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Correlations between the Effects of Pressure and Molecular Weight on Polymer Blend Miscibility

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ABSTRACT: We examine the effects of pressure on polymer blend miscibility for two polyolefin blends as well as for blends of polystyrene (PS) and polybutadiene (PB). Each of the blends studied exhibits an upper critical solution temperature (UCST), and for the PS/PB blend we report experimental results on the pressure dependence of the UCST for different molecular weight combinations. We make use of the Born−Green−Yvon integral equation theory to exploit the connection between the pressure dependence of the UCST and the sign of the volume change on mixing, leading us to predict that through judicious choice of polymer molecular weights the response of the UCST to pressure may be controlled.

1. Introduction

To those interested in using statistical thermodynamics to analyze and understand experimental data, the area of polymer blend miscibility has continued to present challenges. Contributions to both the entropy and enthalpy of mixing are small, and therefore variables that might not play an important role in the case of small molecule analogues can have a strong effect on the ability of polymers to mix. An example is the role of pressure, which has been of recent interest in the literature[1−8] and which is relevant with respect to processing of polymer blends. In the past most multicomponent polymer systems were considered to be immiscible. However, there are now numerous examples of both blends that phase-separate upon lowering the temperature (thereby exhibiting an upper critical solution temperature, or UCST) and those that phase-separate upon raising the temperature (showing a lower critical solution temperature, or LCST). The effect of pressure on an LCST system is well-understood:[9] the LSCT increases with pressure, and so does the blend miscibility. However, for a UCST mixture the situation is more complicated and therefore more interesting. In essence, given that a UCST blend is an endothermic mixture (the enthalpy of mixing is positive), the pressure dependence of the critical temperature can be directly correlated with the sign of the volume change on mixing.[9] This correlation is merely a property of the bulk thermodynamics of a compressible mixture; to make use of it in understanding the statistical thermodynamics of polymeric systems, both experimental data and a statistical mechanical theory are needed.

The Born−Green−Yvon (BGY) lattice theory is an integral equation technique which has been applied to the study of alkane mixtures, polyethylene (PE) solutions, and polyolefin blends.[10] With respect to the scope of this paper, two of the previous applications are of particular interest: In a study of *n*-alkane mixtures,[10a] the BGY equation of state was fit to thermodynamic data for the pure *n*-alkane fluids in order to obtain their characteristic parameters. Then, using a simple combining rule (i.e., not fitting any mixture data), the theory generated predictions about numerous properties of the mixture, including the total vapor pressure, the pressure−volume−temperature (*PVT*) surface, and the volume change on mixing. The BGY theory was very successful in predicting mixture properties, and in particular, the predictions were in excellent agreement with experimental data for the pressure dependence of the volume change of mixing over a range of 200 MPa. The other study of interest involved polyolefin blends,[10b] wherein two of the experimental blends that were studied exhibited a UCST: polyethylene (PE) blended with an ethylene−propylene copolymer (PEP) and the PEP copolymer blended with head-to-head polypropylene (hhPP). In this study the BGY equation of state was again used in conjunction with *PVT* data for the pure polymers, along with a slightly more complicated mixing rule (more details to be given in section 2) in order to make predictions about the effects on miscibility of changing pressure, temperature, and component molecular weights. The work presented in the current paper represents application of the BGY theory to systems that combine the sets of variables referred to in these two studies.

The results outlined in this work are divided into two sections: The first set focuses on the PE/PEP and PEP/hhPP polyolefin blends. While we generated testable predictions (for the PEP/hhPP blend, in particular), we were limited by the absence of experimental data on the pressure dependence of miscibility. Hence, we turned to previously unpublished data on polystyrene (PS) and polybutadiene (PB) blends.[11] For this study we have the advantage of using a consistent set of results from one experimental lab over a pressure range of 100 MPa and a series of component molecular weights.

As a result of this work we predict that, at least for some UCST blends, it should be possible to manipulate the component molecular weights so as to control the sign of the volume change on mixing, thereby affecting

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Table 1. Pure Component and Blend Parameters

polymer	ϵ (J/mol)	r	v (L/mol)	MW (g/mol)
hdPE	−1977.5	1969.4	0.007496	23560[a,10b]
PEP	−2000.0	2464.4	0.007504	29450[a,10b]
hhPP	−2027.8	14040.0	0.009724	171780[a,10b]
PS	−2062.0	1180.0	0.006615	9000[14]
PB	−1988.3	347.9	0.009007	3000[14]

blend	v (L/mol)	g	notes
PE/PEP	0.013	0.999560	see ref 10b
PEP/hhPP	0.013	0.999925	see ref 10b
PS/PB[b]	0.009007	0.9952	using exptl UCST value for PS(1200)/ PB(2350)

[a] These were the MW values used in the experimental blend studies.[10b] For other values of MW the value of r is obtained as $r_2 = r_1(\mathrm{MW}_2/\mathrm{MW}_1)$. [b] The following molecular weight combinations (PS/PB) were used in the experimental studies: (3900/920), (1200/2350).

the pressure dependence of the critical temperature. In fact, in such cases there lies the additional possibility that, by judicious choice of component molecular weights, a blend can be formulated whose UCST is impervious to changes in the pressure.

The work of this paper is organized as follows: In section 2, we provide a brief description of the theoretical and experimental background. In section 3, we focus on two polyolefin blends and make a connection between the pressure dependence of the UCST and the molecular weight of the blend components. In section 4, we pursue this connection by combining experimental data and theoretical analysis of the PS/PB blend. Finally, in section 5, we summarize our results and draw conclusions.

2. Experimental and Theoretical Background

Experiment. Details regarding the polyethylene (PE), ethylene−propylene copolymer (PEP), and head-to-head polypropylene (hhPP), as well as the experiments on their blends, are described in refs 12 and 13. The characteristic parameters for the polymer fluids and the PE/PEP and PEP/hhPP blends are given in Table 1.

