Synthesis of Polystyrene Brushes on Silicate Substrates via Carbocationic Polymerization from Self-Assembled Monolayers

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ABSTRACT: This paper describes the synthesis of polystyrene (PS) brushes on silicate substrates via carbocationic polymerization from self-assembled monolayers (SAMs). Carbocationic initiators, 2-(4-(11-triethoxysilylundecyl)phenyl-2-methoxypropane and 2-(4-trichlorosilylphenyl)-2-methoxy-d_3-propane, and their corresponding SAMs have been prepared. Monolayers were characterized by FTIR-ATR, contact angles, and X-ray reflectometry. Growth of PS brushes from these SAMs through carbocationic polymerization has been successfully achieved; factors that influence PS thickness include solvent polarity, additive, and $TiCl_4$ concentration. Sequential carbocationic polymerization on the same silicate substrate results in thicker PS films. FTIR-ATR study using a deuterated initiator indicates that the initiator efficiency is low, and the second carbocationic polymerization on the same sample involved initiation from both PS chain ends and unconsumed surface-immobilized initiators. Atomic force microscopy reveals a uniform and smooth PS brush surface with a roughness value of 0.3 nm (rms) for a 30 nm thick PS layer.

Introduction

Polymer brushes have attracted considerable attention in recent years. Many theoretical and experimental studies have been directed to elucidate structure and explore novel properties of polymer brushes.[1−11] In good solvents, densely grafted polymer chains are forced to stretch away from the interface to avoid overlapping, which is driven by steric repulsion between polymer chains. As a result, the system's entropy decreases. This behavior is fundamentally different from solution behavior in a good solvent in which polymer chains assume a random coil conformation. Research on polymer brushes has not been restricted to solvent effects, but also extended into pH sensitivity,[9] thermal sensitivity, oxidation−reduction,[10] and light response.[11] Polymer brushes have found applications in broad areas, including colloidal stabilization, tailoring surface properties,[12] and "chemical gates".[9,11]

Generally, there are two ways to fabricate polymer brushes: physisorption and covalent attachment. For polymer physisorption, block copolymers adsorb onto a suitable substrate with one block interacting strongly with surface and the other block interacting weakly with substrate.[13] Disadvantages of these systems include thermal and solvolytic instabilities due to the weak interaction between the substrate and the block copolymer, difficulties in the synthesis of block copolymers suitable for physisorption, and poor control of polymer chain density. Some of these drawbacks could be overcome by covalently tethering polymer chains to substrates. Tethering can be accomplished by either "grafting to" or "grafting from" techniques. In the "grafting to" technique,[14] preformed, end-functionalized polymer molecules react with an appropriate substrate to form an anchored polymer thin film. This approach is limited by steric hindrance for surface attachment. Macromolecules must diffuse through the formed polymer layer to reach the reactive sites; as a consequence, it is not easy to obtain a polymer film with high thickness and high grafting density. Compared to macromolecules, monomers can easily diffuse to reactive sites. Thus, the "grafting from" approach is a very promising method. "Grafting from" can be accomplished by treating a substrate with plasma or glow discharge to generate initiators followed by polymerization.[9] However, "grafting from" well-defined self-assembled monolayers (SAMs) is more attractive due to high density of initiators on the surface and a more well-defined initiation mechanism.[15,16] Also, progress in polymer synthesis techniques makes it possible to produce polymer chains with controllable lengths. Polymerization methods that have been used to synthesize polymer brushes include cationic,[17] anionic,[18] TEMPO-mediated radical,[19] atom transfer radical polymerization (ATRP),[20] and ring-opening polymerization.[21,22] Recently, we reported the synthesis and properties of diblock copolymer brushes by a sequential carbocationic polymerization and ATRP.[23]

Many of the literature studies have not directly dealt with the initiator efficiency of immobilized initiators. This issue is important especially in initiation systems in which a co-initiator or catalyst is needed to interact with initiator to produce active species, such as living carbocationic polymerization or atom transfer radical polymerization. It seems unlikely that all initiators bound to the surface can initiate polymerization because of steric hindrance from tethered chains. In this paper, we report the synthesis of tethered polystyrene (PS) brushes on silicate substrates from SAMs by carbocationic polymerization and present a discussion of initiator efficiency. We used nondeuterated and deuterated initiators to form SAMs on silicate ATR prisms or silicon wafers. FTIR-ATR was used to estimate the initiator efficiency. The factors that affect the thickness of the tethered PS layer will be discussed.

