Self-Assembled Morphologies of Linear and Miktoarm Star Triblock Copolymer Monolayers

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ABSTRACT: Monolayers of linear and miktoarm star ABC triblock copolymers with equal A and C blocks were investigated using self-consistent field theory. Monolayers of ABC triblock copolymers were formed between two parallel surfaces that were attractive to the A and C blocks. The repulsive interaction parameter $\chi_{AC}N$ between the A and C blocks was chosen to be weaker than the A/B and B/C interactions, quantified by $\chi_{AB}N$ and $\chi_{BC}N$, respectively, such that the B blocks were confined at the A/C interface, resulting in various B domains with different geometries and arrangements. It was observed that two variables, namely, the strength of the surface fields and the film thickness, were dominant factors controlling the self-assembly of the B blocks into various morphologies. For the linear triblock copolymers, the morphologies of the B domains included disks, stripes (parallel cylinders), and hexagonal networks (inverse disks). For the miktoarm star triblock copolymers, the competition between the tendency to align the junction points along a straight line and the constraint on their arrangement from the surface interactions led to richer ordered morphologies. As a result of the packing of the junction points of the ABC miktoarm star copolymers, a counterintuitive phase sequence from low-curvature phases to high-curvature phases with increasing length of B block was predicted. The study indicates that the self-assembly of monolayers of ABC triblock copolymers provides an interesting platform for engineering novel morphologies.

INTRODUCTION

Block copolymers consisting of covalently bonded blocks of chemically distinct components have attracted extensive research interest from both industry and the scientific community because of their remarkable ability to form various ordered nanostructures.¹⁻⁵ The simplest block copolymer is an AB diblock copolymer, which can self-assemble into a variety of ordered phases including hexagonally close-packed (HCP) and body-centered-cubic (BCC) spheres, hexagonal cylinders, gyroid and Fddd (O70) networks, and lamellae.⁶⁻⁸ As the synthesis techniques advance, block copolymers with diverse chain architectures can be accessed by experiments, creating a vast phase space for the fabrication of ordered structures.⁹⁻ For example, ABC triblock copolymers, obtained by adding one additional block of a third component C onto an AB diblock, have much more complicated phase behaviors because of their expanded parameter space, which is at least five-dimensional.¹⁷ Furthermore, multiblock copolymers can have various topological variances. For example, linear triblock copolymers can have three different sequences, namely, ABC, ACB, and BAC, that exhibit different phase behaviors. A large multitude of complex ordered morphologies have been observed with linear and miktoarm star ABC triblock copolymers by experiment and theory.^{9,18–29} For ABC linear triblock copolymers, the ordered phases can be classified as "nonfrustrated" and "frustrated" phases according to whether the domain arrangement frustrates the block sequence.³⁰ In contrast, for ABC miktoarm star copolymers, the three blocks are joined at a common junction point, and therefore, there is no explicit block sequence. This topological constraint drives ABC copolymers to self-assemble into ordered structures where the junction points are forced to be aligned along straight lines, resulting in polygon-tiling

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patterns,^{9,26} among other ordered phases. Numerous studies have demonstrated that ABC triblock copolymers provide a powerful platform for forming structures beyond those from AB diblocks.³¹

Many practical applications involve thin films of block copolymers. Accordingly, the equilibrium phase behavior of block copolymers confined in thin films is of particular importance and has thus been extensively studied by experiment and theory.^{32–40} In thin films, block copolymers are usually confined between a bottom substrate surface and a top deformable air interface. Theoretically, thin films of polymers are usually modeled as two impenetrable parallel rigid surfaces on which appropriate surface potentials are imposed, mimicking the bottom surface interaction and the top interfacial tension.^{32,40} Many simulations have provided useful insights into the understanding of experimental observations.^{37,41} It is also worth mentioning that the self-assembly of block copolymers under two- or three-dimensional confinement has also attracted extensive interest.^{42,43}

