PROTEIN REPELLING COATINGS BASED ON STIMULI-RESPONSIVE AQUEOUS MICROGELS DECORATED WITH OLIGO ETHYLENE GLYCOLS

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In the present work novel, biocompatible, thermo-responsive microgels were synthesized by surfactant-free precipitation copolymerization of *N*-vinylcaprolactam (VCL) with 2-methoxyethyl acrylate (MEA). MEA was chosen as comonomer because its polymer is known for his excellent blood compatibility and low protein adsorption[1,2] and therefore is already in use as coating material for artificial organs.[3]
Using optimized precipitation polymerization procedure we could incorporate up to 32 mol% of MEA into the PVCL-based microgels without loss of colloidal stability. The microgel composition was quantified by Raman-Spectroscopy. Both, a high resolution transverse relaxation NMR study and calorimetric measurements delivered that MEA is located mainly in the microgel shell due to its lower polymerization rate in comparison to VCL. With increasing comonomer content the swelling degree $\Delta R_{h(20°C-50°C)}$ of the microgels decreased. This behavior can be explained by the temperature-responsivity of both monomers. While pure PVCL microgels exhibit a LCST = 31 °C,[4] linear PMEA has a very low LCST = 0-5 C°C.[5,6] It follows that with increasing MEA-content the VPTT of the microgels is shifted to lower values. Additionally, the microgel shell is already collapsed at room temperature which prevents the swelling of the PVCL-rich core. Consequently the PVCL/MEA microgels become more rigid and less temperature-sensitive with increasing MEA-content. While the particles with low MEA-content exhibit a core-shell like structure which indicates that the core is denser than the shell, the particles with high MEA-content are rigid and compact that can be approved by AFM measurements.
Furthermore, the protein repellent properties of microgel films were tested. High protein repellence could be obtained for PVCL/MEA microgels, as expected (Figure 1). At last different functionalities like carboxylic acid groups or epoxy groups were integrated into the PVCL/MEA microgels by copolymerization with acrylic acid (AA) or glycidyl methacrylate (GMA). While the carboxylic acid groups lead to additional pH-dependence of the microgels that can be used for pH-triggered uptake and release mechanisms, the epoxy groups are known to react specifically with primary amines and thiols. Therefore proteins, drugs and dyes can be bound to the microgels covalently.
Because of the temperature-sensitivity, high biocompatibility and integrated functionalities, these new microgels might be very interesting for clinical studies and for further modifications like loading with drugs.

Figure 1 - AFM image of a PVCL/MEA 20 microgel film (left), fluorescence microscopy image of a PVCL/MEA 20 microgel film after incubation with tetramethylrhodamine-BSA (middle) and pure glass after incubation with tetramethylrhodamine-BSA as reference (right).

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