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Thermodynamic interactions and correlations in mixtures of two homopolymers and a block copolymer by small angle neutron scattering

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Thermodynamic interactions in mixtures of two homopolymers and a block copolymer were obtained from small-angle neutron scattering (SANS) measurements. Experimental SANS profiles from homogeneous, ternary mixtures of model polyolefins—poly(ethyl butylene)/poly(methyl butylene)/poly(methyl butylene)-*b*-poly(ethyl butylene)—were compared with theoretical predictions based on the multicomponent random phase approximation (RPA). The polymers were nearly monodisperse and were synthesized by saturating the double bonds in anionically synthesized polydienes with H₂ and D₂, thus yielding polyolefins with neutron scattering contrast. The theoretical scattering profiles depend on 16 structural parameters and six Flory–Huggins interaction parameters χ , all of which were obtained independently. The χ parameters were obtained from SANS measurements on binary poly(ethyl butylene)/poly(methyl butylene) blends. The SANS profiles obtained from the ternary blends were in quantitative agreement with theoretical predictions over the observable q range (0.01–0.08 Å^{−1}) and over a wide range of block copolymer concentrations (from 10 to 80 vol. % copolymer). This suggests that the measured χ parameters are consistent with the original ideas of Flory and Huggins that χ is a measure of monomer–monomer interactions, and is thus independent of block copolymer concentration. Partial structure factors, related to correlations in the concentration of individual components, were examined by selective labeling and were also found to be in quantitative agreement with the predictions of the multicomponent RPA.

INTRODUCTION

The application of the random phase approximation (RPA)¹ to small angle neutron scattering data (SANS) obtained from binary polymer blends has led to considerable insight into these materials. Flory–Huggins interaction parameters^{2,3} (χ) for several polymer pairs have been estimated by this approach.⁴ These include polystyrene (PS)/poly(vinyl methyl ether),^{5–8} PS/polybutadiene,⁹ PS/poly(*o*-chlorostyrene),¹⁰ PS/poly(phenylene oxide),¹¹ poly(vinylidene fluoride)/poly(methyl methacrylate),⁵ isotopic polymer blends,^{12–14} blends containing polyisoprenes and polybutadienes with different microstructures,^{15,16} and blends of model ethylene–butene polyolefins.^{17–19}

However, many technologically important polymer blends consist of more than two polymeric components. A well-known example is high impact polystyrene (HIPS), which is a two-phase blend of two homopolymers—polystyrene and polybutadiene—and a polystyrene–polybutadiene graft copolymer. In such systems, the copolymers serve as interfacial agents, improving adhesion between the phases and preventing coalescence of the dispersed phase, and are hence referred to as the “compatibilizers.” The superior properties and commercial success of this class of materials has motivated numerous studies on mixtures of homopolymers and a block copolymer.^{20–27}

Bulk morphologies and their dependence on blend composition and processing conditions have been examined.^{20,21} Direct studies of the interphase have also been conducted.²⁰ Roe and co-workers^{21,22} have followed the kinetics of phase separation in polystyrene/polybutadiene/polystyrene-*b*-polybutadiene mixtures after quenching from the single-phase region into the two-phase region. Dai *et al.*²³ and Budkowski *et al.*²⁴ have studied thin films of homopolymer/homopolymer/block copolymer systems. Lohse *et al.* are studying the properties of compatibilized polypropylene/ethylene–propylene copolymer blends using graft copolymers.²⁵ Theoretical studies aimed at exploring the phase behaviors of these ternary systems have also been conducted.^{26–28}

A quantitative understanding of the interfacial and bulk properties of these multicomponent systems rests on the availability of a model for the free energy of mixing. While the Flory–Huggins theory can readily be generalized to multicomponent systems,²⁹ measurements of the χ parameter are largely restricted to binary blends.³⁰ In particular, we are not aware of any measurements of χ parameters in mixtures of two homopolymers and a block (or graft) copolymer. If the original assumptions of Flory and Huggins are valid, then the thermodynamic properties of multicomponent polymer mixtures should be predictable from binary χ parameters. However, recent theories^{31,32}

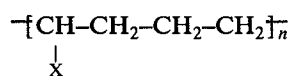
and experiments^{33,34} suggest that the *measured* χ parameter is related not only to monomer–monomer interactions, but that it is affected by other factors such as connectivity and shape of the monomers and equation-of-state effects. If this is true then the ternary χ parameters may differ substantially from those obtained from binary mixtures.

In this paper, we present the first SANS estimates of χ parameters in blends of two homopolymers and a diblock copolymer. Experiments were conducted on binary and ternary mixtures of model polyolefins—poly(ethyl butylene), poly(methyl butylene) and poly(methyl butylene)-*b*-poly(ethyl butylene)—which were synthesized via anionic polymerization. The multicomponent RPA framework, due to Akcasu and Tombakoglu,³⁵ and Benoit *et al.*,³⁶ is used to interpret the SANS data. We find that χ parameters obtained from binary mixtures are in *quantitative* agreement with those obtained from the ternary mixtures over a wide range of block copolymer compositions, suggesting agreement with the original ideas of Flory and Huggins.^{2,3}

The scattered intensity from multicomponent mixtures depends on a matrix of partial structure factors S_{ij} which quantify correlations in the concentration of species i and j in the mixture. By selectively labeling different components, we have isolated different components of the structure factor matrix. These measurements reveal the concentration fluctuations of individual components in the ternary mixture. We find that the measured partial structure factors are also in quantitative agreement with the predictions of the multicomponent RPA.

EXPERIMENTAL SECTION

Nearly monodisperse, model polyolefins were synthesized in two steps.³⁷ First, diene monomers were polymerized anionically under high vacuum in cyclohexane at 25 °C with sec-butyl lithium as the initiator and methanol as the terminator. Standard high vacuum procedures were used to purify the reagents.³⁸ Under these conditions dienes polymerize primarily (about 93%) by 1,4 addition. Second, separate portions of the polydiene were saturated with either H₂ or D₂ in cyclohexane under pressure (250 psi), at 100 °C, in the presence of a palladium catalyst. Isoprene and ethylbutadiene were used as monomers to yield poly(methyl butylene) and poly(ethyl butylene)



model polyolefin

X=CH₃–poly(methyl butylene) (PM),

X=C₂H₅–poly(ethyl butylene) (PE).

