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Thermodynamics of Mixing for Blends of Model Ethylene–Butene Copolymers

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ABSTRACT: This paper describes a study of thermodynamic interactions in binary blends of A_yB_{1-y} copolymers. The blend components are hydrogenated polybutadienes, consisting of chains with branched C_4 and linear C_4 units and corresponding to model ethylene–butene copolymers. Overall compositions range from nearly polyethylene ($y = 0$) to nearly poly(butene-1) ($y = 1$) through a series of nearly random branched C_4–linear C_4 copolymers. Values of the Flory–Huggins interaction parameter χ were determined by small-angle neutron scattering (SANS) from binary blends (one component deuterated) and then corrected for the effect of isotopic substitution. The reduced interaction parameter $\chi/(y_2 - y_1)^2$ was found to be a strong function of the average blend composition, contrary to classical copolymer theory. Higher order theories, based on diad or triad interactions, could be made to fit, but the physical significance of the fits was unclear. The same results were also expressed in terms of a relative solubility parameter, $\delta - \delta_{ref}$, for each copolymer. These values were found to agree well with calculations based on *PVT* properties of the pure components. Thus, it seems clear that, for this system at least, departures from the copolymer equation are foretold in the pure component properties and have nothing to do with anomalies associated with mixing. More generally, inferences about the mixing process that are based on the temperature dependence of χ alone must be viewed with great caution.

Introduction

Statistical copolymers are widely used as components in polymer blends.[1] Thermodynamic interactions play a major role in determining blend morphology and properties, and how these interactions depend on copolymer composition is a question of some importance. Flory–Huggins (FH) theory suggests a simple relationship between copolymer interactions and interactions of the corresponding homopolymers.[2] In this paper we present data for binary blends of A_yB_{1-y} statistical copolymers which demonstrate very large departures from this relationship, called the copolymer equation. The components are hydrogenated polybutadienes, consisting of chains with branched-C_4 and linear-C_4 co-units.[3] They are model ethylene–butene copolymers, and they cover nearly the entire composition range from polyethylene at one end (all linear-C_4 units, $y = 0$) to ideally atactic poly(butene-1) at the other (all branched-C_4 units, $y = 1$). Departures were already evident from earlier work: the polyethylene–polybutene interactions inferred from measurements on "butene-rich"[3] and "ethylene-rich"[4,5] copolymer blends are quite different. Here we confirm those differences and find a smooth transition through the intermediate range. We consider interpretations based on diad[6] and triad[7] interactions, and we develop an alternative method for estimating the homopolymer interactions. Finally, we view the results from the standpoint of a solubility parameter formalism,[8] evaluate the parameters relative to a standard, and compare those results with predictions of solubility parameter based on *PVT* properties of the individual components.

Table 1. Molecular Structures and Physical Properties of Hydrogenated Polybutadienes

sample	N	r_1r_2	ρ (g cm^{-3})[a]	T_g (°C)	T_m (°C)
H97A	1600		0.8658	−22	
H97B	865		0.8651	−25	
H88	1610	0.66	0.8642	−34	
H78	1290	0.73	0.8630	−45	
H66	2040	0.81	0.8635	−54	
H52	1510	0.69	0.8604	−61	
H38	1830	0.74	(0.8598)[b]	(−62)[b]	42
H35	1390	0.65	(0.8589)	(−54)	56
H32	1720	0.71	(0.8643)	(−56)	60
H25	1720	0.66	(0.8798)	(−51)	68
H17	2200	0.68	(0.9978)	(−40)	84
H08	1180	0.24	(0.9104)	(−30)	113

[a] Measured at 23.0 °C in a density gradient column. [b] Values in parentheses measured on partially crystalline samples.

Experimental Section

Polybutadiene precursors were synthesized anionically in the presence of various polar modifiers to provide samples with vinyl contents (1,2 enchainments) from 8% to 97%.[3,9] Separate aliquots of each were catalytically saturated with H_2 to provide hydrogenated polybutadiene (HPB) and with D_2 to provide for each a partially deuterated, but structurally matched counterpart (DPB).[3] All the products have narrow molecular weight distributions ($M_w/M_n < 1.06$) and were extensively characterized by methods described elsewhere.[3,9–11] We follow the nomenclature of the earlier papers; e.g., H52 is an HPB derived from polybutadiene with 52% 1,2 enchainment, D52 is the corresponding DPB, and both have $y = 0.52$ mole fraction of branched-C_4 units. Polymerization index N (total C_4 units per chain), reactivity ratio product r_1r_2, and selected physical properties are given in Table 1. The values of r_1r_2, obtained by ^{13}C-NMR,[12] characterize the sequencing statistics of branched-C_4 and linear-C_4 units; r_1r_2 units = 1 corresponds to random (Bernouillian) sequencing along the chain. The values obtained

