Weak Polyelectrolyte Brush Arrays Fabricated by Combining Electron-Beam Lithography with Surface-Initiated Photopolymerization

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We present a simple "top-down/bottom-up" strategy to fabricate nano- and micropatterned polymer brush arrays composed of pH- and salt-sensitive, weak polyelectrolyte copolymers [poly(*N*-isopropylacrylamide-*co*-methacrylic acid, 3:1, poly(NIPAAM-*co*-MAA)]. In our approach, a silicon surface is first patterned with gold, using "lift-off" electron-beam lithography ("top-down"), and the resulting pattern is then amplified by surface-initiated photopolymerization by conventional, UV-light-induced free radical polymerization ("bottom-up") from an immobilized 2,2′-azobisisobutyronitrile (AIBN) type initiator. The use of pH- and ionic-strength-sensitive comonomers in the copolymer brush enables large, externally triggered conformational changes of the micro- and nanopatterned polymer brushes. We observed that the height of nanopatterned ionized polymer brushes increases with increasing feature size of the pattern. The design and fabrication of surfaces with conformationally switchable, patterned polymeric structures is important for sensing and actuation applications on the micro- and nanoscales.

Introduction

The fabrication of patterned macromolecular architectures on surfaces is aimed at the realization of complex, often multimolecular, entities in which various interacting organic, biomolecular, and inorganic components are positioned in such a way as to give rise to unique properties and precisely defined structure-dependent function. Stimulus-responsive polymer brushes composed from weak polyacids or polybases have attracted significant interest[1] since they undergo large conformational changes in response to external stimuli such as changes in pH and salt concentration.[2,3] These polyelectrolyte or polypeptide systems can serve as basic building blocks in the assembly of complex structures that range from templates for protein or cell adhesion[4,5] and 2D

particle networks[6,7] to polyelectrolyte multilayers.[1,8] Polymer brushes with triggerable phase transition behavior can also be exploited in sensing and actuation devices on the nano- and microscales.[9] Although detailed aspects of the synthesis and characterization of polyelectrolyte brushes have been recently reviewed,[1] there is still little experimental data available for the preparation of nano- and micropatterned pH-sensitive polyelectrolyte brushes; only photolithographic,[10−14] and microcontact printing[15] approaches have been reported. Here, we report the fabrication and characterization of micro- and nanopatterned, pH- and ionic-strength-sensitive polymer brushes. In our approach, a silicon

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Scheme 1. Preparation of Poly(NIPAAM-*co*-NaMAA) (3:1) Copolymer Brush Patterns by Combining Lift-off Electron Beam Lithography (EBL) and Photoinitiated Polymerization, Using a Surface-Tethered Azo Initiator (1) Immobilized on Gold Templates
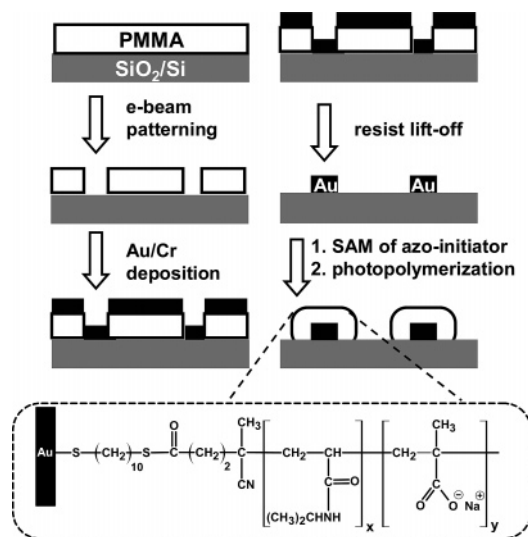
surface is patterned with gold templates, using lift-off electron-beam lithography ("top-down"),[16] and the resulting templates are then amplified by surface-initiated polymerization ("bottom-up") from an immobilized azo-initiator, using UV-light-induced free radical polymerization (Scheme 1).[17,18]

