Pure Component Properties and Mixing Behavior in Polyolefin Blends

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ABSTRACT: This paper summarizes an extensive investigation of the thermodynamic interactions that govern phase behavior in blends of polyolefins and examines their relationship to pure component *PVT* properties. Interaction strengths, obtained by small-angle neutron scattering (SANS) measurements, were classified as regular or irregular according to their consistency with a solubility parameter formalism. Characteristic pressure P^* and temperature T^* were obtained from *PVT* data on the pure components with various liquid-state models. For the regular blends, a close correspondence was found between the SANS-based and *PVT*-based solubility parameter assignments, the latter being closely related to P^*, as expected. The pattern of deviations for the irregular blends, positive in some and negative in others, effectively ruled out equation-of-state contributions as a general explanation. However, the results suggest that mismatches in both P^* and T^* play some role, and we offer some tentative attempts at generalization.

Introduction

During the past few years, we have investigated extensively the molecular interactions that govern phase behavior for polyolefin blends in the melt state.[1−9] Our primary technique has been small-angle neutron scattering (SANS), which provides information on blend interactions through their effect on the local concentration fluctuations.[10,11] Model polyolefins were used; labeling one component with deuterium supplied the necessary scattering contrast. The scattering data were interpreted through the random phase approximation as applied to the Flory−Huggins (FH) expression for free energy of mixing.[12,13] The interaction contribution for each blend and temperature was expressed as an FH parameter for scattering, $\chi_{\rm SANS}$, based on a reference volume v_0:[2]

$$\chi_{\rm SANS} \equiv \frac{v_0}{2}\left(\frac{1}{\phi_1 V_1} + \frac{1}{\phi_2 V_2} - \frac{k_{\rm N}}{I(0)}\right) \qquad (1)$$

in which the ϕ_1 and V_i are component volume fractions and molecular volumes, respectively, $k_{\rm N}$ is the contrast factor, and $I(0)$ is the coherent SANS intensity extrapolated to the forward direction. In effect, $\chi_{\rm SANS}$ is defined in terms of the observed difference from the prediction for scattering by a noninteracting FH blend of the same polymers. The values of $\chi_{\rm SANS}$, or equivalently $\chi_{\rm SANS}/v_0$, were found to be insensitive to component molecular weight[8] and also to component volume fraction in the midrange ($0.25 < \phi_i < 0.75$).[4] Accordingly, $\phi_1\phi_2\chi_{\rm SANS}k_{\rm B}T/v_0$ is the free energy of mixing per unit volume in excess of that for a noninteracting FH blend of the same composition, and

$$X \equiv \chi_{\rm SANS}k_{\rm B}T/v_0 \qquad (2)$$

is the coefficient of this excess free energy density, which we call the interaction strength.[14] Deuterium labeling influences X to some extent. The values from SANS were corrected for the labeling by methods described elsewhere,[3,5] and those used throughout this paper refer to fully hydrogenous components only.

Values of X are now available at several temperatures, typically $27 \le T \le 167$ °C, for approximately 40 pairwise combinations of 18 species. All are saturated hydrocarbon polymers, mostly of the model polyolefin variety. The present paper focuses on the species dependence of the interaction strength and particularly on the relationship among the various values of X that are generated when one such species is mixed with others.

We have already established that the interaction strengths for a large majority of these blends are consistent with a Hildebrand formalism:[6,8]

$$X(T) = [\delta_1(T) - \delta_2(T)]^2 \qquad (3)$$

in which $\delta_i(T)$ is a physical property that is unique to each polymer species i and traditionally called the solubility parameter. We were able to construct a relative scale of solubility parameters for the 18 species using only the SANS data for their blends.[6−8] Thus, the mixing behavior of a blend is classified as either *regular* or *irregular*, according to whether or not its observed interaction strength $X(T)$ is consistent with the prediction based on eq 3 and observed interaction strengths for blends of each of its two components with some common third component. Consistency, a necessary condition for uniqueness, has turned out to be common enough that 17 of the 18 species were parts of some multiconnected network of regular blends. Dif-

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Table 1. SANS-Based Solubility Parameters for Model Polyolefins Relative to the Reference Species H97

	$\delta(T) - \delta_{\mathrm{ref}}(T)$ (MPa$^{1/2}$)				
species	27 °C	51 °C	83 °C	121 °C	167 °C
75SPI	−0.17	−0.17	−0.17	−0.16	−0.16
H97	0	0	0	0	0
H88	0.23	0.22	0.21	0.20	0.18
PP	0.22	0.22	0.25	0.26	0.25
H78	0.49	0.48	0.46	0.44	0.41
50SPI	0.51	0.50	0.48	0.45	0.43
H66	0.73	0.72	0.69	0.66	0.62
PEB	0.72	0.72	0.71	0.69	0.66
hhPP	0.82	0.79	0.76	0.72	0.67
PEP	0.92	0.91	0.90	0.89	0.88
H52	1.01	0.98	0.95	0.91	0.86
H38		1.20	1.16	1.11	1.05
H35			1.17	1.13	1.07
H32			1.28	1.22	1.15
H25			1.37	1.31	1.23
H17				1.37	1.30
H08				1.54	1.43
H00				(1.60)	1.48

Table 2. Extra Interaction Strength for Blends with Irregular Mixing

	X_{E} (MPa) × 10^2 [a]				
blend	27 °C	51 °C	83 °C	121 °C	167 °C
hhPP/PEP	3.0	1.8	0.8	0.3	−0.1
PEB/H66	2.9	2.3	1.9	1.4	1.4
PEB/hhPP	4.2	4.1	3.8	3.4	3.5
H66/hhPP	5.5	3.4	1.7	0.4	0.2
PP/H97	10.2	6.8	2.7	−1.0	
PP/hhPP	−26	−24	−19	−16	
PP/PEP	−40	−35	−28	−23	−22
PEP/H100[b]	−45	−43	−42	−40	−40
PEP/H08[b]				−16	−14
H08/H100[b]				−136	−102
PIB/H52[c]	−47	−41			
PIB/H66[c]	−82	−67	−53		
PIB/H78[c]	−108	−104	−100		
PIB/hhPP[c]	−91	−67	−56		−43

[a] For the blends classified as regular, the values for X_{E} lie in the range $\pm 0.25 \times 10^{-2}$ MPa, which corresponds at least approximately to the experimental uncertainty.[6,8] [b] Obtained using diblock copolymer data of Bates et al.,[15] as explained in ref 6. [c] Obtained using values of $(\delta - \delta_{\mathrm{ref}})_{PVT}$, as explained in ref 9.

ferences in solubility parameter among the 17 could thus be assigned with reasonable confidence. One species was chosen as the reference (H97; see below), and values of $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ were assigned to the other species by repeated application of eq 3 to the connected regular sequences. Details of these considerations are described elsewhere;[6,8] the values so obtained are listed in Table 1.

Seven of the 40 pair combinations were found to mix irregularly: the SAN-determined interaction strength for those blends differs significantly from the value obtained with eq 3 and independently confirmed $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ assignments (Table 1). Both negative departures (favoring mixing) and positive departures (favoring phase separation) were found,[6,8] and we have expressed them simply as an "extra" interaction strength:

$$X_{\mathrm{E}} = X - (\delta_2 - \delta_1)^2 \tag{4}$$

Values of $X_{\mathrm{E}}(T)$ are given for the seven irregular blends in Table 2. Also included in Table 2 are three additional examples,[6] inferred more indirectly by comparisons with interaction strengths obtained from the microphase separation temperatures of block copolymers.[15] Four further examples, all for blends containing polyisobutylene,[9] are also listed. Values of $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ are not known for PIB since all of its blends tested so far are irregular. Values of $(\delta - \delta_{\mathrm{ref}})$ based on *PVT* measurements (see below) were used in eq 4 to obtain the estimates of X_{E} for the PIB-containing blends.

