Measurements of the Flory−Huggins Interaction Parameter Using a Series of Critical Binary Blends

Alisyn J. Nedoma,[†] Megan L. Robertson,[†] Nisita S. Wanakule,[†] and Nitash P. Balsara*[,†,‡,§]

Department of Chemical Engineering, University of California, Berkeley, California 94720, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, and Environmental Energy and Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

The Flory−Huggins interaction parameter, χ, for a series of critical binary blends of polyisobutylene and deuterated polybutadiene was measured by small-angle neutron scattering. χ was determined by fitting the scattering intensity profiles single-phase blends to the well-established random-phase approximation. Our experiments, which covered a wide range of chain lengths, suggest that χ depends on both blend composition and the ratio of the homopolymer chain lengths.

Introduction

The Flory−Huggins theory continues to be the starting point for quantifying the interactions between chemically dissimilar polymer chains.[1,2] In this theory, the free energy per unit volume for mixing two polymers labeled "1" and "2", ΔG_m, is

$$\frac{\Delta G_m \upsilon}{kT} = \frac{\phi_1 \ln \phi_1}{N_1} + \frac{(1-\phi_1)\ln(1-\phi_1)}{N_2} + \chi\phi_1(1-\phi_1) \quad (1)$$

where ϕ_1 is the volume fraction of component 1 in the mixture, υ is a reference volume which we set equal to 0.1 nm^3, k is the Boltzmann constant, T is the absolute temperature, and N_i is the number of repeat units per chain of type i ($i = 1, 2$), where each repeat unit is assumed to have a volume equal to υ. We compute N_i using

$$N_i = \frac{\hat{N}_i \upsilon_i}{\upsilon} \quad (2)$$

where $\hat{N}_i$ is the number of chemical repeat units in chain i and υ_i is the volume of each chemical repeat unit. The volume fraction of component 1 at the critical point is given by

$$\phi_{1,c} = \frac{1}{1 + (N_1/N_2)^{1/2}} \quad (3)$$

For blends that are in perfect agreement with the Flory−Huggins theory, χ should be independent of ϕ_1 and N_i. In many systems, however, this is not the case.[3−12] It is generally assumed that χ depends on blend composition but is independent of component molecular weight, i.e., $\chi(\phi_1)$.[3−12] This implies that a quantitative understanding of polymer blend thermodynamics will require more sophisticated theories that go beyond the one-parameter Flory−Huggins theory. There is, however, no consensus on how to improve upon the Flory−Huggins theory.

Measurements of χ for a chosen pair of polymers are typically made using one set of polymers, i.e., for a particular value of N_1 and N_2.[13] There are relatively few cases where polymer blend thermodynamics are studied as a function of component molecular weight (e.g., ref 3). In this study we examine a series of blends composed of polymers with N_i ranging from about 200 to 3600. We use small-angle neutron scattering (SANS) measurements from single-phase blends to determine χ, as first suggested by de Gennes.[14] The SANS technique works best when the blend is at the critical composition, because small changes in χ near the critical point result in large changes in the scattering profile. We thus report data obtained from critical blends, calculated using eq 3 for our polymer pairs.

Experimental Section

Component 1 in the polymer blends was polyisobutylene (PIB), and component 2 was deuterated polybutadiene (dPBD) with 63% 1,2-addition. Deuterated polybutadiene was synthesized via anionic polymerization using techniques described in ref 15. The C═C double bonds were saturated under high pressure using deuterium gas. Polyisobutylene was synthesized via cationic polymerization, also described in ref 15. The polymers used in this study are listed in Table 1. Binary blends were prepared according to the methods described in ref 15. The compositions of the blends studied in this paper are listed in Table 2. Blends are labeled B[x], where x denotes the value of the ratio N_1/N_2 of the polymers used to make each blend. SANS measurements were made on beamline NG7 at the National Institute of Standards and Technology in Gaithersburg, MD. The raw data were corrected for detector sensitivity, background, empty cell, incoherent scattering, and scattering due to inhomogeneous deuteration using standard methods;[16] then they were converted to absolute coherent scattering intensity, I, versus magnitude of the scattering vector, q ($q = 4\pi\sin(\theta/2)/\lambda$, where θ is the scattering angle and λ is the wavelength of the incident beam).

