Enlarged Stable Phase Region of Hybrid Lamella-sphere Phase Enabled by $A_1B_1A_2(B_2)_m$ Branched Tetrablock Copolymer

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Abstract Hybrid nanostructures possess a great potential for application in advanced nanotechnologies due to the anisotropic properties from different nanophases. Our previous work demonstrated that a linear $A_1B_1A_2B_2$ tetrablock copolymer of symmetric overall volume fraction can self-assemble into a hybrid lamella-sphere (LS) structure by tuning the relative length of the two $A$-blocks through self-consistent field theory (SCFT), where the spherical and the lamellar domains are mainly composed of the long $A_1$- and short $A_2$-blocks, respectively. However, the phase region of LS is limited. In order to expand the stable region of LS, we change the linear $A_1B_1A_2B_2$ copolymer to a branched $A_1B_1A_2(B_2)_m$ copolymer resulting in an increase of the local spontaneous curvature between $A_2$- and $B_2$-blocks. We examine the impact of the branching number $m$ of $B_2$-block on the stable region of LS in the phase diagram with respect to $f_2$ and $\chi_N$ for fixed $f_2=0.5$ and $f_1=0.26$, and find that $m=2$ expands the LS region significantly in contrast to the linear architecture. On the other hand, the stability window of LS does not change notably when $m=2$ is increased to 3 in our calculated parameter space.

Keywords Block copolymer; Self-assembly; Self-consistent field theory; Hybrid structure

INTRODUCTION

Hybrid nanostructures, which combine two types of nanophases, have great potential application in advanced nanotechnologies due to the anisotropic properties from different nanophases.[$^1$–$^5$] For example, the hybrid lamella-sphere (LS) phase, where lamellar and spherical domains are composed of the same chemical component, can simultaneously regulate the spacing distance of the lamellae as well as the spatial arrangement of the spheres to adjust the chemical and physical characteristic of the formed nanostructures.[$^6$] It has been demonstrated that the lamellar structures can be utilized to tune the diffusion rates of the water by controlling the domain space and the corresponding constituents,[$^7$] while the spherical phases are fascinating materials for creating numerous soft mesocrystals with domain size at $5–100\ \text{nm}$.[$^8$–$^{11}$] Generally, the anisotropic properties from different nanophases can influence the diffusion of water in the self-assembled nanostructures. Therefore, due to the presence of sphere domains in the hybrid lamella-sphere phase, the diffusion of water in the lamellar nanostructures can be significantly modulated. Specifically, we can make the spherical domain formed from $A_2$-blocks more attractive to impurity substances in water, e.g., particles pollution and organic matter. When the nanoscale pores are designed to cross the spheres and be parallel to $B$-lamella, the polluted water flow through the nanoscale pores can be purified. So we believe that the hybrid LS nanostructures may be treated as the potential structures for water purification.[$^7$]

The first observation of LS nanostructure was reported in linear $A_1B_1A_2B_2$ tetrablock copolymer by using self-consistent field theory (SCFT). The $A_1$ and $A_2$-blocks locally segregate into lamellar and spherical microdomains respectively to reduce the loss of entropy.[$^6$] It is also showed that the sandwiched lamella (L') is a crucial nanostructure to form the LS, where enthalpy drives the transition from L' to LS. Interestingly, our theoretical predictions were confirmed by the ingenious design of polystyrene-$b$-polyisoprene-$b$-polystyrene-$b$-polyisoprene ($S_1\text{I}_1S_2\text{I}_2$) tetrablock copolymers from Kim's group, where gyroid, hexagonally packed cylinder as well as L' were observed.[12,13] Interestingly, they also found that the order-order transition from cylinder to lamellae was induced by decreasing $\chi N$ (or increasing temperature), which was in good accordance with the predictions of SCFT.[$^6$] However, this transition sequence is different from AB diblock and ABA triblock copolymer systems, where larger $\chi N$ leads to lamellar nanostructures. These results show that SCFT is a powerful tool to design target morphologies from a variety of possible...
molecular architectures based on effective design principles. However, there is no report about the observation of LS nanostructures in Kim’s experiment due to the narrow LS phase regime and high critical phase separation \(\chi N\) (\(\chi N = 74\) predicted in our previous work). Therefore, it is critically important to increase the phase region of LS nanostructure by using a proper design route to achieve the observation of LS structure experimentally. However, for the linear polymer, to obtain the spherical domains, a large asymmetric \(A_2\) and \(B_2\) block ratio is needed, which leads to the increase of critical phase transition \(\chi N\). On the other hand, spherical morphologies have attracted persistent attention, since a series of crystal phase can be produced by the proposed new concept. Notably, Li and coworkers obtained the Frank-Kasper phase and A15 phase theoretically in AB-type block copolymer, where the phase region of spherical morphologies in miktoarm star \(A\) and \(B\) \((m = 2, 3, 4)\) block copolymers is much wider than that in AB diblock copolymer. That is not a surprise because highly asymmetric architecture between \(A\) and \(B\) block creates a large tendency of forming high spontaneous curvature toward the \(A\)-domain. Interestingly, even though spherical domains are formed by the majority of A blocks \(f_A > 1/2\), expanded spherical phase region was achieved by using a dendron like AB-type block copolymers, which breaks the general understanding that the spherical phases can only be stable at the condition that spherical domains are composed of minority component. These results show that branched architecture leads to the formation of spherical morphologies, which could be used to enlarge the phase regime of spherical nanostructures.

