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Frank-Kasper sigma phase stabilized by tailored architectures of block copolymers. WEIHUA LI, MEIJIAO LIU, NAN XIE, FENG QIU, State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, AN-CHANG SHI, Department of Physics, McMaster University — Block copolymer self-assembly forms diverse interesting ordered morphologies, of which the spherical phase is of particular interest because it resembles the similar space symmetry as atomic crystals and has a tunable period on nanoscale. Moreover, the packing lattice of spherical domains dictated by the adjustable competition between the entropic and interfacial energies is programmable. For AB diblock copolymers, it has been known that the stable spherical phase is mainly bcc except for a very narrow region of fcc at the vicinity of the order-disorder transition. When introducing variable number of blocks and architectures to form complex AB-type block copolymers, the A15 phase was predicted as stable. However, a striking experiment observed a new spherical phase, the complex Frank-Kasper sigma phase that consists of 30 spheres in a unit cell, in the PI-b-PLA diblock copolymer as well as a SISO tetrablock terpolymer. Inspired by this experiment, we studied the stability of all known spherical phases of fcc, bcc, A15 and sigma in various block copolymers including conformationally asymmetric AB diblock, ABm miktoarm, and BABC tetrablock copolymers. We have revealed the formation mechanism of the nonclassical A15 and sigma phases due to the tailored architectures.

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State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan U

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