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Table 2. Thermal Expansion Coefficient, Isothermal Compressibility, and *PVT* Solubility Parameter for Selected Samples of Hydrogenated Polybutadiene

sample	T (°C)	$\alpha \times 10^4$ (K^{-1})	$\beta \times 10^4$ (MPa^{-1})	δ (MPa$^{1/2}$)
H08	121	7.4_5	8.8_7	18.1_9
	167	7.6_5	10.9_4	17.5_4
H32	51	$(7.0_2)^a$	$(6.3_8)^a$	$(18.8_8)^a$
	83	7.3_0	7.6_5	18.4_2
	121	7.4_1	9.1_6	17.8_4
	167	7.7_1	11.4_5	17.2_1
H66	27	6.9_2	5.9_0	18.7_6
	51	7.2_4	6.9_0	18.4_4
	83	7.1_7	7.8_7	18.0_0
	121	7.3_0	9.3_6	17.5_3
	167	7.4_3	11.7_7	16.6_5
H97A	27	6.9_4	6.3_1	18.1_7
	51	7.1_2	7.3_2	17.7_6
	83	6.9_9	8.5_2	17.0_8
	121	7.1_4	10.0_9	16.6_9
	167	7.2_5	12.6_8	15.8_6

[a] Values in parentheses are based on small extrapolations into the semicrystalline region.

indicate statistical uniformly throughout the series (the uncertainty for H08 is very large) with only a slight bias toward alternation ($\overline{r_1r_2} = 0.70$ without the H08 result). The physical properties are in excellent accord with values reported in an earlier study of HPB.[13]

The *PVT* properties of selected samples were generously provided by Dr. Gregory Dee of DuPont Central Research. The instrument (Gnomix) and previous work on similar polymers are described elsewhere.[14,15] Density ρ was measured as a function of temperature T (30–250 °C in 10 °C increments) and pressure P (10–200 MPa in 10-MPa increments). The data were used to obtain the thermal expansion coefficient $\alpha = -(\partial \ln \rho/\partial T)_P$ and the isothermal compressibility $\beta = (\partial \ln \rho/\partial P)_T$ at 1 atm (0.1 MPa). The extrapolations require care, especially for β, which changes relatively rapidly through the low-pressure range. The data analysis will be described in more detail in a later publication. The results are given in Table 2.

Small-angle neutron scattering (SANS) was used to determine the thermodynamic interactions in binary blends containing one HPB component and one DPB component. Results were obtained for both labeling configurations, e.g., D52/H66 and H52/D66, for all HPB/DPB blends. Some blends of DPB with fractions of linear polyethylene (H00, $y = 0$) were also studied. The measurements were made at the NIST Cold Neutron Research Facility (CNRF) in Gaithersburg, MD. Blend preparation, experimental procedures, and data analysis have been described previously.[3] Data were obtained for blends in the single-phase region at temperatures ranging from 27 to 167 °C. Crystallization limited this to some extent for blends with ethylene-rich (small y) components, and liquid–liquid separation placed restrictions on the tolerable difference in component compositions (typically $|y_1 - y_2| \lesssim 0.15$ for our range of molecular weights, $N \sim 10^3$).

The SANS results were interpreted[3] through the incompressible random phase approximation as applied to the FH expression for the free energy of mixing in binary blends:

$$\frac{\Delta G_m}{k_B T} = \frac{\phi_1 \ln \phi_1}{v_1 N_1} + \frac{\phi_2 \ln \phi_2}{v_2 N_2} + \frac{X}{k_B T}\phi_1\phi_2 \tag{1}$$

in which k_B is the Boltzmann constant, T is the absolute temperature, N_1 and N_2 are polymerization indices, ϕ_1 and ϕ_2 are volume fractions, and v_1 and v_2 are the volumes per monomeric unit. The interaction energy density X is commonly expressed as

$$X = \frac{\chi k_B T}{v_0} \tag{2}$$

where v_0 is an arbitrary reference volume and χ is the FH interaction parameter with respect to that volume. The values of χ for the blends in this study, evaluated with $v_0 = (v_1v_2)^{1/2}$ in all cases, are based on results given elsewhere.[3,10,11] They were determined for midrange compositions ($\phi \sim 0.5$), where χ is insensitive to ϕ.[16] The hydrogenous pair value χ_{hh} was deduced by averaging the corresponding singly-labeled results, χ_{hd} and χ_{dh}, as described in ref 10. (As explained there, an alternative, proposal for making such adjustments[17] proved to be too unwieldy for our system.[18]) The values thus obtained, $\chi_{hh} \equiv \chi$ are listed in Table 3.

