

Patterning Thin Films of Poly(ethylene imine) on a Reactive SAM Using Microcontact Printing

Lin Yan, Wilhelm T. S. Huck, Xiao-Mei Zhao, and George M. Whitesides*

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138

Received July 6, 1998. In Final Form: December 2, 1998

This paper describes the patterning of poly(ethylene imine) (PEI) on a surface into structures having submicron edge resolution. This procedure consists of three steps: (1) formation of a reactive self-assembled monolayer (SAM) terminating in interchain carboxylic anhydride groups on gold and silver; (2) patterning of this SAM by microcontact printing (μ CP) using a poly(dimethylsiloxane) (PDMS) stamp inked with PEI (this polymer contains primary and secondary amines that are reactive toward the anhydride groups); (3) hydrolysis of the unreacted anhydride groups with base and removal of noncovalently bound PEI. The patterned thin films of PEI are attached covalently to the SAM by amide bonds. The pendant, unreacted primary and secondary amines of the attached PEI can be used as reactive nucleophilic groups in further steps of chemical modification. This type of postmodification has been illustrated by allowing the amine groups of the covalently attached PEI to react with perfluorooctanoyl chloride, palmitoyl chloride, palmitic anhydride, and poly(styrene-*alt*-maleic anhydride). The PEI films and their derivatives were characterized using atomic force microscopy (AFM), scanning electron microscopy (SEM), polarized infrared external reflectance spectroscopy (PIERS), contact angles of water, and X-ray photoelectron spectroscopy (XPS).

Introduction

This paper presents a straightforward method for patterning thin films of amine-containing polymers having submicron-scale edge resolution on the surface using a combination of microcontact printing (μ CP)¹⁻³ and chemical modification of a reactive self-assembled monolayer (SAM) on gold and silver.^{4,5} This approach consists of three steps (Figure 1): (1) preparation of a reactive SAM presenting interchain carboxylic anhydride groups on gold and silver; (2) patterned delivery of poly(ethylene imine) (PEI)—a representative amine-containing polymer—to the SAM by μ CP using a poly(dimethylsiloxane) (PDMS) stamp that is inked with PEI; (3) hydrolysis of unreacted anhydride groups with aqueous base and removal of noncovalently bound polymers. This method provides a readily accessible route to stable and continuously patterned thin films of PEI attached covalently to the SAM by amide bonds.

Patterned thin films of polymers have a wide range of applications, for example, in preventing etching,⁶ in molecular electronics,⁷⁻⁹ in optical devices,^{10,11} in biologi-

cal¹² and chemical sensors,¹³⁻¹⁵ and in tissue engineering.¹⁶ Thin films of polymers that incorporate reactive functional groups provide a surface that can be further modified by chemical reactions.^{15,17-20} Crooks, Bergbreiter, Grainger, Rubner, Hammond, and others have developed methods for attaching polymers to SAMs using, for example, electrostatic adsorption of polyelectrolytes to an oppositely charged surface,²¹⁻²⁴ chemisorption of polymers containing reactive groups to a surface,^{25,26} and covalent attachment of polymers to reactive SAMs;^{13,14,17,18,27-29} this work extends these techniques to the formation of *patterned* surfaces. There are presently only a few methods available

(10) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47-49.

(11) Healey, B. G.; Foran, S. E.; Walt, D. R. *Science* **1995**, *269*, 1078-1080.

(12) Knoll, W.; Matsuzawa, M.; Offenhausser, A.; Ruhe, J. *Isr. J. Chem.* **1996**, *36*, 357-369.

(13) Wells, M.; Crooks, R. M. *J. Am. Chem. Soc.* **1996**, *118*, 3988-3989.

(14) Liu, Y.; Zhao, M.; Bergbreiter, D. E.; Crooks, R. M. *J. Am. Chem. Soc.* **1997**, *119*, 8720-8721.

(15) Bruening, M. L.; Zhou, Y.; Aguilar, G.; Agee, R.; Bergbreiter, D. E.; Crooks, R. M. *Langmuir* **1997**, *13*, 770-778.

(16) Langer, R.; Vacanti, J. P. *Science* **1993**, *260*, 920-926.

(17) Sukhishvili, S. A.; Granick, S. *Langmuir* **1997**, *13*, 4935-4938.

(18) Zhou, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M.; Wells, M. *J. Am. Chem. Soc.* **1996**, *118*, 3773-3774.

(19) Liu, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2114-2116.

(20) Chance, J. J.; Purdy, W. C. *Langmuir* **1997**, *13*, 4487-4489.

(21) Ferreira, M.; Onitsuka, O.; Stockton, W. B.; Rubner, M. F. *ACS Symp. Ser.* **1997**, No. 672, 437-444.

(22) Decher, G. *Science* **1997**, *277*, 1232-1237.

(23) Hammond, P. T.; Whitesides, G. M. *Macromolecules* **1995**, *28*, 7569-7571.

(24) Clark, S. L.; Montague, M. F.; Hammond, P. T. *Macromolecules* **1997**, *30*, 7237-7244.

(25) Stouffer, J. M.; McCarthy, T. J. *Macromolecules* **1988**, *21*, 1204-1208.

(26) Lenk, T. J.; Hallmark, V. M.; Rabolt, J. F.; Haussling, L.; Ringsdorf, M. *Macromolecules* **1993**, *26*, 1230-1237.

(27) Löfås, S.; Johansson, J. *J. Chem. Soc., Chem. Commun.* **1990**, 1526-1528.

(28) Rozsnyai, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 5993-5994.

(29) Mao, G.; Castner, D. G.; Grainger, D. W. *Chem. Mater.* **1997**, *9*, 1741-1750.

