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Anomalous Attractive Interactions in Polypropylene Blends

Glenn C. Reichart,[†] William W. Graessley,* and Richard A. Register

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

Ramanan Krishnamoorti

Department of Chemical Engineering, University of Houston, Houston, Texas 77204

David J. Lohse

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

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ABSTRACT: Some new results on thermodynamic interactions in blends of model polyolefins are reported, including more examples of the anomalous attraction found earlier for polyisobutylene (PIB) blends. Small-angle neutron scattering (SANS) data demonstrate a significant suppression of concentration fluctuations in two polypropylene (PP) blends, meaning a net attraction between components relative to the pure liquid states and corresponding to negative values of the Flory−Huggins interaction parameter χ. As in the PIB blends, the temperature dependencies indicate LCST phase behavior but with much higher critical temperatures for the PP blends. The two PP blends with net attraction also differ from PIB blends in that all their components behave conventionally (net repulsion, positive χ) in blends with other species. The other five PP blends in the study exhibit net repulsion but a wide range of mixing behavior, regular to highly irregular, depending on the second species.

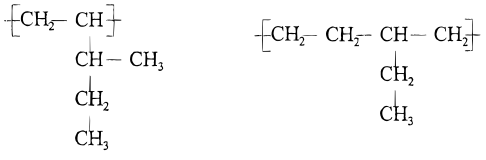
Introduction

In a recent paper,[1] we reported finding large negative values of the Flory−Huggins interaction parameter χ for several blends of saturated hydrocarbon polymers, results that indicate a net attraction between components relative to pure liquids. The values of χ diminish with increasing temperature, cross zero, and then become increasingly positive, leading finally to phase separation. Behavior of this sort is commonly observed when miscibility is driven by some specific association between the components,[2] but finding it for blends with nonpolar components that have no functional groups at all is unprecedented. The cohesive energy for nonpolar liquids is governed by the interactions of induced dipoles. Our results seemingly contradict the underlying theory of those interactions, which would appear invariably to predict a net repulsion between components[3,4] and hence a positive value of χ.

Polyisobutylene (PIB) was a component in all the blends showing large negative χ. That polymer is also somewhat anomalous among saturated hydrocarbon polymers in other ways.[1] So far at least, uniquely among the many nonpolar polymers we have investigated,[5] PIB forms blends with large net attractions, and it seems incapable of mixing in a more normal fashion with any species. We have now found, however, some examples of net attraction in blends that do not contain PIB. The common component in this case is polypropylene (PP). As we show here, blends of PP with other species span a wide range of behavior, including regular mixing,[6] both attractive and repulsive irregularity,[7] and even the PIB-like net attraction.

The polymers in this study, as in earlier ones, are model polyolefins, made by saturating the double bonds of nearly monodisperse polydienes.[8] The main technique for determining the blend interactions is small-angle neutron scattering (SANS) in the single-phase region.[9] We also include some results on the *PVT* behavior of the components. The deuterium labeling required for SANS is obtained by using D_2 instead of H_2 for the polydiene saturations.

Results for blends of various model polyolefin species are described—polypropylene (PP), head-to-head polypropylene (hhPP), saturated polyisoprenes with a range of 3,4 contents (PEP, 50SPI, and 75SPI), saturated polyethylbutadiene with elevated 3,4 content (50PEB), and saturated polybutadienes with 90% and 97% 1,2 content (H90 and H97). Except for 50PEB, the detailed structure and characteristics of these species have been described in previous papers. The polypropylene sample PPC is new here, as is sample H90. The microstructure of 50PEB, like that of 50SPI, consists of an approximately random distribution of saturated 3,4 and 1,4 units along the chain:



50% 50%

Experimental Section

As described elsewhere,[8] hydrogenous and partially deuterated samples were prepared by saturating the double bonds of anionically synthesized, nearly monodisperse polydienes ($M_w/M_n < 1.05$) with H_2 and D_2. All samples are amorphous and atactic with glass transition temperatures well below the temperatures of the *PVT* and SANS measurements. Molecular weights were determined by static light scattering measurements on dilute solutions of the polydiene precursors and are specified in Table 1 by values of N, the number of monomeric units per chain. Size exclusion chromatography before and after saturation confirmed that the large scale molecular structure of the chains was not changed by the saturation reaction. Sample densities, determined at 23 °C in a density

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[†] Present address: Air Products and Chemicals, Inc., 7201 Hamilton Boulevard, Allentown, PA 18195.

