A Monte Carlo Simulation of Asymmetric Random Copolymers at an Immiscible Interface

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Received October 11, 1995; Revised Manuscript Received February 22, 1996[⊗]

ABSTRACT: The distribution of a random copolymer $P(A_f\text{-}r\text{-}B_{1-f})$ at the interface between immiscible A and B phases as a function of the copolymer composition, denoted by the fraction f of A monomers, and as a function of the monomer−monomer interactions, or χ values, has been studied via lattice Monte Carlo simulations. A symmetric distribution of the copolymer was found for compositionally symmetric chains ($f = 0.5$) when the χ values were independent of the copolymer composition. In contrast, an asymmetric distribution of the copolymer was found for a compositionally asymmetric copolymer ($f = {}^2/_3$) with composition-independent χ values. It was found that a symmetric distribution of the compositionally asymmetric copolymer can result only when the χ values are allowed to depend upon the copolymer composition. Such a symmetric distribution of a compositionally asymmetric copolymer is in qualitative agreement with miscibility, neutron reflectivity, and adhesion studies of polystyrene/poly(methyl methacrylate) systems.

Introduction

The segregation of diblock copolymers to the interface between immiscible homopolymers, where they can serve to stabilize and strengthen the interface, has been the object of much study (e.g., refs 1−4). Recently, it has been shown that random AB copolymers at the interface between A and B homopolymers make multiple crossings of the interface and can, under certain conditions, yield better interfacial properties than those obtained from AB block copolymers.[5,6] Recent theoretical studies indicate that the maximum interfacial strength should be obtained for a compositionally symmetric AB random copolymer, i.e., a copolymer composed of an equal number of A and B units.[7,8] This result is consistent with studies of adhesion at polystyrene/poly(2-vinylpyridine) interfaces, where the best adhesion promotion was found using a random copolymer with a styrene fraction of 0.48.[6]

In contrast to these results, adhesion studies on polystyrene (PS) and poly(methyl methacrylate) (PMMA) systems, having the random copolymer $P(S_f\text{-}r\text{-}MMA_{1-f})$ at the interface, show that the fracture toughness is maximized when f, the styrene fraction in the copolymer, is 0.68.[9] Neutron reflectivity studies reveal that the interfacial broadening on the PS and PMMA sides of the interface is symmetric only when $f = 0.68$.[9] In these studies, copolymers with styrene fractions ranging from $f = 0.30$ to $f = 0.89$ were examined.

In addition to the reflectivity and adhesion studies, miscibility studies of binary mixtures of $P(S_f\text{-}r\text{-}MMA_{1-f})$ copolymers with PS and PMMA homopolymers were performed as a function of copolymer composition.[9] The random copolymer was found to be miscible with the PS homopolymer only when the styrene content was very high. The $f = 0.89$ copolymer was miscible with PS for all concentrations investigated, while the $f = 0.78$ copolymer was miscible only at very low copolymer concentrations. The remaining copolymer compositions ($f < 0.78$) were found to be immiscible with PS. In contrast, miscibility of the random copolymer with PMMA homopolymer did not require a correspondingly high methyl methacrylate content. The random copolymer was found to be miscible with PMMA homopolymer for all concentrations investigated for $f < 0.60$, or a methyl methacrylate content greater than 0.40. It has also been observed that a $P(S_f\text{-}r\text{-}MMA_{1-f})$ random copolymer with a composition $f = 0.52$ is more miscible with PMMA than with PS.[10,11] These miscibility results indicate that the interaction of the $P(S_f\text{-}r\text{-}MMA_{1-f})$ random copolymer with PS is different than that with PMMA; i.e., the interaction of the random copolymer with the homopolymers is not symmetric. As a consequence, the distribution of the compositionally symmetric $P(S_{0.5}\text{-}r\text{-}MMA_{0.5})$ copolymer, which is miscible in PMMA but not PS, will not be symmetric at the interface between PS and PMMA, but will be broader in the PMMA phase, consistent with reflectivity studies.[9]