The phase behavior of block copolymers in thin films differs significantly from that of the corresponding bulk system because of the effect of the surface interactions on each block, as well as the geometrical confinement imposed by the two surfaces.^{32,40} In other words, the formation of structures is dictated not only by the characteristic parameters of the block copolymers themselves but also by the variables due to the film properties, namely, the film thickness w and the surface interactions characterized by their affinity (i.e., attractive or repulsive) and strength. For example, for AB diblock copolymers confined between two identical selective surfaces, a large number of equilibrium ordered morphologies have been predicted by self-consistent field theory (SCFT).40 In particular, the breaking of the translational symmetry along the normal of the surfaces results in space symmetries of the morphologies in thin films that are different from those of the corresponding bulk phases. For example, the gyroid phase in the bulk transforms into layering network morphologies in thin films. Furthermore, the geometry of the polymeric domains is altered by the confinement effect; that is, the order-order transitions (OOTs) of block copolymer thin films are considerably affected by the film thickness and surface interactions.

Because of their rich array of ordered bulk phases, the selfassembly of ABC triblock copolymers in thin films is of great interest not only for fundamental research but also for practical applications. It is well-known that the phase behavior of ABC triblock copolymers is typically governed by multiple variables, at least including two compositions f_A and f_B , with $f_C = 1 - f_A$ $-f_{\rm B}$, and three interaction parameters $\chi_{\rm AB}N$, $\chi_{\rm BC}N$, and $\chi_{\rm AC}N$, where the Flory–Huggins interaction parameter χ_{ii} (*i*, *j* = A, B, C) quantifies the immiscibility between components i and j and N denotes the total number of statistical segments of a copolymer. When the two confining surfaces are introduced, the parameter space expands further, thus making the study of the phase behavior of triblock copolymer thin films a formidable task. One effective route forward is to explore some two-dimensional cross sections of the high-dimensional phase space with respect to two crucial variables while keeping other parameters constant and focusing on the stability region of the desired ordered phases.^{44,45}

It is important to note that the formation of an ordered structure in a block copolymer is dictated by its thermodynamic equilibrium as well as its kinetics.¹⁶ There are often many

metastable states intervening between the initial disordered state and the final stable structures. When the self-assembly process is trapped in one long-lived metastable state with a large free-energy barrier, the desired stable structure becomes difficult to reach or requires an extremely long annealing time.⁴⁶ In this work, we study the self-assembly of linear and miktoarm star ABC triblock copolymers with equal A and C blocks confined in thin films. Specifically, the two surfaces are set to asymmetrically attract the A and C blocks, with the aim of confining the self-assembly of the B blocks onto the twodimensional (2D) A/C interface, leading to monolayer morphologies. The domain geometries are regulated by the composition $f_B [f_A = f_C = (1 - f_B)/2]$, the film thickness *w*, and the field strength V_0 . In contrast to the spontaneous phase separation, the surface-field-induced spinodal aggregation of the A and C blocks is much faster,⁴⁷ and thus it could speed up the whole self-assembly process of the desired monolayer morphologies.

THEORY AND METHODS

We consider an incompressible melt of ABC triblock copolymers (linear or miktoarm star) of *N* segments confined between two impenetrable surfaces with a separation *w*. The three blocks in each copolymer chain contain f_AN , f_BN , and f_CN ($f_A + f_B + f_C = 1$) segments, and their repulsive interactions are specified by three Flory–Huggins interaction parameters $\chi_{AB}N$, $\chi_{BC}N$, and $\chi_{AC}N$. The radius of gyration of an unperturbed linear copolymer chain is chosen as the spatial unit length. Based on the standard mean-field theory for *n* Gaussian chains,^{48,49} the free energy per chain at temperature *T* can be expressed as

$$\frac{F}{nk_{\rm B}T} = -\ln Q + \frac{1}{V} \int d\mathbf{r} \{ \sum_{\alpha \neq \beta} \chi_{\alpha\beta} N \phi_{\alpha}(\mathbf{r}) \ \phi_{\beta}(\mathbf{r}) - \sum_{\alpha} w_{\alpha}(\mathbf{r}) \ \phi_{\alpha}(\mathbf{r}) + H(\mathbf{r}) [\phi_{A}(\mathbf{r}) - \phi_{C}(\mathbf{r})] + H_{\rm B}(\mathbf{r}) \ \phi_{B}(\mathbf{r}) - \eta(\mathbf{r}) [1 - \sum_{\alpha} \phi_{\alpha}(\mathbf{r})] \}$$
(1)

