Macromolecules **2002,** *35,* 1905−1910

Entropic Effects of Copolymer Localization at Semiflexible Polymer Interfaces

Wentao Li,[†] Glen H. Ko,[‡] and Dilip Gersappe*,[†]

Department of Materials Science and Engineering, State University of New York at Stony Brook, Stony Brook, New York 11794-2275, and Mitsubishi Chemical Research and Innovation Center, One Broadway, Cambridge, Massachusetts 02142

Received September 21, 2001; Revised Manuscript Received December 7, 2001

ABSTRACT: We use a self-consistent mean-field theory which accounts for polymer semiflexibility to study the effects of semiflexible copolymers localized at the interface between a flexible and a semiflexible homopolymer. Our studies show that, in contrast to copolymers located at the interface between flexible polymers, entropic effects tend to dominate the behavior of the copolymers at semiflexible polymer interfaces. We find that the reduction in interfacial tension caused by the copolymer is a nonmonotonic function of the rigidity of the copolymer and the amount of copolymer added to the system.

Introduction

The ability to form polymer blends from mixtures of rigid and flexible polymers can have distinct advantages over blends in which both components are flexible. The rigid (or semiflexible) polymeric component offers the possibility of forming a blend with enhanced mechanical strength. In addition, the electrical and photoactive properties that rigid polymers such as liquid crystal polymers often manifest can result in blends with unique electrooptic properties. The high interfacial energy between the rigid and the flexible components, however, results in poor adhesion between the two phases, and this compromises the structural integrity of the blend.[1] While theoretical and experimental studies have determined the most efficient copolymer architecture that can compatibilize blends with flexible components[2−4] (by localizing at the interface and reducing the interfacial tension), there has been little theoretical work done on the compatibilization process in semiflexible systems. As a result, experimental attempts at designing copolymer compatibilizers for semiflexible blends have largely used ideas from the literature on flexible blends and consequently do not account for the entropic effects that result from the semiflexibility of the polymers.[5,6] In this paper, we examine the effects of introducing a copolymer into a blend in which one of the components is semiflexible. We show that, in contrast to the compatibilization process in flexible blends, the additional entropy loss due to the semiflexible components of the blend results in a interfacial tension reduction that is a nonmonotonic function of both the rigidity of the copolymer and the amount of copolymer present at the interface. Our results will thus provide guidelines for the rational design of compatibilizers to stabilize semiflexible polymer blends.

In one of the first studies on the interface between semiflexible polymers, Morse and Fredrickson[7] used the wormlike chain model in their self-consistent mean-field calculation to analyze a symmetric interface between two immiscible, semiflexible polymers. Using the ground-state approximation for the chain, they were able to derive an analytical expression for the interfacial tension and the interfacial width. They predicted that in the limit of high chain rigidity there would be a narrow region of polymer interpenetration and a limiting form for the interfacial tension. Other studies have also looked at the interfacial structure in semiflexible blends, but they have been limited to study either a wide interface[8] or cases when one of the polymers is completely rigid.[9]

While all these studies showed clear entropic effects that arise from the semiflexibility of the components, the question still remains: How does this entropic effect manifest itself when a copolymer compatibilizer is added to the system? In this work, we use a self-consistent field lattice model with the incorporation of the rotational isomeric state (RIS) scheme to account for chain rigidity to study the compatibilization process for semiflexible polymer blends. We consider the effect of introducing a semiflexible compatibilizer on the interfacial structure of the polymer blend.

Model

The model we used is based on the self-consistent mean-field (SCF) lattice theory developed by Scheutjens and Fleer[10] and later modified by Leermakers and Scheutjens[11] to account for chain stiffness by using the RIS scheme. In RIS-SCF, bond reversal is prohibited, and the rigidity of the chain is controlled by the energy difference, U_g (in units of kT), between the trans and the gauche states. The gauche and trans probabilities, λ^g and λ^t, respectively, can be obtained from U_g with $\lambda^g = 1/[2 + \exp(U_g/kT)]$ and $\lambda^t = 1 - 2\lambda^g$. The persistence length of the chain, q (in units of a, where a is the length of a polymer segment), can be calculated from

$$q = [5\exp(-U_g/kT) + 4)]/[(6\exp(-U_g/kT)] \quad (1)$$

The main difference between the RIS-SCF and the SCF methods is that the process of generating the polymer chain is now a third-order Markov process in contrast to a first-order process. As a result, to account for chain connectivity, the chain end distribution function for a molecule i, $G_i(z,s^{\alpha\beta}|1)$, defined as the weighting factor of finding a segment s with orientation $\alpha\beta$ in layer z

---

[†] State University of New York at Stony Brook.

