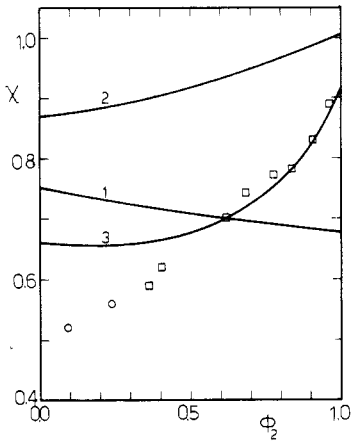

Figure 7. Comparison between experimental and calculated values of χ for the system *n*-pentane (1)–PIB (2) at 25 °C. Squares and circles represent experimental results.[36,41] Curves 1, 2, and 3 were calculated by the Sanchez–Lacombe theory,[6] the present one-parameter model, and the present three-parameter model, respectively, using the binary parameters in Table I.

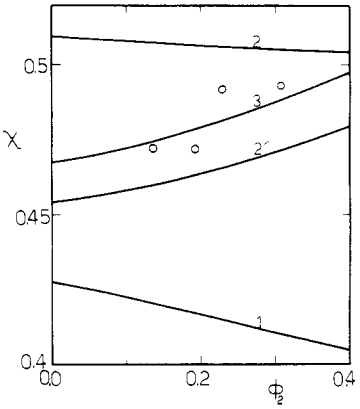

Figure 8. Comparison between experimental and calculated values of χ for the system *n*-octane (1)–PIB (2) at 25 °C. Circles represent experimental results.[42] Curves 1, 2, and 3 were calculated by the Sanchez–Lacombe theory,[6] the present one-parameter model, and the present three-parameter model, respectively, using the binary parameters in Table I. Curve 2′ was calculated by the present model with $\xi_{12} = 1.0$, $q_{12} = 0$, $s_1/s_2 = 1.47$, and $\zeta_{12} = 1.0429$.

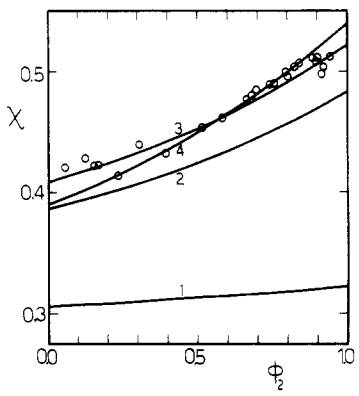

Figure 9. Comparison between experimental and calculated values of χ for the system benzene (1)–natural rubber (2) at 25 °C. Circles represent experimental results.[43] Curves 1 and 2 were calculated by the Sanchez–Lacombe theory[6] and the present one-parameter model, respectively. Curves 3 and 4 were calculated by the present three-parameter model with $s_1/s_2 = 1.0$ and $s_1/s_2 = 1.1$, respectively, using the binary parameters in Table I.

$= 0) = 0.66$ and $\chi(\Phi_2 = 1) = 0.94$.

The fourth PIB–solvent system considered is ***n*-octane (1)–PIB (2)**. Excess volumes for this system were measured by Flory et al.[42] at 25 °C. Delmas et al.[37] found for the same system $\Delta H_\infty = -0.61$ J g^{-1}. χ interaction parameters were also determined at 25 °C by Flory et al.[42] and are shown by circles in Figure 8.

Natural Rubber (NR) Solutions. NR solutions are another class of polymer solutions where an "entropic" correction Q_{12} to the binary parameter X_{12} in Flory's theory[4] is needed in order to reach agreement with experiment. In the present work we will consider only the system **benzene (1)–NR (2)**, for which experimental data for all basic thermodynamic quantities of mixing are available. Excess volumes for this system were measured by Eichinger and Flory[43] at 25 °C. The experimental value of ΔH_∞ for this system is[44] 5.7 J g^{-1}. χ interaction parameters determined from high-pressure osmometry and vapor sorption measurements[43] are shown in Figure 9.

Equation-of-state parameters for NR in the lattice–fluid theory obtained from *PVT* data by Eichinger and Flory[43] are $T^* = 595$ K, $P^* = 439$ mN/m^2, and $\rho^* = 982$ kg/m^3.

