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Synthesis of Polymer Thin Film Gradient with Nanometer Thickness through Water Diffusion Controlled Surface Polymerization

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ABSTRACT: We report here a unique, simple method for synthesizing polymer film gradients with nanometer thickness through diffusion controlled surface polymerization. Polar solvents, especially water, have previously been shown to increase the rate of atom transfer radical polymerization (ATRP) of numerous monomers. That result made it apparent that the rate of ATRP polymerization could be regulated by the concentration of water in the polymerization solution. On the basis of this observation, we successfully developed a simple method for preparing polymer thin film gradients on substrates by water concentration gradient formed along the surface of substrates. An initiator attached substrate was placed in a two-layer system of water and a polymerization solution in which the diffusion of water into the polymerization solution resulted in a monomer concentration gradient, leading to varied polymerization rates along the substrate, and finally polymer thin film gradients. Poly(ethylene glycol) methacrylate (PEGMA) gradient thin films formed on silica surfaces have thickness ranging from a few of hundreds of angstroms to more than 1000 Å.

Introduction

Polymeric thin films are of increasing importance for their applications in electronic, optical, medical, and chemical devices, and for chemical and biological separations as both passive and active components.[1] In the past decade, a variety of synthetic methods have been developed to grow organic and polymeric thin films.[2−7] Recently, polymer thin film gradients have received much attention.[8,9] Gradient surfaces are substrates having a directional continuous variation in variety of physicochemical properties. A key advantage of the gradient surfaces is that a single sample can be used to investigate the effects of variation on multiple surface parameters; this advantage should significantly improve the efficiency of research and development.[10]

Some recent exciting developments for surfaces with continuous molecular gradients are taking place at the interdisciplinary areas between chemistry and biology, with examples that include substrates for biological separations[11−13] and for investigation of protein adsorption and cell adhesion.[14−18] Surfaces having gradient thickness of PEG-based building blocks have received particular attention.[19−23] Because PEG has superior resistant toward nonspecific protein adsorption,[24] it is a commonly used surface patterning material for designing biosensor matrices.[25−27] PEG gradient surfaces have also been used to monitor protein adsorption and cell adhesion.[19,28−30]

Various methods have been developed for generating polymer gradients on surfaces. Among other methods, surface-initiated polymerization is one commonly used approach to generate polymer brush gradients. Various surface polymerization methods have been developed for this purpose, including living radical polymerization on a molecular gradient of an initiator,[10,31,32] physical immersion of a substrate,[33] polymerization solution draining method,[34,35] dynamic potential gradient by electrochemistry,[36,37] and temperature gradient through controlled heating.[10,38]

One of our major interests is to develop better materials for separation of biomacromolecules such as proteins. Our assumption is that a gradient surface should interact with biomacromolecules in a continuously changing manner so that superior separation of biomacromolecules can be achieved. In pursuit of this goal, the present study seeks to develop a new and effective method for preparing a PEG-based polymer thin film gradient. Herein, we wish report a simple, efficient method by creating a monomer concentration gradient on the surface of a substrate during surface-initiated atom transfer radical polymerization (ATRP). In this study, a water-soluble monomer, poly(ethylene glycol) methacrylate (PEGMA), which can introduce PEG chains to the thin film gradient, is employed to demonstrate our strategy. Aqueous ATRP of numerous monomers has been reported and shown to be living and fast.[39] The high dielectric constant of polar solvents, especially water, has been shown to significantly accelerate the polymerization rates of ATRP.[40,41] On the basis of this observation, our idea is to create a water and monomer concentration gradient along a substrate, which leads to a polymerization rate gradient and finally forms a polymer film gradient. Experimentally, we used a two-layer system of water and a polymerization solution where diffusion of reaction molecules created the monomer concentration gradient (Scheme 1). In this paper, the process, synthesis, and characterization of the polymer thin film gradient will be described.

