

Polymer brush resist for responsive wettability

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Well-defined polymer films which change their wettability in response to external stimuli are extensively used within the microelectronics industry, and are rapidly becoming equally beneficial in the field of microfluidics and lab-on-a-chip technologies. The fabrication of a self-contained polymer brush resist, by using the chemistry of surface initiated atom transfer radical polymerization (SI-ATRP) and photoacid generators (PAGs), and its subsequent responsive wettability will be the subject of this paper. Since UV light is used to trigger the responsive behaviour, spatially addressable patterning could be achieved, without the use of sacrificial layers, allowing for the formation of single films with regions of different wettabilities.

Introduction

Protecting group chemistry of free carboxylic acid groups is extensively used in synthetic chemistry.¹ However, it is the drastic switch in solubility observed upon deprotection which has sought considerable interest from the microelectronics industry, and has been harnessed for use in photolithographic resists.^{2–4} Poly(*tert*-butyl methacrylate) (PtBMA) is commonly found as the major component of chemically amplified resists; the *tert*-butyl (tBu) esters being integral to their performance.⁵ The inherently hydrophobic tBu ester groups liberate hydrophilic carboxylic acid groups, and methyl propene thereby regenerating the proton, upon acid catalyzed elimination, as shown in Fig. 1.

Chemical amplification relies on photochemical acid generation, in which the acid created catalyses a large number of reactions without being consumed. PAGs are ideal for this purpose, and indeed their development has largely been driven by this technology.^{6–8} Incorporation of a PAG into a resist film ($\leq 5\%$ by weight) provides a latent acid poised for activation by an external light source. Incorporation is usually achieved by mixing the PAG into a polymer resist solution prior to spin-coating. However, more recently attempts have been made to incorporate PAG units directly into the resist polymer chains since the copolymers formed would minimize phase separation and enhance stability.^{6,9–11} Selective activation of the acid through a mask results in the conversion of any PtBMA into poly(methacrylic acid) (PMAA) in the exposed region. The subsequent change in solubility of the exposed regions allows the formation of a pattern upon development in an appropriate solvent.¹²

The change in solubility of PtBMA in response to the photolytic generation of acid was seen as a potential route to the creation of responsive surfaces. Resist technology relies on

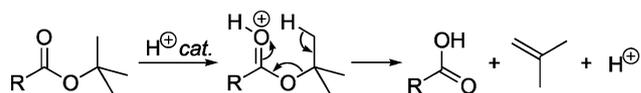


Fig. 1 General mechanism for the acid catalyzed deprotection of a tBu ester.

spincoating—a non-covalent deposition technique—in which removal of reacted polymer during the development stage is necessary. Non-covalent attachment also means that the remaining pattern is unstable to harsher conditions or contact with solvents other than that used for development.

If, however, the PtBMA chains could be covalently anchored to a surface, the resulting hydrophobic film should in principle switch to a hydrophilic state when converted to PMAA. This hydrophilic film would not wash away during (or post) development due to its covalent attachment to the surface; unlike a spin-coated film. Inducing this switch by using a PAG can be thought of as an indirect photo-responsive surface, since light is used as the triggering stimulus but it is the photolytically generated acid which performs the chemical modification.

This paper will discuss in detail the SI-ATRP of tBMA; a new synthetic route to a PAG monomer; and the fabrication of block-copolymer brushes containing both these monomers, in order to create a self-contained responsive surface without the need for sacrificial layers.

Experimental

Materials and methods

All chemicals were 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 dimethyl sulfoxide (DMSO, Fisher), which were analytical reagent grade and used as received. Deionised water with a resistance of 18.2 M Ω cm was obtained from a Millipore Simplicity 185 system. Poly(styrene) (PS), MW 125 000–250 000, was obtained from Polysciences, Warrington, UK. Athene Sjostrand multiple slot nickel TEM grids, with 55 μ m and 125 μ m wide slots, were obtained from Agar Scientific, UK. tBMA

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inhibitor was removed by elution over a neutral alumina plug before use. Silicon wafers (Compart Technology Ltd, 100 mm diameter, boron-doped, <100> 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 minutes 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 visualised 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 µL min⁻¹ were used. Advancing (θ_{AW}), static (θ_{SW}) and receding (θ_{RW}) contact angles were measured. At least three different measurements per sample were taken with their average and standard deviation values reported. Fourier-transform infra-red (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. Spectra were taken with a resolution of 4 cm⁻¹ by accumulating at least 128 scans on each run. The sample compartment was carefully purged with nitrogen to reduce the interference of water and carbon dioxide absorption from the gas phase. 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, ¹³C, and ¹⁹F NMR spectra were collected using a Bruker AVANCE 500 CRYO Ultrashield spectrometer. Shift values were recorded as chemical shift (δ , ppm) relative to Me₄Si. Relative integral, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), coupling constants (in Hz), and acquisition frequency, were assigned where possible. ¹³C spectra were recorded with attached proton test (APT). UV reactions were performed using a water cooled Hanovia high pressure mercury UV lamp (254 nm).

