Polymer Brush Grafted from an Allylsilane-Functionalized Surface

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ABSTRACT: To graft polymer chains from the surface, a uniform and dense initiator layer on the silicate substrate is indispensable. The initiator monolayer can be fabricated in many ways, of which self-assembly of trichlorosilanes on silicate substrates is widely used. However, uniformity is always going to be an issue when using multifunctional silanes. Although uniformity is not so problematic for monofunctional silanes, purification of the surface-active materials is difficult. To obtain a uniform initiator monolayer, an allylsilane was synthesized and used to functionalize a flat silicate substrate in this research. The allylsilane can also be purified using conventional chromatography techniques. Using AFM, the monolayer was found to be more uniform than the corresponding trichlorosilane-functionalized one. Finally, atom transfer radical polymerization was applied to graft polystyrene brushes. The ability to successfully perform sequential monomer additions was consistent with a living polymerization. Tensiometry, ellipsometry, ATR−FTIR, and AFM were used to characterize the films for each surface modification step.

Introduction

Polymer chains tethered to a surface or an interface have been studied extensively both theoretically[1−10] and experimentally[11−14] due to the many possible applications such as colloidal stabilization,[15] adhesion,[16,17] lubrication,[18] nanotechnology,[19] microelectronics,[20] and biology.[21] Covalently grafted polymer brushes have been proven to be an effective means by which one can tune the surface properties such as wettability,[22] adhesion, and surface activity.[23] Polymer chains can be covalently grafted to a surface via either the “grafting to” or “grafting from” technique. Because of its high tethering density, the “grafting from” technique is more attractive. This technique first involves the introduction of an initiating monolayer onto the solid substrate. Then polymer brushes can be grown from the surface-bound initiators. The initiator monolayer can be fabricated in many ways, of which self-assembly of trichlorosilanes on silicate substrates is widely used. However, McCarthy and co-workers[24] suggested that self-assembly is not the only reaction possible between trichlorosilanes and surfaces. Thus, uniformity is always going to be an issue when using multifunctional silanes. McCarthy has recommended the use of monofunctional silanes as the preferred materials for surface modification.

Shimada and co-workers[25] reported the functionalization of silica gel with allylsilanes which are stable toward hydrolysis and can be purified by silica gel chromatography. To obtain a uniform initiator monolayer, an allylsilane was used to functionalize a flat silicate substrate in this research. Using AFM, the initiator monolayer was found to be more uniform than the corresponding trichlorosilane-functionalized surface. Finally, atom transfer radical polymerization (ATRP) was applied to prepare polymer brushes because it can provide good control over brush thickness and polydispersity.

Experimental Section

Reagents. 10-Undecen-1-ol, 2-bromoisobutyryl bromide, *tert*-butyldimethylsilyl chloride, imidazole, allylmagnesium bromide *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%), ethyl 2-bromoisobutyrate (98%), anhydrous anisole, and anhydrous dimethylformamide (DMF) were obtained from Aldrich and used as received. Chlorodimethylsilane and trichlorosilane were from Gelest. Styrene (Aldrich) was passed through a column of activated basic alumina. CuBr (Aldrich, 98%) was purified as described in the literature.[26] Silicon ATR crystals were obtained from Harrick Scientific. Silicon wafers were purchased from Polishing Corporation of America. All other reagents were purchased from Aldrich.

