

NIRT: Nanoengineered Responsive Polymer Surfaces for Micro/Nanofluidic Bioanalytical Systems

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The ultimate success of micron/nanofluidic bioanalytical systems heavily hinges on new micro/nanofluidic technologies to meet the demands of practical applications. A critically important technological challenge involves the ability to modify and functionalize surfaces in such systems. We explore nanoengineered stimulus-responsive polymer brushes [2] as an innovative platform for surface modification and functionalization in micro/nanofluidic devices. Stimulus-responsive polymers undergo strong reversible conformational changes in response to

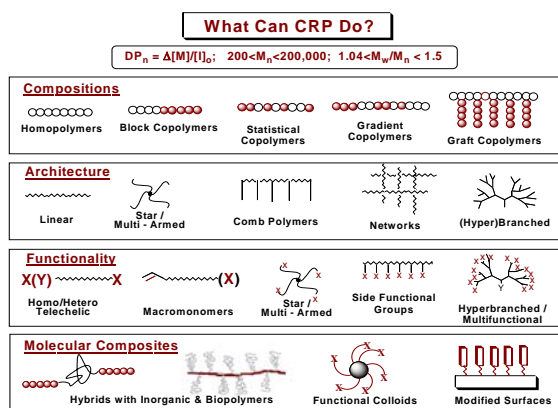


Figure 1. Controlled molecular structures by CRP

molecular transition from a hydrophilic, swollen state to a hydrophobic, collapsed state at their lower critical solution temperature (LCST). In synthesis, controlled/living radical polymerization (CRP) techniques (e.g., atom transfer radical polymerization, or ATRP) [3] are used to graft polymers from/to silicon and gold surfaces. We initially focus on unconfined substrates, and then explore preparation of patterned polymer brushes and *in-situ* polymerization within microchannels. In characterization, atomic force microscopy (AFM), surface plasmon resonance (SPR), and contact angle measurements are used to understand the effects of chain density, composition and topology on the nanoscale morphology and thermal responses (e.g., temperature-dependent changes in film thickness, wettability, and protein adsorptivity).

Thermally responsive polymer brushes are applied to two important micro/nanofluidic

small changes in environmental parameters (e.g., temperature, pH, and electric field). A salient feature of this project involves using recent advances in macromolecular engineering techniques to produce polymer surfaces with precisely controlled chain length, uniformity, composition, topology and functionality. Micro/nanofluidic surfaces modified as such would have optimal intelligent behavior with excellent robustness and long-term stability.

We focus on synthesis, characterization, and micro/nanofluidic applications of thermally responsive polymer brushes that undergo

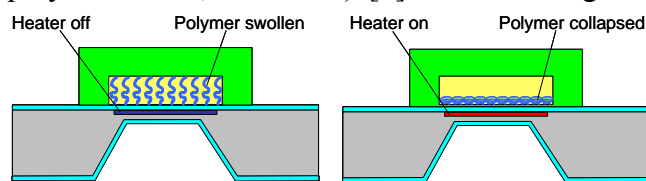


Figure 2. Nanofluidic valve enabled by responsive polymer brushes. The valve is (a) closed and (b) open.

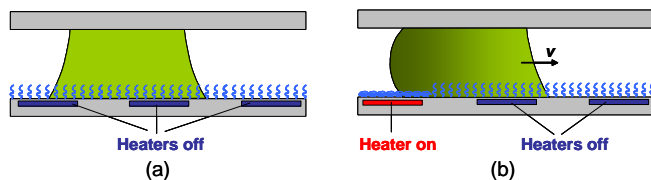


Figure 3. Transport of a droplet in a channel whose bottom wall is coated with a responsive polymer (hydrophilic when unheated). The top wall as shown is hydrophobic.

applications: fluid handling and chromatography. For fluid handling, we exploit thermally induced, fast and reversible changes in polymer thicknesses to demonstrate flow control devices such as valves (Figure 2), pumps and mixers, as well as use such changes in surface wettability to manipulate (e.g., transport) femtoliter-scale droplets in microchannels (Figure 3). Thermally induced wettability changes are also exploited in chromatography, where sequence-specific separation of DNA oligomers is achieved by binding a nonpolar PNA-surfactant complex to target sequences followed by recovery in microchannels by altering the temperature (Figure 4).

