

Direct Patterning of Intrinsically Electron Beam Sensitive Polymer Brushes

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Stable and functional polymer brushes have been used as high-tech coatings on flat or curved organic and inorganic substrates for a variety of applications. Polymer brushes refer to an assembly of polymer chains tethered by one end to a surface. This tethering is sufficiently dense and due to this high steric crowding, the grafted chains extend from the surface, thus residing in an entropically unfavorable conformation.^{1,2} Generally, end-tethered polymer brushes, with covalent attachment of polymers on the substrate surface are assembled by either the “grafting to” or the “grafting from” approach. In the “grafting to” approach, preformed polymers are made to react with the reactive sites on the surface. The “grafting to” technique produces brushes with low grafting density and relatively low thickness due to the increased steric hindrance of grafted chains. This steric hindrance inhibits diffusion of large free polymer chains to diffuse to open surface reactive sites.³ The “grafting from” approach, often referred to as surface-initiated polymerization, is attracting a lot of scientific interest mainly because it offers a way to assemble polymer brushes with tunable grafting density and brush thickness in a controllable fashion. Surface-initiated polymerization involves polymerizing a monomer from an immobilized monolayer of surface initiators. Several polymerization reactions such as conventional radical polymerization,⁴ iniferter,⁵ ring-opening metathesis polymerization (ROMP),⁶ cationic,⁷ anionic,⁸ aminoxyl mediated,⁹ radical addition–fragmentation chain transfer (RAFT),¹⁰ and atom transfer radical polymerization (ATRP)¹¹ have been used to grow dense end-tethered polymer brushes.

ABSTRACT The fabrication of patterned polymer brushes has attracted considerable attention as these structures can be exploited in devices on the nano- and microscale. Patterning of polymer brushes is typically a complex, multistep process. We report the direct patterning of poly(methyl methacrylate) (PMMA), poly(2-hydroxyethyl methacrylate) (PHEMA), poly(isobutyl methacrylate) (PIBMA), poly(neopentyl methacrylate) (PNPMA), and poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) brushes in a single step by electron beam (e-beam) lithography, to obtain nanopatterned polymer brush surfaces. PMMA, PHEMA, PIBMA, PNPMA, and PTFEMA brushes were grown on silicon substrates *via* surface-initiated atom transfer radical polymerization. Surface analysis techniques including ellipsometry, contact angle goniometry, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) were used to characterize the thickness, hydrophilicity, roughness, and chemical composition of the polymer brushes. Tapping-mode AFM imaging confirmed the successful electron beam patterning of these brushes. Using this direct patterning method, highly resolved nanostructured polymer brush patterns down to 50 nm lines were obtained. This direct patterning of brushes eliminates the need for complex lithographic schemes. The sensitivity of these polymer brushes toward direct patterning with e-beam was studied and compared. The sensitivity curves indicate that the structure of the e-beam degradable methacrylate polymer has a significant effect on the sensitivity of the polymer brush toward e-beam patterning. In particular, the effect of the chemical functionality at the β -position to the carbonyl group on the polymer brush sensitivity toward direct patterning was studied using groups of varying size and polarity.

KEYWORDS: polymer brushes · methacrylates · direct patterning · nanopatterns · e-beam lithography.

The fabrication of patterned polymeric nanostructures has received significant interest because of its applications that range from the production of integrated circuits, information storage devices, and light emitting displays to the fabrication of semiconductor microelectronics, microelectromechanical systems (MEMS), miniaturized sensors, micro- or nanofluidic devices, biochips, and for the production of optical components such as gratings and photonic crystals.^{12–14} The past decade has witnessed the rapid development of a broad range of strategies used to pattern polymer brushes. Conventionally, patterned polymer brushes are produced from the initiator monolayer immobilized on patterned

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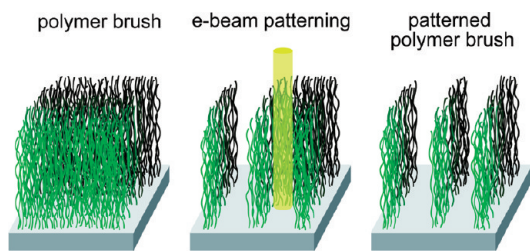


Figure 1. Schematic representation of the direct patterning of polymer brushes using electron beam lithography.

surfaces.^{15–19} Here, the substrate is first patterned using complex lithographic schemes. Then a suitable initiator is immobilized in the patterned regions to grow polymer brushes in these confined regions. Patterned brushes have also been obtained *via* surface initiated polymerization from initiator containing self-assembled monolayers (SAMs) patterned by microcontact printing,^{20–25} two-dimensional gradients,²⁶ contact molding,²⁷ scanning probe microscopy²⁸ or chemical lithography with electron irradiation^{29–31} and subsequent surface initiated polymerization of a desired monomer. Kang and co-workers prepared self-assembled monolayers (SAMs) containing patterns of two different initiators, which they subjected to sequential orthogonal polymerization steps.³² Zhou *et al.* prepared binary brushes of poly(methyl methacrylate) (PMMA) and poly(2-hydroxyethyl methacrylate) (PHEMA) *via* photoetching and reinitiation.³³ Andruzzi *et al.* have reported the patterning of polymer brushes using a modified photolithographic process involving the chemical vapor deposition of parylene.³⁴ In this method, the polymer brushes were first grown off the silicon surface. The parylene was deposited, coated with photoresist by spin-casting, exposed, developed, and reactive ion etched. Using this technique patterned brushes with 10 μm lines with 40 μm pitch size were prepared. Luzinov recently reported the use of an imprinted masking layer to form binary brushes.³⁵ New patterning methods such as nanografting, dip-pen nanolithography, contact lithography, atomic force microscopy lithography, and microelectrochemical patterning have produced surface motifs with resolution down to tens of nanometers.^{36–40} Most of these patterning methods require many steps in between and each of these steps may impose the possibility of losing information or pattern distortion.

