Blend Miscibility and the Flory−Huggins Interaction Parameter: A Critical Examination

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ABSTRACT: The Flory−Huggins interaction parameter, χ, is often used in the literature to describe the binary interactions of polymer blends, yet to what extent does this widespread analysis yield valuable thermodynamic insight? In this work we think critically about χ and creatively about alternatives. Making use of a simple lattice theory to model binary polymer mixtures, we follow a different, less ambiguous route and show connections between the microscopic characteristic parameters of a system and its macroscopic thermodynamic behavior. To this end we analyze experimental data, including results from neutron scattering experiments, cloud point curves, and pressure−volume−temperature (*PVT*) surfaces for a series of blends, including deuterated polystyrene/poly(tetramethyl bisphenol A polycarbonate) (dPS/TMPC), deuterated polystyrene/poly(vinyl methyl ether) (dPS/PVME), polystyrene/polybutadiene (PS/PB), deuterated polystyrene/poly(*p*-methylstyrene) (dPS/PpMS), polypropylene/deuterated head-to-head polypropylene (PP/dhhPP), polystyrene/deuterated polystyrene (PS/dPS), polystyrene/polychlorostyrene (PS/PCS), deuterated poly(methylbutylene)/poly(ethylbutylene) (dPMB/PEB), and poly(ethylmethylsiloxane)/deuterated poly(dimethylsiloxane) (PEMS/dPDMS). We conclude by suggesting that there is a temperature- and concentration-independent parameter which may prove to be a more characteristic indicator of blend behavior than χ.

1. Introduction

The Flory−Huggins binary polymer−polymer interaction parameter, or χ, can be obtained from several experimental methods such as analyses of melting-point depressions,[1,2] heats of mixing,[3,4] cloud points,[5,6] comparisons of solubility parameters,[7] light scattering data,[8] osmotic pressures,[9] recoil spectrometry calculations,[10,11] and inverse gas chromatography measurements.[12−14] One disadvantage of so many methodologies is that the χ parameters determined using two different techniques will often demonstrate significant inconsistencies. For example, diffusion experiments produce χ parameters for a polystyrene/tetramethylbisphenol A polycarbonate system that are an order of magnitude smaller than those determined from small-angle neutron scattering (SANS) experiments.[15] In recent work the focus has been on using SANS data,[15−21] although Flory−Huggins interaction parameters determined by this route typically exhibit composition dependence whose source is not well understood.[1] Adding to the confusion, as Sanchez[1] and others have noted, χ may be derived from the free energy, its first derivative, or its second derivative with respect to composition, with varying results depending on which definition is implemented. This ambiguity has served to diminish the utility of χ as a means of providing insight into blend behavior.

The temperature dependence of the χ interaction parameter provides insight into blend thermodynamics and has usually been described (empirically) by[22]

$$\chi = a + \frac{b}{T} \tag{1}$$

where the constant a represents an entropic contribution to χ and b the enthalpic contribution. For most systems, both a and b depend on the blend composition. A positive value for the constant b is associated with the mixture exhibiting an upper critical solution temperature (UCST), while a negative b corresponds to lower critical solution temperature (LCST) behavior. Although eq 1 has proven useful, it is important to note that more complex relationships may occur. For example, χ may show a parabolic dependence on T, reflecting the simultaneous existence of both a UCST and an LCST.[23]

Comparing χ parameters of different blends is not as useful as one might hope, as specific values of the parameters do not appear to allow definitive conclusions regarding miscibility or critical behavior. In the Discussion section of this paper we report on results for polymer blends that exhibit very comparable critical behavior (and more fundamental similarities, such as similar repeat unit structures) yet show large discrepancies in their respective χ parameters. Alternatively, we also discuss mixtures that exhibit nearly identical χ values but at the same time have different critical temperatures and opposite phase separation behavior. Along with the χ analysis we present a theoretical approach to quantifying the binary interactions of polymeric systems using the Born−Green−Yvon (or BGY) lattice theory.[24−26] This approach combines the simplicity of a lattice model with the sophistication of a description that includes, naturally in its derivation, the effects of compressibility as well as nonrandom mixing. With respect to the latter, in particular, it differs from some of the commonly used theories, for example the lattice fluid (LF) model.[27] In this work we demonstrate the applicability of the BGY lattice theory by using it to think critically about effective routes to predictions about mixture behavior. As part of this process we calculate χ values for a variety of blends as a function of temperature, pressure, and composition and compare with experimental results. It is worth emphasizing that our route to χ matches that followed in

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Table 1. Characteristic Parameters for Several Partially Miscible Blends

blend	ϵ_{11}	ϵ_{22}	r_1	r_2	v	g	MW ratio	χ exp data source	BGY exp data source
dPS/TMPC	−2105.5	−2209.5	21444.39	4390.80	0.009900	1.00028	253000/42000	SANS[15]	SANS[29]
dPS/PVME	−2251.1	−2000.9	35860.17	19701.18	0.009500	1.00230	402000/210000	SANS[16]	SANS[16]
PS/PB	−2062.0	−1988.3	115.57	272.52	0.009007	0.99520	1200/2350	cloud point[5]	*PVT*[28] and T_c[5]
dPS/PpMS	−2251.1	−2282.6	2916.98	5751.10	0.009021	0.99978	32700/58000	SANS[17]	SANS[16] and *PVT*[28]
PP/dhhPP	−2040.7	−2027.8	2859.13	7052.10	0.013000	0.99985	85890/29610	SANS[18]	*PVT*[25] and T_c[25]
PS/dPS	−2228.2	−2251.1	11158.99	8626.06	0.009500	0.99920	119770/96700	SANS[19]	SANS[16] and *PVT*[28]
PEMS/dPDMS	−1744.2	−1808.2	1984.67	2655.48	0.012445	0.99981	26280/34680	SANS[21]	*PVT*[28] and T_c[21]
dPMB/PEB	−2285.9	−2239.6	17955.64	4485.03	0.011079	0.99950	180000/48000	SANS[20]	*PVT*[28] and ΔV_{mix}[20]
PS/PCS	−2228.2	−2409.5	8017.99	7439.87	0.009333	1.00241	90000/918000	cloud point[36]	*PVT*[28] and T_c[36]

analyzing SANS data, and that our results are *predictions* for χ. Values for the characteristic parameters of both pure components and the mixture, which are needed for the predictions, are obtained by analyzing a variety of other data, described below, *not including* χ *data*. In presenting an alternate means of representing the binary interactions of polymer blends, we hope to develop a route that may be used to gain immediate insight into blend behavior.

