

Stabilizing Phases of Block Copolymers with Gigantic Spheres via Designed Chain Architectures

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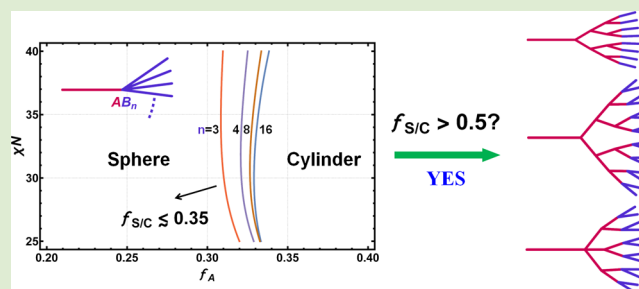


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Supporting Information

ABSTRACT: It is generally believed that the spherical domains self-assembled from AB-type block copolymers are composed of the minority A blocks with a volume fraction of $f_A < 1/2$. Breaking this generic rule so that the spherical domains are formed by the majority A blocks ($f_A > 1/2$) requires mechanisms to drastically expand the stable region of spherical packing phases. Self-consistent field theory predicts that dendron-like AB-type block copolymers, composed of $G - 1$ generations of A blocks connected with the outermost generation of B blocks, exhibit a stable region of spherical packing phases extending to $f_A \sim 0.7$. The extremely expanded spherical regions shed light on the mechanisms governing the self-assembly of amphiphilic macromolecules, as well as provide opportunities to engineer complex spherical



Self-assembly is a ubiquitous phenomenon in soft matter in general and in block copolymers in particular. The rich phase behavior of block copolymers with controlled molecular architectures and composition provides a paradigm system to study the emergent order in condensed matter, as well as a facile route to engineer nanoscopically structured materials.

Based on experimental and theoretical studies in the past decades, the general self-assembly mechanism of block copolymers has been established.^{1,2} Usually, AB-type block copolymers exhibit a robust phase sequence from disorder to sphere, cylinder, gyroid, and lamella when their composition increases from asymmetric to symmetric.^{3,4} Recently, much attention has been paid to the possibility of designing the architecture of block copolymers to obtain novel and even unconventional ordered phases.^{5–9} However, an understanding of the mechanisms for the formation of complex ordered phases is far from being complete, which restricts the engineering of novel structured materials and thus the applications of block copolymers. One challenge in the engineering of novel ordered phases is to shift the composition of ordered phases drastically,^{5,6,10–12} e.g., obtaining unusually large polymeric domains.

Among the ordered phases of block copolymers, the spherical packing phases are unique and important. On one hand, the spherical domains could be regarded as artificial atoms, and thus their packing is helpful for understanding the emergence of different crystalline orders.^{7,13} On the other hand, spherical packing phases as typical mesocrystals exhibit potential applications in many fields.^{14–18} Recently, the

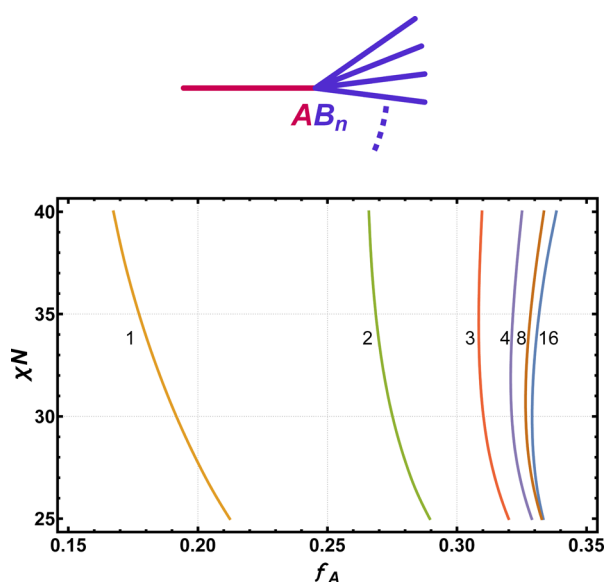
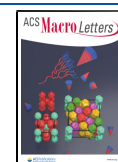


Figure 1. BCC/ C_6 phase boundaries at the f_A - χN plane for AB_n copolymers with different values of n , determined by the spectral method of SCFT.

