Nanotechnology

Locking and Unlocking of Polyelectrolyte Brushes: Toward the Fabrication of Chemically Controlled Nanoactuators**

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Polymers are ideal building blocks for nanofabrication and the engineering of surfaces because of their response in shape and size to environmental changes in polymer concentration, ionic strength, pH, temperature, and solvent. Furthermore, since they are easy to synthesize, as well as chemically and mechanically robust, polymers are ideal materials to bridge the gap between biological nanomachines and silicon-based devices. Of particular interest herein is the exploration of the use of polymer brushes as nanoactuators.[1]

Polyelectrolytes, that is, polymers containing charged monomers, change from an extended conformation in a solution of low ionic strength to a coiled conformation in solutions of high ionic strength.[2] When polyelectrolytes are covalently attached to a surface to form a brush, the polymer chains show a strongly extended (stretched) conformation in pure water, as a result of both the repulsion between neighboring chains and the repulsion between the monomers.[3–6] In contrast, when polymer brushes are placed in electrolyte solutions, the charges of the pendant groups in the polymer chains are screened, and the minimization of the electrostatic repulsions leads to entropically more favorable collapsed conformations.[4–8] This collapse is comparable to transitions from extended to coil-like conformations commonly observed for polyelectrolytes in solution.[3,4] In the case of polymer brushes, there are constraints on the degrees of freedom related to conformational changes, and as a result the height and the amount of water on the inner brush environment are reduced.[5,8]

Our aim is to use the ionic-strength-sensitive behavior of polyelectrolyte brushes[9–11] in combination with specific binding interactions and ion-size-exclusion effects to design smart polymer surfaces that can be switched between a permanently collapsed and an extended state, where both states have different surface properties. In addition, we aim to find a route toward a "fast switch" that reversibly alternates between different polymer brush conformations, and as a consequence gain control over surface properties[12,13] such as wettability, hydration, and stiffness. Reversibly manipulating the polymer-brush conformation in a chemically selective way (not only by changing the ionic strength) will be a crucial step toward the use of surface-confined polyelectrolytes as nano-actuators.

Cationic brushes of [2-(methacryloyloxy)ethyl]trimethyl-ammonium chloride (METAC)[14] were grown from gold surfaces, patterned into regions containing either initiator or methyl-terminated monolayers (Figure 1 a,b), by atom-transfer radical polymerization (ATRP) in an oxygen-free methanol/water (4:1) mixture.[15,16] The responsive behavior of the METAC brushes in different electrolyte environments (NaCl and MgSO$_4$) was studied under liquids using atomic force microscopy (AFM) and a quartz crystal microbalance with dissipation (QCM-D).[17]

The conformational changes in the METAC brush in the presence of 1 M NaCl electrolyte solution can be followed with QCM-D,[18,19] where additional information about the water content and the rigidity of the polymer brush can be obtained. Furthermore, QCM-D is well-suited to study the kinetics of the collapse process, which is not possible with AFM, since it takes approximately 15 min before stable images can be acquired after the addition of salt. QCM-D measurements on 50-nm-thick METAC brushes (thickness measured in the dry state with ellipsometry) clearly show an immediate increase in the frequency (Figure 2 a) and a decrease in the dissipation (Figure 2 b) of the METAC brush/quartz crystal system upon addition of 1 M NaCl. The timescales involved in this collapse