In section 2 we provide a brief experimental and theoretical background. In section 3 we compare our theoretical determinations with experimental results for a diverse series of polymer blends: deuterated polystyrene/poly(tetramethyl bisphenol A polycarbonate) (dPS/TMPC), deuterated polystyrene/poly(vinyl methyl ether) (dPS/PVME), polystyrene/polybutadiene (PS/PB), deuterated polystyrene/poly(*p*-methylstyrene) (dPS/PpMS), polypropylene/deuterated head-to-head polypropylene (PP/dhhPP), polystyrene/deuterated polystyrene (PS/dPS), polystyrene/polychlorostyrene (PS/PCS), and deuterated poly(methylbutylene)/poly(ethylbutylene) (dPMB/PEB). In addition, the effects of pressure will be studied using the blends polyethylmethylsiloxane/deuterated poly(dimethylsiloxane) (PEMS/dPDMS) and dPMB/PEB. The trends and inconsistencies in the χ parameter analysis will be discussed in section 4, and in section 5 we summarize our results and draw conclusions.

2. Experimental and Theoretical Background

Experimental Data. All of the experimental χ results, as well as the data used in the BGY prediction of χ parameters, were obtained from the literature. Procedural details concerning the recorded measurements for the different blends may be found in the references given in Table 1, the text, and the figure captions. With the exceptions of PS/PB and PS/PCS (both determined from cloud point examinations), all experimental χ results from the literature were obtained using small-angle neutron scattering (SANS) measurements. Additional literature SANS data (usually given as zero angle scattering intensities) have been used to generate BGY parameters. *PVT* data used to generate sets of BGY characteristic parameters are from the Zoller and Walsh compendium.[28] Those data, recorded as specific volume as a function of temperature at a series of fixed pressures, are reported to an accuracy of 0.002 cm^3/g (specific volume), ±0.1 K (temperature), and 0.1 MPa (pressure).

The following procedural description will serve as an example of small-angle neutron scattering experiments, as neutron scattering intensities were used to generate the BGY parameters which characterize both the dPS/PVME and dPS/TMPC blends. This summary outlines the experimental routine followed when using the PAXE spectrometer located in Saclay, France.[29,30] Neutron scattering data were recorded for dPS/PVME samples, first equilibrated at the measurement temperature, in a q range of 0.008−0.078 $Å^{-1}$. The mean incident wavelengths for all measurements were 6 Å, and the sample−detector distance was maintained at a constant 5 m. The samples were prepared from solutions in toluene at 10% w/v and cast on glass as thin films. They were then dried under vacuum for 4 weeks at steadily increasing temperatures until reaching a temperature of 20 K over the glass transition temperature (T_g). A stack of 10 samples was wrapped in aluminum foil so as to have a thickness of 1 mm. Careful attention was paid to removing the background scattering and to normalize measured scattering intensities to an absolute scale. The normalized scattering intensities from these samples were typically plotted as inverse scattering intensity, $I(q)^{-1}$, against wave vector, q, extrapolated to $q = 0$ in order to provide values for the second derivative of the free energy of mixing.

The critical temperature of the PS/PB mixture was used to determine the blend's mixed interaction energy. The critical data were measured as a function of pressure at Imperial College in London, where an apparatus was used to determine the blend's phase behavior at temperatures up to slightly over 430 K.[5] The experiment utilized a sample holder mounted onto a platform that allowed for control over the sample's positioning. The sample vessel was a Pyrex tube, placed inverted in a thermostatic mercury bath, and fit with controlled heating/cooling and stirring devices. Magnetic stirring was used to ensure homogeneous mixing. A sapphire window allowed easy viewing of the sample, which was particularly useful as the cloud point was determined visually. The sample was heated at a constant rate of 1 K/h. The phase separation temperatures were recorded with an accuracy of ±0.1 K, while the cloud point was reported to be accurate within ±0.5 K. The cloud point curves were determined for a pressure range of 0.1−100 MPa with a recorded accuracy of ±0.1 MPa.

Theory. The BGY lattice theory for compressible fluids was developed by Lipson and co-workers and has previously been applied to pure fluids and mixtures of both *n*-alkanes and polymers as well as *n*-alkane/polymer solutions.[24,26] This theoretical approach yields analytic expressions for the free energy of mixing and its derivatives which allows for calculation of the thermodynamic properties of a system consisting of an arbitrary number of components, although thus far the applications have been limited to compressible pure fluids and binary mixtures. In this work we have generated sets of characteristic parameters for a series of polymer blends using pure fluid and binary blend pressure−volume−temperature (*PVT*) data, SANS results, and cloud point curves. We have then used these parameters in calculating χ values for comparison with experimental results. The characteristic parameters include the pure and mixed interaction energies (ϵ_{ii}, ϵ_{ij}), the number of segments in a polymer chain (r), and the volume per mole of lattice sites (v). Trends in these parameters have lead us to observations regarding correlations between component properties and mixture phase behavior with the ulterior motive of providing a simple alternative to χ.

The BGY theory uses a simple cubic lattice with a coordination number of $z = 6$ for all calculations. The total volume of the lattice is given by V, where $V = \upsilon(N_0/N_A)$, υ is the volume per mole of lattice sites, N_0 is the total number of lattice sites, and N_A is Avogadro's number. The parameter r_i accounts for the number of contiguous lattice sites occupied by a single molecule of species i. For a binary mixture (where i may be either 1 or 2) the site fractions are defined as $\phi_i = r_i N_i/N_0$, $\phi_h = N_h/N_0$, and $\phi = 1 - \phi_h$. Here, N_i is the total number of molecules of component i and N_h is the number of holes or unoccupied lattice sites. The product $r_i z$ is the maximum number of interactions possible for r_i separated segments; however, the number of interactions available to a molecule occupying r_i *contiguous* lattice sites is given by the quantity $q_i z = r_i(z - 2) + 2$. This relationship, introduced by Guggenheim,[31] leads to the definition of the concentration variables $\xi_i = q_i N_i/(N_h + \sum_j q_j N_j)$ and $\xi_h = N_h/(N_h + \sum_j q_j N_j)$, which reflect the molecule's nearest-neighbor connectivity. The interaction energy of nonbonded nearest neighbors of the same species is characterized by a temperature-independent energy of magnitude ϵ_{ii}, while unlike nearest-neighbor interactions are characterized by ϵ_{ij}. Both the blend *PVT* and neutron scattering routes yield the mixed segment interaction energy as a result of a single fit to mixture data; however, the third route, which makes use of pure fluid *PVT* data, requires that the theoretically calculated critical temperature (that is, the temperature at which the mixture phase separates) be "pinned" to the experimental datum point in order to determine ϵ_{ij}.

