Segregation at the Interface between a Homopolymer and a Binary Polymer Blend

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Low-energy forward-recoil spectrometry studies show that the interface between polystyrene (A) and a miscible blend of two poly(styrene-co-4-bromostyrene)s (B:C) has an interfacial excess of $B$, $z_B^B$, where B is the component with the lower bromostyrene level. At 170°C, $z_B^B$ increases with the bulk volume fraction of $B$, $\phi_B$, has a maximum near 0.25, and then decreases. These results are in qualitative agreement with self-consistent field (SCF) calculations. SCF calculations of the interfacial tension and interfacial width predict that $B$ has an optimum compatibilizing effect for $\phi_B \sim 0.25$.

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Many properties of multiphase polymer systems, such as polycarbonate and poly(acrylonitrile-butadiene-styrene) blends, are controlled by the nature of the interface between the phases. For example, multiphase materials with a high degree of molecular interpenetration across the phase boundary can exhibit good mechanical properties such as a high fracture toughness. As another example, interfacial tension has been found to control the morphology of three-component, multiphase materials [1]. One route for controlling the interfacial properties is through the addition of compatibilizers, such as block copolymers [2], which increase fracture toughness and reduce interfacial tension. Using self-consistent mean-field (SCF) theory, Helfand has proposed that the interfacial properties of an immiscible polymer blend A/C may be varied by adding a third homopolymer $B$, which is miscible with $C$ but not with $A$ [3]. In Helfand’s model, the free-energy density is governed by the Flory-Huggins interaction parameters $\chi_{AB}$, $\chi_{AC}$, and $\chi_{BC}$, which are chosen to ensure B:C miscibility ($\chi_{BC} < 0$) and A/C and A/B immiscibility ($\chi_{AC}, \chi_{AB} > 0$). If the A-B interactions are favored over the A-C ones ($\chi_{AB} < \chi_{AC}$), Helfand predicts that the $B$ component will enrich the interface, whereas the $C$ component will be driven away from the interface. As a result of the segregation of $B$, the interfacial tension decreases while the interfacial width broadens. The interfacial properties are also influenced by the favorable B-C interactions because the demixing of $B$ and $C$ costs free energy. Because the $A$, $B$, and $C$ polymers are chosen to have infinite molecular weight, the free-energy density in the Helfand model is governed solely by the excess free energy. In our approach, entropic contributions are taken into account by considering polymers with finite chain lengths. This improvement is of practical importance because many systems involve materials with moderate degrees of polymerization.

In this Letter, we present the first experimental measurement of interfacial segregation at the A:B:C interface.

The interfacial excess of $B$, $z_B^B$, is found to increase with the bulk volume fraction of $B$, $\phi_B$, appears to reach a maximum near $\phi_B = 0.25$, and then decreases. SCF calculations of $z_B^B$ are found to be in qualitative agreement with the measured values. SCF predictions of the interfacial tension and width demonstrate the compatibilizing effect of $B$ on the A/C system.

We have chosen a ternary system of polystyrene (PS) and two miscible random copolymers of poly(styrene-co-4-bromostyrene), $d$-PBr$_S$ and PBr$_S$, having $x$ and $y$ mole fractions of 4-bromostyrene monomers, respectively. The random copolymers were prepared by brominating deuterated polystyrene $d$-PS and polystyrene PS, using the procedure of Kambour, Bendler, and Bopp [4]. The $x$ and $y$ values as determined by elemental analysis were 0.093 and 0.131, respectively. At these bromine levels, the $d$-PBr$_S$/PBr$_S$, PBr$_S$/PS, and PBr$_S$/PS blends were completely miscible, partially miscible, and completely immiscible, respectively [5]. The polymer characteristics are given in Table I. To simplify the nomenclature in this Letter, we will denote PS, $d$-PBr$_S$, and PBr$_S$ as A, B, and C, respectively. To minimize the solubility of $B$ in A and C in A, we chose the number of A segments to be large. The number of B and C segments was chosen to ensure the miscibility of B and C, and to provide a measurable interfacial excess of B.

