

Photoresponsive Polymer Brushes for Hydrophilic Patterning

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The use of photolabile protecting groups (PGs) as a means to create latent hydrophilic surfaces is presented. Naturally hydrophobic PGs, based on *o*-nitrobenzyl chemistry, are used on polymer side chains, poised for cleavage upon exposure to UV light. Removal of the PGs liberates the hydrophilic polymer, thereby switching the surface wettability from hydrophobic to hydrophilic. This switch can be augmented by increasing the surface roughness. Additionally, this system is also shown to be spatially addressable, a highly desirable property for applications which require specific regions of a surface to switch their wettability.

Introduction

Light is one of the least invasive stimuli available in order to elicit responsive behavior. Light can be used to perform direct chemical modification, or indirect modification by generating reactants in situ which will ultimately perform the desired modification.^{1–5} Biomolecular research is an area of science in which photochemistry has played a pivotal role. An abundance of protecting groups have been generated for specific biomolecular reactions,^{6–11} with the photolabile protecting groups (PGs) taking precedence when light-sensitive compounds such as tryptophan or nucleosides are present.^{12–14} Typically, ultraviolet light with a wavelength between 315 and 380 nm (UVA) is employed, since its relatively long wavelength, in terms of bond cleavage capabilities, will result in targeted PG removal without causing damage to the rest of the molecule.^{15–17} An interesting illustration of this particular strategy was demonstrated by Fodor and co-

workers, in which they used photolabile PGs to fabricate oligonucleotide arrays through light-directed spatially addressable parallel chemical synthesis in the solid state.¹⁷

Polymers and monolayers utilizing direct chemical modification upon exposure to light have also been reported. Of particular interest were the examples in which a hydrophilic group was released upon removal of a hydrophobic PG after exposure to a mild UV source.^{17–21} The cumulative effect of changes on each monomeric unit within a surface tethered polymer film can bring forth a significant change in polymer properties. As such, polymers taking advantage of this type of mild photochemistry were envisaged as potential responsive surfaces. Naturally hydrophobic polymers, containing side chains capped with photolabile PGs, would reveal their latent hydrophilic nature upon exposure to UVA, a noninvasive stimulus. Confinement of these polymers to a surface should result in a wettability change dependent upon the external stimulus (UVA radiation). This UV-induced change in surface properties could be used to manipulate fluid flow through microdevices.^{22,23}

The design and synthesis of photoresponsive monomers and their subsequent surface initiated polymerization will be discussed. The ability to create an irreversible switch in surface wettability upon UV irradiation, and the ability to spatially pattern this wettability, will be shown.

Experimental Section

Materials and Methods. All chemicals were of analytical reagent grade, unless otherwise stated, and were used as received from Aldrich or Lancaster. Solvents were distilled prior to use, except ethanol, methanol, and DMSO (Fisher), which were of analytical reagent grade and used as received. Deionized water with a resistance of 18.2 MΩ·cm was obtained from a Millipore Simplicity 185 system. Monomers were stored in the dark at 4 °C until required. Copper(I) bromide (99.999%) was stored under vacuum until needed. TEM fine mesh nickel grids, size 2000, with pitch = 12.5 μm, hole = 7.5

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μm , and bar = 5 μm , were obtained from Agar Scientific, U.K. Fumed silica beads, Cabosil M5, BET surface area = 200 m^2/g , were obtained from Cabot Corp. (Univar, Cheadle), U.K. Silicon wafers (Compart Technology Ltd., 100 mm diameter, boron-doped, $\langle 100 \rangle$ orientation, one side polished), and quartz substrates (UQG optics Ltd., Spectrosil 2000) were cleaned using an Emitech K1050X Plasma Asher in air plasma mode, 100 W, for 10 min prior to use. Thin layer chromatography (TLC) was performed using glass plates coated with a 250 μm layer of silica gel 60 (Merck). TLC spots were visualized under short-wave UV light or by developing the plate thermally after being dipped in ceric sulfate solution.

