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Pressure Effects on the Thermodynamics of Polymer Blends

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ABSTRACT: Simple thermodynamic arguments are evoked to show that the pressure dependence of the Flory interaction parameter of miscible polymer blends, as derived from small-angle neutron scattering experiments, is directly related to the volume changes on mixing for these systems. This approach is validated by comparison to available experimental data. We make contact with existing theoretical approaches and show that it is thermodynamically inconsistent to model a blend with nonzero χ as having no volume change on mixing. Since the entropic contributions that arise from these volume changes on mixing account for more than 50% of the pressure dependence of χ, the use of regular solution theory, where the pressure dependence is purely enthalpic in origin, gives an imperfect understanding of these situations. We finally show that, since the volume change on mixing is directly proportional to the χ parameter under ambient pressures, the critical temperature for any polymer blend will vary in an apparently “universal” fashion on pressurization. This conclusion is in agreement with experimental data for a large number of polymer blends.

Introduction

The role of pressure on the thermodynamics of polymer mixtures has been intensely studied in the past few years since it has direct applications to processing and to novel synthesis schemes involving environmentally benign supercritical fluids. Pressure effects are also of interest from a fundamental standpoint since the thermodynamics of typical polymer blends are understood in the framework of the incompressible random phase approximation.[1−6] A rigorously incompressible system should be unaffected by pressure. However, since experimental results show that the critical temperature for polymer−polymer demixing, T_c, is strongly affected by pressure, typically $dT_c/dP \approx 25-50$ K/kbar, it is clear that polymer blends show significant departures from this ideal limit.[5,7] Most successful approaches in this area incorporate free volume effects, either into the free energy of the system or into an equation of state. The pressure dependence of T_c and χ, the Flory−Huggins interaction parameter, is then numerically derived.[7−14] While these methods have been quite successful at explaining the measured dT_c/dP, they provide little physical insight into the effect of pressure.

A line of thinking that helps build a picture at the molecular level for the effect of pressure on polymer blend thermodynamics is presented by Rabeony et al.[6] Here it is postulated that the central quantity is the interaction energy density, $X \equiv (\chi/v_0)RT$. χ is the Flory interaction parameter,[15] v_0 is an arbitrary reference volume, R is the gas constant, and T is the temperature. The X values obtained from some of the blends considered appear to be unique functions of system density, and data from several pressures and temperatures for each of these systems can be collapsed onto a master curve. Since this approach explicitly assumes that volume changes on mixing are negligible, it suggests that the only role of pressure is to modify the energetics [i.e., the cohesive energy density] of the two *pure* polymers, in a manner that is describable by a corresponding states principle.

These results, however, are in disagreement with the fact that the pressure-induced shift in critical temperature for the phase separation of a polymer blend correlates with the volume change on mixing.[5,7] Similar results have been found for the role of pressure on the order−disorder transition of block copolymers.[2] Further, since volume changes on mixing can affect both the energetics and entropy of a system, the purely enthalpic ideas embodied in the regular solution approach discussed above could be inadequate to describe the role of pressure on system thermodynamics. We have shown recently that, under atmospheric pressure conditions, compressibility and volume changes on mixing for typical polymer blends played such a small role that the small-angle neutron scattering from these systems were affected by less than 1%.[16] Since the typical uncertainties in these experiments is ≈5%, it is clear that compressibility-related effects play a negligible role at ambient pressure.[17] However, when pressure effects were considered, we suggested through a simplified approach that experimental data on a polyolefin blend could be interpreted as being direct manifestations of volume changes on mixing.[4] There are therefore two conflicting approaches to modeling the role of pressure on system thermodynamics. Since these are philosophically quite different in their conclusions, it is imperative that we have a better understanding of the various assumptions inherent in them and that we attempt to reconcile these different methodologies.

In this paper we focus on the pressure dependence of small-angle neutron scattering (SANS) from polymer blends. We start with the exact expression for the zero wavevector limit of the scattering intensity and, with reasonable approximations valid for typical polymer blends, show that it reduces to the familiar RPA form used routinely. We then derive a simple expression relating pressure effects on χ to the volume changes on mixing for these blends. Numerical predictions for the volume change on mixing, as obtained from the pressure dependence of χ, are in reasonable agreement with available experimental data for this quantity. We then proceed to examine the suggestions of Rabeony and co-

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workers[6] and find that this approach, when applied in a thermodynamically consistent fashion, also implies a direct connection between the pressure dependence of χ and the volume changes on mixing. As a corollary, we deduce that it is inappropriate to model systems with nonzero χ values as having zero volume changes on mixing, since this ignores important entropic contributions to the pressure dependence of χ.[6] The apparent discrepancy between the two formalisms is thus resolved. We also derive the P dependence of T_c and show to zeroth order that all polymer blends display the same, apparently "universal" behavior in this context. This result is also in good agreement with experiment.