Table 1 also includes characteristic parameters for PS and PB, which were obtained by fitting *PVT* data tabulated in Zoller and Walsh's reference book.[14] The measurements on PS/PB blends were carried out at Imperial College, where an apparatus was set up to measure the effects of changing pressure on polymer compatibility over the range of 0.1−100 MPa up to a temperature of 423 K. The apparatus comprised a pressure reactor containing a sample holder mounted on an adjustable platform to regulate the position of the sample holder so as to view the sample through a sapphire window. The pressure vessel was mounted in a thermostatic bath, fitted with controlled cooling, heating, and mechanical stirring devices. The samples were held in Pyrex tubes inverted into a mercury bath which acted as a pressure-transmitting material. The homogeneity of the sample was ensured by the inclusion of a magnetic stirrer. The sample temperature was accurate to ±0.1 °C, and the cloud points were determined at a heating rate of 1 °C/h to an accuracy of ±0.5 °C.[11]

Theory. In this work we apply the polymer Born−Green−Yvon (BGY) theory[15] to the case of a three-dimensional lattice model, fixing the lattice coordination number, z, at a value of six (representing the simple cubic lattice). The volume of the lattice is $V = v(N_0/N_A)$, where N_0 is the total number of lattice sites, N_A is Avogadro's number, and v is the volume per mole of lattice sites. A molecule of species i is assumed to occupy r_i contiguous sites. The site fractions ϕ_i, ϕ_h, and ϕ are defined as $\phi_i = r_iN_i/N_0$, $\phi_h = N_h/N_0$, and $\phi = 1 - \phi_h$, where N_i is the number of molecules of component i and N_h is the number of empty sites or holes. Each molecule of species i has $q_iz = r_i(z - 2) + 2$ interaction sites, leading to the definition of concentration variables $\xi_i = q_iN_i/(N_h + \sum_j q_jN_j)$ and $\xi_h = N_h/(N_h + \sum_j q_jN_j)$ which account for the nearest-neighbor connectivity of the molecules. The interaction energy associated with nonbonded nearest neighbors of the same species is ϵ_{ii}, while ϵ_{ij} corresponds to interactions between unlike nearest neighbor segments. The Born−Green−Yvon integral equation hierarchy links distribution functions of successively higher order. By closing the hierarchy at the level of pairwise interactions using the Kirkwood superposition approximation and then assuming pair independence for all but the particular pair of interest, Lipson[15] was able to derive simple expressions for the probabilities of the different types of nearest neighbor contacts. Summing the product of these probabilities times the relevant energetic contributions, ϵ_{ii} or ϵ_{ij}, yielded a closed-form expression for the internal energy of the lattice mixture. Chain connectivity is accounted for through the site fractions, ξ,[16] and the three parameters ϵ r, and v completely characterize each component. For multicomponent systems there will also be energetic contributions arising from mixed-component interactions, and these are characterized by the ϵ_{ij} terms. It is useful to note that we do not use a literal mapping of the structure of each polymeric repeat unit onto the lattice, as is done in lattice cluster theory,[17] and therefore the values of these parameters reflect both the chemical and the structural nature of each fluid in the system. In addition, at finite pressures (i.e., all experimentally realizable pressures) the system is compressible, and therefore all of the energetic parameters will contribute. The temperature dependence of the internal energy is used to obtain an analytic expression for the free energy via a Gibbs−Helmholtz relationship. This requires an approximation for the entropy of the system at infinite temperature, and for this we use Guggenheim's result.[18] Of course, it is only at infinite temperatures that the system is considered to be randomly mixed; at finite temperatures nonrandom contributions to the entropy play a role, and these arise out of the BGY theory itself. The BGY result for the dimensionless configurational Helmholtz free energy per lattice site, $\hat{a}$, of a K-component mixture is given by

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

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

$$A/VT = k_B\hat{a}/v + a_0 \quad (2)$$

where a_0 is a caloric background not needed in this work. All thermodynamic properties of a mixture can now be derived from the thermodynamic relation

$$\mathrm{d}(A/VT) = (U/V)\,\mathrm{d}(1/T) + \sum_{j=1}^{K}(\mu_j/T)\,\mathrm{d}(\rho_j) \qquad (3)$$

where U is the internal energy of the system, and where $\rho_j = N_j/V = \phi_j/r_jv$ and μ_j are the number density and chemical potential of component j, respectively. The pressure P and the chemical potentials μ_i, for example, are given by

$$P = -\frac{1}{\beta v}\left[\hat{a} - \sum_{j=1}^{K}\phi_j\left(\frac{\partial\hat{a}}{\partial\phi_j}\right)_{\beta,\phi_{k\neq j}}\right], \quad \mu_i = \frac{r_i}{\beta}\left(\frac{\partial\hat{a}}{\partial\phi_i}\right)_{\beta,\phi_{k\neq i}} \qquad (4)$$

Phase transitions in binary blends are conveniently discussed in terms of the total molar density $\rho = \rho_1 + \rho_2$ and the mole fraction $x = \rho_2/\rho$. The thermodynamic field conjugate to the mole fraction x is the difference of the chemical potentials $\mu = \mu_2 - \mu_1$. In terms of these variables, the conditions for a point T_c, P_c, x_c on the critical line of a binary mixture are[9]

$$\left(\frac{\partial\mu}{\partial x}\right)_{T,P} = 0, \quad \left(\frac{\partial^2\mu}{\partial x^2}\right)_{T,P} = 0 \qquad (5)$$

