Emergence of ordered network mesophases in kinetic pathways of order–order transition for linear ABC triblock terpolymers†

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Applying the string method to the self-consistent field theory (SCFT) of ABC linear triblock copolymers, we developed a new strategy to design kinetic pathways for the formation of stable or metastable network mesophases in order–order transition (OOT) processes. The design principle regarding the kinetic pathways between distinct mesophases is based on the matching relationships of both domain spacing and dominant Fourier components of the density distributions. The results suggest that complex ordered network mesophases, such as alternating diamond (D⁴) and alternating plumber’s nightmare (P⁶) could be obtained in kinetic pathways between simple phases covering lamellae, cylinders and spheres. By virtue of the minimal free energy pathway (MEP) obtained, we could acquire the epitaxial relationship and phase transition mechanism. Furthermore, we managed to regulate the MEP by changing the block composition to adjust packing frustration. Two new metastable networks, core–shell five-pronged and six-pronged morphologies, were found in the kinetic pathways, further demonstrating the regulating mechanism. The results will contribute to a better understanding of the kinetic relationship between simple phases and complex networks, thus providing a platform for soft materials design via the OOT route and guiding experimental procedures to fabricate ordered network mesophases.

I. Introduction

Block copolymers can self-assemble into various periodic ordered mesophases with intriguing properties, and thus have attracted a tremendous amount of attention.1–5 The phase behavior of simple AB diblock copolymers is primarily dictated by two parameters, the volume fraction $f_A$ of block A and the immiscibility degree characterized by the product $w_{AB}N$, where $N$ is the number of statistical segments in a chain and $w_{AB}$ is the Flory–Huggins interaction parameter. The equilibrium structures formed by AB diblock copolymers include lamellae (L), cylinders (C_Hex), gyroids (G), Fddd network, and body-centered cubic spheres (S^{bcc}).3 With regard to ABC triblock copolymers, which provide a significantly enlarged parameter space and thus form much more complicated and fascinating morphologies than AB diblock copolymers,6–10 exploring their micro-phase separated behavior thoroughly is particularly formidable.6,9 Customarily, the so-called frustrated and nonfrustrated systems are classified according to the comparison of the interaction between distinct blocks.6 When the interaction parameter between the endblocks, $w_{AC}N$, is larger than those between the two neighboring blocks, $w_{AB}N$ and $w_{BC}N$, the ABC copolymer is referred to as a nonfrustrated system. In contrast, when $w_{AC}N$ is smaller than $w_{AB}N$ or $w_{BC}N$, the A/C interfaces, which are not favored by the molecular architecture, tend to be formed, accordingly leading to a frustrated system. Among the numerous ordered mesophases formed by ABC triblock copolymers, multiple continuous networks containing two or more chemically distinct and intertwining domains have attracted enormous interest as an extremely fascinating class.11 In particular, periodic and interconnected network structures with high order connectors prove to be advantageous in many technological areas such as three-dimensional (3-D) photonic crystals,12,13 and solar cells.14

For amphiphilic molecules with low molecular weight, cubic network structures with multi-pronged nodes as well as their phase transformations have been reported.15–18 The G phase is three-pronged, the diamond (D) is four-pronged, and the plumber’s nightmare (P) is six-pronged. Increasing the number of prongs would lead to a larger excess volume of the nodes. It is well known that the intricate phase behavior is dictated by an
exquisite balance between interfacial tension and packing frustration. When the composition remains constant, surfaces with a constant mean curvature (CMC) tend to develop to satisfy the requirement of minimizing the interfacial area, which is favored by the interfacial tension. At the same time, the system prefers relatively uniform domains to distribute the entropic stretching energy equally among the molecules and thus alleviate packing frustration. It has been elucidated based on the theoretical calculation that ordered bicontinuous double diamond (OBDD) is usually an unstable network mesophase compared to ordered bicontinuous double gyroid (OBGD) in diblock copolymers. The OBDD structure possesses more spacious opening between the three struts around each node, and its CMC surfaces produce more uniform domains between nodes and struts. Thus, the relative variation in its mean curvature is smaller, which makes OBGD a stable phase. In addition to OBDD, a number of metastable ordered networks in diblock copolymers, such as single gyroid (SG) and single diamond (SD), have been captured based on self-consistent field theory (SCFT). For ABC triblock copolymers, it is important to closely pack A and C domains due to the need of reducing the stretching of the bridging block B. For example, ordered tricontinuous double diamond (OTDD or D\(_3^1\)) found to be stable by Qin according to the weak-segregation description, possesses two interpenetrating networks formed by A and C blocks, respectively. And then a novel promising class of ordered network mesophases, with diamond-like morphology (DLM) observed in thin films, was described comprehensively on the basis of both the weak segregation theory and SCFT.

Mitigating packing frustration may stabilize network structures for block copolymers. For example, a thermodynamically stable OBDD structure in an AB diblock copolymer composed of a stereoregular block has been reported. The release of the free energy due to local packing of the conformationally ordered blocks may explain the stabilization of the OBDD structure. Other reported methods include coordinating polydispersity of different blocks, regulating molecular architectures, and tethering nanoparticles. In particular, with appropriate homopolymers added into the copolymers, packing frustration can be significantly relieved, resulting in stable OBDD,\(^{35,36}\) D\(^3\),\(^{37}\) and even P structures.\(^{35,37,38}\) It was concluded by Dotera that homopolymers tend to gather in the bulky nodes rather than in the narrow struts with severe space limitations, which is responsible for the formation of D\(^4\) and alternating P (P\(_3\)) structures.\(^{39}\) Unfortunately, in a pure triblock copolymer system, excessive stretching of A and C blocks makes it impossible to form a stable P phase. On the other hand, for copolymer–nanoparticle hybrid materials, the P structure has been observed as a stable state in experiments.\(^{40,41}\) Jain, et al. reported a straightforward approach to obtain 3-D connected robust networks based on a cubic bicontinuous bulk hybrid material with P morphology. Nevertheless, to the best of our knowledge, network mesostructures with six-pronged connectors have not been substantiated in a purely polymeric system.