In this article, we report the direct patterning of poly(isobutyl methacrylate) (PIBMA), poly(neopentyl methacrylate) (PNPMA), and poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) brushes using electron beam lithography. The polymer brushes were grown on silicon substrates *via* controlled atom transfer radical polymerization and patterned in a single step by degrading specific regions of the brush under an electron beam (Figure 1). Using this direct patterning method, highly resolved nanostructured polymer brush patterns down to 50 nm lines were obtained. For our

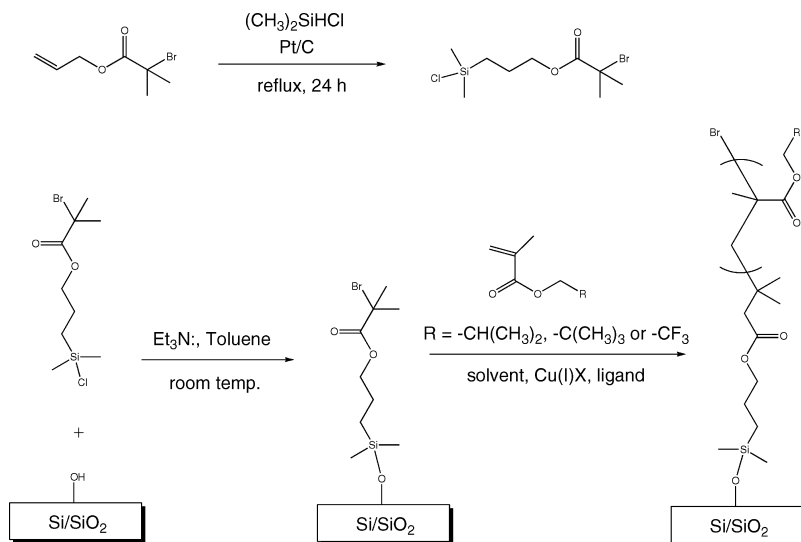
work, we have concentrated on patterned polymer brushes on oxidized silicon wafers since silicon wafers are relatively more stable and smooth compared to gold-coated surfaces. The silane/silicon interface is stronger than the thiol/gold interface. Additionally, patterning on oxidized silicon wafers may be compatible with integrated circuit technology.

It is well established that patterning of positive tone (meth)acrylate photoresists by electron beam (e-beam) exposure is based on the scission reactions that occur on the backbone chain.⁴¹ The scission reaction leads to the degradation of polymers into smaller fragments. For our studies, we chose different positive tone, e-beam methacrylate polymer brush systems with varying chemical functionalities at β -position to the carbonyl group. PMMA and PHEMA are classical positive tone photoresists for e-beam lithography. Recently, we showed that PMMA and PHEMA brushes could be directly patterned, in a single step using e-beam lithography, to achieve patterned brush surfaces with features down to sub-50 nm.⁴² In this paper, the sensitivity of PIBMA, PNPMA, and PTFEMA brushes toward e-beam patterning was studied and compared to the sensitivity of PMMA and PHEMA brushes. The contrast curves obtained for these e-beam degradable polymeric systems indicates that a polymer brush that degrades to form a more stable main chain radical is more sensitive to e-beam irradiation. The order of sensitivity of the methacrylate polymer brush systems was evaluated and explained on the basis of the trend of the molecular free energy values of the main chain radicals and R^\bullet radicals (Scheme 2). High quality quantitative predictions for the methacrylate systems were performed using *ab initio* methods.

RESULTS AND DISCUSSION

Preparation and Characterization of Polymer Brushes.

Synthesis and Characterization of Initiators on Silicon Substrates. The silane ATRP initiator, 3-(chlorodimethylsilyl)propyl 2-bromo-2-methylpropionate, was synthesized in one step using a literature procedure. The disappearance of the alkene protons in the ^1H NMR spectra of the hydrosilylated product confirmed the completion of the reaction after 24 h. The covalent attachment of the silane initiator on to the silicon substrate was carried out in a single step. The formation of a monolayer of initiator was confirmed by ellipsometry and AFM. The dry ellipsometric thickness of the covalently attached monolayer was measured to be 1.6 ± 0.3 nm (the error is due to uncertainties present during the calculation of the film thickness from the optical data). This value is in good agreement with the theoretical height of the initiator containing SAM. The surface topography and roughness was measured by AFM. The root-mean-square (rms) roughness of the initiator-coated silicon substrate was 0.2 nm in a $0.5 \times 0.5 \mu\text{m}^2$ scanning area.



Scheme 1. Synthesis of the polymer brushes: synthesis of the ATRP silane initiator, immobilization of the initiator on the silicon substrate, and surface initiated polymerization of the methacrylate monomer.

This is similar to the rms roughness measured for clean bare silicon pieces.

Preparation and Characterization of Polymer Brushes. PMMA and PHEMA brushes were prepared using a literature procedure.⁴⁴ Jones and Huck reported the controlled surface initiated polymerization of MMA and HEMA to grow thick polymer brushes using aqueous atom transfer radical polymerizations at room temperature. This strategy resulted in controlled brush growth without the addition of sacrificial initiator. Polymerization in aqueous media allows rapid increase in rate of polymerization to grow brushes without losing control over the reaction. We applied the same concept to grow poly(isobutyl methacrylate) (PIBMA) and poly(neopentyl methacrylate) (PNPMA) brushes. To date there is no report of surface-initiated polymerization of isobutyl methacrylate (IBMA) and neopentyl methacrylate (NPMA) to grow PIBMA and PNPMA brushes. Both monomers were polymerized *via* ATRP in isopropyl alcohol (IPA) and water mixture at 32 °C. The formation of PIBMA and PNPMA brushes is fast in this solvent mixture. Chen and co-workers have reported the surface-initiated polymerization of TFEMA on silicon substrates.⁴⁶ They showed that the ATRP reaction of TFEMA is better controlled in a fluorinated solvent such as α,α,α -trifluorotoluene. The use of dNnbpy as the ligand gave a more linear kinetic plot of monomer conversion with polymerization reaction time. The reaction for the synthesis of the ATRP silane initiator and preparation of polymer brushes is shown in Scheme 1. No sacrificial initiator was added to the solvent mixture and the polymerization was surface initiated and surface confined. This prevents the formation of undesirable polymer in solution, resulting in easy retrieval of the delicate polymer brush surfaces. Clean polymer brush surfaces were obtained simply by washing the polymer brushes with water, acetone, and ethanol.

