

Intramolecular and Intermolecular Signatures of Incipient Ordering in a Multicomponent Polymer Blend

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Neutron scattering experiments were performed on a homogeneous blend of two homopolymers and a block copolymer, in the vicinity of an ordering transition. The concentration fluctuations of individual components were examined in separate experiments on contrast matched systems. The homopolymers exhibit intermolecular aggregation, while the block copolymer exhibits intramolecular segregation. [S0031-9007(97)04335-4]

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The relationship between the molecular architecture of the components and the final properties of polymer blends is of scientific and technological interest [1]. The fundamental challenge lies in predicting the effect of thermodynamic interactions between the constituent molecules on the structure of the blend. This effect is well understood in binary polymer blends [2], and studies of the concentration fluctuations by small-angle neutron scattering (SANS) played an important role [3]. This paper is concerned with the thermodynamic properties of a multicomponent mixture composed of two homopolymers and a block copolymer. The concentration fluctuations of the individual components were examined in separate neutron scattering measurements on contrast matched systems. The random phase approximation (RPA) [2,4–6] was used to relate the observed scattering to intermolecular and intramolecular factors.

Mixtures of two homopolymers and a block copolymer are of considerable interest because the amphiphilic nature of the block copolymer results in the formation of modulated phases [7–10]. Microemulsions are obtained at low copolymer concentrations, and ordered phases are obtained at high copolymer concentrations. In this respect, these blends are similar to small molecule mixtures composed of oil, water, and a surfactant [11]. The structure of the isotropic phase in small molecule systems, in the vicinity of an ordering transition, has been examined theoretically [12] and experimentally [13]. The ordering transition is announced by the formation of transient, intermolecular aggregates. In this paper we demonstrate that the ordering transition in a mixture of two homopolymers and a block copolymer is announced by both intermolecular and intramolecular signatures. The homopolymers form transient intermolecular aggregates. The block copolymer chains, on the other hand, remain homogeneously distributed, but exhibit intramolecular segregation.

Model polyolefins—polyethylene (PE), head-to-head polypropylene (PP), and a polyethylene-*block*-head-to-head polypropylene copolymer (PE-PP)—were synthe-

sized and characterized by methods described in Ref. [14]. Separate aliquots of anionically polymerized dienes were saturated with hydrogen and deuterium to give fully hydrogenated polyolefins (*h*PE, *h*PP, and *h*PE-*h*PP), and partially deuterated polyolefins (*d*PE, *d*PP, and *d*PE-*d*PP). Small-angle neutron scattering experiments on blends of these materials were conducted on the NG5 beam line at the National Institute of Standards and Technology in Gaithersburg, Maryland. The procedure for obtaining the absolute coherent scattering intensity, $I(q)$ [$q = 4\pi \times \sin(\theta/2)/\lambda$, θ is the scattering angle, and λ is the wavelength of the incident neutrons], from the raw data is described in Ref. [15].

The characteristics of the components used in this study are summarized in Table I; details will be presented in a full paper [16]. A monomer for both PE and PP chains is defined as a C₆ unit, the number of monomers per chain, N_i was determined by light scattering, the volume occupied by each monomer v_i is based on measured densities of the polymers, and scattering lengths of the monomers b_i are based on atomic composition. The statistical segment lengths l_i which specify the dependence of the radius of gyration of the chains on molecular weight were estimated from neutron scattering measurements from binary homopolymer blends and the pure *d*PE-*d*PP block copolymer, using well-established procedures [15,17]. The binary *h*PE/*d*PP blend with $\phi_{hPE}/\phi_{dPP} = 1.62$ exhibited a liquid-liquid phase transition at 143 ± 3 °C, while the pure *d*PE-*d*PP block copolymer exhibited an order-disorder phase transition at 149 ± 2 °C.

In this paper, we discuss data from two PE/PP/PE-PP blends with $\phi_{PE}/\phi_{PP} = 1.62$ and $\phi_{PE-PP} = 0.50$ (ϕ_i is the volume fraction of species *i*): blend BH, which is composed of *h*PE, *d*PP, and *h*PE-*h*PP, and blend BB which is composed of *h*PE, *h*PP, and *d*PE-*d*PP. The two blends are identical in composition, except for the fact that the labeled species in blend BH is the PP homopolymer, while the labeled species in blend BB is the block copolymer. Since the scattering contrast between the hydrogenated polyolefins is negligible (see Table I), blend BH

TABLE I. Parameters used in RPA calculations at 148 °C.