As a detailed description of the theoretical approach is available in the literature;[24,25] here we will briefly outline the premise, give the main results, and then discuss the BGY methodology for calculating the χ parameter. The BGY integral equation hierarchy links distribution functions (pair to triplet, for example) and in this work is closed off at the level of the pair interactions using the Kirkwood superposition approximation. All segment pairs except for the pair of interest are then assumed to act independently. The results for the remaining pair probabilities represent the probability of having different types of nearest-neighbor interactions.[31] The summation of the product of the probabilities multiplied by the associated energetic contribution produces an expression for the internal energy of the blend that is a function of both temperature and composition, if the system consists of more than one component. Lattice sites may be occupied by segments of either component or of vacancies. Therefore, the system is compressible at finite (experimental) pressures; an additional implication is that each of the interaction energies contributes to the blend's total internal energy, not just a simple combination as in incompressible Flory−Huggins theory. The free energy of the mixture is obtained from the temperature-dependent internal energy through the Gibbs−Helmholtz relationship; for the purposes of integration, it is assumed that at infinite temperature the system is randomly mixed (as described by Guggenheim[32]). We emphasize that at finite temperatures there are important nonrandom contributions to the entropy of the mixture which arise naturally from the integration. The BGY expression for the dimensionless configurational Helmholtz free energy, $\hat{a}$, of a K-component blend on a lattice is given by[24]

$$\hat{a} = \sum_{i=h,1}^{K}\left(\frac{\phi_i}{r_i}\ln\phi_i + \frac{q_i z\phi_i}{2r_i}\left\{\ln\left[\frac{\xi_i}{\phi_i}\right] - \ln[\xi_h + \sum_{j=1}^{K}\xi_j \exp(-\beta\epsilon_{ij})]\right\}\right) \quad (2)$$

where $\beta = 1/(k_B T)$, k_B is Boltzmann's constant, and T is the temperature. The Helmholtz free energy density, A/VT, is given by

$$A/VT = k_B\hat{a}/\upsilon + a_0 \quad (3)$$

where a_0 is a caloric background that is not required for this work. The blend's thermodynamic properties may be calculated using the following derivative of the Helmholtz free energy density:

$$\mathrm{d}(A/VT) = \frac{U}{V}\mathrm{d}(1/T) + \sum_{j=1}^{K}\frac{\mu_j}{T}\mathrm{d}(\rho_j) \quad (4)$$

where U is the internal energy of the system, ρ_j is the number density of component i, and μ_j is the chemical potential of component i. The chemical potential of species i is given by

$$\mu_i = \frac{r_i}{\beta}\left(\frac{\partial\hat{a}}{\partial\phi_i}\right)_{\beta,\varphi_{k\neq i}} \quad (5)$$

Phase transitions for binary mixtures are usually represented in terms of the molar density ($\rho = \rho_1 + \rho_2$) and mole fraction ($x = \rho_2/\rho$). Conjugate to the mole fraction is the difference between the chemical potential of each component, where $\mu = \mu_2 - \mu_1$. These terms allow for the critical line for the blend to be expressed as

$$\left(\frac{\partial\mu}{\partial x}\right)_{T,P} = 0, \quad \left(\frac{\partial^2\mu}{\partial x^2}\right)_{T,P} = 0 \quad (6)$$

where the initial term defines the spinodal line and the second equation defines a critical point as an extremum of the spinodal. The lower critical solution temperature, or LCST, represents the minimum of the spinodal, and conversely, the upper critical solution temperature (UCST) denotes the maximum. Therefore, at pressure P, the coexisting phases satisfy the following two expressions: $\mu(T,P,x_1) = \mu(T,P,x_2)$ and $\mu_1(T,P,x_1) = \mu_1(T,P,x_2)$.

For a pure, compressible fluid the BGY equation of state is

$$P = -\frac{1}{\beta\upsilon}\left\{\ln\phi_h + \frac{z}{2}\ln\left(\frac{\xi_h}{\phi_h}\right) + \phi\left(1 - \frac{1}{r}\right) + \frac{z\phi}{2}\left(\frac{q}{r} - 1\right) + \frac{z\xi^2}{2}\left[\frac{\exp(-\beta\epsilon) - 1}{\xi\exp(-\beta\epsilon) + \xi_h}\right]\right\} \quad (7)$$

The equation may be fit to experimental pressure−volume−temperature (*PVT*) data, producing values for the BGY characteristic parameters r, υ, and ϵ for either pure fluids or mixtures. The mixed interaction energy, given by ϵ_{12}, may be estimated using one of several routes. In a few cases (e.g., mixtures of *n*-alkanes or solutions of polyethylene in *n*-alkanes) a satisfactory result may be obtained using the Lorentz−Berthelot mixing, or geometric mean, approximation, but most mixtures require a slight modification to the geometric mean. This modification is given by the following expression

$$\epsilon_{12} = g(\epsilon_{11}\epsilon_{22})^{1/2} \quad (8)$$

where g is a fit parameter describing the nature of the mixed interactions in terms of their deviation from the geometric mean. A single value, independent of temperature and composition, quantifies the mixed interactions of the system of interest. For blends in which the pure component parameters are already known, the g factor is determined by modifying its value so that BGY calculations of the critical temperature of the mixture

equal the results measured experimentally, in essence "pinning" the calculated coexistence curve to the correct critical temperature. Alternatively, g may be determined by analyzing blend data, such as blend *PVT* surfaces, or neutron scattering intensities. By analyzing these types of data, parameters characterizing both pure components and the mixture are obtained from a single fit. A more detailed explanation is available in the literature.[26]

The Flory−Huggins Interaction Parameter. The Flory−Huggins χ parameter was originally defined in terms of the difference between the mixed interaction energies (ϵ_{ij}^*) and the sum of the pure component energies (ϵ_{ii}^*,ϵ_{jj}^*)[33]

$$\chi_{ij} = (\epsilon_{ii}^* + \epsilon_{jj}^* - 2\epsilon_{ij}^*)/kT \tag{9}$$

This was then related to the enthalpy of mixing (ΔH_{mix}) as

$$\Delta H_{\mathrm{mix}} = \chi k_{\mathrm{B}} T \phi_1 \phi_2 \tag{10}$$

The free energy of mixing (ΔG_{mix}) was then obtained by adding an entropic contribution from random mixing of the components[34]

$$\frac{\Delta G_{\mathrm{mix}}}{kT} = \chi \phi_1 \phi_2 + \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 \tag{11}$$

If the mixture is not ideal, there will be additional contributions, not accounted for in this theory, to both the enthalpy and entropy of mixing (ΔS_{mix}). Thus, according to eq 10 for real mixtures the χ parameter incorporates all contributions to the free energy of mixing, *except* for the combinatorial entropy of mixing. Note that that since the volume fraction will always be less than one, the combinatorial entropy of mixing will always be positive. For small molecule mixtures the magnitude of ΔS_{mix} is typically large, which means that the free energy of mixing may be negative even if the enthalpy change of mixing is very unfavorable (i.e., large and positive). However, in polymeric mixtures ΔS_{mix} is very small due to the large configurational entropy of the pure components. This means that if the enthalpy of mixing is unfavorable, it must be very small if the mixture is to be even partially miscible. In fact, it is found experimentally that both small positive and small negative values of the χ parameter[35] are associated with partial miscibility. Typical "small" values for χ are on the order of $\sim 10^{-3}$.[33]