In addition to stable morphologies, numerous metastable structures, which may be useful in more technological applications, have been investigated as well.\(^{23,42}\) It has been well established that adding more types of blocks will generate more intricate structures.\(^4\) In addition, the chain topology plays a crucial role in the formation of ordered phases.\(^{43-47}\) Changing the molecular topology may allow some metastable structures for linear copolymers, such as perforated lamellae,\(^{48}\) to stabilize. Due to the appearance of more stable and metastable mesophases, especially the ordered networks, the dynamical investigation of order–order transition (OOT) and order–disorder transition (ODT) has become an attractive topic accordingly. Given the peculiarity of long molecular chains characteristic of polymers, the mechanisms of OOT and ODT have become more intricate and fascinating than those for surfactant systems. Well-ordered mesophases could be obtained via regulation of the kinetic pathways of OOT and ODT, thereby instructing their fabricating routes.

The vast range of soft matter systems involves the kinetics of OOT, during which epitaxial intergrowth between different ordered morphologies exists extensively.\(^{49-51}\) The epitaxial intergrowth relationship represents the correspondence of certain crystallographic directions between two ordered phases. Therefore, this enables an easy transformation between the two morphologies due to the low barrier for phase transition. OOTs including C\(^{\text{HEX}}\)-G,\(^3\) \(L\)-G,\(^{53-56}\) L-C\(^{\text{HEX}}\),\(^5\) and S\(^{\text{HEX}}\)-C\(^{\text{HEX}}\) transitions\(^{58,59}\) have attracted massive attention. It was demonstrated in the melt of a poly(oxyethylene)–poly(oxybutylene) diblock copolymer\(^{54}\) that the (211) planes of the G phase are epitaxially related to the (001) planes of the L phase. The same epitaxial relationship was also confirmed in certain block copolymer mixtures.\(^{52}\) With regard to ABC triblock copolymers, aligned metastable morphologies formed in the film followed by thermal annealing prove helpful for developing stable oriented networks. Suzuki, et al.\(^{60}\) observed the phase transition of an ABC triblock terpolymer from L to ordered tricontinuous double gyroid (OTDG or G\(_3\)) in the experiment. It was demonstrated that it is the epitaxial intergrowth that drives G\(_4\) to preferentially orient with (110) planes perpendicular to the solvent cast film.

Utilizing various experimental measurements, the metastable or transient mesophases in the kinetic pathways could be observed. Encountered in numerous experiments involving the phase transition from L to G,\(^{53-56}\) as a metastable structure, PL with different symmetries can be classified into three categories: tetragonally perforated lamellae (TPL), hexagonally perforated lamellae (HPL), and PL with apparently poor spatial order. Besides PL structures, complex network mesophases are another kind of metastable mesophases in kinetic pathways. Investigating the phase transition from L to G induced by a pressure jump and monitored by time-resolved X-ray diffraction, Squires, et al. suggested a mechanism whereby the transformation proceeds via the D structure.\(^{61}\) By solving a set of amplitude equations derived from the TDGL formula, Yamada, et al. demonstrated O\(^{70}\) (Fddd) to be a metastable phase which would convert into the G structure.\(^{62}\) Two metastable structures, O\(^{70}\) and cylinder-like networks, were observed in the L-G phase transition pathway for diblock copolymers in our recent work.\(^{61}\) The cylinder-like network displays an interesting...
characteristic that three adjacent cylinders are interconnected with each other. In addition to the traditional phase transition process, those between different network mesophases such as OBDG–SG, OBD–OBDD, and OBD–SG have also been investigated in recent years.

Despite this progress the phase transition kinetics involving various structures, especially the relationship between simple phases (lamellae, cylinders and spheres) and complex networks is still an open question. It has been demonstrated that string method, which is a robust technique to probe into the free energy landscape, is particularly effective to investigate the kinetic pathways. Aiming at capturing the minimal free energy pathway (MEP) for bistable systems, the string method was proposed by E et al.63–65 Exploiting suitable initialization procedures to exert physical restrictions, the string method can generate the MEP between two ordered structures undergoing nucleation and growth.70 Cheng, et al.71 studied the nucleation of ordered phases in diblock copolymers by examining the free energy landscape using SCFT combined with the string method. The concrete information regarding nucleation, including the shape, size and free energy barrier of the critical nuclei, was obtained from the MEP. Furthermore, it was concluded that the gyroid nucleus develops from the metastable lamellae via a two-step mechanism, starting from a nucleus with hexagonally modulated layers to intermediate hexagonally perforated layers, and then from the perforated layers to the gyroid with networked cylinders. In our recent work, the epitaxial relationship and metastable structures obtained during the OOT between L and G phases of diblock copolymers were explored in detail.51 The one-step and two-step nucleation mechanisms were differentiated particularly. By simulating the spinodal decomposition mechanism, various metastable structures were yielded in the kinetic pathways. The optimal epitaxy between ordered structures was researched by Wang, et al.72 and it was concluded that the epitaxial relationship derives from the matching of the dominant Fourier components of the density distribution. In addition, it is the domain spacing rather than the orientation of different phases that plays a dominant role in an epitaxial transition process.63 Indeed, if the phase periodicity remains invariable during the OOT process, only a local rearrangement is necessary to realize the structural evolution, leading to an easier epitaxial transition.