Synthesis of 4-(methylthio)phenyl methacrylate

A solution of methacryloyl chloride (14.1 cm³, 145 mmol) in dry CH₂Cl₂ (40 cm³) was added dropwise to a mixture of 4-(methylmercapto)phenol (20.3 g, 145 mmol) and *N,N'*-diisopropylethylamine (27.7 cm³, 159 mmol) in dry CH₂Cl₂ (60 cm³) at 0 °C under nitrogen. The solution was stirred for 1 hour at 0 °C and then overnight at room temperature. The solvent was then removed *in vacuo*. Tetrahydrofuran (THF) (100 cm³) was added to dissolve the crude product; and the insoluble *N,N'*-diisopropylethylamine hydrochloride salt was filtered off. The THF was removed *in vacuo*, and the product redissolved in CH₂Cl₂ (50 cm³). The organic layer was washed with HCl (0.01 M aqueous; 20 cm³) then water (2 × 20 cm³), dried over anhydrous MgSO₄, and filtered. The dried organic phase was concentrated *in vacuo*, giving the pure product, 4-(methylthio)phenyl methacrylate, as pale yellow crystals, in quantitative yield (30 g, 100%). *R*_f (2 : 1,

hexane : ethyl acetate) 0.60; elemental analysis: found; C, 63.25; H, 5.85. C₁₁H₁₂O₂S requires C, 63.43; H, 5.81; O, 15.36; S, 15.40%; λ_{\max} (CH₃CN)/nm 256 (ϵ /dm³ mol⁻¹ cm⁻¹ 10 370); ν_{\max} /cm⁻¹ 1728s (α,β -unsaturated ester), 1640 (conj. aromatic); ¹H-NMR δ (500 MHz; CDCl₃): 2.05 (3 H, t, *J* 1, H₂C=C-CH₃), 2.47 (3 H, s, SCH₃), 5.74 (1 H, quin, *J* 1.5, H₂C=C), 6.33 (1 H, t, *J* 1, H₂C=C), 7.05 (2 H, dt, *J* 2.5 & 9, OCCH aromatic), 7.27 (2 H, dt, *J* 2.5 & 9, SCCH aromatic); ¹³C-NMR δ (125 MHz; APT; CDCl₃): 16.5 (SCH₃), 18.4 (H₂C=C-CH₃), 122.1 (OCCH aromatic), 127.3 (H₂C=C-CH₃), 128.0 (SCCH aromatic), 135.5 (SC aromatic), 135.8 (H₂C=C-CH₃), 148.6 (OC aromatic), and 165.8 (C=O); *m/z* (ESI) 231.0450 [(M + Na)⁺. C₁₁H₁₂O₂SNa requires 231.0456].

Synthesis of dimethyl-(4-methacryloyloxy)phenylsulfonium triflate (PAGMA)

A solution of iodomethane (4.82 cm³, 77 mmol) in acetonitrile (20 cm³) was added dropwise to a mixture of 4-(methylthio)phenyl methacrylate (16.1 g, 77 mmol) and silver trifluoromethanesulfonate (19.9 g, 77 mmol) in acetonitrile (100 cm³) at 0 °C under nitrogen in the dark. The silver iodide precipitate was filtered off and washed with acetonitrile (2 × 20 cm³). The collected filtrates were concentrated *in vacuo*. The crude product was recrystallized from hot THF, giving the pure product, PAGMA, as white crystals (18.3 g, 64%). Elemental analysis: found; C, 41.94; H, 4.07. C₁₃H₁₅F₃O₅S₂ requires C, 41.93; H, 4.06; F, 15.31; S, 17.22; O, 21.48%; λ_{\max} (H₂O)/nm 194 (ϵ /dm³ mol⁻¹ cm⁻¹ 33 910), 224 (14 100); ν_{\max} /cm⁻¹ 1732s (α,β -unsaturated ester), 1637 & 1585 (conj. aromatic), 1250s & 1214s (CF₃), 1172s & 1123s (anti-SO₃), and 1029s (symm-SO₃); ¹H-NMR δ (500 MHz; D₂O): 1.90 (3 H, s, CH₃), 3.12 (6 H, s, SCH₃), 5.81 (1 H, t, *J* 1, H₂C=C), 6.28 (1 H, t, *J* 1, H₂C=C), 7.39 (2 H, dt, *J* 2.5 & 9, OCCH aromatic), 7.90 (2 H, dt, *J* 2.5 & 9, SCCH aromatic); ¹³C-NMR δ (125 MHz; APT; D₂O): 17.1 (CH₃), 28.5 (SCH₃), 119.5 (1 C, quartet, *J*_{CF} 315 Hz, CF₃), 122.3 (SC aromatic), 124.5 (OCCH aromatic), 129.4 (H₂C=C), 131.2 (SCCH aromatic), 134.8 (H₂C=C), 154.9 (OC aromatic), 167.5 (C=O); ¹⁹F-NMR δ (376 MHz; D₂O): -79.0 (3 F, s, CF₃); *m/z* (ESI+) 223.0793 [M⁺. C₁₂H₁₅O₂S requires 223.0787]; *m/z* (ESI-) 148.9519 [M⁻. CF₃O₃S requires 148.9526].

