Effect of Copolymer Architecture on the Interfacial Structure and Miscibility of a Ternary Polymer Blend Containing a Copolymer and Two Homopolymers

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ABSTRACT: The effect of copolymer architecture on the phase behavior of a ternary polymer blend containing two homopolymers and a copolymer as well as the interfacial characteristics of this blend in the phase-separated state are examined using Monte Carlo simulation. At low copolymer concentration (*ca.* 1%), the phase transition from miscible to immiscible does not change within the resolution of the simulation for any of the copolymer structures studied here, which include block, random, and alternating architectures. It is found, however, that the copolymer does migrate to the biphasic interface in the phase-separated regime and that the configuration of the copolymer at the interface is a function of sequence distribution within the copolymer. This effect is interpreted in terms of the efficiency of the copolymer to strengthen the biphasic interface. These results suggest that both block and alternating structures show promise as interfacial modifiers, while the purely random copolymer will have the weakest effect on interfacial strengthening. It is also found that a variation of the sequence distribution away from a purely random structure can dramatically affect the ability of the copolymer to modify the interface. As most polymers which are not block or alternating are termed "random", this differentiation may have an effect on experimental studies of random copolymers as compatibilizers in polymer blends.

Introduction

It is well known that blending two or more polymers will not usually form a thermodynamically miscible mixture due to the low entropy gain upon mixing of the two components. This change in the entropy is not sufficient to overcome the usually detrimental enthalpic interactions between unlike polymer segments.[1] Regardless, many incompatible polymer blends are commercially important, such as coextruded fibers and impact-modified plastics.[2] In these products, the ultimate properties depend intimately on the interfacial adhesion between phases. Indeed, the interfacial strength limits the flow and strength properties of these polymer blends. One method to improve the interfacial characteristics of these systems is to add a third polymer (polymer C) which has an affinity for both initial polymers (polymers A and B). Polymer C can be a homopolymer[3−5] or a copolymer.[6−9] In this ternary mixture, polymer C can migrate to the interface of a phase-separated polymer blend and can serve to reinforce the biphasic interface by acting as a physical thread that binds the two phases together. The addition of polymer C will also reduce the number of unfavorable contacts between polymers A and B, which, in turn, will enhance the degree of compatibility of the polymer blend and possibly form a miscible blend, *i.e.*, compatibilize the polymer blend. The term "compatibilization" has two primary meanings in the polymer community. First, it is used in the context of true thermodynamic compatibilization:[10] the presence of a third component mediates enthalpic interactions between the first two components, which, in turn, creates a *single homogeneous* phase. Hereafter, this meaning will be referred to as thermodynamic compatibilization. Second, the term has come to be used to describe the ability of a third component to lower the surface tension between the two original components, promote adhesion between the phases, and therefore modify the morphology of the phase-separated blend as well as improve its ultimate properties. This meaning will be referred to as interfacial compatibilization. In the following study, we will examine characteristics of ternary systems that pertain to both definitions of a compatibilizer.

The ability of a copolymer to act as a compatibilizer in a polymer blend has garnered much attention recently, both experimentally[6,7,11] and theoretically.[6,12] Experimental results and Flory−Huggins-type calculations suggest that a random copolymer will act as a true thermodynamic compatibilizer over a wide concentration range ($\Phi_3 < 40\%$, where Φ_3 is the percent copolymer present) and that the shift in the cloud point temperature is linear with Φ_3.[6] A block copolymer which is similar to the random copolymer, however, exhibits limited compatibilizing effect for $\Phi_3 < 10\%$. This limiting behavior has been attributed to the interplay of microphase separation of the block copolymer and the compatibilizing effect of the copolymer on the polymer blend.

Recently, Balasz and DeMeuse[12] studied the effect of the sequence distribution of a copolymer on the miscibility of ternary mixtures which contain a copolymer and two homopolymers. Using a formalism that incorporates terms that depend on the sequence distribution of the monomers in a copolymer, phase diagrams were determined for various copolymers. Balasz and DeMeuse characterize the copolymer architecture by the parameter θ, which essentially defines the proportion of unlike nearest-neighbor monomers in the copolymer chain. The limiting values of θ for a symmetric copolymer (*i.e.*, 50% A and 50% B) are $\theta = 0$ for a block copolymer, $\theta = 1$ for an alternating copolymer and $\theta = 0.5$ for a random copolymer. The results show that the sequence distribution plays an important role in the phase behavior of these ternary mixtures and that a block copolymer may not be the best thermodynamic compatibilizer in a ternary mixture.