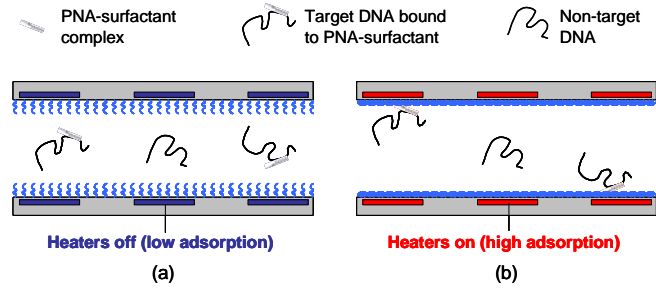


Figure 4. Chromatography in a channel coated with responsive polymer brushes: channel walls are (a) non-adsorptive when unheated and (b) adsorptive when heated.

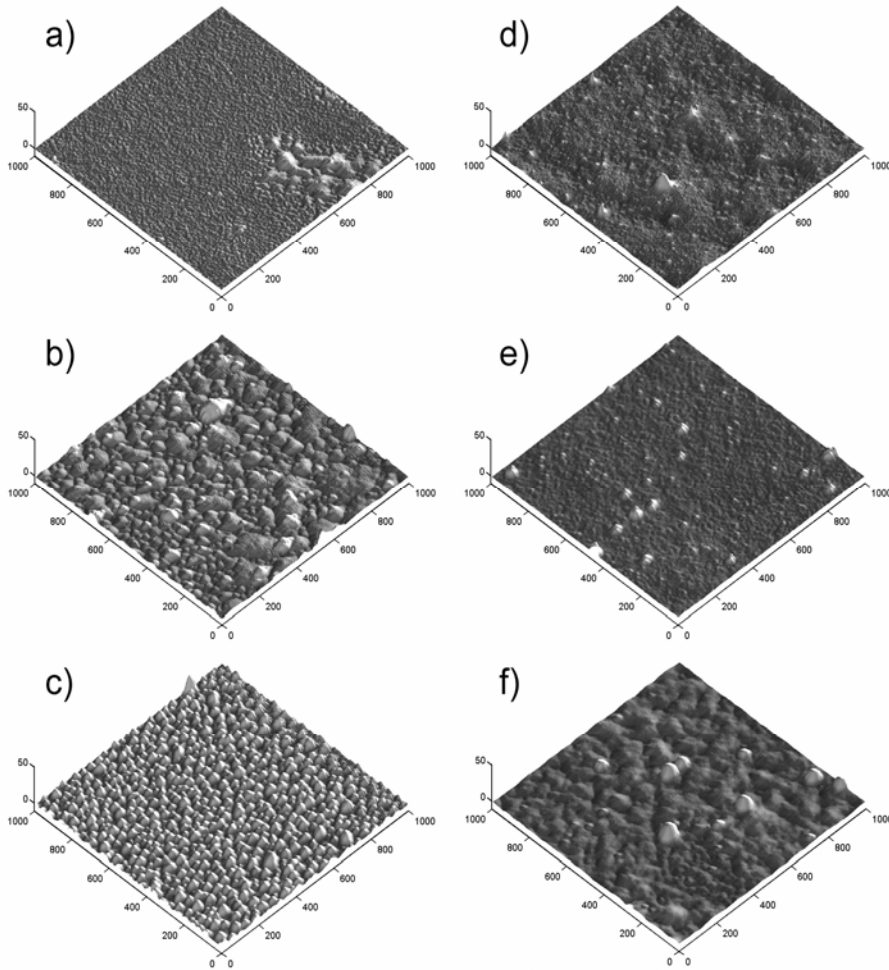


Figure 5. AFM images of Si-OH (a-c) vs. Si-H (d-f) substrates covered with a pDMAEMA layer synthesized by ATRP with different coverage with initiating groups: (a) 20% ($M_n = 95\,000$ and $M_w/M_n = 1.24$), (b) 13% ($M_n = 78\,000$ and $M_w/M_n = 1.26$), (c) 1% ($M_n = 78\,000$ and $M_w/M_n = 1.26$); and for Si-H: (d) 20% ($M_n = 78\,000$ and $M_w/M_n = 1.4$), (e) 13% ($M_n = 78\,000$ and $M_w/M_n = 1.4$), and (f) 1% ($M_n = 78\,000$ and $M_w/M_n = 1.26$). All scales are in nm.