Synthesis of PtBMA brushes

tBMA (15 cm³, 92 mmol), CuBr₂ (4.1 mg, 0.018 mmol), and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) (0.12 cm³, 0.55 mmol) were dissolved in DMSO (15 cm³) at 21 °C and degassed by passing a continuous stream of dry nitrogen through the solution whilst stirring for 30 minutes. CuBr (26.5 mg, 0.18 mmol) was then added under positive nitrogen and the solution degassed for a further 30 minutes. A silicon wafer coated with a silane initiator monolayer was prepared, as described elsewhere,^{13,14} ready for SI-ATRP. Initiator coated wafer samples (~1 cm² each) were sealed in reaction vessels, degassed and left at 21 °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 acetone,

CH_2Cl_2 and methanol, and dried under a stream of nitrogen. The substrates were then stored under nitrogen, until needed.

Synthesis of PPAGMA brushes

PAGMA (4 g, 10.8 mmol) was dissolved in DMSO (11 cm^3) at 21 °C. CuBr_2 (4.8 mg, 0.022 mmol), and PMDETA (0.135 cm^3 , 0.65 mmol) were dissolved in DMSO (10 cm^3) at 21 °C. Both solutions were degassed by passing a continuous stream of dry nitrogen through the solutions whilst stirring for 30 minutes. CuBr (31 mg, 0.22 mmol) was then added under positive nitrogen to the CuBr_2 -PMDETA solution and it was further degassed for a further 30 minutes. A tenth of the catalyst solution (1 cm^3) was then transferred to the monomer solution, and the final polymerization solution left to degas for a further 10 minutes. Initiator coated silicon wafer samples ($\sim 1 \text{ cm}^2$ each) were sealed in reaction vessels, degassed and left at 21 °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 methanol, and dried under a stream of nitrogen. The substrates were then stored under nitrogen in the dark until needed.

tBMA and PPAGMA polymerizations with different monomer concentrations, solvents, or temperatures, were performed following the above procedures changing the appropriate values where applicable.

Synthesis of PPAGMA-block-PtBMA brushes

PPAGMA brushes were synthesised as outlined above. These were then used as the initiating surface (instead of a silane initiator monolayer) for the synthesis of the PtBMA block.

Results and discussion

Surface polymerization of tBMA

The low cost, commercially available monomer tBMA possesses both an acid labile tBu ester group and a methacrylate group, suitable for ATRP.¹⁵ Previous studies which synthesized thick ($\sim 100 \text{ nm}$) poly(*tert*-butyl acrylate) (PtBA) or PtBMA brushes used sacrificial initiator. This provided control over the polymerization but also led to unwanted solution polymer.^{12,16} Copper mediated SI-ATRP on the other hand would provide a surface-confined polymerization, needing only a simple solvent rinse for substrate retrieval.

Typical polymer brush synthesis is shown schematically in Fig. 2. A catalyst complex composed of CuBr , CuBr_2 , and PMDETA, at a fixed molar ratio of 1 : 0.1 : 3 respectively, was used for all polymerizations performed. A monomer to CuBr molar ratio of 500 : 1 was employed. The use of CuBr_2 provides a deactivation route which helps to control the rate of polymerization.¹⁷ Acetone and DMSO¹⁸ were found to be the best solvents for PtBMA brush growth, with typical contact angles of $\theta_{\text{AW}} = 93^\circ \pm 2^\circ$, $\theta_{\text{SW}} = 82^\circ \pm 1^\circ$, and $\theta_{\text{RW}} = 72^\circ \pm 2^\circ$ observed for all brushes.

To assess the control over PtBMA growth, polymerization kinetics were assessed for these two solvents. Polymerization in acetone was performed at 50 °C whilst that in DMSO was

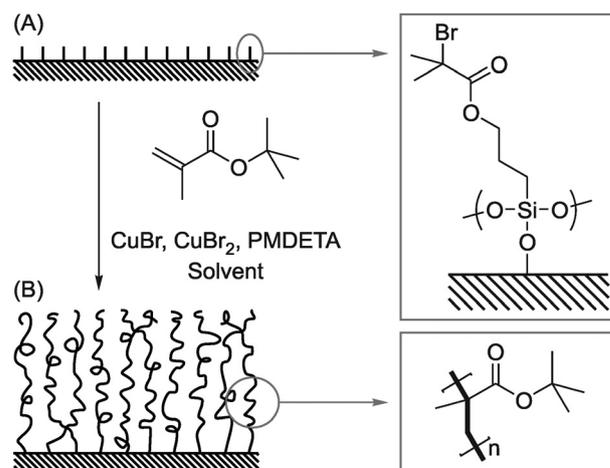


Fig. 2 Schematic representing PtBMA brush synthesis from a silane initiator monolayer on silicon. (A) Silane initiator monolayer. (B) PtBMA brush.