In the current work, combing the string method with SCFT for ABC linear triblock copolymers, we aim at exploring the formation of stable or metastable networks encountered in kinetic pathways. In particular, we focus on possible transition pathways via spinodal decomposition. Thus, the initial density distributions of the states along the string are set to evolve gradually from one end to the other in the whole computation box. Utilizing this initialization procedure, we obtained complex network mesophases in the free energy landscapes of phase transitions between simple phases, including lamellae, cylinders and spheres. The epitaxial relationship and metastable or transient states in the kinetic pathways were systematically analyzed. In particular, the formation of ordered network mesophases could be regulated by adjusting the kinetic pathways via changing the block composition or interaction between the endblocks. More importantly, the OOT between simple morphologies proves to be a robust strategy for obtaining novel networks, such as the five-pronged and six-pronged networks. The results reveal the kinetic relationship between simple phases and complex networks and demonstrate the potential of the OOT route for designing soft materials with specific structures.

II. Theory and computation method

A. Self-consistent field theory (SCFT)

Here, we introduce briefly the theoretical framework of the SCFT for linear ABC triblock copolymers. The derivation, in detail, is the same as our previous paper and the references therein.6 We consider a system composed of n linear ABC triblock terpolymers in a volume $V_j$ which satisfies the incompressible conditions. Block compositions, i.e. the average volume fractions $f_A$, $f_B$, and $f_C$ ($f_A + f_B + f_C = 1$) respectively. All the chains are assumed to have the same degree of polymerization $N$ and polymer segments have the same statistical segment length $b$ (the Kuhn length). In the SCFT, the polymer segment probability distribution function $q(r,s)$, which represents the probability of finding segment $s$ at position $r$, is the fundamental quantity to be calculated. It satisfies a modified diffusion equation which is based on a flexible Gaussian chain model:

$$\frac{\partial q(r,s)}{\partial s} = \frac{1}{6} b^2 \nabla^2 q(r,s)$$

$$- [\gamma_A(s)\omega_A(r) + \gamma_B(s)\omega_B(r) + \gamma_C(s)\omega_C(r)]q(r,s)$$

(1)

where $\omega_k(r)$ is the mean field acting on the species $k$, and $\gamma_k(s)$ is 1 if $s$ belongs to block $k$ and 0 otherwise. The initial condition of the above equation is $q(r,0) = 1$. As the two ends of the triblock chains are disparate, a second end-segment distribution function $q^*(r,s)$ is defined. It satisfies eqn (1) with the corresponding initial condition becoming $q^*(r,0) = 1$. The total partition function for a single copolymer chain is found by integrating all possible configurations for the chains subjected to the external fields and thus can be written as $Q = \int q^*(r,s)q^*(r,1-s)dr$ in terms of $q(r,s)$ and $q^*(r,s)$. The free energy functional of the system satisfies the following equation:

$$F/nk_B T = -\ln(Q/V) + (1/V)\int\mathrm{d}r [\chi_{AB}N\varphi_A(r)\varphi_B(r)$$

$$+ \chi_{BC}N\varphi_B(r)\varphi_C(r) + \chi_{AC}N\varphi_A(r)\varphi_C(r)$$

$$- \omega_A(r)\varphi_A(r) - \omega_B(r)\varphi_B(r)$$

$$- \omega_C(r)\varphi_C(r) - \zeta(r)(1 - \varphi_A(r) - \varphi_B(r) - \varphi_C(r))]$$

(2)

where $\varphi_A(r)$, $\varphi_B(r)$ and $\varphi_C(r)$ are the monomer densities whose periodic distributions characterize the ordered phase. The potential field $\zeta(r)$ is a Lagrange multiplier used to enforce the incompressibility conditions. The minimization of the free energy in eqn (2) with respect to the monomer densities and the
mean external fields leads to the SCFT equations that describe the equilibrium morphology. The solutions can be obtained by using the powerful pseudo-spectral method originally proposed by Rasmussen et al. For each phase, by minimizing its free energy with respect to the cubic box size $D$, the characteristic length scale of the phase in unit of the radius of gyration of the block copolymer $R_g$ is determined.

B. String method
The free energy and morphologies of the system, obtained by solving the SCFT equations can be used as the two ends of the string for the string method. The main objective of the string method is to obtain the MEP $\psi$ on the energy landscape. A MEP is a curve (string) in the configuration space, connecting two states A and B, i.e. the two ends of the string, whose free energies are denoted by $F_A$ and $F_B$, respectively. The MEP obtained is indicated as the evolution of $F – F_0$, the free energy difference along the string between the different states and the initial state A. The MEP satisfies

$$\nabla F^{\perp}(r) \cdot \psi = 0$$

(3)

where $\nabla F^{\perp}$ is the component of $\nabla F$ normal to the string $\psi$ and $s$ (string) is a parameter distinguishing the different states of the system. The whole string is discretized into 40 points where each point corresponds to a state with specific morphology. In addition to the two ends of the string, other initial states on the string can be set up by different initialization procedures. Initializing the string is a case-by-case problem and the converged MEP solution depends significantly on the choice of the initial string. Normally, two kinds of initialization means can be utilized to explore different mechanisms of OOT. On the one hand, when we focus on the nucleation of phase A in phase B, the evolution of the initial states can be defined as a series of concentric spheres formed by A and the remaining volume of the computation box is occupied by B. On the other hand, if we would like to obtain possible metastable states during the phase transition, adopting the same initialization route would be difficult. In this case, the initial density distribution of each state along the string can be dictated to change gradually in the evolution of the initial states can be identified according to the converged MEP. If the free energy barrier of the converged MEP is zero, then the actual phase transition proceeds via spinodal decomposition. Otherwise, the metastable state encountered in the MEP can be regarded as the intermediate structure during the process of nucleation and growth from A to B. Herein, we aim to screen the metastable phases in the kinetic pathways and to explore the possible phase transition via the spinodal mechanism. Accordingly, the initial density distribution should evolve simultaneously in the entire calculation cell, also see our recent paper:63

$$\phi_j(r) = \phi_A(r) + \frac{j}{M}(\phi_B(r) - \phi_A(r)), \quad j = 0, 1, \ldots, M$$

