

Phase Behavior and Interfacial Properties of Diblock Copolymer-Homopolymer Ternary Mixtures: Influence of Volume Fraction of Copolymers and Interaction Energy*

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Abstract We use a Monte Carlo method to study the phase and interfacial behaviors of A-*b*-B diblocks in a blend of homopolymers, A and B, which are confined between two asymmetric hard and impenetrable walls. Our results show that, when the interaction strength is weak, the block copolymers are uniformly distributed in the ternary mixtures under considered concentrations. Under strong interaction strength, distribution region of the block copolymers changes from a single smooth interface to a curved interface or multi-layer interface in the ternary mixtures. Furthermore, our findings show that with increasing volume fraction of A-*b*-B diblock copolymer (ϕ_C), copolymer profiles broaden while $\phi_C \geq 0.4$, a lamellar phase is formed and by further increasing ϕ_C , more thinner layers are observed. Moreover, the results show that, with the increase of ϕ_C , the phase interface first gradually transforms from plane to a curved surface rather than micelle or lamellar phase while with the increase of the interaction between A and B segments (ϵ_{AB}), the copolymer chains not only get stretched in the direction perpendicular to the interface, but also are oriented. The simulations also reveal that the difference between symmetric and asymmetric copolymers is negligible in statistics if the lengths of two blocks are comparable.

Keywords Ternary mixtures; Phase behavior; Interfacial property; Copolymer compatibilizers; Monte Carlo simulation

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INTRODUCTION

Compared with synthesizing new polymers, it is an economical and convenient route to create high performance materials by simply blending existing polymers with desired properties to form mixtures^[1–3]. However, a common drawback in fabricating multicomponent blends is that most of the polymer mixtures are immiscible because of the negligible entropy contribution to the free energy of mixing^[3, 4] and thus, the components phase separate into distinct, macroscopic domains, resulting in relatively poor mechanical properties^[5]. To enhance the structural integrity and mechanical properties, copolymers are often added as polymeric surfactants, which preferentially localize at the interface between immiscible polymers, lower the interfacial tension, disperse the incompatible polymers into smaller domains, and improve the interfacial mechanical strength of polymer blends^[6–10].

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The phase behavior and interfacial properties of homopolymer/copolymer/homopolymer (A/A-*b*-B/B) ternary mixtures are controlled by many parameters, including monomer-monomer interaction energies, the volume fraction of copolymers, chain lengths, and copolymer architectures. Therefore, the parameter space of the mixtures is extremely large. In the past decades, the phase behavior and interfacial properties of these mixtures have been extensively investigated^[1–3, 6–10]. The inhomogeneous self-consistent mean-field theory (SCFT) developed by Noolandi and Hong^[11, 12] provides some insights of the free energy of the block copolymers at the interface, providing a qualitative prediction of the copolymer excess at the interface. For instance, the interfacial tension decreases to zero at a smaller copolymer volume fraction when shorter homopolymers are employed in the mixtures. Later, Leibler^[13] provided a basic understanding of the copolymer segregation at the interface. Israels *et al.*^[14] also applied self-consistent field calculations to study the interfacial behavior of block copolymers based on the explicit consideration of the formation of micellar or multilamellar phases. It is worth mentioning that SCFT was commonly used to generate phase diagrams for copolymer-homopolymers blends^[15–17], but the mean-field approximation ignored fluctuation effects. Some extensions have been made to include the fluctuations into SCFT^[18, 19], however, these extensions have not been implemented in the context of lamellar swelling induced by adding homopolymers. Nevertheless, numerous experimental studies have indicated that the addition of homopolymers to a block copolymer melt swells and stabilizes the lamellae^[20–24].

Besides, computer simulation methods have been proved to be a valuable tool to elucidate the microscopic structure of interfaces of these ternary mixtures. Using Monte Carlo (MC) simulations, Balazs *et al.*^[25] investigated the behavior of a single multiblock AB copolymer near the penetrable interface between two immiscible fluids A and B. Wang and Mattice^[26] and Wang *et al.*^[27] applied the Monte Carlo simulation to symmetric and asymmetric diblock copolymers at the narrow interface between the two monometric homopolymers. Schmid and Müller^[28], Werner *et al.*^[29] and Müller *et al.*^[30] found that the interfacial width increases with copolymer concentration at small and modest segregation strengths while the increase becomes trivial at strong segregation limit, based on which a phase diagram was constructed^[30]. From the simulation data, a 3-phase region was sketched, in which two phases, each one mainly composed of a single type of homopolymer, coexisted with a copolymer-rich phase. The latter phase is apparent in the form of a microemulsion. At lower temperatures, the microemulsion becomes an ordered lamellar structure. By employing dissipative particle dynamics (DPD) simulations, Qian *et al.*^[31] and Bai and Guo^[5] systematically investigated the interfacial properties and their relevance to the phase transitions in the ternary mixtures. These previous theoretical and computational studies provided valuable guidance for the design and optimization of ternary polymer blends. However, the effects of the parameters such as the volume fraction of copolymers and the interaction energies between unlike segments on the interfacial structure and property remain unclear.

It is well-known that, at very low interaction energy between unlike segments, the mixture is in a disordered state (denoted by D); at the opposite interaction energy limit, a macrophase-separated phase (2P) and a lamellar phase (L) could form on the homopolymer-rich side and on the copolymer-rich side, respectively; between the 2P and L phases, a bicontinuous microemulsion phase (B μ E) could be formed under appropriate conditions^[32, 33]. Moreover, for a small amount of added copolymers, the interfacial tension is reduced, the interface is taken to be saturated by copolymers and the associated interfacial area occupied by each copolymer chain. When the volume fraction of copolymers in the mixture increases, dispersion size shrinks to tens of nanometers and becomes thermodynamically stable. In this case, the microemulsion can form^[34], which can become a template to structure the mixtures. The homopolymers would serve as interpenetrated elastomers and tunable porous membranes^[33] or as templates for nanoporous materials^[35, 36]. To date, most of the works on this topic have focused on understanding and exploiting the polymeric bicontinuous microemulsion (B μ E) morphology and characterizing the critical behavior on the homopolymerrich side of the B μ E channel^[5]. Although the interfacial properties of polymer mixtures depend significantly on the interfacial structures, the direct measurement of interfacial structure, for instance, the determination of the concentration profile of each component at the interface is not always possible. A few groups have attempted to experimentally measure the concentration profile at the interface using forward recoil spectrometry^[37, 38] or neutron reflectivity^[38, 39] *via* the deuteration of one or more

components comprising the polymer blends. Computer simulations can provide valuable microscopic insights into the interfacial behaviors, but to the best of our knowledge, the relationships between the molecular conformations of copolymers and the interfacial tension or interfacial thickness are also rarely investigated in previous theoretical and simulation studies under the conditions of different volume fractions of copolymers and interaction energy. However, such an investigation is necessary and helpful for our understanding of the interfacial efficiency of copolymers and can offer useful insight into the applications of real polymer mixtures.

