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Emergence and Stability of a Hybrid Lamella−Sphere Structure from Linear ABAB Tetrablock Copolymers

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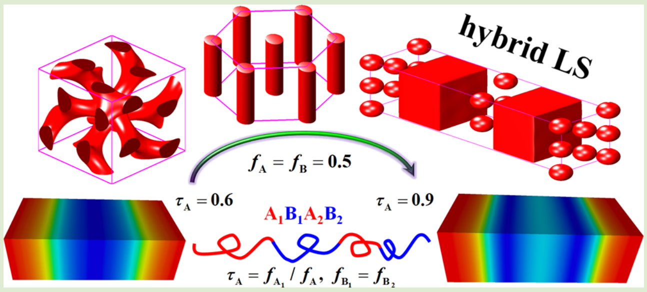
Supporting Information

ABSTRACT: The self-assembly of linear $A_1B_1A_2B_2$ tetrablock copolymers is studied using the self-consistent field theory, aiming to target the formation of stable hybrid structures composed of lamellar and spherical domains of the same component, i.e., the lamella−sphere (LS) phase. Two types of lamellar morphologies, regular (L) and sandwich-like (L′), are observed, and their transition is identified as first-order. The formation of L′ is a prior condition for the formation of LS because the disordered short A_2-blocks sandwiched in the B domain in L′ aggregate into spheres as χN increases, leading to the formation of LS. The separation of A_2-blocks from A_1-blocks in L′ or LS causes extra interfacial energy, which is compensated by the gain of configurational entropy. The tail B_2-block is demonstrated to play a critical role in enlarging the gain of configurational entropy. In a word, the formation of L′ is driven by entropy, while the transition from L′ to LS is driven by enthalpy.



The self-assembly of block copolymers has attracted long-lasting interest due to its remarkable ability of forming rich ordered nanostructures that exhibit promising potential applications in a wide range of fields.[1−5] Though it is easy to understand that the general mechanism that block copolymer self-assembly is governed by the competition between the interfacial energy and the entropic energy,[6] it is still challenging to predict the geometry of the resulting structures. Even for the ideal model system, i.e., the simplest AB diblock copolymer, it has taken a long period to obtain the relatively complete phase diagram under the concerted interplay of theory and experiment,[7] which consists of several ordered phases: hexagonally close-packed (HCP) and body-centered-cubic (BCC) sphere, hexagonal cylinder (C), double Gyroid (G) and *Fddd* (O^{70}) bicontinuous network, and lamella (L).[8−10] However, recent insightful experiments observed more complex spherelike phases in some specific diblock copolymers,[11−15] Frank−Kasper (FK) phases, whose stabilization mechanism was revealed by relevant self-consistent field theory (SCFT) studies.[16,17] Instructively, these complex FK phases were also predicted as stable in other AB-type block copolymer systems by SCFT.[17,18] On one hand, these observations confirm the difficulty with the prediction of phase behaviors. On the other hand, it implies a possibility to generate more ordered phases with AB-type copolymers by tailoring the chain architecture.[19,20]

The phase behaviors of various AB-type block copolymer melts have been systematically explored by SCFT.[10,16,21−32] Though many of them resemble the similar phase sequence as the AB diblock copolymer, their phase boundaries are significantly shifted.[10] A typical example is the linear ABA triblock copolymer,[24] which could be obtained by adding an additional A-block onto the end of the B-block of the AB diblock. In particular, for asymmetric A_1BA_2 with $\tau = N_{A_2}/(N_{A_1} + N_{A_2})$, where N_{A_1} and N_{A_2} indicate the number of statistical segments of A_1- and A_2-blocks, respectively, interesting phase re-entry like L → G → C → G → L as τ increases for fixed volume fraction was observed, which has been confirmed by very recent experiments.[33] This observation demonstrates the important role of architecture as an additional factor to the volume fraction and the interaction parameter even for linear AB-type block copolymers. Nevertheless, most of the structures in AB-type block copolymers consist of only one type of geometry of minority domains, such as sphere, cylinder, or lamella, while stable hybrid structures containing different geometries are rarely reported. For example, lamellar and spherical domains are formed simultaneously with the same chemical component, referred to as the hybrid lamella−sphere (LS) phase. Note that this kind of hybrid phase is capable to produce lines and dots simultaneously, thus having a promising application perspective in block copolymer lithography.[5] Recently, the LS phase was observed in highly asymmetric A_1BA_2 triblock copolymers by Monte Carlo (MC) simu-

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lations;[34] however, quantitative verification of its stability is lacking.

