

Two New Approaches for Patterning Polymer Films Using Templates Prepared by Microcontact Printing

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ABSTRACT: Two new methods for preparing micron-scale patterns of hyperbranched polymer films are reported. Both approaches rely on passivation of a reactive surface by microcontact printing (μ -CP) followed by polymer grafting to unpassivated regions of the surface. The first method involves patterning of a hyperbranched polymer composite film containing poly(amidoamine) dendrimers and Gantrez (an active anhydride copolymer) onto Au. These structures are prepared by partial passivation of an Au surface with an *n*-hexadecanethiol self-assembled monolayer (SAM) using μ -CP, followed by multiple covalent grafting iterations of the dendrimer/Gantrez polymer film onto the unpassivated regions. The second patterning method involves partial passivation of an activated mercaptoundecanoic acid (MUA) SAM, followed by modification of the unpassivated SAM with a layered poly(acrylic acid)/poly(ethylene glycol) (PAA/PEG) nanocomposite. The approach for fabricating these structures consists of formation of an activated MUA SAM, μ -CP of *n*-hexadecylamine (C16NH₂) to partially passivate the MUA SAM, and sequential covalent grafting of PAA and then PEG onto the unpassivated regions. Ellipsometry, Fourier transform infrared–external reflection spectroscopy (FTIR-ERS), optical microscopy, and tapping-mode atomic force microscopy (TM-AFM) provide evidence for the viability of these methods. For both types of films, lines of polymer having lateral dimensions of ~ 20 μ m and edge resolutions of < 1 μ m are obtained. The polymer thicknesses are on the order of 20–50 nm depending on the number of iterative polymer grafting steps.

Introduction

This paper describes two simple, microcontact printing-based methods for preparing micropatterned polymer films. The first approach involves patterning of a hyperbranched polymer composite film containing dendrimers and Gantrez (an active anhydride copolymer) onto Au.^{1–3} These structures are prepared by a two-step process: partial passivation of an Au surface with an *n*-hexadecanethiol (C16SH) self-assembled monolayer (SAM)⁴ using microcontact printing (μ -CP),^{5,6} followed by covalent grafting of the dendrimer/Gantrez polymer film onto the unpassivated regions.^{1–3} The second patterning method involves partial passivation of an activated mercaptoundecanoic acid (MUA) SAM, followed by modification of the unpassivated SAM with a layered poly(acrylic acid)/poly(ethylene glycol) (PAA/PEG) nanocomposite.^{7–9} The approach for fabricating these structures consists of three basic steps: formation of an activated MUA SAM, μ -CP of *n*-hexadecylamine (C16NH₂) to partially passivate the MUA SAM,¹⁰ and sequential covalent grafting of PAA and then PEG onto the unpassivated regions.^{7,9}

Patterned polymer films have applications as etch resists,¹¹ scaffolds for tissue engineering,^{12–15} components in molecular electronic¹⁶ and optical devices^{17,18} and in biological¹⁹ and chemical²⁰ sensors. Such polymers have been patterned by photolithography of spin-cast and covalently linked thin films,^{21–24} using layer-by-layer electrostatic adsorption onto patterned SAMs,^{25–27} by templating phase separation in diblock copolymers,^{28,29} and also by anisotropic spinodal dewetting.³⁰ Recently, we showed that polymers could be covalently grafted to SAMs patterned by μ -CP,^{13,31} and

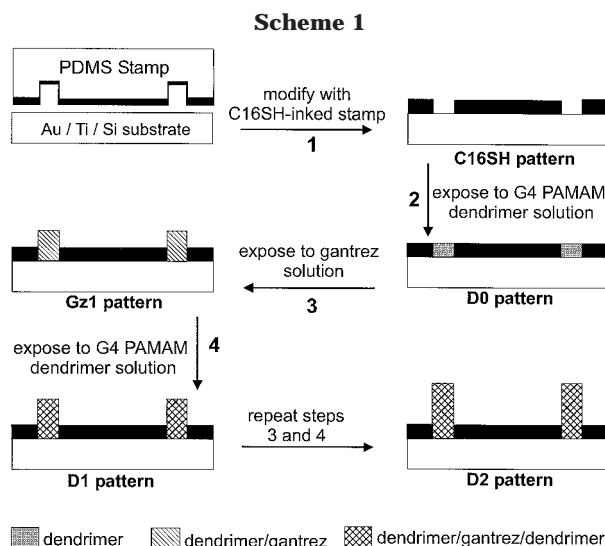
others subsequently demonstrated a number of ingenious alternative strategies that greatly expand the scope, resolution, and chemical flexibility of this approach.^{32–36}