[‡] Mitsubishi Chemical Research and Innovation Center.

* To whom correspondence should be addressed.

10.1021/ma011661z CCC: $22.00

while the segment 1 may be located anywhere in the lattice, is given by the recursion relationship

$$G_i(z,s^{\alpha\beta}|1) = G_i(z,s^{\alpha\beta})\sum_{\gamma'}\lambda^{\beta''-\alpha''-\gamma''}G_i(z',(s-1)^{\gamma'\alpha'}|1) \quad (2)$$

In this case segment s at site z with the first bond in direction α is connected with segment $s-1$ at site z' with the second bond in direction α'. For a one-dimensional system z' takes values of $z-1$, z, $z+1$. $\lambda^{\alpha''-\beta''-\gamma''} = \lambda^{t}$ if the connection of segment s to $s-1$ forms a trans conformation such that $\alpha'' = \gamma''$ and $\lambda^{\alpha''-\beta''-\gamma''} = \lambda^{g}$ if the connection of segment s to $s-1$ forms a gauche conformation such that $\alpha'' \neq \gamma''$. $G_i(z,s^{\alpha\beta})$, also called the free segment weighting factor, is equal to 0 if $\alpha = \beta$ and is equal to $\exp(-\mu_{ik}(z)/kT)$ otherwise. $\mu_{ik}(z)$ is the mean potential experienced by segment k of molecule i at site z. A similar relationship can be written for the segment weighting factor starting from the other end of the chain. The calculation then proceeds in a manner similar to the SCF model, and we refer the reader to ref 11 for more details.

We have extended this model to study copolymers of various architectures and can implement semiflexibility along specific segments of the polymer. Further, although our model is for semiflexible homopolymers and diblock copolymers, we can easily extend it to study more complicated architectures, such as random copolymers, graft copolymers, combs, etc. All our calculations were performed on a tetrahedral lattice with a lattice size = 300 lattice units. Our calculations were performed in one dimension assuming the random mixing approximation within each lattice layer.

Results and Discussion

In the first set of calculations, as a test of our model, we studied the interfacial tension, γ, and the interfacial width, ξ, of a semiflexible polymer blend as a function of the rigidity and the chain length. The system we chose was similar to one that was used by Morse and Fredrickson. However, to compare our results with theirs, we first need to find the relationship between the wormlike model for the chain that they used and our RIS scheme.

In the wormlike chain model, the polymer chain is given a bending modulus κ, which is related to the persistence length q by $q = \kappa a$, where a is the length of a polymer segment. In the RIS model, the persistence length q is related to the gauche and trans energy difference, U_g, by eq 1. In all our calculations the value of q reported is in units of a, the length of a polymer segment. Using these two equations, we can calculate the bending modulus for our RIS chain and directly compare our results to the findings of Morse and Fredrickson.

In Figure 1 we plot the interfacial tension as a function of the chain length for chains of different persistence length. Note that the interfacial tension calculated in the lattice-based SCF model $\gamma a_s/kT$ (where a_s is the surface area of a lattice site) is equivalent to the expression $\gamma/a\rho kT$ (where a is the polymer segment length and ρ is the density) in the continuum limit. The two expressions have the same numerical value for a fixed χ parameter in the long chain limit. In our calculations we set the rigidity of both components of the blend to be the same. From the figure we can see that as the rigidity is increased the interfacial tension also increases, in agreement with Morse and Fredrickson's work. Further, from Figure 1, we can also see that for a given rigidity, for chain lengths >1200 the interfacial tension saturates. This indicates that the ground-state approximation is valid in the regime of chain lengths >1200. While the limiting interfacial tension we see in our system is smaller than the Morse and Fredrickson model (0.8 as opposed to 1.1), the origin of this limiting interfacial tension, however, is the same. The limiting interfacial tension corresponds to the free energy loss of two rigid chains approaching an impenetrable interface. In our case the lower value is a result of the lattice structure, which manifests itself when the interfacial width is on the order of a lattice size.

