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Monitoring of Water Penetration in Polymer Brushes by Time-Resolved Fluorescence of Solvatochromic Dye

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The (de)wetting of e.g. polymer-coated surfaces with various liquids is of fundamental importance in equilibrium and molecular dynamics in confined mesoscale media and is also vital in many materials and applications. In particular, the response of switchable polymer layers to an externally applied thermal, optical, electrical or chemical stimulus causes alternation of local properties, in particular local polarity and molecular mobility. To model such switching, two factors are of crucial importance: (1) the relaxation rate and (2) the width of the contact region, which influences the apparent contact angle for water drop on the surface. Because of the experimental limitations, however, fast subsecond relaxation processes, which may be involved in the dynamic wetting, have been hitherto not addressed for fluorescence imaging.

In the second phase of this SPP we plan to visualize this by analyzing the time-resolved fluorescence of novel polarity sensitive solvatochromic dyes. In this contribution we introduce the overall project idea and discuss our preliminary work with the well-known dye Nile red (NR). The absorption and fluorescence spectra of NR are significantly shifted to the red when solvent polarity increases. In addition, the fluorescence lifetime increases in polar solvents and decreases in protic solvents. These two measurable quantities allow one to image the spatial xyz-distribution of media polarity as well as protic solvent (water) content in different transient states of polymer layers during (de)wetting with water.

In order to overcome the μm-limited optical z-resolution in the nanoscale layers, specially designed depth-gradient dye-labelled polymer brushes will be prepared. There the growing grafted from the surface polymer chain will be labelled with the reporter dye at different nanoscale depth (z). The depth will be gradually changed with respect to the macroscale lateral axis (x). In this experiment the fluorescence color image and/or fluorescence lifetime images (FLIM) of the polymer layer map the liquid diffusion in the layer as well as polymer reorganization during (de)wetting process in the front and in the tail of droplets moving along the x-direction.

Our preliminary data, which shows that this idea is feasible, are based on thermally-switchable poly(di(ethylene glycol) methyl ether methacrylate) (PDEGMA) polymer brush layers that were grown from glass surfaces. From the fluorescence spectra of NR loaded via simple partitioning without control of z in the PDEGMA brushes, the polarity of the polymer is estimated to be between that of ethyl acetate and acetone. PDEGMA also shows a LCST behavior. It is hydrated below 32℃ and collapses above this temperature. The fluorescence of NR in PDEGMA brushes decays double exponentially with major long-lived (4.6 ns) and minor short-lived (2.1 ns) components. When the temperature varies from 20 to 50 ℃, strong deswelling of PDEGMA (swelling ratio from 3 at 25 to 1.5 at 50 ℃) is accompanied with a substantial reduction (from 0.22 to 0.12) of the contribution of NR short-lived decay component. The random distribution of NR in the brushes does not allow one to map these observables in a depth resolved manner. This is overcome in the SPP project by gradient brushes.

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