μ -CP is a soft lithographic method that employs an elastomeric stamp to print a chemical ink onto surfaces with submicrometer resolution.^{5,6,37–39} Although most μ -CP studies have involved patterning of *n*-alkanethiol monolayers directly onto metals and semiconductors, the methodology has recently been extended to stamping of *n*-alkylamines¹⁰ and amine-terminated polymers^{40,41} onto activated MUA SAMs confined to metal surfaces. Additionally, we recently reported a method for patterning hyperbranched polymer films onto activated, oxidized polyethylene surfaces using μ -CP of an *n*-alkylamine to selectively passivate particular regions of the surface, followed by polymer grafting to the unpassivated surface.⁴²

Here we expand upon our previous findings by reporting two new approaches for preparing patterned, functional, three-dimensional polymer films. The first involves μ -CP of C16SH to template the grafting of covalently linked thin films consisting of homogeneous composites of fourth-generation (G4) poly(amidoamine) (PAMAM) dendrimers and poly(maleic anhydride)-*c*-poly(methyl vinyl ether) (Gantrez) capped with a conformal layer of the PAMAM dendrimer. We have previously shown that unpatterned films of this type exhibit fully reversible, pH-switchable permselectivity for both cationic and anionic redox-active probe molecules.¹ The patterning strategy reported here opens the door to the fabrication of micron-scale devices incorporating this function.

We also show that μ -CP of C16NH₂ onto a reactive MUA surface can be used to construct patterns of relatively thick, covalently linked hyperbranched poly(acrylic acid) films capped with a conformal layer of

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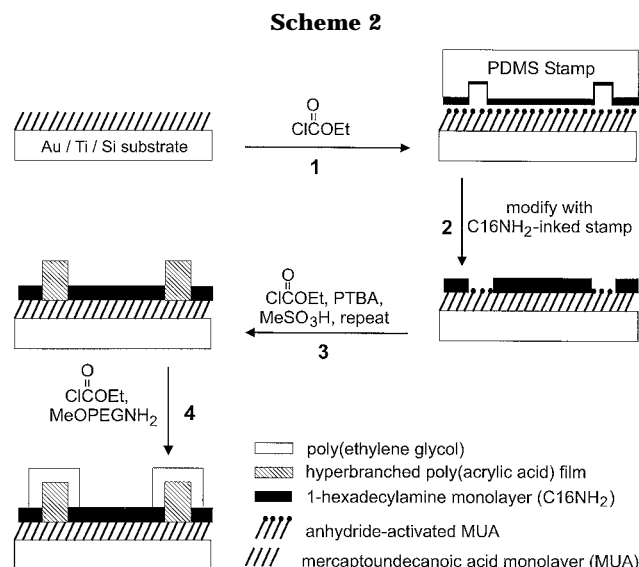


poly(ethylene glycol).^{8,13} Previously we demonstrated that similar structures could be prepared by printing *n*-alkanethiols directly onto Au. This new approach greatly expands the scope of this template approach for polymer growth onto surfaces. Specifically, any surface that contains a monolayer or submonolayer coverage of acid groups can be used to template polymer growth. This includes many types of oxidized plastics, inorganic materials such as carbon that can be oxidized to yield acid functionalities, and any other type of substrate that can be at least partially coated with acid-bearing monomers or polymers. Such materials have applications to corrosion passivation and chemical sensing.^{43–45}

Experimental Section

Materials and Chemicals. Gantrez, which is poly(maleic anhydride)-*c*-poly(methyl vinyl ether) ($M_n = 6.2 \times 10^4$, $M_w/M_n = 3.4$), was generously donated by GAF-ISP (Wayne, NJ). The amine-terminated, fourth-generation Starburst poly(amidoamine) (PAMAM) dendrimers (G4-NH₂) were purchased from Dendritech, Inc. (Midland, MI). 1,1'-Carbonyldiimidazole, 4,4'-azobis(4-cyanovaleric acid) (75+%), ethylenediamine (99%), 11-mercaptopundecanoic acid (MUA), *n*-hexadecanethiol (C16SH), *n*-hexadecylamine, *N*-methylmorpholine, ethyl chloroformate, methanesulfonic acid, *tert*-butyl acrylate, and all anhydrous solvents were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification, except for the *tert*-butyl acrylate, which was distilled before use to remove polymerization inhibitors. Methoxy poly(ethylene glycol) amine (molecular weight 5000, Shearwater Polymers, Huntsville, AL) was used as received.

