

# Comparing the Morphology and Phase Diagram of H-Shaped ABC Block Copolymers and Linear ABC Block Copolymers

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Received: December 14, 2005; In Final Form: March 14, 2006

By using a combinatorial screening method based on the self-consistent field theory (SCFT) for polymers, we have investigated the morphology of H-shaped ABC block copolymers ( $A_2BC_2$ ) and compared them with those of the linear ABC block copolymers. By changing the ratios of the volume fractions of two A arms and two C arms, one can obtain block copolymers with different architectures ranging from linear block copolymer to H-shaped block copolymer. By systematically varying the volume fractions of block A, B, and C, the triangle phase diagrams of the H-shaped ABC block copolymer with equal interactions among the three species are constructed. In this study, we find four different morphologies (lamellar phase (LAM), hexagonal lattice phase (HEX), core-shell hexagonal lattice phase (CSH), and two interpenetrating tetragonal lattice (TET2)). Furthermore, the order-order transitions driven by architectural change are discussed.

## Introduction

Block copolymers provide an ideal route to engineering well-controlled structures on nanometer scales. There are many different methods to control the microphase structures of block copolymers such as changing the composition of different blocks, varying the temperature of the system (namely  $\chi N$ ), and tuning the chemical structure of block copolymers. Through controlling the molecular architecture, block copolymers can be tuned to self-assemble into periodic structures of an astounding variety. A lot of work has been devoted to studies on block copolymers of different architectures because they may self-organize and undergo phase separation, leading to various morphologies and interesting properties.<sup>1–11</sup> However, most of the works focused on linear block and star block copolymers.<sup>9–11</sup> With the development of synthetic methods, block copolymers with more complex architectures, such as H-shaped,  $\pi$ -shaped, comb, centipede, and barbwire shape, were synthesized.<sup>3–5</sup> This inspires theoretical work into the effect of different architectures on morphological behavior. In our previous work, we have studied the microphases of  $\pi$ -shaped block copolymers by using self-consistent field theory.<sup>12</sup>

An H-shaped block copolymer has four sidearms (2A, 2C) attached to the end of the backbone (B), two A arms at one end, and two C arms at the other end. A schematic representation of the architecture is shown in Figure 1. By decreasing the volume fractions of A1 and C1, one can see that the H-shaped ABC block copolymer gradually changes to be a linear ABC block copolymer. Therefore, the H-shaped ABC block copolymer is a very interesting prototype to study the effect of molecule architecture on morphology and the order-order transitions driven by architectural change.

The self-consistent field theory (SCFT) has been widely used to study the interface between immiscible polymers and the microphase ordering of block copolymers.<sup>12–24</sup> In this work,

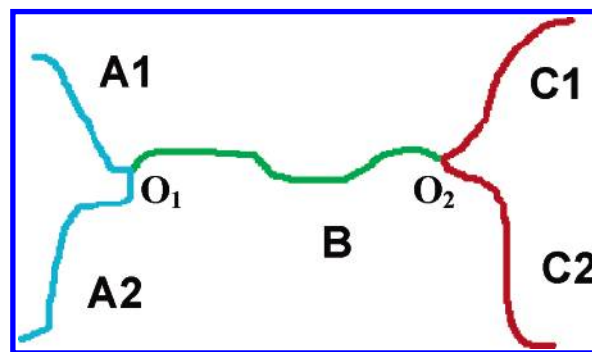


Figure 1. Molecular architecture of the H-shaped block copolymer.

we use the combinatorial screening method based on the self-consistent field theory<sup>22,23</sup> to study the equilibrium morphologies of H-shaped ABC block copolymers. The screening method involves the direct implementation of SCFT for polymers in real space in an adaptive arbitrary cell, which does not require the assumption of the microphase symmetry.<sup>22</sup> Moreover, the order-order transitions driven by the architectural change are investigated.

