# Polymer Brushes with Phototriggered and Phototunable Swelling and pH Response[a]

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Photolabile polymer brushes with tailored length containing a photoremovable protecting group (NVOC) are prepared via the SI-ATRP method. Upon light irradiation, the NVOC group is removed to generate controlled densities of free amine groups (PAMA) randomly distributed along the brush. The presence of the ionizable groups induces a photo-triggered swelling response. The swelling degree can be tuned by the irradiation dose. A dual (light and pH), tunable response is demonstrated.
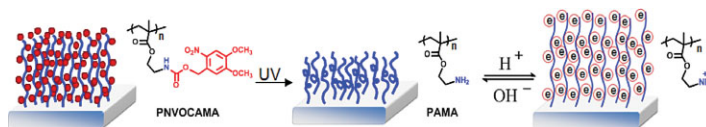
Introduction

Polymer brushes allow surface properties, such as wettability, biocompatibility, cell, bacteria or protein resistance, adhesion or lubrication, to be tailored due to their varied chemical composition and functionality.[1] When stimulus-responsive chains are used,[2] the physicochemical properties of the brush can be changed upon application of a external field (temperature,[3] pH and ionic strength,[4] particular solutes (i.e., glucose),[5] light,[6] voltage[7] or a combination of two of these[8]) that triggers the transition between the extended and the collapsed states. Applications of these systems in microfluidics,[9] mechanical actuators,[10] cell culture technologies,[11] anti-fog systems[12] or in membranes for separation technologies[13] have been envisioned and in part demonstrated.

Amongst the different stimuli, light offers particular advantages for triggering a brush response. Precise spatial and temporal control and tunable dosage, remote modula-tion, room temperature operation and biocompatibility can be achieved if excitation occurs at wavelengths longer than 320 nm.[14] The reported photoresponsive brushes are based either on the azobenzene unit to photoinduce molecular reorientations in the brush,[6e,f] or on photo-removable chromophores that generate ionizable and charged groups along the brush upon light exposure by different mechanisms: (i) release of a photolabile group attached to side chain COOH groups;[6b] (ii) hydrolysis of t-butyl esters by means of neighbouring photoacid generators;[9] (iii) isomerization of side-chain spiropyran moieties.[6d,e] Charge generation in the brush structure after irradiation increased hydrophilicity at the exposed regions and significant wettability changes were demonstrated in all cases. However, no evidence of a tunable response was seen and no analysis of the brush conformational changes upon controlled light exposure were reported. In this work we describe a light-responsive brush obtained from the surface-initiated ATRP of methacrylate monomers containing ionizable $-NH_2$ side groups that are caged with the photoremovable group 4,5-dimethoxy-2-nitrobenzyl (NVOC). In the caged form, the polymer brush (PNVOCAMA) is neutral and hydrophobic due to the presence of the aromatic chromophore. Upon irradiation, the NVOC group is removed and a polycation (poly(2-aminoethyl methacrylate), PAMA) chain is generated. As a consequence, the brush can swell or collapse depending on the pH (dual response). We demonstrate here (i) a phototunable response and (ii) a phototriggered pH-tunable response.

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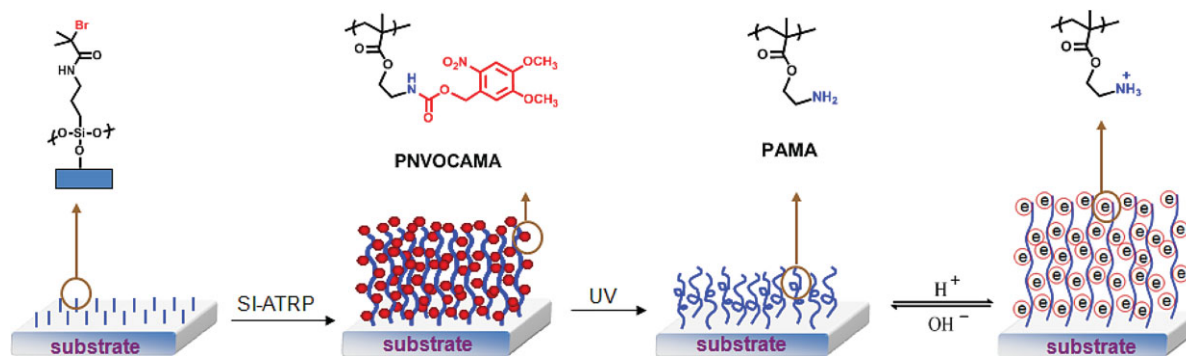
■ *Scheme 1.* Schematic of the chemical structure, photolysis and swelling processes of the photosensitive polymer brush PNCOCAMA.

