# Microstructures controlled by nanoparticles in complicated star terpolymers

**Ling Zhou**[1]

School of Science, Nantong University, Nantong, 226019, China

E-mail: ZL7103@163.com

**Abstract.** Self-consistent field and density functional theories are applied to investigate microstructure transitions in $A(BC)_4$ star terpolymers due to the addition of nanoparticles when $B$ block is a minority. With increasing nanoparticles that have a preferential affinity to $B$ block, a variety of order-to-order transitions are observed, such as the transitions from a hexagonal structure to a core-shell hexagonal structure, from a hexagonal structure with beads at the interface to a core-shell hexagonal structure, from a lamellar structure with beads at the interface to a three-phase lamellar structure, and from a two-phase lamellar structure to a three-phase lamellar structure. The results are helpful in the fabrication of controllable functional materials through the role of nanoparticles.

## 1. Introduction

The self-assembly of copolymers provides a lot of opportunities to fabricate novel functional materials [1]. The components and their interaction energies, the entropy effect caused by the extension of chains and the system incompressibility play an important role in determining the phase behavior of copolymers [2, 3]. Recently, more and more researches indicate that the addition of few nanoparticles can dramatically change structures and properties of copolymers [4-6]. Based on electrostatic interactions, hydrogen bond, hydrophobic interactions and biological recognition between nanoparticles and copolymers, the mixed systems can realize all kinds of self-assemblies, which open up a new developing space by using nanoparticels as sensors and vastly widen the range of application. In this paper, we add several nanoparicles into $A(BC)_4$ star terpolymers. The combined self-consistent field and density functional theories [7] are used to investigate the influence of few nanoparticles on the microstructure transitions. It is well known that the increase of monomer and the change of topological structures may greatly increase the complexity of the self-assembled microstructures. Especially the star constraint of star copolymers can promote the formation of singular microstructures [8]. The $A(BC)_4$ star terpolymers are just this kind of copolymers whose complicated topological architecture leads to the appearance of various complex microstructures that cannot be observed in simple copolymers [9]. The motivation of this work is to study whether nanoparticles can effectively control the microstructure transitions in such complicated terpolymers and what the main factors influencing the microstructures are. Finally four kinds of microstructure transitions are observed.

## 2. Model and method

[1] Address for correspondence: Ling Zhou, School of Science, Nantong University, Nantong, 226019, China. E-mail: ZL7103@163.com.


Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

We select a nanoparticle/terpolymers mixture as our model system. In this model, $A(BC)_4$ star terpolymers consist of one homopolymer arm $A$ and four copolymer arms $BC$. The ends $A$ and $B$ of the five chains are attached to a core. Blocks $A$, $B$ and $C$ have $N_A$, $N_B$ and $N_C$ segments, respectively. The statistical length $b$ of each segment is same. Therefore each segment has a common volume $\rho_0^{-1}$. In addition, we assume that the length of blocks $B$ and $C$ on four arms are same. Therefore the polymerization index of $A(BC)_4$ star terpolymers $N = N_A + 4N_B + 4N_C$. We use $M_i$ to denote the monomer fraction of block $i$ ($i$=$A$, $B$, $C$). Due to the incompressibility constraint of the system, we have $M_A = N_A / N$, $M_B = N_B / N$, $M_C = N_C / N = 1 - M_A - M_B$. Once nanoparticles are added into the $A(BC)_4$ star terpolymers in the volume $V$, the free energy $F$ of the system can be written as:

$$\frac{NF}{\rho_0 k_B T V} = -\phi_{Ter}\ln(\frac{Q_{Ter}}{V\phi_{Ter}}) - \frac{\phi_n}{\alpha_n}\ln(\frac{Q_n\alpha_n}{V\phi_n}) + \frac{1}{V}\int dr(\chi_{AB}N\varphi_A(\vec{r})\varphi_B(\vec{r}) + \chi_{AC}N\varphi_A(\vec{r})\varphi_C(\vec{r}) + \chi_{BC}N\varphi_B(\vec{r})\varphi_C(\vec{r})$$
$$+\chi_{An}N\varphi_A(\vec{r})\varphi_n(\vec{r}) + \chi_{Bn}N\varphi_B(\vec{r})\varphi_n(\vec{r}) + \chi_{Cn}N\varphi_C(\vec{r})\varphi_n(\vec{r}) - W_A(\vec{r})\varphi_A(\vec{r}) - W_B(\vec{r})\varphi_B(\vec{r}) - W_C(\vec{r})\varphi_C(\vec{r})$$
$$-W_n(\vec{r})\rho_n(\vec{r}) - P(\vec{r})(1-\varphi_A(\vec{r})-\varphi_B(\vec{r})-\varphi_C(\vec{r})-\varphi_n(\vec{r})) + \rho_n\Psi(\bar{\varphi}_n)). \quad (1)$$

In above equation, $k_B$ denotes the Boltzmann's constant and $T$ denotes the temperature. $\phi_n$ is the nanoparticle average volume fraction, and $\phi_{Ter}$(=1-$\phi_p$) is the terpolymer average volume fraction. $\varphi_i(\vec{r})$ and $\chi_{ij}$ (=$\chi_{ji}$, $i$, $j$=$A$, $B$, $C$, $n$) are the local volume fraction and the interaction parameter of components $i$ and $j$. $W_i(\vec{r})$ $(i = A,B,C,n)$ is a mean chemical potential field that acts on the component $i$. $Q_{Ter}(=\int d\vec{r}q_A q_A^+ = \int d\vec{r}q_{BC}q_{BC}^+)$ is a partition function of a single teropolymer chain. $Q_n(=\int d\vec{r}\exp[-W_n(\vec{r})])$ is a nanoparticle partition function. According to the architecture of $A(BC)_4$ star terpolymers, we should introduce four distribution functions $q_A(\vec{r},s)$, $q_A^+(\vec{r},s)$, $q_{BC}(\vec{r},s,l)$, $q_{BC}^+(\vec{r},s,l)$ to determine $Q_{Ter}$. These four functions satisfy the following modified diffusion equations:

$$\partial q_A/\partial s = (Na^2/6)\nabla^2 q_A - W_A(\vec{r})q_A; \quad (2)$$
$$\partial q_A^+/\partial s = -(Na^2/6)\nabla^2 q_A^+ + W_A(\vec{r})q_A^+; \quad (3)$$
$$\partial q_{BC}/\partial s = (Na^2/6)\nabla^2 q_{BC} - W_B(\vec{r})q_{BC} \quad \text{if } 0 < s < M_B/4; \quad (4)$$
$$\partial q_{BC}^+/\partial s = -(Na^2/6)\nabla^2 q_{BC}^+ + W_B(\vec{r})q_{BC}^+ \text{ if } 0 < s < M_B/4; \quad (5)$$
$$\partial q_{BC}/\partial s = (Na^2/6)\nabla^2 q_{BC} - W_C(\vec{r})q_{BC} \quad \text{if } M_B/4 < s < (M_B+M_C)/4; \quad (6)$$
$$\partial q_{BC}^+/\partial s = -(Na^2/6)\nabla^2 q_{BC}^+ + W_C(\vec{r})q_{BC}^+ \quad \text{if } M_B/4 < s < (M_B+M_C)/4. \quad (7)$$