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Table 1. Molecular Characterization of the Blend Components

			density at 23 °C		
sample	monomeric units per chain *N*	carbon atoms per monomeric unit	ρ_H (g/cm^3)	ρ_D (g/cm^3)	deuterium atoms per monomeric unit
H90(D90)	520	4	0.8660	0.9011	2.10
HPPC(DPPC)	495	6	0.8525	0.9137	5.96
H50SPI(D50SPI)	1485	5	0.8630	0.9126	4.66
H50PEB(D50PEB)	1000	6	0.8680	0.9057	3.58

Table 2. Equation of State Properties for Various Blend Components

species	*T* (°C)	α × 10^4 (K^{-1})	$\beta \times 10^4$ (MPa^{-1})	δ_{PVT} (MPa$^{1/2}$)
H97	27	6.93	6.25	18.24
	51	6.82	7.17	17.54
	83	6.72	8.42	16.86
	121	6.91	10.13	16.39
	167	7.30	12.78	15.86
PEP	27	7.67	6.02	19.55
	51	7.18	6.99	18.26
	83	6.97	8.10	17.51
	121	7.19	9.77	17.03
	167	7.45	12.25	16.37
50PEB	27	7.55	5.87	19.64
	51	7.20	6.82	18.50
	83	6.81	7.90	17.52
	121	7.05	9.61	17.01
	167	7.45	12.22	16.39
50SPI	27	6.69	5.90	18.45
	51	6.85	6.76	18.12
	83	6.83	7.94	17.50
	121	7.14	9.55	17.17
	167	7.55	12.04	16.61
75SPI	27	6.50	5.57	18.72
	51	6.52	6.50	18.08
	83	6.41	7.80	17.12
	121	6.65	9.39	16.71
	167	6.98	11.79	16.14

gradient column, are also listed in Table 1. Deuteration level was calculated from the densities of the hydrogenated and deuterated versions as described in ref 8, with results given in Table 1. Sample coding follows the conventions of earlier papers: prefixes D and H indicate labeled and unlabeled versions, a suffix (A, B, ...) distinguishes (when necessary) different samples of the same species. Thus, HPPC and DPPC are a "matched pair" of polypropylenes, and they differ in molecular weight from samples PPA and PPB, which were used in previous work.[7]

Data on *PVT* properties were provided by Dr. Gregory Dee of the Du Pont Central Research and Development Department, and were analyzed by methods described elsewhere[5] to obtain the values of thermal expansion coefficient α and isothermal compressibility β that are listed in Table 2. The SANS measurements were made at the NIST Cold Neutron Research Facility in Gaithersburg, MD. Scattering intensity was recorded as a function of scattering angle θ for nearly all the blends on the 8m beamline (NG5) for neutrons with wavelength $\lambda = 9.0$ Å ($\Delta\lambda/\lambda = 0.25$). The scattering vector magnitude, $q = (4\pi \sin\theta/2)/\lambda$, ranged from 0.009 to 0.08 Å^{-1}. The only exception was the blend H75SPI/DPPA, for which the 30m beamline (NG7) was used with neutron wavelength $\lambda = 6.0$ Å ($\Delta\lambda/\lambda = 0.21$) to produce a scattering vector magnitude that ranged from 0.007 to 0.08 Å^{-1}. Sample preparation, experimental procedures and data reduction were as described elsewhere;[8] temperatures ranged from 27 to 167 °C.