(4)

where $M$ is the total discretization number of states. $\phi_0(r) = \phi_A(r)$ and $\phi_M(r) = \phi_B(r)$ represent the density distribution of the A and B structures at the two ends of the string, respectively. It should be noticed that there is no generic means to initialize the string, and different means may lead to distinct efficiency of the string method. Here, we adopt the simplest method, i.e. direct combination of the two states A and B to generate a homogeneous variation of density distribution along the initial string from A to B, which has proven to be an effective means to identify the metastable structures observed in experiments.63 The parameter $s$ ranges from 0 to 1:

$$s_{\text{string}} = \frac{\sum (\phi_j - \phi_A)^2}{\sum (\phi_j - \phi_A)^2}$$

(5)

Once the initialization procedure is accomplished, the next step is to iterate the states on the string via SCFT. After several iteration steps in running the SCFT, such as five, the string would be regulated using the difference method to read just the density distributions of all of the states along the string. In other words, it is significant to continually adjust the string to guarantee a close correlation between various states on the string. Otherwise, the states along the string would converge to a local minimum and fail to generate an effective MEP. It should be noticed that for any initialization procedure, maintaining the shape of the string in the configuration space, i.e. maintaining a constant distance between various states on the string, would be important. Repeating the procedures of iterating and adjusting the string, we would ultimately obtain the MEP satisfying eqn (3). Sufficient relaxation of the string can be indicated by the constant free energy for all of the states along the string.

III. Results and discussion
1. Stable alternating networks for linear ABC triblock copolymers
We focus on the kinetic pathways for the formation of stable and metastable network mesophases in ABC triblock copolymers, so herein we first introduce briefly the stable ordered alternating network mesophases, which contain two interpenetrating and chemically distinct single networks formed by A and C blocks, respectively. The phase behavior of nonfrustrated ABC triblock copolymers has been investigated comprehensively by Qin, et al. To simplify the calculation and analyze the alternating network structures, we pay attention to the phase behavior in the B-rich corner in the phase diagram along the isopleth $f_A = f_C$. In this reduced parameter space, ABC triblock melts behave much like the simpler AB diblock melts. We choose a nonfrustrated system by setting the Flory–Huggins parameter $\chi_{AB} = 13$, $\chi_{AC} = 35$ according to Qin, et al. The stable network morphologies are shown in Fig. 1. To avoid any ambiguity, we specify that the alternating diamond (D$^w$), alternating gyroid (G$^w$), and alternating spheres in which A and C spheres are packed in a CsCl lattice (S$^w$) correspond to the symmetries Fd$\bar{3}m$, I$\bar{4}$32 and Pm$\bar{3}m$, respectively. It should be indicated that the S$^w$ and alternating plumber’s nightmare (P$^3$) structures belong to the same space group Pm$\bar{3}m$. Therefore, we represent S$^w$ here as a P$^3$-like
structure, which is an alternating version of the plumber’s nightmare-like morphology and evolves into a P^A structure when the midblock length is decreased. The strong incompatibility between endblocks is responsible for the formation of G^A, D^A and S^A (P^A). It is significant to place the A and C domains closer together because of the need to relieve the stretching of the bridge block B.\textsuperscript{24,25} As a result, the spherical phase exhibits the body-centered cubic packing of minority domains, and a closer packing may lead to the formation of P^A. As the bridge block fraction $f_B$ increases, the mismatch of the stretching energy between the endblocks and midblock produces a spontaneous interfacial curvature that causes the minority domains to evolve from L to G^A, D^A, S^A (P^A).\textsuperscript{19} With regard to the G^A, D^A and P^A network mesophases, their area-averaged mean curvature increases with the increase in the number of the struts connected in each node as the midblock fraction increases, which explains the phase sequence G^A $\rightarrow$ D^A $\rightarrow$ P^A.

The P^A structure possesses two interpenetrating, six-fold connected networks, whose evolution with $f_B$ is shown in Fig. 2. As $f_B$ decreases from 0.6 to 0.25, the morphologies formed by A blocks evolve from bulkier junctions and narrower struts to relatively uniform domains, which can be interpreted by the tendency to relieve the packing frustration.\textsuperscript{19,75,76} At compositions corresponding to the complex phase region, the constant mean curvature (CMC) surfaces tend to form bulky junctions connected by narrow struts. In this case, the packing frustration would be serious due to a large mismatch of the stretching energy between the blocks forming the bulky junctions and those existing in the narrow struts. To alleviate the packing frustration, the surface deviates from CMC to achieve the match of the stretching energy between the nodes and struts.\textsuperscript{19} When $f_B = 0.6$, the A-rich and C-rich domains form P^A-like structures with an approximately constant curvature, resulting from two facts. Firstly, as the endblock volume fraction is relatively small, the midblock is long enough and its stretching degree can be very low. Secondly, as shown in the third row of Fig. 2, the midblocks, \textit{i.e.} the B blocks tend to distribute within the whole unit cell when $f_B = 0.6$. In contrast, when $f_B = 0.4$ and 0.25, the B blocks incline to form domains restricted tightly around the A and C domains. Therefore, the packing frustration of B domains formed by longer blocks is significantly relieved. To minimize the interfacial energy, a CMC interface is formed at higher $f_B$, which generates nonuniform A domains. In contrast, the A blocks at $f_B = 0.25$ form a much more uniform domain than those at $f_B = 0.6$, and thus more obvious six-fold-coordinated networks are formed. The single chain free energy at $f_B = 0.25$ is 5.5018 and that at $f_B = 0.6$ is 4.5170, which indicates that the system becomes more unstable due to the increase in the non-CMC degree. In the following part regarding the dynamical analysis for the different network mesophases, we will further demonstrate that complex networks would become difficult to observe in kinetic pathways due to the packing frustration-induced non-CMC interfaces. With respect to the D^A phase, a similar tendency has also been observed (Fig. S1, ESI\textsuperscript{†}).