Results and Discussion

Synthesis of Immobilized Carbocationic Initiators. Silanes-**1** and **-2** are initiators for carbocationic polymerization.[24,32,34] The preparation of these two silanes are illustrated in Schemes 1 and 2. In the synthesis of silane-**1**, the coupling reaction between Grignard reagent **4** and compound **5a** was affected by

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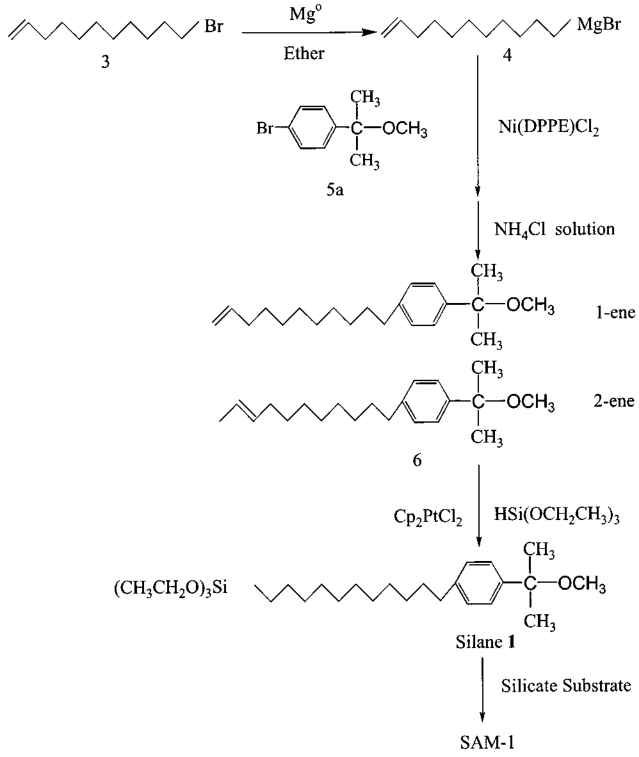
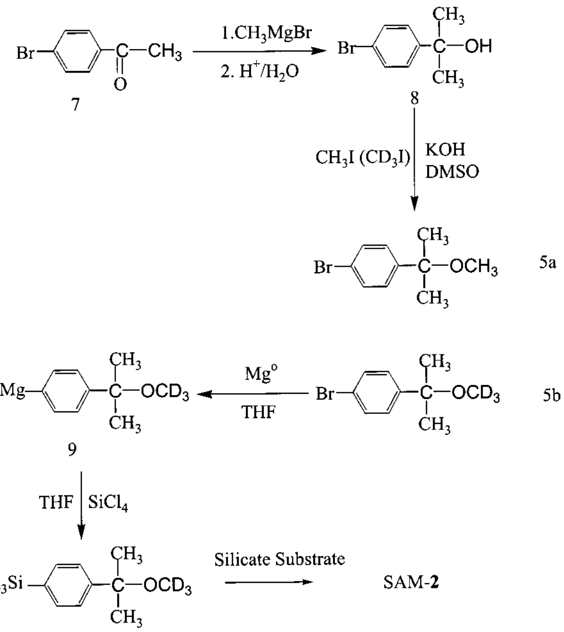
Scheme 1



Scheme 2



several factors including the catalyst concentration, reaction temperature, and reaction time. More catalyst, higher reaction temperature (refluxing temperature instead of room temperature), and longer reaction times produced higher yields of coupling. However, increasing catalyst concentration also increased double-bond isomerization; both the 1- and 2-alkene were obtained from coupling.[25] The optimal reaction conditions are described in the Experimental Section. Triethoxysilane-**1** was successfully prepared by a platinum-catalyzed (Cp_2PtCl_2) hydrosilylation of the terminal double bond with triethoxysilane ($HSi(OEt)_3$). ^1H NMR indicated that the 2-alkene was inert to triethoxysilane under this hydrosilylation condition. Since the 2-ene has no effect on the formation of SAMs, no attempt was made to remove it. The cumyl methyl ether carbocationic initiators are sensitive to acid. Our attempt to prepare the corresponding trichlorosilane initiator from **6** by hydrosilylation was unsuccessful. The trichlorosilyl group can induce an elimination reaction of the cumyl methyl ether to produce α-methylstyrene. In the preparation of triethoxysilane-**1**, Cp_2PtCl_2 was used in the hydrosilylation reaction instead of H_2PtCl_6 because H_2PtCl_6 is an acid that can also cause the elimination reaction of cumyl methyl ether. The synthesis of Cp_2PtCl_2 followed the literature procedure.[26]

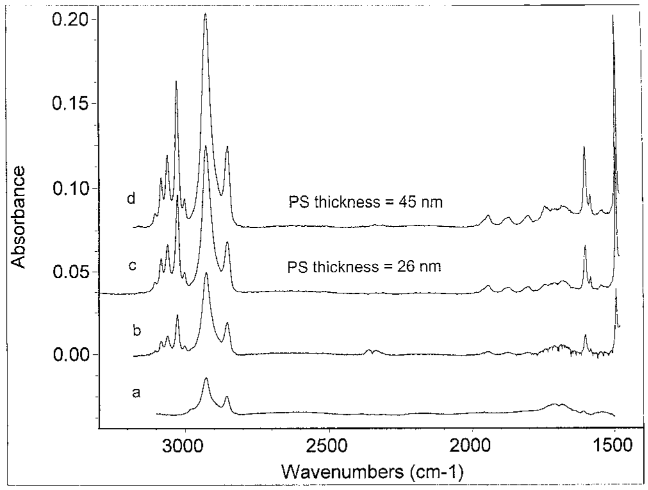


Figure 1. FTIR-ATR spectra of SAM-**1** (a) and tethered PS films from first (b), second (c), and third (d) carbocationic polymerization on SAM-**1**. See Table 3 for polymerization conditions.