Results and Discussion

Synthesis and Characterization of PNVOCAMA Brushes

The structure of the monomer and polymer brush is presented in Scheme 1 and the synthesis is described in the Supporting Information. Polymer brushes were prepared by surface-initiated ATRP (SI-ATRP) on quartz slides.[15] The growth of the polymer brush was followed with UV spectroscopy.[16] The UV absorbance (i.e., the brush thickness) increased linearly with polymerization time during the first 13 h and slowed down for longer reaction times (see Figure S1 in the Supporting Information). The film thickness in the dry state was 8 nm (40 h reaction), as measured in a scratch-test with AFM. In order to estimate the molecular weight of the brush, free initiator PEGBr was added into the SI-ATRP solution and after 13 h polymerization in solution the obtained polymer was isolated and characterized. PNVOCAMA chains with a molecular weight ($\overline{M}_n$) of 8900 g·mol^{-1} and a polydispersity index (PDI) of 1.52 were obtained. The PDI was obtained by GPC and $\overline{M}_n$ was determined from the ratio between the integration of the ^{1}H NMR signals of the aromatic protons (6.5–7.8 ppm) and the alkyl protons corresponding to the initiator (2.8–4.4 ppm). Assuming that the chains generated from free initiator in solution have the same molecular weight as those from free initiator at the surface,[17] the grafting density of the brushes at the surface, Γ, was estimated from the UV absorbance according to Equation (1):[18]

$$\Gamma = 1/2[A_\lambda \varepsilon_\lambda^{-1} n^{-1} N_A] \qquad (1)$$

where A_λ is the absorbance at a given wavelength, ε_λ is the molar extinction coefficient of the chromophore in solution at λ, n is the average degree of polymerization and N_A is Avogadro's number. The factor 1/2 refers to the fact that the quartz slides are modified on both sides. Taking $\varepsilon_{348} = 6300$ M^{-1}·cm^{-1} (as measured from solution experiments), an average grafting density of 0.34

chains·nm^{-2} was obtained. For comparison, the reported grafting density for SI-ATRP synthesized poly(methyl methacrylate) brushes is 0.3–0.8 chains·nm^{-2}, and for poly[2-(2-methoxyethoxy)ethyl methacrylate] (containing bulkier side groups) is 0.33 chains·nm^{-2}.[19]

Light Exposure and Uncaging Reaction

Substrates modified with PNVOCAMA brushes were irradiated at 365 nm (4.7 mW·cm^{-2}). Light exposure cleaved the NVOC from the PNVOCAMA chain (Scheme 1). The removal of the chromophore after exposure and a washing step was reflected in a decay of the UV absorbance of the substrates (Figure 1). The photolytic reaction was almost completed after 10 min irradiation, i.e., longer irradiation times did not significantly change the UV spectrum of the substrate. A residual absorbance
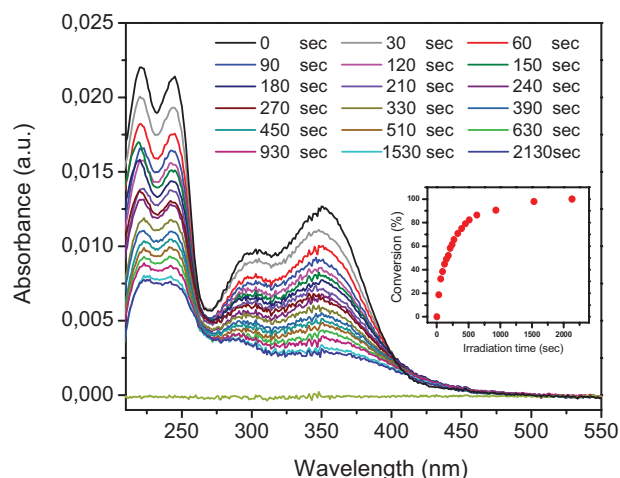

Figure 1. UV spectra after light exposure and washing of quartz substrates modified with PNVOCAMA and irradiated for increasing times. The inset represents the conversion (%) of the photolytic reaction as calculated from the absorbance values at $\lambda_{max} = 348$ nm assuming full conversion (100% chemical yield) for 2130 s. The brush was obtained with a polymerization time of 13 h.

