Polymer Immobilization to Alkylchlorosilane Organic Monolayer Films Using Sequential Derivatization Reactions

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Received August 29, 1996. Revised Manuscript Received May 20, 1997[⊗]

Covalent immobilization of hydrophobic and hydrophilic polymers in sequential reactions to surfaces of olefin-terminated alkylsilane monolayers results in fabrication of polymer-modified ultrathin films. Film surface chemistry and interfacial energy are modified significantly using this approach, resulting from sandwich-type layers bearing pendant poly(ethylene glycol) or perfluoroalkyl chains exposed on the film surface. Photoaddition chemistry has been used to react a thiol-bearing polysiloxane to olefin-terminated alkylsilane monolayers. Additionally, hydrosilylation reactions have also been used to covalently attach Si−H polysiloxanes to olefin-terminated alkylsilane monolayers. XPS and static SIMS have been used to confirm chemistry and yields after these sequential immobilization reactions. Both surface analysis methods provide evidence for the surface chemistry of each immobilization step at the surface.

Introduction

Alkyl chains bearing sulfur or silane terminal anchor groups are well-known to form compact, well-defined monolayer adlayer films on certain metal (e.g., gold, copper, silver, platinum) and oxide surfaces (SiO_2, Al_2O_3, TiO_2), respectively, under controlled conditions. Because of their novel properties, these self-assembled monolayers (SAMs) have been characterized exhaustively over the past decade.[1−12] While debate persists about certain aspects surrounding the formation mechanisms and structures of these organic overlayers, most data support the general contention that carefully prepared SAM films are high-density, organic overlayers approximating monolayer thicknesses.

Significantly, much has been touted about potential use of SAMs in diverse applications including new lubricants, photoresist and lithographic materials, biosensors, new biocompatible materials, and photo- and electrochemical coatings. Alkylthiolate monolayers on copper have been shown to protect the metal against oxidation by air,[14] indicating their passivating nature. Densely packed alkylsilane monolayers have also been shown to protect olefins in monolayer assemblies from oxidation by $KMnO_4$ solution,[15] due to their high lateral organization and chain packing density. Nevertheless, while such surfaces exhibit a number of properties of substantial fundamental interest, their utility in a wide variety of technological and commercial applications is compromised by an intrinsic inability of these monolayers to withstand thermal, mechanical, electrochemical, and other environmental challenges. Enhanced ultrathin-film durability under a number of conditions would be a great advantage.

Polymerized organic monolayers provide one route to increasing monolayer stability. Two general strategies—post assembly in situ film polymerization and directed polymer surface attachment—are logical ap-

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[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1997.

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S0897-4756(96)00450-4 CCC: $14.00

proaches. While in situ film polymerization has been pursued using a wide variety of strategies,[16] prepolymerized directed chemisorption or covalent assembly of macromolecules as thin film structures on surfaces is less studied. Examples, to date, include the early work by Stouffer and McCarthy[17] using polystyrene copolymers containing thiol anchoring groups on gold, polyacrylate monolayer films on gold,[18,19] polysiloxane graft copolymers on gold,[20] redox-active polymer surface attachment,[21] and polyoxazoline surface grafting to oxide solids.[22]

Polymer self-assembled monolayers exhibit higher thermal stability but are less compact and relatively disorganized structures compared to monomer monolayers.[19] The polymer backbone provides monolayers with common side-chain interconnects and multipoint binding stability from anchoring side chains along shared backbones, enhancing the adherent capacity of these films. Nevertheless, limited side chain density and polymer backbone steric constraints also restrict side chain organization and lateral assembly into dense films. Lateral organization and defect density in monomeric self-assembled films is influenced by monomeric alkyl chain length and their functional end groups.[19] Large terminal anchoring groups also reduce regular packing conformations due to steric hindrance and unfavorable binding geometries.

In this paper, we demonstrate a new stepwise approach to obtain high-density polymer-stabilized organic monolayers exhibiting the advantages of both monomer and polymer assemblies. The strategy involves fabrication of bifunctional alkylsilane monolayers on solid oxide surfaces. Previous work[1,15] has shown that this strategy yields compact, high-density self-assembled alkylsilane monolayers on silicon oxide having exposed terminal olefinic functional groups. Sagiv's group has also pioneered methods to react the olefinic surfaces of these monolayers to produce a reactive surface foundation for fabricating layered assemblies.[1,15]

In our approach, these alkylsilane terminal olefinic groups are subsequently reacted with a multifunctional linear polymer, coupling the polymer to the surface of the anchored monolayer. Additionally, other oligomers and organic compounds of diverse nature can be subsequently reacted along the immobilized polymer main chain, forming a new covalently attached surface with interfacial properties reflecting the nature of the immobilized groups. Significantly, this sequential approach forms high-density monomeric films in the first conventional silanization step, stabilizes them with an overlayer of immobilized polymers to provide an organic foundation in the second subsequent step, and permits derivatization of this foundation in the third step. The overall strategy for these procedures is schematically shown in Figure 1, showing one-step, two-step, and three-step derivatization schemes. Through this approach we use monomeric organosilanes as a dense-packed organic foundation to both stabilize and functionalize this organic array via polymer attachment. While stabilization is perhaps more of an issue with metal−thiolate SAMs than with silanes, the strategy is a general method to approach sequential reactions on well-organized organic thin films.

Experimental Methods

Materials. Polyhydrogen methylsiloxane (PHMS, mol wt 4500, viscosity 85 cps), poly(methylmercaptopropyl)siloxane (viscosity 100 cps), 7-oct-1-enyltrichlorosilane, platinum divinylsiloxane complex and H_2PtCl_6 were purchased from Hüls America and used as received. α-Methoxy-ω-allyl ether poly(ethylene glycol) (PEG, mol wt 400 and 600) or analogous semitelechelic ethylene glycol−propylene glycol copolymer (PEG−PPG, mol wt 1400 and 3800, 18% and 58% propylene glycol units, respectively), gifts from Dr. Joachim Venzmer (Universität Mainz, Germany), were purified by reaction with excess anhydrous acetic acid for 12 h, followed by azeotropic distillation in toluene 5 times and drying in vacuo. Allyl chloride (Aldrich), 1*H*,1*H*,2*H*-perfluoro-1-decene (Riedel-de-Haen), 1*H*,1*H*-pentadecafluoro-1-octanol (PCR) and 1-perfluorohexene (PCR) were used as received. Toluene was refluxed over sodium metal and lithium aluminum hydride and then distilled before use. Hexane and triethylamine (Chempure, HPLC grade) was used without purification. Azobis(isobutyronitrile) (AIBN) was purified by recrystallization. Chloroform was washed with deionized water five times, followed by drying over anhydrous calcium chloride for 24 h, and distillation. Perfluorooctylallyl ether was synthesized according to a reported method[20b,22] with a minor modification. *n*-Pentadecafluoro-1-octanol (8.50 g, 21.25 mmol) was added to a 50% caustic soda solution (60 mL) containing 0.76 g (4.0 mmol) of tetramethylammonium hydrogen sulfate (TMAHS) as a phase-transfer catalyst. The mixture was vigorously stirred for 10 min. After 20.0 g (261.3 mmol) of allyl chloride was added, the mixture was stirred at 40 °C for another 12 h. The reaction suspension was then diluted with 20 mL of water, and crude product was extracted with 30 mL of methylene chloride. After drying over anhydrous $MgSO_4$, methylene chloride was removed at 0 °C under reduced pressure, and a colorless liquid was collected. Final distillation of crude product gives a clear liquid of bp 81.5−82.5/24 mmHg, yield 8.98 g (96%). Reverse-osmosis filtered water was further treated with a Millipore (Milli-Q) apparatus.