These polyolefins are essentially derivatives of polyethylene and are chemically equivalent to strictly alternating ethylene–propylene and ethylene–butene copolymers. In this paper, we refer to the poly(methyl butylene) chains as PM and the poly(ethyl butylene) chains as PE, where the letters M and E refer to the methyl and ethyl branches

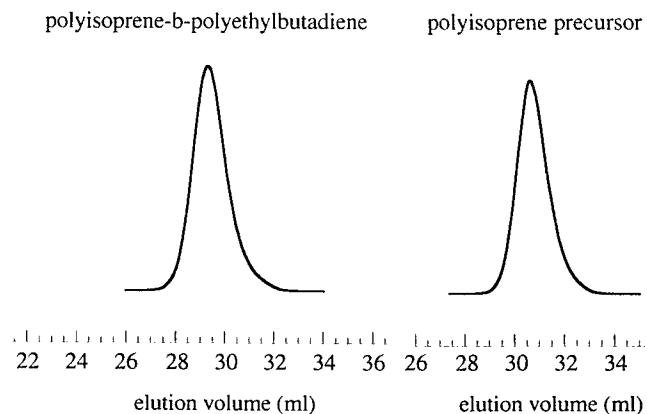


FIG. 1. GPC traces of the polyisoprene-*b*-polyethylbutadiene block copolymer and the polyisoprene precursor. These traces are typical of the polymers used in this study.

emanating from the C–C backbone. Hydrogenous and partially deuterated polyolefins synthesized from the same polydiene are referred to as matched pairs.

A polyisoprene–polyethylbutadiene block copolymer (50 mol % polyisoprene) was synthesized under identical conditions by sequential addition of isoprene followed by ethylbutadiene to the reactor, and then saturated to give PM–PE diblock copolymers. An aliquot of the polyisoprene precursor was removed from the reaction mixture prior to the addition of ethylbutadiene for characterization purposes. Gel permeation chromatography (GPC) traces (measured on a Waters Model 590 instrument with THF as the solvent) obtained from the polyisoprene–polyethylbutadiene block copolymer and the polyisoprene precursor (which represents the polyisoprene block) are shown in Fig. 1 and are typical of the polymers used in this study. The composition of the block copolymers was confirmed by ¹H and ¹³C NMR measurements on a General Electric Fourier transform nuclear magnetic resonance (FT NMR) machine. A section of the ¹H NMR spectrum from the polyisoprene–polyethylbutadiene block copolymer is shown in Fig. 2(a) where the signatures of the polyisoprene and polyethylbutadiene segments are clearly evident. Visual inspection of the spectrum suggests that the block copolymer chains contain roughly equal numbers of polyisoprene and polyethylbutadiene units. However, quantitative analysis was not attempted due to excessive overlap of the peaks. The ¹³C NMR spectrum, shown in Fig. 2(b), was used to estimate the block copolymer composition. The spectrum was analyzed for saturated 1,4 and 3,4 polyisoprene and polyethylbutadiene units. The absence of 1,2 units was established by Fourier transform infrared (FTIR) and ¹H NMR. The peaks associated with saturated polyisoprene units were analyzed using the assignment of Randall,³⁹ while those of the saturated polyethylbutadiene were analyzed on the basis of assignments on two model hydrogenated polyethylbutadiene polymers, one with 93% 1,4 units (and 7% 3,4 units) and the other with 50% 1,4 units (and 50% 3,4 units).⁴⁰ Triad compositions based on these assignments were used to determine

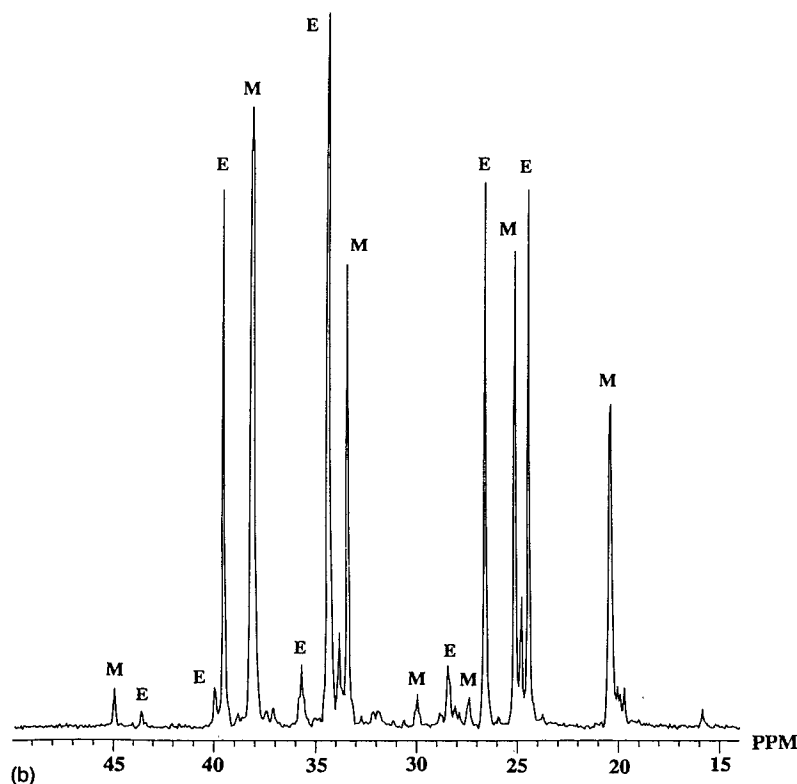
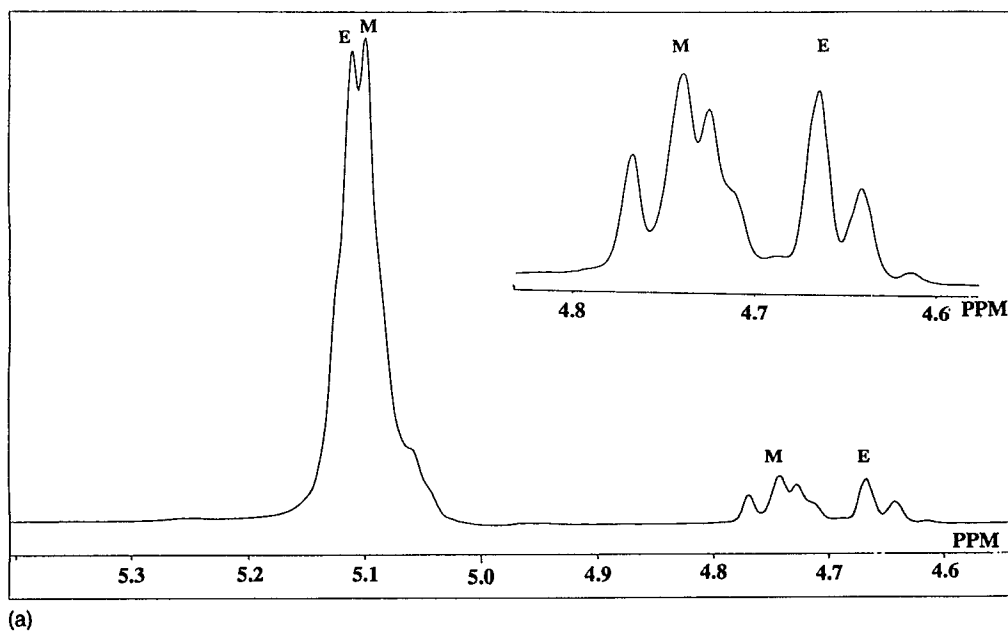


FIG. 2. (a) The ^1H NMR spectrum of the polyisoprene-*b*-polyethylbutadiene block copolymer. (b) The ^{13}C NMR spectrum of *h*PM-*h*PE. Features associated with the PM block are labeled M, while those associated with the PE block are labeled E.

the composition of the block copolymer. The mole fraction of PM monomers thus obtained was 0.50 which is within 1% of the target composition.

