

Synthesis of High-Density Grafted Polymer Layers with Thickness and Grafting Density Gradients

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Received June 23, 2005. In Final Form: September 30, 2005

A novel approach was developed for the synthesis of tethered polymer layers with thickness and grafting density gradients. Poly(glycidyl methacrylate) (PGMA) was employed as a primary anchoring layer to attach the polymer chains to the surface of a silicon wafer. A linear temperature gradient heated stage was used for the generation of a gradual variation in the thickness of the anchoring PGMA film along the substrate. The obtained gradient was translated into the polymerization initiator gradient via the reaction between the epoxy groups of PGMA and the carboxyl functionality of 2-bromo-2-methylpropionic acid (BPA). The attachment of BPA to the surface modified with the monolayer of PGMA was confirmed by X-ray photoelectron spectroscopy experiments. To complete the experimental procedures, surface-initiated atom transfer radical polymerization was performed to synthesize the grafted polymer layers with thickness and surface densities that were varied along the substrate. The grafting density of the samples created in this three-step process ranged from 0.75 ± 0.05 to 1.5 ± 0.25 chains/nm². It was estimated, from a comparison of the surface densities of the initiator and the attached polymer, that the efficiency of the initiation from the surface was on the order of 5–10% and was dependent upon the surface concentration of the initiator and the time of polymerization.

Introduction

Gradient surfaces are substrates with a directional continuous variation in a variety of parameters, for example, the number of functional groups,¹ molecular weight,² chemical compositions,³ grafting density,^{4,5} and the number of nanoparticles^{6,7} or nanostructures.⁸ A key advantage of the gradient surface is that a single sample can be used to investigate the effect of surface parameter variation. The employment of gradients significantly reduces time and improves the efficiency of research and development. These combinatorial/high-throughput methods have led to the discovery of new catalysts and have been widely used for the optimization of inorganic, semiconducting, and superconducting materials.⁹ Gradient surfaces have also been successfully employed in biomedical/biomaterials research.^{10–14}

The high-throughput characterization methods have also changed the productivity of polymer research. Not

only have a significant number of experimental facts been collected, but also novel phenomena have been revealed. Continuous variation in thickness and annealing temperature was utilized for the investigation of the dewetting behavior of thin polystyrene (PS) films.¹⁵ A similar approach was effectively used to measure the cloud points of polymer blends.¹⁶ The combinatorial method through the generation of gradient surfaces was also employed to study surface pattern formation in thin block copolymer films^{17,18} and investigations of polymer adhesion.^{19,20} Recently, the high-throughput technique was applied to the synthesis/characterization of grafted polymer layers reported in our work^{21–24} and in that of others.^{2–5,25,26} Two major grafting techniques available for the preparation of the grafted layers, namely, the attachment of end-functionalized polymers (“grafting to” method) and polymerization initiated from solid surfaces (“grafting from” method), were used for the synthesis.

In our prior research, the “grafting to” approach was employed to synthesize anchored polymer layers with variation in the grafting density along a silicon substrate.

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The density gradient was induced by a gradient in the grafting temperature.^{21–24} The tethered polymer layers demonstrated gradual changes in wetting properties and surface morphology. Next, the synthetic approach was applied to the preparation of mixed polymer brushes with a one-dimensional gradient of composition.²⁴ The combinatorial method allowed for the investigation of phase segregation and responsive behavior as a function of the grafted layer composition and solvent selectivity. It is necessary to note that the values of the grafting density reported were not particularly high because of the well-known limitations of the “grafting to” method.²⁷

The “grafting from” approach, offering the possibility of synthesizing grafted polymer layers possessing higher grafting density, was utilized by several groups to obtain the gradient grafted polymer layers. The methods developed are based on the formation of self-assembled monolayers (SAMs) of polymerization initiators on a substrate surface. Genzer et al.^{2–5} developed two “grafting from” methodologies that allow for combinatorial variation in the grafting density and molecular weight of the grafted polymer layers, respectively. The first technique includes covering a substrate with a molecular gradient of a polymerization initiator, followed by atom transfer radical polymerization (ATRP) from the substrate-bound initiator centers. Grafted macromolecules, with a gradual variation of molecular weight on a silicon wafer, were prepared by ATRP employing an apparatus that controls the polymerization time with a micropump. Beers et al. employed a microfluidic system to vary the molecular weight of the grafted polymer along a substrate.²⁶ Zhao described the synthesis of gradient mixed poly(methyl methacrylate) (PMMA)/PS brushes from a gradient mixed initiator-terminated monolayer by combining ATRP and nitroxide-mediated radical polymerization.²⁵

In this paper we discuss a novel effective approach to preparing high-density grafted polymer layers with variation in the grafting density along a substrate employing surface-initiated ATRP. Poly(glycidyl methacrylate) (PGMA) was utilized as an anchoring layer to attach polymer chains to the surface. (In previous studies, it was found that PGMA could serve as an effective anchoring layer for the synthesis of grafted polymer layers with the ATRP process.^{28,29}) Specifically, a gradient in the density of polymerization initiator was created on the substrate surface through the generation of a thickness gradient in the PGMA anchoring layer. The anchoring layer approach permitted initiator surface densities that were significantly higher than the densities reported for SAMs of polymerization initiators. Therefore, densely grafted gradient polymer layers were obtained by subsequent ATRP initiated from the substrate. The developed method of grafting gradient polymer layers may be applied to various substrates since we demonstrated that the PGMA anchoring film could be successfully deposited on various organic polymeric and inorganic surfaces.³⁰

