



PAPER

Post-polymerization modification of styrene–maleic anhydride copolymer brushes†

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Post-polymerization modification (PPM) has been broadly employed to achieve functional polymer brush surfaces *via* immobilization of functional moieties on the brush using efficient organic transformations. Here, we demonstrate the amine–anhydride reaction as a modular PPM route to functional brush surfaces using poly(styrene–maleic anhydride) (pSMA) copolymer brushes as a platform. The amine–anhydride reaction on pSMA surfaces proceeds to high conversions, with rapid kinetics, under ambient reaction conditions, and exploits a readily available library of functional amines. Using cystamine as a modifier, a convenient route to thiol-functionalized brushes was developed that enables sequential PPM modifications with a large library of alkenes using both base-catalyzed thiol–Michael and radical-mediated thiol–ene reactions. The high fidelity PPM reactions were demonstrated *via* the development of multifunctional, micropatterned brush surfaces.

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Introduction

Engineering polymer brush surfaces with desired chemical functionality is interesting for various applications, including antifouling¹ and antibacterial surfaces,² thermal,³ solvent,⁴ pH,⁵ and ion responsive surfaces,⁶ biosensors,⁷ protein⁸ and cell immobilization,⁹ membranes,¹⁰ and low friction surfaces.¹¹ Two strategies have been developed to fabricate functionalized polymer brush surfaces, including (i) direct polymerization of monomers containing the desired functional group, and (ii) post-polymerization modification (PPM) of the polymer brush. The direct polymerization method, while seemingly straightforward, is limited by the intrinsic intolerance of monomers carrying reactive functional groups with various polymerization mechanisms and conditions (*e.g.* thiols and radical polymerization). To address the disadvantages of the direct polymerization method, the PPM approach is often preferred.^{12–14} In the PPM approach, monomers carrying chemoselective functional groups that are unreactive under polymerization conditions are first subjected to surface-initiated polymerization to incorporate these moieties into a polymer brush precursor. Subsequently, the chemoselective groups serve as reactive handles for further modification enabling a versatile and modular transformation of the physical and chemical properties of surfaces using efficient modifi-

cation chemistries.^{12–14} Commonly used modification chemistries in PPM of polymer brushes are based on reactions with high efficacy, such as aminolysis of active esters,^{15–17} copper catalyzed azide–alkyne cycloaddition (CuAAC),^{18–20} epoxy ring opening reactions,^{21–23} Diels–Alder cycloadditions,^{24,25} nitroxide photoclick reactions,²⁶ and thiol-based reactions.^{27–33}

Amine/anhydride reactions exhibit fast reaction rates, high conversions and have attracted significant attention as a post-polymerization modification process for maleic anhydride copolymers since the 1970s. Early efforts primarily focused on modification of maleic anhydride copolymers with amines for bioconjugates^{34–37} with a few reports aimed at immobilization of biomolecules (*e.g.* enzymes, proteins) on the surface of maleic anhydride copolymer films.^{38,39} However, amine–anhydride reactions remain an underutilized post-modification chemistry for polymer brush surfaces.⁴⁰ In one of few examples, Blomberg *et al.* employed diamines to crosslink styrene–maleic anhydride copolymer brushes grafted from silica nanoparticles for the preparation of hollow nanocapsules albeit under rather harsh conditions.⁴⁰ The lack of examples in literature exploiting amine–anhydride reactions on brush surfaces is particularly surprising considering anhydrides are readily incorporated into polymers *via* copolymerization of commodity monomers (*e.g.* styrene/maleic anhydride) and exhibit orthogonal reactivity under radical polymerization conditions.

Herein, we demonstrate the amine–anhydride reaction as a modular post-polymerization modification route to functional surfaces using poly(styrene–maleic anhydride) (pSMA) copolymer brushes as a platform. SMA copolymer brushes are easily

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accessible *via* surface-initiated radical polymerization of low-cost, commercially available monomers. An extensive library of amines is employed for PPM of the PSMA brushes; however, this manuscript focuses primarily on cystamine dihydrochloride as a modifier. Modification of the brush surface with cystamine provides an immobilized thiol precursor that is readily deprotected *via* reductive cleavage under mild conditions to yield a brush surface with pendent thiol functionality. This approach eliminates the challenges associated with the synthesis of thiol-functionalized brush surfaces (*e.g.*, chain transfer to unprotected thiols under radical polymerization conditions, deprotection of thiol precursors under harsh conditions) and opens the door to sequential modification with a wide range of functional acrylates, methacrylates, and maleimides.^{28,31} We show that the thiol-containing polymer brush surface readily serves as a modular PPM platform using base-catalyzed thiol-Michael and radical-mediated thiol-ene reactions as routes to multifunctional, micropatterned surfaces.