Table 3. Interaction Parameters for Blends of Hydrogenated Polybutadiene and Linear Polyethylene Components

	$\chi \times 10^4$				
blend	27 °C	51 °C	83 °C	121 °C	167 °C
H97A/H88	$13._5$	$11._8$	$10._6$	$8._9$	7.0
H97B/H88	$13._0$	$11._5$	$9._7$	$7._8$	5.6
H88/H78	$18._4$	$16._4$	$14._2$	$12._0$	9.8
H78/H66	$15._6$	$14._1$	$12._4$	$10._7$	9.1
H66/H52	$19._7$	$17._6$	$15._1$	$12._9$	$10._6$
H52/H38	$(13._2)^a$	$11._7$	$9._6$	7.7	6.3
H52/H35	$(15._8)$	$(14._1)$	$11._0$	8.8	7.2
H38/H32	(6.0)	(5.1_4)	$4._3$	3.3	2.5
H38/H25	$(14._8)$	$(12._8)$	$10._7$	7.9	6.3
H35/H17	$(23._0)$	$(19._0)$	$(14._6)$	$10._1$	6.3
H32/H00	(71)	(60)	(48)	(36)	24
H25/H08	$(23._3)$	$(19._4)$	$(15._3)$	11	7.0
H25/H00	(42)	(37)	(29)	(22)	$14._7$
H17/H00	$(20._1)$	$(16._9)$	$(13._5)$	$(10._1)$	6.7

[a] Values in parentheses are extrapolations of single-phase melt results into the semicrystalline region.

Results and Discussion

Copolymer Equation. Application of FH theory to binary blends of random A_yB_{1-y} copolymers yields the following expression:[2]

$$X(y_1,y_2) = (y_2 - y_1)^2 X_{A/B} \tag{3}$$

in which $X_{A/B}$ is the interaction energy density for blends of the A and B homopolymers. The reference volume $(v_1v_2)^{1/2}$ differs by less than 3% among all HPB blends, so with negligible error eq 3 predicts the following relationship among the values of χ at each temperature (Table 3):

$$\chi(y_1,y_2) = (y_2 - y_1)^2 \chi_{H00/H100} \tag{4}$$

where $\chi_{H00/H100}$ is the interaction parameter for blends of polyethylene (H00) and poly(butene-1) (H100). Accordingly, $\chi/(\Delta y)^2$ should depend on temperature alone. In particular, it should be independent of both the difference in copolymer composition, $\Delta y = y_2 - y_1$ and the composition average, $\bar{y} = (y_1 + y_2)/2$, for any pair of HPB components.

The values of $\chi/(\Delta y)^2$ for several HPB blends are shown as functions of temperature in Figure 1a,b. Results for a wide range of $\bar{y}$ are shown in each figure. If eq 4 were valid, all these data would collapse to a single curve, and there are obviously large discrepancies. At each temperature $\chi/(\Delta y)^2$ increases strongly and systematically with increasing $\bar{y}$. Figure 2 shows these data replotted as $\chi(T)/\chi(167\ °C)$, testing the possibility of a common temperature dependence for HPB blends. The values at other temperatures are, in fact, rather similar for $\bar{y}$ larger than about 0.4 but then begin to depart systematically at smaller $\bar{y}$. The dependence of $\chi/(\Delta y)^2$ on average blend composition is shown for the 167 °C data in Figure 3. The values increase smoothly from ~0.02 for small $\bar{y}$, in reasonable agreement with the results of Crist et al.,[4,5] to ~0.09 for large $\bar{y}$, in the range we reported earlier.[3]