The results given in Tables 1 and 2 (aside from those involving PIB) are based solely upon the interaction strengths for binary blends as determined by SANS. The values of $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ in Table 1 are strictly empirical, chosen only for their ability to describe, through eq 3, the interaction strengths for a large number of blends. The values of X_{E} in Table 2 are also empirical. They do no more than quantify the magnitude of departures for pairs of species that, according to the criteria specified, mix irregularly. Thus, $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ is a property that depends on the species alone, while X_{E} is one that depends on both species through attributes whose effects on X are not captured by the values of $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$. Our interest here is in the connection of both $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ and X_{E} with observable properties of the species, mainly their *PVT* (pressure−volume−temperature) properties in the liquid state. Some work along these lines was described in earlier papers.[6−9] We extend the range of saturated hydrocarbon polymer species examined, including now some commercial polyolefins as well as the model materials, and we consider the parallels in thermodynamic properties between homopolymers and their low molecular weight analogs. We also suggest some possible connections between X_{E} and quantifiable features of the component *PVT* properties.

Background

The solubility parameter, according to its original definition, is the square root of the cohesive energy density of the pure liquid (internal energy change with evaporation per unit volume of liquid):[16]

$$\delta_{\mathrm{CED}} = (U/V)^{1/2} \tag{5}$$

The cohesive energy density U/V is equal to the internal pressure, $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$, for a van der Waals liquid; Hildebrand and co-workers have shown that U/V and $(\partial U/\partial_V)_T$ are, in fact, numerically very similar in nonassociating organic liquids.[16] The internal pressure can be determined by *PVT* measurements, and for liquids at low (~atmospheric) pressures,

$$\delta_{PVT} = \left(\frac{T\alpha}{\beta}\right)^{1/2} \tag{6}$$

where α is the thermal expansion coefficient of the liquid $(\partial \ln V/\partial T)_P$, and β is the isothermal compressibility $-(\partial \ln V/\partial P)_T$.

Some years ago, Allen et al.[17] compared the independently measured values of δ_{CED} and δ_{PVT} for a wide range of organic liquids, finding a close although not exact correspondence. Thus, for a fairly wide range of saturated hydrocarbon liquids

$$\delta_{PVT} = \mu \delta_{\mathrm{CED}} \tag{7}$$

in which $\mu \sim 1.04$ for linear alkanes from C_5 to C_{14} with values that drift weakly upward with chain length, and $\mu \sim 1.07$ for branched alkanes. The values of $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ in Table 1 have no necessary connection with either δ_{CED} or δ_{PVT}. However, we have already found that some of our $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ assignments correspond fairly closely with $(\delta - \delta_{\mathrm{ref}})_{PVT}$, the latter calculated from measurements of α and β with eq 6.[6−8]

Table 3. Polymer Species Used in the Study

sample designation	description	source
EP*XX*	statistical copolymers of ethylene and propylene: *XX* gives the weight percent of propylene	direct polymerization of the monomers[1]
iPP	isotactic polypropylene	direct polymerization of the monomer[1]
PP	atactic polypropylene	hydrogenation of 1,4-poly(2-methylpentadiene)[8]
hhPP	atactic head-to-head polypropylene	hydrogenation of 1,4-poly(2,3-dimethylbutadiene)[5]
PEP	alternating copolymer of ethylene and propylene	hydrogenation of 1,4-polyisoprene[6]
PEB	alternating copolymer of ethylene and 1-butene	hydrogenation of 1,4-poly(2-ethylbutadiene)[6]
H*XX*	statistical copolymers of ethylene and 1-butene: *XX* gives the weight percent of 1-butene (H00 is linear polyethylene, H100 is atactic poly(1-butene))	hydrogenation of mixed microstructure polybutadienes[7]
iPB	isotactic poly(1-butene)	direct polymerization of the monomer[1]
PIB	polyisobutylene	direct polymerization of the monomer[1,9]
50SPI, 75SPI	statistical copolymers containing 50 and 75 wt % of 3 methyl-1-butene units	hydrogenation of mixed-microstructure polyisoprenes[8]

PVT measurements can also provide additional predictions about blend interactions through the application of equation-of-state (EOS) theories.[18−22] The effects of interaction on *PVT* properties are usually too small to be obtained from measurements on the blends themselves. They are instead inferred by fitting the pure component data to some liquid-state model and applying a molecularly-motivated combining rule to obtain the excess properties of mixing. A variety of theoretical equations of state have been proposed. A recent review compares the ability to several to fit *PVT* data for polymeric liquids.[23] We use two of these—the Prigogine square well cell model (CM) equation, which fits the pure component data better than most, and the Flory−Orwoll−Vrij (FOV) equation, which fits less well but has been used more extensively—to predict the equation-of-state contributions.[24] Both take on a corresponding states form:

$$\text{CM:}\quad \frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 0.8909} - \frac{2}{\tilde{T}}\left(\frac{1.2045}{\tilde{v}^2} - \frac{1.011}{\tilde{v}^4}\right) \qquad (8)$$

$$\text{FOV:}\quad \frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{T}\tilde{v}} \qquad (9)$$

where P, T, and v are the experimental values; $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$, and $\tilde{v} = v/v^*$ are the reduced pressure, temperature, and volume; and P^*, T^*, and v^* are fitting parameters that characterize the liquid. The solubility parameter defined in eq 6 has the form

$$\delta_{PVT} = f(\tilde{v})(P^*)^{1/2} \qquad (10)$$

in which

$$\text{CM:}\quad f(\tilde{v}) = \left[\frac{2}{\tilde{v}}\left(\frac{1.2045}{\tilde{v}^2} - \frac{1.011}{\tilde{v}^4}\right)\right]^{1/2}\Big/\tilde{v} \qquad (11)$$

$$\text{FOV:}\quad f(\tilde{v}) = 1/\tilde{v} \qquad (12)$$

The FOV combining rules for predicting the equation-of-state contribution to interaction strength X_{EOS} and the volume change on mixing $\Delta v/v$ are described in detail elsewhere.[24]

Experimental Section

The samples used for *PVT* measurements are listed in Table 3. They include both the model polyolefins, made by hydrogenating the double bonds of nearly monodisperse polydienes (the H*XX* series, PP, hhPP, PEP, PEB, 50SPI, and 75SPI), and polyolefins made by direct polymerization (the EP*XX* series, iPP, iPB, PIB, and H00). All molecular weights are large enough (M_n > 20 000) to ensure that the *PVT* properties depend only on the chemical microstructure of the polymer.

The measurements were made with Zoller (Gnomix) instruments.[25] Specific volume was determined as a function of temperature (20 ≤ T ≤ 300 °C, intervals of 8−10 °C) and pressure (10 ≤ P ≤ 200 MPa, intervals of 10 MPa). The data for one group of polymers were gathered over a period of about 2 years with different instruments, operators, and sometimes different experimental protocols.[1] Data for the second group[6−8] were gathered more recently and over a period of only 2−3 months, using a newer version of the instrument and the same protocols for each run.[6,8] The reference species H97 was run with both groups, and the two sets of results were found to be somewhat different, particularly at lower temperatures. Because of this discrepancy and the differences in protocols, we distinguish the groups by designating the earlier results[14] with a "(w)".