## Theoretical Method

We assume that the total degree of polymerization of the H-shaped block copolymer is  $N$ , and the A, B, and C blocks consist of  $f_A N$ ,  $f_B N$ , and  $f_C N$  monomers, respectively. The H-shaped block copolymer can be divided into five parts, namely A1, A2, B, C1, and C2, as shown in Figure 1. The free energy of the system is given by

$$\begin{aligned} \frac{F}{nk_B T} = & -\ln\left(\frac{Q}{V}\right) + \frac{1}{V} \int d\mathbf{r} [\chi_{AB} N(\phi_A(\mathbf{r}) - f_A)(\phi_B(\mathbf{r}) - f_B) + \\ & \chi_{BC} N(\phi_B(\mathbf{r}) - f_B)(\phi_C(\mathbf{r}) - f_C) + \chi_{AC} N(\phi_A(\mathbf{r}) - f_A)(\phi_C(\mathbf{r}) - \\ & f_C) - W_A(\mathbf{r})(\phi_A(\mathbf{r}) - f_A) - W_B(\mathbf{r})(\phi_B(\mathbf{r}) - f_B) - \\ & W_C(\mathbf{r})(\phi_C(\mathbf{r}) - f_C) - P(\mathbf{r})(1 - \phi_A(\mathbf{r}) - \phi_B(\mathbf{r}) - \phi_C(\mathbf{r}))] \quad (1) \end{aligned}$$

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where  $V$  is the volume of the system;  $\phi_A$ ,  $\phi_B$ , and  $\phi_C$  are the monomer density fields normalized by the local volume fractions of A, B, and C, respectively;  $\chi_{AB}$ ,  $\chi_{BC}$ , and  $\chi_{AC}$  are Flory–Huggins parameters between different species;  $P(\mathbf{r})$  is the potential field that ensures the incompressibility of the system,  $W_\alpha(\mathbf{r})$  is the self-consistent field which conjugates to the density field  $\phi_\alpha$  of the block species  $\alpha$ . Minimizing the free energy with respect to  $\phi_A$ ,  $\phi_B$ ,  $\phi_C$ ,  $W_A$ ,  $W_B$ ,  $W_C$ , and  $P(\mathbf{r})$  leads to the following SCFT equations that describe the equilibrium morphology:

$$W_A(\mathbf{r}) = \chi_{AB}N(\phi_B(\mathbf{r}) - f_B) + \chi_{AC}N(\phi_C(\mathbf{r}) - f_C) + P(\mathbf{r}) \quad (2)$$

$$W_B(\mathbf{r}) = \chi_{AB}N(\phi_A(\mathbf{r}) - f_A) + \chi_{BC}N(\phi_C(\mathbf{r}) - f_C) + P(\mathbf{r}) \quad (3)$$

$$W_C(\mathbf{r}) = \chi_{AC}N(\phi_A(\mathbf{r}) - f_A) + \chi_{BC}N(\phi_B(\mathbf{r}) - f_B) + P(\mathbf{r}) \quad (4)$$

$$\phi_A + \phi_B + \phi_C = 1 \quad (5)$$

$$\phi_A(\mathbf{r}) = \frac{V}{NQ} \int_0^{f_{A1}N} ds q_{A10}(\mathbf{r}, s) q_{A11}(\mathbf{r}, f_{A1}N - s) + \frac{V}{NQ} \int_0^{f_{A2}N} ds q_{A20}(\mathbf{r}, s) q_{A21}(\mathbf{r}, f_{A2}N - s) \quad (6)$$

$$\phi_B(\mathbf{r}) = \frac{V}{NQ} \int_0^{f_{B1}N} ds q_{B0}(\mathbf{r}, s) q_{B1}(\mathbf{r}, f_{B1}N - s) \quad (7)$$

$$\phi_C(\mathbf{r}) = \frac{V}{NQ} \int_0^{f_{C1}N} ds q_{C10}(\mathbf{r}, s) q_{C11}(\mathbf{r}, f_{C1}N - s) + \frac{V}{NQ} \int_0^{f_{C2}N} ds q_{C20}(\mathbf{r}, s) q_{C21}(\mathbf{r}, f_{C2}N - s) \quad (8)$$