The aim of the present work is twofold. On the one hand, we use coarse grained MC simulation technique based on a simple lattice model developed by Shaffer^[40] to describe phase behavior of diblock copolymer homopolymer ternary mixtures in a thin film. We expect to validate the results calculated by SCFT and specify the conditions for the formation of different phases in more detail, as well as the corresponding molecular chain conformation of diblock copolymers at the interface. On the other hand, we investigate the effects of the volume fraction, the interaction energy between unlike segments, and chain asymmetry of copolymers on the phase morphology, component density distribution, interface width, and interface energy.

The rest of this paper is organized as follows. In the part “simulation method and model”, we describe the details of the simulation method and the model used in this work. The calculated thermodynamic quantities characterizing the system are also shown within this part. Results and discussion are presented in the part “results and discussion”, where we focus on the following five aspects: (1) phase morphology and concentration profile of each component; (2) the interfacial thickness; (3) the interfacial fluctuations and tension; (4) the molecular conformations of copolymers, including stretching and orientation; (5) the effects of the asymmetry of diblock copolymers. In the part “summary” we provide some concluding remarks.

SIMULATION METHOD AND MODEL

The lattice-based MC simulations combined with bond fluctuation model are performed^[40, 41]. The details of the algorithm can be found elsewhere^[40]. In brief, polymer segments are placed on a simple cubic lattice, where excluded volume interactions are implemented by allowing only a single segment to occupy one lattice site simultaneously. Segments are connected by bonds of variable length $1, \sqrt{2}, \sqrt{3}$ in units of lattice spacing. Elementary movement is achieved by randomly moving a segment to one of the six closest neighboring sites. Since MC simulation employs only local moves of single segment, Rouse dynamics is reproduced for any isolated chain^[42]. The MC simulation time can be mapped directly onto a physical time scale. Because of the geometry of the cubic lattice, chain uncrossability can simply be switched “on” and “off” by forbidding the intersection of the midpoints of the bonds. In this work, in order to accelerate relaxation of chain conformations, the polymer chains are allowed to cross through each other freely. Although this unphysical movement can alter the chain topology, the static properties of crossing and non-crossing chains are indistinguishable from each other^[40]. Therefore, this method is nonetheless appropriate because we are mainly interested in the interfacial properties at a thermodynamical equilibrium state rather than segregation kinetics of the block copolymers.

The systems examined in this study are ternary mixtures of A and B homopolymers and A-*b*-B diblock copolymers. In general, the chain lengths of the two homopolymers are identical $N_A = N_B = 50$. These homopolymers are filled into the simulation box with equal volume fraction $\phi_A = \phi_B = 1/2(1 - \phi_C)$, where subscript C denotes A-*b*-B copolymer. The total segment density is set to 0.5, so that the system could be considered as bulk^[40]. In order to describe the interactions between different types of segments, we adopt the model proposed by Shaffer^[40] to include repulsions. For simplicity, only the interaction between A and B segments (ϵ_{AB}) within a distance of no less than $\sqrt{3}$ lattice constant is considered. Here, a positive value of ϵ_{AB} corresponds to a repulsive interaction. Thus, interaction energy is set as follows: $\epsilon_{AB} = \epsilon k_B T > 0$ and $\epsilon_{AA} = \epsilon_{BB} = 0$. With this choice of the interaction energies, the system can be characterized by a single interaction parameter ϵ . In order to enforce a well-defined interface between an A-rich and a B-rich phase, we place the system in a thick film of thickness D confined between two asymmetric walls which respectively favor A or B type segments. The two walls are treated as hard and impenetrable surfaces. The repulsive potentials are chosen by $\mu_w = \epsilon k_B T$ so that each component wets its corresponding wall. As a result, the interface is located averagely in the middle of the

film. Every attempted move must satisfy both the excluded volume requirement and the bond length restriction. The conformational sampling is governed by the Metropolis *et al.*^[43] rule. The updated conformation is accepted with a probability of $p = \exp(-\Delta E/k_B T)$, where $\Delta E = (N_{AB}^a - N_{AB}^b)\varepsilon_{AB}$ defines the energy change, N_{AB}^a and N_{AB}^b respectively are the numbers of the nearest-neighboring pair of sites taken by the pair of segments after and before the trial move.

In this work, both the symmetric and asymmetric block copolymers are used to examine the effect of chain structure on the interfacial properties. For symmetric chains, the length of A block, N_C^A , is equal to that of B block, N_C^B , i.e., $N_C^A = N_C^B = 25$. For asymmetric chains, $N_C^A = 30$ and $N_C^B = 20$. The segregation strength ε varies from 0.01 to 0.2. The volume fraction of block copolymers ϕ_C varies from 5% to 80%. Periodic boundary conditions are applied on X- and Y- directions to minimize finite size effect. Specifically, we use $L_X = L_Y = 60$ and $D = 60$, which ensures that the film is thick enough so that the interfacial properties are not affected by the impenetrable walls^[44]. All simulations are initiated by equilibrating the systems in a thermal limit. Once the initial configurations are generated, the systems are then sufficiently equilibrated for 2×10^6 Monte Carlo steps (MCS) at a given interaction energy. Note that one MCS is defined as $N \times N_p$ attempted moves. The equilibration period of simulations is much longer than 10τ , where τ defines the longest relaxation time associated with the decay of the end-to-end vector autocorrelation function, which guarantees the results are independent on initial configurations. Thereafter, configurations are stored every 10^4 MCS for further analysis. Totally, 200 configurations are collected. Five parallel runs are carried out to minimize statistical errors. Furthermore, due to size effect, it is always challenging to obtain quantitatively reliable measurement of interfacial properties. To evaluate this effect, we implemented additional simulations in a larger simulation box of $L_X = L_Y = 120$, $D = 60$ with energy strength $\varepsilon = 0.1$. Our model system does not show any significant finite size effect on the phase behaviors and interfacial properties. Accordingly, we are sure that our results are not an artifact of the finite size effect, but of general relevance for real ternary blend systems.

