Tuning Semicrystalline Polymer Brush Morphology and Surface Properties via Solvent-Mediated Crystallization

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Functional polymer brush coatings have significant potential for a wide range of industrial applications due to their responsiveness to environmental stimuli, enabling precise tuning of surface properties. Here, we demonstrate that in semicrystalline poly(octadecyl methacrylate) (P18MA) brushes, surface roughness and interfacial properties can be controlled by tuning crystallization conditions. Using solvent-mediated crystallization, the brush morphology can be reversibly tuned from smooth (Rq ≈ 3nm), spherulitic structures to highly porous architectures with feature sizes of several hundred nanometers (**Fig. 1**). This morphological control enables tunable wetting behavior, with direct implications for adhesion and fluid transport. [1] Control over morphology can be achieved both macroscopically, via solvent infusion followed by cooling and solvent evaporation, and locally, using a focused laser beam to generate patterned regions with distinct roughness. Previous work on the same system showed that melting induces a coupled swelling and wetting transition upon exposure to liquid alkanes, with the top surface exhibiting a higher melting temperature than the bulk. This allows independent control of bulk-driven swelling and surface-driven wetting transitions. [2] In contrast, the morphological changes reported here originate from bulk side-chain crystallization in the presence of solvent. By varying solvent quality, concentration, and crystallization rate, a wide range of morphologies can be accessed, from dense to highly porous structures. This behavior can be understood in analogy with thermally induced phase separation (TIPS), where the interplay between phase separation and crystallization governs structure formation, e.g. for polymeric membranes. [3] Such control over surface topography enables precise tuning of wetting properties, opening new opportunities for the design of functional and adaptive interfaces.

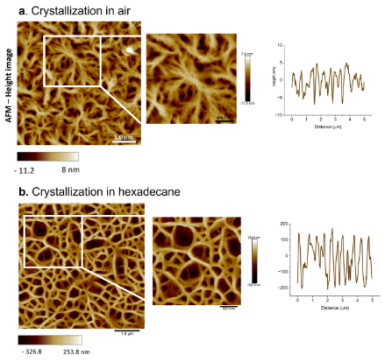

Fig. 1. AFM tapping-mode height images of semicrystalline P18MA brushes, together with corresponding cross-sectional height profiles (right) showing surface height variation along the x-direction.

References:

[1] Buonaiuto L., et al. "Polymer Brush-Enhanced Extraction and Spreading of Oil from Lubricating Greases." *Tribology Letters* 74.2 (2026): 44.
[2] Buonaiuto L., et al. "Thermally Activated Swelling and Wetting Transition of Frozen Polymer Brushes: a New Concept for Surface Functionalization." *Advanced Materials* 37.26 (2025): 2502173.
[3] Pochivalov K. V., et al. "Thermally induced phase separation in semicrystalline polymer solutions: How does the porous structure actually arise?." *Materials Today Communications* 28 (2021): 102558.