Interaction parameters were obtained from the SANS data by extrapolating an experimental "excess function" to $q = 0$:[8]

$$E(q) = \frac{v_0}{2}\left[\frac{1}{v_1 N_1 \phi_1 P_1(q)} + \frac{1}{v_2 N_2 \phi_2 P_2(q)} - \frac{k_N}{I_c(q)}\right] \qquad (1)$$

$$\lim_{q \to 0} E(q) = \chi \qquad (2)$$

in which v_i, N_i, ϕ_i, and $P_i(q)$ are the volume per mer, mers per chain, volume fraction, and the normalized form factor for component *i*; k_N is the contrast factor; $I_C(q)$ is the coherent SANS intensity expressed in absolute units. As before, we used $(v_1 v_2)^{1/2}$ as the reference volume v_o. The component form factors were represented by the Debye equation for monodisperse random coils:

$$P(q) = \frac{2}{u^2}[\exp(-u) - 1 + u] \qquad (3)$$

in which $u = q^2 R_g^{\,2}$, and R_g is the radius of gyration. Values of R_g were obtained for each component by fitting the SANS intensities for its matched pair mixture:[8]

$$\frac{k_N}{I_c(q)} = \frac{1}{\phi_H \phi_D N P(q)} - 2\chi_{HD} \qquad (4)$$

Values of the fitting parameters R_g and χ_{HD} are given in Table 3.

The values of χ obtained by fitting the scattering data to eqs 1 and 2 are given in Table 4. The counting statistics and estimated uncertainties in molecular weights and SANS calibration propagate to uncertainties of approximately ±3% for R_g and $\pm 1.5 \times 10^{-4}$ for χ.[8]

Results and Discussion

The 50SPI/PP and 50PEB/PP Blends. The excess function $E(q)$ at 167 °C is shown in Figure 1 for H50SPI/DPPC and its label-switched version D50SPI/HPPC. Two features are noteworthy. First, the values of χ (the $E(0)$ intercept) differ significantly for the two blends. This is an example of the Rhee–Crist effect,[10] widely observed and discussed in our previous studies;[11,12] we will return to a discussion of that effect below. Second, the values of χ are negative, indicating a net attraction between the components—a highly unusual result for blends of nonpolar species, as discussed in the Introduction. The normally expected positive χ is clearly ruled out as shown by Figure 2, which compares the absolute intensity profile for the D50SPI/HPPC blend at 83 °C with predictions for several choices of χ. Figure 3 shows the temperature dependence of χ for the 50SPI/PPC blends. The data are described reasonably well by nearly parallel straight lines in plots of χ vs T^{-1}, as found for many polyolefin blends. The slopes in this case are negative, however, suggesting LCST behavior with critical temperatures in excess of 300 °C.

Blends of 50PEB with PP also display a net attraction between components. In Figure 4, the SANS intensities for H50PEB/DPPC at three temperatures are compared with the predicted profile for the blend without interactions ($\chi = 0$). The observed intensities are lower, indicating suppression of concentration fluctuations, and, equivalently, a net attraction between components or a negative value of χ. The increase of $I_C(q)$ in the low *q* range with increasing temperature indicates a lessening of the net attraction (an algebraically increasing χ) and thus LCST behavior, as in the 50SPI/PP blends. Figure 5 shows χ vs T^{-1} for the 50PEB/PP blends. The behavior of the 50PEB/PP and 50SPI/PP

Table 3. Chain Dimensions and Isotopic Interaction Parameter for Matched-Pair Mixtures

	27 °C		51 °C		83 °C		121 °C		167 °C	
matched pair	R_g (Å)	$10^4\chi_{HD}$	R_g (Å)	$10^4\chi_{HD}$	R_g (Å)	$10^4\chi_{HD}$	R_g (Å)	$10^4\chi_{HD}$	R_g (Å)	$10^4\chi_{HD}$
H90/D90	51.6	*a*	52.3		53.1		53.7		54.6	
HPPC/DPPC	72.7	−1.8	71.3	−1.5	70.3	−1.4	69.2	−2.0	69.1	−2.0
H50PEB/D50PEB	85.4	3.2	86.3	2.4	87.4	1.3	87.0	0.8	87.7	1.2

[a] The combination of low molecular weight and small deuteration level make estimation of χ_{HD} for H90/D90 unreliable.

