1 Introduction

The self-assembly of block copolymers has attracted tremendous attention because the resulting rich array of ordered nanoscale structures provides materials for potential applications in a wide range of areas,\textsuperscript{1,2} as well as a valuable model system for the study of phases and phase transitions of complex soft matter.\textsuperscript{4} It is generally understood that the self-assembly of diblock copolymers is driven by a competition between two opposing contributions to the free energy of the system, viz. the repulsive interactions between the different blocks and the connectivity of the polymer chains which prevents phase separation at the macroscopic scale. For multiblock copolymers, the phase behaviour is further complicated by the relative strengths of the monomer–monomer interactions and the chain topology.\textsuperscript{5,6} The delicate balance between all these factors results in a very complex free energy landscape for multiblock copolymer systems. In principle, the local minima of this free energy landscape correspond to the candidate ordered phases of the system. Therefore, the phase diagram of a multiblock copolymer melt could be constructed by locating the local minima of the free energy landscape and comparing the free energy of these candidate phases. In practice, locating all the local minima of a complex free energy landscape is an unsolved mathematical problem. One possible strategy to study the phase behaviour of a complex block copolymer system is to use various initialization schemes to obtain a large number of candidate structures. The free energy of these candidate structures is then computed and compared to construct the phase diagram of the system.\textsuperscript{7}

Due to the existence of a large number of possible candidate structures, the determination of a full phase diagram for a given block copolymer is a challenging task. The difficulty of constructing a full phase diagram for block copolymers is evidenced by the simplest block copolymers, \textit{i.e.} AB diblock copolymers composed of A and B sub-chains tethered at their ends. For these seemingly simple block copolymers, it had taken a few decades to obtain a relatively complete phase diagram since the early theoretical work by Helfand in 1975\textsuperscript{8,9} and by Leibler in 1980.\textsuperscript{10} Initially, the phase diagram included the lamellae, hexagonally packed cylinders and spheres packed on body-centre-cubic (bcc) lattice. Subsequent experimental and theoretical studies extended the accessible ordered phases to include the bicontinuous networked structures, or the gyroids and the Fddd phases in the phase diagram.\textsuperscript{11–13} Very recently, it has been discovered in experiments and theory that the conformational asymmetry of the A- and B-blocks could lead to the formation of complex spherical packing phases such as the Frank–Kasper phases.\textsuperscript{14–18} In principle, the knowledge of the phase diagram of a given block copolymer provides full information about the phase...
behavior of the system. In practice, it is very difficult, if not impossible, to determine the full phase diagram due to the complexity of the free energy landscape. On the other hand, because many new block copolymers are usually designed to obtain certain desired structures for specific applications, it is more practical and useful to make theoretical predictions about the region of stability of the targeted ordered phases.\textsuperscript{19–21} This approach amounts to finding a solution to the inverse problem of identifying the stability region of a desired structure in the phase space. Furthermore, for a high-dimensional phase diagram, it is informative to construct two-dimensional (2D) phase diagrams by searching 2D cross-sections of the full phase diagram with respect to two critical variables.\textsuperscript{22–24} Furthermore, the study of the stability region of specific structures provides useful insight into the self-assembly mechanism of the given block copolymer systems. In turn, this knowledge about the stability region and formation mechanism can be used to rationalize the design of block copolymers by optimizing the interaction parameters or compositions, and even the topological architectures, to obtain the desired ordered phases.

