Thermodynamic Interactions in Multicomponent Polymer Blends

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ABSTRACT: Small-angle neutron scattering (SANS) was used to probe the thermodynamic interactions in multicomponent polymer blends including ternary blends containing two homopolymers and a block copolymer, mixtures of a homopolymer and a block copolymer, and a blend of two block copolymers. The polymers used for this study were model polyolefins—poly(ethylbutylene) and poly(methylbutylene) homopolymers and a poly(ethylbutylene)-*block*-poly(methylbutylene) copolymer. SANS profiles from homogeneous blends were measured over a wide range of blend composition, component molecular weights, and temperature. The Flory−Huggins interaction parameters, χ, in multicomponent mixtures were obtained from comparisons between the SANS data and theoretical predictions based on the multicomponent random phase approximation (RPA). At all temperatures, the multicomponent χ parameters were independent of blend composition, molecular weight and molecular architecture of the components. They were thus within experimental error of those obtained from binary homopolymer blends. All our measurements on this system are in agreement with the Flory−Huggins theory of polymer blends.

Introduction

Polymer blends are of considerable scientific and commercial interest. Several blends of commercial importance are multicomponent in nature. In some cases, chemical species are created inadvertently due to the nonspecificity of polymerization reactions and unavoidable side reactions. Commercial polyethylenes, which consist of a variety of branched and linear molecules, are examples of such blends. Most commercial polymers have wide molecular weight distributions. Hence, blends of two commercial polymers are inherently multicomponent in nature. In other cases, the properties of a polymeric product are optimized by alloying it with other components. A well-known example of such a system is high-impact polystyrene in which appropriate amounts of polybutadiene and polystyrene−polybutadiene graft copolymer are added to the polystyrene matrix. Two-phase materials containing graft or block copolymers are collectively known as "compatibilized" polymer blends. In spite of their importance, relatively little is known about the thermodynamics of multicomponent mixtures. Most of the fundamental studies on polymer blend thermodynamics are restricted to binary systems.[1]

In this paper we examine the thermodynamic behavior of multicomponent blends comprising poly(methylbutylene) (PM) and poly(ethylbutylene) (PE) chains in the form of either homopolymers or block copolymers (PM−PE). Included in this study are (1) blends of a homopolymer and a block copolymer (PM/PM−PE and PE/PM−PE), (2) blends of two homopolymers and a block copolymer (PM/PE/PM−PE), and (3) a blend of two PM−PE diblock copolymers. Polymers with narrow molecular weight distributions were synthesized via anionic polymerization under high vacuum. Small-angle neutron scattering (SANS) profiles were measured from homogeneous blends over a wide range of compositions, component molecular weights, and temperature. Thermodynamic information was extracted from these measurements using the multicomponent random phase approximation (RPA).[2−4] This paper is one of a series on the subject of multicomponent polymer blends.[5−7] In previous work we studied thermodynamic interactions and correlations in single-phase[5] and two-phase[6] multicomponent blends. We also studied the effect of molecular architecture on the thermodynamics of diblock and triblock copolymer melts.[7]

The Flory−Huggins theory,[8,9] used traditionally to describe binary systems, has been generalized to multicomponent systems.[10] In this theory, a single parameter, χ, is used to characterize the interactions between component pairs. In principle, χ should depend only on the chemical identity of monomer pairs and should be independent of blend composition and component molecular weight. Thus the results of binary experiments may be used to predict the properties of multicomponent blends. There are, however, several issues that need to be resolved before such predictions can be made with confidence. Problems arise due to the approximate nature of the Flory−Huggins theory. Extensive investigations on blends of small molecules have shown that two-parameter models are required to accurately predict mixture properties.[11] It is thus highly unlikely that a one-parameter model, like the Flory−Huggins theory, would be adequate for polymeric mixtures. The observation that measured χ parameters in binary systems show a composition dependence[12,13] is a manifestation of this inadequacy. Additional parameters required for characterizing polymer blends will become evident when we understand the origins of such observations. At this juncture it is not clear if any

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Table 1. Characteristics of Polymers

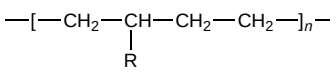
sample designation	no. of deuterium per monomer	mol wt (wt av)[b]	polydispersity index[c]	vol fr of PM in block copolymer[d,e]
*h*PM1	0	7.7×10^4	1.06	
*d*PM1	5.52	8.4×10^4	1.06	
*h*PM2	0	1.7×10^5	1.07	
*d*PM2	6.11	1.8×10^5	1.07	
*h*PE1	0	4.8×10^4	1.07	
*d*PE1	6.38	5.2×10^4	1.07	
*h*PE2	0	2.2×10^5	1.08	
*d*PE2	6.15	2.4×10^5	1.08	
*h*PM-*h*PE	0	4.6×10^4	1.09	0.452
*d*PM-*d*PE	3.67[f]	4.8×10^4	1.09	0.452

[a] Average number of deuterium per monomer, based on density measurements using a density gradient column. [b] From light scattering on polydiene precursors. [c] From GPC, based on polyisoprene calibration, uncorrected for column dispersion. [d] Based on ^{13}C NMR on *h*PM−*h*PE and densities of *h*PM and *h*PE. [e] Based on SANS data and density of *d*PM−*d*PE.[5]

polymer blend can be adequately represented by the Flory−Huggins theory.[14−19] A pronounced composition dependence is observed in "simple" systems such as blends of protonated and deuterated polymers that are otherwise identical (isotopic blends)[20] and polyolefin blends.[21] A "model" system with a composition independent χ parameter would be useful at this juncture. We show that blends comprising poly(methylbutylene) and poly(ethylbutylene) chains have the characteristics of such a system. The χ parameter in *binary* and *multicomponent* blends is independent of blend composition, component molecular weight, and molecular architecture over the accessible temperature range.

Experimental Section

Nearly monodisperse, model polyolefins were synthesized by anionic polymerization followed by saturation of the C=C bonds by hydrogen and deuterium.[22,23] Isoprene and ethylbutadiene were used as monomers to yield poly(methylbutylene) and poly(ethylbutylene) homopolymers and a poly(methylbutylene)-*block*-poly(ethylbutylene) copolymer.



model polyolefin

R = CH_3, poly(methylbutylene) (PM)

R = C_2H_5, poly(ethylbutylene) (PE)

The poly(methylbutylene) chains and poly(ethylbutylene) chains are referred to as PM and PE, respectively, where the letters M and E indicate the methyl and ethyl branches emerging from the C−C backbone. The characteristics of the polymers (deuterium content, molecular weight, and polydispersity index) were determined using procedures described in reference 5 and are listed in Table 1. The prefix "*h*" refers to hydrogenated polymers, and the prefix "*d*" refers to the partially deuterated polymers. The number 1 following the homopolymer designations identifies the lower molecular weight species, while number 2 identifies the higher molecular weight species.

