Microstructures of $A_4(BC)_4$ star copolymers and the influence of architecture

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Abstract. The self-consistent field theory is used to investigate the microstructures of $A_4(BC)_4$ star copolymers. The phase diagram is mapped out to show different phase regions. Compared with $A(BC)_4$ star copolymers, several microstructures are lost, and more lamellar structures are found due to the stronger topological constraint of the junction. The results may be helpful to understand the influence of molecular architectures on microstructures and provide an effective way to design controllable microstructures.

1. Introduction
The self-assembly of block copolymers has attracted much attention in recent years for its promising applications in material science, nanotechnology and biology. For the simplest linear $AB$ diblock copolymers, the fascinating periodic morphologies have been deeply understood both experimentally and theoretically [1-4]. As the distinct components increase, say $ABC$ triblock copolymers, the variety and complexity of microstructures may increase dramatically [5, 6]. Especially, once the topological architecture changes from line shape to star, comb-like or other complicated shapes, more novel structures can be found [7-10]. The star architecture imposes a strong topological constraint on the polymer chain and may lead to new phenomena. In particular, the development of synthesis technology allows us to obtain more complex copolymers, which provides an opportunity to find new periodic microstructures due to the additional entropic effect. By far, systematic investigations on how the microstructures relate to the architectures are still desired. In this work, we use the self-consistent field theory (SCFT) to investigate the microstructures of $A_4(BC)_4$ star copolymers, where four $A$ chains and four $BC$ chains are attached to the junction $O$ by the $A$ ends and $B$ ends, respectively. Each chain $A$ consists of $N_A$ segments, and each chain $BC$ consists of $N_B$ $B$ segments and $N_C$ $C$ segments. All segments have the same volume $\rho_0^{-1}$ and the statistical length $a$. The only difference between two kinds of copolymers is the connection mode of chain $A$. For $A(BC)_4$ copolymers, only one $A$ chain is attached to the junction $O$. In both copolymers, the number of the segment component $A$ is same. Therefore, the length of $A$ chain in the
$A_d(BC)_4$ star copolymers is one fourth of that in the $A(BC)_4$ star copolymers, which means that two kinds of copolymers have same polymerization $N = 4N_A + 4N_B + 4N_C$ though their architectures are different.

![Figure 1](image)

**Figure 1.** (Colour online) A schematic of (a) $A_d(BC)_4$ and (b) $A(BC)_4$ star copolymers. Green, red and blue curves represent $A$, $B$ and $C$ blocks, respectively.

As an important mean-field theory for polymers, the SCFT has been widely used in the prediction of phase behavior of block copolymers and other related systems [11, 12]. For the $A_d(BC)_4$ or $A(BC)_4$ copolymer melts in a volume $V$, the free energy $F$ can be written as

$$F = \frac{N\bar{F}}{k_BT} = \frac{1}{V} \int d\bar{r} [\chi_{AA}N\varphi_A(\bar{r})\varphi_A(\bar{r}) + \chi_{BB}N\varphi_B(\bar{r})\varphi_B(\bar{r}) + \chi_{CC}N\varphi_C(\bar{r})\varphi_C(\bar{r}) - W_A(\bar{r})\varphi_A(\bar{r}) - W_B(\bar{r})\varphi_B(\bar{r}) - W_C(\bar{r})\varphi_C(\bar{r}) - \zeta(1 - \varphi_A(\bar{r}) - \varphi_B(\bar{r}) - \varphi_C(\bar{r})) - \ln \frac{\Omega}{V}].$$

In the equation (1), $T$ is the temperature and $k_B$ is the Boltzmann’s constant. The variables $\varphi_i, W_i(i = A, B, C)$ and $\zeta$ are the functions of the position $\bar{r}$, $\varphi_i$ is the local densities of different components, $\chi_{ij}(=\chi_{ji}, i, j = A, B, C)$ is the Flory-Huggins interaction parameter between two different components. $W_i$ is the effective chemical potential field acting on the different component. $\zeta$ is a Lagrange-multiplier potential field ensuring the system incompressibility. $\Omega$ is the partition function of a single star copolymer and is defined by

$$\Omega = \int dq_0(\vec{r},s)q^*_0(\vec{r},s).$$

In the equation (2), $q_i$ and $q^*_i(i = A$ or $BC)$ are the propagators and denote the probability that finds the segment $s$ at the position $\vec{r}$.