Experimental section

Materials

Maleic anhydride, acetonitrile, cystamine dihydrochloride, triethylamine (TEA), tris(2-carboxylethyl) phosphine hydrochloride (TCEP), phosphate-buffered saline (PBS) buffer solution, 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU), 2-hydroxyethyl acrylate (HEA), lauryl acrylate (LA), poly(ethylene glycol) methacrylate (PEGMA, MW 360), *N*-phenylmaleimide (NPhM), 2,2-dimethoxy-2-phenylacetophenone (DMPA), 5-norbornene-2-carbonitrile, mixture of isomers (NB-CN), ethylene glycol vinyl ether (EGVE), dodecyl vinyl ether (DVE), fluorescein *O*-methacrylate (FMA), propylamine (PAM), allylamine (AAM), propargylamine (PgAm), dopamine hydrochloride (DAM), were purchased from Sigma-Aldrich and used as received. 1*H*,1*H*-Perfluoro-*N*-decyl acrylate (FA) was purchased from Gelest. Norbornenylethylethyl POSS (NB-POSS) and aminopropylisobutyl POSS (POSSAM) were purchased from Hybrid Plastics and used as received. Styrene was purchased from Sigma-Aldrich and was purified by passing through an alumina column to remove inhibitor before use. Silicon wafers (orientation <100>, native oxide) were purchased from University Wafer. The silicon substrates were plasma cleaned using a plasma cleaner from Harrick Plasma with air as the feed gas. An azo-based trichlorosilane initiator for surface-initiated polymerization was synthesized per literature procedures.^{41,42}

Instrumentation and characterization

Ellipsometry measurements were carried out using a Gartner Scientific Corporation LSE ellipsometer with a 632.8 nm laser at 70° from the normal. Multiple thickness measurements were taken for each sample to determine the uncertainty in the measurements. Grazing angle attenuated total reflection FTIR (gATR-FTIR) analysis was carried out using a Thermo Scientific FTIR (Nicolet 8700) equipped with a VariGATR™ accessory (grazing angle 65°, germanium crystal; Harrick

Scientific). Spectra were collected with a resolution of 4 cm⁻¹ by accumulating a minimum of 128 scans per sample. All spectra were collected while purging the VariGATR™ attachment and FTIR instrument with nitrogen along the infrared beam path to minimize the peaks corresponding to atmospheric water and CO₂. Spectra were analyzed and processed using Omnic software. Static water contact angles (WCA) were measured using 6 μL water droplets on a Rame-hart goniometer. UV assisted reactions were performed using an Omnicure Series 1000 UV light source (λ range 300–500 nm) with a 5 mm collimating adaptor. Fluorescent microscopy was conducted on a Zeiss 510 META laser confocal scanning microscope using a λ = 488 nm argon laser.

Cleaning of silicon substrates

Silicon wafers were cut into 1.2 cm × 1.2 cm pieces and cleaned sequentially in DI water, ethanol, THF, and toluene under ultrasonication before drying using nitrogen. Cleaned wafers were then plasma cleaned for 15 min. Clean substrates were stored in an oven at 120 °C before initiator functionalization.

Immobilization of initiator onto silicon substrates

Clean silicon substrates were transferred into dry, septum-sealed test tubes containing a toluene solution of azo-initiator (4 mmol, 13 mL) and TEA (0.2 mL). The immersion time was 45 min. Substrates were then removed, sonicated in toluene and dried under a stream of nitrogen. If not used immediately, initiator functionalized substrates were stored in the dark at –20 °C in toluene.

Surface-initiated polymerization of pSMA brush

A substrate with the azo-based initiator was placed in a sealed test tube and purged with nitrogen. In a separate Schlenk tube, styrene (1.0 mL, 0.91 g, 8.7 mmol) and maleic anhydride (1.0 g, 10.2 mmol) were dissolved in anhydrous acetonitrile (10.0 mL) and the solution was subjected to three freeze-pump-thaw cycles to remove oxygen. For each polymerization, 1.5 mL of the degassed monomer solution was transferred *via* cannula into the test tube containing the substrate. The SMA solution containing the initiator-functionalized substrate was heated at 95 °C for various times to obtain polymer brushes of different thickness. After polymerization, pSMA brush modified substrates were removed from the monomer solution and cleaned by repeated rinsing and ultrasonication in acetonitrile to remove any physically adsorbed polymers from the surface. Brush samples were finally dried with nitrogen.