Experimental Section

Highly polished single-crystal silicon wafers (56 mm long and 12 mm wide) of {100} orientation (Semiconductor Processing Co) were used as the substrate. The wafers were first cleaned

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in an ultrasonic bath for 30 min, placed in a hot piranha solution (3:1 concentrated sulfuric acid/30% hydrogen peroxide) for 1 h, and then rinsed several times with high-purity water. Glycidyl methacrylate and styrene (Aldrich) were purified employing an inhibitor-removing column (Aldrich) and vacuum distillation. Glycidyl methacrylate was polymerized via a free radical method to give PGMA. Gel permeation chromatography (GPC) using PS standards showed that, for PGMA, $M_n = 84,000$ and polydispersity index (PDI) = 3.4. *tert*-Butyl bromoacetate (tb-BA) and 4,4'-dinonyl-2,2'-bipyridyl (dNbP) were used as received from Aldrich. Copper(I) bromide (CuBr), Copper(II) bromide (CuBr₂), and 2-bromo-2-methylpropionic acid (BPA) were used as received from Acros.

A layer of PGMA (6 nm thick) was deposited onto the silicon surface by dip-coating from methyl ethyl ketone (MEK) solution (dip coater, Mayer Fientechnik D-3400). The temperature gradient stage was constructed from a copper bar in which the two opposite sides of the bar were connected to the heating and cooling elements. Five pairs of thermocouples at different locations along the sample monitored the temperature of the bar. The stage was covered to ensure that the samples were kept in N₂ atmosphere.

The attachment of the BPA to the PGMA gradient films was conducted from the gaseous phase in an argon atmosphere under reduced pressure (10 mmHg) at 90 °C for 12 h. Unattached BPA was removed by multiple washings with ethanol, including washing in an ultrasonic bath.

The ATRP of styrene was carried out with maximum precautions to avoid oxygen. In a typical polymerization experiment, CuBr (0.31 g, 2.2 mmol), dNbP (1.88 g, 4.6 mmol), free initiator (tb-BA, 0.11 mmol), CuBr₂ (0.024 g, 0.11 mmol), and styrene (50 mL, 0.44 mol) were sealed in a flask and immediately exposed to several repeating freeze–pump cycles. The mixture was stirred at ambient temperature until the solids were completely dissolved and a deep-brown homogeneous solution was formed. The final mixture was distributed between test tubes in an oxygen-free glovebox. The silicon wafers were immersed into each test tube in the glovebox and sealed. For polymerization, the test tubes were immersed into a preheated silicon oil bath (110 °C) for different times. Ungrafted PS was removed from the wafers by multiple washing with toluene, followed by washing with the solvent in an ultrasonic bath. Samples of the ungrafted PS formed in the bulk were isolated by precipitation with ethanol and purified by multiple precipitations from a tetrahydrofuran (THF) solution into ethanol and dried in a vacuum oven.

The thickness of the PGMA layer and the synthesized brushes was determined by ellipsometry. Ellipsometry was performed with a COMPEL discrete polarization modulation automatic ellipsometer (InOmTech, Inc.) at an angle of incidence of 70°. The reproducibility of the ellipsometry measurements was better than ± 5%. The original silicon wafers from the same batch were tested independently and were used as reference samples for the analysis of the polymer layers deposited. A three-layer model (silicon substrate + silicon oxide layer + PGMA layer + grafted polymer layer) was used to simulate experimental data using COMPEL software. The refractive index for PS is 1.59.³¹ The indexes for PGMA ($n = 1.525$) and BPA ($n = 1.478$) were calculated using the group contribution method.³¹ Since the PGMA and BPA indexes were close, we used a value of 1.5 for the estimation of the PGMA layer thickness and the thickness of the layer treated with BPA.

The surface coverage (adsorbed amount), Γ (mg/m²), was estimated from the ellipsometry thickness of the layer, h (nm) by the following equation:³²

$$\Gamma = h\rho \quad (1)$$

in which ρ (g/cm³) is the bulk density of the attached (macro)molecule. The density of BPA (1.50 g/cm³) used in the calculations was obtained from the CRC handbook.³³ The density of PS was 1.05 g/cm³.³¹

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To estimate the amount of BPA attached to the PGMA film, the thickness of the anchoring PGMA layer was measured first. Then, the thickness of the PGMA film treated with BPA was also determined by ellipsometry. The difference in thickness between the untreated and treated layer was used to estimate the amount of BPA initiator attached to the surface.

The surface density, Σ ((macro)molecules/nm²), that is, the inverse of the average area per adsorbed (macro)molecule, was approximated by:

$$\Sigma = \Gamma N_A \times 10^{-21} / M = (6.023\Gamma \times 100) / M_n \quad (2)$$

in which N_A is Avogadro's number and M (g/mol) is the molar mass of the attached (macro)molecule.

Surface characterization of the brushes obtained was performed by scanning probe microscopy (SPM) in the tapping mode, on a Dimension 3100 (Digital Instruments, Veeco.) microscope. Silicon tips with spring constants of 50 N/m and radii of 10–20 nm were used. Imaging was done at a scan rate of 1 Hz. M_w/M_n was determined by GPC (Waters).