Ellipsometric measurements were carried out on a DRE ELX-02C ellipsometer with a 632.8 nm laser at 70° from the normal. Refractive indices of 1.45 and 1.5 were used for initiator and polymer layers, respectively. At least five different measurements per sample were taken with their average and standard deviation values reported. Contact angle goniometry was performed using a homemade stage with a computer-controlled microsyringe and digital camera. Infusion and withdrawal rates of 4 $\mu\text{L min}^{-1}$ were used. At least three different measurements per sample were taken with their average and standard deviation values reported. Fourier transform infrared (FTIR) spectra of compounds were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer. FTIR spectra of surface polymers were recorded in transmission mode using bare Si wafer as the background on a Bio-Rad FTS 6000 spectrometer. UV spectra were recorded on a Varian Cary 4000 UV-vis spectrometer. Optical microscopy was performed with a Nikon DN100 digital net camera attached to a Nikon Eclipse ME600 microscope. ^1H , and ^{13}C NMR spectra were collected using a Bruker AVANCE 500 CRYO Ultrashield spectrometer. Shift values were recorded as chemical shift (δ , ppm) relative to Me_4Si . Relative integral, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), coupling constants (in Hz), and acquisition frequency were assigned where possible. Melting points were taken using a Gallenkamp melting point apparatus. UV reactions were performed using a UVP Blak-Ray B100 (100 W, 115 V, 350–380 nm) AP lamp.

Synthesis of 4,5-Dimethoxy-2-nitrobenzyl Methacrylate. A solution of methacryloyl chloride (6.6 cm^3 , 67 mmol) in dry DMF (10.0 cm^3) was added dropwise to a mixture of 4,5-dimethoxy-2-nitrobenzyl alcohol (13.0 g, 61 mmol) and *N,N'*-diisopropylethylenediamine (16.3 cm^3 , 91 mmol) in dry DMF (70 cm^3) at 0 °C under nitrogen. The solution was stirred for 1 h at 0 °C and then overnight at room temperature. The solvent was removed in vacuo; the crude crystals were washed with HCl (0.01 M aqueous; 100 cm^3) and filtered. The crystals were redissolved in CHCl_3 (100 cm^3) and washed with H_2O (50 cm^3) until the yellow aqueous layers became colorless. The combined aqueous layers were extracted with CHCl_3 (20 cm^3). The combined organic layers were washed with NaHCO_3 (saturated aqueous, 20 cm^3), dried over anhydrous MgSO_4 , and filtered. The dried organic phase was passed through a silica plug and the solvent removed in vacuo. The product was then recrystallized from hot ethanol, filtered, washed with ice-cold water ($2 \times 25 \text{ cm}^3$), and dried, to yield 4,5-dimethoxy-2-nitrobenzyl methacrylate as pink crystals (12.3 g, 72%). The product was stored at 4 °C in the dark.

R_f (1:1, hexane:ethyl acetate) 0.51; mp 120–121 °C (EtOH). Elemental analysis: Found; C, 55.3; H, 5.4; N, 4.9. $\text{C}_{13}\text{H}_{15}\text{NO}_6$ requires C, 55.5; H, 5.4; N, 5.0; O, 34.1%. λ_{max} (CHCl_3)/nm 243 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 10 990), 302 (4920), 343, (6580). $\nu_{\text{max}}/\text{cm}^{-1}$ 1708s (α,β -unsaturated ester), 1580s (conj aromatic), 1522s (anti- NO_2), and 1324s (symm- NO_2). $^1\text{H NMR}$ δ (500 MHz; CDCl_3): 1.99 (3 H, t, J 1.2, CH_3), 3.94 (3 H, s, OCH_3), 3.95 (3 H, s, OCH_3), 5.58 (2 H, s, OCH_2), 5.64 (1 H, m, $\text{H}_2\text{C}=\text{C}$), 6.19 (1 H, m, $\text{H}_2\text{C}=\text{C}$), 7.02 (1 H, s, *HC*-aromatic), and 7.71 (1 H, s, *HC*-aromatic). $^{13}\text{C NMR}$ δ (125 MHz; APT; CDCl_3): 18.3 (CH_3), 56.3 (OCH_3), 56.4 (OCH_3), 63.4 (OCH_2), 108.2 (CH aromatic), 110.1 (CH aromatic), 126.2 ($\text{H}_2\text{C}=\text{C}$), 127.3 (C- CH_2 -O aromatic), 135.9 ($\text{H}_2\text{C}=\text{C}$), 139.9 ($\text{O}_2\text{N}-\text{C}$ aromatic), 148.1 (C- OCH_3 aromatic), 153.4 (C- OCH_3 aromatic) and 166.6 (C=O). m/z (ES) 304.0787 [(M + Na) $^+$. $\text{C}_{13}\text{H}_{15}\text{NO}_6\text{Na}$ requires 304.0797].

