Macromolecules **1993**, *26*, 1137–1143

Effect of Deuterium Substitution on Thermodynamic Interactions in Polymer Blends

William W. Graessley* and Ramanan Krishnamoorti

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544

Nitash P. Balsara,[†] Lewis J. Fetters, David J. Lohse, Donald N. Schulz, and Joseph A. Sissano

Corporate Research Laboratories, Exxon Research & Engineering Company,
Annandale, New Jersey 08801

Received September 21, 1992; Revised Manuscript Received November 12, 1992

ABSTRACT: We have investigated the effect of deuterium labeling on the thermodynamic interactions in blends of labeled and unlabeled saturated hydrocarbon polymers. Small-angle neutron scattering (SANS) was used to evaluate the Flory–Huggins interaction parameter χ at several temperatures and compositions. Light scattering was also used in several cases to confirm the location of phase boundaries. We find that deuterium labeling changes χ relative to the value for hydrogenous components and that the direction of the change depends on which of the two components is labeled. For blends of hydrogenated polybutadienes, χ always increases when the more branched component is labeled, a pattern first noted by Crist and Rhee and also consistent with the expectation that deuterium substitution reduces the cohesive energy density (solubility parameter) of hydrocarbon substances. A solubility parameter formalism is developed by which χ for hydrogenous components can be estimated with reasonable accuracy from SANS data obtained for the two combinations of singly-labeled components. It also provides a method for assigning relative values of the solubility parameter for a wide class of saturated hydrocarbon polymers.

Introduction

Deuterium labeling now plays an essential role in many areas of research on polymers in the liquid state. Various differences in the properties of protons and deuterons are exploited in depth profiling studies of diffusion,[1] interfacial and coexistence phenomena,[2] and surface segregation.[3] Their large difference in neutron scattering length provides the basis for studies of chain dimensions,[4] local chain dynamics,[5] surface structure,[6] and thermodynamic interactions.[7] The aim, of course, is to achieve a better understanding of behavior for ordinary, fully protonated systems, and indeed most liquid-state properties are virtually indistinguishable for hydrogenous and deuterated polymers of the same species. On the other hand, the studies themselves involve mixtures of labeled and unlabeled components, and the isotopic contribution to their interactions, although small on the segmental level, can become important when summed over the entire chain.[8,9]

The effects of deuterium substitution are most directly observable near phase boundaries, and in particular near critical points, where the overall interactions are delicately balanced and even small additional contributions can shift the critical temperature significantly. The upper critical solution temperature for blends of oligomeric polystyrene and polybutadiene was increased by about 14 °C when perdeuterated polybutadiene of comparable chain length was used[10] and by about 30 °C when a comparable perdeuterated polystyrene was used.[11] The lower critical solution temperature for blends of polystyrene and poly(vinyl methyl ether) increases by as much as 40 °C when perdeuterated polystyrene is used.[12–15] The Θ temperature is affected by deuterium substitution;[16] Θ for polystyrene in cyclohexane is 35 °C when both components are hydrogenous and 36 °C when both are deuterated, but 40 °C when only the solvent is deuterated and 30 °C when only the polymer is deuterated. Deuteration substitution also affects the critical temperature for small-molecule mixtures.[17,18] The changes are usually smaller, and the behavior is complicated by labile exchange and hydrogen bonding in most of the systems investigated, but where these effects are not too large, such as the methanol–cyclohexane system, the results seem to parallel the Θ temperature behavior. Flory–Huggins interaction parameters in the range of 10^{-3} have been measured for mixtures of hydrogenous and perdeuterated components in several polymer species, and values of this order have been predicted theoretically from differences in the length and polarizability of CH and CD bonds.[9]

We have found sizable isotope effects during the course of investigating thermodynamic interactions in the blends of simple hydrocarbon polymers.[19] The components were prepared by catalytically saturating the double bonds of nearly monodisperse polybutadienes with various vinyl contents, using H_2 in one case to obtain the fully hydrogenous form and D_2 in another to obtain the partially deuterated ($f_D = [D]/([H] + [D]) \sim 0.35$) form. Upper critical solution behavior was observed in all cases. In one instance the critical temperature T_c was changed by ~60 °C when the deuterium label was simply switched from one blend component to the other. Crist and Rhee have also observed such shifts with label swapping[20] in blends of polymers that are similar to ours,[21,22] and they also noted a consistent pattern in the shift direction, depending on the structure of the components. In this paper we report several additional instances of shifts in T_c obtained by small-angle neutron scattering (SANS) and light scattering measurements. We also include some data for blends in which either both components are hydrogenous or both are deuterated. We confirm the Crist–Rhee pattern and offer a tentative explanation, leading to a scheme of correction for the isotopic contribution as well as a method for establishing relative values of the solubility parameters for saturated hydrocarbon polymers.

Experimental Procedures

Polybutadienes were synthesized by anionic polymerization[19,23] in the presence of modifiers (1,2-dipiperidinoethane, tetrameth-

---

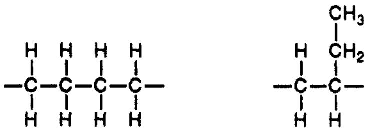
[†] Permanent address: Department of Chemical Engineering, Polytechnic University, Brooklyn NY 11201.