X-ray photoelectron spectroscopy (XPS) experiments were performed in the Center for Microanalysis of Materials at the University of Illinois at Urbana-Champaign using an AXIS ULTRA spectrometer (Kratos) with a monochromatized Al K α X-ray source of 300 W at 20 mA. The analyzer's pass energy was set to 160 eV to record survey spectra and 20 eV to take high-resolution spectra.

Results and Discussion

PGMA Gradient Layer. To synthesize gradient brushes via the “grafting from” technique, two key features of the surface modification with PGMA anchoring layers were utilized. First, the amount of ATRP initiator attached to the surface is directly proportional to the thickness of the primary PGMA layer.²⁹ Thus, if the PGMA thickness is changing gradually along the substrate, a gradient of the polymerization initiator on the surface can be created. The obtained initiator gradient can be readily transformed into the corresponding grafting density variation during the controlled/living ATRP process.^{28,29} A second feature of the PGMA modification is that the thickness of the PGMA layer permanently attached to the surface is dependent upon the temperature and time of the fabrication process. Namely, if a relatively thick PGMA film is deposited onto the substrate, part of the PGMA material can be extracted from the film by being rinsed with solvents. Annealing the film at elevated temperatures leads to an increase in the PGMA amount permanently attached to the surface. Annealing time also increases the anchored amount. Thus, a linear temperature gradient heated stage can be employed for the generation of a gradient PGMA layer.

In our typical experiment, a uniform PGMA layer with the thickness of 6 nm was deposited onto a silicon wafer by dip-coating from a PGMA/MEK solution. The thickness of the reactive layers was kept at a level below the end-to-end distance of the polymer coils to ensure a monolayer formation (for PGMA of 84 000 g/mol, $\langle r^2 \rangle^{1/2} \approx 14$ nm).³⁴ A copper bar was heated at one end by an embedded heating device; the other end was cooled by water. The temperatures of the hot and cold ends of the stage were 110 and 20 °C, respectively. Figure 1a shows the temperature gradient along the copper bar surface measured by the imbedded thermocouples. An almost linear temperature gradient was observed. The wafer covered with the PGMA layer was brought into close contact with the copper bar. After a certain period of annealing in the apparatus, the modified wafer was taken out and rinsed

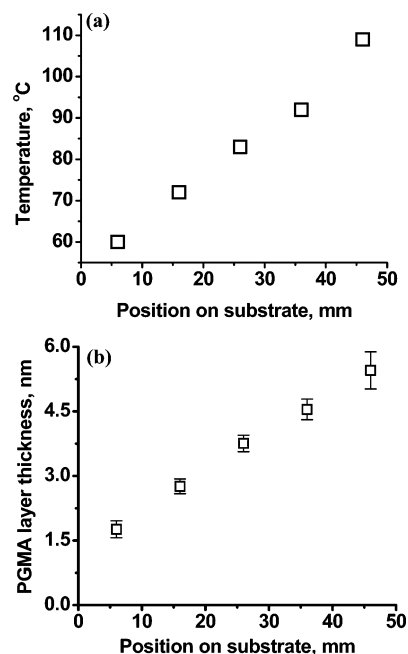


Figure 1. (a) Temperature gradient along the substrate surface. (b) Thickness of the PGMA anchoring layer vs position along the substrate. Each point is the average of the thickness measured at the same position for 6 parallel samples.

with MEK (a good solvent for PGMA) to remove the unattached PGMA.

Ellipsometric measurement revealed that the temperature gradient was effectively translated into the gradient thickness of the PGMA anchoring layer. The thickness of the PGMA film attached to the surface was found to depend on the annealing time. For the shorter time, (10 min) the variation of the anchoring layer thickness along the substrate was between 1 and 4 nm. When the time was increased (up to 30 min), a continuous gradient from 1.5 to 6 nm was created. A series consisting of 6 wafers was prepared under the latter conditions (60–110 °C temperature gradient, 30 min) to check the repeatability of the approach developed. No significant difference was observed between the samples (Figure 1b). The PGMA gradient layers prepared were, indeed, in the range from 1.5 to 6 nm. SPM study revealed (images are not shown) that the PGMA films evenly covered the substrate regardless of the film thickness. These virtually identical samples were utilized in our further investigations.

PGMA/BPA Macroinitiator Gradient Layer. The ATRP macroinitiator gradient was created on the substrate surface by the reaction between the epoxy groups of PGMA and the carboxyl functionality of BPA. The reaction produces a methylpropionic ester derivative of PGMA. Such α -bromoesters are known as effective initiators for the ATRP of styrene, acrylic, and some other vinyl monomers.³⁵ Therefore, a gradient in the surface concentration of the ATRP macromolecular initiator, covalently anchored to the silicon surface, was synthesized. Variation in the PGMA layer thickness along the substrate allowed for control over the amount of BPA attached to the surface. There was a nearly linear correlation between the quantity of the epoxy polymer attached to the surface and the amount of the initiator anchored (Figure 2).

