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Anionic Synthesis of Block Copolymer Brushes Grafted from a 1,1-Diphenylethylene Monolayer

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ABSTRACT: A new method to prepare diblock copolymer brushes on oxide surfaces by anionic polymerization has been developed using a surface bound 1,1-diphenylethylene monolayer. Properties of the brushes were characterized by X-ray photoelectron spectroscopy (XPS), AFM, FTIR-ATR, X-ray reflectometry, and contact angle measurements. Films of thickness as high as 24 nm (by ellipsometry) were obtained by a "grafting from" strategy. Reacting a covalently attached monolayer of 1,1-diphenylethylene units with *n*-butyllithium created an initiator layer for the "grafting from" strategy. The corresponding 1,1-diphenylhexyllithium derivatives initiated the polymerization of a smooth brush of polyisoprene. AFM measurements of polyisoprene brushes indicated a surface microroughness of 0.3−0.5 nm (rms). The living chains ends in a polyisoprene brush were first functionalized to yield hydroxy-terminated polyisoprene before formation of a poly(ethylene oxide) block. Successful functionalization was evidenced by both a change in water contact angles, from $\theta_{\mathrm{adv}} = 86 \pm 2°$ for "grafting from" polyisoprene to $\theta_{\mathrm{adv}} = 47 \pm 3°$ for "grafting from" hydroxy-terminated polyisoprene, and changes in the XPS carbon (1s) scans. The presence of a peak at 286.7 eV in the XPS carbon (1s) scan of the hydroxy-terminated polyisoprene was consistent with the presence of carbon bonded to alcohol groups. The hydroxy-terminated poly(isoprene) brush was converted to the corresponding potassium alkoxide with diphenylmethylpotassium and used to initiate ethylene oxide polymerization. Successful polymerization of the PEO block was substantiated by a reduction in the water contact angle (to $\theta_{\mathrm{adv}} = 35 \pm 2°$) and XPS carbon (1s) scans.

Introduction

Tethered diblock copolymer brushes have generated much interest for use in nanolithographic patterning,[1] catalysis, and membranes.[2−4] The tendency of tethered diblock copolymers to microphase segregate and form unique periodic arrays and ordered nanostructures makes them ideal for the study and control of interfacial behavior.[3,5] Theoretical predictions[6,7] of unique, solvent-dependent micellar structures have also been verified experimentally.[8−12] Methods for preparation of tethered block polymers on surfaces have used physical adsorption of preformed polymers[13−15] or covalent attachment[16] by coupling of polymer functional groups with complementary groups on the grafting surface ("grafting to"). The "grafting to" methods are self-limiting because the grafted chains hinder the approach of additional polymer chains to the surface.

An alternative is to utilize "grafting from" techniques whereby self-assembled monolayers of initiators are used to grow chains outward from the surface. For example, conventional radical polymerization has been used to form polymer brushes utilizing surface-bound azo initiators.[17,18] However, recent studies have applied controlled and living polymerization methodologies for the preparation of tethered polymer brushes with well-defined structures and to prepare block copolymer brushes and chain-end functionalized polymer brushes. The use of controlled radical polymerizations such as ATRP,[11,12,19−21] TEMPO-mediated,[22] RAFT,[9] and iniferter methodologies[23] as well as controlled cationic[24,25] and anionic[26−42] polymerizations for surface grafting have been described. Living anionic polymerization, especially alkyllithium-initiated polymerizations of styrenes and dienes, should provide an excellent methodology for the synthesis of tethered polymer brushes with well-defined structures. Of course, not all anionic polymerizations are living or controlled.

Controlled anionic polymerization requires the proper choice of initiator, monomer, and solvent as well as high-purity reagents and an inert atmosphere. In each of several of the reported applications of anionic polymerization for the preparation of tethered polymer chains by the "grafting from" methodology, some aspect of the synthesis fails to meet the requirements necessary for controlled, living anionic polymerization even in homogeneous solution.[26−28,35,37] For example, controlled molecular weight requires the use of reactive, efficient initiators, e.g., alkyllithium compounds for styrenes and dienes. Initiating systems analogous to phenyllithiums are inefficient and unreactive even in polar media and insoluble in hydrocarbon solution.[43,44] *tert*-Butyllithium has been shown to be an inefficient initiator for styrene polymerization in hydrocarbon solution and should not be expected to be effective for initiating surface bound styrene units.[45−47] Anionic grafting reactions in tetrahydrofuran and toluene are not controlled because simple alkyllithium compounds and polymeric organolithium compounds are not stable in the presence of tetrahydrofuran,[48−50] and the use of toluene as solvent leads to chain-transfer reactions.[51,52] In addition, the use of tetrahydrofuran as solvent for alkyllithium-initiated grafting has been reported to lead to attack of Si−O−Si bonds and removal of the surface-attached monolayer of initiator or co-initiator moiety.[26] Finally, anionic polymerization of polar vinyl monomers such as acrylonitrile using alkyllithium initiators is not a living polymerization.[53−55] To exploit the full potential of anionic "grafting from" procedures for the preparation of well-defined, tethered polymer brushes, it is essential that procedures that would lead to controlled, living

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anionic polymerization in solution be utilized.

Recently, two groups have described the use of surface-bound monolayers of 1,1-diphenylethylene groups as co-initiating sites for anionic preparation of polymer brushes on flat silica and on clay surfaces.[29−31,37−42] These 1,1-diphenylethylene (DPE) groups provide sites for both "grafting to" and "grafting from" methodologies. DPE reacts quantitatively with simple alkyllithiums to form the corresponding monoaddition product, a 1,1-diphenylalkyllithium initiating species.[56] The absence of homopolymerization, due to steric hindrance, makes DPE chemistry very useful for a surface bound monolayer since this co-initiator will not homopolymerize on the surface as would styrene moieties.[26] 1,1-Diphenylalkyllithiums are reactive, useful initiators for the polymerization of styrenes and dienes at room temperature and above in hydrocarbon media, and they efficiently initiate controlled, anionic polymerization of (meth)acrylates and vinylpyridines at low temperature in polar solvents such as THF.[56]

A preliminary report[30] described the use of a surface-bound DPE monolayer on flat silica surfaces with *n*-butyllithium as initiator in benzene for isoprene polymerization for preparation of ω-hydroxy-functionalized polyisoprene brushes by functionalization of the resulting poly(isoprenyl)lithium chain end with ethylene oxide. A unique, living "grafting to" procedure has also been used to prepare tethered polystyrene chains by addition of poly(styryl)lithium to a 1,1-diphenylethylene self-assembled monolayer on silica.[30] An analogous preparation of polystyrene brushes has been reported using either *n*-butyllithium or *sec*-butyllithium;[37−42] however, these authors effected many of their polymerizations in the presence of unspecified amounts of THF,[37,39] in the presence of which organolithium compounds exhibit limited stabilities.[48−50] DPE co-initiating groups have also been used for surface-initiated polymerization of styrene from clay surfaces.[40]

Herein the utility of the DPE surface grafting methodology has been extended to the surface-initiated polymerization of diblock copolymers of poly(isoprene-*block*-ethylene oxide). For comparison, living α-functionalized poly(isoprenyl)lithium and telechelic polyisoprene polymers were grafted to a silicon wafer using the living "grafting to" methodologies with a DPE monolayer and via silyl chloride surface linking chemistry, respectively.