For our purpose, we preferred to use polymer brushes with thicknesses less than 100 nm. The reaction time was determined by measuring the dry ellipsometric thicknesses of the polymer brushes prepared at various polymerization reaction times. The polymerization reactions appeared to be well controlled. We have reported elsewhere that the thickness of the PTFEMA brushes increases linearly with respect to reaction time up to approximately 24 h.⁴⁷ Figure 2 shows the plot of ellipsometric thickness *versus* polymerization reaction time for the PIBMA and PNPMA brushes. The formation of these brushes is fast and thick polymer brushes were obtained within 2 h at 32 °C. NPMA polymerized at a relatively faster rate than IBMA. PNPMA brushes as thick as 120 nm were obtained in an hour. About 100 nm thick PIBMA brushes were obtained after 2 h. The addition of water to the ATRP reaction speeds up the reaction considerably. At longer reaction times, the increase in brush thickness seems to slow down. This is attributed to the loss of active chain ends or to the increase in deactivator concentration that slows down the activation/deactivation cycles, which in turn slows down the polymer brush growth.

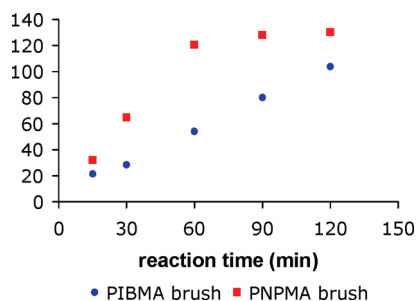


Figure 2. Dry ellipsometric thickness of the PIBMA and PNPMA brushes as a function of polymerization reaction time. A linear increase in brush thickness over times suggests that the brush growth is controlled. NPMA polymerizes at a faster rate than IBMA.

The polymer brushes were characterized by ellipsometry, tapping-mode AFM, water contact angle goniometry, and XPS. The dry thicknesses of the polymer brushes were measured by ellipsometry at a 70° incident angle. The value of $n = 1.50$ was used as the refractive index to determine the thickness of PMMA, PHEMA, PIBMA, and PNPMA brushes. Value of $n = 1.437$ was used as the refractive index for PTFEMA brushes. Tapping mode AFM images of all polymer brushes showed a rms roughness between 0.32 and 0.46 nm, indicating that the polymer brushes were homogeneous throughout the silicon substrate. At room temperature, in ambient air, the advancing and receding water contact angles for the PIBMA brushes were 93° and 72°, respectively. The advancing and receding contact angles for PNPMA brushes were 113° and 55° and those for the PTFEMA brushes were 94° and 70°, respectively. The PIBMA brushes were rinsed with acetone and dichloromethane, THF, or IPA and dried at room temperature in a vacuum oven before measuring the water contact angles. As expected, the PIBMA, PNPMA, and PTFEMA brushes caused the surface to be much more hydrophobic than bare silicon. The surface composition of the polymer brushes was determined using X-ray photoelectron spectroscopy (Figure 3). The C 1s (285 eV), O 1s (533 eV), and F 1s (687 eV) peaks were clearly observed in the XPS spectrum. The relative areas of these peaks are in good agreement with the known composition of PIBMA, PNPMA, and PTFEMA. The atomic percentages from the XPS spectra were C (81.5%), O (18.5%) for PIBMA brushes, C (83.4%), O (16.6%) for PNPMA brushes and C (53.4%), O (17.2%), F (29.41%) for PTFEMA brushes.

Direct Patterning of Polymer Brushes Using e-Beam Lithography.

The fabrication of nanopatterned polymer brush architectures on surfaces is of paramount importance in many areas of modern science and technology as these surfaces are much more robust compared to traditional polymer films. Generation of patterned polymer brushes is traditionally achieved by optical lithography. Some of the conventional approaches involve the immobilization of initiators on surfaces patterned using photolithography. In another approach, an initiator containing self-assembled monolayer is patterned to form a patterned initiator layer. Surface-initiated polymerization of a suitable monomer on these surfaces gives rise to patterned polymer brushes. These methods are quite complex and require multistep lithographic schemes that can increase the chances of surface contamination. Whitesides and co-workers introduced the concept of microcontact printing for the preparation of patterned SAMs on planar and curved surfaces.⁴⁸ This method offers advantages in applications where photolithography is ineffective. However, it does not enable the fabrication of nanometer-scale patterns and requires a minimum of three steps to obtain the patterned brush surfaces. Moreover, Patra and Linse used

computational simulations to show that the growth of brushes from patterned initiator layers lead to lower resolution features when the polymer brush height is comparable in length to the pattern width due to chain relaxation in the voided regions during growth.⁴⁹ Andruzzi *et al.* reported the micropatterning of polymer brushes using a photolithographic process involving the chemical vapor deposition of parylene.³⁴ Though successful, this method can damage the delicate brush surface and the functionalities on the surface during the parylene peel-off step.

In an attempt to prepare nanopatterned polymer brushes in a single step, we investigated the direct patterning of methacrylate polymer brushes using electron beam lithography. Electron-beam lithography enables the fabrication of nanometer-scale patterns as small as 20 nm. The primary advantage of e-beam lithography over photolithography is that the e-beam process uses electrons of wavelength less than 0.1 nm and is not diffraction limited. Besides high lateral resolution, e-beam lithography makes it possible to write complex patterns by adjusting the irradiation dose. Electron beam processing has been used to boost properties by creating controlled degradation or chain scission of certain polymers. Electron beams have been used to break down polymeric materials to create micropowders used in inks, coatings, and lubricants. Doses ranging from 65 to 689 $\mu\text{C}/\text{cm}^2$ were used for the PMMA, PHEMA, and PNPMA brushes. The PIBMA brushes were patterned at doses ranging from 130 to 1378 $\mu\text{C}/\text{cm}^2$. PTFEMA brushes were patterned at e-beam doses ranging from 5 to 150 $\mu\text{C}/\text{cm}^2$ with a beam current of 0.5 nA. After electron beam exposure, followed by development in a suitable organic solvent, a contrast curve was generated in which the normalized thickness was plotted as a function of the log of the exposure (Figure 4). Using the appropriate dose ascertained from the contrast curve, higher resolution lines of patterned PIBMA, PNPMA, and PTFEMA brushes were imaged. Factors such as the electron beam diameter, beam current, and dose were optimized to improve the resolution of the patterned brushes.

