Effect of Molecular Weight on the Interfacial Excess, Tension, and Width in a Homopolymer/Binary Polymer Blend System

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ABSTRACT: The interfacial properties of a three-component, two-phase A/B:C blend are investigated to understand the effect of the A and B chain lengths on the interfacial excess of B, \( z_0^* \), the interfacial tension, \( \gamma_{ABC} \), and the interfacial width, \( w_{ABC} \). The A/B:C components are polystyrene/poly(d$_p$-styrene-co-4-bromostyrene)/poly(styrene-co-4-bromostyrene), where B and C have 4-bromostyrene mole fractions of 0.154 and 0.177, respectively. Low-energy forward recoil spectrometry (LE-FRES) is used to measure \( z_0^* \) as a function of the B volume fraction in the B:C blend, \( \phi_{BC} \). The experimental \( z_0^* \)'s are found to be in excellent agreement with those calculated using the self-consistent field (SCF) model of the A/B:C interface. In addition, the SCF model is used to evaluate \( \gamma_{ABC} \) and the widths for the A/B:C, A/B, and A/C interfaces (i.e., \( w_{ABC} \), \( w_{AB} \), and \( w_{AC} \), respectively). Our results demonstrate that increasing the number of B segments, \( N_B \), greatly increases the magnitude of \( z_0^* \), particularly at low \( \phi_{BC} \). On the other hand, varying \( N_A \) has only a minor effect on \( z_0^* \). Concurrent with the segregation of B, \( \gamma_{ABC} \) and \( w_{AB} \) rapidly decrease and increase, respectively, as \( \phi_{BC} \) initially increases. Upon calculation of the entanglement length, \( w_e \), for each component, \( w_{AB} \) is found to approach \( w_e \) when \( \phi_{BC} \approx 0.30 \). As a result the mechanical strength of the interface should greatly improve. The optimum amount of B to achieve good compatibilization correlates with the \( \phi_{BC} \) at which \( z_0^* \) is a maximum.

1. Introduction

Blending has proven to be a convenient method to improve and adjust the properties and processability of polymeric materials.1,2 Polymer blends usually contain two or more components selected such that the principal advantages of one polymer will compensate for deficiencies of the other polymer and vice versa. Because of strong chemical incompatibility between most polymer pairs (i.e., large positive interaction parameter, \( \chi \)), simple blending usually results in macroscopically phase-separated materials with little practical use. For such a blend, the bulk properties are strongly influenced by the interfacial properties between immiscible phases. The interfacial tension and width are two critical parameters that characterize the interface. For example, the interfacial tension controls the phase morphology. Due to strong incompatibility, the interfacial tension is typically quite high,3 resulting in morphologies with widely-separated, large phases. In addition, narrow interfacial widths result in poor adhesion and low fracture toughness because of the limited interpenetration across the interface.4

Compatibilizers added to these immiscible polymer blends can overcome the above deficiencies in several ways. First, they usually reduce the interfacial tension which leads to a fine dispersion of the minority phase. In addition, compatibilizers broaden the interfacial width thereby providing improved interfacial stress transfer and adhesion. Third, compatibilizers can stabilize the minority phase by slowing down its growth during processing. In practice, these effects will occur to various degrees depending on the particular compatibilizer. Other properties, such as rheology, can also be modified and controlled. Typical compatibilizers include block copolymers, graft copolymers, reactive/functional copolymers, in-situ grafting agents, etc.1,2,5

In particular, block copolymers6,6 and graft copolymers7 can greatly improve the mechanical properties and decrease the interfacial tension between immiscible polymer pairs, A/C. For example, the fracture toughness of a polystyrene (PS)/poly(methyl methacrylate) (PMMA) interface was increased by a factor up to 50 upon adding a PS-b-b-MMA) block copolymer to the interface.8 Recently, random copolymers (A-co-C) were found to also improve the fracture toughness of A/C systems.9

There are several limitations associated with using block copolymers as compatibilizers. First, block copolymers are expensive compared to most commercial polymers. Second, if not applied directly to the interface, block copolymers have to diffuse to the interface and therefore their effectiveness can be limited by kinetics. Also, at concentrations greater than the critical micelle concentration (cmc), block copolymers form micelles. In many cases, the cmc can be as small as 1%. The formation of micelles thus limits the availability of block copolymers which can span the A/C interface. In addition, copolymer micelles usually tend to segregate at the A/C interface which reduces the “effective space” for compatibilization. On the other hand, homopolymers (or random copolymers) can be very attractive compatibilizing agents because of their lower cost. Indeed, recent theoretical10-12 and experimental13,14 studies have demonstrated that homopolymers can be used as effective compatibilizing agents. Recently, Helfand11 and Yoon and co-workers12 calculated that the interfacial properties of an immiscible A/C pair can be improved by the addition of component B, which is miscible with C but not with A. Using the self-consistent field (SCF) method, these studies demonstrated that B segregates to the A/B:C interface, if \( \chi_{AB} \)
< $\chi_{AC}$ As B adsors to the A/B:C interface, the 
interfacial tension, $\gamma_{ABC}$, was found to decrease whereas the 
interfacial width, $\lambda_{ABC}$, increased.

