

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

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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.<sup>1</sup> The results are interpreted in terms of the internal energy change of mixing,  $\Delta U$ , using the Flory–Huggins theory.<sup>2</sup> 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.<sup>3</sup> 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.<sup>4</sup> 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 ( $\Delta G$  is the Gibbs energy change of mixing per unit volume of the mixture and  $\phi$  is the volume fraction of one of the polymers). This follows from the fact that<sup>5</sup>

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

where  $\Delta V$  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,  $\phi$  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  $i$ ,  $\chi$  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,  $149 \text{ \AA}^3$ . Note that this formalism automatically accounts for differences in the monomer volumes of the components. From this point on, we express thermodynamic potentials ( $\Delta G$ ,  $\Delta U$ , and  $\Delta H$ ) in units of  $kT$  per unit volume. In the original Flory–Huggins theory,  $\chi$  was interpreted as a purely energetic interaction parameter, and the second term in eq 2 is equal to  $\Delta H$  (enthalpy change of mixing). Since all other non-idealities of mixing (e.g.,  $\Delta V$ ) are ignored,  $\Delta H = \Delta U$  (internal energy change of mixing).

We now include cases where  $\Delta V$  is non-zero and extend the definition of  $\chi$  to account for this nonideality of mixing. Differentiating eq 2, first with respect to  $P$  and then twice with respect to  $\phi$ , and substituting eq 1, it follows that<sup>6</sup>

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

For illustration, if  $\Delta V$  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  $\Delta V$  has been used to interpret pressure-dependent data from small-molecule mixtures.<sup>5</sup> Equation 3 can be used to obtain equivalent expressions relating  $\partial\chi/\partial P$  and  $\Delta V$ , if the composition dependence of  $\Delta V$  is more complicated. If  $\chi$  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 “ $\chi$  parameter” in a manner that makes contact with previous literature on polymer blends. Thus if  $\chi$  is a linear function of  $P$ , then the intercept is related to  $\Delta U$  in the  $P = 0$  limit (the more traditional interpretation of the  $\chi$  parameter) and the slope is related to  $\Delta V$ .

Model polyolefins, deuterium-labeled polymethylbutylene ( $dPMB$ ) and polyethylbutylenes ( $hPEB1$  and  $hPEB2$ ), were synthesized and characterized by methods described elsewhere.<sup>8</sup> 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  $dPMB$  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-

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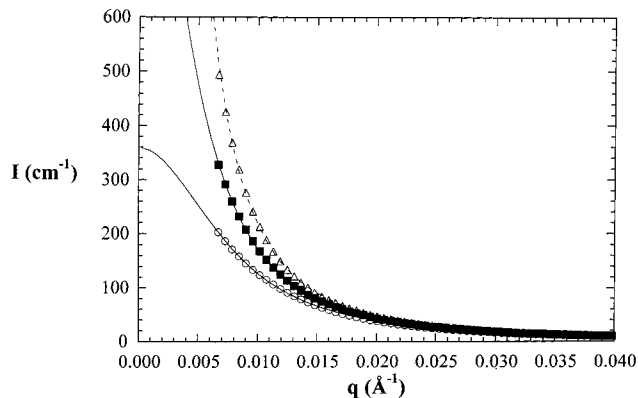
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**Table 1. Composition of Blends Studied**

blend	components		$\Phi^a$
	A	B	
B1	<i>d</i> PMB1	<i>h</i> PEB1	0.414
B2	<i>d</i> PMB1	<i>h</i> PEB1	0.203
B3	<i>d</i> PMB1	<i>h</i> PEB2	0.161
B4	<i>d</i> PMB1	<i>h</i> PEB2	0.099

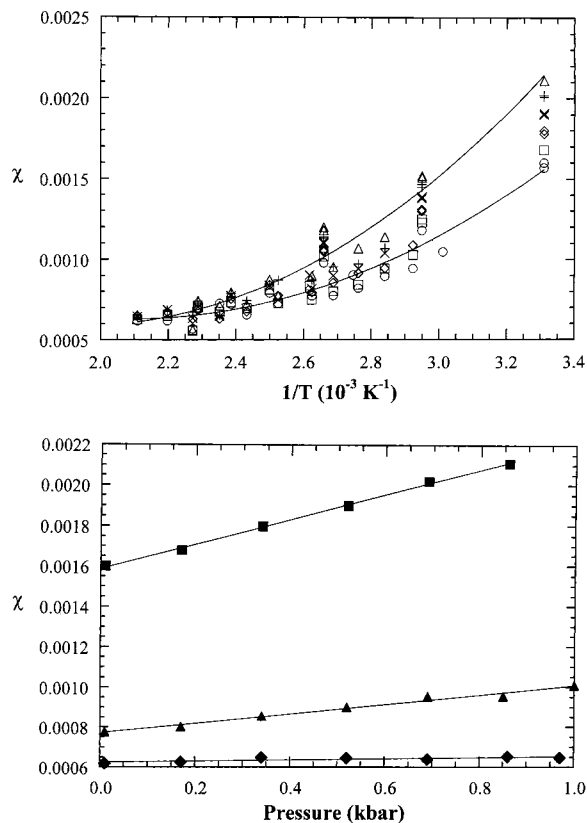
<sup>a</sup> Volume fraction of component A is computed at 30 °C and atmospheric pressure, on the basis of weight fraction of the components and measured densities of the components.<sup>6</sup> The magnitudes of  $\Delta V$  obtained are too small to have a significant effect on  $\phi$ .