Table 4. SANS Interaction Parameters for Binary Blends

	$\chi \times 10^4$						
blend	27 °C	51 °C	83 °C	98 °C	121 °C	142 °C	167 °C
H50SPI/DPPC	−11.7	−10.3	−9.2		−7.6		−6.3
D50SPI/HPPC	−17.4	−16.6	−14.8		−13.1		−11.1
H50PEB/DPPC	−48.7	−38.6	−29.4		−20.3		−12.4
D50PEB/HPPC	−53.8	−44.2	−34.5		−24.7		−15.8
H50PEB/D50SPI	3.1	3.1	2.9		2.9		2.0
D50PEB/H50SPI	0.2	0.0	−0.3		−0.3		−0.1
H50PEB/D90	2 phase			24.9	22.9	21.4	19.6
D50PEB/H90	26.0	24.1		21.6	20.1	18.7	15.5
HhhPPA/DPPC	45.3	38.2	31.1		26.0		21.2
DhhPPA/HPPC	22.8	18.2	14.8		13.0		8.9
H75SPI/DPPA	57.5	47.4	38.4		33.3		30.6
D75SPI/HPPA	60.6	51.5	44.4		...		...

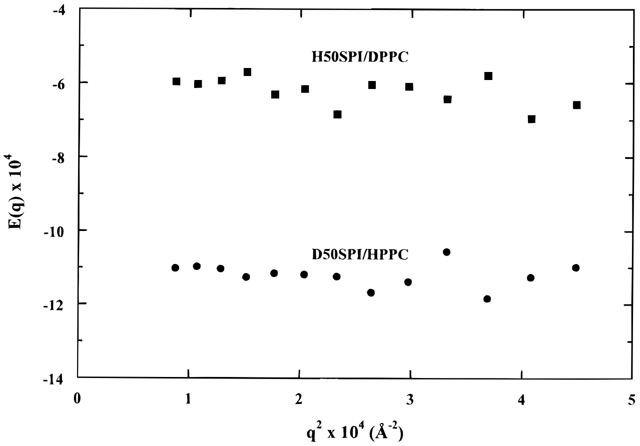

Figure 1. Excess function $E(q)$ in the low q range for HPPC/D50SPI and DPPC/H50SPI blends at 167 °C.

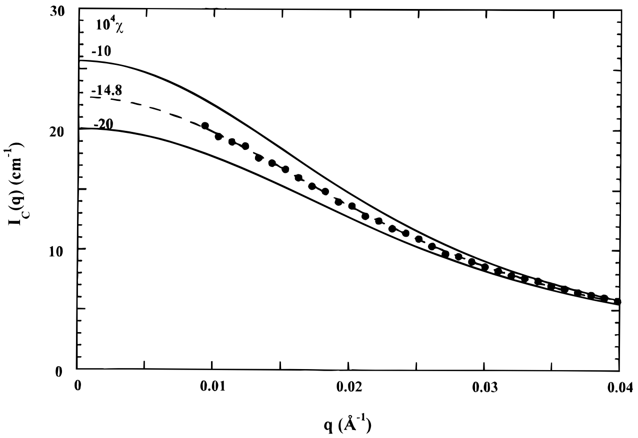

Figure 2. Observed SANS coherent intensity and the intensity predicted with various values of the interaction parameter for the HPPC/D50SPI blend at 83 °C.

blends is quite similar, except that the values of χ at lower temperatures are more negative for 50PEB/PP and they increase more rapidly with temperature. The trends in χ for 50PEB/PP also indicate critical temperatures in excess of 300 °C.

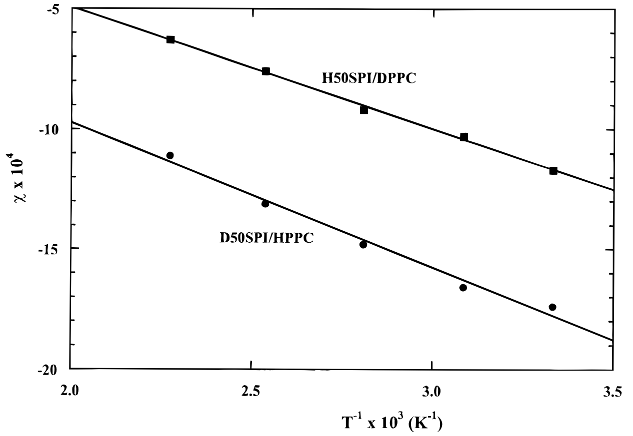

Figure 3. Temperature dependence of the interaction parameter for PPC/50SPI blends.