The attachment of BPA to the PGMA gradient films was conducted from the gaseous phase under reduced

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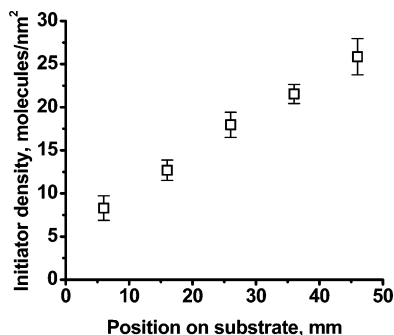


Figure 2. Initiator density ($\Sigma_{\text{Initiator}}$, calculated by eq 2) as a function of the position on the substrate. Each point is the average of the data measured at the same position for 6 parallel samples.

pressure at 90 °C for 12 h. (In our previous paper,²⁹ we reported that the deposition of the initiator from vapor produced a layer of the macroinitiator possessing smoother and more uniform surface morphology than that of the layer produced by deposition from a liquid phase.) These experimental parameters allowed for reaching the maximum possible surface concentrations of the initiator for a given thickness of the PGMA layer. Overall, the anchoring layer approach permitted initiator surface densities ($\Sigma_{\text{Initiator}}$ calculated by eq 2) significantly higher than the value of $\sim 3\text{--}4$ molecules/ nm^2 reported for the SAMs of ATRP initiators.^{36,37} In fact, the minimum initiator density achieved in this work (7–8 molecules/ nm^2) was twice as high, and the maximum initiator density (24–27 molecules/ nm^2) was nearly a magnitude higher than the surface concentration of the initiator obtained by the self-assembly process. It is necessary to note that in our previous study (employing bromoacetic acid (BAA)) we demonstrated that variation in the time and temperature of the BAA deposition allowed control over the amount of BAA attached to the surface.²⁹ Thus, it is possible to control (reduce) the amount of BPA attached to the PGMA gradient by decreasing the time/temperature of the initiator deposition. However, in this work, we concentrated on the generation of the gradient with the highest grafting density possible.

XPS experiments were conducted to confirm the attachment of BPA to the surface modified with the monolayer of PGMA. Specifically, XPS spectra were recorded for three samples: 5-nm PGMA as-deposited film, the film after annealing at 110 °C for 30 min, and the PGMA (annealed)/BPA macroinitiator film. The survey spectra (not shown) for the original and annealed PGMA samples showed the presence of O, C, and Si (from the silicon substrate) elements and were virtually identical. The macroinitiator sample showed the occurrence of Br (71 eV, Br 3d; 182 eV Br 3p and 3p_{3/2}; 189 eV Br 3p_{1/2}) element in addition to the oxygen, carbon, and silicon.³⁸ The presence of a signal from Si indicated that the signal was collected from the entire PGMA/BPA macroinitiator film and not just from the top of the anchoring layer.

Carbon 1s high-resolution XPS spectra were also recorded for these samples (Figure 3). The spectra for the initial and annealed PGMA films were very similar, demonstrating that, for the most part, the epoxy groups survived the annealing. After the treatment of the

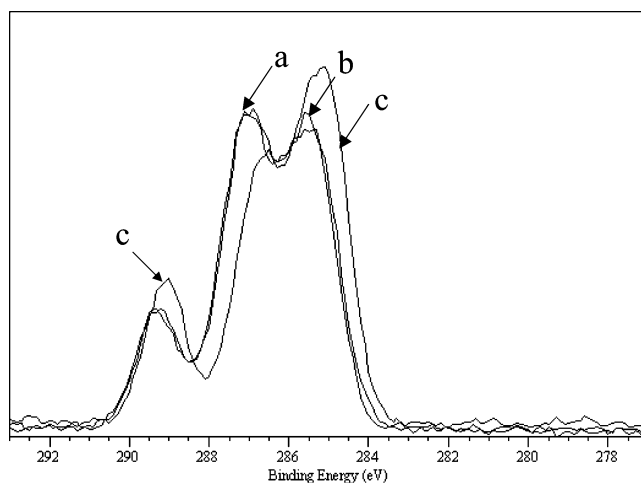


Figure 3. C 1s high-resolution XPS spectra: (a) 5-nm PGMA as-deposited film; (b) 5-nm PGMA after annealing at 110 °C for 20 min; (c) 5-nm PGMA (annealed)/2.7-nm BPA macroinitiator film.

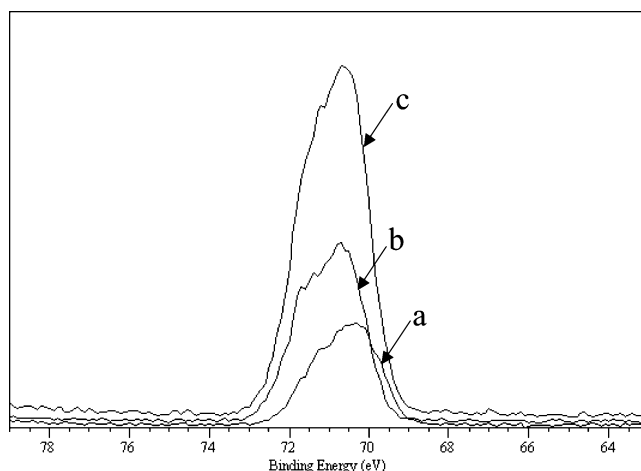


Figure 4. Angular dependence of the XPS high-resolution spectrum of the Br 3d region. TOA: (a) 15°; (b) 45°; (c) 90°. 5-nm PGMA (annealed)/2.7-nm BPA macroinitiator film.

anchoring layer with BPA, considerable changes in the XPS spectrum were observed. Specifically, the spectrum of the macroinitiator showed a significant shift of the peak corresponding to the C in the epoxy group (287.02–288.207 eV)³⁹ to the peak position that corresponds to the C in C–OH (286.7 eV).³⁹ The appearance of the hydroxyl groups suggests a reaction between the epoxy functional groups from PGMA and the carboxyl functionalities in BPA. An increase in the intensity of the aliphatic carbon (285 eV)³⁹ and the carbon in the carbonyl group (289 eV)³⁹ signals also evidenced BPA anchoring.

