

Supplementary Material (ESI) for *Soft Matter*  
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## Electronic Supporting Information (ESI)

### Temperature responsive polymer brushes with *clicked* rhodamine B: synthesis, characterization and swelling dynamics studied by spectroscopic ellipsometry

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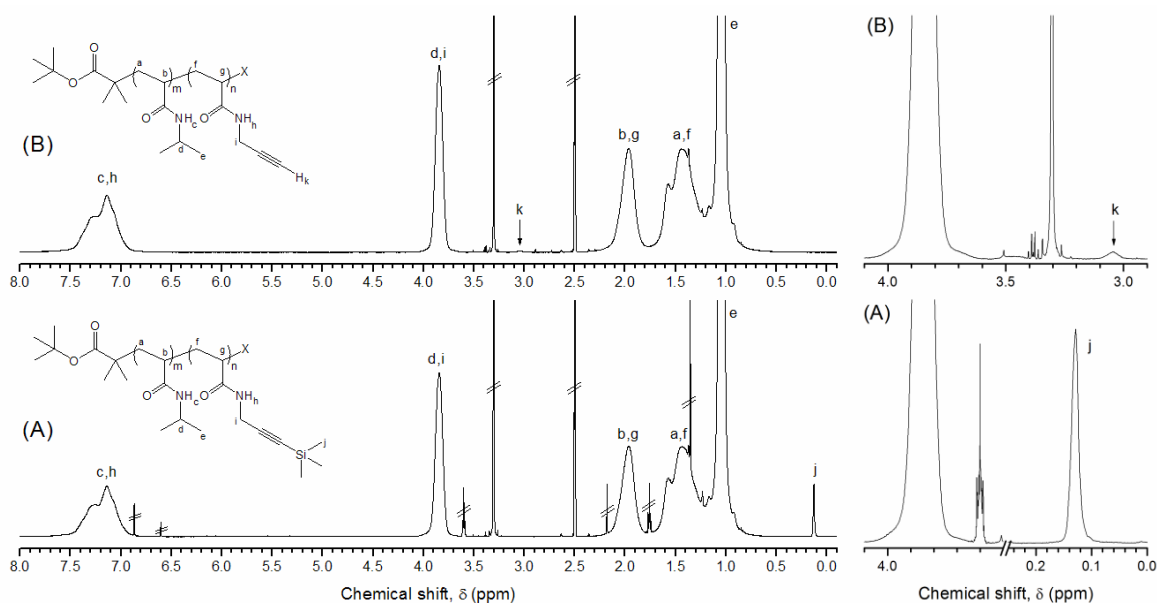
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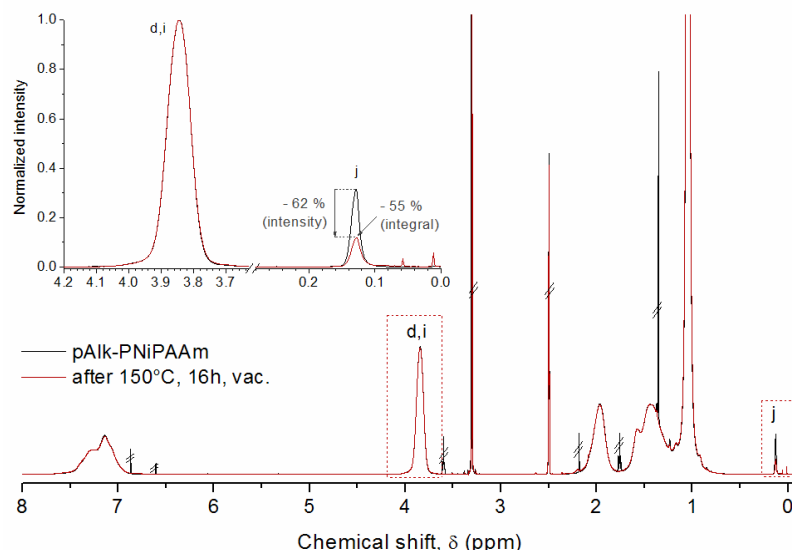