Pressure Dependence of Scattering Intensity

Theoretical Development. In previous work we showed that a SANS measurement, when properly corrected for density fluctuations and for the dissimilar volumes of the two components, yields estimates of the osmotic susceptibility $[\partial^2\Delta g/\partial\phi^2]^{-1}_{T,P}$.[16,17] Here we briefly discuss these previous findings, and also connect them to the standard random phase approximation (RPA) expression, which is traditionally used to analyze SANS data from polymer blends. Note that we consider experimentally relevant isothermal–isobaric conditions, and hence x, the mole fraction of monomers of species 1, and Δg, the Gibbs free energy of mixing per mole of monomers, are the natural variables. x and ϕ are related through the equation

$$\phi = \frac{xv_1}{xv_1 + (1-x)v_2} \tag{1}$$

where v_i is the total volume occupied by a mole of monomers of *pure* component i. We begin with the exact expression for the scattering from a compressible binary mixture, $I_{\text{compress}}(0)$ [see p 202 of ref 18]:

$$I_{\text{compress}}(0) = \langle b\rangle^2(RT\,\rho^2\kappa_T) + k'_{\text{N}}\,\rho^3(\bar{v}_1\bar{v}_2)^2\left[\frac{\partial^2(\Delta g/RT)}{\partial x^2}\right]^{-1}_{T,P} \tag{2}$$

Here κ_T is the isothermal compressibility of the mixture, ρ is the monomer density, and $\bar{v}_i$ is the partial molar volume of component i.[19] $\langle b\rangle = b_1x + b_2(1-x)$ is the average scattering length of the sample, and $k'_{\text{N}} \equiv (b_1/\bar{v}_1 - b_2/\bar{v}_2)^2$ is the scattering contrast factor, where b_i is the scattering length of species i. The first term on the right side of eq 2 derives from density fluctuations and is one manifestation of system compressibility. Since this term is typically 100–1000 times smaller than $I_{\text{compress}}(0)$,[16] and since the background scattering from both pure components is subtracted in the analysis of experimental data, this term is ignored in the analysis that follows. Note that, as a consequence, our analysis is only good to a 1% level. The contribution of system compressibility to the second term in eq 2 is then the primary focus of this paper. In general, the analysis of experimental data involves consideration of the quantity $k_N/I_{\text{compress}}(0)$, where $k_N = (b_1/v_1 - b_2/v_2)^2$ is the experimentally defined contrast factor based on the molar volumes of the pure components, v_i. This yields

$$\frac{1}{S(0)} \equiv \frac{k_N}{I_{\text{compress}}(0)} \approx \frac{k_N}{k'_N}\frac{v^3}{(\bar{v}_1\bar{v}_2)^2}\left[\frac{\partial^2(\Delta g/RT)}{\partial x^2}\right]_{T,P} \tag{3}$$

where $v = 1/\rho$. We are concerned with the pressure dependence of $1/S(0)$. The free energy per unit volume is now considered, where the system volume is defined in the incompressible limit, v_{incom}, i.e., in the case where the volume changes on mixing are identically equal to zero. This is done to be consistent with the volume fraction definition in eq 1,

$$v_{\text{incom}} = x_1v_1 + x_2v_2$$

We now use the identity

$$\left[\frac{\partial^2(\Delta g/v_{\text{incom}})}{\partial\phi^2}\right]_{T,P} \equiv \frac{v^3_{\text{incom}}}{(v_1v_2)^2}\left[\frac{\partial^2\Delta g}{\partial x^2}\right]_{T,P} \tag{4}$$

in conjunction with eq 3 to obtain

$$\frac{1}{S(0)} = \frac{k_N}{k'_N}\frac{v^3\;(v_1v_2)^2}{v^3_{\text{incom}}(\bar{v}_1\bar{v}_2)^2}\left[\frac{\partial^2(\Delta g/v_{\text{incom}}RT)}{\partial\phi^2}\right]_T \tag{5}$$

For typical polymer blends, where the volume changes on mixing are much smaller than 1%, we can approximate this form to better than 1% by [see Appendix I],

$$\frac{1}{S(0)} \approx \left[\frac{\partial^2(\Delta g/[v_{\text{incom}}RT])}{\partial\phi^2}\right]_T \tag{6}$$

This is the standard random phase approximation expression, commonly employed in polymer thermodynamics. Note that we have *not* assumed the system to be incompressible, and hence the formula presented above represents a general prescription to calculate the static scattering from binary polymer mixtures. Δg still refers to the Gibbs energy change on mixing for the compressible polymer blend and hence includes all nonideal contributions such as nonzero excess volumes of mixing. To our knowledge no one has shown that this simple functional form for the scattering intensity, which was derived previously for truly incompressible systems, applies equally well for typical, compressible polymer blends.