The interfacial composition is driven by two independent combinations of the chemical potentials^[45],

$$\Delta\mu = \mu_A - \mu_B \quad (1)$$

$$\delta\mu = \mu_C - \frac{1}{2}(\mu_A + \mu_B) \quad (2)$$

where μ_A , μ_B , and μ_C are the chemical potential of the homopolymer A, homopolymer B, and copolymer C. Two phase coexistence between an A rich and a B rich phase was found at $\Delta\mu = 0$. $\Delta\mu$ determines the volume fraction of copolymers. In the following, we examine the interfacial thickness, the interfacial fluctuations and tension, as well as the copolymer conformations varying the copolymer concentrations.

The thickness of a wedge shaped profile is employed to measure the overlap between the phases^[46]:

$$H_{ABC} = \sum_{z=1}^D [\phi_A(z)\phi_B(z) + \phi_A(z)\phi_C(z) + \phi_B(z)\phi_C(z)] \quad (3)$$

where $\phi_A(z)$, $\phi_B(z)$, and $\phi_C(z)$ are the volume fractions of homopolymers A and B, and A-b-B diblock copolymer. The measurement of H_{ABC} is useful to understanding the mixture interface.

The interfacial tension γ of a system at temperature T can be determined from knowledge of the coexistence properties $\mu(T)$, $p(T)$ and the Helmholtz free-energy of the system $F(T)$. γ can be written as^[47]:

$$\gamma = \frac{F + pV - \mu N}{S_{\text{box}}} \quad (4)$$

where p , V , μ correspond to the pressure, volume, and chemical potential, respectively. N is the number of molecules, while S_{box} represents the interfacial area of the system. If the interfacial monolayer is not highly curved, γ can also be estimated from the spectral intensities of undulating modes. Height fluctuations $h(x, y)$ of the monolayer can be formulated in terms of wavelength dependent undulation modes *via* a Fourier transform.

Here, $h(x, y)$ is defined as the displacement of the midpoint of each copolymer chain $z(x, y)$ from the central plane of the interface. According to the equipartition theorem, for small wave vectors $\mathbf{q}$, both the interfacial tension γ and the bending modulus k can be related to these undulation modes^[5, 48, 49].

$$\langle |H(\mathbf{q})|^2 \rangle = \frac{k_B T (\gamma \mathbf{q}^2 + k \mathbf{q}^4)^{-1}}{S_{\text{box}}} \quad (5)$$

here $H(\mathbf{q})$ is the Fourier component of $h(x, y)$. From simulations, one can compute the spectral intensities of undulatory modes by $S(\mathbf{q}) = \langle |H(\mathbf{q})|^2 \rangle S_{\text{box}}$. Therefore, the interfacial tension γ can be evaluated by fitting the plot $1/[q^2 S(\mathbf{q})] \sim q^{-2}$ ^[50, 51]. In this work, we do not give any concerns of the magnitude of γ , so we use another simple method to calculate the amount of interfacial height fluctuations, the mean squared distance $\langle \Delta R_c^2 \rangle$ between the centers of mass of copolymers and the central plane. At the same time, we also calculated the mean inter-facial energy W_{AB} of the segments in the central two planes. When ϕ_c is not too large, these two physical quantities can well reflect the interfacial tension γ .

To investigate the conformational information of the copolymers at interface, we now take a closer look at the stretching and orientation parameters of the copolymer chains. As for the copolymer stretching, two variables are monitored. First, the mean squared end-to-end distance is employed, which is defined as:

$$\langle R_e^2 \rangle = \frac{1}{N_C} \sum_{i=1}^{N_C} (\mathbf{r}_N^i - \mathbf{r}_1^i)^2 \quad (6)$$

where N_C is the number of copolymers enriched at interface. $\mathbf{r}_N^i$ and $\mathbf{r}_1^i$ are the Cartesian coordinates of the chain ends of i -th copolymer. Second, the radius of gyration is computed as follows:

$$\langle R_g^2 \rangle = \frac{1}{NN_C} \sum_{j=1}^{N_C} \sum_{i=1}^N (\mathbf{r}_j^i - \mathbf{R}_{\text{C.M.}}^i)^2 \quad (7)$$

where $\mathbf{R}_{\text{C.M.}}^i$ is the coordinate of center of mass of the i -th copolymer.

To acquire information of the copolymer orientation, two quantities are also collected. One is the chain orientation parameter which characterizes the difference of the normal and the transversal components of the dimension of the block copolymer molecules^[31] and can be written as:

$$\lambda_{\text{or}} = \frac{\langle R_{gz}^2 \rangle - 0.5(\langle R_{gx}^2 \rangle + \langle R_{gy}^2 \rangle)}{\langle R_g^2 \rangle} \quad (8)$$

where $\langle R_{gx}^2 \rangle$, $\langle R_{gy}^2 \rangle$, and $\langle R_{gz}^2 \rangle$ are the x , y , and z component of $\langle R_g^2 \rangle$, respectively. The other parameter we recorded is the mean projection distance between the two centers of mass in Z direction,

$$\langle L_{ABZ} \rangle = \left[\frac{1}{N_C} \sum_{i=1}^{N_C} (R_{ZA}^i - R_{ZB}^i)^2 \right]^{\frac{1}{2}} \quad (9)$$

where R_{ZA}^i and R_{ZB}^i are the coordinates of center of mass of the block A and B of the i -th copolymer on Z direction.

RESULTS AND DISCUSSION

Phase Morphology and Concentration Profiles

Although the phase behavior and interfacial properties of diblock copolymer-homopolymer ternary mixtures have been considered theoretically from various aspects, the mechanism of how the volume fraction of copolymers and interaction energy influence the phase behavior and interfacial properties is still unclear. Thus, it has been desirable to make contribution with Monte Carlo simulations for a better understanding of this problem.