Materials and Methods

Materials. Sodium methacrylate (NaMAA, 99%) monomer, *N*-isopropylacrylamide (NIPAAM, 97%) monomer, and methanol (MeOH, 99.9%) were obtained from Sigma-Aldrich (Milwaukee, WI). NIPAAM was purified by recrystallization from toluene−hexane before use. Other chemicals were used without further purification. Milli-Q water (18 MΩ/cm, Millipore, Billerica, MA) was used in all experiments. To adjust the pH, 0.1 M HCl or 0.1 M NaOH was used, and different salt concentrations were obtained by dilution of a stock solution of 0.2 M KCl. The synthesis of SAM initiator (**1**) has been described elsewhere.[19]

Methods. *Fabrication of Gold Patterns by Electron-Beam Lithography.* A 130 nm thick one-layer electron-sensitive resist film of poly(methyl methacrylate) (PMMA, Mw = 950000 g/mol) was spin-coated onto a cleaned Si substrate and was annealed at 160 °C on a hot plate for 20 min. The resist layer was then patterned by exposure to an electron beam, using a Philips FEI XL30 Thermal Field Emitter SEM (operating current 144 pA, accelerating voltage 30 kV, working distance 7.5 mm, e-beam spot size 3 nm, chamber pressure 1.0×10^{-5} Pa) controlled by Nano Pattern Generator System (NPGS) software. The exposed PMMA layer was developed in a solution of methyl isobutyl ketone and isopropyl alcohol (MIBK:IPA) (1:3, v:v) for 80 s, quenched by IPA for 20 s, and finally isolated by rinsing with deionized water. A layer of chromium (50 Å) and a layer of gold (260 Å) were thermally

evaporated onto the patterned PMMA/silicon substrate under a vacuum (2×10^{-4} Pa) at room temperature to obtain geometrically well-defined gold features on the exposed SiO$_2$ surface. The Au-coated, developed resist was lifted-off (dissolved) by immersing the substrate in boiling acetone (60 °C), leaving behind 31 nm thick Au patterns on the silicon substrate. The patterned silicon substrate was finally rinsed with copious amounts of acetone and blown dry in a stream of N$_2$.

Preparation of Initiator Monolayers. The 2,2′-azobisisobuty-ronitrile (AIBN)-type photoinitiator, 4,4′-azobis[(1,10-dimercapto-decyl)-4-cyanopentanoate] (**1**), was synthesized as previously reported.[18] A self-assembled monolayer (SAM) of the AIBN-type initiator on the gold patterns was obtained by immersing the substrate into a dilute (1 mM) tetrahydrofuran (THF) solution of initiator (**1**) for 24 h. These samples were then removed from the initiator solution, rinsed thoroughly with THF and MeOH, and finally dried in a stream of dry nitrogen. Polymerization experiments were initiated immediately after monolayer deposition.

Surface-Initiated Polymerization. We used UV-light-induced photopolymerization[17,19] to prepare surface-attached, random poly-(NIPAAM-*co*-NaMAA) copolymer brushes (Scheme 2). Prior to use, all solutions and scintillation vials were thoroughly flushed with dry nitrogen gas to remove oxygen. A polymerization solution was prepared in a nitrogen atmosphere by injecting 2.46 mL of deoxidized, deionized water into a nitrogen flushed-scintillation vial containing a 0.189 g (1.67 mmol) of NIPAAM monomer and 0.081 g (0.75 mmol) of sodium methacrylate monomer, which resulted in 9.9 wt % monomer solution with a fixed molar comonomer feed ratio of NIPAAM to NaMAA of 7:3. The polymerization solution was then transferred into nitrogen-flushed scintillation vials containing the initiator-functionalized substrates. The patterned poly-(NIPAAM-*co*-NaMAA) copolymer brushes were photopolymerized by irradiation with UV light (Blak Ray, 100 W mercury lamp) with a wavelength of around 365 nm for 2 h without stirring at 20−25 °C under nitrogen. The polymerization temperature was kept below the lower critical solution temperature of ∼32 °C of poly-(NIPAAM). Substrates were then removed from the polymerization solution and immediately rinsed with copious amounts of Milli-Q water and MeOH to remove all traces of the polymerization solution and subsequently dried under a stream of nitrogen. The activation process of AIBN-type initiators produces two radicals, only one of which is tethered to the surface. The free radical thus generates free polymer in the bulk. To minimize polymerization in the bulk, we used a 10 times lower monomer concentration (9.9 wt %) than that reported by others.[17,19] Physisorbed copolymer was removed from a patterned substrate by rigorous rinsing with water and MeOH. Dyer et al.[18] also reported that physisorbed polymer can be removed from either clean gold or polymer-modified gold substrates by a simple rinsing step; while entangled physisorbed polymer is more persistent, more rigorous extractions have only a minor effect on the brush height. AFM images of the patterned polymer features showed no traces of physisorbed copolymers.