0024-9297/93/2226-1137$04.00/0

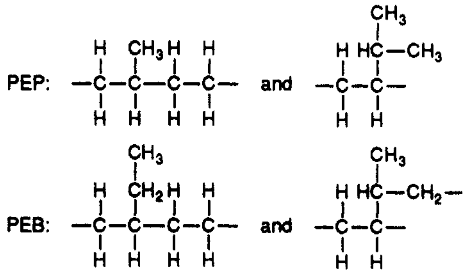
Table I
Characterization of Samples

sample code	degree of polymerization N	fractional deuteration f_D
H97A, D97A	1600	0.34_9
H97B, D97B	865	0.33_6
H88, D88	1610	0.37_0
H78, D78	1290	0.29_6
H66, D66	2030	0.40_6
H52, D52	1510	0.34_4
H38, D38	1830	0.37_9
HPEB, DPEB	550	0.26_5
HPEP, DPEP	855	0.47_0

ylethylenediamine, tetrahydrofuran, and triethylamine) to prepare a series of nearly monodisperse samples representing a range of vinyl contents. An aliquot of each was saturated with H_2 to produce statistical, stereoirregular copolymers of the following linear and branched C_4 units.[19]



Seven saturated polybutadienes, ranging from 38 to 97 mol % of the branched C_4 units, were used in the study. One sample each of polyisoprene and poly(2-ethylbutadiene) was also synthesized anionically, but without modifiers in order to maximize the fraction of 1,4 enchainments, and then saturated with H_2 to produce polymers containing the following chain units.



The structure on the left is the major constituent in each polymer (~93 mol %), corresponding to strictly alternating, stereoirregular copolymers of ethylene with propylene (PEP) and of ethylene with butene-1 (PEB). The minor constituent (~7 mol %) is assumed to be distributed statistically along the backbone.

Separate aliquots of all the polydiene precursors were saturated with D_2 to provide a partially deuterated companion for each of the nine hydrogenated polymers. Apart from deuterium substitution, the fully hydrogenous and partially deuterated versions of each polymer are structural twins,[19] and we refer to them as matched pairs.

According to DSC measurements, samples H38 and D38 are slightly crystalline and melt at 42 °C. The others are amorphous at room temperature and above. Chemical microstructures and sequencing were established by NMR, deuteration content by density measurements, and molecular weights by dilute-solution light scattering.[19] The molecular weight distributions are nearly monodisperse ($\bar{M}_w/\bar{M}_n \leq 1.06$) and unchanged during saturation according to size-exclusion chromatography. Polymerization index N (number of saturated diene units per chain) and fractional substitution f_D in the partially deuterated version are listed in Table I. Percentages of the branched C_4 units in the seven saturated polybutadienes are given in their code names.

SANS measurements were performed on the 8-m instrument at the NIST Cold Neutron Research Facility in Gaithersburg, MD. Sample preparation, experimental procedures, and data workup are described elsewhere.[19] The static structure factor $S(q)$ for each blend was obtained at several temperatures from 27 to 167 °C for a range of scattering vector magnitudes, $0.008 < q$ (Å^{-1}) < 0.075, where $q = (4\pi/\lambda)\sin(\theta/2)$, λ is the neutron wavelength (9.0 Å), and θ is the scattering angle. The light scattering apparatus and procedures used to establish phase boundaries for the blends are also described elsewhere.[19]

Table II
Isotopic Interaction Parameters from Matched Pair Data[a]

sample	$(\chi_{HD})_{apparent} \times 10^4$ 27 °C	52 °C	83 °C	121 °C	167 °C
H97A/D97A	−1.5	−1.9	−2.4	−3.0	−3.7
H97B/D97B	0.6	0.3	−0.1	−0.6	−1.0
H88/D88	1.6	1.2	0.3	−0.8	−1.6
H78/D78	0.4	0.3	−0.6	−0.9	−1.2
H66/D66	2.4	2.0	1.4	1.0	0.5
H52/D52	3.4	2.4	1.8	1.5	0.7
H38/D38	3.8	3.6	3.2	2.6	2.5
HPEB/DPEB	0.9	0.7	−0.3	0.0	0.2
HPEP/DPEP	3.2	2.5	1.9	1.2	0.6

[a] Estimated uncertainty in $(\chi_{HD})_{apparent}$ is $\pm 1.5 \times 10^{-4}$.

Analysis of SANS Data

The structure factors were analyzed in the framework of Flory–Huggins (FH) theory[24] and the random-phase approximation (RPA),[25] leading to the following relationship between $S(q)$ for a two-component polymer blend in the single-phase region and the form factors $P_i(q)$, the number of monomeric units per molecule N_i, the monomeric unit volumes v_i, and the volume fractions ϕ_i of the individual components:

$$\frac{1}{S(q)} = \frac{1}{v_1N_1\phi_1P_1(q)} + \frac{1}{v_2N_2\phi_2P_2(q)} - \frac{2\chi}{v} \qquad (1)$$

where χ is the FH interaction parameter for the blend, and $v \equiv (v_1v_2)^{1/2}$ is a reference volume.

The form factor of each component was obtained from $S(q)$ for an equal volume mixture of its matched pair, for which case eq 1 reduces to

$$\frac{1}{S(q)} = \frac{4}{NP(q)} - 2\chi_{HD} \quad \text{(matched pair)} \qquad (2)$$

where χ_{HD} is the isotopic interaction parameter. The fitting procedure to determine χ_{HD} and $P(q)$ from matched pair data is described elsewhere;[19] the values obtained for χ_{HD} are listed in Table II. Values of χ for the blends, consisting of the hydrogenous version of one component and the deuterated version of another, were then obtained from $S(q)$ by computing the difference function[19]

$$E(q) = \frac{v}{2}\left[\frac{1}{v_1N_1\phi_1P_1(q)} + \frac{1}{v_2N_2\phi_2P_2(q)} - \frac{1}{S(q)}\right] \qquad (3)$$

and extrapolating to obtain $E(0) \equiv \chi$. The extrapolation was always a relatively easy one, as shown by the examples in Figure 1.