In these models,$^{11,12}$ the free energy density of the 
system is governed solely by the enthalpy of mixing. Therefore these models are only valid in the infinite 
molecular weight limit where the entropy of mixing is 
eglected. Moreover, these models are limited to systems 
having $\chi_{BC} < 0$. The former simplification pre-
vents direct experimental testing of the model whereas the 
latter greatly limits the number of polymer systems to 
which these models can be applied. To overcome 
these difficulties, we have modified the SCF model to 
include the contribution of the entropy of mixing to the 
free energy of the system.$^{15}$ This model can then be 
tested on finite molecular weight systems and B:C pairs 
having $\chi_{C} > \chi_{BC} > 0$, where $\chi_{C}$ is the critical value of 
$\chi_{BC}$. An important result from this modified model is 
that the A/B:C interfacial properties depend strongly 
on the number of B segments, $N_B$, but rather weakly 
on $N_A$.

In an earlier study, low-energy forward recoil spec-
trometry (LE-FRES) was used to measure $Z_{B*}$ as a 
function of B volume fraction in the B:C mixture, $\phi_{B enriched$ for the case where $\chi_{AB} < \chi_{AC}$.$^{16}$ These measurements 
provided the first experimental detection of segregation 
at the homopolymer/binary polymer blend interface. In 
subsequent experiments neutron reflectivity (NR) was 
used to determine the shape of the polymer volume 
fraction profiles.$^{17}$ These NR measurements also pro-
vided a direct measure of the interfacial width between 
the A and B:C phases. In the present study, we revisit 
the issue of interfacial segregation using a slightly 
different blend system designed to more rigorously test 
the SCF model. One objective is to investigate the effect 
of $N_A$ and $N_B$ on the A/B:C interfacial properties. As 
before, LE-FRES is used to measure $Z_{B*}$. In contrast 
to previous studies, $Z_{B*}$ is measured over a much 
broader range of $\phi_{B enriched$. We find that an increase in $N_B$ 
leads to a dramatic increase in $Z_{B*}$, a smaller $\gamma_{ABC}$, and 
a larger $\lambda_{ABC}$. However, an increase in $N_A$ by ca. 1.5 
orders of magnitude does not measurably change the 
interfacial properties. Qualitatively and quantitatively, 
the behavior of $Z_{B*}$ as a function of $\phi_{B enriched$ is in excellent 
agreement with SCF predictions.


2. Experiment

2.1. Materials and Sample Preparation. Similar to 
previous experiments, the two-phase, three-component system 
consists of polystyrene, PS, and blends of two miscible random 
copolymers of poly(styrene-co-4-bromostyrene), dPBr,S and 
PBr,S, having $x = 0.154$ (or $x = 0.157$) and $y = 0.177$ mole 
fractions of 4-bromostyrene (4-BrS), respectively. The random 
copolymers were prepared by brominating dPS and normal 
PS, respectively, using the procedure of Kambour and co-
workers.$^{18}$ The values $x$ and $y$ were chosen such that the PS/p 
dPBr,S and PS/PBr,S pairs were immiscible. One of the 
drawbacks of the system studied in refs 16 and 17 was the 
partial miscibility of the B component in the A phase. This 
complicated the comparison of the experimental and calculated 
volume fraction profiles of B. To minimize the solubility of B 
and C in A, the 4-BrS mole fraction in B and C was increased 
relative to B and C in refs 16 and 17. By choosing $x$ to be 
slightly less than $y$, the interaction parameter between dPBr,S 
and PS was tuned and designed to be smaller that than 
between PBr,S and PS (i.e., $\chi_{AB} < \chi_{AC}$). In addition, the 
difference between $x$ and $y$ was small enough to guarantee 
complete miscibility between dPBr,S and PBr,S at all composi-
tions studied. The polymer characteristics are listed in Table

1. To simplify the nomenclature, PS, dPBr,S, and PBr,S are 
referred to as A, B, and C, respectively. Because the 4-BrS 
mole fractions in B1 and B2 are nearly equal, the values of 
$\gamma_{AB}, \chi_{AC}$, and $\gamma_{BC}$ are taken to be the same for the two systems.

Samples were prepared by spin-coating toluene solutions 
of B:C mixtures on silicon wafers previously etched for 10 min 
in a 7% v/v HF/water solution. The samples were then dried 
in a vacuum oven for ca. 12 h at 90 °C. A top film was spin-
coated on a glass slide from a toluene solution of A, scored 
around the edges, floated on a deionized water bath, and 
picked up with a B:C/silicon sample. These bilayers were 
again dried in a vacuum oven for 12 h at 90 °C. Film 
thicknesses determined by ellipsometry were ca. 600–1000 
and 2000–3000 Å for the A and B:C films, respectively. The 
samples were then annealed at 181 °C. The volume fractions 
of the B component were determined in both the as-cast and 
annealed samples using LE-FRES.

