

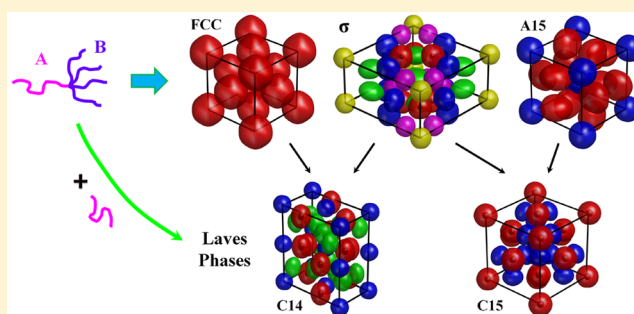
Laves Phases Formed in the Binary Blend of AB₄ Miktoarm Star Copolymer and A-Homopolymer

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Supporting Information

ABSTRACT: Formation of complex Frank–Kasper spherical phases from the self-assembly of block copolymers has attracted renewed interest. In this work, we have studied the emergence and stability of the Laves phases (C14 and C15), belonging to the class of Frank–Kasper phases, in the binary blend of AB₄ miktoarm star block copolymers and A-homopolymer using self-consistent field theory. Neat AB₄ copolymer with a large conformational asymmetry exhibits a large spherical phase region consisting of four different spherical phases: the face-centered-cubic (FCC), body-centered-cubic (BCC), and Frank–Kasper σ and A15 phases. In contrast, the addition of A-homopolymers into AB₄ copolymers leads to the formation of new Frank–Kasper phases, i.e., the Laves phases of C14 and C15. Our work unveils that the Laves phases with more nonuniform domains than the σ and A15 phases are mainly stabilized by the redistribution of A-homopolymers among different A-domains that reduces the interfacial energy between the A-homopolymers and the B-blocks of AB₄. At the same time, it implies that the conformational asymmetry should not be necessary for the formation of the Laves phases.



INTRODUCTION

Particle packing has been attracting long-standing interest as it is ubiquitous in our daily life as well as in industry. The simplest well-known packing problem is the ideal model of uniform hard spheres that pack into the hexagonally close-packed (HCP) crystalline lattice.¹ In practice, particles are not ideally hard, i.e., deformable and nonuniform. These two factors of particles could impact their packing behaviors significantly. For example, it has been revealed that highly deformable bubbles of equal size form the Frank–Kasper A15 lattice,² which is in contrast to the HCP packing lattice of uniform hard spheres. Even for hard spheres of nonuniform sizes, the packing problem also becomes very complicated, which could lead to different crystalline structures.

As the simplest polydisperse system of particles, the binary blend of hard spheres has been intensively studied.^{3–5} Many interesting crystalline structures are observed, of which the Laves phases are particularly attractive. Laves phases, generally composed of large (L) and small (S) particles in the form of LS₂, belong to the class of Frank–Kasper phases and are topologically close-packed structures.^{6,7} L and S particles sitting in the centers of a 16-particle Frank–Kasper polyhedron and an icosahedron have coordination numbers (CN) of 16 (4 L and 12 S particles) and 12 (6 L and 6 S particles), respectively.⁴ The closest packing of hard spheres of L and S is obtained for the radius ratio $r_L/r_S = (3/2)^{1/2}$.⁶ In fact, Laves phases are originally observed in metallic alloy crystals.^{6,8} The radius ratio of metallic atoms also

plays an important role in the formation of crystalline structures in binary metallic alloys apart from other factors such as valence electron numbers and electronegativities.⁹ Binary intermetallic compounds can form a large number of Laves phases due to largely variable properties of metallic atoms, which provide the prototypical structures for other particle systems.⁶ According to the stacking sequences of L/S layers of particles, Laves phases can be divided into different polytypes such as C14 and C15. The thermodynamic stability of the Laves phases is a complicated and unsolved problem in intermetallic compounds because it is dictated by multiple factors.^{10,11}

Very recently, the spherical Laves C14 and C15 phases were observed in the self-assembly of poly(isoprene)-*b*-poly(lactide) (PI-*b*-PLA) diblock copolymer melts annealed under a special thermal process.¹² The self-assembly of block copolymers provides an excellent model for one to probe into the formation mechanism of complex crystalline structures in soft matter systems because of the great advances in experiment and theory.^{13–18} In experiment, modern synthesis techniques can make block copolymer with precisely controlled topology and composition. At the same time, a powerful self-consistent field theory (SCFT) based on the Gaussian-chain model as well as its efficient numerical methods has been built up.¹⁹ On one hand,

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SCFT can accurately calculate the free energy of different ordered phases and thus identify their relative stability. On the other hand, it can calculate the different contributions of the free energy and the distribution of each segment of the copolymer, which is critical to revealing the self-assembly mechanism of every ordered structure.

In the past decades, great success has been achieved in understanding the formation mechanism of complex ordered phases in block copolymers via the concerted interplay between experiment and SCFT. One recent example is about the formation of Frank–Kasper σ ^{20–30} and A15^{24,26,31–35} phases in various block copolymer systems. Inspired by the experimental discovery of the σ phase in PI-*b*-PLA copolymers,²⁰ SCFT reveals that the σ phase is stabilized by the conformational asymmetry between the two blocks.^{23,24} Furthermore, the theoretical work has proposed that the conformational asymmetry can be increased in a large extent by branching the majority blocks, i.e., forming AB_{*n*} miktoarm star copolymer with *n* the number of arms. With a large conformational asymmetry such as *n* ≥ 3, a general spherical phase sequence from FCC to BCC, σ , and A15 is predicted.²³ Encouragingly, the mechanism of conformational asymmetry is confirmed by further experiments in which three diblock copolymers with different degrees of conformational asymmetry are ingeniously designed.³⁰

Bates and co-workers have proposed that the formation of the spherical phases is dictated by the competition between the tendency to form spherical domains and the need to uniformly fill the space under the constraint of the crystalline lattice.²² In other words, the shape of each minority domain deforms from spherical under the influence of the polyhedral shape of its Wigner–Seitz (WS) cell, which in return increases the interfacial energy. Larger domain, which could be formed in conformation-symmetric copolymers, usually exhibits larger deformation.^{23,24} To lower the interfacial energy, domains tend to pack into the crystalline lattice with rounder shape of WSCs, which is quantified by the isoperimetric quotient (IQ), $IQ = 36\pi v^2/s^3$, where *v* and *s* are the volume and surface area, respectively.²² The average values of IQ ($\overline{IQ}$) of FCC, BCC, σ , and A15 are in the ascending order, which qualitatively rationalizes their appearance sequence in the phase diagram.³⁶ In contrast to the classical FCC and BCC lattices, the formation of the complex σ and A15 lattices containing two or more non-equivalent domains with different sizes and shapes should be disfavored by entropy. The σ and A15 phases are stabilized only when the gain in the interfacial energy could compensate for the energy penalty from the loss of entropy.

On the basis of the above argument about the formation of Frank–Kasper phases, Liu et al. proposed a simple binary blend composed of two different conformation-symmetric AB diblock copolymers (AB/A'B') to target the complex spherical phases.^{26,36,37} By tuning the lengths and compositions of the two copolymers, one can achieve stable Frank–Kasper σ and A15 phases with considerable parameter windows.²⁶ In contrast to the mechanism of conformational asymmetry, the Frank–Kasper phases are stabilized by the local segregation between the two different diblock copolymers. Specifically, the segregation occurring along the radial direction and at the interface within every domain favors the formation of large “core–shell” domains of nonspherical shape, whereas the segregation among the different domains favors the formation of domains of different sizes. As a consequence, large domains with tunable shapes are packed into the complex crystalline lattices.