Instrumentation. Film thicknesses were determined by ellipsometry using a Gaertner model L116C ellipsometer. The light source was a He−Ne laser ($\lambda = 632.8$ nm) at a fixed incident angle of 70°. For the initiator monolayer, the refractive index was taken as $n = 1.42-1.44$. Altering this value by 0.05 resulted in less than a 0.1 nm change in the calculated thickness of the monolayer.[29] For polystyrene layer, $n = 1.589$.[13] Water contact angles were determined using a Ramé Hart NRL-100 goniometer with a controlled environment chamber and a tilting base mounted on a vibrationless table. The relative humidity in the chamber was maintained by adding two drops of water in the wells of the chamber. Advancing and receding angles were determined using the tilting stage method. ATR−FTIR spectra were obtained using a Nicolet System 730 spectrometer with a modified 4XF beam condenser (Harrick Scientific). 500 scans were collected, and the spectral resolution was 2 cm^{-1}. To study surface topography, AFM studies were made at ambient conditions on a multimode scanning probe microscope (Digital Instruments) in tapping mode with a silicon tip (Multi-75) that was purchased from NanoDevices, Inc. The molecular weights of free soluble polymers were measured in THF by gel permeation chromatography (GPC) using a Waters 501 pump, Waters HR4 and HR2 styragel columns, a Waters 410 differential refractometer, and a Viscotek 760A dual light scattering and viscosity detector.

Preparation of Silicate Substrates. Silicon wafers were cut into 3 cm × 1 cm strips. ATR crystals and silicon pieces were cleaned using a “piranha” solution (70/30, v/v, concentrated H_2SO_4/30% H_2O_2). It should be noted that the “piranha” solution is extremely reactive and should be handled with care. After heating at 90 °C for 1 h, the samples were cooled to room temperature and immediately rinsed with distilled water repeatedly. The cleaned substrates were dried by a stream of clean air followed by characterization using ATR−FTIR and elipsometry. The samples were stored in fluoroware containers for no longer than 30 min before use.

Initiator Monolayer Prepared from Allylsilane. Initiator monolayer preparation involves the following steps: (i) reaction

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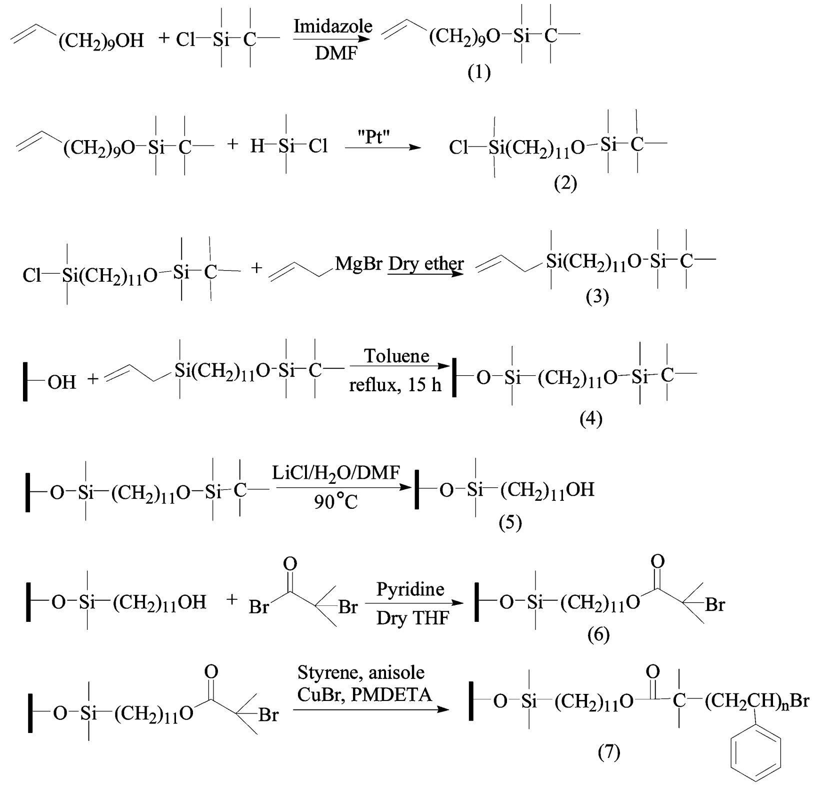

Figure 1. Reaction scheme for allylsilane synthesis, deposition, introduction of ATRP initiator, and ATRP of styrene from silicon substrates.