Microfabrication of Polymer-Patterned Surfaces. Au-coated, Ti-primed Si wafers (100–200 nm of Au sputtered onto an adhesion layer of 5–10 nm of Ti) were cleaned in an ozone cleaner (Boekel Industries, Inc., model 135500, Feasterville, PA) for 10 min prior to patterning. The substrates were then immersed in ethanol for 10 min, followed by ultrasonic cleaning for 1 min (Bransonic 52 ultrasonic cleaner, 47 kHz). Patterned dendrimer/Gantrez composite films were prepared using the five steps as outlined in Scheme 1. A TEM grid (Electron Microscopy Sciences, 300 mesh, Fort Washington, Pa) was used as a master from which poly(dimethylsiloxane) (PDMS) stamps were prepared using a published procedure.⁶ To pattern Au substrates with the G4-NH₂/Gantrez composite, C16SH ink (1 mM in EtOH) was applied to the PDMS stamp, dried under flowing N₂, and then transferred onto the Au substrates via mechanical contact for 30 s. The surface was then rinsed with EtOH and dried with flowing N₂. The unpassivated Au regions of the surface were subsequently modified with G4-NH₂ by direct chemisorption (~12 h, 0.1 mM



G4-NH₂ in EtOH) to the Au surface via multidentate Au/amine bonds.⁴⁶ Exposure of this G4-NH₂ layer to Gantrez (20 min, THF, occasional mild heating) yields the first Gantrez layer (Gz1).² After thorough rinsing in THF, the Gz1-coated substrate was immersed in the ethanolic G4-NH₂ solution for 10 min at room temperature to yield a dendrimer-terminated layer (D1).² One additional repetitive sequential deposition of Gantrez and G4-NH₂ leads to additional film growth (Gz2 and D2, respectively).¹ We have previously reported that this procedure can be continued for at least four reaction cycles (D4) with a resulting linear increase in film thickness.² The substrate was sonicated in ethanol after the dendrimer grafting steps and in THF following Gantrez grafting for 5 min to remove physically adsorbed polymer that might be present on the passivated regions of the surface.

Patterned poly(acrylic acid)/poly(ethylene glycol) (PAA/PEG) nanostructured composite films on active monolayer surfaces were prepared using the four steps outlined in Scheme 2. TEM grids (Electron Microscopy Sciences, 300 and 400 mesh Fort Washington, Pa) were used as masters for preparing the poly(dimethylsiloxane) (PDMS) stamps. To prepare the patterned films, a conformal MUA SAM is prepared on a Au surface by immersion in a 1 mM ethanolic solution, and then the acid groups are activated with ethyl chloroformate.⁷ Second, the activated MUA substrate is patterned by μ -CP (ink: 5 mM C16NH₂ in EtOH) to passivate selected regions of the surface.¹⁰ Third, unpassivated regions of the active MUA substrate are reacted with α,ω -diamino-terminated poly(*tert*-butyl acrylate) (H₂NR–PTBA–RNH₂, R = (CH₂)₂NHCO(CH₂)₂C(CN)(CH₃))⁶ to yield the amide-grafted polymer layer. Hydrolysis of PTBA with MeSO₃H yields the first layer of PAA, and two additional cycles of activation, grafting, and hydrolysis yield a thick, hyperbranched, three-layer PAA film (3-PAA). All activation, grafting, and hydrolysis steps were carried out at room temperature. After each step the substrate was sonicated in ethanol for 5 min to remove physically adsorbed polymer that might be present on the passivated regions of the surface. Finally, the 3-PAA regions of the surface could be functionalized with methoxypoly(ethylene glycol) amine (PEG) using a grafting procedure similar to that reported previously.³¹ The details of the syntheses and properties of unpatterned dendrimer/Gantrez and PAA/PEG composite films covalently linked to Au surfaces have been reported previously.^{1–3,7–9}

Characterization. FTIR-ERS measurements were made using a Bio-Rad FTS-6000 spectrometer equipped with a Harrick Scientific Seagull reflection accessory and liquid-N₂-cooled narrow-band MCT detector. All spectra were the sum of 256 or fewer individual scans with p-polarized light at an 84° angle of incidence with respect to the Au substrate.

