

Using Atom Transfer Radical Polymerization To Amplify Monolayers of Initiators Patterned by Microcontact Printing into Polymer Brushes for Pattern Transfer

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ABSTRACT: We report the use of atom transfer radical polymerization (ATRP) to amplify initiators patterned on films of gold into polymer brushes of poly(methyl methacrylate) (PMMA), poly(hydroxyethyl methacrylate) (PHEMA), poly(*tert*-butyl methacrylate) (PTBA), poly(isobornyl methacrylate) (PIBMA), and poly((dimethylamino)ethylmethyl acrylate) (PDMAEMA). Pattern transfer into gold substrates underlying polymer brushes was achieved by using the patterned brushes as barriers to wet chemical etchants of gold. The surface-confined initiators for ATRP were prepared by the self-assembly of (BrC-(CH₃)₂COO(CH₂)₁₀S)₂ (**I**) on films of gold. These monolayers were assembled from solutions of hexadecane at 60 °C so as to prevent their thermal desorption during ATRP (also performed at 60 °C). By measuring the resistance offered by these brushes to etching of underlying films of gold by aqueous solutions of KI/I₂, KCN/K₃Fe(CN)₆, and 50 vol % aqua regia (70 vol % HNO₃ and 30 vol % HCl), we conclude that both the thickness and chemical functionality of the polymer brushes as well as the choice of etchant can be tailored to control the etch resistance of polymer brushes. Thick brushes formed from hydrophobic monomers were found to be the most effective in resisting all etchants. The etch resistance of a PMMA brush was observed to be greatest when using aqua regia or KI/I₂ to etch an underlying film of gold. For example, when using PMMA brushes (thickness 450 Å), we measured the brushes to slow the etching of the underlying films of gold by KI/I₂ by almost 2 orders of magnitude as compared to monolayers formed from **I**. By using microcontact printing to pattern SAMs formed from **I**, we demonstrate the usefulness of ATRP in schemes for transferring patterns present in monolayers of molecules into underlying substrates.

Introduction

Microcontact printing provides the capability to deliver with submicrometer spatial resolution a variety of organosulfur compounds to surfaces of gold and silver¹ and organosilane² or organophosphonate³ compounds to surfaces of metal oxides. Patterns of molecules on surfaces so-formed have been used to direct a multitude of phenomena, including the spreading of liquids,⁴ the adsorption of proteins,⁵ the growth of cells,⁶ and orientations of liquid crystals.⁷ Patterned monolayers prepared by this experimental procedure have also been widely investigated as barriers for wet chemical etchants, thereby transferring the pattern present in the monolayer of molecules into a variety of underlying substrates.^{8–10} While wet chemical etching of microcontact printed monolayers of molecules has led to levels of pattern transfer that are useful for the prototyping of microstructures,^{8–10} the presence of defects within the patterned monolayers has not permitted pattern transfer with the reliability that is routinely accomplished when fabricating microstructures based on procedures that combine spin-coated polymer films and photolithography.^{8–10}

In this paper, we report the use of polymerization as a means to chemically amplify monolayers of molecules patterned on surfaces into polymer brushes that possess

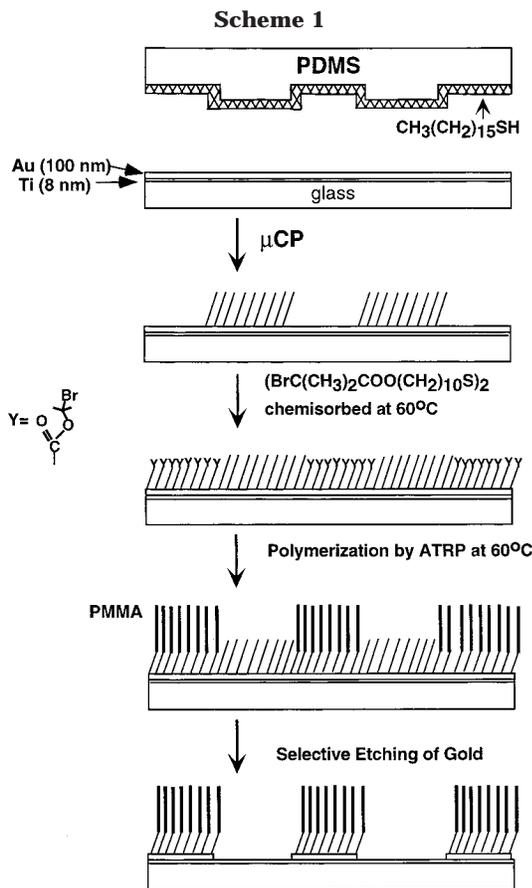
barrier properties to wet chemical etchants that are substantially better than the barrier properties of the patterned monolayers from which they are grown. The approach, which is illustrated in Scheme 1, is based on the use of microcontact printing to deliver to surfaces a patterned monolayer of an initiator for atom transfer radical polymerization (ATRP). The initiator is (BrC-(CH₃)₂COO(CH₂)₁₀S)₂ (**I**).¹¹ Atom transfer radical polymerization is used to amplify the patterned monolayer formed from **I** into a polymer brush that possesses a controlled thickness and as well as physical properties which are tailored by the choice of monomer. We demonstrate that appropriate combinations of polymer brush properties (e.g., thickness and hydrophobicity) and wet chemical etchant can lead to experimental procedures that permit the transfer of patterns from microcontact printed monolayers of **I** into underlying substrates under conditions that lead to poor levels of pattern transfer when using monolayers formed from **I** alone. We demonstrate this capability by patterning regions of surfaces with polymer brushes that have lateral dimensions of micrometers and by selectively etching regions of the substrate not protected by the patterned polymer brushes.

The research described herein builds on a recent investigation in which we combined microcontact printing of hydroxyl-terminated monolayers and surface-initiated ring-opening polymerization of ϵ -caprolactone to form patterned polymer brushes.¹² In this paper we move to ATRP to amplify initiators patterned by mi-

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crocontact printing into polymer brushes for three reasons: (1) ATRP permits control of the molecular weight of polymers and thus the thickness of polymer brushes. (2) ATRP permits polymerization of a range of commercially available vinyl monomers. This characteristic allows the properties of the polymer brushes, such as etch resistance, to be tailored over a wide range. (3) ATRP is relatively easy to perform, is tolerant to the presence of water and oxygen, and, with the correct choice of catalyst, can be performed at relatively low temperatures (see below). By using the procedure illustrated in Scheme 1, we exploit these characteristics of ATRP to transfer patterns formed by microcontact printing into substrates that support the patterned monolayer.