Blends were made by dissolving the polymers in cyclohexane and then drying to constant weight in a vacuum oven at 70 °C. All the blends examined in this paper were optically clear, indicating that they were single-phase. Two-dimensional SANS patterns were measured using 1 mm thick samples held within quartz windows, on the 8 m SANS machine (on the NG5 beam line) at the National Institute of Standards and Technology. All the reported data were obtained using the following instrument configuration: neutron wavelength $\lambda = 9.0$ Å, wavelength spread $\Delta\lambda/\lambda = 0.25$, sample-to-detector distance = 3.6 m, sample aperture = 1.2 cm, source-to-sample distance = 4.1 m, and source size = 2.7 cm. The SANS measurements were carried out at temperatures raging from 27 to 167 °C. The measured scattering data $I(q)$ ($q = 4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle) were converted to an absolute scale using secondary standards described in ref 5, azimuthally averaged, and then corrected for background, empty cell scattering, and detector sensitivity. The incoherent scattering for each blend was estimated from SANS measurements on pure *h*PM1, assuming that it is proportional to the H-atom concentration in the blend. The total scattered intensity was also corrected for scattering due to nonuniformity of deuterium labeling in the partially deuterated chains present in the blend.[24] The coherent SANS intensity, $I(q)$, is given by

$$I(q) = [I(q)]_{\text{measured}} - I_{\text{incoherent}} - \sum_{\substack{\text{sum over} \\ \text{all deuterated} \\ \text{species}}} \phi_{\text{d},i} I_{\text{c},i}(q) \quad (1)$$

where $I_{c,i}(q)$ is the measured coherent SANS intensity of the pure partially deuterated species i and $\phi_{\text{d},i}$ is its volume fraction in the blend. The coherent scattering intensity is thus obtained from the raw data without resorting to any adjustable parameters.

Theory

In this section we present RPA-based predictions for the scattered intensity from multicomponent polymer blends. We define a *component* to be a connected chain of identical monomers. In our framework a mixture of two homopolymers and a diblock copolymer is a four-component system. The scattering intensity of an incompressible ($n + 1$) component polymer blend is given by the following matrix equation[2−4]

$$I(q) = \mathbf{B}^{\mathrm{T}}\mathbf{S}(q)\mathbf{B} \quad (2)$$

where $\mathbf{B}$ is an n-dimensional column vector whose elements, B_i are the scattering length densities of component i. $\mathbf{S}$ is an $n \times n$ structure factor matrix whose elements S_{ij} describe correlations between components i and j. The incompressibility constraint is conveniently incorporated by defining one of the components to be a "background" component. Component 0 is defined as the background component. Vector $\mathbf{B}$ is then given by the following equation:

$$B_i = b_i/v_i - b_0/v_0 \quad (3)$$

where b_i is the scattering length and v_i is the monomer volume of component i. Note that the correlations between the background component and other component are no longer independent due to incompressibility.

Direct information about $S_{ij}(q)$ of multicomponent blends can be obtained from scattering measurement in two cases.

Case (1). If all elements in vector $\mathbf{B}$ are zero except the jth one ($B_i = 0$, $i = 1$ to n, where $i \neq j$), then

$$I(q)/B_j^2 = S_{jj}(q) \quad (4a)$$

Case (2). If all elements of vector $\mathbf{B}$ are identical ($B_1 = B_2 = ... = B_n = B$), then

$$I(q)/B^2 = \sigma(q) = \sum_{\substack{i=1 \text{ to } n \\ j=1 \text{ to } n}} S_{ij}(q) \quad (4b)$$

For the general case, where $B_1 \neq B_2 \neq ... \neq B_n$, the scattering intensity is given by the contrast factor weighted sum of partial structure factors.

The structure factor matrix, $\mathbf{S}(q)$, in eq 2 is given in eq 5 according to RPA,[4]

$$\mathbf{S} = \left[(\mathbf{S^0})^{-1} + \frac{\mathbf{Y}\mathbf{Y}^{\mathrm{T}}}{S^0_{00} - m_0} + (\mathbf{K})\right]^{-1} \tag{5}$$

where $\mathbf{S^0}$ is the "bare" structure factor matrix which describes ideal correlations between components in the absence of interactions (all χ's are zero). The elements of $\mathbf{S^0}$ depend on the molecular architecture of each individual polymer. S^0_{ii}, the correlation between monomers of each component, is given by the Debye function for flexible chains:

$$S^0_{ii}(q) = N_i\phi_i v_i P_i(q) \qquad (i = 0, n) \tag{6a}$$

where N_i, ϕ_i, and v_i are the number of monomer units in component i, the volume fraction of component i in the mixture, and volume of each monomer in component i, respectively, and P_i is the Debye function.

$$P_i(q) = (2/x_i^2)[\exp(-x_i) - 1 + x_i] \quad (i = 0 \text{ to } n) \tag{6b}$$

In eq 6b, $x_i = q^2N_il_i^2/6$, and l_i is the segmental length of the component i. If components i and j are not portions of the same chain, then they are uncorrelated in the absence of interactions, and

$$S^0_{ij}(q) = S^0_{ji}(q) = 0 \qquad (i \text{ and } j \text{ are not on the same chain}) \tag{7a}$$

If, on the other hand, components i and j belong to the same chain, then they are correlated even in the absence of interactions and $S^0_{ij} \neq 0$. If, for example, components i and j are covalently bonded to form a diblock copolymer, then

$$S^0_{ij}(q) = S^0_{ji}(q) = (N_i\phi_i v_i N_j\phi_j v_j)^{1/2}F_i(q)F_j(q) \qquad (i \neq j, \text{ diblock copolymer}) \tag{7b}$$

where F_i is the Leibler function for component i and is given by

$$F_i(q) = \frac{1 - \exp(x_i)}{x_i} \tag{7c}$$

The definition of vector $\mathbf{Y}$ in eq 5 is given by

$$\mathbf{Y} = (\mathbf{S^0})^{-1}\mathbf{S}^0_{\mathrm{R0}} + \mathbf{I} \tag{8}$$

where $\mathbf{S}^0_{\mathrm{R0}}$ describes the ideal correlations between background component 0 and the rest of components (elements are S^0_{i0}, $i = 1$ to n) and $\mathbf{I}$ is the identity vector. The intercomponent Flory−Huggins interaction parameters are included in an $n \times n$ matrix $\mathbf{K}$, given by

$$K_{ij} = K_{ji} = \frac{\chi_{ij}}{v} - \frac{\chi_{i0}}{v} - \frac{\chi_{j0}}{v} \tag{9}$$

where χ_{ij} is the Flory−Huggins interaction parameter between components i and j, and v is the reference volume. The scalar quantity of m_0 in eq 5 is given by

$$m_0(q) = (\mathbf{S}^0_{\mathrm{R0}})^{\mathrm{T}}(\mathbf{S^0})^{-1}(\mathbf{S}^0_{\mathrm{R0}}) \tag{10}$$

Equations 5−10 can be used to obtain the structure factor of any multicomponent blend of flexible chains.

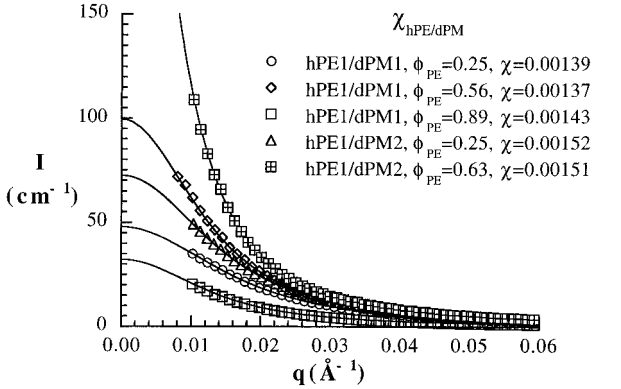


Figure 1. SANS intensity, I, versus scattering vector, q, from binary blends of *h*PE/*d*PM at 27 °C. The solid lines through the data represent best binary RPA fits. The composition and χ parameters are shown in the figure.

