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Reversible Nanostructures Assembled from Amphiphilic Block Copolymers CHEN XU, XUEFENG FU, MICHAEL FRYD, BRADFORD WAYLAND, KAREN WINEY, RUSSELL COMPOSTO, University of Pennsylvania — We present a novel route to assemble perpendicular cylinders by converting an asymmetric diblock copolymer from poly(styrene-b-tert butyl acrylate) (PS-b-PtBA) to poly(styrene-b-acrylic acid) (PS-b-PAA) using an auto-catalytic reaction. Upon exposing films of PS-b-PAA to water, PAA cylinders constrained by the continuous, glassy PS phase protrude 10 nm above the surface and swell laterally to form mushroom caps, rendering the entire surface hydrophilic. The swelling dynamics of the PAA mushrooms is captured by a two-stage mechanism, where domain growth is controlled by super case II diffusion of water into PAA followed by the slow relaxation of the PAA chains. Upon partial drying in air, the mushroom collapses as stretched hydrophilic chains relax, which results in nanometer depression in the center of each cap. The nanostructures revert to their initial dimensions and area fractions upon complete drying, demonstrating reversibility of swelling. This finding provides a new route to fabricate stimuli-responsive materials for sensors, microactuators, and microfluidic devices.

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