Because ATRP is routinely performed at elevated temperatures ($\geq 60^\circ\text{C}$) and because past studies of the thermal stability of self-assembled monolayers (SAMs) on gold have demonstrated substantial levels of desorption at elevated temperatures,¹³ a significant outcome of the work described in this paper is a simple procedure that leads to the formation of SAMs from **I** that are largely stable in toluene at 60°C . We found that SAMs formed from **I** at 60°C on the surface of films of gold are sufficiently stable at 60°C so as to permit the use of ATRP for their amplification into patterned, polymer brushes. In contrast, SAMs of **I** formed using conventional procedures (formation at 25°C) were found not to be stable at 60°C and not to lead to formation of polymer brushes with useful barrier properties.

This paper is organized into four parts. First, we describe the synthesis of compound **I** and procedures that permit the formation of thermally stable SAMs from **I**. Second, we demonstrate the use of SAMs formed from **I** and ATRP to synthesize polymer brushes of

controlled thickness that possess different chemical functionality and physical properties. Third, we report the extent to which the polymer brushes prepared by ATRP act as barriers to various wet chemical etchants of gold. Finally, we report the use of ATRP to amplify patterned, SAMs formed from **I** into polymer brushes and thereby effect pattern transfer from the monolayer into the underlying substrate.

Materials and Methods

Materials. $\text{H}_3\text{C}(\text{CH}_2)_{15}\text{SH}$, 11-mercapto-1-undecanol, methyl methacrylate (99%), isobornyl methacrylate, *tert*-butyl methacrylate, 2-hydroxyethyl methacrylate, 2-(dimethylamino)ethyl methacrylate, potassium hydrogen carbonate, iron(II) bromide (98%), triphenylphosphine (99%), ethyl 2-bromoisobutyrate (98%), magnesium sulfate (99%), hexadecane (99%), and toluene (99%) were purchased from Aldrich (Milwaukee, WI) and used without further purification. Ethanol was purchased from Aaper (Shelbyville, KY). Hexanes and glass microscope slides were purchased from Fisher (Los Angeles, CA). Titanium (99.999%) and gold (99.999%) were purchased from Advanced Materials (Spring Valley, NY).

Synthesis of $(\text{BrC}(\text{CH}_3)_2\text{COO}(\text{CH}_2)_{10}\text{S})_2$ (I**).** Dichloromethane (150 mL), 10% potassium hydrogen carbonate (20 mL), and 11-mercapto-1-undecanol (4.09 g) were added to a round-bottom flask. A solution of bromine (10 mmol, 1.6 g) was slowly added to the well-stirred mixture. The color of the bromine quickly disappeared upon addition to the flask. The organic phase was separated, and aqueous phase was extracted with dichloromethane (50 mL). The organic phases were combined and dried with magnesium sulfate. Evaporation of the solvent gave nearly pure disulfide (2.84 g, 70%). ^1H NMR (250 MHz, CDCl_3): $\delta = 1.21$ (36 H, CH_2), 1.58 (4 H, CH_2), 2.60 (t, $J = 7.3$, 4 H, SCH_2), 3.60 (t, $J = 5$, 4 H, OCH_2).

2-Bromo-2-methylpropionyl bromide (1.83 mL, 14.8 mmol) was added drop by drop to a solution of the disulfide (2.5 g, 6.17 mmol) and triethylamine (4.18 mL, 31.5 mmol) in 150 mL of dichloromethane at 0°C under an argon atmosphere. The solution was stirred for 1 h at 0°C and then at 25°C for another 2 h to complete the reaction. Triethylamine hydrobromide was filtered off, and the solution was extracted with aqueous 2 N sodium carbonate saturated with ammonium chloride. The dichloromethane was evaporated, and the crude product was purified by column chromatography resulting in a viscous, pale yellow liquid, **I** (2.78 g, 64%). The initiator, **I**, was characterized by NMR, ^1H and ^{13}C , and elemental analysis. ^1H NMR (250 MHz, CDCl_3): $\delta = 1.24$ – 1.32 (bm, 28 H, CH_2), 1.57–1.66 (m, 8 H, CH_2), 1.89 (s, 12 H, CH_3), 2.64 (t, $J = 7.5$, 4 H, SCH_2), 4.13 (t, $J = 5$, 4 H, OCH_2). ^{13}C NMR (63 MHz, CDCl_3): $\delta = 25.8$ (CH_2), 28.3 (CH_2), 28.5 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 30.8 (CH_3), 39.2 (SCH_2), 56.0 (C), 66.1 (OCH_2), 171.7 (C=O). Calculated elemental composition of **I** ($\text{C}_{30}\text{H}_{56}\text{Br}_2\text{O}_4\text{S}_2$): C, 51.13%; H, 8.01%; O, 9.08%; Br, 22.68%; S, 9.10%. Measured elements in **I**: C, 50.90%; H, 7.85%; O, 9.45%; Br, 22.90%; S, 8.9%.

Methods. Cleaning of Substrates. Microscope slides were cleaned in piranha solution (70% H_2SO_4 , 30% H_2O_2) using a nitrogen bubbler to provide agitation (1 h at 50°C). **Warning: piranha solution should be handled with extreme caution; in some circumstances, most probably when it has been mixed with significant quantities of an oxidizable organic material, it has detonated unexpectedly.** The slides were then rinsed thoroughly in deionized water (18.2 $\text{M}\Omega\text{-cm}$), ethanol, and methanol and dried under a stream of nitrogen. The clean slides were stored in an oven at 110°C . All other glassware was cleaned in piranha solution prior to use.

Deposition of Gold. Films of gold with thicknesses of ~ 1000 Å were deposited onto glass slides by using an electron beam evaporator manufactured by Telemark Industries (Fremont, CA) and CHA Industries (Fremont, CA). The gold was deposited at normal incidence. A 85 Å thick layer of titanium was used to promote adhesion between the glass and the film of

gold. The rate of deposition of gold and titanium was ~ 0.2 – 0.4 Å/s. The pressure in the evaporator was lower than 2×10^{-6} Torr before and during each deposition.

Formation of SAMs. Self-assembled monolayers were formed on the surfaces of gold films by immersion of the films into 1 mM solutions of $(\text{BrC}(\text{CH}_3)_2\text{COO}(\text{CH}_2)_{10}\text{S})_2$, **I**, using as solvents either hexadecane or toluene at 60 °C or room temperature or ethanol at room temperature. The time used to form each SAM is indicated with the result of each experiment. After formation, each SAM was rinsed sequentially in ethanol and hexanes and then dried under a stream of nitrogen. The SAMs were characterized by ellipsometry, wettability, and X-ray photoelectron spectroscopy (see below).