was still detected and was associated with photolytic products retained in the brush structure or to a possible side-reaction between the benzaldehyde photofragment and the free amine group on the brush that reattaches the chromophore to the surface. This has been already reported for amines protected with the same cage.[22] The conversion of the photolytic reaction for the different exposure times was calculated and is represented in Figure 1. Following the photokinetic equation model for photolysis at surfaces,[20] the quantum yield of the uncaging reaction was obtained from the conversion curves. A quantum yield (Φ_{365}) of 0.026 was obtained, in agreement with reported quantum yield values from solution experiments (0.023[21]) and suggesting that the caged group maintains similar activity when attached to the polymer brush.

Light-triggered Exposure of Ionizable Groups and Photo- and pH-tunable Swelling of the Polymer Brush

A quartz crystal microbalance (QCM) was employed for in situ monitoring of interfacial gravimetric and viscoelastic changes in PNVOCAMA brushes under light irradiation and pH cycling. To this end, we used a window-cell for the experiments that allowed direct illumination of the QCM crystal during measurements.

Figure 2(a) represents the Δf and ΔD of the PNVOCAMA brush during light exposure at pH 4. The uncaging of PNVOCAMA brushes caused an initial steep change in frequency and dissipation curves, indicating a rapid gravimetric/viscoelastic change upon irradiation. This stage was followed by a slower increase in rate for the dissipation, whereas the frequency reached a plateau after 50 min irradiation. The photolytic reaction generated a hydrophilic brush with charged ammonium side groups that swelled and took up water at pH 4. The detected mass increase corresponds to the balance between the water uptake and loss of chromophore from the brush layer. The apparent mass increase after the photodeprotection, as calculated by the Sauerbrey equation, was $\approx 310 \ ng \cdot cm^{-2}$. It is worth noticing that QCM crystals modified with caged (hydrophobic) brushes did not show any variation in Δf or ΔD at different pHs, indicating that the brush is not swollen in the 100×10^{-3} M KCl aqueous electrolyte solution (inset in Figure 2(a)).

The D factor is defined as the ratio between the energy dissipated per cycle of oscillation and the total energy stored in the oscillating system, that is, sensor surface + film. During recent years there has been an increased effort to understand and relate dissipative losses (changes in D) to physical processes (interfacial and/or internal friction) occurring at polymeric interfacial layers.[23] If the immobilized film is rigidly anchored, implying no changes in the coupling between the sensor and the liquid environment, no changes in the energy dissipation are detected. On the
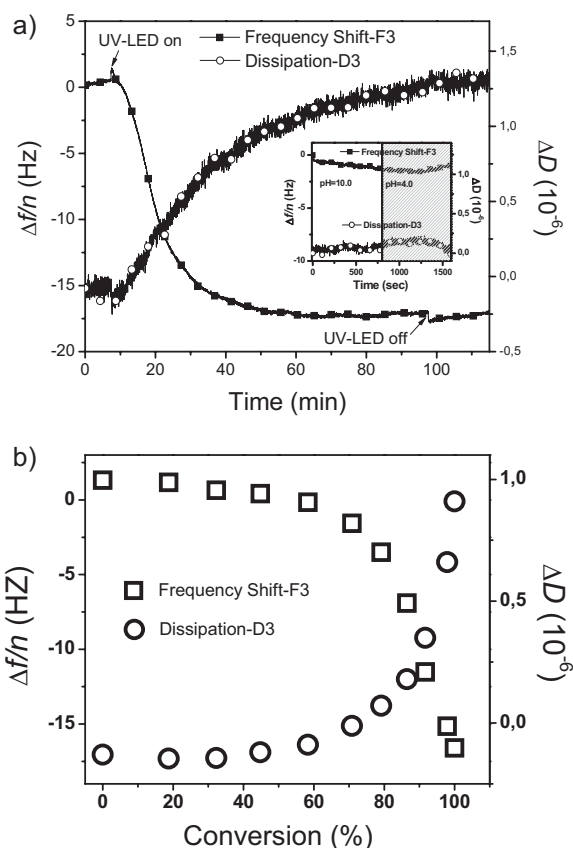
Figure 2. (a) The Δf and ΔD of the third overtone of a SiO$_2$ QCM crystal coated with PNVOCAMA brush under irradiation in buffer at pH 4. The inset represents PNVOCAMA brush under different pHs. Note that a different intensity as in Figure 1 was used for irradiation and therefore irradiation times are not the same. The brush was obtained with a polymerization time of 13 h; (b) the Δf- and ΔD-versus conversion plots.