Attachment of Heterobifunctional Alkylsilanes onto Silicon Oxide Surfaces. Silicon wafers (Wacker Siltronic, p-type, SEMI standard, native oxide ~13 Å thick) were first cleaned in a pirhana acid−peroxide solution for 2 h *(warning: this mixture reacts violently with organic materials and must be handled with extreme care)*, rinsed with Millipore water and dried under nitrogen. These wafers were cut into 1 × 3 cm pieces immediately using a diamond scribe as previously described.[16] These silicon oxide pieces were immersed into 1% triethylamine chloroform solution for 2 h, then washed with chloroform, dried with N_2, and kept in a 120 °C oven for 10 min. The monolayers were formed by immersing these pieces into 5 mM 7-oct-1-enyltrichlorosilane−hexane solution for 24 h at room temptperature. Wafer pieces were then washed with

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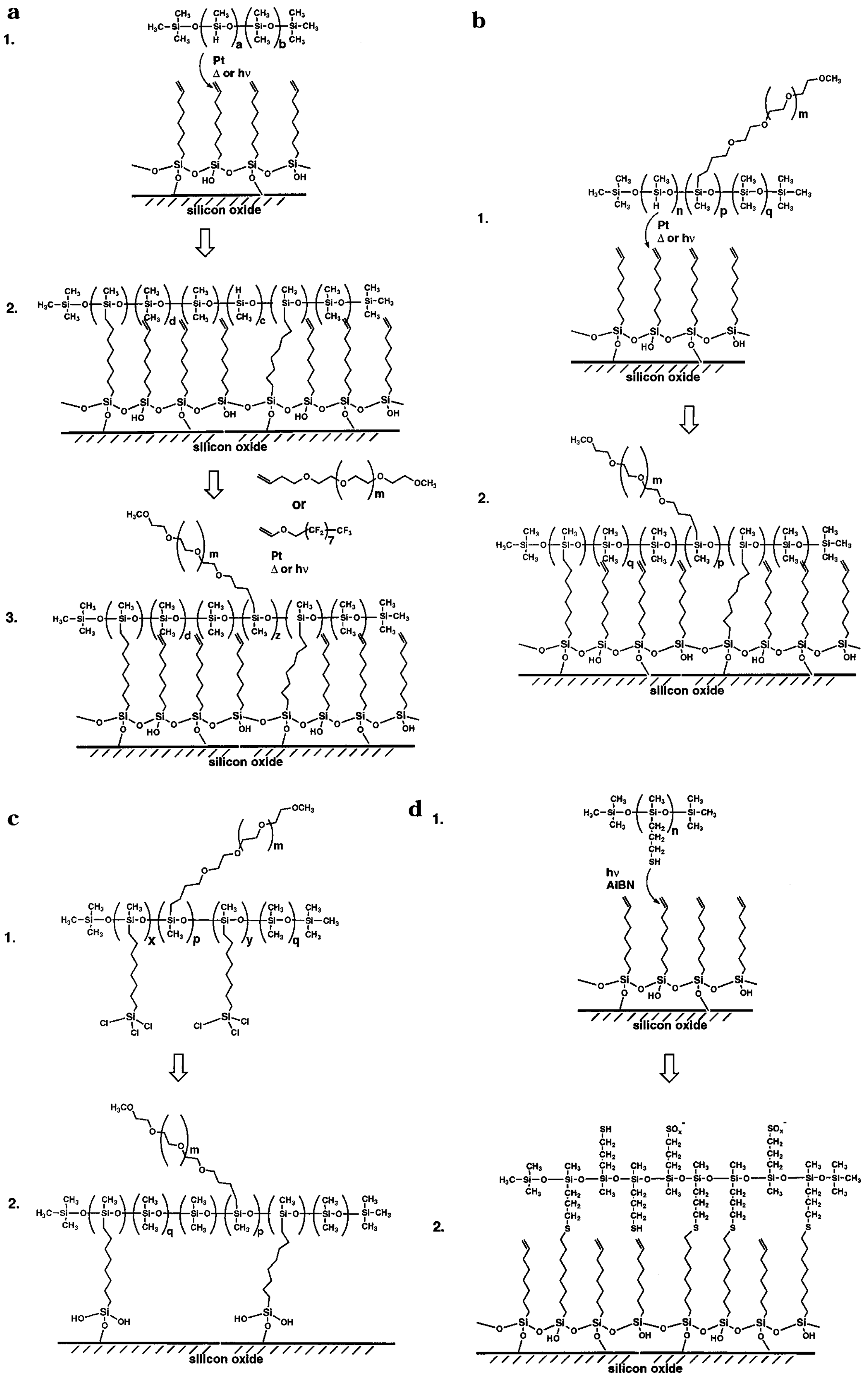

Figure 1. Fabrication scheme for polymer reactions with olefin-terminated alkylsilane monolayers by sequential reactions: (a) three-step approach, (b) two-step approach, (c) one-step approach, and (d) photochemical addition using PMMPS.

fresh hexane, toluene, chloroform, and ethanol in sequence and dried under nitrogen.