In applying the BGY theory to the calculation of χ, we make use of eq 11, rearranged and with r's substituted for N's to give

$$\chi = \frac{\Delta G_{\mathrm{mix}}}{\phi_1 \phi_2 kT} - \frac{\ln \phi_1}{\phi_2 r_1} - \frac{\ln \phi_2}{\phi_1 r_2} \tag{12}$$

Alternatively, the χ interaction parameter can also be calculated using the second derivative of the free energy of mixing with respect to composition, via the following:[27]

$$\chi = \frac{1}{kT} \frac{\partial^2 \Delta G_{\mathrm{mix}}}{\partial \phi_1^{\,2}} - \frac{1}{\phi_1 r_1} - \frac{1}{\phi_2 r_2} \tag{13}$$

As noted by Sanchez, the extent to which the two expressions differ is a reflection of the concentration dependence of χ.[1] We found the results obtained using the different routes to be the same within experimental error. For example, for dPS/PVME at 383 K the value obtained using eq 12 was -1.455×10^{-2} and using eq 13 was -1.458×10^{-2}.

3. Analysis of Experimental Data

Characteristic Parameters. In previous work we have shown that the BGY theory accurately models the pressure−volume−temperature behavior of both pure fluids and mixtures as well as the effects of temperature on the scattering intensities of deuterated polymer blends, which means that these kinds of data may be used to determine an optimized set of characteristic parameters. In this paper we will use parameters so derived, along with eqs 12 or 13, to calculate χ values as a function of temperature, composition, and pressure (where appropriate) and then compare our results with experimentally determined χ values. In doing so, we emphasize the essential point that the characteristic parameters obtained through the BGY analysis are *transferable*, in the sense that they are useful in making predictions about behavior beyond that which has been fit. We believe that demonstrating that there is good agreement between the BGY results for χ and the experimental values provides credibility for the discussion which follows, in which we take a critical look at the utility of χ in predicting, or even explaining, blend behavior.

Table 1 contains details concerning the BGY characteristic parameters used to calculate χ parameters for a series LCST and UCST blends. The two rightmost columns indicate the type of data used to determine both the experimental χ results and the BGY characteristic parameters. For example, the experimental measurement of the χ parameter for PS/PCS was determined by a visual estimation of the cloud point of the blend, while the BGY parameters were obtained by fitting to pure fluid *PVT* data (to produce the pure component parameters) and the critical temperature (to obtain a value for g, which characterizes the mixed interaction energy). The BGY parameters make use of eq 12 to calculate χ values that are compared to the experimental results of ref 36. The r parameter values given in Table 1 are associated with the molecular weights (MW) listed; however, the experimental χ values are usually associated with MWs which are different than those used in the data analyzed to obtain the characteristic parameters. To account for molecular weight differences, the r parameter is rescaled according to the relationship $r_{\mathrm{new}} = r_{\mathrm{old}}(\mathrm{MW_{new}}/\mathrm{MW_{old}})$; our experience with a variety of polymers having a array of molecular weight indicates that at this level of rescaling the other characteristic parameters are not expected to change. To avoid a mixture lattice with composition-dependent site volumes, a single v value is used to describe both pure components and the mixture. Several methods for determining the blend v exist: choosing a "reasonable" value, using the arithmetic average of the two pure component values (which range between 0.0077 and 0.0130 L/mol), or selecting the v value of either pure component. For the results shown here, we use the arithmetic average. After the v value is specified, the r parameter is then rescaled so as to maintain a constant hard-core volume, given by the product of r and v.

The description above includes a route to the mixed interaction through knowledge of the blends' critical temperatures; in essence, the coexistence curve is "pinned" to the critical temperature (the rest of the coexistence curve in its entirety, including the critical composition would therefore constitute a BGY prediction). Other routes to g are via fits of SANS data and of mixture *PVT* surfaces.

Comparison of Calculated χ Values with Experiment. In Figure 1 BGY calculations (lines) for χ as a function of temperature for three LCST mixtures are compared with experimental results (symbols). From left to right, the lines are associated with the blends dPS/TMPC, PS/PCS, and dPS/PVME. The experimental measurements were all recorded at a pressure of 0.1 MPa. Only a single datum point was available for the dPS/TMPC mixture, and the BGY calculation at that

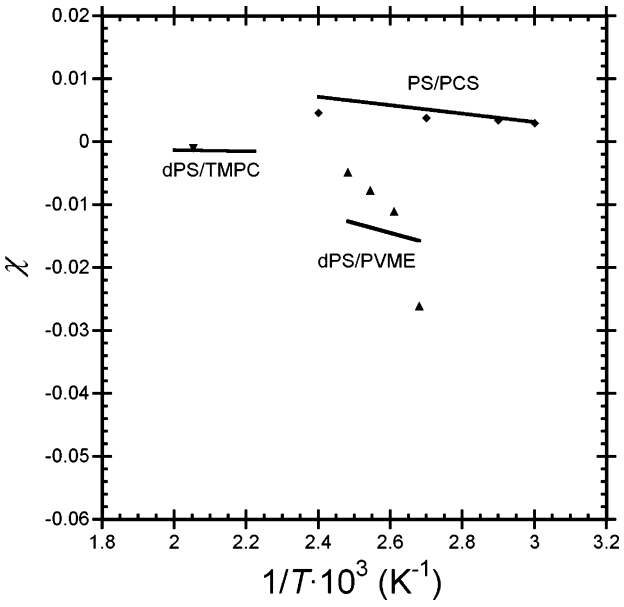

Figure 1. Flory−Huggins interaction parameter as a function of inverse temperature, units of K^{-1}; symbols represent experimental data and lines the BGY predictions. The downward triangles represent dPS/TMPC[15] (253000/42000 g/mol), the diamonds PS/PCS[36] (50000/139500 g/mol), and the upward triangles dPS/PVME[16] (402000/210000 g/mol). The experimental data were measured at concentration ratios of 66/33 dPS/TMPC, 53/47 PS/PCS, and 70/30 dPS/PVME all at pressures of 0.1 MPa.