Experimental Section

Materials. Benzene, cyclohexane, and tetrahydrofuran were purified according to known procedures;[57] solvents were distilled, as needed, directly into polymerization reactors. Isoprene, styrene, and ethylene oxide were dried sequentially over CaH_2 and Bu_2Mg according to known procedures before being distilled into glass ampules.[57] *n*-Butyllithium and 3-(*tert*-butyldimethylsiloxy)-1-propyllithium were used as received from FMC Lithium Corp., and the concentrations were determined by the Gilman double titration method.[58] Imidazole was dried over P_2O_5 and purified by sublimation. Naphthalene was purified and dried by sublimation over P_2O_5 and taken into the drybox. Potassium metal and diphenylmethane were used as received from Aldrich. The polymerizations were carried out in all-glass, sealed reactors using standard high-vacuum techniques.[57] The silicon wafers (Semiconducting Processing) and FTIR-ATR crystals (Harrick Scientific Corp., 25 × 5 × 1 mm) were treated with a piranha solution (70% H_2SO_4/30% H_2O_2)[59] for 2 h at 90 °C and rinsed with copious amounts of Milli-Q water (18.2 MΩ) and absolute ethanol and dried under a stream of dry nitrogen (99.998%, Praxair). (**Caution***: "piranha" solution will react violently with organic materials and should be handled with care.*)

Characterization. Size exclusion chromatography (SEC) was performed using a Waters 150-C Plus instrument equipped with an differential refractometer, a viscosity detector (model 150R), and four Phenomenex Phenogel columns (500, 10^3, 10^4, and 10^5 Å). The SEC analysis was run in THF at 30 °C at a flow rate of 0.5 mL/min after calibration with polystyrene standards. X-ray photoelectron spectra were acquired using a PHI 5600 ESCA system with an Al Kα X-ray source, a 800 μm spot size, and a 45° take-off angle. Ellipsometry data were obtained on a Gaertner Scientific ellipsometer (model L116C) with a fixed angle of incidence (70°) and a He−Ne laser (633 nm). The advancing and receding water (Milli-Q) contact angles were measured using the sessile drop technique. FTIR-ATR spectra were recorded at 2 cm^{-1} resolution (500 scans) with a Nicolet System 730 spectrometer equipped with a Harrick Scientific 4XF beam condensor. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in $CDCl_3$ (99.8% D, Cambridge Isotope Laboratories) on a Varian Mercury 300 MHz spectrometer at room temperature. The NMR sample concentrations were 10 wt %. AFM images were obtained on a Park Scientific Instruments AutoProbe M5 using the tapping mode.

X-ray reflectivity (XR)[60,61] of the monolayers was performed using Cu Kα radiation ($\lambda = 1.54$ Å) generated by a rotating anode (Rigaku) operated at an excitation voltage of 50 kV and filament current of 200 mA. A constant relative wavelength resolution of $\delta\lambda/\lambda = 0.022$ and incident angle resolution of $\delta\theta/\theta = 0.002$ were used. Information on the structure of the samples was derived from the reflectivity curves by seeking the parameter values for a structural model that provided the best agreement between the experimental data and a calculated reflectivity curve for that model. The reflectivity was calculated using an optical matrix formalism with a four-layer model for monolayers and a five-layer model for polymer tethered to the monolayer.[62] This involved calculating first a continuous scattering length density profile using estimates for the parameters of the model. The reflectivity expected from this model structure was then calculated and compared with the XR data. The parameters were varied to optimize agreement between the calculated and experimental reflectivities. The "best fit" values of the model parameters may not have been unique, but considerable effort was expended to attempt to fit the data with other reasonable models and none provided superior agreement with the data.

Synthesis of 1-(4-Bromophenyl)-1-phenylethanol (1).[29] Diethyl ether (100 mL, >99.0%, Fisher Scientific) was transferred by cannula to a flask containing 4-bromobenzophenone (2.0 g, 0.0076 mol) (Aldrich) under argon. After addition of methylmagnesium iodide (3.0 M, 3.0 mL, 0.009 mol), the solution was heated under reflux overnight. The reaction was quenched by addition of a 10% aqueous HCl/MeOH solution. The product was recovered in 95% yield (2.0 g) and further purified using silica gel column chromatography (Silica Gel 60). IR: 3447 (OH), 3000−3100 (aromatic CH st), 2963 and 2872 (aliphatic CH, st), 1392 (CH_3, sy) and 1264 cm^{-1} (C−O st). ^1H NMR ($CDCl_3$): $\delta = 7.38$ (m, 9H, aromatic C−H) and 1.93 ppm (s, 3H, CH_3).

Synthesis of 4-Bromodiphenylethylene (2).[29] 1-(4-Bromophenyl)-1-phenylethanol (1) (2.01 g, 7.25 mmol) and *p*-toluenesulfonic acid (0.055 g, 0.29 mmol) were added to 200 mL of toluene. The solution was heated at reflux with a Dean Stark trap for 12 h. The product was purified by column chromatography (Silica Gel 60) using toluene as the eluent. The purity by HPLC was determined to be 99% using a HP diode array UV detector. IR: 3079 ($=CH_2$ st), 3055 (ar C−H st), 3026 (=CH− st), 1610 and 1485 cm^{-1} (ar C−C). ^1H NMR ($CDCl_3$): $\delta = 7.48$ (d, 2H, aromatic C−H), 7.34 (s, 5H, aromatic CH), 7.23 (d, 2H, aromatic CH) and 5.48 ppm (d, 2H, $=CH_2$). ^{13}C NMR ($CDCl_3$): $\delta = 114.99$ ($=CH_2$).

Synthesis of 1-(4-Dimethylchlorosilylphenyl)-1-phenylethylene (4) and 1-(4-Trichlorosilylphenyl)-1-phenylethylene (5). A small portion of 4-bromodiphenylethylene (BrDPE) (0.21 g, 0.81 mmol) in 20 mL of THF was added to magnesium (0.081 g, 3.32 mmol) (99+%, Aldrich) and heated under reflux temperature to start the reaction. The remaining BrDPE was added dropwise using an addition funnel, and the solution was heated at 45−50 °C for 5 h. The resulting Grignard derivative **(3)** was poured into a side ampule equipped with a Rotoflo stopcock and taken into the drybox; 2.0 mL (0.080 mmol) of the Grignard solution **(3)** was added to $(CH_3)_2SiCl_2$ (0.50 mL, 4.0 mmol). ^{1}H NMR ($CDCl_3$): $\delta = 5.47$ (d, 2H, $=CH_2$) and 0.14 ppm (s, 6H, $-SiMe_2Cl$). ^{13}C NMR ($CDCl_3$): $\delta = 114.5$ ($=CH_2$) and 0.42 ppm ($-SiMe_2Cl$). A similar reaction was performed by adding the Grignard derivative **(3)** (2.0 mL, 0.080 mmol) to excess $SiCl_4$ (0.46 mL, 4.0 mmol). The excess $SiCl_4$ was removed from the Schlenk flask under vacuum before adding solvent for monolayer deposition.

DPE Monolayer Formation (M-1 and M-2). Freshly cleaned silicon wafers (20 × 5 mm) and ATR crystals (25 × 5 × 1 mm) were taken into the drybox and added to a 20 mM solution of DPE-SiCl **(4)** in DMF with 0.009 g (0.13 mmol) of imidazole (Aldrich, 99+%). Different monolayer deposition times were used. After 30−44 h at room temperature, the wafers were removed, extracted with copious amounts of methylene chloride, and dried in a stream of dry nitrogen to yield M-1. A similar monolayer deposition was performed using a 20 mM solution of DPE-$SiCl_3$ **(5)** in DMF (Aldrich) with 0.009 g of imidazole (0.13 mmol) to yield M-2. The solution was decanted, and the wafers were washed with methylene chloride and dried under a stream of dry nitrogen. The silicon substrates for X-ray reflectometry analysis were 25 × 50 mm.

Preparation of Hydroxy-Terminated Polymer Brush (9) from M-1 (50/50 vol % Monomer Concentration). A silicon substrate (20 × 5 mm) with a DPE monolayer (M-1) was added to an all-glass reactor that was evacuated overnight. A solution of *n*-BuLi (25 mL, 2 mM) in benzene was added. After 8 h, the excess *n*-BuLi in benzene was transferred to a side ampule, and the wafer was rinsed five times with benzene by back-distillation. The side ampule containing the *n*-BuLi and 17.5 mL of benzene was removed by heat-sealing with a hand torch. A break-seal was smashed to introduce isoprene (7.5 mL). The concentration of isoprene was 50 vol % in benzene. After 87 h, ethylene oxide (7.5 mL, 150 mmol) was distilled from dibutylmagnesium into the reactor and reacted for 40 h. The quantity of ethylene oxide was sufficient to fully submerge the silicon wafer.

Preparation of Hydroxy-Terminated Polymer Brush (9) from M-1 (Neat Monomer). A silicon substrate with a DPE monolayer (M-1) was placed in a reactor that was evacuated overnight. The substrate was submerged in a solution of *n*-BuLi (25 mL, 2 mM) in benzene. After 8 h, the excess *n*-BuLi in benzene was transferred to a side ampule, and the substrate was rinsed multiple times with benzene from the side ampule to remove *n*-BuLi. The side ampule containing the *n*-BuLi and benzene was removed by heat-sealing with a hand torch. Ampulized isoprene (5 mL) was added neat by smashing the break-seal. After 3 days, ethylene oxide (2.0 mL, 40 mmol) was added to the isoprene and allowed to react for 2 days. A brush with the lowest contact angle was obtained by distilling isoprene from dibutylmagnesium in an attached ampule directly into the reactor without added solvent. The reactor was opened, and the substrates were removed and quenched with 10 mL of a 5 mM solution (0.05 mmol) of acetic acid in THF. After 1 h the wafers were washed multiple times with Milli-Q deionized water and absolute ethanol. Approximately 300 mg of polyisoprene with $M_n = 5 \times 10^6$ g/mol was recovered from solution. A similar reaction utilized degassed methanol to terminate the living poly(isoprenyl)lithium chain ends **(8)**. The polymer brushes on the silicon substrates were extracted overnight in a Soxhlet extractor using methylene chloride under reflux and dried under a stream of dry nitrogen.