Reaction of 7-Oct-1-enyltrichlorosilane Self-Assembled Monolayers with Siloxane Polymers in Solution. Wafer pieces treated with monolayers of 7-oct-1-enyltrichlorosilane were immersed in toluene for 30 min and then either immersed for 2 h into a toluene solution at 50 °C containing PHMS (50 mM hydrosilyl functional group content, 5 mL) and 20 mg of platinum vinylsiloxane catalyst complex (hydrosilylation) or, alternatively, mercaptan-containing PMMPS and 10 mg of AIBN (photoinitiated addition reaction). In the latter case, solutions containing the wafer pieces bearing alkylsilane monolayers were purged for 10 min with N_2 and subsequently irradiated in the presence of PMMPS and AIBN using a 100 W high-pressure Hg lamp with an aqueous infrared filter for 4 h at room temperature. Wafer pieces were subsequently removed, placed into an excess volume of toluene immediately, shaken using forceps for several minutes, or, in some cases, ultrasonicated for several minutes then shaken with forceps, to remove noncovalently adsorbed polymer from the wafer surface, and rinsed with 5 mL of fresh toluene prior to further treatment. Direct exposure of prepared surfaces to air was avoided.

Further Derivatization of Unreacted Functional Groups of Immobilized Polymer Coupled to Alkylsilane Monolayers. Silicon oxide surfaces treated with both 7-oct-1-enyltrichlorosilane and either of the aforementioned siloxane polymers were subsequently placed in either (1) 5 mL toluene solutions containing α-methoxy-ω-olefin semitelechelic PEG allyl ether (or PEG−PPG copolymer allyl ether) oligomer (50 mM) and 20 mg of platinum vinylsiloxane catalyst complex or (2) 1,1,2-trichlorotrifluoroethane solutions (5 mL) containing the perfluoroalkyl allyl ether and 20 mg of platinum vinylsiloxane complex. These hydrosilylation surface immobilization reactions were carried out at 50 °C for 48 h. Wafer pieces were subsequently washed thoroughly with toluene or 1,1,2-trichlorotrifluoroethane, chloroform, and ethanol in sequence, and dried under nitrogen.

Surface Reactions of 7-Oct-1-enyltrichlorosilane Monolayers with Grafted Siloxane Polymers. Polysiloxanes partially grafted with either PEG oligomers or perfluoroalkyl chains were prepared by hydrosilylation reactions in bulk solution. PHMS polymer was reacted with PEG−allyl ether or perfluoroalkyl allyl ether under the same platinum-catalyzed hydrosilylation conditions we have described previously,[20] using a ratio of olefin C=C to siloxane Si−H groups of 0.2 in toluene for 48 h. This procedure has been shown to result in quantitative yields for hydrosilylation of polymer Si−H units, in this case producing a siloxane polymer containing 20 mol % side-chain grafts of either PEG or perfluoroalkyl units with the remaining Si−H units left unreacted. Pieces of silicon oxide presilanized with 7-oct-1-enyl trichlorosilane monolayers were immersed into toluene for about 30 min prior to reaction, then immersed directly into a toluene solution (5 mL, 50 mM) containing either of the bulk-grafted polysiloxanes and 20 mg of platinum vinylsiloxane hydrosilylation catalyst complex. Surface−polymer hydrosilylation coupling reactions were carried at 50 °C for 48 h. The derivatized wafer pieces were subsequently washed with toluene, chloroform, and ethanol in sequence and dried under nitrogen.

One-Step Polymer Surface Immobilization. The polymers used in one-step surface immobilization were synthesized first in bulk via cohydrosilylation reactions to attach various olefin-terminated side chains to PHMS polysiloxane precursors. These reactions were carried out in toluene using a ratio of [C=C]:[Si−H] = 1.1:1 at 90−100 °C for 48 h using H_2PtCl_6 or platinum divinyltetramethylsiloxane complex at 50 °C as catalysts. Flasks used in this reaction were first treated with 1% dichlorodimethylsilane in chloroform and dried with a Bunsen burner under the nitrogen prior to reaction. The reactions were sealed under nitrogen gas. For PEO ω-methyl α-allyl ether/chlorosilyloctene cohydrosilylation, grafting reactions were performed in toluene with a desired ratio of [PEO ω-methyl α-allyl ether]:[PHMS Si−H] for 24 h at 90−100 °C with the same catalyst followed by addition of 7-oct-1-enyltrichlorosilane at a ratio of [C=C]:[Si−H] 1:1 and another 24 h reaction period. Final polymer products were filtered quickly to another dry, silanized 50 mL flask and dried in vacuum at 110 °C. A light gray viscous liquid remained, and its composition was determined by NMR. The product was stored as 5−10% dry toluene solution to prevent gelation.

Polymer monolayer films were prepared in one step by immersing previously described clean silicon oxide wafers into 0.01−10 mg/mL of the grafted polysiloxane copolymer solutions in purified chloroform at room temperature. After 24−48 h, the wafers were removed, rinsed thoroughly with chloroform, and sonicated in chloroform at room temperature for 5 min and then dried again under nitrogen.

Monolayer Characterization. Static contact angles for water and hexadecane were determined using the sessile drop method with a Ramé-Hart Model 100 contact angle goniometer in a controlled environment (saturated vapor). Measurements were taken on both sides of water drops at ambient temperature 30−40 s after 2 μL drops were applied to surfaces and the needle tip was removed from each drop. Contact angle data reported are the average of three drops at different locations on each surface.

Film thicknesses were measured using a Gaertner L117 ellipsometer with a wavelength of 6328 Å (He−Ne laser) at an incident angle of 70°. Each underivatized, bare silicon wafer was used as its own internal reference, and 3−4 measurements were made on each sample with each derivatization step. Thicknesses were calculated numerically assuming a refractive index of 1.45 for the monolayer.[17b] Errors associated with varying the refractive index from 1.36 to 1.46 were approximately ±5 Å for a two-layer model.

X-ray photoelectron spectroscopy (XPS) experiments were performed on a Surface Science SSX-100 spectrometer equipped with a monochromatic Al Kα source, hemispherical analyzer, and a multichannel detector. Typically, spectra were collected with the analyzer at 55° with reference to the sample surface normal, and the operating pressure was approximately 3×10^{-9} Torr. High-resolution spectra were obtained at a pass energy of 50 eV using a 1000 μm spot size. Both survey spectra and data for quantitative analysis were collected at a pass energy of 150 eV and a spot size of 1000 μm. The binding energy (BE) scales for all spectra were referenced to the C1s peak at 285.00 eV. Peak fitting of the high-resolution spectra was done using Gaussian and Lorentzian peak shapes with commercial software supplied by Surface Science Instruments. For calculation of XPS elemental composition, the analyzer transmission function was assumed not to vary with photoelectron kinetic energy (KE),[23] the photoelectron escape depth was assumed to vary as $KE^{0.7}$, [23] and Scofield's photoionization cross sections[24] were used.

