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Thermodynamic Interactions in Polybutadiene Blends

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ABSTRACT: This paper describes a study of thermodynamic interactions in binary blends of statistical copolymers of 1,4- and 1,2-polybutadiene using differential scanning calorimetric measurements. The Flory−Huggins interaction parameter (χ) obtained for blends with component compositions ranging from 8% to 90% 1,2-polybutadiene were found to be inconsistent with the simple random copolymer theory. The reduced interaction parameter, $\chi/\Delta y^2$, was found to be a strong function of the average composition of the blend, in close analogy to an earlier study on ethylene−butene-1 copolymers prepared by saturation of 1,4-polybutadiene−1,2-polybutadiene copolymers. However, values for $\chi/\Delta y^2$ for the polybutadiene blends were considerably smaller than those present in the ethylene−butene-1 copolymers over comparable ranges of copolymer composition. The *PVT* properties of the polybutadiene copolymers, on the other hand, suggest a much larger interaction as well as adherence to the random copolymer theory.

Introduction

In addition to interest in the rubber industry, the thermodynamic interactions in binary blends of polybutadienes are of intense scientific interest, as they represent the first level of complications beyond the simple thermodynamic interactions present in saturated hydrocarbon polymers, that is, polyolefins.[1,2] The purpose of this work is two-fold—to understand the thermodynamic interactions in polybutadiene blends as well as to compare these interactions to those in corresponding model ethylene−butene-1 copolymer blends, obtained by saturation of the same polybutadienes.[3]

Recently, small angle neutron scattering (SANS) measurements have been utilized to determine the thermodynamic interactions in several polymer blend systems.[2−5] These data are typically interpreted in terms of the incompressible mean-field Flory−Huggins theory,[6] which describes the free energy of mixing per unit volume (ΔG_{mix}) as

$$\frac{\Delta G_{\mathrm{mix}}}{k_{\mathrm{B}}T} = \frac{\phi_1}{N_1 v_1}\ln\phi_1 + \frac{\phi_2}{N_2 v_2}\ln\phi_2 + \frac{\chi}{v_0}\phi_1\phi_2 \qquad (1)$$

where ϕ_i, N_i, and v_i are the volume fraction, the degree of polymerization, and the monomeric unit volume for species i, and χ is the Flory−Huggins segment−segment interaction parameter based on a reference volume v_0. On the basis of this expression for the free energy of mixing and the random phase approximation (RPA),[7] the SANS measured intensities are related to χ. However, deuterium labeling of one of the components, essential to provide labeling for the SANS measurements, introduces additional complications to the thermodynamic measurements by way of an isotopic contribution to the interactions.[4] This isotopic contribution can even cause a blend system, whose protonated components exhibit an upper critical solution temperature, to exhibit a lower critical solution temperature when one of the components is deuterated.[8]

In this paper we report on the phase behavior and the thermodynamic interactions (at 25 °C) in blends of polybutadienes with differing microstructures obtained by differential scanning calorimetric (DSC) measurements. The components are statistical copolymers of 1,2- and 1,4-polybutadiene with microstructures ranging from 8 to 90 mol % 1,2-polybutadiene and are the unsaturated analogues of the ethylene−butene-1 copolymers previously studied.[2,3] Only protonated materials are used in this study, so as to avoid any complications that may arise due to isotopic substitution. These results are presented in the context of earlier SANS work on blends and interpreted in terms of the random copolymer theory and its variants.[9,10] Following that, we discuss the interaction parameters in the polybutadiene blends in relation to those present in ethylene−butene-1 copolymer blends with a comparison of their equation of state (*PVT*) properties[11] to provide an attempt at understanding the interactions in polymer blends.

