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Determination of χ from Liquid–Liquid Phase Data and the Computation of Phase Diagrams for Quasi-Binary Polymer Solutions and Blends

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ABSTRACT: A generalized Flory–Huggins theory is described that permits the investigation of the phase behavior for quasi-binary polymer solutions or blends in which, for blends, both components may be polydisperse. A temperature- and concentration-dependent χ interaction parameter is used. It is demonstrated that the χ parameter may be readily extracted from experimental phase data. This is illustrated by using a robust fitting procedure to obtain the composition and temperature dependence of χ for the cyclohexane/polystyrene system from experimental phase data. The result (eq 22) is in excellent agreement with previous determinations of χ for this system, and the method employed here has several advantages over other approaches. Relative merits of a number of methods are discussed. The composition- and temperature-dependent χ determined here (eq 22) is used to predict cloud-point curves for solutions of polystyrene with various bimodal distributions in cyclohexane. These computed CPCs are found to be in quantitative agreement with experimental data.

Introduction

The χ interaction parameter is often interpreted generally as an empirical quantity that can be used to bridge the gap between simple Flory–Huggins[1,2] theory and the diverse range of phase behavior observed experimentally for polymer systems. It is now generally accepted that in order to obtain quantitative agreement between Flory–Huggins theory and experimental observations for most systems, χ must be considered to be a function of both temperature and composition.[3–5] To this end, a form of χ,

$$\chi(T,\varphi_2) = [1 + b_1\varphi_2 + b_2\varphi_2^{\,2}][d_0 + d_1/T + d_2 \ln(T)] \quad (1)$$

has been described previously[6] where the coefficients b_i and d_i are adjustable constants. This form of the temperature dependence follows from the assumption that the change in heat capacity upon mixing, Δc_p, is independent of temperature. The quadratic composition dependence was chosen because it has been found to be sufficient to describe most of the experimentally determined χ parameters for solutions.[3,4,7] Finally, it is assumed that the temperature dependence of χ is uniform for all compositions. This expression for χ may be used to represent[6] the five most common types of experimentally[8,9] observed phase diagrams: LCST, UCST, combined LCST/UCST with the former occurring at higher temperature than the latter, hourglass, and closed loop. Furthermore, this form for χ is sufficient to investigate some more unusual phase phenomena in polymer systems, such as the occurrence of multiple critical concentrations[10] and the coalescence of cloud-point curves.[11] Bae *et al.*[12] have also utilized this approach to describe both vapor–liquid and liquid–liquid equilibria in a number of binary polymer systems.

It is known both theoretically and experimentally that the average molecular weight and the molecular weight distribution can have a significant effect on the location and shape of phase boundaries.[13,14] Consequently, in order to accurately represent the phase behavior of real polymer systems the effects of polydispersity must be incorporated into the model. The effect of molecular weight distribution on the form of phase diagrams of quasi-binary polymer solutions has been studied previously in a quantitative manner,[15,16] and this has been extended to quasi-binary polymer blends.[17] Based closely on earlier work by Koningsveld and co-workers and by Solc, a method has been described that permits the computation of phase diagrams for quasi-binary polymer systems in which one component may be polydisperse.[18] This is generalized here so that both components may be polydisperse.

Table 1. Methods for the Determination of χ for Polymer Solutions

method	approx range of φ_2	ref
osmotic pressure	0.0–0.3	8, 11
vapor sorption	0.3–0.9	8, 11
gas–liquid chromatography	→1.0	8, 11
freezing-point depression of polymer	high only	11
freezing-point depression of solvent	low only	11
swelling equilibrium[a]	high only	11
intrinsic viscosity[b]	→0.0	11
light scattering and sedimentation equilibrium[c]	→0.0	8, 11
critical solution temperature[d]	0.0–0.3	23
temperature dependence of the relative amount of precipitate with the CPC	wide range	24

[a] Relatively low accuracy. [b] Extraction of χ is dependent upon the theory assumed. [c] Determined from second virial coefficients; polymer must be monodisperse. [d] Demonstrated high accuracy, particularly in the region of the critical point, providing φ_2^{crit} and T^{crit} are precisely measured.