We estimate the absolute error in both χ_{HD} and χ to be about $\pm 1.5 \times 10^{-4}$, due mainly to the uncertainties in absolute SANS calibration, molecular weight, and deuteration level.[19] Most values of χ_{HD} are zero within these error bars. Some are larger, however, and all drift downward with increasing temperature. These features, as well as the large negative values for H97A/D97A, are unexpected.[19] For all these reasons we have designated the matched pair interaction coefficients as $(\chi_{HD})_{apparent}$ in Table II. Relative errors should be much smaller than $\pm 1.5 \times 10^{-4}$ among values for the same blend at different temperatures and between values when the labels are switched from one component to the other, since those comparisons are insensitive to calibration and molecular weight errors.

In some cases the spinodal temperature of a blend, T_s, was obtained by light scattering measurements. This was

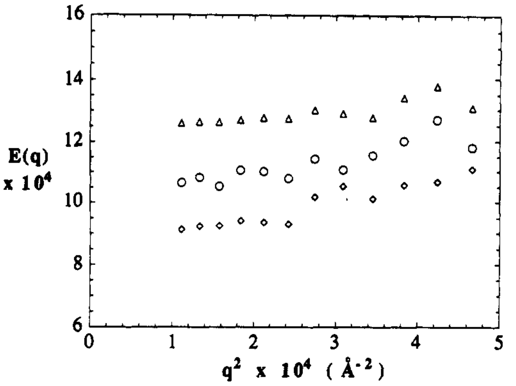


Figure 1. Excess function at low q for the H88/D78 ($\phi = 0.50$) blend. Values at 83 (△), 121 (○), and 167 °C (◇) yield $10^4\chi$ = 11.0, 10.3, and 8.5 when extrapolated to the $q = 0$ intercepts.

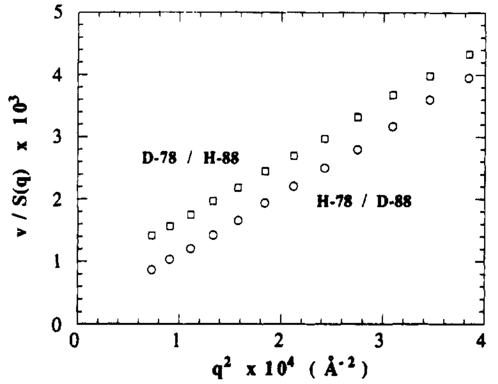


Figure 2. Comparison of structure factors for the H88/D78 and D88/H78 ($\phi = 0.50$) blends at 138 °C.

compared with the SANS estimate of T_s, obtained by extrapolation of the experimental $\chi(T)$ data from midrange compositions ($0.25 \le \phi \le 0.75$) to $\chi(T_s)$:

$$\chi(T_s) = \frac{v}{2}\left[\frac{1}{v_1 N_1 \phi_1} + \frac{1}{v_2 N_2 \phi_2}\right] \qquad (4)$$

Results

The effect of label swapping shows up clearly in $S(q)$ for the blends. Structure factors for the H88/D78 and D88/H78 blends at the same composition and temperature ($\phi = 0.50$, T = 138 °C) are compared as Ornstein–Zernike plots of the low q data in Figure 2. The lines have the same slope, which indicates that chain dimensions are the same in the two blends, but they are displaced vertically from one another, which indicates that the interactions are different.

The temperature dependence of χ for the same two blends is shown in Figure 3. The data for each blend agree well with the conventional form

$$\chi = A/T + B \qquad (5)$$

but χ is larger for the D88/H78 blend by an amount $\Delta\chi \sim 3 \times 10^{-4}$, decreasing slightly with increasing temperature. The phase-separation temperature of the two blends is significantly different, being 68 ± 3 °C for H88/D78 and 133 ± 3 °C for D88/H78 from light scattering determinations. From SANS (eq 5) the values of T_s at $\phi = 0.50$ are 60 and 115 °C, respectively.

Values of χ for the HPEB/DPEP and DPEB/HPEP blends at $\phi = 0.50$ are compared in Figure 4. The temperature dependence of both blends departs considerably from eq 5, yet the difference between HPEB/DPEP and DPEB/HPEP follows the same pattern as the 78/88 blends; $\Delta\chi$ is $\sim 1.5 \times 10^{-4}$ in this case, again with a weak trend toward smaller values at the higher temperatures. The pattern is repeated for the H78/DPEB and D78/HPEB blends, shown for $\phi = 0.50$ in Figure 5. In this case χ is nearly independent of temperature in both, and $\Delta\chi$ ranges from 6.5×10^{-4} at 27 °C to 3.5×10^{-4} at 167 °C. Aside from the magnitude of $\Delta\chi$, which varies from one blend pair to another, the effect of switching labels persists in a similar fashion regardless of the temperature dependence of χ.

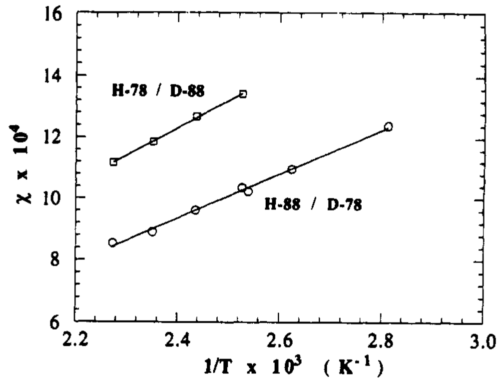


Figure 3. Interaction parameter versus temperature for the H88/D78 and D88/H78 ($\phi = 0.50$) blends.

