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PAPER

# The influence of volume fractions on the phase behaviors of linear A(BC)<sub>n</sub>BA' multiblock terpolymers

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The phase behaviors of A(BC)<sub>n</sub>BA' linear multiblock terpolymers are investigated using the pseudo-spectral method of self-consistent field theory by varying the volume fractions of different blocks. The relative stability among the lamellae-in-lamellae structures with different BC internal layers is tuned by the volume fraction of the two long tails. A larger A volume fraction favors the formation of structures with fewer BC thin layers. When the volume fraction of A is increased further, a hierarchical cylinder phase can be formed because of the effect of the spontaneous curvature and *vice versa*. The separation between B and C significantly reduces the phase regime of the cylinder, especially for the case of small A volume fraction.

## I. Introduction

Because of a number of main features, the self-assembly of block copolymers has attracted the continuing research interest of scientists from a wide range of fields, including chemistry, physics, materials, *etc.* One feature is that many previous reports of block copolymers elucidated a technique for obtaining dense periodic arrays of nanostructures that possess great potential for application in the fabrication of functional materials, including lithographic templates for quantum dots,<sup>1</sup> nanowires,<sup>2</sup> high density magnetic storage media<sup>3</sup> and silicon capacitors.<sup>4</sup> Another important feature is that the self-assembly of block copolymers itself provides a great physical model that contains rich physics, like those classical models in physics, for example, the Ising model. For the simplest model of block copolymers, a diblock copolymer, consisting of two chemically connected polymer blocks, it can self-assemble into a number of ordered nanostructures, including lamella, cylinder, gyroid, sphere and Fddd (orthorhombic network) phases with length scales in the order of 10–100 nm.<sup>5–7</sup> Without considering the difference in monomer sizes, the phase diagram is determined by two parameters: the volume fraction of one of the blocks,  $f$ , and the product  $\chi N$  of the chain polymerization  $N$  and the Flory–Huggins interaction parameter  $\chi$ , which characterizes the immiscibility of the two species. By introducing one more component, more complex block copolymers can be synthesized. Even in a simple case, where there is only one block for each component, there are a few types of triblock copolymers

distinguished by their molecular architectures. Two of them, ABC linear and star triblock copolymers, are extensively studied by both experiments and theories. Either of them has much richer self-assembling behaviors than the diblock copolymer because the parameter number increases to be five, three interaction parameters,  $\chi_{AB}N$ ,  $\chi_{BC}N$ ,  $\chi_{AC}N$ , and two independent volume fractions,  $f_A$ , and  $f_B$ .

Addition of blocks onto a polymer chain is another useful way to synthesize various complex block copolymers, *i.e.*, multiblock copolymers. For the case of three components, a number of linear multiblock terpolymers are synthesized. Matsushita and coworkers synthesized an undecablock terpolymer, PISISISIP, which is composed of two long tail poly(2-vinylpyridine) (P) blocks, five polyisoprene (I) short blocks, and four polystyrene (S) short blocks.<sup>8</sup> Recently, Fleury and Bates synthesized a hexablock terpolymer, poly(cyclohexylethylene-*b*-ethylene-*b*-cyclohexylethylene-*b*-ethylene-*b*-cyclohexylethylene-*alt*-propylene) (CECEC-P).<sup>9</sup> One of attractive features in these multiblock copolymers is that they can self-assemble into ordered nanostructures with double periodicities, *i.e.*, structure-in-structure, referred to as hierarchical structures. With the nearly symmetric PISISISIP terpolymer, Matsushita *et al.* observed lamellar-in-lamellar morphologies where the middle I/S blocks separate to form five thin layers of ISISI between the two major layers of P.<sup>8</sup> In the system of CECEC-P with compositions of  $f_P = 0.5$  and  $f_C = f_E = 0.25$ , Fleury and Bates observed a perpendicular lamellar-in-lamellar phase.<sup>9</sup> The feature of double periodicities in hierarchical morphologies may make them have more potential applications in soft biological materials and composite functional materials.

The main self-assembling mechanism in block copolymers is dominated by the competition between the entropic energy of polymer chains and the interfacial energy between different

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domains. However, there is some delicate difference between the simple diblock copolymers and the complex multiblock copolymers. In the PISISISP polymer system, one interesting issue is about why five I/S thin-layers are formed in the lamellar-in-lamellar morphology. As a matter of convention, we refer this type of linear multiblock terpolymers as  $A(BC)_nBA'$ , where  $n$  denotes the repeating number of B/C short blocks, and the two end blocks of A and A', which are composed of the same component, can be equal length (symmetric) or non-equal length (asymmetric). When the length of A' is zero, the terpolymer becomes  $A(BC)_nB$  type, and it can model the CECEC-P terpolymer with  $n = 2$ . To rationalize the observation, a geometric model, based on counting possible configurational paths of B/C blocks in B/C domains, was proposed by Matsushita *et al.* This simple model gives a qualitative prediction of the number of B/C thin-layers by estimating the entropic contribution and ignoring the interfacial energy. This entropic contribution, from the configurational paths only, becomes trivial by comparison to the stretching entropy in simple block copolymers. It is necessary to carry out a careful theoretical calculation to obtain a more thorough understanding of the relative stability among the hierarchical lamellar phases with different B/C internal layers. Based on this, Li and Shi systematically investigated the hierarchical lamellar phases formed in the symmetric terpolymer of  $A(BC)_nBA$  by using self-consistent field theory (SCFT).<sup>10</sup> Their results demonstrated that more than one hierarchical lamellar phase with various numbers of "internal" BC layers can be stable for an  $A(BC)_nBA$  terpolymer with given compositions, and their relative stability can be tuned by its three interactions of  $\chi_{AB}N$ ,  $\chi_{AC}N$ , and  $\chi_{BC}N$ . This prediction is consistent with those of the strong-segregation theory (SST) and the dissipative particle dynamic (DPD) simulations by ten Brinke and coworkers.<sup>11</sup> In addition, a number of linear multiblock copolymers in bulk such as  $A(BA)_nBA$ ,  $A(BA)_n$ , and  $A(BC)_nBA$ , have been studied by SCFT<sup>12–14</sup> and SST,<sup>15–17</sup> and some multiblock copolymers confined between patterned surfaces or confined in nanopores have been studied by computer simulations.<sup>18–21</sup> In our previous work,<sup>22</sup> the phase behaviors of perpendicular/parallel hierarchical lamellae of the asymmetric terpolymer of  $A(BC)_nB$  have been carefully investigated by real-space SCFT calculations. The conclusion that the perpendicular phase becomes stable instead of the parallel one when  $\chi_{BC} > \chi_{AB} \gg \chi_{AC}$  is consistent with the experimental observations. Most of those studies focus on the influence of interaction parameters, but the study on the influence of volume fractions is very limited.

