COMBINATORIAL POLYMER BRUSHES FORMED BY TEMPERATURE-RESPONSIVE POLYMERS WITH TUNABLE ONSET OF RESPONSE

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Introduction

When grafted on solid surfaces, temperature-responsive polymers provide convenient means to define switchable surface properties (wettability, adhesion, topography), because of the ease of altering the conformation of the grafted polymers through changes in temperature. These switchable properties can also further lead to more complex phenomena, such as the controlled movement of small particles on polymer-bearing surfaces [1,2], a movement that is facilitated by topography and adhesion factors.

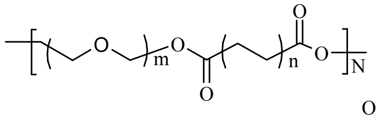
Given the opportunities for application in biomedical and biological systems, water-soluble polymer which undergo a first-order phase transition in solution, i.e. change their hydrophilicity over a narrow temperature range, such as polymers with a sharp, tunable lower critical solution temperature (LCST) are of particular interest. Here, we synthesized and studied end-tethered polymers on solid substrates, with a systematic grafting-density variation that spans the range from dense brush to isolated end-tethered chains, and explored the behavior of such systems in aqueous media as we cross their LCST temperature.

Experimental

Synthesis of end-tethered polyamides on a solid substrate. Amide polymers were end-tethered on a self-assembled monolayer (SAM) covered surface, where a fraction of the SAM surfactants had a CN ω-functionalization. The amide polymers were synthesized by chlorinated α,ω-bis(carboxymethyl)-(m)ethylene oxide (m=13) and reacting it with α,ω-diamine-(n)ethylene (n=5). Both reactants were dissolved in THF and pure THF was used in to wash any unreacted oligomers or homopolymers dissolved in the brush or adsorbed on the surfaces. The reaction was carried out at room temperature in the presence of NaOH. After the reaction, warm THF was used to wash the polymer-covered surfaces

Results and Discussion

Temperature-Responsive Polymers. We synthesized alternating copolymers [3] based on m-oligomers of ethylene-oxide (m-EO) and n-oligomers of ethylene (n-EE) that exhibit cloud points, which directly correlate with the hydrophilic/hydrophobic balance of the polymer (m/n), and resemble a true LCST phase transition. The general structure of these polymers is shown in **Figure 1**. The LCST in aqueous solutions of these polymers can be varied systematically between 10ºC and 80ºC by simply altering the (m/n) ratio [3]. The m-EO and n-EE units can be connected through a variety of linking groups (e.g., esters and amides), and the alkyl groups can be substituted by any other hydrophobic group (e.g., aromatic or cycloaliphatic moieties[3]). We have previously established that the temperature responsive character of the polymer is not affected by end-tethering on flat solid surface. In this work, we prepared arrays of the temperature-responsive polymers on solid surface by utilizing the "grafting from" methodology.



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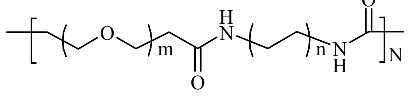

(2)

Figure 1. The general structure of our temperature-responsive polymers. [3]

Molecular and Polymer Gradients. We formed molecular gradients from ω-cyanide-α-silane-alkyl SAM using the initiator vapor deposition method [4]. We then grew the polymer brushes via a "grafting from" approach carrying out monomer-by-monomer polycondensation reactions. The gradient in the surface density of cyanide groups in the CN-SAM resulted in a gradient of the grafting density of the polymers, which also manifested itself in the macroscopic properties of the brush. In **Figure 2** we plot the contact angle of DI water (θ_{DIW}, red squares), the brush grafting density (blue circles), and the adhesion energy (green triangles) as a function of the position on the substrate for the gradient brushes. The grafting density was evaluated from variable-angle spectroscopic ellipsometry (VASE) experiments, the adhesion energy was determined by force-distance atomic force microscopy (AFM) having a $10\mu m$ diameter sphere attached to the AFM tip. Also shown in **Figure 2** is the concentration of the CN-SAM as a function of the position on the substrate (purple line). The latter was determined from the position-dependent near-edge X-Ray absorption fine structure (NEXAFS) signal collected at E=397.2 eV. At all grafting densities these polymeric brushes remain temperature-responsive, as illustrated by changes in adhesion, as well as by direct AFM observation of the brush morphology, while varying the solution temperature.

