Covalent Immobilization of Ultrathin Polymer Films by Thermal Activation of Perfluorophenyl Azide

Mingdi Yan* and Jin Ren

Department of Chemistry, Portland State University, P.O. Box 751,
Portland, Oregon 97207-0751

Received September 26, 2003. Revised Manuscript Received February 2, 2004

The attachment of thin films on solid materials is an effective way to tailor the chemical and physical properties of the surface layer. In this article, we report an alternative approach to the covalent immobilization of ultrathin polymer films. The immobilization chemistry is based on the C−H/N−H insertion reaction of perfluorophenyl nitrenes that were generated by the thermal activation of perfluorophenyl azides (PFPAs). In the process, a silicon wafer was treated with PFPA-silane **1** to give a monolayer of azido groups on the surface. A polymer was then spin coated on the functionalized wafer and the sample was heated. Thermolysis produced perfluorophenyl nitrenes which underwent insertion reactions with the neighboring polymer chains. Removal of the excess polymer by solvent extraction resulted in nanometer-thick polymer thin films covalently attached to the wafer surface. Using polystyrene and poly(2-ethyl-2-oxazoline) as examples, covalently immobilized thin films with thicknesses ranging from a few to over a hundred Å were obtained. The thickness of the film could be controlled by the type and the molecular weight of the polymer. Patterned polymer films were also fabricated using this method.

Introduction

Chemical and physical properties of the surface layer play important roles in determining the function and uses of a material. Because the composition and structure of a material's surface can influence properties such as wettability,[1,2] adhesion,[3] and biocompatibility,[4,5] the ability to tailor the surface characteristics has become exceedingly desirable. Many applications require an ultrathin or monomolecular layer of coating on a bulk material. Recent interests and advances in molecular-scale devices also rely heavily on the ability to immobilize, manipulate, and assemble molecules on a solid substrate.[6−8]

Modification of surfaces with polymer thin films has emerged as an important method to control the physical and chemical properties, and to introduce functional groups to the surface layer. The variety of polymers that are commercially available, the ability to tailor the structural, physical, and chemical properties by design and synthesis, and the larger number of functional groups on polymers in three dimensions as compared to self-assembled monolayers in two dimensions, have given polymers unique advantages over other materials as surface coatings. Both noncovalent and covalent approaches have been developed to generate polymer thin films on solid substrates. Solution casting is a commonly used method to prepare polymer thin films, with spin coating the most popular technique when a flat substrate is used. However, these films are physisorbed and can be easily removed from the substrate by just rinsing with a solvent. Covalently immobilized films are firmly attached to the substrate and are therefore more robust toward environmental and processing conditions. These are especially desirable for applications such as sensors and devices operating under fluidic conditions. Techniques used to covalently attach polymer thin films on solid substrates include graft polymerization,[9−14] electrostatic adsorption,[15−19] self-assembly,[20−25] and photochemistry.[26] Most covalent immobilization methods involve chemical derivatization

---

* Corresponding author. Phone: 503-725-5756. Fax: 503-725-9525. E-mail: yanm@pdx.edu.

(1) Öner, D.; McCarthy, T. J. *Langmuir* **2000**, *16*, 7777−7782.
(2) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 5897−5898.
(3) Baker, L. A.; Zamborini, F. P.; Sun, L.; Crooks, R. M. *Anal. Chem.* **1999**, *71*, 4403−4406.
(4) Inglis, W.; Sanders, G. H. W.; Williams, P. M.; Davies, M. C.; Roberts, C. J.; Tendler, S. J. B. *Langmuir* **2001**, *17*, 7402−7405.
(5) Bruening, M. L.; Zhou, Y.; Aguilar, G.; Agee, R.; Bergbreiter, D. E.; Crooks, R. M. *Langmuir* **1997**, *13*, 770−778.
(6) Keren, K.; Krueger, M.; Gilad, R.; Ben-Yoseph, G.; Sivan, U.; Braun, E. *Science* **2002**, *297*, 72−75.
(7) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791−804.
(8) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2002**, *408*, 541−548.
(9) Crooks, R. M. *ChemPhysChem* **2001**, *2*, 644−654.
(10) Zhao, M.; Liu, Y.; Crooks, R. M.; Bergbreiter, D. E. *J. Am. Chem. Soc.* **1999**, *121*, 923−930.
(11) Zhou, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M.; Well, M. *J. Am. Chem. Soc.* **1996**, *118*, 3773−3774.
(12) Zhang, Y.; Tan, K. L. *Langmuir* **2001**, *17*, 211−218.
(13) Pieracci, J.; Crivello, J. V.; Belfort, G. *Chem. Mater.* **2002**, *14*, 256−265.
(14) Velten, U.; Tossati, S.; Shelden, R. A.; Caseri, W. R.; Suter, U. W.; Hermann, R.; Muller, M. *Langmuir* **1999**, *15*, 6940−6945.
(15) Hammond, P. T. *Curr. Opin. Colloid Interface Sci.* **2002**, *4*, 430−442.
(16) Clark, S. L.; Montague, M. F.; Hammond, P. T. *Macromolecules* **1997**, *30*, 7237−7244.
(17) Hiller, J.; Mendelsohn, J. D.; Rubner, M. F. *Nature Mater.* **2002**, *1*, 59−63.
(18) Yang, S. Y.; Rubner, M. F. *J. Am. Chem. Soc.* **2002**, *124*, 2100−2101.
(19) Caruso, F.; Niikura, K.; Furlong, D. N.; Okahata, Y. *Langmuir* **1997**, *13*, 3427−3433.