Various phases are identified by snapshots. We begin our discussion for the region from $\phi_C = 0.05$ to $\phi_C = 0.8$ under the condition of relatively high interaction energy $\varepsilon_{AB} = 0.1$, typical morphologies observed in simulations are shown in Fig. 1. At low ϕ_C , two types of incompatible homopolymers separated as expected, forming an interface (Fig. 1a2) populated with copolymers, which is driven by enthalpy. In other words, this is corresponding to separated phase. Upon increasing ϕ_C , the central region of the film cannot accommodate these copolymer chains, which induces a curved lamella (Fig. 1d2) or micelles (Fig. 1g2) in homopolymer phase. In the end, copolymers weave across the system and form lamellar phase. However, when the interaction energy is very small ($\varepsilon_{AB} = 0.01$), the block copolymer is uniformly distributed in the ternary mixtures under considered concentrations. For other ε_{AB} , a similar trend of the morphology evolution is observed with different concentration threshold. Furthermore, we find the higher ε_{AB} , the smoother the phase interface, and with the increase of ϕ_C , the system is more willing to form a curved interface, rather than the formation of micelles. More details can be found in supporting information (see Figs. S1–S7 in supporting information, SI).

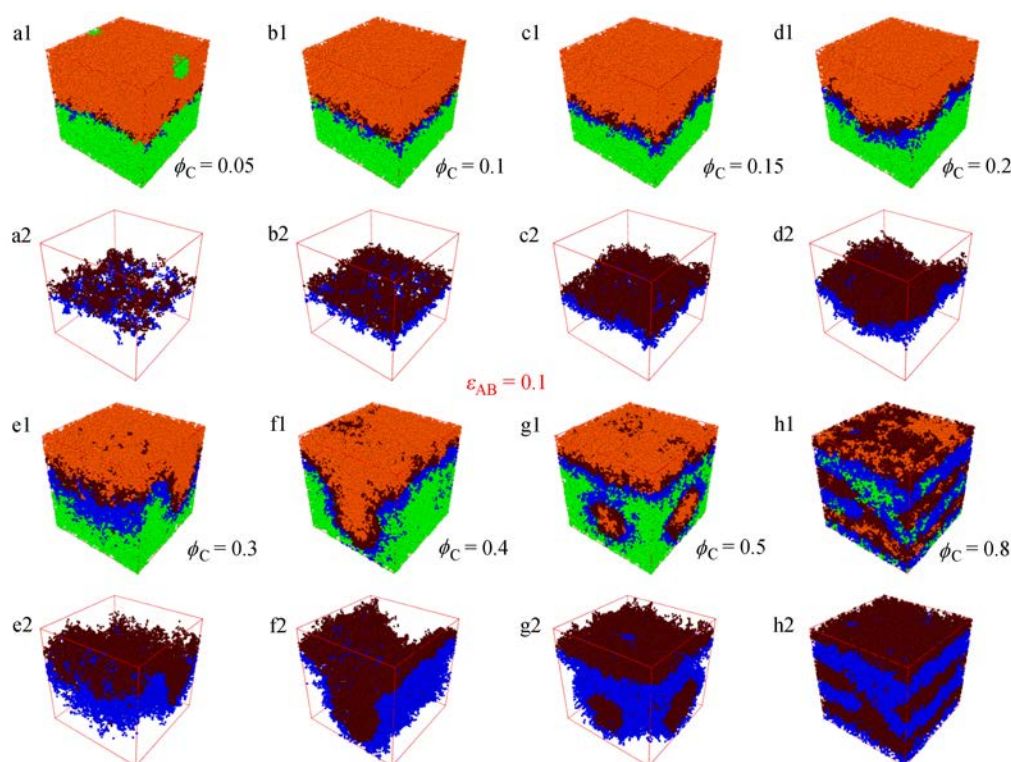


Fig. 1 Simulation snapshots of the system (a1–h1) and diblock polymers (a2–h2) after equilibrium

Here, the interaction energy $\varepsilon_{AB} = 0.1$. From left to right and from top to bottom, the copolymer concentration ϕ_C are 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, and 0.8, respectively. Homopolymers A and B are shown in green and orange colors while blocks A and B are shown in blue and brown, respectively.

Because many physical properties of a blend are related to the segmental distributions, we plot the segment density profiles when the interaction energy $\varepsilon_{AB} = 0.1$ in Fig. 2. At low ϕ_C , most copolymers merely localize within the interface and each block penetrates into its corresponding phase, thereby stabilizing the interface. This three-phase coexistence is in agreement with the SCFT^[52, 53]. With increasing ϕ_C , copolymer profiles broaden, because more copolymers populate at the interface to lower the free energy. When $\phi_C \geq 0.4$, copolymer profiles show periodic fluctuation along Z direction, indicating the formation of a lamellar phase. Further increasing ϕ_C , the number of layers augments whereas the thickness of layers shrinks. This variation of density profile shown in Fig. 2 is consistent with the morphologies displayed in Fig. 1. This consistency is also observed for other ε_{AB} , which could also be found in supporting information (see Figs. S8–S12 in SI). Combining Fig. 1 and Fig. 2, it

can be concluded that there is a transition from the separated phase to lamellar phase by gradually adding copolymer in the system. Meanwhile, the interaction energy determines phase boundary. Additionally, this transition is in accordance with the density profiles of the two blocks of copolymer about Fig. 2 (see Fig. S13 in SI).