performed at 21 °C. The results are presented in Fig. 3, and indicate polymer brush growth in both solvents can be achieved with reasonable control. In both cases an initial period of rapid growth is observed followed by a slower, more linear regime. This type of profile is indicative of fast initiation resulting in a high concentration of active surface radicals, which subsequently cause the termination or burial of chains by their neighbours.¹⁹ Once this process equilibrates, the remaining lower concentration of active, accessible, chain-ends continue to grow in a linear fashion. It is interesting to note that Baker and co-workers also found that rapid uncontrolled SI-ATRP of a number of monomers, including tBA, could be performed in highly polar media.²⁰

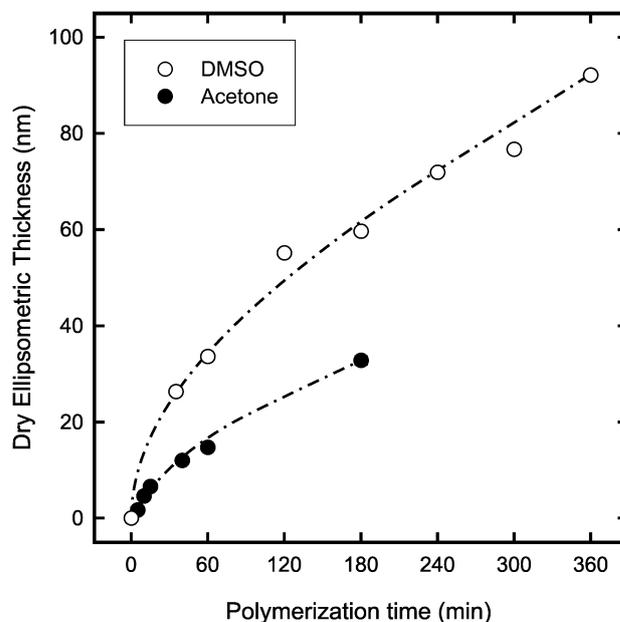


Fig. 3 Time resolved synthesis of PtBMA brushes in acetone at 50 °C and DMSO at 21 °C. Lines are added to guide the eye, and the symbols are larger than the error bars for each measurement.

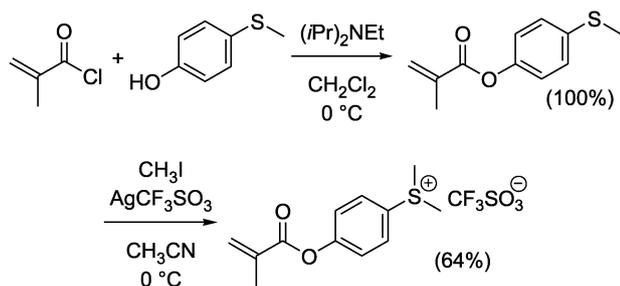


Fig. 4 Synthetic route to PAGMA.

Synthesis of the PAG monomer

The use of trifluoroacetic acid (TFA), or sacrificial layers within device applications is not desirable. As such, a covalently bound polymer brush with a PAG incorporated within its structure would be a more elegant way of providing a latent acid and advantageous when considering possible device fabrication. Since the initial PtBMA brushes were fabricated by a grafting-from technique,²¹ an obvious method to include the PAG within the polymer chains is to synthesize a PAG monomer which can then be incorporated into the brush by polymerization. Gonsalves and co-workers have synthesized such a PAG monomer, and copolymerized it with a number of different monomers in solution *via* free radical polymerization.^{22–24} We attempted the same four step synthesis of PAGMA, but abandoned this route after poor yields and loss of the triflate in the final step. Therefore, a less demanding two step synthesis with higher yields was designed, shown in Fig. 4.^{25–28}

The first step involves ester formation between an acid chloride and a phenol, and proceeds with quantitative yield. Methyl aryl sulfides will only react readily with alkyl halides when in the presence of silver salts, since the aryl ring significantly lowers the nucleophilicity of the sulfide. The stability of the silver halide byproduct which precipitates helps drive the reaction despite the low nucleophilicity of the sulfide. This phenomenon is the basis behind the second step of the reaction which produces silver iodide and the final product, PAGMA, in a reasonable yield of 64%. Elemental analysis, mass spectrometry, and NMR confirmed the existence of the final product with no loss of the triflate counterion.

Surface polymerization of PAGMA

Having successfully synthesized the monomer, PAGMA, surface initiated homopolymerisation was investigated. For consistency, similar conditions to those used for pure PtBMA brush growth were employed. A polymerization time of 3 hours, a temperature of 50 °C, a 0.89 M monomer concentration and a molar ratio of PAGMA, CuBr, CuBr₂, and PMDETA, of 500 : 1 : 0.1 : 3, respectively, were used. The resulting poly(dimethyl-(4-methacryloyloxy)phenylsulfonium triflate) (PPAGMA) brushes were washed with acetone, and ethanol, and dried under nitrogen. An ellipsometric thickness of 14.5 ± 0.4 nm was found. Thicker films could be achieved with a higher monomer concentration but this caused increased surface roughness as evidenced by a poor fit to the ellipsometric model. Contact angles of the 14.5 nm films were: $\theta_{AW} = 72^\circ \pm 3^\circ$, $\theta_{SW} = 70^\circ \pm 3^\circ$, and $\theta_{RW} = 0^\circ$. UV

analysis was also performed for PPAGMA brushes grown in parallel on quartz. The λ_{max} values of the PPAGMA brush were found to lie at 198 and 224 nm. A bathochromic shift from 194 nm in the monomer to 198 nm in the polymer was seen and is probably due to the change in environment of the chromophores from a dilute aqueous solution to a polymer matrix. For the same reason a flattening and small shift in the signal corresponding to the phenyl-sulfonium group at 224 nm was seen.