10.1021/cm034921v CCC: $27.50

of the substrate and/or the polymer; and sometimes, the synthetic chemistry can be complicated and challenging.

We have employed functionalized perfluorophenyl azides (PFPAs) to immobilize ultrathin polymer films on silicon wafers.[27−29] The approach is based on the photochemistry of PFPAs. Upon UV irradiation, perfluorophenyl nitrenes are generated that undergo C−H and/or N−H insertion reactions with the neighboring polymer chains. An attractive feature of this method is its versatility, as no special functional groups are needed on the polymer. The photochemical method has been popular especially for molecules and materials that are labile at elevated temperatures. In addition, patterned structures can be readily generated using conventional photolithography techniques. However, the photochemical approach is effective only for surfaces that can be accessed with light. Also, it is not always practical, especially for large-scale industrial applications.

We have now explored the PFPA-initiated polymer immobilization chemistry by way of thermal activation. It has long been established that thermolysis is equally effective as photolysis to generate arylnitrenes from aryl azides.[30] These highly reactive nitrene intermediates also underwent C−H/N−H insertion reactions with the adjacent molecules. For example, perfluorophenyl azides were used to functionalize C_{60} by heating a solution of a PFPA and C_{60} in chlorobenzene at 105−130 °C.[31] Bisazides were shown to be effective cross-linkers for the vulcanization of polyisobutylene and the cross-linking of polypropylene in the solid state.[32] Compared to photochemical activation, thermolysis is less frequently used in film immobilization because of the high temperature needed (>100 °C) to initiate the thermal decomposition of azides, which, for example, can denature biomolecules. However, the development of a thermal activation method will provide an additional tool for the fabrication of covalently immobilized polymer thin films. It should also extend the range of substrates and devices that could be modified with this surface chemistry. In this article, we present studies on the thermal immobilization chemistry of a hydrophobic polymer, polystyrene, and a hydrophilic polymer, poly(2-ethyl-2-oxazoline). These results are compared with those obtained by photochemical activation. Patterned polymer films were also generated by a combination of photochemical and thermal activation.

Experimental Section

Materials. 3-Aminopropyltrimethoxysilane (United Chemical Technologies) was fractionally distilled and stored under argon. Poly(2-ethyl-2-oxazoline) (average M_w 50 000, 200 000, and 500 000), polystyrene of average M_w 280 000, and silica gel (200 mesh) were purchased from Aldrich and were used as received. Monodisperse polystyrene standards of molecular weights 115 700, 223 200, 393 400, 1 015 000, and 1 815 000 were obtained from Scientific Polymer Products Inc. (Ontario, NY). Water used in the contact angle measurements was obtained from a Millipore Milli-Q system with at least 18.2 MΩ resistivity. Methylene chloride was distilled from P_2O_5. Toluene, chloroform, and methanol were used as received from Fisher. All deuterated solvents were used as received from Cambridge Isotope Labs (Andover, MA). Silicon wafers with a native oxide layer of ~30 Å thick were cut with a diamond pen and cleaned in piranha solution (7:3 v/v concentrated H_2SO_4/35 wt % H_2O_2) for 2 h at 80−90 °C, washed thoroughly with boiling water for 1 h, and dried under a stream of nitrogen. UV glass filters were purchased from Schott Glass Technologies Inc. (Fullerton, CA). The quartz mask used in photolithography was obtained from Electro Scientific Industries, Inc. (Portland, OR). The light-penetrable regions of the photomask were comprised of 5.5-μm circles.