Formation of Homogeneous Polymer Brushes by ATRP. Polymer brushes (not patterned) were prepared by placing a gold film supporting a SAM formed from **I** into a reaction flask with iron(II) bromide (0.33 mmol), triphenylphosphine (1 mmol), ethyl 2-bromoisobutyrate (0.33 mmol), and a monomer (such as methyl methacrylate, 0.1 mol). The thickness of the brush was controlled by the ratio of the monomer (methyl methacrylate) to the initiator (ethyl 2-bromoisobutyrate) in bulk solution. For example, 0.1 mol of methyl methacrylate (MMA) and 0.33 mmol of initiator leads to a film thickness of 30 nm and a bulk polymer with a molecular weight of 30 000 Da. Whereas past studies based on the use of copper (II) bromide were performed at 80 °C,¹¹ we used iron(II) bromide as the catalyst in our experiments because it permits ATRP to be performed at 60 °C. After loading the reactants into the reaction vessel, the vessel was degassed with argon for 15 min and heated to 60 °C for 3 h. The flask was then cooled. The bulk polymer was dissolved into dichloromethane and then precipitated into methanol. To remove any bulk polymer incorporated into the polymer brushes grown from the film of gold, we extracted each brush using dichloromethane at 25 °C for 24 h. After extraction with dichloromethane, the brush was rinsed in ethanol. The thickness of the polymer film was observed to decrease with time of extraction in dichloromethane for times up to 24 h. Beyond 24 h, the thickness remained constant. The catalyst, FeBr_2 , was also removed from the sample by this washing step. The polymer brushes were then characterized by ellipsometry, atomic force microscopy (AFM), and contact angle goniometry.

Ellipsometry. Ellipsometric thicknesses of SAMs and polymer brushes were measured by using a Rudolph Auto EL ellipsometer (Flanders, NJ) at a wavelength of 6320 Å and an angle of incidence of 70°. Ellipsometric constants were measured immediately following removal of the gold films from the evaporator. The ellipsometric thickness of SAMs were estimated by using a three-layer model and by assuming a refractive index of 1.46 for the monolayer and a refractive index of 1.49 for the polymer layer.¹⁴

Gel-Permeation Chromatography. Gel-permeation chromatography (GPC) was performed on a Waters 410 (Milford, MA) chromatograph using a differential refractometer as the detector. Measurements of the average molecular mass were made relative to polystyrene standards with tetrahydrofuran as the carrier solvent.

X-ray Photoelectron Spectroscopy (XPS). X-ray photoelectron spectroscopy (Perkin-Elmer PhiX 5400) was used to determine the atomic composition of SAMs formed from **I** at 25 and 60 °C. XPS was also used to assess the displacement of SAMs formed by microcontact printing of hexadecanethiol (HDT) when these SAMs were immersed into a solution of **I** at 60 °C.

Because bromo-terminated SAMs are susceptible to damage by X-rays and secondary electrons during XPS,¹⁵ we determined the rate of damage of SAMs formed from **I** by exposing these SAMs to X-rays with a pass energy of 35.75 eV. The Br peak intensity was monitored against exposure time for 40 min. Our measurement of the Br peak required 4 min of acquisition, which results in a $\sim 5\%$ decrease in the Br peak area. Only one sample point was measured on each sample, and the reported atomic percentages reflect the corrected Br peak area (corrected for X-ray damage).

The chamber pressure during acquisition of all XPS spectra was approximately 5.0×10^{-9} Torr, and the spot size was $250 \mu\text{m} \times 1000 \mu\text{m}$. Nonmonochromatic X-rays were generated from a Mg-K α source. Survey scans were acquired at one location on a sample with a pass energy of 100 eV. Acquisition was performed in multiplex mode centered on the O(1s), C(1s), Br(3p), and Au(4f) peaks with a pass energy of 35.75 eV at a takeoff angle of 45°. The area of the Au(4f_{5/2}, 4f_{7/2}) peaks varied by less than 5% from sample to sample. The binding energies were referenced to the Au(4f_{7/2}) peak at 84 eV.

Contact Angles. Advancing and receding contact angles of deionized water were measured in air using a Ramé-Hart model 100 (Mountain Lakes, NJ) goniometer at room temperature.¹³

Etchants. The extent to which the polymer brushes prevented etching of underlying gold films was determined using three aqueous etchants: (a) 20 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 0.10 M KCN, 0.25 M KOH; (b) 0.25 M KI, 0.025 I₂; and (c) 50 vol % aqua regia (70 vol % HNO_3 and 30 vol % HCl).⁸ The rate of etching of an untreated film of gold in these solutions was determined to be 25–30 Å/s. To achieve uniform etching of the gold films, all solutions were vigorously mixed and sparged with nitrogen gas in an Erlenmeyer flask.

Characterization. Images and cross-sectional profiles of the polymer films were obtained by atomic force microscopy (AFM) using a Digital Instruments Nanoscope III (Santa Barbara, CA) operating in contact mode. Samples were imaged under ambient conditions using a cantilever made from silicon nitride (spring constant 0.58 N/m). Images of the surface were collected at a scan rate of 150 $\mu\text{m/s}$ with 512 sample points per line.

Preparation of Patterned Polymer Brushes. First, an elastomeric stamp was formed by pouring a mixture of Sylgard 184CA PDMS (Dow Corning, MI) prepolymer and its curing agent in a 10:1 ratio onto a silicon master patterned with relief. The width of the relief was 15 μm and the depth $\sim 20 \mu\text{m}$. Entrained air bubbles were removed by applying a vacuum over the mixture of prepolymer and curing agent. The polymer mixture was allowed to cure for 12 h at 50 °C. The elastomeric stamp was then gently removed from the master and rinsed in ethanol.^{8,10} The stamps were "inked" by placing a drop of an ethanolic solution of 3 mM HDT onto the surface of the stamp. The stamp was then dried under a stream of nitrogen. The stamp was placed by hand into contact with the surface of a gold film and withdrawn after a period of ~ 5 s.^{8,10} The stamped film of gold was then rinsed in ethanol and placed into a 1 mM solution (see above) of **I** maintained at 60 °C for 5 min. The polymer brushes were then formed using these surfaces, as described above. To permit direct comparison of the properties of homogeneous polymer brushes and brushes formed from the patterned SAMs, only one-half of each sample was patterned with the SAM formed from HDT. The resulting patterned polymer brushes were then analyzed by AFM whereas homogeneous regions of polymer brushes prepared on the same sample were analyzed by ellipsometry.