In an attempt to synthesize trichlorosilane-**2** by coupling the Grignard reagent prepared from precursor **5b** and $SiCl_4$ in THF, a complex of silane-**2** and THF was obtained. ^1H NMR showed a 1:1 ratio of silane-**2** to THF. We believe this is an electron donor−acceptor complex, which was demonstrated by chemical shift changes of the THF peaks and a yellowish color.[27] Normally, the δ values of THF peaks are 1.82 and 3.71 ppm, while these two peaks shift to 1.90 and 4.00 ppm in the complex. THF is a Lewis base and can interact with a trichlorosilyl moiety which is a Lewis acid.

Preparation and Characterization of Self-Assembled Monolayers (SAMs). Deposition of silanes-**1** and -**2** on silicate substrates was performed using conventional techniques. Because triethoxysilanes are less reactive than trichlorosilanes, longer deposition times were used for silane-**1**. Pyridine was added in the deposition of silane-**2** to prevent acid-catalyzed elimination of the cumyl methyl ether group.

FTIR-ATR, contact angles, and X-ray reflectometry were used to characterize monolayers. For the SAM of silane-**1**, the IR intensities of the ν_{as} and ν_s CH_2 absorptions are in a reasonable range for a monolayer with an alkyl chain length of 11 carbon atoms (Figure 1a). The peak positions are 2927 and 2855 cm^{-1}, which indicate the monolayer is in a disordered or liquidlike state.[28] For the SAM of silane-**2,** the IR intensities of peak are weak; the FTIR-ATR spectrum (Figure 2a) is similar to initiator precursor **5b** (Figure 2b) except for subtle differences in peak positions of ν(C−D) which are attributed to the different substituents on the para position of benzene ring. Table 1 summarizes the contact angle results. Although the end groups in the two

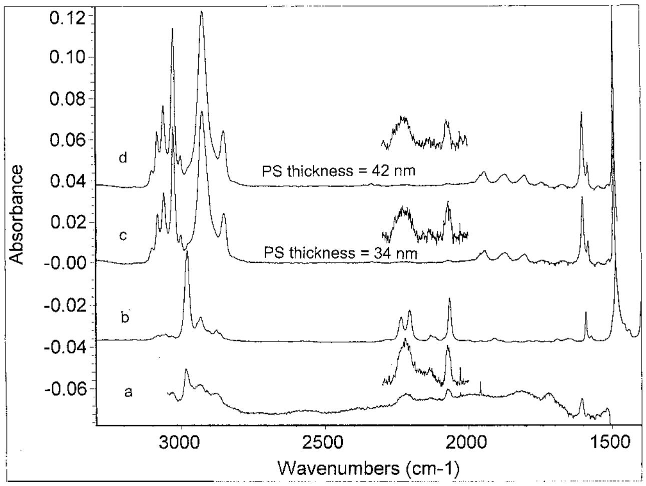


Figure 2. FTIR spectra of (a) SAM-**2** (ATR mode, absorption intensity is magnified 5×), (b) **5** (transmittance mode, intensity is arbitrary), and FTIR-ATR spectra of the tethered PS films from first (c) and second (d) carbocationic polymerizations carried out on SAM-**2**. Experimental conditions for first and second polymerizations of styrene are as follows: −78 °C, CH_2Cl_2 as solvent, $[St]_0 = 0.75$ M, $[DtBP]_0 = 0.012$ M, $[TiCl_4]_0 = 0.0236$ M.

Table 1. Water Contact Angles (deg) of SAMs-1 and -2 and Tethered PS Layers[a]

	θ_a	θ_r
SAM-**1**	88	69
SAM-**2**	67	51
PS layer from SAM-**1**	99	82
PS layer from SAM-**2**	99	82

[a] Standard deviation of contact angles ≤2°.

monolayers are the same, θ_a and θ_r are different. As discussed before, monolayer **1** is in the liquidlike state, and the presence of the alkyl chain makes a contribution to the contact angle.

X-ray reflectometry (XR) was performed on both monolayers. The results for SAM-**1** indicate a poorly organized monolayer compared to well-defined SAMs described in a previous publication.[25] The slower reactivity of the triethoxysilane and the steric hindrance of the aromatic cumyl methyl ether group may be responsible for imperfect monolayer. However, good results were obtained from the XR analysis of SAM-**2**. The thickness of SAM-**2** (0.98 nm) from XR matches the theoretical calculation (0.92 nm) very well.[29]

Surface-Initiated Carbocationic Polymerization. Our surface-initiated carbocationic polymerization primarily involved SAM-**2** due to the easier synthesis of silane-**2**.

Factors that influence surface-initiated carbocationic polymerization include solvent polarity, additives commonly used in living carbocationic polymerization, and $TiCl_4$ concentration. These factors directly influence the thickness of the tethered polystyrene (PS) layer. Table 2 summarizes the results of carbocationic polymerization carried out on SAM-**2** under various conditions. A common additive used in the solution living carbocationic polymerization is dimethylacetamide (DMA). DMA is an electron donor that coordinates to the Lewis acid, $TiCl_4$, and forms a complex. The polarity of the solvent and the presence of the additive have a strong influence. Di-*tert*-butylpyridine (DtBP) was used as a proton trap to suppress unwanted initiation by protons.

