Nonclassical Spherical Packing Phases Self-Assembled from AB-Type Block Copolymers

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ABSTRACT: Among the various ordered morphologies self-assembled from block copolymers, the spherical packing phases are particularly interesting because they resemble the familiar atomic crystals. The commonly observed spherical morphology of block copolymers is the body-centered-cubic phase. Recently, a number of novel spherical packing phases, i.e., the complex Frank−Kasper phases originally obtained in metallic alloys, have been observed in block copolymer melts. Theoretical studies have revealed that conformational asymmetry of the different blocks provides a key mechanism to stabilize the Frank−Kasper phases. Furthermore, local

segregation of different copolymers in blends of diblock copolymers and copolymer architectures provides additional mechanisms to enhance the stability of the complex ordered phases. In this Viewpoint we summarize recent advances in our understanding of the formation of the nonclassical spherical packing phases in AB-type block copolymers, emphasizing the formation mechanisms of these fascinating complex ordered structures.
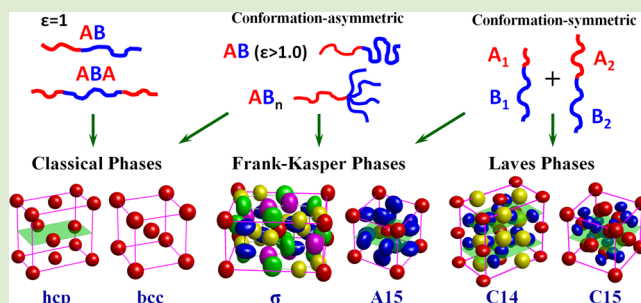
B lock copolymers (BCPs) are known to self-assemble into a rich array of ordered morphologies at the mesoscale.[1−3] Besides potential applications in a wide range of fields,[4−6] the self-assembly of block copolymers provides a model system for the study and understanding of phases and phase transitions in soft condensed matter systems. The simplest block copolymer is an AB diblock copolymer composed of A- and B-blocks covalently linked at their ends. The phase behavior of AB diblock copolymers is controlled by a set of molecular parameters including the Kuhn lengths of the two blocks (b_A and b_B), the volume fractions of the blocks ($f_A = f$ and $f_B = 1 - f$), and the interaction strength χN where N denotes the total number of segments and χ is the Flory−Huggins interaction parameter characterizing the immiscibility of the A and B monomers.[7] Extensive experimental and theoretical studies have established that AB diblock copolymers exhibit an order-to-order phase transition sequence from hexagonally close-packed (hcp) spheres to body-centered cubic (bcc) spheres, hexagonal cylinders (C_{p6mm}), bicontinuous networks (gyroid or $Fddd$), and lamellae (L) as f increases from 0 to $\frac{1}{2}$.[8,9] This generic phase transition sequence is also observed in other AB-type block copolymers with more blocks and/or different architectures, such as ABA triblock, ABAB··· multiblock, and $(AB)_n$ star copolymers.[10]

Among the various ordered morphologies, the spherical packing phases of block copolymers are of particular interest because they resemble the familiar atomic crystals. The spherical packing phases of block copolymers could be regarded as macromolecular mesocrystals with lattice constant at the

10−100 nm range. The unique property of the macromolecular mesocrystals is that their "atoms" or the spherical domains are soft, and their lattice constant could be tuned by the molecular weight of the polymers. As such, the macromolecular mesocrystals provide a model system for the study of the packing problem of soft particles. The two limiting cases of the packing problem are the packing of hard spheres and equal-sized bubbles with well-known solutions given by the hcp and the Frank-Kasper A15 structures, respectively.[11,12] In contrast, the spherical domains in the BCP mesocrystals are deformable with a finite deformation energy. Therefore, the packing of BCP domains represents an intermediate case between the two extrema, leading to opportunities to form novel spherical packing phases[13] beyond the classical hcp and bcc structures (Figure 1).