However, the equations simplify considerably when the background component is a homopolymer. In this case, the concentration fluctuations of the other components are "linked" to that of the background component due to the thermodynamic interactions only and not due to chemical linkages. Thus, for blends comprising at least one homopolymer, the structure factor is given by[3]

$$\mathbf{S} = [(\mathbf{S^0})^{-1} + \mathbf{V}]^{-1} \tag{11}$$

Elements of matrix $\mathbf{V}$ are given by

$$V_{ii}(q) = \frac{1}{S^0_{00}(q)} - \frac{2\chi_{i0}}{v} \tag{11a}$$

$$V_{ij}(q) = V_{ji}(q) = \frac{1}{S^0_{00}(q)} - \frac{\chi_{i0}}{v} - \frac{\chi_{j0}}{v} + \frac{\chi_{ij}}{v} \quad i \neq j \tag{11b}$$

The structure factor of a blend containing two homopolymers labeled 1 and 2 can be obtained from eqs 1−11 by setting all intercomponent correlations to zeros and $n = 1$ (eq 12).

$$S(q) = \frac{I(q)}{\left(\frac{b_2}{v_2} - \frac{b_1}{v_1}\right)^2} = \left[\frac{1}{\phi_1N_1v_1P_1(q)} + \frac{1}{\phi_2N_2v_2P_2(q)} - \frac{2\chi_{12}}{v}\right]^{-1} \tag{12}$$

This is the familiar result first derived by de Gennes.[2]

We define a monomer unit as a C_5 unit for the PM chain and C_6 unit for the PE chains and the reference volume $v = 148.6$ Å^3, which is the geometric mean of the monomer volumes at 27 °C (136.4 Å^3 for PM and 162.0 Å^3 for PE).

Binary Blends of Two Homopolymers

In Figure 1 we show the SANS data obtained from a series of binary PE1/PM1 and PE1/PM2 homopolymer mixtures. All of the data shown in Figure 1 were obtained at 27 °C. The increase in low-q scattering is due to increasing proximity to the spinodal curve. In this series, this effect is produced by changing blend composition and component molecular weight. These data were analyzed using the standard, binary RPA given in eq 12. The estimation of statistical segmental

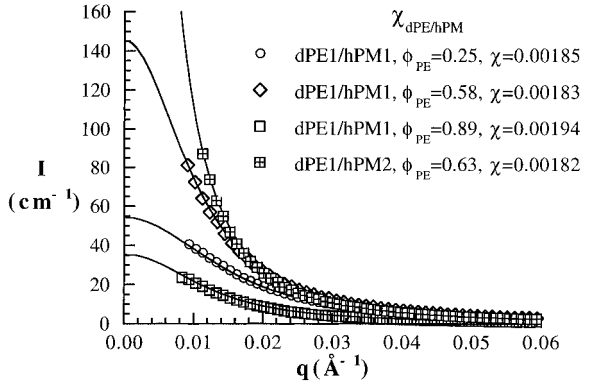


Figure 2. SANS intensity, I, versus scattering vector, q, from binary blends of dPE/hPM with compositions identical to those in Figure 1, but the deuterium labels in these blends are swapped. The solid lines through the data represent best RPA fits. The composition and χ parameters are shown in the figure.

Table 2. Flory−Huggins Interaction Parameters, χ, Obtained from Binary Blends

ϕ_{PE}	27 °C	52 °C	83 °C	121 °C	167 °C
$\chi_{hPE1/hPM1} \times 10^4$ ($\Delta\chi$ x 10^4), blends of PE1 and PM1					
0.250	16.2 (4.35)	12.0 (2.78)	9.0 (3.26)	7.0 (4.46)	6.0 (3.07)
0.575	16.0 (4.57)	12.4 (3.30)	9.5 (2.95)	7.9 (1.84)	6.5 (0.86)
0.891	17.0 (5.21)	12.6 (3.60)	9.2 (3.22)	6.3 (4.73)	5.0 (2.18)
$\chi_{hPE1/hPM2} \times 10^4$ ($\Delta\chi$ x 10^4), a blend of PE1 and PM2					
0.630	17.0 (3.80)	12.7 (3.50)	11.0 (3.60)	8.2 (2.78)	6.4 (2.62)

[a] All χ parameters are based on a reference volume of 148.6 Å^3.

lengths (l_{PM} and l_{PE}) and other parameters is discussed in the Appendix. It is evident that the scattered intensities at all scattering angles are consistent with the reported $\chi_{hPE/dPM}$ and statistical segmental lengths.

In Figure 2 we show scattering data from a series of binary dPE/hPM blends. This series is similar to one described in the preceding paragraph, except for the fact that the deuterium label has been switched from the PM chains to the PE chains. Similar procedures were used to obtain $\chi_{dPE/hPM}$ from these data, and the solid curves in Figure 2 represent the RPA-based calculations of $I(q)$. These results are similar to those shown in Figure 1, but χ values are larger by about 30%. A similar label swapping effect has been reported by Rhee and Crist[25] and by Graessley, Lohse and co-workers.[26] The interesting feature of the present data, however, is the fact that χ is, within experimental error, independent of composition and molecular weight.

We assume that the χ_{ij}, between polyolefins with no labeling contrast ($\chi_{hPE/hPM}$ and $\chi_{dPE/dPM}$) are approximately given by

$$\chi_{hPE/hPM} = \chi_{dPE/dPM} = \frac{\chi_{hPE/dPM} + \chi_{dPE/hPM}}{2} \quad (13)$$

This is an empirical relationship, consistent with data obtained from several binary polyolefin blends.[25,26] In Table 2 we summarize $\chi_{hPE/hPM}$ parameters of all of the binary blends with different compositions and molecular weights at temperatures ranging from 27 to 167 °C. These estimates were obtained by applying eq 13 to SANS measurements on hPE/dPM and dPE/hPM mixtures. It is evident that χ is independent of component molecular weight and blend composition at all temperatures. This is encouraging because it indicates that the thermodynamic interactions in binary PE/PM blends are in agreement with the predictions of Flory−Huggins theory. It is thus appropriate to test this system further and see if adding a PM−PE diblock copolymer to these blends changes the measured χ parameters.

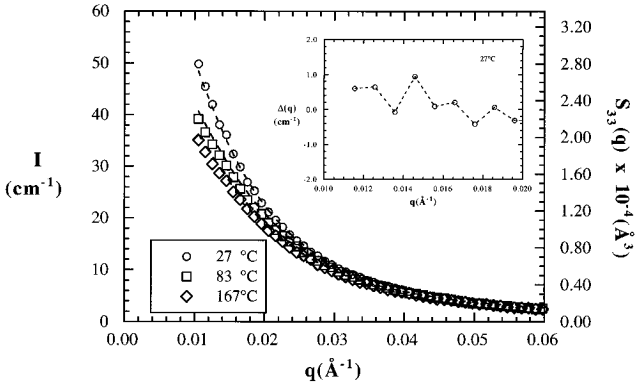


Figure 3. SANS intensity, $I(q)$, and partial structure factor $S_{33}(q)$ from a ternary blend of hPE1/dPM1/hPM−hPE ($\phi_{PE_1}/\phi_{PM_1} = 1.32$, $\phi_{PM-PE} = 0.2$). The dashed lines through the data are RPA calculations using binary χ's. The scale of the S_{33} axis was adjusted so that the same symbols can be used to represent both $I(q)$ and $S_{33}(q)$. The low-q scattering data at 27 °C are shown in the inset where symbols represent the intensity difference between the measured data and the RPA calculations ($\Delta(q)$).