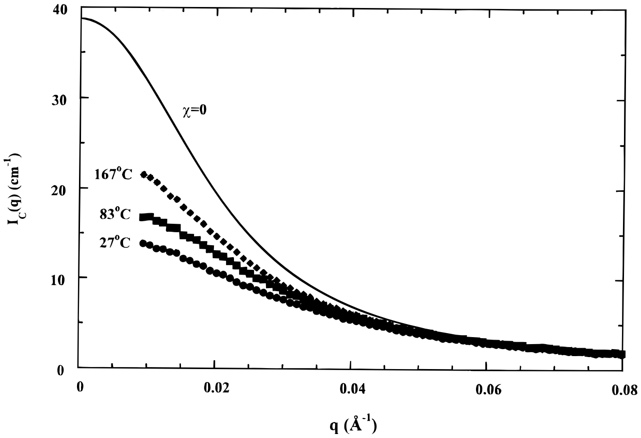

Figure 4. Observed SANS coherent intensity for the H50PEB/DPPC blend at three temperatures. The solid line is the prediction for $\chi = 0$.

All three species in the blends with net attraction—PP, 50SPI, and 50PEB—behave in the more usual fashion when blended with other species. Thus, for example, the blends of PP with head-to-head polypropylene (hhPP) have positive values of χ that decrease with

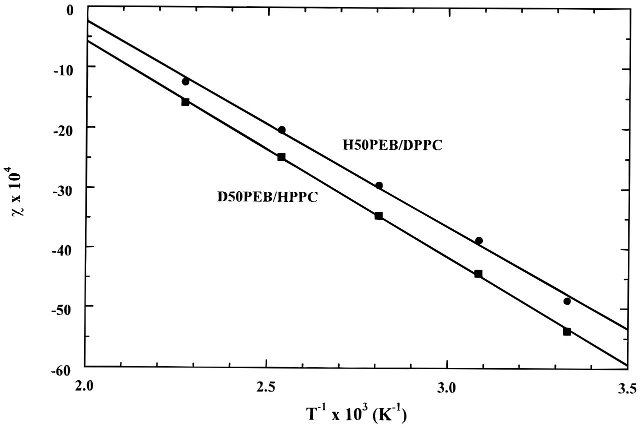

Figure 5. Temperature dependence of the interaction parameter for 50PEB/PPC.

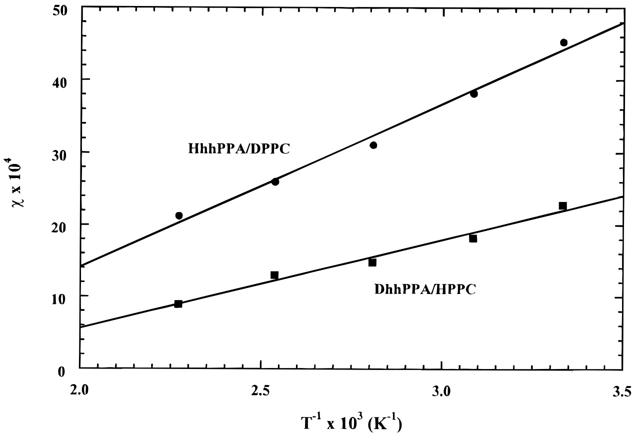

Figure 6. Temperature dependence of the interaction parameter for hhPPA/PPC.

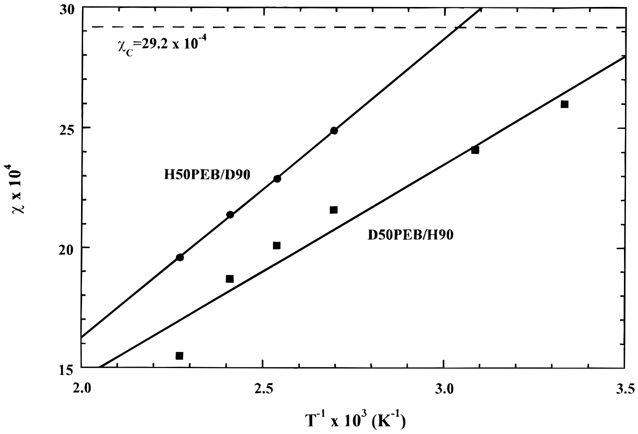

Figure 7. Temperature dependence of the interaction parameter for 50PEB/90. The dashed line indicates the critical value of χ from Flory–Huggins.

increasing temperature,[7] the conventional UCST behavior. The more recent results for the PP/hhPP system, HhhPPA/DPPC, and DhhPPA/HPPC are shown in Figure 6. The blends of 50PEB and H90 also behave conventionally, as shown in Figure 7. Blends of 50SPI with hhPP, and also with H88, have positive χ and UCST behavior as well.[7] The blends of 50SPI with H78 have negative χ, but small enough values to be essentially zero within the errors.[7] Aside from this last possible exception, the blends of these three species (PP, 50SPI, 50PEB) behave conventionally except 50PEB/PP and 50SPI/PP.