The observed correlation between fracture toughness and the interfacial broadening on the PS and PMMA sides of the interface for the $PS/P(S_f\text{-}r\text{-}MMA_{1-f})/PMMA$ system is intuitively reasonable; the maximum fracture toughness occurs when the interfacial broadening is symmetric.[9] Thermodynamically, this symmetry is also reflected in the fact that the $f = 0.68$ copolymer, which provides the maximum interfacial toughness, is immiscible with both PS and PMMA. The unexpected result is that this symmetry does not occur for the compositionally symmetric $f = 0.5$ copolymer. These observations have led us to the following supposition: the behavior of the $PS/P(S_f\text{-}r\text{-}MMA_{1-f})/PMMA$ system

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

may be consistent with intermolecular monomer–monomer interactions, or χ values, which depend upon the composition of the copolymer, i.e., the fraction of A monomers f in the copolymer chain. This putative dependence of the χ values on the copolymer composition is different from the concentration dependence of χ found in many PA/PB homopolymer mixtures. In the case of homopolymer mixtures, the concentration dependence of χ reflects moderation in A–B segmental interactions due to the proximity of similar or dissimilar segments. While such effects may be present in PS/PMMA systems, they cannot account for the observed asymmetry in the miscibility of binary mixtures of P(S$_f$-r-MMA$_{1-f}$) with the homopolymers. In this work, we demonstrate that the observed behavior of the P(S$_f$-r-MMA$_{1-f}$) copolymers may be attributable to composition-dependent χ values which could arise, for example, from segmental interactions that are influenced by neighboring monomers in the copolymer chain.[11]

Model

Unlike a previous study,[12] where the influence of the binary sequence distribution in the copolymer on the miscibility of AB copolymers and C homopolymer was considered, our interest is not in the details of the chain architecture which might lead to composition-dependent χ values. Rather, we assume the existence of composition-dependent monomer–monomer interactions and seek to determine the nature of the resulting distribution of a random copolymer P(A$_f$-r-B$_{1-f}$) at the interface between two immiscible phases A and B. Below, we employ free energy arguments to determine how a copolymer with arbitrary composition and χ values will be distributed at the interface between immiscible phases. We then perform lattice Monte Carlo simulations to confirm the derived relationship between χ values, f, and the symmetry of the copolymer distribution.

Consider the free energy of mixing of a binary mixture of a copolymer PA$_f$B$_{1-f}$ and a homopolymer PA. This is given by[12–15]

$$\Delta G_{a'b':a}/RT = (\phi_{a'b'}/N_{a'b'}) \ln \phi_{a'b'} + (\phi_a/N_a) \ln \phi_a + \phi_{a'b'}\phi_a\{f\chi_{a'a} + (1-f)\chi_{b'a} - f(1-f)\chi_{a'b'}\} \quad (1)$$

where ϕ_a and $\phi_{a'b'}$ are the volume fractions of PA and PA$_f$B$_{1-f}$, respectively, while N_a and $N_{a'b'}$ are the corresponding degrees of polymerization. The primes indicate units which comprise the copolymer. The change in free energy for mixing of the copolymer with PB is

$$\Delta G_{a'b':b}/RT = (\phi_{a'b'}/N_{a'b'}) \ln \phi_{a'b'} + (\phi_b/N_b) \ln \phi_b + \phi_{a'b'}\phi_b\{f\chi_{a'b} + (1-f)\chi_{b'b} - f(1-f)\chi_{a'b'}\} \quad (2)$$

The difference between the free energy of mixing a given amount of copolymer with (equal volumes of) PB and PA is given by the difference of these expressions, or

$$\Delta G_{a'b':a-b}/RT = (\phi/N_a) \ln \phi + \phi_{a'b'}\phi\{f\chi_{a'a} + (1-f)\chi_{b'a} - f(1-f)\chi_{a'b'}\} - [(\phi/N_b) \ln \phi + \phi_{a'b'}\phi\{f\chi_{a'b} + (1-f)\chi_{b'b} - f(1-f)\chi_{a'b'}\}] \quad (3)$$

where ϕ is the volume fraction of PA or PB. If we assume that the degree of polymerization of PA is the same as that of PB ($N_a = N_b$), then eq 3 simplifies to

$$\Delta G_{a'b':a-b}/(RT\,\phi_{a'b'}\phi) = f(\chi_{a'a}(f) - \chi_{a'b}(f)) + (1-f)(\chi_{b'a}(f) - \chi_{b'b}(f)) \quad (4)$$

