Thermodynamics of Mixing for Statistical Copolymers of Ethylene and α-Olefins

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ABSTRACT: The melt-state interactions that govern phase behavior in polyolefin blends were evaluated by small-angle neutron scattering (SANS) and compared with earlier results for structurally similar model polymers. The materials are statistical copolymers of ethylene with a range of propylene, 1-butene, 1-hexene, and 1-octene contents, made by metallocene catalysis. They are modestly polydisperse ($M_w/M_n \sim 2$) and not available in deuterated form, thus requiring modification of the procedures used for the nearly monodisperse and easily deuterated model polymers. The SANS intensity expression for polydisperse components was confirmed independently, and two experimental procedures, employing binary and ternary blends with deuterated model components, were used. The interactions obey a solubility-parameter formalism, in agreement with the earlier studies. Moreover, the values of $\delta - \delta_{ref}$ obtained for the α-olefin copolymers were found to depend only on w, the weight fraction of α-olefin comonomer. Finally, this $\delta - \delta_{ref}$ vs w relationship is the same as that found earlier for model copolymers with different side-chain sequencing, indicating that variations in comonomer sequencing have little effect on the mutual solubility of statistical olefin copolymers.

Introduction

Over the past several years we have been investigating the thermodynamic interactions that govern liquid−liquid phase behavior in the blends of saturated hydrocarbon polymers. The aim is an improved understanding of polyolefin blends, but until now we have used mostly *model polyolefins*, materials made by saturating the double bonds of nearly monodisperse polydienes.[1] Structural uniformity and relative ease of labeling with deuterium makes the model materials especially convenient for methods based on small-angle neutron scattering (SANS),[2] our primary means for evaluating the interactions. Those features permitted an extensive exploration of the effects of labeling on the interaction strength, leading to methods for correcting the SANS-derived interactions of purely hydrogenous and partially deuterated components to those for the more relevant case of purely hydrogenous components.[3−5] They also allowed various tests to be made of the Flory−Huggins expression for the free energy of mixing, confirming it to be a reliable framework for quantifying the interactions in the midrange of compositions for saturated hydrocarbon polymer blends.[6−10] Finally, the interaction strengths for a large majority of these blends were found to obey a solubility-parameter formalism.[7,9] However, many examples of inconsistency with that formalism were also observed, including even in some cases a net attraction between components.[11,12] Current work includes molecular dynamics simulations, seeking some microscopic understanding of such diverse sorts of behavior.[13,14]

In this paper we describe an extension of the study to polyolefins that are made in direct fashion, by the copolymerization of ethylene with various α-olefins, propylene, 1-butene, 1-hexene, and 1-octene. The polymerizations were conducted with metallocene catalysts, single-site systems that can produce copolymers that are statistically more uniform in microstructure and narrower in molecular weight distribution than the products of conventional multisite catalysts.[15] One reason for doing this work is to test how well the model polyolefin results apply to *real polyolefins*. Thus, for example, extensive data are already available for model ethylene−butene copolymers, made by hydrogenating polybutadienes of various 1,2 (vinyl) contents.[8] The sequencing of ethyl branches along the chain will certainly be different for real ethylene−butene copolymers, and the question is whether such differences matter. That is, do the mixing characteristics of the two series differ when compared at the same overall ethyl branch content? Including real polyolefins also offers the possibility of expanding the range of structures in the database. The effects of *n*-butyl and *n*-hexyl branches can be determined in this way, for example, whereas obtaining such structures by the polydiene route would be awkward at best.

Although the statistical uniformity of the metallocene-derived polyolefins is probably adequate for quantitative work, such polymers do suffer two significant disadvantages relative to the model materials: they are polydisperse ($M_w/M_n \sim 2$), and there is no practical way to produce structurally matched labeled and nonlabeled pairs.[1] How these problems were handled is explained in the three parts of the Results and Discussion. The first part describes the outcome of a test for adequacy of the SANS scattering equations for blends of polydisperse components. The second describes the results for binary blends of the olefin copolymers with labeled model materials, interpreted through the solubility-

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Table 1. Polyolefin Characterization Data

sample	$10^{-4} \times M_w$	M_w/M_n	ρ(g cm^{-3})[a]	T_m (°C)[b]
EP13	7.1	2.2	0.9088	104
EP15	7.2_5	2.1	0.9024	95
EP53[c]	15.1	2.0	0.8529	~25
EB10	10.5	2.0	0.9061	110
EB14	7.6_5	1.9	0.9026	103
EB16	9.5	2.0	0.8966	98
EB17	9.9_5	2.0	0.8942	94
EB22	10.8	1.9	0.8831	87
EB27	7.9	1.9	0.8799	80
EB31	5.8	2.0	0.8680	71
EH7	9.3	2.2	0.9213	122
EH10	7.7	2.2	0.9179	121
EH13	10.1	1.9	0.9082	110
EH18	7.6_5	2.0	0.8962	106
EH37	19.9	2.4	0.8702	~114
EH40	17.1	2.1	0.8572	~60
EH43	16.9	2.2_5	0.8549	~54
EH46	12.7	2.1_5	0.8533	~40
EO22	9.4	2.3	0.8969	116
EO43	20.2	2.5_5	0.8738	~128
EO51	14.3	2.2_5	0.8546	~55
EO54	15.9	2.3_5	0.8540	~45

[a] Measured at 23 °C. [b] Final melting temperature. [c] Sample JBG-11.

Table 2. Model Polymer Characterization Data

sample	$10^{-4} \times M_w$	ρ (g cm^{-3})[a]	n_D[b]	n_C[c]	T_m (°C)[d]
H08 (D08)	6.2_5	0.9165	3.6	4	113
H17 (D17)	12.4	0.8878	3.0	4	84
H25 (D25)	9.6_5	0.8798	3.5_5	4	68
H32 (D32)	9.6_5	0.8643	2.7_5	4	60
H35 (D35)	7.8	0.8589	3.4_5	4	56
H38 (D38)	10.2	0.8598	3.0_5	4	42
H52 (D52)	8.5	0.8604	2.8_5	4	
HPEP (DPEP)	8.8	0.8540	5.1_5	5	
HhhPP (DhhPP)	2.7	0.8726	3.9_5	6	

[a] Measured at 23 °C. [b] Average number of deuterium atoms per monomeric unit. [c] Number of carbon atoms per monomeric unit. [d] Final melting temperature.