The data were analyzed in two ways, one to obtain α and β at low pressures and several temperatures for calculating δ_{PVT} with eq 6, the other to determine P^*, T^*, and v^* by fits to the FOV and CM equations. For the crystallizable species, only the data obtained well above the final melting temperature were used.

Various extrapolation procedures were used in the evaluations of α and β, the object being to establish these first-derivative properties in the most accurate and consistent manner possible. Small blocks of data at low pressures were fitted to various functional forms, such as the CM and FOV equations, or to simple polynomials. We found that the resulting values of α and β (and the values of δ_{PVT} calculated from them) varied somewhat with the extrapolation procedure. The accurate determination of β is especially difficult because it is so sensitive to pressure.[26,27] We did find, however, that the resulting differences between species in the values of δ_{PVT} were, within the errors, *independent* of extrapolation procedure.[28] For consistency, we settled on the FOV-based extrapolations with the pressure block from 10 to 40 MPa and temperature blocks of 50 °C, centered around each of the five temperatures in Table 1. The resulting values of α, β, and δ_{PVT} are listed in Table 4.

Larger blocks of data were used to evaluate the fitting parameters for CM (eq 9) and FOV (eq 10). Values of P^*, T^*, and v^* were obtained for the amorphous polymers in both the low-temperature range, 50−150 °C and 10−200 MPa, and the high-temperature range, 150−250 °C and 10−200 MPa. Only the high-temperature range was used for the crystallizable species. Fitting to obtain P^*, T^*, and v^* was accomplished by a nonlinear leasthsquares procedure which minimizes

$$s^2 = \frac{\sum_{i=1}^{n} [P_i(\text{data}) - P_i(\text{fit})]^2}{n - 3} \qquad (13)$$

where n is the number of data points, typically about 200. Goodness of fit is thus specified by $(s^2)_{\min}$. The resulting values of P^*, T^*, v^* (hard-core volume per gram in all cases), and $(s^2)_{\min}$ are listed in Table 5.

Table 4. Thermal Expansion Coefficients, Isothermal Compressibilities, and Solubility Parameters from Liquid-State *PVT* Data

species^a	T (°C)	$\alpha(T) \times 10^4$ (K^{-1})	$\beta(T) \times 10^4$ (MPa^{-1})	$\delta_{PVT}(T)$ (MPa$^{1/2}$)	species^a	T (°C)	$\alpha(T) \times 10^4$ (K^{-1})	$\beta(T) \times 10^4$ (MPa^{-1})	$\delta_{PVT}(T)$ (MPa$^{1/2}$)
iPB$^{(w)}$	167	6.9_2	12.4_1	15.6_6	PP	27	7.2_8	6.4_7	18.3_7
H97$^{(w)}$	27	5.9_0	5.9_9	17.1_9		51	7.5_5	7.5_4	18.0_2
	51	5.9_6	6.7_8	16.8_9		83	7.3_1	8.7_3	17.2_5
	83	6.2_2	8.2_4	16.3_8		121	7.3_0	10.4_4	16.6_0
	121	6.3_3	9.9_3	15.8_4		167	7.5_2	13.1_4	15.8_7
	167	7.0_1	12.2_3	15.8_7	EP84$^{(w)b}$	27	6.9_7	6.0_1	18.6_5
H97	27	6.9_4	6.3_1	18.1_7		51	7.0_6	6.9_0	18.2_2
	51	7.1_2	7.3_2	17.7_6		83	6.9_7	8.0_6	17.5_4
	83	6.9_9	8.5_2	17.0_8		121	7.1_6	9.6_7	17.0_8
	121	7.1_4	10.0_9	16.6_9		167	7.6_0	12.0_2	16.6_8
	167	7.2_5	12.6_8	15.8_6	EP76$^{(w)b}$	27	6.7_0	5.9_8	18.3_4
H88	27	6.8_1	6.1_6	18.2_2		51	6.9_8	6.9_0	18.1_1
	51	7.0_8	7.1_4	17.9_3		83	6.9_7	8.0_6	17.5_4
	83	6.9_8	8.2_5	17.3_5		121	7.2_3	9.6_1	17.2_1
	121	7.1_6	9.8_1	16.9_6		167	7.5_9	12.0_8	16.6_2
	167	7.3_7	12.3_3	16.2_2	EP57$^{9w)b}$	27	6.7_7	5.8_9	18.5_7
H66	27	6.9_2	5.9_0	18.7_6		51	7.0_6	6.8_8	18.2_4
	51	7.2_4	6.9_0	18.4_4		83	7.1_2	7.8_7	17.9_4
	83	7.1_7	7.8_7	18.0_0		121	7.4_1	9.2_8	17.7_3
	121	7.3_0	9.3_6	17.5_3		167	8.1_0	11.4_9	17.6_1
	167	7.4_3	11.7_7	16.6_6	EP23$^{(w)b}$	121	8.3_6	8.9_0	19.2_3
H52	27	6.9_7	5.8_4	18.9_3		167	7.4_5	11.0_7	17.2_1
	51	7.2_5	6.8_3	18.5_6	PEP$^{(w)}$	27	6.6_0	5.8_2	18.4_5
	83	7.1_2	7.9_6	17.8_3		51	6.7_8	6.7_4	18.0_6
	121	7.3_5	9.4_7	17.4_9		83	6.6_9	7.8_7	17.3_9
	167	7.5_0	11.9_0	16.6_5		121	6.8_8	9.3_0	17.0_7
H34$^{(w)}$	83	6.7_0	7.2_3	18.1_6		167	7.3_3	11.5_0	16.7_4
	121	6.9_3	8.7_2	17.6_9	hhPP	27	6.7_0	5.6_9	18.8_0
	167	7.4_7	10.8_9	17.3_7		51	6.9_2	6.6_0	18.4_5
H32	83	7.3_0	7.6_5	18.4_2		83	6.8_1	7.6_0	17.8_5
	121	7.4_1	9.1_6	17.8_4		121	7.0_2	9.0_1	17.5_2
	167	7.7_1	11.4_5	17.2_1		167	7.1_5	11.3_0	16.6_8
H16$^{(w)}$	121	7.0_9	8.7_8	17.8_3	50SPI	27	6.8_9	5.9_7	18.6_2
	167	7.6_5	11.0_9	17.4_2		51	7.1_2	6.9_4	18.2_4
H08	121	7.4_5	8.8_7	18.1_9		83	6.9_2	8.0_7	17.4_6
	167	7.6_5	10.9_4	17.5_4		121	7.1_0	9.6_8	17.0_0
D08	121	7.4_2	8.7_3	18.3_0		167	7.4_5	11.9_7	16.5_4
	167	7.6_2	11.0_3	17.4_4	PIB$^{(w)}$	27	5.5_2	4.8_0	18.5_8
H00$^{(w)}$	167	7.8_0	10.9_9	17.6_7		51	5.7_2	5.5_2	18.3_3
PEB	27	7.0_9	5.8_0	19.1_5		83	5.5_3	6.2_9	17.6_8
	51	6.9_2	6.5_9	18.4_5		121	5.6_8	7.4_1	17.3_8
	83	6.9_4	7.7_0	17.9_0		167	6.0_8	8.8_5	17.3_8
	121	7.1_8	9.3_0	17.4_4					
	167	7.4_5	11.7_8	16.6_8					

[a] (w) indicates results based on a reanalysis of data used originally in ref 1. [b] These samples had been designated EP*y* in ref 1, *y* in that case being weight percent ethylene. Here the number is weight percent propylene.