The denotation $s$ is the segment that changes continuously from one end to another along the arms. Equations (2)-(7) are solved from the initial conditions: $q_A(\vec{r},M_A)=1$, $q_{BC}^+(\vec{r},(M_B+M_C)/4,l)=1$ ($l$ = $1,2,3,4$), $q_A(\vec{r},0)=\prod_{l=1}^4 q_{BC}^+(\vec{r},0,l)$, $q_{BC}(\vec{r},0,l)=q_A(\vec{r},0)\prod_{J=1,J\neq l}^4 q_{BC}^+(\vec{r},0,J)$. The denotation $l$ refers to the $l$th arm of $BC$ copolymers. $\alpha_n(=\frac{4\pi R^3\rho_0}{3N})$ is a volume ratio of the spherical nanoparticles to terpolymers. $R$ is the radius of spherical nanoparticles. $\varphi_n(\vec{r})(=\frac{\rho_0}{N}\int_{|\vec{r}'|<R}d\vec{r}'\rho_n(\vec{r}+\vec{r}'))$ is the local volume fraction of nanoparticles, where $\rho_n$ denotes the nanoparticle center distribution. $\bar{\varphi}_n(\vec{r})(=\alpha_n/V_{2R}\int_{|\vec{r}'|<2R}d\vec{r}'\rho_n(\vec{r}+\vec{r}'))$ is the weighted density of nanoparticles. $\Psi(\bar{\varphi}_n)(=(4\bar{\varphi}_n-3\bar{\varphi}_n^2)/(1-\bar{\varphi}_n)^2)$ is the excess free energy per nanoparticle. $V_{2R}$ is the spherical volume around $\vec{r}$ with radius $2R$. $P(\vec{r})$ is a potential field enforcing the system incompressibility.

The final microstructures of the system are obtained through minimizing the free energy $F$, with respect to $W_A(\vec{r})$, $W_B(\vec{r})$, $W_C(\vec{r})$ and $W_n(\vec{r})$, $\varphi_A(\vec{r})$, $\varphi_B(\vec{r})$, $\varphi_C(\vec{r})$, $\varphi_n(\vec{r})$ and $P(\vec{r})$. A set of self-

consistent equations are obtained and solved with the periodic boundary conditions in a two-dimensional space. By the self-consistent iteration, the final local volume fractions $\varphi_A$, $\varphi_B$, $\varphi_C$ and $\varphi_n$ at the equilibrium are determined. In the calculation, all of the lengths are expressed in units of $b$.

## 3. Results and discussion

The parameters in the calculation are chosen as $N=600$, $R=2b$, $M_B=0.1$. The nanoparticles have a preferential affinity to $B$ block. The interactions between different components are asymmetrical and are set as $\chi_{AB}N=\chi_{An}N=130$, $\chi_{BC}N=\chi_{Cn}N=160$, $\chi_{AC}N=80$, $\chi_{Bn}N=0$.

First we study the microstructures of the terpolymer melts without nanoparticles. $M_A$ is controlled from 0.1 to 0.7. The increment of $M_A$ is set to be 0.1. Since $M_B$ is fixed to 0.1, $M_C$ changes from 0.8 to 0.2 correspondingly. Four kinds of microstructures changing with $(M_A,M_B,M_C)$ are observed, which are a hexagonal structure (hex) when $(M_A,M_B,M_C)=(0.1,0.1,0.8)$, hexagonal structures with beads at the interface (h+b) when $(M_A,M_B,M_C)$ = $(0.2,0.1,0.7)$, $(0.3,0.1,0.6)$, $(0.4,0.1,0.5)$, lamellar structures with beads at the interface (l+b) when $(M_A,M_B,M_C)=(0.5,0.1,0.4)$ and $(0.6,0.1,0.3)$, and a two-phase lamellar structure (l2) when $(M_A,M_B,M_C)=(0.7,0.1,0.2)$. The detailed distributions of different blocks are shown in figures 1(a), 1(c), 1(e) and 1(g).