More surprisingly, besides the σ and A15 phases, two new spherical phases are predicted to be stable in respective large windows of parameters, i.e., the Laves C14 and C15 phases.^{36,37}

It is necessary to note that $\overline{IQ}$ of the two phases are intermediate between the BCC and σ phases; however, they do not appear as stable in the phase diagram of the neat conformation-asymmetric copolymers which contains both the BCC and σ phases.²³ This implies that the blending system should provide an additional effect to that of conformational asymmetry. It has been observed that the size difference of domains in Laves phases is usually more pronounced than that in the σ or A15 phase.³⁷ Although one could speculate that such large size difference might be realized via the local segregation of the different copolymers among domains in the AB/A'B' blend, there is no direct evidence.

To distinguish the stabilization mechanisms of the Laves phases from those of the Frank–Kasper A15 and σ phases, here we turn to another simple binary blend composed of highly conformation-asymmetric copolymers of AB₄ and A-homopolymers (AB₄/A). We mainly focus on the influence of the addition of A-homopolymers into AB₄ copolymers on the packing of A-domains. In general, A-homopolymer has a tendency to swell every A-domain, enhancing the effective composition of A-component.³⁸ It is interesting to know whether the swollen A-domains might pack into complex crystalline lattices or just simply transform into cylinders. In particular, if the starting phase is already the complex σ or A15 spherical phase, what phase transitions can be triggered by adding A-homopolymers? In contrast to the AB/A'B' blend, there is only one effect from nonuniform distribution of A-homopolymers among A-domains but no other effects like the segregation of the two diblocks within each domain in the AB/A'B' blend. Whether or not this single effect could result in the formation of Laves phases is another intriguing question.

■ THEORY AND METHOD

The considered binary blend in a volume of *V* consists of *n*₁ and *n*₂ chains of AB₄ copolymers and A-homopolymers, respectively. The total number of segments of AB₄ is specified as *N*, which consists of *fN* A-segments, and that of A-homopolymer is denoted by *N*_H = *γN*. Simply, we assume that all segments have equal length *b* and density ρ_0 , thus having *n*₁*N* + *n*₂*N*_H = *Vρ*₀ and the volume fraction of AB₄, $\phi = n_1N/V\rho_0$. The repulsive interaction between A and B components is characterized by the product of *χN* with *χ* the Flory–Huggins parameter. The spatial distributions of volume fractions of A- and B-components, $\phi_A(\mathbf{r})$ and $\phi_B(\mathbf{r})$, are chosen to characterize the ordered phases self-assembled in this blend. Note that $\phi_A(\mathbf{r})$ consists of the volume fractions of A-blocks (denoted as $\phi_A^C(\mathbf{r})$) and A-homopolymers (denoted as $\phi_H(\mathbf{r})$), i.e. $\phi_A(\mathbf{r}) = \phi_A^C(\mathbf{r}) + \phi_H(\mathbf{r})$.

Under the approximations of the mean-field treatment and Gaussian-chain model, the free energy in the canonical ensemble can be expressed as¹⁹

$$\begin{aligned} \frac{NF}{\rho_0 V k_B T} = & -\phi \ln \frac{Q_C}{\phi} - \frac{1-\phi}{\gamma} \ln \frac{Q_H}{1-\phi} \\ & + \frac{1}{V} \int d\mathbf{r} \{ \chi N \phi_A(\mathbf{r}) \phi_B(\mathbf{r}) - w_A(\mathbf{r}) \phi_A(\mathbf{r}) - w_B(\mathbf{r}) \phi_B(\mathbf{r}) \\ & - \eta(\mathbf{r}) [1 - \phi_A(\mathbf{r}) - \phi_B(\mathbf{r})] \} \end{aligned} \quad (1)$$

where *w*_K(*r*) is the mean-field conjugate to the volume fraction $\phi_K(\mathbf{r})$ (*K* = A or B). The spatial function $\eta(\mathbf{r})$ is a Lagrange

