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Relationship between Internal Energy and Volume Change of Mixing in Pressurized Polymer Blends

A. A. Lefebvre,[†] J. H. Lee,[†] N. P. Balsara,^{*,†}
B. Hammouda,[‡] R. Krishnamoorti,[§] and S. Kumar^{||}

Department of Chemical Engineering, Chemistry, and Materials Science, Polytechnic University, Six Metrotech Center, Brooklyn, New York 11201; National Institute of Standards and Technology, Building 235, E 151, Gaithersburg, Maryland 20899; Department of Chemical Engineering, University of Houston, 4800 Calhoun, Houston, Texas 77204; and Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802

Received March 17, 1999

In spite of considerable efforts, a fundamental understanding of the interactions between chemically distinct polymer chains in the melt state is lacking. Subtle effects at the monomer level have a profound effect on phase behavior and macroscopic properties. Small-angle neutron scattering (SANS) has proven to be a powerful tool for studying these effects. The scattering from several polymer blends has been measured as a function of temperature.¹ The results are interpreted in terms of the internal energy change of mixing, ΔU , using the Flory–Huggins theory.² Recent theoretical work suggests that the SANS data may be dominated by other effects such as constraints arising due to chain connectivity and detailed chemical structure, entropic effects, and compressibility.³ Fresh insight into the nature of intermolecular interactions in polymer blends would be useful.

In this paper, we focus on the pressure dependence of SANS from binary polymer blends.⁴ Since SANS measurements yield estimates of the osmotic susceptibility $[\partial^2(\Delta G)/\partial\phi^2]_{T,P}$, pressure-dependent experiments could be used to estimate volume changes of mixing (ΔG is the Gibbs energy change of mixing per unit volume of the mixture and ϕ is the volume fraction of one of the polymers). This follows from the fact that⁵

$$[\partial(\Delta G)/\partial P]_{T,\phi} = \Delta V \quad (1)$$

where ΔV is the volume change of mixing per unit volume. This method for measuring the volume changes of mixing in typical polymer blends (e.g., polyolefins) may be important, due to the lack of sensitivity of standard techniques such as dilatometry. We demonstrate that although the estimated magnitudes of these volume changes are small, they play an important role in determining the pressure dependence of polymer–polymer compatibility.

For simplicity of notation and to make contact with past work on polymer blends, we begin with the incompressible Flory–Huggins formulation for a binary mixture of polymers,

$$\frac{\Delta G}{kT} = \left[\frac{\phi \ln \phi}{v_A N_A} + \frac{(1 - \phi) \ln(1 - \phi)}{v_B N_B} \right] + \frac{\chi}{v_0} \phi (1 - \phi) \quad (2)$$

where k is the Boltzmann constant, ϕ is the volume fraction of component A in the mixture, N_i is the number of monomers per chain of component i , v_i is the volume of each monomer of component i , χ is the Flory–Huggins interaction parameter, and v_0 is an arbitrary reference volume that we set equal to the mean monomer volume of the polymers chosen for this study at atmospheric conditions, 149 Å³. Note that this formalism automatically accounts for differences in the monomer volumes of the components. From this point on, we express thermodynamic potentials (ΔG , ΔU , and ΔH) in units of kT per unit volume. In the original Flory–Huggins theory, χ was interpreted as a purely energetic interaction parameter, and the second term in eq 2 is equal to ΔH (enthalpy change of mixing). Since all other non-idealities of mixing (e.g., ΔV) are ignored, $\Delta H = \Delta U$ (internal energy change of mixing).

We now include cases where ΔV is non-zero and extend the definition of χ to account for this nonideality of mixing. Differentiating eq 2, first with respect to P and then twice with respect to ϕ , and substituting eq 1, it follows that⁶

$$[\partial\chi/\partial P]_{T,\phi} = - (v_0/2kT) [\partial^2(\Delta V)/\partial\phi^2]_{T,P} \quad (3)$$

For illustration, if ΔV can be represented as $\Delta V = v\phi(1 - \phi)/v_0$, where v is a system-dependent parameter, then $[\partial\chi/\partial P]_{T,\phi} \equiv v/kT$. This form for ΔV has been used to interpret pressure-dependent data from small-molecule mixtures.⁵ Equation 3 can be used to obtain equivalent expressions relating $\partial\chi/\partial P$ and ΔV , if the composition dependence of ΔV is more complicated. If χ is a linear function of pressure, then we can simply write

$$\chi = u(T) + Pv/kT \quad (4)$$

where we have defined $\Delta U = u\phi(1 - \phi)/v_0$.

