Adsorption of Ultrathin Films of Sulfur-Containing Siloxane Oligomers on Gold Surfaces and Their *In Situ* Modification

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Received October 5, 1993; Revised Manuscript Received February 24, 1994[⊛]

ABSTRACT: Commercially available poly[methyl(mercaptopropyl)siloxane] oligomers have been chemisorbed to gold surfaces from organic solution via gold–alkanes thiolate bonds. Bound films of monolayer thickness (15–20 Å) are shown to form spontaneously and are compositionally and structurally isotropic, regardless of solution concentration. X-ray photoelectron spectroscopy yields evidence for two distinct sulfur species in these films: one consistent with gold–thiolate bonds and one representing free, unbonded thiol. A high content of unbonded thiol has been used to modify these organic films *in situ* using photochemistry. Subsequent exposure of the assemblies to monomeric organothiols does not change film properties. We demonstrate that these siloxane oligomers can be photochemically modified in bulk and assembled on surfaces or, alternatively, that the siloxanes can be chemisorbed as films and subsequently modified *in situ* to present various functional surfaces. Photochemical derivatizations included alkyl, perfluoor, and polyether chains. Cyclic voltammetry exhibited various redox blocking capabilities for $Fe(CN)_6^{3-}$ probes depending on film preparation conditions and chemistry. Chemical derivatization disrupted film structure and redox blocking ability, in addition to oxidizing unbound thiol groups. Both pure and photoderivatized siloxane films were perturbed by high-temperature (>100 °C) exposure to solution environments.

Introduction

Current broad use of siloxane polymers as surface modification agents is attributable to their thermal properties, environmental durability, and their notable low surface tension compared to hydrocarbon-based polymers. Poly(dimethylsiloxane) (PDMS) is the most common siloxane material used in surface applications. Its surface activity results from the combination of PDMS's uniquely flexible siloxane main chain and accompanying alignment of pendant methyl groups along this backbone.[1,2]

We have been interested recently in ultrathin bonded films of derivatized siloxanes[3,4] and other polymers on solid surfaces.[5,6] These polymer coatings all share common architectural features of flexible main chains and pendant alkyl chains terminated with anchoring groups specific to binding designated solid substrate surfaces. Bonded polymer films having thicknesses of 20–40 Å form spontaneously by polymer adsorption from dilute organic solution on metal and oxide surfaces. Because of their multipoint chemisorptive anchoring, these films are stable to solvent reflux, elevated temperatures, and can also be used as facile organic foundations to undergo chemical modification *in situ*.[3-6]

In this contribution, we describe the formation of ultrathin, bonded films of poly[methyl(mercaptopropyl)siloxane], a commercially available siloxane oligomer with short alkyl side chains terminated in thiol groups, and its derivatized product oligomers. These siloxane oligomers attach to gold surfaces by adsorption from solution to form monolayer films. In addition to thickness and wettability measurements, we have used angular-dependent X-ray photoelectron spectroscopy (ADXPS) to profile the surface composition and chemistry of these ultrathin organic arrays. XPS data show that two distinct sulfur species are present—one bound as a gold thiolate and another as free thiol. We have used the free thiol in photochemical derivatizations to modify the siloxanes both prior to and after surface chemisorption. Cyclic voltammetry studies show that electron transfer from aqueous redox species through these chemisorbed films to the surface of modified gold electrodes is dependent on solution and derivatization conditions. The utility of chemisorbed ultrathin films as organic foundations for tailoring interfacial properties is described.

Experimental Section

Materials. Poly[methyl(mercaptopropyl)siloxane] oligomer (PMMPS; mol wt = 670, DP ≈ 5) was purchased from Hüls (Warrington, PA) and used as received. Azobis(isobutyronitrile) (AIBN; Aldrich) was recrystallized twice from methanol. Other chemicals used as obtained include 1-hexene (Aldrich; 97%), 5-hexen-1-ol (Aldrich; 99%), 1*H*,1*H*,2*H*-perfluorohexene (PCR; 97%), octadecyl mercaptan (Aldrich; 98%), hexadecane (Aldrich; 99%), chloroform (CMS; Chempure), toluene (CMS; Chempure), and ethanol (Quantum Chemical; 190 proof). Methoxypoly(ethylene glycol), ω-allyl ether (allyl-PEO; mol wt 400), and 1,3-bis(heptadecafluorodecyl)imidazole-2-thione were generous gifts from Dr. Joachim Venzmer (University of Mainz) and Dr. Michael Ward (University of Minnesota), respectively. Potassium ferricyanide (99+%) and hexamine ruthenium(III) chloride (95+%) used in electrochemical measurements were purchased from Allied Chemical and Johnson-Mathey, respectively. Millipore-filtered water was used for electrochemical measurements, contact angle and film cleaning (18 MΩ resistivity).

Bulk Modification of PMMPS. A total of 1.00 g (7.4 mmol SH) of PMMPS and 4.50 g (53.5 mmol) of 1-hexene were dissolved in 6 mL of toluene in a 25-mL round-bottomed flask. After 0.050 g (0.30 mmol) of AIBN was added, the solution was stirred under UV radiation (with a 100-W medium-pressure Hg–Xe lamp beam filtered through a 10 × 12 cm Pyrex water-filled cylinder) for 10 h. Solvent and excess hexene were then removed by rotary evaporation, and the residual product was washed with methanol and dried under vacuum. The product was analyzed by FTIR, ^{1}H-NMR, and gel permeation chromatography (GPC) to confirm product formation, compositional data, and reaction degree.

1*H*,1*H*,2*H*-perfluorohexene-modified and poly(ethylene oxide) (PEO)-modified PMMPS samples were also prepared by an analogous procedure except that perfluorohexene or allyl-PEO were used in place of 1-hexene.

Monolayer Preparation. Gold substrates were prepared in a diffusion-pumped thermal evaporator with a base pressure of

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[⊛] Abstract published in *Advance ACS Abstracts*, April 1, 1994.

0024-9297/94/2227-3053$04.50/0

6×10^{-7} Torr. A layer of Ti/W (1000 Å) and a layer of Pd (200 Å) were predeposited on 4-in. polished silicon wafers (Wacker Siltronic; semiconductor grade, 20 Ω·cm resistivity, SEMI-standard, p-type silicon) as adhesive interlayers. Vapor deposition of 99.999% gold from a resistively heated tungsten holder onto the Pd-coated wafer surface generates a 1500–2000-Å-thick gold layer. Immediately following evaporation, the deposition chamber was backfilled with pure N_2 and each wafer was cut into 0.8×8 cm slides by scoring the wafer on the reverse side with a diamond-tipped scribe. Underivatized and derivatized PMMPS monolayers were prepared by exposing these cut slides to a sample chloroform solution of various concentrations at ambient temperature (21 °C) for 72 h. The slides were then removed from the solution, immersed into fresh $CHCl_3$ (20 mL) for 0.5–1.0 min, and rinsed with $CHCl_3$, EtOH (6 mL), and Millipore water (10 mL) in sequence. The slides were subsequently blown dry in a N_2 stream prior to analysis.