Angle-dependent XPS data were collected at nominal photoelectron takeoff angles of 0°, 39°, 55°, 68°, and 80°. The takeoff angle was defined as the angle between the surface normal and the axis of the analyzer lens system. The solid acceptance angle of the analyzer lens was decreased to 12° × 30° by placing an aperture over the analyzer lens to improve the depth resolution at each takeoff angle.[25]

Static secondary ion mass spectrometry (SIMS) experiments were performed with a Physical Electronics 3700 SIMS system (Eden Prairie, MN) mounted on a custom ultrahigh-vacuum (UHV) system. The UHV system has a turbomolecular and Ti sublimation pumped analysis chamber with an $XYZ\Theta$ sample manipulator. The base pressure in this chamber is 1×10^{-10} Torr. Samples are transferred into the analysis chamber from a turbomolecular-pumped sample introduction chamber. The PHI SIMS system contains a 90° adjustable energy filter and Balzers 0−511 amu quadrupole mass spectrometer for detection of positive and negative secondary ions emitted by the sample. A differentially pumped Leybold-Heraeus (Koln, Germany) ion source was used to produce a

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Table 1. Contact Angle and Film Thickness Data for Sequentially Reacted Olefin-Terminated Organic Films

modification method	derivatization sequence	film chemical description	contact angles (deg) Θ_{water}	Θ_{HD}	elllipsometric total film thickness (Å)
one-step	only layer	7-oct-1-enyl trichlorosilane	99	20	13 (±2)
		PHMS-*co*-alkylsilane-*co*-PEG 400	55	wetting	28 (±3)
		PHMS-*co*-alkylsilane-*co*-20% CF	110	45	23 (±3)
two-step	first layer	7-oct-1-enyl trichlorosilane	99	20	13 (±2)
	second layer	PHMS	97	25	22 (±3)
		PMMPS	80	wetting	50 (±5)
		20% PEG 400/PHMS	78	wetting	30 (±5)
three-step	first layer	7-oct-1-enyl trichlorosilane	99	20	13 (±2)
	second layer	PHMS	97	25	22 (±3)
	third layer	PEG-400	67	wetting	38 (±5)
		PEG-600	55	wetting	38 (±5)
		PEG−PPG-1418	51	wetting	35 (±5)
		PEG−PPG-3858	57	wetting	42 (±5)
		perfluoroalkyl allyl ether	100	43	29 (±5)

0.5 nA, 3.5 keV Xe^+ primary ion beam. The ion beam was rastered over a 5 × 5 mm area, and the total exposure time of the sample to the ion beam, including setup and data acquisition, was less than 7 min. This corresponded to a total ion dose per sample of $<5 \times 10^{12}$ ions/cm^2, which is within the generally accepted limit for static SIMS conditions for organic surfaces.[26] Both positive and negative secondary ions were collected over a m/z range of 0−300 with a nominal mass resolution of unity. The data acquisition and control of the energy filter and quadrupole were done using the Physical Electronics SIMS software package.

Results and Discussion

Monomeric Olefin-Terminated Self-Assembled Films. We found that 7-oct-1-enyltrichlorosilane is able to form compact, low interfacial energy monolayers by self-assembly from hexane. Contact angles and ellipsometry data for these films are shown in Table 1. Contact angles for 7-oct-1-enyltrichlorosilane monolayers with both purified water and hexadecane indicate strongly hydrophobic interfaces. However, aqueous contact angles are slightly lower than expected for densely packed olefins. Film thicknesses (13 Å) are slightly higher than expected for high-density alkenyl monolayers of this chain length. The thickness contribution from each methylene group averages 1.5 Å, the length of methylene units in alkylthiol self-assembled films on gold and octadecyltrichlorosilane on silicon oxide surfaces.[2,27,28] Reduced film thicknesses and contact angles for water and hexadecane over those known for octadecyltrichlosilane films[29] are attributed to its shorter overall alkyl chain length and surface-exposed olefin end groups, respectively. Nevertheless, the data taken together would support a disordered silane coating, containing some polymeric, cross-linked and physisorbed material contributing to thickness and wetting.

Polymer Coupling to Silane Monolayer Films. Reactive siloxane polymers are covalently bound to alkenyl silane monolayers via reactions with exposed terminal olefin groups at the monolayer−solution interface. Two routes were chosen: a hydrosilylation reaction between monolayer-bound olefins and hydrosilyl units on the PHMS main chain, or alternatively, a photoinitiated free radical transfer addition reaction between PMMPS side-chain thiol radicals created along the siloxane main chain and monolayer-bound olefins.[20a] The resulting, bound siloxane polymer surfaces exhibit new interfacial properties characteristic of these immobilization methods. Resulting film thicknesses and contact angles for water and hexadecane are shown in Table 1 for this next step. Changes in film thicknesses and contact angles after polymer immobilization reflect the additional presence of the polymers on the alkenyl-derivatized surface. Coexistence of disordered siloxane polymer loops, chains, and tails together with remaining, unreacted olefin groups at the surface is likely: the surface-bound polymers may not be able to fully cover the underlying alkyl monolayer surface and leave some polymer hydrosilyl and alkylsilane olefin functional groups unreacted.

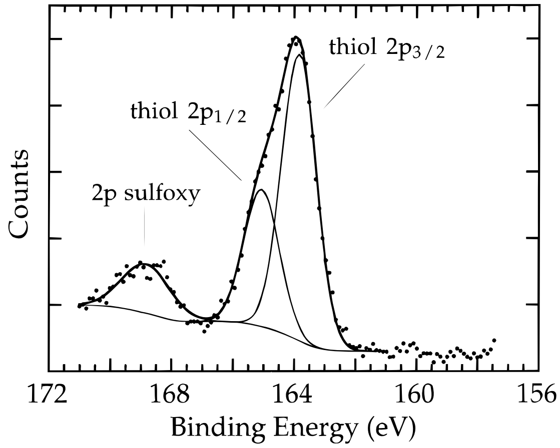

Figure 2. XPS sulfur 2p spectrum for PMMPS-immobilized overlayer on olefin-terminated 7-oct-1-enylsilane monolayers produced by photochemical reaction in solution.

