Beitrag ID: **17** Typ: **Talk**

Thermally activated swelling and wetting transition of frozen polymer brushes: a new concept for surface functionalization

Mittwoch, 19. Februar 2025 11:20 (20 Minuten)

Functional polymer brush coatings have significant potential for a wide range of industrial applications due to their responsiveness to environmental stimuli, which allows for precise tuning of surface properties. Polymer brushes can swell or collapse in response to external stimuli such as temperature changes or variations in the chemical composition of the surrounding medium, leading to changes in interfacial properties and enabling specific functionalities. In addition to these external stimuli, intrinsic polymer transitions—such as melting and glass transitions—offer another effective way to modulate the behavior of polymer brushes. These transitions provide an additional mechanism to control and actuate brush properties, expanding the potential applications of these adaptive coatings.

To investigate this concept, we examine the wetting behavior of liquid n-alkanes on oleophilic bottle brushes composed of poly-n-alkyl methacrylate (PnMA). The melting temperature of these polymer brushes can be precisely tuned by adjusting the length of their side chains. By combining macroscopic wetting experiments, Atomic Force Microscopy (AFM) adhesion measurements, and vibrational Sum-Frequency Generation (SFG) spectroscopy, we demonstrate that the melting transition of a semicrystalline oleophilic poly-octadecylmethacrylate (P18MA) brush drives a coupled swelling and wetting transition when exposed to various liquid alkanes. Notably, the top surface of the P18MA polymer exhibits a slightly higher melting temperature compared to the bulk, allowing for independent control of bulk-driven swelling and surface-driven wetting transitions. These transitions can be activated either through global heating or localized excitation using a focused laser beam. These findings introduce a novel concept for polymer brush-based functional surfaces, enabling controlled fluid transport through independently switchable surface barriers and bulk transport layers.

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Sitzung Einordnung: Short Talks