The fitting parameters for each model are different at low and high temperatures: in the high-temperature block, both P^* and T^* are larger for FOV and smaller for CM. Thus, neither model captures the full span of *PVT* behavior with one parameter set, but other models have similar problems,[23] and such problems are not limited to polymers alone: the *PVT* behavior of all liquids is difficult to model precisely over extended ranges. The fits in both blocks are better for CM as judged by the values of $\langle s^2\rangle_{\min}$, 1−5 MPa^2 for CM but much larger (10−20 MPa^2) for FOV. For each model and temperature block, the hard-core specific volume v^* is nearly the same for all species, the only significant exception being PIB (the low value for D08 merely reflects the higher density caused by deuteration). The reduced volume $\tilde{v}$ at each temperature is also virtually the same for all, so the isothermal variation with species of solubility parameters based on eqs 10−12 reflect primarily the variation in the characteristic pressure with species.

Results and Discussion

A. Regular Mixtures. Comparison of *PVT*-Based and SANS-Based Solubility Parameters.

Values of $(\delta - \delta_{\mathrm{ref}})_{PVT}$ for the various species are listed in Table 6. They were obtained from the results in Table 4 by subtracting δ_{PVT} for the reference species H97 from the values for the others. Values for H97 obtained with the "w" group[1] were used for the "w" species; those obtained for H97 with the later group[6−8] were used for the others. We had hoped this stratagem would compensate for the different treatments of the two groups of measurements. Unfortunately, the evaluation of $(\delta - \delta_{\mathrm{ref}})_{PVT}$ involves small differences of large numbers, so the uncertainties are large even for samples from the same group of runs. That the values of $(\delta - \delta_{\mathrm{ref}})_{PVT}$ for H34(w) and H16(w) are somewhat high relative to the trend with composition of the other H*XX* polymers, all from the latter group, is one indication that cross-group comparisons are still somewhat dubious. In forming judgments, we have weighted the results from the latter group most heavily. The relative uncertainties within that group are perhaps best indicated by the ±0.06 MPa$^{1/2}$ differences in δ_{PVT} for H08 and D08. These polymers differ only in isotopic composition and are almost certainly indistinguishable within the errors of the *PVT* measurements.

In previous work,[6−8] we found a close correspondence between SANS-based and *PVT*-based solubility parameters. A comparison of the two at 167 °C is shown in Figure 1a, $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ being taken from Table 1 and $(\delta - \delta_{\mathrm{ref}})_{PVT}$ from Table 6. A straight line through the

Table 5

A. Characteristic CM Parameters Based on Low-Temperature (50−150 °C) *PVT* Data

sample[a]	P^* (MPa)	T^* (K)	v^* (cm^3/g)	s^2 (MPa^2)	sample[a]	P^* (MPa)	T^* (K)	v^* (cm^3/g)	s^2 (MPa^2)
H97$^{(w)}$	550	4480	1.1015	5	H97	587	4203	1.0868	2
H34$^{(w)}$	630	4270	1.1127	2	H88	592	4181	1.0883	2
EP84$^{(w)}$	593	4179	1.1038	2	H66	628	4091	1.0839	2
EP76$^{(w)}$	596	4168	1.1045	1	H52	621	4122	1.0905	1
EP57$^{(w)}$	613	4203	1.1067	2	PEB	606	4217	1.0952	2
PEP$^{(w)}$	611	4339	1.1115	3	PP	575	4102	1.0975	2
PIP$^{(w)}$	677	4950	1.0593	5	hhPP	632	4245	1.0789	2
					50SPI	597	4233	1.0928	2

B. Characteristic CM Parameters Based on High-Temperature (150−250 °C) *PVT* Data

sample[a]	P^* (MPa)	T^* (K)	v^* (cm^3/g)	s^2 (MPa^2)	sample[a]	P^* (MPa)	T^* (K)	v^* (cm^3/g)	s^2 (MPa^2)
iPB$^{(w)}$	483	4742	1.1300	3	H97	496	4568	1.1137	2
H97$^{(w)}$	511	4696	1.1048	4	H88	508	4501	1.1124	2
H34$^{(w)}$	551	4570	1.1305	2	H66	527	4469	1.1124	2
H16$^{(w)}$	547	4518	1.1201	2	H52	537	4426	1.1141	1
H00$^{(w)}$	567	4324	1.1230	3	H32	555	4370	1.1185	1
EP84$^{(w)}$	518	4439	1.1246	1	H08	564	4302	1.1214	1
EP76$^{(w)}$	523	4431	1.1251	1	D08	557	4318	1.0579	1
EP57$^{(w)}$	542	4404	1.1264	4	PEB	527	4454	1.1145	1
EP23$^{(w)}$	550	4470	1.1325	2	PP	474	4520	1.1297	2
PEP$^{(w)}$	548	4504	1.1251	2	hhPP	532	4590	1.1044	2
PIB$^{(w)}$	614	5041	1.0669	4	50SPI	522	4503	1.1137	2

C. Characteristic FOV Parameters Based on Low-Temperature (50−150 °C) *PVT* Data

sample[a]	P^* (MPa)	T^* (K)	v^* (cm^3/g)	s^2 (MPa^2)	sample[a]	P^* (MPa)	T^* (K)	v^* (cm^3/g)	s^2 (MPa^2)
H97$^{(w)}$	357	6678	0.9822	20	H97	432	6275	0.9716	19
H34$^{(w)}$	452	6449	0.9971	19	H88	438	6256	0.9731	19
EP84$^{(w)}$	431	6229	0.9872	22	H66	471	6201	0.9708	18
EP76$^{(w)}$	435	6224	0.9878	22	H52	462	6230	0.9766	18
EP57$^{(w)}$	432	6348	0.9873	16	PEB	444	6332	0.9804	18
PEP$^{(w)}$	428	6448	0.9953	19	PP	432	6130	0.9801	20
PIB$^{(w)}$	427	7254	0.9513	17	hhPP	461	6413	0.9671	17
					50SPI	437	6329	0.9776	19

D. Characteristic FOV Parameters Based on High-Temperature (150−250 °C) *PVT* Data

sample[a]	P^* (MPa)	T^* (K)	v^* (cm^3/g)	s^2 (MPa^2)	sample[a]	P^* (MPa)	T^* (K)	v^* (cm^3/g)	s^2 (MPa^2)
iPB$^{(w)}$	385	7020	1.0030	14	H97	416	6859	0.9884	12
H97$^{(w)}$	409	7032	0.9829	12	H88	432	6804	0.9879	12
H34$^{(w)}$	466	6917	1.0087	13	H66	447	6797	0.9895	13
H16$^{(w)}$	465	6910	0.9988	13	H52	459	6761	0.9915	13
H00$^{(w)}$	490	6827	1.0044	11	H32	485	6724	0.9957	12
EP84$^{(w)}$	443	6736	0.9993	14	H08	474	6668	0.9977	13
EP76$^{(w)}$	449	6740	1.0000	15	D08	476	6701	0.9424	13
EP57$^{(w)}$	455	6786	0.9981	12	PEB	458	6689	0.9876	11
EP23$^{(w)}$	471	6837	1.0082	15	PP	403	6738	1.0000	14
PEP$^{(w)}$	458	6888	1.0031	11	hhPP	445	6974	0.9831	11
PIB$^{(w)}$	469	7693	0.9558	11	50SPI	444	6836	0.9900	12

[a] (w) indicates values based on a reanalysis of data used originally in ref 1.

origin describes the trend fairly well:

$$(\delta - \delta_{\text{ref}})_{PVT} = \mu(\delta - \delta_{\text{ref}})_{\text{SANS}} \qquad (14)$$

with $\mu = 1.18 \pm 0.09$ obtained from the values at 167 °C. Results for 83 °C are shown in Figure 1b, for which $\mu = 1.04$ u± 0.13 is obtained. The available results for all temperatures are shown in Figure 1c, and for this case $\mu = 1.06 \pm 0.07$. Interestingly, the ratio of these overall values, $(\delta - \delta_{\text{ref}})_{PVT}/(\delta - \delta_{\text{ref}})_{\text{SANS}} = 1.06$, is the same, within the errors, as the ratio of *PVT*-based and CED-based solubility parameters for alkanes,[17] $\delta_{\text{PVT}}/\delta_{\text{CED}} = 1.07$.