Contact angles and film thickness data for PMMPS-derivatized 7-oct-1- enyltrichlorosilane monolayers are shown in Table 1. Decreases in aqueous contact angles (increased aqueous wetting) for this PMMPS surface over that for PHMS is a result of the more-polar mercaptopropyl side chains plus photooxidation of thiol to sulfoxy species (e.g., sulfinate, sulfonate) via photoderivatization.[30] The high-resolution XPS S2p spectrum in Figure 2 shows the presence of two sulfur species. The dominant sulfur species has a S$2p_{3/2}$ BE of 164 eV, consistent with organic thiols and disulfides.[31] Both

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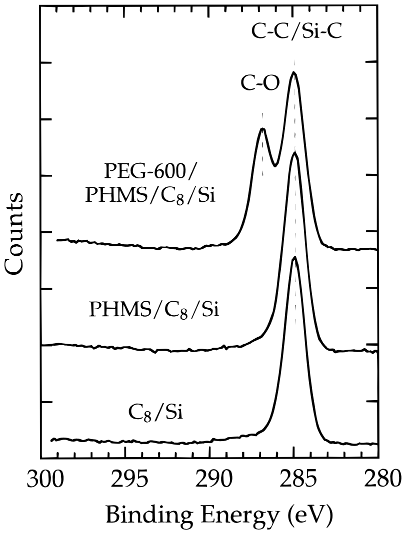

Figure 3. XPS C1s spectra for each step of the three-step sequential derivatization scheme using 7-oct-1-enylsilane, PHMS, and allyl-functionalized PEG in series.

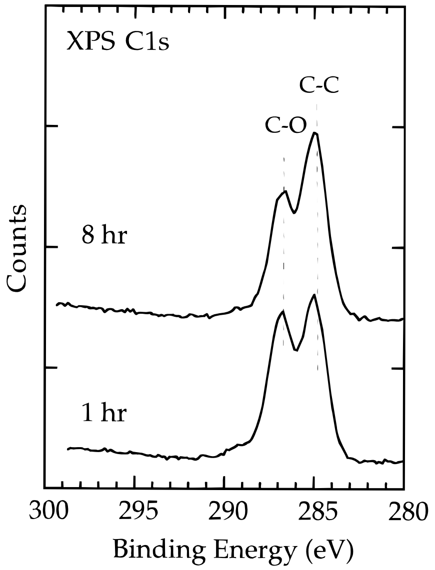

Figure 4. XPS C1s spectra for PEG derivatization of PHMS polysiloxane-immobilized alkylsilane monolayers as a function of PEG reaction time in solution.

unreacted PMMPS mercaptopropyl groups and photoreacted thioether coupled chemistry are consistent with this signal. The small peak near 169 eV is consistent with an oxidized sulfur species.

Derivatization of Siloxane Polymers Immobilized at Self-Assembled Film Interfaces. A demonstration of the general utility of attaching a variety of different functional side chains or molecules onto polymer self-assembled surfaces via this procedure is warranted to provide an array of stable polymer-layered surfaces with specific properties. Our attention has been focused on attachment of PEG or perfluoroalkyl molecules, which provide distinct surface properties and are readily quantified by XPS and SIMS studies and wetting data.

Figure 3 shows XPS high-resolution C1s data tracing the evolution of the surface chemistry for each step of the three-step derivatization sequence using PEG, PHMS, and the 7-oct-1-enyltrichlorosilane on silicon oxide. Assembly of the organosilane is observed by the appearance of a prominent C1s peak centered at 285 eV BE (lowest trace, Figure 3), characteristic of hydrocarbon. Reaction of the olefin-terminated surface with PHMS in the second step serves to increase the intensity of this C1s peak (from $-\mathrm{Si}-C\mathrm{H}_3$ methyl groups) as seen in the second trace in Figure 3. Unchanging wettability and slight film thickness increases, seen in Table 1, are consistent with this reaction. The third reaction—grafting allyl−PEG to the Si−H units remaining along immobilized PHMS—is readily distinguished due to the appearance of a new spectral C1s feature at 287 eV, characteristic of the C−O ether carbon (upper trace, Figure 3). Direct quantification of each step and chemistry is addressed using XPS and is more fully substantiated by wetting and SIMS data presented below.

On the basis of this surface analytical approach, the influence of several factors on surface grafting yields were monitored. Derivatization efficiencies for PEG−allyl ether to these PHMS siloxane-immobilized organosilane monolayer films show that PEG side-chain composition on the final surface depends on the PHMS reaction time with the alkenylsilane underlayer. Short PHMS reaction time increases subsequent PEG immobilization, reaching an optimum time after which PEG composition decreases with prolonged PHMS reaction time. This phenomenon can be explained by a balance of two factors: (1) the quantity of functional PHMS polymer covalently attached to the alkyl surface which dominates the early immersion reaction time and (2) the amount and accessibility of unreacted PHMS Si−H functional groups immobilized on the surface but still available for further reaction steps (with PEG, for example), which becomes an important factor at longer reaction times. Early in the second layer reaction step with PHMS, excess silane olefin groups exist at the immobilized silane monolayer surface: PHMS covalent attachment to the olefin surface occurs readily. At longer times, the amount of covalently bound PHMS remains constant, and prolonging PHMS reaction times does not provide further attachment of PHMS onto the olefin monolayer surface. Longer PHMS reaction times might also increase reactions between alkylsilane surface olefin groups and bound PHMS hydrosilyl functional groups left unreacted, decreasing the availablity of polymer Si−H groups for subsequent PEG immobilization. Figure 4 shows XPS spectra of the final PEG-derivatized products for two different PHMS reaction times. Since only PEG chains contain ether carbon, the detected XPS ether carbon concentration (C1s BE of 287 eV) is directly related to the PEG surface concentration. Different graft chemistries also exhibit different surface reaction efficiencies with PHMS immobilized on organosilane films: perfluoroalkyl species are not immobilized to these polymer surfaces as readily as olefin-terminated PEG chains, and have a reduced surface density in the final surface product. XPS detects only 5−10 atom % fluorine in these films derivatized by the three-step method (data not shown). Low miscibility between polysiloxanes and perfluorinated species might account for low immobilization efficiencies. Figure 4 shows XPS spectra of the final PEG-derivatized products for two different PHMS reaction times. Since only PEG chains contain ether carbon, the detected XPS ether carbon combination (C1s BE of 287 eV) is directly related to the PEG surface concentration.

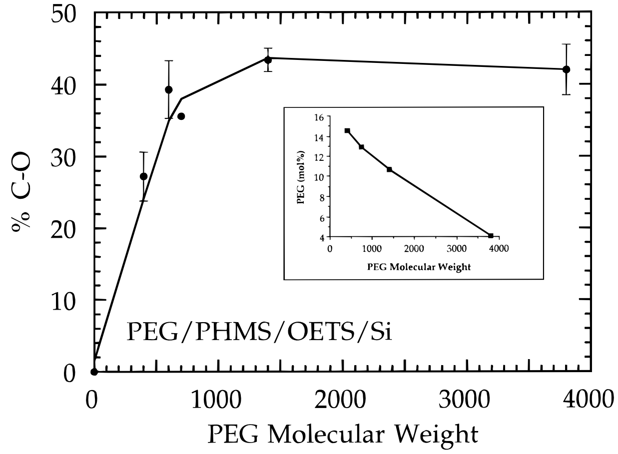

Figure 5. Percent ether carbon signal (from XPS Cls spectra) on sequentially derivatized PEG surfaces as a function of PEG molecular weight. Inset: PEG mol % immobilized on surfaces as a function of PEG molecular weight.