The effect of copolymer architecture on the interfacial structure of a phase-separated polymer blend (*i.e.*, the second definition of compatibilizer above) is also not well

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understood. Recent reflectivity results have shown that a random copolymer will not always migrate to the biphasic interface.[13] One interpretation offered to explain these results is that the intramonomer interactions are not equal, *i.e.*, the energy of A−A ≠ the energy of B−B. If the A−A intramonomer energy is greater than the B−B intramonomer energy, then the A monomer prefers to be near another A monomer more than a B monomer prefers to be near another B. Presumably, this inequality of intramonomer interactions results in a profile in which the random copolymer will favor the A-rich domain, as this profile will maximize the A−A interactions, the preferred interactions. This inequality of intramonomer energies, therefore, leads to a system in which a random copolymer will not migrate to the interface in the phase-separated regime.

These two results suggest that the structure of a copolymer can have a profound effect on the efficiency of its ability to compatibilize a polymer blend, in either sense of "compatibilize". Therefore, an understanding of the role of copolymer architecture in the interfacial profile of a phase-separated ternary polymer blend as well as the miscibility of this blend is certainly needed. It is the goal of this research to describe the effect of the sequence distribution of a copolymer on the interfacial properties and thermodynamics of a compatibilized polymer blend. Copolymer structures that will be studied include an alternating, a random, and a block copolymer. Copolymers whose structures are midway between an alternating and a random copolymer as well as midway between a random and a block copolymer will also be examined. Monte Carlo simulation will be used to characterize the phase behavior and phase-separated structure of the ternary system, polymer A/polymer B/copolymer A−B. These results will serve to describe the effect of copolymer structure on the interfacial structure of a phase-separated blend as well as the miscibility of a compatibilized polymer blend and hopefully will aid in the design and production of commercial products that are composed of a compatibilized polymer blend.

Model and Simulation Technique

The model system in this study consists of 742 chains of length $N = 10$ confined to a cubic lattice. To simulate an infinite set of chains, the system is approximated as a set of infinite identical cells of length L with periodic boundary conditions in all three orthogonal directions (x,y,z). In this study, the only interaction energy is a nearest-neighbor monomer−monomer interaction, ϵ_{A-B}. ϵ_{A-B} is zero if two neighboring monomers are of different type (A−B) and is negative otherwise. In other words, A−A, B−B, A−void, or B−void arrangements have a negative energy, while A−B alignments contribute zero energy. ϵ_{A-B} applies to any two adjacent monomers, whether they are connected by a bond or not. Steric interactions are included as excluded volume; simultaneous occupation of a given lattice site by more than one monomer is prohibited. The density of the system is calculated as the fraction of occupied lattice sites, $\rho = N_pN/L^3$, where $N_p = 742$ is the number of polymer chains present, $N = 10$ is the length of all chains, homopolymers, and copolymers, and $L = 21$ is the size of the cubic lattice. In the present study, $\rho = 80.1\%$.

The initial configuration is created by adding the polymers to the lattice in a completely ordered state. Half of the homopolymers are of type A, and half are type B. The percentage of copolymer present can be varied in the study, though most of the results described here will relate to the system with 1% copolymer concentration. The composition of the copolymer is 50% A and 50% B, while the architecture of the copolymer is controlled by uniformity factors, U_A and U_B. U_A is defined as

$$U_A = \frac{[\sum_{n=1}^{N-1} s_n] + 1}{N_A - 1} \tag{1}$$

where $s_n = 0$ if the nth monomer is of type B, $s_n = 1$ if the nth and $(n + 1)$th monomers are both type A, and $s_n = -1$ if the nth and $(n + 1)$th monomers differ. N_A is the number of A monomers in the copolymer chain. U_B is the same parameter for the B monomer. For the symmetric copolymer in this study, $U_A = U_B = U$. If the copolymer is 50% A and 50% B, this parameter gives the limiting values of $U = -1$ for an alternating copolymer, $U = 0$ for a random copolymer, and $U = 1$ for a block copolymer. Similarly a value of $U = 0.5$ will denote a copolymer that has "blocky" structure but cannot be classified as random, and $U = -0.5$ will represent a copolymer that has some tendency to alternate but is not a pure alternating copolymer. This parameter U can be correlated directly to Balasz's parameter θ. As was previously mentioned, θ is essentially a measure of the proportion of A−B (or B−A) transitions that exist along a copolymer chain. Clearly, the parameters are related, and, indeed, the relation $U = 1 - 2\theta$ maps θ into U for the symmetric copolymer.