Sensitivity of Polymer Brushes Toward e-Beam Patterning. Different positive tone methacrylate polymers were chosen that lead to scission reactions on the polymer backbone on exposure to electron beams. The scission reaction leads to the degradation of polymers by rupture of covalent bonds. This causes a decrease in molecular weight and intrinsic viscosity. The exposed PIBMA and PNPMA brushes were developed in IPA for 90 s at room temperature. Tetrahydrofuran (THF) (90 s at room temperature) was used as the developer for the PTFEMA brushes. The degraded polymer fragments showed good solubility in the two solvents, leaving the covalently attached polymer brushes on the surface unaffected. Polymer brushes were successfully patterned in a single step on exposure to an electron beam and char-

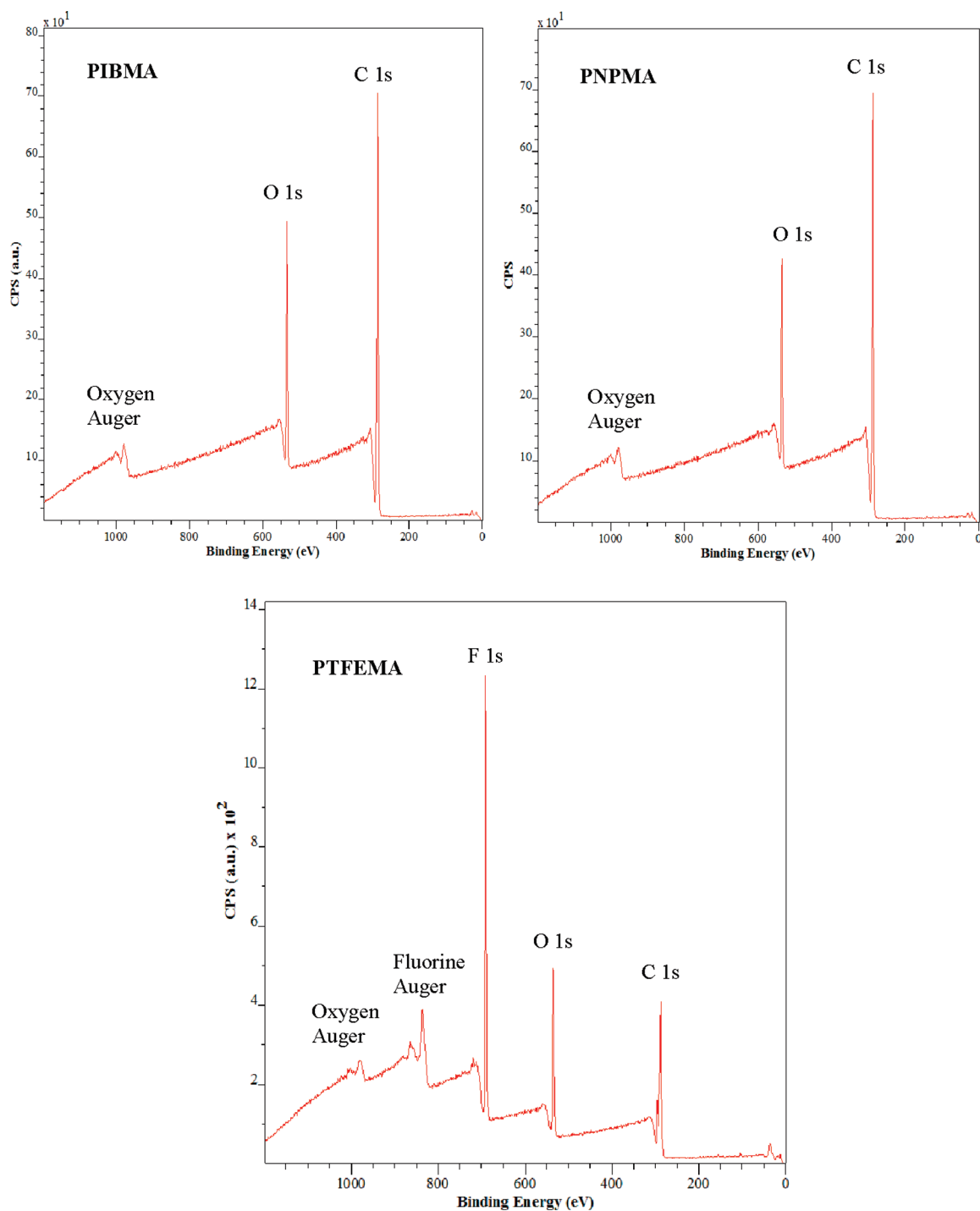


Figure 3. X-ray photoelectron spectroscopy survey spectra of PIBMA, PNPMA, and PTFEMA brushes. The XPS spectra suggest atomic compositions as expected from the structure of each polymer.

acterized and imaged by tapping mode AFM. The contrast curve of the different methacrylate brushes is shown in Figure 4. The contrast curves indicate that PNPMA brushes are the most sensitive to e-beam lithography while PMMA brushes are the least sensitive. The increasing order of polymer brush sensitivity toward direct patterning *via* e-beam lithography is PMMA < PIBMA < PHEMA \approx PNPMA < PTFEMA.