Last, PEG of different molecular weights was immobilized on PHMS−alkenyl silane films to study the influence of molecular size on PEG immobilization efficiency. XPS spectra show that higher molecular weight PEG species exhibit a higher percent ether carbon signal (Figure 5). However, conversion of atomic percent C1s ether carbon signal intensity into PEG mole percent indicates that fewer of the larger PEG molecules are covalently bound to surfaces compared to yields for smaller PEG molecular weights (Figure 5, inset). As with many polymer analogue reactions, immobilization efficiency appears to be controlled by the polymer steric hindrance and reactive site inaccessibility, both of which correlate directly to molecular weight. The thickness of the final surface-bound film also depends on the molecular weight of PEG derivatives (Table 1): higher molecular weights provide thicker layers. This relationship is not linear because the efficiency of PEG immobilization depends on the molecular weight of PEG derivatives: higher molecular weight molecules are less effectively immobilized. Contact angles for these final PEG-grafted product surfaces exhibit the same trends for molecular weight as shown in Figure 5. Aqueous contact angles decrease as PEG molecular weight increases over a certain range (Figure 6), and a more direct relationship shown in Figure 6 (inset) indicates that these contact angles decrease in direct proportion to the number of ether units detected on the surface.

Different XPS sampling depths achieved by varying photoelectron takeoff angles allow determination of film chemical composition as a function of depth. The angle-dependent C1s spectra for PEG-derivatized monolayers indicate that polyether chains slightly enrich the outer surface of these three-layer films (Figure 7). The small difference in ether carbon concentration at the normal and glancing takeoff angles indicates that PEG molecules are not densely packed and comprise a relatively thin indistinct overlayer and remain largely mixed into the underlying film components.

Surface Analysis by Static SIMS. The positive and negative static SIMS spectra obtained for the three-step PEG/PHMS/C8/Si three-step films all exhibited the same trends (spectra not shown). Instead, Figures 8 and 9 show positive and negative ion fragment peak intensity data respectively, as a function of *m*/*z* for each step in a three-step derivatization procedure. Changes in certain fragment intensities are consistent with chemistry occurring at the interface. After the first step (deposition of the C8 silane olefin), nearly all the peaks detected in the positive secondary ion spectra can be attributed to $C_xH_y^+$ ions (e.g., $C_2H_5^+$ at $m/z = 29$). C_xH_y clusters up to $x = 8$ are detectable, but above $x = 4$ their intensity is rather low. The pattern obtained is consistent with the presence of hydrocarbon chains. The SIMS results are in agreement with the XPS C1s spectrum for this sample, which only exhibits a single peak at 285 eV due to hydrocarbon groups (Figure 3). Na contamination is also detected ($m/z = 23$). The main

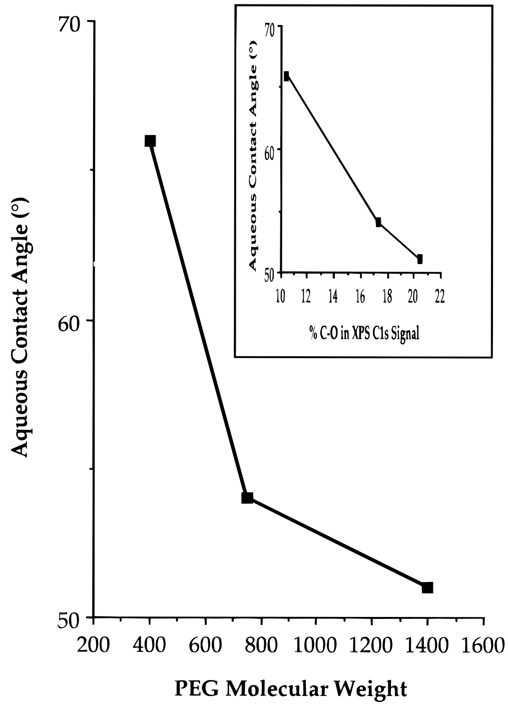

Figure 6. Aqueous wettability of PEG-grafted alkenylsiloxane surfaces as a function of PEG molecular weight. Inset: Aqueous wettability plotted as a function of ether carbon atomic %.

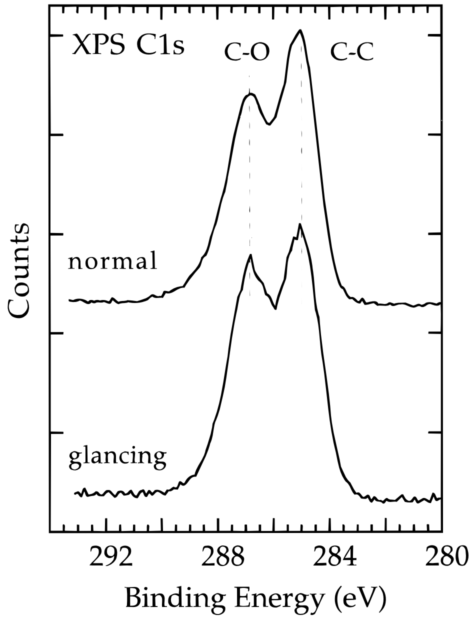

Figure 7. Angular-dependent XPS Cls spectra for PEG-derivatized alkenyl−polysiloxane monolayers.

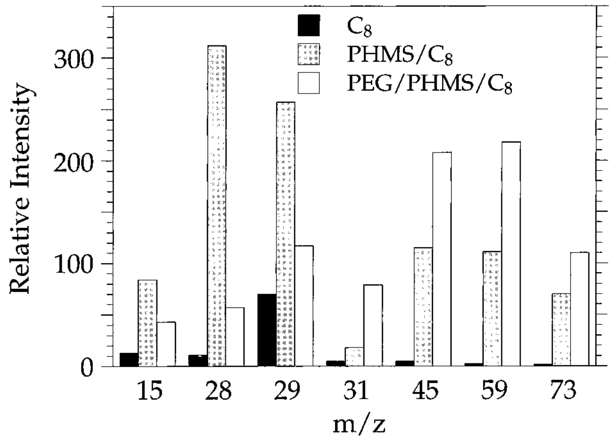

Figure 8. Positive static SIMS results for relevant ion fragments from each step in the preparation of a PEG-derivatized, alkenyl–polysiloxane monolayer (see text for *m*/*z* chemical identification).

