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Water Sensing in Polymers by Time-Resolved Fluorescence of Solvatochromic Dye

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We are interested in the analysis of the (de)hydration dynamics of polymer-coated surfaces monitored with time-resolved fluorescence microscopy. In particular, the reversible changes of the wetting state in thermally-switchable polymer layers is imaged in a confocal microscope via changes of the fluorescence intensity, spectrum and/or decay time of the reporter dye due to changes of local polarity. This may enable the direct detection of water molecules in the vicinity of the polymer chains. In this stage the fluorescence spectra and lifetimes of a solvatochromic dye (Nile red (NR) derivative) were measured in solvents of different polarity and in binary organic solvent/water mixtures mimicking wetted polymer layers on the surface. The absorption and fluorescence spectra of NR are significantly shifted to the red, when the solvent polarity increases. In protic solvents there is an additional substantial longwavelength shift compared to dipolar solvents of the same polarity due to specific interactions of NR with the solvent. The fluorescence lifetime of NR increases in polar solvents and decreases in protic solvents. To estimate the effect of solvent composition on the photophysical properties of the solvatochromic dye, absorption and fluorescence spectra, as well as fluorescence kinetics of NR were investigated in two binary solvent mixtures. One was a mixture of two dipolar aprotic solvents of the same polarity and another one was a mixture of aprotic and protic solvents also the same polarity. The direct detection of water was carried out by using hydroxy- and methoxy-substituted ß-carbolines. In the ground state these derivatives form complexes with water. While with OMe-derivatives only a minor change of fluorescence has been found, the OH-derivatives, being a photoacid, reacts with water leading to a drastic reduction of its fluorescence intensity and lifetime in the presence of water. The mechanism of this fluorescence quenching, static and/or dynamic, is discussed. In addition, to analyze the detection of the wetting state of the thermally-switchable poly(di(ethylene glycol) methyl ether methacrylate) (PDEGMA) layer on glass surfaces, the fluorescence spectra and decay of NR were measured in PDEGMA at different temperatures. With the fluorescence spectra of NR it was shown that PDEGMA layer has a moderate polarity between that of ethyl acetate and acetone. The fluorescence of NR in PDEGMA decays double exponentially with a major long-lived (4.6 ns) and a minor short-lived (2.1 ns) component. The PDEGMA brushes are wetted below 32℃ and are dewetted above this temperature. 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 the short-lived decay component of NR.

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