

Understand the Relative Stability of Single-Gyroid to Double-Gyroid in AB-type Block Copolymer

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The self-assembly of block copolymers provides a versatile way for the fabrication of ordered nanostructures that have broad promising applications. One type of the most intriguing structures is the triply periodic network (TPN) structure. For many AB-type block copolymers, one TPN phase commonly appears between the cylindrical and lamellar phases in the phase sequence along increasing the composition from asymmetric to symmetric, i.e. double-gyroid (DG) [1]. The DG structure consists of two continuous tubular domains that are intercatenated throughout the slab-like matrix and are separated by the triply periodic minimal surface (TPMS). In addition to the double-network TPN structures, there are also single-network structures consisting of only one continuous network spanning throughout the matrix.

It has been commonly accepted that the bicontinuous double-gyroid (DG) network structure is the usual stable phase formed in pure AB-type block copolymer melts. Thus, the emergence of the single-network counterpart, i.e. single-gyroid (SG), is mysterious. In the previous work, it was proposed that the SG phase was stabilized by the synergistic effect of the local segregation between two unequal end B-blocks and the stretched bridging middle B₂-block of linear B₁AB₂AB₃ pentablock, however, which was not sufficiently verified [2]. Here we reexamine the stabilization mechanism of the single-gyroid phase, and we reveal that the bridging middle B-blocks do not play a key role in stabilizing the SG phase over DG due to its negligibly low bridging fraction. Instead, the middle B₂-blocks mainly concentrate nearby the interface in the form of loops, helping short end B₁-block to push long B₃-block to fill the further space and thus relieving the packing frustration of B-blocks in the matrix of SG on the one hand. On the other hand, the middle B-block is distributed more uniformly on the interface in the SG structure than in the DG structure due to the more uniform interfacial curvature of the former. The two factors lower the relative interaction energy of SG to DG, consequently stabilizing SG. Clearly elucidating the stabilization mechanism of SG may provide guide for further improving its stability or for obtaining other single-network phases (e.g. single-diamond).

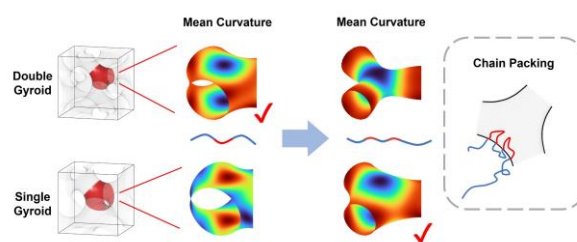


Figure 1 The stability of SG is related to the interfacial curvature and chain packing

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[1] Matsen, M. W.; Schick, M. Stable and Unstable Phases of a Diblock Copolymer Melt. *Physical Review Letters* **1994**, 72, 2660.

[2] Xie, Q.; Qiang, Y.; Li, W. Single Gyroid Self-Assembled by Linear BABAB Pentablock Copolymer. *ACS Macro Letters* **2022**, 11, 205–209.