Prior to 2010, it was believed that the spherical packing phases of AB diblock copolymers are dominated by the hcp and bcc structures. Direct experimental evidence of complex spherical packing phases beyond these classical phases was reported by Bates and co-workers, who have observed a stable Frank−Kasper σ phase in poly(isoprene-*b*-lactide) (IL) diblock copolymers and in the poly(isoprene-*b*-styrene)-*b*-isoprene-*b*-ethelene oxide (SISO) tetrablock copolymers.[14] Subsequent experimental studies[15−21] have firmly established the emergence of a number of nonclassical spherical packing phases, i.e.,
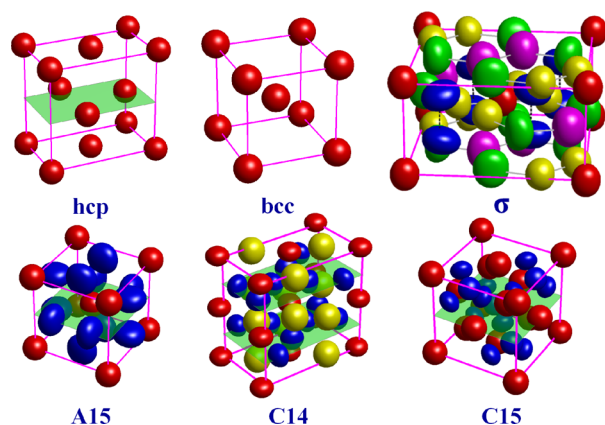
Figure 1. Isosurface plots of various spherical packing phases from the self-assembly of block copolymers, including the two classical phases (hcp and bcc), two Frank−Kasper phases (σ and A15), and two Laves phases (C14 and C15). For the complex spherical packing phases, nonequivalent domains are indicated by different colors.

the complex Frank−Kasper phases (σ, A15, C14, and C15), from the self-assembly of block copolymers (Figure 1). Moreover, the Frank−Kasper σ and A15 phases have been observed in a number of other soft matter systems including hyperbranched amphiphilic liquid crystals,[22,23] nanoparticle superlattices,[24,25] mesoporous silica,[26] giant tetrahedra,[27] and giant surfactants.[28]

Theoretically, the occurrence of complex spherical packing phases beyond the hcp and bcc structures in AB-type block copolymers was predicted by Grason et al.[29,30] Specifically, they showed that the Frank−Kasper A15 phase could become an equilibrium phase of hyperbranched and miktoarm star AB-type block copolymers. Recently, motivated by the experiments from Bates et al. and from early theoretical studies, Li and co-workers carried out extensive self-consistent field theory (SCFT) studies on the emergence and relative stability of various complex spherical packing phases in block copolymer systems.[31−33] In particular, their theoretical results revealed that conformational asymmetry of the different blocks provides a key factor to stabilize the complex spherical packing phases.[31] Furthermore, they predicted that local segregation of different copolymers in blends of diblock copolymers[32,33] and copolymer architectures[34,35] provides additional mechanisms to enhance the stability of these nonclassical complex ordered phases.

In this Viewpoint, we present a discussion on the mechanisms controlling the formation of the complex ordered phases self-assembled from AB-type block copolymers. We will focus primarily on the formation of nonclassical spherical packing phases and their two-dimensional analogues, i.e., cylindrical phases. We will emphasize recent theoretical results and demonstrate that the formation of these complex nonclassical ordered phases could be attributed to three factors, the conformational asymmetry between the different blocks, local segregation of the block copolymers, and the architecture of the block copolymers.