Figure 5a is an AFM image of 50 nm lines of a patterned PIBMA brush with a pitch size of 100 nm that

was patterned by e-beam lithography with an exposure dose of 1060.8 $\mu\text{C}/\text{cm}^2$ and developed in IPA solvent for 90 s at room temperature. Figure 5b is an AFM image of 80 nm lines of a patterned PIBMA brush with a pitch size of 160 nm obtained using similar lithographic and development conditions. Figure 5 panels c and d are AFM images of 100 nm lines/200 nm pitch and 200 nm lines/400 nm pitch of patterned PNPMA brushes, respectively, that were patterned by e-beam lithography with an exposure dose of 185.9 $\mu\text{C}/\text{cm}^2$

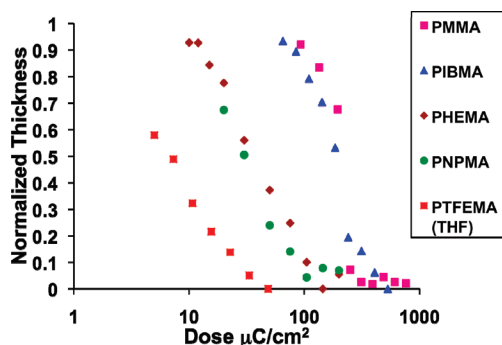


Figure 4. Normalized thickness versus electron beam exposure dose of the PMMA, PHEMA, PIBMA, PNPMA, and PTFEMA brushes.

and developed in IPA solvent for 90 s at room temperature.

With the development of patterned PNPMA brushes in IPA, we observed line broadening of the PNPMA brushes. This is because in the IPA solvent, the PNPMA polymer chains tend to relax or collapse in the patterned silicon regions. This lateral relaxation in the voided regions makes it possible to vary the resolution of the lines formed from the PNPMA brushes. Such strategies have recently gained much interest. Chang and co-workers recently reported the ability to control the resolution of lines and dots formed from PMMA brushes by immersion of the brushes in water or THF.⁵⁰ However, they report the patterning of PMMA brushes using an elaborate, labor-intensive lithographic scheme. One could control the width of the patterned features by varying polymerization time and annealing temperature. THF is a good solvent for PTFEMA and was

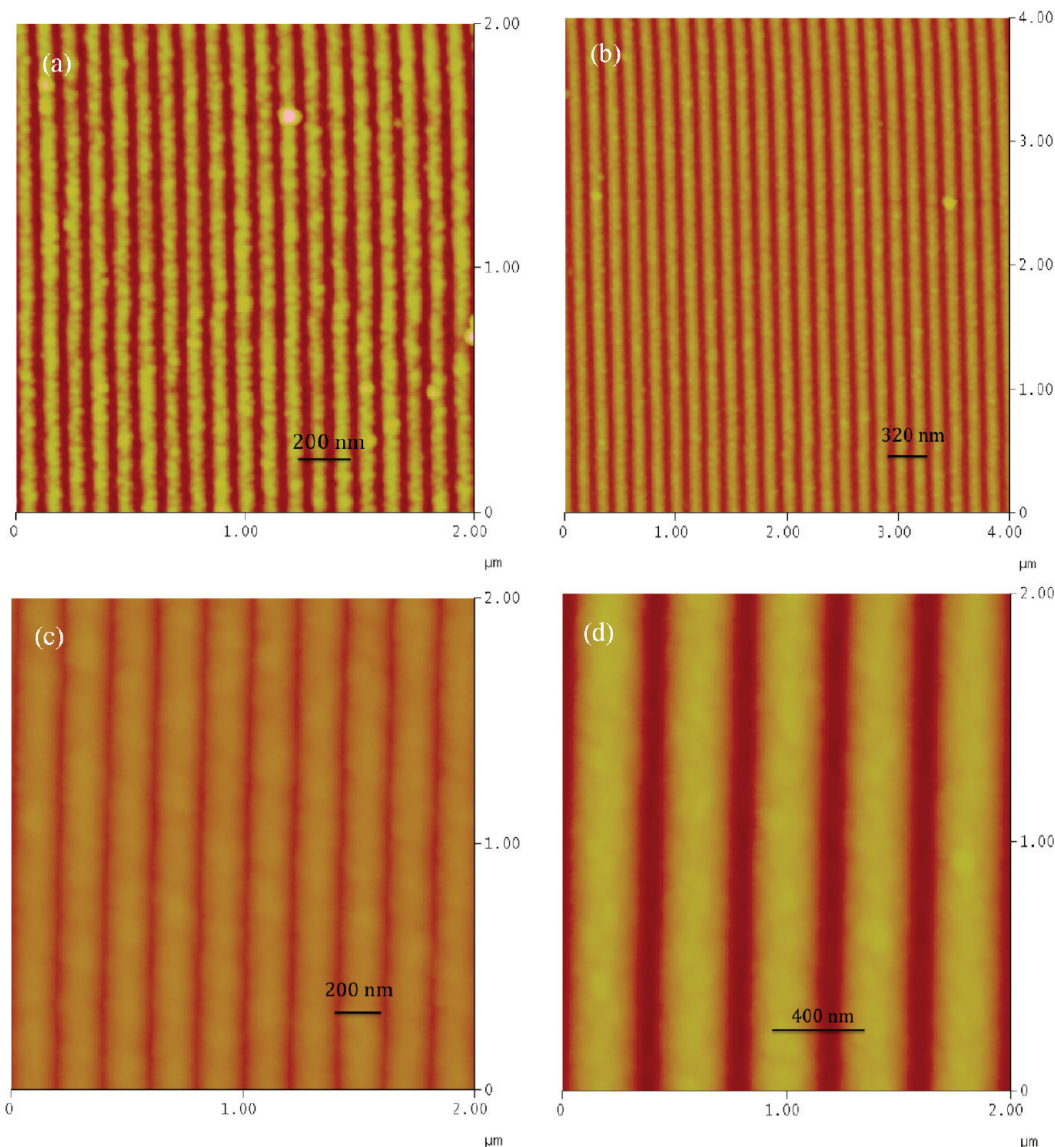


Figure 5. Tapping-mode AFM height images of patterned PIBMA and PNPMA brushes: (a) 50 nm lines/100 nm pitch size and (b) 80 nm lines/160 nm pitch size of a patterned PIBMA brush, patterned by e-beam lithography with an exposure dose of $1060.8 \mu\text{C}/\text{cm}^2$ and developed in IPA for 90 s at room temperature in air; (c) 100 nm lines/200 nm pitch size and (d) 200 nm lines/400 nm pitch size of patterned PNPMA brushes, patterned by e-beam lithography with an exposure dose of $185.9 \mu\text{C}/\text{cm}^2$ and developed in IPA for 90 s at room temperature in air.

