Monolayers on Disordered Substrates: Self-Assembly of Alkyltrichlorosilanes on Surface-Modified Polyethylene and Poly(dimethylsiloxane)

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ABSTRACT: Self-assembled monolayers (SAMs) have been formed on disordered, polymeric substrates. On polyethylene (PE), preparation of the SAM entailed three steps: oxidation of the surface of the PE with an oxygen plasma; formation of a silicate layer anchored to the oxidized surface by reaction with $SiCl_4$; formation of an alkylsiloxane surface layer by adsorption of alkyltrichlorosilanes from the vapor phase, and reaction with SiOH groups (and adsorbed water) on the surface of the silicate layer. On poly(dimethylsiloxane) (PDMS), plasma oxidation produced a surface silicate layer that could be used for subsequent adsorption of an alkylsiloxane layer without additional steps. The wettability of these SAMs is similar to that of comparable SAMs formed by adsorption onto better defined substrates (silicon wafers and gold). Reaction of SAMs on PE or PDMS bearing terminal vinyl groups with an aqueous permanganate/periodate solution produced surfaces bearing carboxylic acid moieties.

Introduction

The objective of this work was to develop a technique that would permit the generation of dense arrays of organic functional groups at the surface of an organic polymer. We used two polymers as substrates: low-density polyethylene film (PE) and poly(dimethylsiloxane) (PDMS). The PE film is made up of mixtures of crystalline and amorphous regions and is intrinsically heterogeneous, even before functionalization. Our stategy involved four steps. First, we introduced polar functional groups at the surface of the polyethylene film by plasma oxidation. These functional groups are undoubtedly heterogeneous in both type and distribution. Second, we formed a thin (probably <100 nm) silicate layer on this functionalized surface, by adsorption and hydrolysis of $SiCl_4$.[2] The functionality formed in the plasma oxidation serves to anchor the silicate layer to the polyethylene. Third, we formed an alkylsiloxane monolayer—self-assembled monolayer (SAM)—on the silicate surface by exposing it to an alkyltrichlorosilane $Cl_3Si(CH_2)_nR$. Fourth, we modified the SAM of alkylsiloxane moieties by appropriate chemical reactions to introduce desired functional groups. The resulting system is a microcomposite comprising four distinct layers: the polyethylene film substrate; a thin silicate surface layer; a monolayer of $(CH_2)_n$ chains, oriented (on the average) perpendicular to the silicate layer; a thin interfacial region between the self-assembled monolayer and contacting vapor or liquid containing the functional groups R (or introduced by chemical transformation of R) present at the termini of the alkyl groups of the alkylsiloxanes. The process used with PDMS was similar, except that plasma oxidation produced a surface silicate layer that served directly as a substrate for formation of a SAM.

We selected a system based on polyethylene and self-assembled monolayers of alkylsiloxanes to develop and test this synthetic strategy, because these components have individually been extensively studied.[3] The surface oxidation of the polyethylene film has been examined using a range of experimental methods, and the stability of the oxidized interfaces is well-characterized. Although oxidation using plasmas is less well understood than oxidations using some other methods (especially oxidation by chromic acid solution), it is among the most widely practiced methods in commercial processes. Its advantages are that it introduces polar functional groups rapidly into the polymer–vapor interphase, it etches the polymer less than most wet-chemical methods, it is applicable to commercial processing, and it requires no solutions. Plasma-functionalized surfaces are substantially more heterogeneous in the type and location of functional groups than are those generated by wet-chemical oxidation and thus less appropriate as substrates for studying organic surface chemistry than more uniformly functionalized materials. Since we used the functionality introduced by the plasma only to link the silicate surface layer covalently to the polyethylene substrate, the heterogeneity of this functionality was relatively unimportant to us.