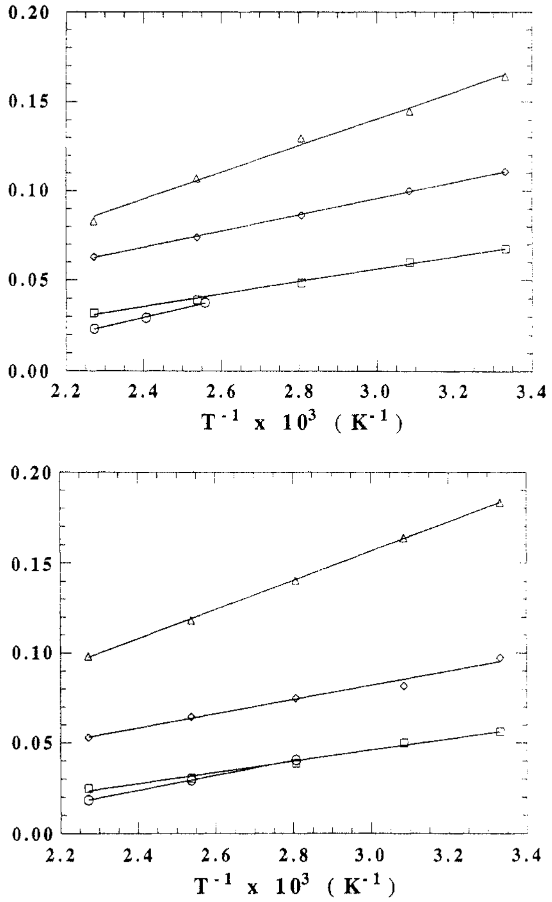

Figure 1. Reduced interaction parameter vs reciprocal temperature for selected HPB blends: (a, top) values of $\chi/(\Delta y)^2$ for H8/H25 (○), H38/H52 (□), H66/H78 (◇), and H88/H97A (△); (b, bottom) values of $\chi/(\Delta y)^2$ for H17/H35 (○), H35/H52 (□), H52/H66 (◇), and H78/H88 (△).

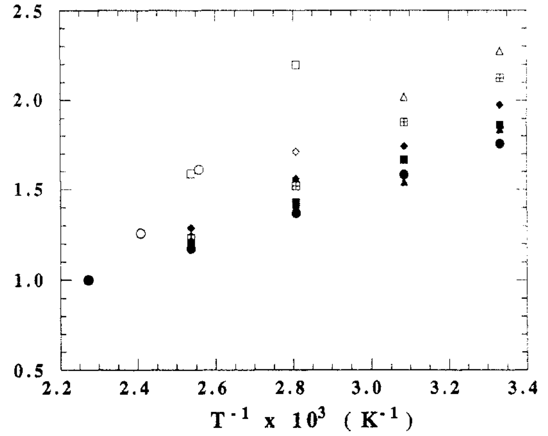

Figure 2. Interaction parameters relative to values at 167 °C *vs* temperature for HPB blends. The following blends are represented: H8/H25 (○), H17/H35 (□), H25/H38 (◇), H35/H52 (△), H38/52 (⊞), H52/H66 (▲), H66/H78 (●), H78/H88 (■), and H88/H97A (◆).

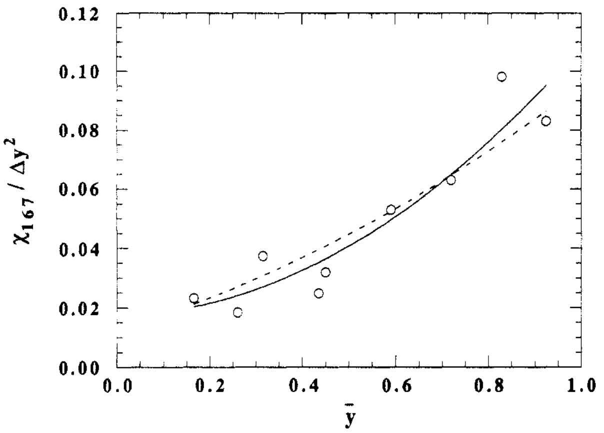

Figure 3. Reduced interaction parameter *vs* mean blend composition at 167 °C. The solid curve was calculated with eq 5 and the parameters in Table 4. The dashed line was calculated with eqs 6 and 8 with parameters in Table 6.