2.2. Low-Energy Forward Recoil Spectrometry (LE-
FRES). The LE-FRES measurements were carried out on a 
Model SSDH Pelletron tandem accelerator (National Electro-
static Corp., WI), interfaced with a custom-designed scattering 
chamber at the ion beam facility of the Laboratory for Research 
on the Structure of Matter at the University of Pennsylvania. 
The technique has been described elsewhere.$^{19}$ Briefly, in LE-
FRES, a monoenergetic beam of 2.0 MeV $^4$He$^+$ ions impinges 
on a sample at an angle of 75° with respect to the sample 
normal. As a result of the interactions of He ions with the 
atoms in the sample, the light nuclei, such as H and D, recoil 
from the sample and travel toward a detector which is placed 
at an angle of 150° with respect to the incident beam. In 
addition to the recoiling D and H nuclei, helium atoms are 
forward scattered from the heavier carbon and silicon atoms 
in the polymer film and substrate, respectively. To prevent 
the helium signal from masking the hydrogen and deuterium 
signals, a 7.5 μm thick Mylar stopper foil is placed before the 
detector. Multiple scattering of the incident and recoiled ions 
with the sample nuclei is the main cause of resolution loss 
below the surface.$^{19}$ Using standards, the depth resolution was 
ca. 500 Å at a depth of 1000 Å beneath the sample surface. The 
resultant LE-FRES spectrum of recoiled yield versus 
detected energy is then converted to a depth profile of the D 
and H nuclei.

3. Results

3.1. Experiment. Previously, we observed that the 
A/B:C interface was enriched with the B component if 
$\chi_{AB} < \chi_{AC}$.$^{16,17}$ As a result of B segregation, 
the interfacial properties such as the interfacial tension and 
width were modified. One result of our SCF calculations 
was that the A/B:C interfacial properties were controlled 
strongly by the number of polymer segments.$^{15}$ In this 
paper we will investigate the effect of $N_A$ and $N_B$ on $Z_{B*}$. 

Figure 1 shows the B1 volume fraction profile in system 
a before (open circles) and after (closed circles) annealing 
for 30 days at 181 °C. In the as-cast sample, $\phi_{B1}$ is 
uniformly 0.392 throughout the B:C blend indicating 
that B1 does not segregate appreciably during spin 
coating. After the sample is annealed, a small excess 
of B1 at the interface is detected, as depicted by the shaded 
area in Figure 1. To conserve B1 in the thin 
film, $\phi_{B1}$ decreases to 0.326. Figure 1 also shows that 
B1 is slightly miscible (ca. 0.07) in A1. Thus, although the 
B1–A1 enthalpic repulsion is strong, the entropy 
of mixing term is large enough to favor partial misci-
bility. The underlying reason for this miscibility is partly 
due to the low molecular weight of B1.

Figure 2 shows the B2 volume profile for system b 
after (open circles) and after (closed circles) annealing 
for 30 days at 181 °C. As in Figure 1, B2 is uniformly 
distributed throughout the as-cast B2:C blend, having a 
$\phi_{B2}$ of 0.400. After the sample is annealed, $\phi_{B2}$
The interface between A1 and B2:C defines the origin of the depth scale. The shaded area represents the interfacial excess of B, $z_B^\infty$.

Figure 1. Volume fraction profile of B1 determined by LE-FRES for the A1/B2:C sample as-cast (open circles) and after annealing for 30 days at 181 °C (closed circles). The bulk volume fractions of B1 are 0.392 (as-cast) and 0.326 (annealed). The interface between A1 and B1:C defines the origin of the depth scale. The shaded area represents the interfacial excess of B1, $z_B^\infty$.

Figure 2. Volume fraction profile of B2 determined by LE-FRES for the A1/B2:C sample as-cast (open circles) and after annealing for 30 days at 181 °C (closed circles). The bulk volume fractions of B2 are 0.400 (as-cast) and 0.310 (annealed). The interface between A1 and B2:C defines the origin of the depth scale. The thick solid line is the volume fraction profile calculated using SCF and corrected for the instrumental resolution of LE-FRES. The shaded area represents the interfacial excess of B2, $z_B^\infty$.

These profiles of B were then used to determine the B component volume fraction, $\phi_B$, for systems Ia and Ib as a function of bulk volume fraction, $\phi_B^\infty$, $z_B^\infty$ is measured by LE-FRES and samples are annealed for 30 days at 181 °C. The solid lines are the results obtained from the SCF model using the numbers of segments listed in Table 1 and the interaction parameters given in the text.

Table 1. Polymer Characteristics

<table>
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<th>Symbol</th>
<th>Polymer A</th>
<th>Polymer B</th>
<th>Polymer C</th>
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<tr>
<td>A2</td>
<td>PS</td>
<td>N=192192</td>
<td>1.20</td>
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<tr>
<td>B1</td>
<td>dPBBr0.15S</td>
<td>3682</td>
<td>1.05</td>
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<tr>
<td>B2</td>
<td>dPBBr0.15S</td>
<td>6333</td>
<td>1.09</td>
</tr>
<tr>
<td>C</td>
<td>PBBr0.17S</td>
<td>3996</td>
<td>1.06</td>
</tr>
</tbody>
</table>

For the polymer characteristics see Table 1.

$^a$ Unless otherwise specified, $N_p$ and p.i. are the number of segments and the polydispersity index of the polymers, respectively.  $^b$ Calculated for a segmental volume of dPS ($v_{\text{dPS}} = 1.645 \times 10^{-22} \text{ cm}^3$).  $^c$ Based on the nominal molecular weight of a PS standard of $2 \times 10^6$ g/mol measured by light scattering in benzene at 25 °C (as reported by vendor).  $^d$ Supplied as dPS.  $^e$ Supplied as PS.