A generic feature of the complex spherical packing phases is that their unit cells contain more than one type of particle or minority domains. Different types of domains have different sizes and shapes. In particular, a unit cell of the Frank−Kasper σ-phase contains 30 domains of 5 types. In an insightful paper, Lee, Leighton, and Bates suggested that the formation of these complex spherical packing phases is dictated by a competition

between the need to uniformly fill the space and the tendency to maintain the spherical shape of the minority domains.[16] The presence of the crystalline lattice necessarily breaks the spherical symmetry of the minority domains. Therefore, these complex structures could be described as ordered phases with broken spherical symmetry of the minority domains. The geometric shape of the deformed polymeric domains follows the symmetry of the polyhedral shape of the Wigner−Seitz cells (WSCs).[16] In general, a WSC with more faces is rounder and thus requires less deformation to its enclosed domain. Quantitatively, the nonsphericity of the domains could be measured by the isoperimetric quotient (IQ), which is defined by $IQ = 36\pi V^2/S^3$, where V and S are the volume and area of the WSC. For a crystalline lattice consisting of more than one type of WSCs, such as the σ and A15 phases, the average value of IQ ($\overline{IQ}$) of all the WSCs could be used to quantify its average sphericity.[16]

For a cubic unit cell, the $\overline{IQ}$ is independent of the size of the cell. Specifically, the $\overline{IQ}$ of the various cubic phases is given by $\overline{IQ} = 0.7405$, 0.7534, and $0.7617(4)$ for fcc, bcc, and A15, respectively.[16,33] For noncubic unit cells, e.g., the Frank−Kasper σ phase, the $\overline{IQ}$ depends on the shape, i.e., the aspect ratio of the unit cells. For example, the Frank−Kasper σ phase, which was originally observed in metallic alloys composed of large and small atoms, has tetragonal symmetry whose unit cell has a nearly constant aspect ratio of 1.89 and an associated $\overline{IQ}_\sigma = 0.7617(0)$. According to these $\overline{IQ}$ values, the nonsphericity of fcc, bcc, σ, and A15 is in a descending order, whereas the two Frank−Kasper phases (σ and A15) have almost the same $\overline{IQ}$.

Intuitively, the shape of the minority domain is less influenced by the shape of its WSC when the polymeric domain is much smaller than the WSC. Conversely, the shape of larger polymeric domains would be strongly affected by the shape of its WSC, resulting in severely deformed domains resembling the WSC itself. The only avenue to reduce the domain deformation is to change the packing lattice to the one with rounder WSCs or larger $\overline{IQ}$. This argument provides a plausible mechanism to stabilize the nonclassical Frank−Kasper σ and A15 phases which have larger values of $\overline{IQ}$ than the classical fcc and bcc structures.[16] The simplest method to increase the domain size is by increasing the volume fraction of the minority blocks. However, it is well-known that the spherical packing phases have a limited stability region when the volume faction of the minority blocks is increased. Instead the cylindrical and lamellar phases would become stable ones.[8] From this argument, it could be concluded that the key factor for the formation of the nonclassical spherical packing phases is to enlarge the stability region of the spherical phases with large spherical domains. Besides the volume fraction of the minority blocks, one possible parameter to control the size of the minority domains is the conformational asymmetry of the A- and B-blocks.

The conformational asymmetry of the different blocks is characterized by the segment properties including the Kuhn length b_K and segment density ρ_K (K = A or B) and by the chain architecture (linear versus branched).[36] For a branched AB_m block copolymer ($m = 1$ corresponds to a linear diblock copolymer), its conformational asymmetry parameter is specified by $\epsilon^2 = m^2(\rho_A b_A^2/\rho_B b_B^2)$. In a previous theoretical study, Matsen showed that a large conformational asymmetry could lead to a larger stability region of the spherical phase.[37]

Furthermore, theoretical calculations of Grason et al. predicted a stability region of the A15 phase between the bcc and C_{p6mm} phases for branched AB_m block copolymers.[29,30] More recently, Xie et al. carried out detailed SCFT calculations for linear and branched AB_m-type block copolymers and examined the emergence and stability of the Frank−Kasper σ and A15 phases.[31] Their theoretical phase diagrams proved that conformational asymmetry of the block copolymers provides a general mechanism to enlarge the stable region of spherical packing phases. Specifically, when the conformational asymmetry parameter ϵ is large enough, both the Frank−Kasper σ and A15 phases emerge as equilibrium phases of the system. Furthermore, the theoretical results revealed a generic phase transition sequence, from fcc to bcc, to σ and A15, as the volume fraction or segregation strength is increased. This predicted phase transition sequence is in agreement with experimental observations from block copolymer systems as well as other self-assembling soft matter systems such as amphiphilic liquid crystals[23] and giant surfactants.[28]