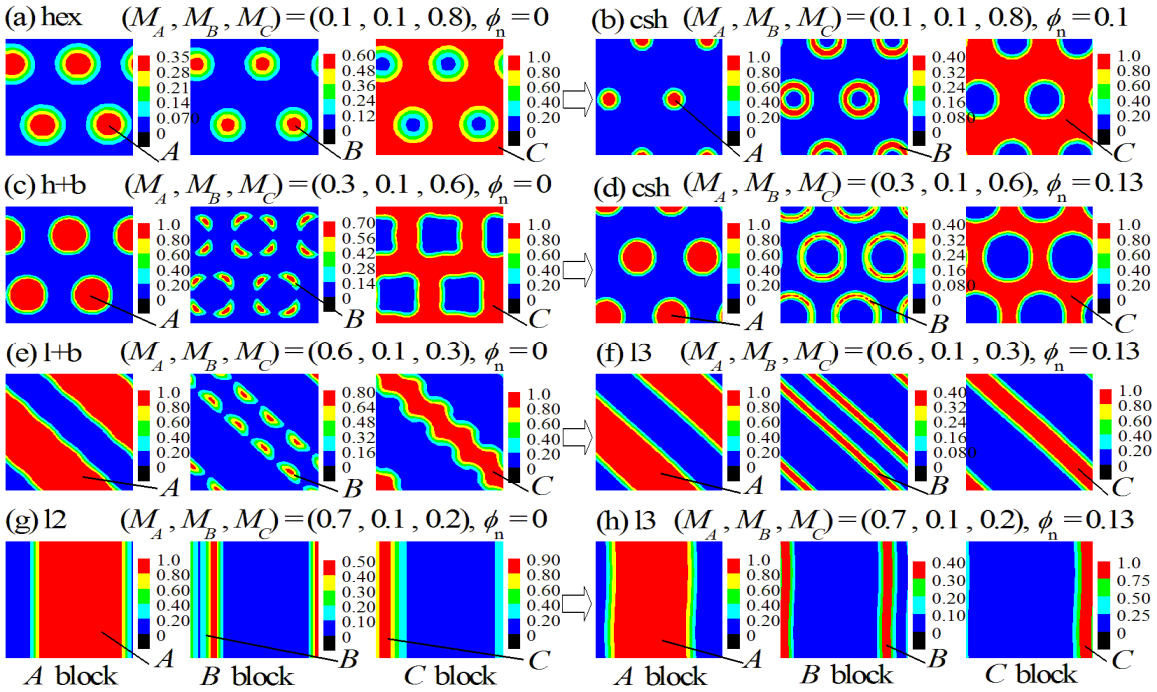



**Figure 1.** The local volume fractions of blocks $A$, $B$ and $C$ (color online).

Then we consider the influence of nanoparticles. Figures 1(b), 1(d), 1(f) and 1(h) illustrate the microstructures due to the addition of few nanoparticles. The color scale on the right of each figure gives the range of local volume fractions of the corresponding blocks $A$, $B$ or $C$. Figure 1(b) gives the core-shell hexagonal structure (csh) when $(M_A,M_B,M_C)=(0.1,0.1,0.8)$ and $\phi_n=0.1$. However, the morphology without nanoparticles is a hexagonal structure (hex) as shown in figure 1(a), where the hexagonal cores consist of $A$ and $B$ blocks, and the matrix consists of the $C$ block. With increasing nanoparticle concentration, the further phase separation occurs between $A$ and $B$ where the block $B$ and nanoparticles form the shells and the block $A$ stays in the hexagonal cores. Therefore the original hexagonal structure (hex) is substituted by the core-shell hexagonal structure (csh) due to the addition of nanoparticles. Figure 1(c) shows the hexagonal structure with beads at the interface (h+b) when