Table 3. Model Polydisperse Components and Characteristics

component	$10^{-4} \times M_w$	W_i[b]
1	2.1_5	0.299
2	4.6_5	0.200
3	6.5	0.202
4	12.9	0.149
5	18.2	0.150

polydisperse sample	$10^{-4} \times M_w$	M_w/M_n	M_z/M_w	n_D[c]	n_C[d]
PH08 or PD08	7.5	1.7_5	1.5_5	3.7	4

[a] Molecular weight of model polybutadiene precursor adjusted for hydrogenation: $M_w = (M_w)_{PBD} \times 56/54$. [b] Weight fraction in the precursor mixture. [c] Number of deuterium atoms per monomeric unit in PD08. [d] Number of carbon atoms per monomeric unit.

parameter formalism but including various tests of consistency with the formalism. The third describes the use of ternary blends, each consisting of two olefin copolymers and a labeled model polymer, to obtain olefin copolymer interaction strengths without invoking the solubility-parameter formalism.

Experimental Section

The metallocene-derived polyolefins are statistical copolymers of ethylene with the comonomers propylene (EP), 1-butene (EB), 1-hexane (EH), or 1-octene (EO). Individual samples are designated EP*xx*, EB*xx*, EH*xx*, or EO*xx* in which *xx* is weight percent of the comonomer. The samples were provided by Exxon Chemical Co. along with their comonomer contents, as determined by high-temperature ^{1}H NMR, and their molecular weight distributions, as obtained by means of size exclusion chromatography (SEC) and a polyethylene calibration. The density at 23 °C was determined with a density-gradient column.[1] The melting temperature was obtained by differential scanning calorimetry at a heating rate of 10 °C/min. An ethylene-propylene statistical copolymer, synthesized by Ziegler−Natta catalysis, was also included in the study. Here designated EP53, it is the well-characterized sample JBG-11 used in an earlier study of viscoelasticity and molecular weight distribution.[16] The characterization data are given in Table 1.

Characterization data for the deuterium-labeled model polyolefins used in the study are listed in Table 2. Most are model ethylene−butene copolymers, made by catalytically deuterating the double bonds of polybutadienes of various vinyl contents. Samples D17, D25, D32, D35, D38, and D52 were used in earlier studies,[8] but D08 is a new sample. Sample DhhPP, a deuterated head-to-head polypropylene, was also used in an earlier study,[5] while DPEP is a new sample of the deuterated ethylene−propylene alternating copolymer. All polydiene precursors were nearly monodisperse ($M_w/M_n \lesssim 1.05$) according to SEC. Molecular weights of the precursors were determined by dilute solution light scattering measurements.[1] Previous work has shown that the saturation reaction does not alter the large-scale molecular architecture.

A model polydisperse precursor was prepared by saturating a mixture of five nearly monodisperse polybutadienes having the same 8% vinyl microstructure but different molecular weights. A matched pair, HP08 and DP08 (labeled and unlabeled samples having the same molecular architecture), was obtained in the usual way, by saturating separate aliquots of the polybutadiene mixture with hydrogen and deuterium.[1] The molecular weights of the five components, obtained by SEC as calibrated with 8% vinyl polybutadiene samples of known molecular weight and then adjusted for hydrogenation, are given in Table 3 along with their weight fractions in the mixture and various other characteristics of the mixture.

The SANS measurements were conducted on both the 8 m (NG5) and 30 m (NG7) beamlines at the NIST Cold Neutron Research Facility in Gaithersburg, MD. Blend preparation, experimental procedures, and data reduction to obtain $I_c(q)$, the coherent SANS intensity as a function of scattering vector magnitude, are described elsewhere.[1] All blends were prepared with equal component volume fractions, $\phi_i = 0.50$ for the binary blends and $\phi_i = 0.33$ for the ternaries. The measurements were conducted at temperatures above the melting temperature of all components.

Analysis of SANS Data. The coherent SANS intensity profile is related to the structure factor of a single-phase blend through the expression[2,17]

$$I_c(q) = \mathbf{B}^T \cdot \mathbf{S}(q) \cdot \mathbf{B} \tag{1}$$

in which **B** is a column vector describing the scattering length contrast among components and **S**(*q*) is the structure factor matrix. The random phase approximation relates **S**(*q*) for a blend to $\mathbf{S}_o(q)$, the “bare” (interactionless) structure factor matrix of the blend, and **V**, a matrix that describes the interactions:

$$\mathbf{S}^{-1}(q) = \mathbf{S}_o^{-1}(q) + \mathbf{V}(q) \tag{2}$$

Both **B** and **S** are scalars for a binary blend, and

$$B = \left(\frac{b_1}{v_1} - \frac{b_2}{v2}\right) \tag{3}$$

in which $(b/v)_i$ is the SANS scattering length density for component *i*. Thus,

$$I_c(q) = \left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2 S(q) \qquad (4)$$

With the Flory–Huggins mixing model, eq 2 leads to the following expression for components of arbitrary polydispersity:[17–19]

$$\frac{1}{S(q)} = \frac{\rho_1}{\phi_1 F_1(u_1)} + \frac{\rho_2}{\phi_2 F_2(u_2)} - \frac{2X_{12}}{RT} \qquad (5)$$

in which R is the universal gas constant, T is the temperature, ρ_i is the mass density of component i in its fully hydrogenous form, ϕ_i is the volume fraction of component i in the blend, and for linear polymers,

$$F_i(u_i) = \int_{\mathrm{o}}^{\infty} M\, P(u_i M)\, W_i(M)\, \mathrm{d}M \qquad (6)$$

in which $W_i(M)$ is the weight distribution function for the hydrogenous version of species i and $P(u_i M)$ is the form factor for monodisperse random-coil linear polymers:

$$P(u_i M) = \frac{2}{(u_i M)^2}[\exp(-u_i M) - 1 + u_i M] \qquad (7)$$

$$u_i = q^2 \left(\frac{R_g^{\,2}}{M}\right)_i \qquad (8)$$

The ratio $(R_g^2/M)_i$ is the chain dimensions coefficient for polymer species i, X_{12} is the interaction density coefficient for the species pair, $\chi = v_o X_{12} RT$ is the Flory parameter for the pair, and v_o is an arbitrary reference volume that sets the magnitude of χ.

For ternary blends,[17]

$$\mathbf{B} = \left\|\begin{matrix} \dfrac{b_1}{v_1} - \dfrac{b_3}{v_3} \\ \dfrac{b_2}{v_2} - \dfrac{b_3}{v_3} \end{matrix}\right\| \qquad (9)$$

$$\mathbf{S}^{-1}(q) = \left\|\begin{matrix} \left(\dfrac{\rho_1}{\phi_1 F_1(u_1)} + \dfrac{\rho_3}{\phi_3 F_3(u_3)} - \dfrac{2X_{13}}{RT}\right) & \left(\dfrac{\rho_3}{\phi_3 F_3(u_3)} + \dfrac{X_{12} - X_{13} - X_{23}}{RT}\right) \\ \left(\dfrac{\rho_3}{\phi_3 F_3(u_3)} + \dfrac{X_{12} - X_{13} - X_{23}}{RT}\right) & \left(\dfrac{\rho_2}{\phi_2 F_2(u_2)} + \dfrac{\rho_3}{\phi_3 F_3(u_3)} - \dfrac{2X_{23}}{RT}\right) \end{matrix}\right\| \qquad (10)$$

in which the various ρ_i, ϕ_i, X_{ij}, and $F_i(u_i)$ are defined as described above for the binary blends.

