

# MISCIBLE ELASTOMER MIXTURES\*

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## INTRODUCTION

The interaction parameter for a blend is positive in the absence of chemical reaction between the components, reflecting a greater attraction between like segments than unlike segments. The magnitude of the van der Waals interactions can be described by a series whose leading term corresponds to the well-known London equation for the dispersion energy<sup>1</sup>,

$$E_{ij} = -(3/4)I_{ij}\alpha_i\alpha_jr^{-6}, \quad (1)$$

where  $\alpha_i$  is the polarizability of the  $i^{\text{th}}$  molecule or chain unit, separated by  $r$  from the  $j^{\text{th}}$  unit, and  $I_{ij}$  is approximately equal to the ionization potential of the species. From Equation (1) it is seen that the mixing enthalpy associated with dispersive interactions always favors phase segregation. Any miscibility is a consequence of the combinatory entropy so that phase separation can be induced by increases in the molar mass of the constituents. The critical point, or minimum on the spinodal curve, defines a value of the interaction parameter below which the system is miscible at all concentrations of the components. The composition at the critical point is deduced by equating the third derivative of the free energy with respect to concentration to zero. For a Flory-Huggins mixture, this critical composition is given by<sup>2</sup>

$$\phi_i^* = N_j^{1/2}/(N_i^{1/2} + N_j^{1/2}), \quad (2)$$

where  $\phi_i$  and  $N_i$  are the respective volume fraction and degree of polymerization of component  $i$ . The corresponding critical value of the interaction parameter is

$$\chi^* = (V_i V_j)^{1/2}[(V_i N_i)^{-1/2} + (V_j N_j)^{-1/2}]^2/2, \quad (3)$$

where  $V$  represents the segment molar volume. From the critical values of molecular weight required to cause phase separation, the magnitude of the interaction parameter for the system can be deduced from Equation (3)<sup>3</sup>. In recog-

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dition of the fact that real mixtures exhibit deviations in behavior from the predictions of simple Flory-Huggins theory that extend the homogenous region of the phase diagram<sup>4-6</sup>, the interaction parameter determined from the component critical molecular weights is probably underestimated.

For macromolecules, the combinatory entropy makes a sufficiently small contribution to the free energy that miscibility is usually restricted to only those mixtures in which the components chemically interact and thereby effect a negative excess enthalpy. The diminution of such specific interactions from increasing thermal agitation may then occasion the observation of a lower critical solution temperature (LCST) in this type of mixture<sup>7-11</sup>. In the less common case of miscibility absent specific interactions, upper critical solution temperatures (UCST) are expected, since the contribution of the combinatory entropy to the free energy of mixing is proportional to temperature<sup>12</sup>. A difference in liquid structure (free volume) of the components, however, can give rise to a negative contribution to the excess enthalpy, entropy, and volume, with the net effect favoring phase segregation<sup>13</sup>. Since such equation-of-state effects are enhanced by increases in temperature, regular mixtures of polymers can also exhibit LCST. The competing effects of the combinatory entropy and of differences in liquid structure can, in principle, give rise to both upper and lower critical solution temperatures.

The present report is concerned with various mixtures involving polybutadiene (both the 1,2- and 1,4-isomers) and *cis*-1,4-polyisoprene. While in all cases associated with positive excess enthalpies reflecting an absence of specific interactions<sup>14-16</sup>, these mixtures exhibit marked differences in their phase behavior.

## EXPERIMENTAL

Atactic polybutadienes (BR) and *cis*-1,4-polyisoprenes (IR) of various molecular weights were either synthesized or obtained commercially. Their microstructure and macrostructure are listed in Table I. Blends were prepared from cyclohexane solutions by precipitation into methanol and vacuum drying at 40°C.

Thermal expansivities were obtained by multiplying by three the linear expansion coefficient, the latter measured using a Perkin-Elmer TMA-7. Densities were determined by the buoyancy method in methanol.

A Perkin-Elmer DSC-2 was used for calorimetry. Heat capacity changes were recorded while heating 5-7 mg samples at 20°/min from -125°C to 30°C. Annealing experiments consisted of heating at 320°/min to the desired temperature, followed by quenching at >200°/min after varying dwell times. This cooling rate was sufficiently rapid that any changes in the phase structure during quenching were not observable. LCSTs were estimated by incrementally increasing the temperature of the annealing (of 5 min duration) until two transitions were observed in the quenched material upon subsequent reheating. These LCST determinations are somewhat approximate in that they correspond to the temperature at which phase segregation can proceed in 5 min to the extent necessary for calorimetric observation of distinct glass transitions.