We now return to the exact definition of the coherent scattering from the system, i.e., eq 3. By following the assumptions used for the derivation of eq 6, and as shown in Appendix II, this directly yields

$$\left[\frac{\partial S^{-1}(0)}{\partial P}\right]_{T,\phi} = \frac{1}{S(0)}\kappa_T + \frac{1}{RT}\left[\frac{\partial^2(\Delta v/v_{\text{incom}})}{\partial\phi^2}\right]_{T,P} \tag{7}$$

κ_T is the isothermal compressibility, and Δv is the molar volume change on mixing of the *compressible* mixture. It is instructional to examine the relative importance of the two terms in eq 7. For illustration purposes, in the rest of this analysis the volume change on mixing is assumed to follow the simplest form,

$$\Delta v \equiv v - v_{\text{incom}} = \mathbf{v}v_{\text{incom}}\phi(1-\phi)$$

where $\mathbf{v}$ is a constant. This last assumption can be relaxed readily. If we adopt representative values of $I(0) = 100\ \text{cm}^{-1}$, $\kappa_T = 0.06\ \text{kbar}^{-1}$, and $k_N \approx 4\times10^{-3}\text{cm}^{-4}$, then the second term in eq 7 will dominate if

$$|\mathbf{v}| \gg 4\times10^{-5}$$

For the dPS/PVME blend, Schwahn and co-workers reported that $\partial S^{-1}(0)/\partial P]_{T,\phi} \approx 4.7 \times 10^{-7}$ mol/(N m) and $1/S(0) \approx 100$ mol/m^3 at $T = 79$ °C for a blend with $\phi_{\mathrm{dPS}} = 0.13$.[7] These results are consistent with recent reports by Hammouda.[20,21] Consequently, the first term in eq 7 is 3×10^{-8} mol/(N m), implying that the contribution of system compressibility to the pressure dependence of scattering is about 5%. Similarly, for the dPS/PMPS blend Schwahn et al. report that $\partial S^{-1}(0)/\partial P]_{T,\phi} \approx 3 \times 10^{-7}$ mol/(m N), again suggesting that compressibility contributions do not play a major role in this context. In these cases we therefore expect $|\mathbf{v}| \approx 5 \times 10^{-4}-10^{-3}$. In contrast, for blends of poly(methylbutylene) and poly(ethylbutylene) the $-\partial S^{-1}(0)/\partial P]_{T,x} = (0.2-2) \times 10^{-7}$ mol/(N m).[4] For the smallest absolute values of $\partial S^{-1}(0)/\partial P$, compressibility contributions can play a significant role in determining the volume changes on mixing, since we expect $|\mathbf{v}| \approx 10^{-5}$. While it is apparent that we have the capability of separating compressibility contributions from the volume changes on mixing, it would be more reasonable if it was not necessary to perform this separation. Below we shall show that the use of Flory–Huggins theory allows us to delineate the volume change on mixing contribution without interference from the compressibility of the system, which thus affords a great deal of simplification.

Predictions of Flory–Huggins Theory. Note that, to this point, our derivation is general and utilizes *no particular form for the free energy of mixing*. Hence, the relationship between the pressure dependence of scattering intensity and volume change on mixing is a special property of mixtures with components with closely matched compressibilities, which *does not* rely on a specific model. For simplicity of notation, as well as to make contact with past work on polymer blends, we shall utilize the Flory–Huggins formulation for describing the free energy of mixing,[15]

$$\frac{\Delta g}{v_{\mathrm{incom}}RT} = \frac{\phi}{v_1 N_1}\ln\phi + \frac{1-\phi}{v_2 N_2}\ln(1-\phi) + \frac{\chi}{v_0}\phi(1-\phi) \tag{8}$$

While χ has been interpreted as a purely enthalpic interaction parameter in the original Flory theory, we expand this definition and include all "nonideal" contributions in it. If we now use this form of the free energy of mixing in the definition of $S(0)$, eq 6, we obtain

$$S^{-1}(0) = \frac{1}{N_1 v_1 \phi} + \frac{1}{N_2 v_2 (1-\phi)} - 2\,\frac{\chi}{v_0} \tag{9}$$

Here it has been assumed that χ is independent of composition. The pressure derivative of eq 9 is calculated under the assumption that the isothermal compressibilities of the two pure components and the mixture are identical. It then follows that

$$\left[\frac{\partial S^{-1}(0)}{\partial P}\right]_{T,\phi} = S^{-1}(0)\kappa_T - \frac{2}{v_0}\left[\frac{\partial\chi}{\partial P}\right]_{T,\phi} \tag{10}$$