Experimental Section

Materials. CuCl (99.5%), $CuCl_2$, 5-hexen-1-ol, H_2PtCl_6, $HSiCl_3$, 2-bromo-2-methylpropionyl bromide, poly(ethylene glycol) methacrylate (PEGMA, average MW 360), 2, 2′-bipyridine were obtained from Aldrich. CuCl was purified according to the published procedure.[42] Toluene was dried over 4 Å molecular sieves before use. Water used in this work was purified

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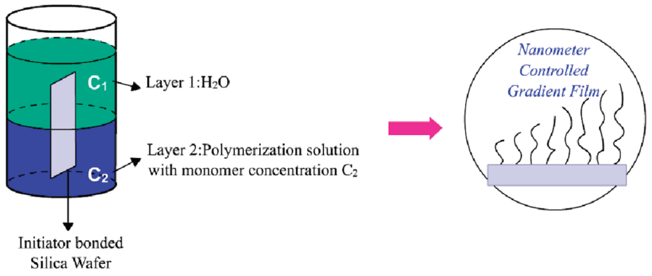
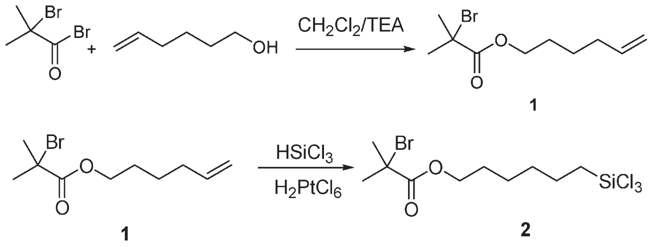
Scheme 1. Using a Two-layer System To Generate a Thin PEGMA Polymer Film Gradient



Scheme 2. Synthesis of Pent-4′-enyl 2-Bromo-2-methylpropionate, 1, and 5-Trichlorosilylpentyl 2-Bromo-2-methylpropionate, 2



to a specific resistance of ca. 18 MΩ·cm using a Milli-Q system. All other reagents were used as received from commercial sources.

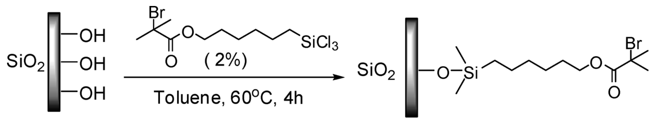
Measurement. The thickness of PEGMA film was measured by a null-ellipsometer (Rudolph Auto EL-II, Fairfield, NJ). The X-ray photoelectron spectroscopy (XPS) analysis was carried out on a ESCALAB 250 XPS, using Al Kα as the radiation, to determine the surface composition. AFM images were collected using a Multimode V atomic force microscope (Veeco Inc.). ^{1}HNMR (500 MHz) spectra were obtained on a Bruker DRX 500 spectrometer.

Synthesis of Pent-4′-enyl 2-Bromo-2-methylpropionate, 1. As shown in Scheme 2, 2-bromo-2-methylpropionyl bromide (27.3 g, 0.12 mol) was added dropwise to a cold solution of 5-hexen-1-ol (10.9 g, 0.11 mol) and triethylamine (13.2 g, 0.13 mol) in dry CH_2Cl_2 at 0 °C. After being stirred under nitrogen atmosphere for 2 h, the solution was warmed to room temperature in 2 h and grew dark in color. The reaction was left overnight. The precipitated triethylamine hydrochloride was removed by filtration, and the solution was washed with saturated aqueous ammonium chloride and water. The organic phase was then dried overnight using $MgSO_4$. After filtration, CH_2Cl_2 was then removed, and the crude product was purified by flash chromatography on a column of silica gel with a mixture of petrol/ethyl acetate = 75/1 as an eluent to yield pent-4′-enyl 2-bromo-2-methyl propionate, 1 as a colorless oil (24.6 g, 90%). ^{1}H NMR ($CDCl_3$, δ in ppm): 1.46 (m, 2H), 1.68 (m, 2H), 1.94 (s, 6H), 2.08 (m, 2H), 4.16 (t, 2H), 4.96−5.06 (m, 2H), 5.75−5.85 (m, 1H).

Synthesis of 5-Trichlorosilylpentyl 2-Bromo-2-methylpropionate, 2. In a 100 mL two-neck round-bottom flask with a magnetic stir bar and rubber septum purged with nitrogen for 15 min were mixed pent-4′-enyl 2-bromo-2-methyl propionate (21.6 g, 87 mmol) and 14.2 mg H_2PtCl_6 in 0.5 g of 2-propanol. The flask was cooled in an ice/water bath for 15 min. Then, trichlorosilane (18.3 g, 135 mmol) was added dropwise in 2 h. The reaction mixture was stirred under nitrogen overnight at room temperature. Unreacted trichlorosilane was completely removed under vacuum to yield the initiator as liquid. (quantitative yield) ^{1}H NMR ($CDCl_3$, δ in ppm): 1.35−1.73, (m, 10H), 1.93 (s, 6H), 4.17−4.20 (t, 2H).