The first of the two equations defines the spinodal while the second one implies that, for a given pressure, the critical point is an extremum of the spinodal in the $T-x$ plane. Hence, lower and upper critical solution temperatures (LCST's and UCST's) correspond to the minimum and maximum of their spinodals, respectively. For temperatures $T <$ UCST or $T >$ LCST, the mixture can separate into two phases of different mole fractions x_{I} and x_{II}. For a given pressure P, the coexisting phases satisfy

$$\mu(T,P,x_{\mathrm{I}}) = \mu(T,P,x_{\mathrm{II}}), \quad \mu_1(T,P,x_{\mathrm{I}}) = \mu_1(T,P,x_{\mathrm{II}}) \qquad (6)$$

The mass fraction c of component 2 is given by

$$c = M_2x/(M_2x + M_1(1-x)) \qquad (7)$$

where M_1 and M_2 are the molar masses of component 1 and 2, respectively. When the BGY lattice model is applied to binary mixtures, eqs 1−4 are evaluated with $K = 2$. The total molar density $\rho = \rho_1 + \rho_2$ and the mole fraction $x = r_2/r$ of the mixture are related to the site fractions ϕ_1 and ϕ_2 by

$$\rho = \frac{1}{v}\left(\frac{\phi_1}{r_1} + \frac{\phi_2}{r_2}\right), \quad \frac{1}{x} = 1 + \frac{\varphi_1}{r_1}\frac{r_2}{\varphi_2} \qquad (8)$$

In addition to the system-dependent parameters r_1, r_2, v, $\epsilon_{11} = \epsilon_1$, and $\epsilon_{22} = \epsilon_2$ which are determined from a comparison with experimental *PVT* data, a value is required for the strength of the mixed interaction ϵ_{12}. In earlier work[10a] on phase coexistence in mixtures of n-alkanes and solutions of polyethylene (PE) in n-alkanes, we found that Berthelot's geometric-mean combining rule, $\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}$, yielded good results. In this work, we represent the mixed interaction, ϵ_{12}, as

$$\epsilon_{12} = g(\epsilon_{11}\epsilon_{22})^{1/2} \qquad (9)$$

The g-factor introduced here thus describes an effective mixed interaction parameter. In previous work[10b] we used exact enumerations in order to predict g values for polyolefin blends, thus allowing us to predict phase diagrams of the blends from pure component properties alone. Here we follow the more common approach of using an experimentally determined result for the UCST in order to determine the value of g.

Given that we have a route to the equilibrium properties of the mixture, we wish to explore the connection between the pressure dependence of the UCST and the volume change on mixing. It can be shown[9] using conventional thermodynamic reasoning that

$$(\partial(\mathrm{UCST})/\partial P)_\phi = T\Delta V_{\mathrm{mix}}/\Delta H_{\mathrm{mix}} \qquad (10)$$

where ΔV_{mix} and ΔH_{mix} are respectively the volume and enthalpy change on mixing. Given that all of these UCST blends exhibit endothermic mixing, the temperature dependence of the UCST is therefore governed by the sign of the volume change on mixing.

3. Two Polyolefin Blends

In the late 1990s, experimental miscibility data appeared[12,13] for a collection of well-defined polyolefin blends. This provided an opportunity for theoretical analysis of a series of polymer mixtures which incorporated closely related components. Some of these mixtures exhibited UCSTs and some LCSTs. Application of the BGY theory to the study of some of blends from this collection[10b] illustrated the ability of this approach to capture and explore the dependence of miscibility on molecular weight, pressure, and local structure. Here we pursue implications from the theory that the effects of pressure and molecular weight may be correlated in some UCST blends. Details regarding the molecular weights of the polymers and the characteristic parameters of the pure fluids, as well as of the mixtures, are given in Table 1.

Our initial expectation was that any experimentally studied UCST blend would exhibit a positive volume change on mixing, and thus its critical temperature would increase with pressure. It was therefore a surprise to find that, of the two UCST polyolefin blends previously studied, one was predicted by the BGY analysis to have positive volume change on mixing and the other a negative volume change upon mixing. Figure 1a shows the results for the PE/PEP blend. The BGY predictions for the volume change on mixing ΔV_{mix} as a function of composition are shown for three temperatures, ranging from 420 to 520 K. ΔV_{mix} is positive, increasing with temperature; the symmetry of the curves about a mole fraction PEP of roughly 0.55 is associated with the fact that the two components have very similar molecular weights. The magnitude of ΔV_{mix} translates to roughly on the order of 10^{-5} mL/g for this blend. According to the analysis presented in section 2, the positive ΔV_{mix} implies that the UCST should increase with pressure, which is confirmed by the results shown in Figure 1b. The experimental UCST is 421 at 0.1 MPa (essentially at the ordinate of the plot), and the points in the plot are the BGY predictions, extending over a pressure range of 100 MPa; the curve is included as a visual guide. In Figure 2 we present analagous results for the PEP/hhPP blend. This time, however, the BGY theory predicts that the volume change on mixing will be negative and decrease as the temperature