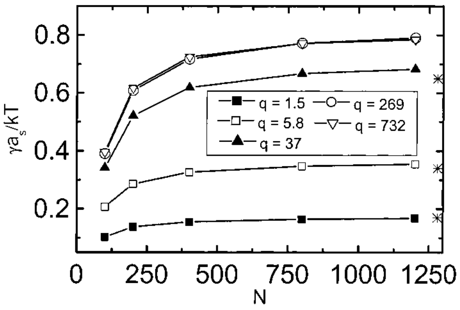

Figure 1. Interfacial tension, γ, as a function of the chain length N and the chain persistence length q. $\chi_{AB} = 0.04$. The stars near the right coordinate indicate the interfacial tension from Morse and Fredrickson.[7] From bottom to top the stars correspond to $q = 1.5$, 5.8, and 14.2, respectively. q is in units of a, the length of a polymer segment.

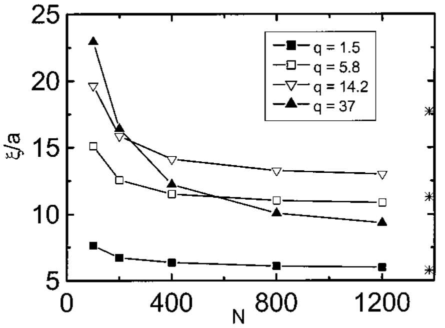

Figure 2. Interfacial width, ξ, as a function of the chain length N and the persistence length q. The width is obtained by fitting the volume fraction profile to a hyperbolic tangential function $\varphi(z) = 0.5(1 + \tanh(2z/\xi))$. The stars indicate values calculated by the equation $\xi = 2a(\kappa/3\chi)^{1/2}$ for $q = 1.5$, 5.8, and 14.2, respectively, from bottom to top. This equation only applies to $\kappa\chi \ll 1$. Therefore it gives a good approximation for the low-rigidity regime. q is in units of a, the length of a polymer segment.

Next we discuss another important parameter, the interfacial width. As shown in Figure 2, an increase of rigidity increases the interfacial width in the low-rigidity regime. The values at $N = 1200$ for $q = 1.5$ and $q = 5.8$ are similar to the values calculated by Morse and Fredrickson. In the limit of low rigidity they derived an expression for the interfacial width (ξ) in terms of the bending modulus and the χ parameter, given as

$$\xi = 2a(\kappa/3\chi)^{1/2} \quad (3)$$

From our calculations we see that significant deviations from the equation start from $q = 14.2$ with $\kappa\chi = 0.85$, as this equation only applies to $\kappa\chi \ll 1$, which is the flexible chain limit, i.e., when the interfacial width, ξ, is large compared to the persistence length of the polymer.

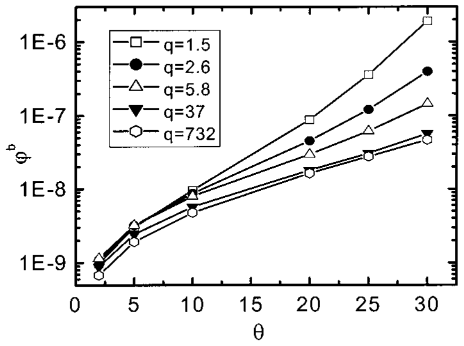

Figure 3. Relationship between the bulk concentration of the copolymer, φ^b, and the amount of the copolymer, θ, in the system. Here a system of A/B/diblock AC is considered. $N_A = N_B = 400$ and $N_{AC} = 200$ with each block length 100. $\chi_{AC} = \chi_{AB} = 0.2$. The A segments are flexible, while B and C are semiflexible. The persistence length of the B homopolymer is fixed at 37. q is the persistence length of the C block.

