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Structural Origin of Thermodynamic Interactions in Blends of Saturated Hydrocarbon Polymers

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ABSTRACT: The thermodynamic interactions in blends of saturated hydrocarbon polymers originate from induced-dipole forces, and they differ in subtle but important ways, depending on the component structures. In this paper we use six model polyolefins, four statistical copolymers and two alternating copolymers, to examine some of the ways that have been suggested for organizing and interpretating these structural effects—statistical segment length mismatch, random copolymer theory, and the solubility parameter formalism. The polymers and their partially deuterated counterparts are components in an interconnected matrix of miscible binary blends for which the interactions were determined by small-angle neutron scattering. The interactions, quantified as Flory–Huggins interaction parameters, were broadly consistent with the length-mismatch idea, but some notable exceptions were found. Interpretations based on random copolymer theory provided homopolymer interaction parameters which conflicted with diblock copolymer results and other blend data. Tests of consistency with solubility parameter ideas were applied to the matrix of blends. The results for one component pair indicated strongly anomalous mixing, but those for all other pairs were consistent with the uniqueness criterion of the theory. Solubility parameters estimated from *PVT* measurements on the pure components agreed fairly well with assignments based on the measured interactions. Some inconsistencies remain, however, between diblock copolymer results and the solubility parameter formulation.

Introduction

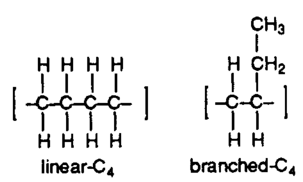
We have studied the thermodynamics of polymer blends by several techniques. Small-angle neutron scattering (SANS) is used to evaluate interactions in single-phase melts, light scattering to locate or confirm phase boundaries, and *PVT* measurements to provide information on the cohesive energies of individual components.[1–3] The blend components are model polyolefins, made by saturating the double bonds in a variety of anionically synthesized polydienes. The net interaction between components is repulsive and appears to be primarily dispersive in origin, as expected for saturated hydrocarbon liquids. UCST behavior (single-phase at high temperature) has been observed in all cases thus far.

We are now attempting, through approaches such as regular solution theory and a solubility parameter formalism,[4] to organize these results into a comprehensive framework. A companion paper[5] uses the label-switching effect[6] to establish an apparent ordering of the solubility parameters for PEP (hydrogenated 1,4-polyisoprene), PEB (hydrogenated 1,4-poly(2-ethylbutadiene), hhPP (hydrogenated 1,4-poly(2,3-dimethylbutadiene), and various members of the HPB family (hydrogenated polybutadienes). The HPB structures range from linear polyethylene to atactic poly(butene-1) through a series of nearly random copolymers of linear-C_4 and branched-C_4 units whose compositions depend on the vinyl content for the parent polybutadiene. For components other than hhPP, the orderings were at least qualitatively consistent with the requirements of solubility parameter uniqueness. A second paper[7] deals with the HPB family alone and demonstrates large departures from the classical theory of interactions for copolymer blends. Numerical values for the HPB solubility parameters, relative to a reference HPB structure, were established. The differences in those values were shown to be reasonably consistent with differences estimated independently from *PVT* measurements on selected HPB components. The results supported the qualitative orderings established in ref 5. They also provided some strong although indirect evidence of both solubility parameter uniqueness and noncomplexity in mixing within the HPB family.

In this paper we examine the numerical self-consistency of solubility parameter differences for blends involving PEP, PEB, and a range of HPB structures; blends of hhPP, already shown to be inconsistent with a solubility parameter formalism,[5] will be considered in a later paper. First, however, we use random copolymer theory to estimate the interactions for some related blends and compare the results with data reported by others. We also consider a recent theory of the interactions that could arise from a mismatch of statistical segment lengths. Last, we provide further comparisons with predictions of interaction strength based on *PVT* data for the pure components.

Experimental Section

A total of 12 polymers was used in this study, six fully hydrogenous and six partially deuterated.[2,5,7] Four are samples of hydrogenated polybutadienes (HPB), which we call model ethylene–butene copolymers. Their chains consist of linear-C_4 and branched-C_4 counits:



$$\left[-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}- \right] \qquad \left[-\mathrm{CH}(\mathrm{CH_2CH_3})-\mathrm{CH_2}- \right]$$

The four HPB samples are designated H38, H52, H66, and H78; their four partially deuterated but structurally matched coun-

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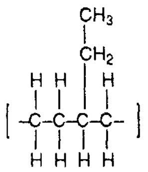
Table 1. Characterization of Samples

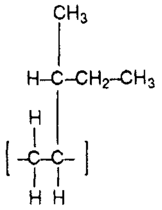
sample code	polymn index N^a	density ρ (g/cm^3)^b	fractional deuteration f_D
H38 (D38)	1828	0.8598	0.378
H52 (D52)	1512	0.8604	0.344
H66 (D66)	2032	0.8635	0.406
H78 (D78)	1286	0.8630	0.296
HPEP (DPEP)	855	0.8540	0.469
HPEB (DPEB)	550	0.8636	0.265

[a] Number of monomeric units per chain: total C_4 units for H38, H52, H66, and H78; total C_5 units for HPEP; total C_6 units for HPEB. [b] Hydrogenous polymer at 23 °C.

terparts (DPB samples) are designated D38, D52, D66, and D78. The code number specifies the vinyl content (% branched-C_4 units) of their polybutadiene precursors.[7] Sequencing of the branched-C_4 and linear-C_4 units is nearly random (average reactivity ratio product $r_1r_2 \sim 0.70$[7].

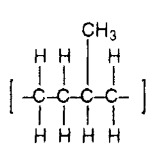
One of the samples is hydrogenated poly(ethylenebutadiene) (HPEB) whose chains also consist of two counits:

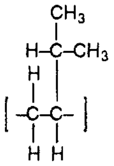

PEB: 93%


PEB: 7%

The partially deuterated version DPEB was derived from the same poly(ethylbutadiene) precursor. The structure of the majority unit corresponds to a strictly alternating copolymer of ethylene and butene-1; HPEB and H66 are nearly the same in overall frequency of ethyl branches but very different in their sequencing.[2]

One of the samples is hydrogenated polyisoprene (HPEP) whose chains also consist of two counits:


PEP: 93%


PEP: 7%

The partially deuterated version DPEP was derived from the same polyisoprene precursor. The structure of the majority unit in this case corresponds to a strictly alternating copolymer of ethylene and propylene. The PEP and PEB structures have essentially the same branch frequency and sequencing, differing only in side group size.[2]

All 12 samples are nearly monodisperse ($M_w/M_n < 1.06$). Synthesis and structural characterization are described elsewhere.[1,2,5] All are amorphous at room temperature except the H38, D38 pair (T_m = 42 °C), and all have glass transition temperatures well below 0 °C. Polymerization index N (number of monomeric units per chain), hydrogenous density ρ at 23.0 °C, and fractional deuteration of the labeled versions f_D[1] are given in Table 1. Radius of gyration R_g was determined by SANS measurements on matched-pair mixtures[1] and are listed in Table 2.