The interface between A1 and B1:C defines the origin of the depth scale. The shaded area represents the interfacial excess of B1, $z_B^\infty$.

For systems IIa and IIb, whose characteristics are given in Tables 1 and 2. As for system I, LE-FRES was used to determine the B component volume fraction profiles for samples annealed for 30 days at 181 °C. These profiles of B were then used to determine $z_B^\infty$ and $z_B^\infty$ in systems IIa and IIb, respectively. Figure 3 shows $z_B^\infty$ (open circles) and $z_B^\infty$ (closed circles) as a function of $\phi_B^\infty$. For systems IIa and IIb, the general behavior of $z_B^\infty$ vs $\phi_B$ is the same as previously observed for systems Ia and Ib. Namely, at small values of $\phi_B$, $z_B^\infty$ increases very rapidly, reaches a maximum at a moderate $\phi_B$, and decreases to 0 as $\phi_B$ approaches unity. In refs 16 and 17, this behavior could only be surmised because of the limited range of $\phi_B$. Figure 3 also shows that the magnitude of $z_B^\infty$ at intermediate values of $\phi_B$ is significantly larger for system Ib. Recalling that $\chi_{AB}$, $\chi_{AC}$, and $\chi_{BC}$ are essentially the same for both systems, the larger $N_B$ in system Ib is mainly responsible for the higher values of $z_B^\infty$.

In addition to the effect of $N_B$, we have also investigated the effect of $N_B$ on the interfacial properties of the A/B/C interface. These experiments were carried out on systems IIa and IIb, whose characteristics are given in Tables 1 and 2. As for system I, LE-FRES was used to determine the B component volume fraction profiles for samples annealed for 30 days at 181 °C. These profiles of B were then used to determine $z_B^\infty$ and $z_B^\infty$ in systems IIa and IIb, respectively. Figure 4 shows $z_B^\infty$ (open circles) and $z_B^\infty$ (closed circles) as a function of $\phi_B$. For systems IIa and IIb, the general behavior of $z_B^\infty$ vs $\phi_B$ is the same as previously observed for systems Ia and Ib. Namely, at small values of $\phi_B$, $z_B^\infty$ increases very rapidly, reaches a maximum at a moderate $\phi_B$, and decreases to 0 as $\phi_B$ approaches 1. The
The main difference between $z_{1B}^*$ and $z_{2B}^*$ is the magnitude of $z_{2B}^*$ at moderate values of $\phi_{B-}$. As discussed earlier this difference is mainly due to the different values of $N_B$.

A brief comparison of Figures 3 and 4 reveals that the values of $z_{2B}^*$ for systems Ia and IIa are practically equal. The same conclusion holds for the $z_{2B}^*$’s in systems Ib and Iib. These observations show that $N_B$ has a strong effect on $z_{2B}^*$ whereas $N_A$ does not greatly influence interfacial segregation. These experimental results are reinforced by SCF calculations which are shown as solid lines in Figures 3 and 4.

3.2 SCF Model. The measured $z_{2B}^*$’s are compared with those predicted by a SCF model. In addition, this model is used to calculate the $A/B:C$ interfacial tension, $\gamma_{ABC}$, and width, $\Delta w_{ABC}$. Because the model determines the volume fraction profiles for each component, the interfacial overlap between the A/B, WAB, and A/C, $W_{AC}$ phases can be found. The details of the model are found elsewhere. Briefly, the A/B/C system is described by seven input parameters, including the number of segments for polymers A, B, and C ($N_A$, $N_B$, and $N_C$), the $A-B$, $A-C$, and $B-C$ segment interaction parameters ($\chi_{AB}$, $\chi_{AC}$, and $\chi_{BC}$), and the B volume fraction in B:C ($z_{ABC}$). The values of $N_A$, $N_B$, and $N_C$ are found in Table 1. The value of $\gamma_{ABC}$ is $3.88 \times 10^{-4}$ is determined from the mutual diffusion coefficient (see Appendix A1). In contrast to our previous approach, the values of $\chi_{AB}$ and $\chi_{AC}$ are allowed to vary to produce the best fits to the experimental $z_{AB}^*$. It is important to note that only one value of $\chi_{AB} = 2.84 \times 10^{-3}$ and $\chi_{AC} = 3.71 \times 10^{-3}$ was used for all the SCF calculations. These values are only slightly different from those previously reported (i.e., $\chi_{AB} = 2.94 \times 10^{-3}$ and $\chi_{AC} = 3.61 \times 10^{-3}$ for $x = 0.154$ and $y = 0.177$, respectively). Because of the small difference in the 4-BrS mole fractions of B1 and B2 (cf. Table 1), the same values of $\chi_{AB}$, $\chi_{AC}$, and $\chi_{BC}$ are used for systems Ia and Ib. Figure 2 shows that the SCF volume fraction of B2 (thick solid line) is in excellent agreement with the experimental data (solid circles). Using the same interaction parameters, similar agreement is found for all other profiles measured. It is quite remarkable that the experimental (circles) and calculated (lines) values of $z_{2B}^*$ for each system shown in Figures 3 and 4 are in such excellent agreement over a wide range of $\phi_{B-}$. Because $z^*$ is small and superimposed on a high background of $\phi_{B-}$, the $z^*$’s measured at high $\phi_{B-}$ have a higher experimental error than those at low $\phi_{B-}$. This may account for the poorer agreement between experiment and SCF at high $\phi_{B-}$.

