Investigation of thermo-responsive properties of poly(di(ethylene glycol) methylether methacrylate) brushes on gold using protein adsorption, cell desorption and adhesive properties

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This study reports on the dependence of the temperature-induced changes in the properties of thin thermo-responsive poly (diethylene glycol) methyl ether methacrylate (PDEGMA) layers of end-tethered chains on polymer thickness. PDEGMA layers with a dry ellipsometric thickness of 5-40 nm were synthesized by surface-initiated atom transfer radical polymerization on gold. To assess the temperature-induced changes, the adsorption of bovine serum albumin (BSA) was investigated systematically as a function of film thickness, and temperature by surface plasmon resonance (SPR). BSA adsorption on PDEGMA brushes is shown to differ significantly above and below an apparent transition temperature. This surface transition temperature was found to depend linearly on the PDEGMA thickness and changed from 35 °C at 5 nm thickness to 48 °C at 23 nm. Finally, irreversibly adsorbed BSA on polymer brushes at temperatures above the transition temperature can be desorbed by reducing the temperature to 25 °C, underlining the reversibly switchable properties of PDEGMA brushes in response to temperature changes <sup>[1]</sup>.

Known to suppress protein adsorption and prevent cell attachment, PDEGMA brushes also possess an interesting and tunable thermo-responsive behavior, if the brush thickness is reduced or the grafting density is altered. PDEGMA brushes with a dry ellipsometric thickness of  $5 \pm 1$  nm can be switched from cell adherent behavior at 37 °C to cell non-adherent at 25 °C. Unlike for tissue culture polystyrene reference surfaces, swelling of the PDEGMA chains below the lower critical solution temperature results in the absence of paxillin and actin containing cellular filaments responsible for cell attachment. These tunable properties of very thin homopolymer PDEGMA brushes render this system interesting as an alternative thermo-responsive layer for continuous cell culture or enzyme-free cell culture systems <sup>[1]</sup>.

Finally, the changes in interaction forces between a hydrophobized colloidal atomic force microscopy (AFM) probe and PDEGMA brushes as well as the mechanical properties and swelling of the PDEGMA layers below and above the reported lower critical solution temperature (LCST) of PDEGMA brushes of 32°C were analyzed. These results corroborate independently acquired data on thermally triggered changes in protein and cell adsorption and release of these brush layers. The determined transition temperatures match those determined by the irreversible adsorption of BSA via SPR. AFM force-displacement and indentation data show a swollen state to three times their dry thickness below the LCST and a collapsed and progressively more adhesive and stiffer state at temperatures above LCST <sup>[2]</sup>. Therefore, such "smart materials" with unique features can be exploited to fabricate thermo-responsive surfaces with finely tunable collapse temperatures located in the physiological range.

- 1. Poly(diethylene glycol) methylether methacrylate homopolymer brushes allow controlled adsorption and desorption of PATU 8988t cells Macromol. Voß, Y.; Wassel, E.; Jiang, S.;, Song, Q.; Druzhinin, S. I., Schönherr, H., Biosci. 2017, 11, 1600337.
- 2. Colloid force probe study of poly(diethylene glycol) methylether methacrylate homopolyer brushes in aqueous media at different temperatures. Wassel, E.; Wesner, D.; Schönherr, H., Europ. Polym. J. 2017, 89, 440-448.