of 10-undecenyl alcohol and *tert*-butyldimethylsilyl chloride to give the protected product undec-10-enyl *tert*-butyldimethylsilyl ether (**1**), (ii) hydrosilylation reaction of **1** with chlorodimethylsilane to afford 1-(*tert*-butyldimethylsiloxy)-11-(chlorodimethylsilanyl) undecane (**2**), (iii) Grignard reaction of **2** with allylmagnesium bromide to produce the allylsilane 1-(allyldimethylsilanyl)-11-(*tert*-butyldimethylsilanyloxy) undecane **(3),** (iv) deposition of the prepared allylsilane onto a silicate surface to afford **4**, (v) deprotection of the *tert*-butyldimethylsilyl group in the organic monolayer on the silicate substrate to give a hydroxyl group-terminated monolayer **5**, and (vi) reaction of terminal hydroxyl groups with bromoisobutyryl bromide to prepare the ATRP initiator monolayer **6**. The six-step immobilization process is illustrated schematically in Figure 1.

Undec-10-enyl tert-Butyldimethylsilyl ether (1). 6.40 g (90% yield) of undec-10-enyl *tert*-butyldimethylsilyl ether (**1**) was prepared according to Keinan and co-workers.[27]

1-(tert-Butyldimethylsiloxy)-11-(chlorodimethylsilanyl)undecane (2). To a solution of 3.2 g (11.25 mmol) of **1** in 15 mL of anhydrous toluene were added 2.5 mL (22.5 mmol) of chlorodimethylsilane and 1 mL of a 2-propanol solution of chloroplatinic acid, H_2PtCl_6 (5 mg). The mixture was heated at 80 °C for 5 h. The solution was then filtered through a short column of silica gel to remove the catalyst. The excess trichlorosilane and toluene were removed under reduced pressure. The product **2** (4.2 g) was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.64 (t, 2H), 1.48 (m, 2H), 1.30 (br s, 18H), 0.98 (s, 9H), 0.40 (s, 6H), 0.08 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 63.45, 33.70, 32.87, 29.88, 29.61, 26.18, 22.89, 19.22, 16.60, 14.30, 0.60, −5.09.

1-(Allyldimethylsilanyl)-11-(tert-butyldimethylsilanyloxy)undecane (3). Into a dry 250 mL two-necked flask equipped with a dropping funnel, a stirring bar, and a condenser to which was attached a guard tube filled with anhydrous calcium chloride were added 12 mL of 1 mol/L diethyl ether solution of allylmagnesium bromide. 4.2 g (11 mmol) of **2** in 20 mL of dry diethyl ether was added dropwise to the flask. The addition is complete after 30 min followed by refluxing for 2 h. After cooling, 40 mL of water was added slowly into the reaction flask followed separation of the layers and two additional ether (2 × 30 mL) extractions. The combined ether extracts were dried over anhydrous magnesium sulfate. The ether was removed on a rotary evaporator, and the product was purified by silica gel column chromatography (hexanes/ethyl acetate 3:1, v/v) to give 4.0 g **3**. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.80 (m, 1H), 4.84 (m, 2H), 3.61 (t, 2H), 1.52 (m, 2H), 1.28 (br s, 16H), 0.91 (s, 9H), 0.52 (m, 2H), 0.06 (s, 6H), −0.01 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 135.59, 112.71, 63.59, 33.85, 33.14, 29.94, 29.88, 29.82, 29.69, 29.59, 26.23, 26.04, 23.97, 23.55, 18.61, 15.06, −3.50, −5.01. Elemental analysis: calculated C 68.67%, H 12.57%; found C 68.71%, H 12.72%.

*Deposition of **3** onto Silicate Substrates.* The cleaned ATR crystal and silicon wafer pieces were placed into a dried round-bottomed flask that was flushed with nitrogen for 15 min. 0.1 g of allylsilane in 15 mL of anhydrous toluene was added to the flask via syringe. The reaction was conducted by refluxing toluene for 15 h; after removal from the deposition solution, the substrates were rinsed in 15 mL of CH_2Cl_2 followed by ethanol washing and drying in a stream of clean air. The samples **4** were characterized by water contact angles, ellipsometry, and ATR−FTIR.