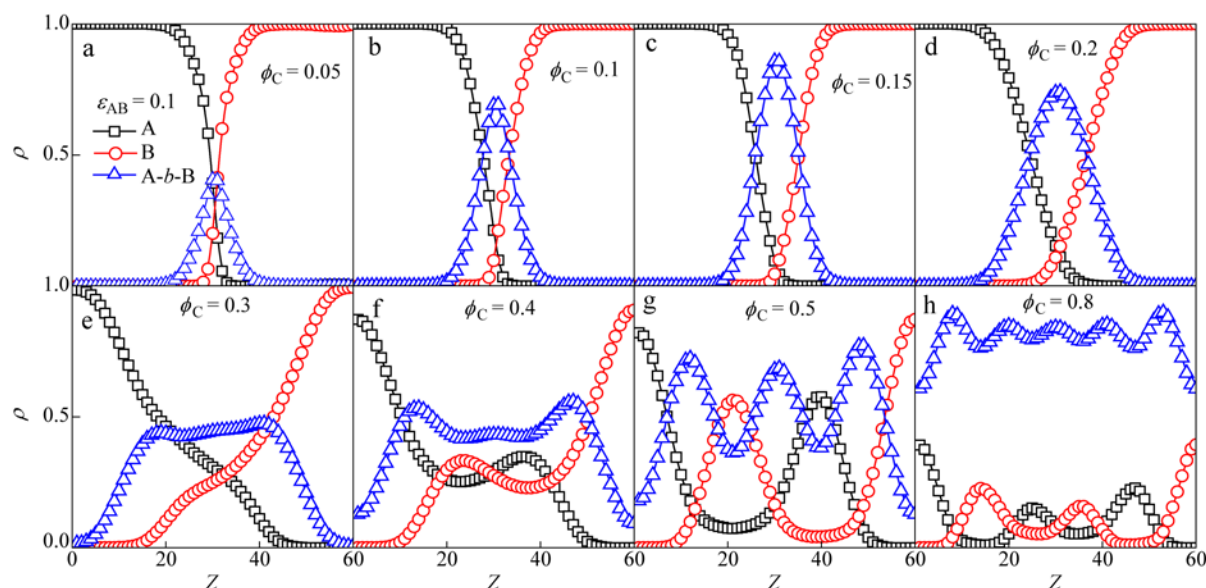


Fig. 2 Segmental density profiles of homopolymer and diblock polymers

Here, the interaction energy $\varepsilon_{AB} = 0.1$. From left to right and from top to bottom, the copolymer concentration ϕ_C are (a) 0.05, (b) 0.1, (c) 0.15, (d) 0.2, (e) 0.3, (f) 0.4, (g) 0.5 and (h) 0.8, respectively. Homopolymers A and B are shown in black square and red circle symbols while diblock polymers A-b-B are shown in blue triangles, respectively.

Interfacial Thickness

We utilize Eq. (3) to calculate the interfacial width and the results are presented in Fig. 3. When ε_{AB} is lower enough, chain segments can not distinguish each other, suggesting that there is no significant energy barrier to mix distinct species. Thus, a wider interfacial region is favorable because the distribution of copolymer segments is uniform in film. At fixed ε_{AB} , H_{ABC} shows a peak as ϕ_C increases, which might be caused by two reasons. First, as shown in Fig. 2, block copolymers concentrate as ϕ_C increases, broadening the interfacial area. The other reason is implicitly involved in Eq. (3) because the phase interface becomes curved when $\phi_C > 0.3$ as shown in Fig. 1. When ϕ_C is fixed, strong interaction ε_{AB} drives the copolymers to occupy the central interface in order to shield the interfacial tension, resulting in decrease of H_{ABC} , which is also in agreement with the above results that the higher ε_{AB} , the smoother the phase interface. It should be noted that this result is valid only for $\phi_C \leq 0.3$, *i.e.* separated phase.

Interfacial Fluctuations and Tension

To confirm the above physical picture, we calculate the mean squared distance $\langle \Delta R_c^2 \rangle$ between the centers of mass of copolymers and the central plane as shown in Fig. 4. At very low ε_{AB} , the copolymers are able to locate far from the central interface because of the low energy barrier. At high ε_{AB} and low ϕ_C , $\langle \Delta R_c^2 \rangle$ is close to zero, because the middle segments concentrate at the interface, which is located in the central plane. With fixed ε_{AB} , it is found that $\langle \Delta R_c^2 \rangle$ increases with the increase of ϕ_C , indicating that phase interface gradually transforms from plane to a curved surface, and the micelle or lamellar phase is present in the system. With fixed ϕ_C , strong interaction results in a plateau with narrow interfacial width. It has to be pointed out that this result holds for separated phase. Figure 5 shows the mean interface energy W_{AB} of the segments in the central two planes. As we expected, the variation of W_{AB} is consistent with $\langle \Delta R_c^2 \rangle$ as displayed in Fig. 4. When ϕ_C is very small, W_{AB}

increases as ϕ_C increases. When ϕ_C reaches a critical value, W_{AB} suddenly drops to a lower value, indicating that the phase interface becomes curved when ϕ_C is larger than this critical value.

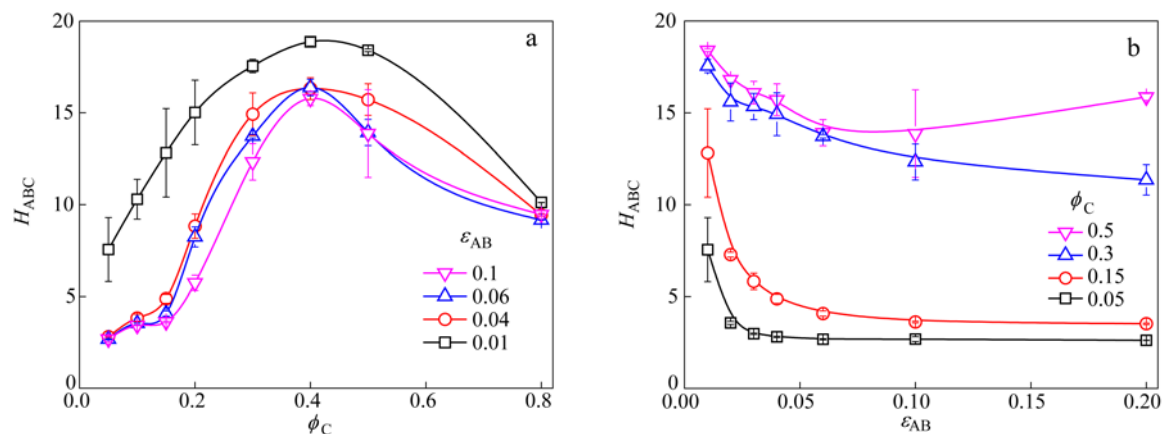


Fig. 3 Interfacial thickness H_{ABC} shown as a function of ϕ_C at different ϵ_{AB} (a) and a function of ϵ_{AB} at different ϕ_C (b). Error bars correspond to 95% confidence intervals for each point.