Silicon Surface Cleanup. The silicon wafers were ultrasonically cleaned for 5 min with acetone. After being washed with DI water, the wafers were treated with piranha solution (70% H_2SO_4 + 30% H_2O_2 (30% concentrate)) for 30 min at 70 °C. The wafers were then rinsed thoroughly with a large amount of Nanopure water (18.2 MΩ-cm), and dried in oven at 120 °C for 1 h.

Scheme 3. Self-Assembling an Initiator Monolayer of 5-Trichlorosilylpentyl 2-Bromo-2-methylpropionate



Surface Functionalization with Initiator Monolayer. As shown in Scheme 3, 5-trichlorosilylpentyl 2-bromo-2-methylpropionate as the initiator (1.0 mL) was added to 50 mL of dry toluene (anhydrous, 99.8% from Sigma), and stirred for 5 min. The solution was then transferred to a shallow beaker loaded with cleaned silicon wafers. The beaker was covered with aluminum foil and heated for 4 h in an oil bath at 60 °C. The reacted wafers were removed from the solution and cleaned by an ultrasonic bath in toluene for 1 min and rinsed again with toluene, methanol and acetone. The wafers were then baked in an oven at 110 °C for 1 h. After baking, the film thickness of the assembled initiator monolayer was measured with an ellipsometer and determined to be 10.3 Å.

Synthesis of PEGMA Films on Silicon Wafer. As shown in Scheme 4, in a typical reaction, a PEGMA monomer mixture having a 1.5 M concentration was prepared by adding 6.0 g of PEGMA (MW = 360, 16.7 mmol) and 5.0 g of water to a 50 mL round-bottom flask. Then, 0.075 g of bipyridyl (0.48 mmol), 0.0054 g of $CuCl_2$ (0.04 mmol) and 0.02 g of CuCl (0.2 mmol) were added to the flask under a nitrogen atmosphere. The flask was sealed with a rubber septum and the mixture was stirred for 10 min. Then 5 mL of the mixture was transferred by syringe to a flask charged with a wafer having an initiator monolayer assembled on the surface. The reaction was allowed to continue for periods of time ranging from 30 min to 8 h. The wafer then was rinsed with nanopure water and air-dried.

Synthesis of PEGMA Film Gradient on Silicon Wafer. In a typical reaction, an aqueous PEGMA monomer solution was prepared by adding 18 g of PEGMA (MW = 360, 50 mmol), 15 g of water, 0.224 g of bipyridyl (1.4 mmol), 0.06 g of CuCl (0.6 mmol), and 0.0164 g of $CuCl_2$ (0.12 mmol) to a 50 mL round-bottom flask under a nitrogen atmosphere. The mixture was stirred for 15 min to form a homogeneous solution. A 24 mm × 30 mm (width × length) silicon wafer piece having an initiator monolayer assembled thereon was placed in a 140 mL beaker in upright end-on-end longitudinal position. The beaker was then placed in an oven filled with N_2. The well-mixed PEGMA monomer solution prepared was carefully added to the beaker so as to form a first layer that covered 2/3 of the silicon wafer. A pipet was then used to gently add 30 mL water to the beaker so as to form a second layer. The beaker was covered with aluminum foil. The oven was then pumped to form a vacuum and slowly filled nitrogen to keep a positive pressure for the polymerization reaction. After reacting at room temperature for 6 h, the wafer were rinsed with nanopure water and dried with air-flow. The thickness of the PEGM film was measured by an ellipsometer.

Measurement of the Thickness of the PEGMA Films. Thickness of the PEGMA films was measured by an ellipsometer at various points across the wafer. The wavelength of the laser beam employed for the measurement was 632.8 nm, and the angle of incidence is 70°. The refractive index of the initiation monolayer and the PEGM film is estimated to be 1.54. The refractive index was calculated using the group contribution method.[43] The thickness is reported as an average of 10 measurements on a given sample of film. The oxide layer (SiO_2) on the bare silicon wafer was determined to be 18.2 Å thick.