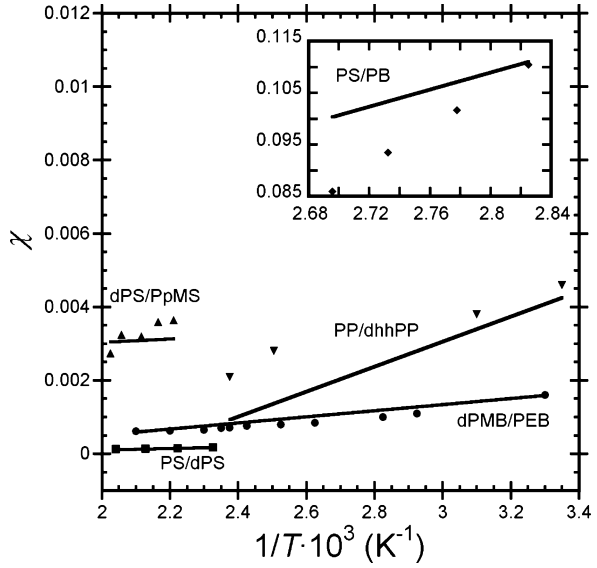

Figure 2. As in Figure 1. The filled triangles represent dPS/PpMS[17] (32700/131000 g/mol), the open squares PS/dPS[19] (119 770/96 700 g/mol), the open diamonds dPMB/PEB[20] (36820/224000 g/mol), the open circles PP/dhhPP[18] (20790/23760 g/mol), and the closed diamonds give PS/PB[5] (1520/235 g/mol); the results for PS/PB are shown in the inset. The experimental data were measured for concentration ratios of 50/50 dPS/PpMS, 80/20 PS/dPS, 41/59 dPMB/PEB, 50/50 PP/dhhPP, and 65/35 PS/PB at a pressure of 0.1 MPa.

temperature nearly equaled the experimental result. The theoretical calculations for the remaining two mixtures demonstrated good agreement with the experimentally derived χ parameters, although the temperature dependence was underestimated for dPS/PVME and slightly overestimated for PS/PCS.

Figure 2 is analogous to Figure 1, but for five UCST blends. From left to right, the lines represent the BGY predictions for dPS/PpMS, PS/dPS, dPMB/PEB, PP/dhhPP, and PS/PB. The PS/PB results are shown in an inset because the χ values are an order of magnitude larger than most of the others. The BGY

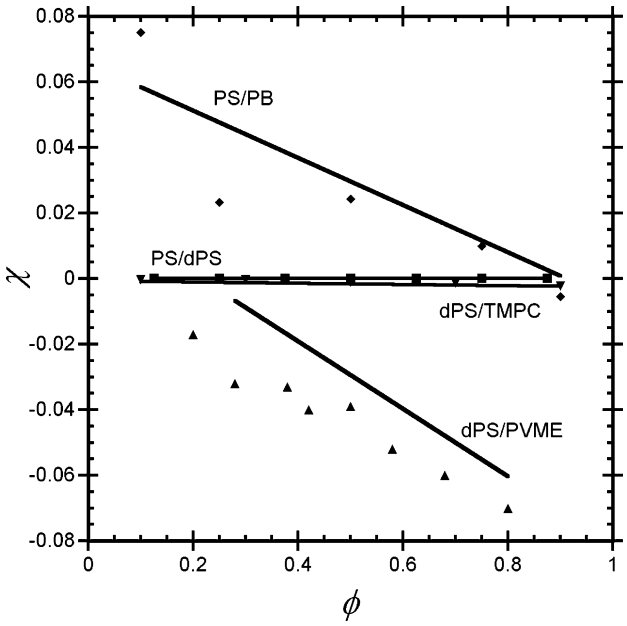

Figure 3. Flory−Huggins interaction parameter as a function of composition (volume fraction). The symbols represent experimental data and the lines the BGY predictions. The downward triangles represent dPS/TMPC,[15] the diamonds PS/PB,[5] the upward triangles dPS/PVME,[16] and the squares indicate PS/dPS.[19] The experimental data were taken at temperatures of 483 K for dPS/TMPC, 388 K for PS/PB, 403 K for dPS/PVME, and 433 K for PS/dPS all at pressures of 0.1 MPa.

predictions show good to excellent agreement with the experimental data; for several of the blends (see, for example, dPMB/PEB) the predicted temperature dependence of χ is extremely close to that observed experimentally.

Figure 3 shows the BGY χ results for two UCST mixtures (PS/PB and PS/dPS) and two LCST blends (dPS/PVME and dPS/TMPC) as a function of composition. The lines represent the BGY calculations and the symbols experimental data for, from top to bottom, PS/PB, PS/dPS, dPS/TMPC, and dPS/PVME. The experimental χ results were record at a pressure of 0.1 MPa and at temperatures 10−30 K into the one-phase region. For each of these (d)PS-containing blends the theory captures both the magnitude and the composition dependence of the χ parameter. In two of the blends (PS/PB, a UCST blend, and dPS/PVME, an LCST blend) χ shows a relatively strong composition dependence. For the remaining two blends (PS/dPS and dPS/TMPC) χ appears to be insensitive to composition, although a closer look at the data for the dPS/PS blend reveals that the composition dependence of χ is parabolic, a feature which has been discussed in the literature and for which numerous theoretical approaches have been formulated.[19,37−39] Taking g to be constant for a given blend, we find that our predictions for χ show a composition dependence which is strictly linear; while allowing g to vary might be appealing in some ways (it would, for example, allow us to predict the appearance of both a UCST and an LCST), the added complication does not seem to be worth the gain in being able to predict phase behavior which is not commonly observed.

In addition to examining the temperature and composition dependencies, the BGY theory may also be applied to predict the effects of pressure on χ. Figure 4 shows results for two UCST blends, PEMS/dPDMS (upper) and dPMB/PEB (lower). The lines represent the BGY calculations, and the symbols indicate the experimental χ results derived from SANS experiments. In each case the data were obtained for temperatures 50 K into the one-phase region. It is clear that the theory

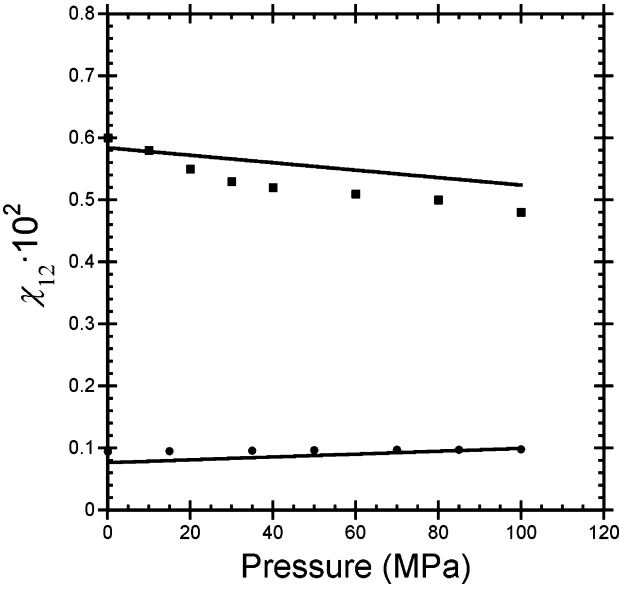

Figure 4. Flory−Huggins interaction parameter as a function of pressure in units of MPa. Symbols give the experimental results and lines the BGY predictions. The squares represent PEMS/dPDMS[21] and the circles give dPMB/PEB.[20] The experimental data were taken at temperatures of 353 K for PEMS/dPDMS (19 450/24 250 g/mol) and 374 K for dPMB/PEB and compositions of 52/48 PEMS/dPDMS and 41/59 dPMB/PEB.