where $\alpha, \beta \in \{A, B, C\}$ and $\phi_{\alpha}(\mathbf{r})$ represents the local volume fraction of component α at position \mathbf{r} . The quantity Q is the partition function of a single polymer chain interacting with the mean fields w_{A} , w_{B} , and w_{C} , which are produced by the surrounding chains. Additionally, the spatial functions $H(\mathbf{r})$ and $H_{B}(\mathbf{r})$ in 1 specify the interaction potentials of the two surfaces with A (or C) and B, respectively. This choice of the surface potentials on A and C implies that the surface that attracts A (or C) is at the same time repulsive to C (or A). As in our previous study,^{40,50} the surface potentials are given by

$$\frac{H(\mathbf{r})}{\chi N} = \begin{cases} -V_0 \{ \exp[(\sigma - d_z)/\lambda] & \text{for } 0 < d_z < \sigma \\ -1 \}, \\ V_0 \{ \exp[(\sigma - d_z)/\lambda] - 1 \}, & \text{for } w - \sigma < d_z < w \end{cases}$$
$$\frac{H_{\rm B}(\mathbf{r})}{\chi N} = V_0 \{ \exp[(\sigma - d_z)/\lambda] - 1 \}, \\ \text{for } 0 < d_z < \sigma \text{ or } w - \sigma < d_z < w \end{cases}$$
(2)

where d_z denotes the smallest distance to either of the two surfaces. All surface potentials are assumed to be short-range and to vanish for $d_z > \sigma$. The variables V_0 , σ , and λ quantify the strength, range, and steepness, respectively, of the surface potentials. Here, σ and λ are fixed as $\sigma = 0.5R_g$ and $\lambda = 0.5R_g$, whereas $V_0 > 0$ is varied to tune the potential strength from weak to strong in a quantitative manner, indicating that one of the surfaces is attractive to A and is simultaneously repulsive to C, the other is attractive to C and is simultaneously repulsive to A, and the two surfaces are repulsive to B.

Minimization of the free-energy functional with respect to monomer densities and mean fields leads to the following standard SCFT equations

$$\begin{split} w_{A}(\mathbf{r}) &= \chi_{AB} N \phi_{B}(\mathbf{r}) + \chi_{AC} N \phi_{C}(\mathbf{r}) + H(\mathbf{r}) + \eta(\mathbf{r}) \\ w_{B}(\mathbf{r}) &= \chi_{AB} N \phi_{A}(\mathbf{r}) + \chi_{BC} N \phi_{C}(\mathbf{r}) + H_{B}(\mathbf{r}) + \eta(\mathbf{r}) \\ w_{C}(\mathbf{r}) &= \chi_{AC} N \phi_{A}(\mathbf{r}) + \chi_{BC} N \phi_{B}(\mathbf{r}) - H(\mathbf{r}) + \eta(\mathbf{r}) \\ \phi_{K}(\mathbf{r}) &= \frac{1}{Q} \int_{0}^{f_{K}} ds \ q_{K}(\mathbf{r}, s) \ q_{K}^{\dagger}(\mathbf{r}, s) \\ Q &= \frac{1}{V} \int d\mathbf{r} \ q_{K}(\mathbf{r}, s) \ q_{K}^{\dagger}(\mathbf{r}, s) \\ \phi_{A}(\mathbf{r}) + \phi_{B}(\mathbf{r}) + \phi_{C}(\mathbf{r}) = 1 \end{split}$$
(3)