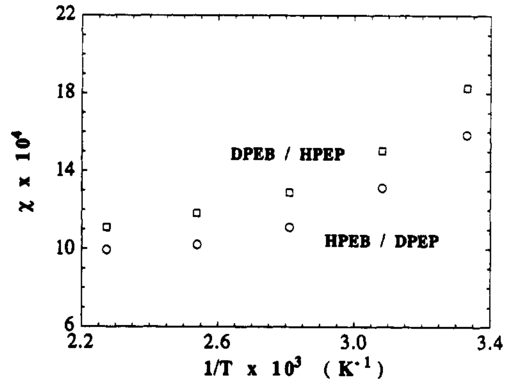


Figure 4. Interaction parameter versus temperature for the HPEB/DEPB and DPEB/HPEP ($\phi = 0.50$) blends.

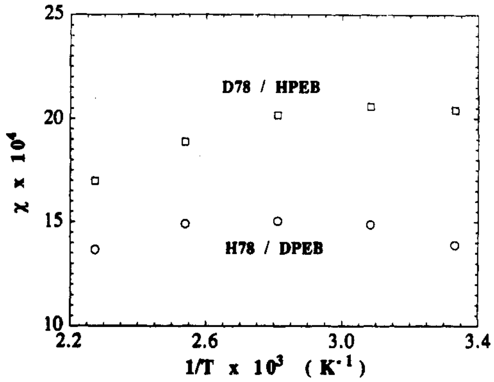


Figure 5. Interaction parameter versus temperature for the H78/DPEB and D78/HPEB ($\phi = 0.50$) blends.

Interaction parameters for the H66/D52 and D66/H52 blends at 167 °C are shown as functions of blend composition in Figure 6. The values for each blend are nearly independent of composition, indicating good agreement with FH theory for $0.1 < \phi < 0.9$, yet χ is consistently larger for D66/H52, $\Delta\chi$ being $\sim 4 \times 10^{-4}$ in this case. From light scattering determinations, the phase-separation temperature at $\phi = 0.50$ is 108 ± 3 °C for H66/D52 and 175 ± 5 °C for D66/H52 (Figure 7a,b). From SANS (eq 5) the values of T_s at $\phi = 0.50$ are 95 and 180 °C, respectively. Again, both SANS and light scattering

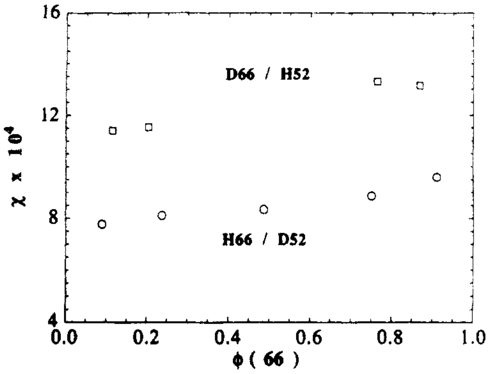


Figure 6. Interaction parameter versus volume fraction of the 66 component for the H66/D52 and D66/H52 blends at 167 °C.

confirm that switching the labels from one component to the other changes the interaction strength.

Interaction parameters obtained at $\phi = 0.50$ and at two representative temperatures, 109 and 167 °C, are listed in Table III for the eight swap comparisons in this study. In all cases the difference in χ that results from switching the labels decreases somewhat with increasing temperature. The magnitude of $\Delta\chi$ ranges rather widely from one blend pair to another, and there is no obvious correlation with the differences in deuteration level of the labeled component (see Table I). Indeed, from Table II, $(\chi_{HD})_{apparent}$ itself also seems uncorrelated with the level of deuteration. Finally, note that, for all six blends of saturated polybutadienes, the interaction parameter is always larger when the more highly branched component carries the labels. This is the pattern found by Crist and Rhee[20] for other blends of saturated polybutadienes, generally in a lower range of branch contents.

Discussion

Several possibilities to account for the label swapping effects were considered. Simple additivity of the isotopic and structural interactions leads directly to $\Delta\chi = \Delta\chi_{HD}$, where $\Delta\chi_{HD}$ denotes the difference in χ_{HD} for the two deuterated components involved. This relationship is clearly incompatible with the values of $\Delta(X_{HD})_{apparent}$ from the matched pair experiments (Table II) and the corresponding values of $\Delta\chi$ in Table III. We also considered the random copolymer approach,[7] which includes cross terms to express the isotopic and structural contributions to the total interaction. Many adjustable parameters are involved, however, so the meaning would be difficult to access. In searching for a simpler explanation, we examined the solubility parameter approach[12,15,16] and found some encouraging results.

From its origins in regular solution theory, the FH interaction parameter can be expressed in terms of δ_1 and δ_2, the solubility parameters of the constituent polymers: [26]

$$\chi = \frac{v}{RT}(\delta_2 - \delta_1)^2 \tag{6}$$

where v is the reference volume, and δ_1 and δ_2 are defined as the positive square roots of the cohesive energy density. The reference volume $v = (v_1 v_2)^{1/2}$ is essentially unchanged by a label switch (v_1 and v_2 change by less than 0.2% with labeling[19]), so χ at each temperature is governed by $(\delta_2 - \delta_1)^2$ alone. The behavior of χ for blends of hydrogenous and deuterated species thus depends on how δ changes with deuterium substitution and chemical structure of the individual components.