The working equations, eqs 4 and 5 for binary blends and eqs 1, 9, and 10 for ternaries, are direct adaptations from equations that are expressed in terms of numbers of monomeric units.[17–19] If ρ_i, ϕ_i, $(b/v)_i$, and W_i(M) are known, the equations relate the SANS profile to the chain dimensions coefficient of the components and the interaction density coefficient of the pairs: $(R_g^2/M)_1$, $(R_g^2/M)_2$, and X_{12} for the binaries; $(R_g^2/M)_1$, $(R_g^2/M)_2$, $(R_g^2/M)_3$, X_{12}, X_{13}, and X_{23} for the ternaries. For matched-pair binaries, $(R_g^2/M)_1 = (R_g^2/M)_2$ and $X_{12} = X_{HD}$, so R_g^2/M for the species and the isotopic interaction coefficient X_{HD} (usually small) are obtained. For binaries of different species and with matched-pair results for each, the only new fitting parameter is X_{12}. However, we generate a second "goodness-of-fit" parameter by permitting $(R_g^2/M)_1$ and $(R_g^2/M)_2$ to float from their matched pair values by a common scale factor α, judging the quality of fit by the closeness of α to unity.[1] This is the procedure used to test the model polydisperse results in part A of the Results and Discussion.

Binaries consisting of a labeled model polymer and a nonlabeled olefin copolymer are discussed in part B. The value of R_g^2/M for the model component is known from matched-pair results, so X_{12} and R_g^2/M for the olefin copolymer are the SANS fitting parameters. Ternaries consisting of a labeled model polymer and two nonlabeled olefin copolymers are discussed in part C. In this case all three values of R_g^2/M are known, from matched-pair data for the model polymer and from the binary blends data for the olefin copolymers. Two of the three values of X are also known from the binaries; the only unknown is the interaction density coefficient for the olefin copolymer pair, which is accordingly the only adjustable parameter for the ternary SANS data.

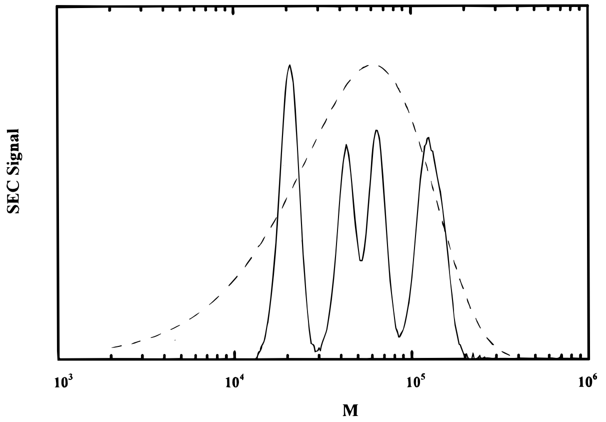

Figure 1. Observed SEC trace for the polybutadiene precursor of the HP08–DP08 model polydisperse polymer (solid line) and the predicted trace for its Zimm–Schulz representation (dashed line).

In each blend, values of the adjustable parameters were assigned by a least-squares, full q-range fit of the coherent SANS profile.[1] As in the earlier studies, most data were obtained in the intermediate scattering regime ($qR_g > 1$). Only the results for blends in the single-phase state, the existence of which having been established according to criteria described earlier,[1] were used in the analysis.

Results

A. Model Polydisperse Polymer. The SANS data for HP08/DP08, a matched pair mixture ($\phi = 0.5$) for the model polydisperse polymer, were interpreted by means of eqs 5–8 to obtain X_{HD} and R_g^2/M for the H08 species. The data in Table 3 were used to model the molecular weight distribution in two ways, as a sum of five monodisperse components with the listed molecular weights and weight fractions and as a Zimm–Schulz distribution[19] having the listed values of M_n and M_w. For linear polymers with a Zimm–Schulz distribution,

$$F_i(u_i) = \frac{2}{\xi_i}\left[\left(\frac{h_i}{h_i + \xi_i}\right)^{h_i} - 1 + \xi_i\right] \qquad (11)$$

in which $h_i = [M_n/(M_w - M_n)]_i$ and $\xi_i = (M_n)_i u_i$.

The SEC curve for the polybutadiene precursor of H08 is compared in Figure 1 with a prediction based on its Zimm–Schulz representation ($h = 1.33$). The shapes are obviously quite different, but as shown in Table 4, the monodisperse-sum and Zimm–Schulz representations lead to values of both X_{HD} and R_g^2/M that differ hardly at all. The values for the polydisperse HP08/DP08 pair are also consistent with the results obtained with nearly monodisperse components.[21] Thus, the values of X_{HD} from both HP08/DP08 and H08/D08 are small, and the values of R_g^2/M they provide are the same within the experimental uncertainties.[1]

A further examination of polydispersity effects was conducted with blends of different species. Results for HP08/D25 and DP08/H25 blends were compared with

Table 4. Matched-Pair and Blend Results for Polydisperse and Monodisperse Model Polymers

	$T = 118$ °C			$T = 142$ °C			$T = 167$ °C		
blend	R_g^2/M^a	α	X^b	R_g^2/M^a	α	X^b	R_g^2/M^a	α	X^b
Polydisperse Model Component									
HP08/DP08									
monodisperse sum fit	0.224		1.00	0.204		0.80	0.195		0.50
Zimm−Schulz fit	0.223		0.90	0.205		0.70	0.195		0.50
HP08/D25									
monodisperse sum fit		0.99	5.90		1.01	5.20		1.00	4.50
Zimm−Schulz fit		1.00	5.60		0.99	5.10		0.98	4.30
DP08/H25									
monodisperse sum fit		1.02	4.30		1.02	3.70		1.01	3.20
Zimm−Schulz fit		1.01	4.50		0.99	3.70		0.98	3.00
Nearly Monodisperse Model Component									
H08/D08									
monodisperse fit	0.208		1.80	0.202		1.60	0.199		1.50
H08/D25									
monodisperse fit		∼1	6.20		∼1	5.40		∼1	4.00
H08/D25									
monodisperse fit		∼1	4.30		∼1	3.60		∼1	3.00

[a] In units of Å^2. [b] In units of MPa × 10^2.