Preparation of Polystyrene Polymer Brush from M-1 (Neat Monomer). A silicon wafer with a DPE monolayer (M-1) was placed in an all-glass reactor that was evacuated overnight. Then the silicon wafer was submerged in a solution of *n*-butyllithium (5 mL, 2 mM) in benzene. After 9 h, the excess *n*-butyllithium in benzene was transferred to a side ampule. The wafer was rinsed four times by back-distillation of benzene from the side ampule. The side ampule containing the excess *n*-BuLi and benzene was removed by heat-sealing with a hand torch. Styrene (3 mL) was added neat by smashing the break-seal. After 4 days, smashing a break-seal to a degassed methanol ampule quenched the polymerization of styrene. The silicon wafer was removed from the reactor and extracted overnight with methylene chloride under reflux.

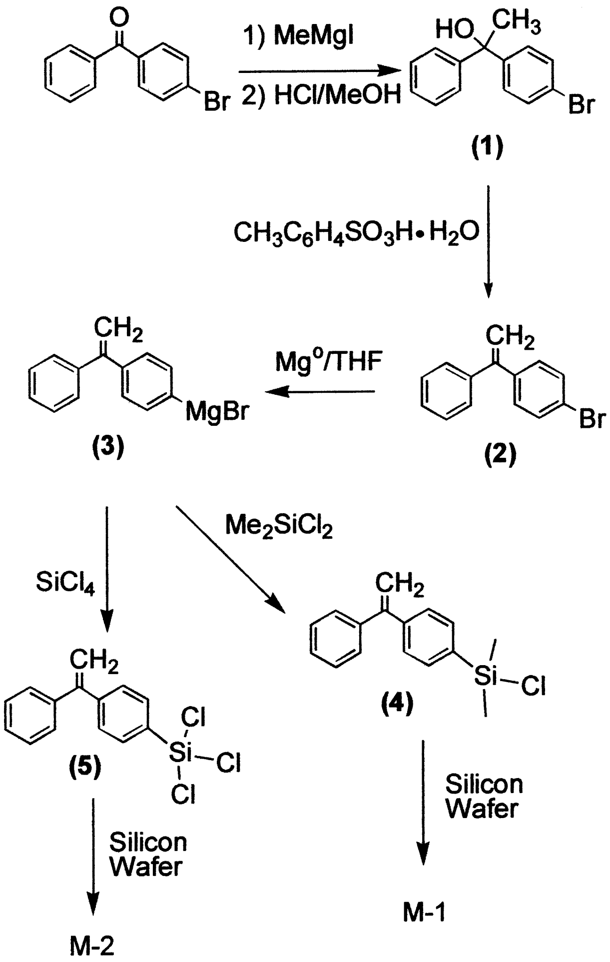
Synthesis of PI-*b*-PEO Diblock Copolymer (10). Diphenylmethylpotassium (DPMK) was prepared in the drybox by adding naphthalene (0.48 g, 3.8 mmol) and potassium (0.15 g, 3.8 mmol) to THF (40 mL). After 3 h, the resulting potassium naphthalenide was treated with diphenylmethane (0.63 g, 3.8 mmol) to yield DPMK. The hydroxy-terminated poly(isoprene) brush **(9)** was converted to the corresponding potassium alkoxide derivative with a 2 mM solution of DPMK in THF (25 mL) for 10 h. The excess DPMK in THF was decanted to a side ampule. After the wafer was rinsed four times by back-distillation of THF from the side ampule, the excess THF was removed by heat-sealing with a hand torch. The resulting surface-grafted potassium alkoxide derivative of polyisoprene was used to initiate polymerization of neat ethylene oxide (10 mL). After 3 days, the reaction was terminated by methanol to give a surface-grafted PI-*b*-PEO diblock **(10)**. The surface-grafted diblock was extracted overnight in a Soxhlet extractor using chloroform at reflux and dried under a stream of dry nitrogen.

Tethering Telechelic Poly(isoprene) (11) to Silicon Wafers and Diblock Synthesis (13). Isoprene (5.2 mL, 52 mmol) polymerization was initiated using 3-(*tert*-butyldimethylsiloxy)-1-propyllithium (5.0 mL, 2.5 mmol, 0.49 M) in cyclohexane at room temperature.[63] The resulting α-functionalized poly(isoprenyl)lithium (M_n = 3000 g/mol, M_w/M_n = 1.07, 2 mmol) was added dropwise to excess Me_2SiCl_2 (12.1 mL, 100 mmol) at 0 °C. After 5 h, the excess Me_2SiCl_2 was removed under vacuum at 40 °C. The telechelic polymer **(11)** (0.46 mmol) in benzene (4 mL) was filtered in the drybox through a 0.45 μm PTFE syringe filter to remove the precipitated LiCl. After filtration, a freshly cleaned silicon wafer, DMF (4 mL), and imidazole (0.69 mmol, 0.046 g) were added in the drybox. After 5 days, the silicon wafer was removed from the solution and rinsed multiple times with $CHCl_3$. The surface-grafted polymer was treated with 1% HCl/THF to give a hydroxy-terminated polymer brush **(12)**. After conversion of **12** to the corresponding potassium alkoxide using 0.05 mmol of DPMK in THF (10 mL), the excess DPMK was decanted to a side ampule. After the wafer was rinsed four times by back-distillation of THF from the side ampule, the ampule containing the excess THF was removed by heat-sealing with a hand torch. Ethylene oxide (10 mL) was distilled from neat Bu_2Mg onto the wafer, and neat monomer was polymerized for 4 days. The reaction was quenched with methanol, and the surface-grafted PI-*b*-PEO diblock **(13)** was extracted overnight with $CHCl_3$ under reflux conditions.

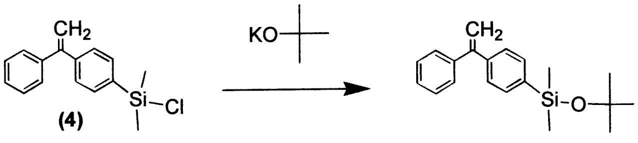
Synthesis of ω-Chlorodimethylsilylpolyisoprene (14) and Tethering Reaction. Isoprene (4.4 mL, 44 mmol) polymerization was initiated by *sec*-BuLi (1.02 mL, 1.45 M) in benzene. The resulting poly(isoprenyl)lithium (M_n = 1930 g/mol, M_w/M_n = 1.03, 1.4 mmol) was added to excess $(CH_3)_2SiCl_2$ (42.0 mmol). The excess silyl chloride was removed under vacuum. ^{1}H NMR ($CDCl_3$): $\delta = 0.44$ ppm (6H, $Si(CH_3)_2Cl$). ^{13}C NMR ($CDCl_3$): $\delta = 2.83$ ppm ($Si(CH_3)_2Cl$). The polymer was tethered to a silicon ATR−IR crystal using known procedures for reacting silyl chlorides with hydroxyl groups.[4,64] ATR−IR: 2962, 2930, and 2855 cm^{-1} (aliphatic C−H st).

Grafting to M-1 and M-2. Poly(styryl)lithium (M_n = 940 g/mol, M_w/M_n = 1.09) in benzene (10 mL, 60 mM) was added to M-1 for 12 h before quenching with methanol and extracted sequentially with methylene chloride and absolute ethanol. In a separate reaction PSLi in benzene (M_n = 22 000, M_w/M_n = 1.01, 15 mL, 8 mM) was added to both M-1 and M-2 for 8 h before quenching with methanol. The silicon wafers were removed from solution and washed sequentially with methylene chloride, THF, and ethanol and dried with nitrogen.