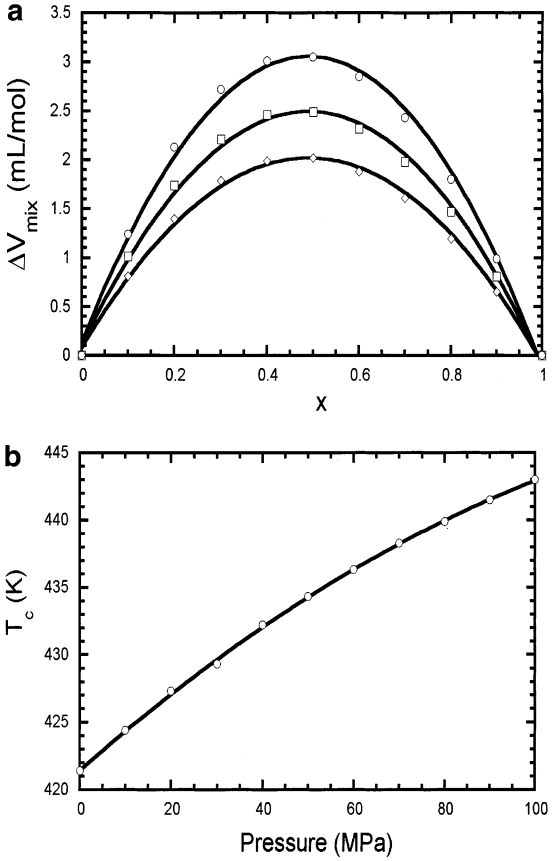

Figure 1. Results for the PE/PEP blend: (a) ΔV_{mix} as a function of mole fraction PEP for (from top to bottom) $T = 520$, 470, and 420 K. The symbols represent the BGY predictions; the lines have been added as a visual aid. (b) BGY prediction for the UCST as a function of pressure; the point at 0.1 MPa is the experimental result,[12] which was used in fitting for the mixed interaction energy.

increases. The corresponding set of predictions for the pressure dependence of the UCST is illustrated in Figure 2b which shows, as expected from the arguments outline above, that the critical temperature should decrease with increasing pressure. Note that the amount by which the UCST changes over a pressure range of 100 MPa is less for the PEP/hhPP blend than for the PE/PEP blend, which is understandable given the slightly smaller values of ΔV_{mix}.

For a blend to exhibit partial miscibility, as opposed to complete miscibility or immiscibility, it is reasonable to expect that $\Delta\epsilon = 2\epsilon_{12} - (\epsilon_{11} + \epsilon_{22})$ values will be relatively small. This leads us to speculate that the prediction for the sign change of ΔV_{mix} might be extremely sensitive to the fits for ϵ_{11}, ϵ_{12}, and ϵ_{12}. To test this, we calculated ΔV_{mix} as a function of temperature for $x = 0.5$ for each of the two blends, keeping the pure component parameter values constant but varying ϵ_{12} so as to change $\Delta\epsilon$. The results are shown in Figure 3a for PE/PEP and in Figure 3b for PEP/hhPP. In both cases increasing ϵ_{12}, therefore $\Delta\epsilon$, by too much yielded an immiscible system; for the PE/PEP blend the experimentally determined $\Delta\epsilon$ value of 1.81 J/mol was close to the maximum possible in order for the blend to be even partially miscible. For $\Delta\epsilon$ values of less than 0.4 J/mol ΔV_{mix} became negative. For the PEP/hhPP blend increasing $\Delta\epsilon_{12}$ from the experimentally determined value of roughly 0.398 to a value of 0.70 J/mol or higher results in a positive volume change on mixing. The different appearance of the two collection of curves was noticeable. In particular, for the PE/PEP plot using the experimentally determined value of $\Delta\epsilon$ the theory predicts a positive ΔV_{mix}, increasing with T. On the other hand, for the PEP/hhPP plot, using the experimentally determined value of $\Delta\epsilon$ the theory predicts that ΔV_{mix} will be negative, decreasing as T increases. In correlating the difference in behavior with differences in parameter values, it is important to recall that the UCST values also differ. Therefore, it makes sense to consider the ratio $\Delta\epsilon/RT_{\mathrm{c}}$, where T_{c} is the UCST of the blend. For the experimental PE/PEP blend studied, this ratio has a value of 5.2×10^{-4}, while for the PEP/hhPP blend the value is 1.4×10^{-4}. Might this factor of 4 difference affect the curvature, and even the values, of the ΔV_{mix} results?

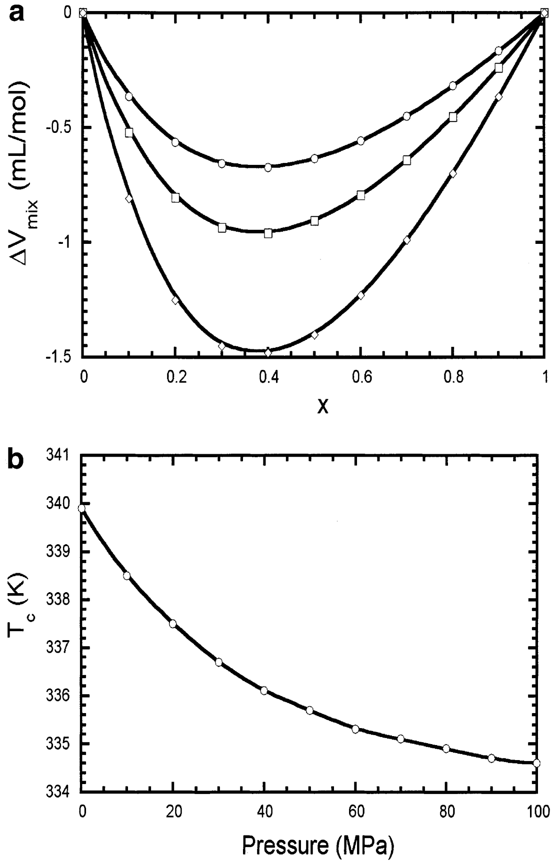

Figure 2. Results for the PEP/hhPP blend: As described in Figure 1, except (a) the abscissa is mole fraction of hhPP and the temperatures are (from bottom to top) 440, 390, and 340 K. The experimental UCST at 0.1 MPa in (b) is from ref 13.