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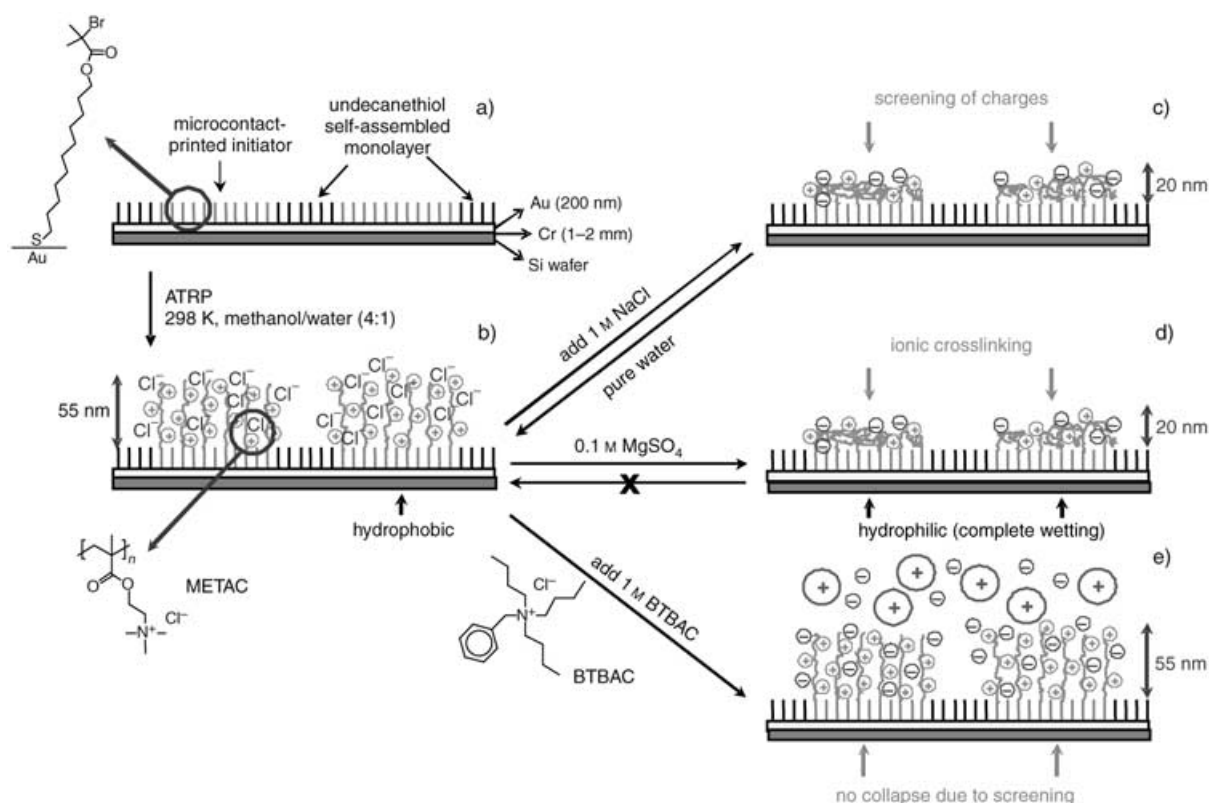
Figure 1. The synthesis (a, b) of polyelectrolyte brushes and their different possible behaviors in response to changes in ionic strength: c) reversible collapse by pure changes in ionic strength, d) irreversible collapse by increases in ionic strength combined with ion pairing, and e) no responsive behavior with the ionic strength because of steric effects.
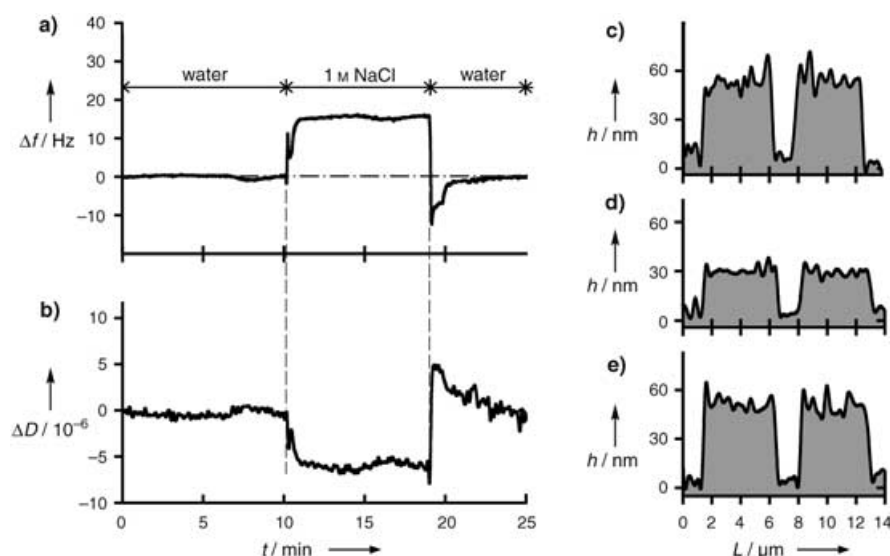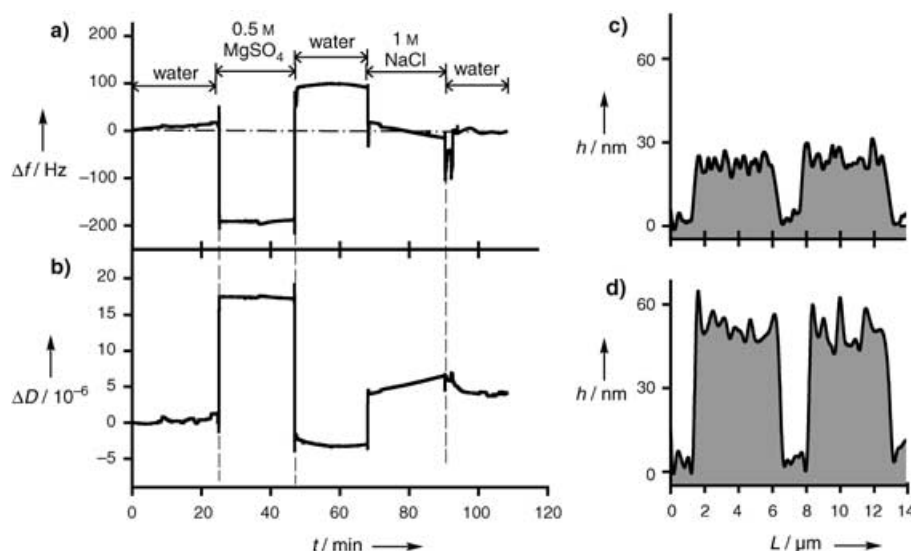