In this study, to increase the stability phase regime of LS nanostructure, we use a branched \(A_1B_2A_1B_2\) \((m = 2, 3)\) multiblock copolymer to increase the local spontaneous curvature between \(A_2\) and \(B_2\)-blocks, where \(m\) indicates the number of \(B_2\)-blocks. First, we investigate the function of branched arms \(m\) on the chain arrangement in the formed nanostructures, where we find more \(A_2\)-blocks tend to stay in the \(B\)-domain for branched polymer \((m = 2)\), resulting in the formation of \(L^*\) nanostructures. Then we explore the influence of \(m\) on the phase transition sequence. Wider phase region of LS is observed at larger \(m\). Finally, we examine the impact of the branching number \(m\) of \(B_2\)-block on the stable region of LS in the phase diagram with respect to \(f_A\) and \(\chi N\) for fixed \(f_B = 0.5\) and \(f_B = 0.26\). We find that the LS region is significantly expanded in \(m = 2\) compared with that of the linear polymer \((m = 1)\). While in the branched polymer, the stability regime of LS changes slightly from \(m = 2\) to \(m = 3\). So, our results can provide an effective method for obtaining hybrid nanostructures, which shows a great application in advanced nanotechnologies.

The rest of this work is organized as follows. Detailed information of the SCFT is given in the next section. In the results and discussion, we first discuss the influence of the branches on the distribution of \(A_2\)-block in formed nanostructures. Then the phase transition sequence for different branches is calculated. The influence of branches on the stability of LS regime is presented in the following section. Finally, we conclude with a summary of this study.

**THEORY AND METHOD**

In this study, the system consisting of \(n\) branching \(A_1B_2A_1B_2\) \((m = 2, 3, 4)\) tetrablock copolymer chains in the volume of \(V^*\) Each branching tetrablock copolymer consists of \(N\) segments with equal segment length \(b\) and density. The length of each block is specified as \(f_A N, f_B N, f_A N, f_B N\) and \(f_A N, f_B N\) \((f_A + f_B = 0.5, f_A + f_B = 0.5)\), respectively. The multiblock copolymer \(A_1B_2A_1B_2\) \((m = 2)\) can be reduced to \(A_1B_2\) at \(f_A = 0\) and \(A_2B_2\) at \(f_A = 0.5\), respectively. The variables \(\phi_A\) and \(\phi_B\) are used to characterize the distribution of volume fraction of \(A\) and \(B\)-blocks in the self-assembled nanostructures. Under the approximation of mean-field treatment of Gaussian chain model, the free energy per chain in the unit of thermal energy \(k_B T\) at the temperature \(T\), where the \(k_B\) is the Boltzmann constant, can be expressed as

\[
\frac{F}{nk_B T} = -\ln Q + \frac{1}{\sqrt{V}} \int dr \left( \chi N \phi_A(r) - \omega_A(r) \phi_A(r) - \omega_B(r) \phi_B(r) \right)
\]

\[
- \eta(r)(1 - \phi_A(r) - \phi_B(r))
\]

(1)