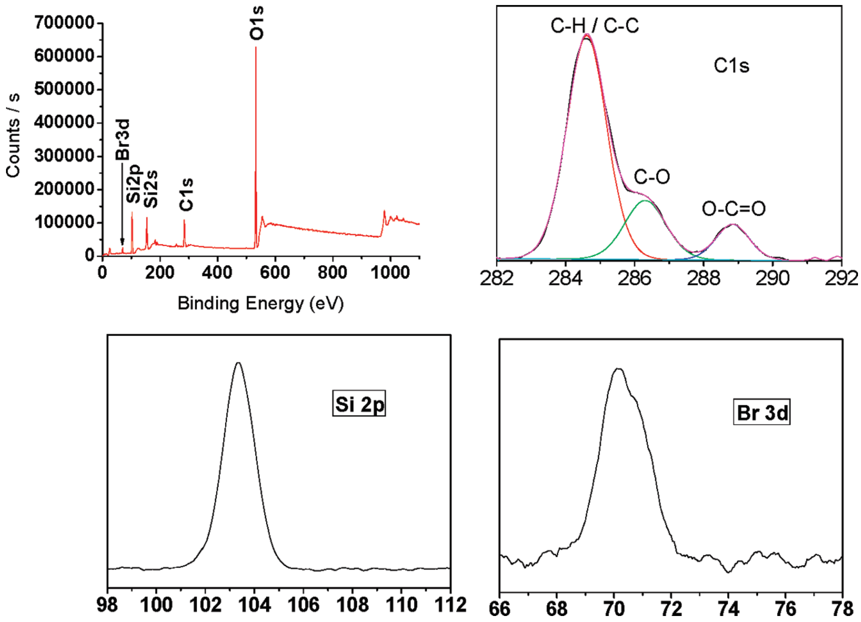
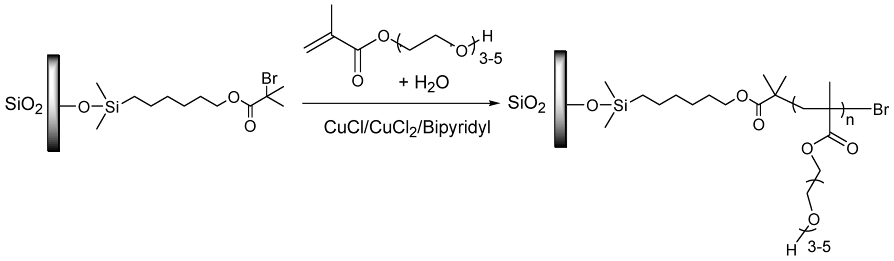


Figure 1. XPS survey spectrum and high-resolution elemental scan of Br 3d, C 1s, and Si 2p of the initiator monolayer modified silicon surface.

Scheme 4. Growing PEGMA Film on Silicon Substrate Using Surface-Initiated ATRP



The thickness of the PEGM film layer in combination with the initiator monolayer was obtained by subtracting the contribution of the oxide layer.

Results and Discussion

The surface initiator molecule was prepared by reaction of 5-hexen-1-ol with 2-bromo-2-methylpropionyl bromide in the presence of triethylamine to give the ester **1**, which was subsequently hydrosilylated with trichlorosilane in the presence of H_2PtCl_6 to afford the trichlorosilyl derivative **2** (Scheme 2). The overall yield for the two steps was 90%, and the structure of **2** was confirmed by ^1H NMR. For the subsequent surface-initiated ATRP, **2** was treated with a cleaned silicon wafer to form a self-assembled monolayer of initiator moieties on silicon substrate (Scheme 3).

Following surface functionalization, XPS was used to confirm the formation of the initiator monolayer. Figure 1 shows the XPS spectrum and high resolution elemental scan of the initiator monolayer film. The survey spectrum showed four elements: silicon (2s, 150 eV; 2p, 103.4 eV), carbon (1s, 285.5 eV), oxygen (1s, 532.7 eV) and bromide (3d, 70.2 eV). The C 1s core-level spectrum of the Si-initiator surface include three peak components having binding energy at about 284.6, 286.3, and 288.8 eV, attributable to the C−H/C−C, C−O, and O−C=O species, respectively. These results indicated that the initiator film for the subsequent ATRP reaction had been successfully immobilized on the silicon surface.

The AFM image reveals that the self-assembled initiator monolayer is smooth and uniform (Figure 2). The surface was homogeneous with rms roughness of ~18 Å.

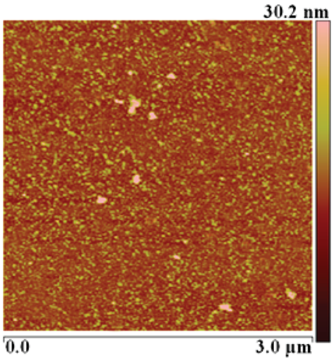


Figure 2. AFM topographic image of the self-assembled initiator monolayer.