Multicomponent Polymer Blends

The theoretical RPA predictions for SANS intensity from any multicomponent blend comprising PM and PE chains (eqs 2−11) can be calculated from the data given in Table 2 and the Appendix (see ref 5 for details). We analyzed the multicomponent data by comparing our measurements with these predictions. When deviations between experiment and theory were observed, $\chi_{hPE/hPM}$ was adjusted to obtain the best least squares fit. All other parameters were kept fixed, including the relative effect of deuterium substitution on χ, $\Delta\chi$. It follows from eq 13 that

$$\chi_{dPE/hPM}\,(\chi_{hPE/dPM}) = \chi_{hPE/hPM} + (-)\,\Delta\chi/2 \quad (14)$$

where $\Delta\chi$ is the difference between binary $\chi_{dPE/hPM}$ and $\chi_{hPE/dPM}$ in Table 2. Note that all three quantities in eq 14 are temperature dependent. Thus, when $\chi_{hPE/hPM}$ was adjusted, $\chi_{dPE/hPM}$ and $\chi_{hPE/dPM}$ were changed using eq 14. Deviations between the theoretical calculations (eqs 1−14) and measured scattering from multicomponent blends are lumped into one parameter: $\chi_{hPE/hPM}$. In all cases we find that adjusting $\chi_{hPE/hPM}$ leads to near-perfect agreement between theory and experiment. The difference between $\chi_{hPE/hPM}$ obtained from the multicomponent blend and that obtained from binary blends (given in Table 2) is a measure of disagreement between multicomponent RPA and experiment.[27]

I. Blends of Two Homopolymers and a Block Copolymer. Figure 3 shows the scattering data at selected temperatures from a ternary blend of hPE1/dPM1/hPM−hPE ($\phi_{hPE1}/\phi_{dPM1} = 1.32$, $\phi_{hPM-hPE} = 0.2$). The RPA structure factors for these blends were computed using eq 11 with hPE1 as the background homopolymer. The individual blocks of the diblock copolymer PM−PE are treated as separate "components" and are labeled 1 (PM block) and 2 (PE block) while the homopolymer PM is labeled as component 3. The dashed lines through the data in Figure 3 represent RPA calculations of the SANS intensities using eq 2. The parameters used for computing theoretical predictions of the SANS intensities from multicomponent

Table 3. List of Structural Parameters Used for Calculations of the Scattering Intensity from Multicomponent Blends at 27 °C[a]

								dPM−*d*PE (*h*PM−*h*PE[+])	
parameter	*h*PM1	*d*PM1	*h*PM2	*d*PM2	*h*PE1	*d*PE1	*h*PE2	PM block	PE block
N_i	1105	1105	2465	2465	525	525	2630	300 (300)	300 (300)
v_i (Å^3)	136.4	136.2	136.4	136.2	162.0	161.8	162.0	136.2 (136.4)	161.8 (162.0)
l_i (Å)	8.19	8.19	8.26	8.26	7.93	7.93	7.60	8.19 (8.19)	7.93 (7.93)
b_i x 10^4 (Å)	−0.415	5.330	−0.415	5.950	−0.498	6.140	−0.498	3.070 (−0.415)	3.650 (−0.498)

[a] See Appendix for parameter estimation at other temperatures. [b] The characterization data of *h*PM−*h*PE are shown in the parentheses.

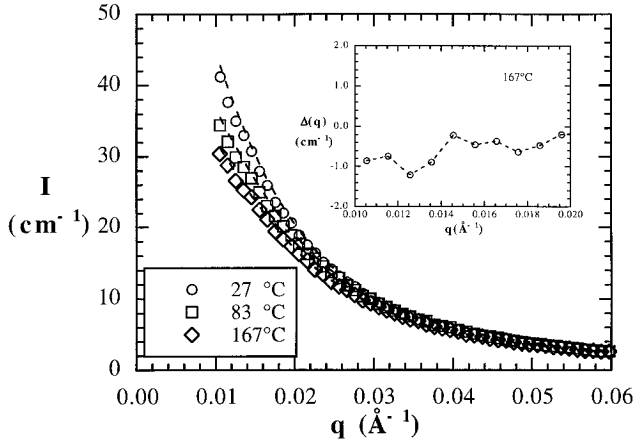


Figure 4. SANS data from a ternary blend of *h*PE1/*d*PM1/*d*PM−*d*PE (ϕ_{PE1}/ϕ_{PM1} =1.32, ϕ_{PM-PE} = 0.2). The dashed lines through the data are RPA calculations using binary χ's. The low-q scattering data at 167 °C are shown in the inset where symbols represent the intensity difference between the measured data and the RPA calculations ($\Delta(q)$).

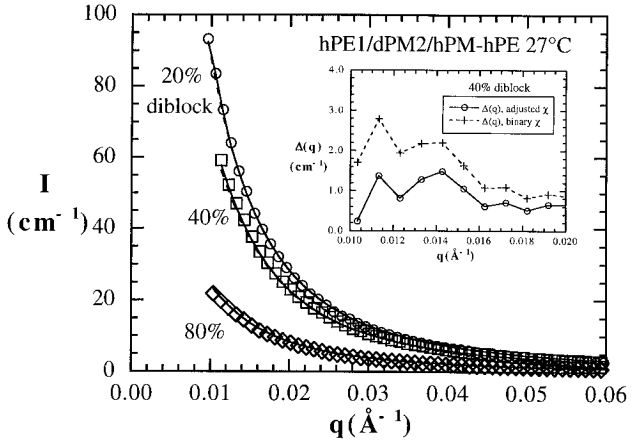


Figure 5. SANS intensity, I, versus scattering vector, q, from *h*PE1/*d*PM2/*h*PM−*h*PE blends with various copolymer volume fractions [(circles) 0.2, (squares) 0.4, and (diamonds) 0.8] at 27 °C. The composition ratio between homopolymers (ϕ_{PE1}/ϕ_{PM1}) is fixed at 1.72. The dashed lines were calculated by multicomponent RPA using binary χ's, while the solid lines were obtained by using $\chi_{hPM/hPE}$ as the adjustable parameter. Inset: Low-q scattering data from the blend with ϕ_{PM-PE} = 0.4. The solid line represents $\Delta(q)$ after adjusting $\chi_{hPM/hPE}$, and the dashed line represents $\Delta(q)$ using binary χ's.

mixtures are given in Table 3. The agreement between theory and experiment at all accessible scattering vectors (q) and temperatures implies that binary χ's can be used to quantify the thermodynamics of mixing in ternary blends of two homopolymers and a copolymer. Also, the statistical segmental lengths of PM and PE chains obtained from *h*PM/*d*PM and *h*PE/*d*PE blends are consistent with the multicomponent blend data.