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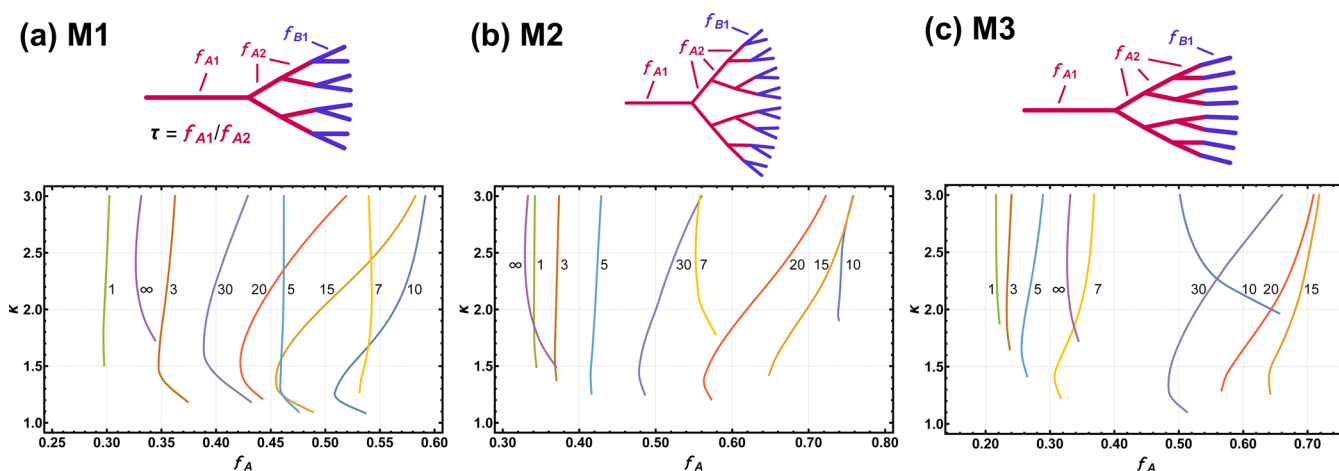


Figure 2. BCC/ C_6 phase boundaries at the f_A - κ plane for three different dendron-like copolymers with different values of $\tau = f_{A1}/f_{A2}$: (a) M1, (b) M2, and (c) M3, where $\kappa = \chi N / \chi N_{ODT,Min}$.

formation of spherical phases in AB-type block copolymers has attracted renewed interest, largely due to the experimental discovery of the complex Frank–Kasper (FK) σ phase self-assembled from diblock copolymers.¹³ The complex FK phases, whose crystallographic counterparts were originally observed in metallic alloys,¹⁹ were also widely observed in a number of amphiphilic molecules.^{20,21} Because of their availability and flexibility, block copolymer melts provide an ideal model system for studying the emergence and stability of the FK phases.^{5,6,9,22–34} Furthermore, the study of block copolymers opens the door to discover new FK phases^{9,22,24,29} as well as to obtain a deeper understanding of the mechanisms for the formation of complex spherical packing phases via the synergistic interplay between experiment and theory.^{23,25,26,32,35} For instance, experimental and self-consistent field theory (SCFT) studies have revealed that the FK σ and A15 phases could be stabilized by expanding the spherical region due to their favorable interfacial energy in contrast to the classical body-centered-cubic (BCC) phase.^{5,6,13,23} Nevertheless, how to expand the stability region of these spherical phases drastically presents a big challenge. Therefore, we focus on exploring a new mechanism for the design of architecture of block copolymers to expand the spherical region. It is noted that the composition of other ordered phases would be concomitantly shifted by the expansion of the spherical region.

It is generally believed that the spherical domains self-assembled from AB-type block copolymers are composed of the minority A blocks with a volume fraction of $f_A < 0.5$. For AB diblock copolymers of asymmetric composition, the AB interface acquires a nonzero spontaneous curvature as a result of minimizing the entropy loss by relaxing the majority block while stretching the minority block. Therefore, in order to obtain large spherical domains, it is important to regulate the chain stretching and the interfacial curvature at the same time. One simple but efficient route to increase the spontaneous curvature is to introduce architectural asymmetry,^{5,6,36–38} e.g., branching one B block into n shorter blocks to form AB_n copolymers.