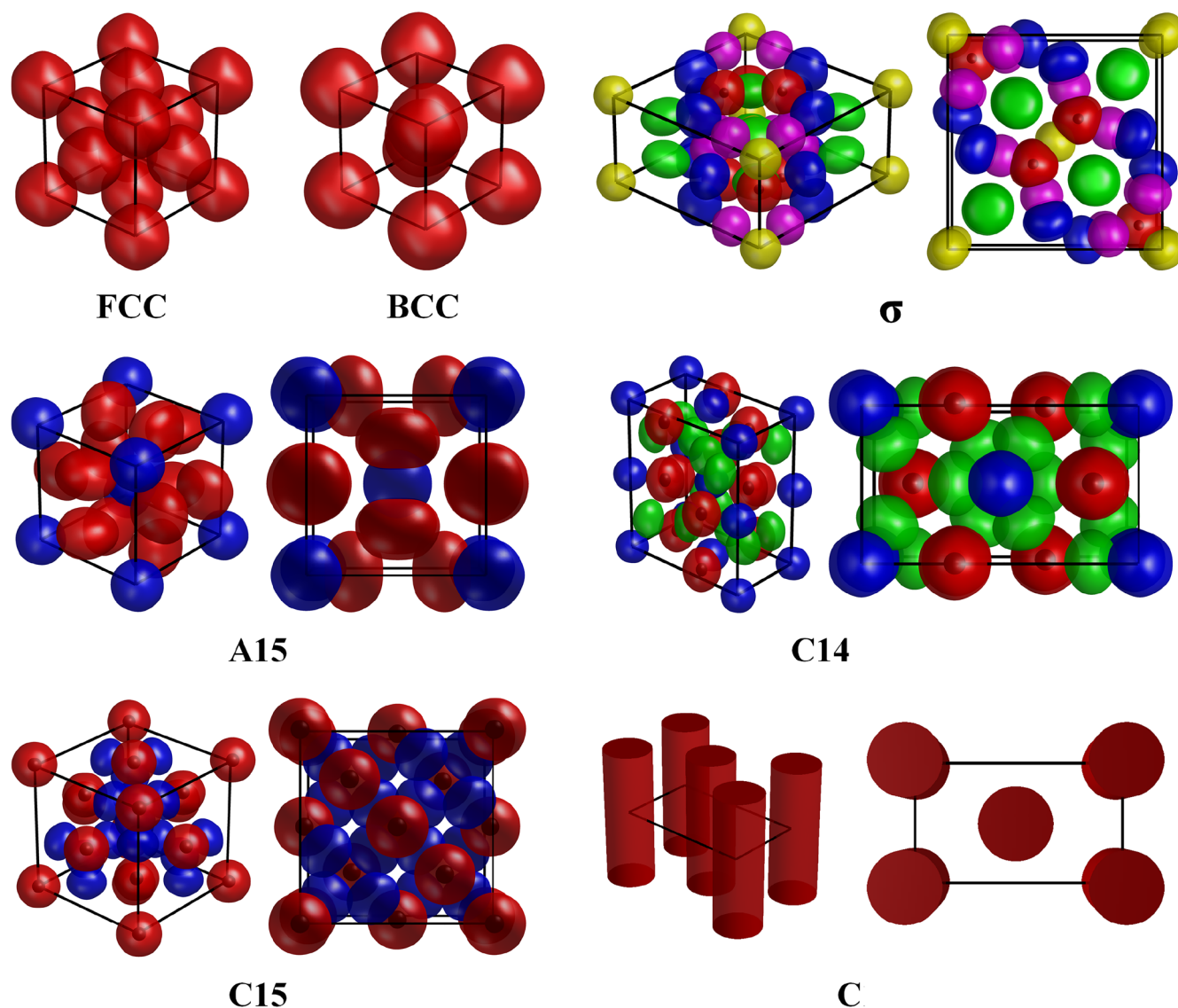


Figure 1. Considered candidate ordered spherical phases including the classical FCC and BCC phases as well as four Frank–Kasper phases of σ , A15, C14, and C15, formed in the AB_4/A binary blend. Moreover, the hexagonal cylindrical phase (C) is considered. For the complex Frank–Kasper phases, the oblique and top views are given, where different domains at nonequivalent positions are shown in different colors. Note that some domains have an inner core but the other do not. The inner core is plotted with the isosurface of A-homopolymers at $\phi_H(\mathbf{r}) = 0.5$ for a typical group of parameters ($f = 0.32$, $\phi = 0.96$, and $\gamma = 0.4$), illustrating the significantly higher content of A-homopolymers in the larger domains (e.g., the red domain of C14) than in the smaller domains (e.g., the blue or green domain of C14).

multiplier used to enforce the incompressibility condition, $\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) = 1$. The two quantities Q_C and Q_H are the partition functions of single copolymer chain and single homopolymer chain interacting with the mean fields of $w_A(\mathbf{r})$ and $w_B(\mathbf{r})$, respectively. Q_C and Q_H are determined by

$$Q_C = \frac{1}{V} \int d\mathbf{r} q_C(\mathbf{r}, s) q_C^\dagger(\mathbf{r}, s)$$

$$Q_H = \frac{1}{V} \int d\mathbf{r} q_H(\mathbf{r}, s) q_H(\mathbf{r}, \gamma - s) \quad (2)$$

Here $q_C(\mathbf{r}, s)$ and $q_C^\dagger(\mathbf{r}, s)$ are the propagator functions of segments of the copolymer starting from the free ends of A- and B-blocks at $s = 0$ and $s = f + (1 - f)/4$, respectively, and $q_H(\mathbf{r}, s)$ is the propagator function for the homopolymer starting from one of its two equivalent free ends. These propagator functions satisfy the following modified diffusion equations:

$$\frac{\partial q_C(\mathbf{r}, s)}{\partial s} = \nabla^2 q_C(\mathbf{r}, s) - w(\mathbf{r}, s) q_C(\mathbf{r}, s)$$

$$-\frac{\partial q_C^\dagger(\mathbf{r}, s)}{\partial s} = \nabla^2 q_C^\dagger(\mathbf{r}, s) - w(\mathbf{r}, s) q_C^\dagger(\mathbf{r}, s)$$

$$\frac{\partial q_H(\mathbf{r}, s)}{\partial s} = \nabla^2 q_H(\mathbf{r}, s) - w_A(\mathbf{r}) q_H(\mathbf{r}, s) \quad (3)$$

In the equations of $q_C(\mathbf{r}, s)$ and $q_C^\dagger(\mathbf{r}, s)$, $w(\mathbf{r}, s) = w_K(\mathbf{r})$ when s belongs to K-blocks in the AB_4 copolymer ($K = A$ or B). In the above equations, $R_g = (N/6)^{1/2}b$, the radius of gyration of an unperturbed linear polymer with N segments, is chosen as the unit of spatial length. Standard initial conditions of the propagator functions for the copolymer and homopolymer are used, e.g., $q_C(\mathbf{r}, 0) = 1$, $q_C^\dagger[\mathbf{r}, f + (1 - f)/4] = 1$, and $q_H(\mathbf{r}, 0) = 1$. At the junction point of $s = f$, $q_C(\mathbf{r}, f) \times [q_C^\dagger(\mathbf{r}, f)]^3$ is set as the initial

value for solving $q_C(\mathbf{r}, s)$ along the B-block from the junction point to the free end at $s = f + (1 - f)/4$, while $[q_C^\dagger(\mathbf{r}, f)]^4$ is set as the initial value for solving $q_C^\dagger(\mathbf{r}, s)$ along the A-block from the junction point to the free end at $s = 0$.

Minimization of the free energy with respect to $\phi_K(\mathbf{r})$ and $w_K(\mathbf{r})$ leads to the following SCFT equations:

$$\begin{aligned} w_A(\mathbf{r}) &= \chi N \phi_B(\mathbf{r}) + \eta(\mathbf{r}) \\ w_B(\mathbf{r}) &= \chi N \phi_A(\mathbf{r}) + \eta(\mathbf{r}) \\ \phi_A(\mathbf{r}) &= \frac{\phi}{Q_C} \int_0^f ds q_C(\mathbf{r}, s) q_C^\dagger(\mathbf{r}, s) + \frac{1 - \phi}{\gamma Q_H} \int_0^\gamma ds \\ &\quad q_H(\mathbf{r}, s) q_H(\mathbf{r}, \gamma - s) \\ \phi_B(\mathbf{r}) &= \frac{4\phi}{Q_C} \int_f^{(3f+1)/4} ds q_C(\mathbf{r}, s) q_C^\dagger(\mathbf{r}, s) \end{aligned} \quad (4)$$

To consider the coexistence of two neighboring phases, we need to construct the phase diagram using the SCFT calculation in the grand canonical ensemble, where the free energy is expressed as

$$\begin{aligned} \frac{NF}{V \rho_0 k_B T} &= -Q_C - z_H Q_H \\ &+ \frac{1}{V} \int d\mathbf{r} \{ \chi N \phi_A(\mathbf{r}) \phi_B(\mathbf{r}) - w_A(\mathbf{r}) \phi_A(\mathbf{r}) - w_B(\mathbf{r}) \phi_B(\mathbf{r}) \\ &- \eta(\mathbf{r}) [1 - \phi_A(\mathbf{r}) - \phi_B(\mathbf{r})] \} \end{aligned} \quad (5)$$

where $z_H = \exp(\mu_H/k_B T)$ is the activity. Here the single-chain partition functions of the two polymers, Q_C and Q_H , have the similar expressions to eqs 2 in the canonical ensemble. And the propagator functions satisfy the same modified diffusion equations as eqs 3.

Minimization of the grand canonical free energy with respect to the distributions of volume fractions and the mean fields leads to the following SCFT equations:

$$\begin{aligned} w_A(\mathbf{r}) &= \chi N \phi_B(\mathbf{r}) + \eta(\mathbf{r}) \\ w_B(\mathbf{r}) &= \chi N \phi_A(\mathbf{r}) + \eta(\mathbf{r}) \\ \phi_A(\mathbf{r}) &= \int_0^f ds q_C(\mathbf{r}, s) q_C^\dagger(\mathbf{r}, s) + z_H \int_0^\gamma ds \\ &\quad q_H(\mathbf{r}, s) q_H(\mathbf{r}, \gamma - s) \\ \phi_B(\mathbf{r}) &= 4 \int_f^{(3f+1)/4} ds q_C(\mathbf{r}, s) q_C^\dagger(\mathbf{r}, s) \end{aligned} \quad (6)$$

