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Polymer Brushes from and to Polymer Crystals: Harnessing the Conformational Similarity

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Abstract

The brush state of polymers occurs when polymers are tethered to an interface that, at sufficient density, encourages chains to orient themselves away from the surface due to interchain repulsion, leading to trans-rich conformations of the side chains. This trans-rich conformational state is also found in ordered polymer and liquid crystals. This dissertation concerns how to harness the conformational similarity of the polymer brushes and crystals to (1) design and synthesize advanced surface polymer brushes with tuned grafting density and morphology and (2) understand the effect of the trans-rich conformation and steric hindrance of molecular brushes on their crystallization behaviors. The first part of this dissertation seeks to expand on the process of fabricating polymer brushes from crystalline states and develop a facile process to synthesize surface polymer brushes via thin film crystallization. Our work demonstrates how, through nonsolvent annealing, the grafting density and, thus, final properties of the brush can be controlled through this facile method. The second part of this dissertation investigates the crystallization behavior of brush polymers using molecular bottlebrushes bearing crystalline side chains as a model system. The effect of grafting density on crystallization kinetics was systematically investigated using thermal analysis and microscopy characterization methods, revealing the influence of brush architecture on the crystallization behavior of such polymers. The third part of this work investigates the crystallization of brush polymers in thin films. The growth of long-range curved fiber-like crystals is reported for the first time for molecular brush systems. The formation of this crystalline state from brush precursors was investigated through select area electron diffraction and *in situ* atomic force microscopy. This dissertation reveals that the unique conformational similarity between the polymer brushes and crystals is essential to the crystal formation of the molecular bottlebrushes. Conformational similarity can also be harnessed for surface brush synthesis, providing a unique approach for materials design.