Scheme 1. Synthesis of Monolayers (M-1 and M-2)



Scheme 2. Synthesis of Derivative of 4 for Mass Spectrometry Analysis



Results and Discussion

Preparation and Characterization of 1,1-Diphenylethylene Monolayers. 1-(4-Dimethylchlorosilylphenyl)-1-phenylethylene **(4)** and 1-(4-trichlorosilylphenyl)-1-phenylethylene **(5)** were synthesized as outlined in Scheme 1. Structure proof for 1-(4-dimethylchlorosilylphenyl)-1-phenylethylene **(4)** was established by analysis with fast atom bombardment (FAB) mass spectrometry. Since silyl chlorides will react with the matrix (nitrophenols or glycerol) employed for fast atom bombardment mass spectrometry, a derivative of the 1-(4-dimethylchlorosilylphenyl)-1-phenylethylene **(4)** was made by reacting the silyl chloride with potassium *tert*-butoxide as shown in Scheme 2. A peak for the molecular ion of the derivative, $[M + H]^+$, was observed at *m/z* 311 (*m/z* calculated 311.17). In addition, peaks for other isotopomers containing ^{13}C were observed at *m/z* 312, 313, and 314.

The 1,1-diphenylethylene unit (DPE) was chosen as the surface-bound co-initiator group because 1,1-diphenylethylene is a nonhomopolymerizable molecule that will react quantitatively with organolithium compounds,[56] cations,[65] and radicals.[66-69] It was assumed that the surface of the silicon wafer after treatment with piranha solution afforded approximately 5 OH groups nm^{-2} as established by other researchers using a deuterium-exchange method.[70] The monolayer was formed on the silicon wafer using well-known procedures for the reaction of hydroxyl groups with silyl chlorides.[4,64] Analogous to conditions for protection of alcohols using *tert*-butyldiphenylsilyl chloride,[64] *N*,*N*-dimethylformamide (DMF) and imidazole were used to catalyze the linking of 4-dimethylchlorosilyl-1,1-diphenylethylene **(4)** and 1-(4-trichlorosilylphenyl)-1-phenylethylene **(5)** onto silicon wafers at room temperature in a nitrogen atmosphere drybox to form monolayers M-1 and M-2, respectively. The advancing contact angle (θ_{adv}) for a freshly cleaned silicon wafer was 10°. The contact angle for DPE monolayers M-1 and M-2 varied with deposition time. As the monolayer deposition time increased from 30 h ($\theta_{adv,M-1} = 79 \pm 2°$, $\theta_{rec,M-1} = 65 \pm 2°$) to 44 h ($\theta_{adv,M-1} = 89 \pm 2°$, $\theta_{rec,M-1} = 83 \pm 2°$), the contact angles increased and the hysteresis decreased, indicating a more well-defined monolayer. The advancing and receding contact angles for M-2 were 66 ± 4° and 50 ± 4°, respectively. The thicknesses of M-1 and M-2 determined by X-ray reflectometry are shown in Table 1. The thickness of M-1 estimated from ellipsometry measurements was 0.9 nm when assuming a two-layer model (silicon oxide and brush) and a value of 1.60 for the refractive index of the grafted layer. The thickness from ellipsometry was larger than that from XR by approximately 0.2 nm. This difference may be rationalized as resulting from differences in the sensitivity of the two techniques to the interface structure between SiO_2 and the monolayer.[71] The monolayers made from 1-(4-dimethylchlorosilylphenyl)-1-phenylethylene **(4)** (M-1) gave more reproducible thicknesses than did monolayers made from 1-(4-trichlorosilylphenyl)-1-phenylethylene **(5)** (M-2). Other researchers have also found that trichlorosilanes are more susceptible to the formation of oligomeric and cyclic structures than monochlorosilanes when performing depositions in the presence of water.[72,73]

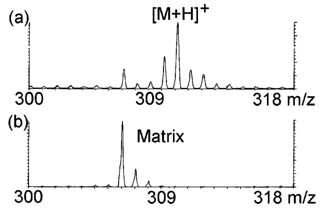


Figure 1. Fast atom bombardment mass spectrum for (a) 1-(4-dimethylchlorosilylphenyl)-1-phenylethylene and (b) pure matrix (*m*-nitrophenol).

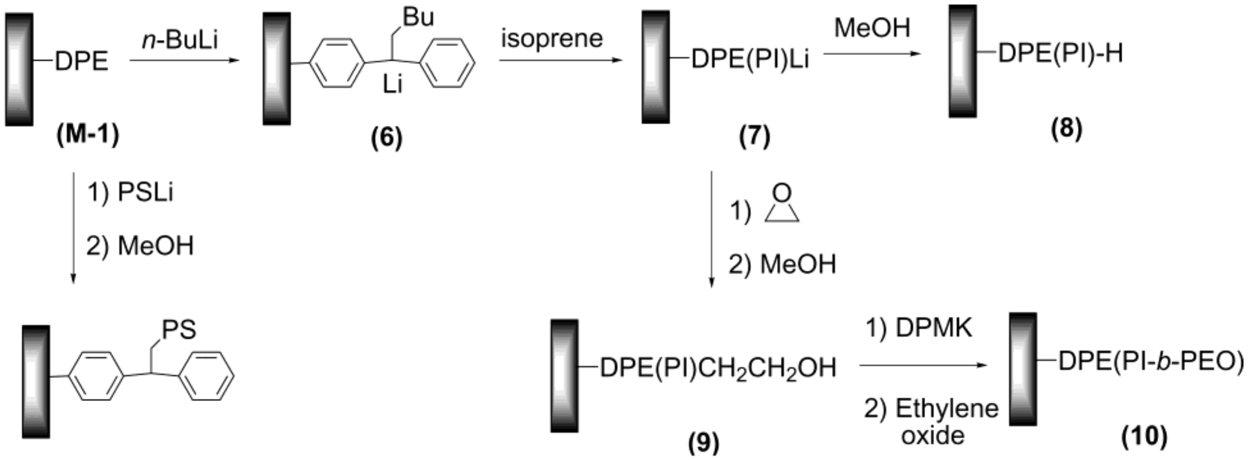
Table 1. Monolayer Parameters from XR and Contact Angle Measurements

	M-1 (Si−Cl based)	M-2 (Si−Cl_3 based)
thickness (nm)[a]	0.72 ± 0.1	0.78 ± 0.1
roughness, rms (nm)[a]	0.17 ± 0.025	0.18 ± 0.025
θ_{adv} (deg)[b]	81 ± 3	66 ± 4
θ_{rec} (deg)[b]	72 ± 2	50 ± 4
area per DPE (1/*A*)[c] (nm^2/DPE unit)	0.41	0.38

[a] Determined by XR. [b] Measured using a sessile drop. [c] Calculated from eq 1.

A determination of the number of DPE molecules per unit area can be made from the electron density, ρ_{el}, of the monolayer obtained from X-ray reflectometry mea-

Scheme 3. "Grafting from" Diblock Synthesis on a Silicon Wafer



surements.[71,74] The average area per molecule, A, can be calculated from eq 1,

$$A = N_e/d\rho_{el} \qquad (1)$$

where N_e is the number of electrons per DPE molecule, d is the thickness of the monolayer (Table 1), and ρ_{el} is the electron density. The electron density was determined by dividing the scattering length density (cm/Å^3) by the classical electron radius (2.82×10^{-13} cm).[61] This yields a value of 0.41 nm^2/DPE unit for M-1 and 0.38 nm^2/DPE unit for M-2. The cross-sectional area of alkyldimethylsilyl groups has been reported to be 0.32–0.38 nm^2 per molecule for densely packed monolayers.[73] The analogous cross-sectional area of 0.41 nm^2 per DPE molecule obtained from X-ray reflectometry for M-1 (Table 1) compares reasonably well with the corresponding values for alkyldimethylsilyl groups, since a DPE molecule would not be expected to pack as well as an alkyl chain in an all-trans conformation (no gauche defects). The monolayer M-2 did not achieve the high packing density of 0.21 nm^2 per molecule reported for the self-assembly of alkylsiloxane monolayers made from trichlorosilanes.[71] However, if each 1-(4-trichlorosilylphenyl)-1-phenylethylene molecule were bonded to two oxygen atoms on the silicon surface,[73] then the surface would be saturated since we expect 5 hydroxyl groups nm^{-2}.[70] This average area per DPE molecule allows surface grafting to be realized since polymer brushes will occupy a much larger cross-sectional area than is occupied by a surface-bound co-initiator group. For example, a "grafting to" polystyrene brush with M_n = 4000 has a surface attachment density of 3.4 nm^2 per chain.[75] The integrity of the monolayers was evidenced by the low values of rms surface roughness determined from XR, 0.17 ± 0.025 nm for M-1 and 0.18 ± 0.025 nm for M-2. The rms surface roughness for M-1 as determined by AFM for multiple 1×1 μm^2 areas was 0.4 ± 0.1 nm.