Results and Discussion

The random-phase approximation (RPA) gives the following expression for the coherent SANS profile, $I(q)$.[14]

$$I(q) = \frac{(b_1 - b_2)^2}{\upsilon}\left[\frac{1}{N_1\phi_1 P_1(q)} + \frac{1}{N_2\phi_2 P_2(q)} - 2\chi\right]^{-1} \quad (4)$$

* To whom correspondence should be addressed. Tel.: (510) 642-8937. Fax: (510) 642-4778. E-mail: nbalsara@berkeley.edu.
[†] Department of Chemical Engineering, University of California.
[‡] Materials Sciences Division, Lawrence Berkeley National Laboratory.
[§] Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory.

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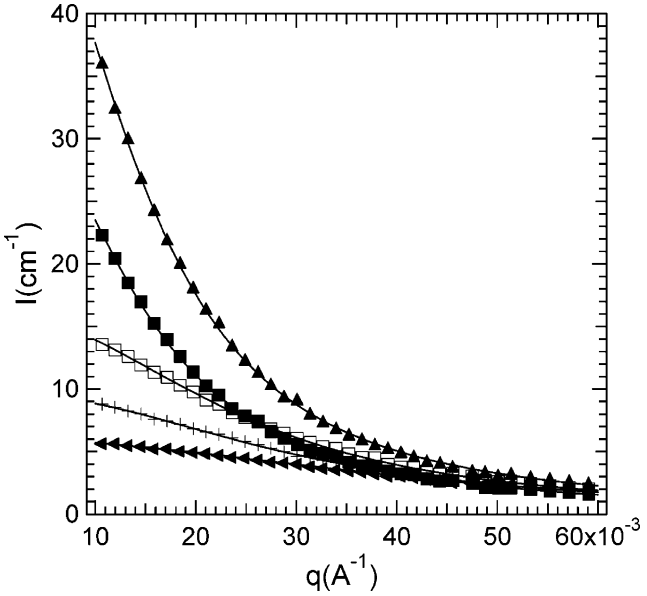

Figure 1. SANS intensity, I, versus magnitude of the scattering vector, q, at 383 K for each blend: B[0.92] (▲), B[0.29] (■), B[4.24] (□]), B[0.20] (+), and B[1.19] (left-pointing solid triangle). The solid curves are the RPA fits to the scattering profile.

Table 1. Characterization of Polymers[a]

name	M_w (kg/mol)	PDI	ρ (g/mL)	N	n_D
PIB(13)	12.5	1.04	0.9134	227	NA
PIB(45)	44.6	1.04	0.9140	810	NA
PIB(57)	56.8	1.02	0.9144	1031	NA
dPB63(10)	10.5	1.02	0.9125	191	3.44
dPB63(58)	62.0	1.01	0.9187	1120	3.65
dPB63(187)	197.2	1.02	0.9123	3589	3.04

[a] M_w is the weight-average molecular weight (for deuterated species the weight in parentheses is that of the hydrogenated analogue); PDI is the polydispersity index M_w/M_n, where M_n is the number-average molecular weight; ρ is the average density measured using a density gradient column; N is the number of reference volumes comprising a single chain; and n_D is the average number of deuterium atoms per C_4 repeat unit.