The binary parameter ζ_{12} in the Sanchez–Lacombe theory[6] obtained from the experimental ΔH_∞ is 0.9901. With this value for ζ_{12} the calculated χ parameters are shown by curve 1 in Figure 9. The calculated volume of mixing at $\Phi_2 = 0.5$ is $\Delta V^M/V^\circ = -0.0019$; the corresponding experimental value is 0.0009.

The binary parameter ζ_{12} is the simple version ($\xi_{12} = s_1/s_2 = 1.0$) of our model determined from the experimental ΔH_∞ is 0.9923. With this value for ζ_{12} the calculated χ parameters are shown by curve 2 in Figure 9 while the calculated volume of mixing at $\Phi_2 = 0.5$ is $\Delta V^M/V^\circ = -0.0027$. Calculated volumes of mixing by both the Sanchez–Lacombe theory[6] and the present simple model are in rather large disagreement with experiment. Agreement between calculated and experimental volumes of mixing can be reached by setting $\xi_{12} = 1.007$. In the case of the studied system, a simple replacement of eq 11 by the mean arithmetic combining rule (equivalent to setting $\xi_{12} = 1.0016$) would not improve significantly the situation. The set of parameters $s_1/s_2 = 1.0$, $\zeta_{12} = 0.9924$, $\xi_{12} = 1.007$, and $q_{12} = 0.0046$ reproduces the experimental values for ΔH_∞ and $\Delta V^M/V^\circ$, while the calculated χ interaction parameters are shown in Figure 9 by curve 3.

Although the one-parameter Flory theory[41] correlates satisfactorily the experimental volumes of mixing, it underestimates significantly the χ parameters in this system. Eichinger and Flory[43] found $\chi(\Phi_2 = 0) = 0.25$ and $\chi(\Phi_2 = 1) = 0.4$; consequently the required "entropic" correction in Flory's theory is significantly larger than the corresponding correction in our lattice–fluid model.

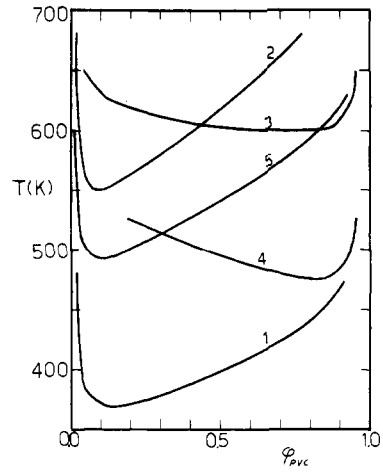

Figure 10. Simulated spinodals for PVC–PCL mixtures: curve 1, $\zeta_{12} = 1.0045$, $s_1/s_2 = 1.0$, $q_{12} = 0.0$; curve 2, $\zeta_{12} = 1.0073$, $s_1/s_2 = 1.0$, $q_{12} = 0.0$; curve 3, $\zeta_{12} = 1.0073$, $s_1/s_2 = 1.35$, $q_{12} = 0.0$; curve 4, $\zeta_{12} = 1.0073$, $s_1/s_2 = 1.40$, $q_{12} = 0.0$; curve 5, $\zeta_{12} = 1.0073$, $s_1/s_2 = 1.0$, $q_{12} = 0.001$.

Liquid–Liquid Equilibria. Critical Temperatures. Polymer solutions show a greater propensity for phase separation at higher temperatures (existence of lower critical solution temperatures (LCST)) than similar mixtures of low molecular weight liquids. Both upper critical solution temperatures (UCST) and LCST as well as the corresponding critical compositions depend on the molecular weight. Sanchez and Lacombe's discussion[6] on the impact to phase stability of the differences in equation-of-state characteristics of polymer and solvent molecules holds, of course, true for the present model as well.

Binodal curves in liquid–liquid equilibria may be calculated, as usual, by equating the chemical potentials for each of the components in the coexisting phases. The shape of binodal curves in polymer mixtures depends strongly on the molecular weight distribution. Since we have not considered molecular weight distributions in the present model, we may confine ourselves to those characteristics of liquid–liquid equilibria in polymer solutions which can be brought about by simple application of the spinodal inequality condition (eq 49).