Ellipsometric thickness measurements were performed on films in air using a Gaertner model L2W26D ellipsometer

(Chicago, IL) with a 70° angle of incidence and a wavelength of 633 nm. To calculate the thickness of “dry” dendrimer/Gantrez, PAA, or PAA/PEG films, a refractive index of 1.54 was used. This value was determined by fitting ellipsometric data obtained from thicker, homogeneous films.^{1,8}

Optical images of patterned films were obtained using a Nikon Eclipse-300 inverted microscope fitted with 10× and 20× objectives. Samples were illuminated with a high-pressure Hg UV lamp. Contrast is observed in the patterned films as a consequence of interference effects arising from the differing film thicknesses and reflective underlayer. The data were collected using a Photometrics SenSys CCD TE-cooled camera with 1 ms exposures. TM-AFM images of patterned dendrimer/Gantrez and PAA/PEG films were obtained in air using a Digital Instruments Nanoscope III (Santa Barbara, CA) fitted with a 200 μm f scanner. Tapping-mode cantilevers (NanoSensors, Wetzlar-Blankenfeld, Germany) had resonant frequencies between 260 and 280 kHz, force constants of 20–100 N/m, and tip apex radii of ~ 10 nm. Images were acquired at 512 \times 512 pixels at 1.0 Hz using a near-minimal contacting force. The resulting images were flattened and plane-fit using Digital Instruments software.

Results and Discussion

Microfabrication of Fourth-Generation, Amine-Terminated PAMAM Dendrimer/Gantrez Composite Patterns. Our approach for preparing patterned composite films consisting of fourth-generation, amine-terminated PAMAM dendrimers and Gantrez (G4-NH₂/Gantrez) and *n*-hexadecanethiol is shown in Scheme 1. First, C16SH from a PDMS stamp was transferred to a cleaned Au substrate, which resulted in formation of a patterned monolayer film.^{13,31} Using the C16SH monolayer as a mask, the remainder of the Au surface was modified with G4-NH₂ via multidentate Au/amine bonds.⁴⁶ The G4-NH₂/Gantrez composite thin film was selectively deposited onto the dendrimer-modified regions of the surface via a layer-by-layer method we reported previously.¹ Specifically, the active-anhydride Gantrez polymer reacts with primary amines on the dendrimer periphery to yield covalent amic acid functional groups. Similarly, amine-terminated PAMAM dendrimers react with underlying Gantrez layers. This sequential dipping process can be carried out indefinitely to yield ever-thicker films (Scheme 1). In the present study, this cycle was carried out twice, leaving the film terminated with G4-NH₂. Although the outermost layer is chemically distinct from those underlying it, the film interior is more or less a homogeneous composite of G4-NH₂ and Gantrez.¹

FTIR-ERS and ellipsometry measurements obtained from unpatterned surfaces initially modified with only C16SH or only G4-NH₂ confirm that grafting occurs exclusively on the dendrimer-modified Au surfaces. Moreover, FTIR-ERS also confirms our earlier finding that contact between the anhydride groups of Gantrez and the primary amines on the dendrimer periphery results in covalent amide linkages.¹ The ellipsometric thickness measured on unpatterned films after the first complete grafting cycle, which we refer to as the D1 layer (Scheme 1), is 12 \pm 1 nm; the D2 layer is 23 \pm 1 nm thick. Both of these values are similar to results reported previously.¹

Figure 1 shows a bright-field optical micrograph of a square-grid pattern (derived from a 300 mesh TEM-grid master). The 20 μm wide grid lines are composed of a D2 (dendrimer-terminated) G4-NH₂/Gantrez nanocomposite, and the interior 63 μm squares consist of a C16SH SAM. TM-AFM confirms pattern transfer of the

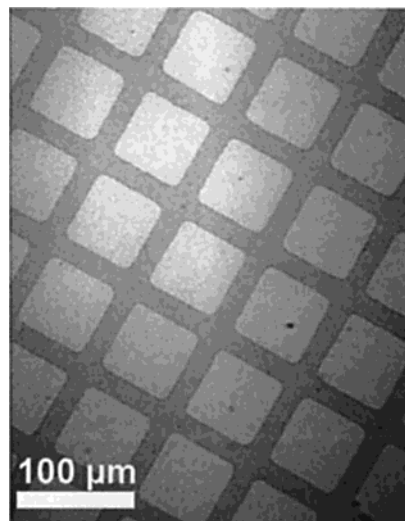


Figure 1. Optical micrograph of a Au surface patterned using μ -CP of *n*-hexadecanethiol (C16SH) followed by sequential grafting of G4-NH₂ dendrimers and Gantrez to the unpassivated regions of the surface. The grid is composed of a 20 μm wide, 23 nm thick dendrimer/Gantrez composite, and the squares are 63 μm wide and consist of a 1.8 nm thick C16SH monolayer. The pattern was derived from a 300 mesh TEM grid master.