Background

Sakurai and co-workers[4] have previously examined blends of hydrogenous and deuterated statistical copolymers of 1,4- and 1,2-butadiene over a range of copolymer compositions. While it is recognized that there indeed exist three different microstructures of polybutadiene—cis 1,4, trans 1,4, and vinyl 1,2 units, the chemical differences between cis 1,4 and trans 1,4 are assumed to be negligible, and these are treated as a single moiety. The temperature dependence of the χ between 1,4- and 1,2-polybutadiene was determined by separating the microstructure and isotopic contributions using the random copolymer theory.[9] This theory relates the thermodynamic interaction χ_{eff} of two random copolymers $A_xB_{(1-x)}$ and $C_yD_{(1-y)}$ to those of the pure

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Table 1. Characterization of Materials

sample code	M_w	T_g (°C)	ΔT_g (°C)	% cis 1,4/ % trans 1,4
08A	20 000	−95.5	2.7	
08B	63 000	−94.1	3.1	36/56
08C	75 000	−96.1	3.0	
08D	124 000	−94.8	2.9	
08E	190 000	−95.2	3.3	
17	120 000	−87.5	3.5	35/48
32	97 000	−76.9	3.5	28/40
35	73 000	−72.3	3.2	27/38
38	102 000	−70.3	3.4	26/36
52	82 000	−59.6	4.1	21/27
66	112 000	−41.9	4.6	15/19
78	70 000	−29.6	4.4	9/13
90	27 000	−16.2	6.1	3/7

homopolymers as

$$\chi_{\mathrm{eff}} = xy\chi_{\mathrm{AC}} + (1-x)(1-y)\chi_{\mathrm{BD}} + x(1-y)\chi_{\mathrm{AD}} + y(1-x)\chi_{\mathrm{BC}} - x(1-x)\chi_{\mathrm{AB}} - y(1-y)\chi_{\mathrm{CD}} \quad (2)$$

where χ_{ij} is the interaction parameter between homopolymers *i* and *j*. Protonated 1,2-polybutadiene, deuterated 1,2-polybutadiene, protonated 1,4-polybutadiene, and deuterated 1,4-polybutadiene species were taken to be the four copolymer constituents, and the effective interactions between protonated 1,4-polybutadiene and protonated 1,2-polybutadiene were obtained from regression of the data. The interactions between 1,4- and 1,2-polybutadiene thus extracted at room temperature were found to be in good agreement with those inferred from diblock copolymers of the same pure component moieties.[12,13] Furthermore several studies of the thermodynamic interaction of copolymers of 1,4- and 3,4-polyisoprene with 1,4- and 1,2-polybutadiene have been undertaken by SANS and have been analyzed in the context of the random copolymer theory.[14]

Previously, we have studied the interactions in statistical copolymers of ethylene and butene-1 (obtained by saturation of statistical copolymers of 1,4- and 1,2-polybutadiene) and have found in that case that the interactions were not consistent with interpretation in terms of the random copolymer theory.[2,3] For the case of blends of copolymers only differing in composition, the random copolymer theory translates to

$$\chi_{\mathrm{eff}} = (y_1 - y_2)^2\chi_{\mathrm{AB}} \quad (3)$$

where χ_{AB} is the thermodynamic interaction between the pure species A and B and y_1 and y_2 represent the composition of each copolymer. The thermodynamic interactions were, however, found to be consistent with a higher order copolymer equation[10] which assumes that the primary interacting elements are diads:

$$\chi_{\mathrm{eff}} = (y_1 - y_2)^2(a_0 + a_1\bar{y} + a_2\bar{y}^2) \quad (4)$$

where $\bar{y}$ is the average composition ($=(y_1 + y_2)/2$) and a_0, a_1, and a_2 represent linear combinations of interactions between the three different types of diads.

The data for the random copolymers of ethylene and butene-1 can also be understood in terms of the solubility parameters of the individual components of that series, obtained from the SANS data and verified using *PVT* measurements.[2,11] The solubility parameters for that series exhibit a quadratic dependence on the copolymer composition, which leads to a χ value, interpreted in terms of the regular solution theory, that exhibits a dependence akin to that seen in eq 4, with only two of the three coefficients a_0, a_1, and a_2 being independent temperature-dependent variables.