PPAGMA-block-PtBMA brushes

If a polymer brush is removed from its polymerization solution while it is still growing, it should in theory retain some chain end α -bromo groups, due to the living nature of ATRP.^{29,30} Re-initiation of polymerization from these groups provides a convenient route to the fabrication of block copolymers, without the need for further chemical modification of the surface between polymerizations.^{17,31,32} After successful synthesis of homopolymer brushes of PAGMA, the next logical step was to investigate re-initiation using tBMA, in order to fabricate a PPAGMA-block-PtBMA copolymer brush. The result would be a discrete polymeric film ready for responsive activation, without the need for any sacrificial layers.

PPAGMA brushes, 14.5 nm thick, were immersed in a polymerization solution containing tBMA, CuBr, CuBr₂, and PMDETA, at a molar ratio of 500 : 1 : 0.1 : 3 respectively, with a monomer concentration of 6.15 M in DMSO. The samples were left to polymerize for 20 minutes at 21 °C, after which a total thickness of 44 nm was found for the block copolymer films, indicating a PtBMA layer of ~30 nm was grown after re-initiation. A schematic of the brush architecture synthesized is shown in Fig. 5.

A typical FTIR spectrum of the block copolymer film is shown in Fig. 6 together with the FTIR spectra of the PAGMA monomer, a PPAGMA homopolymer brush and a PtBMA homopolymer brush for comparison. The shift in the carbonyl peak for PAGMA, 1732 cm⁻¹ for the monomer to 1754 cm⁻¹ for the polymer brush, is expected due to loss of conjugation. It can be seen that both carbonyl stretches from the different blocks are present in the copolymer spectrum, together with the other typical peaks observed for the respective homopolymers. Distinctive signals from deformation modes of the tBu groups

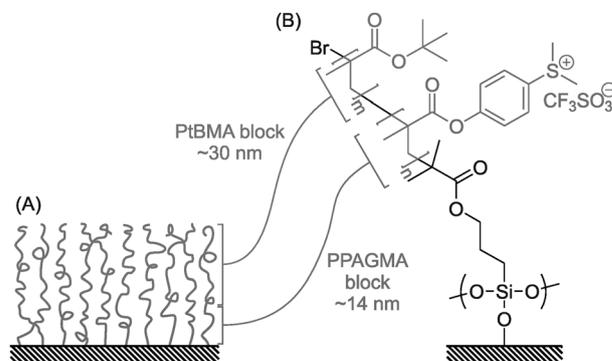


Fig. 5 PPAGMA-block-PtBMA brush. (A) Simple schematic of polymer chain architecture. (B) Chemical structure of block copolymer.

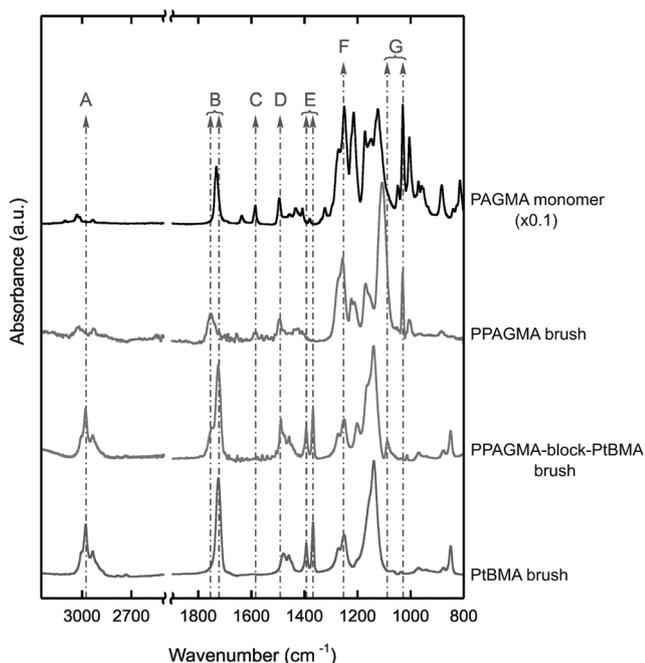


Fig. 6 Comparative FTIR spectra of monomeric PAGMA, a PPAGMA brush, a PPAGMA-block-PtBMA copolymer brush, and a PtBMA brush. Representative peaks are: (A) 2975, CH stretches; (B) 1754 and 1723, carbonyls; (C) 1637 and 1585, conjugated aromatic; (D) 1477, CH deformation; (E) 1392 and 1367, tBu deformation; (F) 1250 and 1214, C–O–C stretches and CF₃; (G) 1087 & 1029 cm⁻¹, SO₃.