If one is to make use of the computational method described here to investigate the phase behavior of real polymer systems, then one needs to be able to obtain accurate values for the coefficients in eq 1 for the system(s) of interest. A large number of experimental methods are available to determine χ, particularly for polymer solutions, and these have been reviewed elsewhere.[4,7] Many of the methods used to determine χ for polymer solutions are summarized in Table 1, together with the approximate range of volume fractions of polymer φ_2 for which the methods are applicable. The application of many of these methods to determine χ for polymer blends has been discussed by Riedl and Prud'homme.[21] Of course, the use of neutron scattering is also of particular

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importance for polymer blends.

To determine accurately the coefficients for the composition dependence of χ (i.e., b_i in eq 1), it is necessary to obtain values of χ over a large range of composition. It can be seen from Table 1 that typically this requires using several complementary techniques to span the required concentration range. We will describe here a robust and convenient method of obtaining all the necessary χ coefficients (b_i and d_i in eq 1), by fitting to phase data. Other methods, such as the last two in Table 1, have also been suggested for obtaining values of similar coefficients, and the approach described here will be contrasted with these. In this paper the underlying theory will be generalized so that both components of a binary system may be polydisperse, but the procedure for extracting χ coefficients will be illustrated by sample calculations performed on the well-studied cyclohexane/polystyrene system. A later paper[22] will extend this work by applying it to a blend of two polydisperse polymers.

Thermodynamic Quantities

In a quasi-binary polymer blend, one or both of the components can be polydisperse. In the general case of two polydisperse components, the free energy of mixing is given by

$$\frac{\Delta G}{RT} = \sum_i n_{1i} \ln \varphi_{1i} + \sum_j n_{2j} \ln \varphi_{2j} + g\varphi_2 \sum_i n_{1i} N_{1i} \quad (2)$$

where the subscripted n's refer to numbers of moles, φ's to volume fractions, and N's to relative molar volumes of the polymer chains. The first subscript (1 or 2) refers to one of the potentially polydisperse components, and the second subscript (i or j) refers to the single molecular weight (monodisperse) constituents that comprise each of the components. The effect of molecular weight on the interaction parameter is typically small[15] and is, therefore, neglected in eq 2. The interaction parameters $g(T,\varphi_2)$ and $\chi(T,\varphi_2)$ are related by[6,15]

$$\chi = g - \varphi_1 g' \quad (3)$$

and upon integration,

$$\int_{\varphi_2}^{1} \chi(T,\varphi)\, \mathrm{d}\varphi = (1 - \varphi_2) g(T,\varphi_2) \quad (4)$$

Furthermore,[6]

$$\chi'(T,\varphi_2) = 2g'(T,\varphi_2) - (1 - \varphi_2) g''(T,\varphi_2) \quad (5)$$

and

$$\chi''(T,\varphi_2) = 3g''(T,\varphi_2) - (1 - \varphi_2) g'''(T,\varphi_2) \quad (6)$$

Here, the prime, double prime, and triple prime denote the first, second, and third derivatives of the appropriate interaction parameter with respect to the volume fraction of component 2.

The chemical potential, $\Delta\mu_{1i}$, of the i-th constituent of the first component is obtained by differentiating

$$\frac{\Delta\mu_{1i}}{RT} = \frac{\partial \Delta G}{RT \partial n_{1i}}\bigg|_{T,P,n_j} = \ln \varphi_{1i} + 1 - N_{1i}\left(\frac{\varphi_1}{N_{1n}} + \frac{\varphi_2}{N_{2n}}\right) + N_{1i}{\varphi_2}^2\left(g - \frac{\partial g}{\partial \varphi_2}\varphi_1\right) \quad (7)$$

where N_{1n} and N_{2n} are the number-average relative molar volumes of the two components. Likewise, the chemical potential of the j-th constituent of the second component is

$$\frac{\Delta\mu_{2j}}{RT} = \frac{\partial \Delta G}{RT \partial n_{2j}}\bigg|_{T,P,n_j} = \ln \varphi_{2j} + 1 - N_{2j}\left(\frac{\varphi_1}{N_{1n}} + \frac{\varphi_2}{N_{2n}}\right) + N_{2j}{\varphi_1}^2\left(g + \frac{\partial g}{\partial \varphi_2}\varphi_2\right) \quad (8)$$