Here, we have allowed for the possibility that the χ values may depend upon the composition f of the copolymer. Regardless of the structure of the copolymer, the composition-dependent χ values will have the folllowing limiting behavior: as $f \rightarrow 1$, $\chi_{a'a}(f) \rightarrow \chi_{aa}$, $\chi_{a'b}(f) \rightarrow \chi_{ab}$, and as $f \rightarrow 0$, $\chi_{b'b}(f) \rightarrow \chi_{bb}$, $\chi_{b'a}(f) \rightarrow \chi_{ba}$.

The quantity $\Delta G_{a'b':a-b}/(RT\,\phi_{a'b'}\phi)$ indicates the relative preference of the copolymer for PA over PB. We define the asymmetry parameter κ as

$$\kappa(f) = f(\chi_{a'a}(f) - \chi_{a'b}(f)) + (1-f)(\chi_{b'a}(f) - \chi_{b'b}(f)) \quad (5)$$

When $\kappa < 0$, the copolymer interacts preferentially with the A homopolymer. For $\kappa > 0$, the copolymer prefers to interact with the B homopolymer. A symmetric distribution of a copolymer at the interface of A and B homopolymers requires that $\kappa = 0$. For the case where the monomer–monomer interactions are independent of composition, i.e., $\chi_{a'a}(f) = \chi_{aa}$, $\chi_{b'b}(f) = \chi_{bb}$, and $\chi_{b'a}(f) = \chi_{a'b}(f) = \chi_{ab}$, a symmetric distribution ($\kappa = 0$) occurs only for the compositionally symmetric copolymer ($f = 0.5$). Note that these conditions are not necessary for a compositionally symmetric copolymer to be symmetrically distributed at the interface, only that the condition $\kappa = 0$ be satisfied.

Monte Carlo Simulations

We have performed lattice Monte Carlo simulations in order to investigate the behavior of a compositionally symmetric random copolymer P(A$_{0.5}$-r-B$_{0.5}$) and a compositionally asymmetric random copolymer P(A$_{0.67}$-r-B$_{0.33}$) at an immiscible interface for cases where $\kappa = 0$ and $\kappa \neq 0$. We have studied three systems using two different models. Simulations were performed using the configurational-bias method described previously.[16] For each simulation, 100 million attempted equilibration and 100 million attempted sampling moves were carried out. The acceptance rate for attempted Monte Carlo moves was approximately 10–20%.

The first system (system 1) represents an interface where the copolymer is present at a very low concentration. A single copolymer chain of 200 monomer units is represented on a 100 (50 × 50) layer lattice. Layers 1–50 are occupied by A monomers, while layers 51–100 are occupied by B monomers. A sharp interface is maintained such that only the single copolymer chain is allowed to cross the interface. The lattice is completely occupied by either the copolymer units or the A or B monomer units. The copolymer chains are alternating A:B copolymers, representing the P(A$_{0.5}$-r-B$_{0.5}$) chains, or A:A:B copolymers, representing the P(A$_{0.67}$-r-B$_{0.33}$) chains. In all simulations, the random copolymers are represented by the corresponding alternating copolymer; differences between the distributions of the alternating copolymers at the immiscible interfaces and distributions found for several randomly generated copolymers were small.