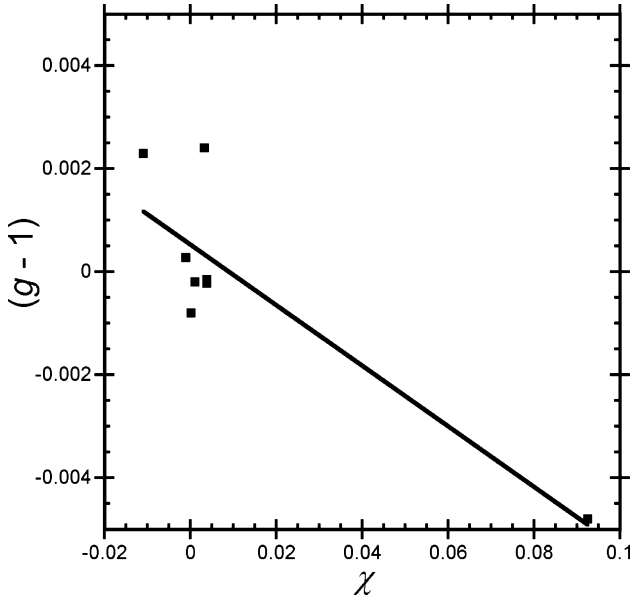

Figure 5. Comparison of the g parameter of BGY theory to the Flory−Huggins interaction parameter for all of the blends listed in Figures 1 and 2. The figure presents the deviation of g from unity vs the experimentally derived value of the χ parameter. The symbols are the individual values; the line shows a linear relationship.

demonstrates excellent agreement with the experimental results for both mixtures across the entire pressure range and correctly accounts for the two mixtures exhibiting large differences in both their χ parameters and their dependencies of χ on pressure.

4. Comparative Analyses

Binary Interactions. The g parameter is introduced into the BGY theory to account for the deviations of the mixed interaction energy from the geometric mean. Given that we now have results for a reasonably broad collection of blends, we expect that a comparison of parameter values should provide some thermodynamic insight. We note that other theoretical treatments employ an analogous parameter; for example, in some of their lattice fluid (LF) results Sanchez and Lacombe implemented a modified geometric mean approximation using the factor, ζ, equivalent to our g. One should not expect to find identical values of the two parameters, even when the same experimental data are being analyzed, however, because the two theories have different results for the free energy. Comparing LF and BGY analyses for LCST blends, we find that with g or ζ values are always found to be greater than unity, meaning that the geometric mean predicts interaction energies which are not favorable enough to account for experimental behavior. Conversely, UCST behavior is associated with g or ζ parameters less than unity, under which circumstances the geometric mean approximation produces an interaction energy that is too favorable.

In contrast to the immediate conclusion one can draw about phase behavior based on having a single g value, a set of $\chi-T$ results are needed in order to determine whether a partially miscible blend has a UCST or an LCST. Ideally, a parameter characterizing blend behavior should also show a trend in its values when the blends being compared exhibit a trend; for example, χ greater than zero is often interpreted as meaning that the components have weakly unfavorable interactions. Presumably those would increase in strength as the value of χ increased. However, such trends are not always observed, and the result is that interpretation of χ values can lead to erroneous conclusions, as the examples discussed below illustrate.

Table 2. Comparisons of χ and g for Selected Polymer Blends

blend	c_c	T_c (K)	c	$g-1$ (BGY)	exp T	notes
PS/PB[5]	0.6	359	0.0925	−0.0048	370	UCST
PS/dPS[19]	0.55	433	0.00018	−0.0008	445	UCST
PP/dhhPP[18]	0.5	303	0.0038	−0.00015	322	UCST
PEMS/dPDMS[21]	0.41	334	0.001	−0.00019	353	UCST
dPS/PpMS[17]	0.5	413	0.0038	−0.00022	435	UCST
PS/PCS[36]	0.53	423	0.0033	0.00241	400	LCST
dPS/PVME[16]	0.73	437	−0.011	0.0023	398	LCST
dPS/TMPC[15]	0.66	514	−0.0011	0.00028	488	LCST

Owing to the typical values of g, we have found that discussing the parameter in terms of $(g-1)$ proves to be more insightful, as important changes in sign and magnitude are made clearly evident. Figure 5 shows a direct comparison between $(g-1)$ values and the corresponding experimental χ results; the line is a visual aid and the symbols indicate results obtained for each of the investigated polymer blends at a temperature approximately $\pm 10-30$ K from the critical point. The corresponding results are also summarized in Table 2. As indicated in the figure, there is not a strong degree of correlation between the two types of parameters. For most of the blends the experimental χ parameters are clustered around a value of zero, and yet this collection of blends exhibits a diverse range of critical temperatures (UCST and LCST), critical compositions, molecular weights, and repeat unit structures. Values of $(g-1)$ have a greater spread, and it is visible at a glance which blends are UCST ($g-1<1$) and which are LCST ($g-1>1$).

In terms of connecting changes in g values with changes in critical behavior, the results of Figure 6 show that relative shifts in $(g-1)$ result in predictable shifts in the critical temperature. This applies even for $(g-1)$ values which differ in orders of magnitude and in sign, which means that it holds regardless of whether the transition in question is a UCST (circles and diamonds) or an LCST (triangles). The unambiguous relationship between the calculated critical temperature and the g