In the first year of the project, we have focused on synthesis and characterization of polymer brushes, choosing Poly-(N,N-dimethylaminoethyl methacrylate) (pDMAEMA), a thermally responsive polymer (LCST: 30-40 °C), as a primary candidate (below) [4,5]. We have also addressed micro-fabrication issues for later creation of functional devices with such polymers. We studied promising approaches to creating patterned pDMAEMA polymer surfaces using UV-induced hydrosilylation (on Si-H substrates) and degradation of methacrylate groups (Si-OH), as well as a technique for room-temperature bonding

of two polymer-functionalized substrates to form thin (down to 0.5 μm currently) channels with an ultrathin intermediate PDMS adhesive layer [6].

pDMAEMA was synthesized in the presence of a sacrificial, “dummy” initiator by surface-initiated ATRP from silicon (Si-OH or Si-H terminated) or gold. Chain densities were controlled by varying the molar ratio of the active vs. dummy initiators, which respectively were: 1-(chlorodimethylsilyl)propyl 2-bromoisobutyrate and chlorotrimethylsilane for Si-OH terminated substrates; 2-bromoisobutyrate ester and non-functionalized 1-octane for Si-H substrates; and hexaethyl bromoisobutyrate disulfide and butyl disulfide for gold coated quartz slides. Tapping mode AFM images of Si-OH based pDMAEMA grafts (in air under ambient conditions) are shown in Figure 5a-c. Images of grafts obtained at higher than 20% initiator coverage (Figure 5a) revealed the presence of dense, relatively smooth films, with occasional patchy defects. Upon lowering the initiator coverage, the grafts were increasingly patchy, and at 1% coverage and below, they had a form of highly uniform, isolated patches. The average apparent volumes of these patches (not corrected for the finite size of the AFM tip) was on the order of 2000 nm^3 , whereas their average height measured with respect to the exposed substrate areas did not exceed 10 nm. This indicates that such patches consisted of just a few individual polymer chains which were collapsed onto the surrounding surface. AFM images of Si-H based grafts are shown in Figure 5d-f. It appears that, in comparison with the Si-OH case with the same assumed initiator coverage, Si-H based films were denser, showing fragmentation into patches only at the lowest initiator coverage (Fig. 5f). Both Si-OH and Si-H substrates seem to yield equally uniform graft layers when the concentration of initiating group on the surface is $\geq 20\%$.

Grafted pDMAEMA brush layers prepared with varying initiator densities on gold were characterized using SPR. Layer densities prepared at 20% and 1% initiator were 2 nm^2/chain and 18 nm^2/chain , respectively. The thermal responsiveness of the layer with 20% initiator has been characterized. The layer thickness decreased by 17% upon heating from 25°C to 40°C (Figure 6). This indicates that SPR is a useful tool for characterization of polymer brushes.

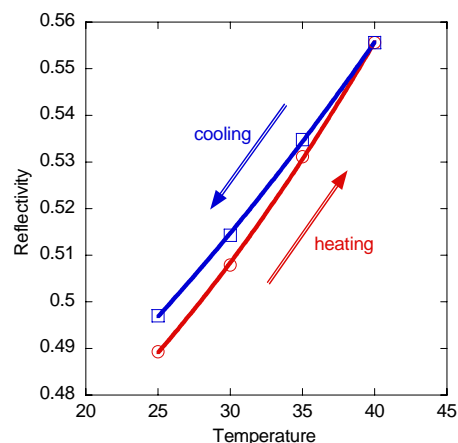


Figure 6. Temperature-dependent reflectivity for pDMAEMA (20% initiator) measured using SPR (incident angle: 55.4°). From this the polymer thickness was estimated to decrease by 17% upon heating from 25°C to 40°C.

References

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