Monolayer Characterization. Static contact angles for water were determined using the sessile drop method with a Ramé–Hart Model 100 contact angle goniometer in a controlled environment (relative humidity = 100%). Measurements were taken on both sides of the water drops at ambient temperature 30–40 s after 1-μL drops were applied to surfaces and the needle tip was removed from each drop. Contact angle data reported are the average of 3 drops at different locations on the 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°. Freshly prepared bare gold was used as reference, and three to four measurements were made with each sample slide. Thicknesses were calculated numerically assuming a refractive index of 1.43 for the monolayer.[7-9]

Infrared spectra of both bulk and adsorbed monolayer films were acquired on a Perkin-Elmer 1800 Fourier transform infrared spectrophotometer with a deuterated triglycine sulfate (DTGS) detector. Transmission IR spectra of bulk samples were measured as neat oligomer samples on NaCl crystal plates. External reflection IR (ER-IR) spectra were obtained on the same spectrometer using a custom optics-optimized single external reflection attachment at an incident angle of 78°. Clean bare gold substrates (measured less than 10 min after gold vapor deposition) were recorded as reference spectra. All ER spectra were taken at 4-cm^{-1} resolution with 1024 scans and are reported as $-\log(R/R_0)$, where R and R_0 are the reflectivities on the sample and bare gold, respectively.

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 Au ($4f_{7/2}$) peak at 84.00 eV. Peak fitting of the high-resolution spectra was done using Gaussian 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),[10] the photoelectron escape depth was assumed to vary as $KE^{0.7}$,[10] and Scofield's photoionization cross sections[11] were used.

Angle-dependent XPS data were collected at nominal photoelectron take-off angles of 0°, 55°, and 80°. Compositional depth profiles (CDP) were determined from angle-dependent data using the regularization method of Tyler et al.[12] The take-off angle was defined as the angle between the surface normal and the axis of the analyzer lens system. The solid acceptance angle of the analzyer lens was decreased to 12° × 30° by placing an aperture over the analyzer lens to improve the depth resolution at each take-off angle.[13]

Cyclic Voltammetry. Cyclic voltammograms of self-adsorbed monolayer films on gold were recorded on an EG&G Model 273, potentiostat/galvanostat connected to a Goerz SE790 X–Y recorder. A single-compartment, three-electron, glass cell containing a Pt gauze counter electrode, a calomel (saturated KCl) reference electrode (SCE), and a monolayer film-covered gold working electrode was used. The size of the working electrode was approximately 0.8×2 cm^2 with an activate surface area (immersed in an electrolyte solution) of 0.8×0.4 cm^2 (the rest of the electrode surface was protected by a tightly wrapped Teflon film from contact with the electrolyte). All electrolyte solutions were freshly prepared using 99+% KCl, together with either $K_3Fe(CN)_6$ or $Ru(NH_3)_6Cl_3$ in Millipore water, and purged with argon for 15 min prior to measurement. Typically, 6–15 scans were run for each sample with potential ranges between +0.5 and −0.9 V referenced to SCE at a scan rate of 0.05 V/s.

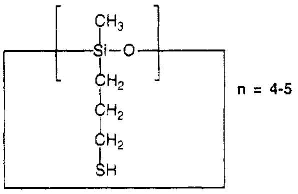

Figure 1. Structure of the thiol-containing cyclic siloxane oligomer PMMPS.

Sequential Monolayer Adsorption. Gold substrates with adsorbed PMMPS monolayer films were immersed into $CHCl_3$ solutions of either octadecyl mercaptan (1.0 mM) or 1,3-bis(heptadecafluorodecyl)imidazole-2-thione (1.0 mM) for an additional 48 h. The substrate was then removed from solution, thoroughly washed with pure solvent ($CHCl_3$) followed by rinsing with $CHCl_3$, ethanol, and Millipore water, and dried in a N_2 gas stream prior to analysis.

***In Situ* Ultrathin Film Modification.** Monolayer films (PMMPS) on gold were immersed into solutions containing 1-hexene (or 1*H*,1*H*,2*H*-perfluorohexene or allyl-PEO) (40% in toluene, v/v) and AIBN (2.5%, w/v). After the solution containing the coated gold substrates was irradiated with an ultraviolet beam (filtered by a water-filled Pyrex cylinder) using a 100-W medium-pressure Hg-Xe lamp for 72 h, the substrate was removed from solution, transferred to $CHCl_3$ solvent for 15 min, and finally rinsed with $CHCl_3$, ethanol, and Millipore water in sequence to remove any physically adsorbed species.

Thermal Testing of Chemisorbed Monolayers. Both dry and wet (under solvent) thermal tests were performed with monolayer films on gold. In dry tests, monolayer films covering gold substrates were placed in clean glass vials and the vial was maintained under N_2 at 110 °C for 15 h. Specimens were cooled gradually to room temperature and transferred into $CHCl_3$ solutions for 2–3 min, rinsed, and dried under N_2 for analysis. In the wet method, toluene (or hexadecane) or water (for poly(ethylene oxide)-modified films) was used as solvent and the film-adsorbed substrates were immersed into these solutions at 85–110 °C for 5–120 min, removed from the solutions, and cleaned as in the dry method prior to further analysis.

Results and Discussion

1. PMMPS Monolayers on Gold. Poly[methyl(mercaptopropyl)siloxane] is a commercial product of Hüls America. This sample has been analyzed by gel permeation chromatography in our lab to have an average molecular weight of 790 (in THF at 30 °C, referenced against polystyrene standards). Our mass spectrum of the same sample reveals a maximum detectable mass of its molecular ion to be 670, together with the cleaved fragments of 461 (assigned to the molecular mass of a tetramer having lost one propylthiol radical) and 445 (a pentamer having lost three propylthiol radicals). Additionally, ^{1}H NMR analysis showed a stoichiometric ratio of mercapto groups versus the backbone silicon-linked methyl group, and no additional protons corresponding to the terminal groups (e.g., absence of trimethylsiloxy end groups and other polar groups, as confirmed also by FTIR, expected for linear siloxane polymers). These results strongly indicate that the sample is a mixture of cyclic siloxane oligomers rather than a polymer, having one SH group with respect to each repeating unit as indicated in Figure 1.

Table 1. Concentration Dependence of Properties for PMMPS Monolayers Chemisorbed on Au⁰

monolayer sample no.	concn[a] (mM)	film thickness[b] (Å)	contact angle[c] (θ_{H_2O}, deg)	$E_{p,c}$[d] (mV)
M-PMMPS0.1	0.1	14.6 ± 1.2	73 ± 1	−210
M-PMMPS1.0	1.0	15.8 ± 1.7	71 ± 1	−290
M-PMMPS10	10	17.3 ± 1.3	68.5 ± 1.5	−350
M-PMMPS60	60	16.7 ± 1.6	77.5 ± 1.5	
M-PMMPS100	100	17.2 ± 1.3	83 ± 3	−410
M-PMMPS1000	1000	17.7 ± 1.7	83.5 ± 1.5	−590

[a] PMMPS oligomer concentration in a $CHCl_3$ solution (calculated based on the mol wt of the repeating unit). [b] Measured by ellipsometry and calculated assuming a refractive index of 1.43 for the monolayers (see ref 9). [c] Static water contact angle obtained with the sessile drop method. [d] Redox [$Fe(CN)_6^{3-}$] reduction peak potential from CV measurements.

Monolayers of PMMPS chemisorbed on gold substrates are formed through spontaneous solution-phase adsorption of oligomer molecules driven by specific Au–S interactions. Our previous study on dithioalkyl polyacrylate monolayers on gold has proven that increasing the density of dithioalkyl anchors along the polymer backbone also increases free, unbound dithio groups in the resulting bound monolayers.[6] A recent study on acrylate polymers containing short alkyl side chains bearing thioether groups has also shown evidence of free unbound side chains.[14] For PMMPS, a high concentration of mercapto anchors versus a backbone siloxane unit makes complete thiolate bonding between the gold substrate surface and mercapto sulfur atoms of each repeating unit in the oligomer highly unlikely. Additionally, if PMMPS maintains its cyclic structure in the chemisorbed state, the cyclic conformation could also prevent complete binding of all pendent thiol groups. The number of successfully chemisorbed units will determine the structure and, therefore, the properties (quality) of the resulting bound monolayers. Variations in PMMPS solution concentration, solvent type, and annealing of preformed monolayers have been studied to understand their influence on the mechanism of monolayer formation and the resulting properties of the monolayers.