Table 2. Composition of Binary Blends Used To Measure χ

blend	component 1	component 2	ϕ_1	N_1/N_2
B[0.06]	PIB(13)	dPB63(187)	0.799	0.0632
B[0.20]	PIB(13)	dPB63(58)	0.690	0.2027
B[0.23]	PIB(45)	dPB63(187)	0.678	0.2257
B[0.29]	PIB(57)	dPB63(187)	0.651	0.2873
B[0.72]	PIB(45)	dPB63(58)	0.540	0.7232
B[0.92]	PIB(57)	dPB63(58)	0.510	0.9205
B[1.19]	PIB(13)	dPB63(10)	0.478	1.1885
B[4.24]	PIB(45)	dPB63(10)	0.327	4.2408
B[5.40]	PIB(57)	dPB63(10)	0.301	5.3979

where $\phi_2 = 1 - \phi_1$ and $P_i(q)$ is the Debye function and is given by

$$P_i(q) = \frac{2}{(qR_{g,i})^2}\{\exp[-(qR_{g,i})^2] + (qR_{g,i})^2 - 1\} \qquad (5)$$

$R_{g,i}$ is the radius of gyration of a chain of species i and is related to the statistical segment length of a chain of type i, l_i, by $R_{g,i}^2 = N_i l_i^2/6$.

Our procedure for extracting χ from SANS is outlined in ref 16. In Figure 1 we show typical RPA fits through the SANS data obtained from selected blends at 383 K with χ and α as the only adjustable parameters. α is given by $\alpha = l_1(T)/l_{1,std} = l_2(T)/l_{2,std}$, where $l_{i,std}$ are the nominal values for the statistical segment lengths established in the literature;[15] $l_{1,std}$ and $l_{2,std}$ are 0.58 and 0.75 nm, respectively. The α values for all of the blends

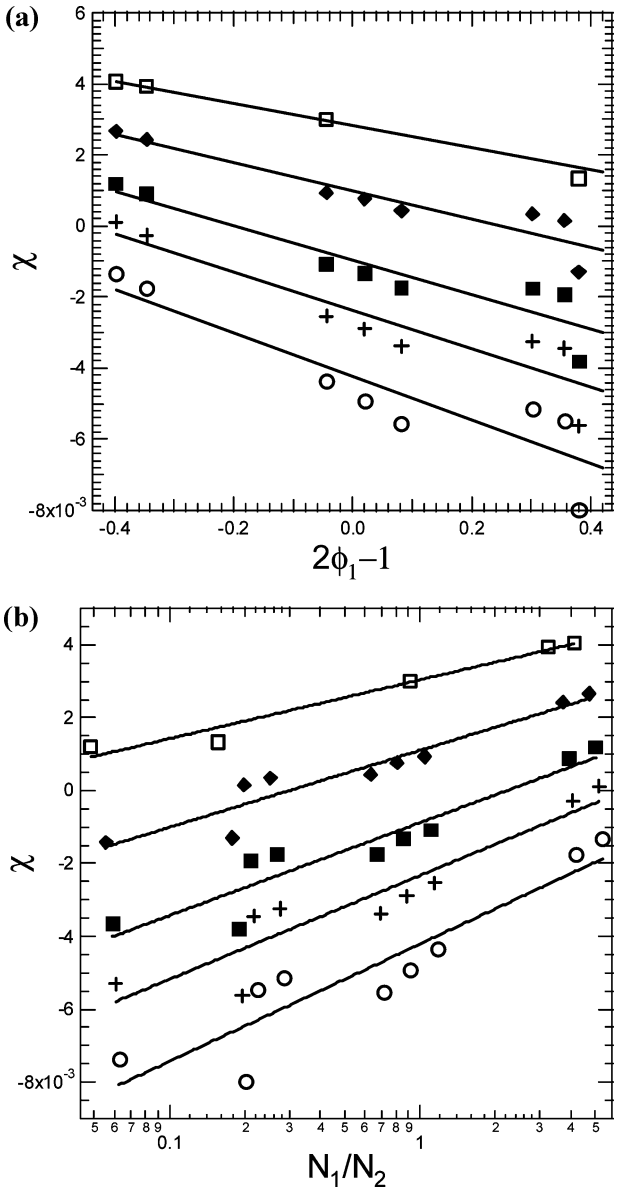

Figure 2. (a) Dependence of χ on blend composition, ϕ_1, at selected temperatures: 474 (□), 383 (◆), 342 (■), 322 (+), and 302 K (○). The solid lines are least-squares linear fits though each data set. Typical uncertainty in χ is about 1×10^{-3}. (b) χ versus N_1/N_2 for selected temperatures: 474 (□), 383 (◆), 342 (■), 322 (+), and 302 K (○). The solid lines are least-squares linear fits though each data set (semilogarithmic). Typical uncertainty in χ is about 1×10^{-3}.