The global tracking of $(\delta - \delta_{\text{ref}})_{\text{SANS}}$ by $(\delta - \delta_{\text{ref}})_{PVT}$ even carries down reasonably well to the finer, more individual distinctions. Thus, for example, the nearly identical values of $(\delta - \delta_{\text{ref}})_{\text{SANS}}$ for PEB and H66, which have the same overall 1-butene content but differ in its sequencing, is found in $(\delta - \delta_{\text{ref}})_{PVT}$ as well, e.g., at 83 °C

$$(\delta_{\text{H66}} - \delta_{\text{PEB}})_{\text{SANS}} = -0.02\ \text{MPa}^{1/2}$$

$$(\delta_{\text{H66}} - \delta_{\text{PEB}})_{PVT} = +0.10\ \text{MPa}^{1/2}$$

The significantly different values of $(\delta - \delta_{\text{ref}})_{\text{SANS}}$ for PP and hhPP, which are geometrical isomers, is also found in $(\delta - \delta_{\text{ref}})_{PVT}$, e.g., at 83 °C

$$(\delta_{\text{hhPP}} - \delta_{\text{PP}})_{\text{SANS}} = +0.51\ \text{MPa}^{1/2}$$

$$(\delta_{\text{hhPP}} - \delta_{\text{PP}})_{PVT} = +0.60\ \text{MPa}^{1/2}$$

The borderline differences in $(\delta - \delta_{\text{ref}})_{\text{SANS}}$ for PP and H97, ideally atactic versions of polypropylene and poly(1-butene), are also found in $(\delta - \delta_{\text{ref}})_{PVT}$, e.g., at 83 °C

$$(\delta_{\text{PP}} - \delta_{\text{H97}})_{\text{SANS}} = +0.25\ \text{MPa}^{1/2}$$

$$(\delta_{\text{PP}} - \delta_{\text{H97}})_{PVT} = +0.17\ \text{MPa}^{1/2}$$

The H*XX* series of statistical enthylene/butene copolymers offers a particularly clear and interesting

Table 6. *PVT*-Based Solubility Parameters Relative to the Reference Species H97

	$\delta(T) - \delta_{\text{ref}}(T)$ (MPa$^{1/2}$)				
sample[a]	27 °C	51 °C	83 °C	121 °C	167 °C
iPB$^{(w)}$					-0.2_1
H97	0	0	0	0	0
H88	0.0_5	0.1_7	0.2_7	0.2_7	0.36
H66	0.5_9	0.6_8	0.9_2	0.8_4	0.8_0
H52	0.7_6	0.8_0	0.7_5	0.8_0	0.7_9
H34$^{(w)}$			1.7_8	1.8_5	1.5_0
H32			1.3_4	1.1_5	1.3_6
H16$^{(w)}$				1.9_9	1.5_5
H08				1.4_9	1.6_8
D08				1.6_1	1.5_8
H00$^{(w)}$					1.8_0
PEB	0.9_8	0.6_9	0.8_2	0.7_5	0.8_2
PP	0.2_0	0.2_6	0.1_7	-0.0_9	0.0_1
EP84$^{(w)}$	1.4_6	1.3_3	1.1_6	1.2_4	0.8_1
EP76$^{(w)}$	1.1_5	1.2_2	1.1_6	1.3_7	0.7^5
EP57$^{(w)}$	1.3_8	1.3_5	1.5_6	1.8_9	1.7_4
EP23$^{(w)}$					1.3_4
PEP$^{(w)}$	1.2_6	1.1_7	1.0_1	1.2_3	0.8_7
hhPP	0.6_3	0.6_9	0.7_7	0.8_3	0.8_2
50SPI	0.4_5	0.4_8	0.3_8	0.3_1	0.6_8
PIB$^{(w)}$	1.3_9	1.3_4	1.3_0	1.5_4	1.5_1

[a] (w) indicates values based on a reanalysis of data used originally in ref 1.

comparison. In earlier work,[7] we showed that the composition dependence of $(\delta - \delta_{\text{ref}})_{\text{SANS}}$ for the H*XX* series could be described rather accurately by the equation

$$(\delta_{\text{H}XX} - \delta_{\text{ref}}) = (\delta_{\text{H100}} - \delta_{\text{ref}}) + (\delta_{\text{H00}} - \delta_{\text{ref}})(1 - y)(1 + \gamma y) \quad (15)$$

in which $y = XX/100$ is the weight (or volume) fraction of 1-butene units. At 167 °C, the fitting parameters for the SANS-based assignments are[7]

$$(\delta_{\text{H100}} - \delta_{\text{ref}})_{\text{SANS}} = -0.06 \pm 0.02\ \text{MPa}^{1/2} \qquad \text{atactic poly(1-butene)}$$

$$(\delta_{\text{H00}} - \delta_{\text{ref}})_{\text{SANS}} = 1.5 \pm 0.02\ \text{MPa}^{1/2} \qquad \text{linear polyethylene}$$

$$\gamma_{\text{SANS}} = 0.47 \pm 0.07$$

The *PVT*-based values for the H*XX* series at 167 °C are shown in Figure 2. The fit of these data to eq 15, shown by the solid curve, gives

$$(\delta_{\text{H100}} - \delta_{\text{ref}})_{PVT} = -0.10 \pm 0.08\ \text{MPa}^{1/2} \qquad \text{atactic poly(1-butene)}$$

$$(\delta_{\text{H00}} - \delta_{\text{ref}})_{PVT} = 1.85 \pm 0.11\ \text{MPa}^{1/2} \qquad \text{linear polyethylene}$$

$$\gamma_{PVT} = 0.51 \pm 0.24$$

The uncertainties are larger for the *PVT*-based results, but the curvature γ_{PVT} is still significant, and it agrees rather well with γ_{SANS}. The ratio of *PVT*-based and SANS-based values for linear polyethylene, $(\delta_{\text{H00}} - \delta_{\text{ref}})_{\text{SANS}} = 1.23 \pm 0.08$, agrees within the errors with the results for all species in Figure 1a at 167 °C, $\mu = 1.18 \pm 0.09$ (eq 14).

From these several comparisons, it is evident that the values of $(\delta - \delta_{\text{ref}})_{PVT}$, derived from measurements on the pure components alone, correspond quite dependably, albeit with more experimental uncertainty, to the values of $(\delta - \delta_{\text{ref}})_{\text{SANS}}$, the latter having been assigned on the basis of mixing behavior alone. In the following, we discuss the species dependence where SANS data are not available, on the basis of *PVT* properties alone.