Comparison of this equation to eq 7 immediately yields the result

$$\left[\frac{\partial\chi}{\partial P}\right]_{T,\phi} = -\frac{1}{2}\,\frac{v_0}{RT}\left[\frac{\partial^2[\Delta v/v_{\mathrm{incom}}]}{\partial\phi^2}\right]_{T,P} \tag{11}$$

which we have employed previously, and where the compressibility contribution has canceled out.[4] Equation 11 is the essential, simple result of our analysis which suggests, to a very good approximation, that the pressure dependence of the effective Flory χ parameter directly yields information on the volume changes on mixing for a polymer blend. A final point we shall assess is the pressure dependence of the quantity $\partial\chi/\partial P$. Again, we shall assume that the κ_T values are independent of composition. Then, we can show to a good approximation that

$$\frac{\partial \ln\left(\frac{\partial\chi}{\partial P}\right)}{\partial P} = -(\kappa_T - \kappa_{T,\mathrm{incom}}) \tag{12}$$

where $\kappa_{T,\mathrm{incom}}$ corresponds to a hypothetical blend with zero volume change on mixing. v_0 is treated as a pressure-independent quantity, as is normally assumed in the analysis of experimental data. For typical polymers we estimate that $\kappa_T - \kappa_{T,\mathrm{incom}} < 0.01$ kbar^{-1}. Thus, eq 12 suggests that $\partial\chi/\partial P$ changes less than 1% for a 1 kbar pressure increase. Since this is within the experimental errors, we conclude that $\partial\chi/\partial P$ is effectively constant over the pressure ranges encountered in many experiments. This conclusion is in good agreement with experiment,[4,6] where it has been found that plots of χ vs P yield straight lines in the pressure range 0–1 kbar. Thus, to better than 1% the role of pressure can be summarized by the simple equation

$$\chi(P) = \chi(P{=}0) - \frac{1}{2}\,\frac{Pv_0}{RT}\left[\frac{\partial^2[\Delta v/v_{\mathrm{incom}}]}{\partial\phi^2}\right]_{T,P} \tag{13}$$

where it is assumed that χ is independent of composition. The free energy of mixing of a typical polymer blend at an arbitrary pressure can then be represented in the corresponding form,

$$\frac{\Delta g}{v_{\mathrm{incom}}RT} = \frac{\phi}{v_1 N_1}\ln\phi + \frac{1-\phi}{v_2 N_2}\ln(1-\phi) + \frac{\chi(P)}{v_0}\phi(1-\phi) \tag{14}$$

where $\chi(P)$ is evaluated following eq 13. Of course, quantities such as v_{incom}, v_1, and v_2 will change with pressure, but these are readily obtained from a knowledge of the isothermal compressibilities of the materials in question.

Application to Real Systems. To our knowledge there is only one case where the change in χ with pressure *and* volume changes on mixing were measured on identical blends. This is the case of PDMS/PEMS, where Fytas et al.[5] reported that the upper critical solution temperature for phase separation was surprisingly depressed on pressurization. In this case it was found that $[\partial\chi/\partial P]_{T,\phi} \approx -5 \times 10^{-6}$ bar^{-1} while $\mathbf{v} \approx -2 \times 10^{-3}$. By employing eq 11 it follows that

$$\left[\frac{\partial^2[\Delta v/v_{\mathrm{incom}}]}{\partial\phi^2}\right]_{T,P} \approx 3 \times 10^{-3}$$

Since these workers found that volume change on mixing varies linearly with the product $\phi(1-\phi)$, we can directly compare our estimates of **v** to experiment. We predict

$$\mathbf{v} \approx -1.5 \times 10^{-3}$$

which is in reasonable agreement with experiment. Note that the agreement between the prediction and experiment is not perfect, and this discrepancy can be attributed to a variety of factors. The χ data of Fytas et al.[5] were obtained from dynamic light scattering, and it is unclear whether the protocol used in the analysis of these experiments tracks the procedure used in the analysis of SANS data. Second, the experimental measurement of small volume changes on mixing are fraught with error. Despite these difficulties, it is clear that pressure-dependent experiments, coupled to this simple thermodynamic analysis, allow for a relatively straightforward determination of the volume change on mixing for this system.

Another system where the pressure dependence of scattering has been extensively studied is the dPS/PVME blend. Schwahn et al.[7] report, as noted earlier, that for a $\Phi_{\mathrm{dPS}} = 0.13$ blend $\partial S^{-1}(0)/\partial P]_{T,\phi} \approx 4.7 \times 10^{-7}$ mol/(N m). Therefore, we estimate

$$\left[\frac{\partial^2[\Delta v/v_{\mathrm{incom}}]}{\partial\phi^2}\right]_{T,P} \approx 1.2 \times 10^{-3}$$