Phase Equilibria in Quasi-Binary Systems

Spinodal. The spinodal curve defines the boundary between unstable and metastable mixtures. Thermodynamically, it is expressed by the determinant[15]

$$Y = \left| \frac{\partial^2 \Delta G}{\partial \varphi_{ij} \partial \varphi_{kl}} \right| = 0 \quad (9)$$

with ij and kl ranging over all constituents of the two polydisperse components, and the spinodal curve is given explicitly by

$$\frac{1}{N_{1w}(1 - \varphi_2)} - [2\chi(T,\varphi_2) + \varphi_2 \chi'(T,\varphi_2)] + \frac{1}{\varphi_2 N_{2w}} = 0 \quad (10)$$

Critical Point. The critical point is the point on the cloud-point curve and spinodal curve where the two phases become identical and form one phase. Thermodynamically, it is determined by simultaneously solving eq 9 and the following equation:[15]

$$Y' = 0 \quad (11)$$

where Y' is the determinant derived from eq 9 by replacing the elements of any horizontal line by $\partial^2 Y/\partial\varphi_{ij}\partial\varphi_{k1l1}$, $\partial^2 Y/\partial\varphi_{ij}\partial\varphi_{k2l2}$, etc. [It is worth noting that eqs 9 and 11, which are necessary conditions for the existence of a critical point, do not constitute a sufficient condition when the cofactors of all the elements in the replaced row are 0. See, for example, refs 23–25.] Explicitly, eq 11 is given by

$$\frac{N_{2z}}{(N_{2w}\varphi_2)^2} - \frac{N_{1z}}{(N_{1w}\varphi_1)^2} + [3\chi'(T,\varphi_2) + \varphi_2 \chi''(T,\varphi_2)] = 0 \quad (12)$$

Here, N_{1w} and N_{1z}, and N_{2w} and N_{2z} are the weight-average and z-average relative molar volumes of components 1 and 2, respectively.

Cloud-Point Curve (CPC). The CPC describes the precipitation temperature, or the χ interaction parameter at this temperature, as a function of solute concentration. Under the conditions of temperature and composition defined by the CPC, two phases may phase separate and exist in equilibrium. Two phases can exist at equilibrium only if the potentials of the corresponding constituents are equal:

$$\Delta\mu_{ij}' = \Delta\mu_{kl}'' \quad (13)$$

Thus, calculation of equilibrium concentrations involves the solution of a system of equations; the number of equations to be solved is equal to the total number of constituents in the two components. If, however, the distribution of relative molar volumes of both polymers is known before phase separation, only two nonlinear equations need to be solved. This dramatic reduction in complexity is facilitated by the introduction of two *separation factors*, σ_1 and σ_2. According to Flory–Huggins theory, the partitioning of each polymer component between two phases obeys the relations

$$\sigma_i = {N_{ik}}^{-1}(\ln {\varphi_{ik}}'' - \ln {\varphi_{ik}}') \quad (14)$$

with ik ranging over all the constituents of component i, where i = 1,2. At the cloud point, where the phase separation begins, one of the phases is identical with the phase existing before phase separation. In this phase, known as the principal phase, the relative molar volume distribution is known. Once σ_i is known, the distribution of relative molar volumes in the second phase (the conjugate phase) can be calculated as well with the help of eq 14. This extra detail enables the reduction of the many equations making up eq 13 to two equations involving temperature, the separation factor σ_2, and the total volume fraction in the principal phase. The solution of this system of equations is known as the cloud-point curve.

The actual derivation of the two equations that define the cloud-point curve is immediate: By eqs 7, 8, and 14,

$$\sigma_2 - \sigma_1 = \varphi_1''^2\left[g(\varphi_2'') + \left.\frac{\partial g}{\partial \varphi_2}\right|_{\varphi_2''}\varphi_2''\right] - \varphi_1'^2\left[g(\varphi_2') + \left.\frac{\partial g}{\partial \varphi_2}\right|_{\varphi_2'}\varphi_2'\right] - \varphi_2''^2\left[g(\varphi_2'') - \left.\frac{\partial g}{\partial \varphi_2}\right|_{\varphi_2''}\varphi_1''\right] + \varphi_2'^2\left[g(\varphi_2') - \left.\frac{\partial g}{\partial \varphi_2}\right|_{\varphi_2'}\varphi_1'\right] \qquad (15)$$