The interfacial tension, $\gamma_{ABC}$, is calculated for systems Ia and Ib by two methods. For Ia, $\gamma_{ABC}$ is evaluated from the SCF model by integrating the incompressibility term, $\Delta w$, in the mean-field potential:

$$\gamma_{ABC} = k_B T \rho_0 \int_{\infty}^{\infty} \Delta w(x) \, dx$$

where $k_B$ is Boltzmann’s constant, $T$ is absolute temperature, and $\rho_0$ is the lattice density. The incompressibility term $\Delta w(x)$ is given by:

$$\Delta w(x) = c [1 - \sum_k \phi_k(x)]$$

where $c$ is a parameter proportional to the bulk compressibility of the mixture. Although eqs 1 and 2 produce reasonable results for Ia (see discussion below), the $\gamma_{ABC}$ values for Ib at intermediate $\phi_{B-}$ are unrealistically low (i.e., less than $\gamma_{AC}$ and $\gamma_{AB}$). To overcome this problem, $\gamma_{ABC}$ for Ib is determined from the Gibbs adsorption equation (GAE) following the procedure of Norton et al. The GAE method is described in Appendix A2. In addition, the GAE approach was used to determine $\gamma_{ABC}$ for system Ia and found to be in excellent agreement with the SCF results.

Figure 5 shows the calculated $\gamma_{ABC}$ as a function of $\phi_{B-}$ for systems Ia (closed circles) and Ib (open circles) at 181 °C. For Ia, $\gamma_{ABC}$ monotonically decreases from 0.520 to 0.428 mJ/m² as the system progresses from a “pure” A1/C to a “pure” A1/B1 interface. As $\phi_{B-}$ increases from 0 to 0.3, $\gamma_{ABC}$ decreases relatively rapidly; however, beyond $\phi_{B-} \approx 0.3$, $\gamma_{ABC}$ decreases more slowly. Similar behavior is observed for system Ib although the transition near $\phi_{B-} \approx 0.3$ is accentuated because $\gamma_{ABC}$ tends to level off for $\phi_{B-} > 0.4$. This plateau-like region is due to the higher value of the pure A1/B2 interfacial tension (0.454 mJ/m²) relative to A1/B1 in system Ia (0.428 mJ/m²). For $\phi_{B-} < 0.3$, the magnitude that $\gamma_{ABC}$ decreases in both Ia and Ib is similar. Thus, at low $\phi_{B-}$ the efficiency of lowering $\gamma_{ABC}$ is nearly equivalent for...
The dependence of the interfacial width, $w_{ABC}$, on the bulk volume fraction of $B$ in the $B:C$ mixture, $\phi_{B*}$, for systems Ia (closed circles) and Ib (open circles) is given in Figure 6. The SCF interfacial width, $w_{ABC}$, is plotted in Figure 6 for systems Ia (closed circles) and Ib (open circles). Comparison of Figure 6 with Figure 5 reveals that the behavior of $w_{ABC}$ with $\phi_{B*}$ mirrors that of $\gamma_{ABC}$. Namely, in Ia $w_{ABC}$ increases gradually from 103.5 to 124.6 Å as the system moves from the A1/C interface to the A1/B1 interface, respectively. $w_{ABC}$ increases quite rapidly as $\phi_{B*}$ initially increases and then more gradually for $\phi_{B*} > 0.3$. In Ib, $w_{ABC}$ qualitatively follows the same trend as in Ia in the region $\phi_{B*} < 0.3$. For $\phi_{B*} > 0.3$, $w_{ABC}$ increases more slowly, reaching a value of 119.6 Å.

To further understand the behavior of $w_{ABC}$, the interfacial widths of component A with B, $w_{AB}$, and of A with C, $w_{AC}$, are plotted in parts a and b of Figure 7, respectively, for systems Ia (closed circles) and Ib (open circles). For Ia, Figure 7a illustrates that $w_{AB}$ rises rapidly as $\phi_{B*}$ increases from 0 to ca. 0.3 and then more slowly as $\phi_{B*}$ continues to increase. For Ib, $w_{AB}$ initially increases more rapidly than in Ia, but then reaches a plateau between 0.3 and 0.6 before increasing again. Note that the difference between $w_{AB}$ in Ia and Ib is significant at low $\phi_{B*}$ (<0.3). For example, at $\phi_{B*} \approx 0.2$, $w_{AB}$ for Ib is about 24% greater than its corresponding value for Ia. These observations indicate that at low $\phi_{B*}$ the overlap between A and B will increase more strongly for systems with higher $N_B$. Whereas $w_{AB}$ increases with $\phi_{B*}$, Figure 7b demonstrates that $w_{AC}$ initially decreases strongly and then near $\phi_{B*} \approx 0.3$ starts to decrease at a much slower rate as $\phi_{B*}$ approaches 1. Recall that $w_{AC}$ is nearly independent of $N_B$ for $\phi_{B*} < 0.3$ (cf. Figure 6). Therefore, the increase in $w_{AB}$ at large $N_B$ must be compensated by the decrease in $w_{AC}$.