On the basis of the comparison between our results for long chains and the ground-state approximation results of an analytical SCF theory by Morse and Fredrickson, the validity of our model has been established. We then proceeded to study the effect of introducing a compatibilizer into the polymer blend. Previous studies have shown that the most efficient compatibilizer for an immiscible flexible/flexible A/B polymer blend is an AB diblock copolymer.[2-4] We therefore consider the following system: polymer A is flexible, while polymer B is semiflexible with $U_g(B) = 4$ (corresponding to $q = 37$). Both A and B have a chain length of 400. AC is a diblock copolymer with a chain length of 100 for each block. C is identical to B (i.e., $\chi_{AC} = \chi_{AB}$) except that the rigidity of C can be varied. In flexible/semiflexible polymer blends, the distinct chemical structures of these two types of polymers often result in a high incompatibility, i.e., a high χ_{AB}.[5,6] In our calculations we set $\chi_{AB} = 0.2$. We denote the total amount of copolymer in the system by θ. The excess amount of copolymer at the interface, θ^{ex}, is then calculated by using

$$\theta_i^{ex} = \sum_z (\varphi_i(z) - \varphi_i^b) \tag{4}$$

where $\varphi_i(z)$ is the volume fraction of copolymer at lattice site z, φ_i^b is the bulk concentration of the copolymer, and the sum is over the entire lattice. At $\chi_{AB} = 0.2$ almost all the diblock is localized at the interface, i.e., $\theta \approx \theta^{ex}$.

To study the effect of adding copolymer to the system, we need to define the control variables of the system. Our two choices are either to fix the bulk concentration of copolymer (φ^b) or to fix the total amount of copolymer (θ) in the system. In Figure 3, we plot φ^b as a function of θ, while varying the rigidity of the C block of the AC copolymer. Figure 3 shows that for the same rigidity φ^b increases almost linearly with θ. This indicates that either quantity can be used as our control variable. In this work, however, we want to understand how the interfacial tension changes with rigidity if the excess amount at the interface is the same or similar. For the same bulk concentration of the copolymer since the excess amount of the copolymer could double for different rigidities, this would not allow us to isolate the effect of the amount of copolymer at the interface on the interfacial tension. Moreover, from a computational standpoint, the bulk concentrations in the system can be so low that some numerical instabilities result from the choice of this quantity as a control variable. Consequently, in our results we choose to plot our curves as a function of rather θ than φ^b.

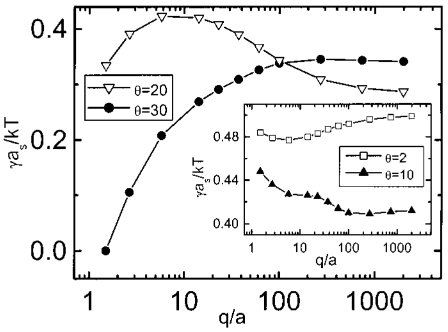

Figure 4. Interfacial tension, γ, as a function of the persistence length, q, of the C block of a diblock copolymer AC for different total amounts of copolymer added (θ). Here a system of A/B/diblock AC is considered. $N_A = N_B = 400$ and $N_{AC} = 200$ with each block length 100. $\chi_{AC} = \chi_{AB} = 0.2$. The A segments are flexible, while B and C are semiflexible. The persistence length of the B homopolymer is fixed at 37. The different curves correspond to different total amounts of the copolymers in the system.

In Figure 4 we plot the interfacial tension, γ, of the system as a function of the rigidity of the C block. From the figure we can see that at low values of θ, as the rigidity of the C block is increased, the interfacial tension passes through a minimum and then increases. With increasing θ, the minimum disappears and then changes to a maximum until finally at high values of θ the interfacial tension monotonically increases as the rigidity of the C block is increased. This behavior implies that, in contrast to compatibilization of flexible blends, the type of compatibilizer that reduces the interfacial tension the most in semiflexible blends depends on the amount of copolymer that you add to the system.

To determine the physical origins of this behavior, we plot the components of the interfacial tension, the excess enthalpy, H^σ, and the negative excess entropy, $-S^\sigma$, as a function of rigidity of the semiflexible diblock in Figure 5. Since $\gamma = H^\sigma - TS^\sigma$, the lower the values of H^σ and $-S^\sigma$, the lower the interfacial tension. From the figure we can see that, except for the highest value of θ, the excess enthalpy shows little change over the range of rigidity studied. Thus, the excess entropy controls the interfacial tension in the system.