and

$$\sigma_1(\varphi_1' + \varphi_1'') + \sigma_2(\varphi_2' + \varphi_2'') = 2\left[\left(\frac{\varphi_1''}{N_{1n}''} + \frac{\varphi_2''}{N_{2n}''}\right) - \left(\frac{\varphi_1'}{N_{1n}'} + \frac{\varphi_2'}{N_{2n}'}\right)\right] + (\varphi_1' + \varphi_1'')\left[\varphi_2'^2\left(g(\varphi_2') - \left.\frac{\partial g}{\partial \varphi_2}\right|_{\varphi_2'}\varphi_1'\right) - \varphi_2''^2\left(g(\varphi_2'') - \left.\frac{\partial g}{\partial \varphi_2}\right|_{\varphi_2''}\varphi_1''\right)\right] + (\varphi_2' + \varphi_2'')\left[\varphi_1'^2\left(g(\varphi_2') + \left.\frac{\partial g}{\partial \varphi_2}\right|_{\varphi_2'}\varphi_2'\right) - \varphi_1''^2\left(g(\varphi_2'') + \left.\frac{\partial g}{\partial \varphi_2}\right|_{\varphi_2''}\varphi_2''\right)\right] \qquad (16)$$

where primed and double-primed symbols denote quantities in the principal and conjugate phases, respectively. Equations 15 and 16 are equations in σ_1, σ_2, φ_1', φ_2', φ_1'', φ_2'', the temperature T, and the different number averages. Obviously, φ_1' is a function of φ_2', and φ_1'' is a function of φ_2'' because

$$\varphi_1' + \varphi_2' = \varphi_1'' + \varphi_2'' = 1 \qquad (17)$$

Once the normalized weight distributions, w_{1j}' and w_{2j}', of the polymer constituents at the cloud point are given, φ_2'' becomes a function of φ_2' and σ_2

$$\varphi_2'' = \sum_j \varphi_{2j}'' = \varphi_2'\sum_j \frac{\varphi_{2j}'}{\varphi_2'}e^{\sigma_2 N_{2j}} = \varphi_2'\sum_j w_{2j}'e^{\sigma_2 N_{2j}} \qquad (18)$$

and σ_1 becomes a function of σ_2 and φ_2',

$$(1 - \varphi_2')\sum_i w_{1i}'e^{\sigma_1 N_{1j}} + \varphi_2'\sum_j w_{2j}'e^{\sigma_2 N_{2j}} = \sum_i \varphi_{1i}'' + \sum_j \varphi_{2j}'' = \varphi_1'' + \varphi_2'' = 1 \qquad (19)$$

If we select χ as the interaction parameter, eqs 15 and 16 take the form

$$\sigma_2 - \sigma_1 = \varphi_2'\chi(\varphi_2') - \varphi_2''\chi(\varphi_2'') + \int_{\varphi_2''}^{\varphi_2'}\chi\,d\varphi \qquad (20)$$

and

$$\sigma_1(\varphi_1' + \varphi_1'') + \sigma_2(\varphi_2' + \varphi_2'') = 2\left[\left(\frac{\varphi_1''}{N_{1n}''} + \frac{\varphi_2''}{N_{2n}''}\right) - \left(\frac{\varphi_1'}{N_{1n}'} + \frac{\varphi_2'}{N_{2n}'}\right)\right] - (\varphi_2'' - \varphi_2')(\chi\varphi_2' + \chi\varphi_2'') - (\varphi_2'' + \varphi_2')\int_{\varphi_2''}^{\varphi_2'}\chi\,d\varphi \qquad (21)$$

Obtaining χ from Experimental Phase Data

The temperature- and composition-dependent coefficients of χ (d_i and b_i, respectively, in eq 1) may be obtained by fitting to experimental phase boundary data. Determining these coefficients in this way has several advantages over the use of many of the other experimental methods listed in Table 1: (i) convenience of using one technique to determine χ over a wide range of concentration; (ii) liquid–liquid phase boundaries are very sensitive to the temperature and concentration dependence of χ, and fitting accurately quantifies these dependences; (iii) utilizes all of the known phase boundary and not just the critical point data, and therefore, does not require highly accurate critical point data; (iv) equally applicable to solutions and blends; (v) binodals, spinodals, or cloud-point curves may be used.

In particular, the method of fitting to an experimental phase boundary is likely to be preferred over the last two methods listed in Table 1 when the required data are already available. If one needs to measure all the required experimental data before proceeding with the extraction of χ, then it may be equally convenient and accurate to use one of these two methods.[19,20] However, there is a much greater likelihood that good phase boundary data will already be available for a particular system than there is that either highly accurate critical points or the temperature dependence of the relative amount of precipitate would have been determined previously.