Figure 2. QCM response on a) frequency and b) dissipation when METAC brushes are in the presence of 1 M NaCl. c) Cross-sectional analysis derived from AFM imaging of METAC brushes in water. d) Cross-sectional analysis of patterned METAC brushes imaged in 1 M NaCl. e) Cross-sectional analysis of METAC brushes in water after treatment with 1 M NaCl.

polymer film (viscoelastically coupled to the solution) to a more rigid collapsed structure. As shown in Figure 2, when the NaCl solution is replaced with pure water, the frequency and dissipation return to their original values, which indicates that the METAC brush resumes the "extended conformation". To estimate the magnitude of the collapse (brush height, h) under different liquid environments we performed in situ AFM measurements on patterned METAC brushes grown as depicted in Figure 1a and b. By combining AFM imaging (at low loads) under liquids with patterned responsive brushes (Figure 1b) it is possible to obtain reliable information about the actual h value of the polymer brush in the liquid environment. When imaged under pure water (Figure 2c), METAC brushes show $h \approx 55$ nm (extended conformation). In

process are less than 3 s. The increase in frequency is related to the loss of water molecules from the polyelectrolyte brush during the collapse process. The decrease in the dissipation (Figure 2b) can be understood as a change from a rather soft the presence of 1 M NaCl electrolyte solutions the polyelectrolyte brushes are completely collapsed, which results in a change in h from ≈ 55 to ≈ 26 nm (Figure 2d). Notably, for NaCl solutions with concentrations lower than 0.1 M the

collapse takes place to a lesser degree. As previously indicated by QCM-D measurements, AFM shows that this collapsed state of the METAC brush in the presence of 1M NaCl can be easily and completely reversed by simply washing the surface-confined polyelectrolyte with pure water (Figure 2e).

A different effect is observed when $MgSO_4$ is used as the electrolyte instead of NaCl. Addition of 0.5M $MgSO_4$ electrolyte solution promotes a frequency decrease, while the dissipation is strongly increased (Figure 3a,b). These effects

electrolytes remain collapsed ($h \approx 28$ nm) in pure water after treatment with 0.5M $MgSO_4$ (Figure 3c).

Figure 3d shows that after treatment of the SO_4^{2-}-collapsed METAC brushes with 1M NaCl and subsequently storage in pure water, the extended conformation of the brushes is clearly restored ($h \approx 53$ nm). The excess of NaCl can be used to displace the equilibrium SO_4^{2-}/quaternary ammonium ion in such a way that the original chemical/ionic (Cl^--coordinated METAC) composition inside the brush is restored. In addition, washing with water depletes the NaCl excess and leads to the fully extended conformation.

The next step was to measure the contact angle to further characterize the surface properties of collapsed and extended brushes. Surfaces modified with METAC brushes ($h \approx 39$ nm) have a static contact angle of approximately 58° (Figure 4a). Treatment of brushes with 0.5M $MgSO_4$ and washing with water results in a completely hydrophilic surface (Figure 4b), and the brush is in a collapsed state. The wettability of the surface is not affected by extensive rinsing with water, which demonstrates the robustness of the switch to the wetting behavior (Figure 4c).

The wetting properties are quite surprising, as we expected that the collapsed state (which involves a significant loss of water) would be more hydrophobic than the fully hydrated extended brushes. We hypothesize that during the collapse a considerable quantity of electrolyte (Mg^{2+} and SO_4^{2-} ions) is retained within the polyelectrolyte brush. This excess of strongly hydrated ions