The SCF $z_{A*}$s for systems I and II (Figures 3 and 4) are found to be in excellent agreement with the measured values. Moreover, the SCF values of the interfacial tension and widths for system I are given in Figures 5, 6, and 7. For completeness, the SCF calculations of $\gamma_{ABC}$ and $w_{ABC}$, along with $z_{A*}$, are presented in Table 3 for system II. Qualitatively, $\gamma_{ABC}$ and $w_{ABC}$ have the same functional dependence on $\phi_{B*}$ both for systems I and II. A quantitative comparison between Ia and Ib reveals that $z_{A*}$ and $w_{ABC}$ are slightly smaller, and $\gamma_{ABC}$ is slightly larger in the system which has the larger $N_A$.

### Table 3. Interfacial Properties Determined from the SCF Model

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<th>$\phi_{B*}$</th>
<th>$z_{A*}$ (Å)</th>
<th>$\gamma_{ABC}$ (mJ/m²)</th>
<th>$w_{ABC}$ (Å)</th>
<th>$z_{A*}$ (Å)</th>
<th>$\gamma_{ABC}$ (mJ/m²)</th>
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<td>111.4</td>
<td>11.0</td>
<td>0.513</td>
<td>107.8</td>
</tr>
<tr>
<td>0.9</td>
<td>5.4</td>
<td>0.489</td>
<td>112.2</td>
<td>3.0</td>
<td>0.511</td>
<td>108.4</td>
</tr>
<tr>
<td>1.0</td>
<td>0</td>
<td>0.484</td>
<td>112.9</td>
<td>0</td>
<td>0.508</td>
<td>109.2</td>
</tr>
</tbody>
</table>

* For the polymer characteristics see Table 1. b Calculated using the GAE approach (see Appendix A2 for details).

A similar relationship is observed upon comparing Ib with IIb. Because increasing $N_A$ by a factor of ca. 50 has only a minor effect on the interfacial properties, we will restrict the discussion section mainly to systems Ia and Ib and focus on the influence of $N_B$.

### 4. Discussion

In this section we provide a physical interpretation of the results presented in the previous part of this
Figure 8. Dependence of the correlation length, $\xi$, on the bulk volume fraction of B in the B:C mixture, $\phi_{Bw}$, for systems Ia (open circles) and Ib (closed circles). The values of $\xi$ were determined from the SCF volume fraction profiles using the procedure outlined in Appendix A3.

As discussed in ref 15, $z_B^*$ is expected to increase as $N_B$ increases for the following reason. For binary polymer blends in contact with air, previous studies (e.g., refs 26 and 27) have shown that the surface excess of the segregating polymer scales with the blend correlation length, $\xi$. Far from the two-phase region, $\xi$ is nearly equal to the radius of gyration of the segregating polymer. However, as the phase boundary is approached, $\xi$ increases rapidly and eventually diverges. If air is replaced by polymer A (as in our case), the previous argument can also describe the segregation of B at the A/B:C interface. Thus, the behavior of $z_B^*$ as a function of $\phi_{Bw}$ should mirror that of the B:C correlation length. Figure 8 shows the variation of $\xi$ with $\phi_{Bw}$ for systems Ia (open circles) and Ib (closed circles). The values of $\xi$ were determined from the SCF volume fraction profiles using the procedure in Appendix A3.

A comparison of Figures 3 and 8 reveals that both $z_B^*$ and $\xi$ have the same functional dependence on $\phi_{Bw}$. In addition, the $\phi_{Bw}$'s at which $\xi$ and $z_B^*$ reach their maxima are nearly identical. However, because of its higher $N_B$, system Ib has higher values of $\xi$ than system Ia.

In addition to the strong increase in $z_B^*$, the interfacial tension $\gamma_{ABC}$ decreases rapidly as $\phi_{Bw}$ initially increases as demonstrated in Figure 5 and Table 3. This behavior can be understood as follows. At low $\phi_{Bw}$, the segregation of B to the A/B:C interface is favored because the system lowers its free energy by replacing more unfavorable A--C contacts with less unfavorable A--B ones. As a result $\gamma_{ABC}$ decreases very rapidly. As $\phi_{Bw}$ continues to increase, $\gamma_{ABC}$ decreases much more slowly. This transition correlates with a reduction in free energy gain upon further replacing A--C contacts by A--B ones at high $\phi_{Bw}$'s. This transition in $\gamma_{ABC}$ occurs at nearly the same value of $\phi_{Bw}$ at which $z_B^*$ is a maximum.

As mentioned earlier in this paper, in addition to reducing the interfacial tension, polymer compatibilizers improve the mechanical properties of a blend by increasing the interfacial strength. For strongly immiscible A/C blends, we now show that the addition of a high molecular weight B component can accomplish this task. In general, an interface between incompatible phases can be strengthened if the interfacial width becomes comparable to the entanglement distance given by

$$w_{ek} = a_k \left( \frac{M_{ek}}{M_{0k}} \right)^{1/2}$$

where $a_k$, $M_{ek}$ and $M_{0k}$ are the segment length, the entanglement molecular weight, and the monomer molecular weight of polymer k, respectively. Fetters and co-workers showed that for a variety of polymers $M_{ek}$ is given by

$$M_{ek} = Kp_k^2 \rho_k$$

where $p_k$ and $\rho_k$ are the packing length and density, respectively. $K$ is temperature dependent and has a value of ca. 226 $A^{-3}$ mol$^{-1}$ at 413 K. Introduced by Witten, Milner, and Wang, the packing length reflects the number of individual chains per unit volume

$$p_k = \frac{M_{0k}}{a_k \rho_k N_A}$$

where $N_A$ is Avogadro’s constant. The values of $a_k$ and $\rho_k$ for polymers B and C were determined using the relations found by Strobl and Urban. The calculated values of $\rho_k$, $a_k$, $p_k$, $M_{ek}$, and $w_{ek}$ for all polymers are listed in Table 4. Note that the entanglement molecular weight decreases as the mole fraction of 4-BrS increases.