G4-NH₂/Gantrez nanocomposite. Parts a and b of Figure 2 are low- and high-resolution TM-AFM images, respectively, of a pattern prepared identically to that shown in Figure 1. The important aspect of Figure 2a is that even at this resolution no defects are evident, and the interface between the SAM and the polymer is remarkably smooth. (The white particulate matter apparent in Figure 2a is tenaciously adsorbed contaminants.)

Figure 2b indicates that the edges of the polymer pattern are uniform and that the interface between C16SH and the polymer composite is < 500 nm. Figure 2c is a line scan representing the height difference (17 \pm 3 nm) between the top of G4-NH₂/Gantrez composite film (D2 in Scheme 1) and the top of the C16SH SAM. Taking into account the 1.8 nm thickness of the C16SH monolayer, the overall height of the composite regions is 19 \pm 3 nm, which is in accord with the previously reported thickness of an unpatterned G4-NH₂/Gantrez film (24 \pm 1 nm).¹ Finally, the tops of the patterned polymers have an average rms surface roughness of 3.0 nm.

Microfabrication of Poly(acrylic acid)/Poly(ethylene glycol) Patterns on Activated MUA Surfaces. Microfabrication of poly(acrylic acid)/poly(ethylene glycol) (PAA/PEG) patterns begins with preparation of a complete, unpatterned MUA SAM on the Au surface and subsequent activation with chloroformate to yield a reactive anhydride (Scheme 2). A fraction of this reactive surface is selectively deactivated by μ -CP using a stamp inked with an *n*-alkylamine (C16NH₂). To form covalent bonds by μ -CP, a high concentration of the active component of the ink is required. Specifically, we used 5 mM C16NH₂ ink, which is significantly higher than that required for direct C16SH passivation of a Au surface (typically 1 mM).¹⁰ We also allowed a longer stamp-contact time (~ 5 min vs 30 s for C16SH on Au) to ensure that the amide-bond formation reaction went to completion.

Regions of the activated MUA surface not passivated with C16NH₂ were selectively modified with up to three layers of PAA. As shown in step 3 of Scheme 2, this was

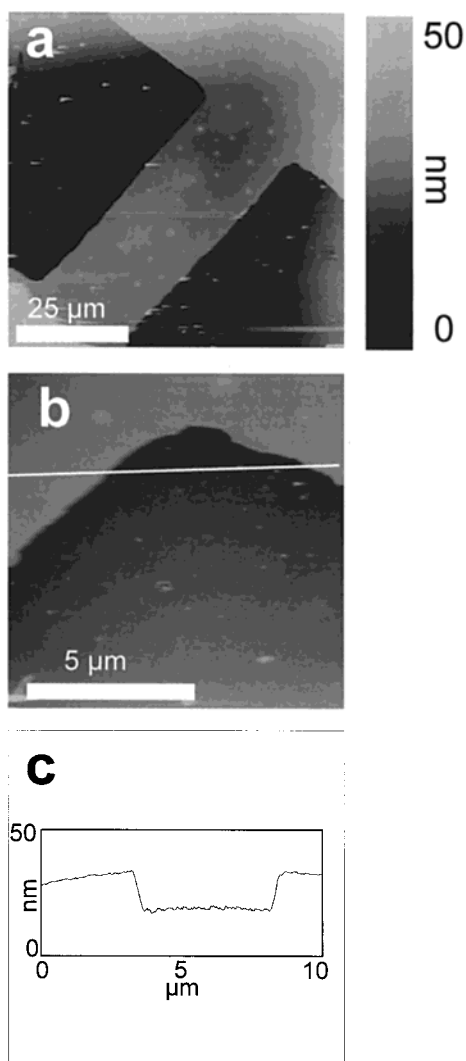


Figure 2. Tapping-mode atomic force microscopy (TM-AFM) data for a G4-NH₂/Gantrez polymer thin film patterned onto a Au substrate: (a) a 75 μm × 75 μm TM-AFM image; (b) a 10 μm × 10 μm TM-AFM image; (c) a line scan spanning the white line in (b). The patterns were derived from a 300 mesh TEM grid master.