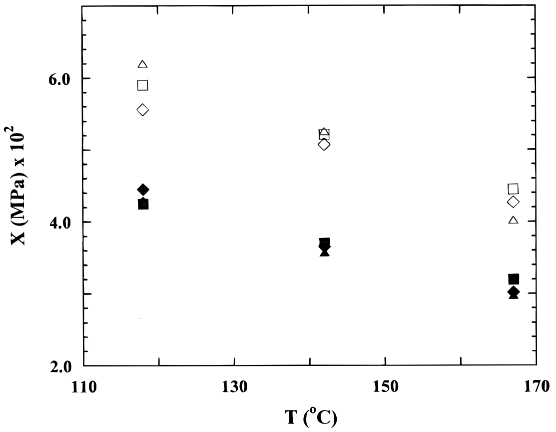

Figure 2. Interaction density coefficient vs temperature for H08/D25 and D08/H25 blends. The various symbols indicate results for nearly monodisperse components,[5,21] H08/D25 (△) and D08/H25 (▲); for blends containing the model polydisperse polymer represented as a monodisperse sum fit, HP08/D25 (◇) and DP08/H25 (◆); and for blends containing the model polydisperse polymer represented by a Zimm−Schulz distribution, HP08/D25 (□) and DP08/H25 (■).

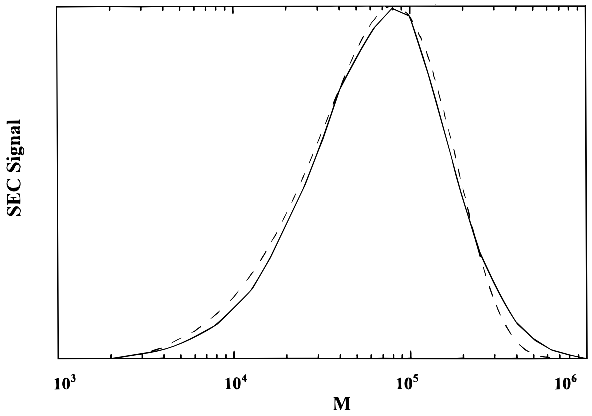

Figure 3. Observed SEC trace for an EP32 polyolefin (solid line) and the predicted trace for a Zimm−Schulz representation of its molecular weight distribution (dashed line).

results for H08/D25 and D08/H25 blends,[5,21] and sensitivity to polydispersity modeling was again tested. The values obtained for interaction density coefficient X and size ratio α are listed in Table 4. The values of α for blends containing HP08 and DP08 are close to unity and thus are consistent with results obtained in earlier studies for many blends of nearly monodisperse components. As shown in Figure 2, the values of X for HP08/D25 blends agree very well with those from H08/D25 blends, and similarly for the DP08/H25 and D08/H25 comparison. Differences in values obtained due to differences in molecular weight distribution modeling are likewise insignificant. From these results at least it would appear that component polydispersity, if modeled in a physically reasonable manner, introduces no inherent limitation to SANS methods for the evaluation of either thermodynamic interaction density or component chain dimensions.

B. Polyolefin Binary Blends. Blends consisting of a nearly-monodisperse, partially deuterated model component and the hydrogenous polyolefin component were used in an attempt to establish a self-consistent database of relative solubility parameters for ethylene−α-olefin copolymers. The methods parallel those in the earlier work with binary blends of model components.[7−9] They are, however, made somewhat more complicated here owing to the lack of matched polyolefin pairs (labeled and nonlabeled versions with identical macromolecular structure). We noted early in the study that interaction strength for the blend was generally small if the model component and the polyolefin had similar comonomer *weight fractions*. Minimizing the interaction strength makes the SANS results more sensitive to the component chain dimensions coefficients. As a result, given the matched-pair value of R_g^2/M for the model component, it was possible to obtain a fairly accurate estimate of R_g^2/M for the polyolefin. Chain dimensions obtained in this way (from "pseudo" matched pairs) were then used to evaluate X for the more strongly interacting mixtures of model and polyolefin components.

In the SANS analyses the polyolefins were represented by Zimm−Schulz distributions with the values of M_w and M_w/M_n given in Table 1 (see eq 11). Figure 3 indicates good agreement between the SEC data for the distribution of another polyolefin made by metallocene catalysis ($M_w = 83\,100$ and $M_w/M_n = 1.7$ from SEC−light scattering data for EP32, the polyolefin used for the comparison) and the corresponding SEC prediction for a Zimm−Schulz distribution. The model polymers were represented in the usual way, as being monodisperse and having the values of $M = M_w$ given in Table

Table 5. Chain Dimensions Parameter for Various Polyolefin Species from the SANS Data for Pseudo-Matched-Pair Mixtures

		R_g^2/M (Å^2)			
polyolefin	mixture	118 °C	142 °C	167 °C	196 °C
EP13	EP13/D17	0.257	0.252	0.244	0.247
EP15	EP15/D17	0.231	0.235	0.240	0.243
EP53	EP53/D52	0.170	0.176	0.173	0.174
EB10	EB10/D08	0.220	0.212	0.211	0.212
EB14	EB14/D08	0.232		0.242	0.254
EB16	EB16/D17	0.202	0.199	0.196	0.195
EB17	EB17/D17	0.208	0.206	0.209	0.210
EB22	EB22/D25	0.206		0.198	0.193
EB27	EB27/D25	0.152	0.155	0.150	
EB31	EB31/D32	0.165		0.161	0.158
EH07	EH07/D08		0.247	0.259	0.261
EH10	EH10/D08		0.278	0.264	0.265
EH13	EH13/D17	0.211	0.208	0.210	0.215
EH18	EH18/D17	0.246	0.258	0.266	0.273
EH37	EH37/D38	0.154		0.138	0.141
EH40	EH40/D38	0.142		0.155	0.167
EH43	EH43/D38	0.136		0.147	0.155
EH46	EH46/D52	0.149		0.137	0.137
EO22	EO22/D17	0.258	0.256	0.257	0.262
EO43	EO43/D38		0.159	0.159	0.168
EO51	EO51/D52	0.163		0.162	0.167
EO54	EO54/D52	0.141		0.135	0.140

2. The chain dimensions coefficient for the various polyolefins from the SANS data for their pseudo matched pair at four temperatures (118, 142, 167, and 196 °C) are listed in Table 5. The corresponding values of interaction density coefficient X for these as well as for the more strongly interacting blends are listed in Table 6. Values of R_g^2/M and X at lower temperatures were also obtained in a few cases and are reported elsewhere.[22,23] The temperature dependence of interaction strength for these various blends is unremarkable, being either insensitive to temperature or decreasing slowly with increasing temperature, as illustrated by the examples in Figure 4.