Results

Thermal Stability of SAMs formed from **I at 25 and 60 °C.** Our initial experiments used SAMs formed from 1 mM solutions of **I** at 25 °C. The ellipsometric thicknesses of SAMs formed from **I** at 25 °C were measured to be 18 ± 1 Å when chemisorbed from solutions of ethanol, toluene, or hexadecane. The ellipsometric thicknesses of the SAMs were also found to be independent of the interval of time over which the SAMs were formed for times greater than 5 min and less than 20 h (Figure 1). Advancing and receding contact angles of deionized water measured on these SAMs were $69 \pm 2^\circ$ and $46 \pm 2^\circ$, respectively. Because we aimed to use SAMs as initiators for ATRP at 60 °C and because SAMs formed from alkanethiols on the surface of gold are known to desorb into organic solvents at elevated

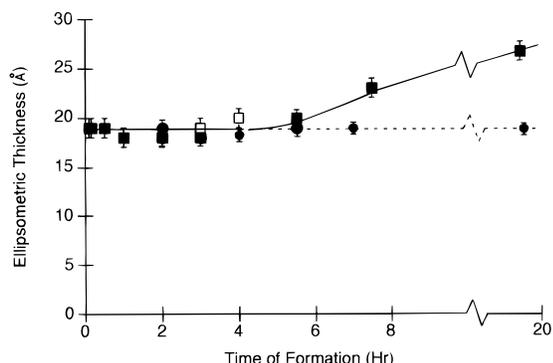


Figure 1. Dependence on time of the ellipsometric thickness of an organic film formed on the surface of gold by immersion into a 1 mM solution of **I**: (filled circles) ethanol and 25 °C; (filled squares) hexadecane and 60 °C; (open squares) toluene and 60 °C. The dashed and dotted lines are drawn to guide the eye.

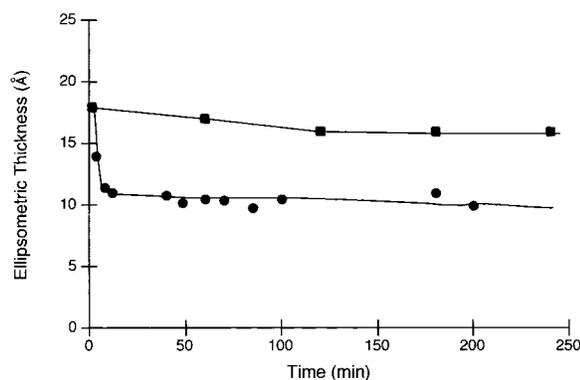


Figure 2. Ellipsometric thicknesses of SAMs formed from **I** and subsequently immersed into toluene at 60 °C for increasing lengths of time: (filled circles) SAMs form on gold at 25 °C using ethanol as the solvent; (filled squares) SAMs formed on gold at 60 °C using hexadecane as the solvent.

temperatures,¹³ we measured the thermal stability of SAMs formed at 25 °C from **I**. We measured the ellipsometric thicknesses of SAMs formed from **I** (using either ethanol, toluene, or hexadecane as the solvent) to decrease from 18 to 11 Å after 5 min of immersion in toluene at 60 °C (Figure 2). Following an initial period of rapid desorption of the SAM, we measured the thickness of the SAM to remain constant at ~10 Å for at least 4 h in toluene at 60 °C. As described below, these SAMs were not sufficiently stable so as to permit their amplification into polymer brushes that served as useful barriers to wet chemical etchants.

To improve the thermal stability of the SAMs, we investigated whether thermally stable SAMs could be prepared by forming the SAMs from solutions of toluene or hexadecane containing **I** at 60 °C (i.e., an elevated temperature). First, we measured the ellipsometric thickness of a SAM formed from **I** at 60 °C as a function of the time of immersion of the gold substrate in a solution of **I**. Whereas the thickness of the SAM formed at 25 °C did not change with time (Figure 1), the ellipsometric thickness of the SAM formed at 60 °C in toluene or hexadecane was observed to increase monotonically after about 3 h of immersion (Figure 1). After 18 h of immersion, the thickness of the surface layer was almost 30 Å and thus greater than that of a monolayer. Over the first 3 h of immersion, however, the thickness of the SAM was observed to remain

constant at ~18 Å, a thickness corresponding to that of a monolayer.

Because the disulfide groups of **I** (or trace thiols) are good nucleophiles and because the α -bromoester groups of **I** are good leaving groups, we speculated that SAMs formed from **I** at 60 °C were comprised of products of a condensation reaction of the disulfide with the α -bromo group.¹⁶ For this reason, we characterized SAMs formed at 60 °C by using ellipsometry, contact angles, and X-ray photoelectron spectroscopy. Because SAMs formed at 60 °C for 2–3 h possessed ellipsometric thicknesses that were indistinguishable from SAMs formed at 25 °C, below we focus our attention on these SAMs. Contact angles measured on SAMs formed for 2 h at 60 °C were the same as contact angles measured on SAMs formed at 25 °C ($\theta_a = 69^\circ$; $\theta_r = 46^\circ$). Furthermore, the atomic composition of SAMs as measured by XPS formed at 25 and 60 °C for 1 h were determined to be indistinguishable. The relative atomic composition of the SAM formed at 25 °C was $3.2 \pm 0.5\%$ Br, $17.0 \pm 2.1\%$ O, and $79.8 \pm 3.9\%$ C whereas the relative composition of the SAM formed at 60 °C was $2.9 \pm 0.4\%$ Br, $18.4 \pm 1.5\%$ O, and $78.6 \pm 4.6\%$ C. These measurements, when combined, reveal minimal differences to exist between the structure and composition of SAMs formed for 3 h (or less) from **I** at 25 or 60 °C even though, as reported below, we observed substantial differences in their thermal stability.

We used ellipsometry to determine the thermal stability of SAMs formed from **I** (for 5 min and 3 h) by immersing these SAMs in toluene at 60 °C for up to 4 h. When using SAMs prepared at 60 °C for 5 min or 3 h with toluene or hexadecane as the solvent, the ellipsometric thicknesses of the SAMs decreased only by 2 Å when immersed in toluene at 60 °C after many hours (Figure 2). These results indicated that thermally stable SAMs can be formed from **I** by assembling the SAMs from solvent held at an elevated temperature. We demonstrate below that SAMs formed from **I** at 60 °C permit the preparation of dense, polymer brushes by using ATRP whereas SAMs formed from **I** at 25 °C do not yield dense polymer brushes.

