Deuteration Effects and Solubility Parameter Ordering in Blends of Saturated Hydrocarbon Polymers

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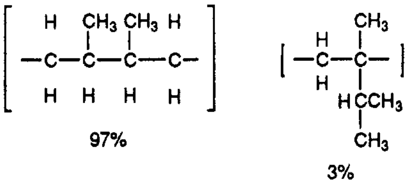
ABSTRACT: This paper presents a continuation of earlier studies on the effects of deuterium substitution on blends of saturated hydrocarbon polymers. The components were model polyolefins, each available in fully hydrogenous (h) and partially deuterated (d) forms, made by saturating the double bonds of polydienes with H_2 and D_2. Values of χ, the Flory–Huggins interaction parameter, were obtained by small-angle neutron scattering with blends of the h form for one component and the d form for the other. According to our earlier proposal, the change in interaction when the deuterium labeling of the pair is reversed, $\chi_{1h,2d} - \chi_{1d,2h}$, permits a numerical ordering of the component solubility parameters, δ_1 and δ_2: $\chi_{1h,2d} > \chi_{1d,2h}$ implies $\delta_1 > \delta_2$. The qualitative consistency of orderings based on this principle, involving blends with common components in many cases, was examined. Although disagreements with group contribution estimates were observed, the internal consistency of the orderings was clearly established for many model random and alternating copolymers. Only in the case of model head-to-head polypropylene were there clear conflicts in ordering assignments, which we had tentatively attributed to specific mixing effects.

Introduction

In a previous paper[1] we discussed the effect of deuterium labeling on the thermodynamic interactions in polymer blends, paying particular attention to the systematic change in interaction strength that occurs when the labels are switched from one blend component to the other.[2] We suggested a possible explanation for the change based on a solubility parameter formalism[3] and found it to be consistent with small-angle neutron scattering (SANS) and light scattering data for several blends of saturated hydrocarbon polymers. In this paper we report many additional results of label switching, provide further tests of qualitative consistency with solubility parameter ideas, and offer brief comparisons with other interpretations of the label switching effect.[4,5] The blend components were labeled (partially deuterated) and unlabeled (fully hydrogenous) model polyolefins, obtained by catalytically saturating the double bonds of nearly monodisperse polydienes with D_2 or H_2. Melt-state interactions were determined by SANS measurements on single-phase blends, interpreted through the Flory–Huggins theory and the incompressible random-phase approximation, as described earlier.[6]

Experimental Section

The blend components were saturated polydienes, each available in fully hydrogenous (H) and partially deuterated (D) forms. The HPB series are saturated polybutadienes (model poly[ethylene-*stat*-butene-1], and, for example, H52 is a member that contains 52% branched C_4 units (from the 52% vinyl content of the parent polybutadiene), while D52 is its partially deuterated but structurally matched twin. Likewise, HPEP and DPEP are a matched pair of saturated 1,4-polyisoprenes (model poly[ethylene-*alt*-propylene]), HPEB and DPEB are a matched pair of saturated 1,4-poly(2-ethylbutadienes) (model poly[ethylene-*alt*-butene-1]), and HhhPP and DhhPP are a matched pair of saturated 1,4-poly(2,3-dimethylbutadiene) (model head-to-head polypropylene). The HPB, PEP, and PEB structures have been described in more detail elsewhere.[1,6] The monomeric units of HhhPP have the following structures:



which result from 97% 1,4 and 3% 1,2 enchainments of the diene.[7]

Synthesis and characterization of the polydiene precursors and their saturated derivatives are described elsewhere.[1,6,8] Weight-average molecular weight M_w was determined by dilute solution light scattering, polydispersity ($M_w/M_n < 1.07$) by size-exclusion chromatography, completeness of saturation by NMR and FTIR, chemical microstructure and sequencing by NMR, and deuteration level by density measurements.[6] The number of monomeric units per chain N and the fractional deuteration of the labeled versions f_D are listed in Table 1. All samples are atactic, and they are noncrystalline at room temperature and above except the "ethylene-rich" saturated polybutadienes which have final melting temperatures that range from 42 °C for H38 to 113 °C for H08.