PPM of pSMA brush with amines

Cystamine dihydrochloride (40 mg, 0.178 mmol) and triethylamine (50 μL, 36.3 mg, 0.359 mmol) were dissolved in 4.0 mL of solvent mixture that contained 50% DI water and 50% acetonitrile. A pSMA brush substrate was placed in the cystamine solution for 20 min at room temperature to ensure high anhydride conversion. PPM with other amines were carried out in acetonitrile for 20 min at room temperature unless stated

otherwise. The reaction conditions for each modifier were: (a) propylamine (0.12 mol L⁻¹), (b) allylamine (0.13 mol L⁻¹), (c) propargylamine (0.16 mol L⁻¹), (d) aminopropylisobutyl POSS (0.057 mol L⁻¹) for 120 min at 50 °C, and (e) dopamine hydrochloride (0.053 mol L⁻¹) with equal molar trimethylamine in 50:50 water/acetonitrile solution for 30 min. The postmodified substrates were thoroughly rinsed with acetonitrile and DI water and dried with nitrogen.

Reduction of cystamine modified pSMA brush

A substrate with cystamine postmodified pSMA brush was placed in a solution of TCEP (60 mg, 0.21 mmol) in 6 mL of acetonitrile: PBS solvent mixture (50:50 by volume) in a sealed test tube. The TCEP solution containing the cystamine postmodified pSMA brush substrate was under constant nitrogen purging for 16 h. The substrate was then removed, rinsed thoroughly using DI water, and dried with nitrogen.

PPM of thiol pendent polymer brush with base catalyzed thiol-Michael reactions

Following reduction of the cystamine-modified pSMA brush, substrates were placed in an acetonitrile solution containing the alkene and DBU (0.022 mol L⁻¹) at room temperature unless stated otherwise. The reaction conditions for each modifier were: (a) *N*-phenylmaleimide (0.096 mol L⁻¹) for 72 h; (b) 2-hydroxyethyl acrylate (0.15 mol L⁻¹) in DI water for 1 h; (c) lauryl acrylate (0.15 mol L⁻¹) for 1 h; (d) 1*H*,1*H*-perfluoro-*N*-decyl acrylate (0.15 mol L⁻¹) in acetone for 1 h; (e) poly(ethylene glycol) methacrylate (0.50 mol L⁻¹) and DBU (0.067 mol L⁻¹) for 72 h. The substrates were removed, rinsed thoroughly using the solvent used in the corresponding PPM reaction, and dried with a stream of nitrogen.

PPM of thiol pendent polymer brush with radical-mediated thiol-ene reactions

Following reduction of the cystamine-modified pSMA brush, substrates were placed in a THF solution containing the alkene (NB-CN, EGVE, DVE 1.5 mol L⁻¹; NB-POSS, 0.36 mol L⁻¹) and DMPA (0.05 mol L⁻¹). The substrates were then exposed to UV light ($\lambda_{\text{max}} = 365 \text{ nm}$, 21.8 mW cm⁻²) for 5 min. The substrates were removed, rinsed thoroughly using THF, and dried with a stream of nitrogen.

Patterning of polymer brush surfaces using micro-capillary stamp

A line-patterned PDMS stamp (linewidth 15.0 μm) was used to create well-defined, micropatterned polymer brush surfaces. The stamp was placed in direct contact with a thiol-functionalized polymer brush surface and a postmodification solution was wicked in subsequently for discrete reaction times yielding a micropatterned surface. For the patterning of thiol containing polymer brush surface, the polymer brush sample was placed in an aqueous solution of HEA (0.15 mol L⁻¹) and DBU (0.022 mol L⁻¹) for 60 min. The reactions were carried out at room temperature. After removing the stamp the sample was

thoroughly washed with DI water and acetonitrile and dried with nitrogen.

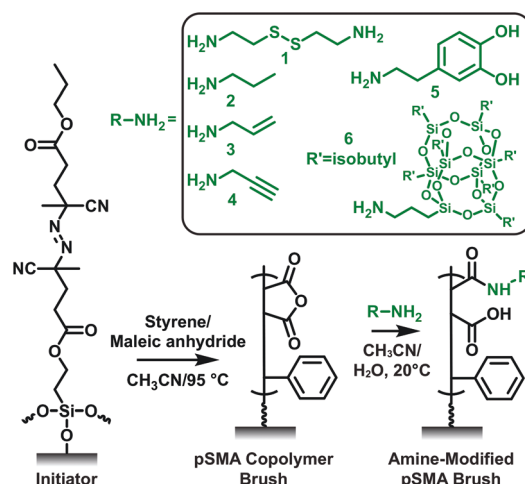
Patterning of thiol containing polymer brush surfaces using photomasks

Photomasks (TEM grids with mesh sizes of 100 and 150) were placed in contact with the brush surface containing thiol groups, immersed in an THF solution of fluorescein *O*-methacrylate (2.5 mmol L⁻¹) and DMPA (0.25 mmol L⁻¹) and irradiated with UV light (λ range 300–500 nm, 21.8 mW cm⁻²) for 5 min. After exposure, the photomasks were then removed from the surface and the substrate was rinsed thoroughly using THF, and dried with nitrogen.