The angular dependence of the XPS high-resolution spectrum of Br 3d region is shown in Figure 4. We used three different takeoff angles (TOAs), 15, 45, and 90°, to evaluate the distribution of BPA throughout the film. (According to the literature,⁴⁰ the probing depth for TOAs of 15 and 90° is about 2 and 8 nm, respectively.) As the TOA and, correspondingly, the penetration depth increased, significant increase in the intensity of Br signal was observed. This result indicated that, in contrast with the SAM, the initiating centers of the synthesized mac-

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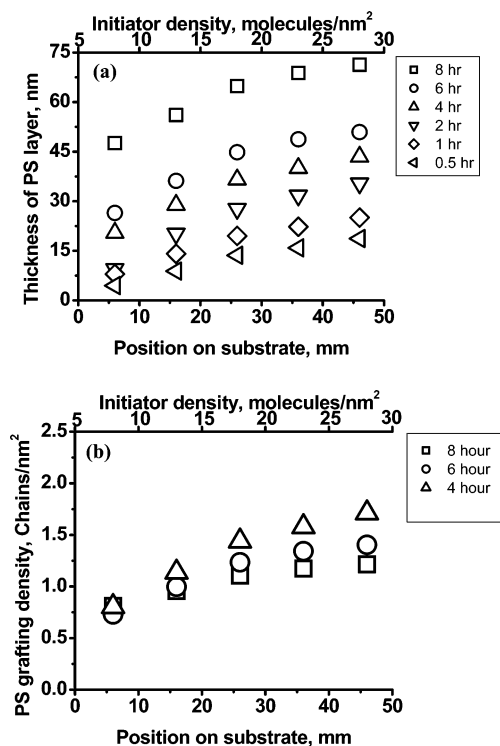


Figure 5. Thickness of PS grafted layer (a) and grafting density (Σ_{Polymer}) (b) versus the position on the substrate and initiator density ($\Sigma_{\text{Initiator}}$).

roinitiator were located not only on the surface of the PGMA layer but also inside the ultrathin film. Hence, the accessibility of the centers to a monomer and/or catalyst may be different in the case of the macroinitiator synthesized. The areas of the Br 3d and C 1s peaks in the survey spectra (not shown) at different TOAs were compared. The C/Br ratio at a 15° TOA was 3.16, whereas the ratios at 45 and 90° were 3.97 and 4.03, respectively. The comparison of the C/Br ratios indicated that the number of Br atoms is somewhat higher at the surface of the macroinitiator layer.

Synthesis of Gradient PS Layers. The ATRP of styrene, initiated from the silicon wafers covered with the macroinitiator gradient, was conducted for different periods of time. Figure 5a demonstrates how the thickness of the PS grafted layer along the substrate varies with the surface density of the anchored BPA initiator and the time of the polymerization. For the same position along the substrate, the thickness of the PS layer increased with the time of reaction. Furthermore, (as expected) the increase in the surface density of the initiating moieties led to an increase in the grafting rate. Obtaining such a result clearly demonstrates that the developed method led to the creation of a thickness gradient of a densely grafted polymer layer along the substrate. By adjusting the steepness of the gradient in the thickness of the PGMA anchoring layer, the conditions of BPA deposition, and/or polymerization time, it is possible to regulate the parameters of the gradient grafted film over a wide range.

The surface morphology of the gradient grafted layers of different thickness was imaged by SPM (Figure 6). For all thicknesses/grafting densities, the surface anchored film completely and homogeneously covered the substrate surface. The roughness of the dry grafted layers increased with thickness (Figure 7), although it was much lower than the layer height. The surface structure of the dry grafted layer was virtually independent of the surface concentration of the PGMA/BPA macroinitiator used for

the synthesis and, consequently, independent of the grafting density of the anchored PS chains. However, surface corrugation was, to some extent, dependent upon the thickness of the grafted polymer layer.

There are several cases of experimental evidence^{37,41,42} that prove that grafted chains have nearly the same molecular weights and closely similar (within 0.1–0.2) molecular weight distributions as the ungrafted (free) polymer being formed in the bulk or solution during a controlled/living grafted polymerization. It was suggested that the free polymer might give a good measure of the molecular weight of the grafted polymer.^{37,42,43} Consequently, to evaluate the efficiency of the initiation in the lack of the intensive polymerization process in the bulk, a very small amount (0.05 mole per 1 mol of CuBr) of *tb*-BA was added to the system. It was assumed that such a small quantity of the sacrificial initiator would not influence the grafting process on the surface but could provide an opportunity for an estimate of the molecular weight of the grafted polymer layers. It was found that the amount of polymer recovered from the bulk after 4, 6, and 8 h of polymerization was sufficient to conduct GPC. The PS obtained had the following parameters: $M_n = 16,051$ g/mol (PDI = 1.24), $M_w = 22,939$ g/mol (PDI = 1.28), and $M_n = 37,103$ g/mol (PDI = 1.38) after 4, 6, and 8 h of polymerization, respectively.