Table 2. Single-Phase Blends

blend	T_g	ΔT_g	χ_s ($\times 10^4$)
08B/38	−84.1	7.7	13.87
08E/38	−85.2	9.9	8.32
08B/52	−80.4	10.6	15.02
08D/52	−79.9	11.2	10.96
08E/52	−76.4	16.0	9.48
08B/66	−73.3	22.0	13.32
08C/66	−75.5	20.2	12.06
08A/78	−69.9	22.7	36.44
08A/78[a]	−56.0	18.5	32.22[a]
17/52	−75.2	9.7	11.16
32/66	−62.6	12.7	10.74
35/66	−57.8	11.0	12.92
38/66	−59.0	11.5	10.39
52/66	−50.7	7.5	11.54
66/78	−35.5	6.5	12.70
78/90	−22.1	5.0	26.98

[a] Composition close to the critical composition—$\phi_{\mathrm{short}} = 0.7$.

Table 3. Two-Phase Blends

	$T_{g,1}$	$\Delta T_{g,1}$	$T_{g,2}$	$\Delta T_{g,2}$	χ_s ($\times 10^4$)
08D/66	−91.5	5.9	−48.2	11.0	9.27
08B/78	−92.6	3.6	−29.6	8.7	16.18
08A/90	−93.8	5.3	−23.9	11.4	47.80
08B/90	−94.5	3.7	−11.6	4.8	27.63
17/66	−83.0	6.1	−49.3	9.8	9.47
17/90	−87.4	3.0	−13.6	4.7	23.78
17/90[a]	−86.0	4.5	−15.0	6.0	21.29[a]
35/78	−70.4	4.7	−29.7	7.5	14.97
38/78	−70.0	5.0	−27.4	6.7	13.25
38/90	−70.3	4.0	−11.2	3.9	24.70
38/90[a]	−69.0	4.6	−14.0	5.0	22.84[a]
52/78	−56.0	7.1	−29.4	7.9	14.39
52/90	−57.4	6.5	−10.5	4.7	25.84
66/90	−36.1	8.6	−10.5	4.6	24.15
66/90[a]	−34.2	10.0	−12.6	5.6	21.91[a]

[a] Composition close to the critical composition—$\phi_{\mathrm{short}} = 0.7$.

Experimental Section

A series of model polybutadienes ranging from 8 to 90% 1,2-polybutadiene were examined in this study. The synthesis and molecular weight characterization of these materials have been described in previous publications.[2,3] The microstructure was determined by ^{1}H NMR and ^{13}C NMR. In addition, it has been confirmed using ^{13}C NMR on the saturated products that the 1,2 and 1,4 moieties were added in a statistical manner. The sample characterization is provided in Table 1. The sample code consists of a number corresponding to the weight % 1,2 and in some cases followed by an alphabetical character to distinguish between materials with identical microstructure but differing molecular weight. In all cases the materials examined were monodisperse with $M_w/M_n \leq 1.07$. The densities of some of the components were measured at 23 °C and found to be in good agreement with values reported in the literature.[4] The densities were found to be a linear function of 1,2 content with the values being 0.896 g/cm^3 for 8% 1,2 and 0.884 g/cm^3 for the 90% 1,2 material.

All the materials used in this study were filtered using a 0.22-μm anodisc filter, as described elsewhere.[2] Blends were prepared by solution blending in cyclohexane followed by precipitation in a mixture of methanol and acetone followed by extensive drying under vacuum. All the blends examined in this study, except as noted in Tables 2 and 3, contained equal volume fractions of both components. DSC experiments were performed on a Seiko model SSC5200H calorimeter equipped with subambient capability. All the calorimetric measurements were performed at a heating rate of 10 °C/min. Glass transitions (T_g) reported in this work correspond to the midpoint of the transition, and the width of the glass transition (ΔT_g) was taken as the difference between the onset and the termination of the thermal transition.