Synthesis of PNVOCA Brushes. 4,5-Dimethoxy-2-nitrobenzyl methacrylate (NVOCMA; 5 g, 18 mmol), CuBr_2 (4.0 mg, 0.018

mmol) and *N,N,N',N''*-pentamethyldiethylenetriamine (PM-DETA; 0.11 cm^3 , 0.53 mmol) were dissolved in DMSO (13.7 cm^3) at 90 °C and degassed by passing a continuous stream of dry nitrogen through the solution while stirring for 30 min. CuBr (25.5 mg, 0.18 mmol) was then added and the solution was degassed for a further 30 min. A silicon wafer coated with a silane initiator monolayer was prepared, as described elsewhere,²⁴ ready for surface-initiated atom transfer radical polymerization (SI-ATRP). Initiator-coated wafer samples (ca. 1 cm^2 each) were sealed in reaction vessels, degassed, and left at 90 °C under nitrogen. The polymerization solution was then injected into each reaction vessel, adding enough solution to submerge each substrate completely. After various polymerization times the samples were removed, washed with CH_2Cl_2 and methanol, and dried under a stream of nitrogen. The substrates were then stored in the dark, under nitrogen, until needed.

Polymerizations with different monomer concentrations were performed following the above procedure, changing the solvent volume to the appropriate value.

Silane ATRP Initiator Coating of Silica Beads. A solution of silane ATRP initiator,²⁴ (75 μL) in dry toluene (20 cm^3), was added to a suspension of fumed silica beads (1 g) and Et_3N (0.5 cm^3) in dry toluene (20 cm^3). The reaction was stirred at 21 °C under nitrogen for 24 h. The initiator-coated beads were collected by filtration and extensively washed with toluene. The beads were collected and dried under vacuum (1.09 g).

PNVOCA Growth on Beads. A polymerization solution was prepared as described for PNVOCA brushes grown from planar surfaces above. A monomer concentration of 2.6 M (1.5 g scale) was used. Once prepared, the polymerization solution was injected over initiator-coated silica beads (0.25 g) under nitrogen at 90 °C. Polymerization was left to proceed for 3 h, after which the particles were collected by filtration and extensively washed with CH_2Cl_2 and water and dried under vacuum.

Results and Discussion

Aromatic nitro moieties connected to a heteroatom via a methylene or methine carbon in the ortho position will readily undergo intramolecular photooxidation when exposed to UVA radiation. This chemistry has been widely used as a protecting group strategy for acidic,^{5,25} basic,^{14,26} and neutral moieties.^{14,16,18} The mechanism of cleavage is thought to be initiated by the UV excitation of the nitro group $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transition which creates a diradical species.²⁷ This is followed by intramolecular hydrogen abstraction from the ortho carbon by the oxygen radical (a 1,5-H shift), with eventual rearrangement to yield a 2-nitrosobenzaldehyde byproduct and the deprotected heteroatom, as shown in Figure 1.^{6,28}

Synthesis of a Photolabile Monomer. The synthesis of latent hydrophilic monomers protected by hydrophobic aromatic nitro groups was envisaged, taking into account the many factors which can influence their degradation.^{14,29,30} Since SI-ATRP provides a convenient route to covalently attach polymeric films, protected hydrophilic methacrylates (specifically methacrylic acid) were the most appropriate choice for target monomers. The monomer synthesized for this study was 4,5-dimethoxy-2-nitrobenzyl methacrylate (NVOCMA), a monomer based on the veratryl skeleton. Additional substituents on the aromatic ring, especially

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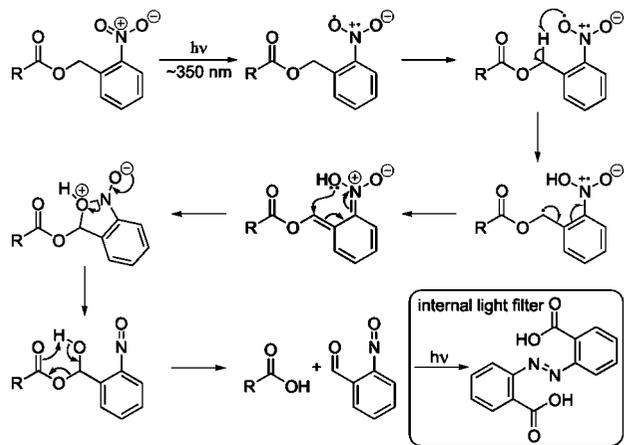


Figure 1. General mechanism of the cleavage of *o*-nitrobenzyl derivatives.