The SANS measurements were performed at the NIST Cold Neutron Research Facility in Gaithersburg, MD.[1,8] Scattering profiles for binary blends (one component deuterated, the other hydrogenous) were obtained in the one-phase region with the 8-m SANS instrument (NG5). The data were analyzed by the incompressible random-phase approximation as applied to the Flory–Huggins (FH) expression for the free energy of mixing per unit volume:

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

Table 2. Radius of Gyration of Samples at Various Temperatures

	R_g (Å) at T (°C)				
sample	27	51	83	121	167
H38		$130._0$	$129._0$	$128._0$	$127._2$
H52	$114._4$ ($114._0$^{a})	$113._8$	$114._0$	$113._6$	$113._5$
H66	$123._3$	$122._9$	$123._0$	$123._3$	$123._2$
H78	$87._7$	$88._1$	$89._0$	$90._3$	$91._5$
HPEP	$95._4$	$94._6$	$93._7$	$92._9$	$92._1$
HPEB	$74._8$	$73._4$	$73._3$	$73._3$	$73._3$

[a] Obtained for a matched-pair mixture with ϕ_{D52} = 0.04; all other values were obtained at $\phi_D = \phi_H = 0.50$.

Table 3. *PVT* Properties for Selected Components

sample	T (°C)	$\alpha(T) \times 10^4$ (K^{-1})	$\beta(T) \times 10^4$ (MPa^{-1})	δ_{PVT} (MPa$^{1/2}$)
HPEP	27	6.6_0	5.8_2	18.4_5
	51	6.7_8	6.7_4	18.0_6
	83	6.6_9	7.8_7	17.3_9
	121	6.8_8	9.3_0	17.0_7
	167	7.3_3	11.5_0	16.7_4
HPEB	27	7.0_9	5.8_0	19.1_5
	51	6.9_2	6.5_9	18.4_5
	83	6.9_4	7.7_0	17.9_0
	121	7.1_8	9.3_0	17.4_4
	167	7.4_5	11.7_8	16.6_8
H88	27	6.8_1	6.1_6	18.2_2
	51	7.0_8	7.1_4	17.9_3
	83	6.9_8	8.2_5	17.3_5
	121	7.1_6	9.8_1	16.9_6
	167	7.3_7	12.3_3	16.2_2
H52	27	6.9_7	5.8_4	18.9_3
	51	7.2_5	6.8_3	18.5_6
	83	7.1_2	7.9_6	17.8_3
	121	7.3_5	9.4_7	17.4_9
	167	7.5_0	11.9_0	16.6_5

where ϕ_i, v_i, and N_i are component volume fractions, volumes per monomeric unit, and monomeric units per chain; k_B is the Boltzmann constant, and T is the temperature. The interaction density X is frequently expressed in terms of an arbitrary reference volume v_0 and the dimensionless FH interaction parameter χ with respect to that volume: $\chi \equiv Xk_BT/v_0$. In previous work we reported χ with respect to the reference volume $v_0(T) = [v_1(T)\, v_2(T)]^{1/2}$, which was quite satisfactory for the purpose of those papers. Here, however, we use copolymer theory[9] in some of the analysis, and that is expressed directly in terms of X. Preferring the convenience of a dimensionless expression for the interaction, we have converted χ for all 20 blends in this study[2,5,7] to the same reference volume for all blends and temperatures, choosing $v_{ref} = 1.0 \times 10^{-22}$ cm^3 (60.2 cm^3 on a g·mol basis), which is close to the monomeric volumes of the HPB components. Thus, for this paper,

$$\chi \equiv \frac{[v_1(T)\, v_2(T)]^{1/2}}{v_{ref}} \chi_{(v_1v_2)^{1/2}} \tag{2}$$

The copolymer equation can now be applied directly to those redefined values. Midrange blend concentrations were used, typically near $\phi_1 = \phi_2 = 0.5$, where the values of χ are insensitive to component concentration.[10]

The *PVT* data for H52, H88, HPEP, and HPEB were provided by David Walsh and Gregory Dee of the DuPont Central Research and Development Department. They were obtained with a Zoller (Gnomix) apparatus[11] by methods described elswhere.[3] Density was measured as a function of temperature (30–250 °C in 10 °C increments) and pressure (10–200 MPa in 10 MPa increments) and used to evaluate the thermal expansion coefficient $\alpha(T)$ and isothermal compressibility $\beta(T)$ at ambient pressures (0.1 MPa). The results are given in Table 3. Values for other HPB samples are reported elsewhere.[7]

Results

The temperature dependence of χ in blends of two HPB components is fairly well described by the form

$$\chi = A/T + B \tag{3}$$

where B is negative, and B/A is relatively insensitive to the choice of components.[1,7] The temperature dependence is quite different for blends that contain either the PEP or PEB structures. Figure 1 compares the interactions of the PEB and 66 structures, which have similar ethyl branch frequencies but different sequencing, with various second components—DPEP with H66 and HPEB in Figure 1a, D52 with H66 and HPEB in Figure 1b, H78 with D66 and HPEB in Figure 1c. Both H66/D52 (Figure 1b) and D66/H78 (Figure 1c) behave according to eq 4; for the other blends, χ is either insensitive to temperature—H66/DPEP (Figure 1a), DPEB/H78 (Figure 1c)—or has an enhanced temperature dependence—HPEB/D52 (Figure 1b), HPEB/DPEP (Figure 1a).

Similar behavior is found if the deuterium labels are "switched" from one component to the other.[2] (The versions used in Figure 1 were chosen to cover the widest available temperature range with the least interpolation). Results for D66/HPEB and the label-switched H66/DPEB are compared in Figure 2. Both versions show an unusually strong dependence at low temperatures and a much weaker one at higher temperatures; neither of course accord with eq 3.

Interaction parameters for blends of DPEP with members of the HPB series are compared in Figure 3. The temperature dependence changes systematically with HPB structure—unusually strong for DPEP/H38, curved and with nearly zero χ at high temperatures for DPEP/H52, and then insensitivity to temperature for DPEP/H66. The progression for DPEP blends with H38, H52, and H66 closely parallels the progression for DPEB blends with H52, H66, and H78. Beyond those subranges of HPB structure, the blends with PEP and PEB are strongly phase-separated for the available ranges of molecular weight. We will explore the implications of these sequences in behavior and their associated "windows of miscibility" in more detail below.

Interaction parameters for DPEP/H52 and the label-switched HPEP/D52 are compared in Figure 4. Even at low temperatures χ is relatively small, suggesting nearly ideal mixing for these components. The values for both blends decrease with increasing temperature, and those for HPEP/D52 cross smoothly through zero. Though small in magnitude, and almost comparable to the $\pm 1.5 \times 10^{-4}$ uncertainties in χ,[1] the negative values for $\chi_{\mathrm{HPEP/D52}}$ at high temperatures appear to be real.