Note that we do not use the original Flory–Huggins theory to explain our pressure-dependent data but rather use its functional form for convenience. We have used the “ χ parameter” in a manner that makes contact with previous literature on polymer blends. Thus if χ is a linear function of P , then the intercept is related to ΔU in the $P = 0$ limit (the more traditional interpretation of the χ parameter) and the slope is related to ΔV .

Model polyolefins, deuterium-labeled polymethylbutylene (*d*PMB) and polyethylbutylenes (*h*PEB1 and *h*PEB2), were synthesized and characterized by methods described elsewhere.⁸ The numbers of repeat units per chain (C_5 units in PMB and C_6 units in PEB) in the three components were determined to be $N_{dPMB} = 2465$, $N_{hPEB1} = 525$, and $N_{hPEB2} = 2630$ and the average number of deuterium atoms per repeat unit in *d*PMB was 6.1. Four binary blends with compositions given in Table 1 were prepared by dissolving the components in cyclohexane and then evaporating the solvent. The blends were placed in a high-pressure cell equipped with sapphire windows that enable the passage of neutrons. Small-angle neutron scattering experiments were con-

[†] Polytechnic University.

[‡] National Institutes of Standards.

[§] University of Houston.

^{||} Pennsylvania State University.

Table 1. Composition of Blends Studied

blend	components		Φ^a
	A	B	
B1	dPMB1	hPEB1	0.414
B2	dPMB1	hPEB1	0.203
B3	dPMB1	hPEB2	0.161
B4	dPMB1	hPEB2	0.099

^a Volume fraction of component A is computed at 30 °C and atmospheric pressure, on the basis of weight fraction of the components and measured densities of the components.⁶ The magnitudes of ΔV obtained are too small to have a significant effect on ϕ .

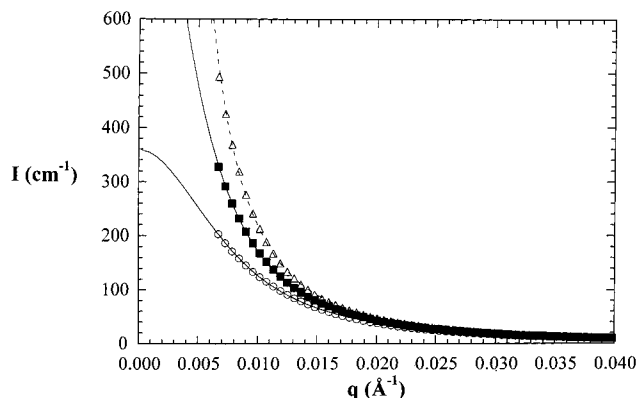


Figure 1. Typical SANS profiles obtained from PMB/PEB blends. Sample B1 at $T = 29$ °C and selected pressures (circles = 0.01 kbar, squares = 0.52 kbar, triangles = 0.86 kbar). The curves through the data represent least-squares fits of the RPA-based theory, which we use to obtain χ . At $P = 0.86$ kbar and $T = 29$ °C, blend B1 is in the two-phase region and the χ parameter obtained from this blend was not used in the analysis.

ducted on the NG3 beam line at the National Institute of Standards and Technology in Gaithersburg, Maryland. The instrument configuration and the procedure for obtaining the absolute coherent scattering intensity, $I(q)$, [$q = 4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle and λ is the wavelength of the incident neutrons] from the raw data are similar to that described in previous papers,^{7,8} and details will be given in a full paper.⁹

Typical SANS data obtained are shown in Figure 1 where we plot $I(q)$ from blend B1 at selected pressures at $T = 29$ °C. It is evident that increasing pressure has a pronounced effect on the scattering from this blend. The theoretical prediction for the scattering profile from polymer blends was obtained by de Gennes¹⁰ using the random phase approximation (RPA). Using this theory to analyze our neutron scattering data is appropriate, because we have assumed identical composition dependencies for ΔU and ΔV . The T and P dependencies of the monomer volumes required for the RPA analysis (eq 2) were obtained explicitly using separate PVT measurements on PMB and PEB homopolymers.¹¹ The solid curves through the data represent least-squares RPA fits through the data with χ and the statistical segments lengths as adjustable parameters.¹² It is evident that the $I(q)$ data are in excellent agreement with RPA predictions. The value of χ determined from the fit at $P = 0.86$ kbar is greater than the value of χ at the binodal, calculated for blend B1 using the Flory–Huggins theory. This implies that at $T = 29$ °C and $P = 0.86$ kbar, blend B1 lies in the two-phase region of the phase diagram. Since the RPA is restricted to single-phase systems and the true limits of metastability in