Table 2. Thickness of Tethered Polystyrene Layer from Surface-Initiated Carbocationic Polymerization Using SAM-2[a]

run no.	solvent	$[TiCl_4]_0$ (mM)	$[DMA]_0$ (mM)	PS thickness[b] (nm)
1	CH_2Cl_2	23.6	none	34
2	CH_2Cl_2/MCH[c]	23.6	none	7
3	CH_2Cl_2/MCH[c]	23.6	9.3	2.5
4	CH_2Cl_2	23.6	9.3	3.4

[a] Polymerization was carried out at −78 °C; $[St]_0 = 0.75$ M, $[DtBP]_0 = 0.012$ M, MCH = methylcyclohexane. [b] Determined by ellipsometry. [c] CH_2Cl_2/MCH (v/v, 1:1).

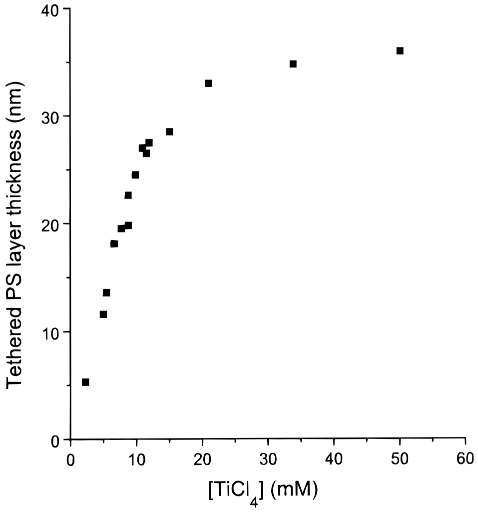


Figure 3. Variation in thickness of polystyrene brush with $[TiCl_4]$.

When 100% CH_2Cl_2 is used as polymerization medium, the thickness of PS layer can be as high as 34 nm. If the mixed solvent CH_2Cl_2/MCH (50/50, v/v) was used, the highest PS thickness achieved was 7 nm. Addition of DMA had the same effect on PS thickness that MCH did. The lowest thickness was obtained when the mixed solvent was used and DMA was added. CH_2Cl_2 is a polar solvent that stabilizes (or solvates) ionic species better than MCH, a nonpolar solvent. Thus, ionization is favored in CH_2Cl_2, and the concentration of active cationic species capable of initiation and propagation is higher than in the less polar solvent mixture of CH_2Cl_2 and MCH. As a consequence, the polymerization rate is higher, which results in a thicker polystyrene brushes.

DMA is an electron donor that forms a complex with $TiCl_4$. The complex is less acidic than the original Lewis acid and also less nucleophilic than the original nucleophile.[30] Thus, the effective $TiCl_4$ concentration decreased, resulting in a decrease in polymerization rate and a lower PS thickness.

Figure 3 shows the effect of $[TiCl_4]$ on PS thickness. The thickness increases with increasing $[TiCl_4]$ initially but levels off at higher $[TiCl_4]$. $TiCl_4$ is extremely sensitive to moisture and can yield protons that initiate carbocationic polymerization. Even though DtBP was added as a proton trap to suppress unwanted side reactions, untethered polystyrene was obtained from simultaneous solution polymerization. Generally, the amount of free PS increases with increasing $[TiCl_4]$, but the conversion is no more than 40%. Since β-proton chain transfer is largely suppressed by low temperature, adventitious moisture may be responsible for the initiation and polymerization of styrene in solution. Solution

Table 3. Thicknesses and IR Intensities of Tethered Polystyrene from Surface-Initiated Polymerization Using SAM-1[a]

run no.	$[St]_0$ (M)	$[DtBP]_0$ (M)	$[TiCl_4]_0$ (mM)	PS thickness (nm)	$I_{3025\ cm^{-1}}$
1	0.75	0.012	2.4	NA	0.0237
2	0.66	0.010	13.7	26	0.0599
3	0.75	0.012	11.8	45	0.0869

[a] Polymerization was carried out at −78 °C in CH_2Cl_2.

polymerization competes with surface-initiated polymerization for $TiCl_4$ and decreases the amount of $TiCl_4$ available to reinitiate the dormant species. As we know, excess BCl_3 or $TiCl_4$ is needed to achieve living polymerization of isobutylene when cumyl chloride or cumyl methy ether was used as initiator.[32−35] Another factor is the limited reaction cross-sectional area available to $TiCl_4$ and monomer near the surface compared with homogeneous solution polymerization. Considering these two factors, increasing $[TiCl_4]$ does not mean the amount of $TiCl_4$ that can reach the surface-immobilized initiators and tethered polymer chain ends increases proportionally. As a result, the increase in PS thickness slows down with increasing $[TiCl_4]$. In solution, the propagation rate is proportional to $[TiCl_4]^2$; we do not know whether the same rate order holds for surface-initiated polymerization.