Table I summarizes the characteristics of the polyolefins used in this work. The prefix *h* refers to hydrogenated polymers and the prefix *d* refers to the partially deuterated polymers. The average number of deuterium atoms per repeat unit in the labeled samples (n_D) was based on density measurements in a density gradient column at 23 °C. The effect of deuteration on monomer volumes is calcu-

lated on the basis that the volume of a perdeuterated polymer is 0.2% less than that of a fully hydrogenated polymer that is otherwise identical to it. The molecular weights of the polymers were determined by light scattering from cyclohexane solutions of the parent polydienes (refractive index increments were measured on a Chromatix KMX-16, and scattered intensities were measured on a Chromatix KMX-6, both at 25 °C). The GPC traces of the parent polydienes and the corresponding matched pairs were essentially superposable, confirming that the satura-

TABLE I. Characterization of polymers.

Sample	Density ^a (g/cm ³)	n_D^b	Molecular weight ^c	Polydispersity index ^d	Volume fr. of PM in block copolymer ^e
<i>h</i> PM	0.8540	...	7.7×10^4	1.06	...
<i>d</i> PM	0.9226	5.52	8.4×10^4	1.06	...
<i>h</i> PE	0.8629	...	4.8×10^4	1.07	...
<i>d</i> PE	0.9297	6.38	5.2×10^4	1.07	...
<i>h</i> PM- <i>h</i> PE	0.8579	...	4.6×10^4	1.09	0.452
<i>d</i> PM- <i>d</i> PE	0.9007	3.67	4.8×10^4	1.09	0.452

^aUsing a density gradient column.^bAverage number of deuterium per monomer based on density measurements.^cFrom light scattering on polydiene precursors.^dFrom GPC, based on polyisoprene calibration, uncorrected for column dispersion.^eBased on ¹³C NMR on *h*PM-*h*PE and densities of *h*PM and *h*PE.

tion step did not alter chain architecture. We therefore assume that the parent polydiene and the corresponding matched pairs have identical degrees of polymerization. The polydispersities were based on GPC measurements with polyisoprene standards for calibration. The 3,4 content of the chains was obtained from ¹H NMR measurements on the polydienes and is similar to that obtained in other laboratories under similar conditions—6%–7% for PM and 7%–8% for PE. The lack of C=C signal in the ¹H spectra of the saturated polydienes was used to confirm complete saturation.

Blends were made by dissolving the components in cyclohexane and then drying to constant weight in a vacuum oven at 70 °C. All the blends were optically clear, indicating that they were single phase. Two-dimensional SANS patterns were obtained from 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. Neutrons with a wavelength $\lambda = 9$ Å ($\Delta\lambda/\lambda = 0.25$) were used. The scattering data were corrected for background, empty cell scattering, and detector sensitivity; converted to an absolute scale using secondary standards; and azimuthally averaged. The incoherent scattering for each blend was estimated from SANS measurements on pure *h*PM, assuming that it is proportional to the concentration of H atoms in the blend, and subtracted from the azimuthally averaged scattering profiles to give the coherent scattering intensity $I(q)$ [$q = 4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle]. All SANS measurements were carried out at 27 °C.⁴¹

THEORETICAL BACKGROUND

The random phase approximation (RPA) for multi-component polymer systems, due to Akcasu and Tombakoglu,³⁵ and Benoit *et al.*,³⁶ yields the following expression for the coherent scattered intensity:

$$I(q) = \mathbf{B}^T \mathbf{S}(q) \mathbf{B}, \quad (1a)$$

where the multicomponent structure factor $\mathbf{S}(q)$ is given by

$$\mathbf{S}(q) = [\mathbf{S}^0(q)^{-1} + \mathbf{V}(q)]^{-1}. \quad (1b)$$

\mathbf{S}^0 contains the structure factors of the components in the absence of interactions, \mathbf{V} contains the interaction parameters between the constituent monomers, and the vector \mathbf{B} characterizes the scattering contrasts in the system. We assume incompressibility and follow the “matrix” method of Akcasu and Tombakoglu^{35,42} to obtain the scattered intensity from a blend of a diblock copolymer (the individual blocks are treated as separate “species” labeled 1 and 2) and two homopolymers (labeled 3 and 4). We write out the components of \mathbf{S}^0 , \mathbf{V} , and \mathbf{B} considering the homopolymer labeled 4 to be the matrix component

$$S_{ii}^0(q) = N_i \phi_i v_i P_i(q) \quad (i=1-3), \quad (2a)$$

$$S_{12}^0(q) = S_{21}^0(q) = (N_1 \phi_1 v_1 N_2 \phi_2 v_2)^{1/2} F_1(q) F_2(q), \quad (2b)$$

$$S_{ij}^0(q) = 0 \quad (i, j \neq 1, 2), \quad (2c)$$

$$V_{ii}(q) = \frac{1}{N_4 \phi_4 v_4 P_4(q)} - \frac{2\chi_{i4}}{v} \quad (i=1-3), \quad (2d)$$

$$V_{ij}(q) = \frac{1}{N_4 \phi_4 v_4 P_4(q)} - \frac{\chi_{i4}}{v} - \frac{\chi_{j4}}{v} + \frac{\chi_{ij}}{v} \quad (\text{all } i \neq j), \quad (2e)$$

$$B_i = \frac{b_i}{v_i} - \frac{b_4}{v_4} \quad (i=1-3). \quad (2f)$$

N_i , ϕ_i , v_i , and b_i are the number of monomers, volume fraction in the blend, monomer volume, and monomer scattering lengths of species i , respectively, and χ_{ij} is the Flory–Huggins parameter between species i and j based on an arbitrary reference volume v . Functions P_i describe the ideal intraspecies monomer correlations due to chain connectivity, and we use the Debye function for flexible chains

$$P_i(q) = 2 \frac{\exp(-x_i) - 1 + x_i}{x_i^2} \quad (i=1 \text{ to } 4), \quad (2g)$$

where $x_i = q^2 N_i l_i^2 / 6$ and l_i is the statistical segment length of species i . Functions F_i describe the ideal interspecies monomer correlations which are absent in all cases except for species 1 and 2, and we use the Leibler function for flexible diblocks:⁴³

$$F_i(q) = \frac{1 - \exp(-x_i)}{x_i} \quad (i=1, 2). \quad (2h)$$

It is implicit in Eqs. (2a)–(2h) that the free energy per unit volume of the homogeneous mixture of two homopolymers and a block copolymer ΔG_m is given by

$$\begin{aligned} \frac{\Delta G_m}{kT} = & \frac{(\phi_1 + \phi_2) \ln(\phi_1 + \phi_2)}{N_1 v_1 + N_2 v_2} + \frac{\phi_3 \ln \phi_3}{N_3 v_3} + \frac{\phi_4 \ln \phi_4}{N_4 v_4} + \frac{\chi_{12}}{v} \phi_1 \phi_2 \\ & + \frac{\chi_{13}}{v} \phi_1 \phi_3 + \frac{\chi_{14}}{v} \phi_1 \phi_4 + \frac{\chi_{23}}{v} \phi_2 \phi_3 + \frac{\chi_{24}}{v} \phi_2 \phi_4 \\ & + \frac{\chi_{34}}{v} \phi_3 \phi_4 - \frac{\chi_{12}}{v} \frac{\phi_1}{(\phi_1 + \phi_2)} \frac{\phi_2}{(\phi_1 + \phi_2)}, \end{aligned} \quad (3)$$

