Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Insights into Ordered Microstructures and Ordering Mechanisms of ABC Star Terpolymers via Integrating Dynamic Self-Consistent Field Theory and Variable Cell Shape Method

Xuguang Cao, Liangshun Zhang, Liquan Wang, and Jiaping Lin**

Shanghai Key Laboratory of Advanced Polymeric Materials, State Key Laboratory of Bioreactor Engineering, Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

Corresponding Authors: Liangshun Zhang (zhangls@ecust.edu.cn),

Jiaping Lin (jlin@ecust.edu.cn)

Content

Part S1: Influences of Relaxation Parameter on Microphase Separation of Asymmetric Diblock Copolymers

Part S2: VCS Simulations for the case of Metastable Structures

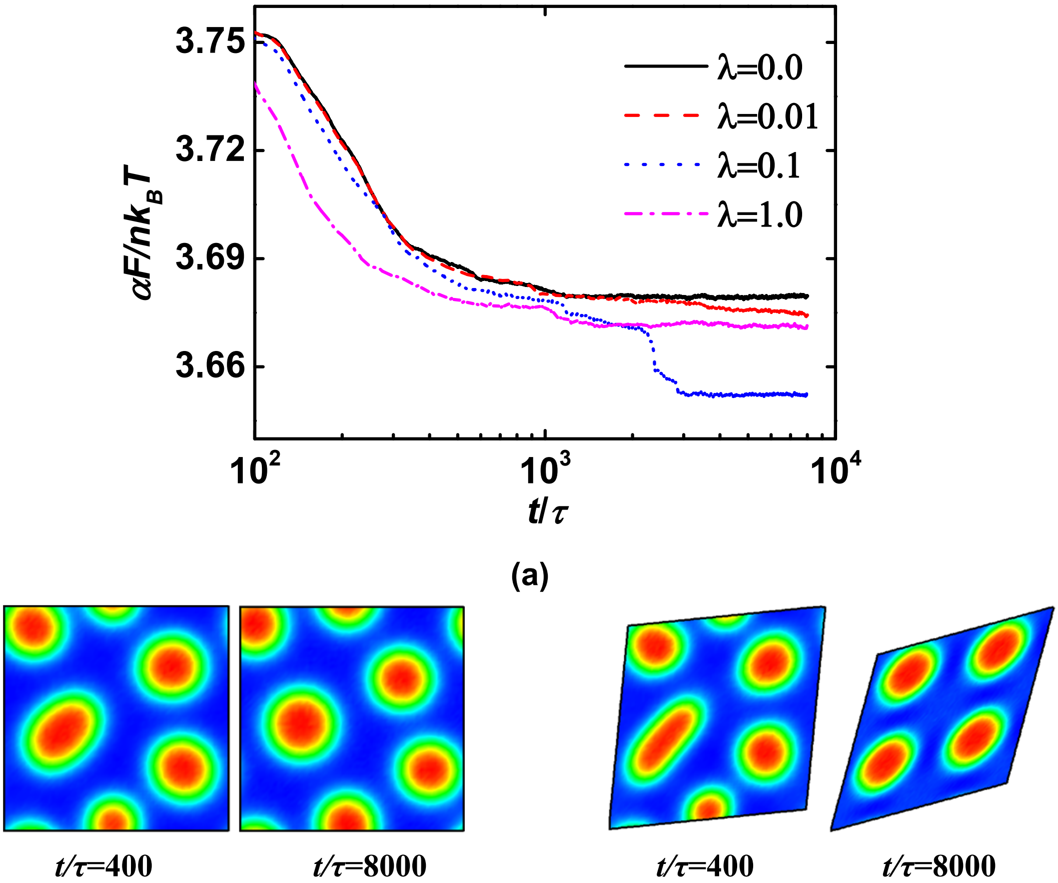
Part S3: Microphase Separation of ABC$_{3.5}$ star terpolymers

Part S4: Determination of Incubation Time and Phase Separation Rate

Part S1: Influences of Relaxation Parameter on Microphase Separation of Asymmetric Diblock Copolymers

Here, the diblock copolymer melts with A-block volume fraction f_A=0.31 are chosen. The system is quenched from an initially disordered state to an ordered state at $\chi_{AB}N$=18.0. For the sake of comparison, the initial shape of cells in the simulations of fix cell shape (FCS) method is also a square with side length 7.2R_{g0}. The temporal evolution of free energy density during the microphase separation with different relaxation parameters is shown in Figure S1(a). The behaviors of temporal evolution of the free energy density are very similar to those of symmetric block copolymers. The relaxation of cell shape promotes the ordering process of block copolymers, and the free energy densities of systems simulated by the variable cell shape (VCS) method are lower than that of system simulated by the FCS method. As the relaxation parameter is set as an intermediate value (λ=0.1), the system manages to escape from a metastable state at time ~2000τ and to reach an ordered configuration with lower free energy density.