XPS showed a carbon (1s) signal at 284.8 eV for the DPE monolayer. Aromatic carbons have been reported at 284.76 eV for polystyrene.[76] A small "shake-up" peak was observed for the π-electrons at 291 eV. The atomic concentration of carbon (1s) was 17%. Because the escape depth of core electrons (5–10 nm) is 4 times larger than the thickness of the monolayer, substantial silicon (2p) (45%) and oxygen(1s) (38%) signals were detected for the DPE monolayer in addition to the carbon (1s) signal.

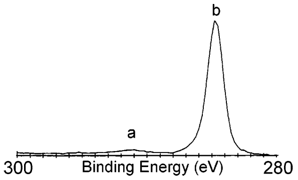


Figure 2. XPS carbon (1s) scan of the polystyrene layer resulting from the grafting of PSLi (M_n = 940 g/mol, M_w/M_n = 1.09) to DPE immobilized on a silicon wafer (M-1) showing (a) the phenyl "shake up" and (b) carbon bonded to carbon.

Table 2. XPS Atomic Concentration for Surface Grafting Poly(styryl)lithium to a 1,1-Diphenylethylene Monolayer

sample	% C$_{1s}$	% O$_{1s}$	% Si$_{2p}$
DPE (θ_{adv} = 79 ± 2°)	17 ± 1	38 ± 2	45 ± 2
(PS)DPE (θ_{adv} = 86 ± 2°)	30 ± 2	32 ± 2	38 ± 2

Preparation of Surface "Grafting to" Homopolymers. To demonstrate the utility of the 1,1-DPE monolayer, poly(styryl)lithium oligomers (M_n = 940 g/mol, M_w/M_n = 1.09) were reacted with monolayer M-1 (Scheme 3). The thickness of the monolayer, measured by ellipsometry, increased from 0.9 to 2.0 nm after reaction with PSLi. From eq 2, the surface coverage, Γ, can be determined from the brush height, h, and the density, ρ, of the polystyrene layer:[77]

$$\Gamma = h\rho \qquad (2)$$

Assuming the bulk density of the brush layer may be approximated by the bulk density of atactic polystyrene (ρ = 1.05 g/cm^3), the grafting density was 2 mg/m^2. This value falls into the typical range of less than 5 mg/m^2 for tethered layers made by the "grafting to" approach.[18] Also, the grafting of carboxylic acid-terminated polystyrene chains (M_n = 4500 g/mol) to epoxide monolayers gave a tethered polymer layer with similar thickness (2 nm by ellipsometry) and surface coverage (2 mg/m^2).[77] In the present work, the atomic concentration of carbon increases with increasing thickness. Figure 2 shows the carbon (1s) scan showing a peak for saturated carbons at 284.8 eV and the shake-up satellite (291 eV) for the π to π* transition as documented for XPS of polystyrene standards.[76] The increase in thickness and increase in the atomic concentration of carbon (XPS) after reaction with PSLi (shown in Table 2) demonstrate that PS was grafted to the DPE monolayer.

Poly(styryl)lithium (M_n = 22 000 g/mol, M_w/M_n = 1.01) was grafted to the monolayer M-2, and the

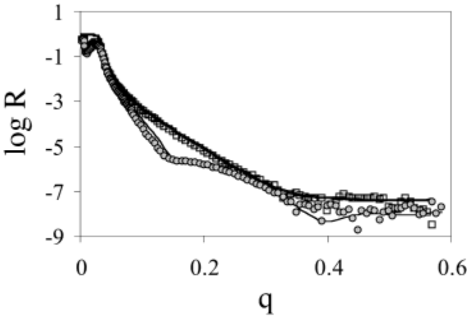


Figure 3. X-ray reflectometry data for DPE monolayer (M-2) before grafting (open squares) and after grafting poly(styryl)lithium (M_n = 22 000 g/mol, M_w/M_n = 1.01) to the surface-bound DPE groups (open circles). The solid lines represent model fits to the data, for which q has units of Å^{-1}.

thickness as measured by XR increased from 0.78 ± 0.18 to 2.03 ± 0.34 nm. The surface roughness (rms) also increased from 0.18 nm for the well-ordered monolayer of initiator to 0.34 nm for a tethered polymer layer. The surface roughness is influenced by the history of the sample. Less surface roughness would occur if the solvent was evaporated slowly compared to rapid removal of the solvent. Because the surface roughness (rms) is less than the film thickness, the surface was presumably completely covered by the tethered polymer layer. Figure 3 shows the reflectivity curves for the monolayer (M-2) before and after grafting poly(styryl)lithium.

Qualitatively, the appearance of well-defined fringes for the grafted layer indicates a thickening of the organic film upon reaction with PSLi. The number of chains on the surface can be approximated from eq 1 using the film thickness from X-ray reflectometry and the value of ρ_{el} from the XR analysis. Determination of the value of N_e was the major source of error (~5%). It was assumed that the value of M_n determined by SEC for free chains in the reaction mixture also pertained to the tethered chains. The free chains had a very narrow molecular weight distribution (M_w/M_n = 1.01). It is noted that others have reported that in the case of tethering amine-terminated polysulfones to epoxide monolayers the fraction of chains tethered at the surface (M_n = 13 160, M_w/M_n = 1.9) had a somewhat lower molecular weight and polydispersity than did the chains in solution (M_n = 13 950, M_w/M_n = 2.3).[78] From eq 1, the average area per chain for the grafted layer was 44 nm^2 per chain. Tethering of ω-primary amine functionalized polystyrene (M_n = 20 000 g/mol) to an epoxide monolayer was reported to give 67 nm^2 per chain at saturation.[75]

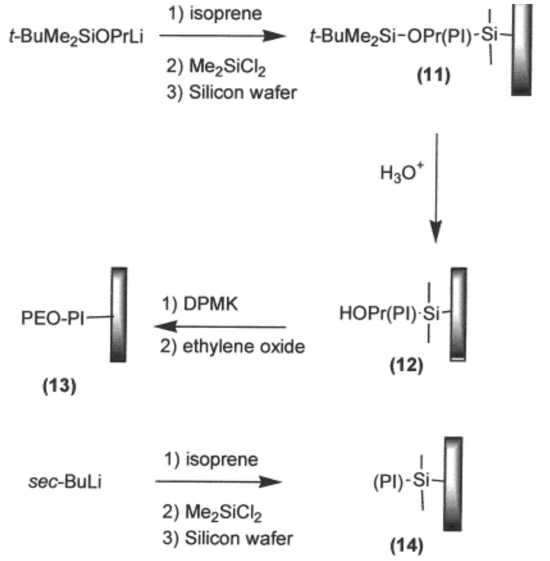
Preparation of Surface "Grafting from" Homopolymer Brushes. Extending a system that offers a controlled living anionic polymerization in homogeneous solution to the surface should provide an excellent methodology for the synthesis of polymer brushes with well-defined structures. For this reason, the 1,1-diphenylethylene monolayer (Scheme 3) was treated with excess *n*-BuLi (2−5 mM) in benzene for 8−9 h. It was assumed that any remaining surface hydroxyl groups (SiOH) not protected by DPE−SiCl were rendered inactive by the treatment with *n*-BuLi. *n*-Butyllithium will react quantitatively with 1,1-diphenylethylene[56] and was chosen as co-initiator because it is less reactive than *sec*-BuLi[50] and should be less likely to cleave the Si−O−Si bonds, damage the monolayer, and produce nonuniformity. In addition, hydrocarbon solvent was used for chain-end stability and to prevent Si−O−Si bond cleavage. The use of THF not only is detrimental to anionic chain-end stability[48−50] but also promotes Si−O−Si bond cleavage by organolithiums.[26] Not all the surface-immobilized DPE units were expected to initiate polymerization. However, ensuring the living nature of the polymerization was judged to be more important than achieving quantitative initiator efficiency. For an analogous cationic system[24] an initiator efficiency of 7% was reported, though film thicknesses up to 30 nm were achieved in that work. Future experiments on high-surface-area substrates will allow the calculation of initiator efficiency.[38,40]

After conversion of M-1 to the corresponding 1,1-diphenylhexyllithium derivative (Scheme 3), isoprene or styrene was added to produce the corresponding "grafting from" poly(isoprenyl)lithium or poly(styryl)lithium brushes. Prior to monomer addition, the excess *n*-butyllithium was poured into a side ampule, and the silicon wafer or ATR crystal was rinsed 4−6 times by back-distillation of benzene to ensure removal of excess initiator. However, even with careful washing, 100−300 mg of polymer with M_n in the range of 5 × 10^6 g/mol was isolated in the washing solutions after polymerizations. The surface-initiated anionic polymerizations were terminated with degassed methanol. All polymer brushes were extracted overnight with CH_2Cl_2 under reflux to remove noncovalently bound polymer. It was found that 4−5 h of heating with CH_2Cl_2 under reflux was sufficient to remove spin-coated poly(oxymethylene) (M_n = 2300 g/mol) or polyisoprene (M_n = 3000 g/mol) films of comparable thicknesses.