Results and Discussion

A summary of the phase behavior as obtained from DSC measurements is presented in Tables 2 and 3. The presence of a single glass transition was found to correlate well with the appearance of a clear mixture (a single-phase mixture) at 25 °C. For mixtures with a cloudy appearance (i.e., signature of phase-separated blends), the calorimetric scan clearly showed the presence of two thermal transitions, confirming the phase-separated nature of the mixture. In many cases, the individual glass transition temperatures observed for the phase-separated mixtures corresponded closely to the pure component glass transition temperatures, indicative of little or no intermixing. Repeated temperature cycling from -130 to $+80$ °C did not change the location or width of the transition, indicating no thermally induced mixing or demixing transition for any of the blends studied. On the basis of the work of Sakurai et al.,[4] these blends are expected to exhibit upper critical solution behavior.

This technique, while not providing a direct measurement of the interaction parameter or its temperature dependence, does in fact, by comparison to the limit of stability, provide bounds for the value of χ. The spinodal condition for a binary mixture is given as

$$\chi_s = \frac{v_0}{2}\left[\frac{1}{N_1 v_1 \phi_1} + \frac{1}{N_2 v_2 \phi_2}\right] \tag{5}$$

and thus for a single-phase mixture $\chi < \chi_s$ and for a two-phase mixture $\chi > \chi_s$. We chose a reference volume v_0 as the geometric mean of the component molar volumes ($v_0 = (v_1 v_2)^{1/2}$). In Tables 2 and 3 values of the right side of eq 5 (i.e., limits of stability), based on this reference volume, are tabulated. On the basis of observation of single-phase or two-phase behavior from light-scattering (i.e., turbidity) measurements and DSC measurements, the value of χ for the system of interest is designated to be greater than or less than the limit of stability value, respectively. With detailed information of the composition dependence and temperature dependence of χ not available, most experiments were carried out for blends with roughly equal volume fractions of the two components (ϕ_i ~0.50 ± 0.01) to minimize any contribution from a possible composition dependence of χ. Furthermore in order to avoid complications arising from interpreting phase behavior data far away from the critical point, additional experiments were performed for blends with disparate molecular weights, near the critical composition, defined by the Flory–Huggins theory as

$$\phi_{1,c} = \frac{\sqrt{N_2 v_2}}{\sqrt{N_1 v_1} + \sqrt{N_2 v_2}} \tag{6}$$

The phase behavior inferred at the critical composition were in good agreement with those at $\phi_i = 0.5$, as indicated in Tables 2 and 3.

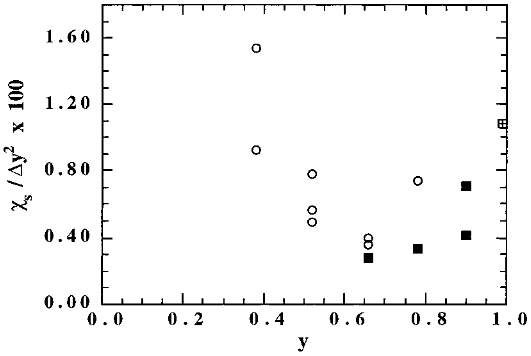

Figure 1. Thermodynamic interactions in blends of polybutadienes, with one of the components 8% 1,2-polybutadiene and the other component of varying composition (y). The calculated spinodal values of χ calculated from eq 5 were normalized by Δy^2, in accord with eq 3. Open circles correspond to single-phase blends, filled squares correspond to two-phase blends, and the hatched square corresponds to the data obtained from diblock copolymers by Cohen and Wilfong.[12]

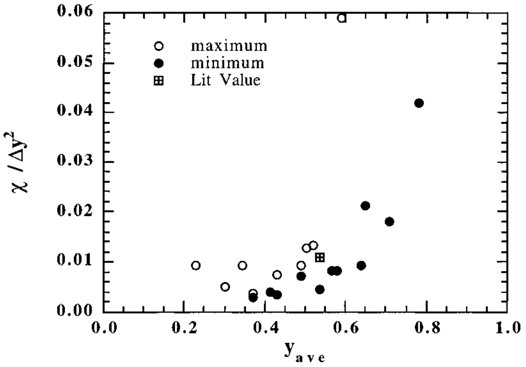

Figure 2. Scaled thermodynamic interactions ($\chi/\Delta y^2$) in blends of polybutadienes as a function of average copolymer composition of blend components, $y = (y_1 + y_2)/2$. Open circles correspond to single-phase blends, filled squares correspond to two-phase blends, and the hatched square corresponds to the data obtained from diblock copolymers by Cohen and Wilfong.[12]

