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Complex Morphology of Oppositely Charged Block Copolymer Micelles MISOOK LEE, KYUNG JEE MIN, SHENG LI, KOOKHEON CHAR, Seoul National University — The morphology of charged block copolymer micelle (BCM) complexes, consisting of polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) and polystyrene-*block*-poly(4-vinyl pyridine) (PS-*b*-P4VP) micelles, was controlled by pH of aqueous solvent as well as solvent quality. To determine the effective pH range for the inter-corona combination of PAA and P4VP blocks in aqueous media, we studied the dissociation behavior of both coronas using Fourier Transform Infrared Spectroscopy. Lower pH region (4.0 <pH <5.0) in aqueous medium offers stronger interactions between oppositely charged corona blocks, resulting in the formation of crystal-like complexes. Furthermore, the crystal habit of the micelle complex was found to be tunable by adjusting the relative size of the block copolymers and/or the pH of the aqueous medium. In the higher pH region (pH >5.5), they first self-assembled into hierarchical bumpy spheres induced by the simple adsorption of small PS-*b*-PAA BCMs on the surfaces of PS-*b*-P4VP large compound micelles since the degree of ionization of P4VP blocks is relatively low. The final micelle morphology is highly dependent on the solvent quality. At low dimethylformamide (DMF) content, the internal structure of the BCM complex resembled spherical micelle. As the concentration of DMF increased, the internal PS-*b*-P4VP block copolymer structure transitioned from micelle-like to that resembled the morphology of the block copolymer in the bulk.

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