Control of Thickness of Brush by ATRP. We used SAMs formed at 60 °C from **I** (3 h of immersion) to grow polymer brushes by ATRP. First, by using procedures described in the Methods section, brushes of poly(methyl methacrylate) (PMMA) were formed. The polydispersity of the bulk polymer was measured by GPC to be 1.1–1.4. Measurements of the ellipsometric thicknesses of brushes of poly(methyl methacrylate) (PMMA) initiated from SAMs that were formed at 25 and 60 °C revealed a linear relationship between the thickness of the polymer brush and the molecular weight of the PMMA formed in bulk solution (Figure 3). For the same molecular weight of polymer formed in the bulk, however, the brushes of PMMA grown from SAMs formed at 60 °C were found to be 1.4–2.1 times thicker than polymer brushes grown from SAMs formed at 25 °C (Figure 3). This result, when combined with the results of the previous section, leads us to conclude that the thermal stability of the SAM formed from **I** affects the overall thickness of the polymer brush grown by ATRP from the SAM.

When the molecular weight of the polymer formed in bulk was measured to be 20 000 Da, as reported in Figure 3, the thickness of the corresponding brush of PMMA was found to be 200 Å. For comparison, we

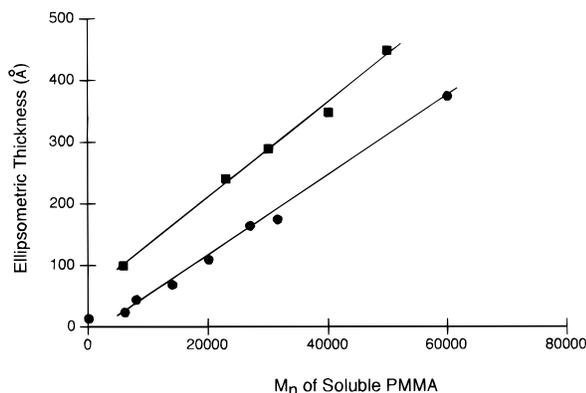


Figure 3. Ellipsometric thicknesses of brushes of PMMA measured as a function of the number-averaged molecular weight (M_n) of the polymer formed in the bulk polymerization. Filled circles indicated polymer brushes grown using SAMs formed from **I** at 25 °C; filled squares indicated polymer brushes grown using SAMs formed from **I** formed at 60 °C.

calculate the contour length of the 20 000 Da PMMA molecule to be ~ 490 Å and the radius of gyration to be ~ 42 Å.¹⁷ These results indicate the polymer chains of PMMA within the brush formed by ATRP to be substantially stretched at the surface. The average cross-sectional area of each chain within a brush, A_x , can be calculated from the molecular weight of the chain, M , and the corresponding brush thickness, t , by $A_x = M/\rho N_A t$, where ρ is the mass density (1.1 g/cm³ for PMMA) and N_A is Avogadro's number. For molecular weights of PMMA of ~ 20 000 Da or greater, we calculate from Figure 3 that the area per PMMA chain within the brushes formed by ATRP is ~ 200 Å². This result suggests a grafting efficiency of approximately one polymer chain for each 10 potential initiator groups within the SAM formed from **I**. For comparison, Jordan et al. report a grafting density of ~ 340 Å² (~ 17 initiators per polymer brush) for the anionic polymerization of polystyrene (~ 40 000 Da) from surface-bound initiators.¹⁸ We also point out that the average area occupied by each PMMA molecule within brushes formed by ATRP is small compared to the area occupied by a PMMA chain anchored to the interface of a lamellar phase of a block copolymer of polystyrene (~ 900 Å²).¹⁹ This observation is consistent with the results of R  he et al.²⁰ and past work on polymerization of polystyrene from silicon oxide surfaces.¹⁹ The high packing densities obtained by the growth of polymers from surfaces (i.e., small cross-sectional area) have not been achieved by the grafting of polymer chains to surfaces (so-called "grafting to" techniques).^{19,21}

Tailoring of Brush Properties. A significant merit of living free radical procedures is the capability to polymerize a wide variety of functionalized monomers. In the case of surface-initiated polymerizations, ATRP also offers the possibility of tailoring surface properties, such as the etch resistance of the resulting polymer brushes. To demonstrate this capability, we formed brushes of poly(*tert*-butyl methacrylate) (PTBA), poly(isobornyl methacrylate) (PIBMA), poly(hydroxyethyl methacrylate) (PHEMA), and poly((dimethylamino)ethyl methacrylate) (PDMAEMA). As shown in Table 1, the contact angles of water measured on these polymer brushes varied widely depending on the type of acrylate monomer used to form the brush. Polymer brushes of PIBMA and PTBA were found to be hydrophobic whereas brushes of PHEMA and PDMAEMA

Table 1. Contact Angles of Water Measured on Polymer Brushes Prepared by ATRP Using SAMs Formed from **I at 60 °C on Films of Gold**

	θ_{adv} (deg)	θ_{rec} (deg)	Thickness (Å)
PTBA 	92	59	50
PMMA 	70	37	480
PIBMA 	95	67	390
PDMAEMA 	35	10	350
PHEMA 	47	8	61

were measured to be hydrophilic. The contact angles of water measured on brushes of PMMA were found to be similar to past measurements performed on dip-coated films ($\theta_a = 72^\circ$, $\theta_r = 59^\circ$),²² thick-casted films ($\theta_a = 73^\circ$),²³ and physisorbed thin films ($\theta_a = 76^\circ$).²⁴ We also measured contact angles of water to be independent of the thickness of the PMMA brush (thickness range between 50 and ~ 500 Å) on which they were measured, a result that is consistent with past studies.²⁵ In summary, the results presented in Table 1 demonstrate that ATRP provides the capability to control physical properties of polymer brushes such as their wettability.

Barrier Properties. The results described above demonstrate that ATRP from SAMs formed from **I** leads to the formation of densely packed, polymer brushes having controlled thicknesses and physicochemical properties. In this section, we exploit this capability to amplify monolayers supported on surfaces into macromolecular barriers for chemical etchants of gold. We measured the etch resistance of polymer brushes formed by ATRP against three different wet chemical etchants of gold (aqueous solutions of KI/I₂, KCN/K₃Fe(CN)₆, and aqua regia) as a function of the thickness and functionality of the polymer brushes. These etches use a ligand that complexes with gold (to lower the oxidation potential of the gold) and an oxidizing agent that oxidizes the gold in the presence of the ligand. Barriers that prevent the etching of gold can act by protecting the gold from the ligand and/or the oxidizing agent. Iodide/iodine and aqua regia etchants contain species that weakly coordinate with gold (I⁻ and Cl⁻, respectively)²⁶ and strong oxidizers (iodine, HNO₃). The cyanide ion, however, significantly reduces the oxidation potential of the gold and requires only a weak oxidizing agent (such as ferrocyanide). In this paper, we define the etch resistance of the polymer brush as the time required to observe complete dissolution of a 1000 Å thick film that supports the polymer brush.