A comparison of the entanglement distances with the A/B:C interfacial width provides a good indication of whether the addition of B will improve the mechanical strength. For a homopolymer/homopolymer interface reinforced with diblock copolymers, Creton and co-workers reported that at least one average entanglement per block is needed for good stress transfer at the interface. The entanglement distances from Table 4 are represented by the solid lines ($w_{A}$), a dotted line ($w_{B}$), and a dash-dotted line ($w_{C}$) in Figure 7. At low $\phi_{Bw}$ (< 0.2), Figure 7b shows that the A/C interpenetration (shaded region) is sufficient to produce an A/B:C interface with good mechanical strength. As $\phi_{Bw}$ further increases, the interface strength attributed to overlap...
Table 4. Entanglement Molecular Weight and Chain Statistics at 413 K

<table>
<thead>
<tr>
<th>symbol</th>
<th>N</th>
<th>x, y</th>
<th>ρ</th>
<th>a</th>
<th>p^2</th>
<th>M_e</th>
<th>R_0^f</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3844</td>
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<td>11657</td>
<td>70.9</td>
</tr>
<tr>
<td>A</td>
<td>3842</td>
<td>0.154</td>
<td>1.216</td>
<td>7.4</td>
<td>3.07</td>
<td>7966</td>
<td>59.5</td>
</tr>
<tr>
<td>B</td>
<td>6333</td>
<td>0.157</td>
<td>1.217</td>
<td>7.4</td>
<td>3.06</td>
<td>7932</td>
<td>59.5</td>
</tr>
<tr>
<td>C</td>
<td>3996</td>
<td>0.177</td>
<td>1.129</td>
<td>7.5</td>
<td>3.01</td>
<td>7060</td>
<td>58.3</td>
</tr>
</tbody>
</table>

^a N is the number of segments, ρ is the density, a is the segment length, p is the packing length, M_e is the entanglement molecular weight, and R_0^f is the square root end-to-end distance. Calculated using ρ = ρ_g - ρ_s + 0.541x and ρ_c = ρ_g + 0.541y. \[ a = a_s(l + 1.4964x) \] and \[ a_c = a_p(l + 1.4964y) \]. Calculated using eq 5. Calculated using eq 4. Calculated using \[ R_0^f = a N_k \].

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Appendix

A1. The Flory–Huggins Interaction Parameter in Poly(styrene-co-4-bromostyrene) Blends. The segmental interaction parameters for the two polystyrene–poly(styrene-co-4-bromostyrene) blends, \( \chi_{AB} \) and \( \chi_{AC} \), were obtained by interpolating values from the literature. However, the interaction parameter for the blends of poly(styrene-co-4-bromostyrene) having different mole fractions of bromine in the interaction parameter \( \chi_{BC} \) was not available. This interaction parameter was determined from the rate at which the B interfacial excess increased with time. This procedure is described below.

For a binary B:C polymer blend, Jones and Kramer showed that the rate of surface segregation is diffusion limited. During the growth of the surface layer, the volume fraction of the adsorbed component, B, is in local equilibrium with its volume fraction in the depleted zone adjacent to the surface, \( \phi_{B-} \). The surface excess of B is then

\[
\frac{z_B*}{\phi_{B-} (\phi_{B-} - \phi_{B-}) \sqrt{D_M}}
\]

where \( D_M \) is the mutual diffusion coefficient and \( r \) is time. By assuming that the B interfacial excess is also diffusion controlled, we use eq A1 to extract \( \chi_{BC} \). Figure 9 shows how \( z_B* \) and \( \phi_{B-} \) (inset) vary with \( r^{1/2} \) at 181 °C. These results indicate that \( z_B* \) increases linearly with \( r^{1/2} \) whereas \( \phi_{B-} \) decreases linearly with \( r^{1/2} \). The bulk concentration of B decreases as the interfacial concentration of B increase because the total amount of B in the B:C thin film must be conserved.

Using an average value of \( \phi_{B-} (\phi_{B-} - \phi_{B-}) \approx 0.0025 \), the slope from eq A1 provides a measure of \( D_M = 3.13 \times 10^{-14} \) cm²/s. Using the fast theory of polymer diffusion and known values of the polystyrene tracer diffusion coefficients, \( D* \), \( \chi_{BC} \) was determined to be ca. 3.88 x 10^{-4}. One assumption in this calculation is that \( D* \) of
normal PS is a good estimate for poly(styrene-co-4-bromostyrene) having low mole fractions of 4-BrS.