Very recently, Bates and co-workers have purposely designed a series of model diblock copolymers with increasing conformational asymmetry: poly(ethylene-*alt*-propylene)-*b*-poly(lactide) (PEP-*b*-PLA) with ϵ = 1.06, PI-*b*-PLA with ϵ = 1.32, and poly(ethylethylene)-*b*-poly(lactide) (PEE-*b*-PLA) with ϵ = 1.68.[20] Their experimental phase diagrams showed that the Frank−Kasper σ phase only becomes stable for larger values of ϵ. Moreover, the stability region of the σ phase in the PEE-*b*-PLA sample is noticeably wider than that in the PI-*b*-PLA sample. These experimental results confirm the SCFT predictions, thus providing experimental evidence to support the proposed conformational asymmetry mechanism for the formation of nonclassical spherical packing phases of block copolymers.

As mentioned above, the most prominent feature of the complex spherical packing phases such as the Frank−Kasper σ phase is that their unit cells contain more than one type of atoms or particles with different sizes and shapes.[38,39] On the other hand, monodisperse block copolymers would prefer the formation of spherical minority domains of the same size. Transforming these uniformly sized spherical domains into nonspherical domains with different sizes involves the deformation of and chain exchange between them. Therefore, the formation of nonclassical spherical packing phases is associated with the free energy cost of changing the domain size and shape. Naturally the stability of the complex spherical packing phases will be enhanced by any mechanisms that could assist the formation of polymeric domains with different sizes and shapes. One such mechanism is the local segregation of different copolymers in a blend of block copolymers. In order to test this hypothesis, Liu et al. designed a binary blend composed of two AB diblock copolymers and examined the emergence and stability of the Frank−Kasper phases in this system.[33] In their model system, the first diblock copolymer self-assembles to form the classical bcc phases, whereas the chain length and block ratio of the second diblock copolymer are used as adjustable control parameters. A very surprising and extremely interesting result from the SCFT calculations of Liu et al. is that the complex Frank−Kasper phases are predicted to be stable in a very large region in the phase diagram of the binary blends.[33] This theoretical study confirms that local segregation of different block copolymers provides a new mechanism and an experimentally more accessible route to form nonclassical complex spherical packing phases.

Specifically, the model binary blend considered by Liu et al. is composed of two conformationally symmetric AB diblock copolymers with chain lengths $N_1 = N$ and $N_2 = \gamma N$, respectively. The A-volume fraction of the first diblock copolymer is chosen as $f_1 = 0.15$ such that its equilibrium phase is the bcc phase composed of minority A-domains. The phase behavior of this diblock copolymer blend is examined using the SCFT formulated in the grand-canonical ensemble. The phase diagram of the blend is plotted in the $\gamma-\phi_1$ plane, where ϕ_1 is the concentration of the first diblock copolymer in the blend. The theoretical phase diagrams reveal that, for a binary blend with $\chi N = 40$, $f_1 = 0.15$, and $N_{B,1} = N_{B,2} = 0.85N$, two Frank−Kasper phases (σ and A15) become equilibrium morphologies in a large window of $0.6 < \phi_1 < 0.9$ for $\gamma > 1.3$. These theoretical results indicate that new mechanisms beyond the conformational asymmetry must be present in the binary blends of diblock copolymers, enhancing the stability of the complex spherical packing phases.