\(\phi_A, (K = A \text{ or } B)\) is the space-dependent monomer concentration, \(\omega_A\) is the corresponding auxiliary field, \(\eta(r)\) is the lagrange multiplier to force the incompressibility condition: \(\phi_A(r) + \phi_B(r) = 1.0\), and the variable quantity \(Q\) is the single chain partition function interacting with the mean field \(\omega_A\) and \(\omega_B\) produced by the surrounding chains, which is determined by:

\[
Q = \frac{1}{\sqrt{V}} \int dq(r, s) q^*(r, s)
\]

(2)

Minimization the free energy leads to the following SCFT equation:

\[
\omega_A(r) = \sqrt{\chi N \phi_A(r) + \eta(r)}
\]

(3)

\[
\omega_B(r) = \sqrt{\chi N \phi_B(r) + \eta(r)}
\]

(4)

\[
\phi_A(r) = \frac{1}{Q} \int_0^{f_A N} ds q^*(r, s) q^*(r, s) + \int_{f_A N}^{f_A N + f_B N} ds q^*(r, s) q^*(r, s)
\]

(5)

\[
\phi_B(r) = \frac{1}{Q} \int_{f_A N}^{f_B N} ds q^*(r, s) q^*(r, s) + \int_{f_B N}^{f_A N + f_B N} ds q^*(r, s) q^*(r, s)
\]

(6)

where the \(q^*(r, s)\) and \(q^*(r, s)\) are the propagator functions of each segment \(s\) starting from the distinguishable ends, satisfying the following modified diffusion equations:

\[
\frac{\partial q(r, s)}{\partial s} = \nabla^2 q(r, s) - w(r, s) q(r, s)
\]

(7)

\[
- \frac{\partial q^*(r, s)}{\partial s} = \nabla^2 q^*(r, s) - w(r, s) q^*(r, s)
\]

(8)

The initial conditions of the propagator functions are \(q(r, 0) = 1.0\) and \(q^*(r, 1) = 1.0\) and the unit length is chosen as \(L = (N/6)^{1/2}\). The Pseudo-spectral method is used to solve the diffusion equation, where the periodic boundary conditions are imposed automatically on the rectangular cubic box, and the Anderson-mixing is implemented in SCFT equations to accelerate the calculation. To obtain reliable results, the lattice length is less than 0.1\(L\) and the chain contour is divided to 200 points. As one of the most successful methods, the SCFT can accurately calculate the free energy of different candidate morphologies and the corresponding distribution of each segment. Therefore, the SCFT can be regarded as the standard tool to reveal the mechanism of forming each morphology.
RESULTS AND DISCUSSION

Based on the established knowledge about the self-assembly behavior of \( A_1B_1A_2B_2 \) tetrablock copolymer under \( f_A=f_B \) condition,\(^{29-40}\) the ordered phases, including not only lamellar structures without spontaneous curvature, but also the cylindrical, spherical, gyroid, Fddd and even the hybrid LS nanostructures with spontaneous curvature, are listed in Fig. 1.

**Distribution of Chain Segments in Formed Nanostructures**

It is interesting to observe the asymmetric nanostructures in symmetric volume fraction (\( f_A=f_B \)). To understand the formation of these nanostructures, the arrangement of chain segments is highly needed. First, we discuss the distribution of chain segments in lamellar nanostructure formed from both linear \((A_1B_1A_2B_2)\) and branched \((A_1B_1A_2(B_2)_2)\) polymers in Fig. 2. Since \( A_2\)-blocks have a great impact on the formation of these...
nanostructures, we calculate the 2D distribution of \( A_2 \)-blocks separately and depict them in the upper panel of Fig. 2. Interestingly, as \( A_1 \)-volume fraction increases, more \( A_2 \)-block favors mixing with \( B \) domain because high \( \chi_N \) is needed for the phase separation from \( B \)-blocks. The result is the same for branched polymer, however, compared Fig. 2(b) with Fig. 2(e), we find that more \( A_2 \)-blocks tend to stay in the \( B \)-domain for branched polymer \( (m=2) \), resulting in the formation of L’ nanostructures.

For the formation of the nanostructures with spontaneous curvature, we depict the possible chain arrangements in the \( G_A/C_A \) phases (Fig. 3) according to the distribution of \( A_2 \) in lamellar nanostructures. Clearly, there are loop and bridge molecules in the \( G_A/C_A \) phases. The effective volume fraction of \( B \)-domain is increased due to the solubility of \( A_2 \)-block in \( B \)-domain, which results in the formation of \( G_A \) and \( C_A \) nanostructures even at symmetric A/B volume fractions.