Instrumentation. Spin coating was performed using a P6204 spin-coater (Specialty Coating Systems, Indianapolis, IN). Irradiation of the polymer films was executed at ambient temperatures with a medium-pressure Hg lamp (450 W, Hanovia). The lamp reached its full power after ~2 min warmup to an intensity of 2.5 mW/cm^2 as measured by a power meter. Contact angles were determined with 2 μL of distilled water and measured at ~1 min after initial contact using a homemade apparatus using an Intel QX3 200× microscope. A digital camera was used to record images, and contact angles were determined graphically. Film thickness measurements were made on a Gaertner model L116A analog ellipsometer with He/Ne laser (2 mW, Melles Griot) at an incident angle of 70° in the manual mode. The following refractive indices: SiO_2 1.465, PFPA-Silane **1** 1.503, PS 1.592, and PEOX 1.520 were used to determine the thicknesses of various film layers. The refractive index of PFPA-silane **1** was determined using a Bausch & Lomb Abbè 3L refractometer. ^1H NMR spectra were acquired on a Nicolet NT-500 MHz FT-NMR spectrometer equipped with a 5-mm ^1H probe. Chemical shifts were reported in delta units referenced to internal $Si(CH_3)_4$ at 0.00 ppm. ^{19}F NMR spectra were recorded on a 90 MHz spectrometer with the chemical shifts reported in delta units internally referenced to Freon 11 (CCl_3F) as δ 0. Infrared spectra were obtained using a Perkin-Elmer Series 2000 FT-IR spectrometer. UV−vis analysis was conducted with a Beckman DU 530 Life Science UV−visible spectrophotometer. Optical images of polymer thin films and photomasks were obtained on an Olympus BHM optical microscope equipped with a digital camera. Atomic force microscopy images were collected on a Nanoscope IIIA (Veeco, Santa Barbara, CA) using a 125-μm cantilever equipped with a silicon nitride tip in the tapping mode at an oscillating frequency of 300 kHz. SEM images were obtained on an ISI SS40 scanning electron microscope equipped with the Oxford ISIS EDX system.

Synthesis of *N*-(3-Trimethoxysilylpropyl)-4-azido-2,3,5,6-tetrafluorobenzamide (1). A solution of *N*-succinimidyl 4-azidotetrafluorobenzoate[33] (102.8 mg, 3.1 mmol), 3-aminopropyltimethoxysilane (65 μL, 3.7 mmol), and CH_2Cl_2 (4 mL) was capped in argon and stirred for 5 h at 23 °C. The mixture was evaporated and approximately 0.3 g of silica gel was added to the dried residue. This sample was purified by column chromatography on silica gel using 1:3 v/v $CHCl_3$/hexane containing 2% methanol as an eluent. Evaporation of

---

(20) Xia, N.; Hu, Y.; Grainger, D. W.; Castner, D. G. *Langmuir* **2002**, *18*, 3255−3262.

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

(22) Sun, F.; Castner, D. G.; Mao, G.; Wang, W.; McKeown, P.; Grainger, D. W. *J. Am. Chem. Soc.* **1996**, *118*, 1856−1866.

(23) Park, J.-W.; Thomas, E. L. *J. Am. Chem. Soc.* **2002**, *124*, 514−515.

(24) Stafford, C. M.; Fadeev, A. Y.; Russell, T. P.; McCarthy, T. J. *Langmuir* **2001**, *17*, 6547−6552.

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

(26) Yan, M. *Polym. News* **2002**, *27*, 6−12.

(27) Bartlett, M.; Yan, M. *Adv. Mater.* **2001**, *13*, 1449−1451.

(28) Yan, M.; Bartlett, M. *Nano Lett.* **2002**, *2*, 275−278.

(29) Yan, M.; Bartlett, M.; Harnish, B. *8th IEEE Inter. Symp. Adv. Packaging Mater.* **2002**, 311−316.

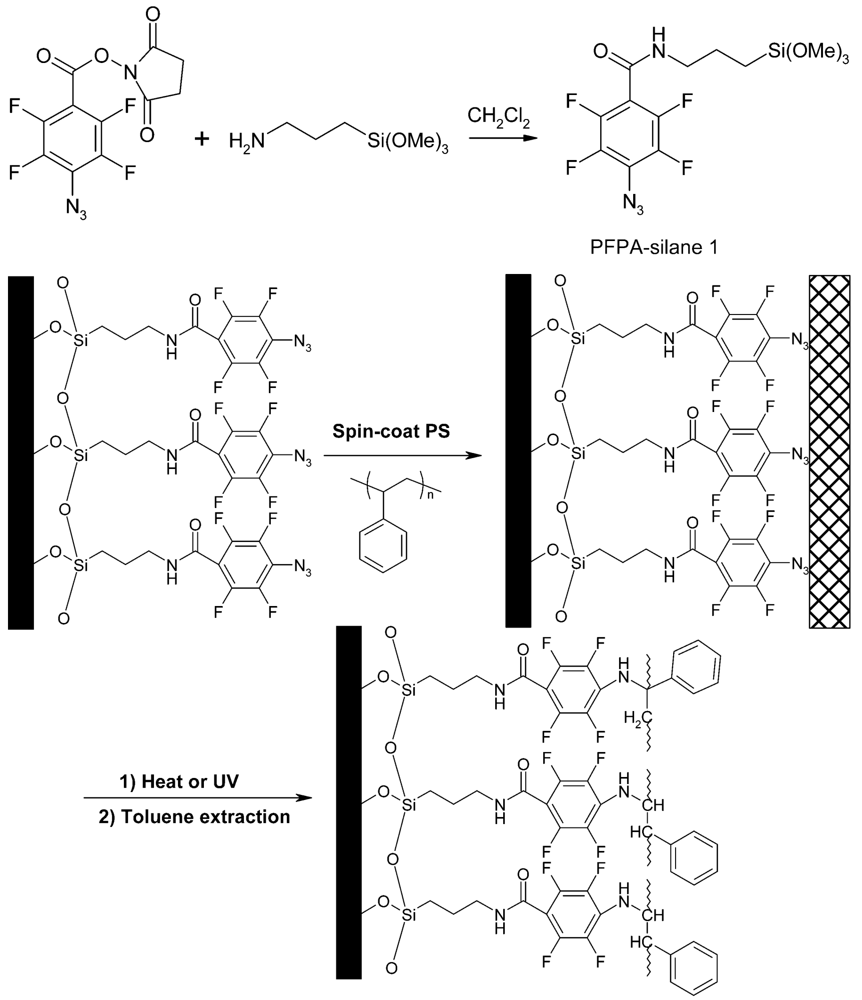
(30) Smith, P. A. S. Aryl and Heteroaryl Azides and Nitrenes. In *Azides and Nitrenes Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic Press: New York, 1984; pp 95−204.