In systems with a nonzero "entropic" correction term ($q_{12} \neq 0$), we must add to the left-hand side term in the spinodal inequality (49) the term

$$2q_{12}\frac{\vartheta_1\vartheta_2}{\varphi_1\varphi_2}\left(1 + \frac{\varphi_1 - \vartheta_1}{\varphi_2}\right)$$

As an example of polymer–polymer systems, we consider the mixture poly(vinyl chloride) (PVC) (1)–poly(ε-caprolactone) (PCL) (2), known to be compatible over the complete range of composition.[45] Phase separation characteristics of this system were also studied through the spinodal condition from Flory's theory[4] by Olabisi.[46] On the basis of his *PVT* data for both pure polymers, the lattice–fluid equation-of-state parameters are for PVC $T^* = 661$ K, $P^* = 754$ mN/m^2, and $\rho^* = 1485$ kg/m^3 and for PCL $T^* = 570$ K, $P^* = 500$ mN/m^2, and $\rho^* = 1189$ kg/m^3.

In Figure 10 are shown five spinodal curves calculated by the present model for the system PVC–PCL. The effect of the binary interaction parameter ζ_{12} on the simulation of phase separation behavior is most emphatically shown by comparing curves 1 and 2; an increase in ζ_{12} makes interchange energy parameter X_{12} more negative, thus favoring miscibility. The most interesting characteristic in Figure 10 is the effect of the surface to volume ratio s_1/s_2 on the shape of the spinodal curve. This is shown by comparing curves 2, 3, and 4 of the figure. At very low pressures the effect of increasing ξ_{12} on the shape of the spinodal curve is not significant except for a slight broadening of the complete immiscibility region. Comparison of curves 2 and 5 shows the effect of considering a nonzero "entropic" correction term ($q_{12} \neq 0$). These theoretical predictions cannot be tested experimentally due to thermal instability of PVC. Figure 10, however, may be used as a guide in phase separation simulation studies of other compatible polymer pairs.

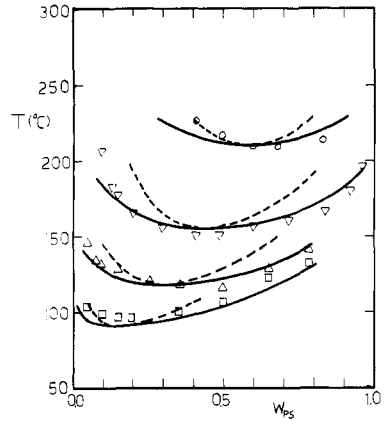

Figure 11. Phase diagrams for PS–PVME mixtures[47] where $\bar{M}_w$ for PVME is 51 500 and $\bar{M}_w$ for monodisperse PS is (○) 10 000, (▽) 20 400, (△) 51 000, and (□) 200 000. W_{PS} is the weight fraction of PS. Solid lines are calculated binodals while broken lines are the corresponding spinodals.

It would be certainly interesting to apply the present model to an actually observed demixing system. The overwhelming majority of real systems, however, consist of polydisperse polymers. Extension of the model to account for polymer polydispersity is postponed for a subsequent publication.

Our model, as developed here, might still be applied to a mixture of near-monodisperse polymers. Nishi and Kwei[47] have reported LCST-type phase diagrams for such systems, namely, mixtures of a poly(vinyl methyl ether) (PVME) sample of $\bar{M}_w = 51\,500$ with various near-monodisperse polystyrene (PS) samples.

PVT data for PVME are rather limited in the open literature.[48] On the basis of this limited information the estimated equation-of-state parameters for PVME are $T^* = 628$ K, $P^* = 418$ mN/m^2, and $\rho^* = 1117$ kg/m^3. The corresponding parameters for PS have been obtained from the literature.[6]

In Figure 11 are shown experimental data along with the predicted binodals and spinodals of the present model for the system PS–PVME. The simple version of our model ($\xi_{12} = s_1/s_2 = 1.0$, $q_{12} = 0$) has been used. The binary interaction parameter ζ_{12} has been adjusted to give an adequate description of the phase behavior for the system PS($\bar{M}_w = 51\,000$)–PVME; its value is $\zeta_{12} = 1.00466$. Calculated binodals and spinodals are very sensitive to the value of ζ_{12}; this is why we report its fifth decimal here.