Next, we carried out surface-initiated ATRP of PEGMA on the self-assembled initiator monolayer surface. We grew PEGMA thin films on silicon wafers with three different monomer concentrations: 1.0, 1.5, and 2.1 M. The thickness of the PEGM thin films was measured by an ellipsometer. The correlation of the PEGMA film thickness with the polymerization time is summarized in Figure 3. For each of the measurements, the relative standard deviation (% RSD) is less than 3%, indicating that the film surface is uniform. The results show the PEGMA film thickness increases with the increase of the polymerization reaction time. In all cases, the film thickness increases linearly with the reaction time after the initial introduction period of polymerization (about 1 h). The results also show that a less concentrated

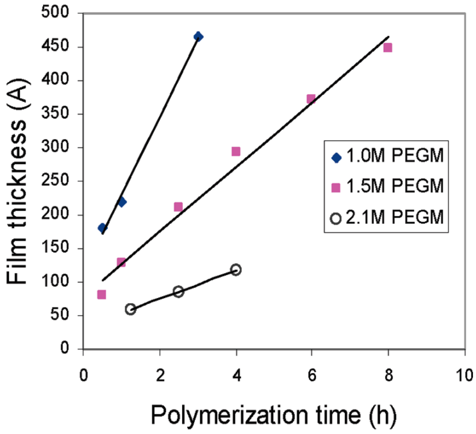


Figure 3. Correlation of PEGMA film thickness versus surface polymerization time on silicon wafers.

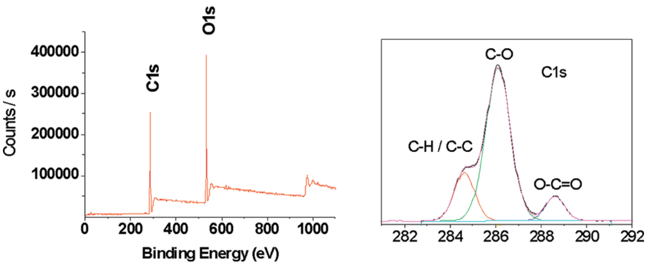


Figure 4. XPS survey spectrum and high-resolution elemental scan of C 1s of the PEGMA film modified silicon surface (monomer concentration, 1.5 M; reaction time, 3 h).

monomer solution leads to the formation of a thicker film on the wafer at constant polymerization time. The slope of PEGMA film growth is 21.5, 48.1, and 111.9 Å/h, respectively, for monomer concentration of 2.1, 1.5, and 1.0 M, respectively. After 4 h of polymerization, the PEGMA thickness is increased to 293.3 and 118.3 Å for 1.5 and 2.1 M polymerization solutions, respectively. Clearly, water accelerates this surface ATRP considerably and this acceleration increases with higher water concentration. At lower PEGMA concentration, water concentration was higher, and hence, the surface ATRP was faster. Our surface polymerization result is consistent with the finding that water plays an important role as an accelerator in solution ATRP reaction rather than merely acting as a diluent.[41]

After surface-initiated ATRP of PEGMA, the chemical composition on silicon surface changed significantly. Figure 4 shows the XPS spectrum of a PEGMA film formed by ATRP polymerization (1.5 M, 3 h). While the bromide and silicon signal disappeared, the increasing intensity of the oxygen peaks relative to the carbon signal agrees with the introduction of PEGMA film to the surface. The C 1s core-level spectrum of the PEGMA film surface shows three peak components having binding energy at about 284.6, 286.1, and 288.6 eV, attributable to the C−H/C−C, C−O, and O−C=O species, respectively. These results confirmed that the surface-initiated ATRP reaction was successful in immobilizing PEGMA layer onto the silicon surface.

With the successful demonstration that water concentration can control the surface ATRP rate, we began to investigate conditions for generating PEGMA polymer thin film gradient. The basic concept for our approach is schematically illustrated in Scheme 1. Specifically, a silicon wafer functionalized with a monolayer of initiator molecule was placed in a beaker in an upright, end-on-end longitudinal fashion. A PEGMA polymerization solution was poured gently to form layer 1, which was followed by the formation of a water layer 2 on top of the organic layer. Water in layer 2 will gradually diffuse into PEGMA monomer layer (layer 1), whereas the monomer and the other reagents in layer 1 will slowly diffuse into water layer. Those diffusions form a monomer concentration gradient across the surface of the initiator-bonded silicon wafer, thereby resulting in the formation of a PEGMA film gradient with a graded increase in thickness across the surface of the silicon wafer.