In this set of equations, $q_K(\mathbf{r},s)$ and $q_K^{\dagger}(\mathbf{r},s)$ ($K \in \{A, B, C\}$) are end-segment distribution functions, determining the probabilities of finding the *s* segment at position **r** along two nonequivalent directions of each block, respectively. These distribution functions satisfy the modified diffusion equations,

$$\frac{\partial q_{K}(\mathbf{r}, s)}{\partial s} = \nabla^{2} q_{k}(\mathbf{r}, s) - w_{K}(\mathbf{r}, s) q_{K}(\mathbf{r}, s)$$
$$-\frac{\partial q_{K}^{\dagger}(\mathbf{r}, s)}{\partial s} = \nabla^{2} q_{k}^{\dagger}(\mathbf{r}, s) - w_{K}(\mathbf{r}, s) q_{K}^{\dagger}(\mathbf{r}, s)$$
(4)

which have different initial conditions for linear and miktoarm star copolymers. For the linear copolymers, the initial conditions are,

$$\begin{aligned} q_{\rm A}(\mathbf{r},\,0) &= q_{\rm C}^{\dagger}(\mathbf{r},\,f_{\rm C}) = 1 \\ q_{\rm B}(\mathbf{r},\,0) &= q_{\rm A}(\mathbf{r},\,f_{\rm A}), \quad q_{\rm C}(\mathbf{r},\,0) = q_{\rm B}(\mathbf{r},\,f_{\rm B}) \\ q_{\rm B}^{\dagger}(\mathbf{r},\,f_{\rm B}) &= q_{\rm C}^{\dagger}(\mathbf{r},\,0), \quad q_{\rm A}^{\dagger}(\mathbf{r},\,f_{\rm A}) = q_{\rm B}^{\dagger}(\mathbf{r},\,0) \end{aligned}$$
(5)

whereas those of the miktoarm star copolymers are

$$q_{K}^{\dagger}(\mathbf{r}, f_{K}) = q_{L}(\mathbf{r}, f_{L}) q_{M}(\mathbf{r}, f_{M})$$

$$q_{K}(\mathbf{r}, 0) = 1$$
(6)

where K(L, M) = A, B, or C, and $L \neq M \neq K$.

To focus on the self-assembly of B blocks into monolayer morphologies at the A/C interface, we fix $\chi_{AB}N = \chi_{BC}N = 60$, $\chi_{AC}N = 30$, and $f_A = f_C = (1 - f_B)/2$, and consequently, we have three adjustable parameters, namely, f_B , w, and V_0 , to control the phase behavior of the linear or star triblock copolymers under this specific confinement. The SCFT equations were solved numerically in real space, whereas the modified diffusion equations were solved using the pseudospectral method.^{51,52} Periodic boundary conditions were imposed along the x and y directions, whereas reflective boundary conditions were applied in the z direction. The calculation box was discretized into a space lattice of $N_x \times N_y \times$ $N_z = 64 \times 64 \times 64$, and the grid spacing of the chain contour was set as $\Delta s = 0.01$. In addition, the Anderson mixing algorithm was employed to accelerate the convergence process.⁵³

Within the considered range of parameters, we explored the possible candidate morphologies using SCFT coupled with a specialization scheme.⁴⁰ Then, we calculated the free energy of each morphology for a give set of parameters that was optimized with respect to the box sizes in the xy plane. Comparison of the free energies between morphologies led to phase diagrams, revealing the stability of the desired structures as well as their formation mechanism.

RESULTS AND DISCUSSION

As mentioned before, we fixed the interaction parameters as $\chi_{AB}N = \chi_{BC}N = 60$ and $\chi_{AC}N = 30$, which could lead to frustrated morphologies favoring the formation of A/C interfaces.³⁰ Moreover, we chose a symmetric composition of $f_{\rm A} = f_{\rm C}$ and an asymmetric surface potential attractive to A and C blocks. With this set of fixed parameters, the phase behavior of the system was controlled by three variables, namely, the block ratio $f_{\rm B}$, the film thickness w, and the potential strength V_0 . To focus on the self-assembly of monolayers composed of B domains under the constraint of A/C interfaces, we restricted the thin-film thickness within the range $2R_g < w < 3.5R_g$. This specific confinement made the ABC miktoarm star copolymer have the topological sequence of ABC along the normal direction of the film, which is similar as that of the ABC linear copolymer. Because of the extra constraint from the alignment of the junction point, the ABC miktoarm star copolymers should be able to self-assemble into more types of morphologies. Therefore, we first explored the possible candidate morphologies for the ABC miktoarm star copolymer and examined their stabilities, after which we turned to the study of the phase behavior of the ABC linear copolymer as a comparison.

