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Nanostructured Multi-Responsive Coatings for Tuning Surface Properties

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Abstract : Stimuli-responsive polymer coatings can be used as functional elements in nanotechnologies, such as valves in microfluidic devices, as membranes in biomedical engineering, as substrates for the culture of biological tissues or in developing nanomaterials for targeted therapies in different diseases. However, such coatings usually suffer from major shortcomings, such as a lack of selectivity and poor environmental stability. The study will present multi-responsive hierarchical and hybrid polymer-based coatings aiming to overcome some of these limitations. Hierarchical polymer coatings, consisting of two-dimensional arrays of thermo-responsive cationic PNIPAM-based microgels and surface-functionalized with non-responsive or pH-responsive polymers, were covalently grafted to substrates to tune the surface chemistry and the elasticity of the surface independently using different stimuli. The characteristic dimensions (i.e., layer thickness) and surface properties (i.e., adhesion, friction) of the microgel coatings were assessed using the Surface Forces Apparatus. The ability to independently control the swelling and surface properties using temperature and pH as triggers were investigated for microgels in aqueous suspension and microgels immobilized on substrates. Polymer chain grafting did not impede the ability of cationic PNIPAM microgels to undergo a volume phase transition above the VPTT, either in suspension or immobilized on a substrate. Due to the presence of amino groups throughout the entirety of the microgel polymer network, the swelling behavior was also pH dependent. However, the thermo-responsive swelling was more significant than the pH-triggered one. The microgels functionalized with PEG exhibited the most promising behavior. Indeed, the thermo-triggered swelling of microgel-co-PEG did not give rise to changes in the microgel surface properties (i.e., surface potential and adhesion) within a wide range of pH values. It was possible for the immobilized microgel-co-PEG to undergo a volume transition (swelling/shrinking) with no change in adhesion, suggesting that the surface of the thermal-responsive microgels remains rather hydrophilic above the VPTT. This work confirms the possibility of tuning the swelling behavior of microgels without changing the adhesive properties. Responsive surfaces whose swelling properties can be reversibly and externally altered over space and time regardless of the surface chemistry are very innovative and will enable revolutionary advances in technologies, particularly in biomedical surface engineering and microfluidics, where advanced assembly of functional components is increasingly required.

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