Component parameter	<i>h</i> PE- <i>h</i> PP				<i>d</i> PE- <i>d</i> PP			
	<i>h</i> PE	<i>d</i> PE	<i>h</i> PP	<i>d</i> PP	<i>h</i> PE	<i>h</i> PP	<i>d</i> PE	<i>d</i> PP
N_i	83	83	178	178	36	376	367	376
$v_i(\text{Å}^3)$	179.0	178.8	174.8	174.6	179.0	174.8	178.8	174.6
$l_i(\text{Å})$	10.79	10.79	8.61	8.61	12.65	10.10	12.65	10.10
$b_i(\text{Å}) \times 10^4$	-0.498	4.952	-0.498	5.156	-0.498	-0.498	6.327	3.784

enables the study of concentration fluctuations of the PP homopolymer, while blend BH enables the study of the concentration fluctuations of the block copolymer. Both blends exhibited signatures of an order-to-disorder transition at 125 ± 5 °C that were qualitatively similar to those seen in the pure *d*PE-*d*PP block copolymer [16].

The SANS data from these multicomponent blends were analyzed using the incompressible, mean-field theory of polymer blends, based on the random phase approximation [2,4–7]. A “component” is defined as a chain of identical monomers, and the scattering intensity from blends comprising $(n + 1)$ components is given by

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

where \mathbf{B} is an n dimensional column vector whose elements B_i quantify the neutron contrast of component i ($B_i = b_i/v_i - b_0/v_0$) and the subscript zero refers to *h*PE, which is common to both blends. $\underline{\underline{S}}(q)$ is an $n \times n$ structure factor matrix whose elements S_{ij} describe correlations between components i and j . For mixtures of two homopolymers and a block copolymer, $n = 3$, and S_{ij} can be expressed as

$$S_{ij}(q) = f_{ij}(\phi_k, N_k, v_k, l_k, \chi_{kl}, v; q) \quad (k, l = 0-3), \quad (2)$$

where ϕ_k is the volume fraction of component k in the blend, and χ_{kl} is the Flory-Huggins interaction parameter between component k and l , based on a reference volume v which we set equal to 161.5 Å^3 . Details regarding the computation of functions f_{ij} are given in Ref. [15].

The scattering profiles from blend BH at selected temperatures are shown in Fig. 1(a). At 167 °C, the scattering intensity is a monotonic function of q . The scattering intensity in the vicinity of $q = 0.013 \text{ Å}^{-1}$ rises sharply with decreasing temperature, and a scattering peak is evident at temperatures below 148 °C. The solid curves through the data are multicomponent RPA calculations—Eqs. (1) and (2)—with the Flory-Huggins interaction parameter $\chi_{hPE/hPP}$ as the only adjustable parameter. The effect of deuterium substitution on χ has been taken into account, using independent experiments [15]. It is evident that the mean-field theory with one adjustable parameter provides an adequate description of the data. Further, the χ parameters used to obtain the match between experiment and theory are

in reasonable agreement with those measured in binary PE/PP blends. For example, $\chi_{hPE/hPP} = 1.48 \times 10^{-2}$ at 148 °C in BH, while SANS data from binary *h*PE/*d*PP mixtures (not shown) give $\chi_{hPE/hPP} = 1.24 \times 10^{-2}$ at 148 °C.