To test this, we decided to produce an extended version of Figure 3a, taking the calculations for PE/PEP out to a temperature which would be high enough so that, were the critical temperature that high, the ratio $\Delta\epsilon/RT_{\mathrm{c}}$ would be approaching the value for the PEP/hhPP blend. The results are shown in Figure 4, which illustrates that, indeed, the behavior of the PE/PEP curves can shift from that associated with Figure 3a (curves include those which show a positive ΔV_{mix}, increasing with T) to that associated with Figure 3b (ΔV_{mix} values are mainly less than zero, decreasing as T increases). Looking back to Figure 1a, we chose to investigate the behavior of ΔV_{mix} in the temperature region between 420 and 520 K because that range was relevant to the experimental UCST. Under what circumstances would the higher temperature region shown in Figure 4 be relevant? Figure 5 shows how the UCST

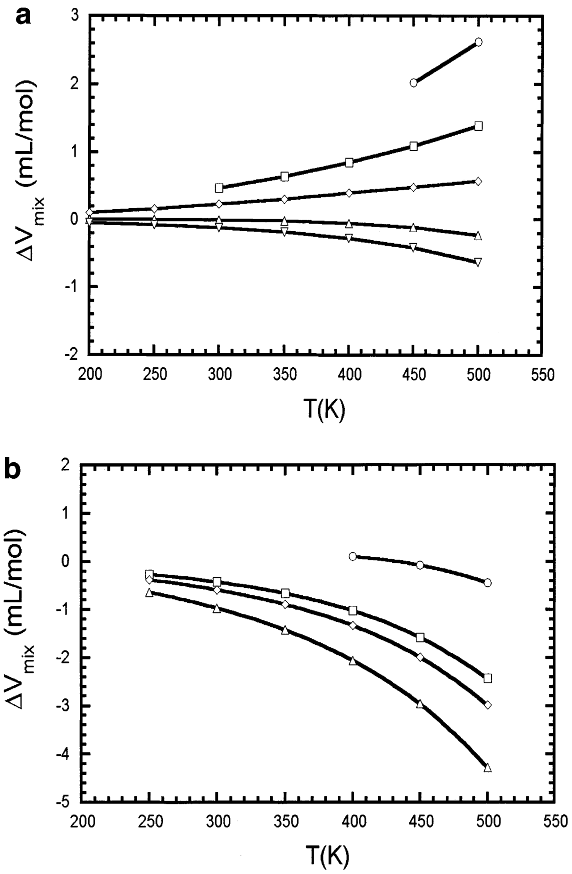

Figure 3. ΔV_{mix} as a function of temperature for $x = 0.5$ and $P = 0.1$ MPa (a) PE/PEP blend with $\Delta\epsilon$ (J/mol) equal to (from top to bottom) 1.81 (using g from experimental fit), 1.20, 0.80, 0.40, and 0.20. (b) PEP/hhPP blend with $\Delta\epsilon$ (J/mol) equal to (from top to bottom) 0.70, 0.40 (using g from the experimental fit), 0.30, and 0.10. Symbols represent BGY predictions; curves are added as a visual aid.

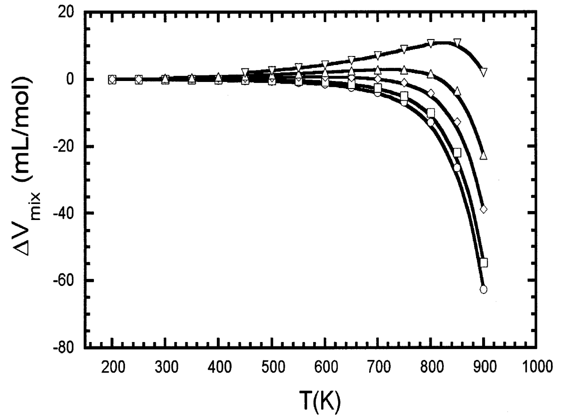

Figure 4. ΔV_{mix} of PE/PEP blend, with $x = 0.5$ and $P = 0.1$ MPa. From top to bottom values of $\Delta\epsilon$ (J/mol) are 1.81 (using g from experimental fit), 1.20, 0.80, 0.40, and 0.20. Symbols represent BGY predictions; curves are added as a visual aid.

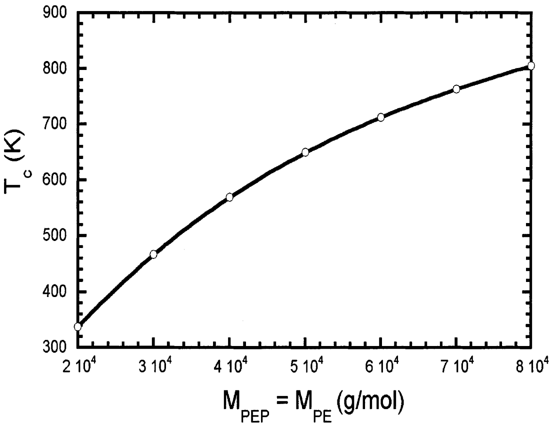

Figure 5. UCST as a function of molecular weight for PE/PEP blend with $M_{PE} = M_{PEP}$. Symbols represent BGY predictions; curves are added as a visual aid.

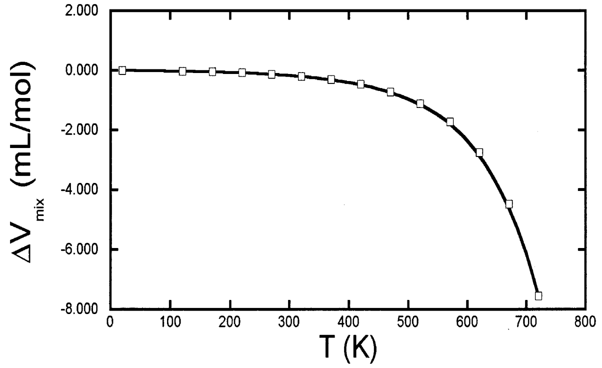

Figure 6. ΔV_{mix} as a function of T for PEP(38 850)/hhPP(35 482); $x = 0.5$ and $P = 0.1$ MPa. Symbols represent BGY predictions; curves are added as a visual aid.

of the PE/PEP blend is expected to increase with the molecular weight of the components; here we set the molecular weight of the PE equal to that of the PEP for the purposes of simplicity, since the two values in the experimental blend were not very different. Recall that the experimental UCST for the blend, yielding an $\Delta\epsilon/RT_c$ value of 5.2×10^{-4}, is associated with an average molecular weight of 27 000 g/mol. From Figure 4 we see that a critical temperature of over 900 K would be needed to pull all of the curves down so that ΔV_{mix} values are negative. Figure 5 shows that such a critical temperature would likely require component molecular weights of over 10^5 g/mol.