A "grafting from" polyisoprene brush **(8)** ($\theta_{adv} = 86 \pm 2°$, $\theta_{rec} = 76 \pm 2°$) was formed by polymerization of neat monomer for 1.5 days to give a 5 nm thick film (by ellipsometry) after extraction overnight by methylene chloride under reflux. In contrast, a "grafting to" polyisoprene layer **(14)** ($\theta_{adv} = 83 \pm 3°$, $\theta_{rec} = 76 \pm 2°$) was deposited for 5 days from a benzene/DMF solution to give a 1.4 nm (by ellipsometry) thick film. The contact angle results for the polyisoprene brushes were in agreement with expectations based on measurements of a polyisoprene film ($\theta_{adv} = 87 \pm 3°$) cast from a toluene solution. AFM experiments (tapping mode) on the unfunctionalized PI brush **(8)** revealed surfaces with small microroughnesses of 0.3−0.5 ± 1 nm (rms) for multiple 1 × 1 μm^2 regions.[30] The surface roughness, as measured by AFM, for multiple 1 × 1 μm^2 regions of the "grafting to" poly(isoprene) **(14)** was 0.9 ± 0.2 nm (rms). Ellipsometric thicknesses as high as 24 nm for polystyrene brushes ($\theta_{adv} = 91 \pm 2°$, $\theta_{rec} = 85 \pm 2°$) and 10 nm for polyisoprene brushes were obtained with the "grafting from" strategy using M-1. The largest brush thicknesses (by ellipsometry) were obtained by polymerizing neat monomer. The 24 nm thickness for the "grafting from" polystyrene brush is larger than the 16.1 nm thickness reported elsewhere for a polystyrene "grafting from" a DPE monolayer,[37] the 18 nm thickness for a PS brush "grafting from" a biphenyl monolayer,[27] and the ~10 nm thickness for a PS brush "grafting from" surface bound styrene units.[26]

Atomic concentrations of surface components can be accurately determined in many cases using the analysis of peak areas in X-ray photoelectron spectroscopy spectra.[79] A low-energy electron gun (5−10 eV) was used to prevent charging of the polymer surface, and the carbon (1s) and silicon (2p) peak positions were used

Scheme 4. Surface Grafting of Telechelic Polymers To Give a Hydroxy-Terminated PI Brush (9) and PI-*b*-PEO Diblock (10)



as charge references. The atomic concentration of carbon from the carbon (1s) scans was 39% for the 5 nm thick "grafting from" PI brush **(8)**. The significant amount of silicon (29%) and oxygen (32%) detected for the 5 nm thick "grafting from" PI brush (8) was expected. The sampling depth, corresponding to 95% of the signal using Al Kα radiation at a 45° take-off angle, is 6.9 nm for silicon (2p) and 5.2 nm for oxygen.[80]

Preparation of Surface "Grafting from" and "Grafting to" Hydroxy-Terminated Polyisoprene. After addition of isoprene to **6**, the resulting poly(isoprenyl)lithium **(7)** chain ends were functionalized[81,82] by addition of ethylene oxide **(9)** (Scheme 3). Ethylene oxide will react with polymeric organolithiums to give a hydroxy-terminated polymer in quantitative yield without oligomerization of ethylene oxide for stoichiometric amounts of ethylene oxide ($[EO]/[Li] = 3-4$).[81-83] Although the reaction of the living chain ends of the polymer brushes would be expected to exhibit different kinetics than dilute solution species,[84] it was assumed that the chemistry of functionalization would be analogous to dilute solution chemistry. Since no precedent exists in the literature for functionalization of living carbanion chain ends on silicon wafers with ethylene oxide, a separate "grafting to" strategy was used (Scheme 4) to prepare an analogous surface-grafted ω-hydroxy-functionalized polyisoprene brush **(12)** for comparison. Although the grafting density of **12** was expected to be lower than that provided by the "grafting from" strategy, the relative amount of functionalization and the effects of functionalization on the surface properties could be compared since every chain end for **12** formed by "grafting to" will have a hydroxyl functional end group. The thickness of **12** was 2 nm (ellipsometry) after a grafting time of 5 days. In the "grafting from" strategy (Scheme 3), the thickness of the monolayer (M-1) increased from 0.9 ± 0.2 to 5 ± 1 nm for the HO(PI)DPE brush **(9)** after a neat polymerization time of 1.5 days.

That the brushes in fact contained hydroxy-functionalized chains was proven using both XPS and contact angle measurements. In interpreting the contact angle measurements, it is necessary to note that the water contact angle observed for a brush of hydroxy-terminated PI may well vary with the conditions under which the measurement is made since the surface of this brush is capable of rearrangement. In covalently bound SAMs of short chains, such as silanes,[72] the tethered molecules are fully stretched, tightly packed, and permanently tethered. They cannot easily rearrange, so the functionalities at the ends of the chains have to present themselves at the surface of the layer. The chains in a brush of hydroxy-terminated PI, on the other hand, are quite mobile, and one would expect that after storage for some time in a drybox the high-energy OH groups would be buried beneath the surface because dry air represents a nominally hydrophobic, apolar medium. When exposed to a polar solvent, or even the water used in a contact angle measurement, the surface may rearrange to place the OH groups next to polar medium to reduce the interfacial energy.[85-87]

Here it was observed that after immersion in methylene chloride under reflux the water contact angle ($\theta_{adv} = 47 \pm 2°$, $\theta_{rec} = 37 \pm 2°$) of the "grafting from" hydroxy-terminated poly(isoprene) brush **(9)** (measured within 20 s) approached the range of advancing contact angles ($\theta_{adv} = 20-50°$)[88-90] reported for hydroxy-terminated aliphatic SAMs. It would be expected that the lowest obtainable advancing contact angle for **9**, the hydroxy-terminated chains, would depend on the percentage of polymer chain ends containing a hydroxyl group. Utilizing more stringent experimental techniques to remove air and moisture (i.e., distillation of isoprene from dibutylmagnesium into the reactor) gave the lowest contact angle ($\theta_{adv} = 47 \pm 2°$) for a brush **(9)** of hydroxy-terminated chains and presumably the highest degree of functionalization. A layer of hydroxy-terminated polyisoprene **(12)** prepared by "grafting to" a silicon wafer (Scheme 4) exhibited a contact angle of $\theta_{adv} = 67 \pm 1°$ after extraction overnight with methylene chloride under reflux. It is important to emphasize that every chain end of **12** has a hydroxyl group and that the "grafting from" hydroxy-terminated polyisoprene brush gave lower contact angles ($\theta_{adv} = 47 \pm 2°$) and thicker films (5−10 nm). However, the advancing contact angles of the hydroxy-terminated brushes are not expected to remain constant over time (>1 h). After submerging **9** in benzene for several hours, the advancing contact angle increased from 47 ± 2° to 67 ± 2°. This increase is consistent with a reorganization of the chain ends near the surface to bury the hydroxyl groups away from the interface with the hydrocarbon solvent.

XPS measurements were also used to characterize the hydroxyl-functionalized polyisoprene brushes. Figure 4 shows a comparison of the XPS spectra from "grafting to" and "grafting from" hydroxy-terminated brushes, **(9)** and **(12)**. Both spectra show a C−O peak from the hydroxyl groups at 286.7 eV. Poly(isoprene) gives a carbon (1s) "shake-up" satellite at around 289 eV which results from the π electrons. The intensity of the "shake-up" is small and, as expected, only 4% of the main peak.[80] The remainder of the asymmetry at high binding energy probably results from a variety of loss processes and is generally noticeable at high resolution.[76,91] The atomic concentrations corresponding to the carbon (1s) binding energy peak (285 eV) were 25% for a 5 nm thick "grafting from" hydroxy-terminated brush and 51% for a 10 nm thick hydroxy-terminated "grafting from" poly(isoprene) brush. The hydroxy-terminated "grafting to" brush **(12)**, which is expected to have a lower grafting density, exhibited an atomic carbon concentration of

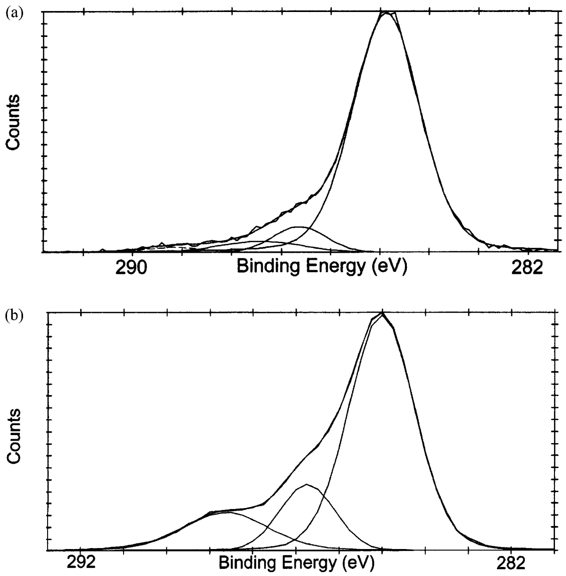


Figure 4. High-resolution XPS data with curve fit for carbon (1s) scans for (a) "grafting to" HO(PI) **(12)** and (b) "grafting from" HO(PI) **(9)**.