Figures S1(b) and S1(c) show the morphological snapshots of asymmetric block copolymers via the FCS and VCS methods, respectively. Because the square shape of simulation cell is not compatible with the perfect arrangement of the cylinder microstructures, the cylinder domains are distorted in the FCS simulation and the system is trapped into a metastable configuration with higher free energy (Figure S1(b)). On the other hand, by using the VCS method, the simulation cell progressively evolves from a square to a rhombus with 60° angle, and a perfect arrangement of cylinder microdomains is achieved at the end of simulation (Figure S1(c)). These results suggest that the VCS method still helps the systems to escape the metastable states for the case of asymmetric block copolymers.



(a)

(b)

(c)

Figure S1 (a) Temporal evolution of free energy density during microphase separation of asymmetric block copolymers after a quench from homogenous states for various values of relaxation parameter λ. The reference simulation with λ=0 corresponds to the case of fixed cell shape method. (b) Pattern evolution in a simulation with the fixed cell shape method at times 400τ and 8000τ. (c) Pattern evolution in a simulation with the variable cell shape method at relaxation parameter λ=0.1. Red and green colors represent A-rich and B-rich regions, respectively.

Part S2: VCS Simulations for the case of Metastable Structures

Here, the initial configurations of VCS simulations are chosen from the metastable structures of FCS method shown in Figures 1(b) and S1(b) at time 8000τ. Figure S2 displays the final configurations of symmetric and asymmetric block copolymers simulated by the VCS method. For the case of symmetric block copolymers, the initially square cell deforms into a parallelogram shape to further relax the residual stress. As shown in Figure S2(a), the zigzag structure of symmetric block copolymer melts is evolved to a well-aligned straight lamellar structure. For the case of asymmetric block copolymers, the simulation cell progressively deforms from a square to a parallelogram. As a result, a cylinder domain is temporarily deformed and is coalesced by the nearby domains. In the final configuration of simulation with the VCS method, the side lengths of the cell are not equal and the cylinder domains are not well aligned in the cell (Figure S2(b)). By comparing the free energy densities of the configurations of Figure S2(b) and Figure S1(c) at time 8000τ, it is found that the difference of free energy between them is very small. This suggests the fact that the final configuration obtained by the VCS method is still a metastable state. However, the free energy of conformation in Figure S2(b) is lower than that of Figure S1(b) at time 8000τ, implying that the VCS method is a convenient way to further lower the free energy of system.

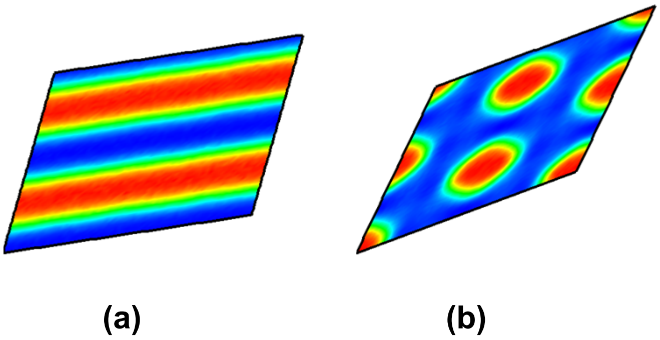
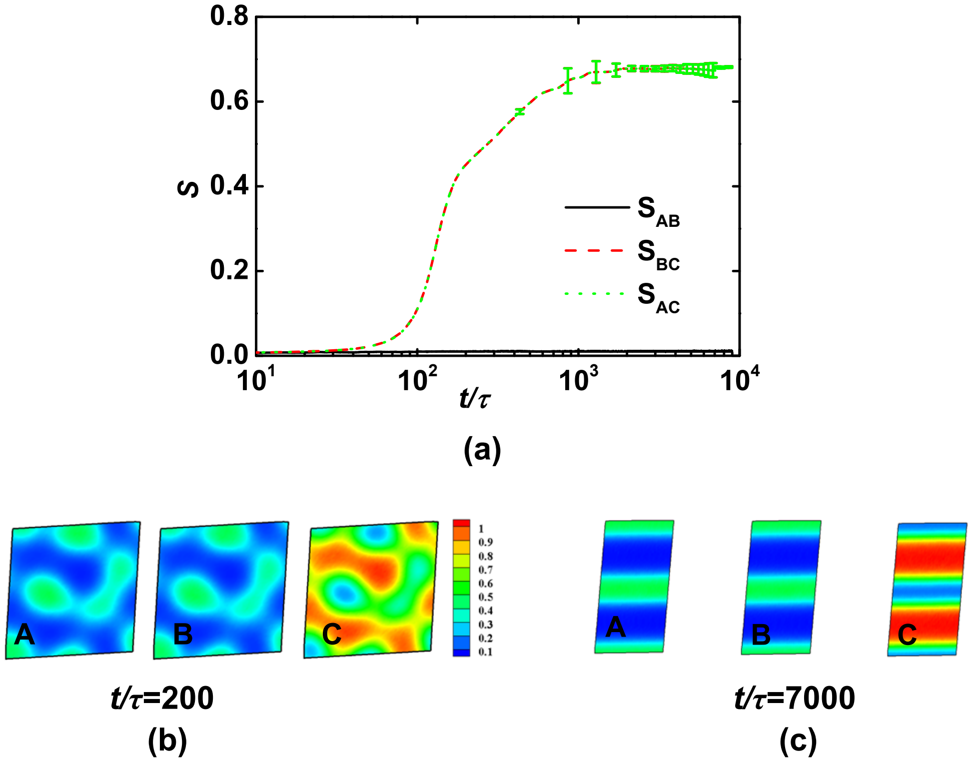