* To whom correspondence should be addressed. Tel: (617) 495-9430. Fax: (617) 495-9857. E-mail: gwhitesides@gmwgroup.harvard.edu.

(1) Kumar, A.; Abbott, N. A.; Kim, E.; Biebuyck, H. A.; Whitesides, G. M. *Acc. Chem. Res.* **1995**, *28*, 219-226.

(2) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 550-575.

(3) Xia, Y.; Whitesides, G. M. *Annu. Rev. Mater. Sci.* **1998**, *28*, 153-184.

(4) Yan, L.; Marzolin, C.; Terfort, A.; Whitesides, G. M. *Langmuir* **1997**, *13*, 6704-6712.

(5) Yan, L.; Zhao, X.-M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1998**, in press.

(6) Xia, Y.; Mrksich, M.; Kim, E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 9576-9577.

(7) Nishizawa, M.; Shibuya, M.; Sawaguchi, T.; Matsue, T.; Uchida, I. *J. Phys. Chem.* **1991**, *95*, 9042-9044.

(8) Burn, P. L.; Kraft, A.; Baigent, D. R.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Jackson, R. W. *J. Am. Chem. Soc.* **1993**, *115*, 10117-10124.

(9) Dai, L.; Griesser, H. J.; Hong, X.; Mau, A. W. H.; Spurling, T. H.; Yang, Y.; White, J. W. *Macromolecules* **1996**, *29*, 282-287.

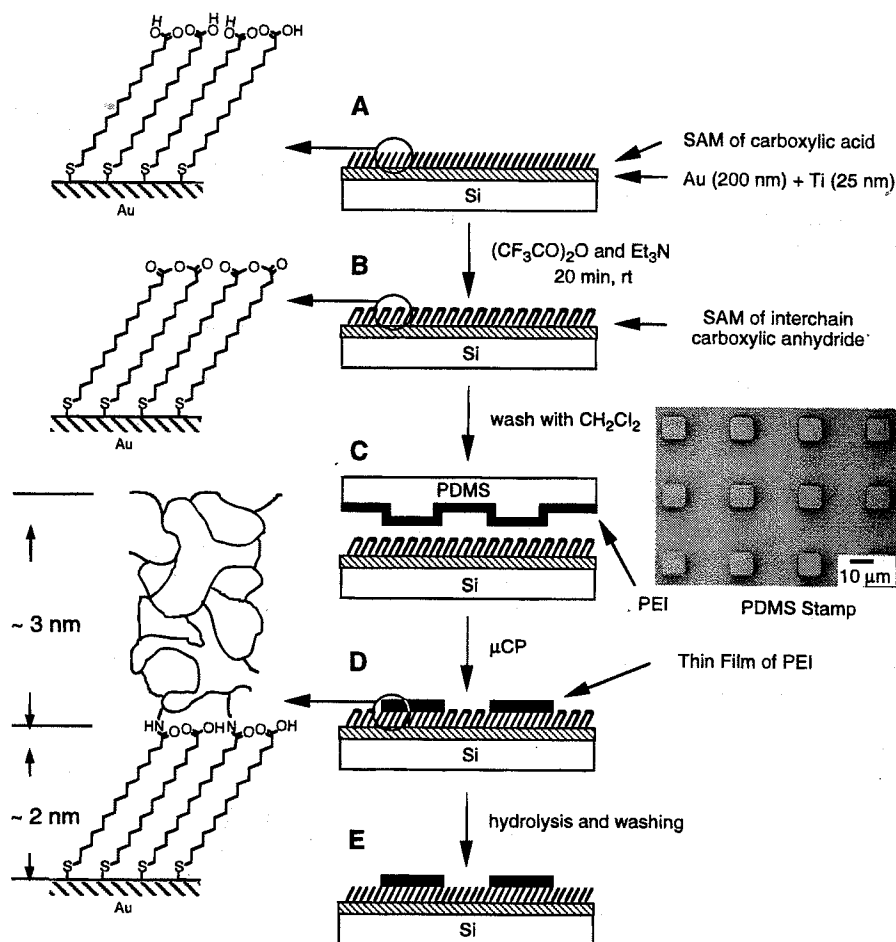


Figure 1. Schematic representation of the procedure for patterning thin films of PEI on the surface using μ CP and a chemical reaction. The scheme suggests the composition of the SAM but not the conformation of the groups in it; it also makes no attempt to represent either the conformation of the polymer or the distribution of functional groups on the polymer backbone. The optical microscope image shows the stamp (10×10 mm squares, separated by 20 mm) used in these studies.

for patterning thin films of polymers on SAMs; these include procedures based on photolithography,^{28,29} templating the deposition of polymers using patterned SAMs,^{23,24,30} and templating phase separation in diblock copolymers.^{31,32} Patterned thin films of polymers attached covalently to the surface are more stable than are ones only physically adsorbed. Photochemical pattern transfer offers only limited control over the surface chemistry, the properties, and the structure of the modified surfaces.