Exploring possible candidate phases self-assembled by block copolymers that correspond to local minima in a complex highdimensional free-energy landscape presents a difficult mathematical problem. Even for the seemingly simple AB diblock copolymers, it required a few decades to obtain a relatively complete phase diagram through the concerted efforts of experimenters and theoreticians. Usually, for a given block copolymer system, special initial conditions for the mean fields can be designed according to well-established self-assembly of intensively studied block copolymers. For the current systems, the phase behaviors of a number of block copolymer systems, including AB diblock, AB diblock in thin films, and ABC linear and miktoarm star triblock copolymers, provided helpful insights for the initialization of the SCFT calculations.

The first set of morphologies consisted of a wetting A layer on the bottom surface, a wetting C layer on the top surface, and a sandwiched layer of B domains located at the A/C interface, and they can be distinguished by the geometry of B domains. In the monolayer geometry, the B blocks can self-assemble into a complete layer, hexagonal network, equally spaced cylinders, or hexagonally arranged disks, which are referred to as lamella (Lam), perforated lamella (PL), cylinder ($C^{(2)}$), and disk ($D^{(1)}$), respectively (Figure 1). The integer number in the superscript of denotations such as $C^{(2)}$ and $D^{(1)}$ indicates the number of triphase junction-point lines of each separated B domain, which is equivalent to the number of lines of the junction points for ABC miktoarm star copolymer.



Figure 1. Density plots of considered candidate morphologies for ABC miktoarm star triblock copolymers confined in thin films whose two surfaces asymmetrically attract A and C blocks. Components A, B, and C are indicated by red, blue, and green, respectively. These morphologies are denoted according to the geometry of the B domains. Moreover, the integer number in parentheses in the superscript is used to indicate the number of the junction-point lines, and an extra number of 1 or 2 is used to distinguish two nonequivalent arrangements of A and C domains for the same number of the junction-point lines when the wetting A/C layer is disrupted by the alignment of the junction points. For example, both $C^{(6)-1}$ and $C^{(6)-2}$ are derived from the bulk phase of [6.6.6], but they have nonequivalent arrangements of A and C domains due to the asymmetric surface potentials. Note that there are two integers connected by a + sign in $C^{(6+2)}$, indicating that there are two types of B domains with 6 and 2 junction point lines, respectively.

The self-assembly of the ABC miktoarm star copolymers in thin films is dictated by the competition between the tendency to coordinate the alignment of the junction points and the preference for the formation of A and C wetting layers due to the surface interactions. When the surface interactions are strong enough, the self-assembly leads to the first set of morphologies. On the other hand, the self-assembly becomes more complicated, leading to complex morphologies in which the complete A and C wetting layers are replaced by alternatively arranged A and C domains on each surface to reduce the energy loss due to the misalignment of the junction points. The polygon-tiling rule still holds for this confining system except that the corresponding A or C domains are deformed to minimize the interaction energy with the top or bottom surface. As the length of the B block increases, the effect of aligning the junction points into straight lines plays a more important role during the self-assembly, leading to polygon-tiling-like patterns. With the symmetric composition of $f_A = f_C$, the first polygon-tiling pattern is [8.8.4], where the A and C blocks form two octagonal domains whereas the B blocks self-assemble into a square domain.²⁶ Accordingly, C⁽⁴⁾ and R⁽⁴⁾ (where R denotes the ring shape of the B domains) morphologies are considered as candidates in our calculations. In contrast to C⁽⁴⁾, the ring morphology R⁽⁴⁾ has unfavorable interfacial and entropic energies, but a preferred surface energy.