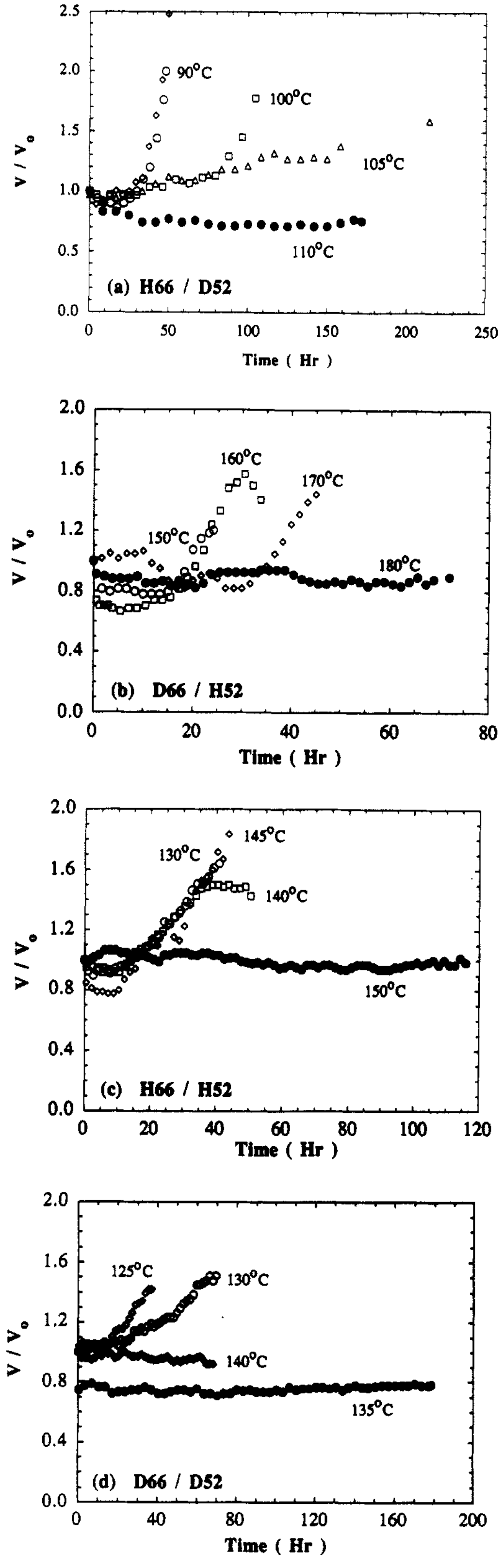


Figure 7. Normalized light scattering intensity versus time after quenching to various temperatures for 66/52 ($\phi = 0.50$) blends with four labeling combinations: (a) H66/D52, spinodal temperature 108 ± 3 °C; (b) D66/H52, spinodal temperature 175 ± 5 °C; (c) H66/H52, spinodal temperature 148 ± 3 °C; (d) D66/D52, spinodal temperature 133 ± 3 °C.

Suppose deuterium labeling always changes the solubility parameter of a polymer in the same direction. That seems reasonable at least for hydrocarbon polymers where only dispersive interactions are involved. Both C–H bond length and bond polarizability are reduced by deuterium

Table III
Interaction Parameters for Blends ($\phi = 0.50$)

sample	$\chi \times 10^4$ at 167 °C	$\chi \times 10^4$ at 109 °C	temp range (°C)
H97A/D88	6.7	8.9	52–170
D97A/H88	6.8	9.3	52–170
H97B/D88	5.4	8.2	27–170
D97B/H88	5.9	8.7	27–170
H88/D78	8.5	11.0	84–170
D88/H78	11.1	14.3[a]	125–170
H78/D66	8.5	10.6	84–170
D78/H66	9.7	11.9	110–170
H66/D52	8.4	11.7	110–170
D66/H52	12.4[b]	16.1[b]	140–170
H52/D38	5.1	7.1	52–170
D52/H38	7.6	10.1	110–170
HPEB/DPEP	9.9	10.5	27–170
DPEB/HPEP	11.1	12.2	27–170
H78/DPEB	13.7	15.0	27–170
D78/HPEB	17.0	19.3	27–170

[a] Extrapolated from higher temperatures. [b] Interpolated from data for blends at $\phi = 0.25$ and 0.75.

substitution,[9,27] and the relative magnitudes of those changes suggest that δ would in fact decrease with labeling. Reduction in δ with deuterium substitution is also consistent with the observation that deuterated species migrate to free surfaces in isotopic mixtures of similar chain lengths.[3]

Consider now a set of saturated hydrocarbon polymers with systematically varying chemical microstructure, such as the hydrogenated polybutadiene (HPB) series. It seems reasonable to expect that δ would vary monotonically with the microstructure, specified for example in the HPB series by the fraction of branched C_4 units in the chains. There are no data to support that supposition directly, but group contribution methods for estimating δ[28] are at least consistent with it. Moreover, solubility parameter estimates for the two end points of the HPB sequence, polyethylene and polybutene-1, based on the group assignments in ref 28, suggest that δ would decrease with increasing branched C_4 content. That inference is also supported by the reduction in δ with branching in small-molecule homologs.[29] It is also consistent with the decrease in P^*, the characteristic pressure from P–V–T measurements, with branching for saturated hydrocarbon polymers.[30]

Now consider the effect of labeling for blends of two members of the HPB series, denoting the more branched member as component 1. According to the arguments above, δ_2 would be larger than δ_1 when both components are hydrogenous. Since δ is reduced by deuterium substitution, the difference $\delta_2 - \delta_1$ would increase if the more branched component 1 were labeled with deuterium. The difference would decrease, however, if the labels were placed instead on the less branched component 2. Then, from eq 6, the observed interaction parameters for blends of saturated polybutadiene should always be larger when the more highly branched component is deuterated, which is the Crist–Rhee pattern that was discussed earlier.

