Development of a Directly Patterned Low-Surface-Energy Polymer Brush in Supercritical Carbon Dioxide

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ARTICLE

ABSTRACT Carbon dioxide (CO_2) is a sustainable solvent because it is nonflammable, exhibits a relatively low toxicity, and is naturally abundant. As a selective, nonpolar solvent, supercritical CO_2 ($scCO_2$) is an ideal fit for the development of low-surface-energy polymers. The development of directly patterned poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) brushes in $scCO_2$ was investigated. PTFEMA, in particular, was selected over other fluorinated polymers because of its very high electron-beam (e-beam) sensitivity. PTFEMA brushes were grown on silicon substrates via controlled surface-initiated atom-transfer radical polymerization of TFEMA. Surface analysis techniques including ellipsometry, contact-angle goniometry, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy were used to characterize the thickness, hydrophilicity, roughness, and chemical composition of the polymer brushes. PTFEMA brushes were directly patterned in a single step using e-beam lithography and were processed in an environmentally benign $scCO_2$ solvent. Tapping-mode AFM imaging confirmed the successful e-beam patterning and development of these brushes. The sensitivity of PTFEMA brushes toward direct patterning with the e-beam, followed by $scCO_2$ development, was studied and compared to development in tetrahydrofuran solvent. Using this direct-patterning method, followed by dry development in $scCO_2$, highly resolved nanostructured polymer brush lines down to 78 nm could be prepared. This method can be generalized to prepare fluorinated low-surface-energy polymer brush surfaces in a single step for various applications.

KEYWORDS: direct patterning • polymer brush • low surface energy • supercritical carbon dioxide • environmentally benign • e-beam lithography • poly(2,2,2-trifluoroethyl methacrylate)

INTRODUCTION

Carbon dioxide (CO_2) has continued to emerge as an environmentally benign solvent in the area of polymer synthesis and processing. CO_2 is nontoxic, nonflammable, and unreactive under most conditions, leaves no liquid waste, and is one of the most promising candidates for a more environmentally friendly replacement for organic and aqueous solvents in many applications. Supercritical fluid technology has been widely used as a processing tool in polymer synthesis, coatings, biomaterials, and microelectronics (1, 2). A supercritical fluid is a substance at a temperature and pressure above its thermodynamic critical point. Supercritical CO_2 ($scCO_2$) has the advantage of having an easily accessible critical point ($T_c = 31.1$ °C; $P_c = 72.8$ atm). Under these conditions, CO_2 exhibits properties such as high gaslike diffusivity, zero surface tension, ease of solvent removal by depressurization, the ability to be recycled, and the possibility of being tuned to achieve the desired density and solvent properties (3). These unique properties associated with $scCO_2$ offer a range of possibilities in polymer chemistry (4−6). One area in which $scCO_2$ has been studied in detail is as a development solvent for photoresist patterning (7−10).

Surface modification using end-tethered polymer brushes (11) is an attractive, versatile, and effective method of tailoring the surface properties of a material to specific needs. Polymer brushes have been utilized to prepare "smart" or responsive surfaces for a variety of applications in the area of microelectronics and biotechnology (12, 13). 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 (14). For kinetic and thermodynamic reasons (12, 13), the "grafting-to" approach is often limited to the formation of polymer brushes of relatively low thickness. The "grafting from" method, usually referred to as surface-initiated polymerization, has become the method of choice mainly because it offers a way to assemble polymer brushes with tunable grafting density and high polymer brush thickness in a controllable fashion. Surface-initiated polymerization involves polymerization of a monomer from an immobilized monolayer of surface initiators. Surface-initiated polymer brushes have been grown using conventional radical polymerization (15), iniferter (16), ring-opening (17), cationic (18), anionic (19), and aminoxyl-mediated (20) radical addition−fragmentation chain-transfer (21), and atom-transfer radical polymerization (ATRP) reactions (22).

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The fabrication of patterned polymer brushes has attracted great interest in recent years and is typically a complex, multistep process. Nanopatterned polymer arrays with controlled chemical functionality, shape, and feature dimensions have a wide range of potential applications in microelectromechanical systems, in the development of biosensors, biochips, and combinatorial arrays, in the study of cell—surface interactions, and in micro/nanofluidic devices (23, 24). Conventionally, patterned polymer brushes are produced from the initiator monolayer immobilized on patterned surfaces (23, 25, 26). Patterned brushes have also been grown from self-assembled monolayers (SAMs) patterned by microcontact printing (27—31), two-dimensional gradients (32), scanning probe microscopy (33), or chemical lithography with electron irradiation and subsequent surface-initiated polymerization of a desired monomer (34, 35). New patterning methods such as nanografting, dip-pen nanolithography, contact lithography, and atomic force microscopy (AFM) lithography have produced surface motifs with resolution down to tens of nanometers (36—38). More recently, we demonstrated the direct patterning of poly(methyl methacrylate) and poly(2-hydroxyethyl methacrylate) brushes using electron-beam (e-beam) lithography. Using this single-step patterning approach, high-resolution polymer brush patterns down to 50-nm lines were obtained (39).