Volume fractions of block copolymers also play an important role during the formation of structures. In simple diblock or triblock copolymers, the volume fractions directly determine the symmetry of structures. In  $A(BC)_nBA'$  multiblock terpolymers, the volume fractions can vary the sub-structures besides the symmetry of the main structures, for example, the B/C internal layers in the hierarchical lamellar phase. How the volume fractions influence the formation of B/C sub-structures when the symmetry of the main structure is unchanged, and how the B/C phase separation influences the symmetry transition of the main phase are two interesting problems. Compared with the interaction parameters, the volume fractions are easier to be controlled in experiments.

Therefore, to understand the role of volume fractions in the formation of hierarchical phases in multiblock copolymers is helpful for experiments and applications in future.

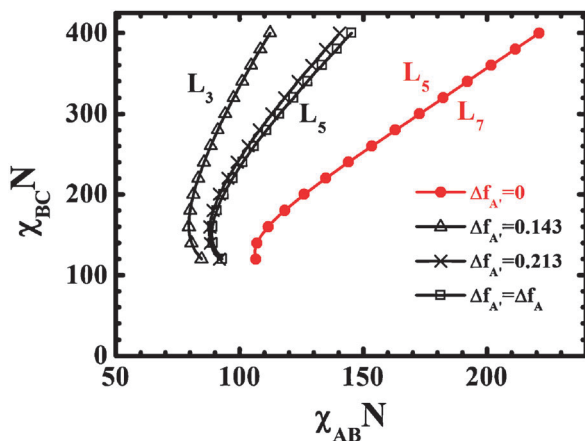
In the present work, we focus on the influence of volume fractions on the phase behaviors in  $A(BC)_nBA'$  multiblock terpolymers. First, we investigate the relative stability of lamellar-in-lamellar phases with different internal layers in the asymmetric terpolymer of  $A(BC)_nBA'$  by varying the length of one tail. Second, we calculate the change of phase transition between different hierarchical lamellar phases induced by the volume fraction of two equal-length tails in the symmetric case of  $A(BC)_nBA$  for a number of  $n$ . Third, we calculate the phase transitions between hierarchical cylinder and lamellar phases for the symmetric terpolymer with a given  $n$ . One of the aims of the third part of our research is to give an estimation that the volume fractions in the second part are varied in the stability region of the lamellar phases. During the construction of the phase diagram, two types of cylinder phases are considered. One type is that the cylinders are formed by A blocks when the A volume fraction is small, and the matrix is a B/C separated structure, and the other is the opposite case, where the cylinder domain is composed of B/C alternate concentric lamellae. Here we ignore the presence of a gyroid phase between the lamellar phase and the cylinder phase as its phase region should be tiny for our choice of A/B or A/C interaction parameter.

In order to calculate the free energy of different morphologies, we employ the real-space method of SCFT in our study. It is known that SCFT is a powerful theoretical framework that is capable of connecting molecular architecture and composition to equilibrium ordered phases.<sup>23,24</sup> In our study, solutions of SCFT equations corresponding to hierarchical morphologies are obtained. Comparison of the free energy of these phases leads to the construction of phase diagrams of the terpolymers. The phase diagrams reveal the stability region of different morphologies.

## II. Theory

We consider an incompressible melt of  $A(BC)_nBA'$  multiblock terpolymers with a degree of total polymerization  $N$ , and volume fractions  $f_A$ ,  $f_B$ , and  $f_C$  ( $f_A + f_B + f_C = 1$ ), in a volume of  $V$ . The length of each B/C block is  $\Delta f_B N / \Delta f_C N$  ( $\Delta f_B = f_B / (n + 1)$  and  $\Delta f_C = f_C / n$ ), and the lengths of two ends are  $\Delta f_A N$  and  $\Delta f_{A'} N$  ( $\Delta f_A + \Delta f_{A'} = f_A$ ), respectively. The radius of gyration of the polymer chain,  $R_g$  is used as the length unit in our calculations. Within the mean-field approximation to statistical mechanics of the Edwards model of polymers,<sup>23,24</sup> at a temperature  $T$ , the free energy functional  $F$  for  $n$  Gaussian multiblock terpolymer chains is

$$\begin{aligned} \frac{F}{nk_B T} = & -\ln Q + \frac{1}{V} \int d\mathbf{r} \{ \chi_{AB} N \phi_A(\mathbf{r}) \phi_B(\mathbf{r}) \\ & + \chi_{AC} N \phi_A(\mathbf{r}) \phi_C(\mathbf{r}) + \chi_{BC} N \phi_B(\mathbf{r}) \phi_C(\mathbf{r}) \\ & - \omega_A(\mathbf{r}) \phi_A(\mathbf{r}) - \omega_B(\mathbf{r}) \phi_B(\mathbf{r}) - \omega_C(\mathbf{r}) \phi_C(\mathbf{r}) \\ & - \eta(\mathbf{r}) [1 - \phi_A(\mathbf{r}) - \phi_B(\mathbf{r}) - \phi_C(\mathbf{r})] \}. \end{aligned} \quad (1)$$