Solubility Parameter Assignment. Our past work has shown that the interaction for many pairs of saturated hydrocarbon polymer species can be organized remarkably well by a solubility parameter formalism.[6,7] The values of $\chi(T)$ for the majority of blends we have investigated obey the Hildebrand equation[3]

$$\chi = \frac{v_0}{k_B T}(\delta_1 - \delta_2)^2 \tag{5}$$

in which k_B is the Boltzmann constant, T is the temperature, and δ_i is the solubility parameter of species i. In our work their values are assigned empirically and solely on the basis of their ability to fit, in a self-consistent way, the interaction data for an interconnected matrix of pair combinations. Only differences can be obtained in this way, so we arbitrarily choose one species, H97, as the reference and developed a catalog of $[\delta(T) - \delta_{\mathrm{ref}}(T)]_{\mathrm{SANS}}$ values for the others. Its construction and verification is described in detail elsewhere.[6,10,13] A species pair for which $\chi(T)$ is consistent with the catalog prediction is said to mix *regularly*. A pair for which the measured $\chi(T)$ disagrees significantly with the prediction is said to mix *irregularly*. For irregular mixtures the departure is expressed as an *extra* interaction strength[7]

$$X_E(T) = X(T) - [\delta_1(T) - \delta_2(T)]^2 \tag{6}$$

in which the $\delta_i(T)$ values are from the catalog and $X(T)$ is the observed interaction strength:

$$X(T) = \frac{k_B T}{v_0}\chi(T) \tag{7}$$

The 50SPI/PP and 50PEB/PP blends are obviously irregular since no choice of solubility parameters can give negative χ, but even some blends with positive χ values are irregular.[6,7]

Relative solubility parameters have been assigned to all species in this study except 50PEB (see ref 5). With eq 5, values for any new species can be obtained from χ for its blend with some species whose values of $(\delta(T) - \delta_{\mathrm{ref}}(T))_{\mathrm{SANS}}$ are already known, provided the mixing for that blend can be shown to be regular ($X_E = 0$). The sign ambiguity for $\delta_2 - \delta_1$ can be removed by qualitative tests for mutual solubility with other species that have known solubility parameters. The effect of deuterium substitution on χ, which seems always to reduce δ for saturated hydrocarbons, is also helpful;[12] labeling the blend component that already has the smaller solubility parameter increases χ, while labeling the other reduces it. The average, $(\chi_{\mathrm{hd}} + \chi_{\mathrm{dh}})/2$, provides a good estimate for χ_{hh}, the value for blends of nonlabeled components. Of course, the regularity assumption for a blend containing some new species can always be tested by the ability of the $[\delta(T) - \delta_{\mathrm{ref}}(T)]_{\mathrm{SANS}}$ values so obtained to predict χ for blends of the new species with still other known species.

All these sources of information were used in assigning the values of 50PEB given in Table 5. Thus, 50PEB/90 blends were assumed to mix regularly, and averages of $\chi_{\mathrm{H50PEB/D90}}$ and $\chi_{\mathrm{D50PEB/H90}}$ were used in eq 2 to calculate $|\delta_{\mathrm{H50PEB}} - \delta_{\mathrm{H90}}|$. From the observation of $\chi_{\mathrm{H50PEB/D90}} > \chi_{\mathrm{D50PEB/H90}}$ (Table 4), we infer $\delta_{\mathrm{H50PEB}} > \delta_{\mathrm{H90}}$. This numerical ordering of solubility parameters is also supported by the separate observation that H50PEB and H97B are immiscible up to very high

