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Adaptive Wetting: Surface ordering-induced wetting transition on thermos-responsive oleophilic polymer brushes

Stimulus-responsive polymer brushes exhibit a remarkable ability to adapt and transform their properties in response to specific external triggers. Here, we investigate the wetting behaviour of oil on hydrophobic temperature-responsive poly(n-octadecyl methacrylate) (PODMA) brushes below and above the bulk melting temperature. Upon depositing a hexadecane droplet on top of PODMA brushes at ambient temperature, a distinctive high contact angle (31^0) prevents the droplet from spreading on the surface. However, above the melting temperature, a first temperature range characterized by brush swelling without spreading is observed, followed by a second temperature range characterized by a transition from partial to complete wetting. AFM adhesion measurements initially conducted on dry (and later also on oil-wetted) brush layers also exhibit a two-stage transition. At low temperature, the layer behaves like a hard solid surface with minimal deformation as the tip is pulled off the surface. At high temperature, polymer chains are liquified and hence very mobile. Individual chains can stick to the AFM tip and stretch before detaching. At intermediate temperature, the behaviour is more variable and depends also on the details of the measurement procedure in a manner that suggests that the surface layer is still solid while the underlying bulk of the brush layer is already liquid. Comparison to the literature on bulk polymers led to the conclusion that the surface layer, which remains solid at intermediate temperature, consists of a densely packed layer of aligned alkyl side chains. It is indeed known that linear hydrocarbon chains ($16 < n < 50$) exhibit surface freezing: an ordered crystalline layer is formed atop a liquid bulk [1]. Non-linear optical sum frequency generation (SFG) measurements confirmed the scenario of a highly ordered and CH3-terminated layer at low and intermediate temperatures and their melting at the upper transition temperature observed in the adhesion measurements. AFM, and the SFG measurements thus provide a consistent scenario of the wetting and swelling behaviour of PODMA, in which the swelling is controlled by the melting of the bulk of the brush layer, whereas the wetting of HD is controlled by the melting of the ordered surface layer of alkyl chains that remain frozen up to a few degrees above the bulk melting temperature. This offers the ability to induce a wetting and swelling transition that can be tuned by varying the length of the side chains. Furthermore, from our observations, PODMA brush layers emerge as a promising platform for finely controlling the entrapment and release of picolitres of fluid locally.

[1] B. M. Ocko, X. Z. Wu, E. B. Sirota, S. K. Sinha, O. Gang, M. Deutsch ”Surface freezing in chain molecules: Normal alkanes.”APS 1997, 55 3164-3182.

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