One example of complex ordered phases formed from block copolymers is the complex spherical packing phases. Early studies indicated that the commonly observed spherical phase of AB diblock copolymers is the bcc phase. In contrast, the Frank–Kasper A15-phase was predicted in the self-assembly of superbranching\textsuperscript{14} or miktoarm AB-type block copolymers.\textsuperscript{16} However, recent experiments have revealed that a complex spherical packing structure, the Frank–Kasper \( \sigma \)-phase,\textsuperscript{25} could be self-assembled from the melts of SISO tetrablock terpolymers and PI-b-PLA diblock copolymers.\textsuperscript{17} The Frank–Kasper \( \sigma \)-phase is a complex spherical packing structure with an unusually large unit cell. Each unit cell of the \( \sigma \) phase contains 30 spherical domains, and these spherical domains are divided into five categories according to the equivalent positions on the crystalline lattice.\textsuperscript{26} Furthermore, the \( \sigma \) phase has attracted additional interest because it is an approximate phase of the dodecagonal quasicrystals.\textsuperscript{27–29} In order to understand the formation of the complex spherical packing phases in block copolymers, Xie \textit{et al.}\textsuperscript{18} examined the phase behavior of AB diblock copolymers with nonuniform segment sizes (\textit{e.g.} conformational asymmetry) using the self-consistent field theory (SCFT). In particular, two more candidate spherical phases, A15 and \( \sigma \), were included in their calculations. A comparison of the free energy of different ordered phases predicted that the \( \sigma \) phase could be stabilized for highly conformationally asymmetric diblock copolymer and its region of stability increases as the conformational asymmetry increases. These theoretical results rationalize the experimental observation of the \( \sigma \) phase from the conformationally asymmetric PI-b-PLA diblock copolymer. Furthermore, the theoretical study revealed that one critical factor affecting the formation of complex spherical phases is the conformational asymmetry, which could be in the form of different Kuhn lengths or different architectures. This conclusion is similar to that of the study on branching AB-type block copolymers by Grason \textit{et al.} except that they did not include the \( \sigma \) phase.\textsuperscript{14,16} In particular, the SCFT study predicted that the \( \sigma \) phase has a significant stability region for block copolymers with \( \text{AB}_m \) miktoarm architectures and its stability region increases as the number of B-blocks is increased, thus effectively enhancing the asymmetry of the chain architecture. In addition, the SCFT study of Xie \textit{et al.} also predicted that the A15 phase becomes stable in the region of a larger volume fraction \( f \) and higher \( \chi N \) (or lower temperature for temperature sensitive \( \chi \) materials) for \( m \geq 3 \). This predicted phase transition sequence from face-centered-cubic (fcc) to bcc, \( \sigma \), and A15, is consistent with experimental observations of the self-assembly of block copolymers as well as amphiphilic liquid crystals.\textsuperscript{36,30,31} These theoretical results indicate that branching or superbranching AB block copolymers offers a more flexible and effective route to control the conformational asymmetry than the conformationally asymmetric AB diblock copolymers, thus facilitating the formation of the \( \sigma \) phase or the A15 phase.

In the experiments by Lee \textit{et al.},\textsuperscript{17,32} the \( \sigma \) phase was also observed in the SISO tetrablock terpolymers, in which the S- and I-blocks are weakly segregated and the O- and S-blocks form core–shell spherical domains. It is very interesting to examine whether the conformational asymmetry mechanism found in the AB-type block copolymers still applies to the SISO tetrablock copolymers, or there are other factors governing the stability of the \( \sigma \) phase. Recently, Bates and coworkers argued that a general self-assembly mechanism of spherical phases is the competition between the tendency to form spherical domains and the need to uniformly fill the space.\textsuperscript{28} When spherical domains are small, their shape is hardly influenced by the filling constraint, \textit{i.e.} the packing lattice. The stable phase is bcc because of the minimal packing frustration of the majority blocks. As the spherical size increases, the shape of each domain experiences a much stronger influence imposed by its neighbors. In order to make the domain shape approach sphericity, more neighboring domains are preferred. In other words, the Wigner–Seitz cell of each domain is favored to have more faces or a rounder shape. There are two known crystalline lattices whose Wigner–Seitz cells have more faces on average than the bcc lattice, which are the \( \sigma \) and A15 phases.\textsuperscript{18} In contrast to bcc, both the lattices consist of more than one type of Wigner–Seitz cells that benefit the space filling rule but lead to non-uniform sizes of domains. Therefore, it is of importance that the size of domains can be optimized to a significant degree for the two complex phases. In conformationally asymmetric AB-type block copolymers, spherical phases can be stabilized in the region of large volume fraction, and thereby large domains bestow them with stronger ability to adjust the relative sizes of domains in each unit cell. As the A15 phase has on average a relatively round shape of Wigner–Seitz cells, it becomes stable at a larger \( f \) and higher \( \chi N \) compared with the \( \sigma \) phase.

In contrast to AB-type block copolymers, the multiblock BABC terpolymer is more complex because of its complex architecture and more molecular parameters. However, in general these two samples should share a common formation mechanism of the \( \sigma \) phase in which the sizes of large spherical domains could be adjusted considerably in the unit cell. In principle, they should have different factors increasing the tendency of forming an interfacial curvature. In AB-type copolymers,
the key factor is the conformational asymmetry (or branching).\textsuperscript{14,16,18} Although there is also conformational asymmetry arising from non-uniform segment sizes in the specific terpolymer of SISO, there must be additional factors increasing the relative stability of the $\sigma$ phase over bcc. Very recently, Champurya et al. have systematically studied the effect of the block ratio of the two S blocks on the phase behaviors by both experiment and theory, and have revealed that this symmetry parameter plays a critical role in the formation of diverse spherical phases.\textsuperscript{22} It has been established that spherical domains are effectively enlarged by the core–shell structure in which the shell is formed by the S-blocks. More importantly, the three I- and S-blocks can form either bridging or looping configurations, and thus the adjustable ratio of these two configurations adds more flexibility to optimize the domain sizes, i.e. more looping configurations enlarge the looping-back domain and oppositely more bridging configurations enlarge the bridge-connected neighboring domain by swelling its shell.