TABLE II. A list of parameters used to obtain theoretical estimates of neutron scattering intensities.

Parameter	<i>h</i> PM	<i>d</i> PM	<i>h</i> PE	<i>d</i> PE	<i>h</i> PM- <i>h</i> PE		<i>d</i> PM- <i>d</i> PE	
					PM block	PE block	PM block	PE block
N_i	575	575	1105	1105	300	300	300	300
v_i (Å ³ /monomer)	136.4	136.2	162.0	161.8	136.4	162.0	136.2	161.8
l_i (Å)	8.19	8.19	7.93	7.93	8.19	7.93	8.19	7.93
b_i (Å)	-4.15×10^{-5}	5.33×10^{-4}	-4.98×10^{-5}	6.14×10^{-4}	-4.15×10^{-5}	-4.98×10^{-5}	3.07×10^{-4}	3.65×10^{-4}

Interaction parameters based on a reference volume $v = 148.6 \text{ Å}^3$
 $\chi_{hPM/dPM} = 3.8 \times 10^{-4}$ $\chi_{hPE/dPE} = 3.2 \times 10^{-4}$
 $\chi_{hPE/dPM} = 1.45 \times 10^{-3}$ $\chi_{dPE/hPM} = 1.85 \times 10^{-3}$ $\chi_{hPE/hPM} = 1.65 \times 10^{-3}$ $\chi_{dPE/dPM} = 1.65 \times 10^{-3}$

where k is Boltzman's constant and T is absolute temperature.

PARAMETER ESTIMATION

The scattered intensity from ternary blends of two homopolymers and a block copolymer thus depends on 16 structural parameters (N_i, v_i, b_i, l_i) and six interaction parameters (χ_{ij}). The values of these parameters are summarized in Table II and the sequence of experiments that were conducted to determine them are described below.

(1) We define the PM monomer to be a C_5H_{10} unit and the PE monomer to be a C_6H_{12} unit. The monomer volumes were obtained from the densities of the fully hydrogenated polyolefins, and the geometric mean of these volumes were taken as the reference volume ($v = 148.6 \text{ Å}^3$). Changes in monomer volumes due to deuterium labeling are not significant for these calculations and have been ignored. Values of N_i are based on light scattering molecular weights. The scattering lengths of the homopolymers and the *h*PM-*h*PE block copolymer were based on literature values for atomic scattering lengths,⁴ using average monomer composition, which, in the case of the labeled homopolymers, was determined from density measurements.

(2) SANS measurements on binary homopolymer blends were used to estimate l_i and χ_{ij} following the procedure of Balsara *et al.*¹⁸ For a mixture of two homopolymers labeled 1 and 2, Eqs. (1a) and (1b) reduce to the familiar form

$$\frac{I(q)}{[(b_1/v_1) - (b_2/v_2)]^2} = S(q) = \left[\frac{1}{\phi_1 N_1 v_1 P_1(q)} + \frac{1}{\phi_2 N_2 v_2 P_2(q)} - \frac{2\chi_{12}}{v} \right]^{-1}. \quad (4)$$

The statistical segment lengths of PM and PE chains, and interaction parameters $\chi_{hPM/dPM}$ and $\chi_{hPE/dPE}$, were obtained from SANS experiments on equal volume *h*PM/*d*PM and *h*PE/*d*PE mixtures (i.e., matched pair mixtures), for which case, Eq. (4) reduces to

$$S_m(q) = \left[\frac{4}{N_m v_m P_m(q, l_m)} - \frac{2\chi_m}{v} \right]^{-1}, \quad (5)$$

where quantities with subscript m refer to matched pairs.

The measured $S_m(q)$'s were fit to the functional form given by Eq. (5) using nonlinear regression and the unknown parameters χ_m and l_m were estimated from the best fit. The regression results indicated that χ is relatively small and the scattering profile is dominated by the chain form factors. This is expected due to the chemical similarity of matched pairs. The measured structure factors of the two matched pair mixtures are shown in Fig. 3. The curves through the data represent results of the nonlinear regression from which we estimate $l_{PM} = 8.19 \text{ Å}$, $\chi_{hPM/dPM} = 3.8 \times 10^{-4}$, $l_{PE} = 7.93 \text{ Å}$, and $\chi_{hPE/dPE} = 3.2 \times 10^{-4}$. We use these statistical segment lengths to calculate $P_i(q)$ and $F_i(q)$ of all "species"—homopolymers as well as block copolymers.

The χ parameters between PE and PM segments were determined from SANS measurements on *h*PE/*d*PM and *d*PE/*h*PM mixtures. The ratio ϕ_{PE}/ϕ_{PM} in both blends was 1.3, which is close to the Flory-Huggins estimate of the critical composition. Estimates of $\chi_{hPE/dPM}$ and $\chi_{dPE/hPM}$ were obtained by recasting the blend structure factor in terms of a difference function $E(q)$,¹⁸

$$E(q) = \frac{v}{2} \left[\frac{1}{\phi_1 N_1 v_1 P_1(q)} + \frac{1}{\phi_2 N_2 v_2 P_2(q)} - \frac{1}{S(q)} \right], \quad (6)$$

which would be equal to χ at all q if the data were in perfect compliance with RPA. We use the matched pair

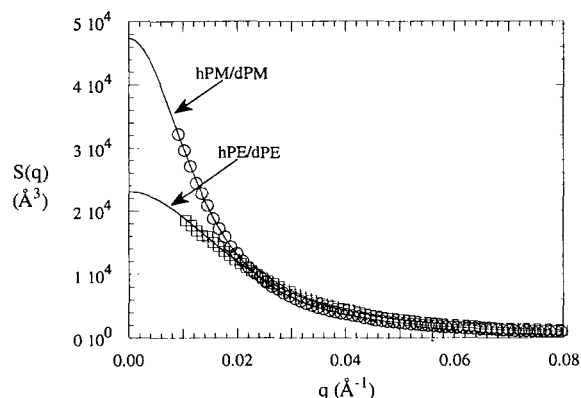


FIG. 3. Structure factor vs q for 50/50 matched pair mixtures. (Circles) *h*PM/*d*PM; (squares) *h*PE/*d*PE. Solid curves through the data are best fits of Eq. (5) from which parameters χ and l are estimated.