**Fig. 1** Phase transition curves of A(BC)<sub>3</sub>BA' terpolymers with various values of  $\Delta f_{A'}$ , with respect to  $\chi_{AB}N = \chi_{AC}N$  and  $\chi_{BC}N$ , for fixed  $f_A = \Delta f_A + \Delta f_{A'} = 0.503$ . The phase boundaries divide the phase regions of  $L_3$  and  $L_5$  for  $\Delta f_{A'} \neq 0$ , and otherwise, the phase boundary divides the phase regions of  $L_5$  and  $L_7$ .

where  $\phi_A$ ,  $\phi_B$ , and  $\phi_C$  are the monomer densities. The partition function  $Q$  is for a single polymer chain interacting with the mean fields of  $\omega_A$ ,  $\omega_B$ , and  $\omega_C$  produced by the surrounding chains. The interactions among the three dissimilar monomers are characterized by three Flory–Huggins interaction parameters,  $\chi_{AB}$ ,  $\chi_{AC}$ , and  $\chi_{BC}$ . Minimization of the free energy with respect to the monomer densities and the mean fields leads to the following standard mean-field equations<sup>23,24</sup>

$$\omega_A(\mathbf{r}) = \chi_{AB}N\phi_B(\mathbf{r}) + \chi_{AC}N\phi_C(\mathbf{r}) + \eta(\mathbf{r})$$

$$\omega_B(\mathbf{r}) = \chi_{AB}N\phi_A(\mathbf{r}) + \chi_{BC}N\phi_C(\mathbf{r}) + \eta(\mathbf{r})$$

$$\omega_C(\mathbf{r}) = \chi_{AC}N\phi_A(\mathbf{r}) + \chi_{BC}N\phi_B(\mathbf{r}) + \eta(\mathbf{r})$$

$$\phi_A(\mathbf{r}) = \frac{1}{Q} \int_{s \in A} ds q_A(\mathbf{r}, s) q_A^\dagger(\mathbf{r}, s)$$

$$\phi_B(\mathbf{r}) = \frac{1}{Q} \int_{s \in B} ds q_B(\mathbf{r}, s) q_B^\dagger(\mathbf{r}, s)$$

$$\phi_C(\mathbf{r}) = \frac{1}{Q} \int_{s \in C} ds q_C(\mathbf{r}, s) q_C^\dagger(\mathbf{r}, s)$$

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

$$\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) + \phi_C(\mathbf{r}) = 1 \quad (2)$$

The integration in the density of  $\phi_A$ ,  $\phi_B$  or  $\phi_C$  is conducted along each block of A, B or C. The quantities,  $q_K(\mathbf{r}, s)$  and  $q_K^\dagger(\mathbf{r}, s)$  ( $K = A, B, C$ ) are end-segment distribution functions which have standard definitions.<sup>23,24</sup> These distribution

functions satisfy the modified diffusion equations

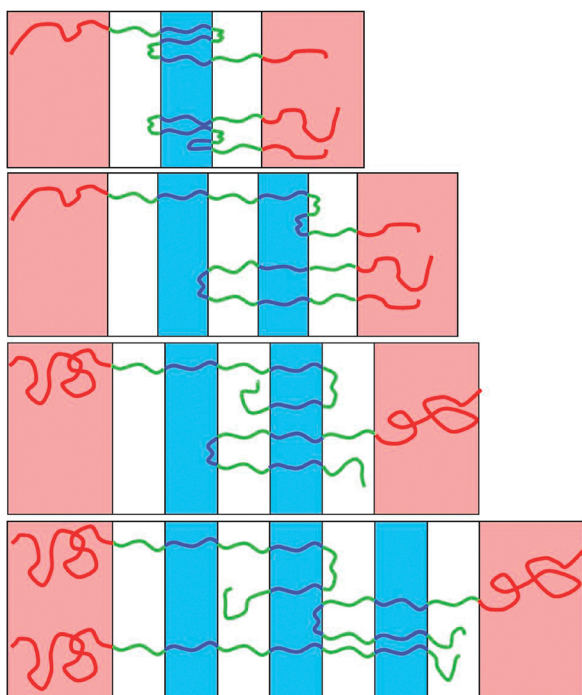
$$\frac{\partial q_K(\mathbf{r}, s)}{\partial s} = \nabla^2 q_K(\mathbf{r}, s) - \omega_K(\mathbf{r}, s) q_K(\mathbf{r}, s) \quad (3)$$

$$-\frac{\partial q_K^\dagger(\mathbf{r}, s)}{\partial s} = \nabla^2 q_K^\dagger(\mathbf{r}, s) - \omega_K(\mathbf{r}, s) q_K^\dagger(\mathbf{r}, s) \quad (4)$$

The initial conditions are  $q_A(\mathbf{r}, 0) = 1$ , and  $q_A^\dagger(\mathbf{r}, 1) = 1$  (or  $q_B^\dagger(\mathbf{r}, 1) = 1$  when  $\Delta f_{A'} = 0$ ). For numerical solutions, we employ the pseudo-spectral method to solve the modified diffusion equations for the end-segment distribution functions.<sup>25,26</sup> Periodic boundary conditions are imposed automatically on each direction of the simulated box, and the free energy is minimized with respect to the box sizes. The discretization degrees along both the chain contour length and on the real space are set so high that the calculated free energy is accurate to determine reliable phase boundaries.<sup>27</sup>