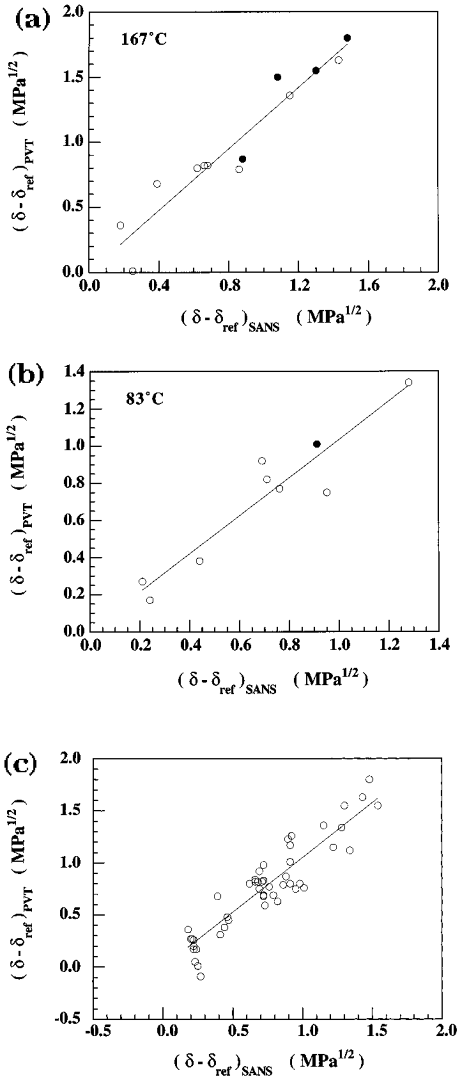


Figure 1. Comparison of solubility parameters from *PVT* measurements (Table 6) with SANS-based values (Table 1): (a) 167 °C; (b) 83 °C; (c) all temperatures. Filled symbols indicate $(\delta - \delta_{\text{ref}})_{PVT}$ obtained with data from ref 1.

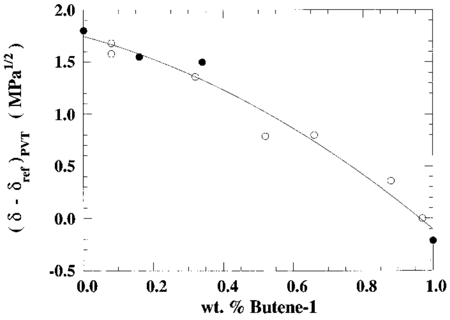


Figure 2. Solubility parameters based on *PVT* data for ethylene−butene statistical copolymers at 167 °C. Filled symbols indicate results obtained with data from ref 1.

Solubility Parameters and the Characteristic Pressure. No SANS data are available for blends that contain iPP, iPB, and members of the EP*XX* series, but we can use *PVT*-derived properties to estimate their locations on the solubility parameter scale. Several are crystallizable, so we use $(\delta - \delta_{\text{ref}})_{PVT}$ only at 167 °C. Also $f(\tilde{v})$ in eq 10 is essentially the same for all species (except PIB) at each temperature, so P^* and δ_{PVT} are equivalent

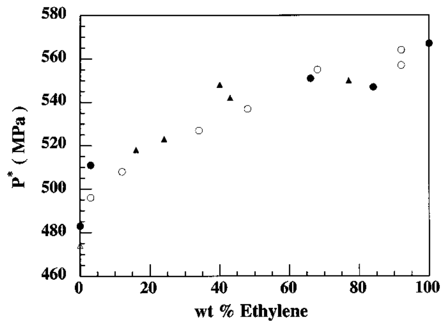


Figure 3. Characteristic pressure (FOV model) as a function of ethylene content for ethylene–propylene and ethylene–butene copolymers. Circles indicate the EB copolymers, triangles indicate the EP copolymers, and filled symbols indicate results obtained with data from ref 1.

for comparison purposes. Thus, we also use P^*, as obtained by the high-temperature fits (Table 5B for CM and Table 5D for FOV), as a correlating parameter.

As noted earlier, isotactic and atactic polypropylene have nearly the same values of P^* (408 and 412 MPa, respectively, for an FOV fit[1]). The PP result here, $P^* = 403$ MPa (Table 5D), supports that result. Apparently, tacticity has little effect on the solubility parameter of polypropylene. The effect of tacticity also appears to be small for poly(1-butene). Thus, at 167 °C, $(\delta_{\mathrm{iPB}} - \delta_{\mathrm{ref}})_{PVT} = -0.2$ MPa$^{1/2}$ from Table 6, and $(\delta_{\mathrm{H100}} - \delta_{\mathrm{ref}})_{PVT} = -0.10 \pm 0.08$ MPa$^{1/2}$ from the fit in Figure 2, so the difference between the isotactic and atactic values is barely significant and certainly small. The comparison of PEP with EP57, both amorphous copolymers of ethylene and propylene with about the same average composition but different sequencing, is more ambiguous. The values of $(\delta - \delta_{\mathrm{ref}})_{PVT}$ for the two are essentially the same at 27 °C but rather different at 167 °C, while the P^* values are very close for both the low- and high-temperature fits.

Some useful information can be drawn from a comparison of P^* values for the H*XX* series (statistical ethylene/1-butene copolymers) and the EP*XX* series (statistical ethylene/propylene copolymers). The P^* values from CM fits (Table 5B) are shown as a function of ethylene content in Figure 3. Aside from some apparent inconsistencies at low ethylene contents—PP (EP100) seems low relative to the EP*XX* trend and also lower than expected relative to H97 (Talble 1)—the values of P^* for both series scatter around a single curve. The solubility parameter appears to depend only on the weight fraction of ethylene in its copolymers with either propylene or 1-butene. It would be interesting to know whether the dependence on weight fraction or equivalently volume fraction, rather than mole fraction for example, would also apply to higher α-olefin comonomers.

Homopolymers and Small-Molecule Analogs. Several species in the study are homopolymers—PE or H00 (linear polyethylene), PP (atactic head-to-tail polypropylene), hhPP (atactic head-to-head polypropylene), H100 (atactic poly(1-butene)), and PIB (polyisobutylene). The PEP (ethylene-*alt*-propylene) and PEB (ethylene-*alt*-1-butene) species are like homopolymers in the sense of being substantially uniform in structure along the chain, so for purposes of discussion, we include them as well. These seven species are listed in Table 7 in descending order of assigned solubility parameter at 167 °C. The values are $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ for all except PIB, for which $(\delta - \delta_{\mathrm{ref}})_{PVT}$ is used.

Some trends with homopolymer structure, such as the decrease in solubility parameter with increasing side group size, are fairly clear. Thus, polyethylene has the largest value, which for polypropylene is considerably smaller, and smaller still for polybutene. The progression from polyethylene to poly(ethylene-*alt*-propylene) to poly(ethylene-*alt*-1-butene) is similar. The successive differences also decrease:

$$(\delta_{\mathrm{PE}} - \delta_{\mathrm{PP}} = 1.23) > (\delta_{\mathrm{PP}} - \delta_{\mathrm{PB}} = 0.31)$$

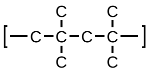
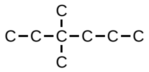
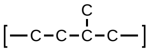
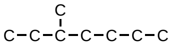
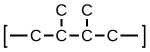
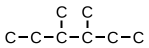
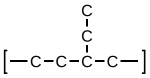
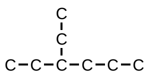
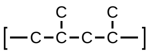
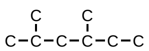
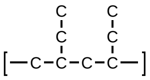
$$(\delta_{\mathrm{PE}} - \delta_{\mathrm{PEP}} = 0.60) > (\delta_{\mathrm{PEP}} - \delta_{\mathrm{PEB}} = 0.22)$$