Inspection of Figure 4A reveals that a polymer brush of PMMA prepared using a SAM formed from **I** at 60 °C can possess resistance to the KI/I₂ etch that is 60 times greater than the etch resistance of the SAM formed from **I**. For example, whereas the gold film supporting a SAM formed from **I** was etched within ~ 25 –30 s, when amplified into a brush of PMMA with

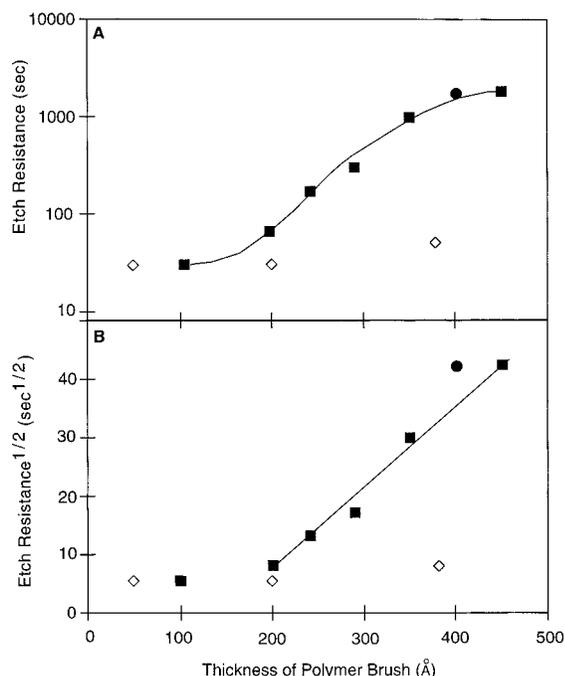


Figure 4. (A) Etch resistance of brushes of PMMA as a function of their ellipsometric thickness: (filled squares) PMMA and (filled circles) PIBMA. Both brushes were grown from SAMs formed from **I** at 60 °C. The etchant was an aqueous solution of KI/I₂. The open diamonds indicate the etch resistance of brushes of PMMA and PIBMA grown from SAMs formed from **I** at 25 °C. (B) Data shown in (A) plotted as a function of the square root of the etch resistance.

thickness 450 Å by using ATRP, the etch resistance of the surface increased to ~1800 s. The resistance to etching by KI/I₂ was found to scale linearly with the square root of the thickness of the polymer film for films greater than 200 Å (Figure 4B). This result suggests that the polymer brushes may act as barriers to diffusion of iodide and/or iodine.

Because we speculated that the hydrophobic polymer brushes might possess the greatest etch resistance in aqueous solutions, we compared and contrasted the capability of polymer brushes of PMMA and PIBMA to act as barriers to the three different etchants. The results of our experiments reveal that the relative etch resistance of the PMMA and PIBMA polymer brushes is specific to the type of etchant (Figure 5). Each result shown in Figure 5 was reproduced with three separate samples. We make three observations using these results. First, the PIBMA brush (thickness of 400 Å) and the PMMA brush (450 Å) were measured to possess similar resistances to etching by KI/I₂. In both cases the resistance to etching is high (~1800 s). Second, when using the alkaline (pH ~ 13.5) KCN/K₃Fe(CN)₆ etchant, the resistance to etching was higher for PIBMA (~600 s) than PMMA (~350 s). Both films, however, were less resistant to etching by the KI/I₂ etchant than the KI/I₂ etchant. We speculate that the polymer brushes were not highly effective as barriers in the alkaline (pH ~ 13.5) cyanide etchants because the alkaline conditions promoted hydrolysis of the ester groups of the side chains of the polymer brushes. Third, when using aqua regia, we measured the etch resistance of the PIBMA brush (~1800 s) to be greater than the PMMA brush (600 s). This difference is plausibly related to the hydrophobic nature of the PIBMA brush as compared to PMMA and thus the greater exclusion of water and

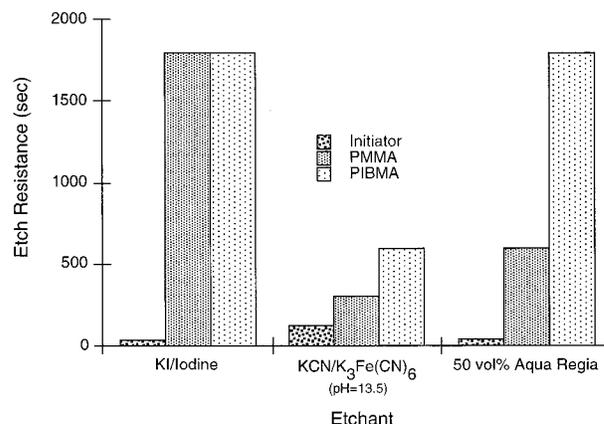


Figure 5. Comparison of etch resistances of SAMs formed from **I** (at 60 °C) and brushes of PMMA (thickness 450 Å) and PIBMA (thickness 400 Å). The chemical compositions of the etchants are described in the text.

ions (H⁺, NO₃⁻, Cl⁻) from the PIBMA brush as compared to the PMMA brush. In summary, our results indicated the effectiveness of the polymer brushes to resist etching of the underlying substrate can be tailored by choice of both the physicochemical properties of the brush and the type of etchant.

We also investigated the etch resistance of polymer brushes grown from SAMs of **I** that were prepared at 25 °C. We observed the gold underlying these polymer brushes to be etched at rates similar to bare gold surfaces (Figure 4A). We believe the poor etch resistance offered by these polymer brushes is likely due to the desorption of the initiator, **I**, from the surface of the gold during the polymerization at 60 °C. Ellipsometric measurements (Figure 1) indicate that roughly half of a SAM formed at 25 °C from **I** will desorb during the first few minutes of the polymerization and that the resulting polymer brush is substantially thinner than that of a polymer brush formed using initiators deposited at 60 °C (Figure 3).