In Figure 1 the upper and lower bounds of χ for the blends of 8% 1,2 material with polybutadienes ranging from 38 to 90% 1,2 are shown. The values of χ are scaled by the factor corresponding to the square of the difference in composition, as required by the random copolymer theory (eq 3). In passing, we observe that we have implicitly assumed, like Sakurai et al., that the structural and chemical differences between cis 1,4 and trans 1,4 are small and that they can be treated as a single moiety. Any complications due to the contrary might be minimized in our case as a result of the relative invariance of the cis 1,4 to trans 1,4 ratio for all the polymers used in this study. Adherence to the random copolymer theory would require the value of $\chi/\Delta y^2$ to be independent of the difference in composition. Figure 1 clearly indicates that a constant value of $\chi/\Delta y^2$ does not describe the blends of 8% 1,2-polybutadiene with polybutadienes containing a higher 1,2 content, at least at room temperature. Furthermore, the data obtained by Cohen and Wilfong[12] on diblock copolymers appear to be consistent with the observations presented in this work.

In Figure 2 the upper and lower bounds for χ for all the polybutadiene copolymer blends examined in this study are shown. The interaction parameters are again scaled by Δy^2 in accord with the random copolymer theory (eq 3). It is clear that the value of $\chi/\Delta y^2$ is not independent of the average composition ($\bar{y}$)—for example, the value of $\chi/\Delta y^2$ for $\bar{y} = 0.37$ is 0.0032 ± 0.0004, while that for $\bar{y} = 0.49$ is 0.0082 ± 0.0011 and the value based on 1,4-polybutadiene–1,2-polybutadiene block copolymers with $\bar{y} = 0.53$ is 0.0108. Furthermore, at

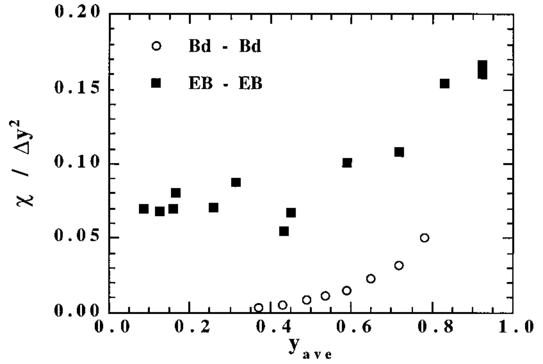

Figure 3. Comparison of the scaled thermodynamic interactions ($\chi/\Delta y^2$) for blends of ethylene–butene-1 copolymers[3] and the best estimates for the copolymers of 1,4- and 1,2-polybutadienes.

higher values of $\bar{y}$, a minimum estimate of $\chi/\Delta y^2$ suggests an extremely sharp increase, with its value being at least 0.021 and 0.042 at $\bar{y} = 0.65$ and 0.78, respectively. The variation of χ with the average composition ($\bar{y}$) appears to follow the trends suggested by eq 4.

The trends observed are very similar to those observed in ethylene–butene-1 copolymer mixtures.[3] A comparison of the best estimates of $\chi/\Delta y^2$ for the polybutadiene series with those for the ethylene–butene-1 copolymer series is presented in Figure 3. However, the interactions in the polybutadiene series are considerably smaller than that observed for the ethylene–butene-1 series.