U is also related to the reactivity ratio of the component monomers. The reactivity ratio r_A is defined as the proportion of the rate of the addition of an A monomer to an A-ended polymer chain to the rate of the addition of a B monomer to an A-ended chain, k_{AA}/k_{AB}. r_B is the corresponding ratio for a B-ended polymer chain, k_{BB}/k_{BA}. As both the reactivity ratio and U relate to the probability of finding two like monomers next to each other on the polymer chain, there should exist a relation between the two parameters. For a symmetric copolymer, it is easy to show that

$$r_A = r_B = \frac{1 + U}{1 - U} \tag{2}$$

For an asymmetric copolymer,

$$r_A = \frac{1 + U_A}{1 - U_A} \qquad r_B = \frac{1 + U_B}{1 - U_B} \tag{3}$$

Once the initial configuration is created, various chain configurations are created by applying a modified reptation technique[14] to the chains. In this modified reptation technique, a void on the lattice is chosen at random. A direction from that void is selected randomly. If the end of a chain resides on that lattice point, the polymer chain is reptated into the void and the other end of the chain is vacated. In this way, the configuration of the polymer chain changes and the void is moved. The new configuration is accepted according to the Metropolis sampling technique.[15] To ensure that there is no bias due to the initially ordered state, the system is equilibrated through 10 000 system configurations before statistics for the system characterization are calculated.

The miscibility and structure of the system are characterized by the following parameters: the heat capacity of the system, C_v, the density profile of the two homopolymers, ρ_A and ρ_B, the density profile of the copolymer, ρ_C, and the radii of gyration of the copolymer along each axis, r_gx, r_gy, and r_gz. The heat capacity is calculated as the fluctuation in the total energy of the system:

$$C_v = [\langle E^2\rangle - \langle E\rangle^2]/(k_bT)^2 \tag{4}$$

where brackets denote the ensemble average. E is the energy of the system and is equal to the number of nearest neighbors that are different. The chain density profile, $\rho_{A(B)}$, is calculated as the proportion of occupied sites in a y−z plane that are populated by homopolymer A(B). The copolymer density profile, ρ_C, is the percentage of copolymer monomers in a given y–z plane. The homopolymer profiles are further characterized by the parameter w, which is inversely related to the width of the profile and is defined as

$$w = \int_{z=0}^{L} |\rho_z - 0.5| \, \mathrm{d}z \tag{5}$$

Finally, the radii of gyration of the copolymer are calculated using the following formula:

$$r_g w = \frac{1}{nch}\sum_{i=1}^{nch}\left[\frac{1}{2N^2}\sum_{l=1}^{N}\sum_{k=1}^{N}(w(i,l) - w(i,k))^2\right] \tag{6}$$

where $w = x$, y, or z, nch is the number of copolymer chains, and $w(i,l)$ is the position on the w axis of the lth monomer on the ith copolymer chain. These parameters allow the analysis of the effect of copolymer architecture on the miscibility temperature of the compatibilized polymer blend through the heat capacity, the morphology of the phase-separated polymer blend through the density profiles, and the configuration of the copolymer at the biphasic interface through the radii of gyration.

Well-known pitfalls in Monte Carlo simulation studies of phase transitions include metastable states, critical slowing down, finite size, and density effects.[16,17] These problems, therefore, must be recognized and accounted for in the present simulation. The model used in this system is a modification of one used previously by the author to study the effect of external perturbations on the phase behavior of liquid crystals.[18,19] In the previous studies, the effects of finite lattice size, density, equilibration time, and long relaxation times near a phase transition on the characteristics of the system were studied. As long as the previously described effects are identified and accounted for, this simulation technique can accurately characterize phase transitions. Therefore, we have used this model to examine the effect of copolymer architecture on the phase behavior and biphasic interface of a compatibilized polymer blend. To minimize statistical deviation and account for the problems discussed above, each point in the following figures (each curve in Figure 2) is an average of at least 7.5×10^6 Monte Carlo steps per chain in the vicinity of the phase transition and at least 2.0×10^6 Monte Carlo steps per chain far from the phase transition.

This simulation was completed on many computers including a Cray Y-MP2 and an IBM RS/6000 at the National Institute of Standards and Technology, a DEC Alpha 400/266 in the Chemistry Department at the University of Tennessee, a DEC Alpha 3000/700 at the University of Tennessee Computing Center, and an IBM SP/2 at the Cornell National Theory Center. The program was run with vector processing and maximum optimization on all machines.

Results

Figure 1 shows the heat capacity, C_v, as a function of the reduced temperature, $\tau = k_bT/\epsilon_{A-B}$, near the miscibility temperature of a binary polymer blend (polymer A/polymer B) and ternary polymer blends with 1% copolymer. In this figure, the structure of the copolymer varies from a block copolymer ($U = 1$) to a random copolymer ($U = 0$) to an alternating copolymer ($U = -1$). Inspection of this figure shows that, to the resolution of this experiment, there is no change in the cloud point temperature of the pure polymer blend through the addition of a copolymer at 1% loading. In each of these samples, the transition from a miscible to an immiscible system occurs at $\tau = 7.5 \pm 0.1$.