In the grand canonical ensemble, the spatial average concentration ϕ is conjugated to z_H , thus determined by

$$\phi = Q_C = 1.0 - z_H \gamma Q_H \quad (7)$$

In either canonical or grand canonical ensemble, the SCFT equations can be solved numerically using a standard iteration scheme. Here we employ the second-order pseudospectral method³⁹ to solve the modified diffusion equations and implement the Anderson mixing iteration scheme⁴⁰ to speed up the converging process toward the equilibrium solutions of SCFT. Although a fourth-order pseudospectral method gives a better accuracy,⁴¹ it has been shown that the second-order pseudospectral method with a fine grid spacing and contour step size can give reliable accuracy of the free energy. In our calculations, the grid spacing is chosen to be smaller than $0.15R_g$ by using a lattice of $128 \times 128 \times 64$ for the σ and C14 phases, 96^3 for the C15 phase, 64^3 for the other 3D phases (FCC, BCC, and A15), and 64^2 for the 2D cylindrical phase. The contour step size

is set up as $\Delta s = 0.01$. For each ordered phase, we carry out the unit cell calculations to determine the free energy. Furthermore, the free energy is minimized with respect to the unit-cell dimensions.^{23,27}

RESULTS AND DISCUSSION

In this work, we mainly focus on the impact of the addition of A-homopolymers into the AB₄ copolymers on the formation of different spherical phases. Accordingly, we consider two classical spherical phases of FCC and BCC together with four Frank–Kasper phases of σ , A15, C14, and C15 (Figure 1). As the cylindrical phase is often a neighbor to the spherical phases, the hexagonal cylindrical phase (C) is also considered for determining the phase boundary of the spherical phases when constructing the phase diagrams. To illustrate the distinguishable characteristics of different Frank–Kasper phases, we list their characteristic parameters in Tables 1–4, respectively, including the occupancy (n_p) of each kind of particle, the number of faces (n_F), the relative volume (v_{WS}), and the approximate IQ value of each WS cell.

Table 1. List of Information of the Polyhedral Wigner–Seitz (WS) Cells in the Frank–Kasper σ Crystalline Lattice Whose Unit Cell Contains Five Kinds of Particles ($\kappa = 1, 2, \dots, 5$), Including the Occupancy (n_p) of Each Kind of Particle, the Number of Faces (n_F), the Relative Volume (v_{WS}), and the Isoperimetric Quotient (IQ) of Each WS Cell^a

Particle Category (κ)	1	2	3	4	5
n_p	4	8	8	8	2
n_F	15	14	14	12	12
v_{WS}	1.068	1.028	1.006	0.950	0.925
IQ	0.782	0.765	0.769	0.745	0.747
Wigner-Seitz Cell					

^aNote that the data of v_{WS} and IQ are slightly dependent on the size ratio of the unit cell.

The phase behavior of the AB₄/A binary blend is mainly controlled by the four parameters χN , f , γ , and ϕ . To focus on the effect of A-homopolymers on the phase behaviors, we calculate the γ – ϕ phase diagrams in Figure 2 by choosing different starting spherical phases of the neat AB₄ copolymers: (a) FCC with $(f, \chi N) = (0.2, 35)$, (b) σ with $(0.28, 35)$, and (c) A15 with

Table 2. List of Information of the Polyhedral WS Cells in the A15 Phase

Particle Category (κ)	1	2
n_p	6	2
n_F	14	12
v_{WS}	1.008	0.977
IQ	0.766	0.749
Wigner-Seitz Cell		

Table 3. List of Information of the Polyhedral WS Cells in the C14 Phase

Particle Category (κ)	1	2	3
n_p	8	4	12
n_F	16	12	12
v_{WS}	1.139	0.937	0.928
IQ	0.810	0.739	0.736
Wigner-Seitz Cell			

Table 4. List of Information of the Polyhedral WS Cells in the C15 Phase

Particle Category (κ)	1	2
n_p	8	16
n_F	16	12
v_{WS}	1.142	0.929
IQ	0.810	0.737
Wigner-Seitz Cell		

(0.32, 35). Each transition point is identified using SCFT in the grand canonical ensemble. It is essential to mention that we have verified that the C14 and C15 phases are not stable in the neat AB_4 copolymers for a fixed $\chi N = 35$ (Figure S1).

Surprisingly, each phase diagram with whatever starting phase exhibits considerable stability regions of the C14 or C15 phase. In Figure 2a, the spherical phase transfers from the starting FCC phase going through σ to C14 as A-homopolymers are added, while the another Laves phase of C15 is observed in the phase diagrams of Figure 2b,c with larger length ratios of A-blocks in the AB_4 copolymer. It is well-known that the addition of A-homopolymers can increase the effective volume fraction of A-component by swelling the A-domains at a limited extent, and otherwise it usually causes macroscopic phase separations in the form of the coexistence of the copolymer-rich ordered phases and the homopolymer-rich disordered phase.³⁸ Obviously, the transition from the spherical A15 phase to the cylindrical phase (C) in Figure 2c is mainly induced by the increasing effective volume fraction of A-component. In fact, the phase transition from FCC to σ may be also induced by a similar mechanism because the σ phase is observed in the region of larger volume fraction than FCC. However, the transition between the σ phase and the C14/C15 phase in Figure 2a,b or between the A15 phase and the σ phase in Figure 2c cannot be solely explained by this simple mechanism based on the change of the effective volume fraction.

Another important parameter controlling the self-assembly behavior of the binary blend is the length of the A-homopolymer. An obvious effect on the phase diagram as γ increases lies in expanding the biphasic region. In other words, the uptake of A-homopolymers by these ordered phases decreases as the length of A-homopolymer increases, which is induced by the increasing entropy loss of A-homopolymer due

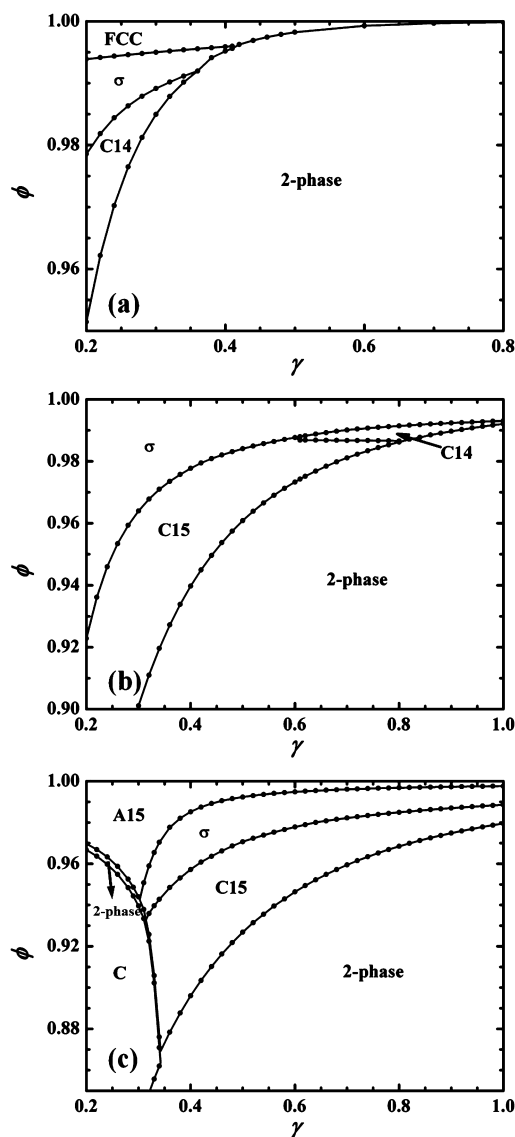


Figure 2. Phase diagrams plotted in terms of the copolymer volume fraction ϕ and the length ratio γ of the A-homopolymer to the AB_4 miktoarm star copolymer for the AB_4/A binary blend with $\chi N = 35$ and (a) $f = 0.2$, (b) $f = 0.28$, and (c) $f = 0.32$. The coexistence region of two neighboring phases is labeled as “2-phase”.