This same argument about the effects of deuterium substitution should apply to any binary liquid whose phase behavior is dominated by dispersive interactions. The results are summarized by the following two rules on the direction of the effect and bracketing of values. First, with the unlabeled system as reference, both $\chi(T)$ and T_c increase when the component with the lower solubility parameter (cohesive energy density) is labeled. Second, both $\chi(T)$ and T_c decrease when the labeling is switched to the other component, and the values for the unlabeled and doubly-labeled systems lie between the two singly-labeled extremes. The Θ temperature for polystyrene in cyclohexane[16] obeys both rules: Θ increases when the component with the lower solubility parameter (cyclohexane) is labeled, and Θ_{hh} and Θ_{dd} lie between Θ_{hd} and Θ_{dh}. The cyclohexane–methanol system[17] does likewise, although in this case nondispersive interactions may also play some role.[18] The only counterexample we have found is the oligomeric polystyrene–polybutadiene system where labeling of either component appears to increase T_c.[10,11]

As discussed above the HPB blends obey the directional rule. To test the bracketing rule, phase-separation temperature was determined by light scattering measurements for H66/H52 ($\phi = 0.50$), a blend of two hydrogenous components (Figure 7c), and for D66/D52 ($\phi = 0.50$), a blend of two deuterated components (Figure 7d). Those values, 148 ± 3 and 133 ± 3 °C, respectively, fall between the results for H66/D52 of 108 ± 3 °C (Figure 7a) and for D66/H52 of 175 ± 5 °C (Figure 7b), as required by the solubility parameter argument. It thus appears that labeling effects in the HPB blends are consistent with the solubility parameter arguments.

Interrelations between χ_{hh} when neither of the blend components is labeled, χ_{dh} when the more branched component 1 is labeled, χ_{hd} when the less branched component 2 is labeled, and χ_{dd} when both are labeled follow directly from adopting the solubility parameter approach (see the Appendix):

$$\chi_{dh}^{1/2} = \chi_{hh}^{1/2} + \chi_{HD1}^{1/2} \tag{7}$$

$$\chi_{hd}^{1/2} = \chi_{hh}^{1/2} - \chi_{HD2}^{1/2} \tag{8}$$

$$\chi_{dd}^{1/2} = \chi_{hh}^{1/2} + \chi_{HD1}^{1/2} - \chi_{HD2}^{1/2} \tag{9}$$

in which χ_{HD1} and χ_{HD2} are the labeling corrections, nominally the matched pair interaction parameters for the two components. The difference between the interaction parameters obtained in swap experiments is thus related to the isotopic contributions by

$$\chi_{dh}^{1/2} - \chi_{hd}^{1/2} = \chi_{HD1}^{1/2} + \chi_{HD2}^{1/2} \tag{10}$$

When the effect of labeling is the same for both components ($\chi_{HD1} = \chi_{HD2}$), the equations simplify to

$$\chi_{hh} = [(\chi_{dh}^{1/2} + \chi_{hd}^{1/2})/2]^2 \tag{11}$$

$$\chi_{dd} = \chi_{hh} \tag{12}$$

We believe that eq 11 is adequate for estimating χ_{hh}, since the deuteration levels are not greatly different among the various components. Calculations using the values of χ_{dh} and χ_{hd} in Table III show that eq 11 can be replaced, with negligible error, by a simple average

$$\chi_{hh} = (\chi_{dh} + \chi_{hd})/2 \tag{13}$$

Estimates of the critical temperature for unlabeled components can also be made, but the averaging depends on how the temperature dependence of χ is changed. Thus, for example, if only the parameter B in eq 5 is affected by labeling,

$$\left(\frac{1}{T_c}\right)_{hh} = \left(\frac{1}{T_c}\right)_{dd} = \frac{1}{2}\left[\left(\frac{1}{T_c}\right)_{hd} + \left(\frac{1}{T_c}\right)_{dh}\right] \tag{14}$$

while if only A is affected,

$$(T_c)_{hh} = (T_c)_{dd} = \frac{(T_c)_{dh} + (T_c)_{hd}}{2} \qquad (15)$$

Considering the other approximations, the simple average is certainly adequate.

Solubility parameter theory is applicable only to systems having positive interaction parameters. That is certainly true for the blends and, within the error bars except for H97A/D97A, to $(\chi_{HD})_{apparent}$ from the matched pair experiments. On the other hand, there is some inconsistency in magnitudes between $(\chi_{HD})_{apparent}$ and the values of χ_{HD} required to explain the observed $\Delta\chi = \chi_{dh} - \chi_{hd}$ for the blends. Consider the example of $\chi_{dh} = 16.1 \times 10^{-4}$ and $\chi_{hd} = 11.7 \times 10^{-4}$ (D66/H52 and H66/D52 blends at 109 °C, Table III). Equation 10 requires $\chi_{HD1}^{1/2} + \chi_{HD2}^{1/2} = 5.9 \times 10^{-3}$, and taking $\chi_{HD1} = \chi_{HD2}$ for estimation purposes, that gives $\chi_{HD} \sim 10^{-5}$. This value is at least an order of magnitude smaller than $(\chi_{HD})_{apparent} \sim 10^{-4}$ obtained for the H52/D52 and H66/D66 match pairs. Similar and even much larger discrepancies in the swapped label–matched pair comparisons are found for the other blends. Taken in isolation, those results are not particularly disturbing because the experimental errors in $(\chi_{HD})_{apparent}$, $\sim 1.5 \times 10^{-4}$, would mask such small χ_{HD} values. However, the χ_{HD} magnitudes required to rationalize the swapped label results ($\leq 10^{-5}$) are also much smaller than estimates for our samples based on SANS data for mixtures of perdeuterated and hydrogenous samples[9] when adjusted for partial deuteration:[31] $\chi_{HD} \sim 2 \times 10^{-4}$. This inconsistency may reflect some fundamental flaw in the solubility parameter approach, or our use of it, but it is at least conceivable that the effects of deuterium substitution are somehow diminished when competing with the much stronger interaction strengths that result from differences in chemical microstructure.