A separate paper discusses adsorptions of alkyltrichlorosilanes from the vapor phase onto the surface of Si/SiO_2 to form SAMs,[4] and we have previously demonstrated the usefulness of SAMs on the surface of PDMS.[5] Others have described adsorptions from the vapor phase onto various substrates.[6,7]

Crystalline polymers—systems that one might expect to have ordered surfaces—often have amorphous or disordered surfaces at equilibrium.[8] Sagiv described the adsorption of mixtures of octadecyltrichlorosilane and various cyanine dyes at the surfaces of stretched poly(vinyl alcohol) (PVA) and of polyethylene coated with PVA and reported that the dye molecules were anisotropically oriented at the surface of the solid.[9] Others have described the preparation of self-assembled multilayers using $Cl_3SiOSiCl_2OSiCl_3$ and PVA.[10]

The ability to prepare SAMs on deformable, polymeric substrates offers several interesting experimental possibilities that are not possible with SAMs on rigid supports. These include (i) preparation of SAMs on substrates that can be shaped into complex geometries, (ii) examination of adhesion between SAMs on elastomeric polymers under (quasi)equilibrium conditions,[5] and (iii) measurement of the dependence of the wetting behavior of these SAMs on strain induced in the film by bending or stretching.

Experimental Section

General Considerations. Heavy mineral oil (Fisher) was used as received or stirred with neutral, grade 1 alumina and was stored over the same alumina until use. Water used in the wetting studies was passed through an ion exchanger (Cole-Parmer) and distilled in a Corning Model AG-1b glass distillation apparatus. Hexadecane was purified by percolation twice through neutral, grade 1 alumina (Fisher) but was not otherwise dried prior to use. The alkyltrichlorosilanes were purchased from Petarch and distilled prior to use. Dichloromethane (Fisher Scientific, HPLC grade) and silicon tetrachloride (Alfa or Petrarch) were used as received.

The polyethylene film (PE-H) used in these experiments was 4 mil thick, low-density, and biaxially blown and was a gift from Flex-o-Film. It was extracted in a Soxhlet apparatus with methylene chloride for 2–6 days under nitrogen to remove film additives. The samples were then dried either in air or *in vacuo* (approximately 10^{-2} Torr) and stored in a desiccator until use. For consistency, experiments were performed on the side of the film facing the inside of the stock roll; this choice of sides was arbitrary.

Silicon substrates were standard n- or p-type semiconductor grade silicon (111 or 100) wafers (3- or 4-in. diameter) from Monsanto. Typically, substrates were cut into 4-cm × 1.5-cm strips. The strips were cleaned immediately before use by soaking in freshly prepared piranha solution (70:30 v/v mixture of concentrated H_2SO_4 and 30% H_2O_2) for at least 30 min. (*Caution: "piranha" solution reacts violently with many organic materials and should be handled with extreme care.*)[34] The clean substrates were rinsed at least 10–15 times with 20-mL portions of deionized and distilled H_2O. The strips were dried under a stream of nitrogen and transferred directly into a glovebag filled with nitrogen or argon. Substrates were used within 30 min of cleaning. Ellipsometric measurements on silicon wafers were made using a Rudolf Research Type 43603-200E thin-film ellipsometer equipped with a He–Ne laser source, as described previously.[17]

Scanning electron micrographs were obtained using a JEOL JSM-35 electron microscope with an acceleration voltage of 35 keV. The working distance was 15 mm with a tilt angle of ca. 60° (tilt correction on) and a load current of 100 μA. The pressure of the analysis chamber was approximately 10^{-6} Torr. Since our samples were insulating, they were first coated with ca. 100 Å of gold using a Hummer II (Technics) sputterer at an ac current of 10 mA under ca. 0.1 Torr of argon for about 30 s.

Oxidation of PE[ox]/SiO$_2$/O$_3$Si(CH$_2$)$_9$CH=CH$_2$ with buffered permanganate/periodate solution was performed as reported for Si/SiO$_2$/O$_3$Si(CH$_2$)$_n$CH=CH$_2$ (n = 4, 9, and 15).[17] Potassium permanganate (KMnO$_4$, Mallinckrodt), sodium metaperiodate (NaIO$_4$, Mallinckrodt), K$_2$CO$_3$ (Mallinckrodt), and NaHSO$_3$ (Fisher) were used as received.

Preparations of the PDMS substrates and PDMS[ox] and the method for adsorption of alkylsiloxane monolayers from the vapor phase have been reported previously.[4,5]

PE[ox]. Samples of PE-H (4 × 1.5 cm) were treated with a low-power, radio frequency oxygen plasma in a Harrick plasma cleaner (Model PDC-23G) for 15 min at a pressure of approximately 0.2 Torr.