In addition to the conventional stable structures, numerous metastable structures might also be observed in experiments and could display broader application prospects. A great wealth of strategies has been developed to explore metastable structures.\textsuperscript{23,42} For example, in the SCFT, by using different

![Fig. 1](image-url)
initialization fields, different metastable structures could be obtained (Fig. S2, ESI†). Fig. S2 (ESI†) displays twelve metastable structures based on the BCC initialization procedure in the phase region of the GA phase. These metastable structures are all obtained via SCFT calculations, but how the different metastable structures develop in kinetic pathways is unknown. In the following parts, we will discuss how we could obtain the complex ordered network mesophases introduced above by designing and regulating kinetic pathways, and develop a new strategy to obtain more novel metastable network phases.

2. Designing kinetic pathways for the emergence of ordered network mesophases

Our design principle of kinetic pathways to explore stable and metastable network mesophases is based on two factors affecting the epitaxial relationship. First, the origin of the epitaxial relationship can be ascribed to the matching of the dominant Fourier components of the density distributions. Second, the domain spacing match is a dominant factor in an epitaxial transition, which can facilitate the epitaxial intergrowth. If the unit cell of the phase remains fixed during the phase transition, polymers just undergo a local rearrangement, so an epitaxial phase transition would be easy to occur. Conversely, if the phase periodicity is mismatched, the phase transition should need macroscopic transport of materials. According to these principles, we can design different kinetic pathways by choosing different initial simple phases as the two ends of the string, and screen possible metastable or stable alternating networks along the transition pathways. From the MEP obtained, we can analyze the epitaxial growth relationship as well as the phase transition mechanisms such as spinodal decomposition or nucleation and growth.

Previous experimental and theoretical investigations have shed light on the phase transition pathway between simple phases and the gyroid phase. The experimental investigations have demonstrated that the epitaxial relationship between L and GA is from the (001) planes of L to the (110) planes of the GA structure. However, in terms of the DA and PA phases, to the best of our knowledge, how they could be formed from simple phases has not been investigated yet. To test the validity of our approach for investigating the kinetic pathways of phase transition, we first apply it to illustrate the formation of the GA structure (Fig. S3, ESI†). It is confirmed that the epitaxial relationship between L and GA is indeed from the (001) planes of L to the (110) planes of the GA structure, which is in good agreement with the experimental observation. In the following parts, we will focus on the formation kinetics of the PA and DA structures, respectively, investigating how the PA and DA structures can be formed from the simple phases epitaxially.

Fig. 2  (P̂A-like) structure with f_B decreasing along the isopleth f_A = f_C with χ_{AB}N = χ_{BC}N = 13, χ_{AC}N = 35. Density profiles of the central cross section of the nodes for block A (the first row) and the corresponding 3D morphology (the second row) as well as the density profiles of the central cross section of the nodes for block B (the third row) are shown. The corresponding compositions for each column are f_B = 0.6, f_B = 0.4 and f_B = 0.25, respectively.
With regard to the P^A phase, one possible pathway for its formation is from the L phase with \{020\} wave vectors, to the C^A phase (alternating cylinders based on a square lattice) with its 10 plane perpendicular to the 001 plane of lamellae. The optimized box sizes of the \{020\} L and C^A phases are both 6.8R_g when \( w_{AB}N = w_{BC}N = 13, w_{AC}N = 35, f_A = f_C = 0.2, f_B = 0.6 \). The thermodynamically stable phase under these conditions is S^A (P^A-like structures), corresponding to the “valley” of the free energy curve shown in Fig. 3(a), and thereby the actual phase transition from L to C^A is difficult to achieve. Instead, the P^A-like phase can be obtained directly from L or C^A indicated by the green arrows. Both of the free energy barriers from L to P^A and from C^A to P^A are close to zero, which manifests that spinodal decomposition happens in these phase transition processes. In the next section, we would discuss how we can regulate the kinetic pathways and obtain a P^A structure as an intermediate state during the phase transition from L to C^A. The transient structures as well as the stable P^A-like phases encountered in the MEP are summarized in Fig. 3(b). The epitaxial growth process between the L, C^A and P^A phases can be clearly seen from the evolution process. It is obvious that a TPL structure (\( s = 0.31 \)) can be observed as a transient structure in the pathway from the L to P^A-like phase. The TPL structure has been observed as a metastable state which appears during the transition from L to G for diblock copolymers.\(^{63}\) Herein, we notice that the TPL structure observed can only be a transient one, which is due to the repelling interaction between A and C perforated lamellae.\(^{5,37}\) The positions of the holes in the TPL structure are determined by the structural characteristics of the P^A phase. After the TPL structure, A perforated lamellae and...
Fig. 4 Discovering the D^A mesophase in kinetic pathways. (a) Minimal free energy pathway (MEP) from L with (111) planes to L with (1–1–1) planes at $\chi_{AB}N = \chi_{BC}N = 13$, $\chi_{AC}N = 35$ and $f_A = f_C = 0.21$, $f_B = 0.58$, the morphologies of which are shown in (c). (b) The MEP from F^A to L with (111) planes at $\chi_{AB}N = \chi_{BC}N = 13$, $\chi_{AC}N = 35$ and $f_A = f_C = 0.21$, $f_B = 0.58$, the morphologies of which are shown in (d). Red and blue represent domains rich in A and C blocks, respectively.
C perforated lamellae pass through each other’s hole and start to interconnect, and thus a P^A-like structure is formed. During the phase transition from the C^A to P^A-like phase, a modulated C^A phase can be observed when $s = 0.72$ as a transient structure. After that, A and C cylinders start to interconnect and form a P^A-like structure constructed from six-fold coordinated junctions with two of them being thicker along the direction of the cylinders ($s = 0.67$). At last, a P^A-like structure with relatively uniform struts is formed.