Although the above analysis provides a qualitative rationalization of the formation of the $\sigma$ phase in BABC tetrablock copolymers, further study is needed to lay a solid foundation for this analysis and to obtain more quantitative understanding. In this work, we focus on the study of the self-assembly of distinct spherical phases in the BABC terpolymers, aiming to reveal the formation mechanism of the $\sigma$ phase, and therefore to identify the parameters facilitating its formation. In practice, we try to understand the influence of each parameter by constructing 2D cross-sections of the full phase diagrams with respect to two variable parameters while fixing others using the well-established SCFT. Many previous studies have demonstrated that SCFT has become one of the most efficient methods for the construction of phase diagrams of various flexible block copolymers because of its strong capacity of dealing with complex topological architectures as well as its high accuracy of free energy calculations.\textsuperscript{3,11,33,34} Similar to our previous work, we use the pseudo-spectral method to solve the modified diffusion equation and apply the Anderson-mixing scheme to speed up the convergence of the iteration process.\textsuperscript{18,22,35} The accuracy and reliability of this method have been justified previously.\textsuperscript{36}

2 Theory and method

We consider an incompressible melt of $B_1A_2B_2C$ tetrablock terpolymers in a volume of $V$, where the subscripts are used to distinguish the two B blocks. Each copolymer chain is specified by the number of statistical segments of the blocks, $Z_A$, $Z_B$, and $Z_C$, and each block is characterized by the segment length $b_k$ and density $\rho_k$ ($K = A$, B, C). The repulsive interactions between dissimilar monomers are given by three Flory–Huggins parameters $\chi_{AB}$, $\chi_{BC}$ and $\chi_{AC}$, respectively. For convenience, a reference density $\rho_0$ is introduced to define the effective degree of polymerization of the polymer chain, $N = N_A + N_B + N_C$, where $N_B = N_B + N_B$. In particular, $N$ is defined such that the product of $N\rho_0^{-1}$ is equal to the volume occupied by a single terpolymer chain, $N\rho_0^{-1} = Z_A b_A^{-1} + Z_B b_B^{-1} + Z_C b_C^{-1}$. The volume fraction of block $K$ is then given by $f_k = N_k/N$ ($f_A + f_B + f_C = 1$ and $f_B = f_{B_1} + f_{B_2}$). Besides the interaction parameters, the different blocks are further characterized by their conformational asymmetry. It has been proposed that the conformational asymmetry can be parameterized by the ratio,\textsuperscript{24,37–39}

\[ \varepsilon_k = \frac{b_k^2 \rho_k}{b_A^2 \rho_A} \]  

Within the mean-field approximation to statistical mechanics of the Edwards model of polymers,\textsuperscript{1,4,33} the free energy functional $F$ of $n$ Gaussian terpolymer chains at a given temperature $T$ is given by

\[ \frac{F}{nk_B T} = -\ln Q + \frac{1}{Q} \int \mathrm{d}r \left( \chi_{AB} N_\phi A(r) \phi A(r) + \chi_{AC} N_\phi A(r) \phi C(r) \right. \]
\[ \left. + \chi_{BC} N_\phi B(r) \phi C(r) - w_A(r) \phi A(r) - w_B(r) \phi B(r) \right. \]
\[ \left. - w_C(r) \phi C(r) - \eta(r) \right) \left[ 1 - \phi A(r) - \phi B(r) - \phi C(r) \right] \]  

where $\phi_k$ ($K = A$, B, and C) are the monomer densities. The quantity $Q$ is the partition function of a single polymer chain interacting with the mean fields of $w_k(r)$, which are produced by the surrounding chains. The field function $\eta(r)$ is a Lagrange multiplier used to enforce the incompressibility conditions, $\phi_A(r) + \phi_B(r) + \phi_C(r) = 1$. Minimization of the free energy with respect to the monomer densities and the mean fields leads to the following SCFT equations:

\[ w_A(r) = \chi_{AB} N_\phi A(r) + \chi_{AC} N_\phi C(r) + \eta(r) \]  

\[ w_B(r) = \chi_{AB} N_\phi A(r) + \chi_{BC} N_\phi C(r) + \eta(r) \]  

\[ w_C(r) = \chi_{AC} N_\phi A(r) + \chi_{BC} N_\phi B(r) + \eta(r) \]  

\[ \phi_A(r) = \frac{1}{Q} \int_{f_A} \mathrm{d}s q(r,s) q^\dagger(r,s) \]  

\[ \phi_B(r) = \frac{1}{Q} \int_{f_A} \mathrm{d}s q(r,s) q^\dagger(r,s) \]
\[ + \int_{f_B} f_A^\dagger \mathrm{d}s q(r,s) q^\dagger(r,s) \]  

\[ \phi_C(r) = \frac{1}{Q} \int_{f_B} \mathrm{d}s q(r,s) q^\dagger(r,s) \]  

\[ Q = \frac{1}{P} \int \mathrm{d}r q(r,s) q^\dagger(r,s) \]  

\[ \phi_A(r) + \phi_B(r) + \phi_C(r) = 1. \]

