From wetting ridge formation to swelling-dependent solvent diffusivity in oil-infused polymer brushes

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Capillary forces induce the spontaneous formation of wetting ridges of oil along the contact line upon depositing aqueous drops onto oil-swollen polymer gels and brushes. Using a combination of confocal fluorescence microscopy and high resolution white light interferometry, we analyze the growth kinetics of such wedges of hexadecane and the concurring depletion of the solvent in partially swollen brushes of polylaurylmethacrylate (PLMA). From the dependence of the wedge growth on the degree of pre-swelling with hexadecane, we infer that the polymer-solvent interaction parameter 'chi' increases from 0.1 (good solvent) to 0.6 (marginal/bad solvent) with decreasing oil saturation. Analyzing the spatio-temporal evolution of the brush thickness next to the drop in terms of Alexander-de Gennes' model (incl. a saturation-dependent 'chi' function) further reveals that the diffusion coefficient of the solvent in the brush decreases by almost two orders of magnitude from fully to weakly swollen polymer brushes. This finding is confirmed by independent Fluorescence Recovery After Photobleaching (FRAP) measurements. These findings reveal that both equilibrium and transport properties of solvents in brushes depend more strongly on the degree of swelling than frequently assumed.

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polymer brushes, wetting, adaptive surface

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