Fluorinated polymers have been extensively utilized in optical devices, biomaterials, and high-quality coatings because of the special properties of these materials such as high thermal and chemical stability, low refractive index, low surface energy, and high hydrophobicity (40). Recently, fluorinated polymer brushes have been prepared by surface-initiated “living” polymerization to prepare low-surface-energy surfaces. Brantley and Jennings used the “grafting to” approach to prepare poly(2-hydroxyethyl methacrylate) brushes on gold substrates. The hydroxyl groups were then fluorinated to obtain fluorinated brushes (41). Andruzzi et al. have grown styrene-based homopolymer and copolymer brushes bearing semifluorinated alkyl side groups by surface-initiated aminoxyl-mediated polymerization (42). Granville et al. reported the synthesis of stimuli-responsive semifluorinated polymer brushes prepared by ATRP (43—45).

2,2,2-Trifluoroethyl methacrylate (TFEMA) has features of typical methacrylate monomers and a fluorine-containing monomer. Poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) is a transparent, amorphous polymer with excellent water repellency and stain resistance. PTFEMA has been used in various coating applications because of its heat and chemical resistance, low refractive index, weatherability, water and oil repellency, and electric insulating properties. Recently, Chen et al. reported the grafting of PTFEMA from silicon wafer surfaces by surface-initiated ATRP (24). However, there is no report of the direct patterning of PTFEMA brushes to obtain nanopatterned polymer brush surfaces.

Previously, we have reported the e-beam patterning of hot-filament fluorocarbon films prepared by chemical vapor deposition, using $scCO_2$ as the developer (46, 47). We have also demonstrated the development of spun-coat fluorinated polymeric photoresists in $scCO_2$ (10). In this paper, we demonstrate the development of directly patterned low-surface-energy PTFEMA brushes in $scCO_2$. PTFEMA, in particular, was selected over other fluorinated polymers because of its very high e-beam sensitivity. PTFEMA degrades into smaller fragments through depolymerization under e-beam exposure at a practically low e-beam dose. Figure 1 shows a schematic representation of the direct-patterning process to obtain nanopatterned PTFEMA brushes. PTFEMA brushes were prepared via controlled ATRP. The brushes were characterized by ellipsometry, water contact-angle goniometry, AFM, and X-ray photoelectron spectroscopy (XPS). The sensitivity of the brushes toward e-beam lithography, after development in the supercritical solvent, was studied and compared to development in tetrahydrofuran (THF) solvent. We show that the use of $scCO_2$ as a processing solvent has no negative effect on the polymer contrast and pattern fidelity of the nanosized features. Using this direct-patterning approach, followed by $scCO_2$ development, we have demonstrated patterns on the order of 80 nm. High-resolution, sub-100-nm features showed line broadening due to lateral relaxation of the polymer brushes in the voided regions. The 50 nm isolated lines showed 56% line broadening in $scCO_2$. The same 50 nm isolated lines showed a much higher line broadening of 88% in THF. This direct method of patterning using e-beam lithography of degradable polymers combined with development in $scCO_2$ is a desirable method to prepare patterned low-surface-energy polymer brushes.

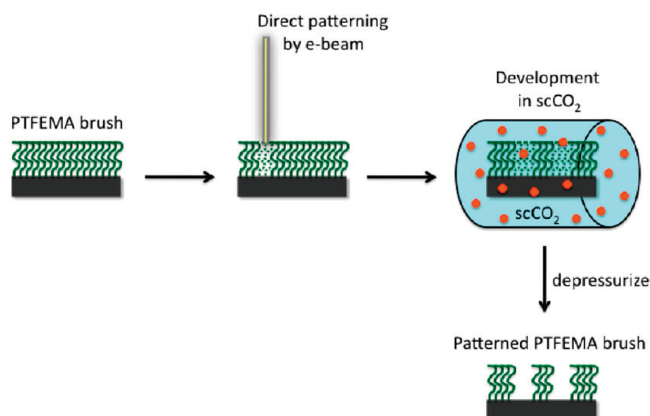


FIGURE 1. Schematic representation of the direct-patterning process. PTFEMA brushes were directly patterned using e-beam lithography and then developed in $scCO_2$ to obtain patterned brush surfaces.