Microcontact printing (μ CP) is a broadly applicable technique for generation of patterns, with submicron edge resolution, by area-selectively *printing* reagents or molecules using an elastomeric stamp. Microcontact printing has been used to pattern alkanethiolates on gold, silver, and copper substrates,² alkylamines on reactive SAMs of alkanethiolates,⁵ alkyltrichlorosilanes on metal oxides,^{6,33} colloids (to pattern catalytical activity),^{34,35} and proteins.^{36,37} Here we demonstrate a procedure for patterning

an amine-containing polymer, PEI, on gold and silver by printing it on SAMs of alkanethiolates terminated in interchain carboxylic anhydride groups (Figure 1). We chose PEI as the reactive soluble polymeric component of the system for four reasons: First, reaction of amines with interchain carboxylic anhydride groups on the surface is a rapid, high-yield reaction.^{4,5} Second, PEI is commercially available. It is an amine-containing polymer that is composed of ethylenimine moieties as the repeating unit. Commercial PEI is highly branched, with a 1:2:1 ratio of primary, secondary, and tertiary amines.³⁸ Third, the PEI, once attached, provides a new, reactive surface that presents residual primary and secondary amine groups. The amine group is one of the most versatile functional groups in organic synthesis, and these remaining, pendant amine groups can be used for further chemical modifications.²⁰ Fourth, SAMs of alkanethiolates presenting amine groups on gold are difficult to make by adsorption of amine-terminated alkanethiols.^{39–41} In this paper, we show that the procedure outlined in Figure 1 generates patterned PEI films having submicron-scale

(30) Kim, E.; Whitesides, G. M.; Lee, L. K.; Smith, S. P.; Prentiss, M. *Adv. Mater.* **1996**, *8*, 139–142.

(31) Karim, A.; Douglas, J. F.; Amis, E. J.; Rogers, J. A.; Jackman, R. J.; Whitesides, G. M. *Phys. Rev. E* **1998**, *57*, R6273–R6276.

(32) Boltau, M.; Walheim, S.; Jurgen, M.; Krausch, G.; Steiner, U. *Nature* **1998**, *391*, 877–879.

(33) Jeon, N. L.; Nuzzo, R. G.; Xia, Y.; Mrksich, M.; Whitesides, G. M. *Langmuir* **1995**, *11*, 3024–3026.

(34) Hidber, P. C.; Helbig, W.; Kim, E.; Whitesides, G. M. *Langmuir* **1996**, *12*, 1375–1380.

(35) Hidber, P. C.; Nealey, P. F.; Helbig, W.; Whitesides, G. M. *Langmuir* **1996**, *12*, 5209–5215.

(36) Bernard, A.; Delamarche, E.; Schmid, H.; Michel, B.; Bosshard, H. R.; Biebuyck, H. *Langmuir* **1998**, *14*, 2225–2229.

(37) James, C. D.; Davis, R. C.; Kam, L.; Craighead, H. G.; Isaacson, M.; Turner, J. N.; Shain, W. *Langmuir* **1998**, *14*, 741–744.

(38) Davis, L. E. In *Water-Soluble Resins*; Davidson, R. L., Sittig, M., Eds.; Van Nostrand Reinhold Co.: New York, 1968; Chapter 11.

(39) Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358–2368.

(40) Tien, J.; Terfort, A.; Whitesides, G. M. *Langmuir* **1997**, *13*, 5349–5355.

(41) Doblhofer, K.; Figura, J.; Fuhrhop, J.-H. *Langmuir* **1992**, *8*, 1811–1816.

edge resolution (<500 nm) and that the PEI films present sufficient numbers of amine groups to react with acyl chlorides and carboxylic anhydrides for (1) introduction of different organic functional groups that modify the surface chemical and physical properties and (2) attachment of other polymers that contain carboxylic anhydride groups to the surface.^{14,19} We have characterized the PEI films and their derivatives using atomic force microscopy (AFM), scanning electron microscopy (SEM), polarized infrared external reflectance spectroscopy (PIERS), contact angles of water, and X-ray photoelectron spectroscopy (XPS).

Results and Discussion

A SAM of 16-mercaptohexadecanoic acid on gold was treated with trifluoroacetic anhydride.⁴ This reaction generated a reactive SAM that presented interchain carboxylic anhydride groups on the surface (Figure 1A,B). A PDMS stamp with protruding squares (~ 10 μm on a side) on its surface was oxidized for ~ 10 s with an oxygen plasma.⁴² The oxidized PDMS stamp was immediately inked with a 1 wt % solution of PEI in 2-propanol and placed in contact with the substrate (Figure 1C): The anhydride groups in the regions that contacted the PDMS stamp reacted with the amine groups of PEI (Figure 1D). Removal of the stamp and hydrolysis of the remaining anhydride groups with aqueous base (pH = 10, 5 min) gave a surface patterned with PEI (Figure 1E). All these procedures were carried out under ambient experimental conditions; the entire process—starting from the readily available SAMs of 16-mercaptohexadecanoic acid⁴³ to patterned PEI films—could be completed in less than 1 h.

Atomic force microscopy (AFM) defined both the edge resolution and the thickness of the patterned thin films of PEI. The AFM images acquired in contact mode showed that μCP delivered a well-defined pattern of PEI to the reactive SAM (Figure 2). The resulting thin films of PEI were nearly continuous, but their surfaces were not smooth at the nanometer scale (Figure 2B). The roughness of these films was controlled in part by the surface topology of the polycrystalline gold substrate.⁴⁴ The presence of gel or dust particles in the PEI probably also played a role;^{45–48} we have not determined the influence of these heterogeneities on the roughness of the surfaces produced by this procedure. Line analysis indicated that the average thickness of the patterned thin films was approximately 3 nm. Figure 2C suggests that the edge resolution of these squares was at the submicron scale (<500 nm); this value is larger than that obtained in μCP of *n*-hexadecylamine on the reactive SAM (<100 nm)⁵ and of alkanethiolates on gold (<50 nm)⁴⁹ but entirely adequate for many applications (especially in biochemistry and cell biology, where great uniformity and high edge-resolution are probably not required).