Figure 2 shows the temperature dependence of the width parameter of the homopolymer A profile, w, for the pure homopolymer blend and the three compatibilized blends. From this figure, it can also be deduced that the width of the interface as characterized by w does not change as a function of copolymer structure at a 1% copolymer loading. This figure also demonstrates that there is no change, within experimental error, in the width of the homopolymer A profile upon the addition of 1% copolymer.

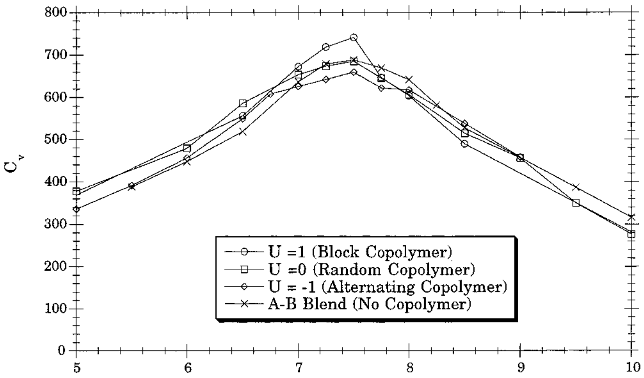

Figure 1. Heat capacity, C_v, vs reduced temperature, $\tau = k_bT/\epsilon_{AB}$, for the binary homopolymer blend and three blends which are compatibilized by copolymers of various architectures. The copolymer structures are $U = 1 \equiv$ block copolymer; $U = 0 \equiv$ random copolymer; and $U = -1 \equiv$ alternating copolymer.

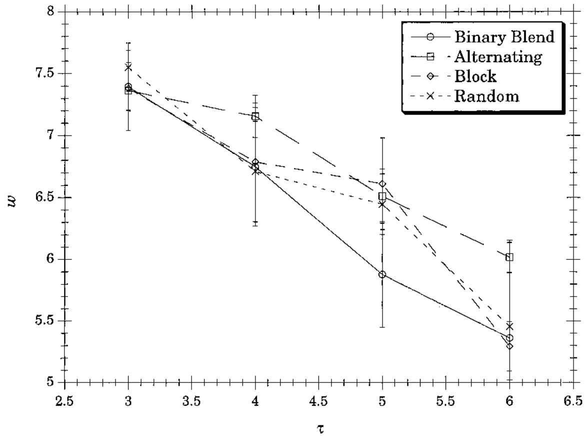

Figure 2. Change in the parameter, w, of the density profile of homopolymer A as a function of reduced temperature for the binary polymer blend and the ternary blends with 1% copolymer. Copolymer structure is identified in the legend. w is inversely proportional to the width of the composition profile.

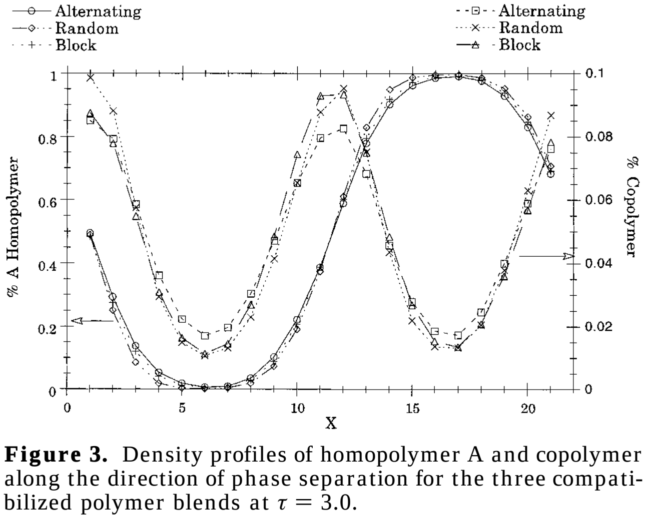

Figure 3. Density profiles of homopolymer A and copolymer along the direction of phase separation for the three compatibilized polymer blends at $\tau = 3.0$.