Results and discussion

Synthesis of styrene/maleic anhydride polymer brushes

Scheme 1 shows the synthetic strategy for the preparation of SMA copolymer brushes *via* surface-initiated polymerization from silicon substrates modified with an asymmetric azobisisobutyronitrile-based trichlorosilane initiator. The average thickness of the initiator layer was $1.6 \pm 0.1 \text{ nm}$ as measured by ellipsometry. The pSMA brushes were synthesized by conventional free radical polymerization initiated by thermal decomposition of the surface-attached initiator; such approach provides a simple and well-studied route to polymer brush surfaces. Polymerizations were carried out in acetonitrile at 95 °C using a 54:46 mole ratio of styrene: maleic anhydride as the monomer feed. Patton and coworkers previously showed that monomer reactivity ratios do not differ significantly when comparing solution copolymerization and surface-initiated copolymerization.^{41,43} Based on styrene and maleic anhydride monomer reactivity ratios, polymer brushes with an alternat-

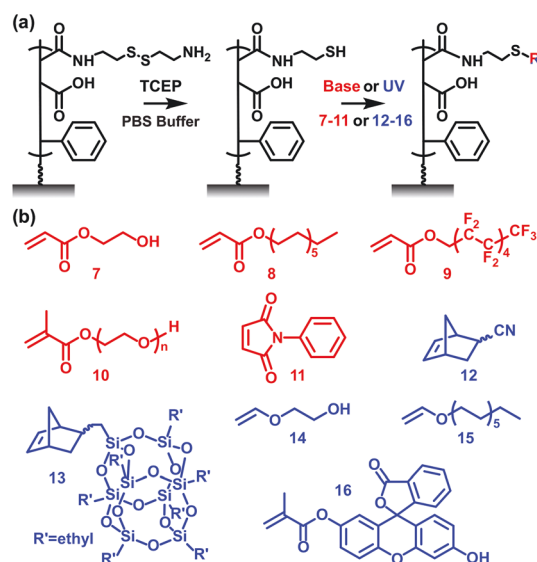


Scheme 1 Initiator immobilization, synthesis of styrene–maleic anhydride copolymer brushes *via* surface-initiated radical polymerization, and post-modification of the pSMA brush using amines (1) cystamine (2) propylamine, (3) allylamine, (4) propargyl amine, (5) dopamine and (6) aminopropyl isobutyl POSS.

ing copolymer structure containing between 46–48 mol% maleic anhydride can be expected;⁴⁴ however, the precise copolymer structure and copolymer composition are not critical for the current work. As expected, brush thickness was observed to increase as a function of polymerization time (Fig. S1†), where under constant monomer concentration and temperature, the increase can be attributed to an increase in brush grafting density.^{45,46} Hereafter, pSMA brushes with an average target thickness of 80 nm were prepared and employed for all postpolymerization modification experiments. The chemical composition of the pSMA polymer brush was characterized using gATR-FTIR. Fig. 1a shows the FTIR spectrum for pSMA with peaks at 1857 cm⁻¹ and 1781 cm⁻¹ attributed to the carbonyl on the five-membered ring of the maleic anhydride.^{47,48} Peaks at 1494 cm⁻¹ and 1454 cm⁻¹ correspond to the aromatic –C–H stretch of styrene.

Postpolymerization modification (PPM) of pSMA with amines

The styrene–maleic anhydride copolymer brushes provide a versatile platform for mild, modular postpolymerization modification reactions with amine-functional molecules (Scheme 1). A library of six amines were selected for PPM; however, we primarily present the results for PPM with cystamine in this manuscript. Modification with cystamine yields a simple route to achieve polymer brush surfaces expressing pendent thiol functionality. The results for amines 2–6 are provided in the ESI (Fig. S2 and Table S2†). PPM was conducted under good solvent conditions (acetonitrile:water, 1:1 by volume) in the presence of triethylamine. As shown in Scheme 2, cystamine modification of the pSMA brush ring-opens the anhydride yielding amide/carboxylic acid moieties along the backbone, with potential to partially crosslink the



Scheme 2 (a) Reduction of cystamine-modified pSMA brush and subsequent base catalyzed thiol-Michael or radical-mediated thiol-ene reaction using (b) a library of commercially available alkenes including (7) 2-hydroxyethyl acrylate (HEA), (8) lauryl acrylate (LA), (9) 1H,1H-perfluoro-N-decyl acrylate (FA), (10) poly(ethylene glycol) methacrylate (PEGMA, MW 360), (11) N-phenylmaleimide (NPhM), (12) 5-norbornene-2-carbonitrile (NB-CN), (13) norbornenylethylethyl POSS (NB-POSS), (14) ethylene glycol vinyl ether (EGVE), (15) dodecyl vinyl ether (DVE), and (16) fluorescent O-methacrylate (FMA).