Figure 5b shows how grafting the density parameter calculated by eq 2 (Σ_{polymer}) changes along the substrate in the course of the synthesis of the PS-anchored layer. (The M_n values obtained for the ungrafted polymer formed by the added sacrificial initiator were used for the Σ determination.) The estimates show that we can, in fact, create a gradient possessing very high grafting density. For the samples created, Σ_{polymer} was varied from 0.75 ± 0.05 to 1.5 ± 0.25 chains/nm² along the substrate. The data showed that, at the lower surface concentrations of the initiator, the calculated grafting densities for various polymerization times were almost identical. When the initiator density increased, the decrease in the values of Σ_{polymer} with polymerization time became obvious.

Efficiency of the Macroinitiator. If the surface grafting follows the general trends observed for the conventional living ATRP conducted in a liquid phase, the same initiator density gradient should generate an identical polymer grafting density gradient, regardless of the polymerization time. In other words, initiator efficiency ($IE = \Sigma_{\text{Grafted-polymer}} / \Sigma_{\text{Initiator}}$) has to be close to 1 and constant during the course of the grafting. Conversely, our results demonstrate that, for the very high surface density of the initiating sites, IE decreases with an increase in $\Sigma_{\text{Initiator}}$ and polymerization time (Figure 8). Moreover, IE values are in the range of 5–10%. This means that only one of every 10–20 initiator groups capable of initiating ATRP reaction finally produces a grafted polymer chain.

The low values of the efficiency may indicate lower accessibility to the monomer and/or catalyst of the fraction of the initiating centers located inside the PGMA layer. However, the low initiating efficiency found for the PGMA/BPA macroinitiator was also observed for the SAMs of low-molecular-weight initiators. For instance, Yamamoto et al.³⁷ varied the concentration of an initiator in a SAM and studied the ATRP of methyl methacrylate initiated by the initiator from the surface. For the maximum (4

(41) Husseman, M.; Malmstrom, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. *Macromolecules* **1999**, *32*, 1424.

(42) Ejaz, M.; Tsujii Y.; Fukuda, T. *Polymer* **2001**, *42*, 6811.

(43) Ramakrishnan, A.; Dhamodharan, R.; R uhe, J. *Macromol. Rapid Commun.* **2002**, *23*, 612.