Experimental measures of the excess volume changes on mixing for the dPS/PVME system are available.[22] These workers report that the excess volume changes on mixing at $T = 298$ K are not symmetric about $\phi = 0.5$ but that the minimum value is $\Delta v/v_{\mathrm{incom}} = -3 \times 10^{-3}$. This value yields a **v** which is about an order of magnitude larger than our estimates. Several possibilities need to be considered to reconcile the experiments and the theory presented here. First, we have made a series of assumptions, the primary one being that the compressibilities of the two components and the mixture are identical. We have attempted to relax this assumption, and a preliminary estimate suggests that even if this assumption is incorrect by 5%, the errors induced by this approximation cannot explain this discrepancy. Second, we have assumed that the excess volume term varies linearly with $\phi(1 - \phi)$ and that χ is independent of composition—these are incorrect in the case of the dPS/PVME blend. While these assumptions can be readily relaxed, the resulting equations are not quite as transparent. Finally, the temperatures and molecular weights employed in the pressure experiments are different from those employed in the volumetric studies. It is therefore clear that more experiments, where both volume changes on mixing and pressure dependence of χ are determined for the same system, are necessary to understand the accuracy of the theory presented here. At this stage evidence exists from two different systems to support that pressure-dependent experiments provide reasonable estimates for the volume changes on mixing for polymer blends, especially in case where dilatometric techniques are incapable of yielding accurate estimates, i.e., when $|v| \leq 10^{-3}$. We have recently begun to critically examine the validity of the assumptions made in this paper by comparisons to the lattice cluster theory and find that the biggest approximation in our analysis follows from assuming χ is independent of composition. While the results of this analysis will be reported in future work, we find that, even with this relatively crude assumption, we can estimate the volume changes on mixing for hydrocarbon blends to within a factor of 2.

Critical Examination of the Ideas of Rabeony et al.[6] We now consider recent suggestions that the role of pressure on a polymer blend is merely to increase the cohesive energy density, δ^2, of a polymer and that volume changes on mixing play a negligible role in this context. Since the χ parameter defined in regular solution theory, denoted as χ_{r}, is[6,23]

$$\chi_{\mathrm{r}} = \frac{v}{2RT}(\delta_1 - \delta_2)^2 \tag{15}$$

it has therefore been argued that pressure effects on the interaction parameter may be rationalized on the basis of this energetically motivated equation alone. To relate these findings to our analysis, we start with the definition of the solubility parameter,[23]

$$\delta \equiv \sqrt{\frac{\Delta u_{\mathrm{vap}}}{v}} \tag{16}$$

where Δu_{vap} is the energy change on vaporization of the liquid, and v is the molar volume of the saturated liquid. The pressure derivative of the solubility parameter is

$$\frac{\partial\delta}{\partial P} = \frac{\kappa_T\delta}{2}\left[\left(\frac{\delta_{\mathrm{ip}}}{\delta}\right)^2 + 1\right] \tag{17}$$

where $\delta_{\mathrm{ip}}{}^2$ is the internal pressure of the polymer liquid,[23,24]

$$\delta_{\mathrm{ip}} = \sqrt{\left[\frac{\partial u}{\partial v}\right]_T} \tag{18}$$

Recent work has shown that $\delta_{\mathrm{ip}} \propto \delta$[24] but that the proportionality constant for polymers can be significantly different from 1.[25] However, simple mean field theories and simulations suggest that this proportionality constant is virtually identical for all polymers considered, $\delta/\delta_{\mathrm{ip}} = 0.72 \pm 0.02$.[25] This assertion, however, cannot be experimentally verified since the δ values for polymers cannot be measured. If we assume that the κ_T and the quantity in square brackets in eq 17 are the same for both polymers, it follows that

$$\chi_{\mathrm{r}}(P) = \chi_{\mathrm{r}}(P{=}0)\left(1 + [\kappa_T P]\left[\left(\frac{\delta_{\mathrm{ip}}}{\delta}\right)^2 + 1\right] - \kappa_T P\right) \tag{19}$$

The last term in the brackets arises due to the volume change on pressurization. Thus, we obtain

$$\left[\frac{\partial\chi_{\mathrm{r}}}{\partial P}\right]_{T,\phi} = \chi_{\mathrm{r}}(P{=}0)\kappa_T\left(\frac{\delta_{\mathrm{ip}}}{\delta}\right)^2 \tag{20}$$

This result is particularly important since, at this juncture, the approach of Rabeony et al.[6] and our methodology predict that pressure causes χ to change linearly. This is in good agreement with available experimental results.[4,6] However, the molecular origins for this pressure dependence are quite different in the two approaches. In the Rabeony approach an increase in pressure causes the δ values, and hence the χ_r parameter, to increase due to changes in system density. In our case we show that pressure effects reflect volume changes on mixing. This second viewpoint is supported by LeChatelier's principle. For example, if a system possesses a negative volume change on mixing, then high pressures will tend to stabilize the single phase of the system. This is in agreement with intuition and also recent experimental results on the PDMS/PEMS polymer blend.[5] Exactly the opposite conclusion is expected if the volume change on mixing were positive, the situation that is more normally encountered in polymer blends. To reconcile these two, apparently conflicting pictures, we compare eq 11 to eq 20. This directly yields

$$-\frac{1}{2}\frac{v_0}{RT}\left[\frac{\partial^2[\Delta v/v_{\mathrm{incom}}]}{\partial \phi^2}\right]_{T,P} = \chi_{\mathrm{r}}(P{=}0)\kappa_T\left(\frac{\delta_{\mathrm{ip}}}{\delta}\right)^2 \tag{21}$$

which simplifies to

$$\mathbf{v} = \chi_{\mathrm{r}}(P{=}0)\frac{\kappa_T RT}{v_0}\left(\frac{\delta_{\mathrm{ip}}}{\delta}\right)^2 \tag{22}$$

if we assume the simplest form for the volume change on mixing. Consequently, eq 22 asserts that for thermodynamic consistency to be achieved, a system with nonzero χ under ambient conditions *must* be accompanied by a volume change on mixing. The implication of these ideas, which was previously anticipated by Hildebrand,[23] is that although the volume changes on mixing for polymer blends are typically small, they play a central role in determining the pressure dependence of χ. Below, we shall show that the neglect of this volume change on mixing by the solubility parameter approach, which thus ignores entropic contributions due to pressurization, can give rise to $[\partial\chi/\partial P]_{T,\phi}$ estimates which can be as much as 50% in error.