Discussion

(a) Effect of Segment Length Difference. Bates et al.[12] have pointed out an apparent correspondence between the interaction strengths in polyolefin blends and Δl, the difference in statistical segment lengths of the component chains. They suggested that segmental mismatch decrease the entropy of mixing and that the effect would therefore appear experimentally as a positive contribution to χ. Liu and Fredrickson suggested that nematic interactions at the segmental level might be responsible.[13] They concluded that, under certain conditions, nematic interactions would contribute to χ an amount on the order of

$$\Delta\chi = v_{\mathrm{ref}} \frac{(\Delta l)^2}{\bar{l}^5} \tag{4}$$

where $\Delta l = l_1 - l_2$ and $\bar{l} = (l_1 + l_2)/2$. Schweizer, though objecting strongly to the nematic mechanism, finds that segment length mismatch can indeed favor demixing but for other reasons.[14]

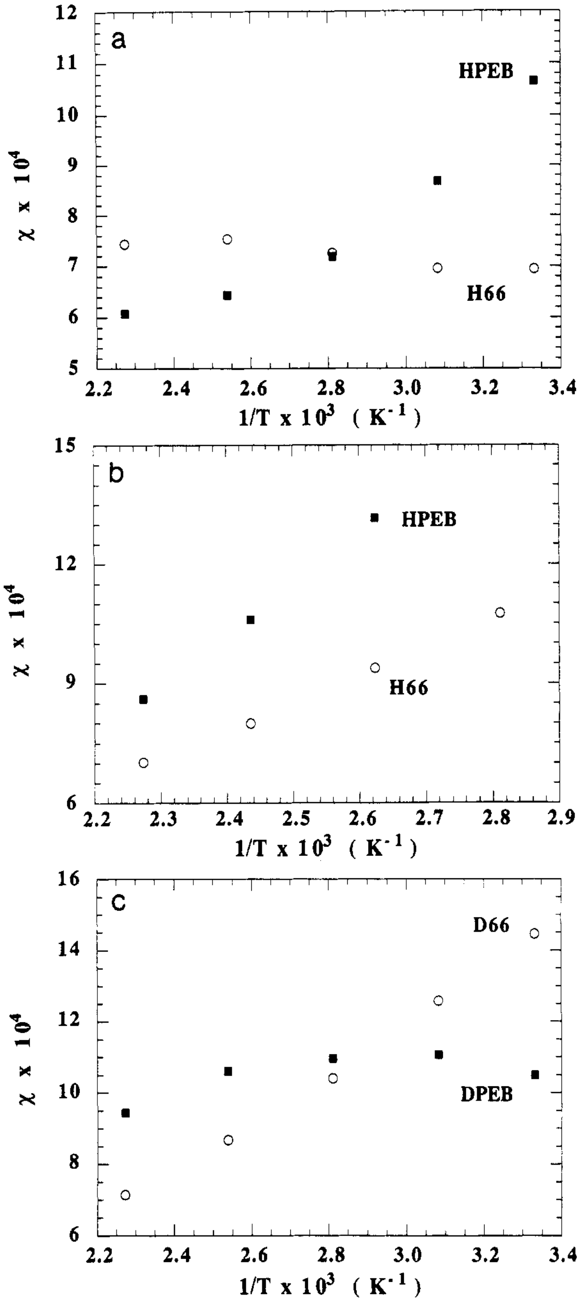


Figure 1. Interaction parameters for blends of PEB and 66 structures with various common components as functions of temperature: (a) HPEB/DPEP and H66/DPEP blends; (b) HPEB/D52 and H66/D52 blends; (c) DPEB/H78 and D66/H78 blends.

Bates et al.[12] suggest that the segment lengths, conventionally defined as $(6R_g^2/n)^{1/2}$, where n is the number of backbone bonds, should instead be compared on the basis of a common FH lattice. We accomplish this for each species i by referring the volume per chain $v_i(T)\,N_i$ to a fixed lattice volume using $v_{\mathrm{ref}} = 1.0 \times 10^{-22}$ cm^3 as before (see eq 2). Thus we define

$$l_i = \left[\frac{6R_g^{\,2}}{N}\frac{v_{\mathrm{ref}}}{v(T)}\right]_i^{1/2} \tag{5}$$

and list those values in Table 4. We then examined our results in terms of eq 4, using mainly the data in Table 4 at 51 and 167 °C.

For the 15 combinations of blend pairs considered in this paper, ignoring label-switch distinctions, $\Delta\chi$ from eq

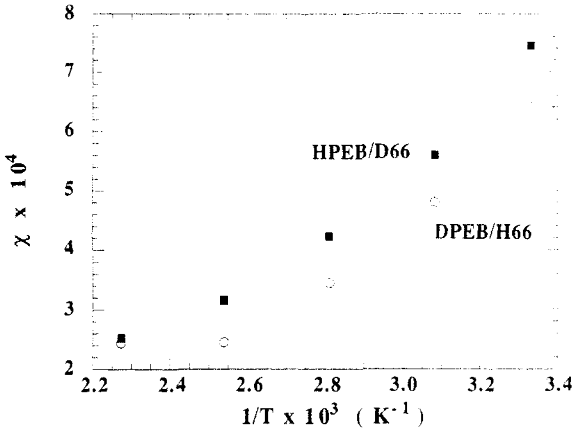


Figure 2. Interaction parameters for HPEB/D66 and DPEB/H66 blends as functions of temperature.

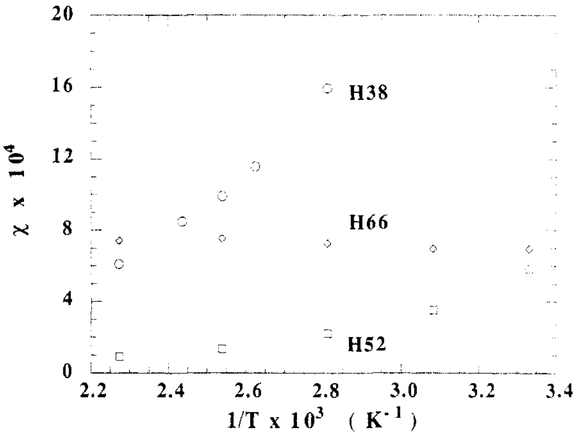


Figure 3. Interaction parameters for blends of DPEP with H38, H52, and H66 as functions of temperature.

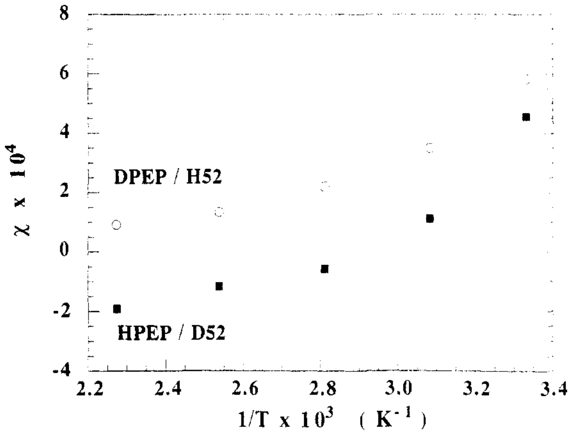


Figure 4. Interaction parameters for HPEP/D52 and DPEP/H52 blends as functions of temperature.

Table 4. Statistical Segment Lengths from Equation 5

	l (Å) at T (°C)				
sample	27	51	83	121	167
H38		7.0_9	6.9_5	6.8_1	6.6_6
H52	6.9_2 (6.9_0[a])	6.8_2	6.7_6	6.6_5	6.5_5
H66	6.4_4	6.3_7	6.3_1	6.2_5	6.1_5
H78	5.7_5	5.7_4	5.7_4	5.7_6	5.7_5
HPEP	6.8_4	6.7_2	6.5_9	6.4_5	6.2_9
HPEB	6.1_3	5.9_8	5.9_1	5.8_4	5.7_6

[a] Obtained for a matched pair with $\phi_{D52} = 0.04$.