The SANS measurements were made at the NIST Cold Neutron Research Facility in Gaithersburg, MD. Data in the single-phase region were obtained at several temperatures (27–200 °C) for a range of scattering vectors ($q = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle and λ the neutron wavelength). Blends consisting of one hydrogenous component and one (partially) deuterated component were used. Specimen preparation, experimental procedures, and data workup are described elsewhere.[6] The interactions are expressed in terms of the Flory–Huggins parameter χ as obtained from SANS. Unless otherwise specified, the values were determined in the concentration mid-range (volume fraction $\phi = 0.50$ of each component), where χ is found to be insensitive to component concentration.[9] Values of $(\chi_{HD})_{apparent}$, nominally the isotopic interaction parameter,[6] were

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Table 1. Characterization of Samples

sample code	degree of polymerization N	fractional deuteration f_D[a]	sample code	degree of polymerization N	fractional deuteration f_D[a]
H78/D78	1290	0.29_6	H25/D25	1720	0.44_2
H66/D66	2030	0.40_6	H17/D17	2200	0.37_2
H52/D52	1510	0.34_4	H08/D08	1180	0.43_5
H38/D38	1830	0.37_9	HPEB/DPEB	550	0.26_5
H35/D35	1390	0.43_4	HPEP/DPEP	855	0.47_0
H32/D32	1720	0.34_6	HhhPP/DhhPP	320	0.33_1

[a] Obtained from density measurements at 23 °C, as described in ref 6. Samples H08, H17, H25, H32, and H38 and their deuterated counterparts are partially crystalline at 23 °C; the others are amorphous.

Table 2. Isotopic Interaction Parameters from Matched Pair Mixtures

	χ_{HD}[a] × 10^4					
T (°C)	H35/ D35	D32/ H32	H25/ D25	H17/ D17	H08/ D08	HhhPP/ DhhPP
27						5.7
52	(C,C)[b]	(C,C)[b]	(C,C)[b]	(C,C)[b]		4.4
83	1.6	2.0	3.0			2.1
89				0.0	(C,C)[b]	
118				0.8	3.8	
121	0.9	1.6	2.7			0.1
142				−1.2	3.3	
167	0.6	1.2	2.3	−1.6	2.9	−1.4

[a] The uncertainties in these values are rather large, ±1.5 × 10^{-4}. They should not be regarded as accurate measures of isotopic interaction strength.[1,6] [b] (C,C) indicates both components are partially crystalline at this temperature and below.

obtained from the scattering of matched pair mixtures ($\phi_H = \phi_D = 0.50$). Those not reported elsewhere[1,6] are given in Table 2.

The form factor $P(q)$ was also obtained for each component from matched pair scattering.[6] The structure factor for each blend, $S(q)$, was used with the form factors of its components, $P_1(q)$ and $P_2(q)$, to extract the interaction parameter:[6]

$$\chi = \lim_{q \to 0} \frac{v}{2}\left[\frac{1}{v_1 N_1 \phi_1 P_1(q)} + \frac{1}{v_2 N_2 \phi_2 P_2(q)} - \frac{1}{S(q)}\right] \qquad (1)$$

in which v_1 and v_2 are the volumes per monomeric unit at each temperature, $v = (v_1 v_2)^{1/2}$ is the reference volume, and χ is the interaction with respect to that reference volume.[6] The interaction parameters and the changes produced by label switching are shown in parts a and b of Table 3. Supplemental observations on mutual solubility, obtained by light scattering,[6] are given in part c of Table 3.

Results and Discussion

General Considerations. The effects of label switching (parts a and b of Table 3) parallel those reported in the previous study.[1] The values of χ for blends of hydrogenous and deuterated components depend upon which of the two components is deuterated. The difference is fairly small for some blends, e.g., the 66/PEB pair, and even zero within the error bars on χ (approximately ±1.5 × 10^{-4} for label switching alone[6]), e.g., the 66/hhPP and PEB/hhPP pairs. For others they are rather large, e.g., the 38/PEP pair, and in some cases they result in liquid–liquid phase separation with one label arrangement but a single-phase liquid with the other, e.g., D32/H08 and H32/D08 at 167 °C. Moreover, for blends of two saturated polybutadienes, a larger χ is always obtained when the more highly branched component is deuterated, a pattern first noted by Rhee and Crist[2] and also observed in our previous study.[1] The difference, $\Delta\chi = \chi_{hd} - \chi_{dh}$, diminishes slightly with increasing temperature.[1,4] It also seems to be independent of both component concentration[1,4] and the temperature dependence of χ for the blend.[1]

Solubility Parameter Interpretation. Our explanation of the label switching effect[1] is based on the following relationship from regular solution theory:[10,11]