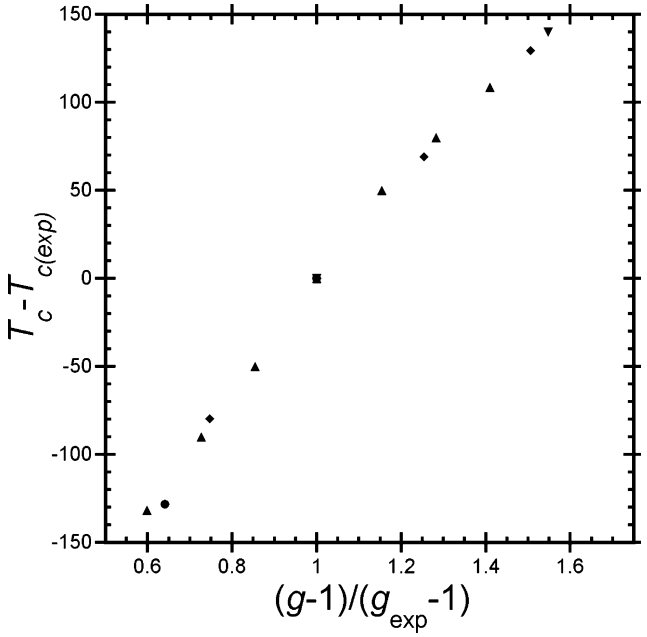

Figure 6. Examination of the dependence of the calculated critical temperature, in units of kelvin, on the *g* parameter. The symbols indicate calculations for various different theoretical mixtures whose pure fluid parameters are based on PE and PEP (circles), dPS and PVME (up-turned triangles), PS and PB (diamonds), and dPS and TMPC (down-turned triangles).

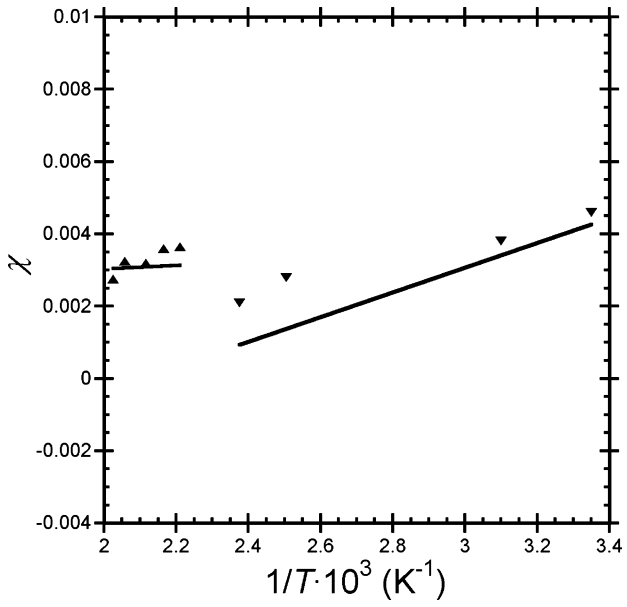

Figure 7. As in Figure 1, for PP/dhhPP (downward triangles) and dPS/PpMS (upward triangles).

parameter lends merit to the idea that *g* would be a useful tool in the analysis of blend coexistence behavior, a notion which is pursued in greater detail below.

Inconsistencies Arising from Using χ To Understand Blend Behavior. For χ to be used as a diagnostic it would be reasonable to expect that two blends which exhibit similar values of χ, and more importantly, trends in χ would have similar polymer blend coexistence behavior. This is not always the case, and in Figures 7−9 we elaborate on this idea by considering a number of examples.

Figure 7 depicts the temperature-dependent χ results for two UCST mixtures: PP/dhhPP (down-turned triangles) and dPS/PpMS (up-turned triangles). At fixed composition (both at $\phi = 0.5$) and nearly analogous temperatures ($T \sim T_c + 20$ K) the χ values for the dPS/PpMS and PP/dhhPP blends are identical at 0.0038. Note that the temperature dependence is needed in order to predict that both are UCST blends; the similarity in $\chi - T$ slopes seems to provide further evidence that the blends must be very similar. It would, however, be a mistake to deduce that the critical temperatures are close; in fact, they differ by over 100 K. On the other hand, turning to $(g - 1)$ as a potential diagnostic parameter, one need only know that the (temperature-independent) values for dPS/PpMS and PP/dhhPP are respectively −0.000 22 and −0.000 15 in order to predict that both must be UCST blends. The small variation in the two blends' *g* parameters may initially seem unimportant; however, the difference is indeed significant as substituting the dPS/PpMS *g* raises the predicted PP/dhhPP critical temperature to 416 K, a shift which should be expected given the results summarized in Figure 5. This close approximation to the experimental dPS/PpMS result of 413 K emphasizes the value of $(g - 1)$ as an analytical tool. In addition, the fact that $(g - 1)$ for the PP/

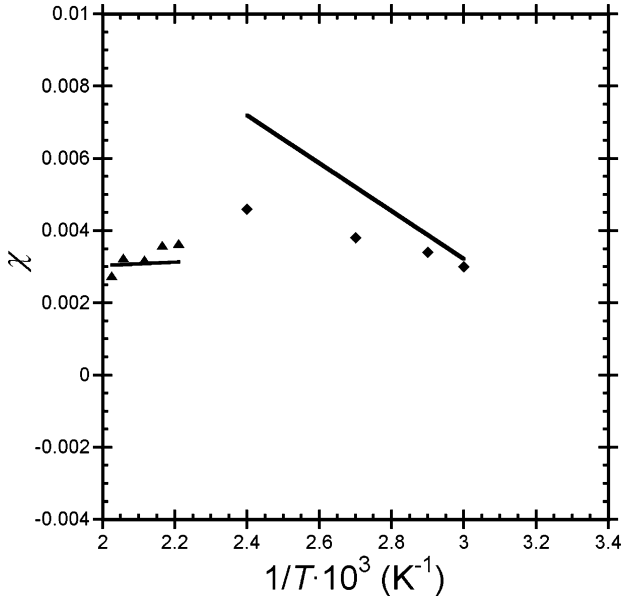

Figure 8. As in Figure 1, for dPS/PpMS (triangles) and PS/PCS (diamonds).

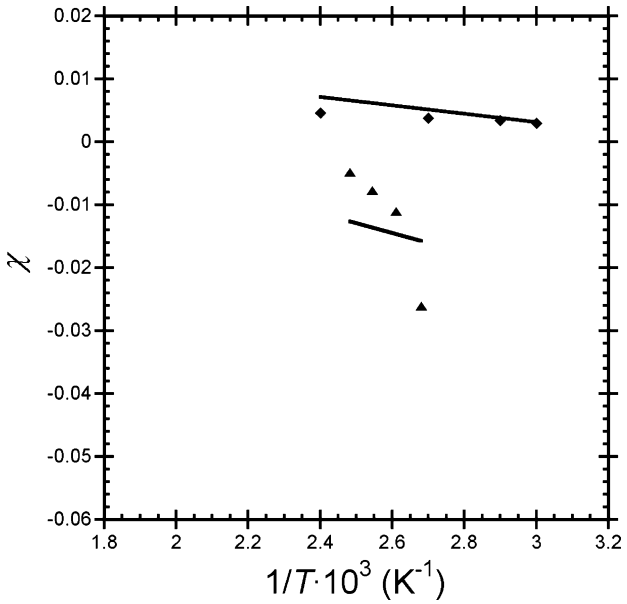

Figure 9. As in Figure 1, for dPS/PVME (triangles) and PS/PCS (diamonds).

dhhPP blend is closer to unity implies a mixed interaction that is closer to what the geometric mean approximation would predict, which should result in greater miscibility and a lower critical temperature; this is indeed reflected in a UCST for PP/dhhPP of 303 K compared to that of 413 K for dPS/PpMS.