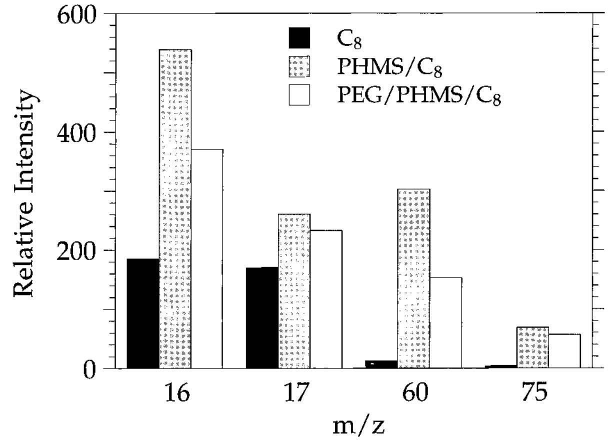

Figure 9. Negative static SIMS results for relevant ion fragments from each step in the preparation of a PEG-derivatized, alkenylpolysiloxane monolayer (see text for *m*/*z* chemical identification).

peaks in the negative secondary ion spectra are observed at $m/z = 13$ (CH^-), 16 (O^-), 17 (OH^-), and 25 ($C2H^-$). The negative ion spectra of pure hydrocarbons are typically rather uninteresting (C_xH^- and C_x^- clusters only), and the negative ion data for the silanization step alone are consistent with that observation. The silicon oxide film below the C8 chains is probably responsible for the observed oxygen-containing peaks since the thickness of this organic overlayer is smaller than the SIMS sampling depth (~20 Å). Cl^- ions are also detected ($m/z = 35$ and 37) in the negative ion spectra.

The attachment of PHMS to the C8 monolayer results in several significant changes in the SIMS data and ion fragment intensities in Figures 8 and 9. The large increase in the positive $m/z = 28$ (Si^+) peak is the most obvious. Other positive ions that exhibit increased intensity are at $m/z = 15$ (CH_3^+), 29 (SiH^+ and $C_2H_5^+$), 43 ($SiCH_3^+$ and $C_3H_7^+$), 45 ($SiOH^+$), 59 ($SiOCH_3^+$), and 73 ($SiC_3H_9^+$). The increase in the intensity of the Si-containing fragments is consistent with grafting of the PHMS on top of the hydrocarbon silane layer. The increase in the $m/z = 15$ fragment may be due to the presence of methyl groups in PHMS, since the C8 chains are terminated with CH_2 instead of CH_3 groups. It is interesting to note that the intensity of fragment at $m/z = 73$ is significantly lower from the grafted PHMS polymer compared to pure poly(dimethylsiloxane) films.[32] The negative secondary ion spectrum also exhibits changes that are consistent with the addition of PHMS to the monolayer. As shown in Figure 9, the intensity of the oxygen fragments (O^- and OH^-) increase due to the oxygen atoms present in the siloxane backbone. Two new molecular fragments are also observed at $m/z = 60$ (SiO_2^-) and 75 ($SiO_2CH_3^-$). Peaks from Na^+ and Cl^- are also detected from the PHMS grafted film, a trace contaminant of unknown origin.

The final step of grafting PEG–PPG chains onto the PHMS/C8 film results in a significant decrease, but not disappearance, of signals that originate from the PHMS component (positive $m/z = 28$ and 29, negative $m/z = 60$ and 75). This means a thin, and possibly patchy layer of PEG covers the PHMS/C8 monolayer. No systematic trend is detectable among the different PEG–PPG grafted samples examined. The presence of PEG–PPG grafted chains on the PHMS/C8 film resulted in the significant increase in peak intensities that can be attributed, at least in part, to the PEG chains (positive $m/z = 31$ (OCH_3^+), 45 ($OC_2H_5^+$ and $SiOH^+$), and 59 ($OC_3H_7^+$ and $SiOCH_3^+$). Again trace Na^+ and Cl^- ions were also detected on all of the PEG–PPG grafted monolayers.

Direct Immobilization of Grafted Siloxane Polymers to Olefin-Terminated Self-Assembled Monolayers. Direct immobilization of hydrosilyl-containing polysiloxanes grafted first in bulk with PEG derivatives or perfluoroalkyl molecules (as depicted in Figure 1) is yet another iteration of this sequential strategy. This method creates surface properties similar to films fabricated by the three-step surface modification scheme using olefin-terminated silanes. This procedure first grafts PEG to PHMS, leaving the majority of Si–H groups intact along the PHMS backbone. This grafted PHMS is then reacted to the alkenylsilane monolayer by an analogous procedure to immobilize the polymer. Contact angle and film thickness data are shown in Table 1: increasing bulk polyether content reduces film aqueous contact angles (increasing film wettability); increasing bound PEG molecular weight results in greater film thickness. Immobilization efficiencies for polysiloxanes containing 20% PEG side-chain grafts decrease with increasing side-chain length. XPS spectra shown in Figure 10 exhibit reduced C1s C–O/C–C ratios as PEG molecular weight bound to PHMS increases. Grafted, pendent PEG side chains appear to block further reaction of residual hydrosilyl units along the polysiloxane backbone with terminal, exposed olefins at the organosilane film interface, resulting in limited attachment of the grafted polymers to the monolayer surface in the two-step reaction.

A One-Step Alternative Method. PHMS bulk-grafted with both alkylsilane anchors and pendant perfluoroalkyl chains can be attached to silicon oxide surfaces by direct, solution-phase chemisorption in a one-step process. Analogous polymers bearing alkyl disulfide anchor chains have been shown to yield stratified, fluorine-enriched monolayers on gold surfaces.[20] One-step modification of silicon oxide from dilute solution using perfluoroalkyl-grafted PHMS de-

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[32] Briggs, D.; Brown, A.; Vickerman, J. C. *Handbook of Static Secondary Ion Mass Spectrometry (SIMS)*; John Wiley & Sons: Chichester, 1989.