Table 4. Coefficients in the Diad Copolymer Equation 5 for Blends of Hydrogenated Polybutadiene and Linear Polyethylene Components

T (°C)	a_0	a_1	a_2
27	0.095 ± 0.024	−0.175 ± 0.108	0.293 ± 0.102
51	0.077 ± 0.021	−0.130 ± 0.096	0.241 ± 0.090
83	0.062 ± 0.018	−0.114 ± 0.081	0.220 ± 0.076
121	0.042 ± 0.014	−0.073 ± 0.066	0.172 ± 0.062
167	0.022 ± 0.013	−0.017 ± 0.058	0.106 ± 0.054

Higher Order Copolymer Equations. Figures 1 and 3 demonstrate that the copolymer equation, though possibly adequate over limited ranges of $\bar{y}$, does not describe the entire span of HPB blends. Furthermore, the homopolymer interaction parameter $\chi_{H00/H100}$ cannot be obtained from the copolymer interactions without some better understanding of this behavior. The copolymer equation is based on monomeric units as the primary interacting elements, and modifications have been proposed that treat diads[6] and triads[7] as the primary elements. In the diad case, three interaction parameters are required for blends of A_yB_{1-y} copolymers—χ_{AB} for AA···BB interactions, χ_{AC} for AA···AB, and χ_{BC} for $\beta\beta$···AB. The triad formulation contains many more parameters and will not be considered further here.

The diad expression for random copolymers ($r_1r_2 = 1$ and the same reference volume for all blends) can be written in the form

$$\chi = (a_0 + a_1\bar{y} + a_2\bar{y}^2)(y_2 - y_1)^2 \qquad (5)$$

in which the a_i stand for linear combinations of χ_{AB}, χ_{AC}, and χ_{BC}.[6] The HPB blend data can be fitted reasonably well with eq 5. The values of a_i are given in Table 4, and the result for 167 °C, where the data are most complete, is shown by the solid curve in Figure 3. The uncertainties in a_i are rather large (Table 4) but appear to be nonsystematic, i.e., reflecting mainly the scatter in the data themselves. The resulting values of $\chi/(\Delta y)^2$ at the extremities (0.022 for $\bar{y} = 0$ and 0.111 for $\bar{y} = 1$ at 167 °C) are consistent with experimental results near those limits.[3-5]

Nevertheless, although the results can be fitted to the diad form, it is not clear how much physical meaning to attribute to the values of a_i, or, in view of their large uncertainties, how to extract from these data believable values of $\chi_{H00/H100}$, the polyethylene–polybutene interaction parameter. Finally, Schweizer explains our observed departures from eq 4 quite differently, suggesting that differences in homopolymer statistical length may be the source and offering some justification based on analytical PRISM theory.[19]

Solubility Parameter Formalism. The same data can also be organized with the following equation from regular solution theory:[8]

$$\chi = \frac{v_0}{k_B T}(\delta_1 - \delta_2)^2 \qquad (6)$$

in which δ_1 and δ_2 are the solubility parameters of the

Table 5. Solubility Parameters of Hydrogenated Polybutadienes and Linear Polyethylene Relative to an H97 Reference

sample	$(\delta - \delta_{ref})$ (MPa$^{1/2}$)				
	27 °C	51 °C	83 °C	121 °C	167 °C
H97	0	0	0	0	0
H88	0.23	0.22	0.21	0.20	0.18
H78	0.49	0.48	0.46	0.44	0.41
H66	0.73	0.72	0.69	0.66	0.62
H52	1.01	0.98	0.95	0.91	0.86
H38	(1.23)[a]	1.20	1.16	1.11	1.05
H35	(1.26)	(1.22)	1.17	1.13	1.17
H32	(1.38)	(1.34)	1.28	1.22	1.15
H25	(1.47)	(1.43)	1.37	1.31	1.23
H17	(1.55)	(1.50)	(1.43)	1.37	1.30
H08	(1.77)	(1.71)	(1.63)	1.54	1.43
H00	(1.88)	(1.78)	(1.71)	(1.60)	1.48

[a] Values in parentheses obtained by extrapolation from data at temperatures above T_m.