The new mechanisms present in block copolymer blends are related to the local segregation of the different block copolymers. The theoretical results of the different ordered phases within the SCFT give the spatial distribution of the different blocks and different copolymers. These distributions provide direct evidence of local segregation of the block copolymers.[33] The segregation of long and short diblock copolymers among the different domains favors the formation of domains of different sizes, whereas the segregation of the different diblock copolymers within a domain favors the formation of domains of nonspherical shapes. Furthermore, the two minority blocks inside the minority domain are preferentially segregated along the radial direction to accommodate the short and long blocks inside the same domain, resulting in an effective "core−shell" structure. Compared with the domain size of the bcc phase formed by the pure short diblock copolymers, the size of the "core−shell" domain is drastically increased due to the swelling by the long copolymers. Therefore, the radial segregation of the short and long blocks has the same effect as conformational asymmetry that stabilizes larger minority domains, thus favoring the formation of complex spherical packing phases. Taken together, the synergetic action of these three effects of local segregation leads to the large stability region of the nonclassical spherical packing phases in the designed block copolymer blends.

It should be noted that no other Frank−Kasper phases beyond σ and A15 are included in the theoretical study of Liu et al.[33] The C14 and C15 phases, also referred to as the Laves phases, were observed in IL diblock copolymers in recent experiments by Bates and co-workers with a special thermal processing, composed of a sudden quench to a very low temperature followed by a heating process to a specific annealing temperature, of the samples.[19] Therefore, if the Laves phases that have more nonuniform domain sizes than the σ and A15 phases are considered as candidate phases by the SCFT calculations, they may be stabilized by the remarkable ability of the binary blend of diblock copolymers to regulate the distribution of domains sizes and shapes.

Besides having "atoms" or minority domains of different sizes and shapes, another important property of the different spherical packing phases is that different ordered phases have different coordination number (CN) or number of nearest neighbors of the lattice. Therefore, it is important to understand mechanisms controlling the CN of an ordered phase. One efficient method to regulate the CN of ordered

phases of block copolymers is to utilize the chain architecture of the copolymers. For example, for spherical packing phases self-assembled from multiblock and star-like block copolymers, a fraction of the polymer chains would necessarily assume bridging configurations linking different spherical domains. The length of the bridge-forming blocks could then be used as a control parameter to regulate the spacing between the bridged spherical domains, which in turn affects the CN of the structure. Therefore, the chain architecture provides a possible control parameter to regulate the formation of complex spherical packing phases of block copolymers.

One example of utilizing chain architecture to induce the formation of complex spherical packing phases is the theoretical study of binary mesocrystals from BABCB pentablock copolymers by Xie et al.[40] It is well-known that for ABC triblock copolymers the stable spherical packing phase is composed of alternating A and C spheres on a bcc lattice or the CsCl structure. Xie et al. demonstrated that changing the ABC triblock copolymer to BABCB pentablock copolymer resulted in an efficient mechanism to regulate the bridging distance via the length of the middle B-blocks that connect a pair of neighboring A and C domains. A smaller spacing between the A and C domains favors the lattice structures with lower CNs. As a result of this mechanism, Xie et al. showed that a large number of binary mesocrystals could be formed from BABCB pentablock copolymers.[40] An interesting question is whether the adjustable bridge mechanism via chain architecture could be generalized to AB-type multiblock copolymers.

One possibility to regulate the bridging faction of block copolymers is provided by star-like block copolymers.[41,42] It is well-known that linear ABA triblock copolymers could adopt bridging or looping configurations in the lamellar morphology [Figure 2(a)] with a fixed fraction (~40%) of bridging
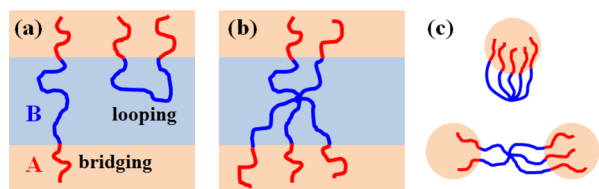

Figure 2. Schematics of looping and bridging configurations for: (a) ABA triblock copolymers in the lamellar phase; (b) $(BA)_5$ star copolymers in the lamellar phase; and (c) $(BA)_5$ star copolymers in the cylindrical phase.