are observed at 1392 and 1367 cm⁻¹ in both the tBMA homopolymer and the copolymer.¹⁷

Responsive behaviour

Pure PtBMA brushes were subjected to acid catalyzed deprotection following two standard methods as control experiments. The first method involved immersion of PtBMA brush coated substrates in a solution of TFA in CH₂Cl₂ (50% v/v) for one hour at room temperature. This is a standard technique for the removal of tBu ester, *tert*-butyloxycarbonyl (tBoc) and 9-fluorenylmethyloxycarbonyl (Fmoc) protecting groups, since the mild nature of TFA allows it to perform the deprotection whilst minimising interference with other functional groups. Before analysis the samples were washed with water and dried under nitrogen. Ellipsometry revealed a 30% decrease in thickness, from 30.3 ± 0.5 nm to 21.4 ± 0.6 nm, after TFA treatment. Contact angle goniometry displayed a dramatic reduction for all three contact angles: $\theta_{AW} = 58^\circ \pm 2^\circ$, $\theta_{SW} = 58^\circ \pm 3^\circ$, and $\theta_{RW} = 0^\circ$. Further evidence for the deprotection was seen by FTIR analysis. The appearance of OH stretches at 3250 cm⁻¹, the almost complete loss of the tBu stretches at 1392 & 1367 cm⁻¹, and the broadening of the carbonyl peak, creating a shoulder at ~1700 cm⁻¹, were all indicative of the loss of tBu groups and the transformation into a PMAA brush.³³

The second standard method used to deprotect PtBMA brushes was adapted from literature procedures using chemically amplified resists and sacrificial PAG layers.¹² The commercially available PAG, triphenylsulfonium triflate (TPSOTf), was

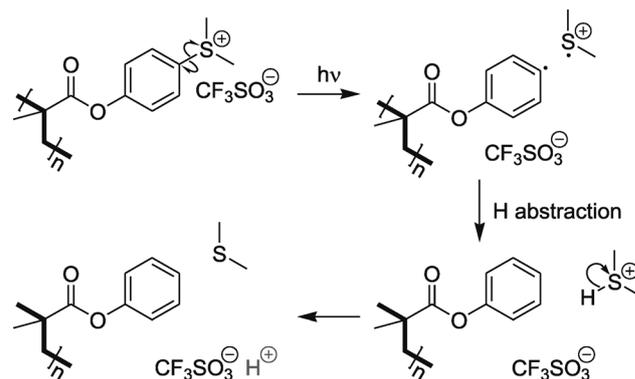


Fig. 7 Possible mechanism for the UV induced decomposition of a sulfonium triflate based PAG. Homolytic cleavage followed by hydrogen abstraction and rearrangement gives triflic acid and varied by-products.

chosen for this study due to its similar structure to PAGMA. Exposure of this compound to UV, at a wavelength of 254 nm (UVC), results in homolytic cleavage of a carbon–sulfur bond as the primary fragmentation pathway. The resulting radical cation then undergoes further reaction ultimately leading to the formation of triflic acid along with other varied photo-products (Fig. 7).^{5,25,34,35}

A mixture of 3% (w/w) TPSOTf in PS was dissolved in CHCl₃ (where [TPSOTf] was 2 mM). Spincoating on top of PtBMA brushes with this solution at 4000 r.p.m. for 60 seconds, resulted in a sacrificial layer of PS infused with PAG, approximately 200 nm thick judging by the thin-film interference colour. The coated films were then exposed to UVC for 5 minutes, followed by a post-exposure bake (PEB) at 120 °C for 5 minutes. The UV light induces the release of acid from the PAG, while the PEB drives diffusion of the acid from the sacrificial layer into the polymer brush. Once complete, the sacrificial PS layer was removed by washing with acetone and the resulting film was washed with water and ethanol, and dried under nitrogen. Contact angle goniometry, ellipsometry and FTIR all confirmed the switch in surface and chemical properties expected, giving similar results to those described already for TFA deprotection of PtBMA to PMAA.

As a control experiment, a 58.9 ± 0.7 nm PtBMA brush was exposed to UVC for 30 minutes, followed by a PEB at 120 °C for 30 minutes. The ellipsometric thickness after exposure and baking was 55.3 ± 2 nm, the decrease most probably being due to loss of trapped solvent and/or reorganization of the polymer; contact angle goniometry and FTIR were also similar to that found before UV exposure indicating that PtBMA brushes are stable to both UVC and baking at 120 °C when acid is not present on the surface.

A control experiment was also performed for the PPAGMA homopolymer brushes. A 14.5 ± 0.4 nm PPAGMA brush was exposed to UVC for 30 minutes followed by a PEB at 120 °C for 30 minutes. The sample was then washed with acetone and water and dried under a stream of nitrogen. Ellipsometry revealed that the brush thickness had reduced by 36% to 9.3 ± 0.1 nm. UV analysis also indicated that a chemical transformation has occurred due to a significant decrease in signal from the λ_{max} at

224 nm. Contact angle goniometry, however, revealed that the wettability remains approximately the same after a typical development.