To form continuous thin films of PEI on the regions contacted by the PDMS stamp, it is essential to make the

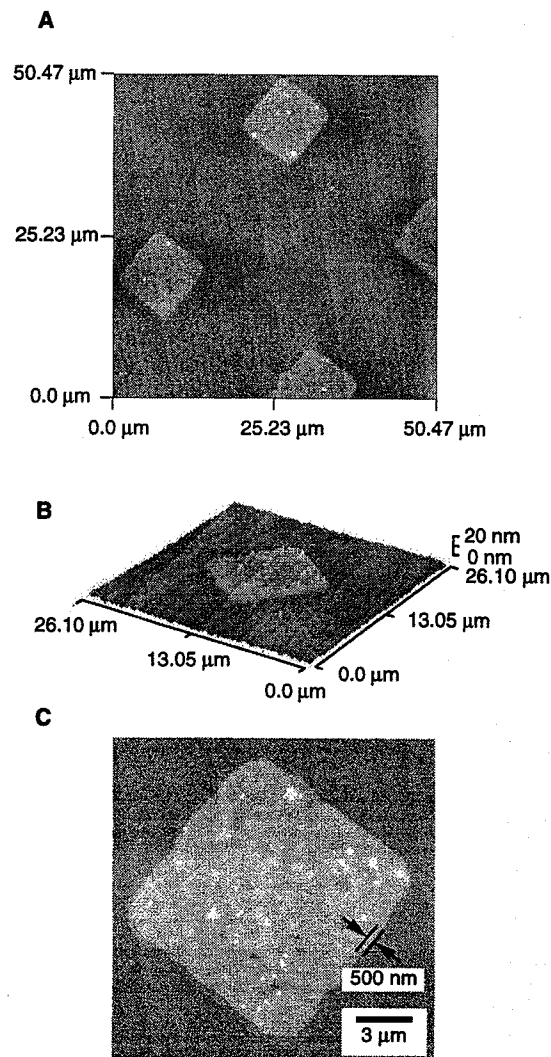


Figure 2. Contact mode AFM characterized the patterned thin films of PEI generated by μCP of PEI on the reactive SAM. These images show a sample patterned by μCP , followed by hydrolysis of the remaining, unreacted interchain carboxylic anhydrides with aqueous base. The light squares in the AFM images (A–C) were thin films of PEI on the regions contacted by PDMS stamp. The AFM image C shows that the PEI film was separated by a well-defined boundary (with roughness < 500 nm) from the regions presenting carboxylic acid groups. The lines in the images were artifacts generated by the instrument.

surface of the stamp hydrophilic prior to inking. We treated the PDMS stamp with an oxygen plasma; this treatment oxidized the $\text{Si}-\text{CH}_3$ groups on the surface of the PDMS and generated (we presume) the silanol groups ($\text{Si}-\text{OH}$) that make the surface hydrophilic.^{42,50} Comparison of the SEM images of the patterned thin films of PEI prepared using the plasma-treated PDMS stamp (Figure 3A–C) with those generated using an unoxidized one (Figure 3D–F) shows the improvement in the coverage of the patterned thin films of PEI on the surface resulting from this oxidative treatment. We hypothesize that, during the evaporation of 2-propanol, the hydrophilic PEI wetted the plasma-treated, hydrophilic PDMS stamp and formed a continuous thin layer of PEI that led to the formation of a continuous thin film of PEI on the SAM. In contrast, PEI dewetted the plasma-untreated, hydrophobic PDMS stamp and formed discontinuous “islands” of PEI on its

(42) Chaudhury, M. K.; Whitesides, G. M. *Science* **1992**, *255*, 1230–1232.

(43) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321–335.

(44) Tidswell, I. M.; Rabedeanu, T. A.; Pershan, P. S.; Kosowsky, S. D. *Phys. Rev. Lett.* **1991**, *66*, 2108–2111.

(45) Huang, K.; Balazs, A. C. *Macromolecules* **1993**, *26*, 4736–4738.

(46) Gersappe, D.; Fasolka, M.; Balazs, A. C. *J. Chem. Phys.* **1994**, *100*, 9170–9174.

(47) Zhao, W.; Krausch, G.; Rafailovich, M. H.; Sokolov, J. *Macromolecules* **1994**, *27*, 2933–2935.

(48) Siqueira, D. F.; Köhler, K.; Stamm, M. *Langmuir* **1995**, *11*, 3092–3096.

(49) Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 4581–4587.

(50) Fakes, D. W.; Davies, M. C.; Browns, A.; Newton, J. M. *Surf. Interface Anal.* **1988**, *13*, 233.

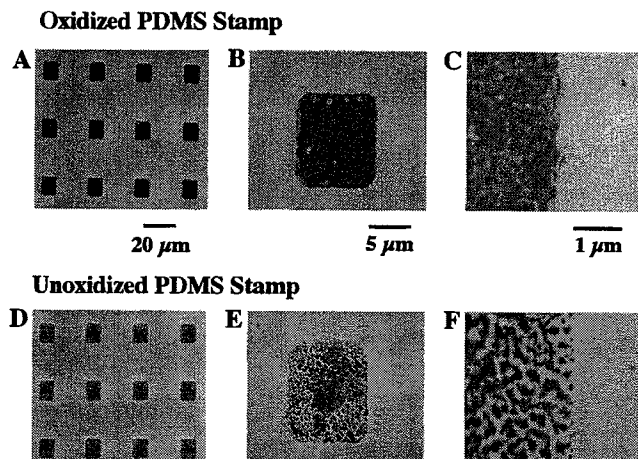


Figure 3. SEM images of patterned thin films of PEI on gold generated by μ CP using (A–C) an oxygen plasma-treated, hydrophilic PDMS stamp and (D–F) a plasma-untreated, hydrophobic one. The black squares or the black dots are PEI.

surface; this texture resulted in the formation of discontinuous, patterned thin films of PEI during the pattern transfer.^{51,52} A continuous thin layer of polymer on the surface of the stamp seems to be a *prerequisite* for transfer of a well-defined, continuous thin film of PEI onto the reactive SAM. We have also used this procedure to pattern thin films of PEI on reactive SAMs on silver; the edge resolution and the roughness of these films are similar to those obtained using SAMs on gold.