The second and third systems (systems 2 and 3) represent cases where a copolymer-rich phase is present at the interface between the immiscible A and B phases. For both systems a 50 (20 × 20) layer lattice was employed. The lattice was 80% filled by 400 chains of 40 monomers. For system 2, 120 PA chains were initially placed in layers 1–15, 160 A:B or A:A:B alternating copolymer chains were placed in layers 16–

Table 1. Copolymer Composition and Interaction Parameters for Monte Carlo Runs

κ	f	χ_{ab}	$\chi_{a'a}$	$\chi_{b'b}{}^a$	$\chi_{b'a}{}^a$	$\chi_{a'b}{}^a$
$^1/_2$	0.000	0.340	0.000	0.000	0.340	0.340
$^2/_3$	−0.113	0.340	0.000	0.000	0.340	0.340
$^2/_3$	0.000	0.340	0.170	0.000	0.340	0.340
$^2/_3$	−0.023	0.340	0.136	0.000	0.340	0.340
$^2/_3$	−0.057	0.340	0.085	0.000	0.340	0.340
$^2/_3$	+0.023	0.340	0.204	0.000	0.340	0.340
$^2/_3$	+0.057	0.340	0.255	0.000	0.340	0.340
$^1/_2$	0.000	0.17	0.000	0.000	0.170	0.170
$^2/_3$	0.000	0.17	0.085	0.000	0.170	0.170

[a] $\chi_{b'a} = \chi_{a'b} = \chi_{ab}$ and $\chi_{aa} = \chi_{bb} = \chi_{b'b} = 0$.

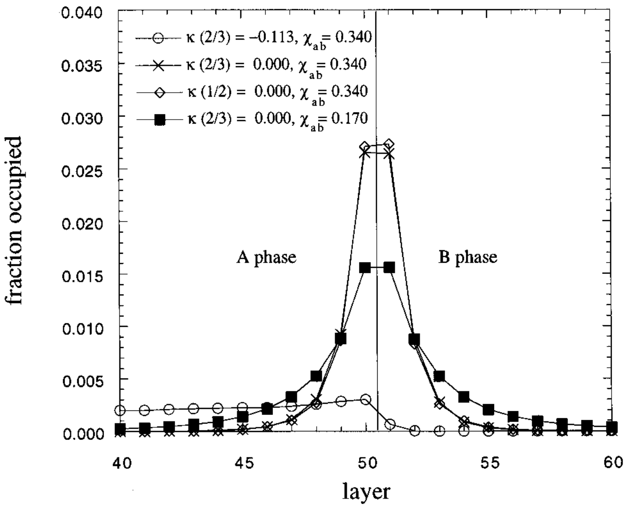

Figure 1. System 1 monomer distribution of the random copolymers at the interface between immiscible phases for various values of the asymmetry parameter κ. The number in parentheses indicates the chain composition. The solid vertical line indicates the location of the A/B interface.

35, and 120 PB chains were placed in layers 36−50. System 3 was initially configured as 176 PA chains in layers 1−22, 48 A:B or A:A:B alternating copolymer chains in layers 23−28, and 176 PA chains in layers 29−50. System 2 contains 20 lattice layers of copolymer chains and results in a well-defined copolymer phase with separate PA and PB interfaces. For system 3, a smaller value of χ_{ab} and relatively few copolymer chains (6 lattice layers) result in an interface where a well-defined copolymer phase is no longer present.

The χ values and the resulting κ values investigated for each system are summarized in Table 1. The value of κ was varied systematically by changing $\chi_{a'b}$ and maintaining $\chi_{b'a} = \chi_{a'b'} = \chi_{ab}$ and $\chi_{a'a} = \chi_{b'b} = \chi_{a'a'} = \chi_{b'b'} = \chi_{aa} = \chi_{bb} = 0$. For this case, eq 5 simplifies to