Table 5. SANS-Based Solubility Parameters Relative to Reference Species H97

	$(\delta - \delta_{\mathrm{ref}})$ (MPa$^{1/2}$)				
component	27 °C	51 °C	83 °C	121 °C	167 °C
75SPI	−0.17	−0.17	−0.17	−0.16	−0.16
H97	0.00	0.00	0.00	0.00	0.00
H90[a]	0.19	0.18	0.18	0.17	0.15
PP	0.23	0.22	0.25	0.26	0.25
50SPI	0.44	0.43	0.41	0.39	0.36
H78	0.49	0.48	0.46	0.44	0.41
50PEB	0.49	0.48	0.47	0.46	0.42
hhPP	0.82	0.79	0.76	0.72	0.67
PEP	0.92	0.91	0.90	0.89	0.88

[a] Values obtained with the solubility parameter vs composition data in ref 9.

Table 6. Comparison of $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ with $(\delta - \delta_{\mathrm{ref}})_{PVT}$ for Selected Species

	51 °C		121 °C	
component	$(\delta - \delta_{\mathrm{ref}})_{PVT}$ (Mpa$^{1/2}$)	$(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ (Mpa$^{1/2}$)	$(\delta - \delta_{\mathrm{ref}})_{PVT}$ (Mpa$^{1/2}$)	$(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ (Mpa$^{1/2}$)
PEP	0.72	0.91	0.64	0.89
50PEB	0.96	0.48	0.62	0.46
50SPI	0.58	0.43	0.78	0.39
75SPI	0.50	−0.17	0.32	−0.16

temperatures. This combination of information places δ_{H50PEB} near, but slightly larger in magnitude than δ_{H50SPI} (see Table 5). Consistency then requires that $\chi_{\mathrm{H50SPI/D50PEB}}$ be larger than $\chi_{\mathrm{D50SPI/H50PEB}}$. Also, χ should be very small for 50PEB/50SPI blends. Both predictions are borne out by the SANS results for 50SPI/50PEB blends (Table 4). The numerical agreement between the values of $(\chi_{\mathrm{H50SPI/D50PEB}} + \chi_{\mathrm{D50SPI/H50PEB}})/2$ and the predictions of $\chi_{\mathrm{H50SPI/H50PEB}}$ with solubility parameters from Table 5 is excellent, being well inside the $\pm 1.5 \times 10^{-4}$ error bars on χ at all temperatures.

We note finally that the effect of label-switching in 50SPI/PPC and 50PEB/PPC blends correctly indicates that δ_{PP} is smaller than both δ_{50SPI} and δ_{50PEB} (Table 5). Remarkably, the algebraic shift in χ when deuterium is switched from one component to the other indicates the correct numerical ordering of solubility parameters even in blends so irregular that χ is large and negative. Perhaps the simple additivity of regular and irregular contributions, as in the arbitrary definition of eq 6, has some fundamental validity.

In previous work,[5−7,13] we found that $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ closely tracks $(\delta - \delta_{\mathrm{ref}})_{PVT}$, the values of which are obtained by equation of state measurements on the pure components. Values of $(\delta - \delta_{\mathrm{ref}})_{PVT}$ were calculated for several species with the data in Table 2 and compared with the SANS-assigned values in Table 6. Some allowance must be made for the rather large uncertainties in $(\delta - \delta_{\mathrm{ref}})_{PVT}$.[5] However, even taking these into account does not explain the substantial discrepancy for 75SPI. This result for 75SPI is the first to conflict with what had seemed a promising alternative approach for estimating the mixing behavior of saturated hydrocarbon polymers from pure component *PVT* data. What would cause 75SPI to behave so differently in this regard is not evident at present.

Comparison with PIB Blends. Results for the 50SPI/PP and 50PEB/PP blends demonstrate that large negative χ can be obtained for binary mixtures of saturated hydrocarbons other than those with polyisobutylene as one of the components. Near room temperature, the magnitudes of χ are larger for some of the PIB blends, but they also change much more rapidly with temperature. As a result, the LCST for PIB blends is relatively insensitive to component chain length,[1] and the highest critical temperature among all PIB blends investigated was only about 180 °C. The temperature dependence of χ is much weaker for the 50SPI/PP and 50PEB/PP blends; the LCST estimated by extrapolating the lines in Figure 3 and 5 to χ_{critical}[8] is well in excess of 300 °C for both 50SPI/PPC and 50PEB/PPC.