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

where v is the reference volume, k_B is Boltzmann's constant, T is the absolute temperature, and δ_1 and δ_2 are pure component properties, called solubility parameters. Each is defined as the positive square root of the cohesive energy density:

$$\delta = (U_v)^{1/2} \qquad (3)$$

where U_v is the internal energy of vaporization per unit volume of a pure component liquid. The energy change with random mixing of two components is assumed to scale as $[2(U_v)_{12} - (U_v)_1 - (U_v)_2]\phi_1\phi_2$. The positive-definite form of eq 2 then follows from eq 3 and Berthelot's conjecture about the crossterm:[11] $(U_v)_{12} = [(U_v)_1(U_v)_2]^{1/2}$. For nonpolar substances, such as saturated hydrocarbons and their deuterated analogs, U_v depends mainly on induced dipole interactions. Accordingly, one expects a rough proportionality between the cohesive energy density of a nonpolar substance and $(\alpha/v)^2$, where α and v are its molar polarizability and molar volume.[11] Both α and v decrease slightly when C–H bonds are replaced by C–D bonds.[12] However, $\Delta\alpha/\alpha$ (~1.6%) is so much larger than $\Delta v/v$ (~0.2–0.4%), at least in such cases as are known,[12] that we were led to the working hypothesis that U_v, and therefore δ, would always decrease with deuterium substitution in saturated hydrocarbons.[1] Other evidence is also consistent with this generalization.[1,13]

It then follows from eq 2 that the numerical ordering of solubility parameters for hydrogenous components, δ_1 and δ_2, can be inferred from the numerical ordering of interaction parameters for their singly-labeled blends:[1]

$$\delta_2 > \delta_1 \quad \text{if} \quad \chi_{1h,2d} < \chi_{1d,2h} \qquad (4)$$

It also follows that $\chi_{1h,2h}$ (unlabeled blends) and $\chi_{1d,2d}$ (doubly-labeled blends) should lie between the two singly-labeled values and should be nearly equal for comparable labeling levels. The same arguments apply to the critical temperatures for the four blend combinations. For comparable labeling levels:[1]

$$(T_c)_{hd} < (T_c)_{hh} \sim (T_c)_{dd} < (T_c)_{dh} \qquad (5)$$

The latter relationship has been confirmed for three blend systems.[1,4] Differences in T_c as large as 75 °C are observed for the two singly-labeled blends along with intermediate and comparable T_c for the nonlabeled and doubly-labeled versions. A fourth example, shown in Table 4, is the T_c variation among the four labeling combinations of PEP/38 blends, obtained by light scattering.[6]

Other Interpretations. The label-switching effect can be explained in other ways. Crist and Rhee[4] emphasize

Table 3. Interaction Parameters for Blends and Light Scattering Observations on Mutual Solubilities

(a) Interaction Parameters for Blends ($\phi = 0.50$)

	χ[a] × 10^4							
blend	27 °C	51 °C	83 °C	108 °C	121 °C	138 °C	167 °C	inferred ordering of solubility param
H52/D35	(L,C)[b]	13.5	9.3		7.1		5.8	$\delta_{35} > \delta_{52}$
D52/H35	(L,C)		(L,L)[c]		10.6		8.6	
H66/DhhPP	19.9	12.2	6.3		2.4		1.4	$\delta_{66} > \delta_{\text{hhPP}}$(?)[d]
D66/HhhPP	19.5	11.6	5.6		1.8		0.9	
H78/DhhPP	33.2	28.2	23.1	20.4		17.2	14.8	$\delta_{\text{hhPP}} > \delta_{78}$
D78/HhhPP	(L,L)			24.2		21.2	18.8	
H66/DPEB	8.7	6.5	4.8		3.5		3.5	$\delta_{\text{PEB}} > \delta_{66}$(?)
D66/HPEB	9.9	7.5	5.8		4.5		3.7	
H66/DPEP	8.5	8.6	9.2		9.8		9.9	$\delta_{\text{PEP}} > \delta_{66}$
D66/HPEP	13.0	13.1	13.2		13.0		12.6	
H52/DPEP	7.1	4.4	2.8		1.8		1.3	$\delta_{52} > \delta_{\text{PEP}}$
D52/HPEP	5.6	1.4	−1.1		−1.8		−2.6	
HPEB/DhhPP	20.7	17.2	13.9		11.2		10.2	$\delta_{\text{PEB}} > \delta_{\text{hhPP}}$(?)
DPEB/HhhPP	19.4	16.7	13.5		11.1		10.0	
HPEP/DhhPP	15.4	11.5	9.2		8.4		10.0	$\delta_{\text{PEP}} > \delta_{\text{hhPP}}$
DPEP/HhhPP	6.1	2.6	0.4		1.1		3.2	