**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  $\chi$ . At  $P = 0.86$  kbar and  $T = 29$  °C, blend B1 is in the two-phase region and the  $\chi$  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  $\theta$  is the scattering angle and  $\lambda$  is the wavelength of the incident neutrons] from the raw data are similar to that described in previous papers,<sup>7,8</sup> and details will be given in a full paper.<sup>9</sup>

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 Gennes<sup>10</sup> 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  $\Delta U$  and  $\Delta V$ . 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.<sup>11</sup> The solid curves through the data represent least-squares RPA fits through the data with  $\chi$  and the statistical segment lengths as adjustable parameters.<sup>12</sup> It is evident that the  $I(q)$  data are in excellent agreement with RPA predictions. The value of  $\chi$  determined from the fit at  $P = 0.86$  kbar is greater than the value of  $\chi$  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

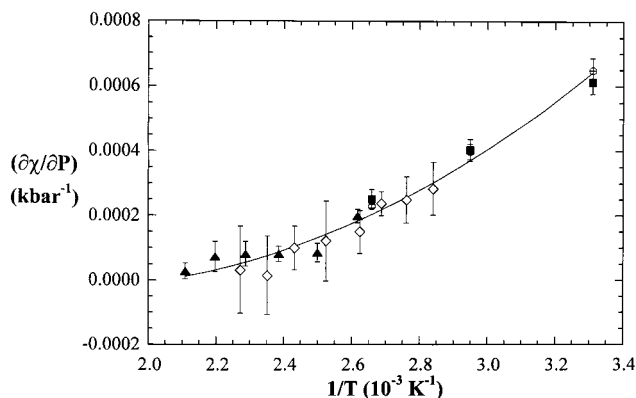


**Figure 2.** (a) Dependence of  $\chi$  on  $P$  and  $T$  for blends B1–4. Circles = 0.01 kbar. Squares = 0.17 kbar. Diamonds = 0.34 kbar. Crosses = 0.52 kbar. Pluses = 0.69 kbar. Triangles = 0.86 kbar. The curves are quadratic fits through the high- (0.86 kbar) and low- (0.01 kbar) pressure data.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

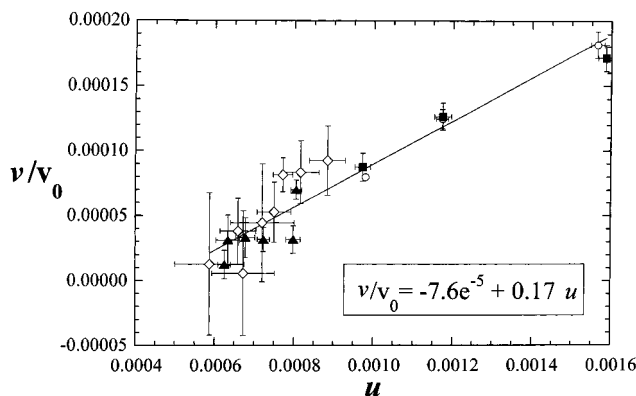
polymer blends have not been established, we ignore data obtained in the two-phase region.

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  $\chi$  versus  $1/T$ . Pressure has a large effect on  $\chi$  at low temperatures. At high temperatures,  $\chi$  is independent of  $P$ . In Figure 2b, we show the typical pressure dependence of  $\chi$  that we have observed. In all cases,  $\chi$  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:  $\nu/v_0 = (kT/v_0)(\partial\chi/\partial P)$ . 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  $\chi$  on  $1/T$  (Figure 1). At low temperatures ( $T < 130$  °C,  $1/T = 0.0025$  K<sup>-1</sup>),  $\partial\chi/\partial P$  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  $6 \times 10^{-5}$  kbar<sup>-1</sup>, 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  $\phi$  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  $\nu/\nu_0$  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  $\nu$  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  $\nu/\nu_0$  versus  $u$  for all of the blends studied. As mentioned before, we obtain  $u$  from the intercept of the  $\chi$  versus  $P$  plots (Figure 2b). A linear relationship between  $\nu/\nu_0$  and  $u$  is evident in Figure 4. Such a relationship was anticipated by Prigogine and coworkers who developed the cell model for liquid mixtures.<sup>13</sup> 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  $\Delta U$  is relatively large and the intermolecular interactions are unfavorable, we find correspondingly large values of  $\Delta V$ . As temperature increases and  $\Delta U$  decreases,  $\Delta V$  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  $\Delta V$  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  $\nu/\nu_0$  was plotted as a function of  $u$ . Note that although  $u$  and  $\nu$  are independent of  $\phi$  and  $N_i$ ,  $\Delta V$  and  $\Delta U$  are not. The observed collapse in Figure 4 thus lends considerable support to the proposed functional forms of  $\Delta U$  and  $\Delta V$ . Since  $\nu$  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  $\Delta H$ . Of course, interactions that are more complex may be found in other polymer blends such as the PS/PVME system.<sup>4,14</sup> There is thus no guarantee that  $u$  and  $\nu$  will be independent of pressure for all systems. A direct proof of the proposed model requires independent measurements of  $(\partial\chi/\partial P)$  and  $\Delta V$ . A polyolefin blend with a measurable  $\Delta V$  would be ideal for this purpose, and efforts to identify such a blend are underway.

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- Identification of equipment and materials does not imply recommendation by the National Institute of Standards and Technology.