In the above equations, $q(r,s)$ and $q^\dagger(r,s)$ are the end-segment distribution functions,\textsuperscript{4} which satisfy the modified diffusion equations:

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

\[ - \frac{\partial q^\dagger(r,s)}{\partial s} = \varepsilon(s) \nabla^2 q^\dagger(r,s) - w(r,s) q^\dagger(r,s), \]
where \( w(r,s) = w_A(r), \sigma(s) = \sigma_A = 1 \) for \( f_{B1} \leq s < f_{B1} + f_A \); \( w(r,s) = w_B(r), \sigma(s) = \sigma_B \) for \( s < f_{B1} \) or \( f_{B1} + f_A \leq s < f_{B1} + f_A + f_{B2} \); and \( w(r,s) = w_C(r), \sigma(s) = \sigma_C \) for \( f_{B1} + f_A + f_{B2} \leq s < 1 \). The initial conditions are \( q(r,0) = q'(r,1) = 1 \). In the above equations, the spatial unit length is set as the effective radius of gyration, \( R_{g,\text{eff}} \), defined by \( R_{g,\text{eff}}^2 = (N b_{B1}^2 \rho_A/\eta_0) \). Here, we employ the pseudo-spectral method \(^{40,41}\) to solve the modified diffusion equations for the end-segment distribution functions, and implement the Anderson mixing iteration scheme \(^{42}\) to accelerate the converging speed toward SCFT solutions. In our calculations, the \( B_1A_B2C \) tetrablock terpolymer chains are placed in a rectangular box with size \( L_x \times L_y \) for 2D systems and a cuboid box of \( L_x \times L_y \times L_z \) for 3D systems. Periodic boundary conditions are imposed automatically in each direction of the box. The grid spacing is chosen to be fine enough (e.g. smaller than 0.15\( R_{g,\text{eff}} \)) to guarantee the accuracy of free energy as high as \( 10^{-6} \).

The key to solving the SCFT equations in the real-space representation consists of generating the possible candidate ordered phases. Usually, we use distinct initialization schemes for different types of morphologies.\(^ {20-22}\) One of the efficient schemes is to generate the initial compositional profiles under the strong segregation approximation according to the space symmetries, thus leading to the initial mean fields. For example, for the crystalline spherical phases (e.g. \( \sigma \) and \( A15 \)), the compositional profiles can be directly constructed from the positions of these spheres that can be readily determined from their space symmetries.

A very useful and convenient feature of this scheme is that the computational unit cell can be appropriately chosen, similar to the spectral method, which facilitates optimizing the domain period. This scheme has been successfully applied to obtaining the knitting pattern\(^ {21}\) and helical supercylindrical phases in linear ABC triblock copolymers\(^ {20}\) and a large number of binary crystal phases in multiblock terpolymers.\(^ {22}\) For complex network phases, this scheme becomes more difficult, but not impossible as long as their interfaces can be described by appropriate mathematical formulae. An alternative scheme to obtain the initial compositional profiles for these network phases is to construct the compositional profiles in terms of a set of superimposing basis functions with appropriate coefficients.\(^ {43,44}\) In practice, we can solve the SCFT equations using the pseudo-spectral method with the initial mean fields from the computed compositional profiles, or directly using the spectral method, to obtain the converged solutions of the network phases for a given set of parameters. Finally, the converged solutions could be used as the input for other calculations. The ordered phases considered are listed in Fig. 1.

### 3 Results and discussion

#### 3.1 \( B_1A_B2C \) tetrablock terpolymers with a uniform conformational parameter

In order to obtain a generic phase diagram of the \( B_1A_B2C \) tetrablock terpolymers, in this subsection we consider a simple case in which all blocks are assumed to have a unique conformational parameter, i.e. \( \sigma_A = \sigma_B = \sigma_C = 1.0 \). Considering that the \( \sigma \) structure observed in the SISO system is composed of core–shell spheres whose sizes are mainly affected by the relative length between the two \( S \)-blocks (referred to as \( B \)-blocks) and the segregation degree between \( B \)-blocks and \( A/C \)-blocks, we calculate the phase diagram in the \( \chi_{AB}N – f_{B1} \) plane (Fig. 2) with a set of fixed parameters: \( f_A = f_{B1} = 0.42, f_C = 0.16, \chi_{BC}N = 15, \) and \( \chi_{AC}N = 45 \). In general, the phase transition follows the sequence sphere, cylinder (C), gyroid (G), and lamella (L) with

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**Fig. 1** Density isosurface plots of 3D morphologies as well as density profiles of 2D morphologies formed by \( B_1A_B2C \) tetrablock terpolymers: body-centered-cubic (bcc), face-centered-cubic (fcc), A15, Frank–Kasper \( \sigma \), hexagonal-close-packed (hcp). Fddd (O\(^{70}\)), gyroid (G), double-diamond (DD), cylinder (C), and lamellae (L). The red, green, and blue colors denote the regions where the majority components are \( A, B, \) and \( C \), respectively, while the A-domain is not shown in the 3D morphologies for clarity.