4 ranges from 10^{-4} to 10^{-2}. Five of those blends, being effectively immiscible even at 167 °C, have large values of χ (38/66, 38/78, 38/PEB, 52/78, 78/PEP), and the largest values of $\Delta\chi$ ($\sim 10^{-2}$) are indeed calculated for four of them. However, $\Delta\chi$ for the fifth ($\sim 0.3 \times 10^{-2}$ for 38/66) is in fact smaller than $\sim 0.5 \times 10^{-2}$ for 52/PEB, 66/78, and PEP/PEB, all of which are miscible over the entire range and have only modest experimental values of χ ($\lesssim 0.15 \times 10^{-2}$). Also, $v_{\mathrm{ref}}(\Delta l)^2/\bar{l}^5$ changes significantly with temperature, usually decreasing but sometimes increasing with temperature, depending on $l(T)$ for the individual components. Accordingly, whatever contribution this term makes to the total interaction would change considerably with temperature, but we were unable to find any correlation between $v_{\mathrm{ref}}(\Delta l)^2/\bar{l}^5$ and the menagerie of $\chi(T)$ shapes found for the various blends.

(b) Random Copolymer Analysis. We have attempted to organize the interactions for blends of HPEP and HPEB with the HPB polymers through random copolymer theory. Thus, aside from ~7% minority units, HPEP and HPEB are essentially homopolymers, while the HPB components are nearly random copolymers of linear- and branched-C_4 units, the respective homopolymers being H00 (linear polyethylene) and H100 [atactic poly(butene-1)]. According to random copolymer theory,[9] the interactions for a homopolymer A with copolymer B_yC_{1-y} are related to those for binary blends of the respective homopolymers—A/B, A/C, and B/C—and the copolymer composition y:

$$\chi_{A/B_yC_{1-y}} = y\chi_{A/B} + (1-y)\chi_{A/C} - y(1-y)\chi_{B/C} \qquad (6)$$

for interaction parameters defined with respect to the same reference volume, eq 2 in our case.

The interactions for four sets of blends are available for analysis by eq 6:

homopolymer	copolymer	homopolymer interaction param
HPEP	D38, D52, D66	$\chi_{D00/D100}$, $\chi_{HPEP/D00}$, $\chi_{HPEP/D100}$
DPEP	H38, H52, H66	$\chi_{H00/H100}$, $\chi_{DPEP/H00}$, $\chi_{DPEP/H100}$
HPEB	D52, D66, D78	$\chi_{D00/D100}$, $\chi_{HPEB/D00}$, $\chi_{HPEB/D100}$
DPEB	H52, H66, H78	$\chi_{H00/H100}$, $\chi_{DPEB/H00}$, $\chi_{DPEB/H100}$

Three copolymer compositions are represented in each set (y = 0.38, 0.52, and 0.66 for the blends with PEP; y = 0.52, 0.66, and 0.78 for the blends with PEB), and χ is available at five temperatures for each, making a total of 15 experimental values to determine 15 homopolymer interaction parameters (three at each of the five temperatures) through eq 6. Values calculated in this way[15] did not differ significantly from those obtained by using eq 3 to describe the three homopolymer interactions, thus requiring only six adjustable parameters (A_i, B_i) to fit the 15 experimental values for each set. The results discussed below were all obtained by this second method.

Previous work on the effects of deuterium substitution[2] suggests the following approximate relationships among interaction parameters for unlabeled (hh), singly-labeled (hd and dh), and doubly-labeled (dd) blends at similar labeling levels:

$$\chi_{hh} = \chi_{dd} \qquad (7)$$

$$\chi_{hh} = (\chi_{hd} + \chi_{dh})/2 \qquad (8)$$

The values of $\chi_{D00/D100}$ and $\chi_{H00/H100}$ from the two PEP sets differed by an average of 20% and those from the two PEB sets by 5%, so an average was used in each case. Values for $\chi_{HPEP/D00}$, $\chi_{HPEP/D100}$, $\chi_{HPEB/D00}$, and $\chi_{HPEB/D100}$ were combined with their label-switched values according to eq 8. The resulting estimates of $\chi_{H00/H100}$, $\chi_{HPEP/H00}$, and $\chi_{HPEP/H100}$ from the blends with PEP, and $\chi_{H00/H100}$ from the blends with PEB, are compared with other determinations of these quantitites in Figures 5–7.

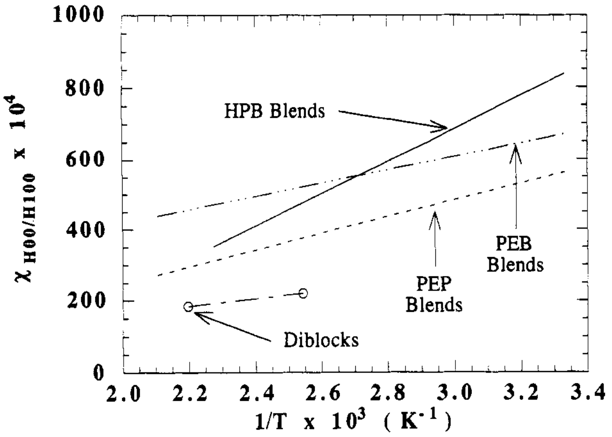


Figure 5. Comparison of H00/H100 interactions obtained from HPEP/HPB and HPEB/HPB blends through random copolymer theory, from HPB/HPB blends,[7] and from H08–H100 diblocks.[12]

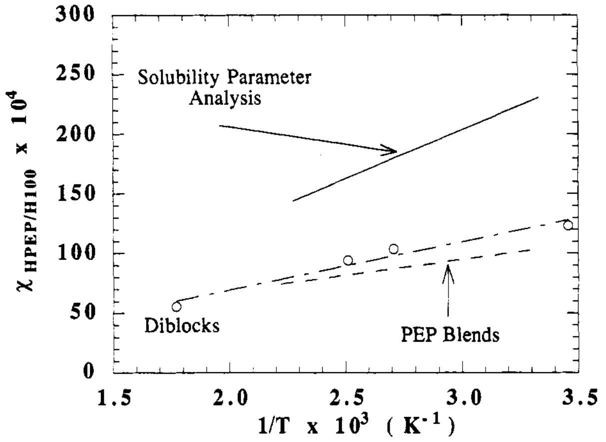


Figure 6. Comparison of HPEP/H100 interactions obtained from HPEP blends through random copolymer theory, from the solubility parameter assignments in Table 4, and from HPEP-H100 diblocks.[12]

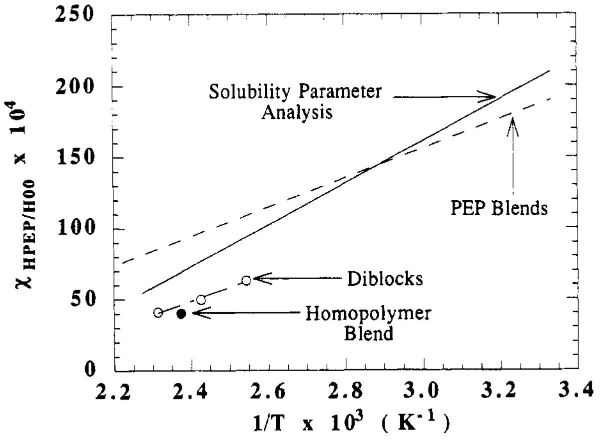


Figure 7. Comparisons of HPEP/H00 interactions obtained from HPEP blends through random copolymer theory, from the solubility parameter assignments in Table 9, and from HPEP-H08 diblocks and blends.[12]