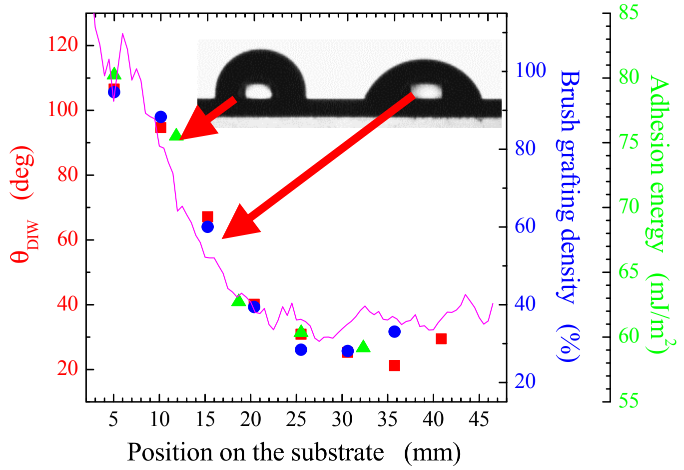

Figure 2. Various properties as a function of the position on the substrate, for a substrate bearing a SAM with a gradient in the surface density of ω-cyanide-surfactants. Plotted are the contact angle of deionized water (θ_{DIW}, red squares), the adhesion energy (green triangles), the surface density of N (ϕ_{CN}, purple line), and the brush grafting density (blue circles).

Temperature Response of the end-Tethered Polymers. The end-tethered polymers as described above form a "smart" responsive polymer gradient, in the sense that their properties can be changed/switched by having

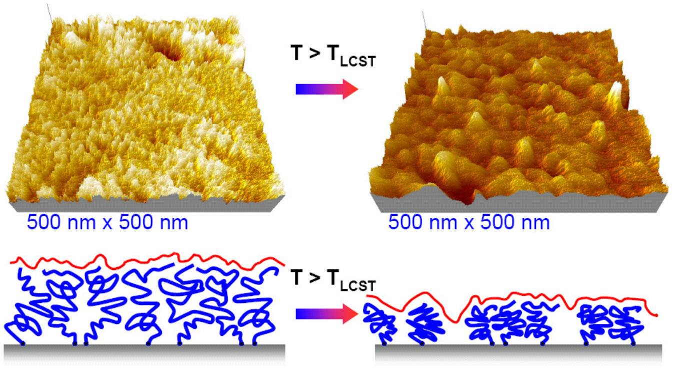

Figure 3. (top) Direct AFM imaging of the polymer brush topography in water, as the temperature is raised above the LCST (45ºC) of the polymer (polyester of structure 1 in fig. 1, with m/n=13/3). **(bottom)** A schematic of the associated brush conformation change, *i.e.* from a swollen polymer brush (low T) to a collapsed multi-chain aggregate structure (high T).

the system temperature cross the corresponding LCST of the polymer. As the temperature *increases* and crosses the LCST, the polymers undergo a transition from a soluble (hydrophilic, expanded-coil state, good-solvent conditions) to a two-phase (hydrophobic, collapsed-coil state, bad-solvent condition) state, a transition that can be directly imaged by AFM mapping of the polymer brush topography (**Figure 3**).

Beyond this topographical reconstruction, there is also an associated change in the surface adhesion. In **Figure 4** we show the surface adhesion as quantified through force-distance measurements by the AFM, employing a tip which bears a 10μm-diameter Tungsten colloidal sphere. There is a clear change in wettability (surface tackiness) at the corresponding LCST of the end-tethered polymer.