Figure 3 shows the A homopolymer and copolymer density profile from the three compatibilized blends, containing 1% alternating, random, and block copolymer at $\tau = 3.0$. This figure shows that the copolymer, regardless of architecture, will migrate to the biphasic

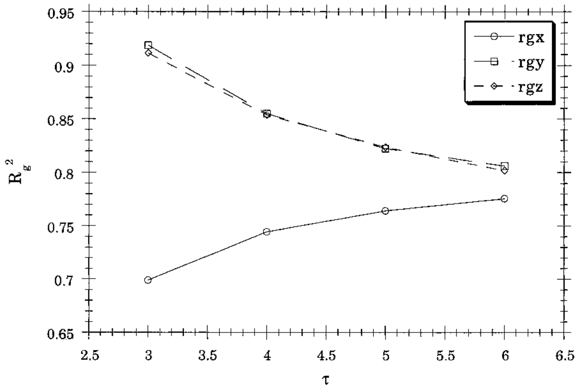

Figure 4. Change in the orthogonal components of R_g^2 of an alternating copolymer ($U = -1$) with reduced temperature at the interface of a phase-separated ternary polymer blend.

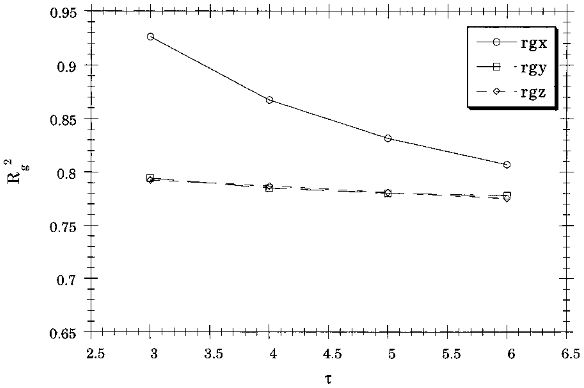

Figure 5. Reduced temperature dependence of the *x*, *y*, and *z* components of R_g^2 of a block copolymer ($U = 1$) in the phase-separated compatibilized polymer blend.

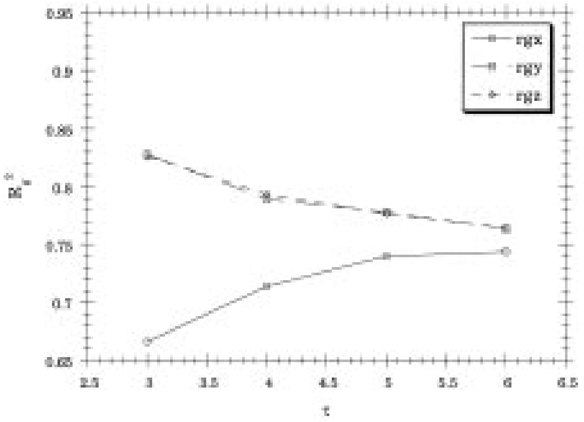

Figure 6. Same as Figures 4 and 5 for a random copolymer ($U = 0$).

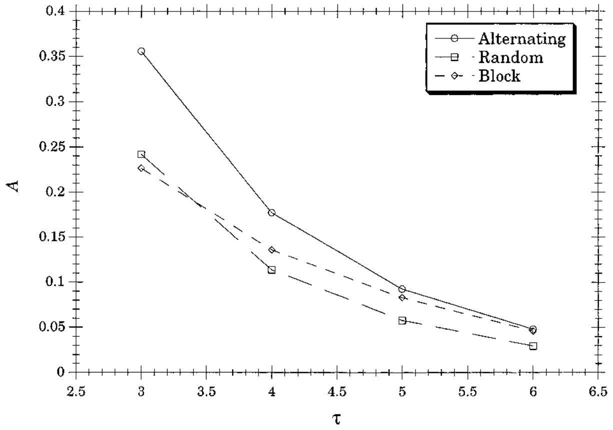

Figure 7. Change in the anisotropy of the three copolymer structures as a function of reduced temperature.

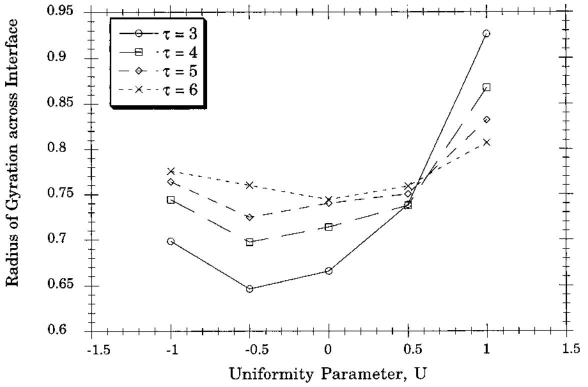

Figure 8. Effect of copolymer structure on the extension of a copolymer across the biphasic interface. $U = 1$, block copolymer; $U = 0$, random copolymer; and $U = -1$, alternating copolymer.