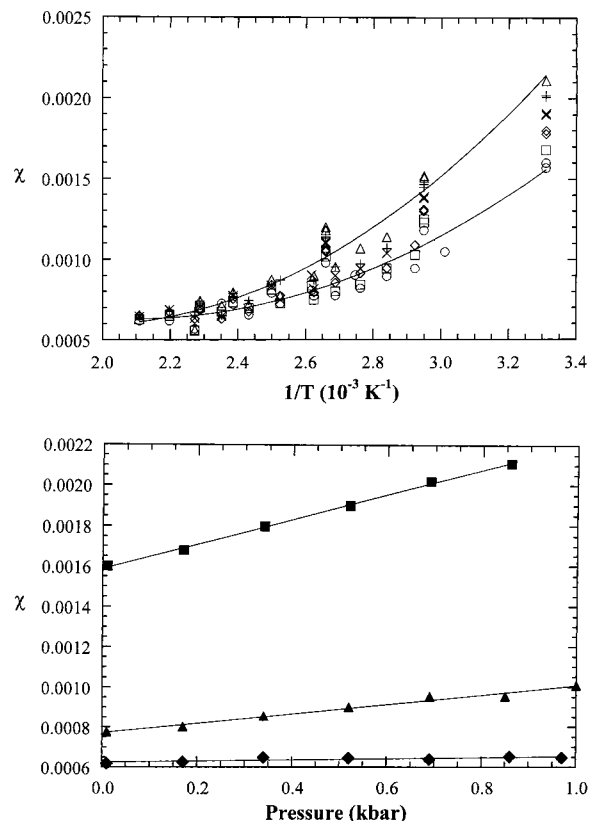


Figure 2. (a) Dependence of χ on P and T for blends B1–4. Circles = 0.01 kbar. Squares = 0.17 kbar. Diamonds = 0.34 kbar. Crosses = 0.52 kbar. Pluses = 0.69 kbar. Triangles = 0.86 kbar. The curves are quadratic fits through the high- (0.86 kbar) and low- (0.01 kbar) pressure data. (b) Typical χ versus P plots. Squares = B2, 29 °C. Triangles = B4, 99 °C. Diamonds = B3, 201 °C. The lines represent least-squares fits through the data.

polymer blends have not been established, we ignore data obtained in the two-phase region.

The SANS data from all of the blends were analyzed by the method described in the preceding paragraph. The results are summarized in Figure 2a where we plot χ versus $1/T$. Pressure has a large effect on χ at low temperatures. At high temperatures, χ is independent of P . In Figure 2b, we show the typical pressure dependence of χ that we have observed. In all cases, χ is a linear function of pressure, as assumed in eq 4. We estimate $\partial\chi/\partial P$ for a given blend at constant temperature by the slope of the least-squares line through the data.

In Figure 3, we show the temperature dependence of $\partial\chi/\partial P$ obtained from all of the blends studied. This quantity is directly proportional to the magnitude of the volume change of mixing: $v/v_0 = (kT/v_0)(\partial\chi/\partial P)$. The curve in Figure 3 is a least-squares quadratic fit through the data. It is evident that the dependence of $\partial\chi/\partial P$ on $1/T$ (Figure 3) is similar to the dependence of χ on $1/T$ (Figure 1). At low temperatures ($T < 130$ °C, $1/T = 0.0025$ K^{−1}), $\partial\chi/\partial P$ is a strong function of temperature. At temperatures between 130 and 200 °C, $\partial\chi/\partial P$ is approximately zero; the average value at $T > 130$ °C is 6×10^{-5} kbar^{−1}, which is comparable to experimental error. In this regime, our model indicates that $\chi = u(T)$, and the PMB/PEB blends are in perfect compliance with the Flory–Huggins theory. The data shown in Figure 3 cover a wide range of blend compositions and pressures. (Note that both ϕ and N_i have been varied in our experiments.) The observed collapse of all of the