**Fig. 2** Phase diagram in the \( \chi_{AB}N – f_{B1} \) plane of the \( B_1A_B2C \) system with \( f_A = f_{B1} = 0.42, f_C = 0.16, \chi_{BC}N = 15, \chi_{AC}N = 45, \) and \( \sigma_A = \sigma_B = \sigma_C = 1.0 \). The filled symbols indicate the transition points determined using SCFT calculations, whereas the solid lines are a guide to the eye.
decreasing \( f_{B_1} \) or increasing \( f_{B_2} \). This is simply because the B-blocks are favored to be intercalated between A- and C-domains to lower their strong interfacial energy, and thus enlarge the effective volume fraction of the minority component by co-forming core–shell minority domains with the C-block. Obviously, the formation of core–shell structures is evidenced in the density plots of the morphologies in Fig. 1. In particular, the \( B_1 \)-block can choose three different configurations to regulate the shell structure, i.e. dangling, looping, and bridging (Fig. 3). Some \( B_1 \)-blocks are dangled in the A/B mixing matrix due to low \( \chi_{AB} \). The looping configurations induce the \( B_1 \)-block to swell the shell of the looping-back domain that is mainly constituted of the \( B_2 \)-blocks, whereas the \( B_1 \)-block of the bridging configurations swell the shell of the bridge-connected neighboring domain.

Importantly, the effective volume fraction of the minority component can be regulated by varying \( \chi_{AB} \). Higher \( \chi_{AB} \) results in more \( B_1 \)-blocks being expelled from the matrix into the shell leading to larger core–shell domains, and accordingly, the phase transition occurs from high curvature phases to low curvature ones from left to right in the phase diagram. The variation of the domain size responsive to \( \chi_{AB} \) is shown by the comparison of the density profiles of four blocks for \( \chi_{AB} = 4 \) and \( \chi_{AB} = 12 \) in Fig. 3(c). For clarity, the hexagonal cylindrical phase is chosen as the example. The conclusion derived from the density profiles of the cylindrical domain applies equally well to the spherical domains except for the dimensional change. Two useful mechanisms can be derived from the density profiles. Firstly, the core–shell structure is clearly confirmed by the presence of a peak for the \( B_2 \)-block, or an additional peak for the \( B_1 \)-block with \( \chi_{AB} = 12 \). More importantly, this suggests that the shell thickness is sensitive to the variation of \( \chi_{AB} \) because of the responsive distribution of \( B_1 \). Secondly, the composition of \( B_1 \) in the matrix is rather high (higher than 0.2), implying that the \( B_1 \)-blocks are weakly segregated from the A-blocks and some of them dangle in the matrix.

The combined effect of the two factors, \( f_{B_1} \) and \( \chi_{AB} \), results in the stable region of spheres at the left-top region of the phase diagram in Fig. 2. Both \( f_{B_1} \) and \( \chi_{AB} \) can effectively change the domain size of the spherical phases. In particular, the shell thickness of each domain is diminished with decreasing \( \chi_{AB} \) or \( f_{B_1} \), thus leading to smaller core–shell domains. In other words, the spherical phase at the region closer to the left-top corner has smaller domains, which effectively corresponds to the larger compositional asymmetry in simple AB-type block copolymers. Accordingly, the stable spherical phase on the left-top corner is hcp, and the bcc phase appears on the left and top boundary areas with vanishingly low \( \chi_{AB} \) or small \( f_{B_1} \). In contrast, the \( \sigma \) phase becomes stable at the region far away from the left-top corner where the factors \( f_{B_1} \) and \( \chi_{AB} \) work in cooperation to form large sizes of core–shell domains whose packing prefers the crystal lattice with rounder Wigner–Seitz cells. In addition, we speculate another factor in the core–shell spherical phase benefiting the stability of the \( \sigma \) phase consisting of non-uniform spherical domains in which the ratio of bridging and looping configurations for each individual domain is tunable to regulate the sizes of domains.