to the confinement of A-domain. However, a more remarkable feature lies in these interesting phase sequences along changing γ for a fixed volume fraction of A-homopolymers. For example, when 1.5% volume fraction of A-homopolymers (i.e., $\phi = 0.985$) is added into the FCC-forming AB_4 copolymers, the stable phase becomes σ for $\gamma < 0.25$ while it becomes the Laves phase of C14 for $0.25 < \gamma < 0.3$ (Figure 2a). The phase transition from σ to C14 is evidenced by the typical free energy comparison for $\phi = 0.985$ in Figure S2. Note that the difference of free energy density between the different spherical phases is typically at the order of $N\Delta F/\rho_0 V = 10^{-4}k_B T$, so the phase transition is sensitive to the calculation accuracy of free energy. Usually, the numerical accuracy of free energy is dependent on two critical factors: the size of grid lattice $N_x \times N_y \times N_z$ and the contour step size Δs . To demonstrate the reliable accuracy, we calculate the typical transition point between the σ phase and the C14 phase in Figure S2 with different lattices and contour step sizes. The results are provided in Table S1, indicating that the lattice size of

$N_x \times N_y \times N_z = 128 \times 128 \times 64$ and the contour step size $\Delta s = 0.01$ are enough for achieving reliable accuracy with the determined transition points in the phase diagrams.

Similar phase sequences such as $\sigma \rightarrow \text{C14/C15}$ in Figure 2b and $\text{A15} \rightarrow \sigma \rightarrow \text{C15}$ in Figure 2c are observed. Typical free energy comparisons for these phase transitions are given in Figures S3 and S4. It is important to conclude that less amount of longer A-homopolymers is needed to drive the transition from the FCC/ σ /A15 phase to the C14 or C15 phase. Very surprisingly, the stable phase changes from the cylindrical phase (C) to the different spherical phases (A15, σ , or C15) as γ increases in Figure 2c. This observation suggests that the stability of spherical phases relative to the cylindrical phase is enhanced by increasing the length of A-homopolymer. More detailed explanations are provided later.

As mentioned above, these complex Frank–Kasper spherical phases not only have larger domains than the classical FCC and BCC phases but also have more kinds of nonequivalent domains with different sizes. Accordingly, controlling the size distribution of domains serves as an additional sophisticated mechanism for stabilizing the Frank–Kasper phases.³⁷ Thus, one could speculate that γ should be a critical factor of controlling the size difference of domains for a given volume fraction of A-homopolymer, thus dictating the relative stability between these Frank–Kasper phases with distinguishable size differences of domains. To verify this speculation, we calculate the average value and the relative standard deviation of volumes of the different domains within the unit cell for these spherical phases along a few typical phase paths, $\bar{v}_{\text{dmn}}$ and $\delta_v = \sqrt{\frac{1}{N_{\text{dmn}}} \sum_i^{N_{\text{dmn}}} (v_{\text{dmn}}^i - \bar{v}_{\text{dmn}})^2} / \bar{v}_{\text{dmn}}$ where N_{dmn} indicates the number of domains within the unit cell, e.g., $N_{\text{dmn}} = 30, 8, 24$, and 24 for σ , A15, C14, and C15, respectively. The volume of each domain is integrated over the space within its enclosing isosurface at $\phi_A(\mathbf{r}) = 0.5$. Note that there is only one kind of domain in the classical FCC and BCC phases, and thus $\delta_v \equiv 0$.

The change of δ_v of the four Frank–Kasper phases (i.e., σ , A15, C14, and C15) along the phase path of $\phi = 0.985$ in Figure 2 is provided in Figure 3. It is shown that $\delta_v(\text{C14}) \approx \delta_v(\text{C15}) > \delta_v(\sigma) > \delta_v(\text{A15})$. Furthermore, as γ increases, δ_v of the two Laves phases increases more rapidly than the other two phases. This observation indicates that the size difference increased by the lengthened A-homopolymers at a fixed concentration should play a critical role in stabilizing the Laves phases. More

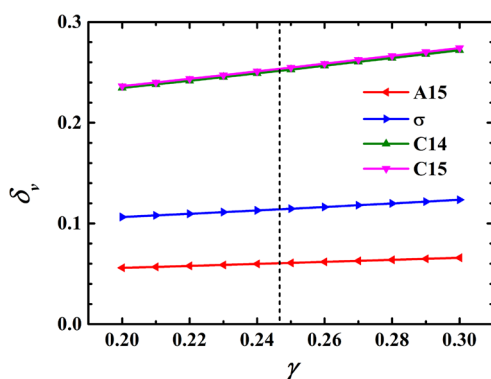


Figure 3. Variation of the relative standard deviation of volumes of the different domains within the unit cell of the four complex phases of A15, σ , C14, and C15, δ_v , for $f = 0.2$ and $\phi = 0.985$. The dashed line indicates the transition from σ to C14.

importantly, the size differences of domains in these complex phases are significantly increased relative to those in the neat AB_4 copolymers by adding A-homopolymers (Figure 4).

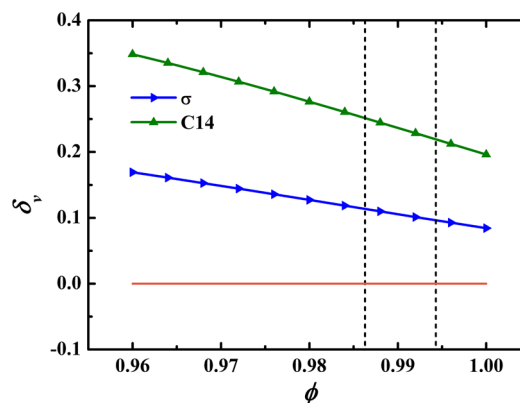


Figure 4. δ_v of the σ and C14 phases along changing ϕ for $f = 0.2$ and $\gamma = 0.26$. The two dashed lines indicate the transition sequence of FCC $\rightarrow \sigma \rightarrow \text{C14}$ along decreasing ϕ . Note that the horizontal solid line indicates $\delta_v \equiv 0$ for FCC.

Similarly, large size differences of domains are also observed in the Laves phases formed by the $\text{AB}/\text{A}'\text{B}'$ blend.³⁷ In addition, the average domain sizes of different phases for the same group of parameters are different, for example, $\bar{v}_{\text{dmn}}(\text{A15}) > \bar{v}_{\text{dmn}}(\sigma) > \bar{v}_{\text{dmn}}(\text{C15}) \sim \bar{v}_{\text{dmn}}(\text{C14})$ (Figure 5). Kim et al. have observed the considerable difference of the domain densities or equivalently the average domain sizes between the BCC and C14 phases.^{12,37} Very interestingly, the content of A-homopolymers in the different domains of each phase, ϕ_{H}^i , varies in different trends as γ increases (Figure 6). ϕ_{H}^i increases when the volume of domain i (v_{dmn}^i) is larger than the average volume of domains ($\bar{v}_{\text{dmn}}$), and otherwise it decreases. The change of ϕ_{H}^i leads to that $v_{\text{dmn}}^i > \bar{v}_{\text{dmn}}$ increases while $v_{\text{dmn}}^i < \bar{v}_{\text{dmn}}$ maintains nearly constant as γ increases.