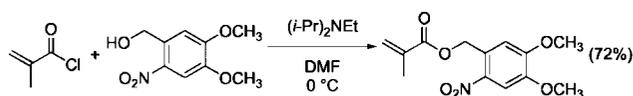


Figure 2. Synthesis of 4,5-dimethoxy-2-nitrobenzyl methacrylate (NVOCMA).

alkoxy groups, increase photosensitivity by shifting the absorption maximum closer to 365 nm,³¹ a less destructive UV wavelength for biological applications. The methoxy group of NVOCMA in the para position is electronically complementary to the nitro group. In this position the chromophore is extended, since the electron-donating group can easily delocalize through the benzene ring to the electron-withdrawing group. NVOCMA was synthesized in a one-step reaction (Figure 2), and easily purified by recrystallization from hot ethanol in good yield (72%). The product was collected as a pink crystalline solid, which is stable to degradation when stored at 4 °C in the dark.

Surface Polymerization of NVOCMA. NVOCMA was dissolved in ethyl acetate at room temperature and also in DMF and DMSO at 90 °C. It was found to be completely insoluble in methanol and water, typical solvents used for ATRP of methacrylates at ambient temperature.³² Using DMSO and DMF as solvents for ATRP has been shown to yield polymers grown with reasonable control and narrow molecular weight distributions.^{33,34} As such, SI-ATRP of NVOCMA in DMSO at 90 °C was first explored and is represented schematically in Figure 3.

A silane ATRP initiator-coated wafer was prepared as described in the literature.²⁴ ATRP solutions consisting of NVOCMA, *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA), CuBr, and CuBr₂, in a molar ratio of 100:3:1:0.1, at 90 °C were prepared. Initiator-coated substrates under nitrogen were then immersed in these polymerization solutions, and left to react at 90 °C under nitrogen for predetermined periods of time to yield poly(4,5-dimethoxy-2-nitrobenzyl methacrylate) (PNVOCMA) brushes. After surface polymerization the samples were washed with dichloromethane and methanol and dried with a stream of nitrogen. Typical contact angles of $\theta_{AW} = 75^\circ \pm 2^\circ$, $\theta_{SW} = 70^\circ \pm 1^\circ$, and $\theta_{RW} = 40^\circ \pm 3^\circ$ were observed (Figure 5), and the ellipsometric thicknesses are presented in Table 1. It can be seen that a 66% increase in polymerization time (6–9 h) results in a 66% increase

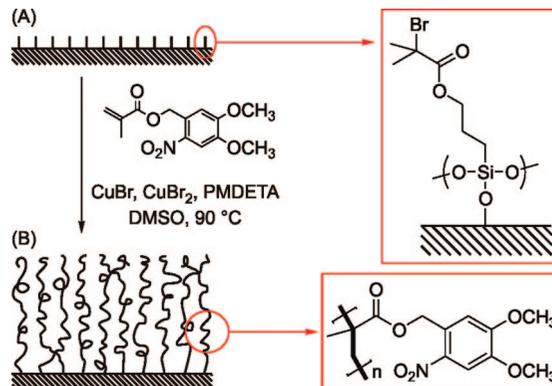


Figure 3. Schematic representing PNVOCMA brush synthesis from a silane initiator monolayer on silicon. (A) Silane initiator monolayer. (B) PNVOCMA brush.

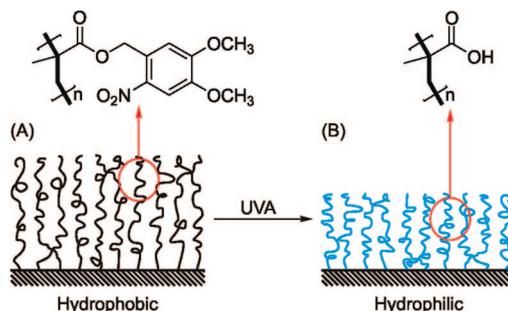


Figure 4. Chemical change that occurs when a PNVOCMA brush is converted to a PMAA brush upon exposure to UVA. (A) Hydrophobic PNVOCMA brush. (B) Hydrophilic PMAA brush.

Table 1. PNVOCMA Polymerization Conditions with Their Corresponding Ellipsometric Thicknesses

[NVOCMA] (M)	time (min)	thickness (nm)
2.6	6	8.7 ± 0.9
2.6	9	13.1 ± 0.4
1.3	9	11.4 ± 0.6

in ellipsometric thickness (8.7–13.1 nm) at a monomer concentration of 2.6 M. Doubling the solvent volume while keeping all other variables the same resulted in only a slight reduction in ellipsometric thickness. The increase in thickness, relative to those of the initiator monolayer (0.7–0.8 nm) is indicative of PNVOCMA brush growth.