***PVT* Measurements.** Equation of state (*PVT*) measurements of the pure component ethylene–butene-1 copolymer series were previously analyzed to obtain values of the solubility parameter[11] δ_{PVT}:

$$\delta_{PVT} = \left(\frac{T\alpha}{\beta}\right)^{1/2} \tag{7}$$

where α and β are the thermal expansion coefficient and the isothermal compressibility, respectively. Using an equation of state theory, such as the Flory–Orwoll–Vrij (FOV) theory[15] which takes on the form

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{T}\tilde{v}} \tag{8}$$

where $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$, and $\tilde{v} = v/v^*$, with P^*, T^*, and v^* being the characteristic pressure, temperature, and volume for the liquid and being obtained by fitting the experimental *PVT* data. The solubility parameter in eq 7 is then related to P^* as

$$\delta_{PVT} = \frac{(P^*)^{1/2}}{\tilde{v}} \tag{9}$$

thereby providing a direct measure of the thermodynamic interactions in terms of the regular solution theory. For a series of copolymers varying in composition, the characteristic volume v^*, representing the hard core volume, is roughly constant.[11] Hence a study of the values of P^* obtained from fitting experimental *PVT* data to the FOV equation of state should provide quantitative information regarding the mixing thermodynamics.

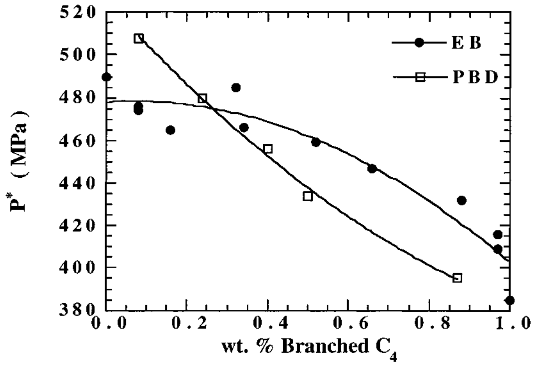

Figure 4. Comparison of the characteristic pressure P^* ($\propto\delta_{PVT}^2$), obtained by fitting *PVT* data to the FOV equation of state, for ethylene-butene copolymers[11] and 1,4-polybutadienes–1,2-polybutadiene copolymers.[16]

Xi et al.[16] have recently studied the *PVT* properties of a series of polybutadienes. The P^* values for that series of polybutadienes are compared to those for the series of ethylene–butene-1 copolymers in Figure 4. The data for the polybutadiene series are roughly linear with copolymer composition. This observation with eq 9 would suggest that the interactions in these blends should be consistent with the random copolymer theory, if their origins were strictly dispersive. Furthermore, such a supposition would suggest that the interactions for a blend of two polybutadienes with a given difference in composition should be larger than that for a corresponding blend of ethylene–butene-1 copolymers—in strong disagreement with the results shown in Figure 3. Also, on the basis of these values of P*, it is expected that, over a considerable range of copolymer compositions, polybutadiene and ethylene–butene-1 copolymers should be miscible—a prediction not observed experimentally.[2] Thus the interactions for blends involving a polydiene appear to be more complicated than accounted for by simple dispersive forces, and ideas based on the mixing of saturated hydrocarbons do not neccesarily translate for systems with unsaturation.

Comparison with Previous SANS Results. The previously published SANS-based χ values for a series of polybutadiene blends[4,8] at room temperature are analyzed in terms of the random copolymer theory. To minimize the number of variables to be determined by fitting the data, we recognize that

$$\chi_{\mathrm{H1,4/D1,4}} = 8.7 \times 10^{-4} \quad \text{and} \quad \chi_{\mathrm{H1,2/D1,2}} = 7.1 \times 10^{-4} \tag{10}$$

as determined by Bates et al.[17] Furthermore, assuming that deuteration decreases the solubility parameter and that the solubility parameter for 1,4-polybutadiene is greater than that for 1,2-polybutadiene[18,19] leads to

$$\chi_{\mathrm{H1,4/H1,2}} = \chi_{\mathrm{D1,4/D1,2}} \tag{11}$$

and

$$\chi_{\mathrm{H1,4/D1,2}} = \chi_{\mathrm{H1,4/H1,2}} + \Delta \quad \text{and} \quad \chi_{\mathrm{D1,4/H1,2}} = \chi_{\mathrm{H1,4/H1,2}} - \Delta \tag{12}$$