TABLE I  
MACRO- AND MICRO-STRUCTURE OF BR AND IR POLYMERS

	Butadiene, %		Isoprene, % 1,4-	$N_w$	$N_w/N_n$
	1,4-	1,2-			
IR <sup>a</sup>	—	—	>95	23000	1.1
IR <sup>a</sup>	—	—	>95	6700	1.1
IR <sup>a</sup>	—	—	>95	4500	1.0
IR <sup>b</sup>	—	—	93	90	1.1
BR <sup>b</sup>	92 <sup>d</sup>	8	—	440	1.1
BR <sup>b</sup>	91 <sup>d</sup>	9	—	100	1.1
BR <sup>c</sup>	3	97 <sup>d</sup>	—	7700	1.2
BR <sup>c</sup>	14	86 <sup>d</sup>	—	7200	1.3
D-BR	—	95 <sup>e</sup>	—	3200	1.3
D-BR	—	95 <sup>e</sup>	—	5200	1.3
BR	3	97 <sup>d</sup>	—	2600	1.2

<sup>a</sup> Polymer Labs Ltd.

<sup>b</sup> Scientific Polymer Products, Inc.

<sup>c</sup> Firestone Tire and Rubber Co.

<sup>d</sup> Atactic.

<sup>e</sup> Deuterated atactic.

## RESULTS AND DISCUSSION

### EXCESS FREE ENERGY OF MIXTURES

The temperature of the glass-to-liquid transition was measured for various blend compositions. The molecular weights required to effect distinct glass transitions for each component, evidencing a heterogeneous phase morphology, were used in Equation (3) to determine the interaction parameter for the IR/BR mixtures. As discussed in detail below, under certain circumstances the transitions measured calorimetrically were very broad (over 40°). Notwithstanding this transition breadth, the thermodynamic miscibility of these particular blends was corroborated by proton and carbon NMR measurements<sup>17</sup> and by observation of spontaneous interdiffusion of the separated pure components<sup>3</sup>.

The interaction parameters determined for blends of IR with BR of varying microstructure are displayed in Table II. It is observed that as the concentration of 1,2 units in the BR increases, there is a large increase in miscibility with IR. At high levels of 1,2 units, phase separation can not be induced even at extremely high molecular weights, indicating a remarkable degree of miscibility given the absence of specific interactions. This miscibility suggests a near equivalence in polarizability between the respective chain units of the 1,2-polybutadiene and the 1,4-polyisoprene, along with a close similarity in liquid structure (or their degree of expansivity). At higher 1,4 content, a larger mixing endotherm restricts miscibility to low molecular weights. The relative contributions to the mixing enthalpy for these blends from changes in van der Waals energy and from equation of state effects are not readily apparent.

TABLE II  
RESULTS FOR MIXTURES OF IR WITH BR COPOLYMERS

1,4 units in BR	$\chi_{exp}^a$	$N^*{}^b$	$\chi_{endo}^c$	$d(\ln V)/dT^d$
92%	$2.4 \times 10^{-3}$	830	$2.8 \times 10^{-3}$	$1.8 \times 10^{-3}$
74%	$1.7 \times 10^{-3}$	1200	—	—
59%	$0.7 \times 10^{-3}$	2900	—	$1.5 \times 10^{-3}$
3%	$<1.7 \times 10^{-4}{}^e$	$>10000{}^e$	$1.6 \times 10^{-3}$	$9.2 \times 10^{-4}$

<sup>a</sup> Experimentally determined for blends containing the critical concentration of components at 27°C.

<sup>b</sup> Critical degree of polymerization ( $-2/\chi_{exp}$ ).

<sup>c</sup> From application of Equation (4) using the data from References 18 and 19.

<sup>d</sup> The thermal expansivity for IR was measured to be  $9.3 \times 10^{-4}$  per degree at 1 atm.

<sup>e</sup> Phase separation not observed.

An assessment of the magnitude of the interchange enthalpies can be made from the solubility parameters of the components, although the solubility parameter data available in the literature are too imprecise for reliable quantitation. According to classical lattice theory, the interchange enthalpy contribution to the free energy is related to the solubility parameters as<sup>13</sup>

$$\chi_{enth} = (V/RT) (\delta_i - \delta_j)^2. \quad (4)$$

The obtained  $\chi_{enth}$  for the IR/BR blends depends on the values for the  $\delta$  selected from among those reported in the literature for these polymers. Results based on the  $\delta$  used by Cohen<sup>18,19</sup> are given in Table II. It is seen by comparison to the measured  $\chi$  that these estimates of  $\chi_{enth}$  are not particularly accurate, nor are assessments of polymer miscibility inferred merely from application of Equation (4). This is partly due to the arbitrary choice of the  $\delta$ , but also reflects limitations of the simple lattice approach. Nevertheless, it is clear that the exchange enthalpy between IR and BR becomes more endothermic (reduced miscibility) as the concentration of 1,4 units in the latter increases. A closer similarity in polarizability between IR and 1,2-BR segments underlies in part the high degree of miscibility of their blends<sup>12,14,15</sup>.