As shown in Figure 11 the description of the phase behavior of this system by theory is essentially correct, albeit qualitative. The model predicts correctly the effect of molecular weight on the phase behavior of the system.

Conclusions

In this work we have presented an approximate thermodynamic theory of polymer solutions. It is based on Sanchez and Lacombe's lattice–fluid theory,[6] which is modified in the following respects: (a) The number of segments per molecule of a fluid is constant in both the pure state and solution. (b) A quadratic mixing rule is used

for the close-packed volume per segment in the mixture (eq 9) along with the classical combining rule (eq 11). (c) Molecular shape characteristics are taken into account through the use of the surface to volume ratio s_1/s_2. (d) An "entropic" correction of the interchange energy parameter X_{12} is introduced in analogy with the corresponding correction in Flory's equation-of-state theory.[4]

An extensive test of the theory has been done against experimental data for the basic thermodynamic quantities of mixing in a number of representative polymer–solvent systems. In parallel, the original Sanchez–Lacombe theory[6] and the simple version of our model[13] ($\xi_{12} = 1.0$, $s_1/s_2 = 1.0$) have been tested against the same set of experimental data. The systems considered (PDMS, PIB, and NR solutions) had been used previously for testing Flory's theory.[4] Some basic conclusions can then be drawn when the performances of all these models are compared. They are the following: (a) Acceptable correlation of all basic quantities of mixing by a one-parameter model of polymer solutions either in the cell approach[4] or in the lattice–fluid approach[6,13] is rather fortuitous; in general, three binary parameters are needed. (b) One convenient set of binary parameters is, ζ_{12} (or X_{12}), ξ_{12}, and q_{12} (or Q_{12}). The physical significance, however, of the parameter q_{12} (or Q_{12}) is not entirely clear.[17] (c) In both the cell and lattice–fluid treatments the proper combining rule for v_{12}^* seems to be dictated, to a great extent, by the nature of the polymer; thus, for PDMS solutions the combining rule of eq 11 is the proper one, while for PIB solutions the mean arithmetic combining rule ($2v_{12}^* = v_1^* + v_2^*$) seems to be superior. (d) The proper trend of χ parameters with composition (slope $d\chi/d\varphi_2$) in polymer solutions can be obtained by considering the surface to volume ratio s_1/s_2. Although the variation of the number of segments per molecule with composition in the original Sanchez–Lacombe theory[6] can be considered to take, to some extent, into account molecular shape characteristics in the mixture, the present work shows that this is insufficient and an explicit consideration of the ratio s_1/s_2 does improve the theory. The inadequacy of the original lattice–fluid theory to reproduce the experimental trend of χ with composition was considered by Sanchez and Lacombe[6] as "the most serious shortcoming of the lattice–fluid theory". (e) If allowance is made in the simple version of our model[13] for a choice of the proper combining rule for v_{12}^*, it appears at least equally if not more quantitative than the original Sanchez–Lacombe theory[6] and Flory one-parameter theory[4]. Notice, however, that the equation-of-state parameters in Flory's theory are temperature dependent, while in the lattice–fluid theory they are not. (f) The theory presented in this work (with ζ_{12}, ξ_{12}, and q_{12} parameters) and the extended Flory theory[17] (δ_{12}, ξ_{12}, and Q_{12} parameters) have many features in common and neither can be considered definitely superior to the other; both are equally good or equally poor models of polymer solutions. However, the fact that the lattice–fluid theory is applicable to both the gaseous and the liquid state is, in our opinion, a definite advantage of the lattice–fluid theory. (g) The incorporation of the ratio s_1/s_2 in the formalism of the lattice–fluid theory increases considerably its versatility in simulation studies of the phase separation behavior in mixtures.