Estimates of $\chi_{H00/H100}$ vs T based on blends with PEP and PEB, obtained as described above, are compared in Figure 5 with values estimated by an analysis of χ for pairs of HPB components[7] and values of $\chi_{H08/H100}$ calculated from the microphase separation transition (MST) temperatures reported by Bates et al.[12] for H08–H100 (PE–PEE) diblock copolymers. The PEP- and PEB-based lines have similar slope, but the values differ by an average of ~60%. The HPB-based line has a clearly different slope, while the diblock-based values are far smaller than any of the others, a difference which cannot be explained by the small difference between the H08 and H00 structures. On the other hand, the results for $\chi_{HPEP/H100}$, in Figure 6, show rather good agreement between the PEP-based values and those from the MST temperatures of HPEP–H100 (PEP–PEE) diblocks.[12] However, values of $\chi_{HPEP/H100}$ obtained by the solubility parameter analysis described in the following section are clearly much larger. Figure 7 compares the PEP-based values of $\chi_{HPEP/H00}$ with those obtained by the solubility parameter method and those calculated from the MST temperatures for HPEP–H08 (PEP–PE) diblocks and an HPEP/H08 blend.[12] In this case the PEP-based and diblock results differ substantially, while those from the solubility parameter analysis agree roughly with the PEP-based values at low temperatures and the diblock values at high temperatures.

The interactions in blends of two HPB components show very large departures from the copolymer equation,[7] so a third method was developed for analyzing the PEP- and PEB-based data that takes those departures into account.[15] The PEP- and PEB-based predictions were changed significantly in some cases, but they led to other inconsistencies that were at least as severe as those so clearly evident in Figures 5–7. We attribute these inconsistencies to a data analysis that relies heavily on random copolymer theory. That theory is inadequate for blends of HPB components,[7] and it may fail for the PEP- and PEB-based blends as well.

(c) Solubility Parameter Analysis. According to regular solution theory,[4] the interaction parameter for binary liquid mixtures can be expressed in terms of pure component properties alone:

$$\chi = \frac{v}{k_B T}(\delta_1 - \delta_2)^2 \tag{9}$$

in which v is the reference volume, and δ_1 and δ_2 are solubility parameters; pure component properties are positive in sign and related in principle to the cohesive energy density. The main assumptions underlying the equation are (1) no volume change with mixing, (2) ideal entropy of mixing, (3) weak forces of the induced dipole type (dispersive interactions), and (4) Berthelot's rule for the cross interactions, which produces the perfect square form of eq 9. Though widely used as an empirical scheme for organizing and estimating interactions in small-molecule liquids,[16] the equation has also been widely criticized for its quantitative shortcomings.[17] On the other hand, the interactions for saturated hydrocarbon polymers are approximately 3 orders of magnitude weaker than those investigated with small molecules, and volume changes with mixing are certainly small.[10] Berthelot's rule and ideality of the mixing entropy are of course much more difficult to establish for any system.

At this point we view eq 9 as a working hypothesis and seek to test its primary supposition, that, in calculating interactions, a unique quantity, called the solubility parameter, can be associated with each component, irrespective of the choice of the second component in its blends. We have already used eq 9 as the basis for explaining label-switching effects on χ^2 and also to assign a qualitative ordering of component solubility parameters from the change in χ when the deuterium labels are switched from one component to the other.[5] We assumed uniqueness in using eq 9 to organize the SANS results for HPB blends.[7] Here we test that supposition directly, by examining the numerical consistency of solubility parameter differences for a matric of interconnected binary blends involving PEB, PEP, and HPB components.

Table 5. Tabulation of Apparent Solubility Parameter Differences

	δ_1–δ_2 (MPa$^{1/2}$)				
comp 1/comp 2	27 °C	51 °C	83 °C	121 °C	167 °C
D38/H52	0.21_2^a	0.20_2	0.18_3	0.16_9	0.16_0
H38/D52	0.25_4^a	0.24_0^a	0.22_6^a	0.21_0	0.19_6
D52/H66	0.25_3^a	0.24_2^b	0.22_3^b	0.21_8	0.20_6
H52/D66	0.31_1^c	0.29_8^c	0.28_3^c	0.26_9^c	0.25_5^c
D66/H78	0.24_4^a	0.23_7^b	0.22_6	0.21_7	0.20_8
H66/D78	0.25_8^a	0.25_0^a	0.24_1^a	0.23_2	0.22_3
DPEP/HPEB	0.21_0	0.19_7	0.18_8	0.18_7	0.19_2
HPEP/DPEB	0.22_6	0.21_1	0.202	0.20_1	0.20_3
DPEB/H78	0.20_9	0.22_3	0.23_2	0.24_0	0.23_9
HPEB/D78	0.25_3	0.26_2	0.26_9	0.27_0	0.26_7
DPEB/H66	0.16_4	0.14_8	0.13_0	0.11_4	0.12_2
HPEB/D66	0.17_6	0.15_8	0.14_5	0.13_0	0.12_2
D52/HPEB	0.33_3^a	0.30_9^a	0.28_2^a	0.25_5	0.22_9
H52/DPEB	0.34_9^a	0.32_4^a	0.29_6^a	0.26_8^d	0.24_0^d
DPEP/H66	0.17_0	0.17_7	0.18_9	0.20_2	0.21_2
HPEP/D66	0.21_0	0.21_8	0.22_7	0.23_4	0.23_9
D52/HPEP	0.13_8	0.07_1	$(-0.003)^e$	$(-0.006)^e$	$(-0.012)^e$
H52/DPEP	0.15_5	0.12_6	0.10_5	0.08_4	0.07_8
D38/HPEP	0.31_0^a	0.25_9^b	0.20_2	0.14_4	0.08_9
H38/DPEP	0.36_2^a	0.32_2^a	0.27_8^a	0.23_5	0.19_2

[a] Extrapolated from higher temperatures. [b] Values from $\phi = 0.25$ and 0.75. [c] Values from $\phi = 0.1, 0.25, 0.75$, and 0.9. No single-phase data were available at $\phi = 0.5$.[5] [d] Values from $\phi = 0.2$ and 0.8. No single-phase SANS data were obtainable at $\phi = 0.5$. [e] Obtained χ was negative; the tabulated value is $\chi k_B T/v_{ref}$ in units of MPa.

According to the results of deuterium switching,[5] the following orderings apply to the solubility parameters for the polymers in this study:

$$\delta_{38} > \delta_{52} > \delta_{66} > \delta_{78}$$

$$\delta_{38} > \delta_{PEP} > \delta_{66}$$

$$\delta_{52} > \delta_{PEP} > \delta_{78}$$

$$\delta_{PEP} > \delta_{PEB}$$

The apparent solubility parameter differences, as computed with eq 9 from χ for their blends, are given in Table 5. The component with the larger solubility parameter is listed first (component 1), so the listed difference, $\delta_1 - \delta_2$, is a positive quantity according to the above orderings. Some values were obtained by extrapolating χ from high temperatures or from values for blend concentrations other than $\phi_1 = \phi_2 = 0.5$ but always in the midrange. (Negative interaction parameters (HPEP/D52 blends at high temperatures only) cannot be accommodated by eq 9 and are listed as $X = \chi k_B T/v_0$ in the compilation.) The question to be examined is whether the differences in Table 5, within the experimental uncertainties, are consistent with solubility parameter uniqueness.