$(M_A, M_B, M_C) = (0.3, 0.1, 0.6)$ and the nanoparticles are absent. In this case, the hexagonal cores consist of *A* blocks, four bead-shape domains of *B* blocks distribute symmetrically around the *A* cores, and the remaining part consists of *C* blocks. Similar microstructures are also found when $(M_A, M_B, M_C) = (0.2, 0.1, 0.7)$ and $(0.4, 0.1, 0.5)$. The only difference of the microstructures is that the numbers of the bead-shape domains. When $(M_A, M_B, M_C) = (0.2, 0.1, 0.7)$, $(0.3, 0.1, 0.6)$ and $(0.4, 0.1, 0.5)$, three, four and six bead-shape domains of *B* blocks appear in turn. The addition of nanoparticles makes the isolated *B* domains change to a shell surrounding the cores *A*. The core-shell hexagonal structure (csh) when $(M_A, M_B, M_C) = (0.3, 0.1, 0.6)$ and $\phi_n$=0.13 is shown in figure 1(d). Figure 1(e) shows the lamellar structure with beads at the interface (l+b) when $(M_A, M_B, M_C) = (0.6, 0.1, 0.3)$. The blocks *A* and *C* separate into two parallel layers, and the blocks *B* shrink into bead-shape domains staying at the interface of two layers when $(M_A, M_B, M_C) = (0.6, 0.1, 0.3)$ and nanoparticles are absent. The same microstructures also can be found when $(M_A, M_B, M_C) = (0.5, 0.1, 0.4)$. With the gradually increased nanoparticles, the domains of block *B* increase and finally form the lamellar structure between layers *A* and *C*. Therefore a three-phase lamellar structure (l3) is observed. Such three-phase lamellar structure (l3) when $(M_A, M_B, M_C) = (0.6, 0.1, 0.3)$ and $\phi_n$=0.13 is shown in figure 1(f). Therefore the addition of nanoparticles successfully realizes the microstructure transition from a l+b structure to a l3 structure. Figure 1(g) shows a two-phase lamellar structure (l2) without nanoparticles when $(M_A, M_B, M_C) = (0.7, 0.1, 0.2)$. Due to the relatively short chains *B* and *C*, and the relatively weak interaction $\chi_{BC}N$, the blocks *B* and *C* form a mixed layer and the block *A* occupies another layer. The addition of nanoparticles leads to the further phase separation of blocks *B* and *C*. Finally block *B* and block *C* completely separate and form two lamellae, respectively. Such three-phase lamellar structure (l3) is shown in figure 1(h) when $(M_A, M_B, M_C) = (0.7, 0.1, 0.2)$ and $\phi_n$=0.13.

## 4. Conclusion

In summary, we theoretically study the microstructures controlled by nanoparticles in $A(BC)_4$ star terpolymers. We find four kinds of microstructures in the terpolymer melts when $\chi_{AB}N = 130$, $\chi_{BC}N = 160$, $\chi_{AC}N = 80$ and $M_B = 0.1$. With the increase of $M_A$, hex, h+b, l+b and l2 structures are observed in turn. In order to capture the microstructure transitions, we add few nanoparticles into $A(BC)_4$ star terpolymers. The interactions between nanoparticles and different blocks are $\chi_{An}N = 130$, $\chi_{Bn}N = 0$ and $\chi_{Cn}N = 160$. The calculations show that the order-to-order transitions, such as hex $\rightarrow$ csh, h+b $\rightarrow$ csh, l+b $\rightarrow$ l3 and l2 $\rightarrow$ l3, can be realized. The strategy in the present study is helpful in the fabrication of controllable functional materials triggered by nanoparticles.

**Acknowledgments**

This work was supported by the Major National Scientific Instrument and Equipment Development Project of China (No. 2011YQ03013403), the National Natural Science Foundation of China (Nos. 61371057 and 11204143) and the Natural Science Foundation for pre-research of Nantong University (Nos. 11ZY005, 10ZY001).

**References**

[1] Xu W Q, Jiang K, Zhang P W and Shi A C 2013 *J. Phys. Chem. B* **117** 5296-305
[2] Subbotin A, Markov V and ten Brinke G 2010 *J. Phys. Chem. B* **114** 5250-6
[3] Shin D O, Mun J H, Hwang G, Yoon J Moon, Kim J Y, Yun J M, Yang Y, Oh Y, Lee J Y, Shin J, Lee K J, Park S, Kim J U and Kim S O 2013 *Acsnano* **7** 8899-907
[4] Zhou L and Ma Y Q 2008 *J. Phys.*: *Condens. Matter* **20** 095006
[5] Zhang L S and Lin J P 2009 *Macromolecule* **42** 1410-4
[6] Pan Q Y, Tong C H and Zhu Y J 2011 *ACS Nano* **5** 123-8

[7] Thompson R B, Ginzburg V V, Matsen M W and Balazs A C 2002 *Macromolecules* **35** 1060-71
[8] Tang P, Qiu F, Zhang H D and Yang Y L 2004 *J. Phys. Chem. B* **108** 8434-8
[9] Zhou L, Liu Y, Peng J and Fang J H 2013 *J. Polym. Res.* **20** 102