(b) Interaction Parameters for Blends ($\phi = 0.50$ Unless Specified)

	$\chi \times 10^4$										
	51 °C	83 °C	108 °C	119 °C	121 °C	113 °C	138 °C	143 °C	167 °C	196 °C	inferred ordering of solubility param
H52/DPEB		(L,L)	(20.5, 20.2)[e]				(16.1, 17.0)[e]		(13.5, 14.3)[e]		$\delta_{52} > \delta_{\text{PEB}}$
D52/HPEB		(L,L)	18.4				15.1		12.5		
H38/DPEP	(L,L)[i]	(20.2)[f]	15.0		(12.9)[f]		11.2		8.2 (9.1)[f]		$\delta_{38} > \delta_{\text{PEP}}$
D38/HPEP	(18.2)[f]	(11.2)[f]	6.0 (7.3)[f]				3.4 (4.0)[f]		1.8 (2.8)[f]		
H38/D25		8.8			5.8						$\delta_{25} > \delta_{38}$
D38/H25			11.1		9.9		9.0		7.8		
H38/D17	(C,L)[g,h]		(L,L)[g]			(11.6)[g]			(L,L)		
H35/D17	(C,L)		10.3			7.6			5.0		$\delta_{17} > \delta_{35}$
D35/H17	(C,L)		(L,L)			10.9			7.5		
H32/D08			(C,L)				(L,L)		8.5	6.7	$\delta_{08} > \delta_{32}$
D32/H08									(L,L)		
H25/D08			(C,L)	9.3				7.4	5.9		$\delta_{08} > \delta_{25}$
D25/H08			(C,L)	13.4				10.9	8.0		$\delta_{08} > \delta_{25}$

(c) Light Scattering Observations on Mutual Solubilities for Blends Not Listed in Parts a and b

blend	concentration	result
H52/D32, D52/H38	$\phi_{52} = 0.50$	two phases up to 200 °C (both versions)
H35/D08, D35/H08	$\phi_{08} = 0.50$	two phases up to 200 °C (both versions)
HPEP/D78	$\phi_{78} = 0.15$	two phases up to 200 °C
HPEP/D97B	$\phi_{\text{PEP}} = 0.10$	two phases up to 200 °C ($N_{97\text{B}} = 865$ (6))
HPEB/D38	$\phi_{\text{PEB}} = 0.10, 0.90$	two phases up to 200 °C
DPEB/H88	$\phi_{88} = 0.08$	two phases up to 200 °C ($N_{88} = 1610$ (6))
DhhPP/H52, HhhPP/D52	$\phi_{52} = 0.50$	two phases up to 250 °C (both versions)
HhhPP/D97A	$\phi_{97\text{A}} = 0.90$	two phases up to 200 °C ($N_{97\text{A}} = 1600$ (6))

[a] Uncertainties in χ here and in Table 3b are roughly $\pm 1.5 \times 10^{-4}$ from one blend to another but somewhat smaller for label-switch differences and smaller still for the same blend at different temperatures.[1,6]
[b] (C,L) indicates one component crystallized at this temperature and below.
[c] (L,L) indicates two liquid phases at this temperature and below.
[d] ? means too close to assign ordering with confidence.
[e] $\phi_{\text{H52}} = 0.20, 0.80$; H52/DPEB at $\phi_{\text{H52}} = 0.50$ is two-phase at 109 °C and below.
[f] $\phi_{\text{H38}} = 0.80$; $\phi_{\text{D38}} = 0.80$.
[g] $\phi_{\text{H38}} = 0.75$.
[h] (C,L) indicates one component crystallized at this temperature and below.
[i] (L,L) indicates two liquid phases at this temperature and below.