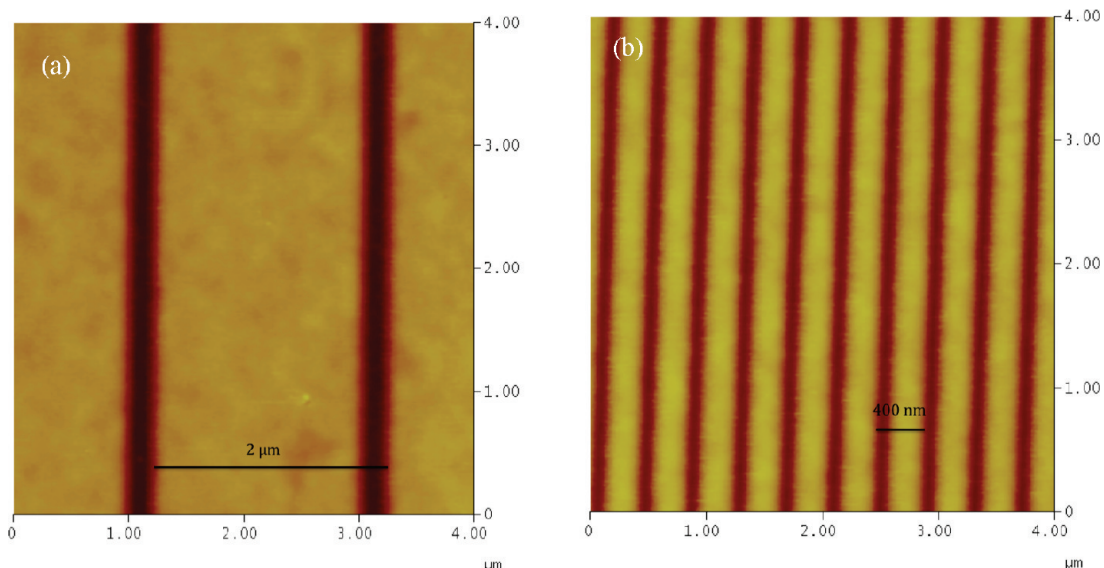


Figure 6. Tapping-mode AFM height images of patterned PTFEMA brushes: (a) 200 nm lines of isolated PTFEMA brush regions. Here the pattern size is 1800 nm with a pitch size of 2 μm ; (b) 100 nm lines/400 nm pitch size of patterned PTFEMA brushes. These patterns were obtained by e-beam lithography with an exposure dose of 48.4 $\mu\text{C}/\text{cm}^2$, followed by development in THF for 90 s at room temperature.

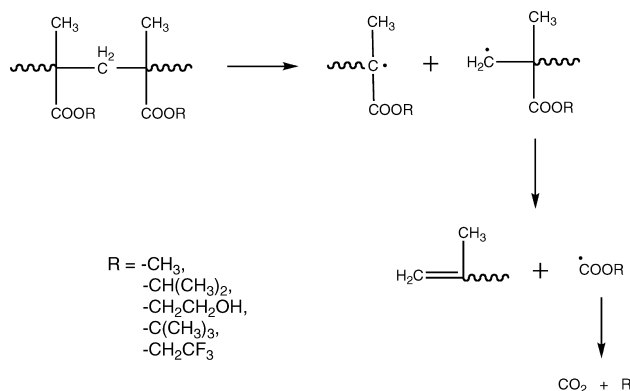
used to develop the exposed regions of the PTFEMA brushes. Figure 6 panels a and b show 200 nm lines of isolated PTFEMA brush regions with a pitch size of 2 μm and 100 nm lines of patterned PTFEMA brushes with pitch size of 400 nm, respectively. These patterns were obtained by e-beam lithography with an exposure dose of 48.4 $\mu\text{C}/\text{cm}^2$, followed by development in THF for 90 s at room temperature.

The observed polymer brush sensitivity toward direct patterning using e-beam lithography was explained on the basis of the stability of radicals formed on e-beam exposure. Bakhru and co-workers reported the degradation of PMMA by electron beam irradiation.⁵¹ Noda *et al.* performed an electron spin resonance study of the free-radical formation of plasma irradiated poly(methacrylic acid) and its esters.⁵² Both these studies suggest the degradation of methacrylate polymers to occur as shown in Scheme 2. We expect the degradability of the other methacrylate systems to be quite similar to the degradation of PMMA. On the basis of this mechanism, it may be hypothesized that the polymer that degrades to form a more stable radical on e-beam irradiation should be the most sensitive as a more stable product would drive the forward reaction. The molecular free energy values for the main chain radicals, formed by scissioning of the polymer backbone was evaluated using computational methods. In addition, the stability of $\cdot\text{CH}_3$ (from PMMA), $\cdot\text{CH}_2\text{CH}(\text{CH}_3)_2$ (from PIBMA), $\cdot\text{CH}_2\text{CH}_2\text{OH}$ (from PHEMA), $\cdot\text{CH}_2\text{C}(\text{CH}_3)_3$ (from PNPMA) and $\cdot\text{CH}_2\text{CF}_2$ (from PTFEMA) radicals that are formed later in the degradation process by decarboxylation was compared.