EXPERIMENTAL SECTION

Materials. Allyl 2-bromo-2-methylpropionate, chlorodimethylhydrosilane, platinum on activated carbon (10 wt %), triethylamine, copper(I) chloride (99.999%), copper(II) dibromide, 4,4′-dinonyl-2,2′-dipyridyl (dNnbpy), α,α,α-trifluorotoluene, and an inhibitor remover packing material were purchased from Sigma Aldrich and used without purification. The monomer 2,2,2-trifluoroethyl methacrylate [TFEMA; inhibited with 50 ppm methylhydroquinone (MEHQ)] was purchased from Scientific Polymer Products, Inc. TFEMA was further purified before use by passing it through a short column of MEHQ and hydroquinone (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. Tetrahyrofuran (THF) was purchased from Fisher Scientific. Carbon dioxide (CO_2; 99.999%) and argon gas were obtained from Airgas Inc. 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 (48). Silicon wafers were diced into 3 × 1 cm^2 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 H_2SO_4/30% H_2O_2 solution) for 30 min. (**Caution!** *Piranha solution reacts violently with organic materials and should be handled carefully*.) After rinsing with copius 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 silicon 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, washed with dichloromethane, and left to stand in dichloromethane for 18 h. The initiator-covered wafers were either used immediately or stored under standard conditions. No loss of activity was observed upon storage for a couple of weeks.

Preparation of PTFEMA Brushes. In a typical reaction, two initiator-coated silicon substrates (3 × 1 cm^2) 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), $CuBr_2$ (8 mg, 0.0324 mmol), and dNnbpy (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 1 h and cannulated into the flask containing the ligand and copper salts. The reaction mixture was stirred at room temperature for 10 min to ensure 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, washed with THF, gently sonicated in THF for 5 min, and dried under a stream of nitrogen.

Characterization of PTFEMA Brushes. Polymer brushes were characterized by ellipsometry, water contact-angle goniometry, AFM, and XPS. The 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 PTFEMA polymer brush. Water contact angles were measured using a VCA optima XE goniometer. Dynamic water contact-angle measurements were performed by the 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 of $<2 \times 10^{-9}$ Torr using monochromatic Al Kα X-rays at 1486.6 eV. Photoelectrons were collected at an angle of 55° from the surface normal using a hemispherical analyzer with a pass energy of 150 V acquired at 1 eV/step for the survey scan. The C–C 1s peak was corrected to a binding energy of 285 eV.

Direct Patterning of PTFEMA Brushes. Patterning of the PTFEMA brushes was done at the Cornell Nanoscale Facility using a JEOL 9300 e-beam lithography system. In order to get an estimate on the patterning conditions needed, contrast curves were generated from 10 × 1 μm^2 areas exposed to the e-beam with linearly increasing electron dosage. A 0.5 nA beam current, 100 kV accelerating voltage, and 5 nm pixel size were used for generation of the contrast curves and for higher resolution patterning. Doses ranging from 5 to 150 $\mu C/cm^2$ were used in this study. After e-beam exposure, the PTFEMA brushes were developed in $scCO_2$ (50 °C, 5000 psi) for 5 min and dried under a stream of nitrogen. Exposed PTFEMA brushes were also developed in THF for 60 s, followed by thorough rinsing in deionized water and then drying under a stream of nitrogen.

Development of Patterned PTFEMA Brushes in $scCO_2$. Patterned PTFEMA brushes were developed in $scCO_2$ using a dissolution-rate monitor apparatus (49). The patterned PTFEMA brush was placed in a 25 mL observation vessel. CO_2 was introduced into this vessel and kept for 5 min at the desired temperature and pressure (50 °C, 5000 psi) to develop the patterned brushes in $scCO_2$. After $scCO_2$ development, the vessel was flushed with fresh $scCO_2$ for 2 min to wash out any of the dissolving polymer residue. The PTFEMA brushes were then removed from the dissolution-rate monitor apparatus and cleaned under a stream of nitrogen for a couple of seconds.

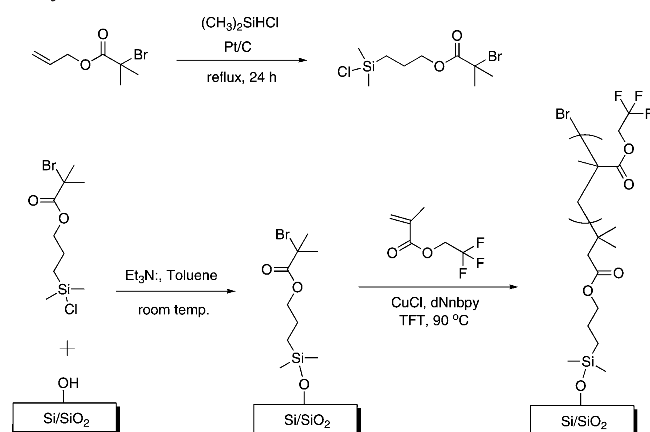
Metrology. Optical microscopy imaging was performed using a Nikon Digital Sight DS-5M-L1 optical microscope. Imaging and depth measurements of the patterned surfaces were done with a Veeco Dimension 3100 scanning probe microscope. Olympus tapping-mode etched silicon probes were used to acquire topographic images in air at room temperature.