### III. Results and discussions

As a matter of convention, the lamellar-in-lamellar structures are denoted as  $L_k$ , where  $k$  indicates the number of internal BC layers. At first, we investigate how the asymmetry of the two tails influences the relative stability of different hierarchical lamellar phases for a given total A volume fraction in A(BC)<sub>3</sub>BA'. According to our previous work,<sup>10</sup>  $L_3$  and  $L_5$  are the main stable phases in the phase diagram when  $f_A$  is around 0.5. The phase boundaries for  $\Delta f_A + \Delta f_{A'} = 0.503$  and  $\chi_{AB}N = \chi_{AC}N$  with various  $\Delta f_{A'} = 0, 0.142, 0.213$ , and 0.2515 are shown in Fig. 1. A(BC)<sub>3</sub>BA' is reduced to be the case of symmetric A(BC)<sub>3</sub>BA for  $\Delta f_A = \Delta f_{A'}$ , while it becomes A(BC)<sub>3</sub>B for  $\Delta f_{A'} = 0$ . The phase boundary between  $L_3$  and  $L_5$  in the symmetric terpolymer of A(BC)<sub>3</sub>BA becomes that between  $L_5$  and  $L_7$  in A(BC)<sub>3</sub>B. In other words, the lamellar-in-lamellar phases with more B/C internal layers are preferred to be formed in the latter terpolymer than the former one. The reason is that the B end in the type of A(BC)<sub>n</sub>B terpolymers can be located in any B thin layer, but the two ends are restricted to be in the two A domains in A(BC)<sub>n</sub>BA terpolymers (see the schematic plots of Fig. 2). From the aspect of ends, the difference between A(BC)<sub>n</sub>B and A(BC)<sub>n</sub>BA is simply similar to that between the equilibrium state and the “mixed” state in ABC triblock copolymers discussed by Maniadis *et al.*<sup>28</sup> From the other aspect of configurational entropy, there is an obvious difference in the two systems. In the multiblock case, the number of configurational paths determined by B/C blocks becomes a significant part of the entropy, which is trivial in the simple ABC triblock copolymer. The configurational paths of the chain in the phase of less B/C layers are only portion of those in the phase of more B/C layers when the restriction of one end is released in A(BC)<sub>n</sub>B. Therefore,  $L_7$  is the main stable phase in A(BC)<sub>3</sub>B instead of  $L_5$  in A(BC)<sub>3</sub>BA. When  $\chi_{BC}N$  increases in a given terpolymer, the other factor of the interfacial energy becomes more and more important compared with the contribution of configurational entropy, and thus the phase with fewer B/C internal layers is preferred. More detailed discussions about the transition between  $L_3$  and  $L_5$  in A(BC)<sub>3</sub>BA or that between  $L_5$  and  $L_7$  in A(BC)<sub>3</sub>B are given in our previous work.<sup>10</sup>

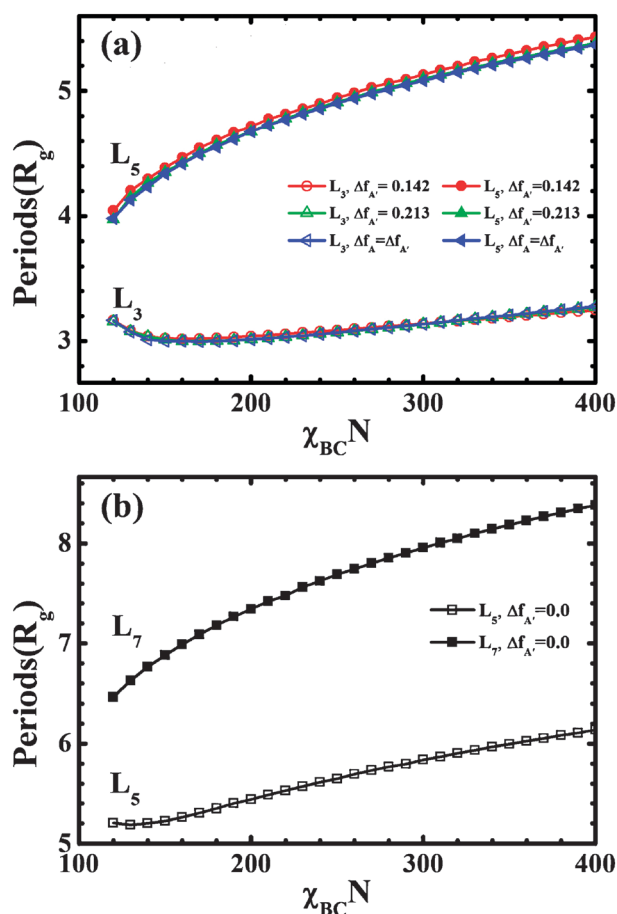


**Fig. 2** Schematic illustrations of possible chain paths of symmetric or asymmetric  $A(BC)_3BA'$  terpolymer through the domains in a number of hierarchical lamellar phases.

Besides above two limit cases, two intermediate cases of phase boundaries of  $\Delta f_{A'} = 0.142$  and  $0.213$  are also determined in Fig. 1. It is found that the two transition curves have shifts toward the  $L_3$  phase region compared with those of the symmetric case, and the shift becomes larger as the asymmetric degree is increased. This shift is attributed to the increased A/B interface induced by the asymmetry of the two end blocks. One effective way to reduce the A/B interfacial energy is to add B/C internal layers, which can stretch the polymer chain to decrease the A/B interfacial energy. Thus the phase region of  $L_5$  is expanded toward  $L_3$ .