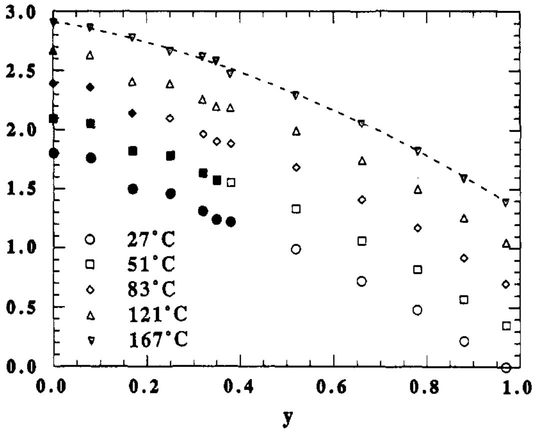

Figure 4. Relative solubility parameter *vs* HPB composition. The values of $\delta - \delta_{ref}$ have been shifted vertically by a constant amount at each temperature. The filled symbols indicate values extrapolated below the melting temperature of crystallizable components. The solid line is a least-squares fit of the 167 °C data to eq 8, with fitted parameters given in Table 6.

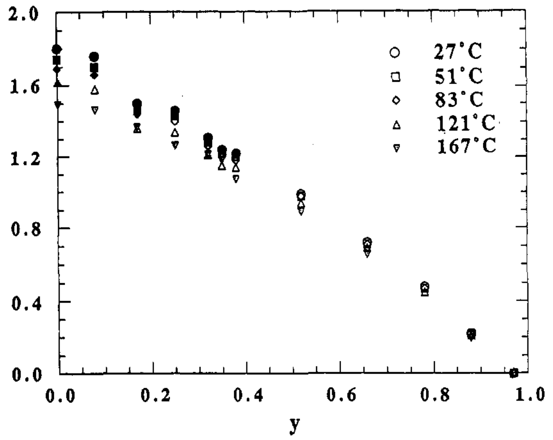

Figure 5. Relative solubility parameter *vs* HPB composition. No vertical shift has been applied; the filled symbols have the same meaning as in Figure 4.

Table 6. Coefficients in the Solubility Parameter Equation 8 for Hydrogenated Polybutadienes and Deduced Interaction Parameter for Polyethylene/Poly(butene-1) Blends

T (°C)	$\delta_{H100} - \delta_{ref}$ (MPa$^{1/2}$)	γ	$\delta_{H00} - \delta_{H100}$ (MPa$^{1/2}$)	$\chi_{H00/H100} \times 10^4$
27	−0.05 ± 0.03	0.27 ± 0.06	1.90 ± 0.03	95_8.
51	−0.05 ± 0.02	0.29 ± 0.06	1.84 ± 0.03	84_3.
83	−0.05 ± 0.02	0.33 ± 0.06	1.74 ± 0.03	70_2.
121	−0.05 ± 0.02	0.39 ± 0.07	1.63 ± 0.03	57_1.
167	−0.06 ± 0.02	0.47 ± 0.07	1.51 ± 0.02	45_3.

components. Many assumptions underlie this form, but for the purpose here we require only that δ be a pure component property, i.e., that its value not depend on the choice of second component in its blends. We find some support for this assumption for HPB materials from blending results with other saturated hydrocarbon polymers,[20] but for the moment we simply view eq 6 as a convenient means for parameterizing the interactions observed in HPB blends. Each member of the HPB series is linked with all the others through a succession of interaction parameters (H97A/H88, H88/H78, etc.), and the sign of $\delta_1 - \delta_2$ is known in each case from the label-switching effect.[10,11] Thus, with one component designated as the reference, $\delta - \delta_{ref}$ can be evaluated for the remainder.

We chose H97A as the reference, with results that are listed in Table 5 and shown in Figure 4. The values of $\delta - \delta_{ref}$ at 51, 83, 121, and 167 °C have been displaced vertically to avoid overlap; the filled symbols represent results extrapolated below the crystallization temperatures of the ethylene-rich components. The values of $\delta - \delta_{ref}$ are replotted in Figure 5 without the vertical shifts. Evidently, $\delta - \delta_{ref}$ is insensitive to temperature for the copolymers that are rich in butene-1, but not so for the ethylene-rich materials, even after allowing for the extrapolation uncertainties in that region of compositions.

In this representation, the copolymer question for the HPB series corresponds exactly to a linear relationship between solubility parameter and HPB composition:

$$\delta(y) - \delta_{ref} = (\delta_{H100} - \delta_{ref}) + (\delta_{H00} - \delta_{H100})(1 - y) \quad (7)$$

where δ_{H00} and δ_{H100} are the solubility parameters for polyethylene ($y = 0$) and atactic poly(butene-1) ($y = 1$). The curvature in Figure 4 and 5 is thus a direct reflection of the departures from copolymer theory as demonstrated in Figures 1 and 3.