For the case of AB_n , the increased stretching of the shorter B blocks would induce a larger spontaneous curvature toward the A domain, resulting in a larger stable region of the spherical phase.³⁹ Indeed, SCFT has demonstrated that the spherical region gradually expands as the arm number n increases.^{23,37}

For simplicity, we estimate the sphere/cylinder boundary $f_{S/C}$ of AB_n by considering the classical BCC and hexagonal cylinder (C_6) phases,⁴⁰ using the highly efficient spectral method of SCFT.^{3,41} The details of the spectral method and SCFT are provided in the Supporting Information. Figure 1 presents the results of $f_{S/C}$ for different values of n , which approaches a limit of $f_{S/C} \sim 0.35$ as $n \rightarrow \infty$ in the intermediate-segregation regime of $25 \leq \chi N \leq 40$, where χ is the Flory–Huggins parameter and N is the number of total segments of the copolymer. In principle, the discrepancy of stretching degrees between the A and B blocks increases continuously as n increases, which should increase the tendency of forming curvature toward the A domain or expand the phase region of A spheres. On the other hand, short B blocks reduce the size of the B domain that, in turn, forces the size of the A domain to decrease. When the A domain continuously decreases as n increases, the conformation of the long A block transfers from stretched to compressed at about $n = 3$ (Figure S1). Large compression results in a severe entropy loss. In contrast to the situation inside a sphere, the entropy loss of the A block inside a cylinder is smaller because the constraint can be released along the axial direction. The conclusion from this simple example is that extreme stretching of B blocks and compression of the A block prevent a larger spherical region.

Based on the study of the AB_n copolymers, it could be concluded that expanding the spherical region further requires mechanisms to manipulate the interfacial curvature and, at the same time, regulate the chain packing or stretching. This task could be achieved by a number of routes. One possibility is the tailored dispersity of the A blocks as demonstrated by the SCFT study of binary mixtures of AB diblock copolymers.^{9,42} Within one spherical domain, the longer A block is stretched to reach the central area, while the shorter A block is mainly located near the A/B interface, leading to a core–shell A domain. The core is mainly filled by the segments on the long A block, whereas the shell is filled by both long and short segments. The bidispersed A blocks favor distributing the segments to fill the growing volume along the radial direction better than a neat A block in AB diblock or AB_n copolymers. On the contrary, a neat A block generates a uniform segment distribution to fill the cone-shaped space within a sphere, and nonuniform stretching along the chain or among the different

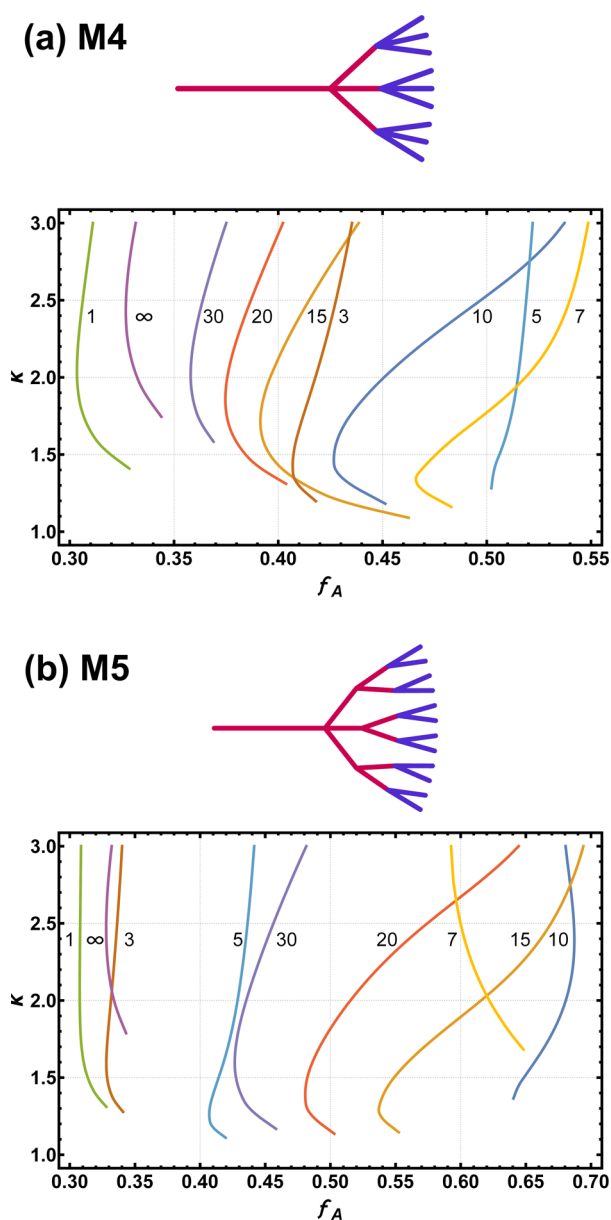


Figure 3. BCC/ C_6 phase boundaries at the f_A - κ plane for two different dendron-like copolymers: (a) M4 and (b) M5.

chains must be unavoidable, which results in an extra entropy loss in addition to stretching.