The q dependence of the partial structure factor S_{33} is also shown in Figure 3 (right hand scale). Note that this is a case 1 blend with B_1, $B_2 \cong 0$, and $B_3 \neq 0$. Hence $S_{33}(q)$ is proportional $I(q)$. In order to quantify the differences between experimental data and RPA calculations, we define a quantity $\Delta(q)$:

$$\Delta(q) = I_{\text{measured}}(q) - I_{\text{RPA calculation}}(q) \qquad (15)$$

The inset in Figure 3 shows $\Delta(q)$ versus q for the 27 °C data at low q. We used the summation of $\Delta^2(q)$ [$\sum\Delta^2(q)$] over the accessible q range to gauge the agreement between the experiment and theory. Adjusting $\chi_{hPE/hPM}$ in the RPA calculations of this blend does not result in a significant decrease in $\sum\Delta^2(q)$.

In Figure 4 we compare the experimental data with theoretical calculations for the ternary blend of *h*PE1/*d*PM1/*d*PM−*d*PE (ϕ_{hPE1}/ϕ_{dPM1} = 1.32 and $\phi_{dPE-dPM}$ = 0.2). This system is similar to that shown in Figure 3 except that we have replaced the *h*PM−*h*PE by *d*PM−*d*PE. The scattering intensity of the blend depends on all nine components of $S(q)$ because B_1, B_2, and B_3 are not zero. Nevertheless, we see good agreement between theory and experiment.

To investigate the effect of molecular weight, we examined blends of *h*PE1/*d*PM2/*h*PM−*h*PE as a function of block copolymer concentration. The molecular weight of PM2 is a factor of 2 larger than that of PM1 (see Table 1). The results are shown in Figure 5. The RPA calculation results of these ternary blends obtained by using binary χ parameters show small deviations from experimental data (dashed lines in Figure 5 and plus symbols in the inset). We then adjusted the $\chi_{hPE/hPM}$ in the RPA calculations to minimize [$\sum\Delta^2(q)$] (solid lines in Figure 5 and circle symbols in the inset). It is evident that adjusting $\chi_{hPE/hPM}$ leads to substantial reductions in $\sum\Delta^2(q)$. However, the difference between $\chi_{hPE/hPM}$ obtained for the multicomponent fit and that obtained from the binary data ranges from 1 to 10%. Note that the radius of gyration (R_g) of PM2 (165 Å) is significantly greater than that of PM1 (115 Å). Since the data were gathered over a fixed q range, the qR_g range covered in these two experiments is quite different. In spite of this, the experimental measurements are in good agreement with theory. We conclude that the multicomponent χ parameters are independent of molecular weight and molecular architecture.

The ratios of the homopolymer volume fractions in ternary blends described above were fixed at values of 1.32 (ϕ_{PE1}/ϕ_{PM1}) for mixtures of PE1/PM1/PM−PE and 1.72 (ϕ_{PE1}/ϕ_{PM2}) for blends of PE1/PM2/PM−PE, respectively (see Table 4). These values correspond to the critical composition for binary PE1/PM1 and PE1/PM2 blends [critical composition of component 1 (PM), $\phi_{c1} = 1/\{1 + (N_1v_1/N_2v_2)^{0.5}\}$]. We also examined some ternary blends with different homopolymer volume fraction ratios to check the dependence of χ parameters on the blend composition. The scattering data and RPA cal-

Table 4. Composition of Blends Discussed in This Paper[a]

blends shown in	blend designation	components A	components B	components A−B	ϕ_A/ϕ_B (ϕ_A)	ϕ_{A-B}
Figure 1	B25A	*h*PE1	*d*PM1		0.333 (0.25)	0
	B056	*h*PE1	*d*PM1		1.273 (0.56)	0
	B089	*h*PE1	*d*PM1		8.091 (0.89)	0
	B25B	*h*PE1	*d*PM2		0.333 (0.25)	0
	B063	*h*PE1	*d*PM2		1.703 (0.63)	0
Figure 2	BS25	*d*PE1	*h*PM1		0.333 (0.25)	0
	BS58	*d*PE1	*h*PM1		1.381 (0.58)	0
	BS89	*d*PE1	*h*PM1		8.091 (0.89)	0
	BS63	*d*PE1	*h*PM2		1.703 (0.63)	0
Figure 3	T046	*h*PE1	*d*PM1	*h*PM−*d*PE	1.345 (0.46)	0.202
Figure 4	T045	*h*PE1	*d*PM1	*d*PM−*d*PE	1.336 (0.45)	0.202
Figure 5	T051	*h*PE1	*d*PM2	*h*PM−*h*PE	1.745 (0.51)	0.197
	T037	*h*PE1	*d*PM2	*h*PM−*h*PE	1.634 (0.37)	0.409
	T012	*h*PE1	*d*PM2	*h*PM−*h*PE	1.561 (0.12)	0.800
Figure 6	T020	*h*PE1	*d*PM1	*h*PM−*h*PE	0.337 (0.20)	0.202
	T019	*h*PE1	*d*PM2	*h*PM−*h*PE	0.314 (0.19)	0.194
Figure 7	HC01		*d*PM1	*h*PM−*h*PE		0.500
	HC02	*d*PE1		*h*PM−*h*PE		0.500
	HC03		*h*PM1	*d*PM−*d*PE		0.500
Figure 11	B050	*h*PE2	*d*PM2		1.000 (0.50)	

blends shown in	blend designation	*h*A−*h*B	*d*A−*d*B	ϕ_{hA-hB}
Figure 8	DB01	*h*PM−*h*PE	*d*PM−*d*PE	0.500

[a] Based on weight fractions, assuming no volume change on mixing.

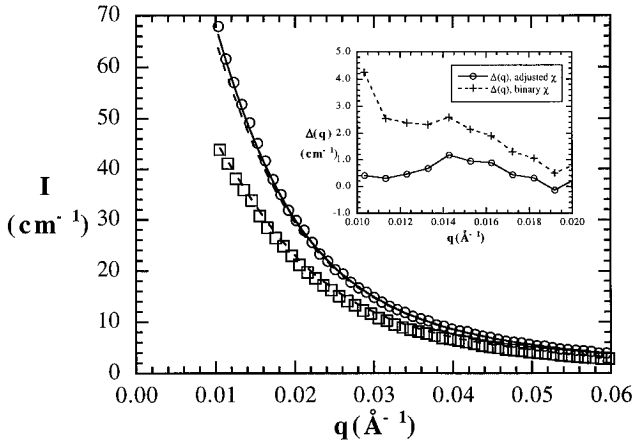


Figure 6. SANS intensity, I, versus scattering vector, q, from ternary blends of *h*PE1/*d*PM1/*h*PM−*h*PE (square symbols) and *h*PE1/*d*PM2/*h*PM−*h*PE (circular symbols) with copolymer volume fraction 0.2, at 27 °C. The composition ratios between homopolymers (ϕ_{PE}/ϕ_{PM}) are 0.33 in both ternary blends. The dashed lines were calculated by multicomponent RPA using binary χ's, while the solid lines were obtained by using $\chi_{hPM/hPE}$ as the adjustable parameter. Inset: Low-q scattering data from the *h*PE1/*d*PM2/*h*PM−*h*PE blend. The solid line represents $\Delta(q)$ after adjusting $\chi_{hPM/hPE}$, and the dashed line represents $\Delta(q)$ using binary χ's.

culations of ternary blends of *h*PE1/*d*PM1/*h*PM−*h*PE and *h*PE1/*d*PM2/*h*PM−*h*PE ($\phi_{hPE1}/\phi_{dPM} = 0.33$ in both cases) are shown in Figure 6. We see small deviations in the SANS data from blends containing higher molecular weight PM2 species (dashed line in Figure 6 and plus symbols in the inset), but good agreement in blends containing lower molecular weight PM1 species.