polymer brush if both amines participate in an intermolecular reaction among brushes. The FTIR spectrum of the cystamine-modified pSMA brush is shown in Fig. 1b. The disappearance of the characteristic carbonyl peaks of the anhydride indicates the total consumption of the anhydride during the PPM. The new peak at 1641 cm⁻¹ corresponds to amide groups, whereas the peaks at 1564 cm⁻¹ and 1405 cm⁻¹ correspond to carboxylate moieties. Surface wettability changed from hydrophobic (WCA 92 ± 2°) to hydrophilic (WCA 69 ± 3°) after cystamine modification which was associated with the opening of anhydride ring and addition of cystamine onto the polymer brush.

The modification of the pSMA brush with cystamine increases the molecular mass of the repeat units resulting in an increase in brush thickness. If we make two simplifying assumptions (e.g. brush grafting density and mass density remain unchanged before and after postmodification), as described by Murata *et al.*,¹⁵ then the change in brush thickness measured by ellipsometry can be used to determine the extent of reaction, and ultimately reaction kinetics, associated with the post-polymerization modification. Full details of these calculations are provided in the ESI.† The conversion *versus* time plot for the cystamine modification of the pSMA brush is shown in Fig. 2. Anhydride conversion greater than 70% was achieved within 10 s with the PPM reaction approaching quantitative conversion (>97%) in less than 1 minute. Due to the large excess of amine modifiers in solution relative to the low concentration of anhydride available on the brush surface, the PPM reaction can be described by the pseudo-first-

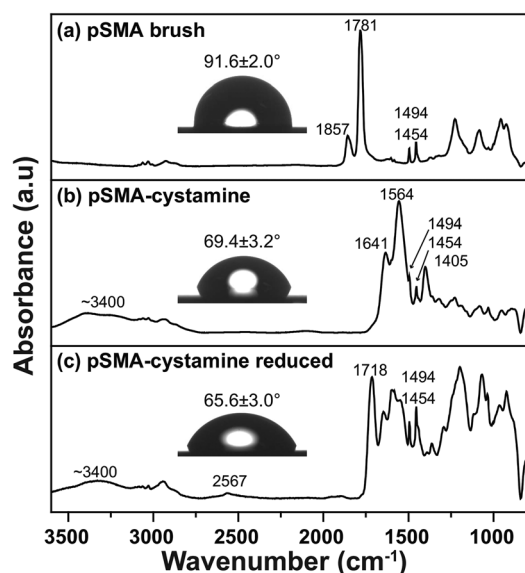


Fig. 1 gATR-FTIR of (a) pSMA brush (b) cystamine-modified pSMA brush and (c) cystamine-modified pSMA after reduction. Inset images show the static water contact angle for each surface.

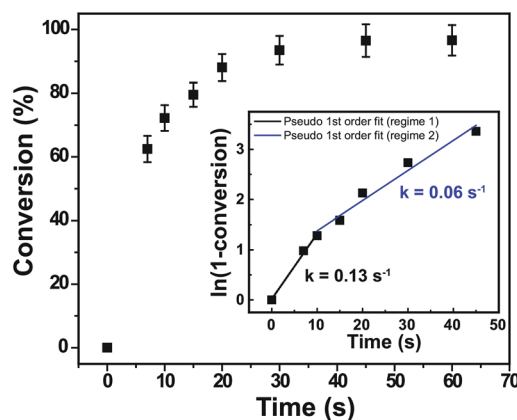


Fig. 2 Anhydride conversion versus cystamine reaction time for pSMA brush under good solvent conditions. Inset shows the pseudo-first-order kinetic plot for the post-modification reaction.

order rate equation $\ln(1 - \alpha) = k't$, where α is anhydride conversion, t is time, and k' is the apparent pseudo-first-order rate constant. Fig. 2 (inset) shows a plot of the kinetic data and the results of linear regression analysis from 0 to 45 s. The data was separated into two regimes, with an initial pseudo-first order rate constant of 0.13 s^{-1} from 0 to 10 s that decreased to 0.06 s^{-1} as the reaction becomes diffusion limited at $t > 10 \text{ s}$. The transition into the diffusion limited regime is attributed to strong segmental repulsion and reduced chain conformational entropy rendering the penetration of the brush by cystamine more unfavorable as PPM proceeds. Similar trends in PPM kinetics have been reported by Orski *et al.*⁴⁹

After post-modification with cystamine, pendent thiol moieties were exposed along the polymer brush chain *via* reductive cleavage of the disulfide linkages using TCEP, as illustrated in Scheme 2. Fig. 1c shows the FTIR spectrum of the reduced pSMA-cystamine brush. The peak at 2567 cm^{-1} is characteristic of the $-\text{SH}$ group and confirms the formation of thiols pendent to the brush backbone. Upon reduction, the thickness of the cystamine-modified pSMA polymer brush decreased from 123 nm to 105 nm – a decrease that can be attributed to the mass loss of cystamine moieties that reacted with the brush by one amine. Again, assuming a constant mass density and grafting density of the polymer brush, the average conversion of the reduction to thiols calculated from the change in brush thickness exceeded 99%.