where  $q_{\alpha\beta}(\mathbf{r}, s)$  is the polymer segment probability distribution function, representing the probability of finding segment  $s$  at position  $\mathbf{r}$ , and satisfies the modified diffusion equation (eq 9) with  $\alpha = A1, A2, B, C1, C2$ , and  $\beta = 0, 1$ .  $\beta = 0$  corresponds to  $s$  of  $q_{\alpha\beta}(\mathbf{r}, s)$  increasing from the free end to the nearer core ( $\mathbf{O}_1$  or  $\mathbf{O}_2$ ) or from core  $\mathbf{O}_1$  to core  $\mathbf{O}_2$ , and  $\beta = 1$  corresponds to  $s$  of  $q_{\alpha\beta}(\mathbf{r}, s)$  increasing from the near core to the free end or from core  $\mathbf{O}_2$  to core  $\mathbf{O}_1$ . The partition function of a single chain subject to the self-consistent field  $W_\alpha(\mathbf{r})$  can be written as  $Q = \int d\mathbf{r} q_{\alpha 0}(\mathbf{r}, s) q_{\alpha 1}(\mathbf{r}, f_\alpha N - s)$ , and the derivation of the single chain partition function is the same as that of the star triblock copolymer and the  $\pi$ -shaped block copolymer.<sup>10,12</sup> It should be noted that  $Q$  is independent of the chain contour length parameter  $s$ . The modified diffusion equation reads:

$$\frac{\partial q_{\alpha\beta}(\mathbf{r}, s)}{\partial s} = \nabla^2 q_{\alpha\beta}(\mathbf{r}, s) - W_\alpha(\mathbf{r}) q_{\alpha\beta}(\mathbf{r}, s) \quad (9)$$

where  $0 < s < f_\alpha N$ . The initial conditions of  $q_{\alpha\beta}(\mathbf{r}, s)$  are

$$q_{A10}(\mathbf{r}, 0) = q_{A20}(\mathbf{r}, 0) = q_{C10}(\mathbf{r}, 0) = q_{C20}(\mathbf{r}, 0) = 1.0$$

$$q_{B0}(\mathbf{r}, 0) = q_{A10}(\mathbf{r}, f_{A1}N) q_{A20}(\mathbf{r}, f_{A2}N)$$

$$q_{B1}(\mathbf{r}, 0) = q_{C10}(\mathbf{r}, f_{C1}N) q_{C20}(\mathbf{r}, f_{C2}N)$$

$$q_{A11}(\mathbf{r}, 0) = q_{A20}(\mathbf{r}, f_{A2}N) q_{B1}(\mathbf{r}, f_{B1}N)$$

$$q_{A21}(\mathbf{r}, 0) = q_{A10}(\mathbf{r}, f_{A1}N) q_{B1}(\mathbf{r}, f_{B1}N)$$

$$q_{C11}(\mathbf{r}, 0) = q_{B0}(\mathbf{r}, f_{B1}N) q_{C20}(\mathbf{r}, f_{C2}N)$$

$$q_{C21}(\mathbf{r}, 0) = q_{B0}(\mathbf{r}, f_{B1}N) q_{C10}(\mathbf{r}, f_{C1}N)$$

which are similar to those in refs 10, 12. Eq 9 is solved by an

alternating direction implicit method.<sup>28</sup> The boundary conditions are periodic.

The density field  $\phi_\alpha$  of species  $\alpha$ , conjugated to the self-consistent field  $W_\alpha(\mathbf{r})$  can be updated by using the equation:<sup>22,23,25</sup>

$$W_\alpha^{\text{new}} = W_\alpha^{\text{old}} + \Delta t \left( \frac{\delta F}{\delta \phi_\alpha} \right)^* \quad (10)$$

where the time step  $\Delta t = 0.05$  and

$$\left( \frac{\delta F}{\delta \phi_\alpha} \right)^* = \sum_{M \neq \alpha} \chi_{\alpha M} N(\phi_M - f_M) + P(\mathbf{r}) - W_\alpha^{\text{old}} \quad (11)$$

The above steps are iterated until the free energy converges to a local minimum, where the phase structure corresponds to a metastable or stable state.<sup>9,10,12</sup> Each minimization is run several times using different initial random guess of the self-consistent fields  $W_\alpha(\mathbf{r})$ . In constructing the phase diagrams, we have encountered metastable structures. In each of these cases, we have identified the most stable structure by comparing the free energies.