(31) Yan, M.; Cai, S. X.; Keana, J. F. W. *J. Org. Chem.* **1994**, *59*, 5951−5954.

(32) Breslow, D. S. Industrial Applications. In *Azides and Nitrenes Reactivity and Utility;* Scriven, E. F. V., Ed.; Academic Press: New York, 1984; pp 491−521.

(33) Keana, J. F. W.; Cai, S. X. *J. Org. Chem.* **1990**, *55*, 3640−3647.

Scheme 1



the solvent afforded *N*-(3-trimethoxysilylpropyl)-4-azido-2,3,5,6-tetrafluorobenzamide (**1**) as a clear viscous liquid (99.5 mg, 88%). Refractive index: n_D^{23} 1.503. FTIR (neat, NaCl plate): 3287, 3088, 2946, 2844, 2126, 1661, 1566, 1489, 1271, 1087, 998, 823, 779 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.56 (s, 9H), 3.47 (q, J = 12 Hz, 2H), 1.76 (m, J = 15 Hz, 2H), 1.61 (s, 1H), 0.72 (t, J = 16 Hz, 2H). ^{19}F NMR (CDCl$_3$): δ −144.0 (br, 2F), −153.8 (br, 2F). UV−vis (in methanol): continuous broad peaks with maxima at 256 and 205 nm, respectively. Anal. Calcd for $C_{13}H_{16}N_4F_4O_4Si$: C, 39.39; H, 4.07; N, 14.13. Found: C, 39.34; H, 4.16; N, 13.81.

Thermal Immobilization of Polymer Thin Films on Silicon Wafers. Cleaned wafers were soaked in a solution of **1** in toluene (10 mg/mL) for 24 h, rinsed in a gentle stream of ethanol, and dried under nitrogen. These wafers were then allowed to cure at room temperature for at least 24 h. The cured wafers were spin-coated at 2000 rpm for 60 s with a solution of PS in toluene or PEOX in chloroform. The film was heated at the designated temperature for various lengths of time. The unbound polymer was removed by sonication in an appropriate solvent (toluene for PS or methanol for PEOX) for 5 min. The resulting film was dried under a stream of nitrogen.

Samples that required additional UV irradiation after heating were prepared as follows. A solution of PS or PEOX was spin coated on PFPA-silane **1**-treated wafers. The films were then heated at the designated temperature for a specified amount of time and irradiated immediately for 5 min with the medium-pressure Hg lamp. A 280-nm optical filter was placed on the film surface during irradiation. Unbound films were removed by sonication in the appropriate solvent and the resulting samples were dried with N$_2$.

Fabrication of Patterned Polymer Thin Films. A PFPA-silane **1**-functionalized wafer was placed in a homemade photolithography apparatus, and the photomask was held in close contact with the sample by applying a vacuum. A 280-nm glass filter was placed on top of the photomask and the entire assembly was irradiated with the medium-pressure Hg lamp for 30 min. The wafer was then spin coated with a 10 mg/mL solution of PS in toluene at 2000 rpm for 60 s, and was heated at 150 °C for 10 min. The film was sonicated in toluene for 10 min, rinsed with fresh toluene, and dried under nitrogen. The patterns were imaged with AFM and SEM.

Results and Discussion

We have designed and synthesized a silane-functionalized PFPA, *N*-(3-trimethoxysilylpropyl)-4-azido-2,3,5,6-tetrafluorobenzamide (**1**), for the photochemical immobilization of polymer films on silicon wafers.[27,28] The same compound is now used to study polymer thin film immobilization by thermal activation.