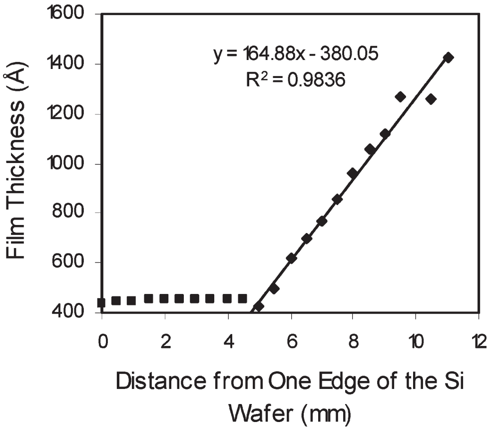


Figure 5. PEGMA film thickness vs the position on the silicon wafer using two layers of liquids: 1.5 M monomer aqueous solution and water.

A specific experiment was carried out as the following. A PEGMA monomer solution (1.5 M) was carefully added to a 140 mL beaker to form a first layer of PEGMA monomer solution covering two-thirds of the silicon wafer (24 mm width × 30 mm height). Into this solution, 30 mL water was gently added to form a second layer. The difference of the monomer concentrations in those two layers caused the diffusion of the monomer and polymerization reagents, forming a monomer gradient along the wafer. After polymerization at room temperature for 6 h, the wafers were rinsed with Nanopure water and dried with air-flow. The thickness of the polymer thin film was measured at intervals beginning at the end of the wafer resting on the bottom of the beaker (Figure 5). The bottom end of the wafer will be identified hereinafter with regard to the 24 mm × 30 mm silicon wafer dimensions as the 0 mm end of the wafer. The PEGM film thickness, measured from 0 mm to 4.5 mm, stayed constant at 450 Å, indicating that 6 h reaction time period was not long enough to enable the water layer to diffuse into the PEGMA monomer layer covering the 0 to 4.5 mm portion of the silicon wafer. The PEGMA film gradient thickness as measured from the 4.5 mm portion of the silicon wafer and up, however, resulted in a linear increase of PEGMA film thickness from 450 to 1400 Å. The linear increase in PEGMA film thickness was attributed to the PEGMA monomer concentration gradient, which was formed when the water layer diffused into the PEGMA monomer layer. The PEGMA film gradient slope is 165 Å/mm. It should be noted that the diffusion should create a PEGMA concentration gradient in the opposite direction from the concentration gradient of water, i.e., at a higher water concentration the PEGMA concentration should be lower. This should create an opposite impact on the polymerization rate: while high [H_2O] increases the rate, lower [PEGMA] should lower the rate. Apparently the water acceleration effect is predominant here. It was noted that the film thickness at the far right side of the wafer had some fluctuation and gradually decreased to zero. We attribute this to the nonlinear diffusion and very low monomer concentration, even approaching zero monomer concentration at the far right end of the wafer.

The AFM images also help to reveal the continuous change of the nanometer thick film gradient (Figure 6). Parts A and B of Figure 6 represent images of PEGMA film gradient in different

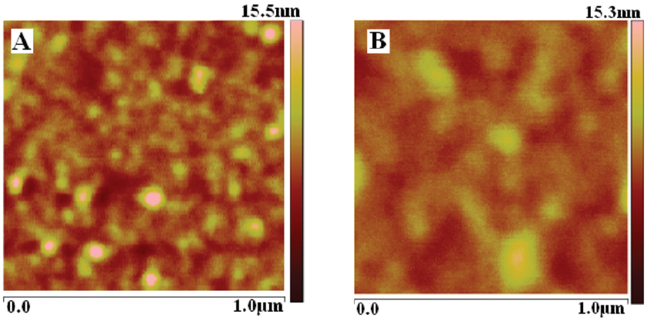


Figure 6. AFM topographic images of (A) PEGMA film imaged at 2 mm distance from the bottom edge of the silicon wafer and (B) PEGMA film imaged at 10.5 mm distance from the bottom edge of the silicon wafer.