The same polymerization method was used to grow PNVOCMA from quartz and silica beads with initiator-coated quartz or beads in place of the initiator-coated silicon wafer.

Responsive Testing of PNVOCMA Polymer Brushes. The synthesis and subsequent polymerization of photolabile monomers has provided a route to hydrophobic surfaces with the potential to switch to a more hydrophilic state in response to UVA radiation. This switch is represented schematically for the PNVOCMA brushes in Figure 4. Elimination of the *o*-nitrobenzyl units from the polymer side chains, following the mechanism detailed in Figure 1, should in principle lead to the formation of poly(methacrylic acid) (PMAA), and hence a polymer film of higher surface energy and therefore wettability.

PNVOCMA brushes, 11.4 ± 0.4 nm thick, were exposed to UV₃₆₅ for 10 min in the dry state and then washed with MilliQ water. The thickness reduced to 7.0 ± 0.3 nm, 61% of the original thickness. Exposure of a sample to UVA while immersed in a 1:1 water:methanol mixture gave a similar result. Further washing with 2 M NaOH and water resulted in a further reduction in

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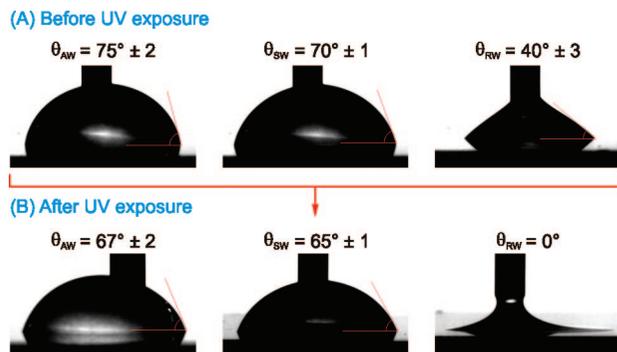


Figure 5. Change in the contact angles of a PNVOCA brush before and after UV₃₆₅ exposure for 10 min.

thickness to 3.8 ± 0.4 nm, 33% of the original thickness. If complete photolysis of the PNVOCA brush were to occur, creating the corresponding PMAA brush, it would proceed with a 60% concomitant loss of mass, since each starting monomeric unit has a molecular weight of 281 and each product unit a molecular weight of 86. If this change in mass is assumed to be proportional to thickness, thereby neglecting swelling and electrostatic effects, an 11.4 ± 0.4 nm thick PNVOCA brush would be expected to be reduced to ~ 3.5 nm upon complete photolysis. The ellipsometric data show that the photolytic step is not dependent on the presence of solvent;¹⁶ however, it does seem that solvent (and NaOH) are needed to aid the removal of cleaved byproducts. The post-UV exposed and washed polymer brushes were further analyzed by contact angle goniometry, UV-vis, and FTIR.

Decreases in all three contact angles were observed, as shown in Figure 5. The most striking change was seen for the receding contact angle, from $\theta_{RW} = 40^\circ \pm 3^\circ$ to $\theta_{RW} = 0^\circ$. Contact angle hysteresis ($\Delta\theta = \theta_{AW} - \theta_{RW}$) usually arises as a result of interactions between the surface and measuring solvent after it has spread over the surface.³⁵ It is observed for almost all cases since ideal surfaces (smooth, rigid, homogeneous) are difficult to achieve in reality. θ_{AW} is largely independent of surface reorganization since it measures the initial state of a surface upon contact with the solvent. However, θ_{RW} is very much influenced by surface reorganization since the contacting solvent has time to interact with the surface before measurement. As such, the value of $\Delta\theta$ is a good indication of the extent of solvent interaction with, and molecular reorganization of, the surface under study.^{36,37} For the PNVOCA brushes here, $\Delta\theta \sim 35^\circ$ before UV exposure while $\Delta\theta \sim 67^\circ$ after deprotection. This larger $\Delta\theta$ implies that the surface becomes more inclined to interact with the hydrophilic solvent, despite the small reduction in θ_{AW} after UV, supporting the hypothesis that the surface has been mostly deprotected to a hydrophilic PMAA state.