We used polarized infrared external reflectance spectroscopy (PIERS) to probe the interaction between PEI and the SAM. A chemisorbed PEI film was prepared by allowing reactive SAMs to react with a 1 wt % solution of PEI in 2-propanol. After the film was washed extensively in both acidic (pH = 4, potassium hydrogen phthalate) and basic (pH = 10, sodium carbonate) buffers and brief sonication, the ellipsometric thickness remained stable around 2–3 nm. In contrast, a physisorbed PEI film—prepared by allowing SAMs of carboxylic acids to react with PEI—desorbed completely from the surface after washing with either acidic or basic buffers. The high stability of the chemisorbed PEI film suggested that PEI was covalently linked to the SAM. Figure 4 shows the PIERS spectra (3200–1300 cm^{-1}) of (A) the SAM presenting carboxylic acids, (B) the unpatterned sample of the physisorbed PEI film, (C) the SAM presenting interchain carboxylic anhydrides, and (D) the unpatterned sample of the chemisorbed PEI film;⁵³ Table 1 lists the key absorption bands of these samples. The appearance of an absorption band at 2816 cm^{-1} that is associated with PEI in both spectra of the physisorbed and the chemisorbed PEI films indicates the adsorption of PEI to the surface; we assigned this band either to an N–H⁺ stretch of

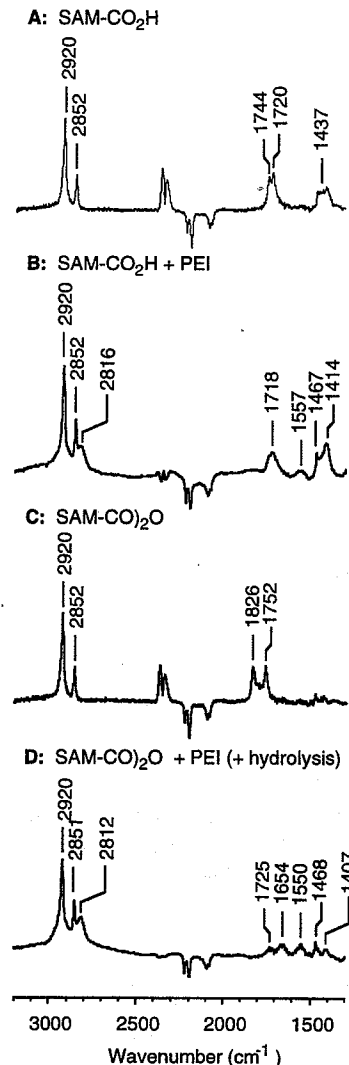


Figure 4. PIERS spectra of (A) the SAM of 16-hexadecanethiolates on gold, (B) the physisorbed PEI films, (C) the SAM of interchain carboxylic anhydrides, and (D) the chemisorbed PEI films. Absorption bands in the range of 2400–2000 cm^{-1} are due to the presence of residual CO_2 in the IR sample chamber and the (C, D) stretching of the background sample.

saturated ammonium salts or to a C–H stretch associated with a lone pair of electrons on nitrogen.⁵⁴ In the range from 1900 to 1300 cm^{-1} , the absorption bands for the C=O stretch of a carboxylic acid (1744 and 1720 cm^{-1})^{55,56} in spectrum A were converted cleanly into the absorption bands for the C=O stretch of a carboxylic anhydride (1826 and 1752 cm^{-1})⁴ in spectrum B; this change indicates a high-yield chemical transformation of carboxylic acids to carboxylic anhydrides on the surface. In the same range, the key difference between the spectra C and D is that an absorption band appears at 1654 cm^{-1} in spectrum D; we assigned this band either to an amide I stretch of a secondary amides or to an amide stretch of a tertiary amide.^{54,57} The presence of this characteristic band argues strongly that the PEI in the stable, chemisorbed PEI film is covalently attached to the surface by amide bonds. The disappearance of the absorption bands characteristic for

(51) During μ CP of *n*-hexadecanethiol on gold, reactive spreading of the thiol has been controlled and utilized to produce smaller features on the surface (Xia, Y.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 7, 3274–3275). Unlike the thiol, PEI is a viscous polymer: Reactive spreading of PEI is probably too slow to form continuous films on the surface during μ CP.

(52) It has been noted previously that the oxidative treatment of the hydrophobic PDMS stamp led to the better coverage of the surface with hydrophilic small organic molecules (Zhang, S.; Yan, L.; Rich, A.; Whitesides, G. Unpublished results) and proteins (see ref 37) during μ CP.

(53) We used a dilute solution (0.01 wt %) of PEI in 2-propanol to prepare both the physisorbed and chemisorbed PEI films. The PEI films formed under this condition did not fully cover the surface; the thicknesses were estimated at ~ 5 Å by ellipsometry. These partially covered PEI films provided unambiguous information about the presence of amide stretches between 1900 and 1300 cm^{-1} in PIERS spectra.

(54) Nakanishi, K. *Infrared Absorption Spectroscopy*; Nankodo Co. Limited: Tokyo, Japan, 1962.

(55) Allara, D.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 52–66.

(56) Tao, Y.-T.; Hietpas, G. D.; Allara, D. L. *J. Am. Chem. Soc.* **1996**, *118*, 6724–6735.

(57) Dolphin, D.; Wick, A. *Tabulation of Infrared Spectral Data*; John Wiley & Sons: New York, 1977.

