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Temperature-Induced, Reversible Swelling Transitions in Multilayers of a Cationic Triblock Copolymer and a Polyacid SVETLANA SUKHISHVILI, Department of Chemistry, Chemical Biology and Biomedical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030, WUI SIEW TAN, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, ROBERT COHEN, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, MICHAEL RUBNER, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 —
We demonstrate large-scale, fully-reversible, thermally-induced volumetric changes in layer-by-layer (LbL) electrostatically self-assembled thin films through the incorporation of A-B-A triblock copolymers, where A is a weak polyelectrolyte block, and B is a temperature-responsive block. Multilayers of a micelle-forming A-B-A triblock copolymer were constructed using LbL deposition with a polyanion. The polyanion type and self-assembly pH were critical parameters for constructing functional films of block copolymer micelles (BCMs). When a polycarboxylic acid was used in self-assembly, films assembled at pH $\geq$ 6 showed fully reversible, 3 to 5-fold changes in film thickness in response to temperature cycling between 6 and 20 °C, enabled by swelling/collapse of the BCM central block.

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