X-ray Photoelectron Spectroscopy/Copolymer Composition. To determine the copolymer composition, we prepared copolymer brush thin films on evaporated gold substrates with three different comonomer feed ratios (8.6%, 30.2%, and 49.5% MAA), using the same polymerization conditions as described above, with exception of the polymerization time, which was kept at 30 min. We then used X-ray photoelectron spectroscopy (XPS) to ascertain the chemical composition of these brush layers by analysis of the O 1s/N 1s peak intensity area ratios, obtained from binding energy survey scans (Kratos Axis Ultra spectrometer using a monochro-matic Al Kα source, scanning from 0 to 1200 eV with 1 eV stepsize, 200 ms dwell time, and 90° takeoff angle). The spectra were

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Scheme 2. Free Radical, Photoinitiated Synthesis of Poly(NIPAAM-*co*-NaMAA) (3:1) Copolymer Brushes by a "Grafting-from" Approach, Using a Self-assembled Layer of Azo Initiator (1)

(AIBN)-type initiator (1)

+

NIPAAM   **NaMAA**
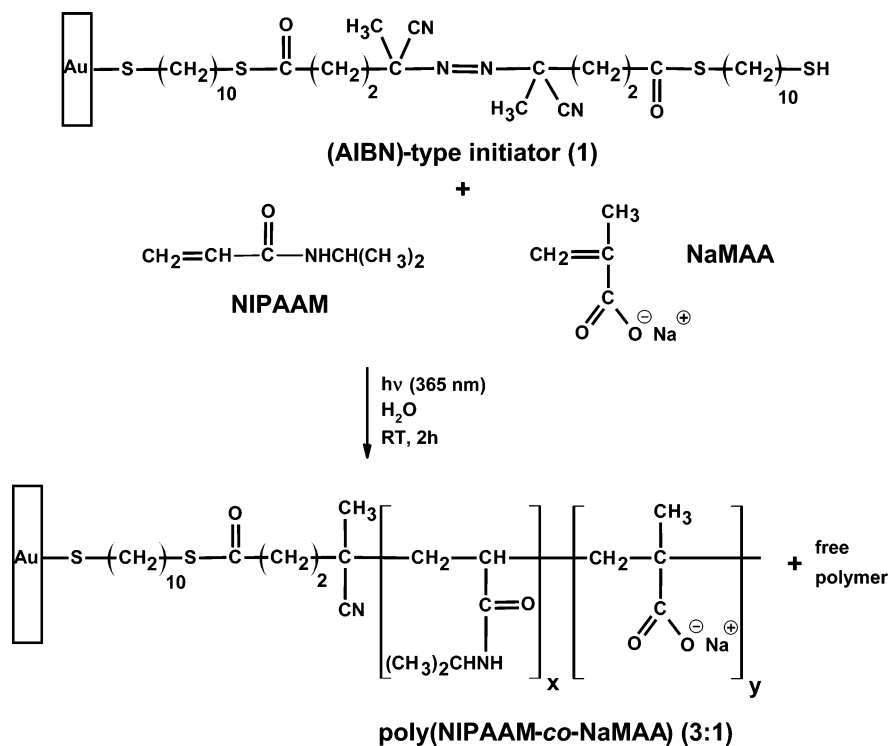
hν (365 nm)
H₂O
RT, 2h

poly(NIPAAM-*co*-NaMAA) (3:1)