Table 4. Critical Temperatures for the 38/PEP Blend Systems

blend system	T_c (°C)	blend system	T_c (°C)
H38/DPEP	90 ± 5	D38/DPEP	60 ± 5
H38/HPEP	52 ± 3	D38/HPEP	<40[a]

[a] Unobservable because it lies below the melting transition of 40 °C for D38.

the volume change associated with labeling. Budkowski et al.[5] consider polarizability changes as well but assume the two are correlated, such that Δv alone would be sufficient, for some range of molecular structures, to express the resulting changes in χ with labeling. For hydrogenous components, both interpretations correspond to

$$\chi = K[f(\rho_2) - f(\rho_1)]^2 \tag{6}$$

where $f(\rho)$ is some monotonic function of hydrogenous component density ρ, and K is a labeling-independent constant. With the stipulation that deuterium substitution always changes molecular volume in the same direction, eq 6 predicts a labeling pattern for T_c with all the features of eq 5. It also leads to the equivalent of eq 4, with δ_1 and δ_2 replaced by $f(\rho_1)$ and $f(\rho_2)$. Thus, for example, the original Rhee–Crist observation[2]—χ is always larger for HPB blends when the more branched component is labeled—becomes consistent with the monotonic increase in melt density with HPB branch content[14] if $f(\rho)$ is a monotonically *decreasing* function of density. Equation 6 is also consistent with the miscibility of H66 and HPEB, since their melt densities are almost identical ($\Delta\rho = 0.0001 \pm 0.0003$ at 23 °C). However, it is seriously inconsistent with the observed miscibility of HPEB and HPEP, where the differences in melt densities are significant ($\Delta\rho = 0.0097 \pm 0.0003$). Apparently, the range of structures that eq 6 can accommodate is rather limited.

For that reason we prefer the solubility parameter interpretation, which, at the simplest level, supposes only that there is *some* physical quantity δ for each pure component that uniquely defines, through eq 2, its thermodynamic interactions with other components. That aspect at least, which does not depend on the validity of eq 3 at all, can be tested for internal consistency by methods already established for solutions of small molecules.[11] In addition, however, the cohesive energy can be estimated, through a series of well-defined approximations, from *PVT* properties of the pure component liquid.[11] This provides a second route to solubility parameter differences, through eq 3, and thus the possibility for separate tests of internal consistency. We focus on the qualitative features below and examine elsewhere the question of numerical uniqueness of assignments[15] and the comparison with *PVT* measurements.[15,16]

Ordering Consistency. We have used eq 4 to infer the ordering of δ for component pairs, shown in the last column of parts a and b of Table 3. The ordering is independent of temperature in all cases. Thus, although the interaction parameters themselves remain nearly constant or increase with decreasing temperature, depending on the pair, the sign of $\chi_{\mathrm{hd}} - \chi_{\mathrm{dh}}$ for any pair never changes. The data on label switching and mutual solubility (results in ref 1 as well parts a–c of Table 3) lead to the following ordering of solubility parameters for hydrogenous components.

(a) The solubility parameter for HPB decreases with increasing branch content across the entire series, from the largest value for H08 to the smallest for H97. As noted previously,[1] that trend is consistent with the group contribution principle as applied to solubility parameter estimation, based on recommended assignments for polymeric $-CH_3$, $-CH_2-$, and $\geqslant CH$ groups.[17] We have assumed that the trend continues on to H00 (linear polyethylene) in analyzing the SANS data for blends of linear polyethylene fractions with several "ethylene-rich" DPB's, as described in the appendix.

(b) The solubility parameter of HPEB is bounded by the values for H52 (Table 3b) and H78,[1] with the ordering

$$\delta_{52} > \delta_{\mathrm{PEB}} > \delta_{78}$$

This ordering is consistent with the observations that HPEB/D38 and HPEB/D88 blends, even far off-critical, remain two-phase up to at least 200 °C (Table 3c) and that χ for PEB/66 blends (Table 3a) is fairly small, at least at high temperatures. In fact, H66 and HPEB have nearly identical ethyl branch frequencies and differ only in their sequencing (statistical for H66, regular in HPEB). Thus, in this case at least, sequencing has relatively little effect on δ, a result also consistent with the group contribution principle.[17]

(c) The solubility parameter for HPEP is bounded by the values for H38 and H66, with the ordering

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

This ordering is consistent with the observations that HPEP/D78 and HPEP/D97 blends, even far off-critical, remain two-phase up to at least 200 °C (Table 3c), that even off-critical PEP/H38 blends are two-phase below ~85 °C, and that χ for PEP/52 blends (Table 3a) is fairly small, at least at high temperatures. The latter result is contrary to the group contribution principle, since the relative concentrations of $-CH_3$, $-CH_2-$, and $\geqslant CH$ groups are quite different for HPEP and H52. Even arbitrary reassignments for $-CH_3$, $-CH_2-$, and $\geqslant CH$ groups cannot reconcile the combination of this result with the HPB ordering in (a).