The film immobilization process started with the functionalization of silicon wafers with PFPA-silane **1** to introduce a monolayer of azido groups on the wafer surface. A polymer solution was then spin coated on the treated wafer and the sample was heated in an oven preheated to the designated temperature. Thermolysis activated the azido group and generated the highly reactive perfluorophenyl nitrene intermediate which underwent C−H insertion reaction to the adjacent polymer chains (Scheme 1). Removal of the unattached polymer by solvent extraction resulted in a thin film that was covalently immobilized on the wafer surface.

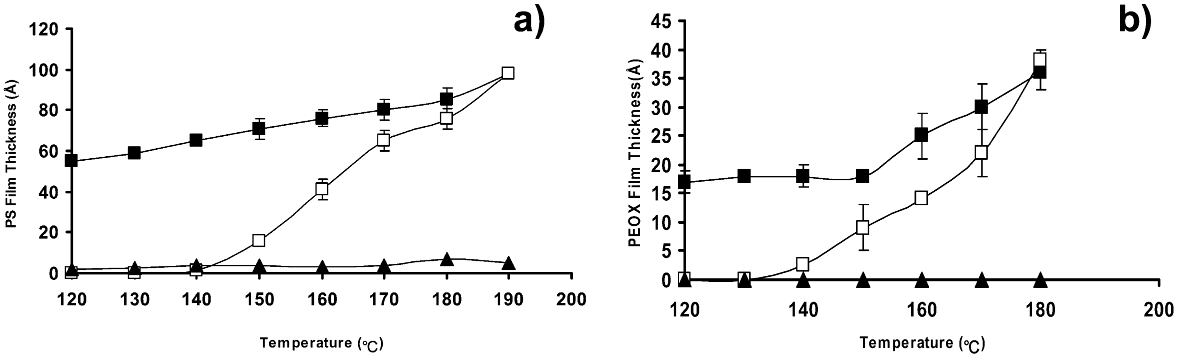


Figure 1. Immobilized film thickness vs heating temperature for (a) PS and (b) PEOX films: (□) samples were heated at the designated temperature for 5 min in air followed by sonication in an appropriate solvent for 5 min; (▲) control samples prepared under the same conditions in the absence of PFPA-silane **1**; (■) samples prepared by heating the films at the designated temperature for 5 min in air, irradiating immediately with the medium-pressure Hg lamp for 5 min, and extracting with an appropriate solvent.

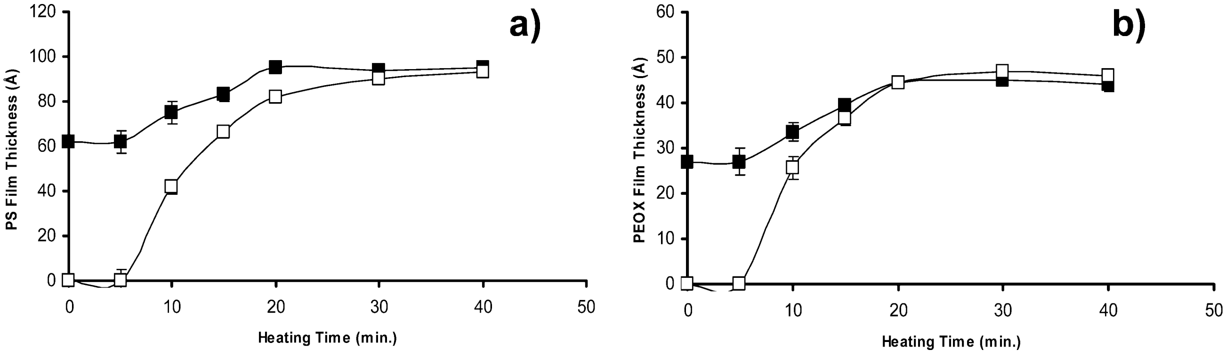


Figure 2. Effect of heating time on the thickness of immobilized films for (a) PS and (b) PEOX: (□) at 140 °C; (■) samples prepared by heating the films at 140 °C for the specified amount of time in air, irradiating immediately with the medium-pressure Hg lamp for 5 min, and extracting with an appropriate solvent.

Comprehensive studies were conducted using a hydrophobic polymer, polystyrene (PS, M_w 280 000), and a hydrophilic polymer, poly(2-ethyl-2-oxazoline) (PEOX, M_w 200 000). A solution of PS in toluene or PEOX in chloroform was spin coated on a PFPA-silane **1**-treated silicon wafer. The thickness of the polymer film was measured to be about 560 Å for PS and 850 Å for PEOX, assuming the refractive indices are 1.592 and 1.520, respectively. The films were heated for 5 min in an oven that had been preheated to temperatures ranging from 120 to 190 °C. Figure 1 shows the thicknesses of the immobilized films after the unattached polymer was removed by solvent extraction. Under these experimental conditions, film immobilization began at 150 °C for PS (Figure 1a) and 140 °C for PEOX (Figure 1b). At below the activation temperature, the azido groups remained unreacted. We confirmed this by irradiating the thermally treated samples with a medium-pressure Hg lamp for 5 min. An increase in film thickness was observed after UV irradiation (solid squares in Figure 1), which demonstrated that the un-reacted azido groups were activated with UV.