copolymers.[42,43] It has been shown theoretically that the ratio of bridging configuration could be drastically increased by increasing the number of arms of $(BA)_n$ star copolymers [Figure 2(b) and (c)], reaching almost 100% when $n \geq 10$.[42] Recently, Gao et al. carried out a detailed SCFT study on AB-type block copolymers and demonstrated that the effect of chain architecture could be used to form nonclassical ordered phases. Specifically, they showed that three nonclassical ordered phases including the stable square array of cylinders, graphene-like array of cylinders, and honeycomb-like network phase, could be induced by adjusting the chain architecture.[35]

In conclusion, the study of the phase behavior of block copolymers has experienced a renaissance in past few years since the discovery of the Frank−Kasper σ phase in block copolymer melts.[14] Significant progress has been made in the study on the formation of nonclassical ordered phases from block copolymers, as illustrated in the schematics shown in

Figure 3. Experimentally, a number of nonclassical spherical packing phases including the Frank−Kasper phases (A15, σ),
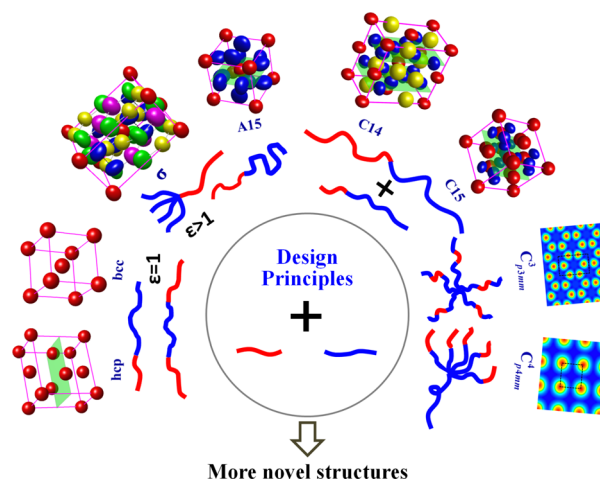

Figure 3. Possible stable spherical packing phases of different AB-type block copolymer systems. Conformationally symmetric copolymers (ε = 1), like AB diblock or ABA triblock, usually form the bcc phase with a very small hcp region, whereas conformationally asymmetric AB-type copolymers (ε > 1 or branched) could self-assemble into the complex Frank−Kasper phases. Binary blends of conformationally symmetric diblock copolymers with properly chosen length ratio and composition could form more stable Frank−Kasper phases, like the Laves phases of C14 and C15. Furthermore, the square lattice and graphene-like lattice of cylinders could form in purposely designed AB-type multiarm copolymers. It is expected that a combination of the different mechanisms could lead to the formation of more novel ordered nanostructures.

the Laves phases (C14 and C15), and quasicrystals have been identified as stable or metastable phases of diblock and multiblock copolymers.[15−21,44] Theoretically, the emergence and relative stability of various nonclassical ordered phases of block copolymers have been examined using the self-consistent field theory.[10,29−33,44] A combination of the experimental and theoretical results has led to a good understanding of the principles stabilizing these complex spherical packing phases.

The emergence of complex spherical packing phases from the self-assembly of block copolymers is accompanied by the appearance of minority domains with different sizes and shapes. Mechanisms favoring the formation of large, nonspherical, and nonuniform minority domains have been identified from theoretical and experimental studies. For AB-type block copolymers, theoretical studies have identified the conformational asymmetry between the A and B blocks as a key factor controlling the formation of the complex spherical packing phases.[29,31] Experiments on purposely designed diblock copolymers with different degree of conformational asymmetry demonstrated the emergence of the Frank−Kasper σ phase is indeed controlled by the conformational asymmetry of the copolymers.[20] Further theoretical studies have shown that local segregation of different block copolymers could lead to the formation of minority domains with different sizes and shapes.[33] As a result of the local segregation, binary blends of AB diblock copolymers exhibit an unusually large window for the formation of the Frank−Kasper phases (A15, σ). The theoretical results on block copolymer blends identified local segregation as a new mechanism to stabilize complex ordered phases and, more importantly, predicted simpler molecular