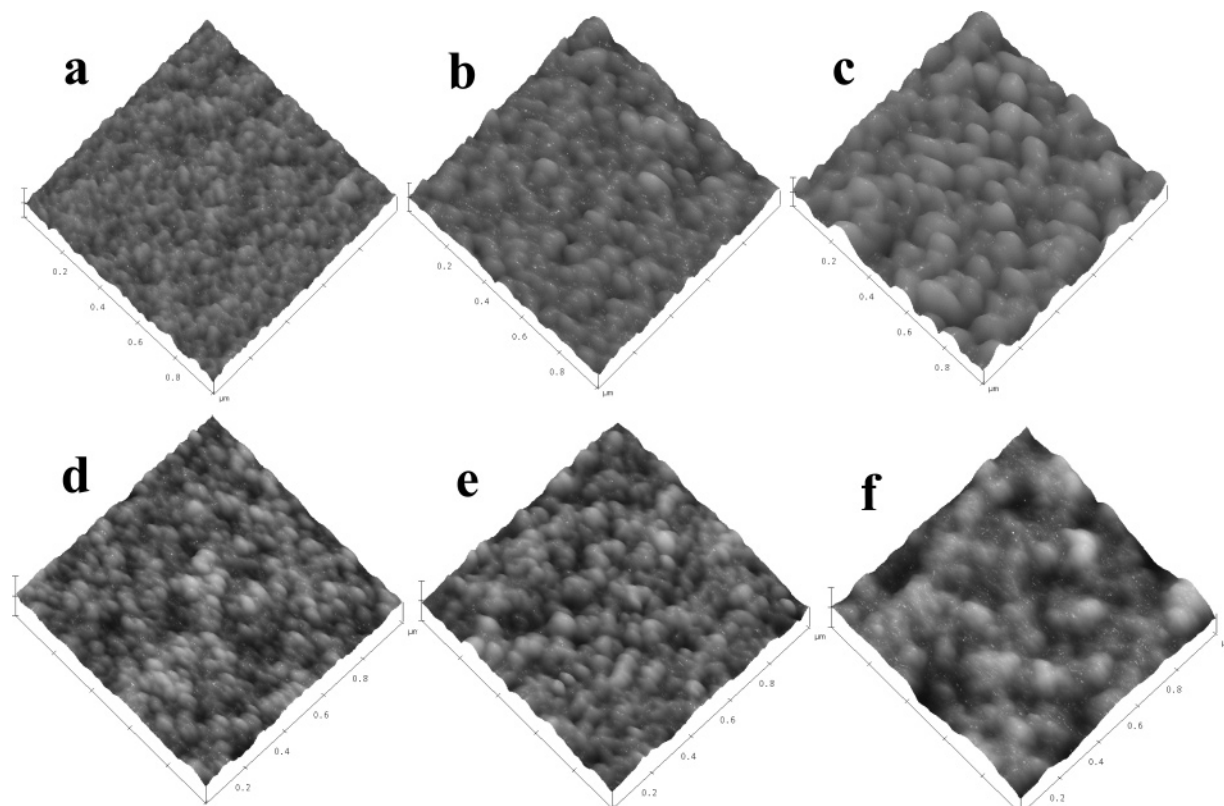


Figure 6. SPM topography ($1 \times 1 \mu\text{m}$) images of PS anchored layers at different positions of the gradient grafted film. (a–c) position: 46 mm; (d–f) position: 6 mm. Thickness of PS layers and time of grafting: (a) 18.7 nm, 0.5 h; (b) 35.4 nm, 2 h; (c) 50.9 nm, 6 h; (d) 4.5 nm, 0.5 h; (e) 9.5 nm, 2 h; (f) 26.5 nm, 6 h. RMS roughness: (a) 1.0 nm; (b) 1.6 nm; (c) 2.6 nm; (d) 0.8 nm; (e) 0.9 nm; (f) 1.2 nm. Vertical scale: 10 nm.

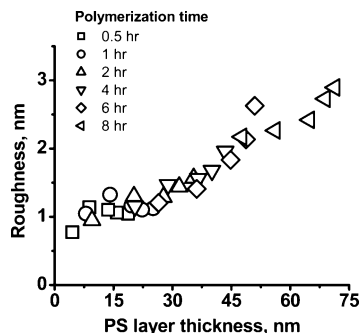


Figure 7. SPM roughness of PS grafted layers (on $1 \times 1 \mu\text{m}$ area) against the thickness of the layers.

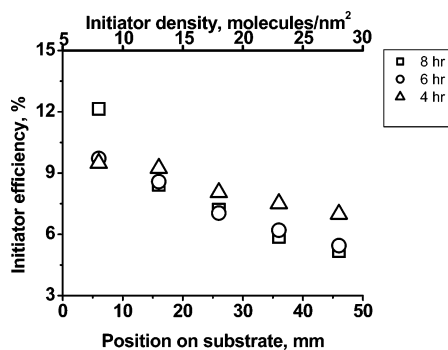


Figure 8. Initiator efficiency ($IE = \Sigma_{\text{Grafted-polymer}} / \Sigma_{\text{Initiator}}$) vs the position on the substrate and initiator density ($\Sigma_{\text{Initiator}}$).

molecules/ nm^2) value of the initiator surface concentration, the efficiency of the initiator was 0.2. With a decrease in the initiator concentration, the efficiency increased, and, according to the authors, might reach 1 at extremely low

concentrations. Jones et al.³⁶ estimated that only 1 of 10 initiating groups in the SAM produced a grafted polymer chain. The surface concentration of the initiator was varied from the maximum value observed for the monolayer to a concentration that was 10 times lower.

In our preceding articles,^{28,29} it was suggested that the early chain terminating mechanism is an important factor causing the low IE during the ATRP initiated from a solid surface. Indeed, at a higher surface density of the initiating sites, many nondormant chains possessing active ends may be found in high proximity to each other. The closeness greatly increases the possibility of recombination/termination. This early termination causes a significant decrease of IE with increase in $\Sigma_{\text{Initiator}}$. On the other hand, a detectable further decrease of IE was observed in the course of grafting. Figure 9 demonstrates how the thickness of the PS brush varies with time throughout the ATRP initiated from the surface by the PGMA/BPA macroinitiator. It is obvious that the grafting rate of the PS layer slowed as the time of polymerization increased up to 6 h. The decrease cannot be explained by monomer consumption because it was very low at this stage of the process. Accordingly, more termination events occurred as the grafting proceeded. At the later stage of the grafting (8 h in our case) the grafting rate began to increase. This autoacceleration was already reported in our preceding paper²⁸ and in work by Jeyaprakash et al.⁴⁴ It was proposed that, at this stage, an uncontrolled growth of the anchored chains starts to dominate the grafting process.

Xiao and Wirth⁴⁵ studied the ATRP of acrylamide initiated from a solid substrate at different temperatures

(44) Jeyaprakash, J. D.; Samuel, S.; Dhamodharan, R.; Rühle, J. *Macromol. Rapid. Commun.* **2002**, *23*, 277.

(45) Xiao, D.; Wirth, M. J. *Macromolecules* **2002**, *35*, 2919.

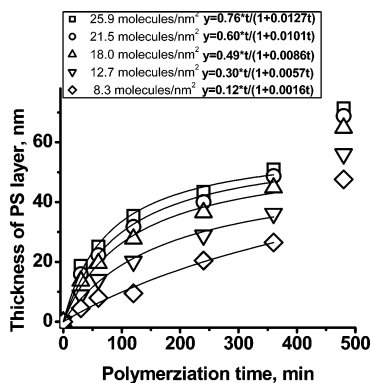


Figure 9. Thickness of PS grafted layer vs polymerization time. The points indicate experimental data, and the curves represent the best fit to eq 3. Different symbols correspond to different initiator densities.