Samples were prepared by spin coating a toluene solution of $B$ and $C$ on a silicon wafer previously etched for 10 min in a 7% vol/vol HF/water solution. The samples were then dried in a vacuum oven for about 12 h at 90°C. A top film was spin coated from a solution of A in toluene, scored around the edges, floated on a deionized water bath, and picked up with a B:C/silicon sample. These bilayer films were dried in a vacuum oven for 12 h at 90°C. Film thicknesses as determined by ellipsometry were about 1000 and 2000 Å for the A and B:C films, respectively. The volume fractions of $B$ in the as-prepared B:C films were 0.15, 0.26, and...
0.52. All samples were annealed in a vacuum oven for 35 days at 170 °C. Using elemental analysis, bromine concentrations were found to be the same before and after annealing. The volume fraction profile of the deuterated B component was determined by low-energy forward-recoil spectrometry (LE-FRES) with a 2.0-MeV He⁺ ion beam at 15° glancing incident and exit angles with the polymer film. Under these conditions, a 7.5 μm Mylar™ foil was sufficient to stop the forward-scattered He⁺ nuclei from masking the ¹³He and ³He signals. The depth resolution was about 500 Å at a depth of 1000 Å beneath the surface. Conventional FRES [6] and LE-FRES [7] have been described elsewhere.

In addition to the LE-FRES measurements, a SCF method was used to calculate the volume fraction profiles of the A, B, and C components. Our calculations followed the framework developed by Hong and Noolandi [8] and Shull and Kramer [9]. A detailed description of our SCF approach will be given in Ref. [10]. In brief, the SCF calculations require solving simultaneously a set of modified diffusion equations [11] for the distribution functions \( q_k(x,t) \), which represent the probability that the \( r \)th segment of polymer \( k \) is found at position \( x \) [12]. These equations can be solved by a numerical iteration technique such as the modified relaxation method described in Refs. [9,10]. The product of \( q_k(x,t) \) and \( q_k(x,N_k - t) \) is proportional to local volume fraction \( \phi_k(x) \). Knowing the volume fraction profiles of A, B, and C, the interfacial properties of the A/B:C system can be calculated. One goal of this Letter is to compare the interfacial excess of B with the values predicted by SCF calculations. Moreover, SCF predictions of the interfacial width and interfacial tension will be presented.

Figure 1 shows the depth profile of B before (○) and after (●) annealing at 170 °C for 41 days. The volume fraction of B in the as-cast sample is 0.15. As highlighted by the shaded region, a large interfacial excess of B, \( z_B^* \), is clearly evident after annealing. As demonstrated later, this segregation lowers the interfacial tension and broadens the interfacial width. Because of the finite film thickness and large \( z_B^* \) value, the bulk volume fraction of B decreases to 0.097 after annealing. Independent LE-FRES measurements on A/B couples revealed that the solubility of A in B is less than the 0.01 volume fraction, whereas the solubility of B in A is 0.06. This latter value is indicated by the arrow in Fig. 1. The lower solubility of A in B is due to the A component having a much higher molecular weight than the B component (see Table I).

As shown graphically in Fig. 1, the volume fraction of B soluble in A is not included in the calculation of \( z_B^* \). Interdiffusion experiments on A/C couples showed that A and C were completely immiscible with each other. To calculate the volume fraction profiles using the SCF method, the numbers of segments for A, B, and C, the bulk volume fraction of B, and the interaction parameters \( \chi_{AB}, \chi_{AC} \), and \( \chi_{BC} \) must be known. The values of \( \chi_{AB} \) and \( \chi_{AC} \) were determined by interpolating the previously measured PS:PBr,S interaction parameters [13] to \( x = 0.093 \) and 0.131. Interdiffusion experiments on B/C couples were carried out to determine the mutual diffusion coefficient. Using the fast theory of mutual diffusion, the value of \( \chi_{BC} \) was then estimated [14]. The values of the interaction parameters used in the calculations are \( \chi_{AB} = 1.51 \times 10^{-3} \), \( \chi_{AC} = 2.45 \times 10^{-3} \), and \( \chi_{BC} = 3.50 \times 10^{-4} \).