Two combination of these two effects, *i.e.* controlled change of the effective surface roughness and the associated change in adhesion, can be exploited to control the surface wettability. For example, in **Figure 5** we show the contact angle of deionized water on two spots along the surface-density gradient (at 20% and 40% fraction of CN in the SAM respectively) for the 13/6 ethyleneoxide/ethylene polyester of Figure 4. As expected, the water contact angle changes as the temperature crosses the LCST of the polymer (26°C), reflecting both the change in surface roughness as well as, and probably more importantly, the change in surface adhesion.

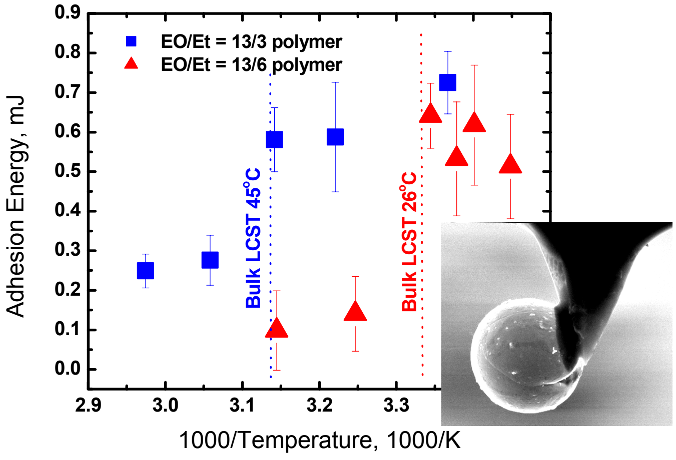

Figure 4. Adhesion energy measured by force-distance AFM in water employing a tip that bears a mounted Tungsten colloidal sphere (of 10μm in diameter, inset). The blue squares correspond to the same polymer as before (a m/n=13/3 polyester), the red triangles correspond to a polymer with a different monomer stoichiometry (a m/n=13/6 polyester) and with a LCST of 26°C.

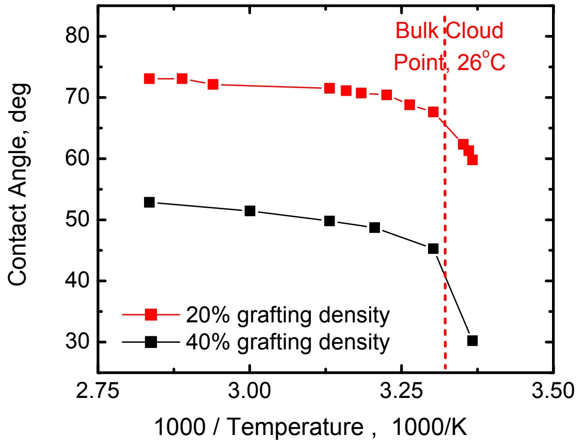

Figure 5. Contact angle of deionized water on two points along the ϕ_{CN} gradient (at about 20% and 40% CN concentration in the SAM) for a surface bearing a 13/6 ethyleneoxide/ethylene polyester with an LCST of 26°C.

Conclusions

Surface-grafted temperature-responsive polymers are used to realize "smart" surfaces, whose behavior is observed for applied temperature-stimuli. A hydrophilic/hydrophobic balance of groups across the polymer allows for the tailoring of the polymer lower critical solution temperature (LCST), which determines the onset of response for these "smart" surfaces. Molecular gradients of an omega-functionalized SAM on a solid surface are used to create a gradient also in the polymer grafting density. The synergistic effects of the grafting-density variation along with the tailoring of the response-onset for the temperature-responsive polymers, allows for the properties of the surface (wettability, topography, adhesion) to be switched on demand via temperature changes. The influence of the grafting density and hydrophobic/hydrophilic balance on the various properties of the polymer brush is reported.

Acknowledgements

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