$$\kappa(f) = -f\chi_{a'b}(f) + (1 - f)\chi_{b'a}(f) \qquad (6)$$

System 1

Symmetric distributions for the P($A_{0.5}$-*r*-$B_{0.5}$) copolymer at the immiscible interface occur when $\chi_{a'b} = \chi_{b'a}$. For the P($A_{0.67}$-*r*-$B_{0.33}$) copolymer, this condition ($\chi_{a'b} = \chi_{b'a}$) results in $\kappa < 0$, with a corresponding distribution that favors the A phase; energetically, the penalty is too high to maintain the A-rich chain in the B phase. These distributions are illustrated in Figure 1. A symmetric distribution ($\kappa = 0$) occurs for the $f = {}^2/_3$ polymer when $\chi_{a'b} = 0.5\chi_{b'a}$. The resulting symmetric distributions for $\chi_{ab} = 0.34$ and $\chi_{ab} = 0.17$ are shown in Figure 1. In these cases, the greater fraction of A units in the copolymer is offset by a moderation of $\chi_{a'b}$ relative to $\chi_{b'a}$, making the B phase as hospitable to the A-rich copolymer as the A phase. The symmetric distributions ($\kappa = 0$) for the $f = {}^1/_2$ and $f = {}^2/_3$ copolymers are nearly identical. The distributions are sharper for $\chi_{ab} = 0.34$ than for $\chi_{ab} = 0.17$. This is a result of the stronger unfavorable interaction between A and B units at the interface for the larger χ_{ab}; the reduction in interfacial energy due to the copolymer at the interface is greater for larger χ_{ab}.

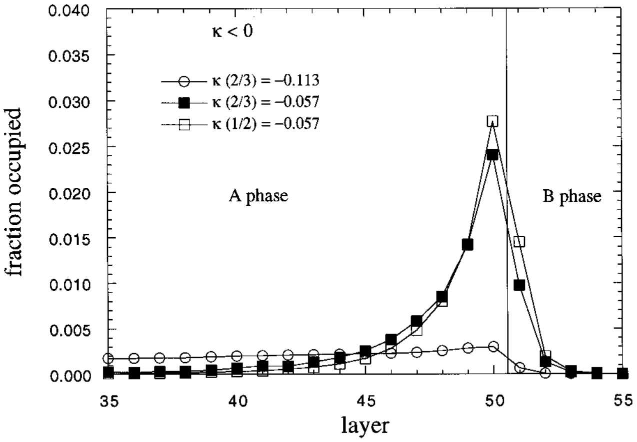

Figure 2. System 1 monomer distribution of the random copolymers at the interface between immiscible phases for values of the asymmetry parameter $\kappa < 0$. The number in parentheses indicates the chain composition. The solid vertical line indicates the location of the A/B interface.

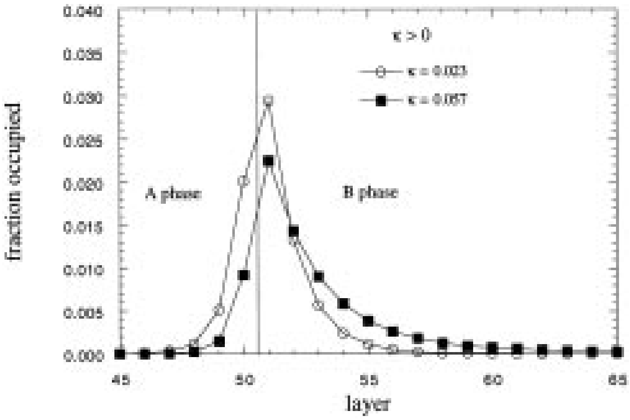

Figure 3. System 1 monomer distribution of a P($A_{0.67}$-*r*-$B_{0.33}$) copolymer at the interface between immiscible phases for values of the asymmetry parameter $\kappa > 0$. The solid vertical line indicates the location of the A/B interface.

Cases where $\kappa < 0$ are plotted in Figure 2 for the P($A_{0.67}$-*r*-$B_{0.33}$) and P($A_{0.5}$-*r*-$B_{0.5}$) copolymers. Here, any moderation of $\chi_{a'b}$ relative to $\chi_{b'a}$ is insufficient to make up for the greater fraction of A units in the copolymer chain and the chain prefers the A phase. As with the symmetric distributions, the distributions of the $f = 0.50$ and $f = {}^2/_3$ copolymers are quite similar for equal values of κ. Differences in the distributions occur on the scale of a single lattice layer or monomer unit and reflect the fact that the chains used are actually alternating copolymers. In Figure 3, cases where $\kappa > 0$ are illustrated for the P($A_{0.67}$-*r*-$B_{0.33}$) copolymers. Here, the moderation of $\chi_{a'b}$ relative to $\chi_{b'a}$ is such that the B phase is preferred.

System 2

The copolymer distributions for system 2 are illustrated in Figure 4 for the P($A_{0.67}$-*r*-$B_{0.33}$) copolymer.