It is instructively observed by MC that short A_2-blocks aggregate into spherical A-domains in the lamellar B-domain, while long A_1-blocks self-assemble into the lamellar A-domain, leading to the LS morphology [Figure 1(a)].[34] Intuitively, if the long A_1- and short A_2-blocks aggregate separately, they could form lamellae and spheres in the same morphology, respectively. The complete separation between A_1- and A_2-blocks means that there is only a unidirectional bridging configuration (e.g., $A_1 \rightarrow B \rightarrow A_2$), while the other directional bridging configuration is not allowed (e.g., $A_2 \rightarrow B \rightarrow A_1$), which is very entropically unfavorable. The mixing bidirectional bridging configurations drive the mixing of A_1- and A_2-blocks. In addition, looping configuration also appears in the lamellar morphology of ABA triblock copolymers,[24] also causing the mixing of the two different A-blocks. No doubt, these mixing configurations lead to the formation of the regular lamellae (denoted by L).

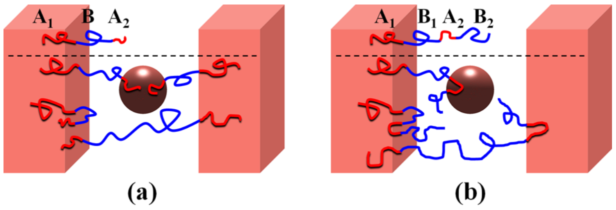

Figure 1. Possible configurations of A_1BA_2 triblock (a) and $A_1B_1A_2B_2$ tetrablock (b) copolymers in a regular lamella or hybrid lamella–sphere (LS) morphologies: A-blocks in red color and B-blocks in blue color. The dangling A_2-blocks in the B-domain are either disordered or aggregated into spheres (above or below the dashed lines).

However, when the A_2-block is very short, its separation from the B-domain leads to a limited gain of interfacial energy but at the expense of configurational entropy. As a result, the very short A_2-block tends to be dangled in B-domain in order to access more configurations at the low expense of interfacial energy, thus increasing the effective volume fraction of B-domain relative to its characteristic value. The probability of the dangling configuration should increase as the A_2-block shortens. As the dangling A_2-blocks aggregate together within the B-domain, the lamellar phase becomes sandwich-like (denoted by L′). The change of the effective volume fraction due to the swollen B-domain by the dangling A_2-blocks governs the phase re-entry. At the same time, the dangling A_2-blocks could aggregate into spherical domains to reduce the A_2/B interfacial energy as long as the local segregation between them and B-blocks is high enough. In a word, LS could be formed when the sandwiched A_2-blocks aggregate into spheres before the layering A-domain transforms into the cylinder as its effective volume fraction decreases.

In contrast to the regular L phase, the separation of A_1- and A_2-blocks in L′ increases the interfacial energy. L′ becomes stable over L if and only if the gain of entropy can compensate the loss of interfacial energy. In other words, the formation of L′ is driven by entropy, while its transition to LS is driven by enthalpy. Our later SCFT calculations will demonstrate that L′ as well as LS is hard to be stabilized in A_1BA_2 due to the limited gain of entropy. To enhance the gain of entropy from the separation of A_1- and A_2-blocks, we purposely attach an additional B-block to the end of the A_2-block, forming a linear tetrablock $A_1B_1A_2B_2$, which is readily accessed by modern synthetic techniques.[35,36] Hence, if a short A_2-block enters the layering domain mainly composed of A_1-blocks, it has to form an extra small loop in any possible configuration of $A_1B_1A_2B_2$ [Figure 1(b)]. To constrain the two junction points of the A_2-block on the A/B interface results in an entropic loss, which becomes more severe as the A_2-block shortens relative to the decreasing A_2/B interfacial energy. Additionally, the looping configuration of the A_2-block also increases the A_2/B interfacial area, which reduces the superiority of the A_1/A_2 blending configuration in the interfacial energy over their separation.