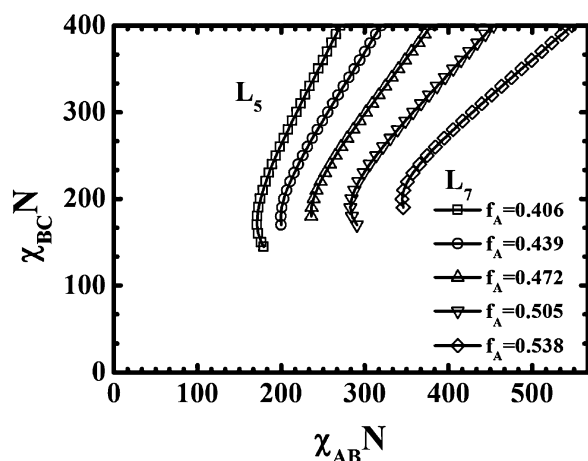
In Fig. 3, the periods of these phases along the phase boundaries in Fig. 1, as a function of  $\chi_{BC}N$ , are calculated. There are two features in the comparison of periods. One feature is that the period difference of the same phase induced by the asymmetry of the tails, is small, when  $\Delta f_{A'}$  is large enough for the  $A'$  block to phase separate from B/C blocks. However, the value of  $\chi_{AB}N$  along these phase curves is different, and it has a larger value for the composition with larger asymmetry. The two factors,  $\chi_{AB}N$  and the composition asymmetry, are near complementary on the influence of periods. The other feature is that the period of the phase  $L_5$  in  $A(BC)_3B$  is significantly larger than those in the other cases. This suggests that there is a swelling behavior in  $L_5$  of  $A(BC)_3B$  arising from the locations of the B end in any inner B domain.

In the hierarchical lamellae formed by a symmetric linear multiblock terpolymer,  $A(BC)_nBA$ , when the volume fraction of  $f_A$  is around 0.5, the number of B/C internal layer is mainly determined by the repeating number of B/C short blocks because of the entropic contribution from the configurations



**Fig. 3** Periods of different morphologies, as a function of  $\chi_{BC}N$ , along the corresponding phase boundaries: (a) the case of double A end blocks; (b) single A end block.

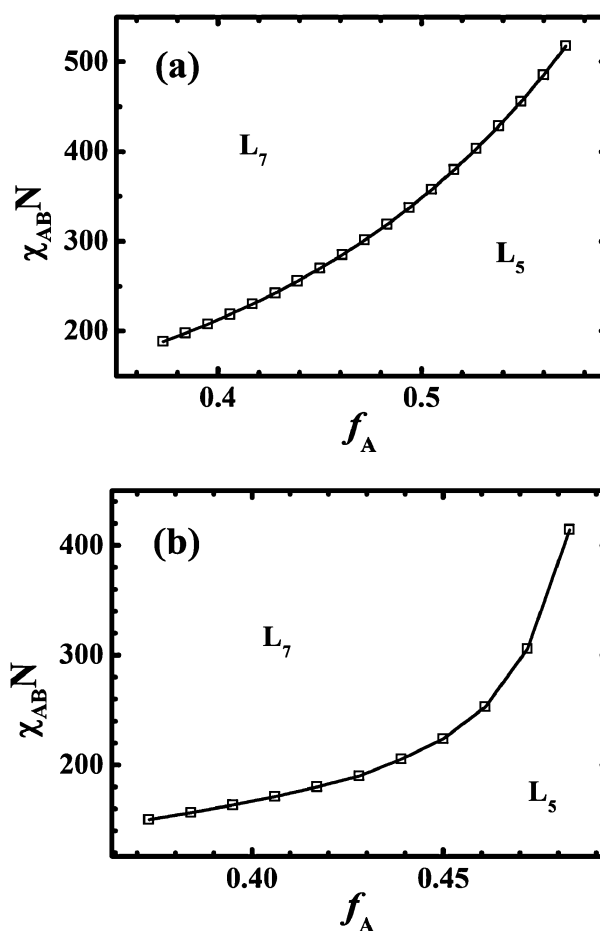
of the polymer. Considering the factors of chain stretching and interfacial energy, the interaction parameters also have significant influence on the relative stability of two neighbor lamellar phases, where the difference of the B/C thin-layer number is two. It is known that the polymer composition is a crucial factor in the formation of morphology in block copolymers. In Fig. 4, a number of phase boundaries between  $L_5$  and  $L_7$  for the symmetric  $A(BC)_5BA$  terpolymer with  $\Delta f_B = \Delta f_C = (1 - f_A)/(2n + 1)$  and  $\chi_{AB}N = \chi_{AC}N$  are determined. From left to right, the volume fraction,  $f_A$  is 0.406, 0.439, 0.472, 0.505, and 0.538, respectively. The obvious shift of the phase boundary from left to right for increasing  $f_A$  indicates that large  $f_A$  prefers the formation of the  $L_5$  phase. In other words, long B/C block is favorable to form more B/C internal layers in the lamellar phase. In fact, the phase region of  $L_7$  becomes more dominant than that of  $L_5$  when  $f_A = 0.406$ . This feature is conflicting with the counting model of configurational paths in which the phase of  $L_5$  with 83 configurational paths is always more stable than  $L_7$  with 68 ones. This suggests that the result of the counting model is only a good approximation in some appropriate situations, like in the case of small B/C blocks. The reason is that the entropic contribution of configurational paths becomes more dominant over the other two contributions of chain stretching



**Fig. 4** Phase boundaries between phases of  $L_5$  and  $L_7$  of symmetric  $A(BC)_5BA$  terpolymer with equal length of B and C short blocks of  $\Delta f_B = \Delta f_C = (1 - f_A)/(2n + 1)$  and  $\chi_{AB}N = \chi_{AC}N$ . From left to right,  $f_A = 0.406, 0.439, 0.472, 0.505, 0.538$ , respectively.

energy and interfacial energy in free energy when the length of B/C blocks is decreased. On the other hand, when B/C blocks become long, the role of the interfacial energy on the structure formation is more pronounced. The reduction of A/B interfaces is enforced to satisfy the decreased length of A blocks, and therefore  $L_5$  transfers to  $L_7$ .