RESULTS AND DISCUSSION

Preparation 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. Covalent attachment of the silane initiator onto 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 rms roughness of the initiator-coated silicon substrate was 0.2 nm in a 0.5 × 0.5 μm^2 scanning area. This is similar to the rms roughness measured for clean bare silicon pieces.

Preparation and Characterization of Polymer Brushes. PTFEMA brushes were synthesized via ATRP using a variation of the procedure described by Chen and co-workers (24) in α,α,α-trifluorotoluene at 90 °C for a set polymerization time. Haddleton and co-workers reported the solution ATRP of TFEMA in toluene with pyridineimine as the ligand (50). Chen and co-workers showed that the ATRP reaction of TFEMA is better controlled in a fluorinated solvent such as trifluorotoluene (24). They also showed that the use of dNnbpy as the ligand gave a more linear kinetic plot of monomer conversion with the polymerization reac-

Scheme 1. Synthesis of the ATRP Silane Initiator and Immobilization of the Initiator on the Silicon Substrate, Followed by Surface-Initiated Polymerization of TFEMA



tion time. The reaction for the synthesis of the ATRP silane initiator and the 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 an undesirable polymer in the solution, and clean polymer brush-covered surfaces were obtained simply by washing the polymer brushes with water, acetone, and ethanol.

For our study, we utilized polymer brushes with thicknesses close to or less than 100 nm. The reaction time was determined by measuring the dry ellipsometric thicknesses of the PTFEMA brushes prepared at various polymerization reaction times. The polymerization reaction was controlled, as indicated by a linear increase in the thicknesses of the brushes with respect to the reaction time (51−55) up to approximately 24 h. Figure 2 shows the plot of ellipsometric thickness versus polymerization reaction time. At longer reaction times, the increase in the brush thickness seems to slow down. This is attributed to the loss of active chain ends or to the increase in the deactivator concentration that slows down the activation/deactivation cycles, which, in turn, slows down the polymer brush growth.

The homopolymer brushes were characterized by ellipsometry, tapping-mode AFM, water contact-angle goniometry, and XPS. The dry thicknesses of the PTFEMA brushes

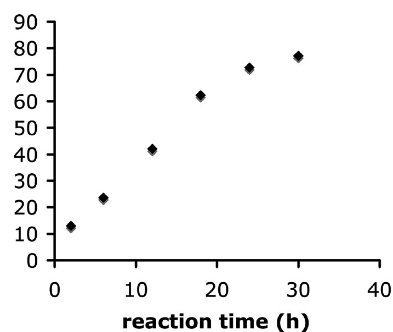


FIGURE 2. Dry ellipsometric thickness of the PTFEMA brushes as a function of the polymerization reaction time. A linear increase in the brush thickness over time suggests that the brush growth is controlled.

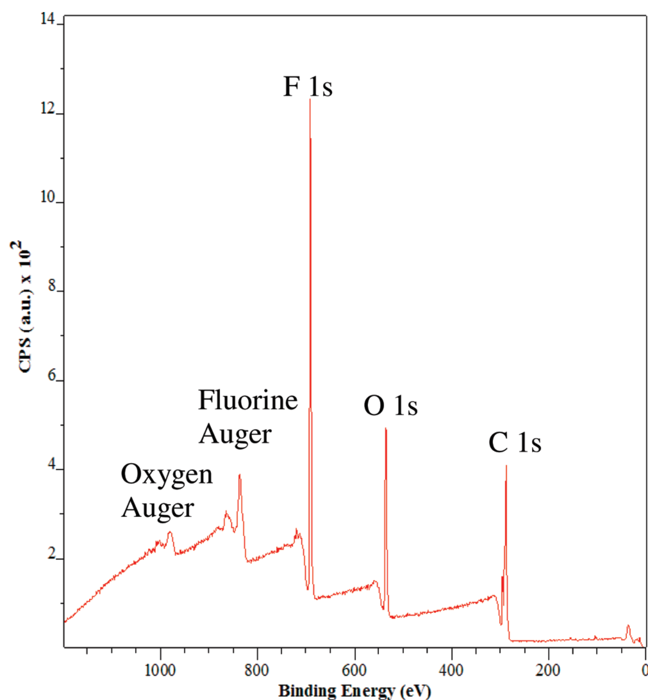


FIGURE 3. XPS survey spectrum of a 50 nm PTFEMA brush grown off a silicon substrate. The XPS spectrum suggests an atomic composition of carbon (53.4%), oxygen (17.2%), and fluorine (29.41%), as expected from the structure of the polymer.

