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Block copolymer films: Hierarchical meshes and bottlebrush morphologies

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Thin films of microphase separated block copolymers have applications in diverse fields including nanolithography, porous membranes, and nanostructured surfaces. Block copolymers with a polydimethylsiloxane (PDMS) block, such as polystyrene-b-PDMS (PS-b-PDMS), are particularly attractive for producing nanoscale patterns due to their high interaction parameter and to the etch selectivity and etch resistance of the PDMS block with respect to the organic block. In this presentation we will first illustrate how sequential multilevel assembly of PS-b-PDMS with different molecular weights can produce nanomesh structures consisting of overlaid orthogonal cylindrical microdomains, without requiring layer-by-layer alignment or high-resolution lithographic templating. The mechanism for orthogonal self-assembly is investigated using both experiment and self-consistent field theory, showing that the height and chemical preference of the underlying surface are critical process parameters. Furthermore, these hierarchical topographical surfaces show extreme hydrophobicity, providing a simple method for surface property modification. We then discuss how the well-known relationship between microdomain period and degree of polymerization, which limits the scaling of block copolymers, can be overcome through the use of novel molecular architectures. Thin films of pseudo-alternating bottlebrush block copolymers show a microdomain period governed by the brush length instead of the backbone length, leading for example to ¡10-nm microdomains from polymers of 600 kg/mol. These patterns can be guided using topographical templates. Finally, we demonstrate the thin-film morphologies of PS-b-PDMS with majority PDMS, including the use of UV irradiation to stabilise the microdomains after solvent vapor annealing. These results illustrate the diversity of possible morphologies, periods and microdomain orientations obtained from PS-b-PDMS block copolymers.