To understand the changes in the excess entropy, first consider the situation at very low values of θ. If the C block is very rigid, it is forced to align parallel to the narrow interface which is a low-entropy state. This strong alignment of the diblock also limits the conformation of the semiflexible homopolymer B to a lower entropy state. The net result is a larger entropy loss and a higher interfacial tension. On the other hand, if both blocks are flexible, replacing the homopolymer with a diblock does not change the entropic state of the system. At these low concentrations, the enthalpic gain is low, and consequently the interfacial tension remains relatively unchanged. The interfacial tension is the smallest at an intermediate rigidity when the block C is not rigid enough to affect the conformation of the homopolymers and also not flexible enough that it can pack well with the semiflexible homopolymer B. As we increase the amount of copolymer in the system, however, the interface becomes wider. Consequently, to

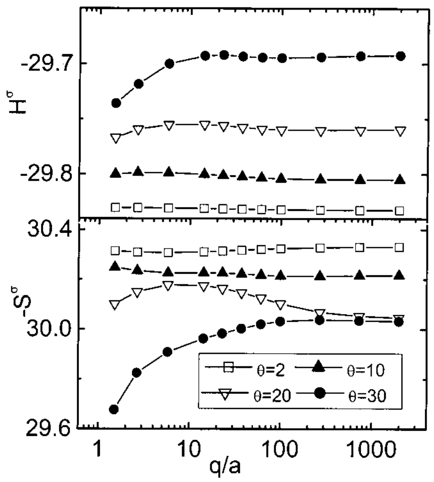

Figure 5. Excess enthalpy, H^σ, and the negative excess entropy, $-S^\sigma$, as a function of the persistence length, q, of the C block of a diblock copolymer AC for different total amounts of copolymer added (θ). Here a system of A/B/diblock AC is considered. $N_A = N_B = 400$ and $N_{AC} = 200$ with each block length 100. $\chi_{AC} = \chi_{AB} = 0.2$. A is a flexible homopolymer, while B is a semiflexible homopolymer with a persistence length = 37 lattice units.

accommodate this increase, chains that have a higher persistence length become more favored, and the minimum in the excess entropy is shifted to higher rigidities of C. As more diblock copolymers are added to the system, the entropic gains that resulted from the rigid chains being present at the interface start diminishing as they become crowded in the interfacial region. At this point a maximum now appears in the excess entropy at some intermediate regime where the effects are most pronounced. This situation worsens as more block copolymers are added to the system. At very high amounts we expect that the diblock copolymer will form a brushlike structure at the interface. In this limit, the homopolymer B will experience a very large entropy loss as the C block becomes more rigid. This results in a monotonic increase in $-S^\sigma$ as a function of the rigidity of the copolymer, and consequently, at higher amounts of copolymer the flexible copolymer reduces the interfacial tension the most.

The effect of packing at the interface suggests that the compatibilization behavior of a diblock copolymer should also be strongly dependent on the width of the interface between the two incompatible polymers. To test this, in the next series of calculations we reduced the interaction parameter to 0.06, a value that results in an interfacial width (in the absence of compatibilizer) that is roughly twice the previous case. The variation of the interfacial tension with the rigidity of the copolymer is shown in Figure 6. As can be seen from the figure, in all cases the flexible diblock is the most effective at reducing the interfacial tension. On the basis of our earlier analysis, this effect can also be explained from an entropic effect as the presence of a wide interface induces more entropic losses in rigid copolymers than for flexible copolymers. Indeed, if we examine $-S^\sigma$ as a function of the rigidity of the C block, it shows a monotonic increase with increasing rigidity. At low values of χ_{AB}, however, not all the copolymer present in the system localizes at the interface. We proceed to examine the amount of copolymer adsorbed at the interface, θ^{ex}, as a function of the rigidity of the C block.