Thus, for regular mixing, the mutual solubility of α-olefin homopolymers increases with increasing size of their side groups. For component molecular weights of about 10^5 and temperatures about 200 °C, an approximate criterion for miscibility of blends that mix regularly is

$$|\delta_2 - \delta_1| < 0.3\ \mathrm{MPa}^{1/2}$$

Accordingly, polyethylene would be strongly immiscible with all α-olefin homopolymers, while blends of polypropylene and polybutene would be borderline. It also appears that side groups on the same or adjacent skeletal carbons can differ significantly in their effects on the solubility parameter from the effects of more widely spaced side groups. Thus, head-to-head polypropylene and head-to-tail propylene have the same size group size and frequency, yet their solubility parameters are significantly different, $\delta_{\mathrm{hhPP}} - \delta_{\mathrm{PP}} = 0.42$ MPa$^{1/2}$. Also, PIB has twice the methyl group frequency of PP,

Table 7. Comparison of Solubility Parameters for Polyolefin Homopolymers and Structurally Similar Octane Isomers

homopolymer species	skeletal C_4 unit	$(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ (MPa$^{1/2}$)	C_8 alkane	$(\delta - \delta_{\mathrm{ref}})_{\mathrm{CED}}$ (MPa$^{1/2}$)
PE	$[\!-\!C\!-\!C\!-\!C\!-\!C\!-\!]$	1.48	$C\!-\!C\!-\!C\!-\!C\!-\!C\!-\!C\!-\!C\!-\!C$	0.97
PIB	 $[\!-\!C\!-\!\overset{C}{\underset{C}{C}}\!-\!C\!-\!\overset{C}{\underset{C}{C}}\!-\!]$	1.25	 $C\!-\!C\!-\!\overset{C}{\underset{C}{C}}\!-\!C\!-\!C\!-\!C$	1.23
PEP	 $[\!-\!C\!-\!C\!-\!\overset{C}{C}\!-\!C\!-\!]$	0.88	 $C\!-\!C\!-\!\overset{C}{C}\!-\!C\!-\!C\!-\!C\!-\!C$	0.61
hhPP	 $[\!-\!C\!-\!\overset{C}{C}\!-\!\overset{C}{C}\!-\!C\!-\!]$	0.67	 $C\!-\!C\!-\!\overset{C}{C}\!-\!\overset{C}{C}\!-\!C\!-\!C$	0.61
PEB	 $[\!-\!C\!-\!C\!-\!\overset{\overset{C}{C}}{C}\!-\!C\!-\!]$	0.66	 $C\!-\!C\!-\!\overset{\overset{C}{C}}{C}\!-\!C\!-\!C\!-\!C$	0.62
PP	 $[\!-\!C\!-\!\overset{C}{C}\!-\!C\!-\!\overset{C}{C}\!-\!]$	0.25	 $C\!-\!\overset{C}{C}\!-\!C\!-\!\overset{C}{C}\!-\!C\!-\!C$	0.25
PB	 $[\!-\!C\!-\!\overset{\overset{C}{C}}{C}\!-\!C\!-\!\overset{\overset{C}{C}}{C}\!-\!]$	-0.06		

yet the solubility parameter is larger for PIB rather than smaller.

Interestingly, these patterns of structural dependence are even found in the isomers of C_8 alkanes. Cohesive energy densities for the C_8 isomers[17a] that most resembled the various homopolymer skeletal structures in Table 7 were used with eq 5 to calculate δ_{CED}. No C_8 equivalent for the polymeric reference species (H97 ~ PB) was available, so we chose a value for δ_{ref} that forced a match with $(\delta - \delta_{ref})_{SANS} = 0.25$ MPa$^{1/2}$ for PP. The results are shown in Table 7. Note that, apart from PIB, the polymeric values of $(\delta - \delta_{ref})_{SANS}$ and the C_8 values of $(\delta - \delta_{ref})_{CED}$ are ordered in the same way. Thus, the PE analog has the largest value, followed by the PEP, hhPP, and PEB analog and then the analog for PP. Even the subtleties of side group adjacency (hhPP vs PP) and "abnormal" positioning (PIB) show up in the C_8 results. Such polymeric-C_8 parallels suggest to us that the interactions in blends that mix regularly are controlled by local structural attributes and that packing on larger scales of chain distance has little to do with mutual solubility. These parallels also offer some hope that computer simulations of even analogs in the range of C_{30} may yield useful and perhaps even quantitative information on interactions in polymer blends that mix in a regular fashion.

B. Irregular Mixtures. The extra interaction strengths, $X_E(T)$, for 14 component pairs that do not mix in a regular fashion are given in Table 2. The first five have positive values, meaning that the interactions are more unfavorable to mixing than expected from the SANS-based solubility parameters of the components. The remaining nine have negative values, indicating that mixing is more favored than expected. The X_E magnitudes are also much larger for these blends, but the total interaction strength $X(T)$ is positive except for the four that contain PB. We note in passing two general characteristics of the irregular blends being considered here. First, their components are mainly homopolymers, i.e., structurally regular as defined previously. Eight of the 14 are homopolymer–homopolymer blends, six are homopolymer–copolymer blends, and none are blends of two copolymers. Second, the absolute value of X_E diminishes with temperature for all 14 irregular blends.

Equation-of-state contributions to the free energy and volume changes on mixing were estimated with equations based on FOV theory[24] for the irregular blends. The prescribed recipes for calculating enthalpy, entropy, and volume changes were followed; values of X_{12}[29] in the plausible range had negligible effect on the results. The composition dependences were roughly of the conventional $\phi_1\phi_2$ form, so the interaction strength X_{EOS} was evaluated as $(h_{EOS} - Ts_{EOS})/\phi_1\phi_2$, where h_{EOS} and s_{EOS} are the enthalpy and entropy values per unit volume of blend at $\phi_1 = \phi_2 = 0.5$. Values of X_{EOS} and the volume change on mixing, $(\Delta v/v)_{EOS}$ at $\phi_1 = \phi_2 = 0.5$, are listed in Table 8. Both negative and positive volume changes are predicted, but all are very small in magnitude ($|\Delta v/v| < 0.001$ in all cases) and near the limit of detection by even very careful density measurements.[9,28] The predicted X_{EOS} values are positive for all 14 blends and hence unfavorable to mixing. At 83 °C they are comparable in magnitude to the corresponding X_E for the first five blends. The disagreements are larger at 167 °C, and of course the predictions of X_{EOS} for the other eight blends are qualitatively inconsistent with the observation of large negative values for X_E.

Table 8. Blend Volume Change and the EOS Contribution to Interaction Strength Calculated with the FOV Method

	83 °C[a]		167 °C[b]	
blend	$(\Delta v/v)_{EOS}$ $\times 10^4$	X_{EOS} (MPa) $\times 10^2$	$(\Delta v/v)_{EOS}$ $\times 10^4$	X_{EOS} (MPa) $\times 10^{-2}$
hhPP/PEP	2.4	21 (0.8)[c]	0.6	9.4 (−0.1)[c]
PEB/H66	0.7	2.4 (1.9)	0.2	1.7 (1.4)
PEB/hhPP	−0.4	8.1 (3.8)	~0	11 (3.5)
H66/hhPP	~0	6.2 (1.7)	−0.3	4.2 (0.2)
PP/H97	−0.2	2.9 (2.7)	−0.8	1.9
PP/hhPP	−3.0	11 (−19)	−4.0	7.2
PP/PEP	1.6	1.1 (−28)	0.5	0.1 (−22)
PEP/H100	3.7	5.3 (−42)	1.9	2.6 (−40)
PEP/H08			~0	0.3 (−14)
H08/H100			3.0	5.2 (−102)
PIB/H52	−8.6	49		
PIB/H66	−7.9	54 (−53)		
PIB/hhPP	−5.2	23 (−56)	−7.3	35 (−43)

[a] Calculated with FOV model with P^*, T^*, and v^* obtained by FOV fits of pure component data in the lower temperature range (Table 5B). [b] Calculated with FOV model and FOV fits in the higher temperature range (Table 5D). [c] Values in parentheses are the experimental values of X_E, taken from Table 2.