Nevertheless, it is more important for one to understand how the size difference or the nonuniform distribution of A-homopolymers is associated with the free energy. In Figure 7, we plot the various contributions of free energy in the canonical ensemble of the different spherical phases relative to the A15 phase along with changing γ for fixed $\phi = 0.985$ in Figure 2a: the total interfacial energy $N\Delta U/\rho_0 V k_{\text{B}} T$, the entropic contribution $-N\Delta S/\rho_0 V k_{\text{B}}$, the interfacial energy between the A- and B-blocks of the copolymer $N\Delta U_{\text{AB}_4}/\rho_0 V k_{\text{B}} T$, and the interfacial energy between the A-homopolymers and B-blocks $N\Delta U_{\text{H/B}}/\rho_0 V k_{\text{B}} T$, of which the expressions are given by

$$\begin{aligned} \frac{NU}{\rho_0 V k_{\text{B}} T} &= \frac{1}{V} \int d\mathbf{r} \chi N \phi_{\text{A}}(\mathbf{r}) \phi_{\text{B}}(\mathbf{r}) \\ -\frac{NS}{\rho_0 V k_{\text{B}}} &= -\phi \ln Q_{\text{C}} - \frac{1-\phi}{\gamma} \ln Q_{\text{H}} \\ &\quad - \frac{1}{V} \int d\mathbf{r} \{w_{\text{A}}(\mathbf{r}) \phi_{\text{A}}(\mathbf{r}) + w_{\text{B}}(\mathbf{r}) \phi_{\text{B}}(\mathbf{r})\} \\ \frac{NU_{\text{AB}_4}}{\rho_0 V k_{\text{B}} T} &= \frac{1}{V} \int d\mathbf{r} \chi N [\phi_{\text{A}}(\mathbf{r}) - \phi_{\text{H}}(\mathbf{r})] \phi_{\text{B}}(\mathbf{r}) \\ \frac{NU_{\text{H/B}}}{\rho_0 V k_{\text{B}} T} &= \frac{1}{V} \int d\mathbf{r} \chi N \phi_{\text{H}}(\mathbf{r}) \phi_{\text{B}}(\mathbf{r}) \end{aligned} \quad (8)$$

It is observed that the C14 phase has the most favorable interfacial energy but the most unfavorable entropic contribution. As discussed above, the C14 phase has considerably more

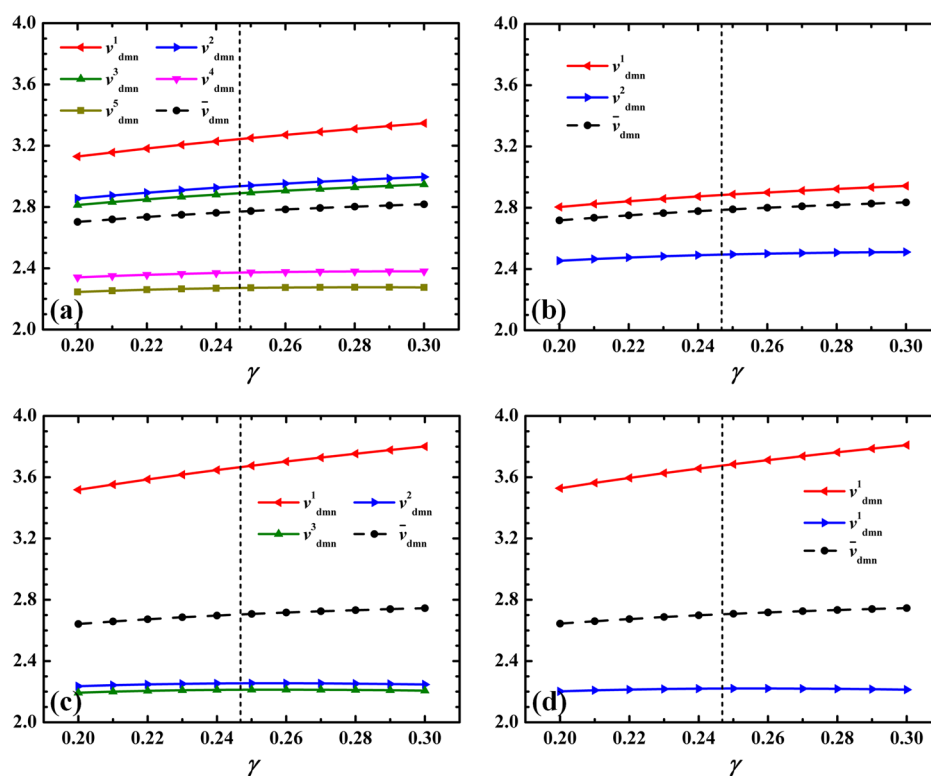


Figure 5. Volume of the different A-domains in the unit cell of the four Frank–Kasper spherical phases with $f = 0.2$ and $\phi = 0.985$: (a) σ , (b) A15, (c) C14, and (d) C15. v_{dmn}^i denotes the volume of type i domain in the units of R_g^3 . The black filled circles indicate the average volume of all A-domains in the unit cell.

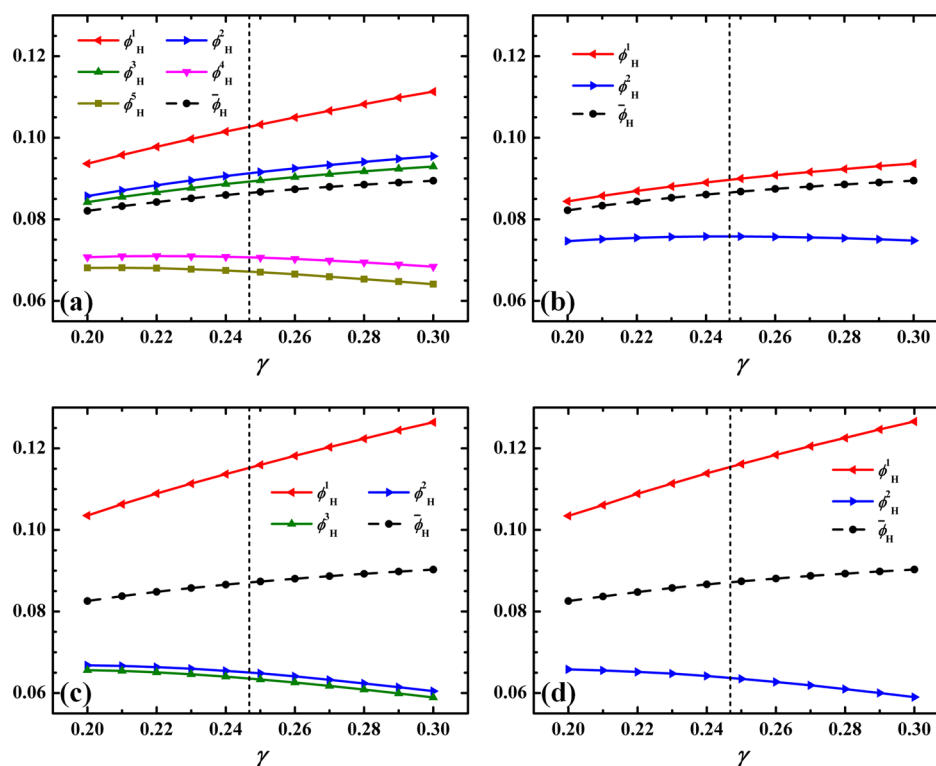


Figure 6. Content of A-homopolymers contained in the different A-domains in the unit cell of the four Frank–Kasper spherical phases with $f = 0.2$ and $\phi = 0.985$: (a) σ , (b) A15, (c) C14, and (d) C15. The black filled circles indicate the average content of all A-domains in the unit cell.

