Stabilizing network phases of block copolymers

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Block copolymers are macromolecules composed of chemically distinct sub-chains or blocks connected via covalent bonds (**Figure 1**) [1]. The most distinguishing property of block copolymers is that they are intrinsically frustrated due to the inter-block repulsion and chain connectivity [2]. Alleviating the frustration leads to the formation of polymeric assemblies in the form of lamellae, cylinders and spheres. The packing of these soft objects results in a rich array of periodically ordered phases (**Figure 2**).

Among the ordered phases, the bicontinuous network phases, consisting of two interweaving networks composed of the minority-blocks embedded in a matrix of the majority blocks, are of particular interest due their intricate structures and potential applications. For linear AB diblock copolymers, extensive experimental and theoretical studies have established that the equilibrium network phase is dominated by the double-gyroids (**Figure 2**). On the other hand, there exists several bicontinuous structures, including the double gyroid ($Ia\bar{3}d$), double diamond ($Pn3m$) and double-primitive ($Im\bar{3}m$) phases. It is therefore desirable to explore the possibility to stabilize different network phases formed from block copolymers.

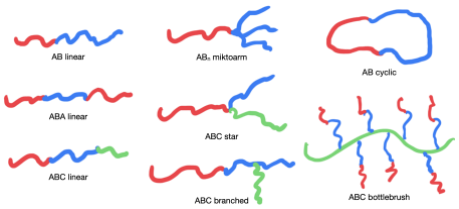

Figure 1 Schematics of block copolymers.

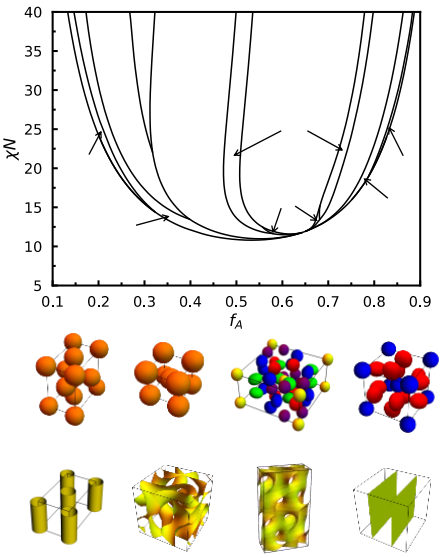

Figure 2 Phase diagram of conformationally asymmetric AB diblock copolymers obtained from SCFT.

In order to the search for block copolymer systems that could stabilize different biconinuous structures, we have studied the relative stability of several network phases in binary blends of linear AB diblock copolymers and nonlinear miktoarm star copolymers by using the self-consistent field theory (SCFT). For binary blends of AB diblock copolymers [3], our theoretical study predicts that the double-diamond and the double-primitive phases can be stabilized in binary blends composed of gyroid-forming and homopolymer-like diblock copolymers. Beyond linear architectures, our theoretical results indicate that a designed $A'(A''B)_5$ miktoarm star copolymer can stabilize double-diamond and double-primitive network phases besides double-gyroid [4]. Mechanisms for stabilizing the networks are shown to be related to the relieving of the packing frustration and the regulation of the AB interfacial curvature. These two mechanisms could act in tandem, resulting in larger stability regions for the novel network phases.

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[4] L. Hou, Z. Xu, Q. Dong, A.-C. Shi and W. Li, *Macromolecules*, **57**, 2165 (2024).