Table 1. Assignment of the Selected Absorption Bands in the Infrared Spectra of the SAM of Acids, the SAM of Anhydrides, the Physisorbed PEI, and the Chemisorbed PEI

wavenumber (cm ⁻¹)					assgnt
SAM of acids	SAM of anhydrides	physisorbed PEI	chemisorbed PEI		
2920	2920	2920	2920	$\nu_{as}(\text{CH}_2)$	
2852	2852	2852	2851	$\nu_s(\text{CH}_2)$	
		2816	2816	$\nu(\text{N}-\text{H}^+)$ or $\nu(\text{C}-\text{H})$ associated with a nitrogen lone pair	
	1826			$\nu(\text{C}=\text{O})$ for anhydride	
	1752				
1744				$\nu(\text{C}=\text{O})$ for acid	
1720		1718	1725		
			1654	amide I band for 2° amide or amide stretch for 3° amide	
		1557	1550	$\delta(\text{N}-\text{H}^+)$ or amide II band for 2° amide	

Table 2. Contact Angles of Water and Characteristic XPS Signals for the Chemisorbed PEI Film and Its Derivatives

substrates	contact angle (deg)		XPS (eV)		
	θ_a	θ_r	N(1s)	F(1s)	C(1s)
SAM-CO ₂ H	<10	<10			289.5 (C=O)
SAM-(CO) ₂ O + PEI	37	<10	400.2		289.8 (C=O)
SAM-(CO) ₂ O + PEI + CF ₃ (CF ₂) ₇ COCl	118	68	400.3	688.6	292.3 (CF ₂₋₃) 289.8 (C=O)
SAM-OCOCF ₃ ^a	96	60		688.5	292.0 (CF ₃) 289.8 (C=O)
SAM-(CO) ₂ O + PEI + CH ₃ (CH ₂) ₁₅ COCl	107	76	400.3		289.0 (C=O)
SAM-(CO) ₂ O + PEI + CH ₃ (CH ₂) ₁₅ (CO) ₂ O	82	53	400.1		289.0 (C=O)
SAM-(CO) ₂ O + PEI + PSMA	78	30	400.3		289.8 (C=O)

^a The SAM of trifluoroacetate was prepared by allowing a SAM of HS(CH₂)₁₁OH to react with trifluoroacetic anhydride in hexane.⁶⁰

carboxylic anhydride after treatment with base suggests that the residual anhydride groups were hydrolyzed by base to generate carboxylic acid groups under the experimental condition. The intensity of the absorption band for the carboxylic acid is weaker in the chemisorbed PEI sample ($\sim 1725 \text{ cm}^{-1}$) than that in the physisorbed PEI substrate ($\sim 1718 \text{ cm}^{-1}$); this result supports the conclusion that part of the carboxylic acids terminated at the SAMs of the chemisorbed PEI substrates was converted into amides that link the PEI films to the SAM.⁵⁸

We have allowed the unpatterned samples of the chemisorbed PEI film that presented pendant, unreacted primary and secondary amines to react with two representative acylating functional groups: acyl chlorides (perfluorooctanoyl chloride and palmitoyl chloride) and carboxylic anhydrides (palmitic anhydride and poly(styrene-*alt*-maleic anhydride)). Figure 5 shows the XPS survey spectra of the original PEI film and its derivatives; Table 2 summarizes the characterization obtained using contact angles of water and XPS. The chemisorbed PEI film was hydrophilic and showed an N(1s) signal at 400.3 eV by XPS; this signal was also present in all the XPS spectra of its derivatives. In addition, the intensities (i.e. photoelectron counts) of the Au peaks were significantly lower than those of the SAM of carboxylic anhydrides. This difference indicates the coverage of the surface with a thin layer of PEI.⁵⁹ Reaction of the PEI film with perfluorooctanoyl chloride generated a surface presenting *N*-perfluorooctyl amides: XPS detected a strong F(1s) signal at 688.6 eV and a C(1s) peak at 292.3 eV; both are characteristic of a perfluoroalkyl group.^{60,61} The advancing contact angle of water on the resulting surface was the same as that of the SAM of CF₃(CF₂)₉SH ($\theta_a^{\text{H}_2\text{O}} = 118^\circ$),⁶²

suggesting that the density of perfluorooctyl chains was close to that of a SAM; the large hysteresis between the advancing and receding contact angles may imply that this perfluorooctyl-derivatized surface is heterogeneous or that the polymer layer swells into microgels on exposure to water. Reaction of the PEI film with palmitoyl chloride and palmitic anhydride both generated a hydrophobic surface. The values of the contact angles of water on the substrates generated using palmitoyl chloride were larger than those prepared using palmitic anhydride and close to that of a SAM of *n*-hexadecanethiolates on gold ($\theta_a^{\text{H}_2\text{O}} = 112^\circ$ and $\theta_r^{\text{H}_2\text{O}} = 110^\circ$);^{43,63} this result suggests that the amine groups of the attached PEI films are more effectively acylated by acyl chlorides than by anhydrides. Reaction of poly(styrene-*alt*-maleic anhydride) (PSMA) and PEI film gave a hydrophobic surface: XPS showed a C(1s) signal at 289.8 eV, which is characteristic of a carbonyl group, and PERS showed adsorption bands at 1861 and 1786 cm^{-1} ; these signatures are characteristic of a carboxylic anhydride.^{54,57} The anhydride groups in the PSMA-derivatized films provide the basis for further postmodification of these films with amines and other nucleophiles. The intensities of the Au peaks were much weaker in this sample than that of other derivatives using small molecules suggests that a thicker bilayer of polymers was formed.