In addition, we construct the phase diagram in the \( \chi_{BC} - f_{B_1} \) plane in Fig. 4 by fixing \( \chi_{AB} = 8 \) instead of fixing \( \chi_{BC} \) in Fig. 2 while keeping the other parameters unchanged. High \( \chi_{AB} \) enforces more \( B_2 \)-blocks to enter the shell and hence increases the effective volume fraction of the minority component. In contrast, high \( \chi_{BC} \) drives more \( B_1 \)-blocks to leave the shell and migrate into the A/B matrix. The influence of \( \chi_{BC} \) on the shell thickness is evidenced by the density profiles in Fig. 3(d), where the peak of \( B_1 \) at the A/C interface vanishes when \( \chi_{BC} \) is increased from 5 to 20. Consequently, increasing \( \chi_{BC} \) leads to the inverse phase transition from low curvature phases to high curvature ones, as shown at the bottom of Fig. 4. A considerable phase region of the \( \sigma \) phase is predicted in the top region where the \( B_1 \)-block has a small but appropriate length. As \( \chi_{BC} \) increases, the \( \sigma \) phase transforms into classical spherical phases. Combining the two phase diagrams given in Fig. 2 and 4, the fundamental formation mechanism of the \( \sigma \) phase stems from the formation of the large core–shell domains which...
makes the interfacial energy more dominant over the entropic energy, and thus causes the domains to be packed on the crystal lattice with rounder Wigner–Seitz cells. In this tetrablock terpolymer system, there are a few critical parameters to regulate the thickness of the shell, such as $\chi_{AB}N$, $\chi_{BC}N$, and the length of $B_2$-block. Note that the alternative diamond structure is predicted to be stable in weakly segregated ABC triblock copolymers. However, in the present systems, the double diamond structure is metastable and transforms into the bcc spherical phase near the order–disorder transition (ODT) boundary because it indeed assumes the core–shell double diamond morphology.

In order to gain full knowledge of the effect of the relative magnitude between $\chi_{AB}N$ and $\chi_{BC}N$ on the stability of the $\sigma$ phase, we determine the phase diagram with respect to the two interaction parameters for a typical group of the other para- and entropic energy $W$. The underlying mechanism is generally independent of block copolymer systems, and has been discussed previously.

In the above paragraphs, we have discussed the influence of a variety of parameters on the stability of the $\sigma$ phase under the constraint condition of $f_A = f_B$, which is not obviously necessary. In experiments, Bates and coworkers have studied the SISO system with $f_A \neq f_B$. Therefore, we identify the phase diagram with respect to $f_A$ and $f_B$, in Fig. 7 when fixing the other parameters as $f_C = 0.16$, $\chi_{AB}N = 10$, $\chi_{BC}N = 15$, and $\chi_{AC}N = 45$, aiming to understand the influence of the change in relative lengths between three blocks of $B_1$, $B_2$ and $A$ on the stability of the $\sigma$ phase. The stability region of the $\sigma$ phase is quite general except that it shrinks slowly as $f_A$ increases. Apparently, a large $f_A$ reduces $f_B$ because of fixed $f_A + f_B = 1 - f_C$, and thus narrows the effective range of $f_B$ for a stable $\sigma$ phase.

### 3.2 B$_1$AB$_2$C tetrablock terpolymer mimicking the SISO systems

Experimentally, the $\sigma$ phase was observed in the SISO systems, and therefore it is interesting to construct a model system mimicking the specific SISO tetrablock copolymers. When the SISO system is referred to as B$_1$AB$_2$C, the interaction parameters are approximately given by $\chi_{AB}N = 11.0$, $\chi_{BC}N = 14.2$, and $\chi_{AC}N = 45.8$, and the conformational parameters are $\epsilon_A = 1.0$, $\epsilon_B = 0.91$ and $\epsilon_C = 2.06$ estimated from $b_1 = 6.07$, $b_2 = 5.47$, $b_3 = 7.80$, $\rho_1 = 0.46$, $\rho_2 = 0.52$, and $\rho_3 = 0.58$. In this terpolymer system, with fixed interaction parameters and conformational parameters, there are still a number of variables including two independent volume fractions and an additional parameter to specify the length of the B$_1$-block relative to the total composition of the B-block. A constraint condition is required to reduce one more parameter for the construction of a 2D cross-section of the phase diagram. Obviously, the length of the C-block is the most dominant factor determining the spherical phase region, and hence we choose $f_C$ as a free variable. In addition, the tail B-block is another critical factor distinguishing the B$_1$AB$_2$C terpolymer from the simple ABC triblock terpolymer. Therefore, we fix $f_A = f_B$, and construct the phase diagram in the $f_C$-$f_B$ plane (Fig. 8).

**Fig. 5** Phase diagram with respect to $\chi_{AB}N$ and $\chi_{BC}N$ for B$_1$AB$_2$C with $f_A = f_B = 0.42$, $f_C = 0.16$, $f_B = 0.30$, $\chi_{AC}N = 45$, and $\epsilon_A = \epsilon_B = \epsilon_C = 1.0$.

**Fig. 6** Free energy as well as its entropic and interfacial contributions of spherical phases relative to that of the reference phase of hcp along the phase path of $\chi_{AB}N = 5$ in Fig. 5.