II. Blends of a Homopolymer and a Block Copolymer. SANS profiles from a series of 50/50 blends containing one homopolymer and a block copolymer were measured. Previous experiments on such blends had revealed a substantial composition dependence in the multicomponent χ parameter.[28,29] Mixtures of a homopolymer and a block copolymer are considered as three-component blends (two components for the block copolymer and one for the homopolymer). We

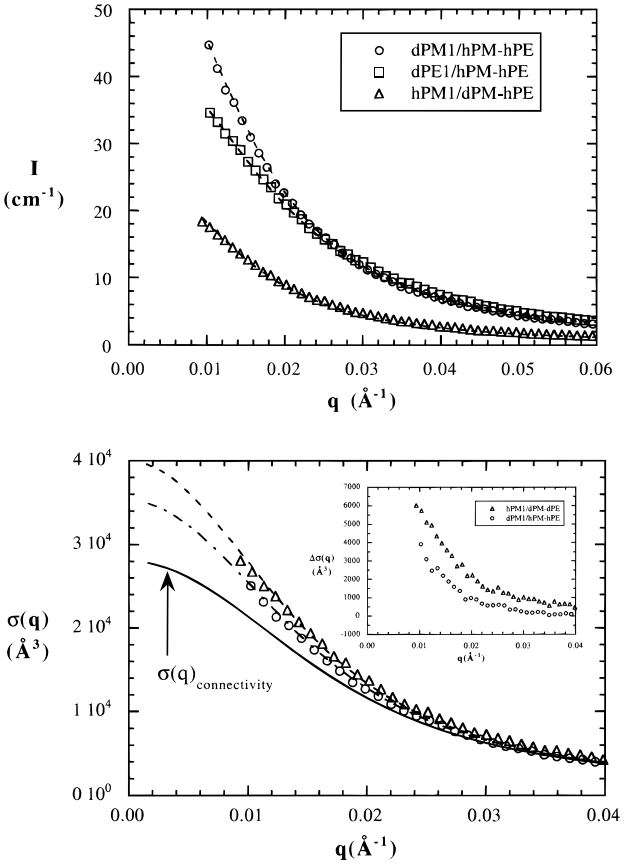


Figure 7. (a) SANS data from a series of 50/50 blends of a homopolymer and a block copolymer at 27 °C [(circles) *d*PM1/*h*PM−*h*PE, (squares) *d*PE1/*h*PM−*h*PE, (triangles) *h*PM1/*d*PM−*d*PE]. The dashed lines are RPA calculations with binary χ's. (b) Sum of partial structure factors $\sigma(q)$ [$\sigma(q) = \sum S_{ij}(q)$] of 50/50 blends at 27 °C [(circles) *d*PM1/*h*PM−*h*PE, (triangles) *h*PM1/*d*PM−*d*PE)]. The symbols are obtained directly from scattering data using eq 4b, and the dashed lines are RPA calculations. The solid line is the $\sigma(q)_{connectivity}$ obtained from RPA calculations by setting all χ_{ij}'s = 0. The contributions to $\sigma(q)$ due to concentration fluctuations are shown in the inset where $\Delta\sigma(q) = \sigma(q) - \sigma(q)_{connectivity}$.

calculated the scattering intensities of these blends by using eqs 2 and 11 with the homopolymer as the background component. The calculation results are compared with SANS measurements in Figure 7a, and the agreement is quite good. Evidently, the χ parameters are composition independent in these blends.

The pair of blends *d*PM1/*h*PM−*h*PE and *h*PM1/*d*PM−*d*PE are identical except for the fact that the deuterium labels are swapped. The scattering intensities from these blends are, however, quite different (see Figure 7a). This is mainly due to contrast differences. Since these are case 2 blends, it is more appropriate to compare the $\sigma(q)$—see Figure 7b. Contributions to $\sigma(q)$ arise due to chain connectivity and due to concentration fluctuations. The connectivity contribution, calculated by computing $\sigma(q)$ under the condition that all $\chi_{ij} = 0$, is identical for both blends and is also shown in Figure 7b. We define an excess scattering function, $\Delta\sigma(q) = \sigma(q)_{measured} - \sigma(q)_{connectivity}$, which reflects concentration fluctuations only. The inset in Figure 7b shows the q dependence of $\Delta\sigma$. It is evident that the magnitude of the concentration fluctuations in the *h*PM1/*d*PM−*d*PE blend are larger than that in the *d*PM1/*h*PM−*h*PE blend (see inset of Figure 7b). The reason for this is that the intermolecular repulsion in the *h*PM1/*d*PM−

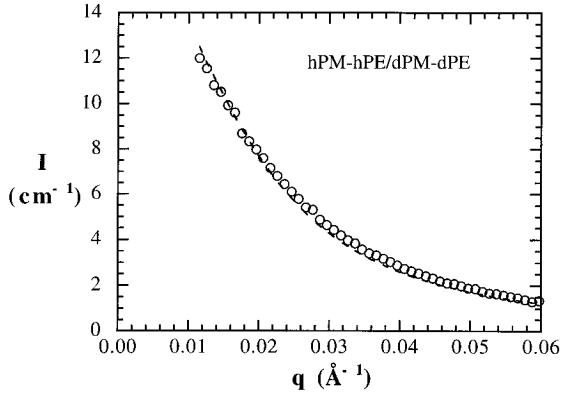


Figure 8. SANS data from a 50/50 blend of two diblock copolymers at 27 °C. The dashed line represents the RPA calculations using binary χ's.

*d*PE blend is mainly due to $\chi_{dPE/hPM}$ while in the *d*PM1/*h*PM−*h*PE blend it is mainly due to $\chi_{hPE/dPM}$. Binary data shown in Figures 1 and 2 show clearly that $\chi_{dPE/hPM} > \chi_{hPE/dPM}$. We then see that the label-swapping effect on χ found in binary mixtures is also manifested in multicomponent mixtures.

III. A Blend of Two Diblock Copolymers. In blends studied thus far, we used the simplified multicomponent RPA formalism (eq 11) to calculate the scattering profiles because all the blends contained at least one homopolymer which could be used as the background component. We now consider a 50/50 mixture of two diblock copolymers *h*PM-*h*PE/*d*PM−*d*PE. To predict the scattering profiles in this system we have to use the more general multicomponent RPA formalism (eq 5). This necessitates the computation of several new quantities such as vectors $\mathbf{Y}$ and $\mathbf{S}^0_{R0}$, which did not enter the previous calculations. The results of the RPA calculations using binary χ parameters are compared with SANS data and are shown in Figure 8. Again, the consistency between the theoretical prediction and experimental data are evident over the accessible q range.