Our successful formation of poly(methyl methacrylate)-*block*-PS brushes by subjecting PS brushes to atom transfer radical polymerization[23] is consistent with chlorine-terminated PS brushes. However, we do not know what percent chain ends are chlorine-terminated versus termination by indanyl ring formation or other side reactions.[31−35] The chlorine-terminated chain end can initiate a second carbocationic polymerization. If further carbocationic polymerization was run on these samples, the thickness should increase. Table 3 summarizes the results of sequential polymerizations performed on SAM-**1** prepared on an ATR crystal. After the first polymerization, the sample was removed from the polymerization mixture and cleaned by extraction with CH_2Cl_2 or THF overnight. The second polymerization was carried out on this same substrate under the described conditions. This procedure was repeated for the third run. The corresponding FTIR-ATR spectra are shown in Figure 1.

The thickness and IR intensities increase as expected. We tried to use X-ray photoelectron spectroscopy (XPS) to detect chlorine atom in a 28 nm thick tethered PS layer, but no chlorine was observed. The reasons for this could be that the concentration of PS chain ends existing in the XPS sampling region is below the detection limit of XPS, and the initiator efficiency is low (will be discussed later). Although the IR intensities and film thickness increase with the second and third polymerizations, it is not clear how the polymerization proceeds on the surface. Does initiation in the second or third polymerization begin from polymer chain ends? To clarify this issue and study initiator efficiency of surface-initiated polymerizations, we prepared deuterated initiator silane-**2** and the corresponding SAM-**2**. The monolayers were prepared on silicon ATR crystals and silicon wafers. FTIR-ATR was employed to monitor how surface-bound initiator concentration changes during the first and second carbocationic polymerization.

Figure 2c,d shows the FTIR-ATR spectra of the tethered PS layers after the first and second carbocationic polymerizations of styrene carried out on SAM-**2**. IR analysis indicated that a low percentage of surface-immobilized initiators were involved in the first polymerization; the intensity of peak located at 2070 cm^{-1} decreased slightly. A “control” polymerization experiment with an uncoated ATR crystal did not produce tethered PS, which confirms that tethered PS resulted from surface-initiated polymerization. We assume that the intensity of the ν(C−D) peak at 2070 cm^{-1} is proportional to the concentration of the immobilized initiator. We also assume that each $-OCD_3$ was converted to −Cl and started a polymerization by interaction of $TiCl_4$. Quantitative IR analysis of the ν(C−D) peak at 2070 cm^{-1} indicates only 7% initiator was consumed in the first polymerization. If we assume one initiator occupies 0.21 nm^2,[36] we calculate that the grafting density is 3 nm^2 per PS chain.

A second, sequential carbocationic polymerization under the similar conditions increased the thickness of polystyrene layer, which was demonstrated by increased IR intensities and film thickness. The initiator peak located at 2070 cm^{-1} decreased, which means the second carbocationic polymerization possibly initiated from both chlorine-terminated polystyrene chain ends and immobilized initiators. CH_2Cl_2 is a good solvent for polystyrene. The tethered PS chains stretch from the interface to avoid adjacent segment contacts. Therefore, the PS density is not high enough near the silicate surface to prevent $TiCl_4$ and monomer diffusion through the PS layer to immobilized initiator molecules. However, it is difficult to explain why the intensity of the ν(C−D) peak at 2070 cm^{-1} decreases more for the second polymerization.

From our FTIR-ATR analysis, most of the immobilized initiator molecules remained unconsumed under the typical polymerization conditions, which means that the propagation is favored relative to initiation from new sites. For the surface-initiated process, the propagation rate is higher than the initiation rate. We may attribute this observation to steric hindrance near to the silicate surface and much lower reaction cross-sectional area available to incoming $TiCl_4$ and monomer compared to solution carbocationic polymerization.

In general, surface chemistry differs from analogous solution reactions. Reasons for this difference may include reduced reagent diffusion to the interface and differences in solvation stabilization due to the underlying monolayer.

The surface of tethered polystyrene film is uniform. Ellipsometry results indicate the thickness variation across surface is 0.6 nm for a 30 nm thick PS film. This result was confirmed by AFM studies. Figure 4 shows a 1 × 1 μm^2 topographic image of a 30 nm thick tethered PS film which was obtained by tapping mode AFM. This image reveals a smooth and uniform polymer brushes surface with a roughness value of 0.3 nm (rms). The small thickness variation reflects a uniform polymerization throughout the silicon surface. We carried out surface-initiated carbocationic polymerizations on SAM-**1** and SAM-**2** under the same conditions described in Figure 2; a 38 nm PS film was obtained from SAM-**1**, and a 34 nm PS film was obtained from SAM-**2**. We attributed this difference to the higher mobility of the carbocationic initiator in SAM-**1**.