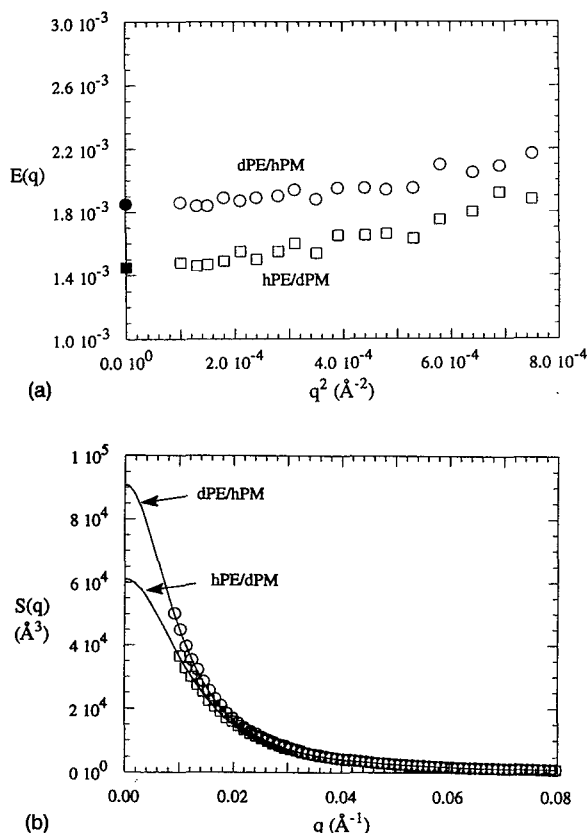


FIG. 4. (a) The difference function $E(q)$ [defined by Eq. (6)] vs q for binary homopolymer blends (circles) hPE/dPM ; (squares) dPE/hPM . ϕ_{PE}/ϕ_{PM} in both blends is 1.3. The solid symbols represent extrapolations to $q=0$ and $\chi=E(0)$. (b) The measured structure factor of binary blends $S(q)$ vs q for binary homopolymer blends (circles) hPE/dPM ; (squares) dPE/hPM . ϕ_{PE}/ϕ_{PM} in both blends is 1.3. The solid curves through the data represent calculated RPA structure factors calculated using χ parameters obtained from $E(0)$ and statistical segment lengths obtained from SANS of matched pair blends.

results for l_i to obtain $P_i(q)$, and thus $E(q)$ is determined solely from experiments. In Fig. 4(a), we show $E(q)$ values at low angles for the hPE/dPM and dPE/hPM blends. The χ parameters for the two mixtures were estimated by extrapolating to obtain $E(0)$ [$\chi \equiv E(0)$], giving $\chi_{hPE/dPM} = 1.45 \times 10^{-3}$ and $\chi_{dPE/hPM} = 1.85 \times 10^{-3}$. These values were obtained by a linear extrapolation of the $E(q)$ vs q^2 data shown in Fig. 4(a). $E(q)$ is a weak function of q , as anticipated, and thus the values of χ are not sensitive to details of the extrapolation procedure. In fact, $E(q)$ values obtained at the lowest angles are very nearly equal to χ itself. In Fig. 4(b), we show the measured structure factors of the hPE/dPM and dPE/hPM blends. The curves through the data are RPA structure factors using the abovementioned χ values and l_i determined from the matched pair blends. It is evident that the estimated parameters are consistent with the data over the entire accessible q window. We can thus conclude that the chains in binary PM/PE blends are unperturbed relative to their state in the matched pair blends. The values of l_i and χ reported here are in agreement with previous measurements on similar materials.^{44–46}

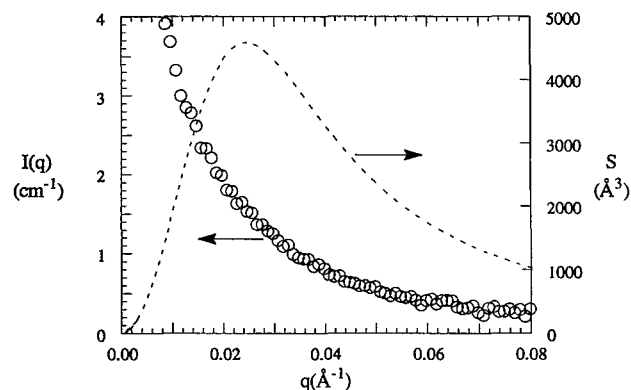


FIG. 5. A comparison between the coherent scattered intensity from $dPM-dPE$ and the RPA prediction for the structure factor of the diblock copolymer. The lack of agreement indicates that there is no scattering contrast between the blocks in $dPM-dPE$.

We now use the result of Rhee and Crist¹⁹ and Graessley *et al.*,⁴⁶ who have shown that the χ parameters between polyolefins with no labeling contrast ($\chi_{hPE/hPM}$ and $\chi_{dPE/dPM}$ in our case) are approximately given by the arithmetic mean of the χ parameters obtained from blends of labeled and unlabeled species ($\chi_{hPE/dPM}$ and $\chi_{dPE/hPM}$ in our case). We thus obtain $\chi_{hPE/hPM} = \chi_{dPE/dPM} = 1.65 \times 10^{-3}$.

(3) SANS data from pure $dPM-dPE$, shown in Fig. 5, were used to determine the deuterium content of the monomers in the block copolymer. If there were systematic differences in the deuterium content of the PM and PE blocks, then the scattering profile would parallel the structure factor of pure diblocks derived by Leibler^{42,43} and have a peak at $q=0.025$ ($1/\text{\AA}$). The dashed curve in Fig. 5 represents $S(q)$ for the $dPM-dPE$ diblock, using statistical segment lengths, monomer volumes, and $\chi_{dPE/dPM}$ determined earlier. It is apparent that the measured scattering profile is not parallel to the RPA prediction for $S(q)$, implying that there is no neutron scattering contrast between the PM and the PE blocks in the $dPM-dPE$ block copolymer ($b_1/v_1 = b_2/v_2$). This relationship and the average deuteration level obtained from density measurements were used to determine b_i of the blocks in $dPM-dPE$. (The

TABLE III. Composition of blends discussed in this paper.