Both PS and PEOX have excellent thermal stabilities as evidenced by the fact that their glass transition temperatures remained constant after heat treatment at over 300 °C.[34] To investigate the possible oxidation of these ultrathin polymer films at elevated temperatures, contact angle measurements were performed. If oxidation had occurred, the film surface would become more hydrophilic due to the polar functional groups introduced by oxidation, leading to a lower water contact angle. However, the water contact angles of the heat-treated (91°) and the immobilized PS film after solvent extraction (94°) were comparable to that of the spin-coated PS film (92°), suggesting the absence of oxidation reactions. The immobilization chemistry was also performed in the absence of O_2 by heating PS and PEOX films in argon atmosphere. No detectable change in the immobilized film thickness was observed.

To ensure that the film immobilization was indeed due to the thermally induced reaction of the surface azido groups to the polymer, control experiments were carried out in the absence of PFPA-silane **1**. PS and PEOX films were spin coated directly on piranha-cleaned silicon wafers. After heating the samples at designated temperatures under the same conditions, no film was detected on the wafer surface after solvent extraction (solid triangles in Figure 1). These results confirmed that film immobilization was indeed initiated by the azido groups on the wafer surface.

Time-dependent studies of the thermal decomposition of surface azido groups were carried out by heating the spin-coated polymer films at 140 °C for various lengths of time. Film immobilization was observed at >5 min of thermolysis (Figure 2). The thickness of the immobilized polymer film increased with increased heating time, and reached a constant value after heating for about 30 min for PS and 20 min for PEOX. This result is consistent with the proposed mechanism that the C−H insertion reactions occur only at the interface where the polymer chains are in contact with the azido

---

[34] Keskkula, H.; Paul, D. R. *J. Appl. Polym. Sci.* **1986**, *31*, 941−950.

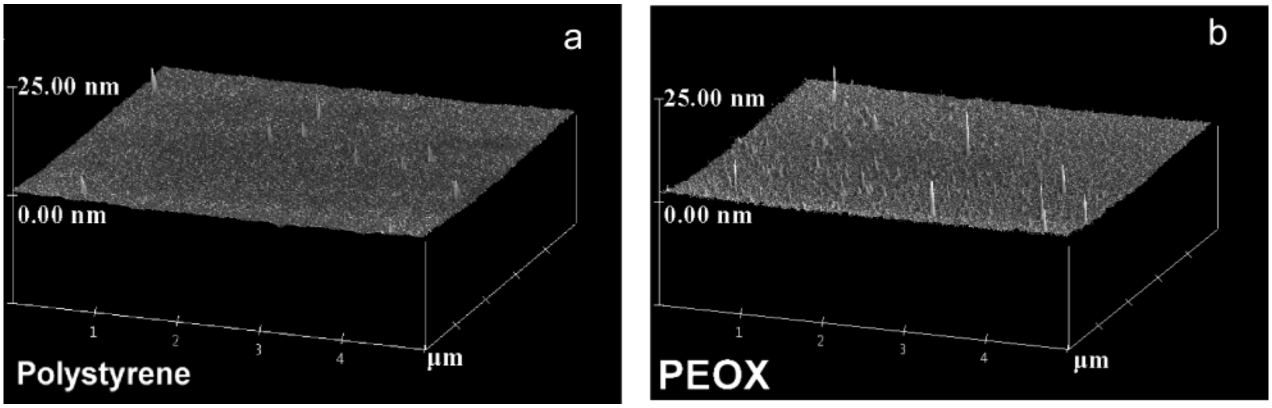


Figure 3. AFM images of the immobilized (a) PS (RMS = 0.489 nm), and (b) PEOX films (RMS = 0.652 nm).