![Fig. 3](image-url)  
**Fig. 3** The schematic plot of possible configurations of \( A_1B_1A_2|B_2|_m \) tetrablock copolymer in \( G_A/C_A \) phases shown in (a) and (b), respectively.

To prove this, we draw the distribution of \( A_2 \)-block in the nanostructures formed in Fig. 4. The upper panel of Fig. 4 is the 2D distribution of \( A_2 \)-block and corresponding 1D density profile along y-direction of \( C_A \) nanostructure in \( A_1B_1A_2B_2 \) \( (m=1) \) polymers with \( f_{A_1}=0.33, 0.37 \) and 0.41, respectively. Interestingly, at a small \( A_1 \)-volume fraction, most \( A_2 \)-blocks stay at the A/B interface, while more \( A_2 \)-block mixed in the B-domains as \( f_{A_1} \) increases. That is in good accordance with the distribution in lamellar nanostructures. Note that the chain conformations are modified by the length ratio between \( A_1 \) and \( A_2 \)-blocks for total \( f_{A_2}=0.5 \), so the phase behaviors are modulated by the length of \( A_1/A_2 \) block. However, as \( m \) increases, more \( A_2 \)-blocks are in \( B \)-domain, which inevitably leads to the increase of stable phase regions of nanostructures with curvature, such as \( G_A \) and \( C_A \). In other words, as the branching \( B_2 \)-blocks \( (m=2, 3) \) fixed on the A/B interfaces, there will be a great loss of entropy compared with the linear architecture \( (m=1) \). Alternatively, the short \( A_2 \)-blocks will prefer to solubilize within the B-domains, which could get more configurational entropy to compensate for the penalty of interfacial energy. Furthermore, the effective volume fraction of A-component decreased relative to its intrinsic volume fraction, while the effective volume fraction of B-component is increased alternatively. So there will be a spontaneous curvature interface between A- and B-blocks, even though the intrinsic volume fraction of A-component equals B-component. These results tell us that branched architecture favors phases with high curvature \( (\text{i.e., cylinder and sphere}) \), leading to the shift of phase boundary towards nanostructure with low curvature, such as lamellae and gyroid. As a result, the phase region of sphere will expand, while the lamellar phase region decreases, which results in the large LS phase regime and small lamellar phase regime. Meanwhile, these results show that the \( A_2 \)-blocks undergo a notable transition both for \( m=1 \) and 2, i.e., the \( A_2 \)-blocks separated from the \( A \)-domain and aggregated in the \( B \)-domain as \( f_{A_1} \) increases. Therefore, the domain spacing of the \( C_A \) phase is expanded as the solubilization effect occurs, which has been reported in previous work.

**Phase Diagrams with Different Numbers of Branching of \( B_2 \)-block**

The above results show that branched architecture favors phases with high curvature \( (\text{i.e., cylinder and sphere}) \), leading to the shift of phase boundary towards nanostructure with low curvature, such as lamellae and gyroid. Therefore, the phase region of the sphere will expand, while the lamellar phase region decreases, resulting in the large LS phase region and small lamellar phase region. However, the phase region of the gyroid and cylinder changes depending on these two factors. On one hand, the gyroid nanostructure expands towards lamellae, on the other hand, phase cylindrical morphology moves to gyroid. The competition between these two factors leads to the corresponding phase region of these formed nanostructures.

To demonstrate the influence of \( m \) on the corresponding phase region, we calculate the free energy of different phases (Fig. 5) and determine the corresponding phase transition points at fixed \( \chi_N=90 \) in Fig. 6.

Interestingly, the phase boundary between L and \( G_A \), shifts from \( f_{A_1}=0.34 \) \( (m=1) \) to \( f_{A_1}=0.314 \) \( (m=2) \) and \( f_{A_1}=0.304 \) \( (m=3) \) for \( \chi_N=90 \). This shifted phase boundary results in the shrinks of gyroid region and the expansion of cylindrical phase region. At \( \chi_N=90 \), the stability regions of gyroid structure are \( f_{A_1}=0.032 \) \( (m=1) \), \( f_{A_1}=0.022 \) \( (m=2) \) and \( f_{A_1}=0.018 \) \( (m=3) \), while the stability regions of cylinder structure expand from \( f_{A_1}=0.049 \) \( (m=1) \) to \( f_{A_1}=0.057 \) \( (m=2) \) and \( f_{A_1}=0.062 \) \( (m=3) \), respectively. The phase diagram changes noticeably from \( m=1 \) to \( m=2 \) due to the influence of polymer topology (from linear polymer to branched polymer), while the phase transition lines shift slightly from \( m=2 \) to \( m=3 \). These results are consistent with those of expanding spherical phase by using branched polymer.