Figure 3. QCM response on a) frequency and b) dissipation when METAC brushes are placed in different electrolyte environments (0.5M $MgSO_4$ and 1M NaCl). Cross-sectional analysis, derived from AFM imaging performed under pure water, corresponding to c) patterned METAC brushes placed in 0.5M $MgSO_4$ for 20 min and d) patterned METAC brushes placed in 0.5M $MgSO_4$ for 20 min, rinsed with water, and then placed for 30 min in 1M NaCl.
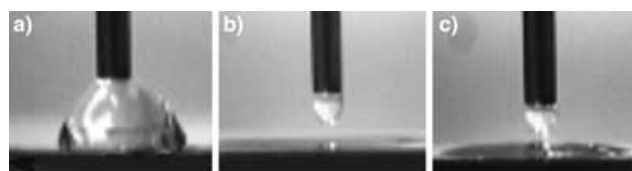
are predominantly a result of the strong changes in viscosity and ionic strength of the liquid environment. AFM imaging (not shown) confirmed, however, that METAC brushes are completely collapsed for $MgSO_4$ concentrations above 10 mM. Surprisingly, the replacement of the 0.5M $MgSO_4$ electrolyte solution by pure water resulted in an increase of the frequency and simultaneous decrease of the dissipation over the values previously obtained in pure water before flushing with 0.5M $MgSO_4$. This result can be interpreted as the METAC brushes remaining in a collapsed state while immersed in pure water. When the samples were stored in the QCM cell in pure water overnight, no changes in frequency or dissipation were detected. This finding implies an irreversible collapse of METAC brushes in the presence of SO_4^{2-} anions. However, these collapsed brushes can be "unlocked" by passing a concentrated NaCl solution (1M) through the QCM chamber and then flushing with water. Figure 3 shows that after this unlocking procedure, both the frequency and dissipation signals return to the original values for fully stretched brushes in water. AFM cross-sectional analysis of METAC brushes ($h \approx 55$ nm in the extended conformation) clearly shows that the surface-confined poly-

Figure 4. Contact-angle measurements of different METAC-modified gold substrates corresponding to a) Cl^--coordinated METAC brushes, b) SO_4^{2-}-treated METAC brushes, and c) SO_4^{2-}-treated METAC brushes after the substrate was stored for 8 min in pure water.

results in a highly hydrophilic behavior of the polymer film. QCM measurements confirmed that the collapsed brushes did not exchange salts with a pure water phase for at least 12 hours. "Unlocking" the brushes with NaCl and subsequent rinsing with water restores the original wetting properties (static contact angle: 58°).

As a further extension of the combination of ionic strength effects and the chemical switching of the brush, we characterized the responsive behavior of METAC brushes with salts of different cation sizes. We treated METAC brushes with NaCl and benzyltributylammonium chloride

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(BTBAC, see Figure 1e). Both electrolytes have the same anion but a very different cation size. The AFM cross-sectional analysis in Figure 5 clearly shows that in the presence of 10 mм BTBAC the brushes remain fully
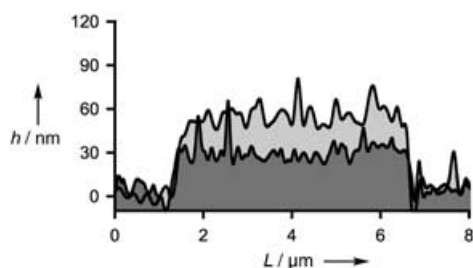
Figure 5. Cross-sectional analysis, derived from AFM imaging performed in 10 mм benzyltributylammonium chloride (light gray) and in 10 mм NaCl (dark gray).

extended, whereas the same brushes collapse to $h \approx 31$ nm in 10 mм NaCl. Chloride anion transport into the brush cannot be separated from the transport of their cationic counterions. When a bulky cation such as BTBA is chosen, whose permeability into the brush is hindered by steric effects, the ionic strength within the brush environment remains low, despite a high concentration of electrolyte outside the brush. As a result, the brushes do not collapse, thus opening up the possibility to decouple the conformational response of the brush from the external solution.

In conclusion, the characterization of polyelectrolyte brushes by using the powerful combination of QCM-D and AFM techniques[20] has enabled us to demonstrate three different cases of brush behavior in the presence of salts: a) their response to the ionic strength, b) strong ion-pairing effects in the case of SO_4^{2-} ions, and c) the exclusion of the ions introducing steric effects. This rich responsiveness can be exploited to create surfaces where the brush is collapsed or extended in either low- or high-ionic-strength conditions (Figure 1). These states not only correspond to changes in thickness, but also to changes in hydration state and wettability. We think that this responsive behavior makes polymer brushes excellent candidates to be used as nano-actuators. By using strong binding interactions between the SO_4^{2-} anions and the quaternary ammonium pendant groups on the METAC brush, we have been able to "lock" the polyelectrolyte conformation in a completely hydrophilic collapsed state. To achieve the actuating character of the polyelectrolyte brush and to "unlock" it we exchanged the "locking" SO_4^{2-} counterions coordinated to the quaternary ammonium pendant groups for Cl⁻ anions, which restored the original extended state and surface properties.

The extended state could also be "locked" by introducing chloride salts with very bulky cations, decoupling the brush response from the ionic strength in solution, and introducing selectivity. The "lock" and "unlock" METAC brush conformation is also a simple and reversible way to change surface properties, thickness, and wettability, which could control the permeability of brushes if used as a barrier on a coating, and

could stop or change the speed of a fluid in a liquid-cell device.

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