The propagators satisfy the modified diffusion equations:

$$\frac{\partial q_A(\vec{r},s)}{\partial s} = \frac{Na^2}{6} \nabla^2 q_A(\vec{r},s) - W_A(\vec{r})q_A(\vec{r},s) \quad 0 < s < N_A(\ A_d(BC)_4) \ \text{or} \ 0 < s < 4N_A(\ A(BC)_4);$$

$$\frac{\partial q^*_A(\vec{r},s)}{\partial s} = -\frac{Na^2}{6} \nabla^2 q^*_A(\vec{r},s) + W_A(\vec{r})q^*_A(\vec{r},s) \quad 0 < s < N_A(\ A_d(BC)_4) \ \text{or} \ 0 < s < 4N_A(\ A(BC)_4);$$

$$\frac{\partial q_{BC}(\vec{r},s)}{\partial s} = \frac{Na^2}{6} \nabla^2 q_{BC}(\vec{r},s) - W_i(\vec{r})q_{BC}(\vec{r},s) \quad \text{if} \ 0 < s < N_B, i = B; \ \text{else} \ \text{if} \ N_B < s < N_C, i = C;$$

$$\frac{\partial q^*_{BC}(\vec{r},s)}{\partial s} = -\frac{Na^2}{6} \nabla^2 q^*_{BC}(\vec{r},s) + W_i(\vec{r})q^*_{BC}(\vec{r},s) \quad \text{if} \ 0 < s < N_B, i = B; \ \text{else} \ \text{if} \ N_B < s < N_C, i = C.$$

Due to the different architectures of the $A_d(BC)_4$ and $A(BC)_4$ copolymers, the initial conditions of above equations are different.

For the $A_d(BC)_4$ copolymers, the initial conditions are given by

$$q_A(\vec{r},0) = 1, \ q^*_A(\vec{r},N_B + N_C) = 1,$$

$$q_A(\vec{r},N_A) = [q_A(\vec{r},N_A)]^1 * [q^*_B(\vec{r},0)]^4, \ q_{BC}(\vec{r},0) = [q_A(\vec{r},N_A)]^4 * [q^*_B(\vec{r},0)]^3.$$  

For the $A(BC)_4$ copolymers, the initial conditions are given by
\[ q_A(\vec{r}, 0) = 1, \quad q_{bc}(\vec{r}, N_B + N_C) = 1, \quad q_A(\vec{r}, N_A) = [q_{bc}(\vec{r}, 0)]^4, \quad q_{bc}(\vec{r}, 0) = q_A(\vec{r}, N_A) \times [q_{bc}(\vec{r}, 0)]^4. \quad (8) \]

Minimizing the free energy \( F \), we obtain a set of self-consistent equations. The field \( W_i \) and the local density \( \phi_i \) at the equilibrium can be determined by using the combinatorial screening method \[12\] to solve the self-consistent equations with periodic boundary conditions.

3. Results and discussion

To compare the microstructures of two kinds of copolymers, we ensure all factors are same except for the architectures. The Flory-Huggins interaction parameters and the polymerization in both copolymers are set as \( \chi_{ab}N = \chi_{bc}N = \chi_{ac}N = 140 \) and \( N = 600 \). All the sizes are in units of \( a \).

Table 1. (Colour online) Summary of observed microstructures of \( A_4(BC)_4 \) star copolymers.

| Name (Abbreviation) | Graphic | Schematic representation |
|---------------------|---------|--------------------------|
| hexagonal microstructure (HEX) | ![Image](hexagonal.png) | ![Image](hexagonal_schematic.png) |
| core-shell hexagonal microstructure (CSH) | ![Image](core-shell.png) | ![Image](core-shell_schematic.png) |
| two-phase lamellar microstructure (L2) | ![Image](two-phase.png) | ![Image](two-phase_schematic.png) |
| three-phase lamellar microstructure (L3) | ![Image](three-phase.png) | ![Image](three-phase_schematic.png) |
| three-phase lamellar microstructure with one mixed phase (L3M) | ![Image](three-phase-mixed.png) | ![Image](three-phase-mixed_schematic.png) |
| interpenetrating tetragonal microstructure (TET) | ![Image](tetragonal.png) | ![Image](tetragonal_schematic.png) |

We can introduce the average densities of different components: \( D_A = 4N_A/N, \) \( D_B = 4N_B/N, \) \( D_C = 4N_C/N. \) With the change of the average densities, the distinct block has different length. The corresponding copolymer may self-assemble into an ordered microstructure. All observed microstructures of the \( A_4(BC)_4 \) star copolymers are shown in table 1, including the hexagonal microstructure (HEX), the core-shell hexagonal microstructure (CSH), the two-phase lamellar...
microstructure (L2), the three-phase lamellar microstructure (L3), the three-phase lamellar microstructure with one mixed phase (L3M) and the interpenetrating tetragonal microstructure (TET).