Solubility parameter theory is based on the theory of dispersive (induced-dipole–induced-dipole) interactions and thus applies, in principle at least, only to the enthalpic part of χ. Strazielle and Benoit[16] apply the isotopic correction only to $\chi - \chi_s$, where χ_s is the entropic part and which they show is not changed by deuteration, and then add χ_s back into the result. There is a significant entropic component in χ for HPB blends,[19] so for consistency eqs 7–9 should be applied in the same way. However, resolving χ into its components is rather uncertain, so we have omitted that refinement.

There is an interesting and potentially useful byproduct of these label-switching effects. To the extent that the solubility parameter formulation is applicable and the reduction of the solubility parameter by deuterium substitution is universal, the effect itself provides a method for assigning solubility parameters to polymers, relative to some reference species, from measurements of χ. Values of χ_{dh} and χ_{hd} for a blend can of course be used to estimate, or at least bracket, χ_{hh} through eq 13 and therefore obtain $(\delta_2 - \delta_1)^2$ for hydrogenous components from eq 6 in the usual way. In addition, however, they provide the sign of $\delta_2 - \delta_1$, based on the rule that the larger of χ_{dh} and χ_{hd} is obtained when the component of the lower solubility parameter is labeled. Thus, for example, δ for PEP must be larger than δ for PEB because χ for that pair is larger when PEB is labeled (Table III). Likewise, δ for PEB must be larger than δ for HPB-78 because χ is larger when HPB-78 is labeled. Self-consistency of the numerical assignments can be tested with "redundant" bridges, e.g., by data on H78/DPEP and its swap in the examples above. The ordering should also be consistent with cohesive energy densities as inferred from P–V–T measurements.[30] In a later publication we will report the results obtained by these assignment procedures for a wide range of saturated hydrocarbon polymers.

Conclusions

We have shown not only that the thermodynamic interactions in polymer blends can change significantly when one of the components is labeled with deuterium but that the direction of that change depends on which of the two components is labeled. From SANS measurements on the eight blends of saturated hydrocarbons considered here, the differences in FH interaction parameter χ that results from label switching range up to 6×10^{-4} and produce differences in critical temperature T_c as large as 70 °C. When neither component is labeled or when both are labeled, T_c lies between these singly-labeled extremes. The magnitude of these differences changes rather unpredictably from one blend to another, but the effect of choice in the labeled component, whether it increases or decreases T_c relative to the nonlabeled value, varies systematically within a homologous series of blends. These observations are shown to be consistent with a simple theory based on solubility parameter arguments. It appears that the thermodynamic interactions in blends of purely hydrogenous components can be estimated reasonably well by a simple averaging of the results for a blend with one component labeled and another with the labeling switched. The direction of the change produced by such single-component labeling indicates which component has the lower solubility parameter, a result which should prove useful in establishing a rank ordering of values for hydrocarbon polymers.

Added in Proof: Recently, Rhee and Crist[32] and Budkowski et al. have presented explanations for the label-switching effect which parallel the treatment presented here.

Acknowledgment. We are grateful to Buckley Crist of Northwestern University for extensive discussions of the labeling effect and to the National Science Foundation (Grant DMR89-05187) for support of W.W.G. and R.K.

Appendix. Effect of Deuteration on Solubility Parameters

From eq 6, the difference in blend component solubility parameters is given by

$$\delta_2 - \delta_1 = \pm(\chi RT/v)^{1/2} \qquad (A1)$$

where the positive root applied if $\delta_2 > \delta_1$. The effect of deuterium substitution can be expressed as

$$\delta_1(h) - \delta_1(d) = \Delta_1 \qquad (A2)$$

$$\delta_2(h) - \delta_2(d) = \Delta_2 \qquad (A3)$$

where the Δ_i can depend on the chemical structure of component i as well as the amount and location of the substitution. We assume that the replacement of hydrogen by deuterium always reduces the solubility parameter, so the values of Δ_i are positive.