Overall Picture

The results of a wide range of experiments at 27 °C are summarized on a ternary composition diagram in Figure 9. The heights of line segments protruding from the composition diagram surface are proportional to values of $\chi_{hPE/hPM}$ parameters at 27 °C. The ternary composition diagram was "traveled" along several different "paths" with fixed homopolymer volume fraction ratios (ϕ_{PE}/ϕ_{PM}). The ternary blends of *h*PE1/*d*PM1/*h*PM−*h*PE are located along paths A ($\phi_{PE1}/\phi_{PM1} = 1.32$) and D ($\phi_{PE1}/\phi_{PM1} = 0.33$), while blends of *h*PE1/*d*PM2/*h*PM−*h*PE are located along paths B ($\phi_{PE1}/\phi_{PM2} = 1.72$) and D ($\phi_{PE1}/\phi_{PM2} = 0.33$). Binary homopolymer blends are located at the bottom of the triangle (path C), and blends containing a homopolymer and a block copolymer are located on the lateral sides of the composition diagram. The deviation between binary and multicomponent χ parameters is at most 10%.

In Figure 10, we show the χ parameters of the blends along paths A−D as a function of the homopolymer PE composition and temperature. The lack of dependence of the measured χ parameter on blend composition, component molecular weight, and molecular architecture is evident at all temperatures.

In Figure 10 we also show SANS data from *h*PE2/*d*PM2 (hatched square). Note that the molecular weight

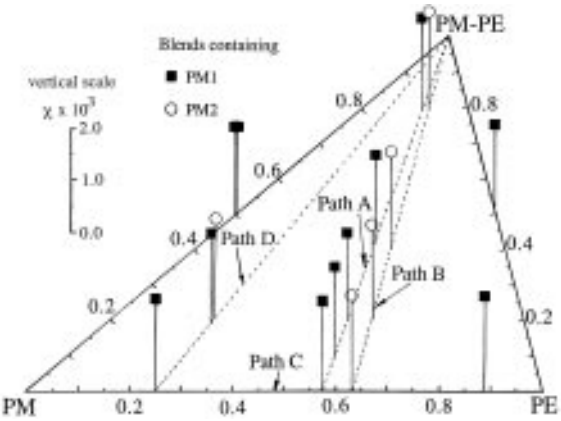


Figure 9. χ parameters of several polymer blends studied at 27 °C on a ternary composition diagram. The magnitude of the χ parameter at each composition is proportional to the heights of the line segments protruding from the surface of the ternary composition diagram. Data from blends containing PM1 are identified by solid squares, while those containing PM2 are identified by open circles. Blends were studied along several paths (A−D), as described in the text.

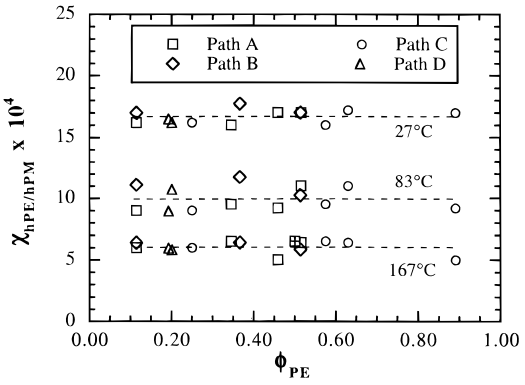


Figure 10. χ parameters of blends along paths A−D (defined in Figure 9) plotted against the volume fraction of homopolymer PE at 27, 83, and 167 °C. See Figure 9 for volume fractions of other components corresponding to each data point. The hatched square represents χ obtained from the binary *h*PE2/*d*PM2 blend measured at 160 °C. The dashed lines through data at each temperature are the average χ values at the given temperatures.

of PE2 is a factor of 5 larger than that of PE1. This binary blend is phase-separated over most of the temperature window in this study (spinodal temperature = 130 °C).[6] The SANS profile obtained at 160 °C (single phase) and RPA calculations of this blend are shown in Figure 11. The value of $\chi_{hPE2/dPM2}$ is consistent with measurements from PE1/PM1 and PE1/PM2 blends. The $\chi_{hPM2/hPM2}$ shown in Figure 10, was extracted using eq 13, using the average of $\Delta\chi$'s listed in Table 2.

The temperature dependence of χ for most of the blends studied is shown in Figure 12. All the data are seen to collapse onto a single quadratic curve (eq 16).

$$\chi = 0.0028 - \frac{2.30}{T} + \frac{584.45}{T^2} \qquad (16)$$

The multicomponent blends studied in this paper contain two kinds of monomers. Our data indicate that the thermodynamic properties of these blends are related to a single χ parameter. We also conclude that the random phase approximation accurately predicts scattering profiles and correlations between individual

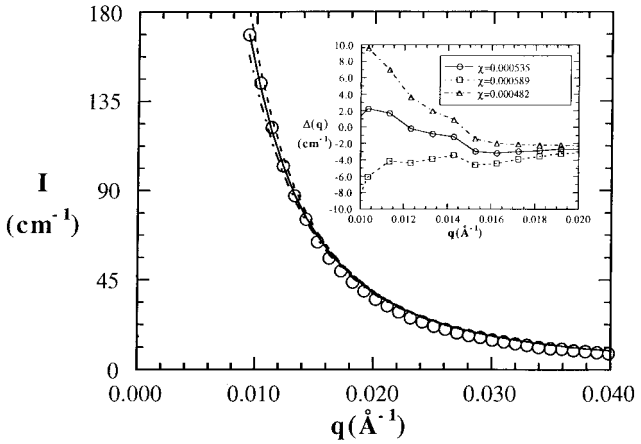


Figure 11. SANS data measured at 160 °C from a 50/50 *h*PE2/*d*PM2 blend compared with RPA calculations. The deviation between experiment and calculations, Δ, is shown in the inset. The solid line represents RPA calculations with $\chi = 5.89 \times 10^{-4}$. The dashed lines correspond to a ±10% variation in χ.

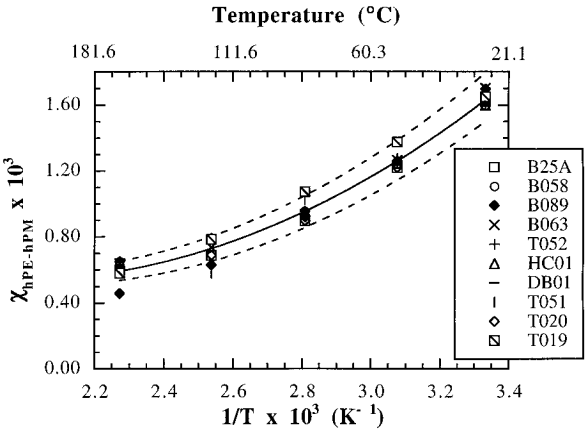


Figure 12. Temperature dependence of the χ interaction parameter for most of the polymer blends studied. The curves represent eq 16 with ±10% uncertainty. See Table 4 for blend compositions.

components in our homogeneous binary and multicomponent blends.