Deprotection of the tert-Butyldimethylsilyl Group. The *tert*-butyldimethylsilyl groups were deprotected from the allylsilane **3**-functionalized ATR crystal and silicate substrates in a neutral medium.[27] ATR crystal and silicate substrates were placed in a rubber septum-sealed dry flask which was flushed with nitrogen for 15 min, to which water (2.76 mmol) and dry LiCl (25 mmol) in 7 mL of anhydrous DMF were added. The reaction was carried out at 90 °C for 24 h. After rinsing the solid substrates with copious water and dichloromethane, the dried samples **5** were characterized by water contact angle measurement, ellipsometry, and ATR−FTIR.

ATRP Initiator Monolayer Preparation. Hydroxyl-terminated substrates **5** were dried by connection to a vacuum line followed by addition of 20 mL of 0.1 M bromoisobutyryl bromide THF (anhydrous) solution and 2 mmol of anhydrous pyridine. The reaction was allowed to proceed at room temperature for 10 min. Then the substrates **5** were taken out and rinsed with copious water and methylene chloride. Water contact angle measurements, ellipsometry, and ATR−FTIR were performed.

Initiator Monolayer Prepared from Self-Assembled Trichlorosilane. To make a comparison, a corresponding trichlorosilane

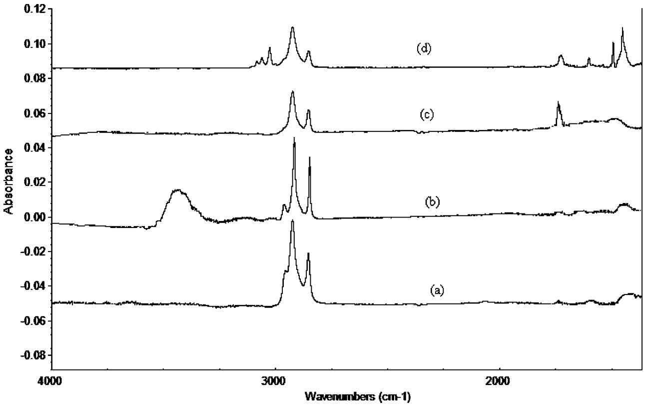

Figure 2. ATR−FTIR spectra for each surface modification step: (a) sample **4** obtained by depositing allylsilane **3**, (b) deprotected monolayer **5**, (c) ATRP initiating monolayer (**6**), and (d) Si/SiO$_2$//polystyrene **7**.

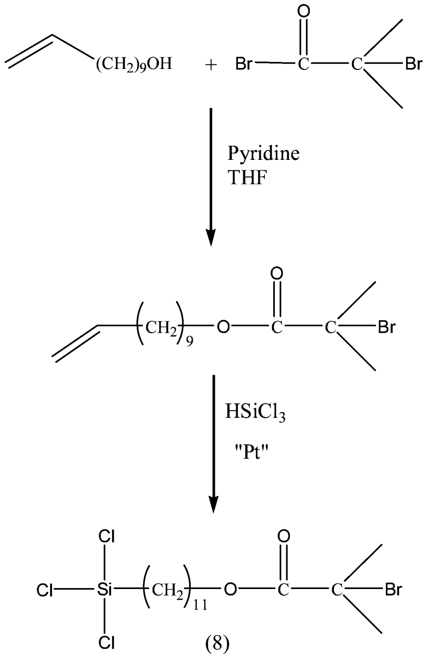

Figure 3. Reaction scheme for trichlorosilane **8** synthesis.

8-functionalized surface was prepared. The synthesis and self-assembly of the trichlorosilane were performed according to Matyjaszewski and co-workers.[28] The reaction scheme is shown in Figure 3.