A2. The A/B:C Interfacial Tension Determined from the Gibbs Adsorption Equation. Recently, Norton and co-workers pointed out that the surface energy difference between components in binary polymer blends can be evaluated from the Gibbs adsorption equation:

\[
d\gamma = -\sum \Gamma_i d\mu_i \tag{A2}
\]

where \(\gamma\), \(\Gamma_i\), and \(\mu_i\) are the surface tension, molecular surface excess, and chemical potential of component \(i\), respectively. This approach was used to determine the A/B:C interfacial tension for some systems in this paper.

The interface between A and B:C phases is defined to coincide with the Gibbs dividing interface for the A component. Because \(\Gamma_A = 0\) following this definition, we can write

\[
\Gamma_B = -\Gamma_C \tag{A3}
\]

The molecular interfacial excess is related to the interfacial excess, \(z_i^*\), of species \(i\) by

\[
\Gamma_i = z_i^* \rho_i / N_i \tag{A4}
\]

where \(\rho_i\) and \(N_i\) are the molar density and number of segments of \(i\), respectively. By combining eqs A2–A4, we have

\[
d\gamma = -\rho_B z_B^* \left[ \frac{d\mu_B}{N_B} - \frac{d\mu_C}{N_C} \right] \tag{A5}
\]

The chemical potentials, derived from the Flory–Huggins free energy, are

\[
\frac{\mu_B}{k_B T} = \ln \phi_B - 1 + \phi_B \chi_{BC} (1 - \phi_B) N_B \tag{A6}
\]

\[
\frac{\mu_C}{k_B T} = \ln \phi_C - 1 + \phi_C \chi_{BC} (1 - \phi_C) N_C \tag{A7}
\]

where \(k_B\) is Boltzmann’s constant, \(T\) is the absolute temperature, \(\chi_{BC}\) is the B–C interaction parameter, and \(N_i\) and \(\phi_{i,\infty}\) are the number of segments and bulk volume fraction of \(i\), respectively. Differentiating eqs A6 and A7 with respect to the bulk volume fractions of B and C, respectively, we obtain:

\[
\frac{d\mu_B}{k_B T} = \left[ \frac{1}{\phi_B} - 1 + \frac{N_B}{N_C} - 2\chi_{BC} (1 - \phi_B) N_B \right] d\phi_B \tag{A8}
\]

\[
\frac{d\mu_C}{k_B T} = \left[ \frac{1}{\phi_C} - 1 + \frac{N_C}{N_B} - 2\chi_{BC} (1 - \phi_C) N_C \right] d\phi_C \tag{A9}
\]

Substituting eqs A8 and A9 into eq A5 yields

\[
d\gamma = -k_B T \rho_B z_B^* \left[ \frac{1}{N_B \phi_B} + \frac{1}{N_C (1 - \phi_B)} - 2\chi_{BC} \right] d\phi_B \tag{A10}
\]

After integrating eq A10, the A/B:C interfacial tension relative to the A/C interfacial tension is found

\[
\gamma_{ABC} = \gamma_{AC} - k_B T \rho_B \int_{x_0}^x [1 - \phi_A (x)] dx + \int_{x_0}^x \phi_A (x) dx = 0 \tag{A12}
\]

The value of \(x_0\) defines the origin for a new depth scale. A reduced volume fraction of B, \(\phi_{B,\text{red}} (x)\), is determined from

\[
\phi_{B,\text{red}} (x - x_0) = \frac{\phi_B (x)}{\phi_B (x) + \phi_C (x)} \quad \text{for} \quad x > x_0 \tag{A13}
\]

Finally, the values of \(\xi\) are found by fitting \(\phi_{B,\text{red}} (x)\) to the function

\[
\phi_{B,\text{red}} (x) = \frac{\phi_{B1} - \phi_{B,\infty}}{h_0} \left[ 1 - \tanh \left( \frac{x - h_0}{2\xi} \right) \right] + \phi_{B,\infty} \tag{A14}
\]

where \(\phi_{B1}\) and \(\phi_{B,\infty}\) are the volume fractions of B at the surface \((x = x_0)\) and in the bulk, respectively, and \(h_0\) is the position of the inflection point of the tanh function with respect to the origin.

References and Notes


(20) The fwhm values were determined from as-cast samples.
(21) Due to the long computation times, the SCF calculations were not performed for very long chain lengths, i.e., \( N_A = 192 \) 192, and the following strategy was followed. Simulations were carried out for \( N_A \)'s of 4000, 5000, 10 000, and 12 000. For each \( N_A \), the corresponding values of \( z_B^* \), \( \gamma_{ABC} \) and \( w_{ABC} \) were plotted as a function of \( 1/N_A \). By extrapolation, \( z_B^* \), \( \gamma_{ABC} \), and \( w_{ABC} \) were found.
(24) The error bars in Figures 3 and 4 were based only on the counting statistics in the LE-FRES spectrum. The uncertainty due to choosing the origin of the A/B:C interface was not included. At high values of \( \phi_B \), this error is particularly important. For example, if the interface shifts by 150 Å toward the B:C phase, \( z_B^* \) can be reduced by ca. 20 Å.
(25) The failure of the SCF model to produce realistic values of \( \gamma_{ABC} \) for system Ib (and also IIb) is not known. The model works well for all systems as \( \phi_B \) approaches 0 and 1. The model fails at a very high \( N_A \) and moderate \( \phi_B \), thus in the vicinity of the B:C binodal. We speculate that this close proximity of the B:C mixture to the two-phase region causes an instability in the SCF calculations.
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