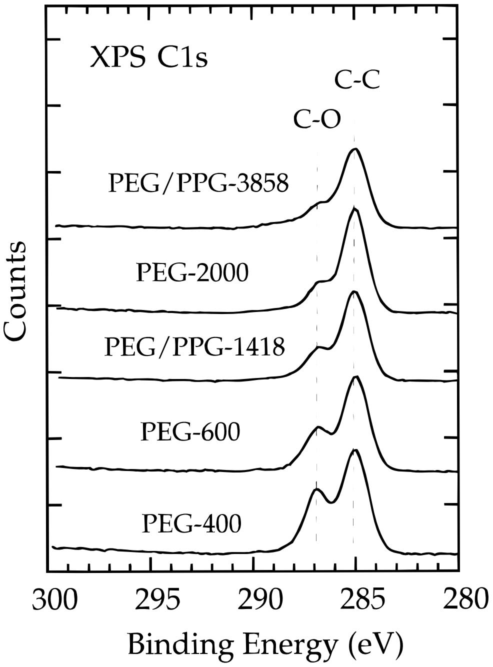

Figure 10. XPS Cls spectra following grafting of polysiloxane-immobilized alkenyl silane monolayers in a two-step procedure.

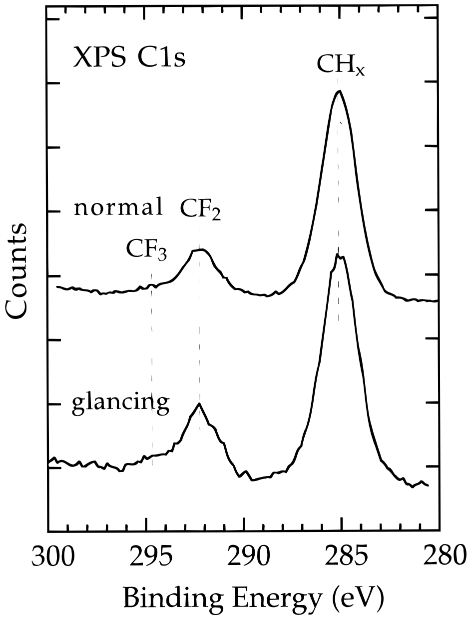

Figure 11. Angle-dependent XPS C1s spectra for a PHMS-*co*-perfluoroalkyl-*co*-alkyltrichlorosilane polymer layer assembled on silicon oxide using a one-step method.

rivatized with alkyltrichlorosilane side chains yields bound chemistry consistent with polymer monolayer formation. Figure 11 shows the angle-dependent XPS C1s spectrum for this one-step reaction using a perfluoroalkyl-grafted polysiloxane-bearing octylsilane anchoring side chains. Peaks associated with $-CF_3$ (294 eV), $-CF_2-$ (292 eV) and $-CH_x-$ (285 eV) are all observed. The contribution of the $-CF_2-$ signal and the $-CF_2-/CH_x$ ratio are more prominent in the glancing angle spectra, consistent with low interfacial energy perfluorochain partitioning to the interface.[20,33] The lack of a clear $-CF_3$ signal signifies, however, that perfluorochain enrichment is low and orientation of these grafts normal to the surface plane to expose the terminal $-CF_3$ groups is unlikely. We have shown that such side chain orientation normal to the film interface is a function of perfluoroalkyl graft density.[20b,34]

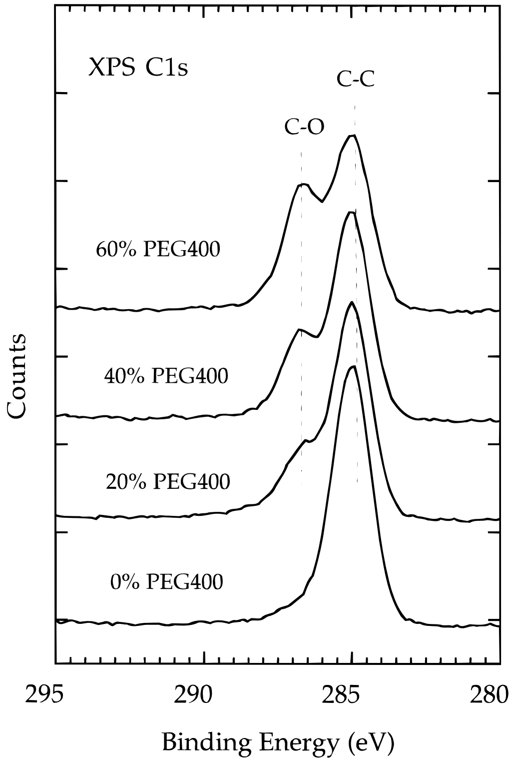

Figure 12. Compositional dependence of the XPS C1s signal for one-step immobilization of PHMS-*co*-PEG400-*co*-alkyltrichlorosilane.

Figure 12 shows XPS C1s results for one-step derivatizations of silicon oxide using PHMS grafted with alkylsilane anchoring chains and different amounts of PEG 400 chains. The spectra show a clear trend correlating the amount of bulk-grafted PEG 400 to an increasing amount of C1s ether carbon signal (287 eV) on the surface. Contact angle and thickness data for terpolymers bearing either 40% PEG 400 or 20% perfluorocarbon grafts are shown in Table 1.

Conclusions

Sequential monolayer derivatization allows fabrication of layered and stable organic thin films to improve or change interfacial properties at solid surfaces. Surface chemistry composition is varied by selecting specific attachment chemistries (e.g., perfluoralkyl vs PEG) and accurately controlling copolymer composition and side chain functionalization prior to chemical immobilization to olefinic silane monolayers. Nevertheless, siloxane polymers with high percentages of PEG grafting proved difficult to immobilize at high density on olefin surfaces, yielding relatively thick immobilized films because of the steric influence of grafted PEG chains. As an alternative, more direct “grafting to” in situ derivatization of previously bound siloxane polymer at residual Si−H functional sites comprised a third sequential PEG reaction sequence. This reaction at the interface is not

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(33) Schnurer, A.; Holcomb, N. R.; Gard, G.; Castner, D. G.; Grainger, D. W. *Chem Mater.* **1996**, *8*, 1475−1481.

(34) Castner, D. G.; Wang, W.; Grainger, D. W., unpublished results.

well controlled because of PEG steric reactivity problems and surface-reactive site access variability. Surface analysis shows that surface composition of PEG can, nevertheless, be altered by changing the concentration of the reactants and reactant time for each subsequent layering process. The third reaction step using PEG grafting is able to produce increased PEG side-chain density over the more direct two-step approach anchoring pregrafted PEG functionalized siloxane polymer. This may be attributed to higher concentrations of surface-exposed siloxane polymer functional groups and favorable immobilized siloxane polymer conformations that can react with small reactants at the interface. The process is different from that of one-step immobilizing of a densely prederivatized polymer where grafted chains hinder surface accessibility to immobilization sites.

Acknowledgment. Support is gratefully acknowledged from National Science Foundation/EPRI joint grant program (NSF MSS-9212496 and EPRI RP-8017) (D.W.G.), National Science Foundation Grant DMR-9357439 (D.W.G.), and National Institutes of Health grant RR-01296 (D.G.C.).

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