other hand, D may suffer significant changes if the deposited film is not rigidly attached to the oscillating sensor surface. In other words, a soft film attached to the quartz crystal is deformed during the oscillation and this renders high dissipation values, while a rigid material is associated with low dissipation values. In the case of the photo-triggered uncaging of PNVOCAMA brushes, the changes in D upon irradiation reflects structural changes in the film layer during the photochemical reaction. The increasing D indicates that the film changes its viscoelastic properties from a rigid to a soft state. This observation is in agreement with the idea of a hydrophobic brush that is gradually transforming into a hydrophilic layer and strongly interacting with the aqueous environment (brush hydration + water uptake). Interestingly, these structural changes occur even after 50 min of irradiation (after 100% conversion), when the frequency curve has already reached a plateau, suggesting that the "softening" of the uncaged brush layer in the final stages might be mostly driven by

film reorganization without implying significant mass changes.

Figure 2(b) displays Δf and ΔD values corresponding to different photolytic conversions. It is evident that water uptake (which implicitly indicates the brush swelling) does not linearly correlate with the uncaging ratio. In fact, photoconversions of up to 50% promoted only slight changes in mass. However, photodeprotection degrees beyond 50% were associated with drastic frequency and dissipation changes, which could be attributed to a significant solvent uptake. This experimental observation can be explained by considering a threshold density of amine groups in the brush above which the brush changes from hydrophobic (i.e., non-swelling) to hydrophilic. The light-tunable swelling and pH response is, therefore, only effective between 50 and 100% conversion values.

Figure 3 shows the pH-sensitivity of the fully uncaged PNVOCAMA brush, i.e., the PAMA brush. At pH 4, the brush was highly charged and adopted a swollen conformation, taking up a significant amount of solvent.[24] By increasing the pH, the charged ammonium groups in the brush turned into non-charged amines and, consequently, the brush collapsed. The gradual increase in frequency upon increasing the pH (Figure 3) is related to the loss of solvent from the polyelectrolyte brush during the collapse process. In a similar vein, the decrease in the dissipation can be understood as a change from a rather soft polymer film (viscoelastically coupled to the solution) to a more rigid collapsed structure. As expected, the sharpest frequency changes occured in the $7 < \mathrm{pH} < 8$ range (close to the pK_a of the amino groups), thus confirming that the uncaging reaction yielded PAMA brushes.[25] It should also be noted that when the pH was returned to 4, the value of Δf also returned to the previous one, indicating that the swelling-collapse process was fully reversible.
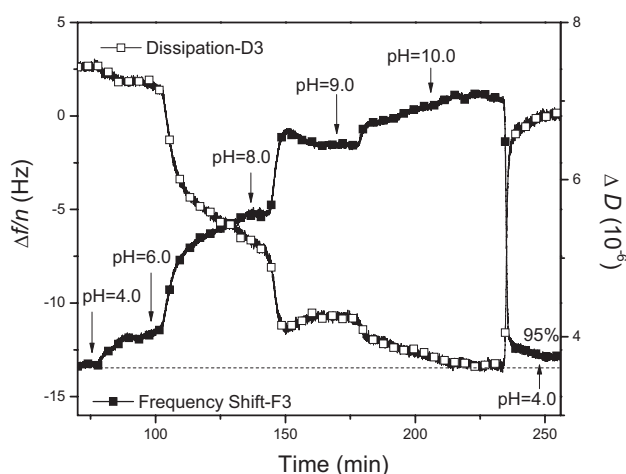
Conclusion

Photolabile polymer brushes with tailored length containing a photoremovable protecting group (NVOC) were prepared via the SI-ATRP method. Upon light irradiation, the NVOC group was removed to generate controlled densities of free amine groups (PAMA) randomly distributed along the brush. The presence of the ionizable groups induced a photo-triggered swelling response. The swelling degree could be controlled by the irradiation dose. A dual response (light and pH) was demonstrated. Our novel systems may have interesting properties for phototriggered biolubrication, wettability, adhesion or remote actuation.

Figure 3. The Δf and ΔD of the third overtone of a SiO$_2$ QCM crystal coated with PAMA obtained from PNVOCAMA brush at different pHs.

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