The BGY theory predicts that by increasing the molecular weights of the PE/PEP components this UCST blend should shift from one whose critical temperature increases to one whose critical temperature decreases with increasing pressure. The predicted molecular weights needed for the PE/PEP blend to exhibit negative volume changes on mixing are experimentally accessible; however, the temperatures required are unrealistically high. Thus, we turn to the experimental PEP/hhPP blend, for which the theory predicts a negative volume change on mixing and a UCST which decreases with increasing pressure. If the same pattern of behaviour is obeyed for this blend as for the PE/PEP blend, it should be possible to shift from a negative to a positive volume change on mixing by *decreasing* the molecular weights of the components, thereby working at lower UCST values, thus a larger value for $\Delta\epsilon/RT_c$. Perhaps an even more intriguing possibility is that, by judicious choice of molecular weights, one can formulate a blend such that $\Delta V_{mix} = 0$ and whose critical temperature would be impervious to pressure changes. Figure 6 shows ΔV_{mix} plotted against temperature for the PEP(38 850)/hhPP(35 482) blend. The UCST for this blend is 44 K, and at that temperature (and for at least 100 K above) the volume changes on mixing are essentially zero (on the order of 10^{-2} mL/mol, well below the capability of experimental detection). This blend is therefore predicted to exhibit pressure-independent behavior in the region of its UCST.

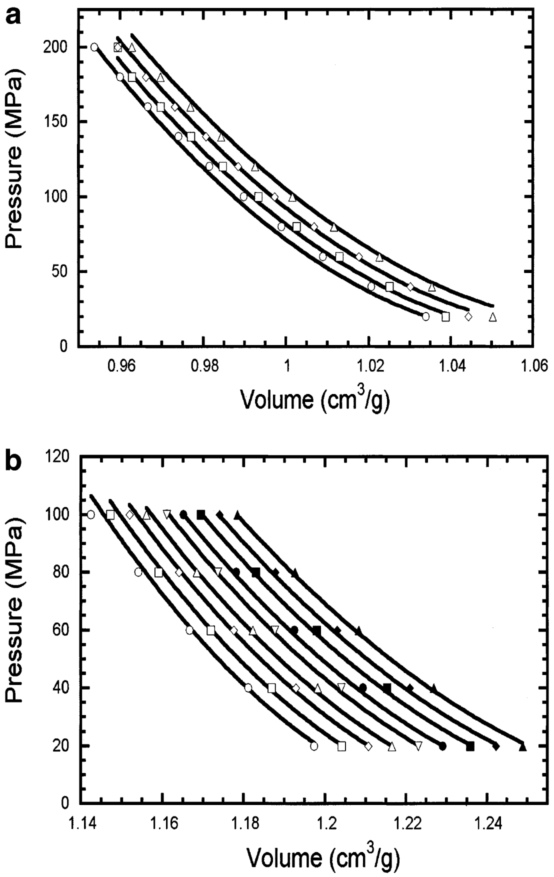

Figure 7. Pressure as a function of volume for (a) PS(9000) at temperatures $T = 503.4$, 492.4, 482.3, and 473.3 K and (b) PB(3000) at temperatures $T = 471.2$, 462.9, 455.1, 446.4, 439.3, 430.7, 423.3, 414.8, and 406.6 K. The symbols represent experimental data points,[14] and the curves represent the BGY fit.

Note that, with the exception of the experimentally determined UCST values for $P = 0.1$ MPa, all of the results from this section are theoretical predictions: the volume changes on mixing, the effects of changing pressure, and the effects of changing molecular weight. Next, we turn to studies on a blend of polystyrene and polybutadiene, for which more experimental data are available.

4. Polystyrene/Polybutadiene

The appeal of this blend lay in the availability of experimental data[11] for the pressure dependence of the coexistence curve over a range of 100 MPa. In addition, *PVT* data were readily available for both PS and PB,[14] allowing us to fit for the pure component parameters using eq 4. The results for PS and PB in Table 1 were based on a fit to experimental PS data for molecular weight 9000 g/mol and PB data for molecular weight 3000 g/mol. The BGY fits (curves) to the experimental data (symbols) are illustrated in Figure 7, which shows pressure plotted against volume for a series of temperatures. The molecular weights used in the Higgins and Tripathi study were 1200, 1520, and 3900 g/mol for the PS and 920 and 2350 g/mol for the PB. The fact that the molecular weights were relatively low did present a challenge, in that we expect the *PVT* surface may be somewhat molecular-weight-dependent for oligomeric systems. This was also a concern in obtaining the PS parameters, since we had to choose between using a data set for PS of 900 or 9000 g/mol, neither of which was ideal. We chose the 9000 g/mol data because it was analogous to the PB data in being beyond the oligomeric range.