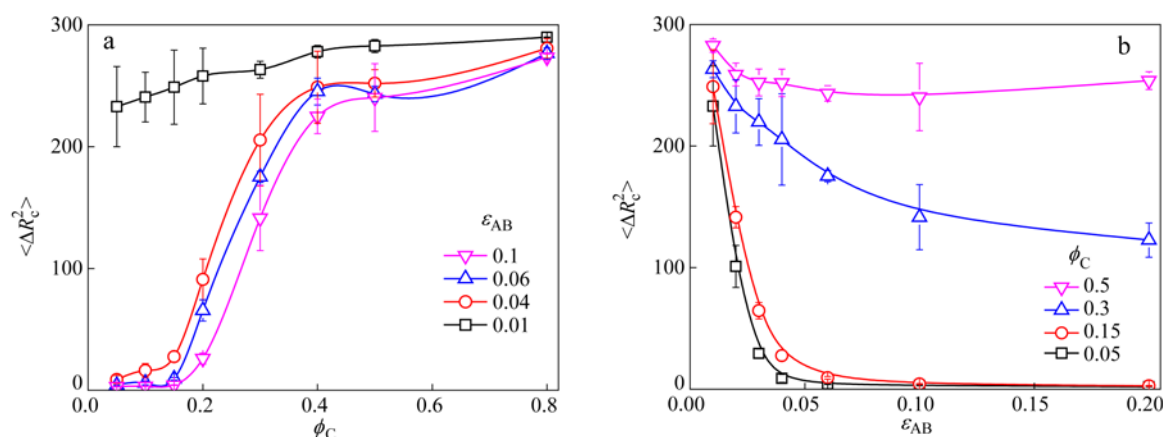


Fig. 4 Mean squared deviated distance $\langle \Delta R_c^2 \rangle$ as a function of ϕ_C at different ϵ_{AB} (a), and as a function of ϵ_{AB} at different ϕ_C (b). Error bars correspond to 95% confidence intervals for each point.

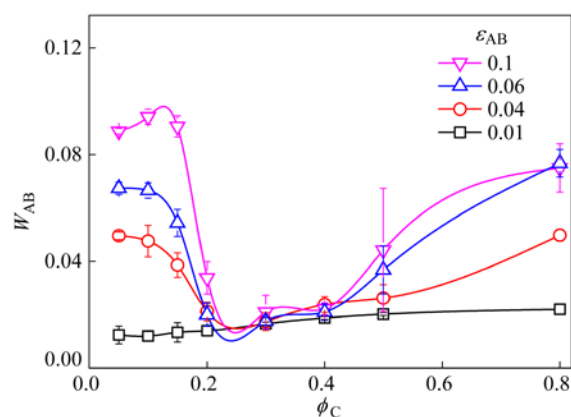


Fig. 5 Mean interface energy W_{AB} of the segments in the central two planes as a function of ϕ_C at different ϵ_{AB} . Error bars correspond to 95% confidence intervals for each point.

Molecular Conformations of Copolymers

An ideal copolymer compatibilizer is the one that maximizes the contact area with homopolymers. Although it is difficult to be quantified directly, an alternative way is to evaluate the size and orientation of the copolymer. Figure 6 depicts the dependence of the dimension of copolymers on ϕ_C and ε_{AB} . Generally, $\langle R_g^2 \rangle$ shows quite similar trend with $\langle R_e^2 \rangle$ so that the interpretation can be made in the same manner. At very low ε_{AB} , copolymer behaves as a homopolymer, thus $\langle R_g^2 \rangle$ is nearly constant when varying ϕ_C . When fixing ε_{AB} , $\langle R_g^2 \rangle$ expands by adding copolymer at first, suggesting that copolymers penetrate deeper into the homopolymer phase. By further increasing ϕ_C , $\langle R_g^2 \rangle$ decreases because of the formation of lamellar phase. With fixed ϕ_C , it is clear that $\langle R_g^2 \rangle$ increases with the increase of interaction energy, implying that the copolymers are stretched by homopolymer chains. Our results are in qualitative agreement with the experimental findings of Shull *et al.*^[54] At the same time, we note that the half-width of the curves corresponding the copolymers in Fig. 2, namely, the thickness of the interface layer, is far broader than $\langle R_g^2 \rangle$. Hence they are not strongly confined to the interface as assumed by the Leibler theory^[13, 55]. That might be the reason that the SCFT usually underestimates the interfacial width and also leads to quantitative discrepancies in the distribution of copolymer segments.

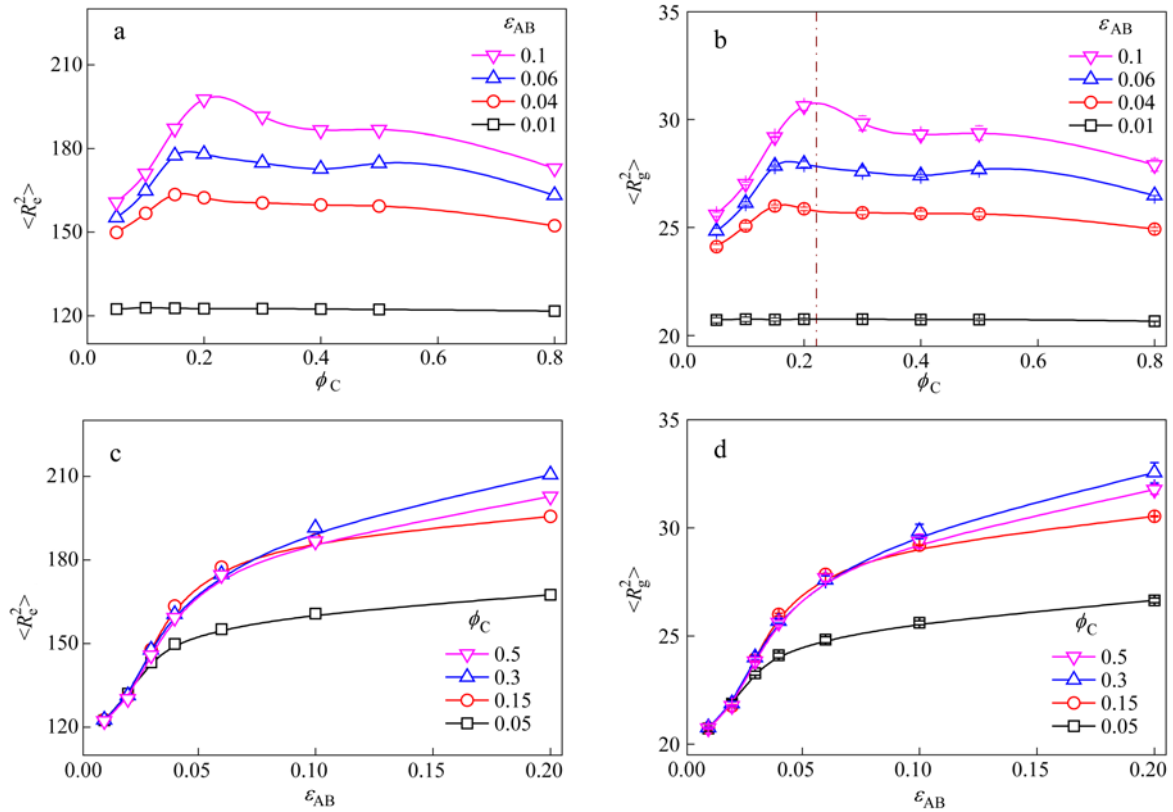


Fig. 6 (a) Mean squared end-to-end distance $\langle R_e^2 \rangle$ and (b) mean squared radius of gyration $\langle R_g^2 \rangle$ of diblock polymers as a function of ϕ_C at different ε_{AB} ; (c) $\langle R_e^2 \rangle$ and (d) $\langle R_g^2 \rangle$ of diblock polymers as a function of ε_{AB} at different ϕ_C . Error bars correspond to 95% confidence intervals for each point.

