187c Visualizing Worm Micelle Dynamics and Phase Transitions of a Charged Diblock Copolymer in Water

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Assemblies of block copolymer amphiphiles are sometimes viewed as glassy, frozen, or static colloids, especially in strongly segregating solutions. Here we visualize by fluorescence microscopy and AFM the dynamics and transitions of single cylindrical micelles and vesicles composed of a charged diblock copolymer in water. In mapping the salt- and pH-dependent phase diagrams of a near-symmetric diblock of polyacrylic acid–polybutadiene, low pH and high salt (NaCl, CaCl2) are seen to neutralize and screen the charged corona sufficiently to foster membrane formation and generate vesicles. Decreased salt and ~neutral pH increases intra-coronal repulsion and drives a transition to multi-branched cylinders and highly stable but fluid and flexible worm-like micelles. Ca2+ both stiffens and stabilizes cylinders. Further increase of intra-coronal repulsion generates spherical micelles by fragmentation and pinch-off at the ends of worms. Both transition kinetics and phase diagrams indicate divalent cation is about 10-fold more effective than monovalent in stabilizing all morphologies.