Table 1. Molar Concentration of MAA in the Comonomer Feed and Corresponding molar Concentration in the Resulting Copolymer as Determined by XPS

MAA in feed (mol %)	MAA in copolymer (by XPS) (mol %)
8.6	3.8
30.2	22.0
49.5	42.1

analyzed off-line with CasaXPS software (Casa Software Ltd., Ver. 2.2.79). The results, summarized in Table 1, suggest that the MAA fraction in the copolymer is in all cases somewhat smaller than the MAA fraction in the monomer feed, and that the copolymer composition depends linearly on comonomer feed composition over the observed range of feed ratios. Our observations are in line with findings by Zhou and Chu on the copolymer composition of pNIPAAm/MAA microgels that were prepared by free radical precipitation polymerization.[20] Using a linear interpolation, we calculated our pNIPAAm/MAA copolymer composition as 76.0 mol % NIPAAm and 24.0 mol % MAA; i.e., ∼(3:1).

Atomic Force Microscopy. AFM images were obtained by contact mode imaging using V-shaped silicon nitride cantilevers (Nano-Probe, Veeco, Santa Barbara, CA; spring constant 0.12 N/m, tip radius 20−60 nm) using a MultiMode and a Dimension 3100 SPM (Veeco, Santa Barbara, CA). Topographic imaging was performed in air, in water at pH 4.0, in water at pH 9.0, and in water with varying salt concentration. Image forces were kept below 1 nN to minimize compression and damage to the polymer brushes. 0.1 M HCl or 0.1 M NaOH was used to adjust pH, and a 0.2 M KCl stock solution was used to prepare solutions of different ionic strengths by dilution. After the ionic strength was adjusted to the desired value, the solution pH was checked and adjusted as necessary. Before AFM measurements, substrates were ion-exchanged by immersion (3 times for 2 min) in a solution that had the same pH and salt concentration as that in the fluid cell of the

AFM. To avoid salt crystal formation due to evaporative losses, we rinsed the substrates with MQ-grade water after each dipping cycle, and after the final water rinse, we rinsed with methanol and dried the substrates in a stream of nitrogen gas.

Results and Discussion

We report the fabrication of micro- and nanopatterned pH- and salt-sensitive poly(NIPAAM-*co*-NaMAA) (3:1) copolymer brushes with lateral dimension ranging from 550 nm to 3.4 μm. We used 30 mol % methacrylic acid (MAA) comonomer in the feed to confer pH and salt sensitivity to the brush; similar molar concentrations have been used successfully for the preparation of pH-sensitive microgel particles.[20−22] Here, we show that micro- and nanopatterned polymer brushes that contain a weak acid or base can undergo large conformational changes in response to changes in solution pH or ionic strength, which suggests the potential of these patterned brushes for actuation and sensing applications.[2,3]

Effect of pH. It is well-known that poly(methacrylic acid) (PMAA) can undergo a marked pH-induced conformational transition in solution.[23] In aqueous media and at low pH, PMAA chains are charge neutral and adopt a compact form, minimizing hydrophobic interactions. At high pH (large degree of ionization) and in the absence of electrolytes, PMAA chains open to an expanded random coil. Thus, the swelling/collapsing behavior of PMAA brushes should be highly pH- and salt-sensitive. Figures 1a and 1b show that