were measured by ellipsometry at a 70° incident angle. The value of $n = 1.437$ was used as the refractive index to determine the thickness. Tapping-mode AFM of the PTFEMA brushes showed the rms roughness as 0.42 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 PTFEMA brushes were 94 ± 1° and 70 ± 2°, respectively. The polymer brushes were rinsed with acetone and THF and dried at room temperature in a vacuum oven before measurement of the water contact angles. Thus, as expected, the fluorinated polymer brush caused the surface to be much more hydrophobic than bare silicon. After polymerization, the surface composition of the PTFEMA brush was characterized using XPS (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 PTFEMA. The atomic percentages of carbon, oxygen, and fluorine were 53.4%, 17.2%, and 29.41%, respectively.

Preparation of Patterned PTFEMA Brushes. ***Direct Patterning of PTFEMA Polymer Brushes Using E-Beam Lithography.*** In recent years, the preparation of patterned polymer brushes has emerged as a robust method for creating surfaces because of the stability of polymer brushes against solvents or harsh conditions. Patterned brush surfaces are routinely produced from an initiator monolayer on a patterned surface. While successful, this method requires complicated lithographic schemes. The inclusion of extra steps leads to additional opportunities for contamination and image degradation. The compatibility of the photoresist is important because the patterned photo-

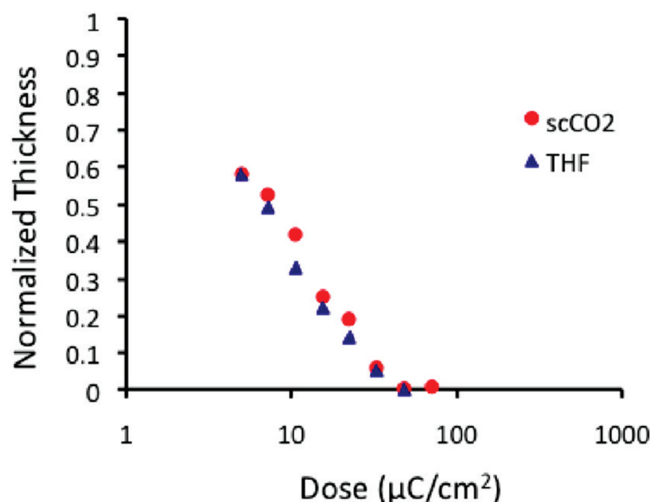


FIGURE 4. Contrast curves of the PTFEMA brushes developed in $scCO_2$ at 50 °C, 5000 psi, for 5 min (shown in red) or developed in a THF solvent at room temperature for 90 s (shown in blue).

resist, if soluble in the initiator solution, will restrict the formation of patterned initiators. To address these challenges, Xia and Whitesides developed microcontact printing for the preparation of patterned SAMs on both planar and curved surfaces (56). These replication methods, such as microtransfer molding, offer advantages in applications where photolithography is ineffective. However, this method requires at least three steps to complete. In addition, as we go down to sub-50-nm features, the impact at contact can cause structure deformation. In addition, there can be clogging from contaminants collected at contacts. Recently, we demonstrated a single-step approach to achieve patterned polymer brushes. In this method, polymer brushes were prepared via ATRP and directly patterned using e-beam lithography to achieve 50 nm patterned PMMA brush surfaces (38).

E-beam processing has been used to boost properties by creating controlled degradation or chain scission of certain polymers. E-beams have been used to break down polymeric materials to create micropowders used in inks, coatings, and lubricants. Upon e-beam exposure, scission reactions occur on the polymer backbone. The scission reaction leads to the degradation of polymers by the rupture of covalent bonds. This causes a decrease in the molecular weight and intrinsic viscosity (57). 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.

PTFEMA is a highly sensitive positive tone e-beam resist that degrades into smaller fragments upon e-beam irradiation. We patterned PTFEMA brushes (ellipsometric thickness of 50 nm) at e-beam doses ranging from 5 to 150 $\mu C/cm^2$ with a beam current of 0.5 nA. After e-beam exposure, followed by a $scCO_2$ or THF development step, a contrast curve was generated in which the normalized thickness was plotted as a function of the logarithm of the exposure dose, as shown in Figure 4. Using the appropriate dose ascertained from the contrast curve, higher resolution lines of patterned PTFEMA brushes were imaged. Factors such as the e-beam diameter, beam current, and dose were optimized to improve the resolution of the patterned brushes.