The interaction data in Table 6 were used to assign solubility parameters to the various polyolefin components. Thus, according to the solubility parameter hypothesis, the interaction density coefficient can be expressed as follows:

$$X_{12} = (\delta_1 - \delta_2)^2 \qquad (12)$$

in which δ_i is a physical property of pure component i called the solubility parameter. In our case, the components consist of a partially deuterated model polymer D1 and a fully hydrogenous polyolefin H2. Solubility parameters relative to a common reference material (the H97 species) have already been assigned to the fully hydrogenous versions of the model polymers, by finding values of $\delta_{H1} - \delta_{ref}$ for each that satisfy eq 12 for a highly overdetermined set of model component pairs.[10,21] We applied that method to the same database of interactions[21] to obtain $\delta_{D1} - \delta_{ref}$, the solubility parameter relative to the same reference material for the partially deuterated model polymers of interest here. The results are given in Table 7; they indicate $\delta_H > \delta_D$ with $(\delta_H - \delta_D)_{avr} = 0.023$ MPa$^{1/2}$. Equation 12 can be expressed as

$$\delta_{H2} - \delta_{ref} = \delta_{D1} - \delta_{ref} \pm (X_{D1/H2})^{1/2} \qquad (13)$$

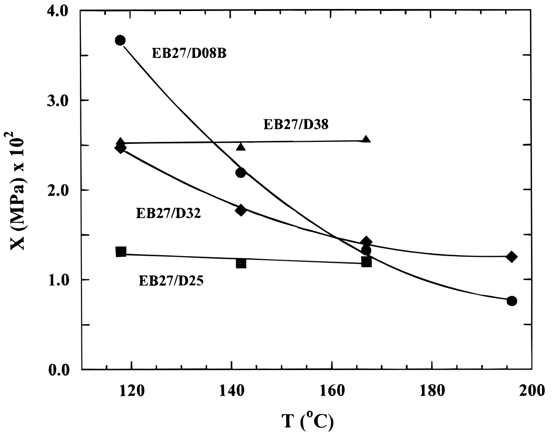

Figure 4. Interaction density coefficient vs temperature for selected blends of polyolefins with model polymers.

in which $X_{D1/H2}$ is the interaction density coefficient for the model polymer/polyolefin blend (Table 6) and the ± indicates the ambiguity in square-root sign. With the values of $\delta_{D1} - \delta_{ref}$ given in Table 7, and the values of $X_{D1/H2}$ for blends of a polyolefin polymer with two or more model polymers, the sign ambiguity can be removed, and the feasibility of identifying a unique solubility parameter for each polyolefin and temperature can be tested.

The tests of self-consistency for the polyolefin EB31 are shown in Table 8. Values of $\delta_{EB31} - \delta_{ref}$ were calculated from eq 13 with both + and − signs for each of several model polymers. Those results make it clear that δ_{EB31} lies between δ_{D17} and δ_{D38}. Furthermore, when the appropriate signs are chosen, excellent agreement is found among the various values obtained from blends of EB31 with different model polymers. Similar behavior was found for the other polyolefins. The self-consistent relative solubility parameters evaluated in this way are given at four temperatures in Table 9.

C. Ternary Blends. A total of 24 ternary blends were investigated, each consisting of two polyolefins and a labeled model polymer. All but two of these (EH37/D25/EH46 and EO22/D17/EO43) were single-phase over at least some part of the available temperature range. Values of X for the polyolefin pair were obtained from the SANS data for each single-phase ternary, as described previously. In four of the polyolefin pairs (EP13/EB31, EB31/EH07, EB31/EH10, and EB31/EO22) the interactions were determined with two different model polymers, as tests for third component sensitivity. All ternary results are listed as observed values of X in Table 10. Also listed there are values of X predicted with eq 12 and the solubility parameters in Table 9.

On the basis of error considerations in the SANS evaluation of interaction strength,[1,21] we estimate the uncertainty in interaction density coefficient to be approximately $\pm 0.5 \times 10^{-2}$ MPa. From Table 10, the values of X that are obtained by the ternary method employing different model polymers are within that uncertainty for all four cases, indicating no significant third component effect. The difference between X predicted by the solubility parameters in Table 9 and the value observed in the ternary blends is displayed graphically in Figure 5. The differences are spread uniformly and symmetrically about zero, and no trend with the strength of the interaction is apparent. The average difference for all blends and temperatures, $|\Delta|_{ave}$, is 0.53×10^{-2} MPa. It would appear that the

Table 6. Interaction Density Coefficient for Blends of Various Polyolefin Species with Model Polymers

	$10^{-2}X$ (MPa)					$10^{-2}X$ (MPa)			
blend	118 °C	142 °C	167 °C	196 °C	blend	118 °C	142 °C	167 °C	196 °C
Ethylene−Propylene Copolymers									
EP13/D08	0.81	0.52	0.70	0.67	EP15/D25		2.35	1.81	1.10
EP13/D17	1.63	0.97	0.57	0.60	EP15/D32			4.93	3.79
EP13/D25		1.75	1.99	1.47	EP53/D35	1.55	1.13	0.95	0.67
EP13/D32		5.02	4.50	4.00	EP53/52	0.98	0.92	0.87	0.74
EP15/D08		1.05	0.99	0.47	EP53/DPEP	1.83	1.47	1.23	1.18
EP15/D17	1.85	1.81	0.46	−0.17	EP53/DhhPP	7.84	7.14	6.72	6.43
Ethylene−Butene Copolymers									
EB10/D08	1.20	0.98	0.57	0.34	EB22/D08	4.34	3.10	2.32	1.78
EB10/D17	2.54	2.22	1.82	1.59	EB22/D25	0.73		0.35	0.35
EB10/D25	PS[a]	4.22	3.67	2.93	EB22/D32	2.10	1.82	1.53	1.43
EB14/D08	−0.81		−1.30	−0.89	EB22/D38	PS	4.48	4.41	3.92
EB14/D17	3.80	3.52	3.19	2.60	EB27/D08	3.67	3.23	2.33	1.84
EB14/D25	6.26	5.53	5.07	4.73	EB27/D25	1.31	1.18	1.20	
EB16/D08	0.24	0.07	0.26	0.25	EB27/D32	2.47	1.77	1.42	1.25
EB16/D17	1.09	0.97	0.99	1.13	EB27/D32	4.55	3.88	3.46	
EB16/D25	3.34	2.08	1.42	1.35	EB31/D08	PS	7.84	6.66	4.86
EB16/D32	PS	4.64	3.90	3.35	EB31/D17	2.04	1.26	0.91	0.56
EB17/D08	0.84	0.49	0.41	0.35	EB31/D32	1.23		0.87	0.77
EB17/D17	0.63	0.51	0.49	0.41	EB31/D38	1.82	1.43	1.21	1.33
EB17/D25	5.30	4.90	4.14	3.84	EB31/D52	PS		7.44	
EB17/D35	PS	PS	PS	4.37					
Ethylene−Hexene Copolymers									
EH07/D08		0.98	0.75	0.52	EH37/D38	2.73		2.11	2.00
EH07/D17		3.30	2.52	1.74	EH37/D52	3.91		4.00	4.13
EH07/D25		4.52	3.59	2.63	EH40/D25	PS		3.53	3.24
EH10/D08		1.23	1.17	0.23	EH40/D32	2.58		1.43	1.21
EH10/D17		1.78	1.12	1.13	EH40/D38	1.85		1.57	1.22
EH13/D08	2.22	2.10	1.86	1.58	EH40/D52	PS		3.52	3.15
EH13/D17	1.05	0.65	0.38	0.23	EH43/D32	PS		2.35	1.87
EH13/D32	PS	3.12	2.78	2.81	EH43/D35	1.87	1.50	1.27	1.03
EH18/D08	2.91	2.30	1.61	1.20	EH43/D38	1.21		0.75	0.53
EH18/D17	0.49	0.25	−0.01	−0.15	EH43/D52	2.89		2.57	2.08
EH18/D32	3.87	3.71	3.40	2.85	EH46/D35	2.15	1.87	1.68	1.21
EH18/D35	PS	5.63	4.68	4.13	EH46/D52	3.11		2.76	2.53
EH37/D25	PS		2.70	2.20	EH46/DPEP	2.62		2.10	1.93
Ethylene−Octene Copolymers									
EO22/D08	2.80	2.41	2.05	1.58	EO51/35	1.72	1.35	0.90	0.57
EO22/D17	0.41	−0.17	−0.28	−0.33	EO51/D52	3.18		2.31	2.01
EO22/D32	4.08	3.31	2.88	2.41	EO51/DPEP	PS		2.21	1.54
EO22/D35	PS	5.94	5.70	5.22	EO54/D32	PS	PS	3.51	2.80
EO43/D25		3.26	2.92	2.54	EO54/D38	2.89		2.21	1.51
EO43/D32		1.05	0.85	0.52	EO54/D52	2.21		1.54	0.95
EO43/D38		0.71	0.47	0.41	EO54/DPEP	PS		2.51	1.93
EO51/32	PS	2.63	1.70	1.08					