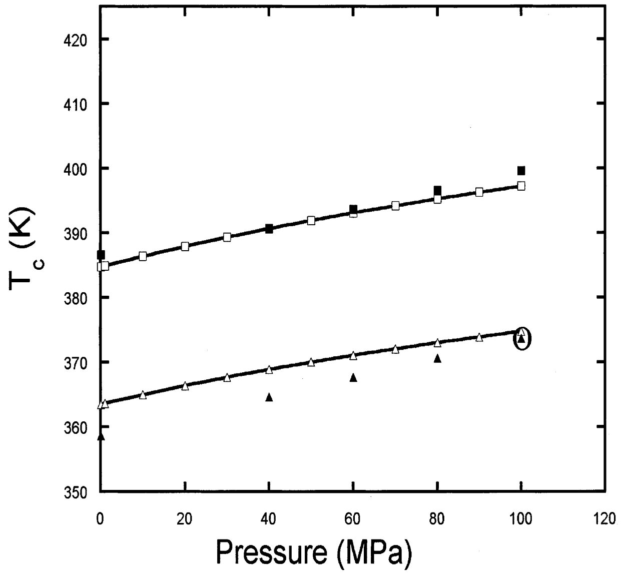

Figure 8. UCST as a function of pressure for (upper curve) PS(3900)/PB(920) and (lower curve) PS(1200)/PB(2350). Black symbols represent experimental data,[11] open symbols are BGY predictions, and the dashed line has been added as a visual aid. The experimental point at $P = 100$ MPa on the lower plot was used in fitting for the g value.

The value of g was fit to reproduce one experimental datum point: the UCST of a PS(1200)/PB(2350) blend at 100 MPa. We chose to fit the UCST at 100 MPa; however, equivalent results were obtained by fitting the UCST at 0.1 MPa. Figure 8 compares the BGY predictions (open symbols) for the blend UCST as a function of pressure with the experimental data (filled symbols); the lines are included as a visual guide. The upper plot is for a PS(3900)/PB(920) blend, while the lower is for the PS(1200)/PB(2350) blend. The experimental datum point used for the fit is circled in the latter plot. The BGY predictions are in good to excellent agreement with the experimental results over the whole pressure range. Note that for both molecular weight blends the UCST is increasing as a function of pressure. One would therefore expect that the volume change on mixing should be positive, and this is indeed what the BGY theory predicts, as shown in Figure 9a. Here, ΔV_{mix} is plotted for the PS(3900)/PB(920) blend over a large temperature range, and one can see at a glance the similarity to Figure 4 for the PE/PEP blend. In Figure 9a for the region of temperature associated with the PS/PB UCST the volume change on mixing is small and positive. For this molecular weight combination the sign of ΔV_{mix} does not become negative until temperatures close to 800 K are reached, which is not experimentally practical. However, the results for the polyolefins suggest that the difference between the UCST and the temperature at which ΔV_{mix} changes sign can be manipulated by changing the molecular weight of the components. Figure 9b illustrates the BGY predictions for the molecular weight dependence of ΔV_{mix} as a function of the molecular weight of PB for blends with PS(3900); the UCST for the PB(950) blend is 390 K. The lower curve shows the PB molecular weight dependence of ΔV_{mix} at a fixed temperature of 400 K, which would be below the UCST for molecular weights greater than PB(1500). The upper curve shows the molecular weight

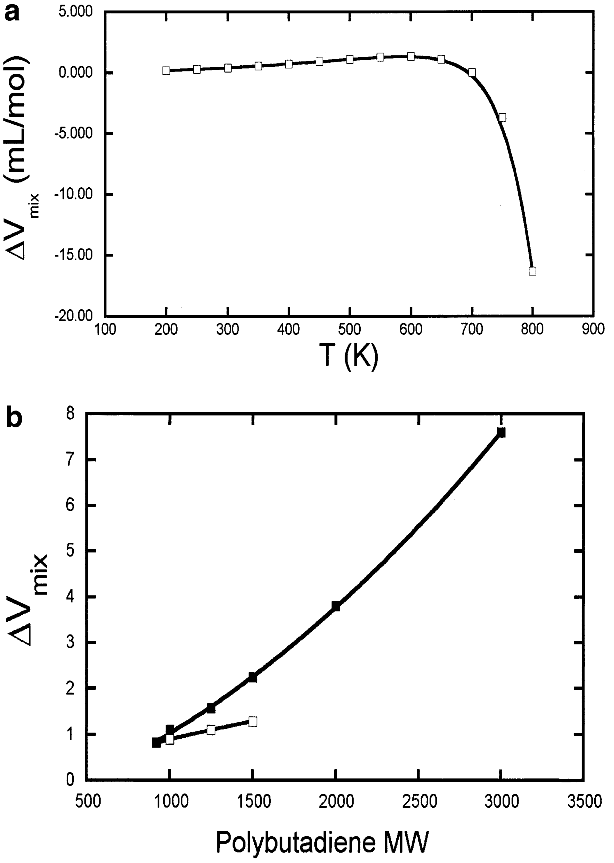

Figure 9. (a) ΔV_{mix} as a function of T for the PS(3900)/PB(920) blend. Symbols represent BGY predictions, and the curve is a visual aid. (b) ΔV as a function of PB MW with PS(3900). The open symbols represent predictions at $T = 400$ K, and the filled symbols at $T = \mathrm{UCST} + 10$ K.

dependence of ΔV_{mix} such that the calculations are done at a temperature which is 10 deg higher than the UCST of the blend. As the plots show, the theory predicts a noticeable molecular weight dependence to the volume change on mixing.