In conclusion, we have successfully prepared tethered PS films on flat silicate substrates. FTIR-ATR analysis of surface-immobilized deuterated initiators indicates

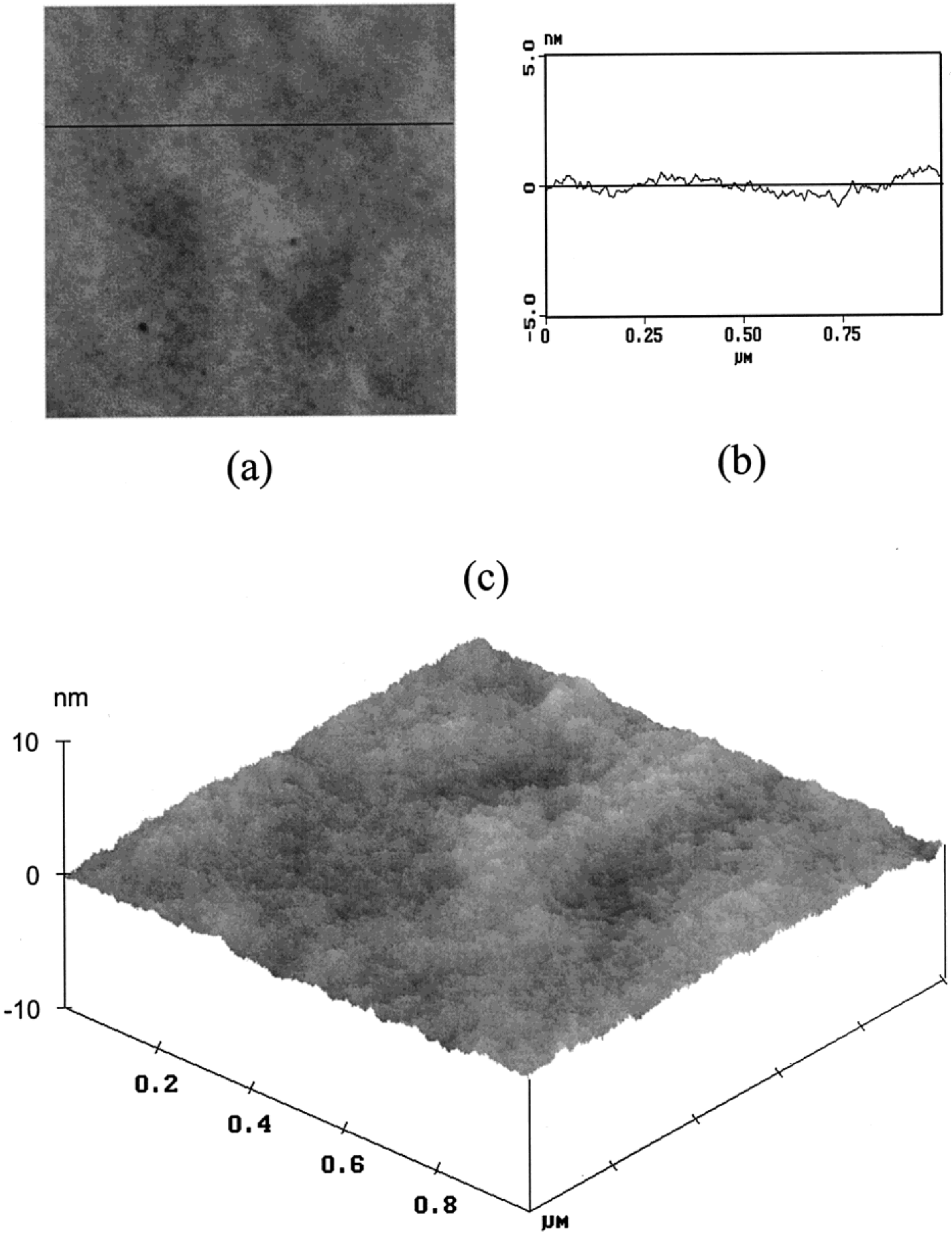


Figure 4. Atomic force microscopy (a) of a 30 nm thick grafted PS film, (b) depth profile along the indicated line, and (c) 3-D image.

only 7% consumption under the typical carbocationic polymerization conditions. FTIR-ATR analysis demonstrated that the second in-situ carbocationic polymerization possibly involved initiation from both tethered polystyrene chain ends and immobilized initiator molecules. Our technique could be applicable to other cationic monomers, such as isobutylene and styrene derivatives.

Experimental Section

Materials. Silicon ATR crystals (25 × 5 × 1 mm) were obtained from Harrick Scientific. Silicon wafers were purchased from Semiconductor Processing, Inc., and cut into the size of 25 × 10 mm using a diamond-tipped glass cutter. Hexadecane (Aldrich, 99%) was dried over 4 Å molecular sieves. THF was distilled from Na^0/benzophenone. 11-Bromoundec-1-ene (Pfaltz & Bauer) was used as received. $TiCl_4$

was used as received and stored in a drybox. Dimethylacetamide (DMA) and methycyclohexane were distilled over CaH_2 and stored in a drybox; CH_2Cl_2 was distilled over P_2O_5 and stored in a drybox. Di-*tert*-butylpyridine (DtBP) was dried over 4 Å molecular sieves and stored in a drybox. Stock solutions of DtBP in CH_2Cl_2, DMA in CH_2Cl_2, and $TiCl_4$ in CH_2Cl_2 were prepared in a drybox. Styrene was distilled from CaH_2 into a flask containing dibutylmagnesium and 1,10-phenanthroline and redistilled after a purple color persisted. The freshly distilled styrene was stored in a refrigerator in a drybox until use. All other reagents were purchased either from Aldrich or Fisher and used as received.