In the inset of Figure 6 we plot the amount of copolymer adsorbed at the interface as a function of the rigidity of the C block of the copolymer. An interesting trend emerges from this plot. The amount of copolymer at the interface increases with an increase of the rigidity of C. In the compatibilization of flexible polymeric systems, the amount of copolymer present at the interface is directly proportional to the amount of reduction in the interfacial tension.[2-4] For semiflexible systems this does not hold true. To understand the discrepancy between the interfacial excess of copolymer and the interfacial tension reduction, it is useful to examine the processes that cause copolymers to localize at the interface. At small amounts of copolymer in the system, the driving force is for the copolymer to minimize the contact between the two homopolymers. As we increase the amount of copolymer in the system, however, the mismatch between the flexibility of the homopolymers and the copolymer starts affecting the system. Studies have shown that even in the absence of any enthalpic interactions, a mismatch in the flexibilities of the polymers can result in segregation between the components.[12,13] It is this effect, we believe, that results in an increase in the amount of the copolymer at the interface. As this excess amount has an unfavorable interaction with the homopolymer, it does not contribute to decreasing the interfacial tension; rather, it increases it. We have confirmed that this effect is present by studying a system in which we use a homopolymer compatibilizer (D) with $\chi_{AD} = \chi_{BD} = 0$. We set the length of D to be $N = 100$. Here too we see that at larger amounts of homopolymer ($\theta = 60$) in the system both the amount adsorbed at the interface and the interfacial tension increase with increasing rigidity of D (Figure 7).

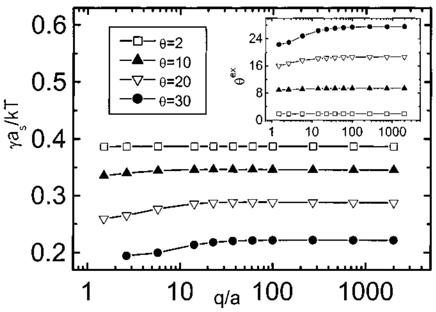

Figure 6. Interfacial tension, γ, as a function of the persistence length, q, of the C block of a diblock copolymer AC for different total amounts of copolymer added (θ). The inset shows the amount of copolymer at the interface, θ^{ex}, as a function of the persistence length, q, of the C block of a diblock copolymer AC for different amounts of copolymer added to the system (θ). Here a system of A/B/diblock AC is considered. $N_A = N_B = 400$ and $N_{AC} = 200$ with each block length 100. $\chi_{AC} = \chi_{AB} = 0.06$. A is a flexible homopolymer, while B is a semiflexible homopolymer with a persistence length = 37 lattice units.

One concern that needs to be addressed here is whether the bulk concentration of the diblock copolymer is above its cmc. The critical micelle concentration (cmc) is a threshold above which the interfacial tension drops very slowly, as the diblock copolymers aggregate to form micelles, instead of segregating to the interface. For a symmetrical semiflexible diblock copolymer studies have shown that the cylindrical micelle is the preferred morphology.[14,15] As a result, the cmc has to be calculated in a two-dimensional model if the semiflexible block in a flexible−semiflexible diblock copolymer is sufficiently rigid. However, for long chains, the two-dimensional SCF model calculation is expensive in terms of both memory and computational time.[16] The diblock copoly-

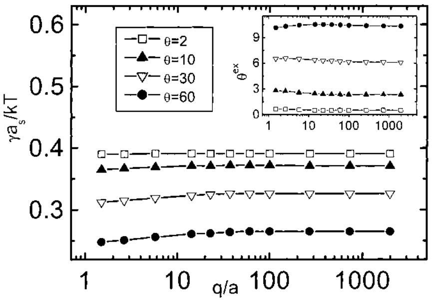

Figure 7. Interfacial tension, γ, as a function of the persistence length, q, of a D homopolymer for different total amounts of D added (θ). The inset shows the amount of D at the interface, θ^{ex}, as a function of the persistence length, q, of D for different amounts of D added to the system (θ). Here a system of A/B/D is considered. $N_A = N_B = 400$ and $N_C = 100$. $\chi_{AB} = 0.06$ and $\chi_{AD} = \chi_{BD} = 0$. A is a flexible homopolymer, while B is a semiflexible homopolymer, with a persistence length = 37 lattice units.