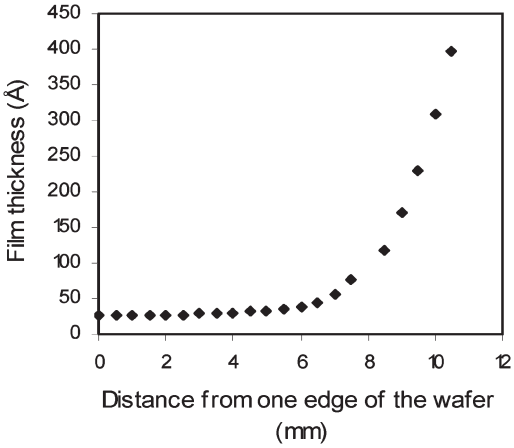


Figure 7. PEGMA film thickness versus the position on the silicon wafer using two layers of liquids: bulk monomer solution and water.

areas. The film thickness for the film in part A is 45.67 nm and the rms roughness was 12 Å; the film thickness for the film in part B is 125.47 nm and the rms roughness is 10 Å. These results showed that the gradient film was smooth and homogeneous. The thickness of polymer thin film increases with the distance from the bottom edge of the silicon wafer, agreeing well with the ellipsometry measurement (Figure 5).

Another PEGMA film gradient was prepared by a two-layer system of water and bulk PEGMA polymerization solution. The bottom layer was prepared by using the same protocol as described above, except without adding any water. After 5 h of reaction at room temperature, the thickness of the thin PEGM film gradient was measured and plotted in Figure 7. Figure 7 indicates that the bulk PEGMA polymerization solution caused a different monomer concentration gradient to be formed, which affected the graded increase in thickness of the PEGM gradient film being grown on the initiator-coated substrate.

Using different monomer concentrations, the film gradient shapes and slopes are different. Those differences are determined by the diffusion of water, monomer, and other reaction participating reagent molecules. The parameters that determine the formation of the monomer gradient include initial monomer concentration, reaction temperature, reaction pressure, the height of the liquid layers, and so on. Despite the simplicity of this method for surface gradient formation, to achieve high accuracy and reproducible results, the multiple parameters for producing the monomer diffusion need to be well designed and carefully controlled. The mechanism of this method for film gradients will be further investigated.

In conclusion, we successfully developed a simple method for preparing polymer thin film gradients by using a new concept for concentration gradient controlled ATRP. The slope of the gradient can be fine-tuned by adjusting the monomer concentration and polymerization time. The PEGMA gradient films have thickness ranging from a few of hundreds of angstroms to more than 1000 Å. Generally, this provides a convenient method to prepare polymer thin film gradients for many potential applications.