interface to act as a compatibilizer. It should be noted that the presence of two interfaces in this figure is a result of the use of periodic boundary conditions but does not affect the results reported below. Figures 4−6 demonstrate that the copolymer configuration at the interface, however, *is* a function of the copolymer architecture. Figure 4 shows the *x*, *y*, and *z* components of R_g^2 of the alternating copolymers at the interface as functions of reduced temperature. Figures 5 and 6 are the same plots for the block and random copolymers, respectively. In these figures, the *x* direction is the axis along which phase separation occurs and the *y* and *z* axes define the plane that is parallel to the biphasic interface. Inspection of the figures leads to some interesting conclusions. At a given temperature, r_gx of the block copolymer is greater than r_gy and r_gz, while the opposite is true for both the random and alternating copolymers ($r_gz \approx r_gy > r_gx$). Therefore, the volume that the block copolymer occupies has a cigar- or cylinder-type shape, while the volume that the random and alternating structures occupy has a disklike shape in the phase-separated blend. These results also show that the expanse of the alternating copolymer at the interface (r_gy or r_gz) is larger than that of the random copolymer at a given temperature. Therefore, the alternating copolymer is more expanded along the interface than the random copolymer. This will be considered further in the Discussion section. It is also interesting that, at a given temperature, the expanse of the alternating copolymer *along* the interface is very close to the expanse of the block copolymer *across* the interface.

An important parameter that defines the configuration of the copolymer is its anisotropy, which is characterized by the parameter $A = |r_gx^2 - r_gy^2|$. Figure 7 shows a plot of *A* versus reduced temperature, showing that all three structures have a maximum anisotropy at the lowest temperature, $\tau = 3.0$. As the temperature is increased toward miscibility, the anisotropy in the copolymer decreases up to the transition temperature, where $A = 0$. Figure 8 demonstrates the effect of the copolymer structure on the configuration of the copolymer at the interface. This plot shows the change in the r_gx with copolymer structure for the reduced temperatures that are listed. Figure 9 is the same plot for r_gy. Figure 8 shows a minimum of the extension across the biphasic interface for the copolymer whose structure is half way between alternating and random (termed alt-

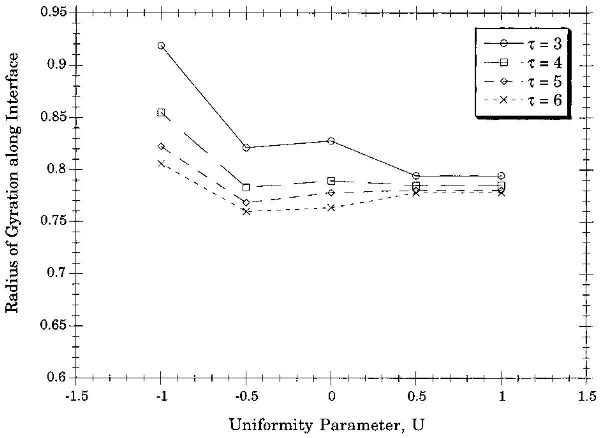

Figure 9. Extension of the copolymer along the biphasic interface as a function of copolymer structure.

ran) at $\tau = 3.0$. The results in Figure 9, however, demonstrate that the extension along the biphasic interface is a maximum for the alternating copolymer and decreases as the structure deviates from the truly alternating architecture and remains unchanged for all other structures, with a slight increase in r_gy for the random copolymer at deep quench depths ($\tau = 3.0$).

Discussion

Thermodynamic Compatibilization. First, the relation of copolymer architecture to the ability to truly compatibilize a polymer blend through mediation of detrimental enthalpic interactions will be discussed. The results suggest that the addition of 1% copolymer, regardless of sequence distribution, to a polymer blend will not change the miscibility or cloud point temperature of the polymer blend and therefore will not act as a thermodynamic compatibilizer. These results are in agreement with the experimental work of Han.[20] In these experiments, the change in the spinodal of a polymer blend of polystyrene and polybutadiene with the addition of block copolymer was examined using neutron scattering. No change in the spinodal with the addition of 1% copolymer was observed, but a change in the miscibility temperature was found when the copolymer concentration was increased to 3%. The results of Rigby *et al.*[6] show a linear decrease in the cloud point temperature with the addition of a random copolymer to a binary blend up to 40% copolymer loading. Close examination of the results of Rigby *et al.*, however, show that the lowest copolymer concentration examined was *ca.* 5 wt %. Therefore, our results cannot be directly compared to this experimental investigation.