Dry Development of Patterned PTFEMA Brushes in $scCO_2$. PTFEMA homopolymers and copolymers have been used as cladding materials in optical fibers, protectives for marble statues, etc. (58). Fluorinated polymers have many unique characteristics, among which the oleophobic−hydrophobic nature of fluorinated polymer surfaces and their remarkable thermal and chemical resistance stand out. The properties arise as a result of the low intermolecular forces present in highly fluorinated organic compounds. The presence of nonpolar $-CF_3$ groups at the surface of the PTFEMA brushes lowers the surface energy of a surface. The nonpolar nature of fluorinated polymers confers a range of properties, including water repellence and solubility in $scCO_2$. Patterned low-surface-energy polymer brush surfaces have the potential of being used in the preparation of superhydrophobic surfaces and in the patterning of hydrophilic inks.

The exposed PTFEMA polymer brushes were developed in $scCO_2$ and in THF. The degraded polymer chains showed good solubility in the two solvents, leaving the covalently attached polymer brushes on the surface unaffected. PTFEMA brushes were successfully patterned in a single step upon exposure to an e-beam and characterized and imaged by tapping-mode AFM. The contrast curves of the PTFEMA brushes, developed in THF (shown in blue) and in $scCO_2$ (shown in red), are shown in Figure 4. The contrast was not as sharp as expected in the environmentally benign $scCO_2$ solvent; however, PTFEMA brushes are highly sensitive to e-beam patterning. Also, the development of patterned PTFEMA brushes in $scCO_2$ does not have a negative effect on the contrast and sensitivity of PTFEMA brushes.

Figure 5a is an AFM image of 200 nm lines of a patterned PTFEMA brush with a pitch size of 2 μm that was patterned by e-beam lithography with an exposure dose of 48.4 $\mu C/cm^2$ and developed in $scCO_2$ solvent for 5 min at 50 °C and 5000 psi. Figure 5b is an AFM image of 150 nm lines of a patterned PTFEMA brush with a pitch size of 400 nm obtained using similar lithographic and development conditions. The $scCO_2$ development step was compared to the development in an organic solvent. THF is a good solvent for PTFEMA and was used to dissolve the exposed regions of the PTFEMA brushes. Parts a and b of Figure 6 show AFM images of 200 nm lines of patterned PTFEMA brushes with pitch sizes of 2 μm and 400 nm, respectively. These patterns were obtained by e-beam lithography with an exposure dose of 48.4 $\mu C/cm^2$, followed by development in THF for 90 s at room temperature.

For sub-100-nm features, reduced line broadening was observed with $scCO_2$ development when compared to the development in an organic (THF) solvent. Parts a and b of Figure 7 show AFM images of 50 nm isolated lines of patterned PTFEMA brushes with pitch sizes of 2 μm that were developed in $scCO_2$ and THF, respectively. The 50 nm patterns exhibited line broadening due to the lateral relaxation/collapse of the extended polymer chains in the voided