24%. In addition, the silicon (2p) peak from the substrate decreased from 45% for M-1 to 20% for the hydroxy-terminated poly(isoprene) brush **(9)**. For the 10 nm hydroxy-terminated poly(isoprene) brush, the presence of substantial signals from silicon (2p) (20%) and oxygen (29%) may be an indication of lateral inhomogeneities.

Successful creation of layers of functionalized PI is evidenced by both the contact angle measurements and XPS results. Both a decrease in contact angle from $\theta_{adv} = 86 \pm 2°$ for "grafting from" polyisoprene **(8)** to $\theta_{adv} = 47 \pm 3°$ for "grafting from" hydroxy-terminated polyisoprene **(9)** and changes in atomic concentration of carbon bonded to oxygen support the premise that the PI chain ends were functionalized with an OH group. The ratio of the atomic concentration of carbon bonded to oxygen may be taken as a measure of the degree to which the region of the sample near the surface is enriched in hydroxyl groups. This ratio is 3 times as large for the "grafting from" functionalized PI layer as for the "grafting to" layer. Thus, on the basis of XPS and contact angle results, it can be concluded that the "grafting from" method gives a higher grafting density and larger density of functional groups near the air interface than does the "grafting to" strategy.

Additional evidence for the presence of terminal hydroxyl groups on the tethered polymer chains comes from ATR−IR data. The ATR−IR spectrum (Figure 5) of the hydroxy-terminated polymer brush **(9)** showed aliphatic C−H stretching bands at 2972, 2930, and 2851 cm^{-1}. A small contribution from the terminal hydroxyl groups **(9)** was observed at 3200−3400 cm^{-1} (O−H stretch). The aliphatic C−H stretching for **9** was consistent with the aliphatic stretching bands at 2962, 2930, and 2855 cm^{-1} seen for the surface "grafting to" hydroxy-terminated polyisoprene brush **(12)**. It was difficult to ascertain the existence of a peak at 3200−3400 cm^{-1} for **(12)** due to the low signal-to-noise ratio. This is consistent with the relative amounts of C−O seen in the XPS carbon (1s) scans (Figure 4) and the contact angle measurements. Other relatively weak absorbance bands for the determination of diene microstructure (839 cm^{-1} for cis-1,4 and 842 cm^{-1} for trans-1,4)[82,92] were obscured by the strong absorbance of the silicon ATR crystal below 1500 cm^{-1}. By way of comparison, FTIR-ATR spectra for hydroxy-terminated aliphatic monolayers ($HOC_{23}Si$) on silicon wafers showed similar aliphatic C−H stretching at 2918 and 2851 cm^{-1} and a broad −OH peak at 3200−3500 cm^{-1}.[88]

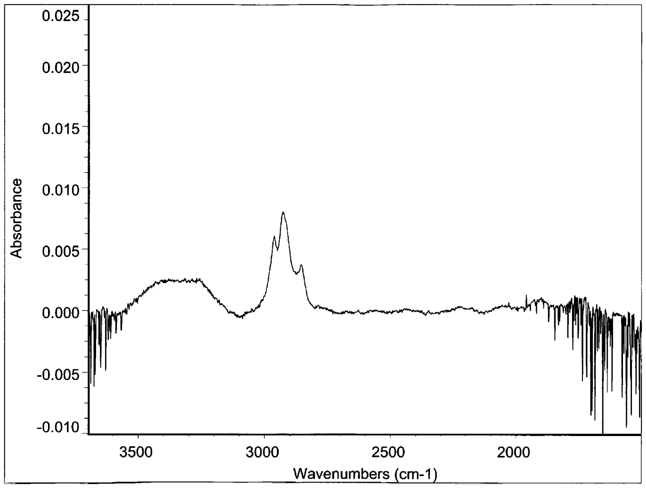


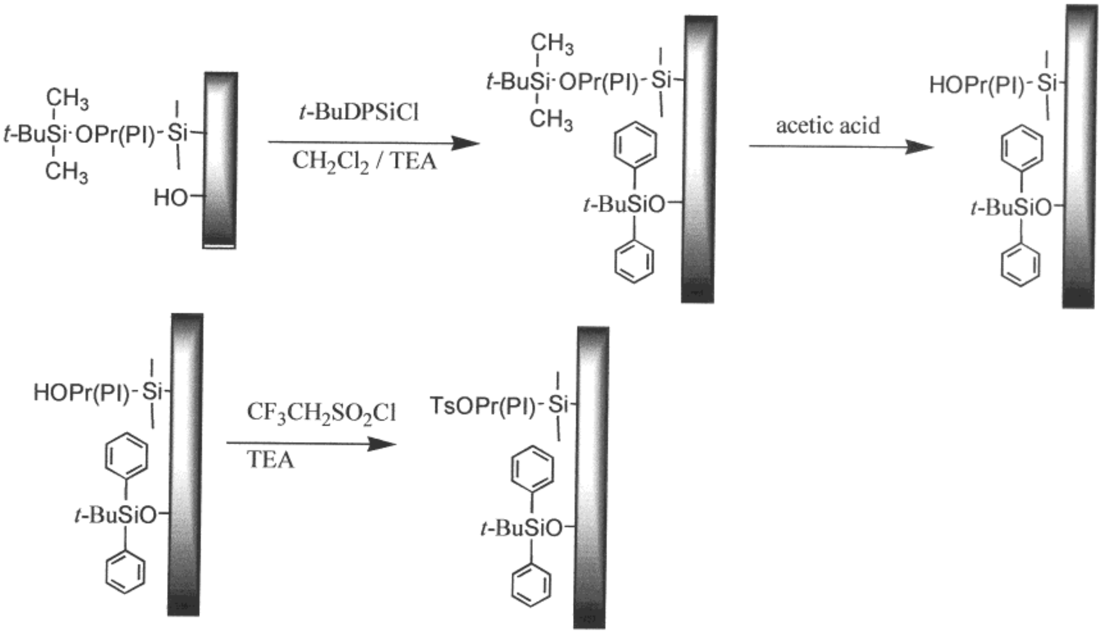
Figure 5. FTIR-ATR spectrum for hydroxy-terminated PI brush **(9)** grafted from a 1,1-diphenylethylene monolayer.

Synthesis of Polyisoprene-*block*-poly(ethylene oxide) (PI-*b*-PEO) Brushes. The hydroxy-terminated PI brush **(9)** was used to make a PI-*b*-PEO diblock copolymer brush as shown in Scheme 3. The synthetic strategy outlined in Scheme 3 allowed characterization of the hydroxy-terminated PI brush **(9)** before formation of the poly(ethylene oxide) block to yield **10**. Diphenylmethylpotassium was chosen to convert the hydroxy-terminated PI brush into the corresponding potassium alkoxide since it is a homogeneous system in THF and gave reasonable thicknesses for the resulting PI-*b*-PEO brushes. The brush thickness after extraction with methylene chloride increased from 5 nm (ellipsometry) for the "grafting from" hydroxy-terminated PI brush to 10 nm (ellipsometry) for the "grafting from" PI-*b*-PEO diblock copolymer brush. If it is assumed that the molecular weight of the tethered polymer layer is much larger than the molecular weight of the solvent molecules, then a large entropic penalty exists for the exclusion of solvent molecules from the tethered polymer layer.[93] Thus, it is reasonable to expect that all the chain ends are accessible to the diphenylmethylpotassium.