**Fig. 7** Phase diagram in the $f_A - f_B$ plane of B$_1$AB$_2$C tetrablock terpolymers for $f_C = 0.16$, $\chi_{AB}N = 10$, $\chi_{BC}N = 15$, $\chi_{AC}N = 45$ and $\epsilon_A = \epsilon_B = \epsilon_C = 1.0$. The red dotted line is the limit of $f_B = 0$, and the blue dotted line indicates the case of $f_B = f_A$. The three black dotted lines denote the ODT boundary.

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During the construction of Fig. 8, more candidate phases beyond the stable phases are considered. Typical free energy comparisons for a given phase path of \( f_C \) are shown in Fig. 9. For example, for the bicontinuous phase, we considered another phase Fddd (O70) besides the gyroid phase. In particular, for spherical phases, we considered all of the other known domains with a high segregation degree in AB diblock when they have the same composition and chain length. Therefore, when a long B-block in B1AC is divided into two short B1- and B2-blocks separated by the A-block in B1AB2C, the effective interaction between A- and B-blocks is reduced even for the case of weak segregation between A- and B-blocks. Lower interaction induces smaller loss of configurational entropy of the B1AB2 triblock, and thus favors the phase separation of C-blocks from the B1AB2 co-formed matrix. As a consequence, the ODT curve tilts toward the direction of decreasing \( f_C \), the region of spherical phases moves toward the direction of decreasing \( f_C \), the region of the \( \sigma \) phase shrinks.

In Fig. 8, the most notable feature is the presence of the considerable region of the \( \sigma \) phase intermediated between the bcc and cylinder phases, and the expanded region of the \( \sigma \) phase compresses the region of bcc to be very narrow. This feature is similar to that of the phase diagram obtained by SCFT in the very recent work, though the parameters are not exactly same. Besides the similarity, there is a difference between the two phase diagrams, which is the presence of the stability regions of fcc and hcp in the area of large \( \tau = f_{B1} / (f_{A1} + f_{B2}) \). This difference should be caused by the different parameters, especially the interaction parameters. In the area of \( \tau \) approaching 1 with our parameters, it is possible for B and C blocks to self-assemble independently into separated B and C domains, thus forming more complex binary phases. As the appearance of other possible phases does not interfere with the conclusion on the formation mechanism of the single spherical phases, we would not include more possible morphologies into our calculations. In brief, this prediction is encouraging because it proves that the \( \sigma \) phase observed in experiments may be stable. When we compare the phase diagram with the experimental results along the phase path of \( f_{B1} = f_{B2} \) (denoted by the gray dotted line), the phase sequence from disorder to sphere, to cylinder, is in qualitative agreement. The shift of phase boundaries should be mainly induced by the inaccuracy of the parameter estimation and other unconsidered factors in theory such as the polydispersity of molecular weight.

Another interesting feature in Fig. 8 is the significant difference between the two limit phase paths of \( f_{B1} = 0 \) and \( f_{B1} = 0 \), which are reduced to two triblock terpolymers AB2C and B1AC, respectively. The unequal interactions of strong \( f_{AC} \) and weak \( f_{AB} \) causes the two triblock terpolymers to be non-equivalent. We can see that the region of the \( \sigma \) phase expands upwards until the limit path of B1AC. As we know, the segregation degree in the symmetric ABA triblock copolymer is only slightly higher than that of the corresponding AB diblock copolymer but with half length of the former. In other words, the segregation degree in the ABA triblock is lower than that of the AB diblock when they have the same composition and chain length. Therefore, when a long B-block in B1AC is divided into two short B1- and B2-blocks separated by the A-block in B1AB2C, the effective interaction between A- and B-blocks is reduced even for the case of weak segregation between A- and B-blocks. Lower interaction induces smaller loss of configurational entropy of the B1AB2 triblock, and thus favors the phase separation of C-blocks from the B1AB2 co-formed matrix. As a consequence, the ODT curve tilts toward the direction of decreasing \( f_C \), the region of spherical phases moves toward the direction of decreasing \( f_C \), the region of the \( \sigma \) phase shrinks.

It has been established that the conformational asymmetry of diblock copolymers acts as a key factor leading to the formation of a stable \( \sigma \) phase. Similarly, it should also play a significant role in the multiple block copolymers. In order to obtain direct evidence, we calculate the stability region of the \( \sigma \) phase with the same parameters as those in Fig. 8 except for the uniform conformational parameter \( \epsilon_A = \epsilon_B = \epsilon_C = 1 \).
These transition curves are superimposed onto Fig. 8 but are plotted in a different color (magenta). In comparison to the case of non-uniform conformational parameters, the $\sigma$ phase region shrinks drastically to become very tiny. This observation directly indicates the effect of the non-uniform conformational parameters. Moreover, the tiny stability region of the $\sigma$ phase along the phase path of the $B_1AC$ triblock originates from the triblock architecture that leads to the formation of the large spherical core–shell domains under the special group of interaction parameters.