Table 7. Extra Interaction Density Coefficients for Irregular Blends

	$X_{\mathrm{E}} \times 10^2$ (MPa)				
blend pair	27 °C	51 °C	83 °C	121 °C	167 °C
PP/50SPI	−8.9	−8.4	−6.4	−5.2	−4.4
PP/50PEB	−20.3	−17.9	−14.1	−11.0	−7.6
PP/hhPP	−27.6	−25.1	−19.6	−15.3	−12.8

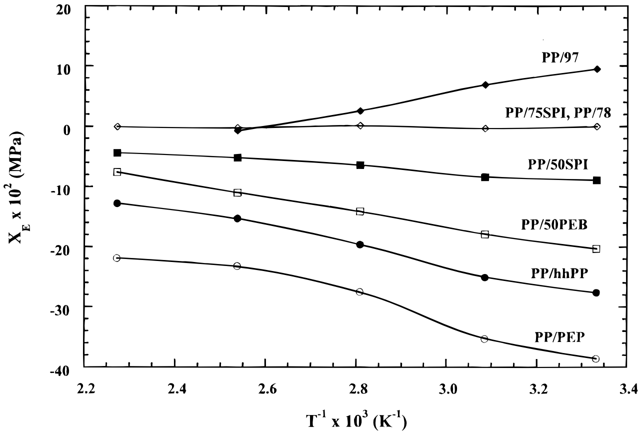

Figure 8. Temperature dependence of X_{E} for blends of polypropylene with various species.

In contrast with the earlier study,[1] where all miscible blends of PIB were irregular, in this work all components of blends with negative χ mix regularly with at least two other species. Solubility parameters could thus be assigned to each component and used in eq 6 to calculate X_{E}. The values for 50PEB/PP and 50SPI/PP blends are listed in Table 7. Included there also are the values of X_{E} for hhPPA/PPC blends. Those now replace the slightly different and less accurate values for hhPP/PP that had been obtained earlier[7] with a polypropylene component of much lower molecular weight (PPA). Interestingly, the extra attraction irregularity is actually smaller in magnitude for both 50SPI/PP and 50PEB/PP, which had large negative χ, than for the hhPP/PP, which has large positive χ. The net repulsion caused by the large difference in solubility parameter for hhPP/PP blends (Table 5) more than offsets the attraction irregularity. A smaller attraction irregularity produces a negative χ in 50SPI/PP and 50PEB/PP blends because in these the contribution of the solubility parameter difference is much smaller.

Blends of PP with PEP have positive χ, but extra attraction irregularities that are even larger than those for hhPP/PP.[7] There appears, in fact, to be a pattern in the extra interaction strengths for polypropylene blends. The extra interaction coefficients for all the blends of polypropylene we have investigated thus far are shown in Figure 8. Four of the pairs show conventional UCST behavior with positive values of χ (75SPI/PP, H97/PP, H78/PP, hhPP/PP), one shows LCST behavior with positive χ (PEP/PP), and two show LCST behavior with negative χ (50SPI/PP, 50PEB/PP). The somewhat contrary data for 75SPI/PP and H78/PP (X_{E}

~ 0) notwithstanding, X_E tends to move toward more negative values as the solubility parameter of the second component increases. Aside from such specific correlations, however, the similarities and trends of X_E vs T^{-1} behavior with the various second components suggest at least the possibility of a common origin for the attraction anomaly.

Finally, we note that the second components in PIB blends with negative X_E have consistently smaller solubility parameters than PIB, whereas those in PP blends with negative X_E have consistently larger solubility parameters than PP. In neither group of blends that display the extra attractions is the span of solubility parameters for the second component centered on the solubility parameter of the first component.

Summary and Conclusions

We have found two new examples of saturated hydrocarbon polymer blends with net attractions between components. Both have polypropylene as a component, and an examination of data for all available polypropylene blends revealed a rather clear pattern of increasingly negative (attractive) departures from regular mixing, as the solubility parameter of the second component increases. The parallels and contrasts in behavior between the blends of polypropylene and the blends of polyisobutylene were noted, but no firm conclusions could be drawn.

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