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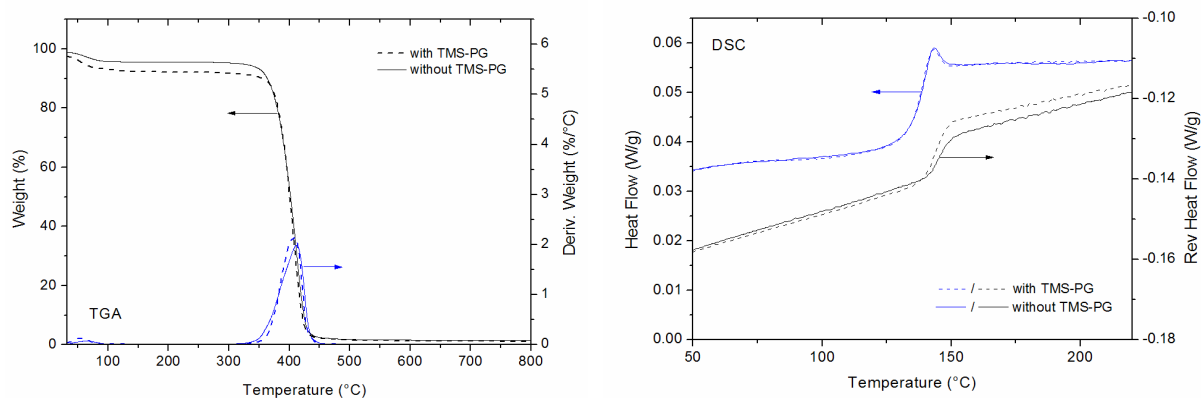
- Figure S1: <sup>1</sup>H-NMR spectra of pAlk-PNiPAAm and Alk-PNiPAAm
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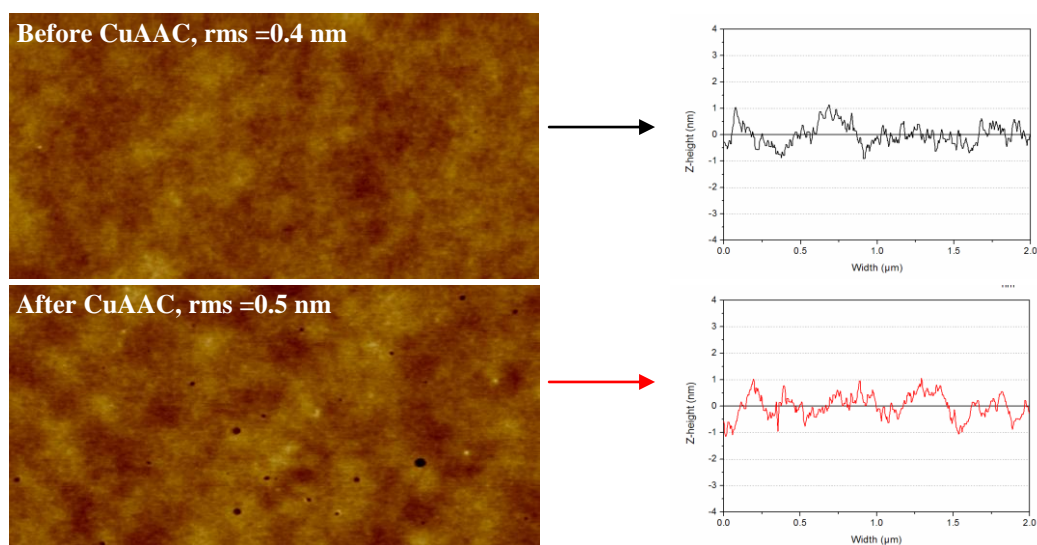
**Figure S1.** <sup>1</sup>H-NMR spectra of bifunctionalized PNiPAAm before (A) and after (B) deprotection of the TMS-group (left) and magnification (right) of the signals used for the calculation of the number of alkyne groups. All spectra were recorded in DMSO-d<sub>6</sub>, (500.13 MHz, 300 K).