Surface-Initiated Atom Transfer Radical Polymerization. The initiator-bound solid substrates were placed into a 100 mL Schlenk flask which was sealed with a rubber septum. The flask was degassed and backfilled with nitrogen three times and left under a nitrogen atmosphere. Styrene (13.5 mL), CuBr (55 mg), and anhydrous anisole (16.5 mL) were added to another 100 mL Schlenk flask which was equipped with a stirrer bar and sealed with a rubber septum. This flask was degassed by purging with nitrogen for 1 h. PMDETA (157 μL) was added to the mixture via a syringe, and the solution was stirred at 100 °C for about 10 min until it became homogeneous. The solution was cannulated to the flask containing the solid substrates, followed by the addition of free initiator ethyl 2-bromoisobutyrate (23 μL) via a syringe. The polymerization proceeded at 100 °C for 12 h, after which the ATR crystal and silicon wafer were removed and rinsed with CH_2Cl_2. To remove physically absorbed polymer chains, the solid substrates were placed into a Soxhlet extractor and extracted with THF for 24 h. Free polymer from the polymerization solution was isolated by evaporating residual monomer and solvent first, then dissolving in THF, and passing through a short column of activated basic alumina to remove any residual catalyst.

Table 1. Properties of Each Surface Modification Step

	contact angle[a] (deg)		film thickness[b] (nm)
	θ_a	θ_r	
4	87	76	2.3
5	65	52	1.5
6	82	70	1.8
Si/SiO$_2$//polystyrene (1st layer)	92	73	10
Si/SiO$_2$//polystyrene (2nd layer)	92	73	10

[a] The standard deviation of contact angles was <2°. [b] Film thickness determined from ellipsometry.

Results and Discussion

Initiator Monolayer Characterization. To graft polymer chains from the surface, a uniform and dense initiator layer on the silicon substrate is important. Self-assembly of trichlorosilanes[29] is widely used for that purpose. However, McCarthy and co-workers[24] demonstrated that self-assembly is not the only reaction possible between trichlorosilanes and surfaces and that uniformity is always going to be an issue when multifunctional silanes are used.

Shimada and co-workers[25] reported an interesting method for the modification of the silica gel surface by using allylorganosilanes. In refluxing toluene, deallylation on the allylsilane takes place to form the Si−O−Si bond with the silicon. This new method of surface functionalization has the merit that allylsilanes are stable toward hydrolysis and can be purified by silica gel chromatography.

In this research, an allylsilane **3** was synthesized and deposited (Figure 1). The presence of the monolayer was confirmed by ATR−FTIR, which showed peaks for the aliphatic C−H stretching (Figure 2a). The water advancing and receding contact angles were 87° and 76°, respectively, and the film thickness measured from ellipsometry was 2.3 nm. Then *tert*-butyldimethylsilyl groups in the organic monolayer **4** were deprotected to afford terminal hydroxyl groups as evidenced by the appearance of a peak at 3400 cm^{-1} in the ATR−FTIR (Figure 2b). The advancing and receding water contact angles decreased to 65° and 52°, respectively. The film thickness measured from ellipsometry was 1.5 nm. To introduce ATRP initiator onto the surface, the terminal hydroxyl groups were reacted with bromoisobutyryl bromide. This step was verified by the disappearance of the hydroxyl peak at 3400 cm^{-1} and the appearance of peak at 1740 cm^{-1}, which was assigned to the carbonyl stretching (Figure 2c). The advancing and receding water contact angles were 82° and 70°, respectively, and the film thickness was 1.8 nm. The contact angle and ellipsometry data are listed in Table 1.

Initiator Monolayer Uniformity. The main purpose of this research was to obtain a uniform initiator monolayer from which polymer chains can be grafted from. AFM was used to study the uniformity of the ATRP initiator monolayer (Figure 4a). The organic initiating monolayer **6** exhibited good uniformity, and the rms roughness from AFM is 0.3 nm.