Characterization Methods. FTIR-ATR spectra were recorded using a Nicolet System 730 spectrometer using a modified 4XF beam condenser (Harrick Scientific). Spectra were recorded at 2 cm^{-1} resolution, and 500 or 1000 scans were collected. Contact angles were determined using a Rame Hart NRL-100 contact angle goniometer equipped with an environmental chamber and tilting base mounted on a vibrationless table (Newport Corp.). Advancing and receding values were determined using the tilting stage method. Drop values were 10 μL. Solution ^1H and ^{13}C NMR spectra were recorded using a Varian Gemini 200 MHz spectrometer. Ellipsometric measurements were performed on a Gaertner model L116C ellipsometer with He−Ne laser ($\lambda = 632.8$ nm) and a fixed angle of incidence of 70°. For the calculation of the layer thickness, a refractive index of $n = 1.500$ for the polystyrene was used. Atomic force microscopy (AFM) of tethered polystyrene (PS) brushes was performed using a Multimode scanning probe microscopy (digital instruments) in tapping mode with a silicon tip of resonance frequency of 260 kHz.

Substrate Preparation. ATR prisms and silicon wafers were cleaned by treatment with freshly prepared "piranha" solution (70/30, v/v, concentrated H_2SO_4/30% H_2O_2) at 90 °C for 1 h and were then rinsed with distilled water and dried with a stream of clean air. (**Caution**: *"piranha" solution reacts violently with many organic materials and should be handled with great care.)*

Preparation of Self-Assembled Monolayers of Silane-1 on Silicon Wafers and ATR Prisms. Freshly cleaned ATR prisms or silicon wafers were immersed into a solution of 0.1 mL of silane-**1** (containing 2-(4-(undec-9-enyl)phenyl)-2-methoxypropane) in 50 mL of hexadecane at 78 °C for 115 h. Following deposition, the substrates were rinsed with CH_2Cl_2. The samples were gently wiped with CH_2Cl_2-soaked cotton-tipped applicators to remove the precipitate on the surface.

Preparation of Self-Assembled Monolayers of Silane-2 on Silicon Wafers and ATR Prisms. A 0.6 g sample of silane-**2** (THF complex) was added to 60 mL of hexadecane, and the mixture was shaken; a cloudy solution was obtained. A 1.0 g sample of pyridine was added into the solution followed by immersion of freshly treated ATR prisms or silicon wafers. After 30 min, the sample was taken out of the solution, cleaned by CH_2Cl_2-soaked, cotton-tipped applicators, and rinsed with CH_2Cl_2.

Synthesis of 2-(4-(11-Triethoxysilylundecyl)phenyl)-2-methoxypropane (1). A solution of 9.95 g (0.05 mol) of 4′-bromoacetophenone (**7**) in 45 mL of anhydrous diethyl ether was added dropwise to 20 mL of a 3.0 M solution of CH_3MgBr in ether. The reaction was refluxed for 2 h followed by addition of a saturated NH_4Cl aqueous solution. The mixture was extracted 3× with diethyl ether. The combined ether extracts were washed with a saturated aqueous Na_2CO_3 and dried over anhydrous Na_2SO_4. Distillation under reduced pressure gave 9.0 g of colorless product (**8**) (84% yield). ^1H NMR ($CDCl_3$, 200 MHz): δ (ppm) 1.52 ($-CH_3$, 6H), 2.40 (1H, $-OH$), 7.34, 7.40 (4H, aromtic). ^{13}C NMR ($CDCl_3$, 200 MHz): δ (ppm) 148.40, 131.42, 126.62, 120.72, 72.31, 31.69.

A 2.5 mL (40 mmol) aliquot of CH_3I was added to a mixture of **8** (4.3 g, 20 mmol), 4.5 g of KOH (80 mmol), and 40 mL of DMSO; the reaction was left to stand overnight. The mixture was poured into 150 mL of water; CH_2Cl_2 was used to extract the aqueous layer. The combined extracts were dried over anhydrous Na_2SO_4. Distillation and silica gel chromatography afforded 2.75 g of product (60% yield). ^1H NMR ($CDCl_3$, 200 MHz): δ (ppm) 1.49 (s, 6H, $-CH_3$,), 3.05 (s, 3H, $-OCH_3$), 7.27 (d, 2H, aromatic), 7.45 (d, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 200 MHz): δ (ppm) 27.97, 50.80, 76.67, 121.05, 127.96, 131.58, 145.53.

The synthesis of **5b** is identical to that of **5a** except that CD_3I is used instead of CH_3I. ^1H NMR ($CDCl_3$, 200 MHz): δ (ppm) 1.49 (s, 6H, $-CH_3$), 7.27 (d, 2H, aromtic), 7.45 (d, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 200 MHz): δ (ppm) 27.77, 48.83, 49.26, 49.69, 50.12, 50.55, 76.31, 120.81, 127.71, 131.56, 145.30.