The exposed thiol moieties serve as reactive handles for subsequent post-modification of the brush surface using facile thiol-mediated reactions, as illustrated in Scheme 2a. Base catalyzed thiol-Michael modifications were carried out with a series of electron deficient alkenes (*e.g.* acrylates, methacrylates, and maleimides, Scheme 2b, 1–5) using 1,8-diazabicyclo (5.4.0)undec-7-ene (DBU) as the catalyst. Fig. 3a–e shows the FTIR spectrum for each thiol-Michael modification. In each modification, conversion from pendent thiol to pendent thioether was observed as indicated by the disappearance of the thiol peak at 2567 cm^{-1} . Conversions calculated from the

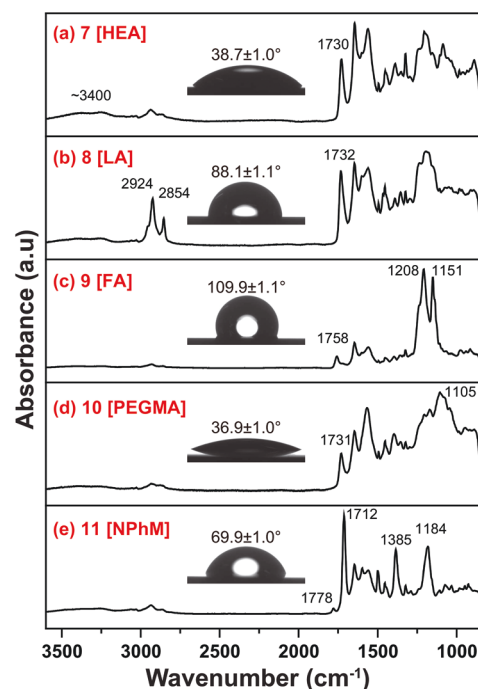


Fig. 3 gATR-FTIR of modified thiol containing polymer brushes using the following alkene modifiers: (a) HEA, (b) LA, (c) FA, (d) PEGMA, MW 360, and (e) NPhM. Inset images show the static water contact angle.

increase in brush thickness after modification are summarized in Table 1. In general, the modifications yielded high or near quantitative conversions demonstrating the efficiency of the thiol-Michael reaction. The lower conversion observed for FA could be attributed to low miscibility of the perfluoroalkyl chain with the thiol-modified brush. Similarly, PEGMA reached only $61 \pm 5\%$ conversion within 72 h, which may result from the lower efficiency of the thiol-Michael reaction when carried out with methacrylates.⁵⁰ The molecular weight of the modifiers also influences the penetration depth into the brush – an effect that has been well-described in the literature.⁴⁶ Additionally, post-polymerization modification of the pendent thiol brushes with multiple modifiers was confirmed using FTIR. For example, brushes modified with acrylates 7–9

Table 1 Brush thickness and conversion of thiol–ene modifications on thiol-functionalized pSMA brush surfaces

Modifier	Thickness (nm)		Conversion (%)
	Before PPM	After PPM	
HEA	73.5 ± 1.0	138.9 ± 2.1	94 ± 6
LA	72.4 ± 0.1	187.0 ± 1.9	99 ± 4
FA	78.1 ± 0.1	273.4 ± 4.3	80 ± 6
PEGMA	71.6 ± 0.1	165.2 ± 3.0	61 ± 5
NPhM	92.7 ± 0.1	190.7 ± 1.2	86 ± 2
NB-CN	71.1 ± 0.6	136.7 ± 2.3	96 ± 6
NB-POSS	72.6 ± 0.4	267.0 ± 6.7	66 ± 8
EGVE	69.7 ± 0.6	122.9 ± 1.4	94 ± 4
DVE	71.7 ± 1.7	175.9 ± 1.1	99 ± 3

show a broad peak centered at 3400 cm^{-1} corresponding to the HEA hydroxyl group (Fig. 3a), sharp peaks at 2854 cm^{-1} and 2924 cm^{-1} attributed to the LA aliphatic C-H groups (Fig. 3b), and peaks at 1208 cm^{-1} and 1151 cm^{-1} consistent with the C-F groups of FA (Fig. 3c), respectively. In Fig. 3d, the peak at 1105 cm^{-1} is characteristic of the -C-O-C- linkages found in PEGMA. Finally, the spectrum for the brush modified with NPhM (Fig. 3e) exhibits peaks centered at 1385 cm^{-1} and 1184 cm^{-1} assigned to the (C-N) bond of the tertiary aromatic amine and the maleimide (C-N-C) stretch, respectively.⁵¹ Static WCA measurements for each brush modification are shown as inset images in Fig. 3 and exhibit the expected changes in wettability associated with each functional moiety immobilized within to the brush surface.