Solution Concentration Effects. A wide range of PMMPS oligomer solution concentrations in the gold substrate immersion solution (0.1–1000 mM) were used to examine any effects on monolayer formation. Table 1 lists the thickness and water contact angle data for PMMPS monolayers obtained from different PMMPS concentrations in solution.

In the only other publication known on this material, Häussling[15] reported that adsorption of this same PMMPS compound on Au⁰ was completed within approximately 2 h (with maximum thickness reached after the first 60 min). Our concentration experiments, however, used immersion times for gold substrates in solution at identical as well as extended (72-h) solution adsorption times, well beyond what was shown to be adequate for kinetically complete monolayer formation (60 min).[15] From Table 1, it is apparent that, as PMMPS concentration increases from 0.1 mM to 1.0 M, the resulting monolayers show no significant increase in monolayer thickness.[9] This suggests that only monolayer films are formed on substrate surfaces. Significantly, side reactions such as sulfur–sulfur oxidation (disulfide cross-linking) which contribute to the formation of multiple layers[16] have not been observed.

The thickness of the PMMPS monolayer from 0.1 mM solutions is very consistent with the reported value (13–14 Å) of the same monolayer from a ca. 0.2 mM solution.[15] However, our water contact angles for the same monolayer do not agree with reported values[15] ($\theta^{adv}_{H_2O}$ = 93°, $\theta^{rec}_{H_2O}$ = 84°). In fact, monolayers prepared from solutions of concentration below 10 mM all show similar wettability toward water. More concentrated solutions (≥60 mM) give monolayers which are increasingly hydrophobic. With solution concentrations of 100 mM or greater, monolayers reach the identical water contact angle (83°) observed for thicker spin-coated bulk films (680 Å).

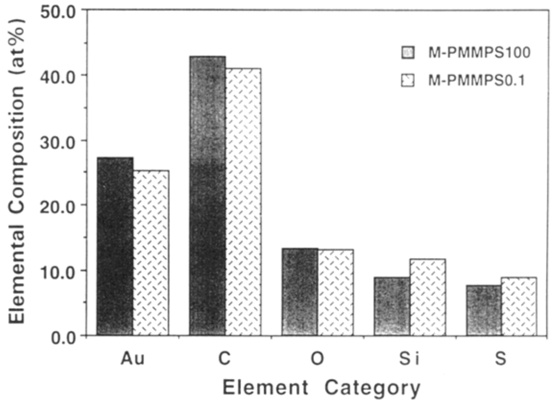

Figure 2. Compositional comparison between M-PMMPS0.1 and M-PMMPS100 oligomeric monolayers as demonstrated from XPS analysis.

Table 2. Angle-Dependent XPS Data for PMMPS60 Ultrathin Oligomer Films on Gold (atomic %)[a]

take-off angle (deg)	sampling depth (Å)	C	Si	O	S	Si/S	O/S
0	90	60.5	12.3	17.6	9.7	1.3	1.8
55	50	60.6	11.9	18.0	9.6	1.2	1.9
80	15	60.7	13.2	17.3	9.0	1.5	2.0
theor	bulk	57.1	14.3	14.3	14.3	1.0	1.0

[a] The Au XPS signal was not included in the experimental composition so a direct comparison with the theoretical composition can be made.

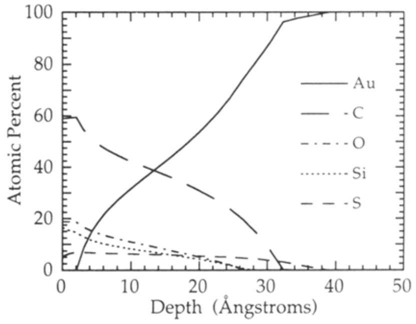

Figure 3. Compositional depth profile (CDP) generated using the regularization method of Tyler et al.[12] applied to angle-dependent XPS data for the M-PMMPS60 monolayer. *X*-axis: Depth into film. *Y*-axis: Atomic percent of each element as a percent of the XPS total signal for each measurement.

A comparison of film composition using XPS studies on monolayers prepared from both 0.1 and 100 mM PMMPS solutions reveals very similar results (Figure 2), indicating that substrate surfaces are covered by PMMPS oligomers at both low and high solution concentrations.

An angle-dependent XPS experiment was carried out for the monolayer prepared from the 60 mM PMMPS solution (Table 2 and Figure 3). Unlike dithioalkyl polyacrylate[6] and (perfluoroalkyl)(dithioalkyl)polysiloxane monolayers,[3] no large changes in PMMPS monolayer composition are observed by changing the XPS take-off angle (sampling depth). The monolayer shows a homogeneous composition: film composition remains constant when the XPS sampling depth changes from ∼90 to ∼15 Å (the take-off angle increases correspondingly from 0° to

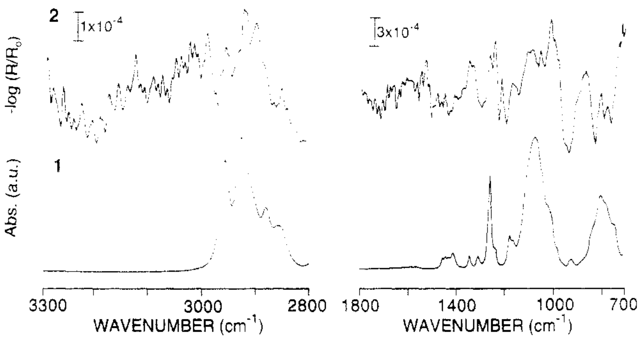

Figure 4. FTIR spectra of PMMPS (1) in bulk and (2) as a monlayer film on gold (M-PMMPS100).

80°). The compositional depth profile (CDP), computed from a published regularization method,[12] also indicates a monolayer thickness of ~18 Å, as determined by the depth where the Au^0 concentration is 50 atomic % (Figure 3). This thickness is within experimental error of the ellipsometric thickness (16.7 ± 1.6 Å) for the same sample.

An almost structurally featureless FTIR spectrum was obtained for PMMPS monolayers on gold, indicating conformational disorder in the film as well (Figure 4). This homogeneity suggests that the monolayer is probably structurally isotropic and can be explained by the presence of short anchoring side chains together with the high density of anchors along the backbone ring. The former does not provide sufficient van der Waals lateral interactions between side chains to stabilize chain orientation and ordering, and the latter contributes free, unbound mercapto groups throughout the monolayer matrix. This results in a nearly isotropic monolayer film.

Incomplete interaction between side-chain mercaptan anchors and the gold substrate is demonstrated by XPS high-resolution S2p spectra as shown in Figure 5. The asymmetric three-peaked S2p line shapes of the monolayers shown result from the presence of two sets of overlapping S2p spin-orbital doublets (Figure 5a).[6] One doublet ($S2p_{3/2}$ BE = 162 eV) corresponds to thiols adsorbed to the Au^0 surface. The second doublet ($S2p_{3/2}$ BE = 164 eV) is identical to that for metal-free sulfur species,[17,18] representing free, unbound thiol.[6] Peak-fitting results show that all monolayers exhibit a similar percentage of bound mercapto groups (35 ± 2%) regardless of solution concentration.