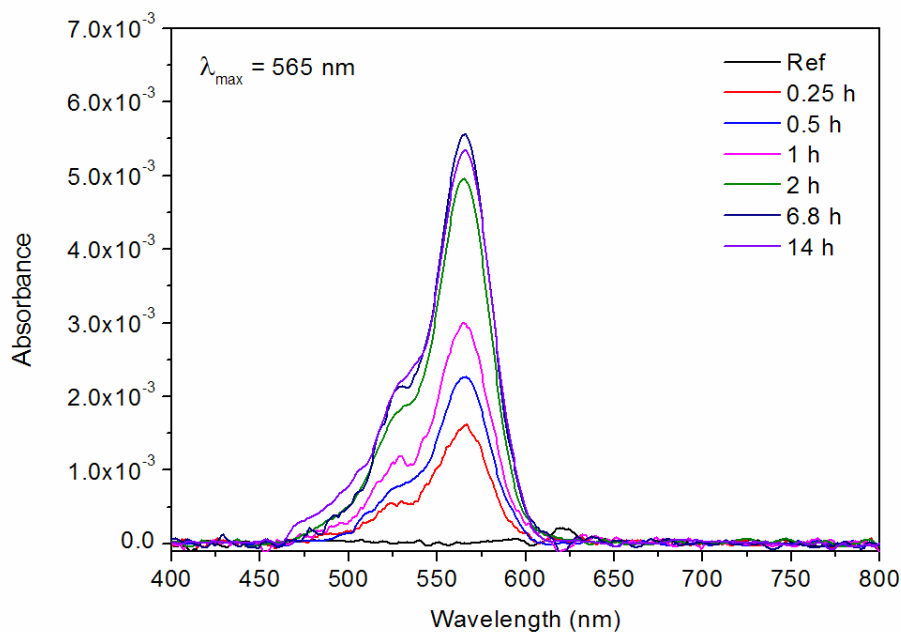
**Figure S2.**  $^1\text{H-NMR}$  spectra of TMS-protected PNiPAAm (pAlk-PNiPAAm) before (black) and after (red) annealing at 150 °C for 16 hours. The spectra were normalized to the signal of the single proton of the isopropyl group. The inset shows the magnification of the reduced signal (~60%) of the TMS-group after annealing. All spectra were recorded in  $\text{DMSO-d}_6$ , (500.13 MHz, 300 K).