When $f_{\rm B}$ increases further, the polygon tiling in the bulk transforms from [8.8.4] to [6.6.6].²⁶ Therefore, it is necessary to consider some candidate morphologies that have alignments of the junction points similar to that of [6.6.6] in the bulk, including $C^{(6)-1}$, $C^{(6)-2}$, $C^{(6+2)}$, and $R^{(6)-2}$ (Figure 1). Although both $C^{(6)-1}$ and $C^{(6)-2}$ are derived from the bulk phase [6.6.6], their A and C domains are nonequivalent because of the asymmetric surface potentials. Obviously, $C^{(6)-2}$ has a lower surface energy and is thus more favorable. This symmetry preference also holds for the ring morphologies $R^{(6)-1}$ (not shown in Figure 1) and $R^{(6)-2}$. Note that $C^{(6+2)}$ is a hybrid morphology that consists of two types of B domains with 6 and 2 junction-point lines.

Once the candidate morphologies are chosen, their stabilities can be determined by computing and comparing their free energies using SCFT calculations, and hence, the relevant phase diagrams can be constructed. Two phase diagrams, in the $f_B - w$ and $f_{\rm B}-V_0$ planes, are presented in Figure 2. In general, the phase diagrams can be divided into two regions: the region dominated by the surface interactions and the region dominated by the effect of aligning the junction points. For example, the phase diagram in Figure 2a can be divided into the left-bottom region and the right-top region. In the left-bottom region, with relatively small $f_{\rm B}$ or w, the surface interactions govern the self-assembly behaviors, resulting in the formation of A and C wetting layers on the two surfaces and thereby constraining the B domains at the A/C interface. Surprisingly, from left-top to right-bottom, the phase sequence goes from Lam to PL, $C^{(2)}$, and $D^{(1)}$, which seems counterintuitive because longer blocks usually tend to form domains with lower curvatures. Indeed, this transition sequence is still dictated by the growing tendency of assembling the junction points into lines as the length of the B block increases. From Lam to $D^{(1)}$, the B domains shrink at the A/C interface as the junction points become more and more localized, thus benefiting the reduction of the interfacial energy by replacing the A/B or B/Cinterfaces of high interfacial tension with A/C interfaces of low interfacial tension. In the lamellar morphology (Lam), the junction points are uniformly distributed. It is interesting to note that a "mixed" domain exists that contains monomers of all three blocks in the lamellar morphology and is also observed in the bulk miktoarm star copolymers.⁵⁴ From the point of view of the B domains, it can be regarded as disordered. In addition, the film thickness has a considerable effect on the phase transition. Lower film thicknesses give rise to smaller stretching for the A and C blocks or higher interfacial areas and, accordingly, favor the phase transition from Lam to D⁽¹⁾, reducing interfacial energy.

The sequence of phase transitions is rationalized by the packing constraint of the junction points; nevertheless, the fundamental mechanism that the domains of longer blocks prefer low interfacial curvature is violated. In other words, for



Figure 2. Phase diagrams of ABC miktoarm star triblock copolymers confined in thin films with $\chi_{AB}N = \chi_{BC}N = 60$, $\chi_{AC}N = 30$, and $f_A = f_C = (1 - f_B)/2$: (a) in the $f_B - w$ plane for fixed $V_0 = 0.1$ and (b) in the $f_B - V_0$ plane for fixed $w = 2.5R_g$. The solid symbols indicate the transition points determined using SCFT calculations, whereas the solid lines are a guide for the eyes. The dashed line in panel a indicates the phase path of W = 0.1.

larger $f_{\rm B}$, the B blocks confined in the spherical domains of D⁽¹⁾ experience higher stretching. As $f_{\rm B}$ increases, the entropy loss becomes more pronounced and, consequently, forces the morphology to transform into more stable one, namely, one approaching the bulk polygon-tiling morphologies but at the expense of destroying the A/C wetting layers. Thus, the phase transitions enter the right-top region. In addition to the length of the B block, the film thickness also plays a critical role on impacting the phase transitions. The main influence of the film thickness lies in the reduced surface energy relative to the total free energy as w increases. As the contribution of the surface interactions is lowered, the effect of aligning the junction points in a manner that favors the interfacial energy as well as the stretching energy becomes increasingly dominant, leading to stable morphologies of $R^{(4)}$ and $C^{(4)}$ that resemble closer alignment of the junction points to the corresponding bulk phases.