Both XPS and wettability analysis indicate that monolayers of PMMPS assembled from different concentration solutions on gold substrate surfaces have similar properties regarding composition, anchoring percentage, and film wettability. Furthermore, the ellipsometric thicknesses for PMMPS monolayers also demonstrate a less significant dependence on solution concentration compared to other reported polymeric systems,[6,15] implying that PMMPS monolayers prepared from a wide range of solution concentrations are macroscopically indistinguishable.

Cyclic Voltammetry. To further examine monolayer properties, electrochemical measurements were undertaken using cyclic voltammetry measurements. Cyclic voltammetry has been shown to be particularly useful for detecting film defects through permeability studies of redox-active probe molecules in organic thin films on electrodes.[18,19]

Figure 6 shows cyclic voltammograms (CVs) of the aqueous redox probe $Fe(CN)_6^{3-}$ (3 mM in a 1 M KCl solution) obtained for gold electrodes with adsorbed PMMPS monolayers prepared from different solution concentrations. Several points are worth noting. First, all CVs for monolayer-adsorbed electrodes show greatly suppressed peaks corresponding to $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ reduction (Figure 6A). Bare gold electrodes with the same redox couple show the well-known, reversible behavior reported by others[17-19] (data not shown, ΔE_p = 60 mV, i_p = 0.15 mA). Redox behavior for monolayer-covered electrodes indicates a significant blocking of the probing redox species by surface-bound monolayers. Second, only a single cathodic peak is observed for all PMMPS-modified electrodes within the cycled potential ranges between +0.5 and −0.5 V (or −0.9 V). However, increasing the incubation solution concentrations yields monolayer films with a continuously increasing cathodic peak ($E_{p,c}$) shifting to a more negative potential relative to the $E_{p,c}°$ (for the bare

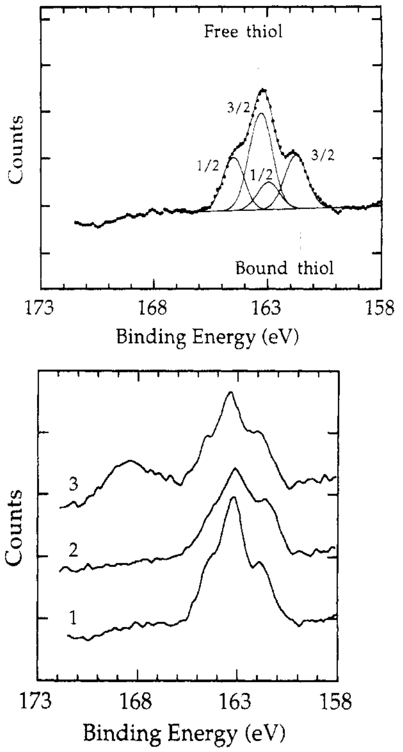

Figure 5. (a) High-resolution XPS S2p spectrum of a PMMPS monolayer showing $S2p_{3/2}$–$S2p_{1/2}$ spin-orbital doublets for both sulfur species within assembled monolayer films. (b) High-resolution XPS S2p spectra for (1) M-PMMPS100, (2) M-EO-PMMPS, and (3) M-PMMPS-EO. See text for experimental details.

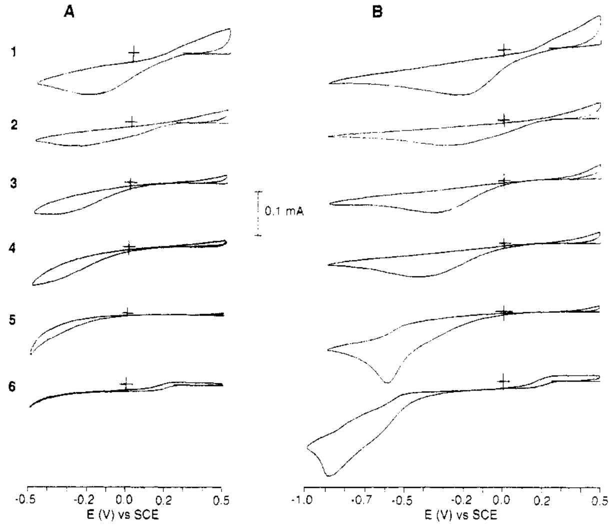

Figure 6. Cyclic voltammograms of PMMPS monolayer modified electrodes (3 mM $Fe(CN)_6^{3-}$, 1.0 M KCl, fourth scan): (A) +0.5 to −0.5 V cycled potential; (B) +0.5 to −0.9 V cycled potential. (1) M-PMMPS0.1; (2) M-PMMPS1.0; (3) M-PMMPS10; (4) M-PMMPS100; (5) M-PMMPS1000; (6) $C_{18}H_{37}SH$ monolayer.

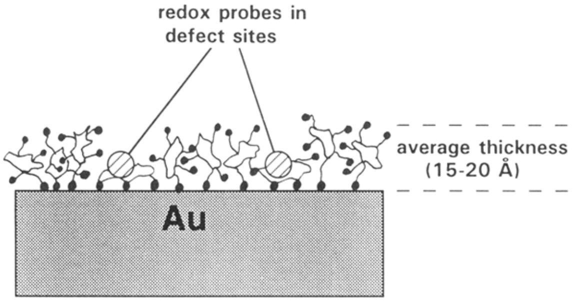

Figure 7. Structural depiction of PMMPS monolayers.

gold electrode, $E_{p,c}° = +180$ mV) (also see Table 1). These results are representative of at least six separate electrode experiments for each system and are reproducible for the first 6–8 scans.

Since the peak-to-peak separation (ΔE_p) value for oxidation and reduction currents is evidence of the blocking effect of probing species by the monolayer barrier,[19,20] it is believed that higher concentration solutions provide monolayers with an improved barrier behavior despite similar layer thicknesses and similar XPS compositions. In other words, monolayers from higher concentration solutions possess less microstructural defects than corresponding films formed from diluted solutions. Third, when electrode potential was cycled between +0.5 and −0.5 V, cathodic peaks are barely detectable for electrodes covered with monolayers from 1000 mM or higher concentration solutions (only capacitive current). The same monolayer-covered electrodes show a considerable probe reduction peak, however, when the applied potential is expanded to cycle between +0.5 and −0.9 V. A similar result was also observed for octadecanethiol (C18SH) monolayer-modified electrodes (Figure 6B, curve 6), suggesting that defects in monolayers from ≥1000 mM solutions are small and widely spaced. In this case, however, the larger negative overpotential (to −0.9 V) could facilitate reductive desorption of the PMMPS from the gold electrodes. Previous work has demonstrated that thiolate reduction for hexadecanethiol occurs at −1.0 V and for octadecanethiol near −1.3 V.[21] A more recent study indicates that monolayer reduction occurs at even more negative potentials.[22] Nevertheless, XPS data show that PMMPS monolayer composition remains constant before and after cyclic voltammetry, supporting the notion that, if such reduction is occurring at the most negative overpotentials, the layer remains intact and surface-localized. Large defects of closely spaced small defects will correspond to a reversible, linear diffusion-dominated cyclic voltammogram.[23,24]

The lack of sigmoidal curves in most CVs supports a primary linear diffusion redox mode where probe species penetrate the monolayer films through small defects linearly. Unlike defects in alkane thiol monolayers which were induced by short, aromatic template molecules,[25] defects in PMMPS monolayers are mainly induced by short-chain disorder in film packing, together with imposed backbone ring conformation restrictions. Monolayers of PMMPS on gold may, therefore, be microscopically uneven in thickness and composed of relatively dense domains of both anchoring side chains and backbone segments as well as small islands (defects) of only backbone chain shielding lacking anchored, aggregated side chains (Figure 7).