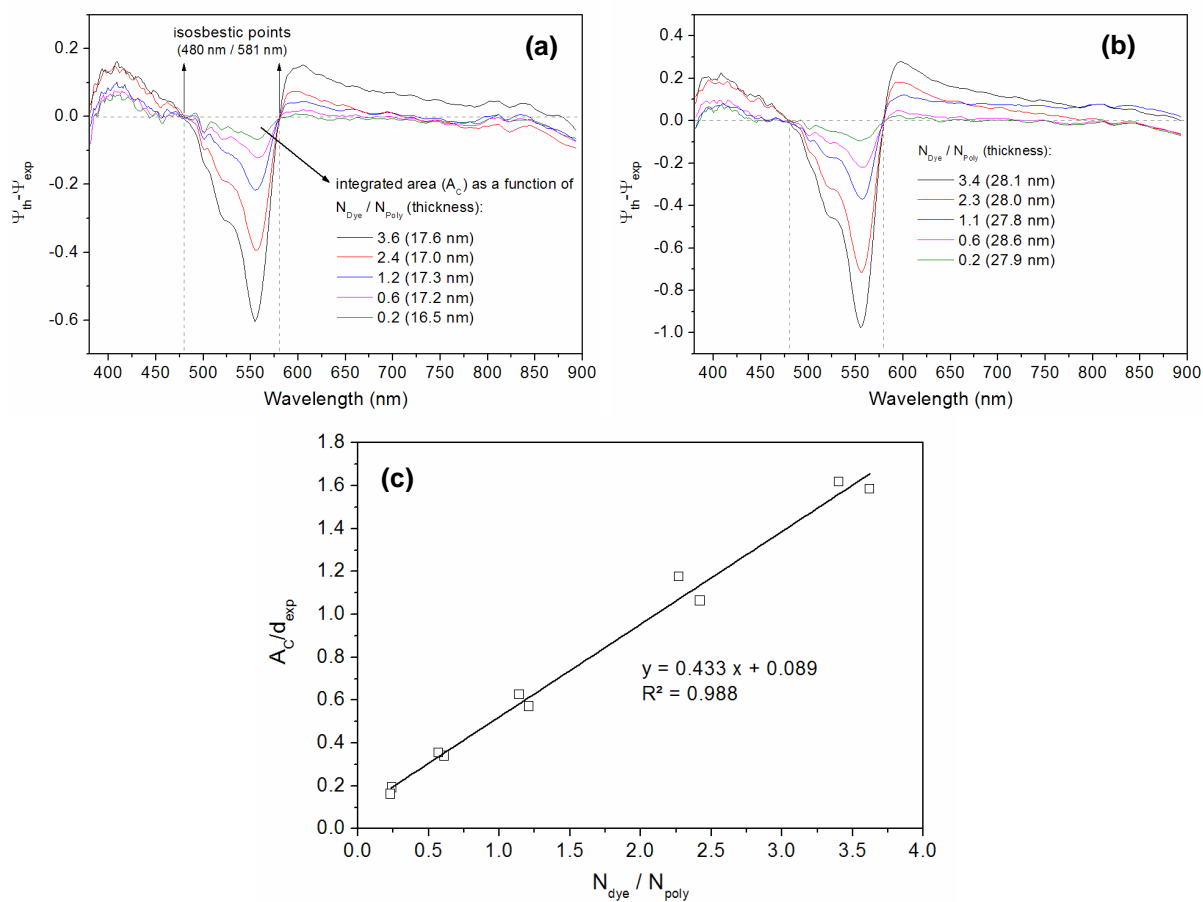
**Figure S3.** TGA (left) and DSC (right) curves of bifunctionalized PNiPAAm with (dotted lines) and without (solid lines) TMS-protecting group (TMS-PG). For both polymers a  $T_g$  of 143 °C was determined using the half-step method.



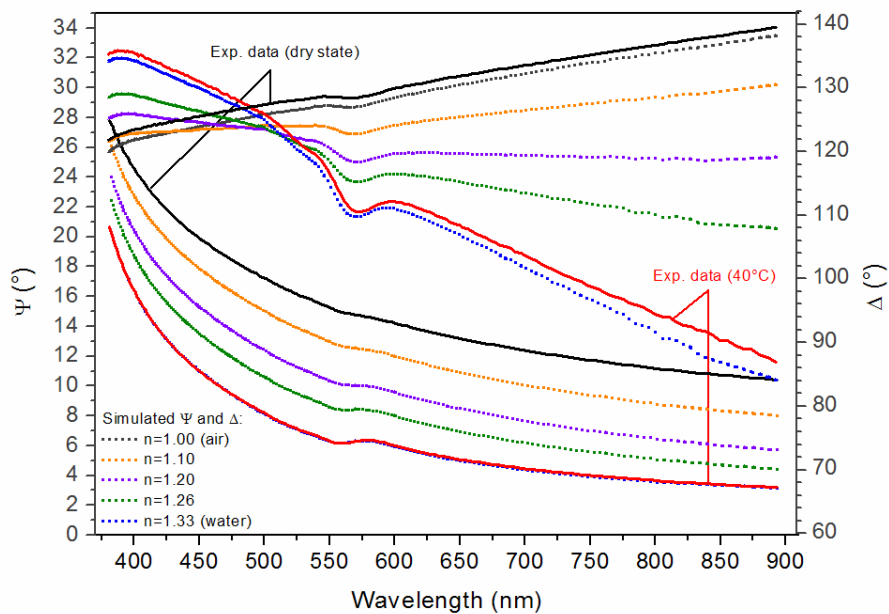
**Figure S4.** Surface topography images (left) and cross section (right), as measured by AFM, of Alk-PNiPAAm before (top, black line) and after (bottom, red line) CuAAC reaction with azide-modified rhodamine B (N3-RhB). AFM was conducted using a scanning force microscope Dimension V equipped with a Nanoscope V controller (Veeco Instruments, USA), operating in TappingMode® in atmosphere at room temperature. We used silicon-SPM-sensors (BudgetSensors, Bulgaria) with spring constant of about 3–4 N/m and with a resonance frequency of about 65 kHz, the tip radius was lower than 10 nm. Data was analyzed using NanoScope Analysis v1.40 (Bruker AXS, Germany). No changes in the surface morphology or roughness of the modified brush system were found after CuAAC with N3-RhB.