The interconnections of components through blends are shown by the sketch in Figure 8. The lines connect components whose interactions have been determined. The solid line indicate those where the assignment of order seems clear; the dashed lines indicate the ones with very small differences in the solubility parameter or some uncertainty in ordering because the label-switching effect was too small. Consistency was checked first by summing solubility parameter differences over only the closed paths defined by the solid lines in Figure 8. Thus, for example, there are four nonredundant blend sequences, with a common component at each step, that begin and end at H38:

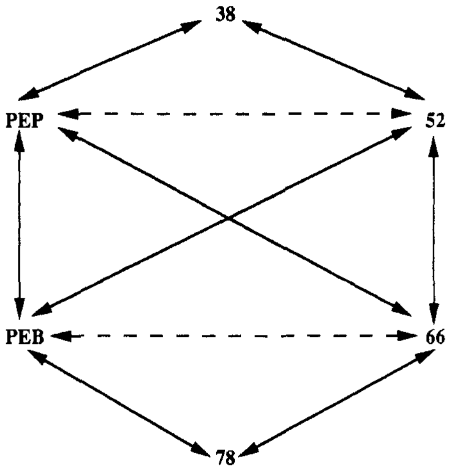


Figure 8. Schematic of binary blend connections among the components. The solid lines indicate pairs with conveniently large interaction parameters and a clear indication of solubility parameter ordering from the label-switching effect; the dashed connections indicate smaller interaction parameters or some ambiguity in solubility parameter ordering.

H38/DPEP, DPEP/HPEB, HPEB/D78, D78/H66, H66/D52, D52/H38

H38/DPEP, DPEP/H66, H66/D78, D78/DPEB, HPEB/D52, D52/H38

H38/DPEP, DPEP/H66, H66/D52, D52/H38

H38/DPEP, DPEP/HPEB, HPEB/D52, D52/H38

There are four others for D38, two for H78, and two others for D78. Consistency requires that the sum of solubility parameter differences for the sequence of blends along each path, with due regard for the algebraic sign at each step, be zero.

The sums for each of these 12 independent paths are listed in Table 6. With some exceptions, most notably the high-temperature sequences that include the D38/HPEP blend, the sums are less than 0.08 MPa$^{1/2}$, which is small relative to the magnitude of the individual terms. Similar tests were performed for several open path sequences along solid lines in Figure 8, leading to apparent values for $\delta_{38} - \delta_{52}$, $\delta_{52} - \delta_{66}$, $\delta_{66} - \delta_{78}$, $\delta_{38} - \delta_{66}$, $\delta_{52} - \delta_{78}$, and $\delta_{38} - \delta_{78}$. Values obtained for sequences along the HEB series only were compared with those that also include the PEP and PEB structures. Again, with the exception of sequences that include the D38/HPEP blend, the agreement was good, with differences never larger than ~0.05 MPa$^{1/2}$. We believe the D38/HPEP anomaly is associated with the relatively small values of χ for that blend, as explained below. Aside from that, however, the sums along the solid lines alone support the idea that solubility parameters can be uniquely assigned to individual components and that there are no significant pair-specific effects, such as local packing changes with mixing, at least within this limited collection of saturated hydrocarbon polymers. The lack of systematic variations in the sums with temperature also suggests that the wide variety of temperature dependences observed for χ simply reflects different variations with temperature in pure component properties alone.

The uncertainties in SANS intensity calibration and molecular weight are estimated to be 7% and 5%, respectively.[1] For the blends in this study we estimate the resulting uncertainties on χ to be $(0.7\text{–}1.5) \times 10^{-4}$, with the smallest uncertainty associated with values obtained nearest the spinodal. In the absence of a detailed

Table 6. Residuals in Consistency Tests of the Solubility Parameter Formulation

		algebraic summations (MPa$^{1/2}$)				
sequence	ref	27 °C	51 °C	83 °C	121 °C	167 °C
H38-DPEP-HPEB-D78-H66-D52-H38	H38	–0.06	–0.05	–0.04	–0.03	–0.02
H38-DPEP-H66-D78-HPEB-D52-H38	H38	0.05	0.06	0.07	0.07	0.06
H38-DPEP-H66-D52-H38	H38	–0.02	–0.02	–0.01	–0.01	0.00
H38-DPEP-HPEB-D52-H38	H38	0.01	0.03	0.04	0.04	0.04
D38-HPEP-DPEB-H78-D66-H52-D38	D38	0.02	0.04	0.06	0.07	0.09
D38-HPEP-D66-H78-DPEB-H52-D38	D38	0.00	0.03	0.06	0.08	0.10
D38-HPEP-D66-H52-D38	D38	0.00	0.02	0.04	0.06	0.08
D38-HPEP-DPEB-H52-D38	D38	0.02	0.05	0.08	0.09	0.11
H78-D66-HPEP-DPEB-H78	H78	0.02	0.02	0.02	0.01	0.01
H78-D66-H52-DPEB-H78	H78	0.00	–0.01	–0.02	–0.02	–0.02
D78-H66-DPEP-HPEB-D78	D78	–0.04	–0.03	–0.03	–0.02	–0.02
D78-H66-D52-HPEB-D78	D78	–0.08	–0.08	–0.08	–0.07	–0.07

Table 7. Estimation of δ_{52}–δ_{PEP} and δ_{66}–δ_{PEB} by Various Sequences

		results of summation (MPa$^{1/2}$)				
sequence		27 °C	51 °C	83 °C	121 °C	167 °C
D52-H38-DPEP	δ_{D52}–δ_{DPEP}	0.11	0.08	0.05	0.02	0.00
D52-HPEB-DPEP	δ_{D52}–δ_{DPEP}	0.12	0.11	0.09	0.07	0.04
D52-H66-DPEP	δ_{D52}–δ_{DPEP}	0.08	0.07	0.04	0.02	–0.01
D52-H66-D78-HPEB-DPEP	δ_{D52}–δ_{DPEP}	0.05	0.03	0.01	–0.01	–0.03
H52-D38-HPEP	δ_{H52}–δ_{HPEP}	0.10	0.06	0.02	–0.02	–0.07
H52-DPEB-HPEP	δ_{H52}–δ_{HPEP}	0.12	0.11	0.09	0.07	0.04
H52-D66-HPEP	δ_{H52}–δ_{HPEP}	0.10	0.08	0.06	0.04	0.02
H52-D66-H78-DPEB-HPEP	δ_{H52}–δ_{HPEP}	0.12	0.10	0.08	0.04	0.02
D66-H78-DPEB	δ_{D66}–δ_{DPEB}	0.04	0.01	–0.01	–0.02	–0.03
D66-HPEP-DPEB	δ_{D66}–δ_{DPEB}	0.02	–0.01	–0.02	–0.03	–0.04
D66-H52-DPEB	δ_{D66}–δ_{DPEB}	0.04	0.03	0.01	0.00	–0.01
D66-H52-D38-HPEP-DPEB	δ_{D66}–δ_{DPEB}	0.01	–0.03	–0.06	–0.09	–0.12
H66-D78-HPEB	δ_{H66}–δ_{HPEB}	0.01	–0.01	–0.03	–0.04	–0.04
H66-DPEP-HPEB	δ_{H66}–δ_{HPEB}	0.04	0.02	0.00	–0.02	–0.02
H66-D52-HPEB	δ_{H66}–δ_{HPEB}	0.08	0.07	0.05	0.04	0.02
H66-D52-H38-DPEP-HPEB	δ_{H66}–δ_{HPEB}	0.07	0.04	0.01	–0.01	–0.02