An examination of the CV response of monolayers upon aging shows that PMMPS monolayers become more leaky to redox probe molecules after repeated cycling during electrochemical measurements (greater than 10 scans) followed by storage in air in a dry state overnight after normal cleaning (Figure 8A). This observation implies that film defects increase due possibly to conformational shrinking of PMMPS molecules under solvent removal. Similar results have also been obtained for dithioalkyl-substituted polyacrylate and cohydrosilylated(perfluoroalkyl)(dithioalkyl)polysiloxane monolayer films on gold electrodes.[26]

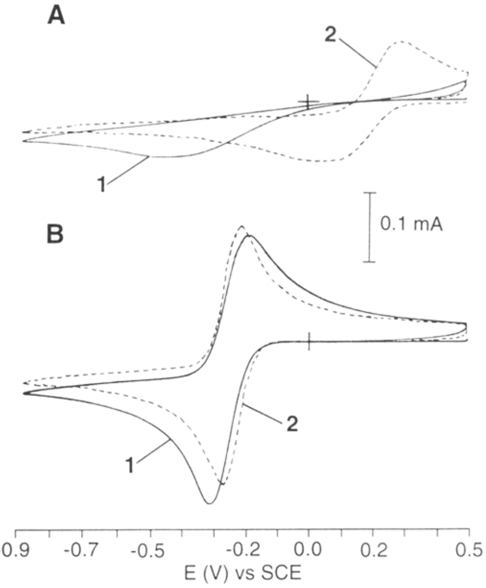

Figure 8. Cyclic voltammetry of PMMPS monolayer (M-PMMPS100) modified electrodes upon aging by drying under nitrogen and storage. (A) Probed by a 3 mM $Fe(CN)_6^{3-}$ redox couple. (B) Probed by a 3 mM $Ru(NH)_6^{3+}$ redox couple. (1) Freshly prepared monolayer (fourth scan); (2) 16-h aging after CV measurements (10 scans).

Figure 8B shows CV data for identical PMMPS monolayer-modified electrodes probed by a $Ru(NH_3)_6^{3+}$ ion redox couple for both the fresh and aged film states as described in Figure 8A for $Fe(CN)_6^{3-}$. $Ru(NH_3)_6^{3+}$ probe molecules appear more permeable through these monolayer surfaces than $Fe(CN)_6^{3-}$ probes. Similar results were already reported for nanoporous monolayer systems comprising mixed long- and short-chain organothiols and were attributed to a monolayer "sieving" effect to $Ru(NH)_6^{3+}$ as opposed to $Fe(CN)_6^{3-}$.[25] Diffusivities of the two probe molecules are similar yet the heterogeneous electron-transfer rate constant for $Ru(NH_3)_6^{3+}$ is considerably larger than that for $Fe(CN)_6^{3-}$.[25] Cyclic voltammetric behavior of these monolayer-adsorbed electrodes toward the $Ru(NH_3)_6^{3+}$ ion may be explained by this kinetic mechanism since little evidence for a radial diffusion component is observed (sigmoid shape). Film defects are possibly large relative to $Ru(NH_3)_6^{3+}$ probes as nearly ideal linear diffusion occurs (Figure 8B, curve 1). Further enlargement of defects by possible shrinking of monolayer conformation upon aging (drying) is evidenced by the completely reversible CV curve obtained under these conditions with ΔE_p of 60 mV (Figure 8B, curve 2), proving again the monolayers of PMMPS are structurally loose and can undergo conformational changes with environmental variation.

Sequential Monolayer Adsorption. CV study of PMMPS monolayers have shown that the molecules are not packed densely enough to afford complete redox blocking. The limited bonding of thiol groups to the gold surface (35 ± 2% of total anchors) probably caused by constraints of the backbone ring configuration and the relatively short anchoring chains which contribute little stability to later chain–chain and dense packing interac-

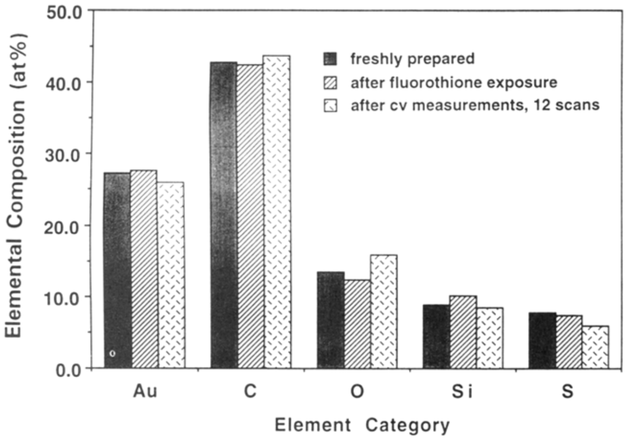

Figure 9. XPS-determined elemental composition for the M-PMMPS100 monolayer before and after secondary exposure to fluorothione and CV measurements, respectively.

tions are the two major causes of this incomplete blocking. To further probe the surface coverage dependence of PMMPS monolayers, a secondary sequential adsorption method[14] using either fluorinated imidazole thione[27] or octadecanethiol (C18SH) as a small molecule "hole-filler" was performed. Figure 9 presents the monolayer film composition results determined by XPS analysis for the sequentially adsorbed PMMPS oligomer–fluoromonomer system.

Fluorinated imidazolethione and C18SH are reported to self-assemble into dense monolayers on gold.[23,27] By exposing the PMMPS monolayer-adsorbed substrate (immediately after PMMPS adsorption) to a chloroform solution of either thione or C18SH, the remaining uncovered gold surface sites should be occupied by monomer thione or C18SH molecules, backfilling the film defect sites.[14] Figure 9 demonstrates that no considerable variations in monolayer compositions are observed for either the fluorothione or C18SH mixed monolayer situations (C18SH data not shown). In addition, no detectable XPS fluorine signal is found for thione adsorption, suggesting that the gold surface is completely shielded by the overlying PMMPS monolayer.

Nevertheless, secondary sequential adsorption has been shown to be a useful method to explore monolayer surface coverage by Lenk et al. in their recent work on monolayers of polyacrylates containing thioether anchors on gold.[14] Their results indicate significant surface occupancy by small-molecule perfluoro species. Differences between our experiments versus Lenk's system can be explained by distinct differences in anchor group concentrations (anchor density versus the backbone repeating unit) between the two systems. Despite obvious defects, PMMPS monolayers seem to exhibit greater Au–S binding than the polyacrylate thioether case, contributing to a higher coverage and greater integral stability.[6]

Figure 9 also shows results for the monolayer after CV measurements. No Fe or N signals were detected in XPS measurements, precluding the possibility of increased monolayer leakage by permeating, embedded probing redox molecules (Figure 8) upon aging.[26] Comparison of XPS substrate Au atomic percent data, combined with ellipsometric measurements, shows that monolayers after CV measurement are identical to freshly prepared PMMPS monolayers or thione-treated samples prior to CV analysis. Aqueous contact angles, however, decreased by ~15° for monolayers after CV measurement, compared to either a freshly prepared PMMPS or thione-exposed monolayers (82–83°). This increasing wettability for monolayers after CV measurement is an indirect proof of film conformational changes which lead to less complete surface coverage (bare gold substrates have water contact angles of 45°).[15]

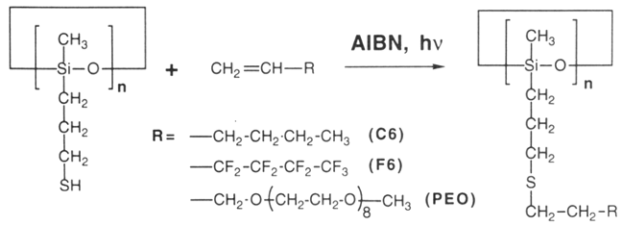

Figure 10. Schematic representation of photo-aided chain-transfer addition reactions.