accomplished by reacting the surface with H₂NR-PTBA-RNH₂ (PTBA) followed by hydrolysis to yield the first layer of PAA (1-PAA). Two more cycles of activation, grafting, and hydrolysis yields the patterned, hyperbranched 3-PAA film. Importantly, hyperbranched PAA films contain a high density of acid groups, which can subsequently be functionalized with a conformal layer of methoxy poly(ethylene glycol) amine (MeO-PEG₅₀₀₀NH₂, PEG) via amidation chemistry.¹³

FTIR-ERS and ellipsometry measurements obtained from unpatterned fractions of a partially patterned substrate confirm that PAA/PEG grafting occurs. Specifically, the measured ellipsometric thickness of 3-PAA on unpatterned regions of the Au surface was found to be 22 ± 1 nm, and after grafting PEG (3-PAA/PEG) the film thickness increased to 50 ± 2 nm. Both of these values are in accord with our previous studies.^{7,13} Control experiments performed on an activated MUA surface contacted by a flat (unpatterned) PDMS stamp inked with C16NH₂ indicated that growth of PAA and PEG was completely inhibited (within the resolution of ellipsometry and FTIR-ERS). Specifically, the thickness of a MUA surface modified with an unpatterned stamp

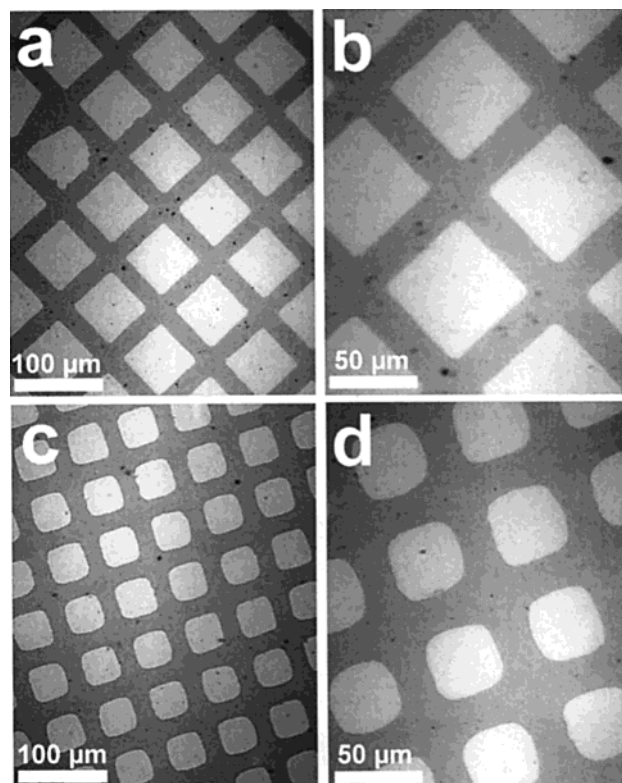


Figure 3. High- and low-resolution optical micrographs of an Au surface patterned by partial passivation of an activated mercaptoundecanoic acid (MUA) SAM using μ-CP of C16NH₂ followed by grafting of PAA and PEG onto unpassivated regions of the substrate. The grid lines are composed of PAA capped with a conformal PEG layer. The squares contain an amide-coupled bilayer. The patterns in parts a and b are derived from a 300 mesh TEM-grid master. The patterns shown in parts c and d were derived from a 400 mesh TEM-grid master.

inked with C16NH₂ was found to be 2.2 ± 0.2 nm even after attempting growth of PAA/PEG. This clearly indicates that the reaction efficiency between the surface-confined activated acid and the C16NH₂ ink is very high.

Parts a and b of Figure 3 are optical images obtained at high and low resolution, respectively, from a patterned 3-PAA/PEG film derived from a 300 mesh TEM-grid master. The grid lines, which consist of 3-PAA/PEG, are 20 μm wide, and the interior squares, consisting of MUA covalently linked to C16NH₂ via amide bonds, are 63 μm. Similarly, parts c and d of Figure 3 are optical images of identically prepared polymer patterns derived from a 400 mesh TEM-grid master. Here, the grid lines are also 20 μm wide, but the interior squares are only 42 μm. Note that there is some rounding of the corners in the smaller pattern.