Here, a robust Nelder–Mead simplex method has been used in the fitting procedure. In all cases, the approach is to minimize a function. The function depends on the phase boundary being fitted, i.e., whether spinodal, binodal, or cloud-point curve. For spinodal curves, the function is obtained by summing the absolute values of the left side of the spinodal equation (10) evaluated for each experimental temperature and volume fraction pair.

For binodal and cloud-point curves, an extra step is needed because the curves are calculated by solving two equations in three variables. Each experimental temperature and volume fraction is substituted into one of the two equations, which is then solved for the third variable. The function is obtained by substituting each set of three variables (two given and one calculated) into the other equation, taking the absolute values and summing.

Cyclohexane/Polystyrene

Extracting χ. The procedure for extracting χ coefficients is illustrated by using the well-studied cyclohexane/polystyrene system as a model. To this end we use the phase data of Shultz and Flory[26] and treat this as binodal data, i.e., assume that the polystyrene fractions are monodisperse. This is a necessary assumption because specific information regarding the polydispersity of the polystyrene fractions is not available.

Shultz and Flory[26] provided data of precipitation temperature, T_p, versus the volume fraction of polystyrene for polystyrene fractions having viscosity-average molecular weights, M_v, of 43 600, 89 000, 250 000, and 1 270 000. The stated accuracy of the T_p values is ±0.1 K over the majority of the composition range. The values of T_p were independent of cooling rate between 0.01 and 0.05 K min^{-1}, and the same values were determined on heating and cooling and independently of whether the solution was stirred or not.

The experimental data[26] are replotted in Figure 1, together with the fitted binodal curves. The expressions fitted to the experimental data were forms of eqs 20 and 21 simplified by the assumption that both components

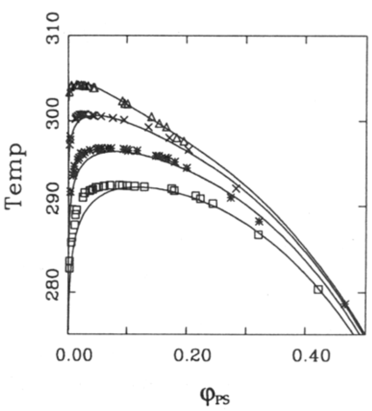

Figure 1. Experimental data[26] (symbols) for the precipitation temperature versus the volume fraction of polystyrene for the cyclohexane/polystyrene system and fitted binodal curves. Different symbols represent different molecular weights of polystyrene: open squares, $M_v = 43600$; stars, $M_v = 89000$; crosses, $M_v = 250000$; open triangles $M_v = 1270000$.

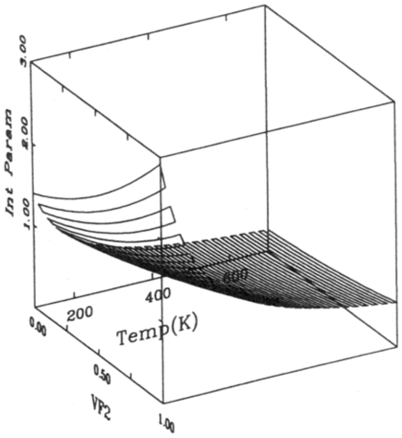

Figure 2. χ interaction parameter determined here (eq 22) for the cyclohexane/polystyrene system plotted as a function of temperature and the volume fraction of polystyrene.

are monodisperse. These expressions are given explicitly in ref 6. The densities[26] of cyclohexane and polystyrene were taken to be 0.7790 and 1.082 g cm^{-3}, respectively. A single set of χ coefficients was determined for all molecular weights of polystyrene. The composition- and temperature-dependent χ parameter

$$\chi(T,\varphi_2) = [1 + 0.51\varphi_2 + 0.60\varphi_2^{\,2}][0.073146 + 131.4/T] \tag{22}$$

resulted from the fitting procedure. This expression for χ is plotted in Figure 2.