in the temperature range of 302−474 K were between 0.89 and 1.02. It is evident from Figure 1 that the RPA fits capture all aspects of the SANS profiles.

In parts a and b of Figure 2, we show the dependence of χ on ϕ_1 and N_1/N_2, respectively. Since the blends are at the critical composition, ϕ_1 and N_1/N_2 are related by eq 3. We use $(2\phi_1 - 1)$ as the abscissa in Figure 2a for convenience as this quantity is zero when $N_1/N_2 = 1$. For the case of blends with $N_1/N_2 \approx 1$, we see excellent agreement between the χ parameters measured from the different blends. The values of χ obtained from blends B[1.19] and B[0.92] differ by about 10% (which is the typical experimental uncertainty in χ determined by SANS) in spite of the large difference in N_1; N_1 is 227 for B[1.19] and 1031 for B[0.92]. The $N_1/N_2 \approx 1$ data seem to imply that the thermodynamics of PIB/dPBD blends are in good agreement with the Flory−Huggins theory. However, the χ parameters measured from blends with N_1/N_2 values that are

Table 3. Intercepts and Slopes, $A(T)$ and $B(T)$, for the Fit of $\chi = A(T) + B(T)[2\phi_1 - 1]$

T (K)	$A(T)$	$B(T)$
302	−0.004 24	−0.006 09
322	−0.002 39	−0.005 39
342	−0.000 97	−0.004 81
363	0.000 14	−0.004 33
383	0.000 98	−0.003 98
403	0.001 57	−0.003 77
423	0.001 98	−0.003 72
443	0.002 37	−0.003 44
463	0.002 69	−0.003 20
474	0.002 82	−0.003 09

Table 4. Intercepts and Slopes, $C(T)$ and $D(T)$, for the Fit of $\chi = C(T) + D(T) \log(N_1/N_2)$

T (K)	$C(T)$	$D(T)$
302	−0.004 21	0.003 22
322	−0.00233	0.002 85
342	−0.000 88	0.002 55
363	0.000 25	0.002 30
383	0.001 10	0.002 11
403	0.001 72	0.001 99
423	0.002 17	0.001 94
443	0.002 58	0.001 79
463	0.002 91	0.001 67
474	0.003 04	0.001 61

significantly different from unity show departures from the values obtained when $N_1/N_2 \approx 1$. Values obtained from blends with $N_1/N_2 < 1.0$ are systematically smaller than those obtained from $N_1/N_2 > 1.0$. These general observations hold for all of the temperatures that were examined (Figure 2). The lines in Figure 2 are least-squares linear fits through the data, and the results of the fits are tabulated in Tables 3 and 4. The data in Figure 2 thus suggest that χ may, in fact, be a function of two variables, ϕ_1 and N_1/N_2. The dependence on ϕ_1 is similar to that reported in polystyrene/polyvinylmethyl ether blends,[3] where it has been argued that compressibility effects are responsible for the linear composition dependence.[12] It is conceivable that similar effects are responsible for the composition dependence of χ in PIB/dPBD blends. The theoretical work in ref 12 also suggests that compressibility effects cause the measured χ to depend on molecular weight. It is clear that further experimental work, wherein both ϕ_1 and N_1/N_2 are varied independently, is needed to establish the variables that affect the Flory−Huggins interaction parameter. Finally, it is worth noting that the compositions of the critical blends studied here were calculated on the assumption that χ is independent of ϕ_1, N_1, and N_2. The proximity of the blends to the true critical composition will have to be reevaluated after all of the variables that affect χ have been identified.