The pressure field  $P(\mathbf{r})$  can be obtained by solving eqs 2–5:<sup>25</sup>

$$P = \frac{(C_2 C_3 (W_A + W_B) + C_1 C_3 (W_B + W_C) + C_1 C_2 (W_A + W_C))}{2(C_1 C_2 + C_2 C_3 + C_1 C_3)} \quad (12)$$

where

$$C_1 = -\chi_{AB}N + \chi_{BC}N + \chi_{AC}N \quad (13)$$

$$C_2 = \chi_{AB}N - \chi_{BC}N + \chi_{AC}N \quad (14)$$

$$C_3 = \chi_{AB}N + \chi_{BC}N - \chi_{AC}N \quad (15)$$

The initial value of  $W_\alpha(\mathbf{r})$  is constructed by  $W_\alpha(\mathbf{r}) = \sum_{M \neq \alpha} \chi_{\alpha M} N(\phi_M(\mathbf{r}) - f_M)$ , where  $\phi_M(\mathbf{r}) - f_M$  satisfies the Gaussian distribution:

$$\langle (\phi_M - f_M) \rangle = 0 \quad (16)$$

$$\langle (\phi_i(r) - f_i)(\phi_j(r') - f_j) \rangle = \gamma f_i f_j \delta_{ij} \delta(r - r') \quad (17)$$

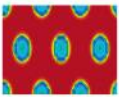
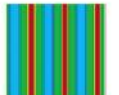
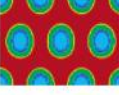
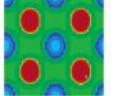
Here,  $\gamma$  is defined as the density fluctuation at the initial temperature. By using a different random seed, we can get a different initial value of  $W_\alpha(\mathbf{r})$ , which can be viewed as a quench.

For the sake of numerical tractability, the implementation of the self-consistent field equations is carried out in a two-dimensional square grid with side length  $L = V^{1/2}$ , which is initially chosen to be a small value and then increased until the changes in free energy are below predefined threshold,  $10^{-5}$ , in this work.<sup>22</sup> Then the free energy of the obtained “equilibrium” structure in the above calculation is minimized with respect to the aspects of the simulation cell.

## Results and Discussion

In the present work, we focus on the effect of block copolymer architecture on the phase behavior, so the interactions between the species are set to be the same, i.e.,  $\chi_{AC}N = \chi_{BC}N = \chi_{AB}N = 35.0$ . By systematically changing the volume

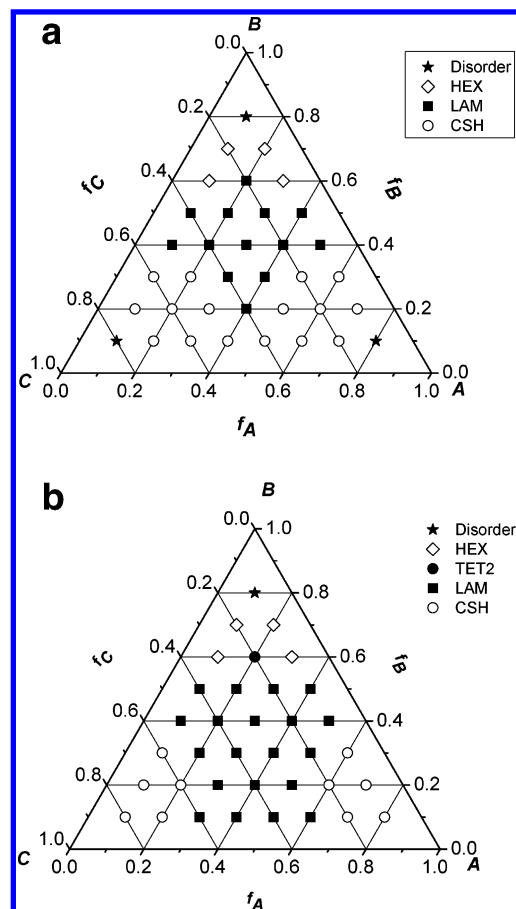
**TABLE 1: Summary of Observed Equilibrium Morphologies**