The above arguments are evidenced by the comparisons of the free energy as well as its different contributions as a function of $f_{\rm B}$ for $w = 2.4R_{\rm g}$ and $V_0 = 0.1$ in Figure 3. The three contributions of the free energy are the interfacial energy of U/ $nkT = (1/V)\int d\mathbf{r} \sum_{\alpha\neq\beta}\chi_{\alpha\beta}N\phi_{\alpha}(\mathbf{r}) \phi_{\beta}(\mathbf{r})$, the entropic energy of $-TS/nkT = -\ln Q - (1/V)\int d\mathbf{r} \sum_{\alpha} w_{\alpha}(\mathbf{r}) \phi_{\alpha}(\mathbf{r})$, and the surface energy of $E_{\rm surf}/nkT = (1/V)\int d\mathbf{r} \{H(\mathbf{r})[\phi_A(\mathbf{r}) - \phi_C(\mathbf{r})] + H_{\rm B}(\mathbf{r})\phi_{\rm B}(\mathbf{r})\}$, where $\alpha, \beta \in \{A, B, C\}$. The free-energy comparison for $0.17 \leq f_{\rm B} \leq 0.23$ reveals the stable phase sequence from Lam to D⁽¹⁾ and then R⁽⁴⁾. The comparison of the surface interactions in Figure 3d illustrates that C⁽²⁾ and $D^{(1)}$ have much lower surface interactions than $R^{(4)}$ and $C^{(4)}$ because of their complete A and C wetting layers on the two surfaces. In contrast, $R^{(4)}$ and $C^{(4)}$ have more favorable entropic energies as well as interfacial energies because of their alignment of the junction points. Moreover, $R^{(4)}$ is less preferred than $C^{(4)}$ by the contributions of interfacial energy and the entropic energy because of the energy penalty for bending B domains into the ring shape. Accordingly, it is natural for $R^{(4)}$ to transform into $C^{(4)}$ when the contribution of the surface interactions attenuates as w increases.

The phase diagram in the f_B-V_0 plane in Figure 2b unveils the influence of the surface potential on the phase transitions in a quantitative manner. Similarly to Figure 2a, the effects of the surface interactions and the junction points work in cooperation to divide the phase diagram into two regions: the surface-interaction-dominated left-top region and the rightbottom region dominated by the junction-point-alignment effect. Obviously more complex morphologies can be explored for $f_B > 0.26$ beyond the two phase diagrams. However, we are more interested in the morphologies where various B domains are softly confined between the A and C wetting layers on the two surfaces, and thus, we do not extend the phase diagrams to larger f_B .

As a comparison, the phase behaviors of ABC linear copolymers with a set of parameters similar to those used in Figure 2 were also obtained in our SCFT calculations (Figure 4). One remarkable difference from the phase diagrams in Figure 2 is that those only composed of three stable morphologies are much simpler. Obviously, this difference is due to the absence of the constraint on the arrangement of the junction points in the ABC linear copolymers. More importantly, the phase transitions take the reverse sequence, from lamella (Lam), to cylinder, perforated lamella, and then lamella again. In fact, this phase sequence provides an analogy to the common sequence of the AB diblock copolymers in the bulk from disordered to sphere, cylinder, gyroidal bicontinuous network, and lamella, and then to gyroid, cylinder, sphere, and disorder except that the 3D space is reduced to a quasi-2D space because of the constraint on the B domains from the A/Cinterface. In such a quasi-2D space, the phase sequence consists of only 2D phases featured by the geometry of B domains, namely, from disordered (i.e., B blocks do not separate from A and C blocks) to disk ("2D sphere"), equally spaced lying cylinders ("2D lamella"), hexagonal network ("reverse disk"), and a complete B layer ("2D reverse disorder"). Except for the disk phase in the sequence, the other phases are observed in the phase diagrams of Figure 4. Note that the two "disordered" phases for small and large $f_{\rm B}$ are denoted as Lam and that their regions join together at the top where the triblock chain are highly stretched, forcing them to form the A/B/C nonfrustrated layering structures because no extra entropy can be paid to generate the A/C interfaces required by the formation of the frustrated morphologies.