Accordingly, here we will study the phase behavior of $A_1B_1A_2B_2$ melts using SCFT, focusing on the emergence and stability of the LS phase. Details of SCFT are provided in the Supporting Information. The numbers of segments on the four blocks are specified as N_{A_i} and N_{B_i} (i = 1 and 2), respectively, with $N_{A_1} + N_{A_2} + N_{B_1} + N_{B_2} = N$, $f_{A_i} = N_{A_i}/N$, $f_{B_i} = N_{B_i}/N$, $f_A = f_{A_1} + f_{A_2}$, $f_B = f_{B_1} + f_{B_2}$, $\tau_A = N_{A_1}/(N_{A_1} + N_{A_2}) = f_{A_1}/f_A$, and $\tau_B = N_{B_1}/(N_{B_1} + N_{B_2}) = f_{B_1}/f_B$. Besides the interaction parameter, χN with χ being the Flory–Huggins parameter and N the total number of segments, three other independent variables are needed to characterize the phase behaviors, e.g., f_A, τ_A, and τ_B.

To give prominence to the effect of architecture, we fix the composition as symmetric, i.e., $f_A = f_B = 0.5$. As mentioned previously, one of the most attractive features in the phase behavior of asymmetric A_1BA_2 copolymers lies in the phase re-entry as τ varies occurred for a fixed composition. This phenomenon should also occur with the phase behavior of $A_1B_1A_2B_2$ because of the possible separation between the two A-blocks as well as between the two B-blocks. Of course, the two re-entry phenomena for A- and B-blocks are mirror symmetric. We calculate the phase diagram of $A_1B_1A_2B_2$ with respect to τ_A and τ_B for $f_A = f_B = 0.5$ and $\chi N = 60$ (Figure 2).

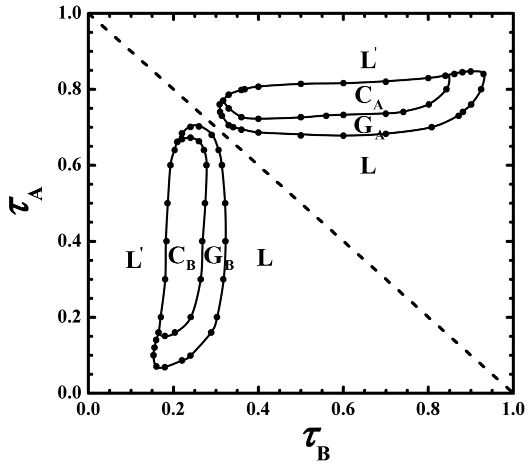

Figure 2. Phase diagram in the τ_B–τ_A plane of $A_1B_1A_2B_2$ tetrablock copolymers with $\chi N = 60$ and $f_A = f_B = 0.5$. The filled circles denote the phase transition points determined by SCFT, while the solid lines are a guide for the eyes.

The considered candidate morphologies are listed in Figure S1. Apparently, the phase diagram is mirror symmetric with respect to the diagonal connecting the top-left and bottom-right corners, which is dictated by the exchange symmetry between A and B blocks. Interestingly, the gyroid and cylinder phases exhibit considerable stability regions besides the lamellar phases for the case of ideally symmetric composition, giving rise to the phase re-entry as τ_A or τ_B varies. Note that the denotation C_α or G_α (α = A and B) indicates the cylinder or gyroid phase whose minority geometry is composed of an α-component.

Without loss of generality, we focus on the phase re-entry as τ_A varies. The typical phase re-entry is $L' \rightarrow C_A \rightarrow G_A \rightarrow L$ as τ_A decreases for $0.3 < \tau_B < 0.85$. For $\tau_A = 1$, corresponding to the AB diblock, there is no doubt the stable phase is lamella. As τ_A decreases from 1, increasing A_2-block divides the B-block into two pieces, B_1- and B_2-blocks. When the A_2-block is short, it would stay within the B-domain instead of joining in A_1-blocks, thus increasing the effective volume fraction of B-blocks, $f_B^{eff} > f_B$. The energy gain from the increased configurations when mixing short A_2-blocks into the B-domain is larger than the cost of interfacial energy. As f_B^{eff} becomes adequately asymmetric, the stable phase transfers from L′ to C_A. However, this increasing trend of f_B^{eff} as τ_A decreases cannot be maintained because the interfacial energy is continuously increased, and thus it would drive A_2-blocks to leave the B-domain. Accordingly, the symmetric volume fraction is restored as more A_2-blocks leave the B-domain, i.e., that f_B^{eff} decreases toward its characteristic value $f_B = 0.5$, leading to the inverse transition from C_A going through G_A into L.