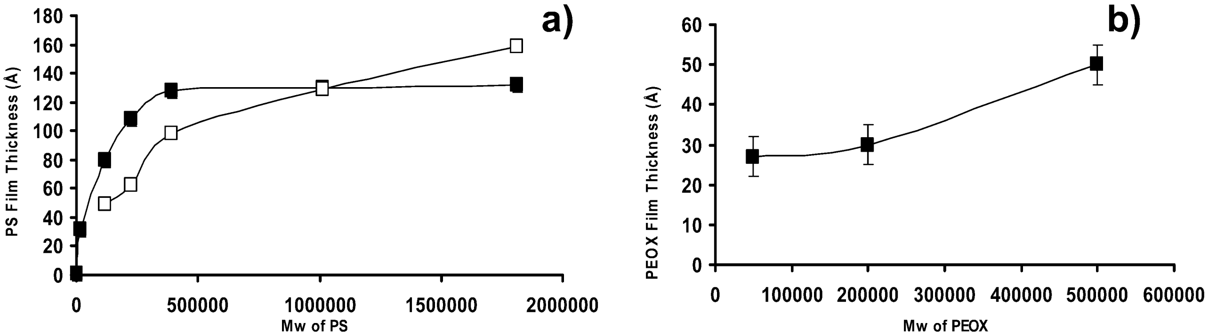


Figure 4. Immobilized film thickness as a function of molecular weight for (a) PS, and (b) PEOX: (■) samples prepared by heating at 165 °C for 10 min; (□) films immobilized by UV irradiation for 5 min at room temperature.

groups, and therefore a monolayer of polymer is attached to the surface after thermolysis (Scheme 1). The surface of the thermally immobilized thin films was examined by AFM. Smooth surfaces were observed for both PS and PEOX films (Figure 3a and b). Again, the un-reacted azido groups could be activated by UV irradiation (solid squares in Figure 2). These samples reached the same maximal film thicknesses as those prepared by heat-treatment alone. These results further support the immobilization mechanism outlined in Scheme 1.

In our previous work where UV was employed to initiate the decomposition of surface azido groups, the immobilized film thicknesses were 63 Å for PS and 32 Å for PEOX.[27] However, under thermal activation conditions, the immobilized film thicknesses were ~90 Å for PS and ~45 Å for PEOX. It was reported that solid-state conditions enhance the yield of C−H/N−H insertion products by preventing diffusion of nitrenes and limiting the reactions to neighboring molecules.[35] On the other hand, for insertion reactions to occur in the solid state, the azido groups need to be in close proximity with the adjacent molecules. Heat treatment increases the chain mobility and therefore enhances the contact between the polymer chains and the azido groups on the wafer surface. The increased film thickness under thermal activation conditions is likely due to the increased chain motion when the polymer was heated above its glass transition temperatures (T_g, 100 and 56 °C for bulk PS and PEOX, respectively, although derivation in T_g was observed for ultrathin films[36,37]). Upon heating, polymer changes from a rigid, stiff, glassy state where the chains have been effectively frozen, to the amorphous state at above its glass transition temperature where the polymer is free to rotate and translate, and long-range segmental chain motions are possible.

The effect of molecular weight on the thickness of the immobilized films was also studied. PS and PEOX of various molecular weights were spin coated on PFPA-silane **1**-functionalized wafers, heated at ~165 °C for 10 min, and sonicated in the corresponding extraction solvent for 5 min. At molecular weights below 500 000, the immobilized film thickness increased with the molecular weight of the polymer (Figure 4). The thickness of the immobilized film is related to the radius of gyration of the polymer coil (R_g) which increases with the molecular weight of the polymer.[27,28] Therefore, the higher the molecular weight of the polymer, the larger the R_g and the thicker the immobilized polymer film. However, unlike the photochemically initiated immobilization where the film thickness continued to increase with molecular weight (open squares in Figure 4a), in the case of thermal activation, the film thickness started to plateau when the molecular weight of polystyrene was greater than 500 000 (solid squares in Figure 4a). We attribute this to the thermal expansion of polymer when the polymer is heated above its glass transition temperature (T_g). As the polymer is heated, its specific volume increases. The rate of this increase accelerates at the onset of T_g. A higher specific volume corresponds to a lower polymer density. A reduction in