[a] Phase-separated.

Table 7. Relative Solubility Parameters for Model Polymers

	$\delta - \delta_{\text{ref}}$ (MPa$^{1/2}$)			
polymer	$T = 118$ °C	$T = 142$ °C	$T = 167$ °C	$T = 196$ °C
D08	1.53 (1.60)[a]	1.46	1.40 (1.48)	1.32
D17	1.33 (1.37)	1.29	1.24 (1.30)	1.19
D25	1.28 (1.31)	1.25	1.21 (1.23)	1.16
D32	1.19 (1.22)	1.15	1.11 (1.15)	1.07
D35	1.12 (1.13)	1.10	1.07 (1.07)	1.03
D38	1.09 (1.11)	1.05	1.02 (1.05)	0.98
D52	0.89 (0.91)	0.87	0.85 (0.86)	0.82
DPEP	0.87 (0.89)	0.86	0.84 (0.88)	0.83
DhhPP	0.72 (0.72)	0.69	0.66 (0.67)	0.63

[a] Value in parentheses is $\delta - \delta_{\text{ref}}$ for the fully hydrogenous version.[10]

solubility parameter formalism describes the interactions of ethylene-rich olefin copolymers very well indeed.

Discussion

A. Interaction Density Coefficient. Having found the polyolefin interactions to obey a solubility parameter scheme, we searched for a relationship between the solubility parameters and polyolefin microstructure. Two of the possibilities are tested in Figure 6. In Figure 6a the values of $\delta - \delta_{\text{ref}}$ for all the ethylene copolymers at 167 °C are plotted as a function of the *weight percent* of comonomer; in Figure 6b the same values are plotted as a function of the *mole percent* of comonomer. Data for different comonomers fall along a common line in Figure 6a but are displaced from one another in Figure 6b. Results at the other temperatures are similar, so the solubility parameters for ethylene copolymers in this range of compositions evidently depend primarily on the weight fraction of comonomer. Weight fraction is equivalent to volume fraction in the copolymers of ethylene with higher α-olefins, so the interactions behave like other thermodynamic properties of polymer blends, such as the combinatorial entropy, in depending primarily on volume fractions as opposed, for example, to mole fractions.

The dependence of solubility parameter on comonomer weight fraction for the ethylene−butene polyolefins are compared with those for model ethylene−butene

Table 8. Resolution of the Sign Ambiguity and Relative Solubility Parameter Assignment for the Polyolefin EB31 Example

		$\delta_{\rm EB31} - \delta_{\rm ref}$ (MPa$^{1/2}$)			
blend	condition[a]	T = 118 °C	T = 142 °C	T = 167 °C	T = 196 °C
EB31/D08	$\delta > \delta_{\rm model}$		1.74	1.66	1.54
	$\delta < \delta_{\rm model}$		**1.18**[b]	**1.14**	**1.10**
EB31/D17	$\delta > \delta_{\rm model}$	1.47	1.40	1.34	1.26
	$\delta < \delta_{\rm model}$	**1.19**	**1.18**	**1.14**	**1.12**
EB31/D38	$\delta > \delta_{\rm model}$	**1.22**	**1.17**	**1.13**	**1.10**
	$\delta < \delta_{\rm model}$	0.96	0.93	0.91	0.86
EB31/D52	$\delta > \delta_{\rm model}$			**1.10**	
	$\delta < \delta_{\rm model}$			0.86	

[a] Assumption in applying eq 13. [b] Values in bold are the internally consistent assignments.

Table 9. Relative Solubility Parameters for the Polyolefins

	$\delta - \delta_{\rm ref}$ (MPa$^{1/2}$)			
polyolefin	T = 118 °C	T = 142 °C	T = 167 °C	T = 196 °C
Ethylene−Propylene Copolymers				
EP13	1.44	1.38	1.33	1.26
EP15	1.43	1.37	1.32	1.26
EP53	1.00	0.98	0.95	0.92
Ethylene−Butene Copolymers				
EB10	1.49	1.45	1.39	1.33
EB14	1.53	1.48	1.43	1.36
EB16	1.47	1.39	1.33	1.27
EB17	1.43	1.38	1.32	1.26
EB22	1.32	1.27	1.24	1.19
EB27	1.32	1.27	1.23	1.18
EB31	1.21	1.18	1.14	1.11
Ethylene−Hexene Copolymers				
EH07		1.47	1.40	1.32
EH10		1.42	1.35	1.30
EH13	1.38	1.32	1.27	1.21
EH18	1.37	1.33	1.28	1.23
EH37	1.09		1.05	1.02
EH40	1.03		1.01	0.98
EH43	1.02	0.99	0.97	0.93
EH46	0.96	0.96	0.95	0.92
Ethylene−Octene Copolymers				
EO22	1.38	1.32	1.28	1.23
EO43		1.06	1.03	1.00
EO51	0.99	0.99	0.98	0.96
EO54	0.92		0.91	0.90

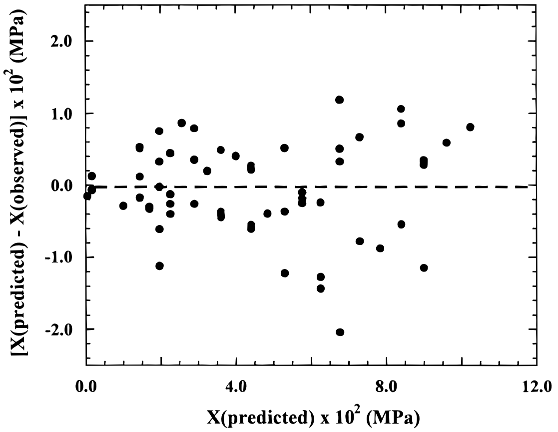

Figure 5. Difference between ternary blend values and solubility parameter predictions of interaction density coefficient in relation to the interaction strength.

