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Aqueous Self-Assembly of Non-Ionic Bottlebrush Block Copolymer Surfactants with Tunable Molecular Shapes[1]

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Polymer amphiphiles provide a robust and versatile platform for the fabrication of nanostructured soft matter. In this research, we explore a new class of polymer surfactants based on comb-like bottlebrush architecture as highly tunable molecular building blocks for aqueous self-assembly. Excluded volume interactions between densely grafted polymer side chains in the bottlebrush architecture are alleviated by backbone stretching, which leads to the formation of shape-persistent cylindrical macromolecules whose molecular dimensions can be precisely tailored during chemical synthesis. Amphiphilic bottlebrush block copolymers containing hydrophobic polylactide (PLA) and hydrophilic poly(oligoethylene oxide methacrylate) (PEO) side chains of various lengths were synthesized by a combination of controlled radical and ring-opening polymerizations. In dilute aqueous solutions, bottlebrush surfactants rapidly assembled into spherical, cylindrical and bilayer aggregates, as visualized by cryogenic transmission electron microscopy (cryo-TEM). Depending on the compositional side chain asymmetry, the formation of spherical micelles with different sizes and dispersities was observed. The molecular shape-dependent assembly was analyzed with help of a packing parameter (p) computed from the molecular composition data akin to small molecule surfactants, with most uniform spherical aggregates observed for bottlebrush amphiphiles with p close to 0.3. The formation of highly uniform micelles and the presence of a rich morphological diagram with relatively narrow compositional windows were attributed to the lack of conformational freedom in bottlebrush surfactants. Similarly, the unusual formation of cylindrical micelles with long aspect ratios for such high molecular weight amphiphiles was attributed to their inability to stabilize morphological defects, such as Y-junctions, with large deviations from mean curvature.

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