Note that the main discrepancy between our theoretical results and the experimental results along the phase path of $f_{B1} = f_{B2}$ is that the experimental phase sequence in whole shifts toward smaller $f_C$. Actually, the interaction parameters in experiments cannot be fixed for different samples because of variable molecular weights. Accordingly, the experimental data only give these approximate phase points in the phase diagram for the constant set of interaction parameters. To examine the effect of interaction parameters on the phase behaviors, we vary all interaction parameters by a unique ratio as $(\gamma_{AB} = \gamma_{BC} = \gamma_{AC} = 11.0, 14.2, 45.8)$, and thereby identify the phase diagram in the $f_C-\gamma$ plane (Fig. 10). Apparently, as $\gamma$ increases to strengthen the interaction parameters, the phase boundary of the $bcc$ and $\sigma$ phases moves toward smaller $f_C$, which is closer to the experimental observation. However, it does not reach the experimental value of $f_C = 0.08$ as it is terminated by the presence of the cylinder phase. When strengthening the interactions synchronically, the impact on the phase separation between $A$- and $B$-blocks is more pronounced because $A$- and $B$-blocks are not fully separated and their segregation degree can be dramatically enhanced by increasing $\gamma$. As more and more $B$-blocks are pulled out from the matrix to form a shell surrounding the $C$-cores, which enlarges the volume fraction of minority effectively, the spherical phase tends to transform into the cylinder phase. This implies that the interactions might be underestimated in unequal degrees, for example, $\gamma_{AB}^{N}$ has a smaller deviation. In addition, one considerably important factor is not included in our theoretical model, i.e. the molecular polydispersity that is 1.04 for the experimental SISO sample.

### 4 Conclusions

In summary, we have systematically studied the formation of the Frank–Kasper $\sigma$-phase in $B_1AB_2C$ tetrablock terpolymers using SCFT calculations. First, we consider a generic model of $B_1AB_2C$ that three types of segments have a unique segment size, by screening the factor of conformational asymmetry that dominates the formation of the $\sigma$ phase in diblock copolymers. The stability of the $\sigma$ phase is investigated by constructing a number of 2D cross sections of phase diagrams with respect to a pair of free parameters while fixing the others. Significant stable regions of the $\sigma$ phase have been identified in these phase diagrams, illustrating another important factor of stabilizing the $\sigma$ phase that originates from the special tetrablock architecture. We find that an appropriate length for the middle $B_2$-block is necessary to form the shell of spherical domains enlarging the domain size. Moreover, the interaction parameter $\gamma_{AB}^{N}$ must be small and significantly smaller than $\gamma_{BC}^{N}$, and the latter is also required to be lower than some critical values for a given $\gamma_{AC}^{N}$.

In brief, these parameters work in cooperation to generate a critical self-assembly environment where the minority $C$-block forms a spherical core surrounded by an appropriate thickness of shell formed by part of $B_1$ blocks together with the $B_2$ blocks. The large core–shell spherical domain makes the contribution of interfacial energy more dominant over the entropic one, and thus benefits the formation of the $\sigma$ phase that has more favorable interfacial energy than the classical phases of $hcp$, $fcc$, and $bcc$.

Then, we choose a specific set of parameters mimicking the SISO sample with equal volume fractions of $S$ and $I$ in experiments, and calculate the stability region of the $\sigma$ phase with respect to the two block ratios $f_C$ and $f_{B1}$, which is intermediated between the $bcc$ and cylinder phases and is considerably large. Our prediction is in qualitative agreement with the experimental results as well as very recent theoretical results. Although the phase behavior is affected tremendously by the relative length between $B_1$ and $B_2$ blocks, there is no obvious evidence that the stability of the $\sigma$ phase is solely dependent on it because the phase region of $\sigma$ expands until reaching the limit of $f_{B1} = 0$, i.e. the case of the $B_1AC$ triblock. The tetrablock terpolymer with a uniform conformational parameter exhibits a significantly smaller stability region of the $\sigma$ phase than that of SISO confirming that the conformational asymmetry between the $A$/B-blocks and the $C$-block plays another critical role in stabilizing the $\sigma$ phase.

More than ten years ago, the complex $\sigma$ phase, which has been known for decades in hard alloy crystals, was discovered in the self-assembly of amphiphilic liquid crystals, and then was observed in the self-assembly of the IL diblock copolymer as well as the SISO tetrablock terpolymer in 2010. The coincident formation of this spherical phase in very diverse soft matter systems must imply some common formation mechanism.
Xie et al. have revealed that the dominant factor for the formation of the $\sigma$ phase in AB diblock copolymers arises from the conformational asymmetry leading to a large spherical domain, and based on this mechanism they have predicted the formation of the $\sigma$ phase in AB$_n$ miktoarm copolymers. This work that explores another formation mechanism originating from the chain architecture completes the understanding of the formation of the $\sigma$ phase and is complementary to the state-of-the-art experiments.

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