Computational chemistry has been used extensively to simulate chemical structures and reactions numerically. Electronic structure methods such as *ab ini-*

tio methods (implemented in the Gaussian package) are used to compute the free energy of a particular molecular structure. We used this method to quantitatively predict the energies of the methacrylate systems. Density functional theory (DFT) calculations were carried at the B3LYP/6-31G(d) level corresponding to the Becke-style 3-parameter density functional theory approximation method using the Gaussian 03 package.⁴⁵

On the basis of the DFT calculations we report the Gibbs molecular free energy values for the optimized low energy conformation for the different main chain radicals. We expect the methacrylate main chain radical with the lowest molecular free energy to be the most sensitive to e-beam exposure. The molecular free energy value of the PTFEMA main chain radical was calculated to be $-722.57 E_h$. It has the lowest molecular free energy among the other methacrylates which explains the high sensitivity of PTFEMA brushes. Molecular free energy calculated for PMMA was $-385.53 E_h$.



Scheme 2. Schematic representation of the degradation of methacrylate polymers on exposure to electron beams.

TABLE 1. Density Functional theory (DFT) Calculations on Optimized Low Molecular Energy Conformation of Each Main Chain Radical and Each R[•] Radical^a

methacrylate	molecular free energy (E _n) (DFT calculations)	
	main chain radical	R
PTFEMA	−722.57	−376.87 [· CH ₂ (CF ₃)]
PNPMA	−542.69	−196.98 [· CH ₂ C(CH ₃) ₃]
PHEMA	−500.02	−154.32 [· CH ₂ CH ₂ OH]
PIBMA	−503.40	−157.70 [· CH ₂ CH(CH ₃) ₂]
PMMA	−385.53	−39.83 [· CH ₃]

^aThe calculations were carried at the B3LYP/6-31G(d) level corresponding to the Becke-style 3-parameter density functional theory approximation method using the Gaussian 03 package.

The low sensitivity of PMMA brushes was attributed to the high energy value. The computationally obtained molecular energy values for main chain radicals of PNPMA, PHEMA, and PIBMA were −542.69 E_n, −500.02 E_n, and −503.4 E_n, respectively. The molecular energy values for the main chain radicals and the R[•] radicals are summarized in Table 1. The stability of the R[•] radicals can also be explained on the basis of the 1,3-hydride shift. The methyl radical is the least stable as it is not stabilized. The ·CH₂C(CH₃)₃ and ·CH₂C(CH₃)₃ radicals are stabilized by a 1,3-hydride shift. ·CH₂CH₂OH is stabilized by hyperconjugation. On the basis of these arguments, we see that the order of sensitivity of the polymer brush systems is similar to the order of radical stability. Though other factors also play a role, the radical stability has a significant effect on polymer e-beam degradation. We conclude, that the e-beam degradable methacrylate polymer brush system forming a more stabilized radical on e-beam exposure is more sensitive to e-beam irradiation. This direct patterning

method makes it possible to obtain nanopatterned polymer brushes in a single step.

CONCLUSIONS

We have demonstrated a single-step approach to form patterned polymer brushes on oxide surfaces by electron beam lithography. PIBMA, PNPMA, and PTFEMA brushes were grown on silicon substrates *via* ATRP. The chemical structure of the different brushes was confirmed by XPS and the physical properties were characterized by ellipsometry, water contact angle measurements. AFM confirmed the successful nanopatterning of the polymer brushes. Using e-beam lithography, polymer brush patterns as small as 50 nm were obtained. The contrast curves for PIBMA, PNPMA, and PTFEMA brushes were obtained and compared to PMMA and PHEMA brushes. The increasing order of polymer brush sensitivity toward e-beam patterning is PMMA < PIBMA < PHEMA ≈ PNPMA < PTFEMA. These studies indicate the e-beam degradable methacrylate polymer brush system that degrades to form a more stable main chain radical and R[•] radical tends to be more e-beam sensitive. Hence one can tailor-make polymer brushes to be highly sensitive for direct patterning using e-beam lithography by chemical modifications at the β-position to the carbonyl group. This direct method of patterning brush is much less complicated compared to conventional lithographic methods. The direct patterning of brushes is an efficient method to fabricate patterned macromolecular architectures with nanoscale precision. This method is not limited to methacrylates and is applicable to polymers that show positive tone behavior under e-beam exposure.

EXPERIMENTAL SECTION

Materials and Chemical Reagents. Allyl-2-bromo-2-methylpropionate, chlorodimethyl- hydrosilane, Pt on activated carbon (10 wt %), triethylamine, copper(I) bromide, copper(II) dibromide, copper(I) chloride, 4,4'-dinonyl-2,2'-dipyridyl (dNn-bpy), α,α,α-trifluorotoluene, 2,2'-bipyridine, inhibitor remover packing material, anhydrous toluene, isobutyl methacrylate (IBMA) (inhibited with 15 ppm monomethyl ether hydroquinone (MEHQ)), methyl methacrylate (MMA) (inhibited with 10–100 ppm MEHQ), and 2-hydroxyethyl methacrylate (HEMA) (inhibited with 200 ppm MEHQ) were purchased from Sigma Aldrich and used without purification unless stated otherwise. Neopentyl methacrylate (NPMA) (inhibited with 100 ppm MEHQ) and 2,2,2-trifluoroethyl methacrylate (TFEMA) (inhibited with 50 ppm MEHQ) were purchased from Scientific Polymer Products, Inc. Monomers were purified by passing through a short column of MEHQ and HQ inhibitor remover packing material. Deionized water with a resistivity of 18.2 MΩ · cm at 25 °C was obtained from Millipore's Milli-Q Synthesis A10 system. All other solvents for rinsing and cleaning were purchased from Fisher Scientific. Doped silicon wafers were obtained from Montco Silicon Technologies, Inc.

Synthesis and Immobilization of the Surface Initiator. Hydrosilylation of allyl 2-bromo-2-methylpropionate was carried out using a literature procedure to obtain the ATRP silane initiator, 3-(chlorodimethylsilyl)propyl 2-bromo-2-methylpropionate.⁴³

Silicon wafers were diced into 3 cm × 1 cm pieces, cleaned by rinsing with acetone, and dried under a nitrogen stream. To remove any organic residues on the surface, the substrates were further cleaned in Piranha solution (3:1 concentrated H₂SO₄/30% H₂O₂ solution) for 30 min. (*Caution:* piranha solution reacts violently with organic materials and should be handled carefully). After rinsing with copious amounts of deionized water, the substrates were washed with dichloromethane and then dried in a vacuum oven for 10 min at 120 °C. The clean Si wafer pieces were immersed in a toluene solution of the silane initiator (2 mM) and triethylamine (0.05 mM) for 24 h. The wafers were then removed from the solution and washed with dichloromethane and left to stand in dichloromethane for 18 h. The initiator-coated wafers were either used immediately or stored under standard conditions. No loss of activity was observed on storage for a couple of weeks.