A comparison of the UV spectra before and after photolysis (together with monomeric NVOCMA 0.1 mM in chloroform) is shown in Figure 6. Brushes grown on quartz were synthesized in the same reaction vessels as those grown on silicon and are therefore assumed to be of an equivalent thickness. Brushes with a thickness of 11.4 nm were used for analysis. The characteristic peaks of the monomer at λ_{max} 243, 302, and 343 nm, can clearly be seen in the polymer brush at λ_{max} 245, 304, and 348 nm, indicating incorporation of the monomer without degradation. The minor bathochromic shift of the peaks is most likely due to

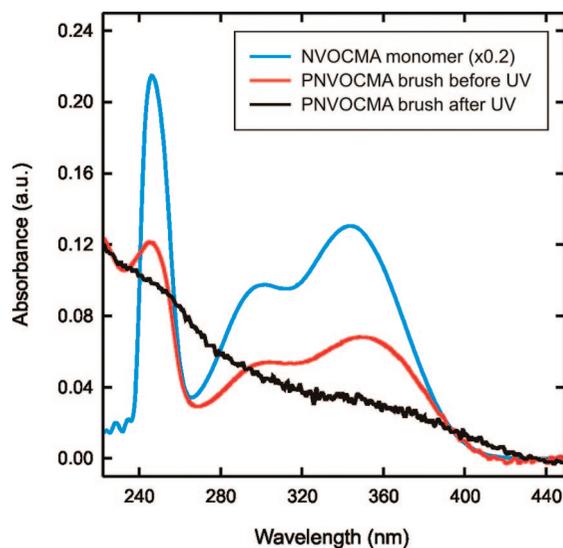


Figure 6. UV spectra of monomeric NVOCMA (0.1 mM in chloroform) and change in UV absorbance of a PNVOCA brush before and after UV₃₆₅ exposure for 10 min with subsequent washing with water. The spectrum of the monomer has been decreased by a factor of 5 for clarity.

the change in environment of the chromophores from a dilute chloroform solution to a polymer film. The UV absorbance (at 343 nm) from a brush grown on quartz decreased considerably upon UV switching, indicative of loss of the *o*-nitrobenzyl groups throughout the bulk of the film.

A comparison between the FTIR spectra of NVOCMA monomer, a PNVOCA brush, and the same brush after UV exposure is shown in Figure 7. The characteristic IR peaks of the monomer are present in the polymer brush. The peak at 1708 cm^{-1} in the monomer corresponds to the α,β -unsaturated carbonyl; the equivalent carbonyl peak in the polymer brush spectrum has shifted to 1733 cm^{-1} , as expected, due to the loss of conjugation. The remaining peaks at 1580 , 1523 , 1330 , and 1278 cm^{-1} corresponding to the conjugated aromatic ring, the symmetric nitro group stretch, the asymmetric nitro group stretch, and the methoxy C–O–C stretch, respectively, can be seen clearly in both spectra, further supporting the presence of a PNVOCA brush. After UV exposure a decrease in the intensity of the nitro group stretches at 1523 and 1330 cm^{-1} can be seen, indicating cleavage of the *o*-nitrobenzyl groups throughout the film. A broadening of the carbonyl stretch at 1733 cm^{-1} , and the appearance of OH stretches at 3250 cm^{-1} , is observed corresponding to the formation of carboxylic acid groups.

The analysis so far indicates that the majority of NVOC groups are cleaved upon exposure to UV₃₆₅ with a concomitant change in surface wettability; however, a wash is needed to remove the byproducts formed.

Spatially Addressable Photodeprotection. To further prove that a distinct switch in surface characteristics occurs, selective photodeprotection was performed through a TEM grid. An 11.4 ± 0.4 nm PNVOCA brush was covered with a TEM grid, with the dimensions of pitch = $12.5\ \mu\text{m}$, hole = $7.5\ \mu\text{m}$, and bar = $5\ \mu\text{m}$. The sample was then exposed to UV₃₆₅ for 10 min in the dry state, washed with water, and dried under nitrogen. The patterned sample was then subjected to condensation imaging by optical microscopy, a technique in which water vapor condenses preferentially on the hydrophilic regions of a patterned sample.³⁸ The results are shown in Figure 8.