To understand this effect, it should be remembered that an important parameter for compatibilization is surface coverage. To lower the surface tension, the compatibilizer must cover the interface between the two phases to mediate the enthalpic interactions. A quick calculation shows that, at 1% copolymer, the phase-separated system does not have a saturated interface. If the biphasic interface is one lattice plane wide, a lower limit, then the interfacial volume is $21 \times 21 = 441$ lattice sites. At 1% copolymer loading, there are eight copolymer chains of length $N = 10$. Therefore, less than one-fifth of the interfacial plane can be covered by the copolymer, and that is only if the copolymer spreads perfectly along the interface. It therefore seems logical that the presence of 1% copolymer is not sufficient to mediate the enthalpic interactions between homopolymers and act as a true thermodynamic compatibilizer. But, at higher copolymer concentrations, when the surface approaches saturation, a deviation in the miscibility temperature should be seen. Experimental results support this conclusion, as the results of Han as well as Rigby *et al.* do show a decrease in the cloud point temperature with an addition of at least 3–5% copolymer. Preliminary Monte Carlo[21] results also show a decrease in the cloud point temperatures for 5% and 7.5% copolymer concentrations. Further studies of systems with higher copolymer concentrations are in progress and will be the topic of future publications.

Interfacial Modification. Figure 3 shows that, regardless of the copolymer structure, the copolymer will migrate to the interface and compatibilize the blend in the sense that it modifies the interface of the phase-separated blend. This disagrees with the recent experimental results.[13] However, these experimental results have been attributed to unequal intramonomer interactions, while the intramonomer interactions in the present study are equal. Future simulations will examine the role of disparate energies of interactions between similar monomers and attempt to duplicate these novel experimental results.

A copolymer is added to a polymer blend with the hope that the copolymer will migrate to the interface and act as a thread between the two phases to "sew" them together. This promotes adhesion between phases and increases the ultimate properties of the blend. The ability to bind the two phases together depends intimately on the configuration of the copolymer that is at the interface. An ideal configuration would be one where the copolymer forms loops across the interface, into which the homopolymer can become entangled.

It therefore seems logical that the copolymer architecture that allows the most entanglements at the interface will act as the best interfacial modifier. Unfortunately, this aspect of the polymers in this system cannot be easily quantified. The measurable properties of the copolymers in the blend, however, can be used to estimate the relative efficiency of each structure as a compatibilizer. An important property that can be quantified is the extent of expansion of the copolymer along and across the interface in the phase-separated structure. A copolymer that is expanded along and across the interface will allow the required entanglements more readily than a compact structure. Using this criterion, inspection of Figures 4–6 leads to some interesting conclusions. Before proceeding, it should be noted that the molecular weights studied in this simulation are undoubtedly below the entanglement molecular weight of most polymers. The following analysis is not meant to imply that entanglements occur but to point out systematic trends which will affect the ability of entanglements to occur in systems where they can occur.

First, the random copolymer, as shown in Figure 5, expands the least of the three structures. Its expanse both along and across the interface is the smallest of each of the copolymer structures. It seems to have crumpled in on itself. This structure will allow fewer entanglements than will a more expanded structure. Therefore, from these results, it is expected that addition of a random copolymer to a binary blend will be the least efficient of the three copolymer structures, alternating, block, and random, at compatibilizing a polymer blend.

The block copolymer, however, exhibits a configuration that is stretched across the interface. In this configuration, the A block is extended into the A-rich phase, while the B block extends into the B-rich phase. This structure is more conducive to entanglements than the random copolymer structure. The block copolymer, however, does not interdigitate across the biphasic interface, a structure which would encourage entanglements. In the stretched configuration of the block copolymer, any entanglement that may occur must be formed between a homopolymer chain and one half of the block copolymer. The block of the copolymer that will participate in this entanglement will behave like a polymer chain which is one-half the length of the copolymer and which is end-adsorbed onto a surface. Therefore, for the block to be an efficient interfacial compatibilizer, the block length must be long enough to allow entanglements even though one end is confined to the interface, *i.e.*, the block length must be above the entanglement molecular weight of an end adsorbed polymer. These results, therefore, suggest that an estimation of the entanglement molecular weight of a polymer that is end-adsorbed onto a surface would be useful to estimate the lower limit for the length of a block copolymer that is an efficient interfacial modifier in phase-separated polymer blends.

Finally, the alternating copolymer displays a structure that is expanded along the interface as well as across it. This expansion both along and across the interface will be very conducive to the introduction of entanglements between the copolymer and the homopolymer; therefore, this structure will be an efficient interfacial modifier in the phase-separated regime. Indeed, the expansion of the alternating copolymer along the interface is similar to the expansion of the block copolymer across the interface. This is evidence that the regular order within a copolymer results in a maximum in the expansion of the copolymer at the interface of a phase-separated polymer blend. In the block copolymer, the expansion occurs across the interface, while the expansion is along the interface for the alternating copolymer. This suggests that, in order to maximize the expansion of a copolymer at the interface of a phase-separated blend, which is desirable to create entanglements, a well-defined order within the copolymer is helpful and may be required.