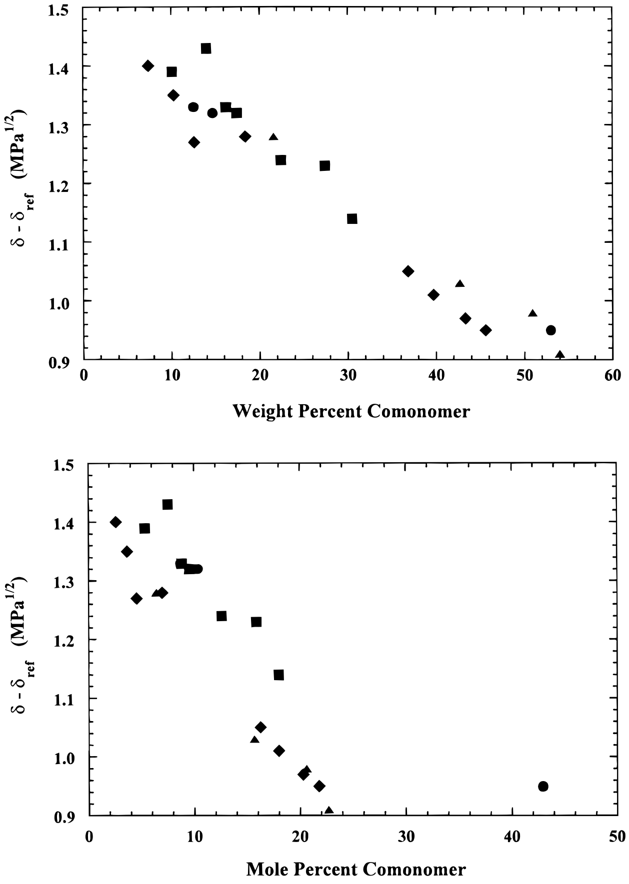

Figure 6. (a) Relative solubility parameter for ethylene copolymers at 167 °C as a function of the weight percent of the α-olefin comonomer. The various symbols refer to ethylene−propylene copolymers (●), ethylene−butene copolymers (■), ethylene−hexene copolymers (◆), and ethylene−octene copolymers (▲). (b) Relative solubility parameter for ethylene copolymers at 167 °C as a function of the mole percent of α-olefin comonomer. The symbol references are the same as in (a).

copolymers (hydrogenated polybutadienes[8,10]) in Figure 7. Over the available range of compositions the dependence of $\delta - \delta_{\rm ref}$ for the two copolymer types is essentially indistinguishable. The data in Figure 7 were all obtained at 167 °C, but the agreement between olefin copolymers and model copolymers holds at other temperatures as well. It is interesting that the inevitable differences in sequencing among these various copolymer species have such little effect on the thermodynamic interactions.

The dashed line in Figure 7 was calculated with an empirical equation[8] fitted to the model ethylene−butene copolymer results at 167 °C:

$$\delta - \delta_{\rm ref} = 1.51(1 - w)(1 + 0.47\,w) - 0.06 \quad (14)$$

in which w is the weight fraction of comonomer units. The parameters of this equation for other temperatures

Table 10. Interaction Density Coefficient for Polyolefin Pairs Determined with SANS Data for Ternary Blends and Predicted by Relative Solubility Parameters

		$10^{-2}X$ (MPa)							
		T = 118 °C		T = 142 °C		T = 167 °C		T = 196 °C	
polyolefin pair	model polymer	predicted	observed	predicted	observed	predicted	observed	predicted	observed
EP13/EB31	D17	5.3	6.5			3.6	4.1	2.3	2.5
	D32	5.3	5.7			3.6	4.0	2.3	2.1
EB31/EH07	D08			8.4	7.4	6.8	5.6	4.4	4.2
	D17			8.4	7.6	6.8	6.3	4.4	5.0
EB31/EH10	D08			5.8	5.9	4.4	4.2	3.6	3.1
	D17			5.8	6.0	4.4	5.0	3.6	4.0
EB31/EO22	D08					2.0	2.6	1.4	2.0
	D32	2.9	3.2			2.0	3.1	1.4	1.6
EP13/EH10	D17			0.2	∼0	0.0	0.2	0.2	0.2
EP15/EB31	D17	4.8	5.2			3.2	3.0	2.3	2.7
EP15/EH40	D32	16.0	PS[a]			9.6	PS	7.8	8.7
EB14/EB31	D17	10.2	11.1	9.0	10.2	8.4	9.0	6.3	7.5
EB14/EH18	D17	2.6	1.7			2.3	1.8	1.7	2.0
EB27/EH07	D08			4.0	3.6	2.9	2.1	2.0	1.2
EB31/EH13	D08					1.7	2.0	1.0	1.3
EB31/EH18	D08					2.0	1.6	1.4	0.9
EH13/EO43	D32			6.8	6.4	5.8	5.9	4.4	4.1
EH18/EH43	D35					9.6	9.1	9.0	8.7
EH18/EO51	D35	14.4	PS			9.0	8.7	7.3	6.6
EH37/EH46	D25		PS		PS		PS		PS
EH37/EO54	D38	2.9	2.5			2.0	2.0	1.4	1.3
EH40/EO22	D32	12.3	PS			7.3	8.1	6.3	7.7
EO22/EO43	D17		PS		PS		PS		PS
	D32			6.8	8.8	6.3	6.5	5.3	4.8

[a] PS means phase separated.

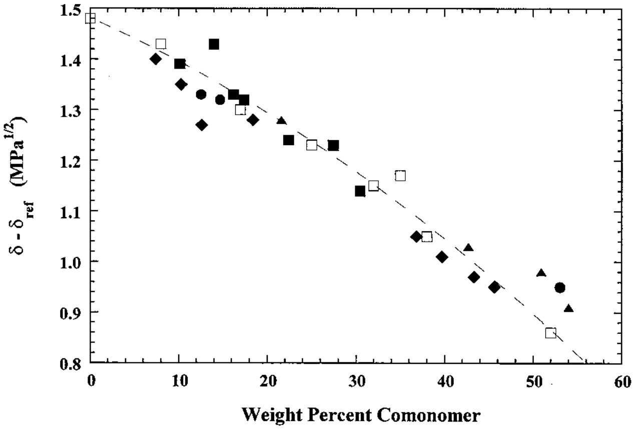

Figure 7. Comparison of solubility parameters for the ethylene copolymers at 167 °C with those for model ethylene–butene copolymers. The filled symbols refer to the ethylene copolymers as defined in Figure 6a; the open squares (□) refer to the model copolymers[8] (hydrogenated polybutadienes). The dashed line is the correlating equation for the model copolymers at 167 °C (eq 14).

are given in ref 8. Evidently, such equations can be used just as well to describe the data for the ethylene–propylene, ethylene–butene, ethylene–hexene, and ethylene–octene copolymers over the range of comonomer fractions, $0 < w < 0.5$.