Table 8. Comparison of Direct and Indirect Estimates for δ_{52}–δ_{PEP} and δ_{66}–δ_{PEB}

		$\delta_1 - \delta_2$ (MPa$^{1/2}$)				
		27 °C	51 °C	83 °C	121 °C	167 °C
indirect[a]	δ_{H52}–δ_{HPEP}	0.09	0.07	0.05	0.02	0.00
indirect[b]	δ_{D52}–δ_{DPEP}	0.11	0.09	0.06	0.03	0.00
direct	δ_{H52}–δ_{HPEP}	0.15	0.10			
indirect	δ_{H66}–δ_{HPEB}	0.03	0.00	–0.02	–0.04	–0.05
indirect[b]	δ_{D66}–δ_{DPEB}	0.05	0.03	0.01	–0.01	–0.02
direct	δ_{H66}–δ_{HPEB}	–0.17	–0.16	–0.14	–0.12	–0.12

[a] Indirect means the values were obtained through blends with third components, when the interactions were large. Direct means the values were obtained through eq 13 from the blends of the components themselves. [b] According to eq 12, these values should be the same as the hh values on the line above.

analysis we assume an error of ±1.5 × 10^{-4} for all blends. The uncertainties in χ propagate in a rather complicated manner to those for $(\delta_1 - \delta_2)_{\text{apparent}}$ in Table 5. Thus, χ = 25 × 10^{-4} translates through eq 9 to $(\delta_1 - \delta_2)_{\text{apparent}}$ ~0.3 MPa$^{1/2}$ with 3% uncertainty, while χ = 10 × 10^{-4} translates to ~0.2 MPa$^{1/2}$ ± 7% and χ = 3 × 10^{-4} to ~0.1 MPa$^{1/2}$ ~ 30%. Even the absolute errors in $(\delta_1 - \delta_2)_{\text{apparent}}$ increase rapidly as χ becomes small. This, of course, must be considered in judging the significance of nonzero sums in Table 6, particularly because some of the sequences involve blends with small χ, especially those at high temperatures. Such considerations can very easily explain the apparent D38/HPEP anomaly noted above. On the other hand, if all values based on small χ—say, $\chi < 5 \times 10^{-4}$—were eliminated, the number of alternative sequences between components, and thus the stringency of the tests, would be reduced significantly.

We have not yet discussed the results for PEP/52 and PEB/66 blends, connected by the dashed lines in Figure 8. The interaction parameters for PEP/52 blends are rather small, so their solubility parameter differences (Table 5), are uncertain, for the reasons explained above. The interaction parameters for PEB/66 blends are larger, but the effect of deuteration switching is small enough to make the sign of $\delta_{HPEB} - \delta_{H66}$ uncertain. The apparent solubility parameter differences for both, however, can be obtained indirectly, through their blends, with other components, e.g.,

$$\delta_{52} - \delta_{HPEP} = (\delta_{D38} - \delta_{HPEP}) - (\delta_{D38} - \delta_{H52}) \tag{10}$$

$$\delta_{D52} - \delta_{DPEP} = (\delta_{H38} - \delta_{DPEP}) - (\delta_{H38} - \delta_{D52}) \tag{11}$$

The results for such sequences are listed in Table 7. The apparent solubility parameter differences for hydrogenous, deuterated, and mixed pairs at similar labeling levels are linked by the following approximate relationships:[5]

$$(\delta_1 - \delta_2)_{hh} = (\delta_1 - \delta_2)_{dd} \tag{12}$$

$$(\delta_1 - \delta_2)_{hh} = \frac{1}{2}[(\delta_1 - \delta_2)_{hd} + (\delta_1 - \delta_2)_{dh}] \tag{13}$$

Averages for the various indirect estimates of $\delta_{52} - \delta_{HPEP}$, $\delta_{D52} - \delta_{DPEP}$, $\delta_{H66} - \delta_{HPEB}$, and $\delta_{D66} - \delta_{DPEB}$ (Table 7) are compared in Table 8 with values estimated from eq 13 for the PEP/52 and PEB/66 blends themselves (Table 5). Note that the direct apparent values for $\delta_{H52} - \delta_{HPEP}$ (only available at low temperatures) agree fairly well with the two indirect values, which also agree well with each other other as required by eq 12. For $\delta_{H66} - \delta_{HPEB}$, however, the direct values and the two indirect values (which do agree

Table 9. Solubility Parameters from SANS Data, Relative to the H97 Reference for the PEP, PEB, and Selected HPB Structures

	$\delta - \delta_{\mathrm{ref}}$ (MPa$^{1/2}$)				
sample	27 °C	51 °C	83 °C	121 °C	167 °C
H97	0	0	0	0	0
H78	0.4_9	0.4_8	0.4_6	0.4_4	0.4_1
HPEB	0.7_2	0.7_2	0.7_1	0.6_9	0.6_6
H66	0.7_3	0.7_2	0.6_9	0.6_6	0.6_2
HPEP	0.9_2	0.9_1	0.9_0	0.8_9	0.8_8
H52	1.0_1	0.9_8	0.9_5	0.9_1	0.8_6
H38	$(1.2_3)^a$	1.2_0	1.1_6	1.1_1	1.0_5
H08	(1.7_7)	(1.7_1)	(1.6_3)	1.5_4	1.4_3

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

Table 10. Comparison of Solubility Parameter Differences from Symmetric Diblock Copolymers[12] and Those Obtained with Table 9

	$\delta_1 - \delta_2$ (MPa$^{1/2}$)			
	100 °C		167 °C	
pair	diblock	from Table 9	diblock	from Table 9
H08, HPEP	0.6_3	0.6_9	0.4_8	0.5_5
H100, HPEP	-0.7_4	-0.9_3	-0.7_1	-0.9_2
H08, H100	1.1_5	1.6_2	1.0_8	1.4_7

between themselves) are substantially different at all temperatures. We interpret this difference as indicating a pairwise effect that is specific to the mixing of HPEB and H66 components. This pair provides the only clear example of irregular mixing among all the component pairs in this study. The blends of both PEB and 66 with other components are consistent with the idea of solubility parameter uniqueness, but a *bona fide* specific interaction appears when they are blended with one another. Aside from the ~7% minority unit in PEB, the two structures differ only in ethyl branch sequencing along the chain, which presumably is somehow responsible for the mixing anomaly. It is curious, but perhaps just coincidental, that the indirectly obtained solubility parameters for PEB and 66 are essentially identical at all temperatures, so that the pair would have formed ideal mixtures if *anomalous* mixing had not intervened. Many other examples of irregular mixing have been identified[15] and will be described in forthcoming publications.

A solubility parameter scale for the HPB series, relative to the value for H97 at each temperature, was established in previous work.[7] The values for HPEP and HPEB on the same scale, determined indirectly from the results for blends with HPB (omitting the PEP/52 and PEB/66 blend results), are given in Table 9. These assignments were used to estimate the spinodal temperature T_s for other PEP and PEB blends, all far off-critical and yet known to be two-phase up to at least 200 °C[5]—HPEP/D78 ($\phi_D = 0.15$), HPEB/D38 ($\phi_D = 0.10$), and HPEP/D88 ($\phi_D = 0.08$). The resulting values of T_s—215, 155, and 170 °C, respectively—are all consistent with two-phase equilibrium states at 200 °C.