For typical polymers considered in this work eq 22 suggests that, if we assume the last term to be 1.5, $\mathbf{v} = 0.05\chi(P{=}0)$. This result is qualitatively in accord with our own earlier results, where we have empirically found that $\mathbf{v} = 0.17\chi(P{=}0) - 7.6 \times 10^{-5}$.[4] However, note that the absolute magnitude of the proportionality constant between $\mathbf{v}$ and $\chi(P{=}0)$ is incorrect by a factor of 3. To understand the origins of the discrepancy between experiment and the regular solution ideas presented above, we start with the thermodynamic identity

$$\Delta g \equiv \Delta h - T\Delta s$$

Δh and Δs are respectively the enthalpy and entropy changes on mixing. A pressure derivative of this equation yields

$$\Delta v = \left[\frac{\partial \Delta h}{\partial P}\right]_{T,x} + T\left[\frac{\partial \Delta v}{\partial T}\right]_{P,x} \tag{23}$$

We now consider the second term on the right-hand side of this equation:

$$\left[\frac{\partial \Delta v}{\partial T}\right]_{P,x} = v\alpha_P - v_{\mathrm{incom}}\alpha_{P,\mathrm{incom}} \approx \alpha_P \Delta v \tag{24}$$

where α_P is the thermal expansion coefficient of the system, and $\alpha_{P,\mathrm{incom}}$ is the corresponding quantity for a system with zero volume change on mixing. The second line is a crude approximation, which we expect at best to be qualitatively valid. Further, if we assume that both the pure materials and the blends have the same κ_T value,

$$\left[\frac{\partial \Delta h}{\partial P}\right]_{T,x} = \left[\frac{\partial \Delta u}{\partial P}\right]_{T,x} - P\kappa_T\Delta v \tag{25}$$

Using eqs 24 and 25 in eq 23 yields

$$\Delta v = \frac{1}{1 - T\alpha_P + P\kappa_T}\left[\frac{\partial \Delta u}{\partial P}\right]_{T,P} \tag{26}$$

We now reiterate that $\chi_{\mathrm{r}}\phi(1-\phi) \equiv \Delta u/RT$ and take the second composition derivative of this equation. Thus, the inclusion of entropic effects modifies eq 22 to the form

$$\mathbf{v} = \frac{1}{1 - \alpha_P T + \kappa_T P}\chi_{\mathrm{r}}(P{=}0)\frac{\kappa_T RT}{v_0}\left(\frac{\delta_{\mathrm{ip}}}{\delta}\right)^2 \tag{27}$$

For many polymers, $\alpha_P \approx 5 \times 10^{-4}$–$10^{-3}$ K^{-1}. Consequently, we suggest that the inclusion of entropic effects modifies the relationship between $\mathbf{v}$ and $\chi(P{=}0)$ at $T = 450$ K to $\mathbf{v} = 0.10\chi(P{=}0)$. This is in much better agreement with experiment than the purely enthalpic approach. It is clear that even better agreement with experiment could be afforded if we relax simplifications such as assuming that α_P and κ_T are independent of the polymer or the blend. Further, it is well-known that the regular solution description of χ, which assumes that cross interactions are defined by a geometric mean approximation, is incorrect even in the case of hydrocarbon blends.[24] Nevertheless, we conclude here that entropic effects, caused primarily by volume changes on mixing, play a profound role in determining the pressure dependence of χ for polymer blends.

Despite these problems, we stress that these approximate approaches correctly suggest that the magnitude of the volume change on mixing, $\mathbf{v}$, must scale with the energetic interactions in the system, $\chi(P{=}0)$. This has been previously confirmed by experiments. However, arguing that pressure effects may be delineated simply by measuring the pressure dependence of the δ parameter might be too simplistic for many real polymer blends. In this context we note that eq 11 is a fundamentally based description for changes that occur on pressurizing a polymer blend, one whose general validity can also be expanded to include situations where the two blend constituents have different compressibilities and where χ is a function of composition. In contrast, the solubility parameter based approach is not as soundly based since it has the fundamental assumption of the validity of regular solution theory built into it. Consequently, this more approximate approach must be used with great caution.