(d) The solubility parameter for HPEP is larger than that for HPEB.[1] This is consistent with the ordering patterns in (a), (b), and (c), but it is clearly inconsistent with the group contribution principle. Thus, HPEP has higher concentrations of $-CH_3$ and $\geqslant CH$ groups than HPEB and therefore should have a lower solubility parameter, at least according to the current assignments.[17] Again, changing those assignments to force agreement with the HPEB–HPEP ordering causes an inconsistency with the HPB ordering in (a).

(e) The solubility parameters for HhhPP is bounded by the values for HPEP and H78, with the ordering

$$\delta_{\mathrm{PEP}} > \delta_{\mathrm{hhPP}} > \delta_{78}$$

This is consistent with the observation that HhhPP/D97A blends, even ones far off-critical, are two-phase up to at least 200 °C (Table 3c). When combined with $\delta_{66} \sim \delta_{\mathrm{PEB}}$ from (b), the miscibilities of hhPP/66 and hhPP/PEB blends (Table 3a) are also consistent. However, the combination of immiscibility for hhPP/52 blends up to at least 250 °C (Table 3c) and miscibility for hhPP/PEP blends down at least to 27 °C (Table 3a) is totally inconsistent with (c), which shows $\delta_{52} \sim \delta_{\mathrm{PEP}}$ with several cross-checks. The blends of hhPP with either 52 or PEP (or both) clearly violate the solubility parameter principle itself, and of course the group contribution principle as well.

Thus, although frequently inconsistent with the group contribution principle, the assignments of solubility parameter ordering for HPEB, HPEP, and the HPB series are at least internally consistent. The numerical uniqueness of solubility parameter assignments for those polymers, a much more stringent test of consistency, is examined elsewhere.[15] The qualitative violation of the solubility parameter principle by hhPP blends is interesting and might indicate changes in local liquid packing with mixing.[18–21] Such departures could also arise from violations of the Berthelot hypothesis, the very basis of eq 2 and apparently seldom obeyed in small molecule mixtures.[22] On the other hand, to produce observable effects in monomeric solutions, the local interactions must be much stronger ($\chi \sim 1$ near T_c), so volume changes and nonrandom mixing might play more prominent roles in those cases. At this point it is encouraging to find even a modest range of polymeric structures which give results that are qualitatively consistent with eq 2.

We also note that eq 2 can accommodate only positive values of χ, yet we find negative values for D52/HPEP blends at some temperatures (Table 3a). Negative values of χ are not necessarily inconsistent with the assumption of purely induced dipole interactions,[23] and in this case they are small, comparable in magnitude to $(\chi_{\mathrm{HD}})_{\mathrm{apparent}}$ in the matched pair mixtures[1,6] (Table 2). The uncertainties are large in both cases ($\pm 1.5 \times 10^{-4}$), and we simply dismiss the negative χ values for now.

Temperature Dependence. In addition to the qualitative observations, there are some interesting parallels in the temperature dependence of χ when PEP and PEB are blended with members of the HPB series. Figure 1 shows χ_{hh}, estimated as $(\chi_{\mathrm{hd}} + \chi_{\mathrm{dh}})/2$,[1] as a function of temperature for blends of HPEP with H38, H52, and H66 ($\phi = 0.5$). Figure 2 is a similar plot for blends of HPEB with H52, H66, and H78. The values are relatively small for HPEP/H52 and HPEB/H66 blends, as pointed out in (b) and (c) above, and their changes with temperature

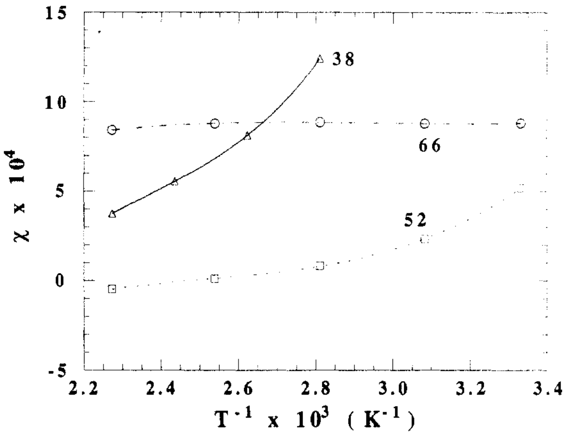

Figure 1. Interaction parameter vs temperature for blends of HPEP with H38, H52, and H66. The lines are drawn as guides to the eye (HPEP/H38 (△); HPEP/H52 (□); HPEP/H66 (○); all at $\phi_{\mathrm{HPEP}} = 0.5$).