It has now been established that no significant change in wettability is observed when homopolymer brushes of PPAGMA, or homopolymer brushes of PtBMA, are taken through a typical development process. The copolymer brush containing both these monomeric units should in theory exhibit markedly different responsive wettability. In principle, acid generated upon UVC exposure of the PAGMA moieties in the brush should go on to deprotect the tBu groups of the co-monomer. A switch in surface wettability should be seen, due to the generation of hydrophilic carboxylic acids in place of hydrophobic tBu polymer side chains. A non-covalent coating of a film of PtBMA containing PAG would not achieve the same goal, since the exposed polymer would be removed during the washing steps.

The PPAGMA-block-PtBMA copolymer brushes were subjected to responsive testing similar to that used for the pure PPAGMA brushes and the PtBMA brushes coated with a sacrificial layer of PS infused with TPSOTf. A 44 nm thick copolymer brush was exposed to UVC for 30 minutes followed by a PEB at 120 °C for 30 minutes. The sample was then washed with acetone and water and dried under a stream of nitrogen. Ellipsometry revealed a 20% decrease in thickness to 36 nm, while a concomitant increase in hydrophilicity was observed by contact angle goniometry as shown in Fig. 8.

The block copolymer presents a PtBMA surface to the surroundings and the $\theta_{AW} = 89^\circ$ confirms this. The reduction of θ_{AW} to 58° after switching, together with the 20% decrease in thickness, correlate to a high degree with the results obtained for the pure PtBMA brushes switched to their PMAA states using TFA or TPSOTf. To further assess this self-contained polymer brush resist as a responsive surface, patterned deprotections through TEM grids were performed.³⁶ The grids chosen contained 55 μm and 125 μm wide slots through which UV radiation could pass. Samples, 44 nm thick, covered with TEM grids were again exposed to UVC for 30 minutes, followed by a PEB at 120 °C for 30 minutes. The samples were then washed with acetone and water, and dried under a stream of nitrogen, before further analysis.

Fig. 9 shows optical micrographs of a section of the TEM grid used, the block copolymer brush after patterned deprotection,

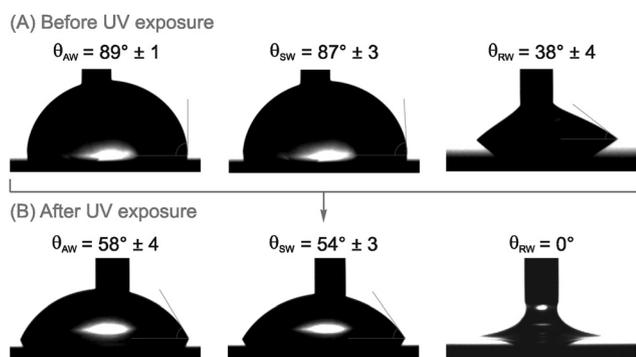


Fig. 8 Change in wettability of a PPAGMA-block-PtBMA polymer brush.

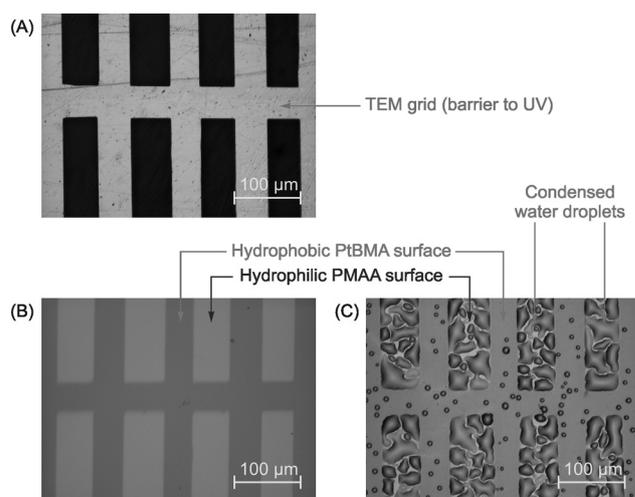


Fig. 9 PPAGMA-block-PtBMA brush patterned through a TEM grid. Optical micrographs of: (A) TEM grid with 55 μm wide features. (B) PPAGMA-block-PtBMA polymer brush after UVC exposure and PEB. (C) Condensation imaging of the same sample revealing the hydrophilicity of the exposed regions.

and the same brush by condensation imaging.^{37,38} The change in brush thickness is indicated by the difference in thin-film interference colours between the exposed and non-exposed regions. Condensation imaging was performed in order to ascertain the change in wettability of the exposed regions. Hydrophilic regions will tend to induce water condensation to a greater extent than hydrophobic regions. As a result, water will tend to nucleate, spread, and coalesce on the hydrophilic regions leading to easy visualization of the patterned surface. Image (C) in Fig. 9 shows how water preferentially condenses on the exposed regions which present a hydrophilic (PMAA) surface. Well-defined edges and