Encouragingly, the phase region of LS is notably enlarged for \( f_{A_1}=0.029 \) \( (m=2) \) and \( f_{A_1}=0.031 \) \( (m=3) \) compared with that for \( f_{A_1}=0.01 \) \( (m=1) \) for linear molecule. The phase region of LS is significantly expanded to nearly three times for \( \chi_N=90 \). To understand the expansion of LS nanostructure, we depict the chain arrangement of linear and branched polymers in Fig. 7, where the loss of conformational entropy from L to LS and L’ transition in a linear polymer is less than that transition in the branched polymer. On the other hand, due to the highly asymmetric stretching degrees between \( A_2 \)- and \( B_2 \)-blocks in branched polymer, the \( B_2 \)-blocks will have a large tendency to form the spontaneous curvature towards the \( A_2 \)-block. Therefore, the LS is more energy favorable rather than L’ to reduce the interfacial energy. Consequently, the \( A_1B_1A_2|B_2|_m \) bran-
hed tetrablock copolymer favors the formation of L’ or LS rather than L. However, the phase region of LS only increases slightly as \( m \) increases from 2 to 3 since the block length of each \( B_2 \)-decreases as \( m \) increases,\(^{10} \) signifying that there is a limit to increase the phase region by increasing the number of branches.

In addition, we find the threshold \( \chi_N \) to form LS nanostructure from linear \( A_1B_1A_2B_2 \) tetrablock is 74. To investigate the influence of branched arms on the formation of LS nanostructure, we decrease the \( \chi_N \) to 70. Notably, we find that LS is still stable at \( \chi_N = 70 \) for \( m = 2 \) and \( f_{A1} = 0.26 \) as shown in Fig. 8, signifying the propensity of LS nanostructures for branched polymers in this condition. To fully understand the stability regime of these nanostructures, it is necessary to calculate the full phase diagram with respect to the volume fraction of \( A_1 \)-block and \( \chi_N \) for different \( m \).

For \( f_{B1} = 0.5 \), the phase behavior of the \( A_1B_2A_2(B_2)_m \) branched tetrablock copolymer is controlled by \( \chi_N, f_{A1}, f_{B1} \) and \( m \). To investigate the influence of the number of branches on the stability of these nanostructures, we calculate phase diagrams of \( A_1B_2A_2(B_2)_m \) tetrablocks with respect to \( f_{A1} \) and \( \chi_N \) for \( m = 2 \) and 3 with fixed \( f_{B1} = 0.26 \) in Fig. 9. For

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Fig. 4 Two dimensional density distribution of \( A_2 \)-block and corresponding one-dimensional density profile of \( A_2 \)-, \( A \)- and \( B \)-blocks along the \( y \)-direction in \( C_A \) phase for \( m = 1 \) and 2 with fixed \( \chi_N = 50 \) and \( L_x = 0 \) at three different \( A_1 \) volume fractions \( f_{A1} = 0.33, 0.37 \) and 0.41 shown in (a), (b), (c), (d), (e) and (f), respectively. The red solid line, red dotted line and blue dotted line represent the density distribution of \( A_2, A \) and \( B \) monomers, respectively.
comparison, the phase diagram of linear tetramblock copolymer (m=1, f_{B1}=0.25) is reproduced from previous work and listed in Fig. 9(a).[6]

From the phase diagrams of Fig. 9, the topologies of the phase diagrams of m=2 and 3 are the same with m=1, however, with shifted phase boundary to the small A_{1}-block volume fraction.[6] The phase diagram changes noticeably from m=1 to m=2 due to the influence of polymer topology (from linear polymer to branched polymer), while the phase transition lines shift slightly from m=2 to 3, as shown in Fig. 10. These results are consistent with those of expanding the spherical phase by using branched polymer.[22] At the same time, the threshold value to form LS decreases from χ_{N}=74 (m=1, f_{B1}=0.25) to χ_{N}=61.5 (m=2, f_{B1}=0.26) and 63 (m=3, f_{B1}=0.26), respectively, which means that the branching B_{2}-blocks facilitate the observation of LS in the experiment. The markedly wide regime of LS is evidenced by the free energy comparison shown in Fig. 5.