The scattering intensity from multicomponent blends with one labeled species is due to two contributions: (1) connectivity of the monomers in that species and (2) nonrandom concentration fluctuations of the constituent components. In order to study these concentration fluctuations, we have to subtract the connectivity contribution to the scattering intensity. We define an excess scattering intensity $I_{EX}(q)$ as follows:

$$I_{EX}(q) = I(q) - I_{\text{conn}}(q), \quad (3)$$

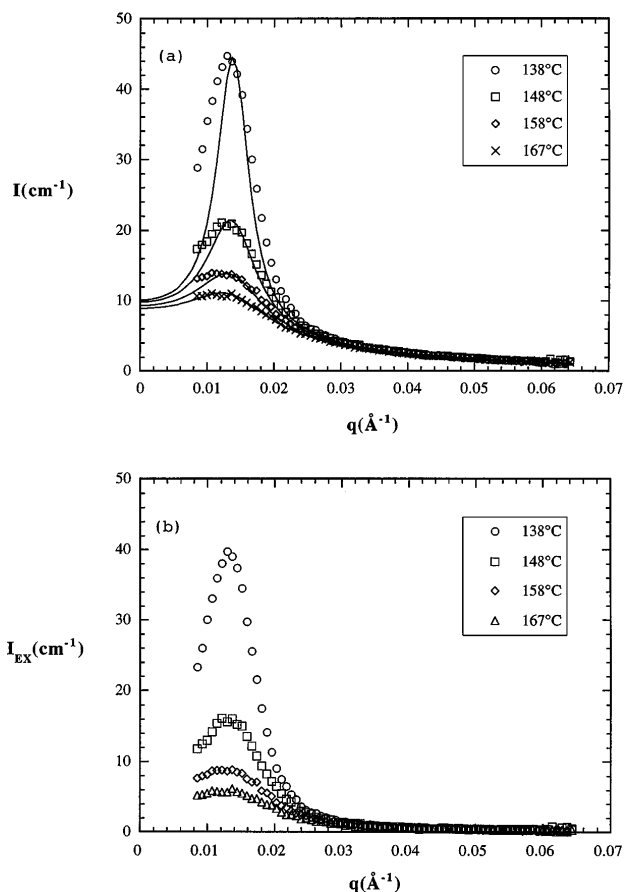


FIG. 1. Temperature dependence of SANS data from blend BH. (a) Coherent scattering intensity I and (b) excess coherent scattering intensity I_{EX} versus scattering vector q . The solid curves are theoretical fits.

where the connectivity contribution $I_{\text{conn}}(q)$ is computed from RPA Eqs. (1) and (2) with all χ_{ij} set to zero,

$$I_{\text{conn}}(q) = \mathbf{B}^T \underline{\underline{S}}(\phi_k, N_k, \mathbf{v}_k, l_k, \chi_{kl} = 0, \mathbf{v}; q) \mathbf{B}. \quad (4)$$

In Fig. 1(b) we plot I_{EX} versus q for blend BH. A well-defined peak at $q = 0.013 \text{ \AA}^{-1}$ is evident at 148°C , indicative of a periodic arrangement of the *d*PP homopolymer chains with a length scale ($1/q_{\text{peak}}$) of about 80 \AA . The length scale of the periodic structure is significantly larger than the radius of gyration of the PP molecules, which is $45 \text{ \AA} [= (N_i l_i^2/6)^{1/2}]$. The peak in I_{EX} becomes sharper with decreasing temperature, indicating that the periodic structure becomes better defined. However, the values of I_{EX} at the lowest accessible q (0.008 \AA^{-1}) also increase substantially with decreasing temperature, indicating the increasing presence of large length-scale (greater than 80 \AA) concentration fluctuations. We thus see that the PP homopolymer exhibits intermolecular aggregation as the ordering transition is approached.

In Fig. 2(a) we show the q dependence of I at selected temperatures from blend BB. The solid lines are RPA fits