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References and Notes

(1) Gritsenko, K. P.; Krasovsky, A. M. *Chem. Rev.* **2003**, *103*, 3607–3649.
(2) Yoshikawa, C.; Goto, A.; Tsujii, Y.; Fukuda, T.; Yamamoto, K.; Kishida, A. *Macromolecules* **2005**, *38*, 4604–4610.
(3) Chen, R.; Zhu, S.; Maclaughlin, S. *Langmuir* **2008**, *24*, 6889–6896.
(4) von Werne, T. A.; Germack, D. S.; Hagberg, E. C.; Sheares, V. V.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2003**, *125*, 3831–3838.
(5) Ohno, K.; Koh, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2002**, *35*, 8989–8993.
(6) Huang, X.; Wirth, M. J. *Anal. Chem.* **1997**, *69*, 4577–4580.
(7) Huang, X.; Doneski, L. J.; Wirth, M. J. *Anal. Chem.* **1998**, *70*, 4023–4029.
(8) Genzer, J.; Bhat, R. R. *Langmuir* **2008**, *24*, 2294–2317.
(9) Morgenthaler, S.; Zink, C.; Spencer, N. D. *Soft Matter* **2008**, *4*, 419–434.
(10) Liu, Y.; Klep, V.; Zdyrko, B.; Luzinov, I. *Langmuir* **2005**, *21*, 11806–11813.
(11) Van Dover, R. B.; Schneemeyer, L. D.; Fleming, R. M. *Nature* **1998**, *392*, 162.
(12) Chaudhury, M. K.; Whitesides, G. M. *Science* **1992**, *256*, 1539–1541.
(13) Liedberg, B.; Wirde, M.; Tao, Y.; Tengvall, P.; Gelius, U. *Langmuir* **1997**, *13*, 5329–5334.
(14) Elwing, H.; Golander, C. G. *Adv. Colloid Interface Sci.* **1990**, *32*, 317–339.
(15) Welin-Klintstrom, S.; Lestelius, M.; Liedberg, B.; Tengvall, P. *Colloids Surf. B* **1999**, *15*, 81–87.
(16) Gunawan, R. C.; Silvestre, J.; Gaskins, H. R.; Kenis, P. J. A.; Leckband, D. E. *Langmuir* **2006**, *22*, 4250–4258.
(17) Lee, S. J.; Khang, G.; Lee, Y. M.; Lee, H. B. *J. Colloid Interface Sci.* **2003**, *259*, 228–235.
(18) Kumar, G.; Ho, C.-C.; Co, C. C. *Adv. Mater.* **2007**, *19*, 1084–1090.
(19) Lee, J. H.; Jeong, B. J.; Lee, H. B. *J. Biomed. Mater. Res.* **1997**, *34*, 105–114.
(20) Lin, Y. S.; Hlady, V.; Gölander, C.-G. *Colloids Surf. B* **1994**, *3*, 49–62.
(21) Mougin, K.; Ham, A. S.; Lawrence, M. B.; Fernandez, E. J.; Hillier, A. C. *Langmuir* **2005**, *21*, 4809–4812.
(22) Mei, Y.; Wu, T.; Xu, C.; Langenbach, K. J.; Elliott, J. T.; Vogt, B. D.; Beers, K. L.; Amis, E. J.; Washburn, N. R. *Langmuir* **2005**, *21*, 12309–12314.
(23) Larsson, A.; Liedberg, B. *Langmuir* **2007**, *23*, 11319–11325.
(24) Harris, J. M. *Poly(ethylene glycol) Chemistry and Biological Applications*; American Chemical Society: Washington, DC, 1997, vol. *680*.
(25) Uchida, K.; Otsuka, H.; Kaneko, M.; Kataoka, K.; Nagasaki, Y. *Anal. Chem.* **2005**, *77*, 1075–1080.
(26) Zhen, G.; Falconnet, D.; Kuennemann, E.; Vörös, J.; Spencer, N. D.; Textor, M.; Zürcher, S. *Adv. Funct. Mater.* **2006**, *16*, 243–251.
(27) Larsson, A.; Ekblad, T.; Andersson, O.; Liedberg, B. *Biomacromolecules* **2007**, *8*, 287–295.
(28) Lin, Y. S.; Hlady, V.; Golander, C. *Colloids Surf. B* **1994**, *3*, 49–62.
(29) Morgenthaler, S.; Zink, C.; Städler, B.; Vörös, J.; Lee, S.; Spencer, N. D.; Tosatti, S. G. P. *Biointerphases* **2006**, *1*, 156–165.
(30) Ionov, L.; Stamm, M.; Diez, S. *Nano Lett.* **2005**, *5*, 1910–1914.
(31) Wu, T.; Efimenko, K.; Genzer, J. *J. Am. Chem. Soc.* **2002**, *124*, 9394–9395.

(32) Wu, T.; Efimenko, K.; Vlèek, P.; Sÿubr, V.; Genzer, J. *Macromolecules* **2003**, *36*, 2448–2453.
(33) Morganthaler, S.; Lee, S.; Zürcher, S.; Spencer, N. D. *Langmuir* **2003**, *19*, 10459–10462.
(34) Tomlinson, M. R.; Genzer, J. *Macromolecules* **2003**, *36*, 3449–3451.
(35) Xu, C.; Wu, T.; Batteas, J. D.; Drain, C. M.; Beers, K. L.; Fasolka, M. J. *Appl. Surf. Sci.* **2005**, *252*, 2529–2534.
(36) Wang, X.; Bohn, P. W. *J. Am. Chem. Soc.* **2004**, *126*, 6825–6832.
(37) Ratcliff, E.; Hillier, A. C. *Langmuir* **2007**, *23*, 9905–9910.
(38) Ionov, L.; Zdyrko, B.; Sidorenko, A.; Minko, S.; Klep, V.; Luzinov, I.; Stamm, M. *Macromol. Rapid Commun.* **2004**, *25*, 360–365.
(39) Jones, D. M.; Huck, W. T. S. *Adv. Mater.* **2001**, *13*, 1256–1259.
(40) Haddleton, D. M.; Perrier, S.; Bon, S. A. F. *Macromolecules* **2000**, *33*, 8246–8251.
(41) Wang, X.; Armes, S. P. *Macromolecules* **2000**, *33*, 6640–6647.
(42) Percec, V.; Barboiu, B.; Kim, H. J. *J. Am. Chem. Soc.* **1998**, *120*, 305–316.
(43) Van Krevelen, D. W. *Properties of Polymers*; Elsevier: Amsterdam, 1997.