Another, perhaps more robust, route to expand the spherical region is to design polymer architectures, which is the focus of the current letter. Without loss of generality, we consider that the spherical domain is formed by the A blocks. According to the above arguments, the key point is to achieve a gradual radial distribution of A blocks, such that the compression of A blocks and the extreme stretching of B blocks are avoided as much as possible. The relief of the packing frustration amplifies the curvature effect, resulting in the enhanced stability of the spherical phase. In order to achieve a robust radial distribution of the A blocks, a dendron-like architecture is considered.^{6,20} Inspiringly, Cho et al. synthesized a type of third-generation amphiphilic dendron extended by a linear polymer chain and demonstrated that these dendritic macromolecules exhibited some unusual phase behaviors.⁶ In particular, they observed the spherical A15 and cylindrical phases at two large volume

fractions of $f = 0.41$ and 0.62 , respectively. Intuitively, this architecture could achieve the required distribution naturally. However, this intuitive guess needs to be validated, and the parameters need to be optimized. In the current study, the SCFT is used to validate the proposed design by calculating the BCC/ C_6 phase boundaries.

Specifically, the dendron-like AB-type block copolymer is composed of $G - 1$ inner generations of A blocks and one outermost generation of B blocks. It should be stressed that the dendron-like copolymer is significantly different from the linear-dendritic copolymer.^{36,38,43} First we consider a typical case where each block in the $(i - 1)^{\text{th}}$ generation is connected with two blocks in the i^{th} generation. The total number of A blocks is $2^{G-1} - 1$, and that of B blocks is 2^{G-1} . In principle, the radial distribution of A blocks could be regulated by tuning the relative lengths of the A blocks in each generation. To enable the copolymer to be reduced to AB_n and, at the same time, reduce the parameter space, we simply assume that only the length of A1 block f_{A1} is different from that of the others f_{A2} (i.e., $f_{A1} + (2^{G-1} - 2)f_{A2} \equiv f_A$) and specify their ratio as $\tau = f_{A1}/f_{A2}$. Obviously, the dendron-like copolymer is reduced to an AB_n copolymer with $n = 2^{G-1}$ arms when $\tau \rightarrow \infty$.

To demonstrate the role played by the parameter τ in controlling the self-assembly behavior, we present the BCC/ C_6 boundaries $f_{S/C}$ for $G = 4$ (denoted as M1) with different values of τ in Figure 2(a). As the segregation degree is sensitively dependent on τ , we rescale χN with $\chi N_{\text{ODT,Min}}$ which is the minimal order-disorder transition with respect to f_A , i.e., introducing $\kappa = \chi N / \chi N_{\text{ODT,Min}}$. For example, $\chi N_{\text{ODT,Min}}$ values for $\tau = 1, 3, 10, \text{ and } \infty$ are determined by random phase approximation (RPA)⁴⁴ and are 39.84, 40.49, 33.19, and 12.75, respectively. The values of $\chi N_{\text{ODT,Min}}$ of all considered copolymers as well as the corresponding values of f_A are listed in Table S1. Surprisingly, $f_{S/C}$ changes nonmonotonically as τ increases. There exists an optimal tail length, $\tau \approx 10$, at which the stability region of the spheres is the largest, i.e., $f_{S/C} > 0.55$ for $2 < \kappa < 3$. This result is in sharp contrast to $f_{S/C} < 0.35$ in AB_8 (i.e., $\tau = \infty$). The dendron-like architecture of M1 with the optimal long tail not only generates an ideal radial distribution of A blocks for filling a spherical space but also maintains the size asymmetry between A and B blocks in AB_n .

Intuitively, the cone shape of the dendron-like copolymer becomes more obtuse as its generations increase, tending to form A domains with a higher curvature. The BCC/ C_6 boundaries of the analogous dendron-like copolymer with $G = 5$ (denoted as M2) are shown in Figure 2(b). Similarly, the largest expansion of the spherical region occurs at $\tau \approx 10$; however, the largest region is remarkably larger than that of $G = 4$, i.e., $f_{S/C} > 0.7$ for $2 < \kappa < 3$. There are two main effects resulting from the increased generation. On the one hand, more generations of A blocks favors optimizing the radial distribution of A blocks inside the A domain. On the other hand, the increased number of B blocks from 8 to 16 drastically increases the obtuseness of cone shape of the molecule.