formulations to generate nonclassical spherical packing phases for practical applications. Last but not least, architecture of block copolymers, i.e., linear versus star-like, is shown to provide a mechanism to control the bridging of different minority domains, thus regulating the coordination number of the ordered structures.[34,35] Taken together, these progresses have led to a good understanding of the principles and mechanisms of the formation of nonclassical spherical packing phases self-assembled from block copolymers. However, despite these significant progresses on the self-assembled complex ordered phases of block copolymers, a number of challenges remain.

The first challenge concerns detailed comparison between experiments and theory. The experimental results on the IL diblock copolymers are in agreement with the SCFT predictions qualitatively. Quantitatively, the emergence of the Frank−Kasper σ phase occurs at a smaller conformational asymmetry than theoretical predictions. This quantitative discrepancy between experiment and theory could be attributed to a number of factors. The SCFT calculations were carried out for monodisperse diblock copolymers which are modeled as flexible Gaussian chains, whereas the experiments were carried out for the IL diblock copolymers with a small but finite polydispersity. From the previous theoretical study on binary blends of diblock copolymers, it could be concluded that polydisperse block copolymers could favor the formation of complex spherical ordered phases due to their ability to locally segregate. Therefore, it is desirable to carry out SCFT calculations for polydisperse diblock copolymers to examine the effect of polydispersity on the formation of nonclassical spherical ordered phases. Furthermore, the SCFT is a mean-field theory valid for polymeric systems with high molecular weight. On the other hand the experiments were carried out for IL diblock copolymers with short PLA blocks. It is possible that thermal fluctuations might have a nontrivial effect on the relative stability of different ordered phases.[45,46] Therefore, more accurate theory is required to model the finite-length polymer or even to include the effect of thermal fluctuations.

The second challenge is related to the extension of theoretical study to aperiodic structures such as quasicrystals, soft glasses, and disordered micellar phase. Quasicrystalline structures have been observed from the self-assembly of the block copolymers in a number of experiments.[14−19,47] On the other hand, the question whether quasicrystals are equilibrium phases of block copolymers has not been resolved. Theoretically, exploring the thermodynamic stability of quasicrystalline structures is of particular interest but also very challenging.[48,49] Developing methods to solve the SCFT equations and calculate the free energy of quasicrystal structures is critical to identify their stability. Furthermore, identifying mechanisms favoring the formation of quasicrystalline phases could lead to the design of experimental systems to obtain stable polymeric quasicrystals.

The third challenge involves the understanding of the kinetic pathways leading to different ordered phases.[6,50,51] Very recently, Bates and co-workers reported that the experimentally observed ordered state of diblock copolymers could be regulated by thermal processing. Specifically, they showed that the C14 and C15 phases were observed in the IL diblock copolymers only when the polymers were treated under special thermal processing conditions.[19] When the sample with f_{PLA} = 0.15 is directly quenched to the annealing temperature 70 and 55 °C, the observed ordered phases were bcc and σ,

respectively. However, the observed ordered phases became C14 and dodecagonal quasicrystal (DDQC) when the sample was first cooled rapidly to −196 °C and then heated to 85 and 35 °C, respectively. Similarly, the C15 and σ phases were observed at different annealing temperatures with this special thermal processing, whereas the hexagonally packed cylinders were observed with the normal annealing processing. These results clearly demonstrated that the nonclassical phases, C14, C15, and DDQC, might be metastable but could be trapped kinetically by the special thermal processing. Therefore, the kinetic pathways leading to different ordered phases could be regulated by thermal processing. Understanding the principles of guiding the transition pathways is a major challenge to soft matter theory.

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Notes
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