**Influence of Number of Branches on the Domain Spacings of LS Phase**

To understand the influence of polymer architecture on LS nanostructure, we calculate the diameter of spherical domain as well as the periods of L_{x} and L_{y} directions of LS phase in Fig. 11. Interestingly, the diameter of the sphere formed by A_{2}-blocks within the B-domain decreases as m increases for fixed f_{A1}, which is shown in Fig. 11(a). This is because that each B_{2}-block in the branched molecule has to be strongly stretched if the spherical domain formed from A_{2}-blocks is equal for linear and branched molecules. In order to decrease the excessive...
stretching of B2-block, the diameter of spherical domain formed from A2-blocks has to decrease to release this extra stretching. In addition, the diameter of sphere decreases as fA1 increases, which is in good accordance with the change of the length of A2-block. On the other hand, the periods at x- and y-axis decrease as m increases for fixed fA1, indicating that the branched architectures prefer to form the small nanostructures to avoid excessive stretching of the blocks, compared with linear architecture. Therefore, our results show that not only the stability region but also the domain spacings of the LS nanostructures can be modulated from the branched multiblock copolymers.

Fig. 9  The phase diagram of A1B1A2(B2)m in the fA1\chiN plane with fixed fA2=fB=0.5 and m=1 for fB1=0.25, m=2 for fB1 = 0.26 and m=3 for fB1=0.26 in (a), (b) and (c), respectively. The phase diagram of m=1 is reported in the previous work (Reproduced with permission from Ref. [6]; Copyright (2018) American chemical Society).

Fig. 10  The stability regime of LS phase for m=1 (fB1=0.25), 2 (fB1=0.26) and 3 (fB1=0.26), in black, red and blue closed regions, respectively.

Fig. 11 (a). The diameter of each sphere formed by A2-blocks formed with 8-domain in LS; (b) The domain spacing of LS, the black and red lines represent the periods of x and y directions, respectively.

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CONCLUSIONS

In this study, we systematically studied the self-assembly of branching A₃B₂A₃B₂ₙ tetrablock copolymer with symmetric overall volume fraction \(f_m = f_b\) focusing on the impacts of branching \(B_2\)-blocks on the formation of LS phase and corresponding order-order transitions. First, we investigate the influence of branched arms \(m\) on the chain arrangement in the formed nanostructures. For the lamellar structures, we find more \(A_3\)-blocks tend to aggregate in the B-domain for branched polymer \((m=2)\), resulting in the formation of \(L_\alpha\) nanostructures at large \(m\). Then we explore the function of \(m\) on the phase transition sequence, where wider phase regions of LS are observed at larger \(m\). These results show that branched architecture favors phases with high curvature (i.e., cylinder and sphere), leading to the shift of phase boundary towards nanostructure with low curvature, such as lamellae and gyroid.

As a result, the phase region of the sphere expands, while the lamellar phase region decreases. Finally, we examine the impact of the branching number \(m\) of \(B_2\)-block on the stable region of LS in the phase diagram with respect to \(f_B\) and \(\chi_N\) for fixed \(f_m = 0.5\) and \(f_B = 0.26\). We find that the LS region is significantly expanded in \(m=2\) compared with that of the linear polymer \((m=1)\). While in the branched polymer, the stability region of LS changes slightly from \(m=2\) to \(m=3\). In addition, the threshold value of forming the LS decreases from \(\chi_N = 74\) \((m=1)\), \(f_m = 0.25\) to \(61.5\) \((m=2)\), \(f_m = 0.26\) and \(63\) \((m=3)\), \(f_m = 0.26\), respectively. Therefore, our results can provide an effective method for obtaining the hybrid nanostructure and are helpful to fully understand the formation mechanism of these nanostructures.