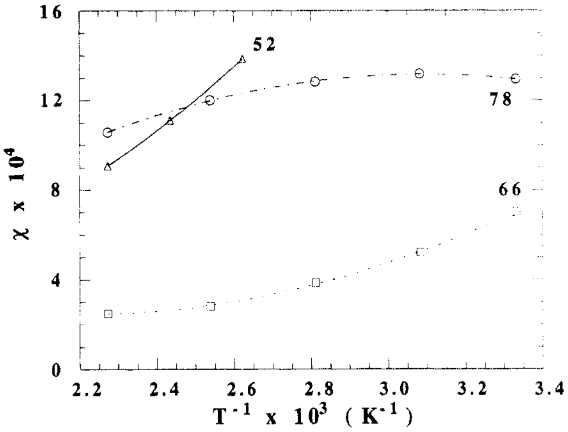

Figure 2. Interaction parameter vs temperature for blends of HPEB with H52, H66, and H78. The lines are drawn as guides to the eye (HPEB/H52 (△); HPEB/H66 (□); HPEB/H78 (○); all at $\phi_{\mathrm{HPEB}} = 0.50$).

(relatively flat at the higher temperatures but then rising as the temperature is decreased) are similar to those for HPEP/HPEB blends.[1] For HPEP/H38 and HPEB/H52 blends the variation in χ with temperature is much more pronounced, while for PEP/H66 and PEB/H78 blends the values of χ are large and practically independent of temperature. Thus, in solubility parameter language, the temperature dependence of χ for blends of HPEP and HPEB with HPB components is similar when compared at similar values of $\Delta\delta$, either $\delta_{\mathrm{HPEP}} - \delta_{\mathrm{HPB}}$ or $\delta_{\mathrm{HPEB}} - \delta_{\mathrm{HPB}}$. When $|\Delta\delta|$ is relatively small (HPEP/H52 and HPEB/H66), the form of $\chi(T)$ closely resembles that for HPEP/HPEB blends. When $\Delta\delta$ is larger but negative (HPEP/H38 and HPEB/H52), χ is a strongly increasing function of temperature. When $\Delta\delta$ is larger but positive (HPEP/H66 and HPEB/H78), χ is essentially independent of temperature.

Such asymmetry appears contrary, at least in spirit, to the solubility parameter idea, since eq 2 certainly requires that the sign of $\Delta\delta$ be irrelevant. On the other hand, the solubility parameters themselves may be temperature dependent,[11] and $\mathrm{d}\delta/\mathrm{d}T$ could differ enough among HPEP, HPEB, and HPB to account for unusual χ vs T behavior as well as the apparent $\Delta\delta$ asymmetries. This possibility will be examined in more detail in the forthcoming papers on quantitative consistency and *PVT* properties.[15,16]

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Table 5. Characterization of Linear Polyethylene Fractions

polyethylene fraction	N	T_m (°C)
PE-1 (SRM-1482)	232	131.4
PE-2 (SRM-1483)	570	132.9
PE-3 (SRM-1484)	2140	136.2

Table 6. Interaction Parameters for PE/DPB Blends

		$\chi \times 10^4$		
blend	ϕ_{PE}	148 °C	167 °C	196 °C
PE-1/D32	0.50	$31._8$	$29._7$	$25._1$
PE-2/D25	0.50	$20._9$	$18._4$	$15._2$
PE-3/D25	0.85	(L,L)[a]	(L,L)[a]	$14._3$
PE-3/D17	0.50	(L,L)[a]	(L,L)[a]	7.3_6

[a] (L,L) means two liquid phases.