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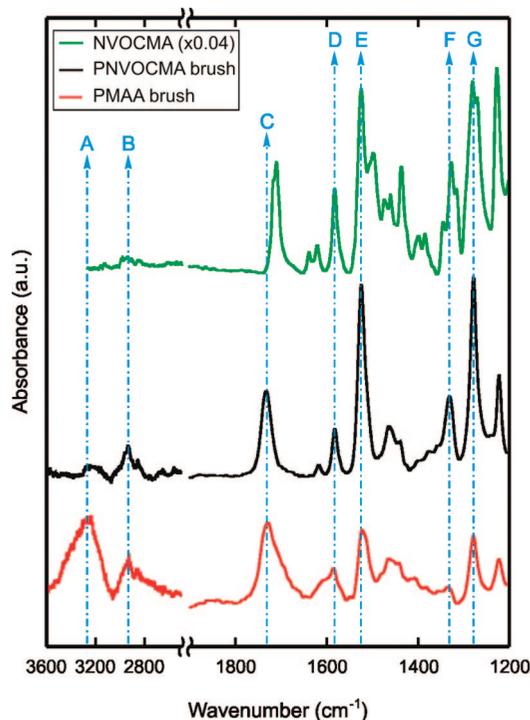


Figure 7. IR spectra of monomeric NVOCMA and a PNVOCMA brush on silicon, before and after UV₃₆₅ exposure. Representative peaks: (A) 3250, OH stretches; (B) 2950, CH stretches; (C) 1733 and 1708, carbonyl; (D) 1580, conjugated aromatic ring; (E) 1523, symmetric nitro group stretch; (F) 1330, asymmetric nitro group stretch; (G) 1278 cm⁻¹, C—O—C stretches. The spectrum of NVOCMA has been decreased by a factor of 25 for comparison.

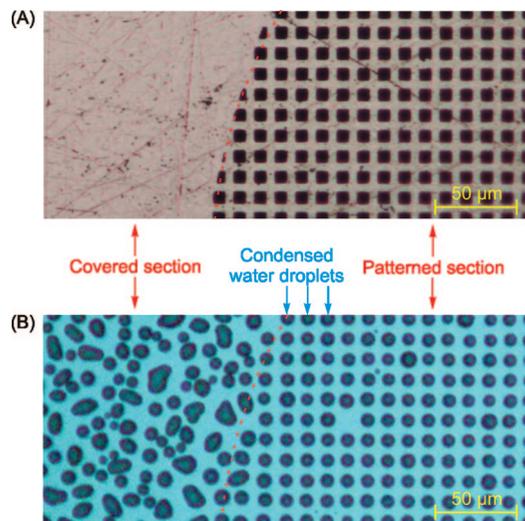


Figure 8. Condensation picture, taken by optical microscopy, of a PNVOCMA brush after patterned deprotection. (A) TEM grid used for patterned deprotection (size 2000). (B) Condensation image (blue contrast has been enhanced for clarity). Dashed red lines are added to guide the eye.

It can be clearly seen in Figure 8 that the areas of the PNVOCMA brush which were exposed to UV₃₆₅ through the mask have switched to the more hydrophilic PMAA state, and hence preferentially nucleate condensation of water into a regular array of droplets in line with the pattern of the TEM grid. The area of the brush which was completely covered, and hence

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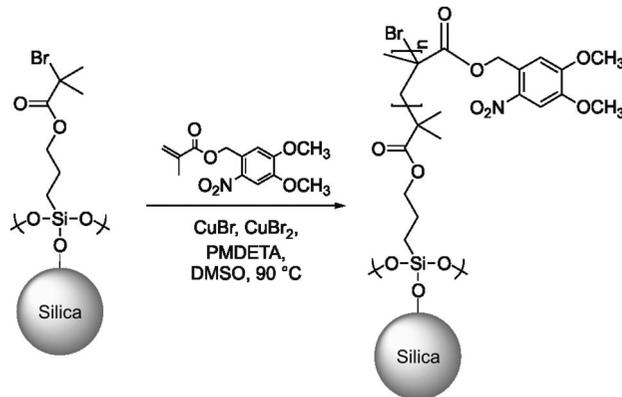


Figure 9. ATRP of NVOCMA from initiator-coated beads.

remained hydrophobic, has no spatial preference for droplet condensation as expected. In contrast, the area patterned by the grid is extensive and regular.

Augmentation of Wetting Change. The augmentation of wettability by increasing surface roughness is a well-established field of study.^{39–41} Coating a rough surface with PNVOCMA should in principle increase the wettability difference between the hydrophobic and hydrophilic states of the brush as seen on planar surfaces. In order to achieve this increased roughness, PNVOCMA brushes were grown from submicron-size (0.2–0.3 μm) fumed silica beads (Cabosil M5) with subsequent deposition onto a planar surface. The native silanol groups of the silica beads were first reacted with the trichlorosilane ATRP initiator, in a way similar to that described for planar surfaces to form an ATRP initiating monolayer.^{24,42,43} Once coated with initiator, a polymerization solution and method similar to that used for brushes grown from planar surfaces were used to create the polymer brush (Figure 9).