There will also be a contribution to the free energy of mixing from any differences in the liquid structure of the two components<sup>3,13,16</sup>. A difference in their degree of thermal expansion will result in a volume contraction upon mixing, which can influence both the mixing enthalpy and the mixing entropy. Displayed in Figure 1 is the density measured for IR blended with 1,4-BR and 1,2-BR respectively. While the volumes of the latter mixtures are simply additive in the volume of the components, 1,4-BR/IR blends exhibit a negative excess volume. These blend densities reflect the differing contribution of equation-of-state effects to the liquid structure of the mixtures.

Although absence of an excess volume upon mixing does not imply nonadditivity of the enthalpy and noncombinatory entropy, any such equation-of-state contributions to the free energy must be vanishingly small in blends of 1,2-BR with IR in order that miscibility be observed at high component molecular weights. The significance of differences in liquid structure with regard to the

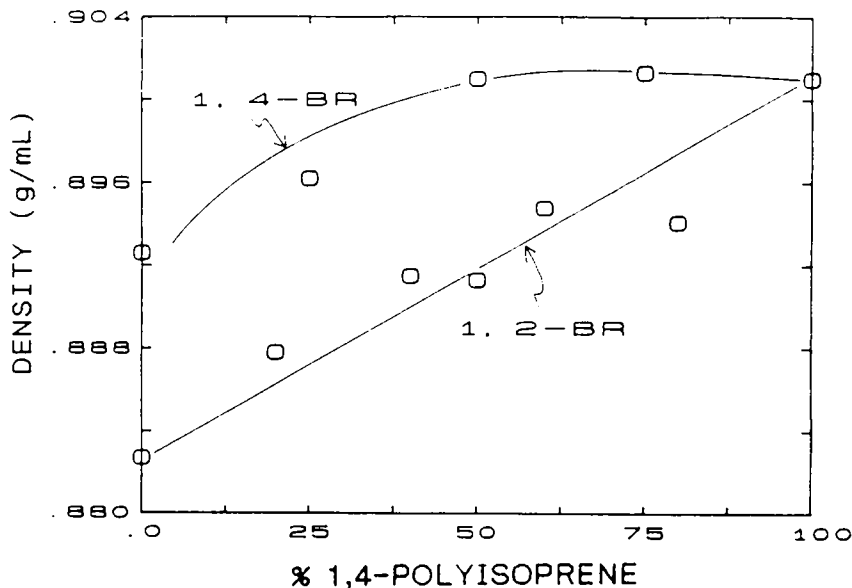


FIG. 1. --The density measured at room temperature for IR mixed with 86% 1,2-BR and 92% 1,4-BR. The latter blends exhibit deviation from additivity indicative of a mismatch in the liquid structure of the pure components.

magnitude of the interaction parameter can be gauged from comparison of the thermal expansion coefficients of the components. The measured thermal expansion coefficient of 1,2-BR and the IR had a difference that only marginally exceeded the experimental error, indicating the similarity in their liquid structure. The expansivity measurements for the BR polymers higher in 1,4 content, however, reveal a distinct mismatch in liquid structure with IR (Table II). These equation-of-state effects are responsible at least in part for the reduction in miscibility that accompanies an increased extent of 1,4 microstructure in the BR.

A further consequence of significant equation-of-state effects is the potential for lower critical solution temperatures<sup>16</sup>. It is expected that when the temperature of a miscible blend of BR and IR is reduced, phase segregation will eventually transpire, since the driving force for miscibility is the combinatorial entropy. Such upper critical solution temperatures, however, are evidently below the glass-transition temperatures of the mixtures herein and thus unobservable. Contrarily, phase separation of miscible mixtures of IR with BR of high 1,4 content were induced by increases in temperature. Representative calorimetry results are displayed in Figure 2 for a blend of 59% 1,4-BR (with  $\phi = 0.38$  and  $N = 1700$ ) and IR ( $N = 4500$ ), for which the LCST is found to be about 50°C. Mixtures of IR and BR having a higher concentration of 1,4 units also exhibited LCST. On the other hand, when the BR microstructure is less than 15% 1,4, no phase separation in blends with IR has ever been observed<sup>3,12,20,21</sup>. The absence