In Figure 8 are shown $\chi-T$ data for PS mixed with poly(chlorostyrene) (PCS), represented by the diamonds and dPS/PpMS (triangles). Once again values for 50:50 compositions at a temperature roughly 20 K into the miscible region are very similar, being 0.0038 for dPS/PpMS and 0.0033 for PS/PCS, which might lead one to surmise similar blend behavior. It is only by knowing about the temperature dependence of χ, shown in the figure, that one realizes the two blends manifest opposite critical behavior, with PS/PCS having a UCST and dPS/PpMS an LCST. On the other hand, signs of the temperature-independent values of $(g - 1)$, which are −0.000 22 for the latter and 0.002 41 for the former, reveal this difference immediately.

Figure 9 shows χ−temperature results for PS/PCS (diamonds) and dPS/PVME (triangles). Once again, the availability of $\chi-T$ data allows one to conclude that both are LCST blends. However, it is also clear from the figure that the χ values themselves are extremely different, being opposite in sign and an order of magnitude apart. On this basis one might expect that the miscibility of the two blends, as evidenced by their critical temperatures, would differ considerably. However, comparison of $(g - 1)$ values, which are 0.0023 for dPS/PVME and 0.0024 for PS/PCS, yields immediately that both are LCST blends and indicates that the miscibility behavior of the two should be extremely close. This is indeed the case, with the LCST for PS/PCS at 423 K and that for dPS/PVME at 437 K. As was the case for the previous two sets of examples, the $(g - 1)$ values correlated strongly with experimental behavior, while the χ data were rather uninformative.

5. Summary

In the course of previous work on partially miscible blends we observed that trends in the parameters characterizing these systems appeared to be strongly correlated with the strength and temperature dependence of miscibility. In this paper we have tested our observations by studying literature data for a series of UCST and LCST blends. Given that the most common method of characterizing such behavior in the literature is through the Flory−Huggins χ parameter, we decided first to make comparisons with such experimental χ results on the blends, including temperature, composition, and pressure dependence (where available). It is worth emphasizing that a strength of the BGY approach is the transferability of the characteristic parameters obtained by matching theory to experimental data. This means that our predictions for χ results, obtained from analyzing other kinds of experimental data, agreed well with the literature values for χ. We then turned to thinking critically about what could be learned regarding miscibility and phase separation via information about χ. Our results suggest that through the BGY theory there is a viable alternative to the Flory−Huggins interaction parameter when conclusions about blend miscibility are of interest.

In section 2 of this paper we presented an overview of the BGY theory and described routes to the parameters which characterize the pure components and the mixtures. The blends of interest in this study encompass three exhibiting an LCST (PS/PCS, dPS/PVME, and dPS/TMPC) and five exhibiting a UCST (PS/PB, PS/dPS, PP/dhhPP, PEMS/dPDMS, and dPS/PpMS). In section 3 we applied the BGY theory to the calculation of χ, making comparisons with experimental values, including temperature, pressure, and composition dependences, where possible. Our results demonstrate good to excellent agreement with experiment for all of the polymer systems that were studied. We believe that having demonstrated the capability of the BGY theory to predict χ values lends credence to our conclusions that the theory provides a more useful alternative.

We began section 4 of the paper with a discussion of the correlations between blend miscibility and values for g, the quantity that characterizes the deviation of the evident experimental result for the mixed interaction energy from the geometric mean approximation. In fact, we found it most telling to work with $(g - 1)$, given that we discovered perfect correlation between the sign of this quantity and the phase behavior of a partially miscible blend, with a positive value signifying an LCST blend and a negative value associated with the appearance of a UCST.[40] Indeed, if we consider the case of a hypothetical partially miscible blend having the rest of its characteristic parameters fixed, we find that the relative change of the critical temperature for the blend appears to be a universal function of $(g - 1)$, regardless of the order of magnitude of this quantity or whether it is greater than or less than unity. In other words, not only is the sign of $(g - 1)$ an immediate indicator of the type of miscibility (UCST or LCST), shifts in this quantity lead to predictable shifts in miscibility, all other factors being unchanged. In this section we also observed that a direct comparison of χ and $(g - 1)$ showed no particular trend, the precursor to results in the next section.

In the final section (section 4) of the paper, we presented three case studies, each of which involved two blends. Two of the case studies involved blends having the same (or extremely similar) values of χ at a temperature approximately 10−30 K into the one-phase region. In all cases a set of $\chi-T$ data were required in order to characterize the blend as UCST or LCST, whereas knowing only a single, temperature (and pressure and composition)-independent $(g - 1)$ value serves the same purpose. In one case both blends were of the UCST type, however, the critical temperatures were over 100 K apart. The experimental χ values were exactly the same, while the $(g - 1)$ value of the less miscible blend was about 50% greater in magnitude than that of the blend having the lower UCST. Indeed, keeping all of the parameters of the second blend fixed and then increasing $(g - 1)$ by 50% yielded a predicted shift in the critical temperature of almost exactly the difference shown between the two experimental blends. In the second example, although the experimental χ values were almost identical, one blend was UCST type and the other exhibited an LCST. Once again, $\chi-T$ data were needed in order to anticipate this difference, while the fact that the $(g - 1)$ values for the two blends were opposite in sign immediately indicated the difference in temperature dependence of miscibility. In the final study the experimental χ values were opposite in sign and a factor of 10 different in magnitude, while the $(g - 1)$ values were within 5% in value (and the same sign). In this case, the blends were both LCST, and their critical temperatures were only about 15 K apart.

We believe that the results presented in this paper suggest that correlations between blend miscibility and experimental results for the Flory−Huggins χ parameter are inconsistent at best and nonexistent at worst. Adding this conclusion to the often-discussed issues in the literature regarding interpretation of the concentration and temperature dependence of χ, it would seem that an alternative would be desirable. In this work we suggest that application of the BGY theory, coupled with use

of the ($g - 1$) parameter, may have a great deal to offer in the study of partially miscible blends. This quantity is truly constant for a particular blend, being independent of temperature, pressure, and composition; its sign is an immediate diagnostic of how the miscibility will change with temperature, being positive for LCST blends and negative for UCST blends; its definition is simple and unambiguous. Indeed, one might ask why such a simple-minded parameter should do so well. We are currently pursuing this question, and the results we obtain will be the subject of a future study.

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