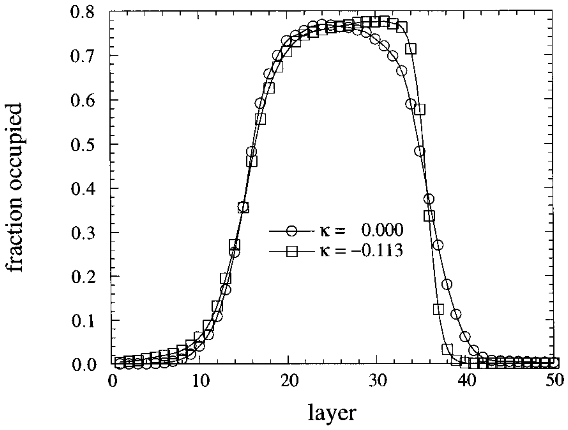

Figure 4. System 2 monomer distribution of the P($A_{0.67}$-*r*-$B_{0.33}$) copolymer in the PA/P($A_{0.67}$-*r*-$B_{0.33}$)/PB system.

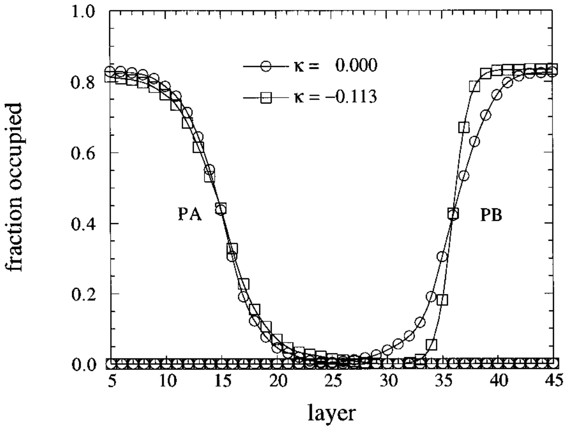

Figure 5. System 2 monomer distribution of the PA and PB homopolymers in the PA/P($A_{0.67}$-*r*-$B_{0.33}$)/PB system.

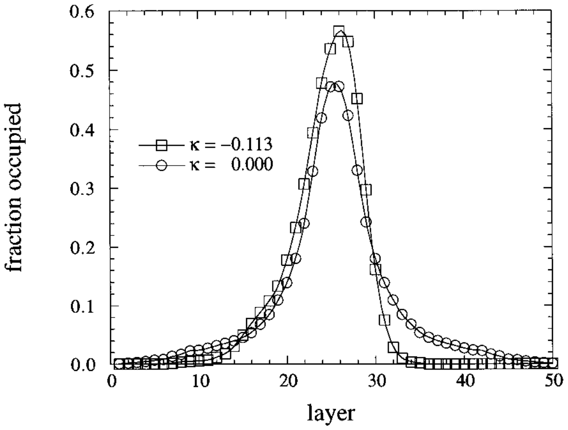

Figure 6. System 3 monomer distribution of the P($A_{0.67}$-*r*-$B_{0.33}$) copolymer in the PA/P($A_{0.67}$-*r*-$B_{0.33}$)/PB system.

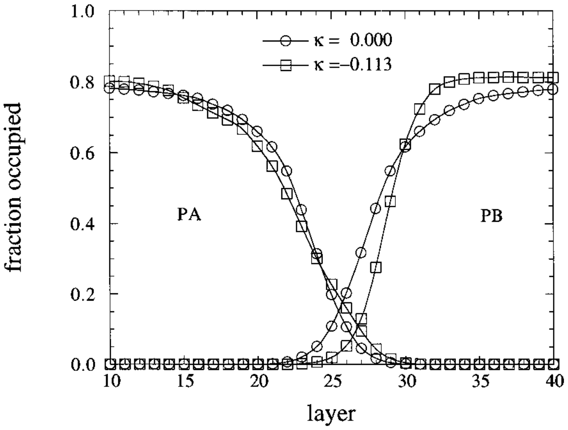

Figure 7. System 3 monomer distribution of the PA and PB homopolymers in the PA/P($A_{0.67}$-*r*-$B_{0.33}$)/PB system.