PE[ox]/SiO$_2$. In a hood, samples of PE[ox] were held at a distance of ca. 1 cm above liquid SiCl$_4$ (inside a 500-mL bottle of SiCl$_4$) for 30 s at room temperature. The surface area of the solution, which was not stirred, was approximately 20 cm^2. As expected, the thickness of the resultant layer of silica was sensitive to experimental conditions, particularly the ambient humidity. No effort was made to exclude air. The sample was removed from the bottle, soaked in distilled water for 5–20 min, and dried with a stream of nitrogen or argon or left to dry in air. The wettability by water of the sample was checked, and if a drop of water did not spread symmetrically across the surface ($\theta_a \approx 0°$), the sample was dried with a stram of nitrogen and treated again with SiCl$_4$. The most reliable test for completeness of the SiO$_2$ layer, however, was the behavior of a drop of hexadecane on the surface of the final product PE[ox]/SiO$_2$/*monolayer* (next section): we interpreted low contact angles ($\theta_a < 5°$) of, and swelling by, hexadecane on these surfaces as evidence for incompleteness of the SiO$_2$ layer. When we found this behavior, we repeated the experiment (with a new piece of PE[ox]) and increased the number of treatments with SiCl$_4$/H$_2$O (vapor). The number of treatments necessary depended on the ambient humidity in the laboratory, and no more than three treatments were ever used. Occasional samples had uneven levels of clarity in different regions of the film, but this variation did not appear to affect the quality of SAMs produced on these surfaces.

SAMs of Alkylsiloxanes on PE[ox]/SiO$_2$. A sample of PE[ox]/SiO$_2$ (4 × 1.5 cm) was attached to a glass microscope slide and transferred into a glovebag under a counterflow of N$_2$ or Ar. The sample was suspended, face down, approximately 1.5 cm above a solution of an alkyltrichlorosilane (0.200 mL) in heavy mineral oil (3.0 g). The surface area of the solution exposed to the slide was approximately 20 cm^2. The assembly was placed into an empty desiccator and adjusted to a pressure of ca. 0.1 Torr. The liquid phase was not stirred. After 2.5 h, the desiccator was filled with nitrogen (argon), and the sample was removed and analyzed. As expected, this procedure was sensitive to the experimental conditions—particularly humidity and integrity of the vacuum. Care was taken to minimize the humidity in the glovebag by flushing several times with nitrogen or argon.

Mineral oil solutions of alkyltrichlorosilanes could be reused after exposure to the laboratory atmosphere and after storage (in a desiccator) if first degassed *in vacuo* to remove HCl and to prevent bubbling that could contaminate the surface with splattered solution.

Contact Angles. Contact angles were measured using a Ramé-Hart Model 100 contact angle goniometer, using a previously published procedure.[16] Probe liquids were dispensed from either a Gilmont syringe with a flat-ended needle or a Micro-electrapipette (Matrix Technologies; Lowell, MA). Unless otherwise stated, contact angles were measured within 10 s of application of the drops. All measurements were taken at ambient laboratory temperatures (17–22 °C). The reported values are usually the average of at least six measurements, taken at different locations on the surface (3 drops, 2 sides each).

The contact angle titrations were performed using standard buffered solutions.[35] For high pH (≥9), the drop spread slowly (for ca. 1 min in some cases) over the surface; contact angles were measured when spreading was no longer perceptible.

X-ray Photoelectron Spectroscopy. XPS spectra were collected on a Surface Science Instruments spectrometer (Model SSX-100) with a monochromatized Al Kα source, concentric hemispherical analyzer operating in fixed analyzer transmission mode, and a multichannel detector. The spectra were acquired with a 50-eV pass energy and 600-μm spot size. The peaks were iteratively fit using 75% Lorentzian/25% Gaussian profiles and a Shirley background subtraction.[36]