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Literature Cited

(1) Flory, P. J. Thermodynamics of high polymer solutions. *J. Chem. Phys.* **1941**, *9*, 660.

(2) Huggins, M. L. Solutions of long chain compounds. *J. Chem. Phys.* **1941**, *9*, 440.

(3) Han, C. C.; Bauer, B. J.; Clark, J. C.; Muroga, Y.; Matsushita, Y.; Okada, M.; Qui, T. C.; Chang, T. H.; Sanchez, I. C. Temperature, Composition and Molecular-Weight Dependence of the Binary Interaction Parameter of Polystyrene Polyvinyl Methyl-Ether) Blends. *Polymer* **1988**, *29*, 2002.

(4) Bates, F. S.; Muthukumar, M.; Wignall, G. D.; Fetters, L. J. Thermodynamics of Isotopic Polymer Mixtures—Significance of Local Structural Symmetry. *J. Chem. Phys.* **1988**, *89*, 535.

(5) Schwahn, D.; Hahn, K.; Streib, J.; Springer, T. Critical Fluctuations and Relaxation Phenomena in the Isotopic Blend Polystyrene Deuteropolystyrene Investigated by Small-Angle Neutron-Scattering. *J. Chem. Phys.* **1990**, *93*, 8383.

(6) Herktmaetzky, C.; Schelten, J. Critical Fluctuations in a Binary Polymer Mixture. *Phys. Rev. Lett.* **1983**, *51*, 896.

(7) Ito, H.; Russell, T. P.; Wignall, G. D. Interactions in Mixtures of Poly(Ethylene Oxide) and Poly(Methyl Methacrylate). *Macromolecules* **1987**, *20*, 2213.

(8) Murray, C. T.; Gilmer, J. W.; Stein, R. S. Neutron-Scattering Investigation of the Interaction between Components in Concentrated, Miscible, Amorphous Polymer Blends. *Macromolecules* **1985**, *18*, 996.

(9) Hahn, K.; Schmitt, B. J.; Kirschey, M.; Kirste, R. G.; Salie, H.; Schmittstrecker, S. Structure and Thermodynamics in Polymer Blends—Neutron-Scattering Measurements on Blends of Poly(Methyl Methacrylate) and Poly(Styrene-Co-Acrylonitrile). *Polymer* **1992**, *33*, 5150.

(10) Krishnamoorti, R.; Graessley, W. W.; Balsara, N. P.; Lohse, D. J. The Compositional Dependence of Thermodynamic Interactions in Blends of Model Polyolefins. *J. Chem. Phys.* **1994**, *100*, 3894.

(11) Mori, K.; Okawara, A.; Hashimoto, T. Order-disorder transition of polystyrene-block-polyisoprene. 1. Thermal concentration fluctuations in single-phase melts and solutions and determination of chi as a function of molecular weight and composition. *J. Chem. Phys.* **1996**, *104*, 7765.

(12) Taylor-Maranas, J. K.; Debenedetti, P. G.; Graessley, W. W.; Kumar, S. K. Compressibility effects in neutron scattering by polymer blends. *Macromolecules* **1997**, *30*, 6943.

(13) Balsara, N. P.; Eitouni, H. B. *Thermodynamics of Polymer Blends*; 2007; Chapter 19.

(14) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(15) Reynolds, B. J.; Ruegg, M. L.; Balsara, N. P.; Radke, C. J.; Shaffer, T. D.; Lin, M. Y.; Shull, K. R.; Lohse, D. J. Thermodynamics of polymer blends organized by balanced block copolymer surfactants studied by mean-field theories and scattering. *Macromolecules* **2004**, *37*, 7401.

(16) Kline, S. *SANS Data Reduction and Analysis*, Version 4.2; National Institute of Standards and Technology: Gaithersburg, MD, 2003.

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