Next we discuss the orientational properties of the polymers. Figure 7 shows the dependence of the orientation of copolymer on ϕ_C and ε_{AB} . At very low ε_{AB} , λ_{or} and $\langle L_{ABZ} \rangle$ are nearly zero, reflecting that the copolymers are isotropically distributed within the film. Combining first peak in Fig. 7(a) and the peak in

Fig. 6(a), it can be concluded that the copolymers are stretched further by adding some copolymer, which enlarges the contact area. The anisotropy (Fig. 7b) increases as the interaction energy strengthens at four selected ϕ_C , revealing that homopolymer phase favors the corresponding copolymer block. Here the orientation of the polymer chains involves two different factors. First, chains may be oriented without volume changes; that is, the $\langle R_g^2 \rangle$ or $\langle R_e^2 \rangle$ remains unaffected by the orientation. Second, chains may get compressed or stretched in one direction. As Fig. 6 illustrates, the latter effect dominates for the system were tested.

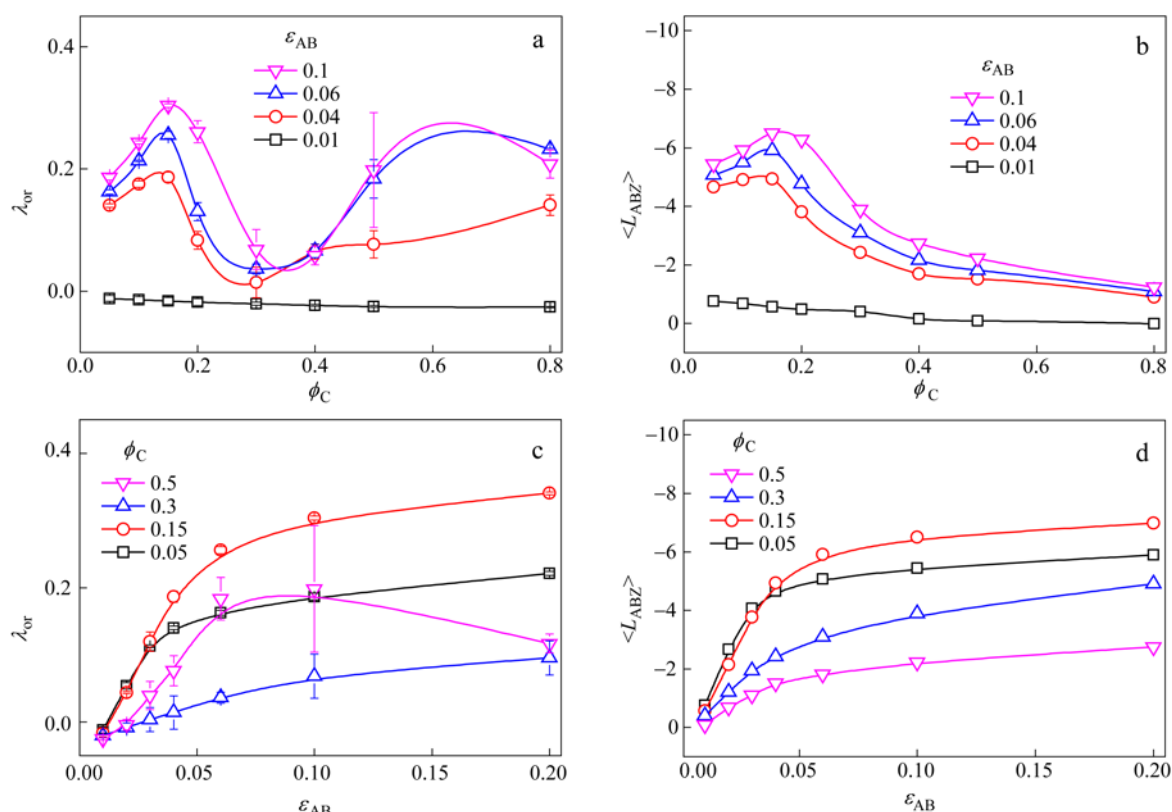


Fig. 7 (a) Orientation parameter λ_{or} and (b) mean projection distance $\langle L_{ABZ} \rangle$ of diblock polymers as a function of ϕ_C at different ε_{AB} ; (c) λ_{or} and (d) $\langle L_{ABZ} \rangle$ of diblock polymers as a function of ε_{AB} at different ϕ_C . Error bars correspond to 95% confidence intervals for each point.

Effects of the Asymmetry of Diblock Copolymers

It is inevitable to yield asymmetric copolymer in practical synthesis of polymers. Thus, the effect of asymmetry of compatibilizers has to be considered. However, systemic investigation of asymmetric copolymer is beyond the scope of this work. A specified case of copolymer is examined to clarify the general role of asymmetry in phase separation. Figure 8 compares the density profiles of symmetric and asymmetric copolymer at four distinct ϕ_C . The difference between two kinds of copolymers is trivial at low ϕ_C , whereas some asymmetric copolymers prefer to distribute in A phase at high ϕ_C . In the former case, all copolymers can be adsorbed within the interface, corresponding to separated phase strictly. However, in the latter case, because some copolymers are away from the interface, the interface bends towards A phase, or forces copolymer to form micelles in A phase, leading to an asymmetric profile. Obviously, there is little difference between two kinds of copolymers at low ε_{AB} (see Fig. S14 in SI). Furthermore, we find that the symmetric copolymer penetrates deeper into the homopolymers than the asymmetric copolymer does. Comparing symmetric and asymmetric copolymers further, Fig. 9 depicts 4 quantities as functions of ϕ_C at different ε_{AB} . There is little difference between two kinds of copolymers in statistics, because of the similar composition ratio used in model.