The data can in fact be fitted rather well if a quadratic term is added to eq 7, such that

$$\delta(y) - \delta_{ref} = (\delta_{H100} - \delta_{ref}) + (\delta_{H00} - \delta_{H100})(1 - y)(1 + \gamma y) \quad (8)$$

where γ is empirical. The fitting parameters $\delta_{H100} - \delta_{ref}$, $\delta_{H00} - \delta_{H100}$, and γ are listed for the five temperatures in Table 6. The fit at 167 °C, where a complete set of results is available without extrapolation, is compared with the data by the dashed line in Figure 4. From eq 8, the difference in solubility parameter for any two HPB components is

$$\delta(y_1) - \delta(y_2) = -(\delta_{H00} - \delta_{H100})(1 - \gamma + 2\gamma\bar{y})\Delta y \quad (9)$$

The result obtained when this expression is used with eq 6 to calculate $\chi/(\Delta y)^2$ *vs* $\bar{y}$ at 167 °C is shown by the dashed line in Figure 3. The agreement with experiment of course does no more than reinforce the point that departures of HPB blends from the copolymer equation are very large indeed. The values of $\chi_{H00/H100}$, obtained from eq 6 with $\delta_{H00} - \delta_{H100}$, are listed in Table 6.

Expressing the data on HPB interactions in the language of solubility parameters rephrases but does not answer the more fundamental question about the source of departures from eq 4. Thus, for example, small changes in local order, dependent on subtleties in molecular geometry, cannot be ruled out, and, by its very nature, eq 6 itself rests on a literal interpretation of the simplest

Table 7. Solubility Parameter Differences from SANS Data, *PVT* Measurements, and Group Contribution Correlations

blend	T (°C)	$\delta_1 - \delta_2$ (MPa$^{1/2}$) SANS	*PVT*	GCC
H08/H97A	27	(1.77)	—	0.88
	51	(1.71)	—	
	83	(1.63)	—	
	121	1.54	1.4_9	
	167	1.43	1.6_8	
H32/H97A	27	(1.38)	—	0.65
	51	(1.34)	(1.1_2)	
	83	1.28	1.3_4	
	121	1.22	1.1_5	
	167	1.15	1.3_6	
H66/H97A	27	0.73	0.5_9	0.31
	51	0.72	0.6_8	
	83	0.69	0.9_2	
	121	0.66	0.8_4	
	167	0.62	0.8_0	

possible theory of the liquid state. On the other hand, the interactions are weak and dispersive in origin, and the volume changes with mixing are very small, all of which are necessary prerequisites for regular solution theory. Although both this theory and eq 6 have serious shortcomings[21] near liquid–liquid transitions in small-molecule mixture ($\chi \sim 1$), they have not been tested extensively with interactions as weak as those considered here ($\chi \sim 10^{-3}$). Thus, it seems worthwhile to take the further step of comparing the results with independent estimates of the solubility parameter based on pure component properties.

Pure Component *PVT* Properties. Solubility parameters are conventionally associated with the cohesive energy density U_V, the decrease in internal energy with evaporation per unit volume of the pure liquid.[8] The solubility parameter was originally defined by $\delta = U_V^{1/2}$. When U_V is unknown by direct measurement it has been replaced by $(\partial U/\partial V)_T$ for the pure liquid, which is exact for a van der Waals liquid and a reasonable approximation for many real liquids.[8] Furthermore, $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$ is a thermodynamic identity, and $T(\partial P/\partial T)_V = T\alpha(T)/\beta(T)$ is much larger than P for dense liquids at low pressures, leading to the following expression for the solubility parameter, based only on *PVT* properties of the pure liquid:

$$\delta_{PVT} = \left[T\frac{\alpha(T)}{\beta(T)}\right]^{1/2} \tag{10}$$

For a closely related class of nonpolar structures, such as saturated hydrocarbon polymers, one might hope that $\delta_{PVT} = \lambda\delta_{PVT}$, where λ is some constant of order unity.