Patterson and Robard[30] separate blend interactions into a contact term, which it seems natural to associate with regular mixing, and a free volume term X_{FV}, which corresponds with what we have called X_{EOS}. They used the following expression for estimating the free volume contribution for blends in which the differences in P^* and T^* for the components are small:

$$X_{FV} = \frac{3P^*\tilde{T}}{2}\left(\frac{\tilde{v}^{1/3}}{4 - 3\tilde{v}^{1/3}}\right)\frac{(T_2^* - T_1^*)^2}{T_1^* T_2^*} \qquad (16)$$

in which P^*, $\tilde{T}$, and $\tilde{v}$ represent averages of the component values. Values of X_{FV} from this equation, like those obtained with the full FOV formulas in Table 8, are always positive. It seems highly unlikely therefore that equation-of-state or free volume effects have any connection at all with the negative values of X_E that we have found in most of the irregular blends.

Although equation-of-state theories seemingly cannot, as presently constituted, provide a general explanation for irregular mixing, there nevertheless are patterns, or at least tendencies, among the irregular blend results which suggest that the difference in component characteristic temperature, $\Delta T^* = |T_2^* - T_1^*|$, plays some role in irregularity. Thus, we note the following observations:

(a) When ΔT^* is relatively small, the interaction strength is dominated by $\Delta P^* = |P_2^* - P_1^*|$. The components mix regularly, $X_E \approx 0$, and the solubility parameter scheme works.

(b) When ΔP^* is relatively small, large values of ΔT^* lead to irregular mixing with $X_E > 0$. The single phase is destabilized, as expected for an equation-of-state effect.

(c) When both ΔP^* and ΔT^* are large, the components mix irregularly, but now $X_E < 0$, so the single phase is stabilized.

To obtain the most reliable tracking, we based these observations on values of P^* and T^* from the CM fits (Table 5A for results at 83 °C, and Table 5C for 167 °C), omitting all results from the earlier "(w)" runs except those for PIB, which had been confirmed separately.[9] The majority of blends mix regularly and conform to the first observation. The first five blends lised in Table 2 are roughly consistent with the second observation. The remainder are, for the most part, consistent with the third observation.

This attempt at generalization has no theoretical basis, but it provides at least some general rationale for the fact that, for example, pairs of the H*XX* series with adjacent compositions mix regularly, while the H08/H100 pair mixes irregularly. Thus, the values of P^* and T^* are found to change monotonically with butene content, but in opposite directions. Adjacent compositions therefore have relatively small ΔT^*, so $X_E \approx 0$. However, ΔT^* and ΔP^* are both large for the H08/H100 pairing, and X_E is large and negative as the generalizations above would suggest. The PIB blends also fit the pattern.[9] Values of ΔT^* are very large for all of them since T^* for PIB is anomalously large, and PIB is also effectively immiscible with species having a similar solubility parameter, i.e., where ΔP^* is relatively small. However, PIB does have a window of miscibility with other species, such that ΔP^* lies within some range of moderately large values. The density and also T^* for hhPP, although still well below the anomalously large values of both these properties for PIB,[9] are at the top of their ranges for the other polyolefins, so perhaps the tendency of hhPP to mix irregularly with other species (Table 2) is some attenuated reflection of whatever produces the strange mixing characteristics of PIB.

Summary and Concluding Remarks

In this work we have examined the relationship between mixture interactions and mechanical properties (*PVT*) of the pure components for numerous species of saturated hydrocarbon polymers. We showed earlier that SANS-derived interaction strengths for most of these blends can be usefully organized by means of a solubility parameter formalism. Relative values of the solubility parameter, $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$, were assigned and confirmed as self-consistent for nearly all the species. Some component pairs, however, mix irregularly in the sense that the interaction strength differed significantly from the solubility parameter prediction. The effect of the irregularity itself ranged from strongly stabilizing to mildly destabilizing with respect to a single liquid phase. The relative solubility parameters derived from interaction strengths were shown to be consistent with values determined independently from the *PVT* measurements, thus paralleling the close correspondence between cohesive energy density and internal pressure for nonpolar monomeric liquids. Even the trends with rather subtle variations in molecular structure were found to be similar for the homopolymers and their alkane homologs.

Parallels were also noted between $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ and the characteristic pressure, the latter obtained by fitting the *PVT* data to equation-of-state (EOS) models. It is also possible that EOF contributions to the free energy of mixing generates the destabilizing irregularities, but not the larger and certainly more interesting irregularities that favor the single phase. For those, we are left with some tantalizing observations suggesting that stabilization is accompanied by large differences between components in both characteristic temperature and pressure. The search for other explanations for mixing irregularity have so far been unsuccessful. Thus, for example, we noted in earlier work[8] an excellent correlation between the statistical segment length of a polymer and its solubility parameter but no correlation at all with mixing irregularity.

In considering possible sources of mixing irregularity, it is important to recall that regular mixing and the solubility parameter concept, when applied to polymers, rely in a rather delicate way on Berthelot's conjecture about the contact energies:[16] $\epsilon_{12} = -(\epsilon_{11}\epsilon_{22})^{1/2}$. A convenient way to parameterize departures from this geometric mean rule is to replace the equality with a proportionality, $\epsilon_{12} = -\lambda(\epsilon_{11}\epsilon_{22})^{1/2}$. Translating that to solubility parameter language[8] with eq 4 gives

$$X = (\delta_1 - \delta_2)^2 + (1 - \lambda)\delta_1\delta_2 \qquad (17)$$

The solubility parameters for saturated hydrocarbon polymers lie in a narrow range, 15.5–19.0 MPa$^{1/2}$ (Table 4), and the solubility parameter difference for regular mixing, $M \sim 10^5$ and $T_c \sim 200$ °C, is about 0.3 MPa$^{1/2}$. Thus, with typical magnitudes,

$$\mathrm{X} \sim 0.1 + 300(1 - \lambda) \qquad (\mathrm{MPa}^{1/2}) \qquad (18)$$

Accordingly, the geometric mean rule must be correct to about one part in 30 000 ($|1 - \lambda| = 1/30\,000$) in order to approximate regular mixing (<10% contribution from the second term in eq 17). Considering both the tenuous foundation for this geometric mean rule[31,32] and the exquisite sensitivity of total interaction strength to any departures, it is remarkable that confirmed examples of regular mixing are ever found in polymeric blends. Thus, for example, the largest positive value of X_E in Table 2 (PP/H97 at 27 °C) corresponds to $1 - \lambda = 3 \times 10^{-4}$ and the largest negative value (H08/H100 at 121 °C) at $1 - \lambda = -4.5 \times 10^{-3}$: both are so small that even minute adjustments in local packing could easily produce them. Interestingly, in the nonpolar mixtures for which the geometric mean rule has been examined,[32] the departures have all been positive ($\lambda > 1$). Thus, the stabilizing irregularities that we find in blends of nonpolar polymers are apparently unprecedented.

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