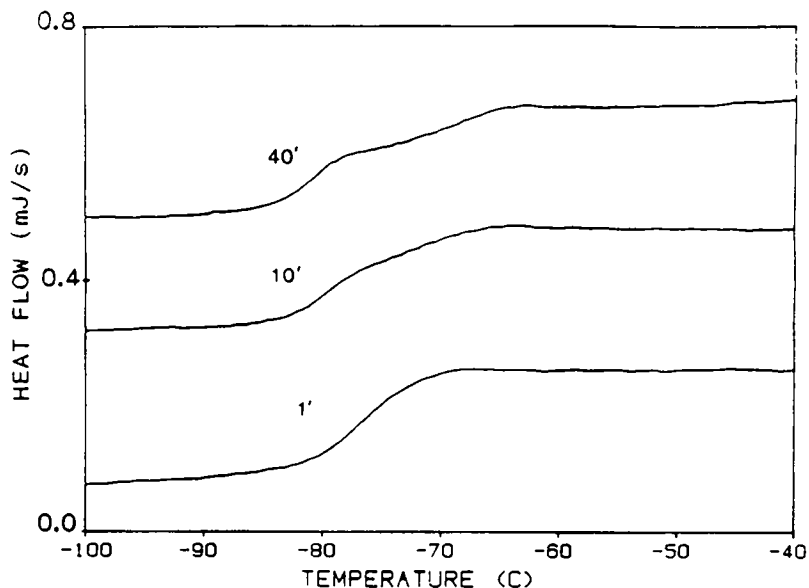


Fig. 2.—The glass-transition behavior of blends of IR ( $N = 4500$ ) with 59% 1,4-BR ( $N = 1700$ ) at the critical concentration of components calculated from Equation (2). The samples were heated from 30°C to 50°C and held at the latter for the indicated time period, followed by quenching to -125°C. The displayed curves, corresponding to measurements made in the ensuing reheating, reflect the increasing extent of phase separation transpiring just above the LCST.

of an LCST is consistent with increased similarity in the expansivities of the components at higher 1,2 microstructure.

#### PHASE MORPHOLOGY AND THE GLASS TO LIQUID TRANSITION

Displayed in Figure 3 are differential-scanning-calorimetry results (measured during heating) for three blends of varying relative concentrations of 1,2-BR and IR. Although only a single transition is observed for each mixture, it can be seen that in some cases, the transition occurs over a broad temperature range (as much as 50° for two of the glass transitions in Figure 3). These are compositions with a higher relative abundance of the higher glass-transition component. When the molecular weights of the components are reduced, effecting an increase in the critical value of the interaction parameter from  $1.7 \times 10^{-4}$  to  $7.6 \times 10^{-3}$  (and hence greater miscibility) the transition remains broad; however, a less miscible sample (for which  $\chi^* = 6.2 \times 10^{-4}$ ) has a relatively sharp glass transition. These results demonstrate that the anomalous transition breadths do not reflect proximity to, or the onset of, a phase separated state.

An influence of blend composition on the abruptness of the heat capacity change at  $T_g$  is not unique to mixtures of 1,2-BR with IR. Blends of 1,2-BR and 1,4-BR are miscible when  $\chi^*$  exceeds  $4.4 \times 10^{-3}$ <sup>16</sup>. Calorimetry measurements for three such mixtures are displayed in Figure 4. A blend sample, with a critical concentration of the components according to Equation (2) and a value for  $\chi^*$