Results

Exposure of the surface of low-density polyethylene film (PE-H) to a low-power, radio frequency, oxygen plasma introduces a variety of oxidized functional groups into the interfacial region.[11,12] Unlike oxidation with aqueous chromic acid, this procedure has the advantage that it does not etch the surface of the polymer severely. Treatment of this modified polymer—designated PE[ox] to emphasize the highly oxidized although unselectively functionalized polymer surface—with silicon tetrachloride in humid air resulted in formation of a layer of silicon dioxide on the surface.[2,13] A similar method has been used to prepare monolithic gels of silica.[14] We indicate this coated surface as PE[ox]/SiO$_2$ by analogy to the interface between silicon and its native coating of silica (Si/SiO$_2$): this nomenclature (PE[ox]/SiO$_2$) is almost certainly inaccurate in suggesting the composition of the silicate layer to be "SiO$_2$" rather than "SiO$_x$(H$_2$O)$_y$" for a hydrated layer, and we use it only for brevity. Treatment of poly(dimethylsiloxane) (PDMS) with an oxygen plasma produced a silicate layer directly (PDMS[ox]).[5]

Adsorption of undecyltrichlorosilane from the vapor phase at ca. 0.1–0.2 Torr onto the surface of PE[ox]/SiO$_2$

Scheme I. Schematic Illustration of the Synthesis of SAMs on PE[ox]/SiO₂ and PDMS[ox][a]
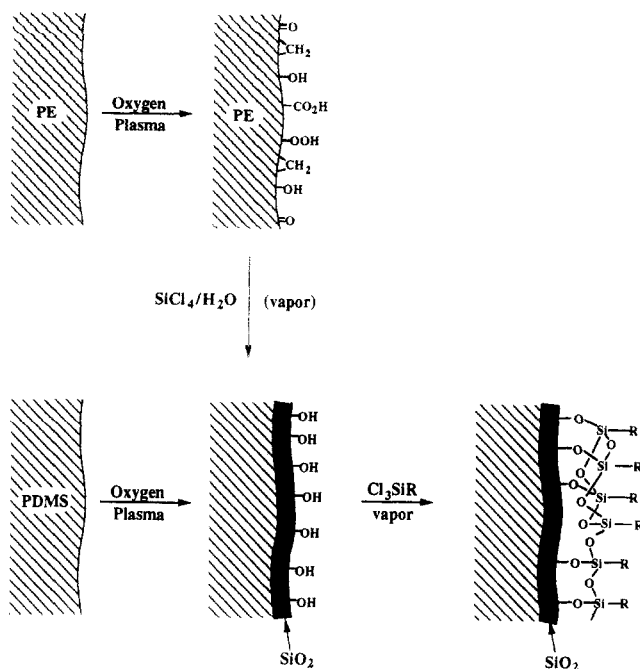
[a] The thickness of the surface film of SiO₂ on polyethylene is probably between 200 and 1000 Å, depending on the number of treatments with SiCl₄ (see Experimental Section) and is not drawn to scale.[14] The thickness of the silicate layer on PDMS[ox] is less than 50 Å.[5]
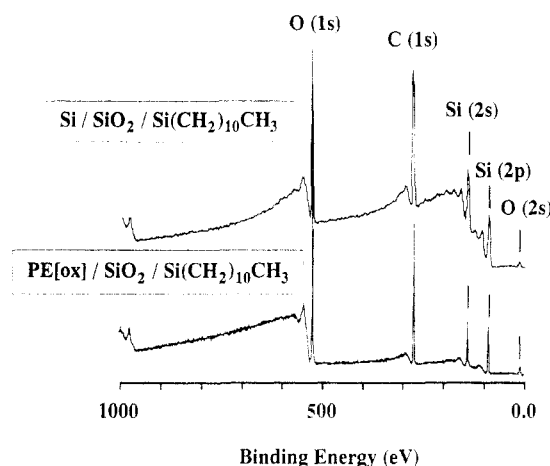

Figure 1. X-ray photoelectron spectra of Si/SiO₂/O₃Si(CH₂)₁₀CH₃ (top) and PE[ox]/SiO₂/O₃Si(CH₂)₁₀CH₃ (bottom).