As for future work, the lattice–fluid theory can be further improved in a number of ways. Correction for nonrandomness can be introduced in the way we described earlier.[49] Consideration of different interacting groups in the same molecule can be done in a way we also described earlier.[50] Improvement of the theory can also be done through improvement of the theory for pure fluids.[7,22] It is hoped that the present work will stimulate both experimental and theoretical work toward clarifying the relation between the nature of the polymers, the obstruction of chain irregularities for efficient packing, and the proper combining rule for v_{12}^* in polymer solutions.

Registry No. PS, 9003-53-6; PVME, 9003-09-2; PVC, 9002-86-2; PCL (SRU), 25248-42-4; PCL (homopolymer), 24980-41-4; PIB, 9003-27-4.

References and Notes

(1) Barker, J. A.; Henderson, D. *Rev. Mod. Phys.* **1976**, *48*, 587.
(2) Gray, C. G.; Gubbins, K. E. *Theory of Molecular Fluids*; Clarendon: Oxford, 1984; Vol. 1.
(3) Prigogine, I.; Trapeniers, N.; Mathot, V. *Discuss. Faraday Soc.* **1953**, *15*, 93.
(4) Flory, P. J. *Discuss. Faraday Soc.* **1970**, *7*, 49.
(5) Patterson, D.; Delmas, G. *Discuss. Faraday Soc.* **1970**, *7*, 98.
(6) Sanchez, I. C.; Lacombe, R. H. *Macromolecules* **1978**, *11*, 1145.
(7) Kleintjens, L. A. Ph.D. Thesis, University of Essex, 1979. Koningsveld, R.; Kleintjens, L. A.; Onclin, M. H. *J. Macromol. Sci., Phys.* **1980**, *18*, 363. Kleintjens, L. A.; Koningsveld, R. *Chemical Engineering at Supercritical Fluid Condition*; Paulaitis, M., Penninger, J. M. L., Gray, R. D., Davidson, P. Eds.; Ann Arbor Science Publishers: Ann Arbor, MI, 1983.
(8) Beret, S.; Prausnitz, J. M. *Macromolecules* **1975**, *8*, 878.
(9) Harmony, S. C.; Bonner, D. C.; Heichelheim, H. R. *AIChE J.* **1977**, *23*, 758.
(10) Schotte, W. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 289.
(11) Simha, R.; Somcynsky, T. *Macromolecules* **1969**, *2*, 342.
(12) Nose, T. *Polym. J. (Tokyo)* **1971**, *2*, 124.
(13) Panayiotou, C. *Makromol. Chem.* **1986**, *187*, 2867.
(14) Gibbs, J. H.; DiMarzio, E. A. *J. Chem. Phys.* **1958**, *28*, 373.
(15) Panayiotou, C.; Vera, J. H. *J. Polym. Sci. Polym. Lett. Ed.* **1984**, *22*, 601.
(16) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80*, 2352.
(17) Panayiotou, C. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 1435.
(18) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953. Tompa, H. *Polymer Solutions*; Butterworths: London, 1956.
(19) Lacombe, R. H.; Sanchez, I. C. *J. Phys. Chem.* **1976**, *80*, 2568.
(20) Panayiotou, C. *Polym. Eng. Sci.* **1984**, *24*, 1219.
(21) Staverman, A. J. *Recl. Trav. Chim. Pays-Bas* **1937**, *56*, 885.
(22) Panayiotou, C.; Vera, J. H. *Polym. Eng. Sci.* **1982**, *22*, 345.
(23) Flory, P. J.; Shih, H. *Macromolecules* **1972**, *5*, 761.
(24) Chahal, R.; Kao, W.; Patterson, D. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1834.
(25) Sugamiya, K.; Kuwahara, N.; Kaneko, M. *Macromolecules* **1974**, *7*, 66.
(26) Lichtenthaler, R. N.; Liu, D. D.; Prausnitz, J. M. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 470.
(27) Sugamiya, K. *Makromol. Chem.* **1977**, *178*, 565.
(28) Hamada, F.; Shiomi, T.; Fujisawa, K.; Nakajima, A. *Macromolecules* **1980**, *13*, 729.
(29) Canovas, A.; Rubio, R. G.; Renuncio, J. A. R *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 783; **1983**, *21*, 841.
(30) Delmas, G.; Patterson, D.; Bhattacharyya, S. N. *J. Phys. Chem.* **1964**, *68*, 1468.
(31) Morimoto, S. *Makromol. Chem.* **1970**, *133*, 197.
(32) Summers, W. R.; Tewari, Y. B.; Schreiber, H. P. *Macromolecules* **1972**, *5*, 12.
(33) Kuwahara, N.; Okazawa, T.; Kaneko, M. *J. Polym. Sci., Part C* **1968**, *25*, 543.
(34) Brotzman, R. W.; Eichinger, B. E. *Macromolecules* **1982**, *15*, 531; **1983**, *16*, 1131.
(35) Shiomi, T.; Izumi, Z.; Hamada, F.; Nakajima, A. *Macromolecules* **1980**, *13*, 1149.
(36) Eichinger, B. E.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *64*, 2053, 2061, 2066.
(37) Delmas, G.; Patterson, D.; Somcynsky, T. *J. Polym. Sci.* **1962**, *57*, 59.
(38) Cuniberti, C.; Bianchi, U. *Polymer* **1966**, *7*, 151.
(39) Krigbaum, W. R.; Flory, P. J. *J. Am. Chem. Soc.* **1953**, *75*, 1775.
(40) Flory, P. J.; Daoust, H. *J. Polym. Sci.* **1957**, *25*, 429.
(41) Baker, C. H.; Brown, W. B.; Gee, G.; Rowlinson, J. S.; Stubley, D.; Yeadon, R. E. *Polymer* **1962**, *3*, 215.
(42) Flory, P. J.; Ellenson, J. L.; Eichinger, B. E. *Macromolecules* **1968**, *1*, 287.
(43) Eichinger, B. E.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *64*, 2035.
(44) Hock, L.; Schmidt, H. *Rubber Chem. Technol.* **1934**, *7*, 462.