The corresponding homopolymer distributions are shown in Figure 5. From these figures, it can be seen that a well-defined copolymer phase exists with essentially independent PA and PB interfaces. For the $\kappa = 0$ case, the distribution of the A-rich copolymer with PA is symmetric with the interface of the copolymer with PB. This is the result of a reduced value of $\chi_{a'b}$ ($\chi_{a'b} = 0.5\chi_{b'a}$). For the case of composition-independent χ values, i.e., $\chi_{a'b} = \chi_{b'a}$, the asymmetry factor $\kappa = -0.113$, indicating a preference of the copolymer for PA over PB. As a result, the interface of the copolymer with PB is much narrower than that with PA. This effect is also reflected in the distributions of PB shown in Figure 5.

System 3

The copolymer distributions for system 3 are illustrated in Figure 6 for the P($A_{0.67}$-*r*-$B_{0.33}$) copolymer. The corresponding homopolymer distributions are shown in Figure 7. Unlike system 2, significant mixing of PA and PB occurs in the copolymer-rich region and hence a well-defined copolymer phase cannot be identified. As for both system 1 and system 2, when $\kappa = 0$ the A-rich copolymer is symmetrically distributed with the PA- and PB-rich phases. Again, as in system 1 and system 2, composition-independent χ values ($\kappa = -0.113$) result in a much narrower interface of the copolymer with the PB-rich phase compared with the PA-rich phase.

Conclusions

The above examples illustrate that a symmetric distribution of a copolymer with a composition $f \neq 0.50$ at the interface between two immiscible phase occurs when $\kappa = 0$. This symmetry was observed for cases ranging from a single copolymer chain at the interface between immiscible phases to the case of a well-defined copolymer phase with separate interfaces with the immiscible phases. Values of $\kappa = 0$ can occur for compositionally asymmetric copolymers when the interaction of a monomer unit comprising a copolymer chain with a monomer unit comprising a homopolymer differs from the corresponding interaction between units comprising the homopolymer chains, e.g., when $\chi_{a'b} \neq \chi_{ab}$. Conversely, when the χ values are independent of composition, $\chi_{a'b} = \chi_{ab}$ and a symmetric distribution occurs only for a compositionally symmetric chain.

The composition of the P($A_{0.67}$-*r*-$B_{0.33}$) copolymer modeled here is quite similar in composition to the P($S_{0.68}$-*r*-$MMA_{0.32}$) copolymer which showed symmetric broadening on the PS and PMMA sides of the PS/P(S_f-*r*-MMA_{1-f})/PMMA interface.[9] Our model indicates that a symmetric distribution of such a random copolymer requires that $\kappa = 0$. When $\chi_{a'a} = \chi_{b'b} = 0$ and $\chi_{b'a} = \chi_{ab}$, this occurs when $\chi_{a'b} = 0.5\chi_{ab}$, as discussed above. So, it is possible that the observed behavior of the PS/PMMA system is a result of moderation of the interaction of styrene units comprising the copolymer with the PMMA homopolymer by a factor of 2 due to the presence of MMA units in the copolymer. However, any combination of composition-dependent χ values which result in $\kappa = 0$ will yield a symmetric distribution for the compositionally asymmetric copolymer. As an example, when $\chi_{a'b} = \chi_{ab}$, a value of $\chi_{a'a} = 0.5\chi_{ab}$ yields a symmetric distribution. So the observed behavior of PS/

$P(S_f\text{-}r\text{-}MMA_{1-f})$/PMMA system could also be due to unfavorable interactions between styrene units comprising the copolymer with styrene units comprising the PS homopolymer due to the presence of MMA units in the copolymer chain. Currently, experimental data are insufficient for determination of the nature of the composition-dependent χ values or the importance of the particular distribution of segmental sequences comprising the copolymer. Despite these limitations, however, we believe that composition-dependent χ values can account for the miscibility and interfacial behavior of PS/$P(S_f\text{-}r\text{-}MMA_{1-f})$/PMMA systems, as demonstrated by our model and simulations.

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MA951515R