Similar to the P^B phase, the D^A phase can also be obtained in the kinetic pathways between the simpler phases. Fig. 4 shows two pathways for the formation of the D^A phase. One of the pathways is from L with (111) planes to L with (111) planes (Fig. 4(a)), and the other pathway is from the spherical phase, referred to as F^A, to the L phase with (111) planes (Fig. 4(b)). The F^A phase is packed in a NaCl lattice, in which A and C domains form a face-centered cubic (FCC) lattice, respectively. Likewise, the epitaxial growth process can be obtained according to the MEP. In particular, the (111) planes of the D^A phase are epitaxially related to the (001) planes of the L phase, which is different from the epitaxial growth process between L and P^A. In addition, the HPL structure is encountered in the pathways located at $s = 0.39$ and $s = 0.64$ in Fig. 4(c) and at $s = 0.59$ in Fig. 4(d). Like the TPL structure shown in Fig. 3(b), the HPL structure observed here can be regarded as an alternating version of A and C perforated lamellae, which is a transient state. It should be noticed that although we obtain the D^A phase in the kinetic pathway between different simpler phases, the D^A phase is actually thermodynamically preferred, as compared with other phases under the chosen parameters. The possible phase transition pathways to D^A are indicated by the green arrows shown in Fig. 4(a) and (b). Both the P^A-like and the D^A phases we obtained under the chosen parameters are very near the ODT, and thus in reality the fluctuation effect could not be ignored. However, it is not considered in a mean field theory, such as SCFT. The free energy differences per molecular chain between different phases encountered in the kinetic pathways to P^A and D^A are of the order of magnitude of $10^{-3}$ and $10^{-3}k_B T$, respectively, leading to the systems extremely susceptible to thermal fluctuations. The effect of composition fluctuations on the phase behavior of diblock copolymers has been illuminated and the former can be suppressed when the polymer chains are long enough. In addition, in terms of the triblock copolymers, the weak segregation theory used to investigate the phase behavior near the ODT has identified S^A (P^A-like) and D^A phases. Clearly, the results presented by our SCFT calculations are in good agreement with the analysis based on weak segregation theory.

The results involving the formation of alternating networks, including G^A, P^A, and D^A, demonstrate that the method we developed to design the kinetic pathways could serve as a promising means to obtain complex network mesophases via the phase transition between simple morphologies such as lamellae, cylinders, and spheres. The complex network mesophases and the corresponding simpler phases are summarized in Table 1. It can be clearly seen in Table 1 that the ordered network structures all have the same optimized box size with their corresponding simpler structures, which demonstrates the validity of our design principle of kinetic pathways.

### Table 1: The optimized box sizes for different ordered network mesophases and the corresponding simple phases with $z_A N = z_B N = 13, z_C N = 35$

<table>
<thead>
<tr>
<th>Composition parameters</th>
<th>Structures</th>
<th>Optimized box size ($R_g$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_A = f_C = 0.23, f_B = 0.54$</td>
<td>C^A</td>
<td>(5.2, 5.2, 5.2)</td>
</tr>
<tr>
<td>$f_A = f_C = 0.23, f_B = 0.54$</td>
<td>BCC</td>
<td>(5.2, 5.2, 5.2)</td>
</tr>
<tr>
<td>$f_A = f_C = 0.21, f_B = 0.58$</td>
<td>D^A</td>
<td>(6.0, 6.0, 6.0)</td>
</tr>
<tr>
<td>$f_A = f_C = 0.21, f_B = 0.58$</td>
<td>D^A</td>
<td>(6.0, 6.0, 6.0)</td>
</tr>
<tr>
<td>$f_A = f_C = 0.20, f_B = 0.60$</td>
<td>P^A</td>
<td>(6.8, 6.8, 6.8)</td>
</tr>
<tr>
<td>$f_A = f_C = 0.20, f_B = 0.60$</td>
<td>P^A</td>
<td>(6.8, 6.8, 6.8)</td>
</tr>
<tr>
<td>$f_A = f_C = 0.20, f_B = 0.60$</td>
<td>C^A</td>
<td>(6.8, 6.8, 6.8)</td>
</tr>
</tbody>
</table>

### 3. Regulating kinetic pathways for the emergence of ordered network mesophases

The method we developed can not only design kinetic pathways for the emergence of ordered network mesophases, but can also regulate the pathways by changing the block length and interaction. Herein, taking the P^B phase as an example, we would firstly display the effect of the block length on the kinetic pathways. As shown in Fig. 5, when the midblock fraction decreases to $f_B = 0.58$ (Fig. 5(a)) and $f_B = 0.56$ (Fig. 5(b)) from $f_B = 0.6$ (Fig. 3), the P^A-like phase evolves from a stable structure at the valley to a metastable one at the saddle point in Fig. 5(a) and an unstable one at the peak in Fig. 5(b). This fact demonstrates that if the midblock length is not long enough, then it may be difficult to observe the P^B structure in the kinetic pathways of phase transition. When the midblock fraction is appropriate such as $f_B = 0.58$ in Fig. 5(a), the P^B structure can be observed as a metastable structure during the phase transition process between L and C^A. However, when the midblock fraction is $f_B = 0.56$, as shown in Fig. 5(b), the P^B structure would convert into L or C^A easily via spinodal decomposition. Accordingly, from a dynamical perspective, we have confirmed the properties demonstrated in Fig. 2 that the packing frustration induces the instability of the P^B structure with decreasing midblock length. Moreover, kinetic pathways and phase transition mechanisms can be regulated by changing the block length to adjust the packing frustration.