It can be seen in Figure 1 that a good quantitative fit of the experimental data has been achieved. The agreement is good over the entire range of polystyrene molecular weights. Considering the quality of the fit as a function of composition, the agreement is worst at the lowest concentrations of polystyrene. In particular, although the critical temperatures are in good agreement over the entire range of molecular weights, calculated and experimental critical volume fractions show greater deviation at lower molecular weights. No attempt has been made to increase the quality of the agreement at the low polystyrene concentrations (at the expense of the other regions), because a basic premise on which eq 2 is based may not be satisfied for dilute solutions, i.e., that all regions of space are equally available to a given molecule. Shultz and Flory argued[26] that this premise is satisfied for solutions of high molecular weight polymers, even at low concentrations of polymer, for temperatures near $T = \Theta$.

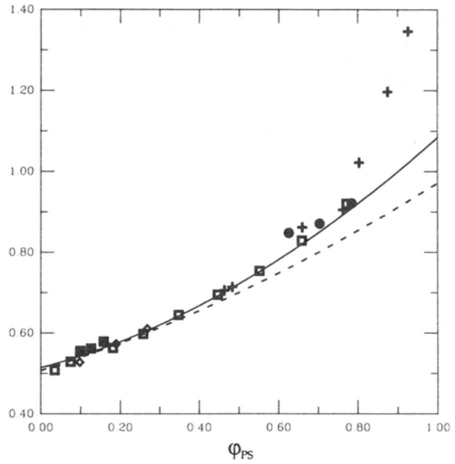

Figure 3. Comparison of the composition dependence of χ at 298 K determined here (bold line) with previously measured values at approximately this temperature.[30] The symbols represent different studies utilizing a variety of experimental techniques: filled squares, osmotic pressure (299 K);[31] filled circles, vapor pressure (298 K, M = 150000);[32] crosses, vapor pressure (297 K, M = 26000);[33] open squares, equilibrium ultracentrifucation (303 K, M = 154000);[34] diamonds, osmotic pressure (297 K, M = 72000).[33] The broken line represents an expression for χ determined by Koningsveld *et al.*[19] from critical solution temperatures.

The observation, from Figure 1, that the agreement between theory and experiment at low concentrations of polystyrene increases as the molecular weight of the polystyrene increases is consistent with this argument.

It should also be noted that Einaga, Fujita, and coworkers have studied extensively phase separation in the cyclohexane/polystyrene system. Their work included determining χ from light scattering measurements on true binary systems[27] and predicting phase boundaries for both true binary[27] and quasi-binary solutions.[28,29] These workers concluded that to accurately predict phase boundaries for the cyclohexane/polystyrene system, χ must be treated as a function of molecular weight in addition to temperature and composition. However, it is clear from Figure 1 that a molecular weight dependent χ is not a prerequisite for accurately representing the phase data of Shultz and Flory.[26]

Comparison with Values for χ Measured Previously. Consistent with previous observations, χ for the cyclohexane/polystyrene system can be seen from eq 22 and Figure 2 to be strongly composition dependent. However, it is interesting to note that the original[1,2] $1/T$ "enthalpic term" dominates the temperature dependence. A comparison is made in Figure 3 of the composition dependence of χ determined here at 298 K with that determined in other studies. In Figure 3, the various symbols represent different studies utilizing a variety of experimental techniques[30] (see the figure caption for further details). Also in this figure, the broken line represents an expression for χ determined by Koningsveld *et al.*[19] from critical solution temperatures, and the bold line represents eq 22 determined in the present study. Equation 22 can be seen to be in good agreement with the other determinations of χ over most of the composition range. This agreement is somewhat better than that observed for the expression determined by Koningsveld *et al.*[19] This is not too surprising because the latter expression[19] was determined over a very limited range of composition (4–18% polymer by weight) and has been significantly extrapolated in Figure 3. However, this underscores a major limitation of determining the com-

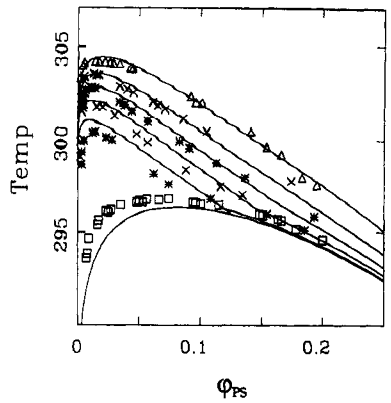

Figure 4. Experimental data[26] (symbols) for the precipitation temperature versus the total volume fraction of polystyrene for solutions of polystyrene with various bimodal distributions of molecular weight in cyclohexane together with CPCs calculated taking eq 22 as the interaction parameter. The symbols represent various volume fractions of the low molecular weight (89 000) polystyrene fraction, φ_L, that were mixed with the high moleclar weight polystyrene fraction to generate the bimodal distributions: open triangles, $\varphi_L = 0.000$; upper crosses, $\varphi_L = 0.500$; upper stars, $\varphi_L = 0.750$; lower crosses, $\varphi_L = 0.900$; lower stars, $\varphi_L = 0.980$; open squares, $\varphi_L = 1.000$.