Patterned Polymer Brushes. We used the etch resistance of polymer brushes formed by ATRP to transfer patterns generated in SAMs into the underlying substrate. This novel strategy relies on the preparation of patterned polymer brushes of PMMA by using microcontact printing of hexadecanethiol (HDT) on the surface of films of gold. Following microcontact printing, the underivatized regions of the gold film were derivatized by immersion into a 1 mM solution of **I** in hexadecane at 60 °C for 5 min. In separate experiments, SAMs formed from **I** for 5 min in hexadecane at 60 °C were demonstrated to be stable when immersed in toluene at 60 °C for up to 3 h.

The patterned SAM was then amplified into a patterned polymer brush by performing ATRP as discussed in the Methods section.

Past studies have reported that ~50% of a SAM formed from HDT (on gold) will desorb into hexadecane when immersed at 83 °C for ~30 min.¹³ Because the procedure reported above involves the immersion of a SAM formed from HDT into a solution of hexadecane and **I** at 60 °C for 5 min, we measured the extent of displacement of the SAM formed from HDT during this procedure. We microcontact printed a SAM formed from HDT (at 25 °C) on a 2 cm by 2 cm area of a film of gold and subsequently immersed it into a 1 mM solution of **I** in hexadecane at 60 °C. The surface was then characterized by using ellipsometry and XPS. We mea-

sured the extent of displacement of HDT by **I** after immersion in the 1 mM solution of **I** for 5 min, 1 h, or 2 h. For reference, the ellipsometric thicknesses of SAMs formed from HDT and **I** are 23 ± 1 and 18 ± 1 Å, respectively. After 5 min of exposure to the 1 mM solution of **I** at 60 °C, the ellipsometric thickness of the SAM formed from **I** was 23 ± 1 Å. Furthermore, measurements by XPS indicated that no bromine was incorporated within the SAM. These results, when combined, demonstrate that a 1 mM solution of **I** does not measurably displace a SAM formed from HDT after 5 min of immersion. Immersion for times substantially greater than 5 min did, however, result in measurable displacement. After 1 and 2 h of immersion, for example, the ellipsometric thickness of the SAM formed initially from HDT (23 ± 1 Å) was reduced to 22 ± 1 and 20 ± 1 Å, respectively. By assuming a linear relationship between composition of a SAM and its thickness, we estimate the composition of the mixed SAM to be 70–80% HDT after 1 h and 50–60% after 2 h. In summary, we conclude that displacement of the SAM formed from HDT by the 1 mM solution of **I** (at 60 °C) is very low (less than a few percent) when the time of immersion in the solution of **I** is maintained at 5 min. This fact permits the formation of patterned polymer brushes by ATRP.

We used AFM in contact mode to image patterned polymer brushes grown from surfaces of gold using patterned SAMs formed from **I** and HDT. Figure 6A shows a real-space image of patterned polymer brushes of PMMA with lateral dimensions of ~ 10 μm. A cross-sectional profile of the patterned brush shows the height difference between the brushes of PMMA and gold substrate in Figure 6B. The average thicknesses of PMMA brushes estimated from the AFM images were generally in good agreement with the thicknesses measured by ellipsometry. For example, the thickness of the PMMA film estimated from the AFM image in Figure 6B is 220 ± 40 Å,²⁷ a value that is in good agreement with the thickness of 210 ± 10 Å measured by ellipsometry on the adjacent, unpatterned region. We also observed that gold films used to support brushes of PMMA were sometimes discolored when the brushes were formed for greater than 3 h using ATRP. The discoloration was caused by a change in the optical constants of the gold. Measurements of the thickness of the polymer layers were not made by using ellipsometry when discoloration was observed.

Finally, we report that patterned brushes of PMMA of the type shown in Figure 6A can be used to pattern the underlying substrate of gold. Figure 6C shows a gold film supporting a patterned brush of PMMA that was etched for 60 s in an aqueous solution of KI/I₂. The image was obtained using parallel polars. The dark lines correspond to regions of gold that were protected from etching by a brush of PMMA. In contrast, the light regions in Figure 6C correspond to gold regions that did not support brushes of PMMA and were subsequently etched away.

Discussion

The principal result of this paper is that ATRP can be used to amplify monolayers of molecules patterned on surfaces by microcontact printing into patterned polymer brushes that serve as effective barriers to etchants of gold. By using ATRP, we have demonstrated that the thickness and physical properties of the pat-