(45) Olabisi, O.; Robeson, L.; Shaw, M. *Polymer–Polymer Miscibility*; Academic: New York, 1979.
(46) Olabibi, O. *Macromolecules* **1975**, *8*, 316.
(47) Nishi, T.; Kwei, T. K. *Polymer* **1975**, *16*, 285.
(48) Shiomi, T.; Kohno, K.; Yoneda, K.; Tomita, T.; Miya, M.; Imai, K. *Macromolecules* **1985**, *18*, 414. Robard, A. Ph.D. Thesis, McGill University, 1979.
(49) Panayiotou, C.; Vera, J. H. *Fluid Phase Equil.* **1980**, *5*, 55. Panayiotou, C.; Vera, J. H. *Polym. J. (Tokyo)* **1982**, *14*, 681.
(50) Panayiotou, C.; Vera, J. H. *Can. J. Chem. Eng.* **1981**, *59*, 501.

Static and Dynamic Solution Properties of Poly(1,4-benzamide) in Dimethylacetamide with 3% (g/mL) LiCl

Qicong Ying† and Benjamin Chu*†‡

Department of Chemistry and Department of Materials Science and Engineering, State University of New York at Stony Brook, Long Island, New York, 11794-3400.
Received August 20, 1986

ABSTRACT: Laser light scattering was used to determine static and dynamic solution properties of five poly(1,4-benzamide) (PBA) samples in dimethylacetamide (DMAC) with 3% (g/mL) LiCl. The results show $\bar{D}^{\circ}_z = 1.24 \times 10^{-3} M_w^{-0.89}$ cm^2/s with M_w expressed in units of grams per mole and a persistence length ρ of 75 ± 3 nm. As the α_D (=0.89) value and the persistence length for PBA in DMAC with 3% (g/mL) LiCl are greater than those for poly(1,4-phenyleneterephthalamide) (PPTA) in concentrated sulfuric acid, PBA in DMAC/LiCl has stiffer chains than PPTA in concentrated sulfuric acid. Concentration and angular dependence of mean line widths as well as molecular weight distributions derived by using different methods of data analysis are presented.