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REFERENCES

1. Bates, C. M.; Bates, F. S. 50th Anniversary perspective: block polymers pure potential. *Macromolecules* **2017**, *30*, 3–22.
2. Darling, S. B. Directing the self-assembly of block copolymers. *Prog. Polym. Sci.* **2007**, *32*, 1152–1204.
3. Bates, F. S.; Hillmyer, M. A.; Lodge, T. P.; Bates, C. M.; Delaney, K. T.; Fredrickson, G. H. Multiblock polymers: Panacea or Pandora’s box? *Science* **2012**, *336*, 434–440.
4. Li, W. H.; Muller, M. Defects in the self-assembly of block copolymers and their relevance for directed self-assembly. *Annu. Rev. Chem. Biomol. Eng.* **2015**, *6*, 187–216.
5. Zhang, J. Y.; Li, T. Q.; Mannion, A. M.; Schneiderman, D. K.; Hillmyer, M. A.; Bates, F. S. Tough and sustainable graft block copolymer thermoplastics. *ACS Macro Lett.* **2016**, *5*, 407–412.
6. Zhao, B.; Jiang, W. B.; Chen, L.; Li, W. H.; Qiu, F.; Shi, A. C. Emergence and stability of a hybrid lamella–sphere structure from linear ABAB tetrablock copolymers. *ACS Macro Lett.* **2018**, *7*, 95–99.
7. Aryal, D.; Howard, M. P.; Samanta, R.; Antoine, S.; Segalman, R.; Truskett, T. M.; Ganesan, V. Influence of pore morphology on the diffusion of water in triblock copolymer membranes. *J. Chem. Phys.* **2020**, *152*, 014904.
8. Lee, S.; Blueneme, M. J.; Bates, F. S. Discovery of a Frank-Kasper \(\sigma\) phase in sphere-forming block copolymer melts. *Science* **2010**, *330*, 349–353.
9. Lee, S. W.; Leighton, C.; Bates, F. S. Sphericity and symmetry breaking in the formation of Frank-Kasper phases from one component materials. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *111*, 17723–17731.
10. Xie, N.; Li, W. H.; Qiu, F.; Shi, A. C. \(\sigma\) Phase formed in conformationally asymmetric AB-type block copolymers. *ACS Macro Lett.* **2014**, *3*, 906–910.
11. Xie, N.; Liu, M. J.; Deng, H. L.; Li, W. H.; Qiu, F.; Shi, A. C. Macromolecular metallurgy of binary mesocrystals via designed multiblock terpolymers. *J. Am. Chem. Soc.* **2014**, *136*, 2974–2977.
12. Ahn, S.; Kim, J. K.; Zhao, B.; Duan, C.; Li, W. H. Morphology transitions of linear \(A_3B_2A_3B_2\) tetrablock copolymers at symmetric overall volume fraction. *Macromolecules* **2018**, *51*, 4415–4421.
13. Ahn, S.; Seo, Y.; Kim, J. K.; Duan, C.; Zhang, L. X.; Li, W. H. Cylindrical to lamellar microdomain transition upon heating for a linear tetrablock copolymer with upper critical ordering transition. *Macromolecules* **2019**, *52*, 9039–9044.
14. Gao, Y.; Deng, H. L.; Li, W. H.; Qiu, F.; Shi, A. C. Formation of nonclassical ordered phases of AB-type multiamorph block copolymers. *Phys. Rev. Lett.* **2016**, *116*, 068304.
15. Chen, L.; Qiang, Y. C.; Li, W. H. Tuning arm architecture leads to unusual phase behaviors in a (BAB)_3 star copolymer melt. *Macromolecules* **2018**, *51*, 9890–9900.
16. Jiang, W. B.; Qiang, Y. C.; Li, W. H.; Qiu, F.; Shi, A. C. Effects of chain topology on the self-assembly of AB-type block copolymers. *Macromolecules* **2018**, *51*, 1529–1538.
17. Xu, Y. C.; Hu, W. G. Formation of multicontinuous 3D network nanostructures with increased complexity in ABC-type block copolymers. *Langmuir* **2020**, *36*, 11324–11331.
18. Xie, Q.; Qiang, Y. C.; Li, W. H. Regulate the stability of gyroids of ABC-type multiblock copolymers by controlling the packing frustration. *ACS Macro Lett.* **2020**, *9*, 278–283.
19. Xie, Q.; Qiang, Y. C.; Chen, L.; Xia, Y. M.; Li, W. H. Synergistic effect of stretched bridging block and released packing frustration leads to exotic nanostructures. *ACS Macro Lett.* **2020**, *9*, 980–984.
20. Li, W. H.; Duan, C.; Shi, A. C. Non-classical spherical packing phases self-assembled from AB-type block copolymers. *ACS Macro Lett.* **2017**, *6*, 1257–1262.
21. Liu, M. J.; Qiang, Y. C.; Li, W. H.; Qiu, F.; Shi, A. C. Stabilizing the Frank-Kasper phases via binary blends of AB diblock copolymers. *ACS Macro Lett.* **2016**, *5*, 1167–1171.
22. Zhao, M. T.; Li, W. H. Laves phases formed in the binary blend of \(A_3B_2\) Miktoarm star copolymer and \(A\)-homopolymer. *Macromolecules* **2016**, *52*, 1832–1842.
23. Qiang, Y. C.; Li, W. H.; Shi, A. C. Stabilizing phases of block copolymers with gigantic spheres via designed chain architectures. *ACS Macro Lett.* **2020**, *9*, 668–673.
24. Tzeremes, G.; Rasmussen, K. Ø.; Lookman, T.; Saxena, A. Efficient computation of the structural phase behavior of block copolymers. *Phys. Rev. E* **2002**, *65*, 041806.
25. Rasmussen, K. Ø.; Kalsakas, G. Improved numerical algorithm for exploring block copolymer mesophases. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 1777–1783.
26. Thompson, R.; Rasmuse, K.; Lookman, T. Improved convergence in block copolymer self-consistent field theory by Anderson.
mixing. *J. Chem. Phys.* 2004, 120, 31–34.