nonuniform domains compared with the σ and A15 phases. The nonuniformity of domains is directly determined by the nonuniform distributions of the copolymer/homopolymer

among different types of domains, resulting in the loss of translational entropy. However, the lower interfacial energy of C14 than σ is rather contradictory to its smaller domain size on

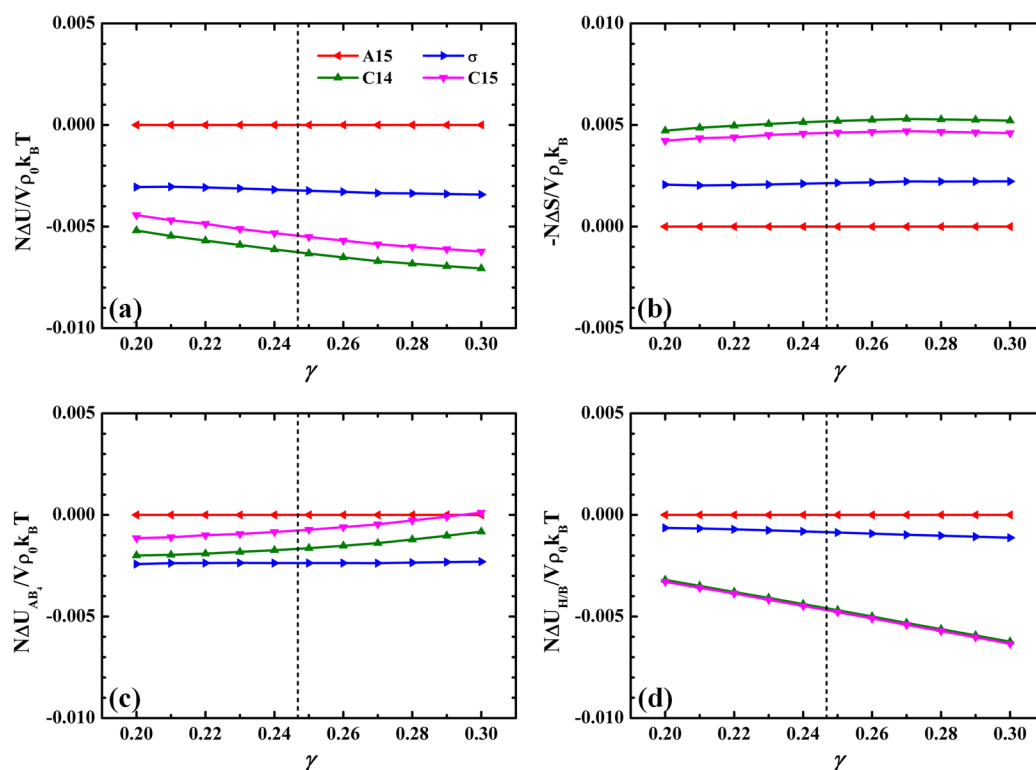


Figure 7. Various contributions of free energy of the different spherical phases relative to those of the A15 phase for $f = 0.2$ and $\phi = 0.985$: (a) the total interfacial energy $N\Delta U/\rho_0 V k_B T$; (b) the entropic contribution $-N\Delta S/\rho_0 V k_B T$; (c) the interfacial energy between the A- and B-blocks of the AB_4 copolymer $N\Delta U_{AB_4}/\rho_0 V k_B T$; (d) the interfacial energy between the A-homopolymers and B-blocks $N\Delta U_{H/B}/\rho_0 V k_B T$.

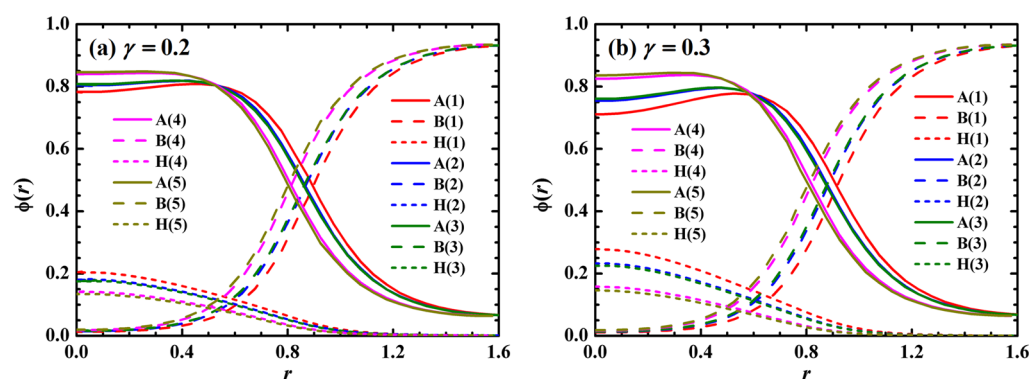


Figure 8. Radial distribution of different components of each domain in the unit cell of the σ phase with $f = 0.2$ and $\phi = 0.985$: (a) $\gamma = 0.2$ and (b) $\gamma = 0.3$. The distributions of the A-blocks, B-blocks, and A-homopolymers within the type i domain are denoted as $A(i)$, $B(i)$, and $H(i)$, respectively.

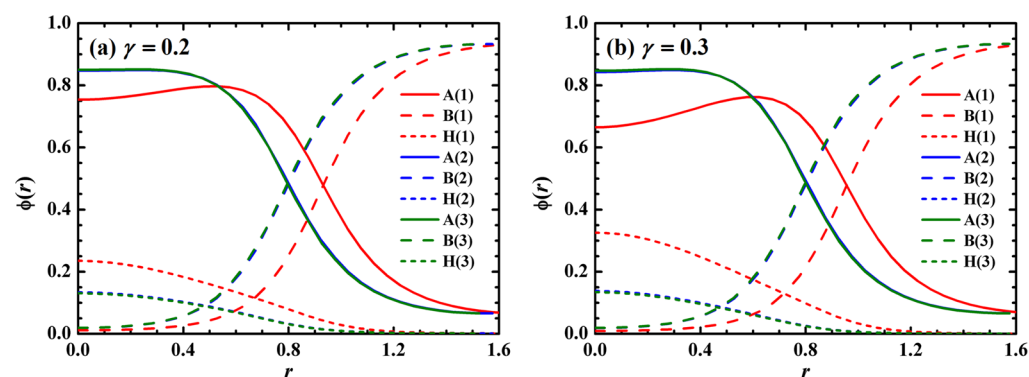


Figure 9. Radial distribution of different components of each domain in the unit cell of the C14 phase with $f = 0.2$ and $\phi = 0.985$: (a) $\gamma = 0.2$ and (b) $\gamma = 0.3$.