Radical-mediated thiol-ene modifications were carried out with a series of electron rich or strained alkenes (*e.g.* norbornenes and vinyl ethers, Scheme 2b, 12–15) under UV light using DMPA as the photoinitiator. All modifications were conducted in THF under ambient conditions (*i.e.* without N_2 purge) with 5 min UV exposure times. As summarized in Table 1, near quantitative conversion was observed for the PPM with norbornene and vinyl ether modifiers, except for NB-POSS. The bulky POSS pendent group likely hinders the penetration of the modifier into the brush within the experimental time frame. Fig. 4a–d shows the FTIR spectrum for each thiol-ene modification. In each case, the disappearance of the thiol peak at 2567 cm^{-1} was observed indicating the conversion from pendent thiol to pendent thioether. Likewise, the FTIR spectra clearly show peaks that are indicative of the incorporated alkene modifiers. For example, brushes modified with NB-CN exhibit a peak at 2238 cm^{-1} corresponding to the

nitrile (Fig. 4a). The peak at 1111 cm^{-1} , as shown in Fig. 4b, corresponds to the Si-O group of the POSS moiety resulting from successful incorporation of NB-POSS. Brushes modified with vinyl ethers show a broad peak centered at 3400 cm^{-1} , 1119 cm^{-1} and 1067 cm^{-1} corresponding to the EGVE hydroxyl and ether groups, respectively (Fig. 4c). Sharp peaks at 2854 cm^{-1} and 2924 cm^{-1} , as observed in Fig. 4d, are attributed to the aliphatic C-H groups of DVE. Static WCA measurements show the expected changes in wettability associated with each functional moiety conjugated to the surface (Fig. 4 insets).

Patterning thiol-functionalized polymer brush surfaces

Materials with micro-engineered surfaces that express multifunctional, spatially defined chemistries are fundamentally important for applications ranging from biosensors and tissue engineering to adhesives and microelectronics.^{12,52} Here, we use the thiol-functionalized polymer brush platform to demonstrate two simple approaches to micropatterned surfaces. First, area selective thiol-Michael modifications were performed using a microcapillary patterning process.²⁹ A PDMS stamp with linear microchannels (linewidth $15\text{ }\mu\text{m}$) was placed in direct contact on a reduced cystamine-modified pSMA brush (thickness $\sim 140\text{ nm}$), as illustrated in Fig. 5a. An aqueous solution of HEA and DBU was wicked into the microchannel *via* capillary action with a contact time of 60 min. After removing the stamp and thoroughly washing the brush surface, the process yields a micropatterned thioether/thiol surface. Fig. 5b shows the AFM height image of the micropatterned surface and the averaged cross section profile of the height image. The height image clearly shows a $\sim 65\text{ nm}$ increase in brush thickness in HEA exposed regions compared with the PDMS protected regions – an increase consistent with near quantitative conversion of the pendent thiols.

Second, area selective thiol-ene modifications were performed using a simple photopatterning technique while

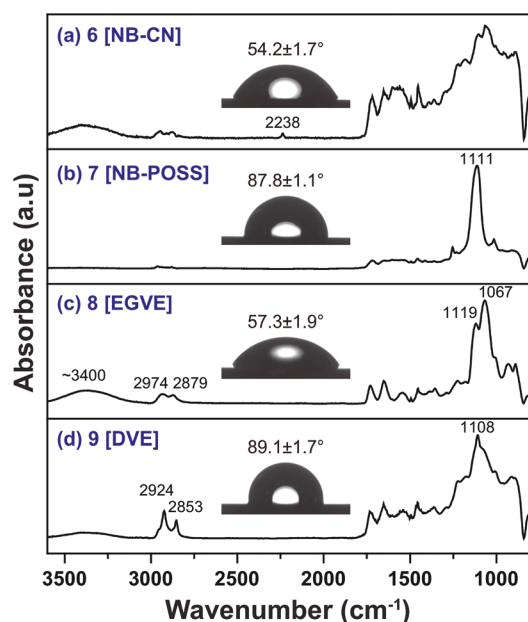


Fig. 4 gATR-FTIR of modified thiol containing polymer brushes using the following alkene modifiers: (a) NB-CN, (b) NB-POSS, (c) EGVE, and (d) DVE. Inset images show the static water contact angle.