27 Shi, A. C. *Developments in block copolymer science and technology*, John Wiley & Sons, Ltd., Hamilton, 2004, p. 265–293.

28 Fredrickson, G. H. *The equilibrium theory of inhomogeneous polymers*, Oxford University Press, New York, 2006.

29 Leibler, L. Theory of microphase separation in block copolymers. *Macromolecules* 1980, 13, 1602–1617.

30 Matsen, M. W.; Schick, M. Stable and unstable phases of a diblock copolymer melt. *Phys. Rev. Lett.* 1994, 72, 2660–2663.

31 Matsen, M. W.; Bates, F. S. Unifying weak- and strong-segregation block copolymer theories. *Macromolecules*, 1996, 29, 1091–1098.

32 Matsen, M. W. The standard Gaussian model for block copolymer melts. *J. Phys.: Condens. Matter* 2002, 14, R21–R47.

33 Matsen, M. W. Equilibrium behavior of asymmetric ABA triblock copolymer melts. *J. Chem. Phys.* 2000, 113, 5539–5544.

34 Matsen, M. W. Effect of architecture on the phase behavior of AB-type block copolymer melts. *Macromolecules* 2012, 45, 2161–2165.

35 Grason, G. M.; Kamien R. D. Interfaces in diblocks: a study of Miktoarm star copolymers. *Macromolecules* 2004, 37, 7371–7380.

36 Arora, A.; Qin, J.; Morse, D. C.; Delaney, K. T.; Glenn, H.; Bates, F. S. and Dorfman K. D. Broadly accessible SCFT for block polymer materials discovery. *Macromolecules* 2016, 49, 4675–4690.

37 Watanabe, M.; Asai, Y.; Takano, A.; Matsushita, Y. Preparation and morphologies of AB₈ block-graft copolymers. *J. Polym. Sci., Part B: Polym. Phys.* 2019, 57, 952–960.

38 Li, W.; Delaney, K. T.; Fredrickson, G. H. Fddd network phase in ABA triblock copolymer melts. *J. Polym. Sci., Part B: Polym. Phys.* 2016, 54, 1112–1117.

39 Tyler, C. A.; Morse, D. C. Orthorhombic Fddd network in triblock and diblock copolymer melts. *Phys. Rev. Lett.* 2005, 94, 208302.

40 Sakurai, S.; Shirouchi, K.; Munakata, S.; Kurimura, H.; Suzuki, S.; Watanabe, J.; Oda, T.; Shimizu, N.; Tanida, K.; Yamamoto, K. Morphology reentry with a change in degree of chain asymmetry in neat asymmetric linear A,B₂₅ triblock copolymers. *Macromolecules* 2017, 50, 8647–8657.

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