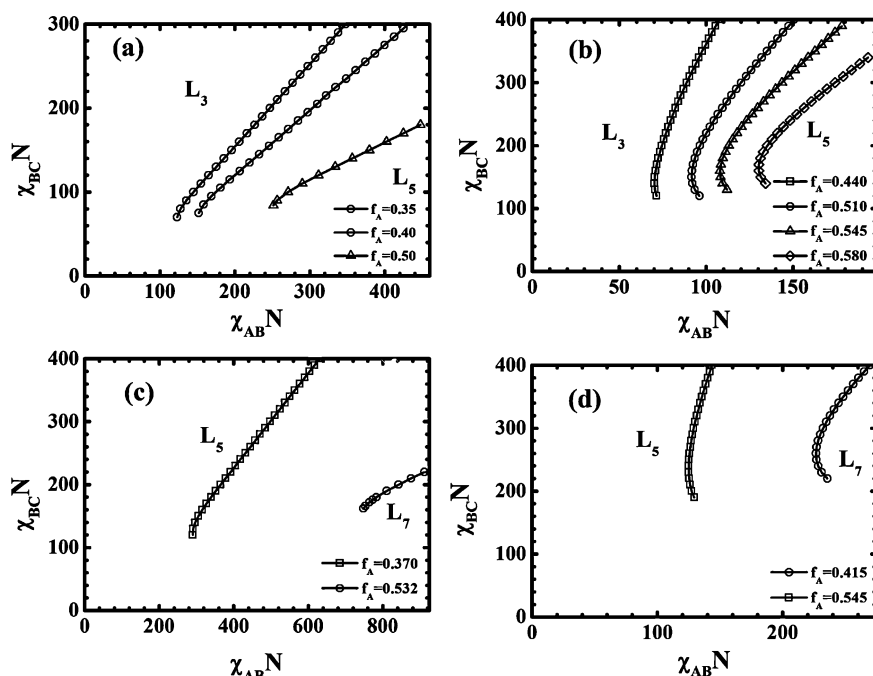
To get a more thorough picture about the influence of the polymer composition on the relative stability of  $L_5$  and  $L_7$  in the  $A(BC)_5BA$  terpolymer, we calculated their phase boundaries as function of  $f_A$  for two typical cases of: (a) fixed  $\chi_{BC}N = 300$ ; and (b)  $\chi_{AB}N = \chi_{AC}N = \chi_{BC}N$  (Fig. 5). The two figures indicate that the composition as well as  $\chi_{AB}N = \chi_{AC}N$  plays a significant role in the determination of the number of B/C thin-layers in the formation of hierarchical lamellae. For strong segregation, the factor of interfacial energy becomes more important, thus the influence of the composition on the phase boundary becomes more dominant. Especially, this point is more obvious in the case of  $\chi_{AB}N = \chi_{AC}N = \chi_{BC}N$  of Fig. 5(b) where  $L_7$  can be hardly stable when  $f_A > 0.49$ . The influence of the composition on the relative stability between two neighbor hierarchical lamellar phases formed by  $A(BC)_nBA$  terpolymers is general for  $n$ . A number of phase transition curves between  $L_3$  and  $L_5$  or between  $L_5$  and  $L_7$ , for  $n = 2, 3, 4, 6$ , are present in Fig. 6. It is found that the phases with the major phase region are consistent with the prediction of the counting model for  $n \leq 4$  in the considered range of compositions. This suggests that the counting model also gives reasonable results for  $n \leq 4$  because the difference of the number of configurational paths is large among the neighbor phases, although the volume fractions or the interaction parameters can change their relative stability. When the number of B/C repeating blocks is increased, the number of configurational paths becomes large, and their relative difference among the neighbor phases becomes small. For example, the path numbers are 229 and 218 for  $L_5$  and  $L_7$ , respectively, in the case of  $n = 6$ . The relative difference is less than 5%. Therefore the result of the counting model is less reliable in this situation. It is concluded that the polymer composition of



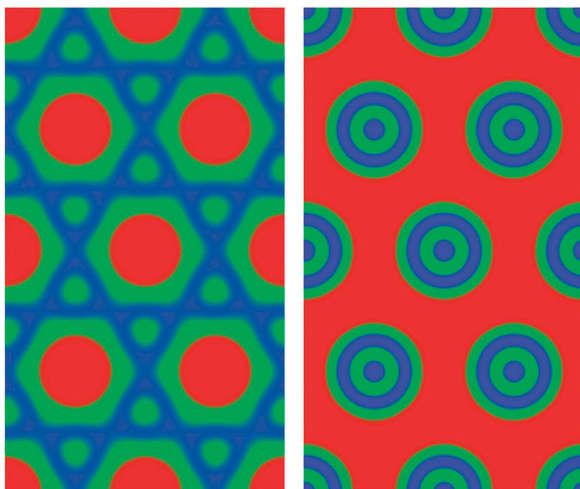
**Fig. 5** Phase boundaries between  $L_5$  and  $L_7$  of symmetric  $A(BC)_5BA$  terpolymer of  $\Delta f_B = \Delta f_C$  and  $\chi_{AB}N = \chi_{AC}N$ : (a)  $\chi_{BC}N = 300$ ; (b)  $\chi_{AB}N = \chi_{AC}N = \chi_{BC}N$ .

multiblock terpolymers can be used as an effective way to fabricate various hierarchical lamellae with different number of B/C internal layers. For example,  $L_5$  is observed by experiments in the  $A(BC)_4BA$  terpolymer with  $f_A = 0.53$ ,  $f_B = 0.26$  and  $f_C = 0.21$ .<sup>8</sup> According to the phase diagram of Fig. 6(c), it is possible to observe  $L_7$  when  $f_A$  is decreased to be 0.37, or even smaller.