The phase diagram in figure 2(a) gives the microstructures varying with the average densities. Three sides of the triangle represent the average densities $D_i$ ($i = A, B, C$). Each of them changes from 0 to 1. The increment is 0.1. Each grid point corresponds to a set of $(D_A, D_B, D_C)$. For example, the grid point in the lower left of the phase diagram corresponds to $(0.1, 0.1, 0.8)$. In this case, $N_A = 15$, $N_B = 60$ and $N_C = 480$, the length of chain $A$ is very short whereas that of chain $C$ is very long. The microstructure is obtained by using the method described in Section 2. The corresponding structural symbol is plotted on the grid point. In the three corners of the phase diagram, the systems can form the hexagonal microstructure. Three kinds of schematic representations of the composition are plotted in table 1. Taking the first schematic representation as an example, the cores consist of two kinds of short blocks $A$ and $B$. The matrix consists of the long block $C$. The cores arrange hexagonally in the matrix. When $(D_A, D_B, D_C) = (0.2, 0.1, 0.7)$ and $(0.7, 0.1, 0.2)$, the core-shell hexagonal microstructures are observed. If $(D_A, D_B, D_C) = (0.2, 0.1, 0.7)$, blocks $A$ form the cores, the mixed blocks $A$ and $B$ form the shells, and $C$ blocks form the matrix. Similarly, if $(D_A, D_B, D_C) = (0.7, 0.1, 0.2)$, $C$ blocks form the cores, the mixed blocks $B$ and $C$ form the shells, and $A$ blocks form the matrix. When $(D_A, D_B, D_C) = (0.1, 0.4, 0.5), (0.2, 0.2, 0.6), (0.6, 0.2, 0.2), (0.6, 0.3, 0.1)$ and $(0.7, 0.2, 0.1)$, the two-phase lamellar microstructures are found. The schematic representations in table 1 show that the two short connected blocks form a mixed layer and the other long block forms another layer. With the separation of the mixed phase, L3M is observed, where most of the long blocks in the mixed layer is separated to form another individual layer, and the rest of the long blocks and the short blocks still form the mixed layer. The further separation can lead to the three-phase lamellar microstructure, where each different component forms an individual layer. When the density of $B$ block is relatively high, the system can form an interpenetrating tetragonal microstructure, where $A$ and $C$ blocks form tetragonal lattices respectively, and $B$ blocks form the matrix. When $(D_A, D_B, D_C) = (0.1, 0.8, 0.1)$, the system cannot be separated and keeps homogeneous (DIS).

![Figure 2](image)

**Figure 2.** Phase diagrams of (a) $A_d(BC)_4$ and (b) $A(BC)_4$ star copolymers.

To further examine the influence of architecture, we compare the microstructures with those of the $A(BC)_4$ star copolymers. For clarity, the phase diagram of the $A(BC)_4$ star copolymers is shown in figure 2(b). Obviously, the microstructure number of the $A(BC)_4$ star copolymers is smaller than that of the $A(BC)_4$ star copolymers. Other structures such as the two-phase lamellar structure with alternating blocks inside a layer (L2AL), the two-phase lamellar structure with beads at the interface (L2BD) and the interpenetrating hexagonal microstructures (INHE) observed in the $A(BC)_4$ star copolymers (see Ref. [8]) cannot be found in the $A_d(BC)_4$ star copolymers. The first two lamellar
microstructures show that the mixed blocks in the lamellar structures may further separate inside the mixed layer which can be attributed to the flexibility of one arm A. In addition, we find that most of the grid points in the phase diagram are occupied by the lamellar structures in the \(A_4(BC)_4\) star copolymers. In comparison with the phase diagram of the \(A(BC)_4\) star copolymers, most of the hexagonal microstructures and the core-shell hexagonal microstructures in the \(A(BC)_4\) star copolymers are replaced by all kinds of the lamellar structures in the \(A_4(BC)_4\) star copolymers. Due to the junction constraint of four chains A, the formation of the lamellar structures may help to lower the free energy by relieving the interfacial crowding. The symmetry of four blocks A and four blocks BC also favours the formation of symmetrical structures. Therefore more lamellar structures are observed in the \(A_4(BC)_4\) star copolymers.

4. Conclusion

We studied the microstructures of the \(A_4(BC)_4\) star copolymers by using self-consistent field theory. Six kinds of different microstructures are observed by varying the average densities of distinct components when \(\chi_{AB}N = \chi_{BC}N = \chi_{AC}N = 140\) and \(N = 600\). Compared with the microstructures of the \(A(BC)_4\) star copolymers with the same parameters, the number of the microstructures decreases and more lamellar structures are found due to a stronger junction constraint of blocks A. It is helpful to understand the influence of architectures on microstructure and provide an effective way to design controllable microstructures with these results.

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