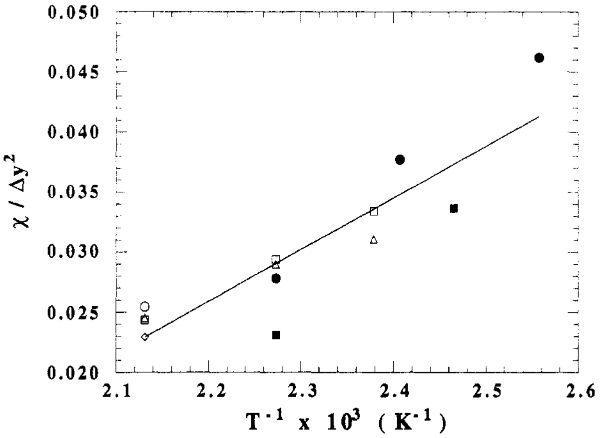

Figure 3. Reduced interaction parameter $\chi/(y_2 - y_1)^2$ vs temperature for PE/DPB and HPB/DPB blends. The pairs represented are PE-1/D32 (◇), PE-2/D25 (□), PE-3/D17 (○), PE-3/D25 (△), H08/D25 (●), and H17/D35 (■).

Appendix. Blends of Linear Polyethylene with Fractions with Saturated Polybutadienes

SANS data were obtained for blends of D17, D25, and D32 with fractions of linear polyethylene (PE). The latter are standard reference materials available from the National Institute of Standards and Technology (SRM-1482, SRM-1483, and SRM-1484). Their values of N (defined for consistency with the HPB's as the number of C_4 units per chain) and melting temperatures[24] are given in Table 5. The resulting values of χ for PE/DPB blends are given in Table 6. Since label switching was not possible for these blends, we estimated χ_{hh} by another method, based on the copolymer equation[25] and data for HPB/DPB blends in the same composition range (Table 3b).

According to the copolymer equation, at constant reference volume the interaction parameter for binary blends of A_yB_{1-y} random copolymers varies quadratically with the composition difference:

$$\chi(T) = \chi_0(T)(y_2 - y_1)^2 \qquad (1A)$$

For our system, $y_2 - y_1$ is the difference in mole fraction of branched $-C_4$ units, and χ_0 is nominally the interaction parameter for blends of polyethylene and polybutene-1. (Corrections of χ to constant reference volume are negligible here.) This relationship only applies over limited ranges of average composition $\bar{y} = (y_1 + y_2)/2$ for blends of HPB.[16] Figure 3 shows the data for the four PE/DPB blends as well as H08/D25 and H17/D35. (The H25/D38 blend already behaves somewhat differently from the others,[16] and its data are not shown.) The more branched component is deuterated in all six of the blends, so the labeling effect will tend to increase χ in all cases.

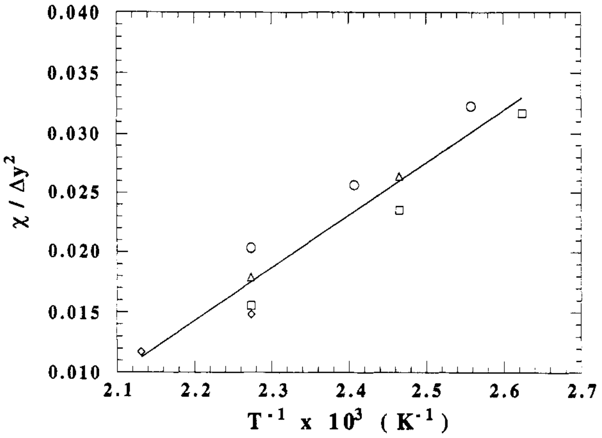

Figure 4. Reduced interaction parameter $\chi/(y_2 - y_1)^2$ vs temperature for DPB/HPB blends. The pairs represented are D08/H25 (○), D08/H32 (△), D17/H35 (□), and D17/H38 (◇).

For this relatively narrow range of ethylene-rich compositions the agreement—within the PE/DPB series, within the HPB/DPB series, and between the two—is fairly good. A similar plot is shown in Figure 4 for the label-switched HPB/DPB blends (deuterium on the less branched component; data for D25/H38 and beyond omitted). The interaction parameters are smaller than those in Figure 3, as expected, but again the agreement within the series is reasonable.

The data in both figures were fitted with least-squares lines, which were then used to estimate interaction parameters for the (hypothetical) label-switched polyethylene blends, and hence the interaction parameters for PE/HPB blends, from $\chi_{hh} = (\chi_{hd} + \chi_{dh})/2$.[1] The homopolymer interaction parameter $\chi_0 = \chi_{hh}/(y_2 - y_1)^2$ is 0.029 at 150 °C, which is near the values reported by Crist and co-workers[26,27] for the same range of PE/HPB compositions.

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