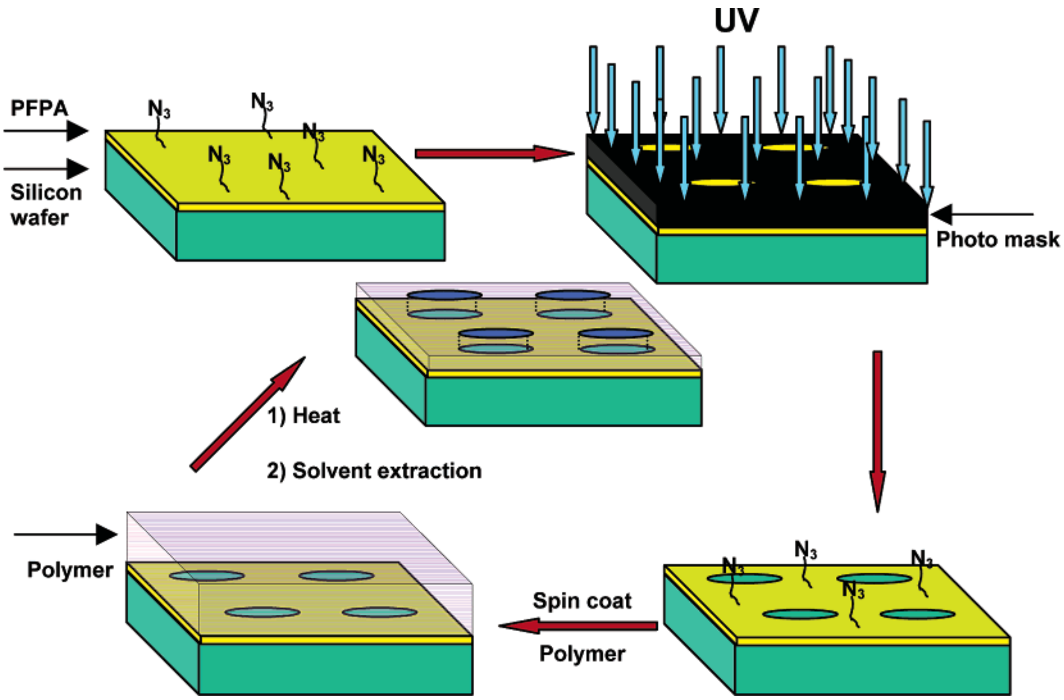
---

[35] Torres, M. J.; Zayas, J.; Platz, M. S. *Tetrahedron Lett.* **1986**, *27*, 791−794.

[36] Kim, J. H.; Jang, J.; Zin, W.-C. *Langmuir* **2001**, *17*, 2703−2710.

[37] Fryer, D. S.; Nealey, P. F.; de Pablo, J. J. *Macromolecules* **2000**, *33*, 6439−6447.

Scheme 2



the amount of polymer on the functionalized surface would lead to a decrease in immobilized film thickness, which compensates for the increase in film thickness as a result of increased molecular weight. To further test that the reduction in film thickness was indeed due to the thermal expansion of the polymer, polystyrene of various molecular weights was spin coated on PFPA-silane **1**-treated silicon wafer, heated at 140 °C for 5 min, and irradiated with UV for 5 min. Results obtained were similar to those in Figure 4a where the immobilized film thickness again leveled off at molecular weight of above 500 000. Note that the thermal treatment at 140 °C for 5 min would not induce film immobilization (open squares in Figure 2a).

This immobilization chemistry was employed to generate patterned polymer thin films. The fabrication process is illustrated in Scheme 2. A silicon wafer that has been functionalized with PFPA-silane **1** was placed in direct contact with a quartz photomask. The sample was then exposed to UV irradiation using a homemade photolithography apparatus. The photomask had an array of 5.5-μm circles that are transparent to UV, and therefore the azido groups in these regions would be decomposed after irradiation. After UV exposure, a solution of polystyrene in chloroform was spin coated on the wafer surface and the sample was heated at 150 °C for 10 min. Thermolysis initiated polymer film immobilization in the regions where the azido groups were unexposed to UV light. After the unattached polymer was removed by sonication in chloroform, patterns were observed under SEM (Figure 5 inset). An AFM cross-section image revealed that polymer films were indeed immobilized in the un-irradiated regions (Figure 5). The height of the microwells correlated well with the thickness of films immobilized under the same condition.

Conclusions

In summary, we have developed a method that allows for the covalent immobilization of ultrathin polymer films on silicon wafers by thermal activation of a silane-functionalized perfluorophenyl azide. The thickness of the film can be tailored by using polymers of different molecular structures, or by varying the molecular weight of the polymer. Thicker films were obtained as compared to those by photochemically initiated immobilization. We attribute the increase in film thickness to the closer proximity of the polymer chains to the azido groups that resulted from the increased polymer chain motions when the polymer is heated above its glass transition temperature.

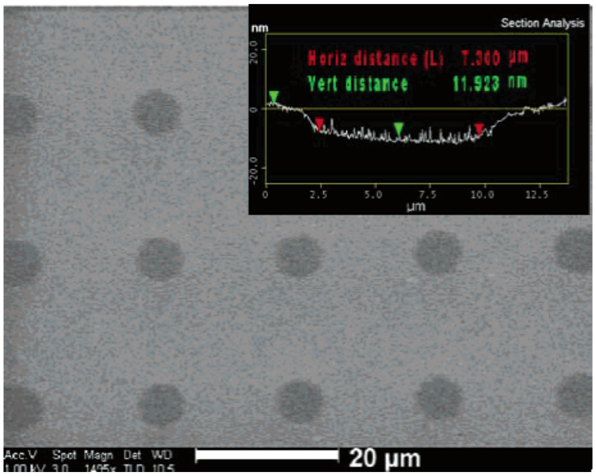


Figure 5. SEM and AFM cross-section image of a patterned PS film. See text for sample preparation procedure.

Acknowledgment. We are grateful to donors of the Petroleum Research Fund, administered by the American Chemical Society, and a Faculty Enhancement Grant from Portland State University for support of this research. Silicon wafers were generously donated by Wacker Siltronics Corp.

CM034921V