The cleaned PNVOCMA-coated beads were resuspended in dichloromethane at a concentration of 0.01 g in 5 cm³ for deposition onto freshly oxidized silicon wafer samples. Drops of the particle suspension were deposited on each sample until complete coverage was achieved. Subsequent evaporation of the solvent resulted in a layer of beads for responsive behavior analysis.

A planar surface with a layer of PNVOCMA-coated beads was exposed to UV₃₆₅ for 5 min in the dry state, with no subsequent washing steps. Analysis of the beads by contact angle goniometry was performed before and after UV exposure to quantify the hydrophobic to hydrophilic switch. The results for analysis with pure water are shown in Figure 10, and it can clearly be seen that all contact angles decrease after UV exposure, indicating a large hydrophobic to hydrophilic switch in surface properties.

It is interesting to note that the increase in surface roughness augments the change in wettability compared with that seen for PNVOCMA brushes on planar surfaces (Figure 5). For example, in the hydrophobic state, an advancing water contact angle of 75° for the planar brush increases to 145° for the rough bead surface. The use of submicron-size beads has the advantage of being able to be incorporated into paint formulations for easy application to surfaces, for example by ink-jet printing. Also, by

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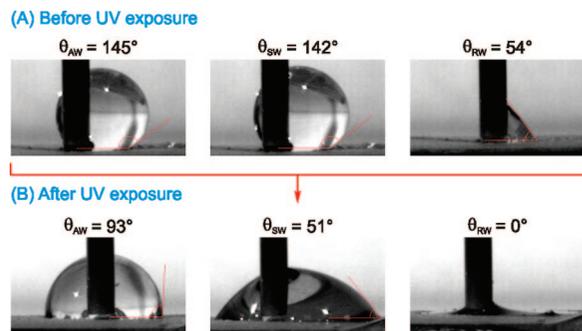


Figure 10. Change in contact angles of PNVOCA-coated beads deposited on a planar surface.

using polymeric materials and accurate device fabrication techniques, such as embossing, specific regions of a channel could be impregnated with the beads, leading to channels with regions with augmented responsive behavior.⁴⁴

Conclusions

Protecting group chemistry applied to polymer side chains as a potential route to new responsive surfaces has been investigated. The advantages of using the noninvasive stimulus, UV light, were considered when screening for possible PG candidates. The monomer, NVOCMA, utilizing the mild photochemistry of *o*-nitrobenzyl groups, was synthesized such that the hydrophobic protected monomeric units would transform into hydrophilic PMAA units upon exposure to UV. NVOCMA was found to have good sensitivity at longer UV wavelengths (λ_{\max} at 343 nm). This was attributed to the electron-donating methoxy groups attached to the benzyl ring extending the chromophore of the monomer.

SI-ATRP of the NVOCMA was achieved, yielding the desired hydrophobic polymer surfaces with θ_{AW} in the 75° – 80° region. Cleavage of the *o*-nitrobenzyl groups was observed upon exposure to UV₃₆₅. As a result, the polymer brushes synthesized from these monomers were shown to switch from a hydrophobic to a hydrophilic state as a result of the collective conversion of the monomeric units within the brush. Analysis by ellipsometry, contact angle goniometry, FTIR, UV–vis, and condensation imaging revealed that although incomplete chemical transformation takes place this is sufficient to produce an observable change in wettability. Further to this, a rough surface was found to augment the switch in wettability. This augmentation was achieved by growing PNVOCA brushes on fumed silica beads which were deposited onto planar surfaces.

Exposure of PNVOCA brushes through a TEM grid, with subsequent pattern visualization by condensation imaging, demonstrated the ability to locally switch the surface on the micron scale, and to reproduce this switch over a large area.

The movement of liquids on the micrometer scale within devices is largely dependent on the surface energy of the channel through which the fluid is moving. A switch from hydrophobic to hydrophilic should in theory allow aqueous fluid flow to begin over a previously “closed” channel. The irreversible nature of the chemistry demonstrated and noninvasive stimulus may prove useful for rapid-throughput, disposable systems which require a single sudden change in wettability, for example, flood release of an aqueous solution within a microdevice.

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