Hierarchical Self-assembly Behaviors of ABC-Type Bottlebrush Copolymers

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Bottlebrush copolymers (BBCPs) can rapidly self-assemble into ordered nanostructures with large domain spacings, offering promising applications in nanotechnology. Recently, experiments have shown that the self-assembly of ABC-type BBCPs is an efficient method for creating hierarchical nanostructures, where the superstructure and substructure can be separately controlled by varying the number or lengths of the side chains. However, the self-assembly behaviors of ABC-type BBCPs are influenced not only by the volume fraction but also by the side chain asymmetry and the rigidity of the backbone, making them complex and therefore not well understood. In order to explore more hierarchical structures and fully understand the self-assembly behavior of ABC-type BBCPs, systematic studies are needed.

In this work, we have performed dissipative particle dynamics simulations to study the self-assembly of ABC-type BBCPs. One portion of the backbone is grafted with pairs of A-blocks, while the other portion is grafted with pairs of B/C-blocks. Our focus is on the effects of the grafting number of A side chains, the length of B side chains relative to C side chains, and the rigidity of the backbone on the formation of hierarchical structures. We observed a multitude of hierarchical structures where the superstructures are formed by the phase separation between A and B/C blocks, and the substructures are formed by the phase separation between B and C blocks. Although the formation of A-superstructures and B-substructures in many hierarchical structures can be independently controlled, there are also hierarchical structures where the transitions of the superstructure and substructures are coupled. Additionally, our results reveal that a rigid backbone favors the normal arrangement of B-substructures relative to A-superstructures. Our work not only deepens the understanding of the self-assembly mechanisms of ABC-type BBCPs but also introduces new design principles for the efficient creation of complex hierarchical structures.

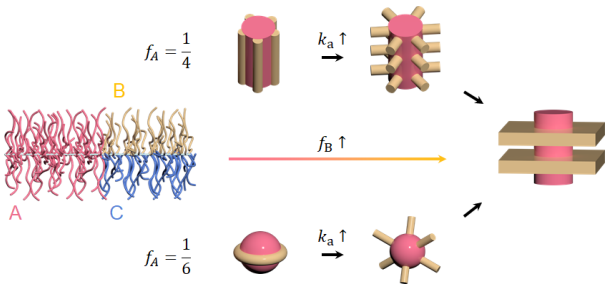

Figure 1 Schematic of the self-assembly behaviors of ABC-type bottlebrush copolymers.

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