To examine the effect of the number of B blocks alone, we replace the branched B blocks connected with each A block in the outermost generation with a single B block in M2. Thus, the number of B blocks is reduced from 16 to 8, while the architecture of A blocks is the same as M2 (denoted as M3). The results of $f_{S/C}$ are presented in Figure 2(c). The largest spherical region is achieved at $\tau \approx 15$, $0.68 < f_{S/C} < 0.71$ for $2 < \kappa < 3$, which is noticeably smaller than that of M2 in Figure 2(b). This result confirms the role of the number of B blocks.

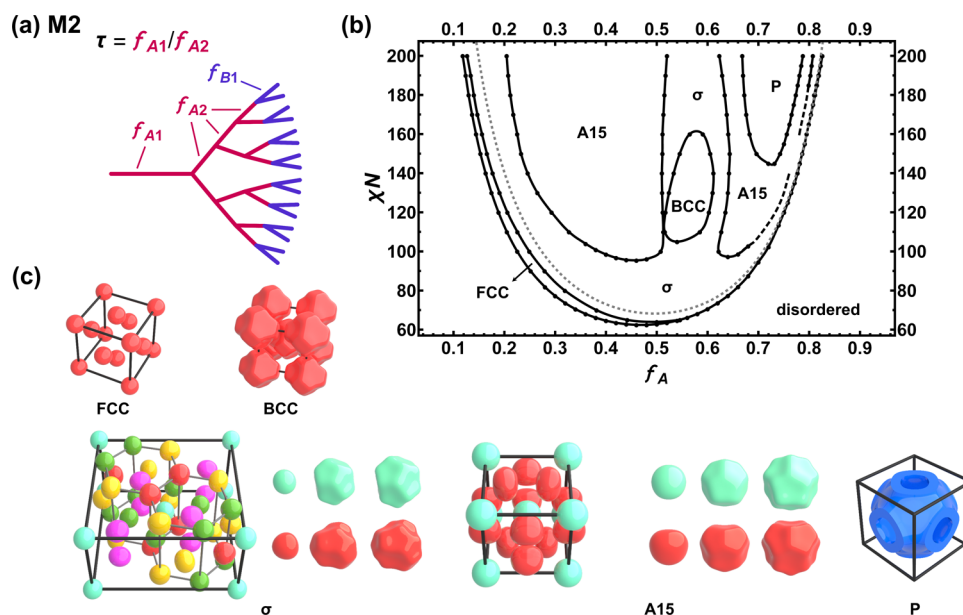


Figure 4. (a) Considered dendron-like copolymer ($G = 5$). (b) Phase diagram for $\tau = 10$. (c) Isosurface plots of different structures at their respective stability points along the path of $\chi N = 150$: FCC ($f_A = 0.16$), BCC ($f_A = 0.58$), σ ($f_A = 0.18$), A15 ($f_A = 0.26$), and P ($f_A = 0.72$). The smallest (top row) and largest (bottom row) domains of σ for $f_A = 0.18, 0.52$, and 0.62 (from left to right columns) and the two different domains of A15 for $f_A = 0.26, 0.48$, and 0.66 , are plotted, respectively.

Moreover, the largest spherical region in Figure 2(c) is considerably larger than that in Figure 2(a), which indicates that the architecture of A blocks provides the most critical effect on the spontaneous curvature. It should be noted that the optimal $\tau \approx 15$ in Figure 2(c) is larger than $\tau \approx 10$ in Figure 2(b) because the B blocks in M3 are longer than those in M2 and thus match the larger coil size of A blocks. In fact, the molecule M3 is similar to that studied in the experiment by Cho et al.⁶ The values of τ of the two experimental samples, about 30 and 90, deviate from the optimal value of about $\tau \approx 15$ for the largest spherical region.

Obviously, various architectures could be designed for the dendron-like copolymer, e.g. by replacing the double-branched junctions by triple-branched ones. In Figure 3(a) and (b), we consider the phase behavior of two more molecules. The first copolymer is a triple-branched dendron-like copolymer with $G = 3$ (denoted as M4), while the second one is a fourth-generation dendron consisting of three branches in the second generation and two branches in the rest (denoted as M5). The largest spherical region of M4 is even smaller than that of M1, although its number of B blocks (i.e., 9) is larger than 8 of M1. The reduction of the spherical region solely results from the decreased generations of A blocks. The value of $0.68 < f_{S/C} < 0.69$ in Figure 3(b) of M5 is only slightly narrower than that of M3 but notably narrower than that of M2. This is because M5 has more B blocks (i.e., 12) than M3 (i.e., 8) but less generations of A blocks, whereas it has less B blocks as well as less generations of A blocks than M2.

