

Approximants of dodecagonal quasicrystals in aqueous diblock polymer dispersions

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Aqueous lyotropic liquid crystals (LLCs) are structured soft materials with long range crystallographic order, which derive from minimal hydration of amphiphilic molecules in water. In certain composition windows, amphiphiles self-assemble into quasispherical micelles that pack on body-centered cubic (BCC), face-centered cubic (FCC) and hexagonally close packed (HCP) lattices [1]. Herein, we describe investigations of the aqueous LLC phase behavior of polyethylene-poly(ethylene oxide) (PE-PEO) diblock polymers using temperature-dependent small-angle X-ray scattering (SAXS). With increasing polymer concentration, we show that these aqueous LLCs self-assemble into FCC, BCC, and Frank-Kasper (FK) A15 phases (Cr₃Si structure type). Upon heating the A15 phase, we find that it undergoes a transition to a BCC phase that gives way to a hexagonally-packed cylindrical micelle phase (H) at high temperatures. Quenching the H phase to room temperature drives formation of a FK σ phase, which transforms into the original A15 structure after several months. These findings suggest that various, complex intermediate phases may form in LLCs depending on their thermal histories. We discuss the formation of these phases in the context of a delicate balance between minimization of free energy at the local micelle length scale against the global LLC unit cell scale. The specific observations of FK A15 and σ phases, both periodic approximants of dodecagonal quasicrystals, suggest the possibility that suitable processing of these aqueous LLCs may lead to soft liquid quasicrystals. In view of recent discoveries of dodecagonal quasicrystals and their approximants in other soft systems[2-5], our discovery provides a new context for understanding the factors driving periodic and quasiperiodic order in soft materials.

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