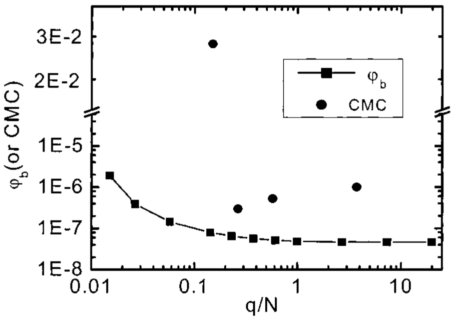

Figure 8. Bulk concentration, φ^b, of the flexible–semiflexible diblock copolymer and its cmc as a function of the ratio between persistence length q and the length N of the semiflexible block. The bulk concentration corresponds to $\theta = 30$ for the diblock in the system. $\chi_{AB} = 0.2$. The cmc of the flexible–semiflexible diblock copolymer is obtained by a two-dimensional RIS-SCF model.

mer in our work here, with a chain length of 100–100, has to be scaled down to a short diblock to perform the two-dimensional calculations.

To perform this scaling down, we have to determine the set of scaled parameters for which the free energy is invariant. The free energy expression for a mixture of a flexible diblock copolymer with a flexible homopolymer is invariant for the same asymmetric factor g (the ratio between the length of the two blocks of a diblock copolymer), χN_c, and N_h/N_c (N_h and N_c are the length of the homopolymer and diblock copolymer, respectively).[17] The free energy expression of a semiflexible polymer, on the other hand, is invariant if both κ/N and χN are kept fixed.[18] As the bending modulus is related to the persistence length q with $q = \kappa a$, it is expected that the cmc is invariant if g, q/N_c, χN_c, and N_h/N_c are kept fixed for a semiflexible copolymer. On the basis of this analysis, the system of a flexible homopolymer A with chain length 400, an AB diblock copolymer with chain length 100–100, and an $\chi_{AB} = 0.2$ can be scaled to a system of a homopolymer A with chain length 40, an AB diblock copolymer with chain length 10–10, and a $\chi_{AB} = 2.0$. In comparing the bulk concentration and cmc as a function of rigidity of the semiflexible block, the abscissa has to be scaled by q/N_c. Here N_c is replaced by the length of the semiflexible block as the other block is always flexible. Our results are shown in Figure 8 for the system with $\chi_{AB} = 0.2$. The cmc corresponds to the bulk concentration of a diblock copolymer in a homopolymer and a diblock copolymer mixture, at which a minimum excess free energy per chain is obtained. It is clear that even the bulk concentrations for the highest amount of diblock copolymer in our work are still far below the cmc. The sharp change of cmc from the first to the second point is due to the different morphology with increasing the rigidity of the semiflexible block. While the lamella was found the stable structure for a diblock copolymer with low rigidity (the first point), a cylinder was the stable structure if the semiflexible block has a higher rigidity (the other three points). As a test, we confirmed that similar cmc values have been obtained in a one-dimensional calculation for the flexible–flexible diblock copolymers using the original (nonscaled) polymer parameters.

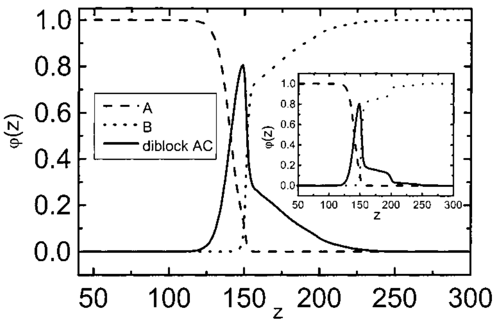

Figure 9. Volume fraction profiles, $\varphi(z)$, from the SCF calculation. The figure shows the volume fraction profiles for the homopolymer A/homopolymer B/diblock copolymer AC system. $N_A = N_B = 400$. The copolymer is of a type A100C100. $\chi_{AB} = \chi_{AC} = 0.2$; $U_g(A) = 0$ ($q = 1.5$), $U_g(B) = 4$ ($q = 37$), and $U_g(C) = 4$. In the inset $U_g(C) = 6$ ($q = 270$). In all these plots the amount of copolymer was fixed at $\theta = 20$.