B. Chain Dimensions Parameter. Effects of polyolefin structure on the chain dimensions parameter R_g^2/M are examined in Figure 8. The values are plotted as a function of weight percent comonomer in Figure 8a and of mole percent comonomer in Figure 8b. In contrast with the solubility parameter correlation, mole percent unifies the results for the various comonomer species fairly well, and weight percent is much inferior. The widely divergent value in Figure 8b is that for EP53, the only product of Ziegler–Natta catalysis that had been included in the study. It is not clear why EP53

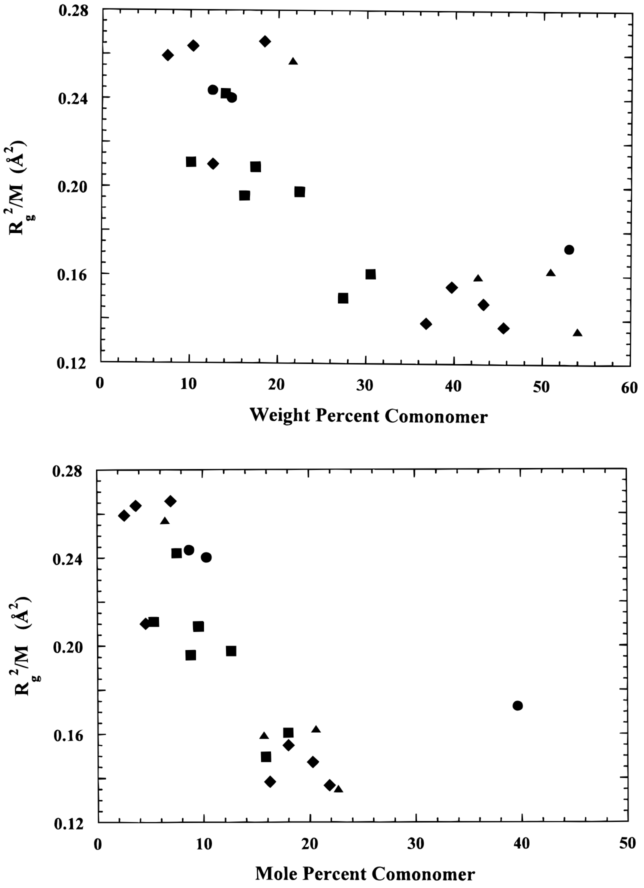

Figure 8. (a) Chain dimensions parameter for the ethylene copolymers at 167 °C as a function of the weight percent of α-olefin comonomer. The symbols refer to ethylene–propylene copolymers (●), ethylene–butene copolymers (■), ethylene–hexene copolymers (◆), and ethylene–octene copolymers (▲). (b) Chain dimensions parameter for the ethylene copolymers at 167 °C as a function of the mole percent of α-olefin comonomer. The symbol references are ther same as in (a).

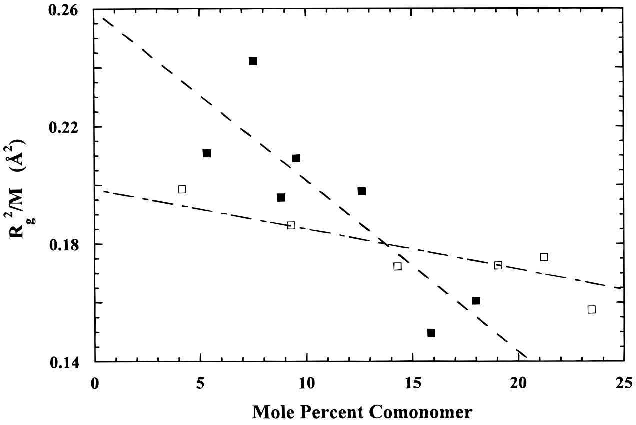

Figure 9. Comparison of chain dimensions parameter for the metallocene-derived ethylene−butene copolymers at 167 °C with those for model ethylene−butene copolymers. The filled symbols (■) refer to the copolymers from metallocene catalysis; the open symbols (□), to the model copolymers[8] (hydrogenated polybutadienes).

should differ in size so much from the others, since its solubility parameter, for example, is not at all unusual. There is another feature of the size behavior, however, that casts some doubt on all the polyolefin values of R_g^2/M obtained in this study. Thus, Figure 9 compares R_g^2/M vs mole percent for the copolymers of ethylene and butene with those for the model ethylene−butene copolymers[8] (hydrogenated polybutadienes). Although somewhat obscured by the scatter in the data, the trends with comonomer content appear to be rather different for the two types. Even more disturbingly, they extrapolate to values of R_g^2/M for the polyethylene limit (zero comonomer) that differ by about 30%.

We have been unable to resolve this inconsistency. Systematic errors in the molecular weight determination for polyolefins would need to be unreasonably large to account for even a part of this discrepancy, i.e., doubling the input M_w, for example, reduces the resulting R_g^2/M by only about 8% (EB10/D08). Representing the distribution by the Zimm−Schulz form might introduce some error as well, but the model polydisperse results would seem to indicate insensitivity to that aspect as well. Thus, we are compelled to leave this annoying discrepancy unresolved. The multitude of internal checks on the interaction density coefficients for polyolefin blends, however, lead us to believe that those results at least are valid.

Conclusions

The interaction density coefficients determined as functions of temperature by SANS for approximately 80 blends of polyolefins with deuterated model polymers were shown to be consistent with a solubility-parameter formalism. Consistency of the assignments of relative solubility parameter, $\delta - \delta_{\text{ref}}$, was further confirmed for the 22 polyolefin components by the SANS results on 24 ternary blends, showing the predicted and observed interaction strengths for polyolefin pairs to agree within the experimental uncertainties. The solubility-parameter values were found to vary in a systematic way with the polyolefin microstructure. Thus, $\delta - \delta_{\text{ref}}$ for this collection of ethylene-rich copolymers decreases smoothly with increasing comonomer content, and for all comonomers investigated (propylene, 1-butene, 1-hexene, 1-octene) the values of $\delta - \delta_{\text{ref}}$ depend only on the weight fraction of comonomer. Finally, the agreement between this relationship and the data for model ethylene−butene copolymers indicates that differences in the monomeric unit sequencing along the chain have little effect on the interactions of statistical olefin copolymers.

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