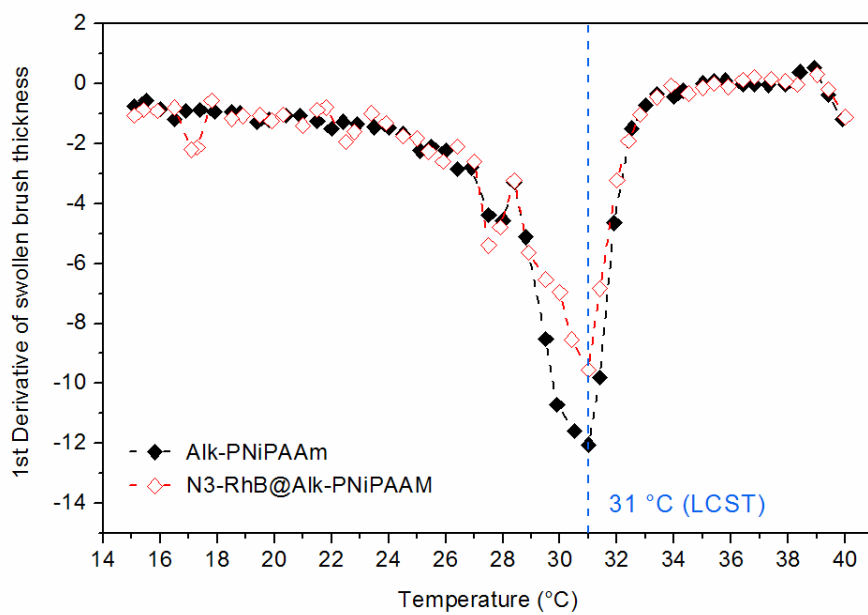
**Figure S5.** UV/VIS spectra (absorbance) of Alk-PNiPAAM brushes (prepared on fused silica substrates) after CuAAC reaction with N3-RhB for different reaction times.



**Figure S6. Calibration curve:** To determine the dye to polymer ratio, two series of spincoated films with thicknesses of (a) 17 nm and (b) 28 nm of pAlk-PNiPAAM with varying N3-RhB concentration were prepared and the experimental  $\Psi$  data analyzed by SE. For this, the integrated area between the resulting isosbestic points (480 nm and 581 nm) was normalized by dividing by the film thickness and correlated with the molar ratio of dye to polymer in solution, which is assumed to be conserved in the spincoated films in dry state.



**Figure S7.** Experimental and simulated  $\Psi$  and  $\Delta$  values of a N3-RhB@Alk-PNiPAAM brush for different ambients.



**Figure S8.** Determination of the LCST of Alk-PNiPAAM brushes before (black) and after (red) CuAAC reaction with N3-RhB.