Figure S2 Final configurations of (a) symmetric and (b) asymmetric block copolymers simulated by the variable cell shape method. The initial configurations for the cases of symmetric and asymmetric block copolymers correspond to the Figures 1(b) and S1(b) at time 8000τ, respectively. The value of relaxation parameter λ is set as 0.1.

Part S3: Microphase Separation of $ABC_{3.5}$ star terpolymers

Figure S3 shows the temporal evolution of the order parameters and patterns during the microphase separation of $ABC_{3.5}$ star terpolymers quenched to the ordered state at $\chi_{AB}N_l=\chi_{BC}N_l=\chi_{AC}N_l=30.0$. Under the circumstances, the C arms are much longer than the A or B arms, and the combined interaction parameter $\chi_{AB}N_l=30.0$ is not enough to assure the segregation between the A and B species. This is confirmed by the order parameter S_{AB} curve of Figure S3(a), where the order parameter S_{AB} keeps zero in the whole process of phase separation of star terpolymers. However, the interaction parameters $\chi_{BC}N_l=\chi_{AC}N_l=30.0$ are enough to trigger the phase separation between the B and C species or A and C species. As shown in Figure S3(b), the system forms the AB-rich domains in the presence of the majority C component, within which one cannot observe the segregation between the minority A and B components. As time elapses, the order parameters S_{BC} and S_{AC} gradually increase, then eventually reach a saturated value. In the ordering process, the cell shape and size are changed and the microdomains rearrange themselves to generate a well-aligned lamellar structure (Figure S3(c)). It should be noted that the behaviors of the $\mathrm{ABC}_{3.5}$ star terpolymers are very similar with those of diblock copolymers.



(a)

t/τ=200
(b)

t/τ=7000
(c)

Figure S3 (a) Temporal evolution of order parameters S_{AB}, S_{BC} and S_{AC} during microphase separation of ABC_z star terpolymers with z=3.5. The melts are quenched from the disordered state at $\chi_{AB}N_l=\chi_{BC}N_l=\chi_{AC}N_l=0.0$ to the ordered state at $\chi_{AB}N_l=\chi_{BC}N_l=\chi_{AC}N_l=30.0$. Profiles of local density field distributions of A (left panel), B (middle panel) and C (right panel) species at times 200τ (b) and 7000τ (c).

Part S4: Determination of Incubation Time and Phase Separation Rate

The determination for the quantities “incubation time” and “phase separation rate” is described as follows: the curves of order parameters at the S1 and S2 stages of simulations are respectively fitted to a linear form, which are shown in Figure S4. The rate of phase separation corresponds to the slope of fitted curve at the S2 stage. The incubation time is obtained from the intersection of fitted curves at the S1 and S2 stages.

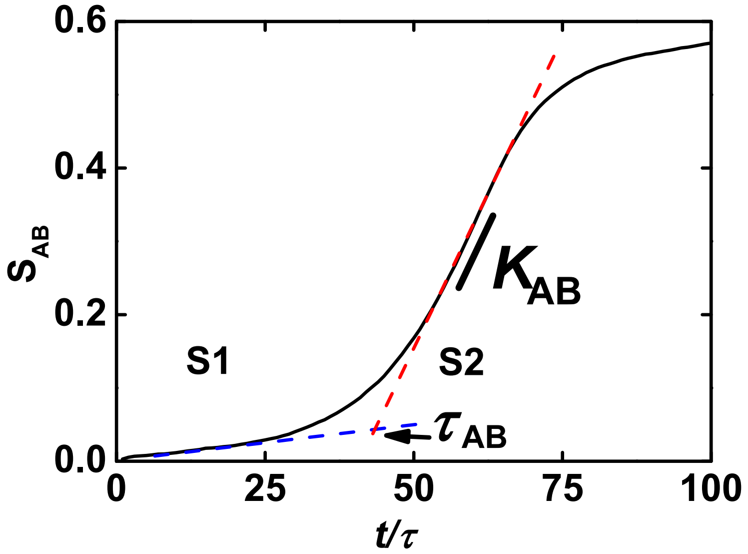


Figure S4 Illustration of determination of incubation τ_{AB} and rate K_{AB} for the order parameter S_{AB} curve.