Blends shown in	Components			ϕ_A/ϕ_B^a	ϕ_{A-B}^a
	A	B	A-B		
Figure 3	<i>hPM</i>	<i>dPM</i>	...	1.041	0
	<i>hPE</i>	<i>dPE</i>	...	1.033	0
Figure 4	<i>hPE</i>	<i>dPM</i>	...	1.355	0
	<i>dPE</i>	<i>hPM</i>	...	1.350	0
Figure 6	<i>hPE</i>	<i>dPM</i>	<i>hPM-hPE</i>	1.344	0.101
	<i>hPE</i>	<i>dPM</i>	<i>hPM-hPE</i>	1.351	0.399
	<i>hPE</i>	<i>dPM</i>	<i>hPM-hPE</i>	1.350	0.800
Figure 7 (blend A)	<i>hPE</i>	<i>hPM</i>	<i>dPM-dPE</i>	1.304	0.202
(blend B)	<i>hPE</i>	<i>dPM</i>	<i>hPM-hPE</i>	1.345	0.200
Figure 9 (blend C)	<i>hPE</i>	<i>dPM</i>	<i>dPM-dPE</i>	1.333	0.202

^aBased on weight fractions, assuming no volume change on mixing.

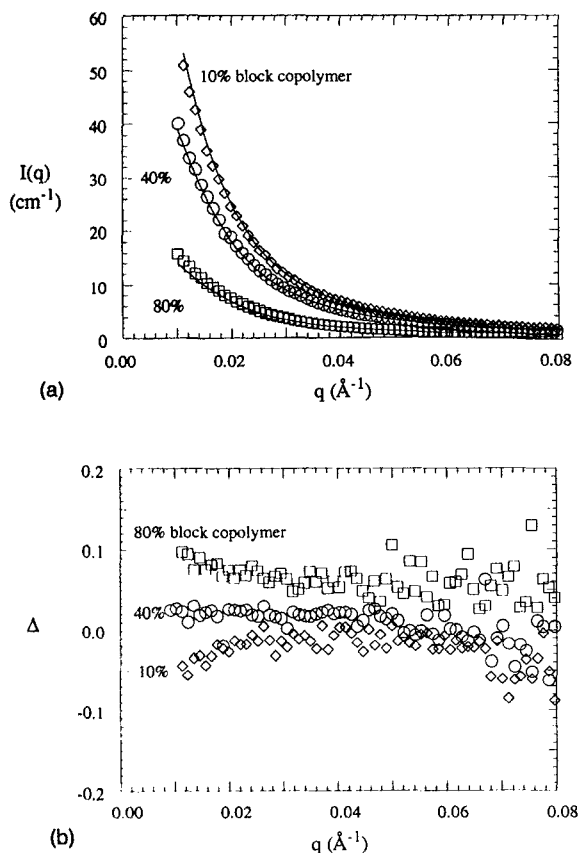


FIG. 6. (a) SANS intensity $I(q)$ vs scattering vector q from ternary $hPE/dPM/hPM-hPE$ blends (diamonds) $\phi_{hPM-hPE} = 0.1$; (circles) $\phi_{hPM-hPE} = 0.4$; (squares) $\phi_{hPM-hPE} = 0.8$. ϕ_{hPE}/ϕ_{dPM} in all blends is 1.3. Solid curves are multicomponent RPA predictions using independently obtained structural and thermodynamic parameters given in Table II. Agreement between experiment and theory is obtained without adjustable parameters. (b) A plot of Δ [defined by Eq. (7)] vs q , showing deviations between experiment and theory for ternary $hPM/dPE/hPM-hPE$ blends (diamonds) $\phi_{hPM-hPE} = 0.1$; (circles) $\phi_{hPM-hPE} = 0.4$; (squares) $\phi_{hPM-hPE} = 0.8$. ϕ_{hPE}/ϕ_{dPM} in all blends is 1.3.

small upturn in the low q scattering from $dPM-dPE$ is consistent with the arguments given in Ref. 47.⁴⁸)

NEUTRON SCATTERING FROM TERNARY BLENDS

In Fig. 6(a), we show comparisons between theory and experiment for ternary $hPE/dPM/hPM-hPE$ mixtures with varying amounts of diblock copolymer ($\phi_{hPM-hPE} = 0.1, 0.4$, and 0.8). The relative homopolymer concentration ϕ_{hPE}/ϕ_{dPM} is kept constant at 1.3, which is identical to that in the binary experiments which gave χ_{ij} between PE and PM segments. For the sake of clarity, we refer to nominal blend compositions in the discussion. The exact compositions of all blends used in this study are given in Table III. The solid lines in Fig. 6(a) represent theoretical predictions for $I(q)$ using Eqs. 1(a) 1(b) and 2(a)–2(h), with structural and thermodynamic parameters listed in Table II. It is apparent that there is good agreement between theory and experiment. We emphasize that the agreement was obtained without any adjustable parameters and can thus be taken as a confirmation of the Flory–Huggins theory and the random phase approxima-

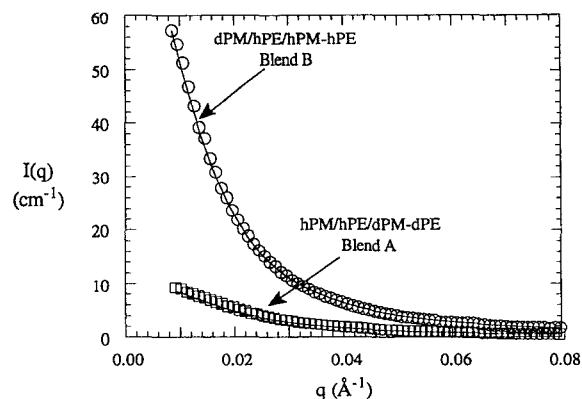


FIG. 7. The effect of label switching on measured SANS intensity from ternary blends. (Squares) $hPE/hPM/dPM-dPE$ blend with $\phi_{hPE}/\phi_{hPM} = 1.3$ and $\phi_{dPM-dPE} = 0.2$ (blend A). (Circles) $hPE/dPM/hPM-hPE$ blend with $\phi_{hPE}/\phi_{dPM} = 1.3$ and $\phi_{hPM-hPE} = 0.2$ (blend B). Solid curves are RPA predictions using parameters given in Table II.

tion in mixtures of two homopolymers and a block copolymer. This implies that the chains in the ternary blend are unperturbed relative to their state in the binary blends and that binary χ parameters can be used to quantify the thermodynamics of mixing in mixtures of two homopolymers and a block copolymer.

The deviations between experiment and theory are shown more clearly in Fig. 6(b). The quantity Δ defined as

$$\Delta = \frac{I(q)_{\text{experiment}} - I(q)_{\text{theory}}}{I(q)_{\text{theory}}} \quad (7)$$

is plotted vs q for the three blends depicted in Fig. 6(a). The observed deviations are well within experimental error; typical uncertainties in the estimate of N_i , b_i , l_i , and χ_{ij} lie between 5% and 10%. If the χ_{ij} values in the ternary blends were different from those in the binary blends, then the disagreement between theory and experiment would be most pronounced at low q . The q dependence of Δ in all cases is weak, suggesting that the minor deviations between theory and experiment are not due to differences in the thermodynamic interactions in binary and ternary blends, but perhaps errors in the estimation of the structural parameters (N_i , b_i , and l_i).