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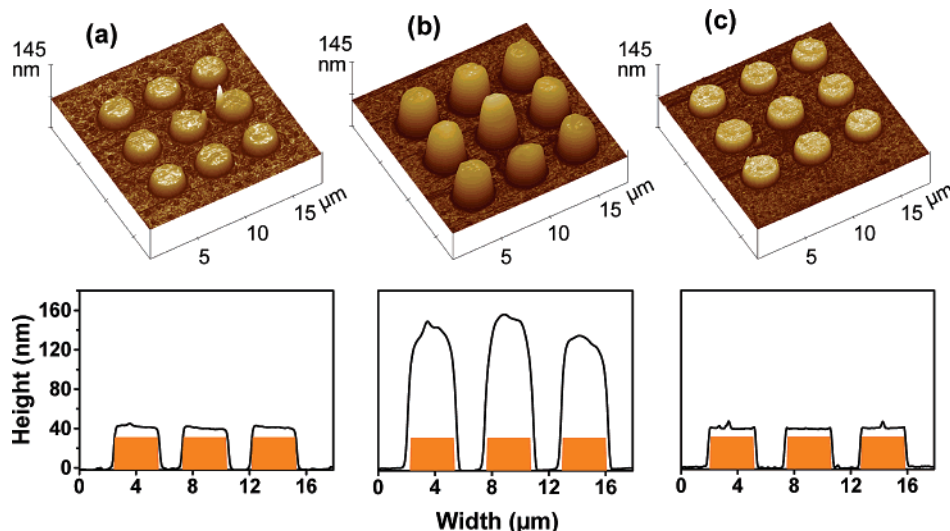(23) Olea, A. F.; Thomas, J. K. *Macromolecules* **1989,** *22,* 1165−1169.

Figure 1. AFM contact mode height images of a poly(NIPAAM-*co*-MAA) brush dot array (3.4 µm feature size) and the corresponding average-height profiles imaged at ~28−30 °C in (a) air (9 nm high after subtraction of 31 nm for the Au−Cr layer), in (b) water at pH 9.0 (112 nm high), and in (c) water at pH 4.0 (9 nm) (2 h polymerization time). The filled squares in the cross-sectional profiles indicate the underlying 31 nm high and 3.0 µm wide Au micropatterned features.
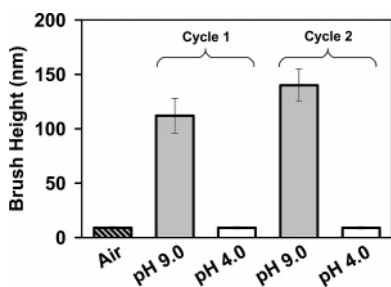

Figure 2. Average height of poly(NIPAAM-*co*-MAA) copolymer brush dot array (3.4 µm feature size) in air (patterned bar; brush collapsed) and for two consecutive, cyclic exposures to water at pH 9.0 (gray bars; brush swollen) and water at pH 4.0 (white bar; brush collapsed).

when a dry polymer brush (9 nm, after substraction of 31 nm for the Au−Cr layer) is exposed to MQ-water at pH 9.0, the polymer brush swells by more than 1 order of magnitude to a height of about 112 nm.

The effect of two extreme pH conditions on the conformation of a micropatterned, stimulus-responsive poly(NIPAAM-*co*-MAA) brush is shown in Figures 1b and 1c. At high pH (pH 9.0) the carboxylic acid groups on the MAA comonomer are completely dissociated (pK_a of ~5.0), causing a large charge density inside the brush. The osmotic pressure buildup, caused by the counterions in the brush, leads to significant chain stretching,[2] and consequently, the average brush height increases dramatically. The average brush height at pH 9 is about 112 nm (Figure 1b). After the brush is exposed to low pH (pH 4.0), it adopts a collapsed conformation with an average height of only about 9 nm (Figure 1c), indistinguishable from the average dry height (Figure 1a). This suggests that at low pH almost all hydration water has left the protonated brush. Cyclic exposure of the patterned brushes to solutions of low pH (pH 4.0) and high pH (pH 9.0) showed that the pH-induced phase transition is quite reversible (Figure 2). The small increase in brush height in the second solvent exchange cycle can most likely be explained by differences in the normal forces applied during imaging the soft, swollen brush structures. Hydrated polymer brushes are soft and susceptible to compression; thus, even