Transfer of 3-PAA to the patterned surface was confirmed by TM-AFM. For example, parts a and b of Figure 4 are TM-AFM images obtained from patterned 3-PAA films derived from 300 and 400 mesh TEM-grid masters, respectively. The AFM-measured height difference between the top of the 3-PAA grid lines and the top of the C16NH₂-passivated region is 21 ± 2 nm (Figure 4, c and d). The thickness of an unpatterned MUA film activated and then stamped with C16NH₂ is 2.2 nm, and therefore the overall height of the 3-PAA film as measured by TM-AFM is 23 ± 2 nm. This value is consistent with those we have measured in the past on unpatterned substrates.^{13,31} The average rms rough-

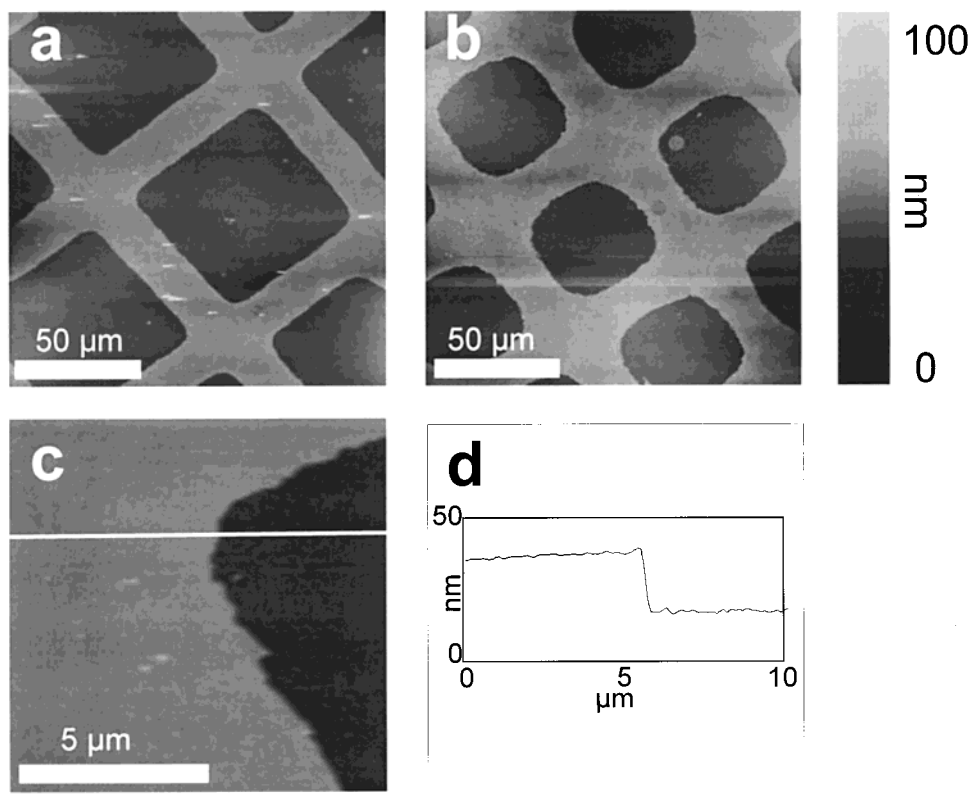


Figure 4. High- and low-resolution TM-AFM data of an Au surface patterned by partial passivation of an activated mercaptoundecanoic acid (MUA) SAM using μ -CP of C16NH₂, followed by grafting of PAA onto unpassivated regions of the substrate: (a) a 150 μ m \times 150 μ m image of a patterned 3-PAA hyperbranched polymer film prepared using a 300 mesh TEM-grid master; (b) same as (a) except the pattern was derived from a 400 mesh TEM-grid master; (c) a 10 μ m \times 10 μ m TM-AFM image of a patterned 3-PAA hyperbranched polymer film derived from a 300 mesh master; (d) line scan spanning the white line in (c).