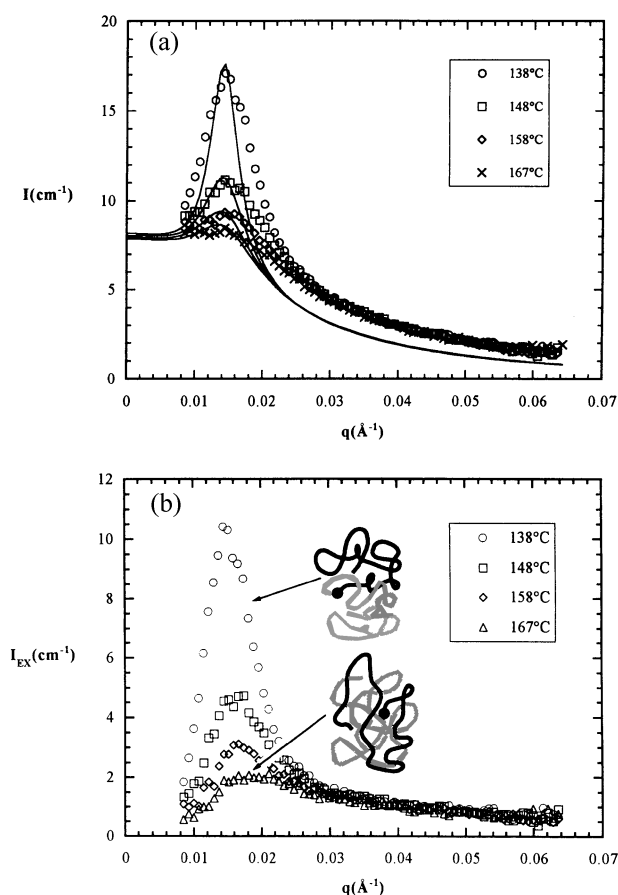


FIG. 2. Temperature dependence of SANS data from blend BB. (a) Coherent scattering intensity I and (b) excess coherent scattering intensity I_{EX} versus scattering vector q . The solid curves are theoretical fits. Inset (b): A schematic of the conformational changes of the block copolymer with temperature.

with $\chi_{h\text{PE}/h\text{PP}}$ as the only adjustable parameter. We find that the agreement between theory and experiment is reasonable, and that the χ parameter used to obtain these fits is similar to those in blend BH ($\chi_{h\text{PE}/h\text{PP}}$ in BB at 148°C is 1.52×10^{-2}). In Fig. 2(b), we plot the q dependence of I_{EX} for blend BB. These data show a well-defined peak at $q = 0.014 \text{ \AA}^{-1}$, which is similar in some respects to the q dependence of I_{EX} of blend BH [Fig. 1(b)]. A careful comparison of Fig. 2(b) with Fig. 1(b), however, reveals an important difference. In blend BB [Fig. 2(b)], I_{EX} arctan approaches zero as $q \rightarrow 0$, while in blend BH [Fig. 1(b)], I_{EX} is finite as $q \rightarrow 0$. We thus see evidence for purely periodic concentration fluctuations and the absence of large length-scale fluctuations in blend BB. With decreasing temperature, these periodic fluctuations grow in amplitude, but not in spatial extent; the location of the peak in q space is temperature independent. These characteristics have been observed by numerous experimenters in melts nearly monodisperse, pure, block copolymers [18]. They represent signatures of the intramolecular segregation of the individual blocks as the ordering transition is approached [4]. The q dependence of I_{EX} in blend BB, shown in Fig. 2(b), contains the signature of intramolecular segregation in a multicomponent blend.

In the case of scattering from a melt of a single molecular species, such as a pure block copolymer, $I_{\text{EX}}(q)$ must necessarily approach zero as $q \rightarrow 0$ [4]. In multicomponent blends, however, this is not at all necessary. One could envision the formation of a variety of aggregates of the copolymer chains such as transient micelles. The fact that I_{EX} is negligibly small at the low q indicates the absence of all forms of pretransitional, intermolecular aggregation of the PE-PP chains. Note that the scattering intensity from sample BB is finite in the limit of $q \rightarrow 0$ [Fig. 2(a)]. The true intramolecular nature of the concentration fluctuations became evident only after the connectivity contribution was subtracted [Fig. 2(b)]. The availability of the RPA based theory was crucial, because the connectivity contribution could be calculated independently, without resorting to data from the multicomponent systems.

To summarize, we have studied concentration fluctuations of individual components in a blend of two homopolymers and a block copolymer, in the vicinity of an ordering transition. The homopolymers exhibit intermolecular aggregation, while the block copolymer exhibits intramolecular segregation. The ability of block copolymer molecules to undergo conformational changes and the lack of such effects in small molecule surfactants is, perhaps, the most important distinction between polymeric and small molecule surfactants.

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