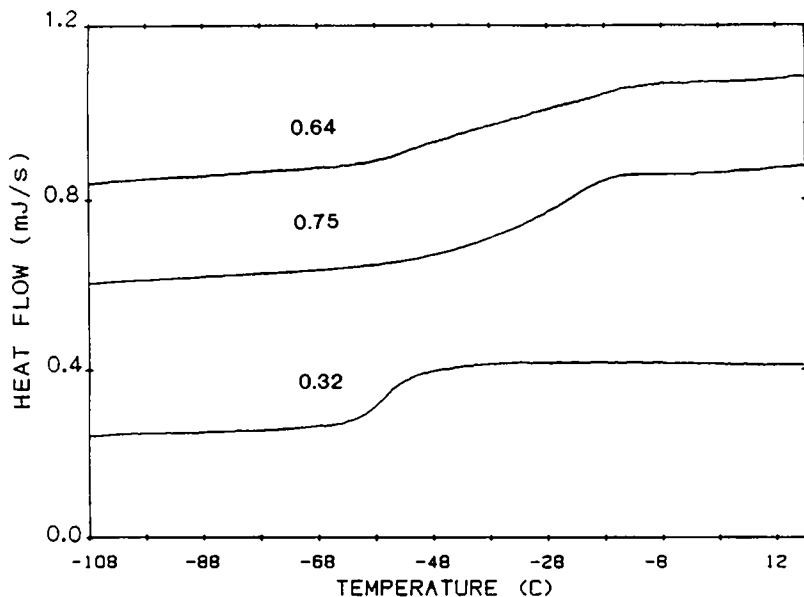


Fig. 3.—Calorimetry results for three miscible blends of IR with 1,2-BR with the indicated volume fraction of the BR. Only the upper curve had a critical concentration of components, and it is, thus, the least miscible (with a critical interaction parameter value equal to  $1.7 \times 10^{-4}$ ). Broad glass transitions are observed in both it and the most miscible of these blends ( $\phi_{BR} = 0.75$  for which  $\chi^* = 7.6 \times 10^{-3}$  for the particular component molecular weights). The sample with 32% BR has the narrowest transition, despite intermediate miscibility ( $\chi^* = 6.2 \times 10^{-4}$ ).

calculated from Equation (3) to be  $7.4 \times 10^{-3}$ , is miscible and exhibits a relatively narrow transition. As the stability of the mixture is increased by altering the composition away from that associated with the critical point, the glass transition broadens when the concentration of the 1,2-BR is increased (Figure 4). At higher component molecular weights (for which  $\chi^* = 2.4 \times 10^{-3}$ ), two distinct glass transitions are observed in Figure 4, reflecting the expected heterogeneous phase morphology. These results demonstrate that the temperature range over which the change in heat capacity associated with  $T_g$  transpires is not necessarily an indication of the degree of miscibility of the composition. The broadening of the transitions herein is only observed in mixtures containing an abundance of 1,2-BR homopolymer. Equivalent mixtures, but in which the polybutadiene has about 15% 1,4 units randomly placed along the chain, do not exhibit such broad glass transitions<sup>12</sup>. Observation of this anomaly is dependent upon the presence of a relative abundance of BR which is, moreover, very high in 1,2 microstructure.

The anomalous breadth of the DSC transitions observed in the blends with a high 1,2-BR concentration is invariant to the thermal treatment imposed. The breadths of these transitions were reproducibly observed irrespective of the rate at which the temperature is changed, and remain essentially the same when  $T_g$  is approached from either direction. The peculiar nature of the glassy

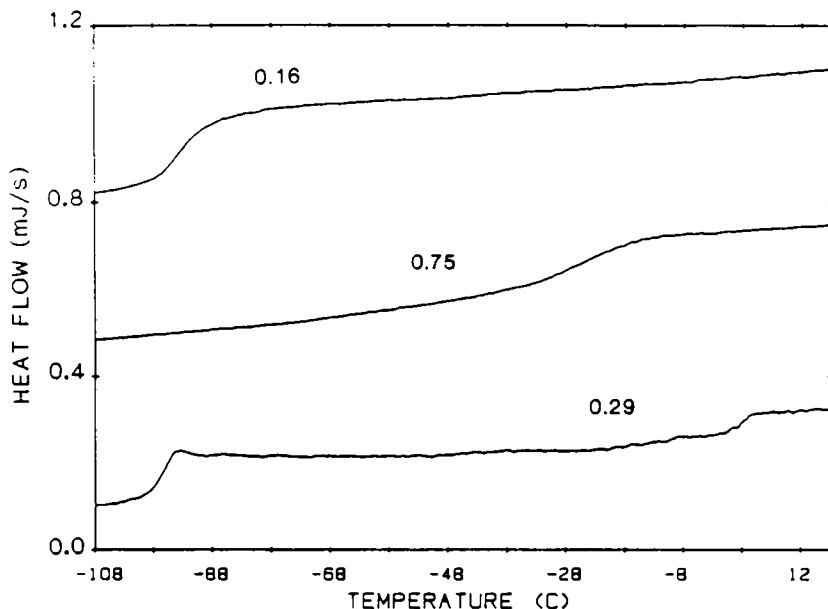


Fig. 4.—Calorimetry results for three blends of 1,2-BR with 1,4-BR, with the indicated volume fraction of the 1,2-BR. It is seen that reducing  $\chi^*$  from  $6.4 \times 10^{-3}$  (the uppermost curve containing a critical concentration of components) to  $2.4 \times 10^{-3}$  (the lowest curve) effects phase separation. A broad  $T_g$  is observed in the sample with a high concentration of 1,2-BR, despite the fact that this is the more stable of the miscible compositions.