The absence of the disk phase between the left Lam and C⁽²⁾ is because the difference between $\chi_{AC}N$ and $\chi_{AB}N = \chi_{BC}N$ is not large enough, which is similar to the phenomenon that the sphere-on-cylinder phase vanishes as $\chi_{AB}N = \chi_{BC}N$ is reduced for fixed $\chi_{AC}N$.²⁸ In fact, the ABC linear copolymer with the considered interaction parameters is quite similar to the experimental sample of PS-*b*-PB-*b*-PMMA or PS-*b*-PEB-*b*-PMMA linear copolymers [where PS represents polystyrene; PB, polybutadiene; PEB, poly(ethylene-*co*-butylene); and PMMA, poly(methyl methacrylate)] whose bulk self-assembly



Figure 3. Comparisons of free energy and its different contributions for w = 2.4 and $V_0 = 0.1$: (a) free energy, ΔF , relative to that of $\mathbb{R}^{(4)}$; (b) entropic energy, $-T\Delta S/nk_BT$; (c) interfacial energy, $\Delta U/nk_BT$; and (d) surface energy, $\Delta E_{surf}/nk_BT$. The dashed lines indicate two phase boundaries of $\mathbb{C}^{(2)} \to \mathbb{D}^{(1)} \to \mathbb{R}^{(4)}$.



Figure 4. Phase diagrams of ABC linear triblock copolymers confined in thin films with the same parameters as those in Figure 2: (a) in the f_B-w plane for $V_0 = 0.1$ and (b) in the f_B-V_0 plane for $w = 2.5R_g$.

has been intensively studied.^{20–22} In particular, an interesting bulk morphology similar to C⁽²⁾ was observed for symmetric PS-*b*-PB-*b*-PMMA with $f_{\rm PB} \approx 0.17$ by experiment.²⁰ In the phase diagram of Figure 4a, the stability region of C⁽²⁾ can extend to $f_{\rm B} = 0.17$ when $w < 2.3R_{\rm g}$.

CONCLUSIONS

In summary, the phase behaviors of miktoarm star and linear ABC triblock copolymers in thin films were investigated using SCFT calculations. The film thickness and the interaction parameters were judiciously chosen to ensure the formation of the desired morphologies consisting of A and C wetting layers on the two surfaces plus inner B domains with variable geometries tuned by the length of the B block $f_{\rm B}$ and the strength of the surface potential V_0 . For the ABC miktoarm star copolymer, the structure formation is dictated by the competition between the surface interactions and the tendency to align the junction points on lines. When the surface interactions are dominant for large V_0 or relative small f_B ensuring the formation of the wetting A and C layers on the two surfaces, a phase sequence from Lam, to PL, $C^{(2)}$, and $D^{(1)}$ is predicted as $f_{\rm B}$ increases. Surprisingly, this phase sequence is counterintuitive because the curvature of the domains increases as $f_{\rm B}$ increases. This abnormal phase sequence is caused by the alignment effect of the junction points in the ABC miktoarm star copolymers. In contrast, when the ABC miktoarm star copolymer is replaced by the ABC linear copolymer, the phase sequence is reversed to the normal order. Interestingly, the phase sequence resembles that of bulk AB diblock copolymers, but it is dramatically simplified by the reduction in dimensions from 3D to 2D. In addition, for ABC miktoarm star copolymers, as the effect of packing the junction points becomes increasingly dominant, the A/C wetting layers are destroyed to form morphologies exhibiting arrangements of the junction points similar to those of the corresponding bulk phases, such as $C^{(4)}$ and $R^{(4)}$.

The results for the self-assembly of the ABC triblock copolymers under the specific confinement considered in this work provide insight into the understanding of the confined self-assembly of block copolymers as well as a platform for the engineering of monolayer morphologies. On one hand, the self-assembly mechanism of the B blocks at the A/C interface sheds light on the self-assembly of block copolymers at interfaces, which has been widely studied by experiments.^{55–57} On the other hand, these morphologies with B domains of variable shapes confined between the complete wetting A and C layers might have promising potential applications in nanotechnology because the constraining conditions are favorable for speeding up their equilibration processes.

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Notes

The authors declare no competing financial interest.

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