### Table I. Polymer characteristics.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Polymer</th>
<th>Number of segments</th>
<th>Polydispersity index</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>PS</td>
<td>15385</td>
<td>1.15</td>
<td>Pressure Chemical</td>
</tr>
<tr>
<td>B</td>
<td>d-PB\textsubscript{0.093}S</td>
<td>6161</td>
<td>1.09</td>
<td>Polymer Laboratories\textsuperscript{b}</td>
</tr>
<tr>
<td>C</td>
<td>PBr\textsubscript{0.113}S</td>
<td>3846</td>
<td>1.06</td>
<td>Pressure Chemical\textsuperscript{c}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Calculated for a segment length of 6.7 Å.

\textsuperscript{b}Supplied as d-PS.

\textsuperscript{c}Supplied as PS.

![FIG. 1. Volume fraction profile of d-PBr\textsubscript{0.09}S (B) determined using LE-FRES for an A/B:C sample as cast (○) and after annealing at 170 °C for 41 days (●). The bulk volume fractions of B are 0.15 (as cast) and 0.097 (annealed). The interface between A and B:C in the as-cast sample defines the origin of the depth scale. The shaded area represents the interfacial excess of B, \( z_B^* \).]
Figure 2 shows the $B$ volume fraction profiles from LE-FRES (•) and the SCF calculation (dotted line). Also shown is the SCF result corrected for finite system resolution (solid line). This correction was performed by convoluting the SCF profile with Gaussian functions having a full width at half maximum (FWHM) which increased linearly from 400 Å at the sample surface to 650 Å at a depth of 2000 Å. These FWHM values are determined from LE-FRES measurements on as-cast polymer samples. The convoluted SCF and experimental profiles are in excellent agreement near the maximum value of $f_B^*$; however, the convoluted SCF profile underestimates $z_B^*$ for two possible reasons. First of all, the SCF profile does not include the partial solubility of $B$ in $A$ and the interfacial broadening resulting from this solubility. As a result, the front edge of the experimental profile is much broader than the SCF profile. Second, in the SCF model, the volume fraction profile is very sensitive to the values of the interaction parameters. In our SCF calculations, these values may not be appropriate because of confinement effects. In fact, Heier et al. [15] have shown that the critical interaction parameters of thin polymer films can be larger than the corresponding bulk value.

Figure 3(a) shows the interfacial excess as a function of the bulk volume fraction of $B$, $\phi_{Bc}$. The closed (•) and open (○) circles represent $z_B^*$ values determined by LE-FRES and SCF methods, respectively. The solid lines are a guide to the eye. The SCF calculations were carried out using the same interaction parameters as in Fig. 2. The SCF and experimental results both show that $z_B^*$ vs $\phi_{Bc}$ is asymmetric, having a maximum near $\phi_{Bc} = 0.25$. For all values of $\phi_{Bc}$ investigated, the SCF method underestimates the experimental values. Possible reasons for this difference were discussed previously. In addition to $z_B^*$, the interfacial tension $\gamma$ and interfacial width $w$ were calculated from the SCF profile. Figure 3(b) shows that $\gamma$ (○) decreases and $w$ (●) increases as a relatively small amount of $B$ is added to the $A/C$ system. For $\phi_{Bc}$ greater than about 0.2 both $w$ and $\gamma$ change more slowly as they approach their asymptotic values for the $A/B$ interface. The bulk volume fraction of $B$ at which $W$ and $\gamma$ start to level off correlates with the maximum $z_B^*$ shown in Fig. 3(a). This observation is important technologically because it provides guidance for choosing the optimal volume fraction of $B$ that effectively modifies (compatibilizes) a strongly immiscible $A/C$ pair.

In summary, we have shown for the first time that a $B$ homopolymer in an $A/B:C$ system can enrich the interfacial region. The interfacial excess of the $B$ compo-
nent measured as a function of bulk volume fraction of B reaches a maximum at about $\phi_{B_c} = 0.25$ in the particular system investigated. This result is in qualitative agreement with the SCF predictions, although the SCF values of the interfacial excess are consistently lower than the experimental values. Using the SCF model, the interfacial tension and interfacial width are calculated and found to decrease and increase, respectively, with increasing $\phi_{B_c}$; these changes become more gradual as $\phi_{B_c}$ increases. For the A/B:C system investigated, these results suggest that the effectiveness of B as a homopolymer compatibilizer is optimum at a bulk volume fraction near 0.25.

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