The scattered intensity from the blends shown in Figs. 6(a) and 6(b) is due to the correlations in the concentration of dPM segments. Incompressible ternary mixtures have two independently fluctuating concentrations. Correlations in the concentration of the other species, say $hPM-hPE$, do not contribute to the scattering because there is no neutron scattering contrast between the $hPM-hPE$ and the matrix component (hPE). Note, however, that the presence of this species does affect the dPM correlations through the interaction matrix V . In order to focus on the block copolymer concentration fluctuations (i.e., the second independently diffusing species), we examined a $hPE/hPM/dPM-dPE$ blend with $\phi_{hPE}/\phi_{hPM} = 1.3$ and $\phi_{dPM-dPE} = 0.2$ (blend A). The SANS profile obtained from this mixture is shown in Fig. 7. For purposes of comparison, we also show the data from a blend with identical

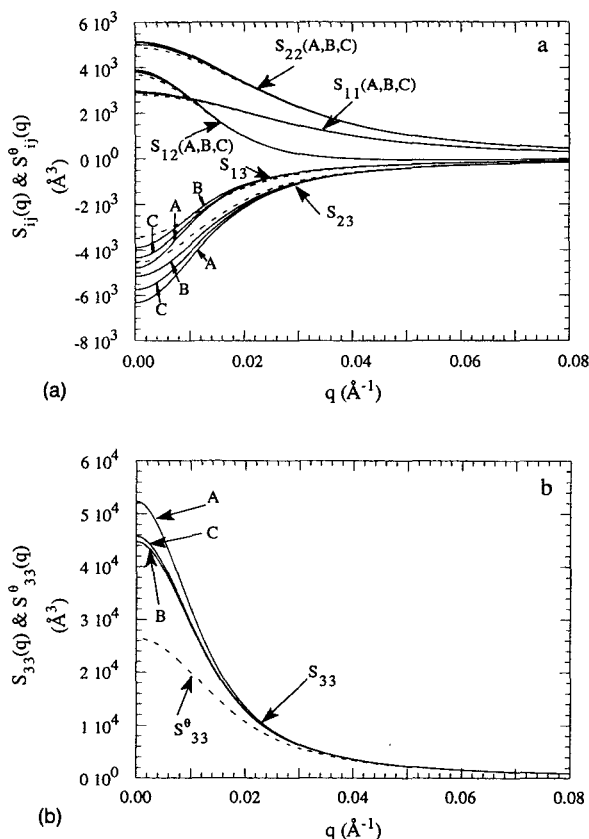


FIG. 8. RPA predictions for the partial structure factors of ternary blends A, B, and C. (Blend A) $hPE/hPM/dPM-dPE$ blend with $\phi_{hPE}/\phi_{hPM} = 1.3$ and $\phi_{dPM-dPE} = 0.2$; (blend B) $hPE/dPM/hPM-hPE$ blend with $\phi_{hPE}/\phi_{dPM} = 1.3$ and $\phi_{hPM-hPE} = 0.2$; (blend C) $hPE/dPM/dPM-dPE$ blend with $\phi_{hPE}/\phi_{dPM} = 1.3$ and $\phi_{dPM-dPE} = 0.2$. Solid curves represent S_{ij} and were obtained using parameters given in Table II. Dashed curves represent S_{ij}^0 and were obtained by setting $\chi_{ij} = 0$. Labels 1 and 2 refer to the PM and PE segments in the block copolymer, respectively, label 3 refers to the PM homopolymer segments, and label 4 refers to hPE . (a) $(i,j) = (1,1), (1,2), (2,2), (1,3), (3,1)$; (b) $(i,j) = (3,3)$.

composition, but with the deuterium labels on one of the homopolymers, instead of the block copolymer— $hPE/dPM/hPM-hPE$ blend with $\phi_{hPE}/\phi_{dPM} = 1.3$ and $\phi_{hPM-hPE} = 0.2$ (blend B).

If we ignore the minor changes in χ due to deuterium substitution, then the distribution of concentration fluctuations in blends A and B would be identical. It is thus somewhat surprising to find a sixfold decrease in the low q intensity from blend A relative to blend B. A threefold change is anticipated because the concentration of labeled chains in blend A is lower than that in blend B (see Table III), and the scattering contrast of the $dPM-dPE$ chains is less than that of the dPM chains (see Table I for values). The underlying physics responsible for the additional two-fold decrease becomes clear when one examines the partial structure factors responsible for the observed scattering. The RPA predictions for the partial structure factors (S_{ij}) of blends A and B are represented by solid curves in Figs. 8(a) and 8(b). In this discussion, the labels 1 and 2 refer to the PM and PE segments in the block copolymer, respectively, label 3 refers to the PM homopolymer segments

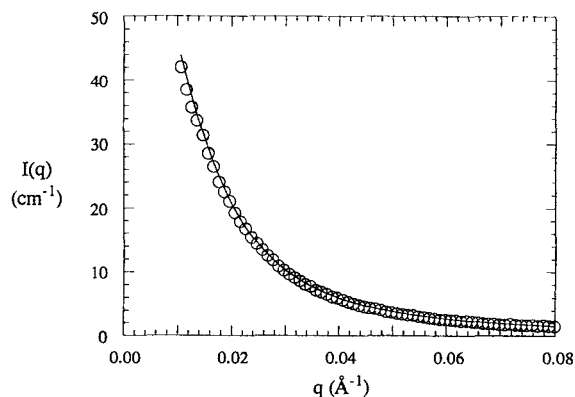


FIG. 9. A comparison between experimental SANS intensity and RPA predictions (solid curve) for the $hPE/dPM/dPM-dPE$ blend with $\phi_{hPE}/\phi_{dPM} = 1.3$ and $\phi_{dPM-dPE} = 0.2$ (blend C). Note that in this blend there is scattering contrast among all three components.

and label 4 refers to hPE (the matrix component in both blends). (Note that $S_{ij} = S_{ji}$ by definition.) The partial structure factors of blends A and B are not identical due to small differences in composition and χ parameters. However, these differences have a negligible effect on S_{ij} , especially in the experimentally accessible q range [see Figs. 8(a) and 8(b)]. The dashed curves in these figures are calculated S_{ij}^0 's with all χ_{ij} 's set to zero, and we refer to these as S_{ij}^0 . S_{ij}^0 thus represents the expected partial structure factors in the absence of thermodynamic interactions. It is apparent from Fig. 8(a) that the block copolymer S_{ij} and S_{ij}^0 ($i,j = 1,2$) are virtually indistinguishable. This implies that the correlations in the block copolymer segment concentrations are unaffected by the thermodynamic interactions in the system and arise only due to connectivity of the segments. In contrast, Fig. 8(b) shows that the homopolymer partial structure factor S_{33} is enhanced by a factor of about 2 at low angles. Recall that the scattered intensity from blend A is proportional to $(S_{11} + S_{22} + 2S_{12})$, since $B_1 = B_2 \neq 0$ and $B_3 = 0$, while that from blend B is proportional to S_{33} , since $B_1 = B_2 = 0$ and $B_3 \neq 0$. The unexpectedly low scattering from blend A is thus due to the fact that the scattering from this blend arises from partial structure factors unaffected by the thermodynamic interactions. Note that the agreement between the measured partial structure factors and multicomponent RPA is quantitative; the solid curves through the data in Fig. 7 are the RPA predictions for $I(q)$ with no adjustable parameters.