Name	Abbreviation	Graphic
hexagonal lattice phase	HEX	
lamellar phase	LAM	
core shell hexagonal lattice phase	CSH	
two interpenetrating tetragonal lattice	TET2	

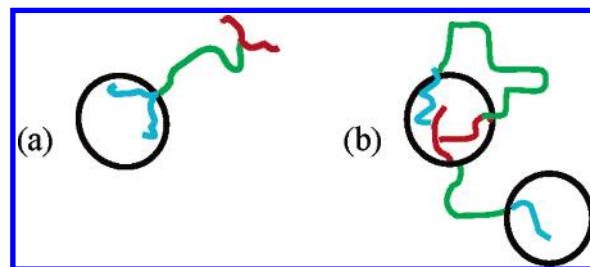
fractions of A, B, and C blocks, the component triangle phase diagrams in the entire range of the copolymer composition are constructed. The increment of the volume fractions  $f_A$ ,  $f_B$ , and  $f_C$  in the phase diagram is 0.1. At each grid point, the most stable morphology is obtained with the method described in the above section. In this work, we only focus on the most stable morphologies. Table 1 shows all the observed ordered microphases that are found for H-shaped ABC block copolymer. Three different colors, blue, green, and red, are assigned to the A, B, and C blocks, respectively. Four microphases are observed: lamellar phase (LAM), hexagonal lattice phase (HEX), core-shell hexagonal lattice phase (CSH), and two interpenetrating tetragonal lattice (TET2). Here, it should be pointed out that the results present in this paper are subject to the 2D model and, hence, many intrinsic 3D structures, such as the cubic bcc and complex tricontinuous gyroid structures, are not obtained. However, our result is useful to understand the effect of architecture on the morphology and may help to guess the 3D morphologies.

Figure 2 gives the phase diagrams of the H-shaped ABC block copolymer and the linear ABC block copolymer, where the interaction parameters of the H-shaped ABC block copolymer and the linear ABC block copolymer are same, namely  $\chi_{AC}N = \chi_{BC}N = \chi_{AB}N = 35.0$ . In Figure 2a, the phase diagram is for the symmetric H-shaped ABC block copolymer with  $f_{A1}/f_A = f_{C1}/f_C = 0.50$ . In Figure 2b, the phase diagram is for the linear ABC block copolymer, which is reproduced from ref 9. The triangle phase diagram of H-shaped block copolymer clearly shows A–C reflection symmetry. Therefore, exchanging the positions of block A and C does not alter the phase symmetry for the system with symmetric interactions between the three distinct blocks, which is similar to that of the  $\pi$ -shaped and linear ABC block copolymers.<sup>9,12</sup>

In the center region of the phase diagram in Figure 2a, where the volume fractions of the three components are comparable, a “three-color” LAM phase is found, which is consistent with the phase diagram in Figure 2b. At nearly equal volume fractions of the three species ( $f_A \approx f_B \approx f_C$ ), the LAM phases with two characteristic lamellar widths are also observed,<sup>9,26,27</sup> i.e.,  $D_A \approx D_C \approx 2D_B$ , where  $D_A$ ,  $D_B$ , and  $D_C$  are the widths of the A, B, and C lamellae, respectively. Compared to the phase diagram



**Figure 2.** (a) Phase diagram of H-shaped ABC block copolymer ( $f_{A1}/f_A = f_{C1}/f_C = 0.50$ ) for  $\chi_{AB}N = \chi_{BC}N = \chi_{AC}N = 35.0$  and (b) phase diagram of linear ABC block copolymer for  $\chi_{AB}N = \chi_{BC}N = \chi_{AC}N = 35.0$ , which is reproduced from ref 9.



**Figure 3.** Schematic representation of the composition of hexagonal lattice. Three different colors, blue, green, and red, are assigned to the A, B, and C blocks, respectively. (a) H-shaped ABC block copolymer, (b) linear ABC block copolymer.

of linear ABC block copolymer (Figure 2b), the region that one can find the LAM phase is decreased obviously.