Values of δ_{PVT}, calculated with eq 10 for selected HPB samples, are listed in Table 2. Differences between components, $(\delta_1 - \delta_2)_{PVT}$, are compared in Table 7 with those from the scattering data, $(\delta_1 - \delta_2)_{\rm SANS}$. Also included there are the values of $\delta_1 - \delta_2$ calculated at 25 °C from the group contribution correlation (GCC) of Coleman et al.[22]

Several points are worth noting. First, δ_{PVT} varies with temperature, and that variation changes slightly with the HPB composition. As a result, $(\delta_1 - \delta_2)_{PVT}$ also changes with temperature. Second, $(\delta_1 - \delta_2)$ from SANS, *PVT*, and GCC decrease monotonically with increasing branched-C_4 (butene-1) content as the various temperatures. Thus, the signs for $(\delta_1 - \delta_2)_{\rm SANS}$ as established by label-switching are consistent with both the *PVT* data and the group contribution correlation. Third, $(\delta_1 - \delta_2)_{PVT}$ is in fact remarkably close to $(\delta_1 - \delta_2)_{\rm SANS}$ in all cases. The calculated values of δ_{PVT} are fairly precise, but the precision of $(\delta_1 - \delta_2)_{PVT}$ is much lower, being a small difference of large numbers, even for such widely different HPB structures as the H08/H97 pair. Thus, the trends with temperature are more uncertain. Fourth, $(\delta_1 - \delta_2)_{\rm GCC}$ is smaller than both $(\delta_1 - \delta_2)_{\rm SANS}$ and $(\delta_1 - \delta_2)_{PVT}$ by a factor of 2. Group contribution correlations predict the correct trends in this system but severely underestimate the strength of the interactions.

The close parallels between $(\delta_1 - \delta_2)_{PVT}$ and $(\delta_1 - \delta_2)_{\rm SANS}$ are encouraging. The data thus far are limited of course, and differences in solubility parameter place a rather heavy burden on the precision of *PVT* measurements. Nevertheless, this correspondence strongly suggests that the interactions in HPB blends can be explained, within the uncertainties, in terms of pure component properties alone. Their departures from the copolymer equation (eq 4) then become merely the consequences of systematic variations with chemical microstructure in the pure component *PVT* properties. There appears to be no need to consider anomalies such as local packing changes with mixing in blends that involve only HPB components. Accordingly, the experimental values of χ can be described in their entirety, and within the errors, by eq 6, i.e., without additional terms to reflect the mutual geometrical restrictions that might be imposed in mixing by differences in the local molecular shapes of HPB components.

From this it follows that the observed temperature dependence of χ reflects mainly the temperature dependence of the various elements in eq 6. Thus from eq 10, for a given component pair,

$$\chi(T) \propto \frac{V_0(T)}{T}[\delta_2(T) - \delta_1(T)]^2 \tag{11}$$

and noting that $V_0(T) \propto [\rho_1(T)\ \rho_2(T)]^{-1/2}$,

$$\chi(T) \propto \left[\left(\frac{\alpha_1(T)}{\beta_1(T)}\right)^{1/2} - \left(\frac{\alpha_2(T)}{\beta_2(T)}\right)^{1/2}\right]^2 / [\rho_1(T)\ \rho_2(T)]^{1/2} \tag{12}$$

Accordingly, almost any variation of χ with temperature is possible, at least in principle, depending only on the temperature of α, β, and ρ for the individual components. In particular, the fact that χ for HPB blends fits the form $A/T + B$ would appear to be only an accidental consequence of pure component physical properties and their correlation with structure across the HPB series. Attributing special significance about the mixing process itself to the signs and relative magnitudes of the coefficients A and B alone is thus somewhat questionable.

Some examples of blends which depart from the pattern described above, and where local packing anomalies may possibly be involved, are described elsewhere.[20,23]

Conclusions

We have shown that the thermodynamic interactions in binary blends of HPB components depart significantly from predictions based on the classical theory for A_yB_{1-y} copolymers. The large and systematic variation in $\chi/(\Delta y)^2$ with $\bar{y}$ can, however, be easily accommodated by theories that consider diads or triads to be the interacting elements, but that approach, while plausible, is difficult to confirm by independent means. We have also recast the interactions in a solubility parameter formalism, thereby associating them tentatively with differences in a property of the individual components alone. Independent estimates of the solubility parameter were obtained by *PVT* measurements on selected HPB components, and their differences were shown to parallel closely the differences deduced from SANS. This correspondence suggests that the departures from the copolymer theory arise simply from a nonlinear variation with composition in the solubility parameter across the HPB series. It also suggests that local packing changes that occur when HPB components are mixed have a negligible effect on the interactions. Finally, noting the component-specific variations in solubility parameter with temperature from both *PVT* and SANS, we emphasize the possible pitfalls of interpreting the temperature dependence of χ in terms of entropic and enthalpic contributions in the mixing process itself.

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