To clearly demonstrate the variation of f_B^{eff}, we estimate its value of the lamellar phase that transforms from L′ to L as τ_A decreases or f_{A_2} increases without considering the intermediate phases of cylinder and gyroid (Figure S2). When f_{A_2} increases from 0, most of the A_2-blocks stay in the B-domain, leading to a nearly linear growth of $f_B^{eff} \approx f_B + f_{A_2} = f_B + (1 - \tau_A)f_A$. As f_{A_2} increases, the amount of A_2-blocks joining in the major A-domain increases, finally leading to the transition from L′ to L when most of the A_2-blocks enter the A-domain. Surprisingly, for fixed $\tau_B = 0.5$, f_B^{eff} abruptly drops off at a critical $\tau_A^C \approx 0.77$, which implies a first-order transition between L′ and L.[37] In addition, the first-order transition is evidenced by their free energy comparison as well as the discontinuous variation of their domain spacing as τ_A increases (Figures S3 and S4). Note that L′ has a notably larger period than L due to its lower content of looping configurations. Interestingly, the first-order transition vanishes at the side of large τ_B where L′ and L become indistinguishable (Figure S5). In particular, for $\tau_B = 1$ corresponding to the case of asymmetric A_1BA_2, the portion of A_2 in the B-domain of L′ is vanishingly small (Figure S6). This implies that the LS phase should be hard to stabilize in asymmetric A_1BA_2 copolymers.

Notice that the above phase re-entry exhibits an asymmetric phase sequence, $L' \rightarrow C_A \rightarrow G_A \rightarrow L$, which is in obvious contrast to the generic phase sequence as composition in AB-type block copolymers. In other words, the Gyroid phase only appears at the lower side of the cylinder phase in the phase region but not at the upper side. This asymmetric feature is attributed to the asymmetric change of f_B^{eff} as τ_A increases at the two sides of the cylinder. At the upper side with $\tau_A > 0.82$, most of the short A_2-blocks enter the B-domain, thus inducing an almost linear increment to f_B^{eff} as the length of the A_2-block. In contrast, at the lower side, f_B^{eff} is dictated by a pair of competing factors. Although longer A_2-blocks are more likely to migrate into the major A-domain by enforcing the polymer chains to adopt some looping configurations [Figure 1(b)], only a proportion of them do so because of the need to balance the loss of configurational entropy and the gain of interfacial energy. On one hand, there is a smaller proportion of longer A_2-blocks as f_A contributing to f_B^{eff}. On the other hand, the increasing length of the A_2-block partially compensates the lowering of f_B^{eff}.

For a given τ_B, the local segregation degree is determined by the length of the A_2-block and χN. With $\chi N = 60$, no stable LS phase is observed because short A_2-blocks prefer to be disorderly dangled in the B-domain for such low segregation between A_2-blocks and B-blocks. To examine the effect of χN on the formation of LS, we construct the phase diagram with respect to τ_A and χN for fixed $\tau_B = 0.5$ and $f_A = f_B = 0.5$ (Figure 3). Surprisingly, a noticeable stability region of LS is observed between L and C_A for $\chi N \gtrsim 74$. A typical comparison of free energy for $\chi N = 80$ is given in Figure S7, while the comparisons of interfacial and entropic contributions are given in Figure S8. As expected, the local aggregation of A_2-blocks makes LS have more favorable interfacial energy but higher entropic energy than L′ in the stability region of LS. Note that the density of A-blocks within the spherical domain of LS is much higher than that of the A-blocks sandwiched in the B-domains of L′, and it increases to become larger than 0.9 at $\chi N = 90$ (Figure S9). This observation evidences that the spherical domains of LS are well separated from the "B-matrix".