transition in these mixtures evidently is not an artifact of nonequilibrium. The broad discontinuity at  $T_g$  was also observed in thermal expansion measurements, as well as in the corresponding mechanical damping transitions<sup>22</sup>. Related to this are some recent results suggesting that, despite spatial homogeneity on the segmental level, the motions of the 1,2-BR and IR chain units do not become liquid-like at precisely the same temperature<sup>17</sup>. The glass-to-rubber transition depends on the available free volume, and this free volume and its fluctuations are equivalent for miscibly blended polymers; however, preliminary indications are that the local accumulation of free volume necessary for the onset of rubbery behavior is different for the IR and 1,2-BR. Despite compositional homogeneity that extends to the subnanometer level, in the vicinity of the glass transition, different chain subunits in the respective components apparently exhibit simultaneously glassy and liquid-like motions due to a difference among the chain segments in the free-volume requirements for rubbery behavior. This aspect of the behavior of BR/IR blends is currently being investigated.

#### ISOTOPE MIXTURES

The interaction parameter was determined for blends of hydrogenous 1,2-BR with deuterated 1,2-BR from nonlinear least-squares fitting of experimental



small-angle neutron scattering intensities to the mean field scattering equation for polymer mixtures<sup>23</sup>,

$$I(Q)^{-1} = [N_i \phi_i g_i(Q)]^{-1} + [N_j \phi_j g_j(Q)]^{-1} - 2\chi, \quad (5)$$

where  $g$  is the Debye scattering function for an ideal chain, and  $Q$  the reduced scattering angle (momentum transfer). The results for one composition at various measurement temperatures are displayed in Figures 5 and 6. These data are in agreement with recently reported results obtained from similar neutron scattering experiments<sup>24</sup>. It is interesting to find that 1,2-BR is less miscible with its deuterated isomer than with the chemically distinct IR. The change in C-H bond length when hydrogens are replaced with deuterons effects an alteration in the polarizability and hence the dispersion energy<sup>25,26</sup>, evidently greater than the difference in van der Waals energy between 1,2-BR and IR.

Using Equation (3), the value of the interaction parameter for this 1,2-BR isotope blend, above which phase segregation can be expected, is calculated to be  $\chi_s = 5.2 \times 10^{-4}$ , with the uncertainty in  $N$  giving an error of less than  $1 \times 10^{-4}$ . As seen from the measured interaction parameter (Figure 6), this isotope mixture is thus predicted to be phase-separated. The neutron scattering results (Figure 5), however, provide clear evidence of miscibility in this blend sample. Both the magnitude and the angle dependence of the SANS measurements are well described by mean field scattering theory and, moreover, the fitting to Equation (5) yielded values of the interaction parameter in good accord with a

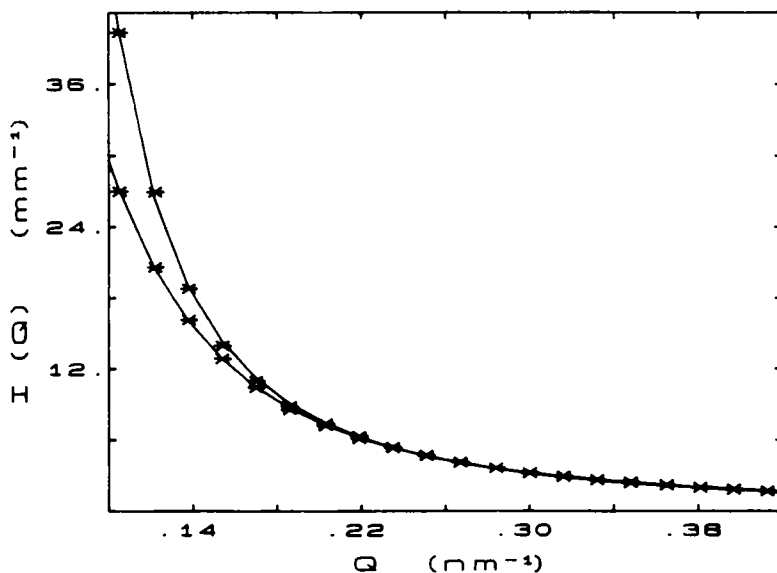


FIG. 5.—The experimental (\*\*\*) and calculated SANS results at 24°C for blends of deuterated 1,2-BR ( $M_w = 192\,000$ ) with respectively 47% by volume by hydrogenous 1,2-BR ( $M_w = 139\,000$ ) and 53% hydrogenous 1,2-BR ( $M_w = 281\,000$ ). For the latter composition (corresponding to the upper scattering curve), the interaction parameter exceeds the Flory-Huggins critical value.