Preparation of PMMA and PHEMA Brushes. PMMA and PHEMA brushes were prepared using a literature procedure.⁴⁴

Preparation of PIBMA Brushes. In a typical reaction, two initiator-coated silicon substrates (3 cm × 1 cm) were placed in a 25 mL Schlenk flask under an argon atmosphere. The flask was evacuated and backfilled with argon three times. CuBr (143 mg, 1.0 mmol), and 2,2'-bipyridine (312 mg, 2.0 mmol) were taken in another 25 mL Schlenk flask equipped with a magnetic stir bar. The air in the flask was evacuated and replaced with argon three times. The solvent mixture (deionized water, 2 mL and IPA, 8

mL) and purified IBMA (5 g, 35.2 mmol) were purged separately with argon for about an hour and cannulated into the flask containing the ligand and copper salts. The reaction mixture was stirred at room temperature for 10 min to ensure the dissolution of the monomer and the copper–ligand complex in the solvent. This solution was then transferred into the flask containing the silicon wafer pieces. Polymerization was carried out for a set reaction time at 32 °C. After polymerization, the substrates were removed from the flask and washed with IPA and acetone, gently sonicated in IPA for 5 min, and dried under a stream of nitrogen.

Preparation of PNPMA Brushes. PNPMA brushes were prepared by surface-initiated polymerization of NPMA (5 g, 32 mmol) via ATRP as described for PIBMA brushes. After polymerization, the substrates were removed from the flask and washed with IPA and acetone, gently sonicated in IPA for 5 min, and dried under a stream of nitrogen.

Preparation of PTFEMA Brushes. PTFEMA brushes were prepared using a modified literature procedure.⁴⁶ In a typical reaction, two initiator-coated silicon substrates (3 cm × 1 cm) were placed in a 25 mL Schlenk flask under an argon atmosphere. The flask was evacuated and backfilled with argon three times. CuCl (32 mg, 0.324 mmol), CuBr₂ (8 mg, 0.0324 mmol), and dNnbp (285.6 mg, 0.712 mmol) were taken in another 25 mL Schlenk flask equipped with a magnetic stir bar. The air in the flask was evacuated and replaced with argon three times. The solvent (α,α,α -trifluorotoluene, 13 mL) and purified TFEMA (8 mL, 56 mmol) were purged separately with argon for about an hour and cannulated into the flask containing the ligand and copper salts. The reaction mixture was stirred at room temperature for 10 min to ensure the dissolution of the monomer and the copper–ligand complex in the solvent. This solution was then transferred into the flask containing the silicon wafer pieces. Polymerization was carried out for a set reaction time at 90 °C. After polymerization, the substrates were removed from the flask and washed with THF and acetone, gently sonicated in THF for 5 min, and dried under a stream of nitrogen.

Characterization of Polymer Brushes. Polymer brushes were characterized by ellipsometry, water contact angle goniometry, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Thicknesses of the polymer brushes were measured using a Woollam variable angle spectroscopic ellipsometer at a 70° angle of incidence. A Cauchy model (Cauchy layer/silicon substrate) was used to fit the data, in which the Cauchy layer was representative of the polymer brush. Water contact angles were measured using a VCA optima XE goniometer. Dynamic water contact angles measurements were performed by addition and retraction of a drop of water on the surface. At least three sample spots were taken on each surface. Surface topography was analyzed and the root-mean-square (rms) roughness was measured using a Veeco Dimension 3100 scanning probe microscope. Olympus tapping mode etched silicon probes were used to acquire topographic images in air at room temperature. The surface composition of the polymer brush was determined by XPS using a Surface Science Instruments SSX-100 spectrometer with an operating pressure <2 × 10⁻⁹ Torr using monochromatic AlK α X-rays at 1486.6 eV. Photoelectrons were collected at an angle of 55° from the surface normal using a hemispherical analyzer with pass energies of 150 V acquired at 1 eV/step. The C–C 1s peak was corrected to a binding energy of 285 eV.

Direct Patterning of Polymer Brushes. Patterning of the polymer brushes was done at the Cornell Nanoscale Facility using the JEOL 9300 electron beam lithography system. To get an estimate on the patterning conditions needed, contrast curves were generated from 10 μm × 1 μm areas exposed to the electron beam with linearly increasing electron dosage. A 0.5 nA beam current, 100 kV accelerating voltage, and 5 nm pixel size was used for the generation of the contrast curves and for higher resolution patterning. Doses ranging from 65 to 689 $\mu\text{C}/\text{cm}^2$ were used for the PMMA, PHEMA, and PNPMA brushes. The PIBMA brushes were patterned at doses ranging from 130 to 1378 $\mu\text{C}/\text{cm}^2$. PTFEMA brushes were patterned at e-beam doses ranging from 5 to 150 $\mu\text{C}/\text{cm}^2$. After e-beam exposure, the polymer brushes were developed in an appropriate solvent, thor-

oughly rinsed in deionized water, and then dried under a stream of nitrogen.

Metrology. Optical microscopy imaging was performed using the Nikon Digital Sight DS-5M-L1 optical microscope. The patterned brush surface was analyzed using a Veeco Dimension 3100 scanning probe microscope. Olympus tapping mode etched silicon probes were used to acquire topographic images in air at room temperature.

Semiempirical Calculations. High quality quantitative predictions for the methacrylate systems were performed using *ab initio* methods. Density functional theory (DFT) calculations were carried at the B3LYP/6-31G(d) level using the Gaussian 03 package.⁴⁵

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