One more effect that we believe is important to consider in the compatibilization of semiflexible polymer blends is the possibility that the rigidity of the copolymer induces a change in the orientation near the interfacial region, since such orientation effects can have a strong influence on the mechanical properties of the interface. In Figure 9, we plot a typical density profile observed from the calculation of a semiflexible copolymer at the interface of a flexible–semiflexible polymer blend. As can be seen from the figure, a kink is observed in the density profile of semiflexible C block instead of the smooth profile that is normally observed in a flexible–flexible block copolymer at flexible/semiflexible polymer interface. We believe this kink is an indication of the orientation of C block. Our calculations show that this orientation increases with increasing rigidity of the compatibilizer (see inset of Figure 9). We believe that this orientation could induce a cocrystallization of semiflexible components. Recent work by Chaffin et al.[19] suggests that an efficient compatibilizer for a semicrystalline polymer blend not only has to segregate to the polymer interface during melt blending to reduce the interfacial tension and the rate of coalescence, but also has to engage in crystallization during the crystallization process. From our results we see that no one copolymer can satisfy these two requirements, since rigid compatibilizers, which show strong orientation effects, are not the most efficient at reducing the interfacial tension. Consequently, experimental design of such compatibilizers has to balance the reduction of interfacial tension (which favors flexible compatibilizers) with the propensity of the compatibilizer to orient at the interface (which favors more rigid compatibilizers).

Summary

In summary, we have shown that the ability of a flexible–semiflexible diblock copolymer to reduce interfacial tension in a semiflexible polymer blend is a complex function of the rigidity of the semiflexible block and the amount of copolymer at the interface. We note that while our results show that flexible diblock copolymers are usually the most efficient in the reduction of interfacial tension for a flexible/semiflexible polymer blend, they may not be the best candidate if cocrystallization between the compatibilizer and the semiflexible homopolymer is necessary to improve the mechanical strength.[19] Only if the semiflexible block of the diblock is sufficiently rigid can it have the degree of orientation necessary for cocrystallization with the semiflexible homopolymer. Consequently, synthetic design of these copolymers will involve a trade-off between the interfacial tension reduction and the cocrystallization effect.

Acknowledgment. We gratefully acknowledge funding from the Mitsubishi Chemical Corporation. We also thank Drs. Y. Shnidman and David Wu for useful discussions.

References and Notes

(1) Seppala, J.; Heino, M.; Kapanen, C. *J. Appl. Polym. Sci.* **1992**, *44*, 1051.
(2) Shull, K. R.; Kramer, E. J.; Hadziiannou, G.; Tang, W. *Macromolecules* **1990**, *23*, 4780.
(3) Lyatskaya, Y.; Gersappe, D.; Gross, N. A.; Balazs, A. C. *J. Phys. Chem.* **1996**, *100*, 1449.
(4) Russell, T. P.; Menelle, A.; Hamilton, W. A.; Smith, G. S.; Satija, S.; Majkrzak, C. F. *Macromolecules* **1991**, *24*, 5721.
(5) Datta, A.; Baird, D. G. *Polymer* **1995**, *36*, 505.
(6) La Mantia, F. P.; Scaffaro, R.; Magagnini, P. L.; Paci, M. *J. Appl. Polym. Sci.* **2000**, *77*, 3027 and references therein.
(7) Morse, D. C.; Fredrickson, G. H. *Phys. Rev. Lett.* **1994**, *73*, 3235.
(8) Drovetsky, B. Y.; Liu, A. J.; Mak, C. H. *J. Chem. Phys.* **1999**, *111*, 4334.
(9) Fukuda, J. *Eur. Phys. J. B* **1999**, *7*, 573.
(10) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619.
(11) Leermakers, F. A. M.; Scheutjens, J. M. H. M. *J. Chem. Phys.* **1988**, *89*, 3264.
(12) Kumar, S. K.; Yethiraj, A.; Schweizer, K. S.; Leermakers, F. A. M. *J. Chem. Phys.* **1995**, *103*, 10332.
(13) Wu, D. T.; Fredrickson, G. H.; Carton, J. P. *J. Chem. Phys.* **1996**, *104*, 6387.
(14) Williams, D. R. M.; Fredrickson, G. H. *Macromolecules* **1992**, *25*, 3561.
(15) Muller, M.; Schick, M. *Macromolecules* **1996**, *29*, 8900.
(16) Li, W.; Gersappe, D. *Macromolecules* **2001**, *34*, 6783.
(17) Shull, K. R. *Macromolecules* **1993**, *26*, 2346.
(18) Matsen, M. W. *J. Chem. Phys.* **1996**, *104*, 7758.
(19) Chaffin, K. A.; Bates, F. S.; Brant, P.; Brown, G. M. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 108.

MA011661Z