small differences in applied normal force during imaging can affect the measured brush heights. We note that the pH was adjusted over the desired range (pH 4.0−9.0) while maintaining the ionic strength of the solution almost constant. The magnitude of the pH-induced height change for the micropatterned poly(NIPAAM-*co*-MAA) brush is significantly larger than that elicited by a co-nonsolvent (MeOH) on a patterned poly(NIPAAM) homopolymer brush that we reported earlier.[24−26] This also agrees with observations made on charged polymer gels, where the degree of swelling in comparison to that of a neutral gel dramatically increases with increasing amounts of ionizable groups.[20] While one would initially expect that, particularly at low pH, a poly-(NIPAAM-*co*-MAA) copolymer brush would also be temperature-sensitive, this was not observed. This is explained by the effect of the MAA comonomer on the poly(NIPAAM) transition temperature and, more importantly, the temperature sensitivity, which are shifted and reduced with increasing MAA concentrations to smaller values.[20] For our copolymer brush with 24 mol % of MAA, the poly(NIPAAM) copolymer remains in a collapsed state at low pH and the AFM imaging temperature (~28−30 °C) used.

Effect of Ionic Strength. We also studied the influence of ionic strength on the conformational mechanics of a fully dissociated poly(NIPAAM-*co*-MAA) (3:1) copolymer brush grown from a micropatterned dot array (dot diameter 1.2 µm) (Figure 3). At pH 9, and in the absence of added electrolyte, the carboxyl groups are fully dissociated and the polymer brush adopts an extended conformation with an average height of about 69 nm (after subtraction of 31 nm for the Au−Cr layer). Figure 3d shows that the brush height decreases dramatically with increasing salt concentration (added KCl) and is explained by the increased screening of

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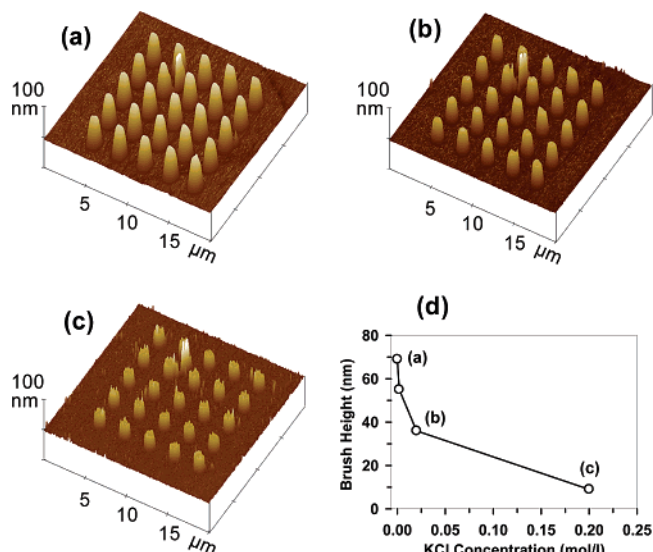
Figure 3. AFM contact mode height images of a poly(NIPAAM-*co*-MAA) brush dot array (1.2 μm feature size) imaged at ~28−30 °C in water at pH 9.0 in (a) absence of KCl (69 nm high after subtraction of 31 nm for the Au−Cr layer), in (b) 0.02 M KCl (36 nm high), and in (c) 0.2 M KCl (9 nm high). (d) Average brush height plotted as a function of salt (KCl) concentration in water at pH 9.0 (the solid line in (d) is a guide to the eye).

the charged COO⁻ groups. At a KCl concentration of 0.2 mol/L (screening length ~0.7 nm), a strongly collapsed state is reached with a brush height of only about 9 nm.

The contribution of the temperature-sensitive NIPAAM comonomer to the salt-induced collapse of the poly(NIPAAM-*co*-MAA) copolymer brush is negligible at the low salt concentrations (KCl ≤ 0.2 mol/L) used here. This is also supported by work of Brooks et al.[27] that showed that the hydrodynamic thickness of particles decorated with a homopolymer poly(NIPAAM) layer remained unchanged at NaCl concentrations below 0.8 mol/L.