In Figure 10a we illustrate the predicted approach of the UCST to the changeover temperature for ΔV_{mix} as the molecular weight of PS is changed while that of PB remains fixed. Two examples of PB molecular weight have been used, and for each case there are two curves; the bottom (dashed) curve in each set shows the effect of increasing the PS molecular weight on the UCST, while the top curve in each pair shows the effect on the changeover temperature for ΔV_{mix}. The idea behind this plot is to find a molecular weight combination which will yield a crossing of the curves at a temperature that is experimentally realizable. The results in this figure, which are all for a pressure of 0.1 MPa, show the PS molecular weight changing between 4000 and 20 000 g/mol, while the two PB samples are 3000 (top) and 2000 g/mol (bottom). Clearly, the relevant temperature range decreases with the PB molecular weight. However, for lower PB molecular weights higher PS molecular weights are needed in order to achieve a UCST which approaches the changeover temperature for ΔV_{mix}. In addition, going to an extremely low PB molecular weight means that the sample is really an oligomer, not a polymer. Using the results in Figure 10a as a guide, we have found that working with slightly lower molecular weight PB samples, and much higher molecular weight PS samples puts us in the desired region, which is shown in Figure 10b. The three sets of plots are for PB samples of 1000 (upper set), 950 (middle set), and 900 g/mol (lower set). The PS molecular weight range is considerably higher ($5.0 \times 10^5 - 2.5 \times 10^6$) although still experimentally accessible. Using PB(1000), the temperature at which the two curves cross is still too high. However, for the PB(950) sample blended with PS(8.0×10^5) the theory predicts the two curves to meet at a temperature of 653 K.[19] This implies that for such a molecular weight combination the UCST should show no pressure dependence. Further, for a PS molecular weight of 1.5×10^6 the theory predicts that the UCST is 663 K, while the crossover temperature for ΔV_{mix} is below the UCST at 654 K, with the separation between the two increasing fairly rapidly for further increases in PS molecular weight.

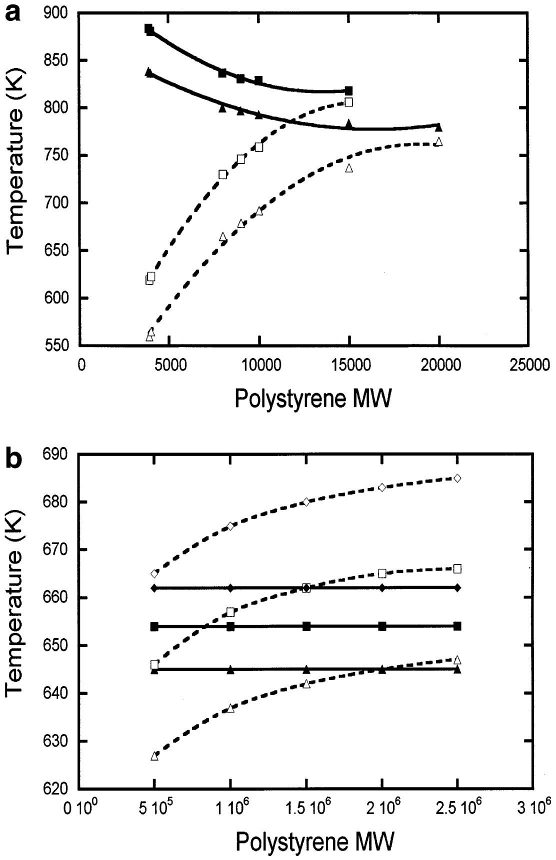

Figure 10. Illustration of the relative approach of the PS/PB blend UCST to the "crossover" temperature, at which ΔV_{mix} for the blend changes from positive to negative; in all cases $P = 0.1$ MPa. For each *pair* of plots, associated with a fixed molecular weight of PB, the solid line represents the change in crossover temperature for ΔV_{mix} and the dashed line represents the UCST. (a) Molecular weight (g/mol) of PB is 3000 (squares) and 2000 (triangles). (b) Molecular weight (g/mol) of PB is 1000 (diamonds), 950 (squares), and 900 (triangles).

5. Summary and Conclusions

In this paper we predict that for some UCST polymer blends the response of the blend miscibility to pressure may be manipulated through choice of the molecular weights of the two components. There is precedent in the case of polystyrene/cyclohexane solutions for finding that the sign of the volume change on mixing may shift with an increase in the polymer molecular weight.[20] However, that is an LCST polymer solution, and here we are making predictions for UCST blends.

For the two polyolefin blends studied, PE/PEP and PEP/hhPP, we used the fit parameters obtained previously from data on the pure fluids and on experimentally studied blends to make predictions for the volume changes on mixing and the change in UCST with respect to pressure. The theory indicates that the volume change on mixing for each of these two blends is small (but should be measurable) and positive for the PE/PEP blend and negative for the PEP/hhPP blend. This implies that the UCST should increase with pressure for the former and decrease as pressure increases for the latter. The theory also suggest that the sign of the volume change on mixing for a UCST blend may be induced to change by altering the molecular weights of the blend components. This leads us to suggest that, for such a system, experimental conditions may be manipulated so as to create a blend whose UCST is impervious to pressure. In fact, we have used the theory to predict that a PEP(38 850)/hhPP(35 482) blend should exhibit a pressure-independent UCST.

We further applied these ideas to the study of a PS/PB blend, making use of unpublished coexistence data for a series of component molecular weights, over a pressure range of 100 MPa. We made use of one experimental datum point, for a single choice of molecular weights at a pressure of 100 MPa, to fit for the mixed-interaction parameter. Subsequently, we used the BGY theory to capture the experimental miscibility trends over a range of pressures and molecular weights. In predicting ΔV_{mix} as a function of temperature we found, as expected from the pressure dependence of the UCST, that the values were positive. However, we also discovered that the extended-temperature plot bore a striking similarity to that of the PE/PEP blend. We therefore explored the possibility that it might be possible to manipulate the PS and PB molecular weights in order to produce a blend showing a crossover temperature for the sign of ΔV_{mix} which would be lower than the UCST. We determined that a blend of PS(8×10^5)/PB(950) should exhibit a pressure-independent UCST at 653 K, while for a blend using PS(1×10^6) the crossover temperature is expected to be at 654 K, 3 deg below the UCST.

Our goal in this paper was to apply the leads we discovered in studying the polyolefin results to the case of a more accessible blend. We have made testable predictions on two polymer blends, although we note here that the studies suggested on the PS/PB blend would still represent an experimental challenge. An additional challenge remains for us, which is to determine whether the intriguing possibilities outlined here may be observed for other UCST polymer blends under more mundane molecular weight and temperature conditions.

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