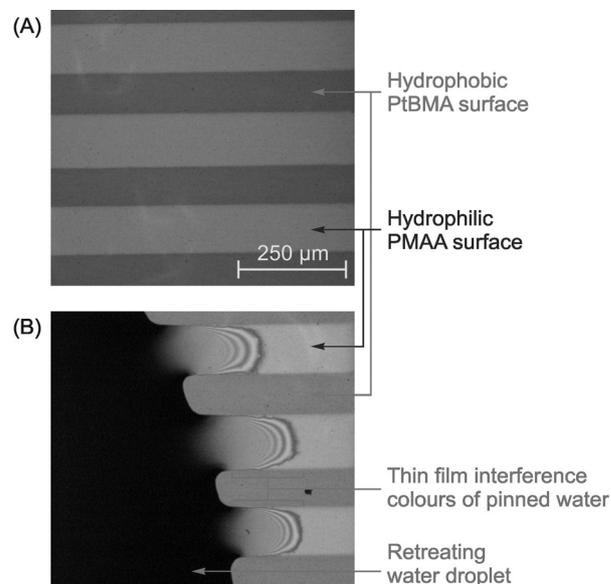


Fig. 10 PPAGMA-block-PtBMA brush patterned through a TEM grid. (A) Patterned block copolymer film with 125 μm wide hydrophilic lines within a hydrophobic background. (B) Retreating water droplet over same patterned sample.

droplet confinement can be observed, indicating a sharp interface between the hydrophilic and hydrophobic regions.

Observations of water dewetting from a patterned surface are shown in Fig. 10. Image (A) shows a section of a patterned block copolymer film with 125 μm wide hydrophilic lines within a hydrophobic background. Image (B) shows the same sample with a retreating water droplet moving over the surface. The bulk of the water droplet appears black due to its thickness. It is interesting to note that the colour of the water droplet remains black over the PtBMA regions right up to the droplet edge, indicative of a high contact angle on the PtBMA regions, as expected. Conversely, the water retreating from the hydrophilic, PMAA, regions lags behind that on the hydrophobic PtBMA regions. Looking more closely at the water on the hydrophilic regions a progression up the thin-film interference colours can be seen moving from the droplet edge to the droplet bulk. This shows that the water has a very low contact angle with, and therefore a high affinity for, the hydrophilic region.

Random copolymer brushes were also synthesised, however the contact angles were much lower than those seen for the block copolymer brush which presents only PtBMA to the contacting phase. This lowering of contact angles for the random polymer was assumed to be due to the presence of the ionic PAGMA units close to the surface. As a result, the changes in contact angles observed after UV exposure were not as significant as those seen for the block copolymer brush. On a molecular level the side reactions of the PAGMA moieties during photolysis would cause crosslinking and the formation of hydrophobic phenyl ester units. For a random co-polymer brush both of these processes would be detrimental to surface wetting behaviour, whereas a block co-polymer architecture helps avoid these problems by confining these side-reactions to the lower layer.

Conclusions

SI-ATRP of the acid labile monomer tBMA has successfully been performed. Both acetone and DMSO were found to produce homopolymer films tens of nanometres thick in under six hours at room temperature with reasonable control. The resulting hydrophobic PtBMA films were susceptible to acid catalyzed deprotection (with TFA or TPSOTf), resulting in the formation of hydrophilic PMAA films. In addition to the switching behaviour, this route to PMAA brushes is in itself useful, since the direct formation of uniform acidic polymer brushes is known to be difficult.³⁹

A new, more efficient, synthetic route to a PAG monomer was developed. It was found that PAGMA could be polymerized from surfaces by ATRP to form brushes in a similar manner to other ionic monomers.^{40,41} Re-initiation from the PPAGMA films was also possible, allowing for the synthesis of PPAGMA-block-PtBMA brushes. The external noninvasive stimulus, UVC radiation, photolytically generates triflic acid from the PPAGMA layer. This acid catalyses the deprotection of the tBu groups in the outer layer resulting in a hydrophilic PMAA surface. This architecture cannot be achieved with random copolymers, or non-covalently attached films.

The data presented shows that PPAGMA-block-PtBMA brushes can act as self-contained polymer brush resists. When the two components, PAGMA and tBMA, are separated into their

respective homopolymer brushes no responsive behaviour is seen. However, when present in the same brush, the cooperative chemistry of the two components results in responsive behaviour unique to the copolymer. Selective exposure through TEM grids containing features on the micron scale demonstrated the versatility of the block copolymer films. Regions of different wettability could be formed with high line-edge definition. Unexposed regions retained their hydrophobicity indicating that heat alone will not degrade the polymer and acid diffusion is minimal on the micron scale,^{6,42} whilst the exposed regions became highly hydrophilic, demonstrating the ability to perform localised switching.³⁶

This simplified system eliminates the need for harsh solution chemistry⁴³ and unwanted sacrificial layers¹² which are not desirable or easy to employ within potential device applications. The large irreversible hydrophobic to hydrophilic change in surface wettability has potential use in microfluidic devices, where surface energy patterns can act as passive elements for controlling biphasic fluid flows.⁴⁴

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