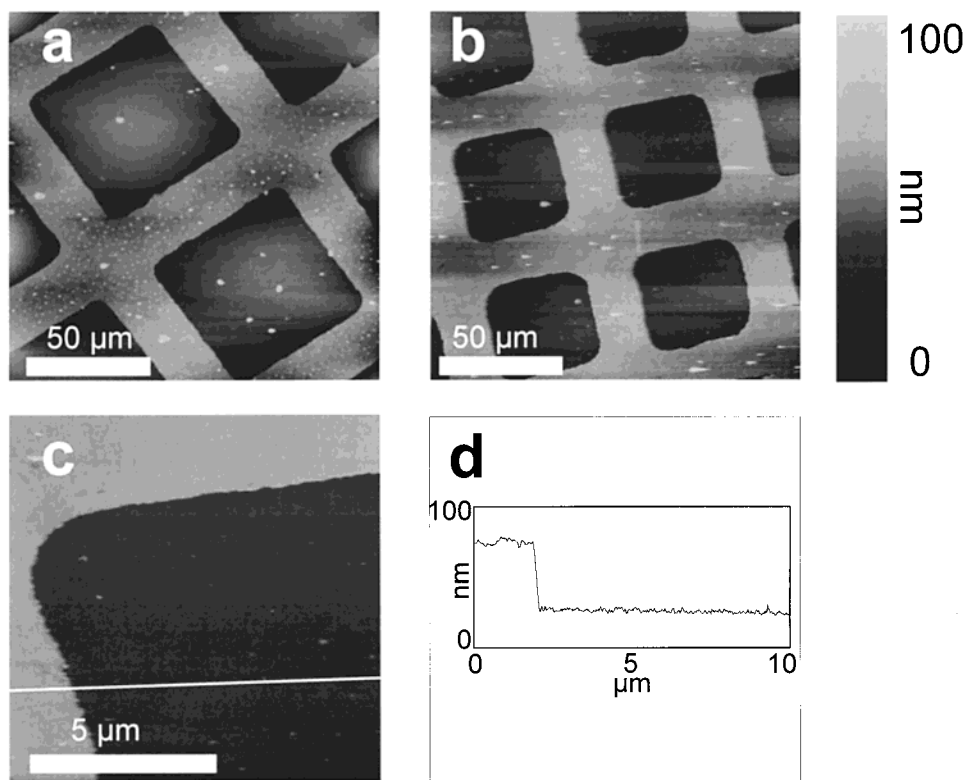


Figure 5. High- and low-resolution TM-AFM data of an Au surface patterned by partial passivation of an activated mercaptoundecanoic acid (MUA) SAM using μ -CP of C16NH₂, followed by sequential grafting of PAA and then PEG onto unpassivated regions of the substrate: (a) a 150 μ m \times 150 μ m image of a patterned 3-PAA/PEG composite polymer film derived from a 300 mesh TEM-grid master; (b) same as (a) except the pattern was derived from a 400 mesh TEM-grid master; (c) a 10 μ m \times 10 μ m TM-AFM image of a patterned 3-PAA/PEG composite polymer film derived from a 300 mesh TEM grid master; (d) line scan spanning the white line in (c).

ness of the 3-PAA fraction of these patterned surfaces is 0.9 nm, which compares favorably with our earlier measurements on unpatterned 3-PAA films (rms roughness = 0.8 nm). Figure 4d shows that the edge resolution for this pattern is $< 1 \mu\text{m}$.

Figure 5 shows TM-AFM images of 3-PAA patterns similar to those shown in Figure 4, but after grafting with a conformal layer of PEG. Parts a and b of Figure 5 are derived from 300 and 400 mesh TEM grids, respectively. The AFM-measured height difference between the top of 3-PAA/PEG film and top of the interior square regions is $45 \pm 4 \text{ nm}$ (Figure 5, c and d), which corresponds to an overall 3-PAA/PEG thickness of $47 \pm 4 \text{ nm}$ after taking into account the thickness of the interior covalently linked bilayer. Recall that unpatterned 3-PAA/PEG films were found by ellipsometry to be $\sim 50 \text{ nm}$ thick.¹³ The rms roughness of the 3-PAA/PEG surface is 3.0 nm. Figure 5d shows that the interface between the bilayer and polymer composite is $< 1 \mu\text{m}$.

Conclusions

The methodology presented in this paper provides a convenient route to polymer thin films patterned with micron-scale edge resolution. Because both methods rely on a layer-by-layer strategy of polymer grafting, the film thickness is easily controlled to within a resolution of a few nanometers. Films having thicknesses on the order of tens of nanometers were described, but additional grafting steps yield even thicker films.

Although the polymeric patterns reported here are somewhat more time-consuming to prepare than those based exclusively on monolayers, we have found them to be more stable, more versatile, and less prone to defects and delamination. For example, unpatterned dendrimer/Gantrez composite films function as supra-molecular gates that are activated by pH changes.¹ Patterned surfaces consisting of 3-PAA/PEG grids surrounding SAMs can be used to pattern mammalian^{13,14} and bacterial⁴⁷ cells. Additionally, the three-dimensional walls, which consist primarily of a polyelectrolyte, can be used to trap and release small molecules⁴⁸ and proteins⁴⁴ in the vicinity of such cells.

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