To confirm the expansion of the spherical region more quantitatively and, more interestingly, to validate the idea that the expanded spherical region provides opportunities to form complex spherical packing phases, we construct a relatively complete phase diagram at the f_A - χN plane for M2 with $\tau = 10$ by considering a large number of candidate ordered phases (listed in Figure S2) using the second-order pseudospectral method.⁴⁵ The candidate phases include the classical phases and some unconventional phases. Note that the accuracy of the

phase boundaries is confirmed using the fourth-order algorithm (Figure S3). The phase diagram in Figure 4 confirms the extremely expanded spherical region with $f_{S/C} > 0.7$. In fact, the whole region of ordered phases is covered by various spherical packing phases, except for the upper-right corner occupied by the Plumber nightmare phase (P) that is rarely observed in neat AB-type block copolymers.⁴⁶ Such a large spherical region leads to many interesting features, and the two most remarkable ones are the vanishing of the classical phases (e.g., C_6 , G, and L) and the multiple reentrant transitions of $FCC \rightarrow \sigma \rightarrow A15 \rightarrow \sigma \rightarrow BCC \rightarrow \sigma \rightarrow A15$ between $106 \lesssim \chi N \lesssim 162$ that are evidenced by the free energy comparison in Figure S4(a). As f_A approaches the close-packing volume fraction of spheres, the domains must be deformed severely to avoid the contact with each other, resulting in not only nonsphericity but also a concave surface in Figure 4(c).³⁷ In fact, the surface changes from convex to concave are one of the main effects accounting for the reentrant transitions. Moreover, the A domains could even become connected at the vicinity of order-disorder boundary with $f_A > 0.7$, resulting in the possible formation of many exotic structures (Figure S4(b)).

In summary, the current work breaks the generic rule that the spherical domains are composed of the minority A blocks of AB-type block copolymers. It is discovered that a gradual radial distribution of A blocks is a key factor for stabilizing gigantic spheres, as validated by the various designed dendron-like copolymers. The mechanism of stabilizing gigantic spherical phases is that the dendron-like topology of the block copolymers alleviates the packing frustration, thus amplifying the effect of the spontaneous interfacial curvature. As a result of this mechanism, all designed copolymers with optimized architectures exhibit an extremely expanded spherical region with $f_{S/C} > 0.5$. In particular, the most overwhelming spherical region even approaches $f_{S/C} \sim 0.7$. Very recently, we noticed that Lequieu et al. predicted a largely expanded spherical region in multiarm AB-type block

copolymers.⁴⁷ In fact, our mechanism of amplifying the effect of the spontaneous curvature can be applied to rationalize their results. In addition, ten Brinke and co-workers obtained inverse spherical morphologies in a linear multiblock copolymer with two-length scale architecture,⁴⁸ where short A- and B-blocks are not significantly separated. As a result, the volume fraction of spherical domains is considerably lower than that of the corresponding blocks.

Although the SCFT calculations do not consider the finite length effect of polymers with low molecular weight and the excluded volume effect of crowding polymers, they should still be predictive.^{9,23,28,34,35} Therefore, the current work not only sheds light on the understanding of the mechanisms stabilizing spherical phases with gigantic polymeric domains but also provides a practical route to engineering such structured materials for various applications.⁶ Furthermore, the mechanisms and understanding developed in the current work could be applied to other soft matter systems such as amphiphilic liquid crystals and giant surfactants.^{20,21,49} In particular, a dendritic architecture has been utilized in the design of amphiphilic liquid crystals to obtain Frank–Kasper phases.²⁰ In contrast to flexible block copolymers, these rigid or semiflexible molecules exhibit stronger capability to transform the dendritic topology into the geometrical cone shape. As a result, the optimal ratios of molecular weights of these blocks at different generations should be quite different. It is expected that a single control parameter τ might not be enough for optimizing the architectures of these rigid or semiflexible self-assembly molecules.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00193>.

Self-consistent field theory, the spectral method, the pseudospectral method, Table S1, and Figures S1–S4 (PDF)

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Notes

The authors declare no competing financial interest.

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