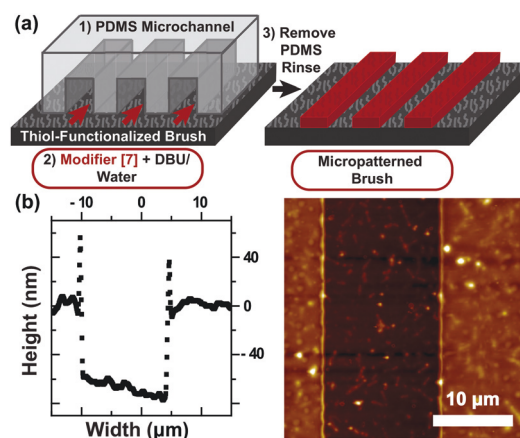


Fig. 5 (a) Microcapillary patterning thiol-functionalized polymer brush surfaces with thiol-Michael reactions. (b) $30\text{ }\mu\text{m} \times 30\text{ }\mu\text{m}$ AFM height image of micropatterned brushes using HEA and the averaged cross section of the AFM height image.

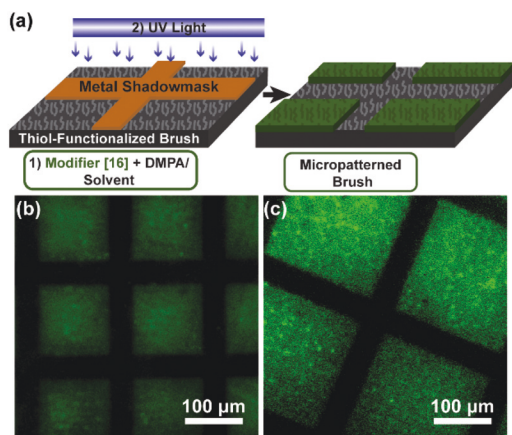


Fig. 6 (a) Photopatterning thiol-functionalized polymer brush surfaces with radical-mediated thiol–ene reactions. Fluorescence microscopy images of patterned brush surface using of fluorescein *O*-methacrylate using (b) 150 mesh and (c) 100 mesh grids. Excitation for microscopy was 488 nm.

employing fluorescein *O*-methacrylate (16, FMA) as the modifier. Copper grids (100 mesh, 149 μm and 150 mesh, 89 μm) were used as shadow masks to develop a spatially patterned polymer brush using radical thiol–ene coupling reaction between the pendent thiols and fluorescein *O*-methacrylate (Fig. 6a). Thiol-functionalized brush surfaces were submerged in a fluorescein *O*-methacrylate/THF solution and a TEM grid was placed in direct contact with the surface. The masked surface was irradiated with UV light (300–500 nm, 21.8 mW cm^{-2}) to facilitate the thiol–ene modification only in the exposed areas. It should be noted that homopolymerization of the methacrylate likely occurs in solution in the UV exposed areas, however, physisorbed polymer can be removed from the surface *via* a thorough rinse step. Fig. 6a and b show the fluorescent micrographs of the patterned brush surface under illumination with an argon laser ($\lambda = 488 \text{ nm}$). The fidelity of the features and the uniformity of the patterned surface highlight the efficiency of both the deprotection and subsequent photoinduced thiol–ene modification. We also note that the thiol–Michael addition between the tethered thiol and the methacrylate can be precluded in the absence of an appropriate catalyst (*e.g.* phosphine). Control experiments in the absence of light under otherwise identical conditions yielded no detectable fluorescence on the brush surface after rinsing.

Conclusions

In this work, we have demonstrated the synthesis and post-polymerization modification of styrene–maleic anhydride copolymer brushes using simple and efficient amine–anhydride reactions. The postpolymerization modification of pSMA brushes exploits the high reactivity of the amine–anhydride reaction, which proceeds rapidly to high conversions under mild reaction conditions. Although a library of amine modi-

fiers was explored, modification of the pSMA brushes with cystamine was the primary focus. Cystamine-modified brushes served as convenient precursors, which upon reductive cleavage of the disulfide linkage, provided thiol-functionalized polymer brush surfaces. We showed that thiol-containing polymer brush surfaces readily serve as a modular PPM platform using base-catalyzed thiol–Michael and photoinduced radical thiol–ene reactions as routes to multifunctional, micropatterned surfaces. Ultimately, the pSMA brush platform offers as an attractive and modular approach to tailor the functionality of polymer brush surfaces and should find widespread use among polymer surface science community.

Conflicts of interest

There are no conflicts to declare.

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