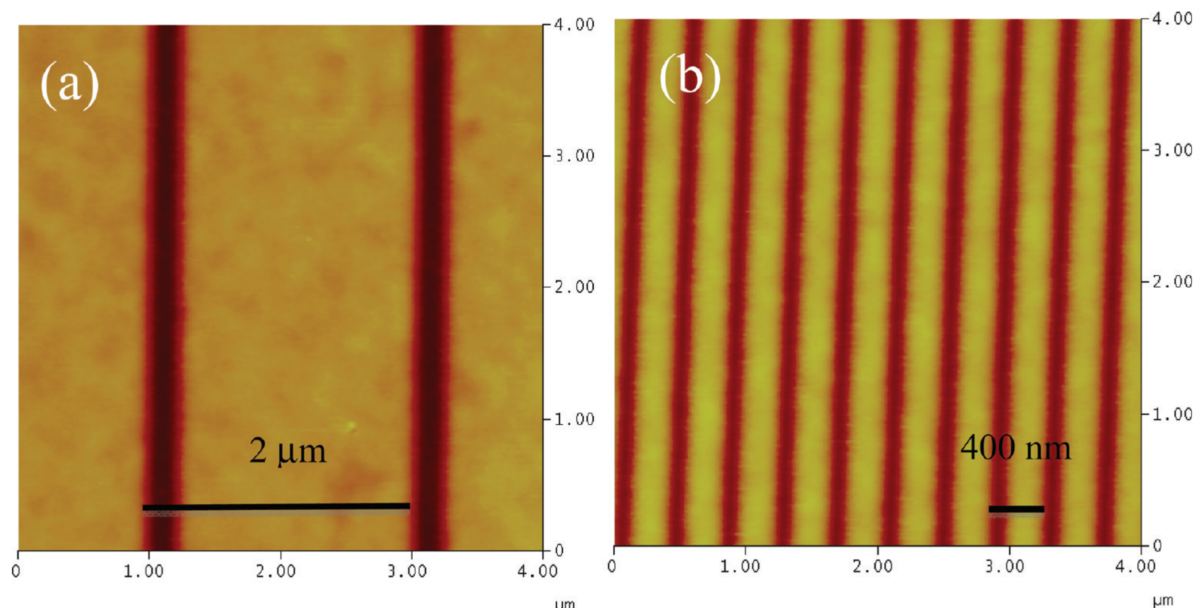


FIGURE 5. Tapping-mode AFM height images of patterned PTFEMA brushes, developed in $scCO_2$ at 50 °C, 5000 psi, for 5 min and imaged at room temperature in air: (a) 200 nm lines/2 μm pitch size and (b) 150 nm lines/400 nm pitch size of patterned PTFEMA brushes.

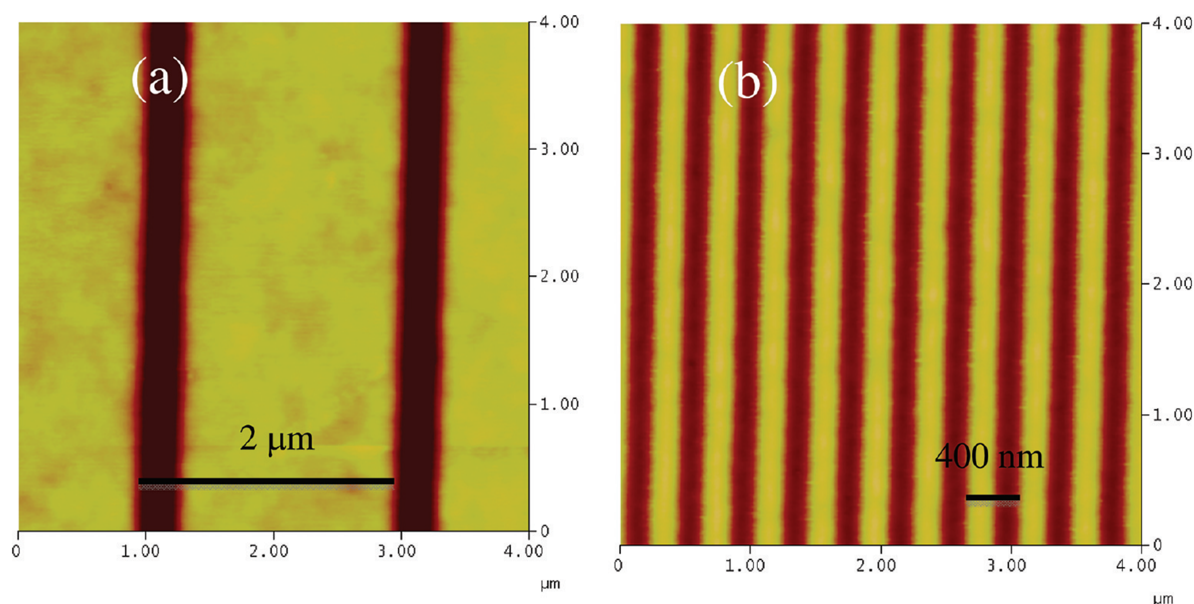


FIGURE 6. Tapping-mode AFM height images of patterned PTFEMA brushes, developed in THF at room temperature for 90 s and imaged at room temperature in air: (a) 200 nm lines/2 μm pitch size and (b) 200 nm lines/400 nm pitch size of patterned PTFEMA brushes.

patterned regions. After $scCO_2$ development, the 50 nm patterns broadened to 78 nm. This is a 56% increase in the pattern size. The same features developed in THF showed 88% line broadening, resulting in 94 nm patterned lines as measured by AFM. This difference in behavior is attributed to the fact that THF is a very good solvent for PTFEMA, which makes the pattern edges much more susceptible to polymer chain relaxation. Because of the increased line broadening with the THF developer, we label THF as a poorer developer compared to $scCO_2$. Residual polymer fragments are not a concern because THF is such a good solvent that it can wash away all of the fragments easily. Usually, a good solvent cannot be used as a developer for traditionally spun-coat polymer resists because not only would the patterned fragments be washed away but the polymer film as well. However, that is not the case for polymer brushes because the chains are tethered to the surface.