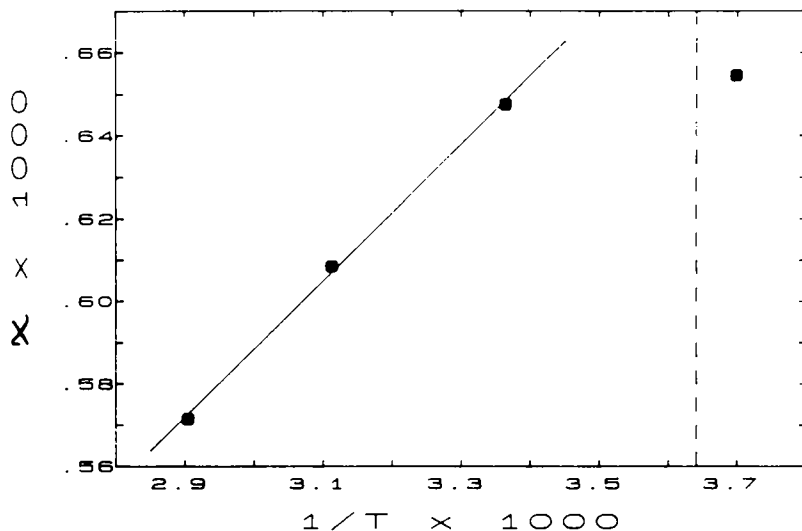


Fig. 6.—The interaction parameter measured for the isotopic mixture of 1,2-BR displayed *versus* the inverse of the various SANS measurement temperatures (in Kelvin). The largest value of  $\chi$  was obtained when the sample was below its glass-transition temperature (denoted by the vertical dashed line). Least squares fitting to the liquid state data yielded the indicated straight line with a slope and intercept of 0.17 degrees and  $9.3 \times 10^{-6}$  respectively.

determination of  $\chi$  for a sample with lower molecular weight components (and thus greater miscibility). SANS measurements on the sample were also found to be time invariant. When a mixture is immiscible, the equilibrium morphology (corresponding to total phase segregation) is never attained due to the high viscosity of the polymeric melt state; nevertheless, when the blend was taken in temperature from ambient (where the viscosity is *circa* 10 GPa·s) to 50° higher, the neutron scattering did not exhibit the time dependence expected for a system in a morphological state of nonequilibrium upon increase in the molecular mobility.

In addition to these neutron scattering results, other indications of miscibility between the components of the mixture were in evidence. For example, if a phase separated morphology was existent, the domains would develop in size over time such that scattering of visible light would be expected (since the molar volume isotope effect gives rise to molecular polarizability differences and, hence, refractive index differences). After annealing for several weeks at room temperature, however, the sample remained transparent, a result consistent with homogeneity. Also, when films consisting of the pure isotopic components were maintained in contact at 50°C, spontaneous interdiffusion was observed. This direct observation of spontaneous mixing of the deuterated and hydrogenous species provides unambiguous evidence of their thermodynamic miscibility. Since the isotope blend is miscible, it is clear that the calculated  $\chi_s$  must be in error. It is emphasized that this error can not be attributed to experimental uncertainties in the molecular weights of the polymers, which could

alter  $\chi_s$ , less than 15%. It must therefore be inferred that the divergence of the experimental phase behavior from the expectations of the calculated spinodal reflects a divergence of the free energy from the simple Flory-Huggins formulation. The inadequacy of Equation (3) in describing the precise location of the spinodal, however, is only made obvious when experiments are carried near the critical region.

The limitations of simple mixing theory in the vicinity of criticality are well established for mixtures of small molecules<sup>27</sup>. It is also well known that the concentration independence of the interaction parameter required by the Flory-Huggins model is rarely observed in polymer mixtures when chemical reaction transpires between the components<sup>28,29</sup>. The failure of the theory to accurately describe the thermodynamics of isotope mixtures, while less expected, is in fact consistent with recent predictions<sup>5,6</sup> of deviations in the combinatorial entropy from the ideal value assumed in the Flory-Huggins model. Local correlation effects, due to chain connectivity<sup>6</sup> and the attractive interactions of like contacts<sup>6</sup>, serve to extend the miscible region in polymer blends.

### CONCLUSIONS

The degree of miscibility of the various IR/BR mixtures is not obvious from inspection of the chemical structures. IR and 1,2-BR, despite their distinct differences in chemical structure, form blends that are always homogenous. On the other hand, the liquid structural differences between IR and 1,4-BR overwhelm their chemical similarities, and it is the former that governs the phase behavior. As the 1,4 content of BR increases, the thermodynamic behavior of BR/IR blends ranges from nearly ideal mixing to the occurrence of an LCST due to negative excess mixing volumes. While the observation of lower critical solution temperatures in polymer mixtures in which no specific interactions exist is unusual, the same mismatch in liquid structure gives rise to the LCST commonly observed in polymer solutions.