2. Photochemically Modified PMMPS Monolayers on Gold. Organic thioethers are known to form self-assembled monolayers on gold substrates.[14,28] Mercapto groups at the end of each propyl side chain on PMMPS can be derivatized readily to thioether via a free-radical transfer addition reaction,[29,30] shown schematically in Figure 10.

Hydrocarbon, fluorocarbon, and polyether (PEO) derivatizing reagents were chosen in order to create monolayers having widely varying surface properties. Bulk reactions were photo (UV)-aided using AIBN as a free-radical initiator and PMMPS thiol groups as chain-transfer agents. Results are summarized in Table 3 for bulk photochemistry.

Monolayers of all three modified PMMPS species on gold were prepared in a way similar to that for pure PMMPS monolayers except that aqueous solutions were used for PEO-modified PMMPS. Table 4 presents results for monolayers of those compounds characterized by ellipsometry, contact angle, and CV measurements.

It is apparent that all three modified PMMPS generate only monolayer-thick films on gold substrates as shown by the ellipsometric data. In fact, ellipsometric thicknesses are consistent with thicknesses derived from ADXPS measurements[12] for the C6- and F6-PMMPS monolayers. Both ether carbon ($\underline{C}$–O, 286 eV) and fluorocarbon ($\underline{C}$–F_2, 291.4; $\underline{C}$–F_3, 293.7 eV) peaks were clearly demonstrated for PEO- and F6-modified monolayers, in addition to the hydrocarbon signal ($\underline{C}$–H, 284.5 eV) for the PMMPS monolayer (Figure 11). A significant amount of unbound thioether sulfur was also found (Figure 5B, spectrum 2).[31] Water contact angles show an effective wettability change upon derivatization, i.e., increased by ~20° for the hexene (C6)-modified PMMPS monolayer and ~10° for the fluorohexene (F6)-modified monolayer and decreased by ~30° for the PEO-modified monolayer, compared to pure PMMPS monolayers (80 ± 2°). Less increase in the hydrophobicity of F6-PMMPS monolayers compared to C6-PMMPS is ascribed to higher residual SH groups in films of the former, due to incomplete conversion of free SH to thioether or possible thiol oxidation to more polar sulfoxy species under fluorocarbon derivatization conditions. XPS film composition data for F6-PMMPS monolayers suggest a 75% perfluoro chain attachment efficiency to side-chain terminal thiols (assuming negligible XPS inelastic collision effects) in good agreement with the bulk composition (Table 3).

The redox blocking properties of modified PMMPS monolayers to the redox probe, $Fe(CN)_6^{3-}$, are less efficient compared to underivatized PMMPS monolayers (Table 4 and Figure 12). All CVs for modified PMMPS monolayers present smaller shifts to negative potentials, together with a narrower peak-to-peak separation than PMMPS monolayers. This observation is highly reproducible and

Table 3. Bulk Characterization of Photochemically Derivatized PMMPS[a]

oligomer[b]	derivatizing reagent	thiol convn[c] (C %)	MW[d]	solubility[e]
B-C6-PMMPS	$CH_2{=}CH(CH_2)_3CH_3$	~100	2270 (0.3) 1280 (0.7)	hexanes
B-F6-PMMPS	$CH_2{=}CH(CF_2)_3CF_3$	75 ± 5	2550 (0.55) 1440 (0.45)	hexanes
B-EO-PMMPS	$CH_2{=}CHCH_2O(EO)_6CH_3$	30 ± 5	2710	hexanes, water

[a] Reaction conditions: [PMMPS]/[reagent] (–SH/[C=]) = 1:4–8; AIBN, 4.5 mol % (based on –SH content of PMMPS); toluene (6 mL), room temperature, 10 h. [b] Product oligomers were named first with a letter (B) indicating the bulk versus monolayer (M) derivatized sample, followed by derivatizing reagent (e.g., F6) and "PMMPS" for bulk photo-aided reaction (reagent first) or *in situ* photo-aided reaction (PMMPS first then reagent). [c] Calculated based on the disappearance of a thiol proton in ^{1}H-NMR spectra, (C %) = 100 $(\delta_{0.65} - 2\delta_{1.36})/\delta_{0.65}$. ($\delta_{0.65}$ and $\delta_{1.36}$ are integration peak heights for protons $SiCH_2$ and *SH*, respectively). [d] Molecular weight determined by GPC based on polystyrene standards (data in brackets indicate the relative percentage of each peak). [e] 0.1 g of sample was dissolved in 2.0 mL of testing solvent to prepare a 5% (w/v) oligomer solution (clear and homogeneous).

Table 4. Siloxane-Based Monolayers on Gold Fabricated from PMMPS Prederivatized by Bulk Photoaddition[a]

monolayer	monolayer thickness[b]	XPS-derived thickness[c]	θ_{H_2O} (deg)	$E_{p,c}$ (mV)	ΔE_p (mV)
M-C6-PMMPS	16.8 ± 1.7	15–16	100 ± 2	+180	125
M-F6-PMMPS	21.3 ± 2.4	17–18	89 ± 1	+120	200
M-EO-PMMPS	17.5 ± 2.2		48 ± 1	+20	

[a] Solution concentration: 2% (w/v). [b] From ellipsometry. [c] From ADXPS depth profile at 50 atomic % substrate (gold) signal (see ref 12).

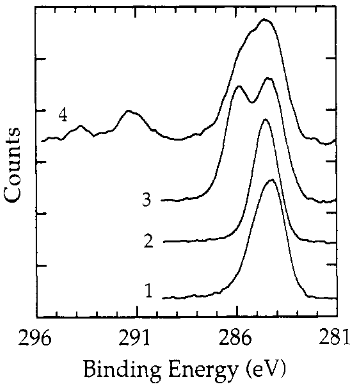

Figure 11. High-resolution XPS C1s spectra for photo-derivatized PMMPS monolayers (see text for details): (1) M-PMMPS 100; (2) M-C6-PMMPS; (3) M-EO-PMMPS; (4) M-F6-PMMPS.

indicates more defects (either large or small, closely spaced) are possibly included in the former monolayers. ADXPS results reveal that all these monolayers are compositionally homogeneous along the surface normal. Isotropic characteristics of the film are ascribed primarily to the unique architecture of the PMMPS molecules in which derivatizing chains are connected directly to the anchoring sulfur atoms. When sulfur anchors bind to gold substrate, connected thioether chains are also brought into the vicinity of the gold surface. Incomplete Au–S bonding as determined by XPS is a second reason for film isotropy since unbound anchors (sulfur species) are uniformly dispersed within the layer thickness. Extra side chains present in modified PMMPS compared to underivatized PMMPS show little effect on altering film thicknesses between the former (Table 4) and the latter (Table 1), implying a difference in film-packing density, i.e., less molecules (anchors) per absolute unit area of substrate surface for modified PMMPS monolayers than for pure PMMPS. This leads to a looser-packed film with increased defect density, consistent with the observed cyclic voltammograms (Figure 12, curves 1–3). This assumption can be rationalized by considering the steric effects of including additional, long side chains on sulfur anchors and differences between thioether sulfur and free thiol sulfur anchors, both of which reduce the reactivity of sulfur in derivatized PMMPS with gold substrates.