Introduction

Dynamic light scattering in combination with static light scattering intensity measurements has been used successfully to determine both the static and dynamic properties of wormlike macromolecules in solution, such as poly(1,4-phenyleneterephthalamide) (PPTA) in concentrated sulfuric acid.[1-3] Poly(1,4-benzamide) (PBA) is another important aromatic polyamide polymer material that yields high-thermal-stability, high-modulus, and high-tensile-strength fibers from solution spinning of anisotropic dopes. PPTA and PBA have similar chemical chain structure, the only difference being the incorporation into the chain of all amide groups in the "head to tail" order for PBA and in the alternating order for PPTA. Thus, the rigidity of the PBA molecular chain greatly exceeds that of PPTA.[4] The static and dynamic solution properties of these two polymers can also be expected to be somewhat different. We have published static and dynamic light scattering characterization of PPTA in 96 wt % sulfuric acid.[2,3] The present work reports recent experimental results on static and dynamic solution properties of PBA in dimethylacetamide (DMAC) with 3% (g/mL) LiCl.

Experimental Section

1. Materials. Five different molecular weight poly(1,4-benzamide) samples were kindly provided by Professor J. Wang of the Shanghai Institute of Resins in Shanghai, China.

The solvent mixture was prepared by dissolving 3% (g/mL) LiCl, which was dried at 450 °C for 3 h, in *N,N*-dimethylacetamide (DMAC) (certified reagent ACS, Fisher Scientific Co.) and kept in a drybox before use.

Solutions at different concentrations were prepared by dilution. The stock solution was made by dissolving 0.13 g of PBA in 10 mL of filtered DMAC/LiCl solvent mixture. The middle portion of each centrifuged solution (after 2 h of centrifugation at 1 × 10^4 gravity) was transferred to a screw-capped (with Teflon packing inside) 16-mm-o.d. light scattering cell and stored in a drybox except during light scattering experiments. All measurements were completed within a few days after preparation of solution, but for sample 4 (see Table I) light scattering measurements were performed periodically over about a 1-mo. period in order to check the solution stability.

The condition for centrifugation was further tested by making light scattering measurements at upper and lower portions of a PBA solution after 6 h of centrifugation at 3 × 10^4 gravity. The agreement signified that PBA was not fractionated by centrifugation, yet our procedure was sufficient to eliminate most of the dust particles in solution.

2. Methods of Measurement. The refractive index n and the refractive index increment (dn/dc) of the DMAC/LiCl solvent mixture were determined at 30 °C by using a Brice-Phoenix differential refractometer. For the measurement of n of the solvent mixture, we used chloroform (n = 1.4446 at λ_0 = 546 nm, 25 °C) as a reference standard. At 30 °C and λ_0 = 514.5 nm, the values of n and $(\partial n/\partial C)_T$ for the solvent mixture are 1.4491 and 0.3426 mL/g, respectively.

The viscosity η_0 of the DMAC/LiCl solvent mixture was determined at 30 °C by using a Ubbelohde viscometer with cyclohexane as a reference standard

$$\eta_0/d = Ft - (B/t) \quad (1)$$

where d is the density, F is an instrument constant, and B is related to the kinetic energy term. When the flow time t is long enough (usually $t > 120$ s), the B/t term in comparison with Ft is negligibly small. At 30 °C the values of η_0 and d for the solvent mixture are 1.354 cP and 0.9596 (g/mL), respectively. The DMAC/LiCl (3% g/mL) solvent showed no absorption peak in the wavelength range between 600 and 400 nm.

The light scattering apparatus has been described elsewhere.[6] We used a Lexel Model 95 argon ion laser operating, nominally, at ~250 mW. All light scattering measurements were performed by using λ_0 = 514.5 nm. Intensity measurements were accumulated automatically every 4.5° between 18° and 135° scattering angles (θ).

Correlation function measurements were made by using a 128-channel Brookhaven Model BI-2030 digital correlator. Only those time correlation function measurements whose base-line difference between calculated and measured values was less than 0.1% were accepted. A few low-angle (18°–24°) data that showed a base-line difference of around 0.2% were also analyzed. Correlation function data were accumulated every 6° between θ = 18° and 60° and every 15° between 60° and 120°. The light

* Author to whom correspondence should be addressed. Send to Chemistry Department address.
† Department of Chemistry.
‡ Department of Materials Science and Engineering.

0024-9297/87/2220-0871$01.50/0