One can view the low angle scattering as that arising from large length-scale correlations (or fluctuations) that emerge, e.g., when a system approaches the spinodal point. The diminutive low angle scattering from blend A indicates that there are substantially fewer large length-scale fluctuations in the block copolymer concentration when compared to those in the homopolymer concentration. We attribute this to the symmetric architecture of the block copolymer (mole fraction of PM units in copolymer is 0.5). Even though there are large fluctuations in the concentrations of the homopolymers in blends A and B (due

to repulsive interactions between the homopolymers, $\chi > 0$), the symmetric block copolymer has equal preference for both homopolymers and is thus found with equal probability in both PM-rich and PE-rich regions. Also, there is no propensity for the block copolymer molecules to partition to the “interfacial zone” between the PM-rich and PE-rich regions. This is diametrically opposite to the conventional “compatibilizing” role of the block copolymers in phase separated systems, where the block copolymers have a strong preference to partition to the interface between the phases.

The ternary blends examined thus far contain only one labeled species. In Fig. 9, we show data obtained from a $hPE/dPM/dPM-dPE$ blend with $\phi_{hPE}/\phi_{dPM} = 1.3$ and $\phi_{dPM-dPE} = 0.2$ (blend C). In this case, there is substantial scattering contrast between the monomers of all three components (see Table II) and thus all nine components of the structure factor matrix contribute to the measured scattering. We note that even in this case, the predictions of multicomponent RPA are in good agreement with the experimental results. Except for deuterium labels, blend C is identical in composition to blends A and B, and its structure factors are also depicted in Figs. 8(a) and 8(b). The quantitative agreement between theory and experiment suggests that the theoretically predicted cross correlations between homopolymer and block copolymer concentrations— S_{13} and S_{23} [see Fig. 8(a)]—are also in agreement with experiment since all the other S_{ij} 's were examined independently in experiments conducted on blends A and B.

It is perhaps appropriate to question whether or not the detailed multicomponent RPA analysis is essential for understanding these data. For instance, one may argue that effects of deuteration on χ are small and thus a single, averaged χ parameter may be used to quantify the PE/PM interactions in these ternary mixtures. To answer this question, we have reanalyzed the data presented in Figs. 6(a) and 6(b) with $\chi_{PE/PM} = 1.65 \times 10^{-3}$, regardless of labeling, and $\chi_{hPE/dPE}$ and $\chi_{hPM/dPM}$ set to zero. This scheme was found to be reasonable at high block copolymer concentrations, but not at low concentrations. For example, for the blend with 10% copolymer, $|\Delta|$ at $q = 0.01 \text{ \AA}^{-1}$ increased from 0.05 to 0.12 when this simplification was used. This indicates that the subtle effects of deuterium substitution on χ observed in the binary systems^{19,46} are also present in these ternary systems. Incorporating such effects requires the use of multicomponent RPA. Similarly, one could simplify the analysis by assuming that the block copolymer is an inert diluent and treat the scattering from the ternary mixture as a pseudobinary mixture. This simplification is justified because the block copolymer is uniformly distributed throughout the sample, and the fact that the relative ratio of PM and PE units does not change significantly as one dilutes the blend with the block copolymer.⁴⁹ Of course, this scheme can only be used to interpret the data shown in Figs. 6(a) and 6(b); it is incapable of addressing the results of the label switching experiments described in Fig. 7. We found that this pseudobinary approximation is accurate at low block copolymer concentrations, but not at

high concentrations. For example, for the blend with 80% copolymer, $|\Delta|$ at $q = 0.01 \text{ \AA}^{-1}$ increased from 0.10 to 0.17 when this scheme was used. Also, both the simplifications considered here gave Δ vs q plots with significant curvature at low q , suggesting that the thermodynamic interactions in the blend are not accurately described. In summary, the full multicomponent RPA treatment was the only one that was quantitatively consistent with all the experimental data presented in this study.

CONCLUSION

Small-angle neutron scattering profiles from homogeneous, ternary mixtures of poly(ethyl butylene)/poly(methyl butylene)/poly(methyl butylene)-*b*-poly(ethyl butylene) (PE/PM/PM-PE) were measured at a fixed homopolymer ratio ($\phi_{PE}/\phi_{PM} = 1.3$) over a wide range of block copolymer concentrations ($0.1 \leq \phi_{PM-PE} \leq 0.8$). Thermodynamic interactions in these ternary mixtures were inferred by comparing the experimentally measured scattering profiles with theoretical predictions of multicomponent RPA, which are based on linear response theory. The structural and thermodynamic parameters required for the theoretical predictions were obtained from independent experiments. The χ parameters were obtained from binary poly(methyl butylene)/poly(ethyl butylene) blends. In all cases, there was quantitative agreement between theory and experiment, implying that binary χ parameters can be used to predict thermodynamics in homopolymer/homopolymer/block copolymer mixtures. Although we are a long way from establishing the microscopic origin of the χ parameter, our experiments lend support to the original ideas of Flory and Huggins that χ is a measure of monomer–monomer interactions and is thus independent of block copolymer concentration.

The χ parameter, both in the Flory–Huggins framework and in our experiments, is related to the scattering at $q = 0$ only. The structure factor of the ternary blends at finite q is related to the correlations between blend components. Correlations in the concentration of individual components were examined by selective labeling. Dramatic differences were observed when the label is switched from one of the homopolymers to the block copolymer, owing to differences in molecular architecture. We find large length-scale fluctuations in homopolymer concentrations which are driven by repulsive interactions between the PM and PE homopolymers. However, the PM–PE block copolymer is not affected by these fluctuations and is distributed homogeneously throughout the sample due to its symmetric architecture. We find that the measured partial structure factors are in quantitative agreement with theoretical predictions of multicomponent RPA over the entire accessible q window, implying the adequacy of linear response theory in these multicomponent mixtures.

The thermodynamic measurements presented in this paper are limited to blends in which the ratio of homopolymer volume fractions ϕ_{PE}/ϕ_{PM} was kept constant at 1.3. Whether or not the observed agreement between theory and experiment persists at other values of ϕ_{PE}/ϕ_{PM} remains

to be seen. We have also not addressed temperature and molecular weight effects, nor have we studied systems close to the phase separation point. Our current experiments are aimed in these directions.

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- ⁴⁹We thank the reviewer for suggesting this simplification.