Network Phases from Self-Assembly of High-χ Block Copolymers and Chiral Block Copolymers

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Network Phases from the self-assembly of block copolymers (BCPs) have attracted extensive attention and intensive study over the years because of their appealing applications due to the effect of deliberate structuring on material properties inspired from nature.

By taking advantage of the effect of solvent selection on BCP self-assembly with tuning solvent evaporation rate for casting, a series of cubic network phases can be obtained from the self-assembly of single-composition, lamellae-forming polystyrene-*block*-polydimethylsiloxane (PS-*b*-PDMS) due to its high-χ character. An unusual network phase in diblock copolymers, double primitive phase (DP) (hexapod network) with space group of $Im\bar{3}m$, can be observed for the first time. With the reduction of solvent evaporation rate, double diamond phase (DD) (tetrapod network) with space group of ($Pn\bar{3}m$) and double gyroid (trigonal planar network) with space group of ($Ia\bar{3}d$) can be obtained due to the reduction on the degree of packing frustration (entropic penalty) within the junction (node).[1]

With the introduction of topology effect on PS-*b*-PDMS self-assembly, the phase window for network phase formation can be enlarged in self-assembled PS-*b*-PDMS. Apart from gyroid and diamond, a peculiar network phase with space group of *Pm3n* (Frank-Kasper structure) can be found for the first time as evidenced by small-angle X-ray scattering. Electron tomography results reveal the network phase with alternating connection of three and four struts. The observed phase behaviors suggest that the network formation is built from the bisectors of dispersive spheres in the Frank-Kasper phase, instead of building connections among them, and thus decipher the origins of complex phase formation due to the adaptive character of malleable mesoatoms.[2]

Block copolymers composed of chiral entities, denoted as chiral block copolymers (BCP*s), were designed for mesochiral self-assembly. A helical phase was discovered for the first time in the self-assembly of BCPs. Homochiral evolution at different length scales in the self-assembly of the BCPs* was found. Generalization of the chirality effect on the self-assembly of BCPs was established.[3] By extending the homochiral evolution concept of mesochiral self-assembly, it is feasible to fabricate nanonetwork phase with controlled helicity from self-assembly for the first time.[4]

[1] C.-Y. Chang, G.-M. Manesi, C.-Y. Yang, Y.-C. Hung, K.-C. Yang, P.-T. Chiu, A. Avgeropoulos*, R. M. Ho* *PNAS* **118**, 11 (2021).
[2] C.-Y. Chang, G.-M. Manesi, W.-E. Wang, Y.-C. Hung, A. Avgeropoulos, R.-M. Ho* *Science Advances*, in press (2024).
[3] H.-F. Wang, K.-C. Yang, W.-C. Hsu, J.-Y. Lee, J.-T. Hsu, G. M. Grason, Edwin L Thomas, J.-C. Tsai*, R. M. Ho* *PNAS* **116**, 4080 (2019).
[4] H.-F. Wang, P.-T. Chiu, C.-Y. Yang, Z.-H. Xie, Y.-C. Hung, J.-Y. Lee, J.-C. Tsai, I. Prasad, H. Jinnai, E. L Thomas, R. M. Ho* *Science Advances* **6**, eabc3644 (2020).