In addition to the block length, the interaction between endblocks imposes remarkable influences on the formation of ordered network structures. By designing kinetic pathways, we have already demonstrated that the P^A phase could be formed during the phase transition from L to C^A. Herein, starting with another kinetic pathway for the formation of P^A between two sphere phases, we try to illuminate the significant role of the block interaction in ABC triblock copolymers. The two ends of the string correspond to the two F^A phases with A and C spheres exchanging positions. As shown in Fig. 6, during the phase transition process between these two F^A phases, the P^A-like structure can be obtained as a metastable structure at the valley of the MEP ($s = 0.5$). The shape of the spheres formed by block A
varies with the morphology evolution of the C phase. At $s = 0$, A and C are both cube-like spheres. When the C phase becomes a network constructed from four-fold coordinated and eight-fold coordinated junctions at $s = 0.31$, the A blocks tend to form perfect spheres, which could be interpreted by the interaction between the endblocks. When the C phase turns into tetrahedron-like structures, the A phase changes into cube-like spheres with different orientations from those at $s = 0$. And when $s = 0.49$, both A and C phases form the plumber’s nightmare-like structures, which constitute metastable structures in this kinetic pathway. It can be assumed that the formation of the P$^A$-like structure in this kinetic pathway is induced by the interaction between A and C blocks.

To demonstrate this mechanism of the interaction between the endblocks leading to the induced formation of the P$^A$-like or P$^B$ structure, we investigate the formation of P$^A$ in the frustrated system with $N_{AB} = 35$, $N_{AC} = 15$. It is obvious that the interaction between block A and block C for the system we have chosen here is the weakest. As shown in Fig. 7(a), with $f_B$ decreasing, the morphologies based on a BCC lattice evolve from A/C-mixed BCC spheres (space group $Im3m$) to S$^A$ spheres (space group $Pm3m$). The S$^A$ spheres are packed in a CsCl lattice and can be regarded as the alternating version of the BCC phase. When $f_B$ is large enough (0.74), block A and block C are not long enough to form stable three-phase structures. 78,79

Because of the weak interaction between block A and block C, the A and C phases mix and form BCC spheres. 9,12 When block A and block C are long enough (i.e. $f_B = 0.54$, 0.4), the interaction between the A phase and the C phase increases so that the A and C domains separate from each other and form the alternating spheres based on a CsCl lattice. However, as a result of the weak interaction between the endblocks, cube-like spheres rather than conventional ones, are formed. Furthermore, it can be seen from the density profiles of block A and block C and the density distribution in Fig. 7(b) that the A and C phases are still mixed but the mixing degree has been reduced at $f_B = 0.54$ and $f_B = 0.4$. At $f_B = 0.4$, within the C-sphere rich region, A spheres almost only gather in the eight corners and their density distribution in the middle of the C spheres is almost zero. As the competition between the particle core sphericity and BCC crystal lattice symmetry dictated by the constraint of constant overall density determines the morphology of the spheres in diblock copolymers, we manage to find more stable structures (Fig. 8) compared to the S$^A$ structures mentioned above. For spheres based on a BCC lattice in diblock copolymers or the A/C mixed BCC spheres in triblock copolymers, every particle has eight nearest and six next nearest neighbors, resulting in a Wigner–Seitz cell that is a truncated octahedron with 14 faces. 46 However, for the S$^A$ spheres packed in a CsCl lattice, the interaction between the endblocks will dictate largely the morphology. As is shown in Fig. 8a, at $f_B = 0.54$ and $f_B = 0.4$, the complex decorated P$^A$ structures, which possess the same space group $Pm3m$ as S$^A$, are obtained. Like the P$^A$ morphology observed in the nonfrustrated system, this type of P$^A$ structure also has two intertwined networks constructed by six-fold coordinated nodes, while in each node there exists a B sphere with a shell composed of the other endblock. When the endblock is not long enough, for example at $f_B = 0.54$, the shell in each node would be nonuniform (also see Fig. S4, ESI†). The existence of the core–shell B spheres, which will not appear in the nonfrustrated systems with large repelling interactions between the endblocks (Fig. 2), indicates that the block interaction dictates the morphology of the P$^A$ structure. At $f_B = 0.2$, block A and block C are long enough and the interaction between the two phases is so large that the core–shell B spheres do not exist in the nodes any more, therefore leading to a structure very similar to the P$^A$ structure observed in the nonfrustrated systems. Likewise, in terms of the G$^A$ and D$^A$ structures, A/C-mixed morphologies would evolve into those in which the A and C phases separate from each other almost completely as the midblock length decreases gradually (Fig. S5 and S6, ESI†). The mechanism of the interaction between the endblocks induced formation of the P$^A$ structure can be further confirmed by the comparison of S$^A$ and P$^A$ with the same parameters, as shown in Fig. 8(b). It can be seen that P$^A$ is more stable than S$^A$. Although the interaction between the endblocks is relatively small in the frustrated systems, thus resulting in S$^A$ structures observed at $f_B = 0.4$ and $f_B = 0.54$, they could not be observed at
$f_B = 0.2$ because the repelling interaction gets larger with increasing A and C block lengths. Therefore, at $f_B = 0.2$, the spheres in a CsCl lattice tend to be interconnected with the same spheres, i.e. the six next nearest neighbors, leading to the formation of the P structure. At $f_B = 0.4$ and $f_B = 0.54$, the decorated P structure is more stable than S, manifesting that the interaction between the endblocks favors the formation of the decorated six-fold connected P structure rather than S spheres within a CsCl lattice.