Concluding Remarks

Small-angle neutron scattering profiles from homogeneous binary and multicomponent blends comprising poly(methylbutylene), poly(ethylbutylene), and a poly(methylbutylene)-*block*-poly(ethylbutylene) copolymer were measured over a wide range of concentrations ($\phi_{PE} = 0.0-1.0$, $\phi_{PM-PE} = 0.0-0.8$), temperatures (27−167 °C), and component molecular weights (M_w of PM = 77 000 and 170 000, M_w of PE = 48 000 and 220 000). Thermodynamic interactions were inferred by comparing experimental SANS profiles with calculations based on multicomponent RPA. SANS profiles obtained from the multicomponent blends were in quantitative agreement (within 10%) with the RPA calculations using χ parameters determined from binary blends. This is within the estimated uncertainties[30] and indicates a consistency between binary and multicomponent χ parameters. Though the microscopic origin of the χ parameters is far from established, our experiments support the original ideas of Flory and Huggins, that χ is a measure of monomer−monomer interactions and is thus independent of blend composition, molecular weight, and molecular architecture. For this particular system, measurements of χ parameters in binary systems may be used to design more complex, multicomponent systems.

Previous experiments on binary polyolefin mixtures revealed a pronounced composition dependence of the χ parameter.[21] It is not clear why the poly(methylbutylene)/poly(ethylbutylene) system does not show such behavior.[32] If we can find the underlying feature of this system that is responsible for the observed compliance with the Flory−Huggins theory, then we may be able to identify the additional parameter (or parameters) necessary to obtain a more complete understanding of polymer blend thermodynamics.

Acknowledgment. It is a pleasure to acknowledge Boualem Hammouda for many educational and stimulating lessons on multicomponent RPA. Financial support from the National Science Foundation through Grants CTS-9308164 and DMR-99307098, and the NSF Young Investigator Program, Grant No. DMR-9457950, is gratefully acknowledged. We thank John Barker and Charles Glinka for their help during the SANS experiments.

Appendix. Estimation of Statistical Segment Lengths and Monomer Volumes

The statistical segment lengths of PM and PE chains were obtained from SANS experiments on *h*PM/*d*PM and *h*PE/*d*PE mixtures. Equation 13 was used to analyze the data and the results are summarized in Table 5 (see ref 5 for details). In theory, the statistical segment lengths must be independent of component molecular weight. The measured statistical segment lengths of PM1 and PM2 chains are within 1% of each other. Slightly larger deviations (about 5%) are found in PE1 and PE2 chains. We used the PM1 and PE1 l_i values to compute the partial structure factor of the diblock copolymer, due to the fact that it is a relatively low molecular weight species. The volumes of PM and PE monomers were estimated from room temperature density measurements and found to be 136 and 162 Å^3. Monomer volumes at other temperatures were calculated using the following equation:

$$v_i(T) = v_i(300\ \text{K}) \exp[-\alpha(T - 300)] \qquad \text{(A.1)}$$

where α is equal to 7.0×10^{-4} (K^{-1}) for the PM chains and 6.5×10^{-4} (K^{-1}) for the PE chains.

Table 5. Values of l_i and χ Obtained from *h*PM/*d*PM and *h*PE/*d*PE blends

	l_i (Å)					$\chi \times 10^4$				
polymer	27 °C	52 °C	83 °C	121 °C	167 °C	27 °C	52 °C	83 °C	121 °C	167 °C
PM1	8.19	8.22	8.00	8.03	8.00	3.80	3.22	2.80	1.53	0.72
PM2	8.26	8.16	8.05	8.01	7.92	3.91	2.99	1.83	1.01	0.30
PE1	7.93	7.75	7.57	7.69	7.76	3.23	2.94	3.00	1.02	−0.10
PE2	7.48	7.54	7.65	7.50	7.43	1.61	1.05	0.50	0.17	0.02

Nomenclature

b_i	scattering length of monomer i
b_0	scattering length of monomer of the background component 0
B_i	contrast column vector of component i
f	volume fraction of block A in the block copolymer
F_i	the Liebler function of component i in a flexible block copolymer
$I_{measured}$	measured SANS scattered intensity
I	coherent SANS intensity
$I_{incoherent}$	incoherent SANS intensity
$I_{c,i}$	coherent SANS intensity arises from the label nonuniformity in a pure partially deuterated sample i
l_i	statistical segment length of component i, obtained by fitting SANS data to mean-field theory
$n + 1$	total number of components in a blend
N	number of repeat units per homopolymer chain based on reference volume, v; $N = N_i v_i/v$
N_i	number of monomers per chain (i =A, B)
$N_{i,b}$	number of monomers per block (i =A, B)
P_i	the Debye function of i component
PM	homopolymer poly(methylbutylene)
PE	homopolymer poly(ethylbutylene)
PM−PE	diblock copolymer with PM and PE blocks
q	scattering vector, $q = (4\pi \sin(\theta/2)/\lambda)$ (Å^{-1})
R_g	the radius of gyration, $R_g = Nl^2/6$
$\mathbf{S}^0$	the bare structure factor matrix
$\mathbf{S}$	the structure factor matrix
T	absolute temperature (K)
v	reference volume (equal to 148.6 Å^3 throughout this paper)
v_i	monomeric volume of the component i
x_i	$x_i = q^2R_g^2$
χ	Flory−Huggins interaction parameter, based on reference volume v
$\Delta\chi(T)$	$\chi_{dPE/hPM} - \chi_{hPE/dPM}$
$\Delta(q)$	the deviation of theoretical SANS intensity from experimental data, $\Delta(q) = I_{measured} - I_{RPA\ calculations}$
ϕ_i	volume fraction of component i
λ	the wavelength of neutron beam (Å)
$\sigma(q)$	the sum of partial structure factors $[\sum S_{ij}(q)]$ in a blend
$\Delta\sigma(q)$	the difference between $\sigma(q)_{measured}$ and $\sigma(q)_{connectivity}$

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(27) In principle, the difference between multicomponent and binary χ's can also result from failures of the label-swapping rule (eqs 13 and 14). However, for this particular blend the effect of label swapping is relatively small ($\Delta\chi/\chi_{dPE/hPM}$ is about 0.1). In addition, if eqs 13 and 14 were inappropriate, then adjusting a single parameter, $\chi_{hPE/hPM}$, would not result in agreement between theory and experiment.
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(30) The major factors that lead to errors in interpreting SANS experiments are (1) errors in absolute calibration, (2) instrumental smearing of scattering profiles, and (3) errors in measurement of polymer molecular weight (N_i) and deuterium content (B_i). In this paper we compare binary and multicomponent SANS measurements that were made on the same instrument with the same instrument configuration, and the same standards were used for absolute calibration. This reduces the uncertainty significantly because factors 1 and 2 are no longer relevant. Estimated errors in measurement of N_i and B_i are ±5% and ±4%, respectively.[31] For comparisons of scattering from binary homopolymer mixtures with that from mixtures of two homopolymers and a diblock copolymer, only uncertainties in the characterization of the diblock copolymer are relevant. The scattered intensity is related to a summation of terms involving products of N_i and B_i. Since the diblock copolymer comprises two components, the estimated error is ±9% [$=\{2(0.05^2 + 0.04^2)\}^{0.5}$].
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(32) There are many reported effects that would cause χ to be composition dependent. A summary of these effects is given in ref 21. Recently, it has been proposed that the composition dependence of χ can be predicted from pure component *PVT* properties (equation-of-state).[16] The "differences" in *PVT* properties of poly(methylbutene) and poly(ethylbutene) are substantial and similar in magnitude to those of other polyolefin blends which show a pronounced composition dependent χ parameter.[33,34]
(33) Krishnamoorti, R.; Graessley, W. W.; Balsara, N. P.; Lohse, D. J.; *Macromolecules* **1994**, *27*, 3073.
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