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Multiple Phases of Binary Micellar Crystals Derived from Aqueous Solutions of Charged Block Copolymers KOOKHEON CHAR, SEYOUNG KIM, Seoul National University, SOO-HYUNG CHOI, Hongik University, SHENG LI, DuPont Central Research and Development — Amphiphilic block copolymers containing weak polyelectrolyte blocks can induce surface-charged block copolymer micelles (BCMs) in aqueous media and, at the same time, their charge densities can be finely tuned by pH of the media. Polystyrene-*block*-poly(acrylic acid) and polystyrene-*block*-poly(vinyl pyridine) BCMs, whose signs of surface charges are opposite in a relevant pH window, can self-assemble together via electrostatic interactions. By mixing of these charge-tuned BCMs, we obtained binary micellar complexes showing strong crystalline habits and assigned their crystal structures with small-angle neutron scattering and other techniques. We demonstrate multiple phases of binary micellar crystals derived from a set of BCM mixtures of which size and charge ratios are varied. The dependence of the size ratio of individual phases is proven to be different from that of rigid nanoparticles such as inorganic nanocrystals. We believe that this deviation from the hard-matter superlattices is due to the deformability of BCMs based on soft building units. That is to say that BCMs can be readily deformed by the swelling in good solvent and can modify their structure from spheres to other anisotropic shapes while they assemble together.

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