4. Exploring new metastable network mesophases

The stability of complex network structures in phase transition processes can be adjusted by regulating the kinetic pathways, which has been shown in the discussion above. By this means,
we manage to discover new metastable network mesophases, including six-pronged (Fig. 9) and five-pronged (Fig. 10) networks. Fig. 9 shows the MEP for the formation of a six-pronged network and the corresponding characteristic morphologies encountered in the kinetic pathways. The six-pronged structure (see the insets of Fig. 9(a) and (b)) is a core–shell single network different from the P\textsuperscript{A} phase, which has two intertwined six-pronged networks. This single six-pronged network is discovered in the kinetic pathways of the phase transition between L with (110) planes and core–shell hexagonally packed cylinders (CS-C\textsuperscript{HEX}), which possess the same unit cell with a size of 6.0\textit{R_g} at \( f_A = 0.17, f_B = 0.25, f_C = 0.58 \) and 6.4\textit{R_g} at \( f_A = 0.27, f_B = 0.25, f_C = 0.48 \), respectively. During the phase transitions from L with (110) planes to CS-C\textsuperscript{HEX} (Fig. 9(a)) or from CS-C\textsuperscript{HEX} to L (Fig. 9(b)), the HPL structure can be obtained as a metastable structure, as shown in Fig. 9(c) (\( s = 0.33 \)) and Fig. 9(d) (\( s = 0.8 \)), respectively. This HPL structure is obviously different from the TPL structure observed during the phase transition from L to P\textsuperscript{A} (Fig. 3) and the HPL structure observed during the phase transition from L to D\textsuperscript{A} (Fig. 4) which are only transient structures because of the repelling interaction of the endblocks. By regulating the block compositions and thus altering the stability of the core–shell single six-pronged network in the kinetic pathway, it would become a metastable structure and hence be easier to observe in experiments. At \( f_A = 0.17, f_B = 0.25, \) and \( f_C = 0.58 \), the core–shell single six-pronged network is exactly at the peak of the MEP, which corresponds to the highest free energy barrier and means that it is a rather...
unstable state. It can be speculated from the MEP that the single six-pronged network tends to develop into a HPL or CS-CHEX structure via spinodal decomposition without any free energy barrier. However, when we fix $f_B$ at 0.25 and increase $f_A$ to 0.27, the core–shell single six-pronged network would locate at the valley of the MEP and thereby become more stable in the kinetic pathway. The regulation of the stability of the single six-pronged network can be attributed to the alleviation of packing frustration because of the fact that the stretching of the three blocks is better matched. Fig. 10 shows the formation of another novel networked structure, the five-pronged network found in the kinetic pathways of the phase transition between CS-CHEX and core–shell double diamond (CS-DD). The optimized cell sizes for CS-CHEX and CS-DD are $6.0R_g$ at $f_A = 0.17$, $f_B = 0.25$, $f_C = 0.58$ and $6.4R_g$ at $f_A = 0.27$, $f_B = 0.25$, $f_C = 0.48$, respectively. Similarly, the five-pronged network would become

![Image](https://example.com/image.png)

**Fig. 8** (a) Morphology evolution based on the $P^A$ structure with $f_A$ decreasing along the isopleth $f_A = f_C$ with $N_{AB} = 35$, $N_{AC} = 15$. Red, green and blue represent domains rich in A, B, and C blocks, respectively. Density profiles of the A block are shown in Fig. S4 (ESI†). (b) Single chain free energy comparison between $P^A$ and $S^A$. 

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a metastable state via regulating the kinetic pathways, as shown in Fig. 10(d) at $s = 0.82$. It should be noticed that besides the five-pronged network at $s = 0.82$, another network at $s = 0.65$ is also observed in the kinetic pathway. This network is a cylinder-like structure in which every three adjacent columns are connected together, and similar to that observed in the L-G phase transition for diblock copolymers. Although different metastable network mesophases could be obtained in the kinetic pathways, we notice that the HPL structure at $s = 0.33$ is more stable than these networks, including CS-DD, single five-pronged network, and cylinder-like structures.

IV. Conclusions

We have demonstrated the design and regulation of OOT pathways for the formation of ordered network mesophases by using SCFT combined with the string method. The results suggest that complex ordered network mesophases, including $G^5$, $D^6$, $P^A$, and other networks could be obtained in the phase transition pathways between lamellae, cylinders, and spheres, which provides a new strategy to explore novel stable and metastable structures. The design principles of kinetic pathways are based on two kinds of matching relationships between distinct phases, i.e. the matching of the dominant reciprocal lattice vectors and the domain spacing. Changing the molecular architecture proves to be an effective means to regulate kinetic pathways, which can be attributed to the properties of packing frustration induced non-CMC surfaces. In addition, the interaction between endblocks plays a critical role in the formation of the ordered network mesophases. By exploiting the mechanism of regulating kinetic pathways, new metastable networks such as single six-pronged and five-pronged networks can be obtained. The approach we developed could be widely used to investigate the formation mechanism of complex network mesophases, especially those structures which are difficult to observe by direct
self-assembly from block copolymers, such as SG and SD. These relatively rare cubic morphologies with triple periodicity are important for basic science such as the geometry of interfaces in soft matters and technological applications. However, they remain a significant challenge for experimental observation and theoretical investigations. The exploration of the kinetic pathways combining SCFT and the string method presented in the current work demonstrates the significant potential of the OOT route to obtain the required networks, thus providing guidelines for the bottom-up means to fabricate materials with complicated networks.

Acknowledgements

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References