Pressure Dependence of Critical Temperature

We now examine our predictions for the pressure dependence of T_{c} in the framework of the generalized Flory–Huggins model, eq 14. For mixture of two polymers, especially those of equal compressibility, it follows from Flory theory that at the critical point,

$$\mathrm{d}\chi = 0 \tag{28}$$

Simple thermodynamic manipulation then suggests that

$$\left[\frac{\partial \chi}{\partial T}\right]_{P,\phi}\mathrm{d}T + \left[\frac{\partial \chi}{\partial P}\right]_{T,\phi}\mathrm{d}P = \mathrm{d}\chi \equiv 0 \tag{29}$$

where we have assumed, in agreement with Flory–Huggins theory, that χ does not vary with composition, and hence the critical composition is unaffected by pressure. This assumption would, of course, be invalid for systems such as dPS/PVME where the experimentally determined χ is well-known to have a linear composition dependence. Thus, the variation of critical temperature with pressure is obtained:

$$\left[\frac{\partial T}{\partial P}\right]_{\mathrm{c}} = -\frac{\left[\dfrac{\partial \chi}{\partial P}\right]_{T,\phi}}{\left[\dfrac{\partial \chi}{\partial \mathrm{T}}\right]_{P,\phi}} \tag{30}$$

This form is well-known in the literature,[1,2,12,26,27] one which has been employed successfully to explain the pressure dependence of the critical temperature of both LCST and UCST systems. Our goal here is to provide an order of magnitude estimate of the dependence of critical temperature on pressure.

The numerator of eq 30 is already known, eq 11, and hence we are left with only the task of evaluating the denominator. We take the temperature derivatives of eqs 6 and 9 and use the assumptions that both the homopolymers and the blend have the same coefficient of thermal expansion, α_P. Then, we obtain

$$\left[\frac{\partial \chi}{\partial T}\right]_{P,\phi} = \frac{v_0}{2}\left[\frac{\partial^2[\Delta h/v_{\mathrm{incom}}RT^2]}{\partial \phi^2}\right]_{T,P} \tag{31}$$

and hence

$$\left[\frac{\partial T}{\partial P}\right]_{\mathrm{c}} = \frac{\dfrac{1}{R}\left[\dfrac{\partial^2[\Delta v/v_{\mathrm{incom}}]}{\partial \phi^2}\right]_{T,P}}{\left[\dfrac{\partial^2[\Delta h/v_{\mathrm{incom}}RT^2]}{\partial \phi^2}\right]_{T,P}} \approx \frac{\mathbf{v}}{R(\chi/v_0)} \tag{32}$$

At this point it is convenient to utilize eq 27 since this permits a direct connection between $\mathbf{v}$ and χ under ambient pressure.

$$\left[\frac{\partial T}{\partial P}\right]_{\mathrm{c}} \approx \kappa_T T\left[\frac{\delta_{\mathrm{ip}}}{\delta}\right]^2 \frac{1}{1-\alpha_T T-\kappa_T P}$$

This approximate relationship suggests that at $T = 400$ K and ambient pressure the critical temperature will change ≈35 K/kbar, independent of the polymer chains in question. This result is remarkable in that it is consistent, within a factor of 2, with many experimental results on polymer blends, some of which display UCST behavior while others have LCSTs. Of course, this analysis is contingent on the applicability of regular solution theory, an assumption that is the weakest link in this analysis. Consequently, unusual effects such as minima in the dependence of the T_{c} on P will be entirely missed. Nevertheless, we stress that our analysis suggests that polymer mixtures may be expected to behave in a "universal" manner when considered in this context, a prediction that seems to be followed by several nonpolar polymer mixtures, including polyolefin mixtures, etc.

Conclusions

Our primary conclusion is that the pressure dependence of the Flory χ parameter is related directly to the volume change on mixing for polymer blends. This conclusion is verified by the small amount of available experimental data. Since this argument is purely thermodynamic, and completely general as long as the two components have the same compressibility, it suggests that it is not necessary to evoke changes in R_{g}, the radius of gyration of the chains, or any other system property on pressurization to explain the molecular basis for pressure effects. We also show that it is inappropriate to model blends with nonzero χ values as having zero volume changes on mixing, since this violates thermodynamic consistency. Thus, modeling these systems through the regular solution approach is incorrect from a fundamental viewpoint, although it could yield numerically reasonable estimates, to within an order of magnitude, for the pressure dependence of χ. Finally, we consider the change of critical temperature with pressure. Since the volume change on mixing scales with the χ parameter at ambient pressure, we conclude that T_{c} must vary ≈35 K/kbar pressure, independent of the chains in question. This result is also in agreement with experiment, suggesting that our simple approach captures all the important experimental observations on pressure effects on these systems.