Effect of Pattern Size. When we reduced the lateral dimension of the Au templates to the sub-micrometer length scale, we observed that the heights of brushes synthesized on nanopatterns and subjected to high pH and low ionic strengths were significantly smaller than those of brushes synthesized on the micropatterns under otherwise identical polymerization conditions (Figure 4). We also noticed that the copolymer brushes grown on top of the Au templates respond strongly to external stimuli (pH and salt), whereas the dimensional response of the brushes grown on the sides of the Au templates are significantly smaller (Figure 1). These observations agree with our previous work,[26] where we argue that at constant grafting density a polymer brush in good solvent adopts a vertically less ordered and laterally more extended conformation, induced by the lack of lateral restraint the brush experiences at its boundaries, leading to less chain crowding and thus less chain stretching. Patra and Linse[28] have recently confirmed this hypothesis by molecular dynamics simulations (MD) of patterned homopolymer

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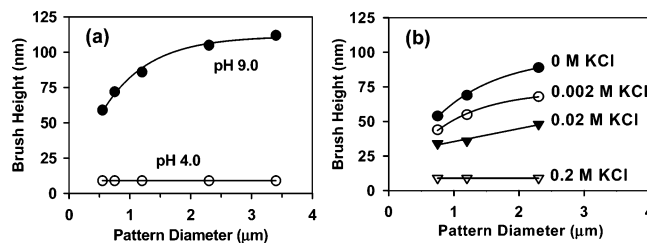(28) Patra, M.; Linse, P. *Nano Lett.* **2005**, *6*, 133−134.

Figure 4. Average height of patterned poly(NIPAAM-*co*-MAA) copolymer brushes plotted as a function of the lateral dimension of the underlying pattern footprint: (a) in water at pH 9.0 (closed circles; brush swollen) and in water at pH 4.0 (open circles; brush collapsed); (b) in water at pH 9.0, in the absence of KCl (closed circles; brush swollen); in 0.002 M KCl (open circles); in 0.02 M KCl (closed triangles), and in 0.2 M KCl (open triangles, brush collapsed). The average brush heights at pH 9.0 in the absence of KCl in Figures 4a and 4b differ slightly because the brushes were prepared on two different substrates, under otherwise identical fabrication and polymerization conditions.

brushes. Their simulations revealed that the polymer brush height (segment density profile) is a function of grafting density and depends strongly on pattern footprint size. For patterns with small lateral extent, the brush lacks conformational constraint and deforms significantly near the pattern edges.

Conclusions

We demonstrated a simple "top-down/bottom-up" strategy to fabricate nano- and micropatterned polymer brush arrays composed of pH- and salt-sensitive, weak polyelectrolyte copolymers (poly(*N*-isopropylacrylamide-*co*-methacrylic acid, 3:1). In our approach, a silicon surface is first patterned with gold, using "lift-off" electron-beam lithography ("top-down"), and the resulting pattern is then amplified by surface-initiated photopolymerization by conventional, UV-light-induced free radical polymerization ("bottom-up") from an immobilized 2,2′-azobisisobutyronitrile (AIBN) type initiator. We have shown that the use of a pH- and salt-sensitive monomer in a copolymer brush enables large, triggerable conformational changes of micro- and nanopatterned polymer brushes. We also observed that the height of nanopatterned ionized polymer brushes increases with increasing pattern feature size. It is clear that, with the current trend in fabricating and manipulating polymer nanostructures on surfaces, an understanding and prediction of this size-dependent phenomena is essential. The design and fabrication of surfaces with conformationally switchable, patterned polymeric structures is important for sensing and actuation applications on the micro- and nanoscales. For example, our patterned stimulus-responsive polymer brushes can be used as sensors, switches, or mechano-chemical actuators.