The interaction parameter for 1,2-BR in blends with IR is *circa*  $2 \times 10^{-4}$ , which is remarkably low given the absence of specific chemical interactions. These mixtures most closely approximate ideal mixing behavior of any known pair of chemically distinct polymers. Even mixtures of BR isotopes are more nonathermal than blends of 1,2-BR with IR; moreover, the thermodynamic behavior of these isotope mixtures are not in conformance with simple Flory-Huggins lattice theory.

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## REFERENCES

- <sup>1</sup> J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.
- <sup>2</sup> P. G. de Gennes, "Scaling Concepts in Polymer Physics," Cornell University Press, Ithaca, N.Y., 1979.
- <sup>3</sup> C. A. Trask and C. M. Roland, *Macromolecules* **22**, 256 (1989).
- <sup>4</sup> C. M. Roland and C. A. Trask, *Polymer Bull.* **20**, 471 (1988).
- <sup>5</sup> P. Cifra, F. E. Karasz, and W. J. MacKnight, *Macromolecules* **21**, 446 (1988).
- <sup>6</sup> J. G. Curro and K. S. Schweizer, *J. Chem. Phys.* **88**, 7242 (1988).
- <sup>7</sup> F. E. Alexandrovich, F. E. Karasz, and W. J. MacKnight, *Polymer* **18**, 1022 (1977).
- <sup>8</sup> M. Shayama, H. Yang, R. S. Stein, and C. C. Han, *Macromolecules* **18**, 2179 (1985).
- <sup>9</sup> A. Maconnachie, R. P. Kambour, M. W. Dwain, S. Rostami, and D. J. Walsh, *Macromolecules* **17**, 2645 (1984).
- <sup>10</sup> S. H. Goh, D. R. Paul, and J. W. Barlow, *Polym. Eng. Sci.* **22**, 34 (1982).
- <sup>11</sup> C. K. Sham and D. J. Walsh, *Polymer* **28**, 804 (1987).
- <sup>12</sup> C. M. Roland, *Macromolecules* **20**, 2557 (1987).
- <sup>13</sup> "Selected Works of Paul J. Flory, Vol. I," L. Mandelkern, J. E. Mark, U. W. Suter, and D. Y. Yoon, Eds., Stanford Press, 1985, p. 409.
- <sup>14</sup> C. M. Roland, *J. Polym. Sci., Polym. Phys. Ed.* **26**, 839 (1988).
- <sup>15</sup> C. M. Roland, *RUBBER CHEM. TECHNOL.* **61**, 866 (1988).
- <sup>16</sup> C. A. Trask and C. M. Roland, *Polym. Commun.* **29**, 332 (1988).
- <sup>17</sup> C. M. Roland, C. A. Trask, K. Mc Grath, and J. Miller, to be published.
- <sup>18</sup> R. E. Cohen, *ACS Symp. Ser. n.* **193**, 489 (1982).
- <sup>19</sup> R. E. Cohen, *Macromolecules* **15**, 370 (1982).
- <sup>20</sup> G. M. Bartenev and G. S. Kongarov, *RUBBER CHEM. TECHNOL.* **36**, 668 (1963).
- <sup>21</sup> A. Ueda, H. Watanabe, and S. Akita, *Int. Rubber Conf.*, Kyoto, Japan, Oct. 1985, p. 199.
- <sup>22</sup> C. M. Roland and C. A. Trask, *Polym. Mater. Sci. Eng.* **60**, 832 (1989).
- <sup>23</sup> P. G. de Gennes, "Scaling Concepts in Polymer Physics," Cornell University Press, Ithaca, 1979.
- <sup>24</sup> F. S. Bates, L. J. Fetters, and G. D. Wignall, *Macromolecules* **21**, 1086 (1988).
- <sup>25</sup> F. S. Bates and G. D. Wignall, *Phys. Rev. Lett.* **57**, 1429 (1986).
- <sup>26</sup> R. R. Singh and W. A. Van Hook, *Macromolecules* **20**, 1855 (1987).
- <sup>27</sup> R. R. Singh and W. A. Van Hook, *J. Chem. Phys.* **87**, 6088 (1987).
- <sup>28</sup> R. S. Stein and G. Hadziioannou, *Macromolecules* **17**, 1059 (1984).
- <sup>29</sup> C. T. Murray, J. W. Gilmer, and R. S. Stein, *Macromolecules* **18**, 996 (1985).