Conclusions

This paper offers a convenient route to patterned thin films of PEI having high coverage and good edge resolution (<500 nm) on gold and silver by printing PEI on a reactive SAM using a hydrophilic PDMS stamp. Our work brings two features: the use of the readily available interchain anhydride groups as the starting point and the application of μCP using an oxidized PDMS stamp to form the initial

(58) The slight shift of the absorption band for carboxylic acid groups in these two samples may be a result of different degrees of hydrogen bonding and salt-bridge interactions in which these carboxylic acid groups participated.

(59) Laibinis, P. E.; Bain, C. D.; Whitesides, G. M. *Phys. Chem.* **1991**, *95*, 7017–7021.

(60) Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074–1087.

(61) Hutt, D. A.; Leggett, G. J. *Langmuir* **1997**, *13*, 2740–2748.

(62) Chidsey, C. E. D.; Loiacono, D. N. *Langmuir* **1990**, *6*, 682–691.

(63) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7152–7167.

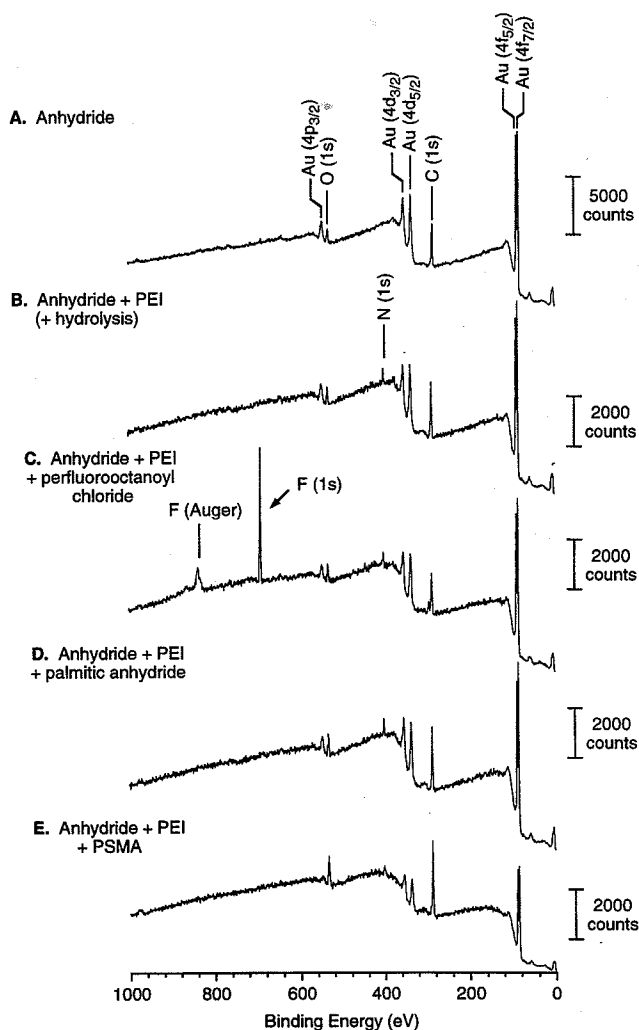


Figure 5. XPS survey spectra of (A) the SAM of interchain carboxylic anhydride groups on gold, (B) the unpatterned sample of the chemisorbed PEI film, (C) the sample of PEI derivatized using perfluorooctanoyl chloride, (D) the sample of PEI derivatized using palmitic anhydride, and (E) the sample of PEI derivatized using PSMA.

pattern. The covalently attached PEI films make a large number of reactive amine groups available for further chemical modification of the surface. These amine groups can react with other functional groups (e.g., acyl chlorides and carboxylic anhydrides) to introduce other organic functionalities into the surface and to attach polymers that have such organic functional groups. Since the wetting of the PEI films derivatized using perfluorooctanoyl chloride and palmitoyl chloride was similar to that of SAMs of $\text{CF}_3(\text{CF}_2)_9\text{SH}$ and of *n*-hexadecanethiolates on gold, respectively, the surface density of available amine groups must be high (for comparison, the density of alkanethiolates in SAMs on gold is $\sim 4.2 \times 10^{14}$ chains/ cm^2 ;⁶⁴ since the polymer films are ~ 3 nm thick, the net interfacial density of amine groups might be $1015\text{--}1016/\text{cm}^2$). The PEI films are covalently attached to the SAM by amide bonds and are stable under both acidic and basic conditions. We have not yet quantified the yield on conversion of carboxylic acid or carboxylic anhydride groups to amide groups during attachment of PEI to the SAMs.

We suggest that this method provides a general procedure of patterning PEI (or other amine-containing

polymers) with submicron-scale edge resolution on a surface that presents carboxylic acid groups. One of the useful characteristics of this method is that it provides a new reactive surface that displays amine groups that can, in turn, be used for further chemical modification. We are currently extending this method to other surfaces and SAMs and exploring the utility of this method for specific applications.

Experimental Section

General Methods. Absolute ethanol (Pharmcoproducts, Inc.), anhydrous *N,N*-dimethylformamide (DMF), 2-propanol, triethylamine, trifluoroacetic anhydride (Aldrich), THF, and CH_2Cl_2 (VWR) were used as received. 16-Mercaptohexadecanoic acid was prepared according to the literature.⁴³ Poly(ethylene imine) (PEI, Mr 750 000, 50 wt % solution in water, Aldrich) was dissolved in 2-propanol, and poly(styrene-*alt*-maleic anhydride) (PSMA, Mr 350 000, Aldrich) was dissolved in THF; both solutions were passed through $0.2\ \mu\text{m}$ filters prior to use.