resulted in the formation of an organic layer at the surface of this material within 2.5 h (Scheme I). The atomic composition, measured by X-ray photoelectron spectroscopy (XPS), indicated a thickness of the organic layer consistent with a monolayer: the change in the silicon signal before and after monolayer formation, as well as comparison of the carbon signal for this SAM with a well-characterized SAM on Si/SiO₂, allowed us to determine the thickness of the organic film directly.[17] Figure 1 shows XPS survey spectra of this SAM and one formed by adsorption of the same adsorbate on Si/SiO₂. A similar treatment produced monolayers on PDMS[ox].[5] The contact angles of water and of hexadecane (Table I) on PE[ox]/SiO₂/O₃Si(CH₂)₁₀CH₃ and on PDMS[ox]/O₃Si-(CH₂)₁₀CH₃ are very similar to those on structurally related alkanethiolates on gold and alkylsiloxanes on Si/SiO₂. This similarity to the well-ordered systems suggests that the outermost portion of the surface is populated primarily by methyl groups. The topology of the surface of PE-[ox]/SiO₂/O₃Si(CH₂)₁₀CH₃ (Figure 2) is smoother than

Table I. Advancing (θ_a) and Receding (θ_r) Contact Angles on Hydrocarbon Surfaces[a,b]

material	water		hexadecane	
	θ_a	θ_r	θ_a	θ_r
PE[ox]/SiO₂/O₃Si(CH₂)₁₀CH₃	113	104	48	40
PE[ox]/SiO₂/O₃Si(CH₂)₉CH=CH₂	106	100	38	31
PDMS[ox]/O₃Si(CH₂)₁₀CH₃	112	103	46	45
PDMS[ox]/O₃Si(CH₂)₉CH=CH₂	104	99	36	35
Si/SiO₂/O₃Si(CH₂)₁₀CH₃	112	102	41	39
Si/SiO₂/O₃Si(CH₂)₉CH=CH₂	101	92	30	24
Au/S(CH₂)₁₀CH₃	115	105	48	42
Au/S(CH₂)₉CH=CH₂	107	97	39	33
PE-CO₂(CH₂)₁₁CH₃	125	≈40	wets	

[a] Values for SAMs on Si/SiO₂ were taken from ref 17; those on gold were taken from ref 16; those on PE-CO₂(CH₂)₁₁CH₃ were taken from ref 37. The high value of θ_a (H₂O) and the low value of θ_r (H₂O) is due in part to the roughness of this surface. [b] Values for SAMs on PE[ox]/SiO₂ were on samples with "complete" silicate layers (i.e., those having high contact angles and the absence or slow swelling by hexadecane).

that of unfunctionalized PE-H and much smoother than that of polyethylene etched by chromic acid ("polyethylene carboxylic acid", abbreviated PE-CO₂H).[15] Adsorption of 10-undecenyltrichlorosilane on PE[ox]/SiO₂ and on PDMS[ox] produced surfaces bearing vinyl groups at the solid/air interface. The contact angles of water and of hexadecane (Table I) on these SAMs were similar to those on SAMs formed by adsorption of 18-nonadecene-1-thiol onto the surface of gold[16] and by adsorption of 10-undecenyltrichlorosilane onto Si/SiO₂.[17] Figure 3 shows contact angles measured at different locations on several samples of the methyl- and vinyl-terminated SAMs on PE[ox] and indicates the level of reproducibility possible in this system *if care is taken to form a complete silicate layer* (see Experimental Section).

Certain experimental variables in our syntheses at the surface of polyethylene were not controlled. The most important of these was probably the ambient humidity, since it may affect the efficiency of the *in situ* hydrolysis of SiCl₄ to give SiO₂. We presumed that, since SiCl₄ is volatile (bp = 56 °C), the atmosphere above its liquid was always rich in its vapor. The partial pressure of atmospheric water in the vapor above the liquid SiCl₄, however, was unknown. Since complete coverage by the silicate layer is necessary for formation of high quality monolayers, these experimental variables required that our syntheses be tailored to the ambient laboratory conditions. More than one treatment with SiCl₄/air was usually necessary for formation of a complete silicate layer. In seven attempts at preparing PE[ox]/SiO₂/O₃Si(CH₂)₁₀CH₃ or PE[ox]/SiO₂/O₃Si(CH₂)₉CH=CH₂ using a single treatment with SiCl₄, the experiment gave high quality monolayers only once; in four attempts using two treatments, it worked four times. The only attempt using three treatments was also successful. Preparations of SAMs on PDMS[ox] were highly reproducible.