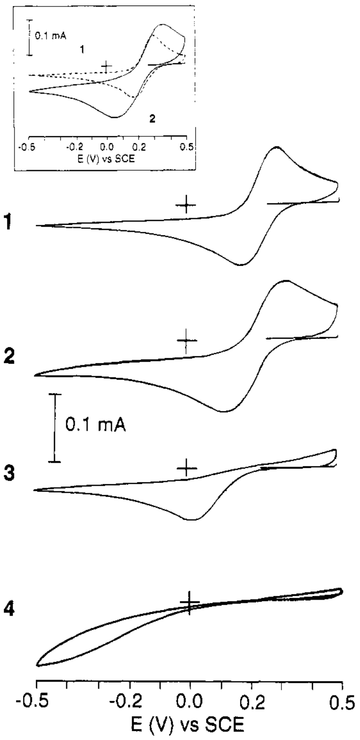

Figure 12. Cyclic voltammograms of bulk photoderivatized PMMPS monolayer-modified electrodes probed by a $Fe(CN)_6^{3-}$ redox couple (1 M KCl, fifth scan). Inset: M-C6-PMMPS monolayer modified gold electrode with (solid line) and without (dashed line) secondary exposure to fluorothione. (1) M-C6-PMMPS; (2) M-F6-PMMPS; (3) M-PEO-PMMPS; (4) M-PMMPS100.

The XPS data for the M-C6-PMMPS monolayer after secondary fluorothione exposure reveal 2.7 atomic % fluorine, in contrast to pure PMMPS monolayers which have no fluorine "backfilling" after the same sequential adsorption treatment (Figure 9), proving that the former has a relatively looser molecular packing containing more defects. Observed improvement in the barrier behavior for C6-PMMPS monolayers treated with C18SH to the same probing redox species (Figure 12, inset curves) is further indirect evidence for looser film structure for modified PMMPS monolayers compared to corresponding underivatized PMMPS monolayers. These results indicate both the efficiency of sequential adsorption in determining structural defects (e.g., loose packing, incomplete surface coverage) for the films[14] and possibly weaker gold–sulfur interactions for thioether anchors over underivatized thiols.

Table 5. *In Situ* Photochemical Modification of PMMPS Oligomeric Monolayers on Au[a]

monolayer	reagent	thickness	water contact angle (deg)	$E_{p,c}$ (mV)	ΔE_p (mV)
M-C6-PMMPS	hexene	20.6 ± 2.3	68.5 ± 1.5	+115	140
M-F6-PMMPS	fluorohexene	17.8 ± 1.8	69 ± 1.0	+175	125
M-EO-PMMPS	allyl-PEO	23.1 ± 1.8	56 ± 1.0	−610	

[a] See Tables 1 and 3 for symbol definitions. *In situ* modification conditions: reagent, 40% (w/v); solvent, toluene; AIBN, 2.5% (w/v); room temperature, 72 h.

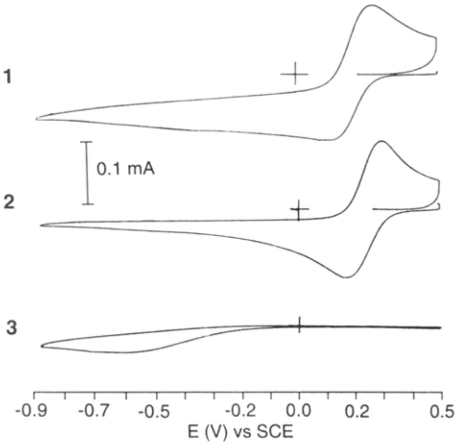

Figure 13. Cyclic voltammograms of *in situ* derivatized PMMPS monolayer-modified gold electrodes probed by a $Fe(CN)_6^{3-}$ redox couple (1 M KCl, fifth scan). (1) M-PMMPS-C6; (2) M-PMMPS-F6; (3) M-PMMPS-EO.

3. *In Situ* Photochemical Derivatization of PMMPS Monolayers on Gold. Comparisons of underivatized and derivatized PMMPS monolayers indicate that the latter have less structural integrity (more defects) than the former, though the former do not exhibit perfect structure. Moreover, XPS results reveal only ~35% conversion of thiol sulfur atoms to thiolate–gold bonds in pure PMMPS films, leaving the majority (~65%) of siloxane-bound mercapto groups free in the monolayer matrix. We have explored the feasibility of further utilizing these unbound, free thiol groups for *in situ* modification of PMMPS monolayers via a similar photochemistry method reported for bulk PMMPS in a previous section, i.e., photo-aided free-radical transfer addition using olefin derivatizing reagents. Table 5 compiles the film properties after several different *in situ* film modifications.

Table 5 shows that all *in situ* modified monolayers have increasing wettability despite using hydrophobic hexene or fluorohexene or hydrophilic PEO derivatizing reagents, while retaining comparable monolayer thicknesses to underivatized PMMPS. Since higher wettability of PMMPS versus PDMS monolayers[32] is ascribed to the existence of free polar SH groups in the film, hexyl or perfluorohexyl chain additions into films should decrease wettability (increasing contact angle) by introducing both hydrophobic segments and simultaneous consumption of polar thiol groups. The results obtained oppose this prediction. One explanation is that, during *in situ* modification, the film structure is perturbed as evidenced by altered CV response (Table 5 and Figure 13). Both CVs for hexene- and perfluorohexene-modified monolayers show a considerably leaky structure compared to unmodified films, indicating a greater defect density. Lower contact angles also result from thiol oxidation in the film during photoreaction. From XPS analysis (Figure 5b), it appears that photo-aided *in situ* film modification generates more oxidized sulfur species than that from bulk photo-modified monolayers and pure PMMPS. These polar, ionized groups contribute to the improved wettability. We have no evidence to quantify the relative importance of monolayer defects generated by structural disturbances versus the creation of oxidized, more polar ionic species in the film during photoreaction to the decreasing contact angles observed.

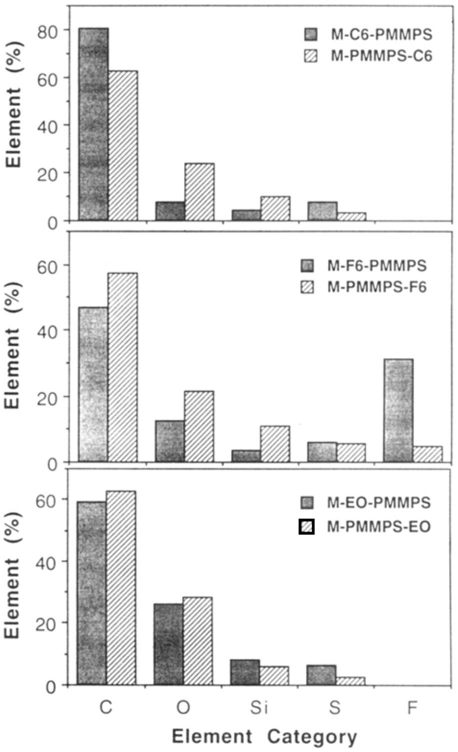

Figure 14. Comparison of bulk and *in situ* derivatized monolayer XPS elemental compositions. The Au XPS signal was not included in the experimental composition to permit direct comparison of the monolayer film compositions.