In those regions at the corner **B** of Figure 2a and b (where the middle block B dominates), the phase behaviors of H-shaped and linear ABC block copolymer are similar, i.e., the HEX morphology is found at the same composition. It should be noted that, in Figure 2a, the majority of A or C species forms the hexagonally packed lattices and the rest dissolves in the matrix formed by B. However, in Figure 2b, block A and C mix together and form the hexagonally packed lattices, as schematically shown in Figure 3. This is attributed to the different architectures of block copolymers and the equal interaction energies. The length of block A and C of this H-shaped ABC block copolymer is half of that of the linear ABC block copolymer, so the longer block A or C consists of the hexagonal

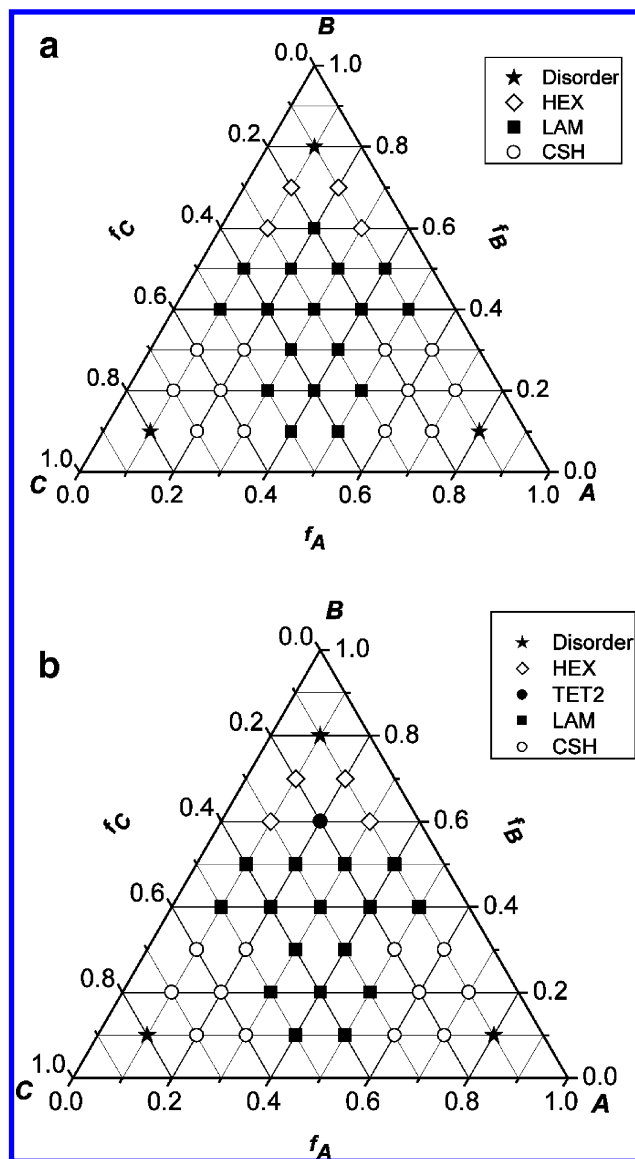
lattice and the shorter block C or A is pulled out of the hexagonal lattice, which makes for the relaxing of block A, B, and C.<sup>29</sup> When  $f_A = 0.2$ ,  $f_B = 0.6$ , and  $f_C = 0.2$ , the TET2 morphology appears for linear ABC block copolymer instead of the “three-color” LAM morphology for H-shaped ABC block copolymer, as shown in Figure 2. Compared with the linear ABC block copolymer, the length of block A and C of the H-shaped block copolymer is half of that of the linear block copolymer in each grid, so the LAM is more stable than the TET2 due to the different interfacial crowding.<sup>2–4</sup> Near corners A and C, the CSH morphology appears. In this morphology, the majority species A forms the matrix, while the minority species C forms the inner cores, and the middle block B forms the shells around the cores, which is the same as that of the linear ABC block copolymer. A similar CSH phase with species C forming the matrix, species B forming the shells, and species A forming the cores is also obtained near the corner C of the phase diagram in Figure 2a. Obviously, the CSH region of the H-shaped block copolymer is larger than that of the linear ABC block copolymer and the LAM region of H-shaped copolymer is decreased, which can also be explained in terms of the interfacial crowding.<sup>2–4</sup>