The assignments in Table 9 were also compared with some blend results reported by Bates et al.[12] The apparent value of $\delta_{\mathrm{H08}} - \delta_{\mathrm{HPEP}}$, estimated from the critical temperature T_c for their PE/PEP blend (H08/HPEP in our terminology), was reasonably consistent with expectations based on Table 9: $\delta_{\mathrm{H08}} - \delta_{\mathrm{HPEP}} = 0.59$ MPa$^{1/2}$ at 148 °C. A similar comparison, based on T_c for their two PEP + PE/PEE blends (HPEP/H43 blends in our terminology), gave mixed results. Agreement with the assignments in Table 9 was good for the blend with higher T_c but poor for the other.

The assignments in Table 9 were also used to evaluate the solubility parameter differences that are relevant for the PE–PEE (H08–H100), PEP–PEE (HPEP–H100), and PEP–PE (HPEP–H08) diblock results reported by Bates et al.[12] The estimates and the values deduced from the MST temperature for the diblocks are compared at two temperatures in Table 10. The temperature dependences from blends and from diblocks agree rather well in all three cases, and the values for $\delta_{\mathrm{H08}} - \delta_{\mathrm{HPEP}}$ are reasonably consistent. However, the numerical discrepancy is larger for $\delta_{\mathrm{H100}} - \delta_{\mathrm{HPEP}}$ and very large indeed for $\delta_{\mathrm{H00}} - \delta_{\mathrm{H100}}$. For symmetric diblocks, moreover, the solubility parameter formalism requires

$$\delta_{\mathrm{PE}} - \delta_{\mathrm{PEE}} = (\delta_{\mathrm{PE}} - \delta_{\mathrm{PEP}}) + (\delta_{\mathrm{PEP}} - \delta_{\mathrm{PEE}}) \tag{14}$$

$$\delta_{\mathrm{H00}} - \delta_{\mathrm{H100}} = (\delta_{\mathrm{H08}} - \delta_{\mathrm{HPEP}}) - (\delta_{\mathrm{H100}} - \delta_{\mathrm{HPEP}})$$

which is clearly not satisfied by the diblock results in Table 10. Thus, it seems inescapable that solubility parameters developed from a body of data for binary blends, and authenticated for uniqueness by tests of internal consistency, still cannot always be applied with confidence to quantitative predictions for block copolymers.

(d) Solubility Parameters from PVT Properties. In earlier work[7] we compared solubility parameter differences from SANS with those estimated from *PVT* measurements on the pure components. Thus, from the thermal expansion coefficient and isothermal compressibility:[4,18]

$$\delta_{PVT} = \left[T\frac{\alpha(T)}{\beta(T)}\right]^{1/2} \tag{15}$$

The values obtained for H52, H88, HPEP, and HPEB are listed in Table 3; those for H08, H32, H66, and H97 are given elsewhere.[7] The values related to H97, $(\delta - \delta_{\mathrm{ref}})_{PVT}$, are compared with $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ at the three higher temperatures in Table 11. (Results at the other temperatures are comparable; values of $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ for H32 were taken from ref 7, the remainder being from Table 9 here.)

The estimates from pure component *PVT* data in Table 11 provide the same rough ordering as the SANS results:

$$\delta_{\mathrm{H32}} > \delta_{\mathrm{HPEP}} > \delta_{\mathrm{HPEB}} > \delta_{88}$$

and the numerical values of $(\delta - \delta_{\mathrm{ref}})_{PVT}$ and $(\delta - \delta)_{\mathrm{SANS}}$ are in fact in remarkably good agreement in most cases. It is not possible to establish a clear ordering of solubility parameters for H52, H66, HPEP, and HPEB on the basis of the *PVT* results alone, and there is simply too much scatter to allow meaningful inferences about the unusual temperature dependence of χ for blends containing HPEB or HPEP components. The experimental errors in $\alpha(T)$ and $\beta(T)$ are, of course, strongly emphasized when the *PVT* predictions are expressed as solubility parameter differences. Nevertheless, the comparisons in Table 11 strongly support the idea that χ for the blends in this study, regardless of their temperature dependence (but excepting PEB/66 blends), are governed primarily by pure component properties alone.

Summary and Conclusions

We have shown that the melt state interactions in binary blends of PEP, PEB, and several members of the HPB family, expressed in terms of the Flory–Huggins interaction parameter χ, display a wide range of temperature de-

Table 11. Comparison of Solubility Parameters from Pure Component *PVT* Data with Those from SANS Measurements on Blends

	83 °C		121 °C		167 °C	
component	$(\delta - \delta_{ref})_{PVT}$	$(\delta - \delta_{ref})_{SANS}$	$(\delta - \delta_{ref})_{PVT}$	$(\delta - \delta_{ref})_{SANS}$	$(\delta - \delta_{ref})_{PVT}$	$(\delta - \delta_{ref})_{SANS}$
H97[a]	0	0	0	0	0	0
H88	0.2_7	0.2_1	0.2_7	0.2_0	0.3_6	0.1_8
H66[a]	0.9_2	0.6_9	0.8_4	0.6_6	0.8_0	0.6_2
HPEB	0.8_2	0.7_1	0.7_5	0.6_9	0.8_2	0.6_6
H52	0.7_5	0.9_5	0.8_0	0.9_1	0.7_9	0.8_6
HPEP[b]	1.0_1	0.9_0	1.2_3	0.8_9	0.8_7	0.8_8
H32[a]	1.3_4	1.2_8	1.1_5	1.2_2	1.3_6	1.1_5
H08[a]	–	(1.6_3)[c]	1.4_9	1.5_4	1.6_8	1.4_3

[a] The *PVT* and SANS values for these samples are given in ref 7. [b] The H97 reference data used to evaluate $(\delta - \delta_{ref})_{PVT}$ for HPEP differ slightly from those used for the other polymers.[7] The HPEP and replacement H97 data were acquired much earlier and with slightly different protocols than the others. [c] Obtained by extrapolation from SANS data above T_m.

pendences. We examined the interactions from several viewpoints—statistical segment length mismatch, random copolymer theory, and a solubility parameter formalism. Interaction strengths increase in a rough way with differences in the segment lengths, but there are exceptions, and we did not find a unifying correlation with the key parameter of the theory, $v_{ref}(\Delta l)^2/\bar{l}^5$. Copolymer theory provided a reasonably coherent account of the observed variety of temperature dependences for χ, but we were unable to establish self-consistent values of the underlying homopolymer interactions amongst the H00 (polyethylene), H100 [poly(butene-1)], and HPEP monomeric units. Consistency with the uniqueness of solubility parameter assignments was demonstrated for the various blend components. These assignments vary with temperature, and the temperature dependence of χ can be explained for the most part by those variations alone, i.e., without the need to invoke local packing changes with mixing that are specific to the component pair. We did, however, identify one component pair, PEB and 66, whose blends displayed clear evidence of specific mixing effects. We also showed that the ordering of solubility parameters inferred from pure component *PVT* properties was consistent with the SANS-based ordering, and we found good numerical agreement between the solubility parameter assignments obtained by the two methods.

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