Figure 14 gives the composition of the PMMPS monolayers after *in situ* modification. For comparison, compositional data for monolayers fabricated from bulk-derivatized PMMPS are also included. Clearly, our *in situ* modification method results in a significantly lower number of thiol groups undergoing reaction compared to the bulk solution modification method. With fluorohexene, for example, only ~15% of the perfluorocarbon chains are attached to the monolayer versus ~75% bulk conversion of the same system even though much higher concentrations of radical initiator (AIBN) and longer reaction times were employed for the *in situ* modification. This observation is consistent with the previously reported results for *in situ* monolayer hydrosilylation reactions[3] indicating a much slower *in situ* reaction process due to heterogeneous phase characteristics.[33]

PEO *in situ* modified layers show both improved wettability and barrier behavior in blocking $Fe(CN)_6^{3-}$ redox probes (Table 5 and Figure 13, curve 3). Though the water contact angle of the monolayer is ~10° higher than those for monolayers of bulk PEO-modified PMMPS (Table 4), the film appears to contain less defects than the latter. This is highly reproducible and possibly indicates that, through the control of limited degrees of reaction, film *in situ* modification could be the ideal way to manipulate the surface with the least structural disturbance.

Table 6. Comparison of PMMPS-Based Monolayer Properties before and after Thermal Tests

				before				after			
monolayer[a]	solvent[b]	T (°C)	t (h)	Th (Å)	θ_{H_2O} (deg)	$E_{p,c}$ (mV)	ΔE (mV)	Th (Å)	θ_{H_2O} (deg)	$E_{p,c}$ (mV)	ΔE (mV)
M-PMMPS100	toluene	110	0.1	16.3 ± 1.8	83 ± 1	−430		17.4 ± 2.1	81 ± 1	−60	530
M-PMMPS100	HD	100	2	17.2 ± 1.3	83 ± 3	−410		11.2 ± 2.0	64 ± 1	+170	100
M-PMMPS100		110	18	17.2 ± 1.3	83 ± 3	−410		16.5 ± 1.7	79 ± 1	−80	
M-F6-PMMPS		110	18	21.3 ± 2.4	89 ± 1	+120	200	14.8 ± 1.4	76 ± 1	+180	95
M-EO-PMMPS	H_2O	100	2	17.5 ± 2.2	48 ± 1	+20		16.1 ± 1.7	49 ± 1	+40	
M-PMMPS-C6	HD	100	2	20.6 ± 2.3	68.5 ± 1.5	+115	140	12.0 ± 1.6	65 ± 1	+160	90
M-PMMPS-EO	toluene	110	0.1	23.1 ± 1.8	56 ± 1	−610		18.4 ± 1.4	58 ± 1	−130	

[a] Refer to Tables 1, 4, and 5. [b] HD = hexadecane.

4. Thermal Effects on PMMPS Monolayers. An improved overall stability of monolayer films on gold surfaces has been observed for polymeric ultrathin films compared to similar monolayers of organic compounds.[4,6] Cooperative, multisite interactions between individual polymer molecules and a substrate surface are responsible for such a difference. In PMMPS and derivatized PMMPS systems, each siloxane oligomer molecule contains only a limited number (~5) of repeating units, each bearing an anchoring thiol/thioether functionality. Moreover, an average of only ~35% (equal to ~1.8 thiolate bonds per oligomer) of the anchoring groups is actually bound to substrate gold. Monolayer film stability, therefore, is expected to be more comparable to that of monomeric organic assemblies[34] than to polymer analogs.[5,6,14] Thermal tests of monolayers were carried out in both dry and wet (solvent) states. Results are summarized in Table 6.

In Table 6, physical data of monolayer films before thermal testing were also compiled for the sake of comparison. Several comments can be made regarding these observations. First, both underivatized (M-PMMPS100) and *in situ* derivatized monolayers (M-PMMPS-EO) maintain almost identical thicknesses and wettabilities after toluene exposure (6 min at 110 °C). This implies that removal of film components upon toluene exposure is negligible within the experimental time scale. However, the barrier properties of the same monolayers toward a $Fe(CN)_6^{3-}$ redox couple show a dramatic decrease after toluene exposure, indicating conformational changes and defect formation within the film. With M-PMMPS-EO monolayers, water contact angles before and after toluene exposure provide another piece of evidence that modifying PEO species were chemically attached to the PMMPS substrate film via a chemical linkage, as physisorbed PEO species would be removed entirely by toluene reflux. Second, when solvent exposure time (HD, 2 h at 100 °C) was lengthened, a considerable change in both thickness and wettability was observed (Table 6, monolayers M-PMMPS100 and M-PMMPS-C6). This observation, together with the significant change in CV response, suggests that surface monolayers have been at least partially removed by this treatment. Third, heating monolayers in a dry state (in N_2 at 100 °C for 18 h) could also result in conformational changes leading to a more leaky structure (monolayers M-PMMPS100 and M-F6-PMMPS). This is especially clear for the M-F6-PMMPS monolayer sample. A simultaneous decrease in the film thickness for this monolayer implies monolayer decomposition with loss of fluorocarbon species. Fourth, in contrast to M-PMMPS100 and M-PMMPS-C6 monolayers in hexadecane, the monolayer M-EO-PMMPS seems to be stable in a water environment under the test conditions (2 h of aqeuous reflux at 100 °C). Moreover, the observed identical wettability after thermal testing supports chemical bonding of PEO species in the monolayer films to the underlying oligomer siloxane chains.

Conclusions

Ultrathin oligomer films of monolayer thickness on gold surfaces have been prepared by spontaneous adsorption of a commercially available poly[methyl(mercaptopropyl)-siloxane] from solution. These monolayer films are structurally and compositionally isotropic. Cyclic voltammetry study indicates that these monolayers can substantially block electron transfer through the films, although considerable film defects do exist. Film defects are assumed to result from imperfect, loose packing of oligomeric film components, leading to microscopically uneven distribution of holes. The packing densities of the films were found to be concentration-dependent, with higher concentration incubation solutions providing monolayers of denser structure than that from more dilute solutions, but both have macroscopically comparable film thicknesses. In most cases, only ~35% of thiol groups present in the siloxane oligomer chains form Au–S thiolate bonds, leaving the remaining 65% of the anchors unbound and dispersed throughout the film matrix. This is likely due to the cyclic nature of the oligomer and resulting conformational constraints which do not permit extensive side-chain anchoring. Further photochemical modification of the siloxane oligomer films by either bulk approaches or *in situ* film reactions generates derivatized surfaces of variable wettability. However, the film structure seems to be perturbed during the modification processes, creating more defects resulting in increased electron transfer. Oxidation of free thiols is also detected after derivatization. A less perturbed film structure is obtained with an *in situ* film modification approach when attachment of modifying species was limited. This last strategy provides a facile and powerful method to manipulate surface properties of materials with stable, bound organic arrays of oligomers.

Acknowledgment. This work was partially supported by the Whitaker Foundation (D.W.G.), NSF/EPRI Grant MSS-9212496 (D.W.G.), NSF Grant DMR-9357439 (D.W.G.), and NIH Grant RR01296 (D.G.C.). We thank Drs. J. K. Hurst and Y. Lei for assistance with cyclic voltammetry experiments. We acknowledge funding from the Research Experience for Undergraduates program from the National Science Foundation (D.W.G.) for supporting Jennifer Peterson and her assistance with film characterization.

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(31) Quantitative comparison of the percentage of bound thiol anchors based on peak fitting of high-resolution S2p XPS spectra for underivatized and photoderivatized monolayers is difficult. This is due primarily to the emergence of a significant amount of oxidized sulfur in the latter case, accompanied by binding energy shifts for both bound and free $S2p_{3/2}$ peaks toward each other. A qualitative estimate for bound thiolate anchors in these monolayers ranges from 30 to 60%.

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(33) Similar results were also reported by Niwa et al.[19] when a fixed *in situ* initiator was adapted to a polymerizable monolayer. Polymerization occurs much more rapidly within the film matrix than that using initiator only in solution.

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