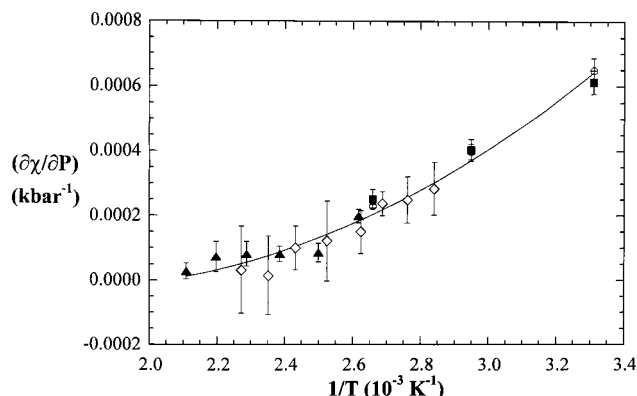


Figure 3. Temperature dependence of $\partial\chi/\partial P$ at constant composition. Circles = B1. Squares = B2. Triangles = B3. Diamonds = B4. The curve is a least-squares quadratic fit through the data.

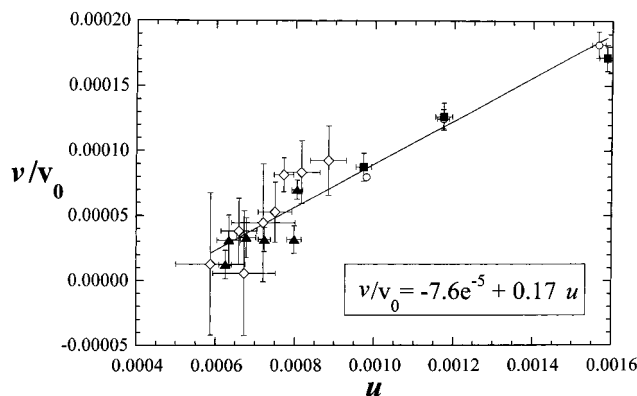


Figure 4. Dependence of the volume change of mixing parameter ν/ν_0 on the internal energy change of mixing parameter, u . The line represents a least-squares fit through the data.

data in Figure 3 indicates that the experimentally determined ν is independent of blend composition and pressure.

We present a simple explanation for the observed temperature dependence of the volume change of mixing seen in Figure 3. In Figure 4, we plot ν/ν_0 versus u for all of the blends studied. As mentioned before, we obtain u from the intercept of the χ versus P plots (Figure 2b). A linear relationship between ν/ν_0 and u is evident in Figure 4. Such a relationship was anticipated by Prigogine and coworkers who developed the cell model for liquid mixtures.¹³ The data in Figure 4 suggest that the observed volume changes of mixing in PMB/PEB mixtures are, in fact, dependent on the internal energy changes of mixing. At low temperatures where ΔU is relatively large and the intermolecular interactions are unfavorable, we find correspondingly large values of ΔV . As temperature increases and ΔU decreases, ΔV also decreases. Extrapolation of the linear fit through the data in Figure 4 suggests that $\Delta V = 0$ when $u = 0.0005$. At this point, the intermolecular interactions, though unfavorable, are sufficiently small in magnitude so that ΔV is nearly zero.

To summarize, we have studied SANS from a series of PMB/PEB blends over a wide range of blend compositions, component molecular weights, temperatures, and pressures. We found that these data were consistent with a simple extension of the Flory–Huggins theory that accounts for finite volume changes of mixing. The data from all of our samples collapsed onto a master

line (Figure 4) when ν/ν_0 was plotted as a function of u . Note that although u and ν are independent of ϕ and N_i , ΔV and ΔU are not. The observed collapse in Figure 4 thus lends considerable support to the proposed functional forms of ΔU and ΔV . Since ν is a unique function of u (Figure 4), the temperature and pressure dependence of the thermodynamics of PMB/PEB blends can be deduced from a single, temperature-dependent parameter, namely, $\chi(T)$, determined at atmospheric pressure. The only effect of high pressure on these blends is to add a $P\Delta V$ contribution toward ΔH . Of course, interactions that are more complex may be found in other polymer blends such as the PS/PVME system.^{4,14} There is thus no guarantee that u and ν will be independent of pressure for all systems. A direct proof of the proposed model requires independent measurements of $(\partial\chi/\partial P)$ and ΔV . A polyolefin blend with a measurable ΔV would be ideal for this purpose, and efforts to identify such a blend are underway.

Educational discussions with Mike Abbott and financial support, provided by the National Science Foundation Grants DMR-9457950 and CTS-9805852 to Polytechnic University and CTS-9704907 to Pennsylvania State University, are gratefully acknowledged. The SANS instrument is supported by Grant No. DMR-9423101 from the National Science Foundation to NIST.¹⁵

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