position dependence of χ from critical concentration data: the composition range accessible for measurement is significantly limited.

The agreement between χ determined here and the values measured in other studies and plotted in Figure 3 is worst at the highest volume fractions of polystyrene. This could be because eq 22 was only determined using data with φ_2 up to about 0.5. Also, a quadratic composition dependence of χ was assumed in parameterizing this equation, but an accurate representation of the data in Figure 3 requires a higher order composition dependence.

Prediction of CPCs for Quasi-Binary Solutions. Having determined the temperature- and composition-dependent χ for a particular solution or blend, one may then use the expressions given earlier in this paper to compute spinodals, CPCs, and critical points for various molecular weights and molecular weight distributions of interest. This procedure is illustrated and validated here by computing CPCs for quasi-binary solutions of (polydisperse) polystyrene in cyclohexane and comparing the results to experimental data.

Shultz and Flory[26] mixed two polystyrene fractions (M_v = 89 000 and 1 270 000) in various proportions to generate bimodal distributions. Experimentally determined CPCs of solutions of these bimodal samples in cyclohexane were analyzed by these authors[26] as ternary systems. Here, we treat them as quasi-binary systems and predict their CPCs using the previously determined temperature- and composition-dependent χ parameter (eq 22). A plot of the experimentally determined[26] values of T_p versus the total volume fraction of polystyrene is shown in Figure 4, together with the computed CPCs. It can be seen that the computed and experimental results are in generally good agreement.

There is an additional feature that is worthy of note in Figure 4. On the calculated CPC corresponding to the solution of the bimodal mixture of polystyrene fractions with the highest concentration of the lowest molecular weight constituent, there is a depression at approximately $\varphi_2 = 0.12$ and some associated structure. This feature is enlarged in Figure 5 and is due to the solution undergoing a separation into three phases.

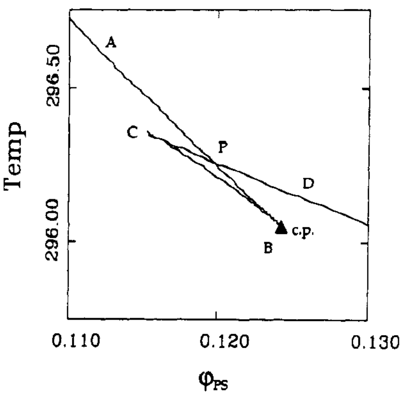

Figure 5. Enlargement of the depression and associated structure on the CPC in Figure 4 corresponding to the solution of the bimodal mixture of polystyrene fractions with the highest concentration of the lowest molecular weight constituent (φ_L = 0.980).

The possibility that a solution of two homologous polymers in a solvent might separate into three liquid phases was first recognized by Tompa.[13] This has been studied by Koningsveld *et al.*[19] and Dobashi and Nakata.[35,36] The cyclohexane/polystyrene system has also been investigated by Einaga, Nakamura, and Fujita[37] and by Sundar and Widom.[38] Theoretical discussions of this and related phenomena in other multicomponent systems have been published by several authors. Specifically, Solc *et al.*[39] describe the projection of these phenomena in multicomponent systems onto a CPC drawn in two dimensions.

In Figure 5, the CPC between A and P is thermodynamically stable. From P to the cusp point B it is metastable. Point B is a singular point which, because in this particular case it coincides with the critical point, is designated as a heterogeneous double critical point.[39] Between B and C the CPC is unstable. Between the cusp point C and P the CPC is metastable again. Continuing out from P toward D, the curve is stable again. Thus, two stable branches of the CPC intersect at point P. Therefore, this phase will be at equilibrium with two other incipient phases of different composition, and point P is referred to as a three-phase point on the CPC.[39]

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