In contrast to the use of THF as a development solvent, the processing of patterned PTFEMA brushes in $scCO_2$ has several advantages. The high diffusivity and low viscosity of $scCO_2$ allow for its efficient removal via depressurization, which allows easy separation from the polymer brushes. Because the solvating power of a supercritical fluid is directly related to its density, a large variation in solubility can be achieved with relatively small changes in operating conditions. Direct patterning by e-beam lithography involves the dissolution of relatively small polymer fragments. Because CO_2 can dissolve small molecules and low-surface-energy

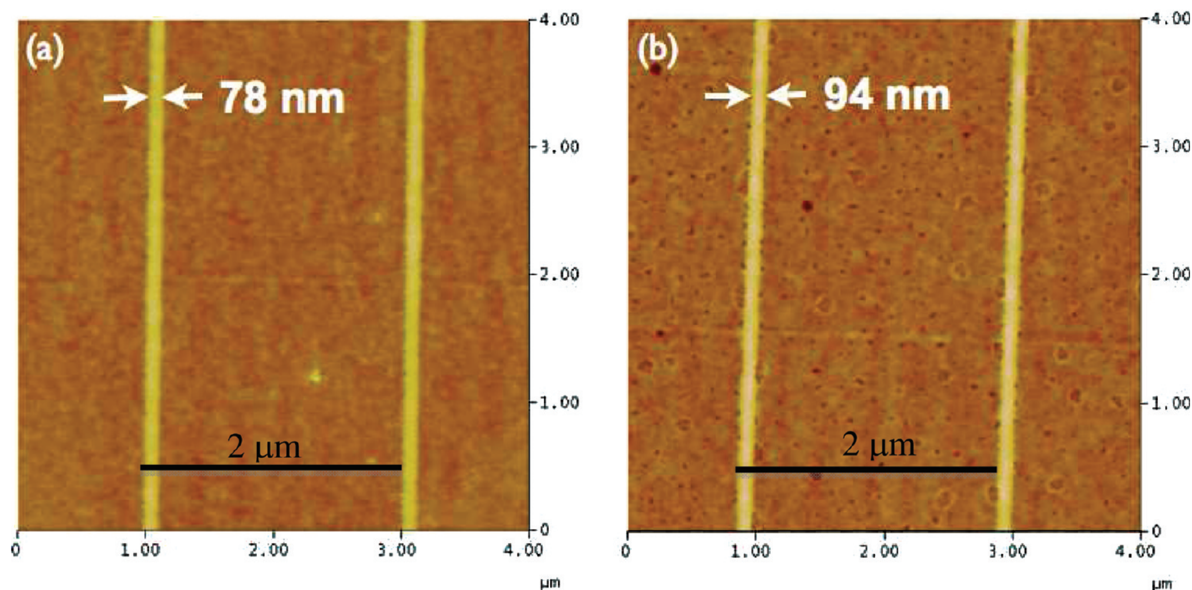


FIGURE 7. Tapping-mode AFM height images of 50 nm isolated lines of patterned PTFEMA brushes imaged at room temperature in air: (a) developed in $scCO_2$ at 50 °C, 5000 psi for 5 min; (b) developed in THF at room temperature for 90 s.

polymers such as fluoropolymers, $scCO_2$ could replace a sizable fraction of the solvents used in the processing of low-surface-energy patterned surfaces. In addition, $scCO_2$ serves as an ecological and economical alternative processing solvent that eliminates the use of toxic and flammable organic solvents.

CONCLUSIONS

Highly e-beam-sensitive PTFEMA brushes were directly patterned in a single step to prepare nanopatterned PTFEMA brush surfaces. The exposed brushes were successfully developed in an environmentally benign, $scCO_2$ solvent at 50 °C and 5000 psi for 5 min. The contrast and sensitivity of PTFEMA brushes were determined and compared to the development of the exposed brushes in THF. The contrast curve for PTFEMA brushes is not very sharp. However, these brushes are very sensitive to e-beam exposure. Using e-beam lithography, followed by development in $scCO_2$, polymer brush patterns as small as 78 nm could be obtained. The 50 nm isolated line patterns showed increased line broadening with both THF and $scCO_2$ development. Line broadening up to 88% was observed in the THF developer. This line broadening was reduced to 56% in $scCO_2$, suggesting that $scCO_2$ is a better developer for sub-100-nm features. The polymer used to prepare the polymer brush surfaces must be degradable under e-beam irradiation. A limitation of this method is that it requires a relatively higher pressure and a longer development time compared to the traditional organic development. This direct method of obtaining patterned brushes is a shorter and cleaner way to prepare patterned brush surfaces. The use of $scCO_2$ as a development solvent eliminates the generation of organic solvent waste and is an environmentally friendly patterning process.

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