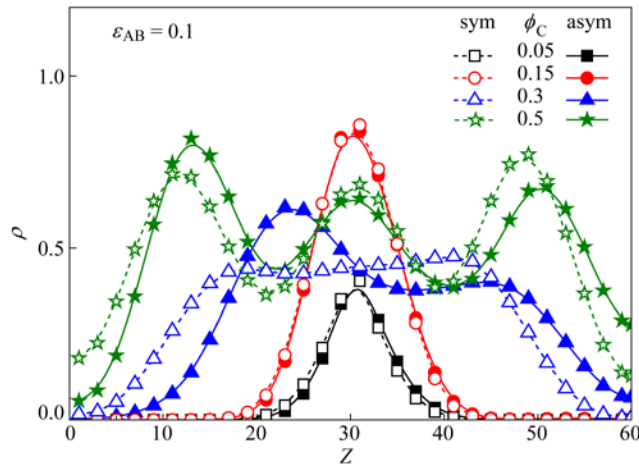


Fig. 8 Comparison for the segmental density profiles of symmetric (vacant) and asymmetric (solid) diblock polymers at different copolymer concentrations ϕ_C . Here, the interaction energy is set to $\varepsilon_{AB} = 0.1$.

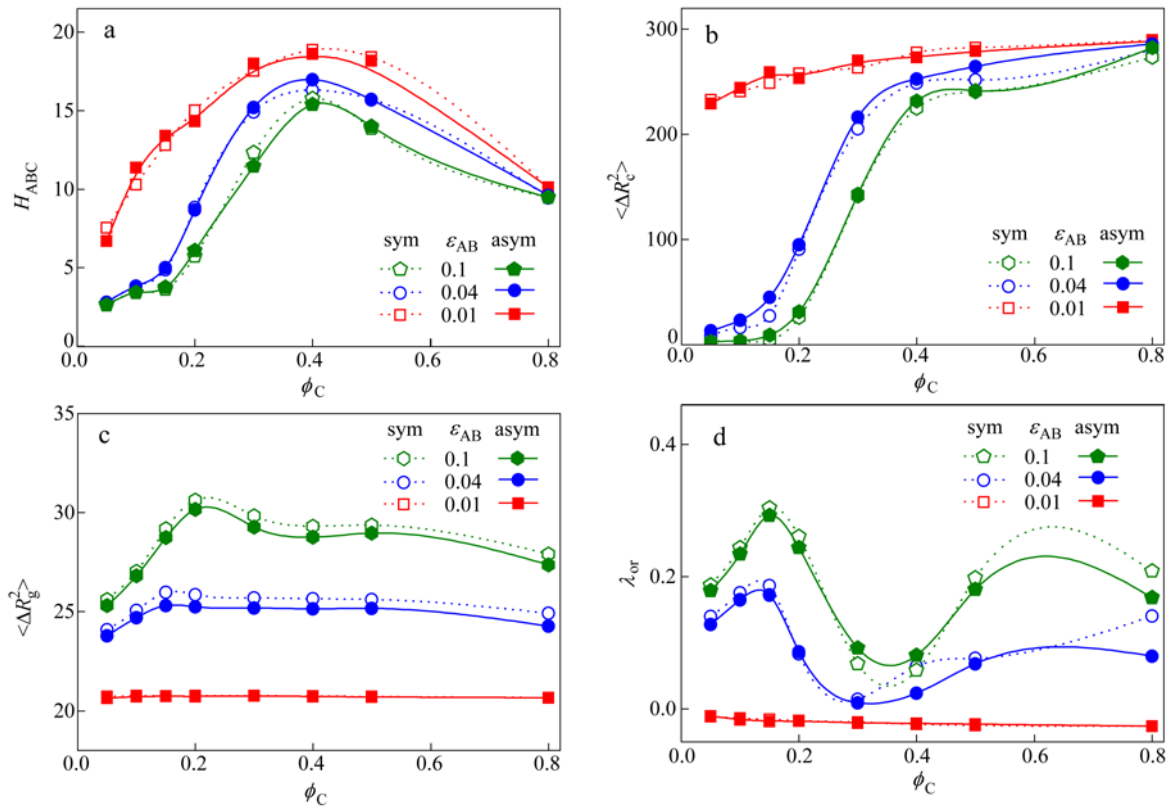


Fig. 9 Comparison for (a) H_{ABC} , (b) $\langle \Delta R_c^2 \rangle$, (c) $\langle \Delta R_g^2 \rangle$, and (d) λ_{or} of symmetric (vacant) and asymmetric (solid) diblock polymers at different interaction energy ε_{AB} .

SUMMARY

We have presented the results from MC simulations for the ternary mixtures of A and B homopolymers and A-*b*-B diblock copolymers confined into a thin film. Both surfaces attract the same component of the diblock *via* a short range potential energy. We have quenched a large number of independent systems from athermal state to

systems employing a series of interaction potentials. For a very weakly repulsive system with $\varepsilon_{AB} = 0.01$, the block copolymer is uniformly distributed in the ternary mixtures under considered concentrations. As the repulsive energy becomes relatively strong, some typical morphologies calculated by SCFT are observed. At low ϕ_C , a macrophase-separated phase is formed as expected. Upon increasing ϕ_C , the central region of the film cannot accommodate these copolymer chains, which induces a curved lamella or micelles in homopolymer phase. At the end, copolymers weave across the system to form lamellar phase. Furthermore, our findings show that, with increasing ϕ_C , copolymer profiles broaden; when $\phi_C \geq 0.4$, a lamellar phase is formed; with ϕ_C continues to increase, the number of layers also increases, but the thickness of layers shrinks.

The information about the detailed interfacial structure in thin film geometry is extremely rich and complex. At lower ϕ_C , the middle segments concentrate at the interface; $\langle R_g^2 \rangle$ expands by adding copolymer at first, suggesting that copolymers penetrate deeper into the homopolymer phase. With the increase of ϕ_C , the phase interface first gradually transforms from plane to a curved surface rather than micelle or lamellar phase. With the increase of ε_{AB} , the copolymer chains not only get stretched in the direction perpendicular to the interface, but also are oriented, revealing that homopolymer phase favors the corresponding copolymer block. The thickness of the interface layer is far beyond $\langle R_g^2 \rangle$, indicating that they are not strongly confined to the interface as assumed by the Leibler theory. In addition, there is little difference between symmetric and asymmetric copolymers in statistics, when the length of two blocks is comparable.

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