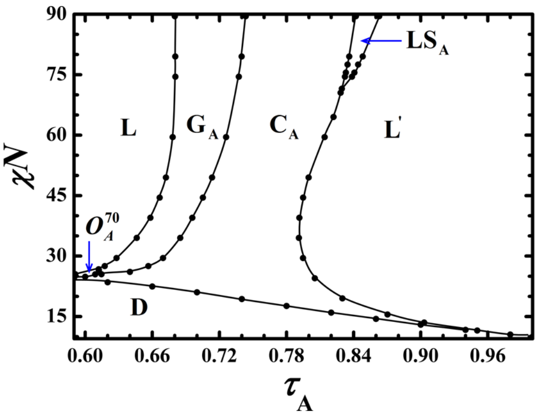

Figure 3. Phase diagram of $A_1B_1A_2B_2$ tetrablock copolymers in the τ_A−χN plane for fixed $f_A = f_B = 0.5$ and $\tau_B = 0.5$.

To demonstrate the key role of the B_2-block on stabilizing L′ and thus LS further, we calculate the peaking densities of A_2-blocks (ϕ_{A2}^P) within the B-domain as a function of τ_A for τ_B = 0.5 and $\chi N = 80$ and compare it with that of $\tau_B = 1$ (i.e., A_1BA_2) (Figure S10). We find that A_2-blocks of L′ locally aggregate into spheres at $\phi_{A_2}^{max} \sim 0.25$ for $\tau_B = 0.5$, thus forming LS. In contrast, the maximum value of $\phi_{A_2}^P$ is only about 0.07 for $\tau_B = 1$, which is far below the threshold value for the aggregation of A_2-blocks. More interestingly, the maximum of $\phi_{A_2}^P$ cannot be simply increased by enhancing χN (Figure S11). This observation reveals that LS may not be stabilized in asymmetric A_1BA_2.

There is still one question to be answered, i.e., whether other hybrid phases such as the lamella−cylinder, gyroid−sphere, and cylinder−sphere are stable. Our answer is yes if we could adjust more parameters such as χN and f_A. For example, according to the transition sequence of A_2-domains within B-domains from disordered to sphere and then to cylinder, the lamella−cylinder phase might become stable in the region with χN far above the LS region. In addition, another critical parameter is the composition. To vary the symmetric composition to be asymmetric offers an opportunity to stabilize the hybrid gyroid−sphere or cylinder−sphere phase.

In summary, we have studied the self-assembly behaviors of $A_1B_1A_2B_2$ tetrablock copolymers using SCFT, predicting a stable hybrid lamella−sphere phase. Our results indicate that $A_1B_1A_2B_2$ exhibits significantly different phase behaviors from A_1BA_2 though similar phase re-entry is observed with both of them. In $A_1B_1A_2B_2$ with symmetric composition, two types of lamellar phases, regular (L) and sandwich-like (L′), are observed, and their transition driven by entropy is identified as first-order. Note that both L′ and LS are formed via the separation of short A_2-blocks within B-domain from long A_1-blocks. Therefore, the formation of L′ at relatively low χN is a prior condition to the formation of LS at high χN because L′ transfers to LS as the disordered A_2-blocks locally aggregate into spheres. The stabilization mechanism of L′ as well as LS is explicitly elucidated, and it is found that the tail B_2-block plays a critical role. Although the stability region of LS is narrow, on one hand, it could be enlarged by further adjusting the control parameters or optimizing the architecture. On the other hand, the stabilization mechanism of LS is instructive for stabilizing other hybrid phases.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.7b00818.

> Further description and figures regarding the self-consistent field theory, the comparisons of free energy, the domain spacing, and so on (PDF)

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Notes

The authors declare no competing financial interest.

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(37) (1) The "phase diagram" in block copolymer literature is not a phase diagram in a rigorous sense, but it is commonly used in in the literature. These phase diagrams should be regarded as phase portraits. (2) In our work, we follow the literature and use the term "phase diagram", but they should be regarded as phase portraits. (3) We thank an anonymous reviewer for pointing this out.