It is known that cylindrical phases can become stable when  $f_A$  deviates far from 0.5 because of the formation of spontaneous curvature to reduce the stretching energy of the polymer chain. There are two types of candidate cylindrical phases. In the first type, the cylinder is constructed by the two long tails of A, and B/C blocks with further phase separation co-form the matrix. The left picture of the monomer density plots in Fig. 7 shows a typical cylindrical phase of this type, which is denoted as  $\bar{C}_{3,5}$ , where C with an overbar indicates the cylinders consisting of A blocks (red), the digit of 3 indicates the layer number between two neighbor cylinders, and .5 indicates the presence of the small B domains (green) at the triangular center of three neighbor cylinders. The second type phase is shown as the right picture in Fig. 7, which is denoted as  $C_4$  where 4 gives the total number of B/C concentric lamellae inside each cylinder. To understand the competition between hierarchical cylindrical phases and lamellar phases,



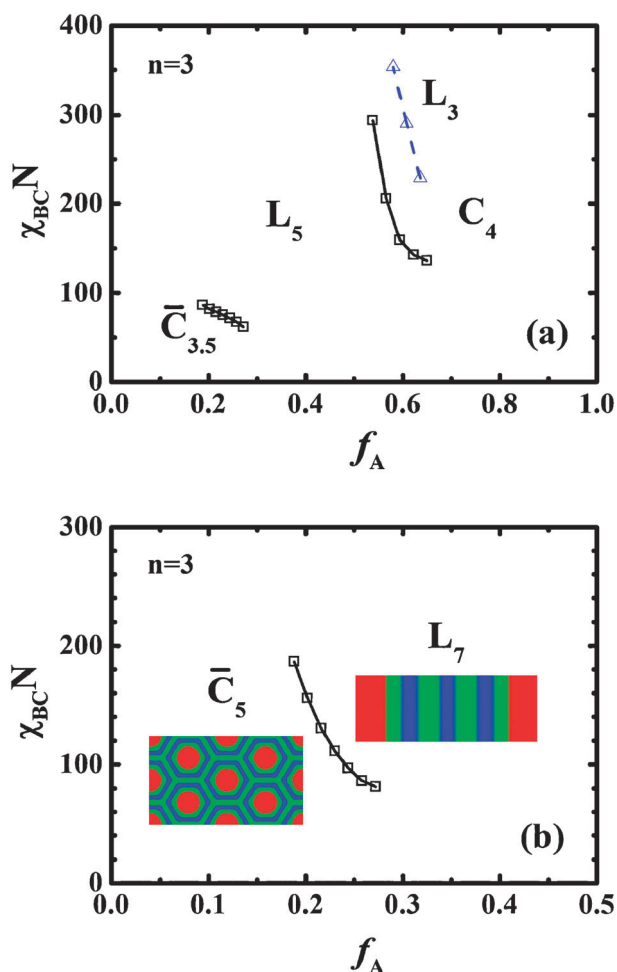
**Fig. 6** Phase transition curves between two neighbor phases in  $A(BC)_nBA$  terpolymers with  $\Delta f_B = \Delta f_C$  and  $\chi_{AB}N = \chi_{AC}N$  for different repeating number of B/C blocks and various compositions: (a)  $n = 2$ ,  $f_A = 0.35, 0.4, 0.5$ ; (b)  $n = 3$ ,  $f_A = 0.44, 0.51, 0.545, 0.58$ ; (c)  $n = 4$ ,  $f_A = 0.37, 0.532$ ; (d)  $n = 6$ ,  $f_A = 0.415, 0.545$ .



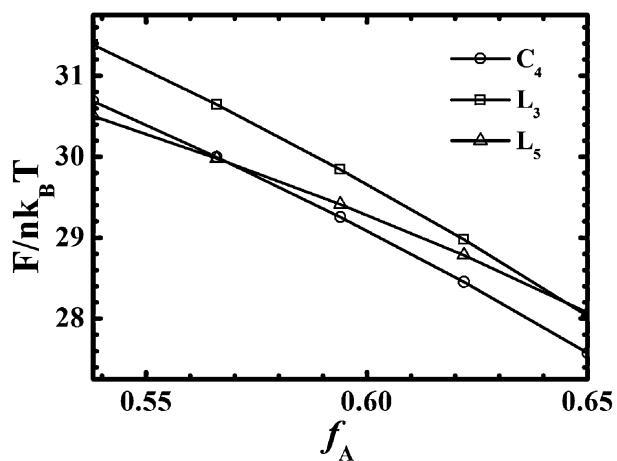
**Fig. 7** Typical monomer density plots of hierarchical cylindrical morphologies. The super-cylinder phase (left) is denoted as  $\bar{C}_{3,5}$ , where C with an overbar indicates the cylindrical structure of A blocks, the digit of 3 indicates the layer number located between two neighbor cylinders, and .5 indicates the presence of the small B domains at the triangular center of three neighbor cylinders. On the other side, the super-cylinder phase (right) consisting of concentric B/C lamellae is denoted as  $C_4$  where the digit of 4 gives the total number of B/C concentric lamellae inside each cylinder.