From eqs A2 and A3, the solubility parameter differences for the four labeling combinations of the blend—hh, dh, hd, and dd—are given by hh: $$\delta_2(h) - \delta_1(h) = \Lambda_0 \qquad (A4)$$

dh: $$\delta_2(h) - \delta_1(d) = \Lambda_0 + \Delta_1 \qquad (A5)$$

hd: $$\delta_2(d) - \delta_1(h) = \Lambda_0 - \Delta_2 \qquad (A6)$$

dd: $$\delta_2(d) - \delta_1(d) = \Lambda_0 + \Delta_1 - \Delta_2 \qquad (A7)$$

where Λ_0 is the solubility parameter difference for unlabeled components, as defined by eq A4. Equations 7–9 of the text, which apply only if Λ_0 is positive and larger than the Δ_i, follow directly from eq A1, applied to eqs A2 and A3 to obtain the isotopic corrections $\chi_{HD1}{}^{1/2}$ and $\chi_{HD2}{}^{1/2}$ and to eqs A4–A7 to obtain $\chi_{hh}{}^{1/2}$, $\chi_{dh}{}^{1/2}$, $\chi_{hd}{}^{1/2}$, and $\chi_{dd}{}^{1/2}$. We ignore the small differences in reference volume v among the four labeling combinations. If Λ_0 is negative, the signs on $\chi_{HD1}{}^{1/2}$ and $\chi_{HD2}{}^{1/2}$ are reversed. In either case, of course, χ increases relative to χ_{hh} when the component having the smaller solubility parameter is labeled.

References and Notes

(1) Green, P. F.; Kramer, E. J. *Macromolecules* **1986**, *19*, 1108.
(2) Budkowski, A.; Steiner, U.; Klein, J.; Schatz, G. *Europhys. Lett.* **1992**, *18*, 705.
(3) Zhao, X.; Zhao, W.; Sokolov, J.; Rafailovich, M. H.; Schwarz, S. A.; Wilkins, B. D.; Jones, R. A. L.; Kramer, E. J. *Macromolecules* **1991**, *24*, 5991.
(4) Zirkel, A.; Richter, D.; Pyckhout-Hintzer, W.; Fetters, L. J. *Macromolecules* **1992**, *25*, 954.
(5) Richter, D.; Farago, B.; Fetters, L. J.; Huang, J. S.; Ewen, B.; Lartigue, C. *Phys. Rev. Lett.* **1990**, *64*, 1389.
(6) Russell, T. P.; Karim, A.; Mansour, A.; Felcher, G. P. *Macromolecules* **1988**, *21*, 1890.
(7) Sakurai, S.; Hasegawa, H.; Hashimoto, T.; Hargis, I. G.; Aggarwal, S. L.; Han, C. C. *Macromolecules* **1990**, *23*, 451.
(8) Buckingham, A. D.; Hentschel, H. G. E. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 853.
(9) Bates, F. S. *J. Appl. Cryst.* **1988**, *21*, 681. Bates, F. S.; Fetters, L. J.; Wignall, G. D. *Macromolecules* **1988**, *21*, 1086.
(10) Atkin, E. L.; Kleintjens, L. A.; Koningsveld, R.; Fetters, L. J. *Makromol. Chem.* **1984**, *185*, 377.
(11) Higgins, J. S. Private communication.
(12) Yang, H.; Hadziioannou, G.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 159.
(13) Yang, H.; Shibayama, M.; Stein, R. S.; Shimizu, N.; Hashimoto, T. *Macromolecules* **1986**, *19*, 1667.
(14) Ben Cheikh Larbi, F.; LeLoup, S.; Halary, J. L.; Monnerie, L. *Polym. Commun.* **1986**, *27*, 23.
(15) Lin, J.-L.; Roe, R.-J. *Macromolecules* **1987**, *20*, 2168.
(16) Strazielle, C.; Benoit, H. *Macromolecules* **1975**, *8*, 203.
(17) Fenby, D. V.; Kooner, Z. S.; Khurma, J. R. *Fluid Phase Equilib.* 1981, *7*, 327.
(18) Singh, R. R.; Van Hook, W. A. *J. Chem. Phys.* **1987**, *87*, 6097.
(19) Balsara, N. P.; Fetters, L. J.; Hadjichristidis, N.; Lohse, D. J.; Han, C. C.; Graessley, W. W.; Krishnamoorti, R. *Macromolecules* **1992**, *25*, 6137.
(20) Rhee, J.; Crist, B. *ACS-PSME Prep.* **1992**, *67*, 209.
(21) Nicholson, J. C.; Finerman, T. M.; Crist, B. *Polymer* **1990**, *31*, 2287.
(22) Rhee, J.; Crist, B. *Macromolecules* **1991**, *24*, 5663.
(23) Lohse, D. J.; Schulz, D. N.; Sissano, J. A.; Balsara, N. P.; Graessley, W. W.; Krishnamoorti, R. Manuscript in preparation.
(24) Scott, R. L.; Magat, M. *J. Chem. Phys.* **1945**, *13*, 172 and references therein.
(25) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(26) Olabisi, O.; Robeson, L. M.; Shaw, M. J. *Polymer–Polymer Miscibility*; Academic Press: New York, 1979.
(27) Rabinovich, I. B.; Tsvetkov, V. G. *Russ. J. Phys. Chem.* **1971**, *45*, 458, as summarized on pp 335–6 of ref 17.
(28) Coleman, M. M.; Serman, C. J.; Bhagwagar, D. E.; Painter, P. C. *Polymer* **1990**, *31*, 1187.
(29) Barton, A. F. M. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press: Boca Raton, FL, 1983.
(30) Walsh, D. J.; Graessley, W. W.; Datta, S.; Lohse, D. J.; Fetters, L. J. *Macromolecules* **1992**, *25*, 5236.
(31) Gehlsen, M. D.; Rosedale, J. H.; Bates, F. S.; Wignall, G. D.; Hansen, L.; Almdal, K. *Phys. Rev. Lett.* **1992**, *68*, 2452.
(32) Rhee, J.; Crist, B. *J. Chem. Phys.*, in press.
(33) Budkowski, A.; Klein, J.; Eiser, E.; Steiner, U. *Macromolecules*, submitted.