Stabilize different continuous network phases by rationally designing block copolymers

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The self-assembly of block copolymers provides an efficient method for the fabrication of ordered nanostructures. One of the most useful nanostructures is the bicontinuous network phase. For most of AB-type block copolymers, the stable network phase is the double-gyroid network structure, but not the other two network structures, i.e. double-diamond and double-primitive. It has been commonly accepted that the superior stability of the double-gyroid phase over the double-diamond or double-primitive phase is due to the packing frustration associated with the nonuniformities of interfacial curvature and domain size. Based on self-consistent field theory (SCFT), we demonstrate that a delicately designed miktoarm star A'(A''B)$_5$ copolymer can stabilize double-diamond and double-primitive network phases besides double-gyroid[1-2]. A number of sophisticated mechanisms for stabilizing the networks are revealed, including amplified effect of spontaneous curvature originating from the cone shape of A-blocks, effect of combinatorial entropy associated with the multiple A''B-arms and the effect of local segregation between the long A' and short A''-blocks. Under the synergistic effect of these three sophisticated mechanisms, the concentrations of the A' and A''-blocks in the nodes and struts are regulated by tuning the architectural parameters, thus controlling the sizes of the node and strut to match the geometry of various network structures. In brief, the A'(A''B)$_5$ copolymer with ingeniously tailored architectures can adopt two largely different forms of conformations to adapt to the local geometries of the node and strut of these three bicontinuous network phases, thus stabilizing them.

For the continuous network phase, another mysteriousness lies in why the double-gyroid phase but not the single-gyroid phase is often formed. Our SCFT calculations predict that the single-gyroid phase can be stabilized in a linear BABAB pentablock copolymer melt with proper block ratios and composition [3]. In this talk, we are also going to discuss about the stabilization mechanism of single-gyroid over double-gyroid [4].

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