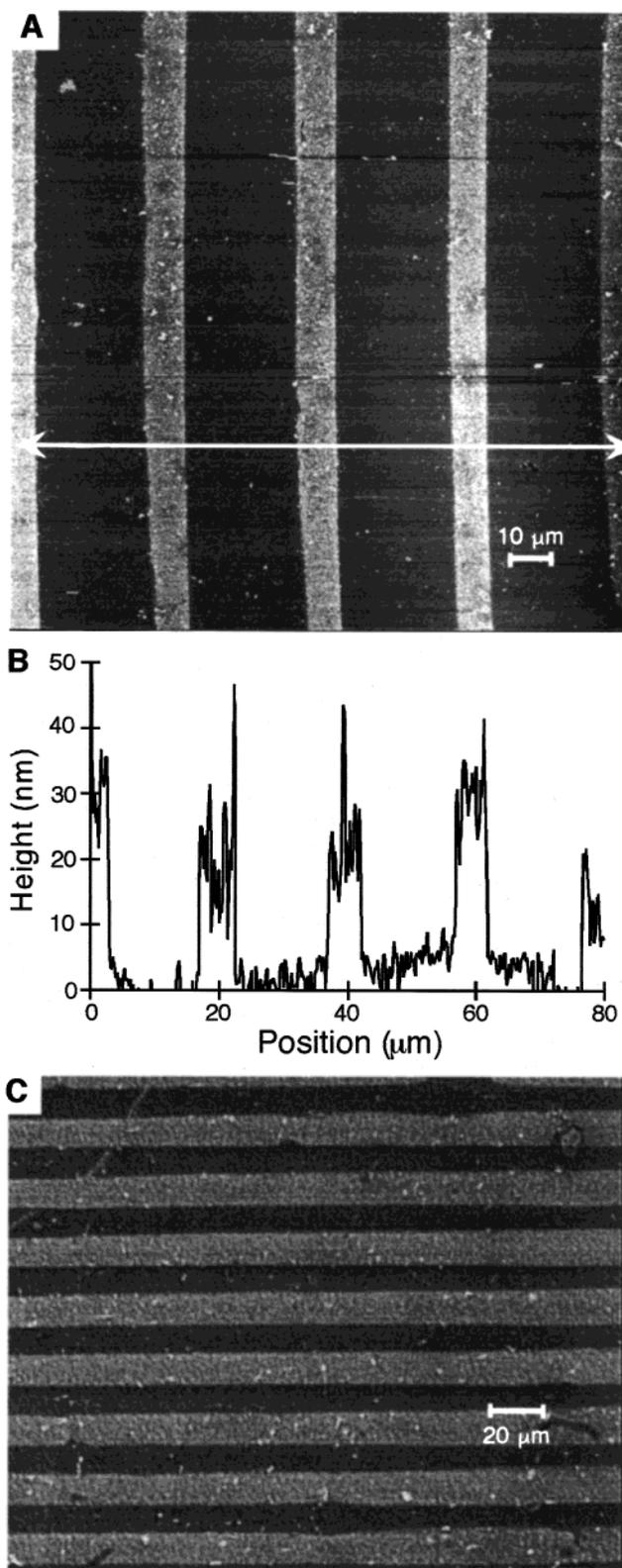


Figure 6. (A) AFM image of a patterned brush of PMMA formed by combination of microcontact printing and ATRP. The bright areas of the image correspond to brushes of PMMA while the dark regions correspond to patterned areas of SAMs formed from HDT. (B) Cross-sectional profile of the patterned PMMA brush shown in (A). The location of the cross-sectional profile is marked in (A) by the double-headed arrow. (C) Optical image of a patterned brush of PMMA after immersion into aqueous KI/I₂ for 60 s. The dark areas of the image are gold protected by the PMMA brush, and the light regions correspond to glass (the substrate underlying the gold film).

terned polymer brushes can be tailored to control the effectiveness of the polymer brushes as barriers to wet chemical etchants of gold.

The work we report builds on past studies that have demonstrated the use of microcontact printed SAMs formed from HDT as resists for the patterning of gold and silver.²⁸ Silver and gold films so-patterned have also been used as secondary masks for pattern transfer into Si, SiO₂, and GaAs.¹ These past studies also reveal, however, that SAMs are susceptible to formation of defects and thus are limited in usefulness as barriers to a variety of wet chemical and conventional reactivation etchants.^{1,10} A principal point of the investigation reported in this paper is the demonstration that polymer brushes grown from patterned SAMs (i) can serve as better barriers to etchants of gold than the SAMs and (ii) can serve as barriers to a broad range of etchants.

We recently demonstrated the capability to amplify patterned SAMs prepared by microcontact printing by utilizing a surface-initiated ring-opening polymerization of ϵ -caprolactone¹² to form patterned polymer brushes. In that study, however, we did not demonstrate the use of these polymer brushes as resists for wet chemical etching. Several past studies have, however, investigated amplification of SAMs spatially patterned by microcontact printing.^{29,30} Tao et al., for example, reported the use of microcontact printing of SAMs to prepare templates that hindered polymerization of polymethylene (PM) from the surface of films of gold.²⁹ The patterned films of PM were used as barriers to aqueous etchants of the underlying films of gold. In a second approach, Lackowski et al. used AFM to image films of gold patterned with SAMs formed from HDT and mercaptohexadecanoic acid that were subsequently amplified by grafting hyperbranched poly(acrylic acid) (PAA) to the patterned SAM.³⁰ More recently, Huck et al. have grafted polymer multilayers to patterned SAMs and used the polymer multilayers as resists for etching of films of gold.³¹

Although the use of ATRP to amplify monolayers of initiators patterned on gold into polymeric barriers for wet chemical etchants has not been reported in the past, we note that ATRP has been used to form homogeneous polymer brushes from a silica surface.^{19,32} Indeed, a number of past studies have described the growth of polymers from surface-confined initiators. For example, Prucker et al.²⁰ reported a free radical polymerization of styrene using azo-based initiators from silicon oxide whereas Jordan et al.¹⁸ reported the anionic polymerization of styrene from SAMs on gold substrates terminated with the biphenyl–lithium moiety. We also note that past studies by Sun et al.,³³ Lenk et al.,³⁴ and Tsao et al.³⁵ have reported the formation and characterization of various polymeric assemblies (polyacrylate, PMMA, poly(dimethylsiloxane)s) by grafting polymers with side chains containing disulfide, thiol, or sulfide moieties, respectively, to the surfaces of films of gold. We believe that combinations of these past approaches leading to the formation of polymeric films, if combined with microcontact printing, will likely also yield useful means by which to amplify monolayers into robust barriers for pattern transfer into underlying substrates.

The work we report in this paper revolves around the use of organosulfur compounds on gold as initiators of ATRP. Because SAMs formed from alkanethiols are known to thermally desorb from the surface of gold when placed into contact with organic solvents¹³ and

because ATRP requires the use of elevated temperatures (≥ 60 °C), in the course of the work reported in this paper we found a simple procedure that permits formation of thermally stable SAMs formed from **I** on gold. These SAMs are sufficiently stable at the elevated temperatures used for ATRP so as to permit formation of dense polymer brushes. We note that a variety of methods have been reported in the past to increase the thermal stability of SAMs, such as substituting silver for gold at the surface of the metallic film,³⁶ designing monomers with multiple S–Au interactions,³³ increasing the intrachain interactions through aromatic moieties or hydrogen bonds,³⁷ and incorporating polymerizable groups.³⁸ For example, underpotential deposition of silver atoms onto the surface of films of gold has been shown to enhance the thermal stability of SAMs (up to 70–105 °C).³⁶ Enhanced stability of SAMs at 85 °C in hexadecane has also been observed on SAMs formed from molecules that establish multiple S–Au interactions.³³ Finally, past studies have shown intrachain interactions at 80 °C in decahydronaphthalene (DHN) to lead to enhanced thermal stability of SAMs formed from chelating aromatic dithiols.³⁷ In contrast to the methods described above, the procedure we report to form thermally stable SAMs from **I** is simple to perform and does not require the synthesis of special monomers or require additional steps in the preparation of substrates. Our procedure involves the immersion of the films of gold into solutions of **I** at elevated temperatures. We point out that a past investigation has reported the formation of SAMs at elevated temperatures. Zhao et al.¹⁰ reported the formation of SAMs from liquid H₃C–(CH₂)_{*n*}SH (where *n* \geq 25) at elevated temperatures (≥ 70 °C). This past study, however, did not address the role of the formation temperature on the thermal stability of SAMs.

Conclusions

The principal result of the work reported herein is a demonstration of the usefulness of ATRP to amplify initiators patterned on surfaces by microcontact printing into polymeric barriers that can serve as robust barriers to a range of wet chemical etchants. The use of ATRP permits a high level of control over the thickness and functionality of polymer brushes and makes possible the tailoring of the physical properties of the brushes such as their wettability and resistance to wet chemical etchants.

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