In the regions near the three edges of the phase diagram in Figure 2b, the linear ABC block copolymers become A–B ( $f_C \rightarrow 0$ ), A–C ( $f_B \rightarrow 0$ ), and B–C ( $f_A \rightarrow 0$ ) diblock copolymers. However, in those regions in Figure 2a, the H-shaped ( $A_2B$ – $(C)_2$ ) block copolymers become ( $A_2B$ ) ( $f_C \rightarrow 0$ ), ( $A_2$ )( $C_2$ ) ( $f_B \rightarrow 0$ ), and  $B(C_2)$  ( $f_A \rightarrow 0$ ) star-shaped block copolymers. Near the AB edge of the phase diagram (Figure 2a and 2b), where  $f_C = 0.10$ , the phase transitions are the same for both of the H-shaped and linear block copolymer, i.e., as the volume fraction  $f_B$  increases, the ordered microphases change from CSH to LAM, and finally to HEX. Near the CB edge, similar transitions are also obtained. Near the AC edge, as  $f_A$  increases, the ordered microphases change from CSH to LAM, and finally to CSH. One can also find that near the AC edge in Figure 2a, where the architecture of the block copolymers is close to the four-arm star block copolymer, the region that one can observe the LAM phase region is very small.

Parts a and b of Figure 4 show the phase diagrams of H-shaped ABC block copolymer with  $f_{A1}/f_A = f_{C1}/f_C = 0.30$  and  $f_{A1}/f_A = f_{C1}/f_C = 0.20$ , respectively, for  $\chi_{AB}N = \chi_{BC}N = \chi_{AC}N = 35.0$ . By comparing Figure 2a, Figure 4a, and Figure 4b, one can see that, as  $f_{A1}/f_A = f_{C1}/f_C$  decreases, the phase behaviors change greatly. When  $f_{A1}/f_A$  changes from 0.3 to 0.2, the TET2 morphology is found, which covers one of the grid of the LAM. When  $f_{A1}/f_A = f_{C1}/f_C$  decreases, the LAM phase region is gradually increased and the CSH phase region is decreased. These transitions are supposed to be the result of the competition between the interfacial contact energy and the chain stretching.<sup>2</sup> When  $f_{A1}/f_A = f_{C1}/f_C$  decrease, the crowding of species AB and BC is gradually decreased, so the phase behavior changes greatly with different value of  $f_{A1}/f_A = f_{C1}/f_C$ .

## Conclusion

By using a combinatorial screening method based on the SCFT for polymers, we have investigated the morphologies of symmetric H-shaped ABC block copolymers ( $A_2BC_2$ ) and compared with those of the linear ABC block copolymers. By changing the volume fractions of A1 and C1, one can obtain block copolymers with different architectures ranging from linear block copolymer to H-shaped block copolymer. By systematically varying the volume fractions of block A, B, and C, the triangle phase diagrams of the H-shaped ABC block



**Figure 4.** Phase diagram of H-shaped ABC block copolymer for  $\chi_{AB}N = \chi_{BC}N = \chi_{AC}N = 35.0$ . (a)  $f_{A1}/f_A = f_{C1}/f_C = 0.30$ , (b)  $f_{A1}/f_A = f_{C1}/f_C = 0.20$ .

copolymer with equal interactions among the three species are constructed. In this study, we obtained four different morphologies LAM, HEX, CSH, and TET2. When  $f_{A1}/f_A = f_{C1}/f_C$  decreases from 0.5 to 0 (i.e., from H-shaped to linear ABC block copolymer), the LAM phase region is gradually increased and the CSH phase region is decreased. When  $f_{A1}/f_A = f_{C1}/f_C$  changes from 0.3 to 0.2, the TET2 morphology is found, which covers one of the grid of the LAM. These results may help with the design and the synthesis of block copolymers with different microstructures.

**Acknowledgment.** This work is supported by the National Natural Science Foundation of China (20574070, 20490220, 50373044, 20620120105, 50340420392) programs and subsidized by the Special Funds for National Basic Research Program of China (2005CB623800).

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