where Δ is a correction factor arising from isotopic substitution. The random copolymer equation in that case reduces to

$$\chi_{\mathrm{eff}} = (xy\chi_{\mathrm{H1,4/D1,4}} + (1 - x)(1 - y)\chi_{\mathrm{H1,2/D1,2}}) = \chi_{\mathrm{H1,4/H1,2}}(x - y)^2 + \Delta(x - y) \tag{13}$$

where x and y are the 1,4 content in the hydrogenous

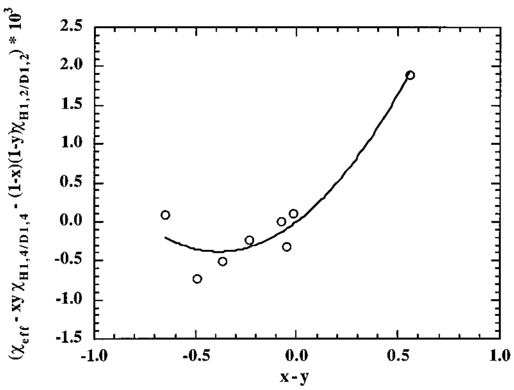

Figure 5. Reexamination of previous SANS-determined χ_{eff} values for blends of protonated and deuterated copolymers of 1,4-polybutadienes–1,2-polybutadiene, as per eq 13. See text for details of the analysis.

and deuterated components, respectively. The data and the fit to the above equation are shown in Figure 5. The data appear to follow the functional form represented by the random copolymer theory and yield a value of $\chi_{H1,4/H1,2} = 0.0026 \pm 0.0004$. This value, however, is lower than any of the estimated values for $\chi_{H1,4/H1,2}$ (or $\chi/\Delta y^2$) in this work. Furthermore, the isotopic correction factor Δ (=0.0020 ± 0.0003) turns out to be much larger than that expected from isotopic interactions determined by Bates et al. (eq 10), thereby making this interpretation questionable.

The SANS data on protonated and deuterated components are not adequate to rigorously test the fundamental conclusions of this work. This could be a result of the limited composition range of the components studied by SANS or of the fact that the isotopic interactions and their influence on the interactions are too dramatic to be able to rigorously test the validity or breakdown of the random copolymer theory. Hence we suggest that the interactions in higher vinyl component polymers be studied by SANS so as to ascertain the exact nature of the thermodynamic interactions. Particularly, deuterating a high-vinyl polybutadiene and studying the thermodynamic interactions of that molecule with other protonated high-vinyl components might lead to the most adequate test of the random copolymer theory for these blends.

Conclusions

We have shown that the thermodynamic interactions in model statistical copolymers of 1,4- and 1,2-polybutadiene depart significantly from the random copolymer theory. Thermodynamic interactions were measured using protonated copolymers over a wide range of compositions using DSC measurements. The data, however, were found to be consistent with previous deviations from the random copolymer theory observed in model ethylene–butene-1 copolymers. Such deviations were shown previously to be consistent with the idea that the primary interacting units were diads or triads. However several points cloud a simple analysis of the data and the molecular origins of the phase behavior of blends of polybutadiene copolymers. The thermodynamic interactions in the polybutadiene blends are considerably smaller than those in ethylene–butene-1 copolymers. The equation of state-determined characteristic pressure P^*, which is proportional to the solubility parameter, suggests that the polybutadiene blends copolymers should obey the random copolymer theory and possess interactions considerably larger than those seen in comparable ethylene–butene-1 copolymer blends. Furthermore, a reexamination of the earlier SANS data for blends of polybutadiene, with one component deuterated, appears to be consistent with the random copolymer theory, with the effective value for $\chi_{H1,4/H1,2}$ being smaller than that determined in this study. It thus appears there is a need to obtain more SANS-based thermodynamic information over a wide range of copolymer compositions and labeling combinations in order to sort out the thermodynamics of polybutadiene copolymer blends.

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