Preparation of the Reactive SAM Presenting Interchain Carboxylic Anhydride. SAMs were prepared by immersing the freshly e-beam evaporated gold substrates (~ 200 nm of gold onto a test grade, $\langle 100 \rangle$ single-crystal silicon wafer primed with 5 nm of titanium—in a 2 mM ethanolic solution of 16-mercaptohexadecanoic acid at room temperature overnight according to a procedure described previously.⁴³ In a freshly prepared solution of 0.1 M trifluoroacetic anhydride and 0.2 M triethylamine in anhydrous DMF, precleaned substrates having SAMs of the acid were immersed without stirring for 20 min at room temperature, removed from the solution, rinsed thoroughly with CH_2Cl_2 , and dried in a stream of nitrogen. The substrates of the reactive SAMs were used immediately.

Patterning of PEI to the Reactive SAMs. A PDMS stamp having the specific feature was prepared according to the published procedure.⁶⁵ The stamp was oxidized with an oxygen plasma for 10 s at 0.2 Torr O_2 pressure in a Harrick plasma cleaner. After evaporation of the solvent, the PDMS stamp was briefly dried under a stream of nitrogen and placed in contact with the substrate for 1 min. The stamp was carefully peeled off, and the substrate was immersed in a basic buffer ($\text{pH} = 10$, sodium carbonate) for 5 min and sonicated for 30 s using Automatic Cleaner (Branson Instruments Inc.), washed with distilled, deionized water ($\text{pH} = 6.0$), and ethanol, and dried in a stream of nitrogen to give a surface patterned with PEI. The PDMS stamp inked with PEI sticks to the reactive SAM. Peeling off causes some damage to the stamp surface, so the stamp can be used only a few times.

Deposition of PEI to SAMs. The unpatterned samples of the chemisorbed PEI film used in some spectroscopic measurements were prepared by allowing the reactive SAM to react with a 1 wt % solution of PEI in 2-propanol for 30 min, followed by washing with copious amounts of water and ethanol, and dried under a stream of nitrogen. The physisorbed PEI sample was generated by immersing the SAM of 16-hexadecanethiolates in the identical solution of PEI for 30 min, followed by the same workup procedure.

Reactions of the PEI Films. The unpatterned samples of the chemisorbed PEI film prepared using a 1 wt % solution of PEI were allowed to react with 10 mM perfluorooctanoyl chloride (or palmitoyl chloride, or palmitic anhydride and 1 mM 4-(dimethylamino)pyridine) and 20 mM Et_3N in CH_2Cl_2 for 20 min. The substrate was washed with CH_2Cl_2 and ethanol and dried in a stream of nitrogen. The PEI film was allowed to react with a 1 wt % solution of PSMA in THF for 20 min, removed from the solution, washed with copious amounts of THF and CH_2Cl_2 , and dried under a stream of nitrogen.

Characterization. AFM measurements were carried out on a Topometrix TMX 2010 instrument. All images were obtained in contact mode in air. The surface area scanned was $70 \times 70\ \mu\text{m}$ with a $70\ \mu\text{m/s}$ scan rate. Force conversion of the triangular cantilever (Topometrix) was $\sim 0.16\ \text{nN/\AA}$. SEM images were acquired using a Leo 982 Digital Scanning Microscopy instrument at 1.0 kV accelerating voltage. PIRS spectra were obtained in single reflection mode using Digilab Fourier transform infrared spectrometer (BioRad, Cambridge, MA). The p-polarized light

(64) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437–463.

was incident at 80° relative to the surface normal of the substrate, and a mercury-cadmium-telluride (MCT) detector was used to detect the reflected light. A spectrum of a SAM of *n*-hexadecanethiolate-*d*₃₃ on gold was taken as a reference.⁶⁶ Typically, 1024 scans were averaged to yield spectra with excellent signal-to-noise ratios. XPS spectra were collected on an SSX-100 spectrometer (Surface Science Instruments) using monochromatic Al K α X-rays ($\lambda = 8.3 \text{ \AA}$). The spectra were referenced to Au(4f_{7/2}) at 84.00 eV. High-resolution core-level spectra were recorded with a 50-eV pass energy, 300- μm spot size with an acquisition time of 30 min. Ellipsometric measurements were made on a Rudolph Research Type 43603-200E ellipsometer using a He-Ne laser ($\lambda = 632.8 \text{ nm}$) at an incident angle of 70.0° relative to the surface normal of the substrate. We used a refractive index of 1.52 to estimate the thickness of the PEI films, using a program written by Wasserman.⁶⁷ At least three separate spots were

measured on each of three individually prepared substrates, and the readings were averaged. Contact angles of water were determined on a Ramé-Hart Model 100 goniometer at room temperature under ambient laboratory conditions. Data presented here were averages of the measurements of at least three spots on each of three individually prepared samples.

Acknowledgment. This work was supported by DARPA, the ONR, and NSF (Grant ECS-9729405). W.T.S.H. gratefully acknowledges a postdoctoral fellowship from The Netherlands Technology Foundation (STW). SEM images and XPS measurements were obtained by using MRSEC Shared Facilities at Harvard. We thank Y. Lu and S. Shephard for their assistance in using SEM, XPS, and photolithography. We also thank Professor Paul Laibinis (MIT) for generously allowing us to use his FTIR instrument and Dr. Noo-Li Jeon (Harvard) for technical assistance.

LA980818M

(65) Kumar, A.; Whitesides, G. M. *Appl. Phys. Lett.* **1993**, *63*, 2002-2004.

(66) Laibinis, P. E.; Bain, C. D.; Nuzzo, R. G.; Whitesides, G. M. *J. Phys. Chem.* **1995**, *99*, 7663-7676.

(67) Wasserman, S. R.; Whitesides, G. M.; Tidswell, I. M.; Ocko, B. M.; Pershan, P. S.; Axe, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 5852-5861.