A 2.0 g (83.3 mmol) sample of Mg^0 turnings and a small iodine particle were placed in a three-necked flask equipped with a reflux condenser and purged with argon. A portion of a solution of 10.21 g (43.8 mmol) of 11-bromoundec-1-ene was added to the flask. The rest was added dropwise once the Grignard reaction initiated. After refluxing for 2 h, the Grignard reagent was transferred to an addition funnel and was added to a mixture of 98.5 mg of [1,2-bis(diphenylphosphino)ethane]dichloronickel(II) (0.5% mole ratio to **5a**), 8.36 g (36.5 mmol) of **5a**, and 10 mL of diethyl ether. The reaction mixture was refluxed for 60 h. The mixture was treated with a saturated NH_4Cl aqueous solution and extracted 4× with diethyl ether; the combined extracts were dried over anhydrous Na_2SO_4. Distillation under reduced pressure and chromatography over silica gel using 2:1 (v/v) of hexane/CH_2Cl_2 eluent afforded 2.2 g of product (20% yield). ^1H NMR ($CDCl_3$, 200 MHz): δ (ppm) 1.33, 1.65, 2.02 (m, $-CH_2$), 1.54 (s, 6H, $-CH_3$), 2.61 (t, 2H, $-CH_2-$), 3.08 (s, 3H, $-OCH_3$), 5.02 (m, 2H, 1-ene), 5.44 (m, 2H, 2-ene), 5.85 (m, 1H, 1-ene). Based on ^1H NMR, the product ratio of 1-ene to 2-ene is 56:44.

A 0.82 g sample of **6** was dissolved in 5 mL of CH_2Cl_2 followed by addition of 2.0 mL of triethoxysilane ($HSi(OEt)_3$) and 5 mg of dicyclopentadienylplatinum(II) chloride (Cp_2PtCl_2). The mixture was refluxed overnight. The solvent and unreacted triethoxysilane were removed in vacuo. ^1H NMR analysis indicated a mixture of the desired product and unreacted 2-ene. No further purifcation was attempted since the 2-ene product does not affect the formation of the SAM. ^1H NMR ($CDCl_3$, 200 MHz): δ (ppm) 1.27, 1.64 (m, $-CH_2-$, $-CH_3$), 1.53 (s, 6H, $-CH_3$), 2.00 (m, $-CH_2$, 2-ene), 2.60 (t, 2H, $-CH_2-$), 3.07 (s, 3H, OCH_3), 3.83 (m, 6H, $-OCH_2-$); 5.43 (s, 2-ene), 7.16 (d, 2H, aromatic), 7.32 (d, 2H, aromatic).

Synthesis of 2-(4-Trichlorosilylphenyl)-2-methoxy-d_3-propane (2). A 2.0 g (83.3 mmol) sample of Mg^0 turnings (activated by stirring in argon for 2 days) and a small iodine particle were placed in a three-necked flask equipped with a reflux condenser and purged with argon. A 4.0 g (17.2 mmol) sample of **5b** was dissolved in 20 mL of dry THF and was added dropwise. The reaction mixture was refluxed for 3 h and then transferred to an addition funnel attached to another flask and added slowly into a mixture of 10 mL of dry THF and 5 mL (7.42 g, 43.6 mmol) of $SiCl_4$. After 3 h, the solid precipitate was filtered off under argon atmosphere. THF and unreacted $SiCl_4$ were removed in vacuo. ^1H NMR shows the product is a 1:1 complex of the desired product and THF. ^1H NMR ($CDCl_3$, 200 MHz): δ (ppm) 1.54 (6H, $-CH_3$), 7.55 (d, 2H, aromatic), 7.79 (d, 2H, aromatic), 4.00 (4H, THF), 1.90 (4H, THF).

Surface-Initiated Carbocationic Polymerization. A typical surface-initiated carbocationic polymerization was conducted as follows. Stock solutions of $TiCl_4$, DtBP, and DMA in CH_2Cl_2 were prepared in a drybox. A stirring bar, an ATR prism and a silicon wafer were placed in a 50 mL Schlenk tube. In a drybox, 10 mL of CH_2Cl_2, 1 mL of styrene, and DtBP solution were added to the Schlenk tube. The Schlenk tube was then sealed with a rubber septum with a long syringe needle penetrating through the rubber septum containing $TiCl_4$ solution in the syringe. The Schlenk tube was removed from the drybox and cooled to −78 °C. The polymerization was started by injection of the $TiCl_4$ solution. The initial concentrations were $[\mathrm{styrene}]_0 = 0.75$ M, $[\mathrm{DtBP}]_0 = 0.012$ M, and $[TiCl_4]_0 = 0.012$ M. After 50 min, the reaction was quenched with prechilled methanol. The samples were rinsed several times with CH_2Cl_2 and extracted with THF or CH_2Cl_2 in a soxhlet extractor overnight. The samples were characterized by FTIR-ATR, contact angles, ellipsometry, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM).

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