What happens when the structure of the copolymer deviates from these ideal structures? In most experimental investigations, a copolymer that is neither an alternating structure nor a block structure is termed a random copolymer. Yet there is a significant difference between a structure that is mostly alternating with a few defects and a structure that is nearly a block copolymer but is not perfect. With this in mind, the copolymer configuration in the phase-separated blend was examined for structures that are characterized by $U = 0.5$ and $U = -0.5$. These structures will be called block-ran and alt-ran, respectively. Figures 8 and 9 show the changes in the radii of gyration with copolymer structure and reduced temperature. Inspection of these plots shows that $U = 0.5$, the alt-ran structure, is a relatively poor interfacial modifier. This structure extends across and along the interface less than any other structure, including the random copolymer, and therefore a minimum number of entanglements will occur. The block-ran structure, however, shows some potential as an efficient compatibilizer. The radius of gyration across the interface is greater than or equal to that of all other structures except the block copolymer, while the radius of gyration along the interface is almost as large as that of all other structures except the alternating copolymer. Therefore, this structure has the possibility to allow entanglements and may be an efficient interfacial compatibilizer.

These results emphasize the difference between experimentally defined "random" copolymers. It must be stressed that, in order to accurately quantify the compatibilizing efficiency of a random copolymer, an accurate description of the sequence distribution of the copolymer must first be obtained. The results of this study show that copolymer architecture, even within the experimentally defined random structure, will play an important role in the ability of a copolymer to modify the biphasic interface of a polymer blend.

Experimental verification of these predictions would be interesting. This should be possible through the correlation of the reactivity ratio of two monomers to the sequence distribution parameter U. A possible experimental test of these results would be the utilization of the reactivity ratios of two monomers to determine the resulting U of the copolymers from eqs 2 and 3. The reactivity ratios can be adjusted to create copolymers with a range of well-defined architectures. Strength experiments on the subsequent phase-separated compatibilized blends will then test the above predictions of the role of copolymer architecture on the efficiency of interfacial modification.

Other predictions, such as the changes in the density profile and radii of gyration as a function of sequence distribution in the copolymers, can also be experimentally verified. Deuterated polymers can be synthesized, and the structure of the copolymer can again be controlled through the reactivity ratios of the initial monomers. With deuterated polymers, the homopolymer and copolymer profile can be determined using neutron reflectivity or secondary ion mass spectrometry, while small angle neutron scattering can be used to measure the radii of gyration of the copolymer along and across the interface.[22] The verification of the predictions could expand the understanding of the underlying driving forces in ternary polymer blends as well as increase the fundamental interest in these complex systems.

Conclusions

The effect of copolymer sequence distribution on the miscibility of a polymer blend containing two homopolymers and a copolymer has been studied. The importance of copolymer architecture in determining the interfacial characteristics of these systems when phase-separated was also examined. The results show that, within the resolution of the experiment, there is no change in the miscibility temperature of these systems with the addition of 1% copolymer, which agrees with recent neutron scattering results.[20] This has been attributed to the fact that the copolymer present is not sufficient to cover the biphasic interface and therefore will not mediate the undesirable enthalpic interactions enough to manifest a lowering of the miscibility temperature. This demonstrates the importance of understanding the interfacial area of a phase-separated polymer blend and its ratio to the amount of copolymer present when examining compatibilized polymer blends.

The copolymer structure at the biphasic interface, however, does vary significantly with copolymer sequence distribution. This variation in configuration was interpreted in terms of the ability of the copolymer to form loops and entangle homopolymer so that a macroscopic reinforcement of the interface will be found. With this interpretation, it is found that both alternating and block copolymers should efficiently strengthen the interface due to their extension along and/or across the interface. The purely random copolymer, however, is less efficient at strengthening the interface, as this copolymer tends to crumple in on itself and does not offer the opportunity for entanglements to occur.

A deviation from a purely random structure has been found to have a significant impact on the copolymer configuration at the biphasic interface and, therefore, the efficiency of the copolymer to strengthen the interface. The structure that is halfway between an alternating and a random copolymer (alt-ran) is less expanded both along and across the interface than the random copolymer and therefore will not readily allow entanglements to occur and strengthen the interface, while the structure that is halfway between a random and a block copolymer (block-ran) exhibits reasonable expansion across and along the interface and therefore will serve to strengthen the interface more efficiently than either the purely random or the alt-ran copolymer structure. This differentiation is important, as any copolymer that is not block or alternating is usually termed “random”. These results show that a random copolymer that is actually alt-ran will have very different compatibilizing effects than a random copolymer that is actually a block-ran copolymer. This disparity of structure should be distinguishable experimentally through the relationship of the theoretical parameter U and the experimental quantity of the reactivity ratios of the two monomers as defined in eqs 2 and 3.

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