Hierarchical gyroid structures in frustrated ABC triblock copolymers

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Frustrated linear ABC triblock copolymer with the repulsive interaction between A and C blocks significantly weaker than those between the other two pairs of adjacent blocks can self-assemble into various hierarchical structures composed of discrete B-subdomains sitting on A/C interfaces. However, whether the hierarchical structures still follow the common transition sequence of sphere → cylinder → gyroid → lamella remains an interesting question to be answered. In this work, the self-assembly of frustrated linear ABC triblock copolymer is investigated using self-consistent field theory (SCFT), focusing on the formation of different hierarchical gyroid structures.

Since these hierarchical gyroid nanostructures may be used to fabricate functional materials with high performance, it is critical to choose the A, B and C monomers for obtaining three proper Flory-Huggins parameters based on the phase diagram. Specifically, we consider that short middle B-blocks form discrete subdomains decorated on the surface of A-domain. We first construct the corresponding part of the triangular phase diagram with respect to three compositions (f_A, f_B and f_C) for fixed $\chi_{AB}N = \chi_{BC}N = 80 \gg \chi_{AC}N = 15$. Surprisingly, the hierarchical gyroid structure is not commonly formed between the hierarchical cylindrical and lamellar structures in the transition sequence with changing f_A. For these hierarchical structures, the formation of B-subdomains on the surfaces of A-domains presents a constraint on the chain configurations, leading to entropy loss. Accordingly, we speculate that the absence of the gyroid structure is mainly caused by its irregular surface of A-domain that does not allow the B-subdomain to form uniform arrangement and thus produces more severe constraint on the chain configurations than the cylindrical and lamellar structures with regular surfaces of A-domains.

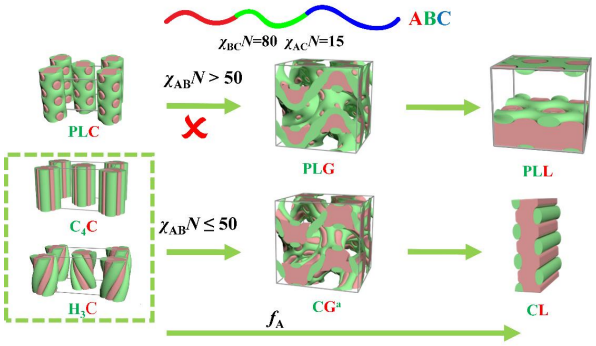

Fig. 1

The stability regions of various gyroid phases appear and expand as $\chi_{AB}N$ is gradually decreased, giving rise to the common transformation from cylinder to gyroid and then to lamella for A-domain. This is because as $\chi_{AB}N$ decreases, the A/B interface widens and B-subdomains move into main A-domain, relieving the constraint on the A/B junction point and thus on the configuration of A-block. This work demonstrates that the substructure of the hierarchical structures imposes a nontrivial effect on the relative stability of various hierarchical structures, which may disrupt the common transition sequence in frustrated linear ABC triblock copolymer.

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