In comparison, AFM was performed on the trichlorosilane **8**-functionalized surface. The synthesis and self-assembly of trichlorosilane were conducted by following the work of Matyjaszewski et al.[28] AFM (Figure 4b) indicated significant aggregation on the surface, and the rms roughness increased to 0.7 nm, which was consistent with McCarthy and co-workers.[24]

Surface-Initiated ATRP. Living polymerization techniques are preferred for making polymer brushes since they can afford better control over brush thickness and polydispersity. The

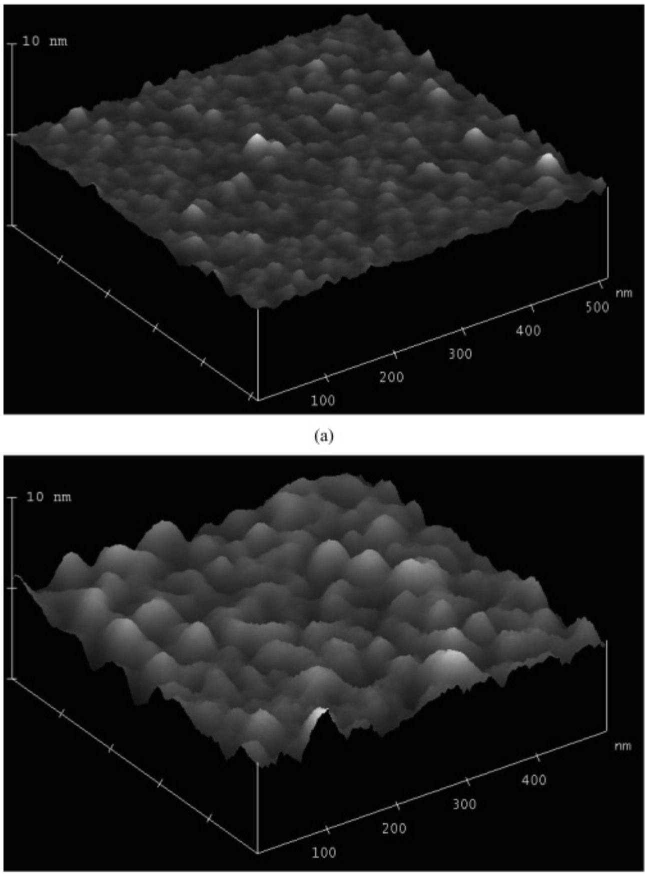

Figure 4. AFM 3D plot of (a) initiator monolayers **6** and (b) from trichlorosilane **8**.

advantage of ATRP over other living polymerizations lies in its tolerance to impurities and polar functionalities in the monomers.

The ATRP of styrene from the modified silicon wafers was conducted. After a 12 h reaction, the film thickness increased by 10 nm, and the advancing and receding water contact angles were 92° and 73°, respectively, which are characteristic of a polystyrene film. Molecular weight analysis (GPC) of the free polymer indicated $M_w = 10\,400$ g/mol and $M_w/M_n = 1.07$. The existence of polystyrene polymer brush was also verified by ATR−FTIR (Figure 2d). To test whether most chain ends were still “alive” after the polymerization, the same substrates were subjected to the same polymerization conditions; after 12 h, the film thickness increased by another 10 nm and showed the same water contact angle values. The free polymer displayed $M_w = 10\,500$ g/mol and $M_w/M_n = 1.08$. This result suggested that most chain ends remain active and were capable of successfully reinitiating additional monomer.

Conclusions

To graft polymer chains from the surface, a uniform and dense initiator layer on the silicon substrate is preferred. The initiator monolayer can be fabricated in many ways, of which self-assembly of trichlorosilanes on silicate substrates is widely used. To obtain a uniform initiator monolayer, allylsilane **3** was synthesized and used to functionalize a flat silicon substrate. Using AFM, the initiating monolayer **6** was found to be more uniform than the corresponding layer made with trichlorosilane **8**. Atom transfer radical polymerization (ATRP) was use to prepare polystyrene brushes **7**. Evidence for a living polymerization was demonstrated by sequential monomer addition. Tensiometry, ellipsometry, ATR−FTIR, and AFM were used to characterize the polymer brushes.

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