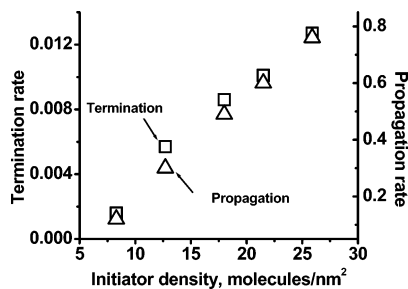


Figure 10. Termination and propagation rates estimated by eq 3 vs initiator density.

and concentrations of the monomer. It was also found that the thickness of the polyacrylamide film formed was not proportional to the reaction time. Specifically, the thickness of the grafted layer had a tendency to level off as the polymerization proceeded. The experimental analysis of the process suggested that the surface-initiated polymerization is strongly affected by the termination from radical combination because of the close proximity of the growing polymer chains. The authors proposed the following model to describe the kinetics of the grafting process

$$[M]_0 - [M] = \frac{[M]_0 k_p [\sim R]_0 t}{1 + [\sim R]_0 k_t t} \quad (3)$$

in which $[M]$ is the monomer concentration (the subscript 0 indicates the initial value); $[\sim R]_0$ is the initial radical concentration; and k_p , k_t , and t are the propagation reaction constant, termination reaction constant, and polymerization time, respectively. It was concluded that the ellipsometric thickness is proportional to $\{[M]_0 - [M]\}$. The thickness versus time plots were fitted, using the above function, to evaluate propagation (polymerization) rate ($[M]_0 k_p [\sim R]_0$) and termination rate ($[\sim R]_0 k_t$) for the grafting polymerization.⁴⁵

We employed eq 3 to treat the grafting versus time dependencies obtained in the present experiment. Figure 10 displays how the polymerization and termination rates varied with an increase in the surface initiator density. Both rates changed almost linearly with initiator density. As $\Sigma_{\text{Initiator}}$ increased from 8.3 to 25.9 molecules/nm², the propagation rate increased from 0.12 to 0.76, and termination rate increased from 0.0016 to 0.0127. The ratios between the propagation and termination rates were reasonably close for different $\Sigma_{\text{Initiator}}$ values. In general, the calculated propagation rate was 50–75 times higher than the termination rate for a given value of the initiator surface density. The results indicated that after extensive

termination at the early stages of the grafting (which decreased IE to the level of 5–10%), the further termination process demonstrates a quasi-stationary character and causes only a moderate decrease in IE .

The low initiating efficiency (observed by us and others) of the ATRP initiators immobilized on a surface might be predetermined by the frontal nature of the polymerization. In fact, for a successful controlled ATRP grafting process, most of the chains growing from the surface should be in a dormant state. The dormant chains cannot recombine. To activate the chain, the catalyst (halogen salt associated with a ligand) should contact the dormant macromolecule. Instantly, the macromolecule has to be contacted again by the catalyst for the sake of deactivating the growing chain. However, there is a strict limitation on the maximum amount of the catalyst located in vicinity of the growing polymer front. This amount is in the same order as that of the catalyst monolayer that may cover the substrate surface. Thus, only a limited number of the growing macromolecules can be readily converted into the dormant state. Other chains are propagating until they recombine with neighboring active chains. In other words, only a certain number (dictated by the capacity of the catalyst monolayer) survive and grow in a fashion relatively close to that of those in a conventional controlled ATRP. Additionally, some initiator molecules, screened by the growing front of polymer chains, might not have any chance to contact the catalyst and originate a growing macromolecule.

The relation $V = M/\rho N_A$ was used to approximate the size of the CuBr/2(dNbP) complex. Here, M is molecular weight (961 g/mol), ρ is density of the substance (1.3 g/cm³, estimated by the weight average method from known densities of components constituting the complex³³), and N_A is Avogadro's number. As a first approximation, it was assumed that the complex has a spherical shape, and the estimated value for the complex cross-section was found to be 1.38 nm². Thus, if the complex is deposited on a surface as a monolayer, the surface concentration is on the order of 1 molecule/nm². This value, in our opinion, should greatly affect the magnitude of the maximum possible grafting density that can be obtained by ATRP from a surface. Our data support this monolayer hypothesis well, since, even after an extremely high surface concentration of initiator was generated, a maximum grafting density of 1.5 chains/nm² was obtained.

Conclusions

A novel approach was developed for the synthesis of tethered polymer layers with thickness and grafting density gradients. PGMA was employed as a primary anchoring layer to attach the polymer chains to the surface of a silicon wafer. A linear temperature gradient heated stage was used for the generation of a gradual variation in the thickness of the anchoring PGMA film along the substrate. The obtained gradient was translated into the polymerization initiator gradient via the reaction between the epoxy groups of PGMA and the carboxyl functionality of BPA. The attachment of BPA to the surface modified by the monolayer of PGMA was confirmed by XPS experiments. To complete the experimental procedures, surface-initiated ATRP was performed to synthesize grafted polymer layers with thickness and surface densities that were varied along the substrate. For the samples created, the grafting density varied from 0.75 ± 0.05 to 1.5 ± 0.20 chains/nm². From a comparison between the surface densities of the initiator and that of the attached polymer, it was estimated that the efficiency of the

initiation from the surface was on the level of 5–10% and was dependent upon the surface concentration of the initiator and the time of polymerization.

Acknowledgment. This work was supported by the National Science Foundation under Award CTS-0456550, the ERC Program under Award No. EEC-9731680, and

the Department of Commerce via the National Textile Center Grants C05-CL04 and C04-CL06. The authors thank Dr. R. Aspland for the useful suggestions, Ms. Kim Ivey for the GPC measurements, and Dr. A. Janorkar for the XPS measurements.

LA051695Q