The chemical accessibility of chain ends was shown in a separate experiment by reacting a solution of tresyl chloride ($CF_3CH_2SO_2Cl$) with the hydroxy-terminated ends of the brush **(12)** as shown in Scheme 5. Before reaction with the tresyl chloride, the excess surface hydroxyl groups at the surface of the substrate were protected by *tert*-butyldiphenylsilyl chloride. After tresylation, analysis by XPS detected the fluorine (1s) XPS signal at 687 eV, indicating that chain ends were functionalized with tresyl chloride. Control experiments with a *tert*-butyldiphenylsilyl monolayer on an ATR wafer showed no fluorine (1s) signal, indicating that the signal in Figure 6 contains only contributions from the reaction of the polymeric hydroxyl chain ends with tresyl chloride.

After formation of the PEO-*b*-PI surface-grafted diblocks, the presence of the PEO block was proven by water contact angle and XPS measurements. Typical contact angle values for PEO films from the literature

Scheme 5. Reaction of Surface "Grafting to" Hydroxy-Terminated Polyisoprene with Tresyl Chloride



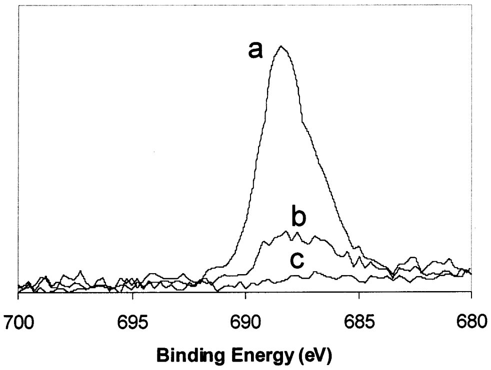


Figure 6. XPS fluorine (1s) overlay for poly(isoprene) chain ends functionalized with tresyl chloride (a), control experiment (b), and untreated *tert*-butyldiphenylsilyl monolayer (c).

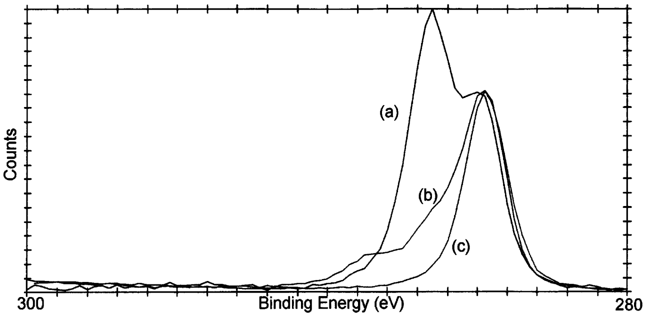


Figure 7. X-ray photoelectron spectra for the "grafting from" (a) PEO-*b*-PI diblock **(10)**, (b) HO(PI) **(9),** and (c) unfunctionalized brush **(8)**.

are $\theta_{adv} = 34-45°$ and $\theta_{rec} = 24-30°$.[94] There was good agreement between the contact angle measurements for the PEO-*b*-PI diblock brushes made by the "grafting to" strategy (Scheme 3) ($\theta_{adv} = 40 \pm 3°$, $\theta_{rec} = 28 \pm 1°$) and those made by the "grafting from" strategy (Scheme 2) ($\theta_{adv} = 35 \pm 2°$, $\theta_{rec} = 24 \pm 2°$), and both results were consistent with the cited literature values for PEO films created by other means. Figure 7 shows an overlay of the XPS spectra for the "grafted from" PEO-*b*-PI diblock copolymer **(10)**, hydroxy-terminated brush **(9),** and unfunctionalized brush **(8)**. In Figure 7a, the C−O peak from the PEO block at 286.7 eV is distinct from the saturated carbon peak at 285 eV. The chemical shift range for carbons bonded to oxygen relative to saturated hydrocarbons (285 eV) is 1.13−1.75 eV.[80] As seen in Figure 7, the C−O peak (286.7 eV) increased after formation of the PEO block. Relative to the saturated carbon peak (285 eV), the C−O peak (286.7 eV) for the "graft from" diblock **(10)** was larger than that for the "graft to" diblock **(13)**. It was not possible to independently confirm the presence of PEO by FTIR-ATR measurements. The ether stretch from the PEO block could not be seen due to a strong absorbance from the silicon wafer below 1500 cm^{-1}.

The reorganization of the tethered PI-*b*-PEO diblock in response to changes in an adjacent solvent was also investigated. It has already been demonstrated by others that tethered diblock copolymers can reorganize in response to stimuli such as changing solvent conditions.[11] Figure 8 shows the XPS carbon (1s) scans for the "grafting to" PEO-*b*-PI diblock copolymer after immersion in methylene chloride overnight and in cyclohexane for 2 h. The change in the surface elicited by varying the solvent next to the surface also resulted in a change in the advancing contact angle from 40 ± 2° after immersion in methylene chloride to 55 ± 2° after submerging in cyclohexane for 2 h. The magnitude of this change in contact angle is somewhat less than the 23° change seen when "grafting from" poly(styrene-*block*-methyl methacrylates) diblock copolymer brushes were contacted first with methylene chloride and then with methylcyclohexane.[9−11]

The reorganization of polar groups attached to the polymer backbone requires some finite time, and the rate at which the minimization of the interfacial energy is achieved can be influenced by rotational mobility of the polymer backbone and cross-linking.[87] The reorganization of amphiphilic diblock copolymer brushes of poly(methyl methacrylate-*block*-acrylamide)[12] is reported to have required 30−60 min after exposure to methylene chloride and 1 h after exposure to cyclohexane as polar and nonpolar media, respectively. By

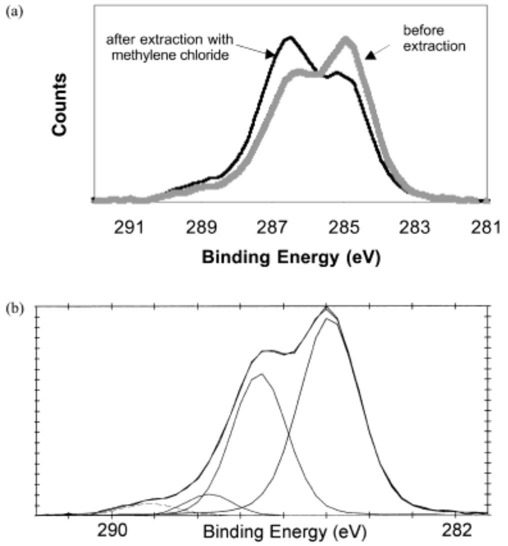


Figure 8. High-resolution XPS carbon (1s) scans of "grafting to" PEO-*b*-PI diblock **(13)** after exposure to different solvents: (a) before methylene chloride extraction (cyclohexane treatment) and after methylene chloride extraction; (b) curve fit for cyclohexane treatment.

design, poly(isoprene-*block*-ethylene oxide) diblock copolymer brushes should provide surfaces with faster reorganization under changing solvent conditions because both the polyisoprene and the poly(ethylene oxide) blocks have flexible backbones with low T_g's. Further elucidation of the kinetics of the reorganization will be the subject of future work.

Conclusions

Living anionic polymerization has been used to prepare polymer chains tethered to a silicon oxide surface using a 1,1-diphenylethylene surface-bound monolayer as co-initiator. It is expected that this method can be extended to other inorganic oxide surfaces. These DPE monolayers react with poly(styryl)lithium to form the corresponding living adducts by a "grafting to" procedure. The DPE monolayer also reacts with *n*-butyllithium to form surface bound 1,1-diphenylhexyllithiums that can initiate living anionic polymerization of styrene and diene monomers. Thicknesses as high as 24 nm (ellipsometry) have been obtained by "grafting from" a 1,1-diphenylethylene monolayer in the presence of neat monomer. The resulting tethered living polymeric organolithium chains ends can be functionalized with ethylene oxide to form the corresponding ω-hydroxyethylated polymers as evidenced by contact angle and XPS measurements. These hydroxyl functional groups can be used to initiate the polymerization of ethylene oxide. The existence of the PEO block was proven by observations of the XPS carbon (1s) peak (286.7 eV) and an increase in layer thickness [5 ± 1 nm for the HO(PI)DPE brush **(9)** to 10 ± 1 nm for the PEO-*b*-PI diblock brush **(10)**] and a decrease in contact angle from $\theta_{\mathrm{adv}} = 47 \pm 3°$ for **(9)** to $\theta_{\mathrm{adv}} = 35 \pm 2°$ for the PEO-*b*-PI diblock brush **(10)**. Future work will include the investigation of free radical and cationic grafting reactions using the surface grafted DPE layers.

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