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Appendix I. Derivation of Approximate Eq 6

It is our role to evaluate the quantities below, which are from eq 5, and to show that they are nearly equal to unity for most polymer blends.

$$\frac{k_N}{k'_{\mathrm{N}}}\,\frac{v^3}{v_{\mathrm{incom}}^3}\,\frac{(v_1v_2)^2}{(\bar{v}_1\bar{v}_2)^2} \tag{33}$$

Let us consider the case where the volume change on mixing is defined in the simple form,

$$v - v_{\mathrm{incom}} = \alpha x(1-x)$$

For most polymer blends of interest, $\alpha < 1 \times 10^{-3} v_{\mathrm{incom}}$. From here we can directly derive the partial molar volumes of the two components in the blend:

$$\bar{v}_1 = v_1 + \alpha(1-x)^2$$

$$\bar{v}_2 = v_2 + \alpha x^2$$

Evaluation of the terms in eq 33, while keeping terms to leading order in α alone, yields

$$\frac{k_N}{k'_N} \approx 1 - \frac{2\alpha}{v_{\mathrm{incom}}}$$

$$\frac{v^3}{v_{\mathrm{incom}}^3} \approx 1 + \frac{3\alpha}{v_{\mathrm{incom}}}$$

$$\frac{(v_1v_2)^2}{(\bar{v}_1\bar{v}_2)^2} \approx 1 - \frac{2\alpha}{v_{\mathrm{incom}}}$$

In deriving these equations, we assumed that $v_1 = v_2 = v_{\mathrm{incom}}$ and that $x = 0.5$. While these simplifications allow us to obtain these expressions in a convenient form, they can be relaxed to cases where these assumptions are not valid. We expect, however, that these conclusions will continue to be approximately valid even in these cases. From here it follows that the correction term represented by eq 33 is of order

$$1 - \frac{\alpha}{v_{\rm incom}}$$

For typical polymer blends, where $\alpha/v_{\rm incom} \ll 0.01$. Thus, neglecting the term represented in eq 33 can only change the result by factors that are clearly smaller than the inherent uncertainties in the experiment.

Appendix II. Approximate Expressions for the Pressure Dependence of Scattering

Let us begin with the definition of the scattering from a compressible polymer mixture, eq 3,

$$\ln S^{-1}(0) = \ln\left(\frac{k_N}{k'_N}\right) + \ln\left(\frac{v^3}{[v_1 v_2]^2}\right) + \ln\left[\frac{\partial^2(\Delta g/RT)}{\partial x^2}\right]_{T,P} \tag{34}$$

We shall now take the pressure derivative of this equation and shall deal with the three terms separately. From the first term we obtain

$$\left[\frac{\partial \ln\left(\frac{k_N}{k'_N}\right)}{\partial P}\right]_{T,x} = 2\kappa_{T,1} + \frac{2b_2}{v_2\sqrt{k_N}}(\kappa_{T,1} - \kappa_{T,2}) - 2\bar{\kappa}_{T,1} - \frac{2b_2}{\bar{v}_2\sqrt{k'_N}}(\bar{\kappa}_{T,1} - \bar{\kappa}_{T,2})$$

$\kappa_{T,i}$ is the isothermal compressibility of pure component i, while $\bar{\kappa}_{T,i}$ is a similarly defined quantity for the partial molar volume of species i in the mixture. For all practical considerations, this derivative is expected to be much smaller than κ_T, the isothermal compressibility of the mixture, since it involves differences in κ_T values. Typical κ_T for pure polyolefins are of order 0.06 kbar^{-1}, and the differences in κ_T values of typical polyolefins are 0.001 kbar^{-1}, thus justifying the assumptions built into this analysis. The second term then yields

$$\left[\frac{\partial \ln\left(\frac{v^3}{[v_1 v_2]^2}\right)}{\partial P}\right]_{T,x} = -3\kappa_T + 2\bar{\kappa}_{T,1} + 2\bar{\kappa}_{T,2} \approx \kappa_T$$

Note that in the last approximation we have again assumed that quantities such as $\kappa_T - \bar{\kappa}_{T,1} \ll \kappa_T$. This seems reasonable given that most polymers have very similar isothermal compressibilities. The last term then yields the most interesting quantity in this analysis,

$$\frac{1}{\left[\frac{\partial^2(\Delta g/RT)}{\partial x^2}\right]_{T,P}}\left[\frac{\partial^2(\Delta v/RT)}{\partial x^2}\right]_{T,P}$$

Combining these expressions finally yields the result

$$\left[\frac{\partial S^{-1}(0)}{\partial P}\right]_{T,x} \approx \frac{1}{S(0)}\kappa_T + \frac{k_N}{k'_N}\frac{v^3}{(\bar{v}_1\bar{v}_2)^2}\left[\frac{\partial^2(\Delta v/RT)}{\partial x^2}\right]_{T,P} \tag{35}$$

Finally, we need to convert the derivative in the second term into one where the independent variable is ϕ, rather than x. To do this, we use an identity similar to that derived in eq 5. One then has several terms multiplying this derivative. However, a closer examination shows that they are identical to those considered in Appendix I, where we have illustrated that the correction they offer is smaller than the inherent uncertainties in our analysis. Consequently, we ignore these factors and end up with eq 7.

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