we focus on the phase behavior of the  $A(BC)_3BA$  terpolymer with fixed  $\chi_{AB}N = \chi_{AC}N = 200$ . The phase diagram with respect to  $f_A$  and  $\chi_{BC}N$  is present in Fig. 8(a). Only cylindrical phases and lamellar phases are considered during the construction of the phase diagram with the assumption that

the phase region of gyroid phase is tiny, which is reasonable for the present value of interaction parameters.<sup>29,30</sup> Three phases,  $C_4$ ,  $L_5$ , and  $\bar{C}_{3,5}$  are stable in this phase diagram, and  $L_3$  is metastable. A typical comparison of free energy among  $C_4$ ,  $L_3$ , and  $L_5$  is given in Fig. 9 for  $\chi_{AB}N = \chi_{AC}N = \chi_{BC}N = 200$ . When  $f_A > 0.5$ , the super-cylindrical phase of  $C_4$  becomes stable instead of  $L_5$ , and the phase transition moves toward small  $f_A$  for high  $\chi_{BC}N$ . Compared with the phase behavior of simple ABA triblock copolymer when ignoring the influence of gyroid phase,<sup>31</sup> the phase region of cylinder has some expansion toward small  $f_A$  when  $\chi_{BC}N$  is strong enough for the phase separation between B and C blocks. In our calculations,  $\Delta f_B = \Delta f_C$  gives  $f_B : f_C = 4 : 3$  for  $A(BC)_3BA$ , which benefits the formation of the spontaneous curvature to form B/C/B/C concentric rings. On the other hand,  $f_A < 0.5$ , the phase region of  $\bar{C}_{3,5}$  is compressed toward the corner of small  $f_A$  and low  $\chi_{BC}N$ . This suggests that the B/C segregation tremendously suppresses the formation of the super-cylindrical phase. The reason is that the matrix co-formed by the phase-separated B/C domains is not a perfect entirety, and thus the total effective volume fraction of B and C is reduced to favor the formation of a lamellar phase. We can conclude that it is easy to observe the second type of super-cylindrical phase with B/C concentric lamellae, and it is hard to observe the first type phase when there is a strong segregation between B and C. This conclusion makes sense in the formation of super-spherical phases. However, in the asymmetric terpolymer,  $A(BC)_3B$ , the cylinder-phase region of the first type has significant expansion toward large  $f_A$  and high  $\chi_{BC}N$  (see Fig. 8(b)) while the B end can be located in any B domain according to the requirement of the polymer entropy.



**Fig. 8** (a) Phase diagram of symmetric  $A(BC)_3BA$  terpolymer of fixed  $\chi_{AB}N = \chi_{AC}N = 200$  with respect to  $f_A$  and  $\chi_{BC}N$ . The solid lines with symbols give the phase transitions between two neighbor stable phases, and the dashed line is the transition curves between  $L_5$  and  $L_3$ , which is metastable. (b) Phase boundary between phases of  $L_7$  and  $\bar{C}_5$  of asymmetric  $A(BC)_3B$  terpolymer for fixed  $\chi_{AB}N = \chi_{AC}N = 200$ .



**Fig. 9** Typical free energy comparison among three phases of  $C_4$ ,  $L_3$  and  $L_5$  as a function of  $f_A$  for equal interaction parameters of  $\chi_{AB}N = \chi_{AC}N = \chi_{BC}N = 200$ .

## IV. Conclusions

In summary, we have studied the formation of hierarchical lamellar structures in linear  $A(BC)_nBA'$  multiblock terpolymers by varying the polymer composition. The asymmetry in the two tails can influence the phase transition between different hierarchical lamellar phases. Especially, in the limit case where there is only one tail, the lamellar phases with more B/C internal layers are preferred to be formed because the B end can be located in any B thin-layer. For the symmetric terpolymer of  $A(BC)_nBA$ , with  $n = 2, 3, 4, 5, 6$ , a systematical research has been carried to study the influence of the polymer composition on the phase boundary between two neighbor lamellar phases. Our results show that small  $f_A$  is favorable for the formation of lamellae with more B/C thin-layers. The phase diagram including super-cylindrical phases indicates that the hierarchical lamellar phases are stable in a large range of A composition for  $A(BC)_nBA$  terpolymer. Therefore, the polymer composition is a useful way to control the number of B/C internal layers in the fabrication of hierarchical lamellae for a multiblock terpolymer with a given repeating number of B/C blocks. In experiments done by Matsushita and coworkers,<sup>8</sup> it is possible to observe the lamellar morphology with seven B/C thin-layers when  $f_A$  is decreased to be as small as around 0.3. According to the comparison between our results and those of the counting model, a simple conclusion can be made that the counting model gives reasonable prediction for the stable lamellar phase when the relative difference of the configurational path number among the neighbor phases is large, *i.e.*, for  $n \leq 5$ . When  $n$  is larger than 5, the composition has more pronounced influence on the relative stability between the neighbor phases compared with the factor of the number of configurational paths. In addition, we have also included the super-cylindrical phases during the construction of phase diagrams for  $A(BC)_3BA$  and  $A(BC)_3B$  in order to estimate the stability region for lamellar phase. It is observed that the region of the first type of cylinder phase, where the cylinder is composed of A blocks, is suppressed by the B/C segregation. The suppression is significantly released in the asymmetric  $A(BC)_3B$  terpolymer because the B end can be located in any B domain. It is expected that our results would motivate further experimental research on the transition between different hierarchical lamellar phases in the linear multiblock terpolymers.

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