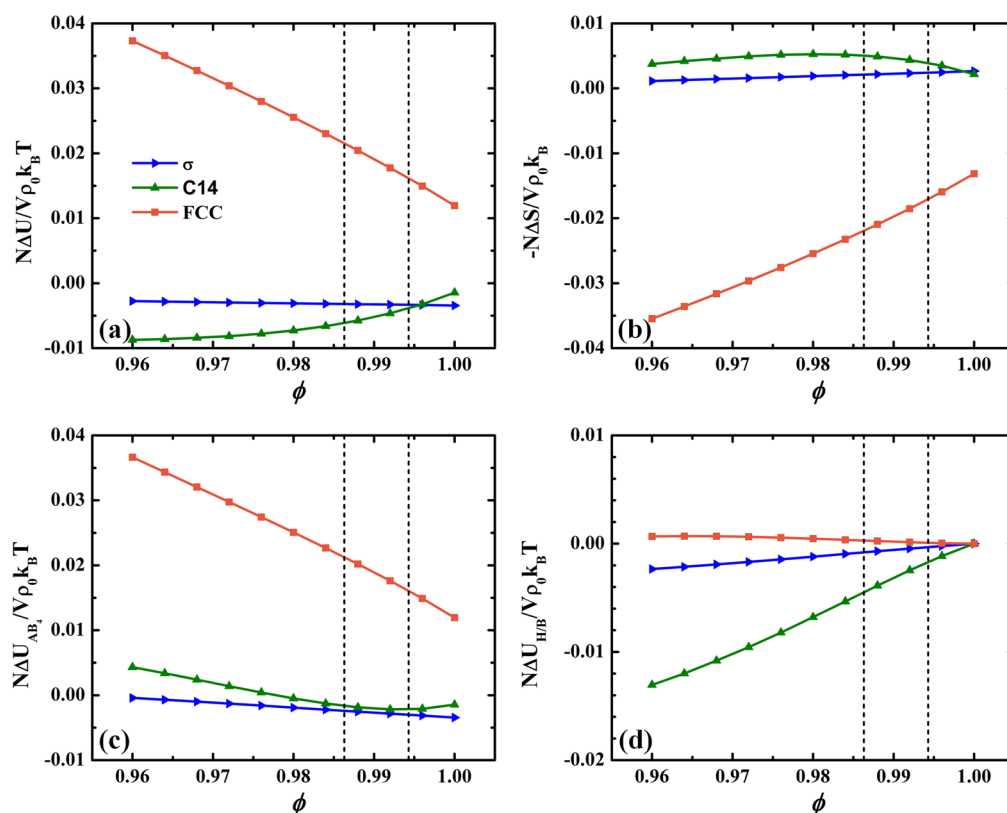


Figure 10. Various contributions of free energy of FCC, σ , and C14 relative to those of the A15 phase for $f = 0.2$ and $\gamma = 0.26$. The two dashed lines indicate the transition sequence of FCC $\rightarrow$ σ $\rightarrow$ C14 along decreasing ϕ .

average. There should be another factor benefiting the interfacial energy, i.e., the size difference.

Instructively, the interfacial energy $\Delta U_{H/B}$ between A-homopolymers and B-blocks of C14 decreases fast as γ increases though the interfacial energy between the A- and B-blocks goes down moderately. This suggests that the fast decrease of $\Delta U_{H/B}$ must result from the growing δ_v . In Figures 8 and 9, we separately plot the radial distributions $\phi(r)$ of A-blocks, B-blocks, and A-homopolymers in every domain of the σ and C14 phases for $\gamma = 0.2$ and 0.3 , respectively, which are obtained by averaging $\phi(r)$ in the spherical shell between r and $r + \Delta r$ with a small thickness Δr . From the comparison of the radial distributions between $\gamma = 0.2$ and 0.3 , we find that the difference of the A-homopolymer distributions within different domains becomes more pronounced as γ increases. For example, the difference between the distributions of A-homopolymers in type 1 domain denoted by H(1) and in type 5 domain denoted by H(5) for $\gamma = 0.3$ in Figure 8b is notably larger than those for $\gamma = 0.2$ in Figure 8a. This feature also exists in Figure 9.

More importantly, the difference of the distributions of A-homopolymers between the different domains in the C14 phase is considerably larger than that in the σ phase, and it becomes more pronounced as γ increases. For example, the difference between the smallest domain and the largest domain of the C14 phase in Figure 9b is much larger than that of the σ phase in Figure 8b. In other words, in the C14 phase, more A-homopolymers are aggregated within the larger domains while less are within the smaller domains. Obviously, the A-homopolymers in the larger domains have smaller interaction area with the B-blocks, thus lowering H/B interfacial energy ($U_{H/B}$). When the reduced interfacial energy $U_{H/B}$ compensates for the marginal penalty from both the interfacial energy

between the A- and B-blocks and the entropic contribution, the C14 phase becomes stable over the σ phase in Figure 2a. This argument can also be applied to explaining why adding longer homopolymers favors stable spheres over cylinders. It is well-known that spheres have unfavorable interfacial energy in contrast to cylinders. When the interfacial energy of spheres is decreased by adding longer homopolymers at the low cost of entropic contribution due to the feature of nonuniform domains in the complex spherical phases, spheres become favorable over cylinders.

Note that the transitions from σ /A15 to C14/C15 in Figure 2b,c along increasing γ share the similar mechanism (Figures S5–S9). In Figures S5 and S6, δ_v and various contributions of free energy between the σ and C15 phases along changing γ for fixed $f = 0.28$ and $\phi = 0.974$ are shown. Similarly, increasingly larger δ_v of C15 than σ when increasing γ leads to favorable interfacial energy and thus stabilizes C15 over σ . Moreover, the mechanism can also be applied for the transitions along adding A-homopolymers or decreasing ϕ . For example, along the path of decreasing ϕ for a given $\gamma = 0.26$ in Figure 2a, FCC transfers to σ at $\phi \approx 0.994$ and then to C14 at $\phi \approx 0.986$ (Figure S10). In Figure 4, obviously the values of δ_v for the C14, σ , and FCC phases are in a descending order, and their differences become more pronounced as adding A-homopolymers. As a result, their interfacial energies are in an ascending order for $\phi > 0.995$ (Figure 10). When the gain of the interfacial energy compensates the energy penalty resulting from the loss of entropy, FCC transfers to σ and then to C14.

CONCLUSIONS

In summary, we have investigated the formation of different spherical phases from the AB₄/A binary blend using SCFT,

particularly focusing on one category of Frank–Kasper phases, i.e., the Laves phases (C14 and C15). It is observed that the C14 phase could be obtained from the FCC- or σ -forming AB₄ copolymers by adding A-homopolymers whereas the C15 phase could be formed from the σ - or A15-forming copolymers. Moreover, the stabilization mechanism of the Laves phases different from that of the Frank–Kasper σ and A15 phases is unveiled. Our SCFT results indicate that the C14 or C15 phase has favorable interfacial energy between the A-homopolymers and the B-blocks ($U_{H/B}$) due to the larger size difference of domains than the σ or A15 phase. The C14 or C15 phase becomes stable over FCC, σ , or A15 when the reduced interfacial energy of $U_{H/B}$ could compensate for the energy penalty from both the interfacial energy between A- and B-blocks of the AB₄ copolymers and the entropic contribution. Furthermore, it is found that longer A-homopolymer drives the formation of the Laves phases at a lower concentration as it facilitates nonuniformly distributing A-homopolymers into different domains and thus favors enlarging their size difference due to the less loss of translational entropy associated with the nonuniform distribution of A-homopolymers. The observation that the Laves phase could be formed from the FCC-forming AB₄ copolymers by adding A-homopolymers implies that the conformational asymmetry should not be necessary for the formation of the Laves phase. Instead, the second polymer such as homopolymer or different block copolymer is essential to modulate the large size difference of the domains in the Laves phases. Therefore, the formation of the C14/C15 phase in the AB/A'B' blend should resemble a similar mechanism. On one hand, this work provides a simple route to fabricate the interesting Laves phases. On the other hand, it enhances our understanding on the formation mechanism of different Frank–Kasper phases in soft matter systems.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b02407.

Table S1 and Figures S1–S10 (PDF)

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Notes

The authors declare no competing financial interest.

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