Treatment of SAMs bearing terminal vinyl groups with an aqueous solution of KMnO₄ (0.5 mM)/NaIO₄ (19.5 mM)/K₂CO₃ (1.8 mM) produced SAMs having terminal carboxylic acid groups. In previous papers, we[17] and others[18,19] have described the oxidation of terminal vinyl groups in SAMs of alkylsiloxanes on silicon dioxide. The advancing contact angle of water on the oxidized surfaces obtained from both PE[ox]/SiO₂/O₃Si(CH₂)₉CH=CH₂ and PDMS[ox]/O₃Si(CH₂)₉CH=CH₂ ranged from 43–51° for drops at pH 1 to 10–19° for those at pH 12 (Figure 4).[20] This variation ("contact angle titration") was similar to that observed for an analogous SAM prepared on silicon/silicon dioxide[17,21] (pH 1, θ_a = 32°; pH 13, θ_a = 9°) and
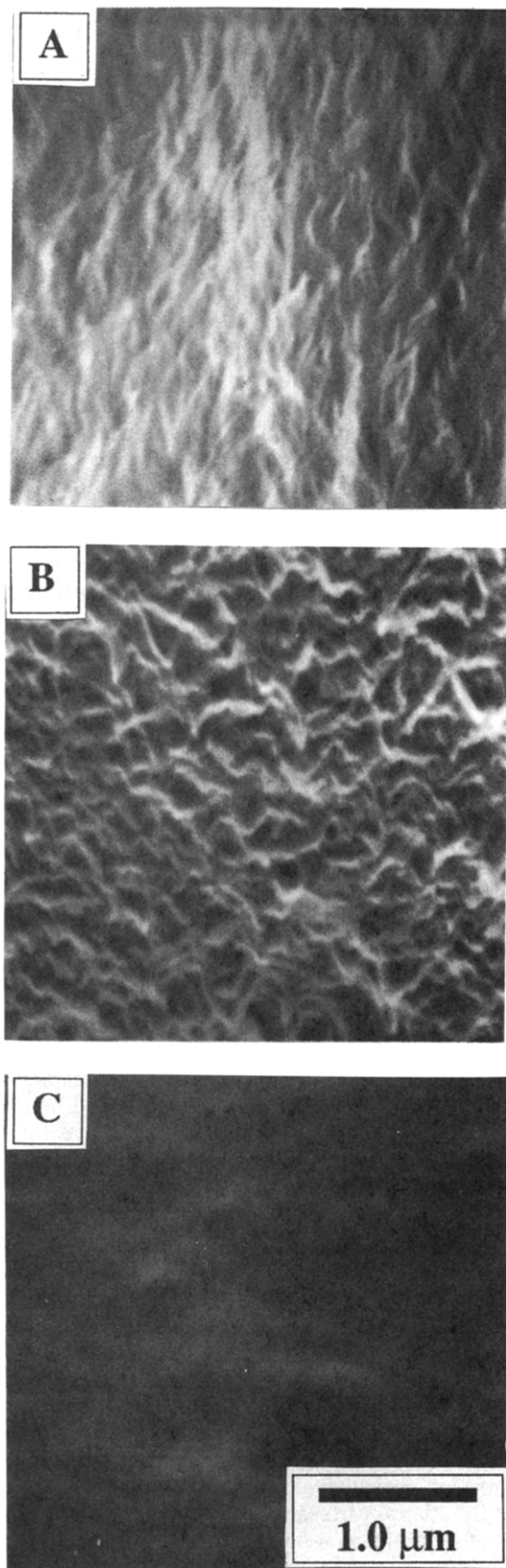
Figure 2. Scanning electron micrographs of PE-H(A), PE-CO$_2$H (B), and PE[ox]/SiO$_2$/O$_3$Si(CH$_2$)$_{10}$CH$_3$ (C). All of these micrographs were obtained at the same magnification. Samples were coated with approximately 100 Å of gold before analysis.

indicated a high density of carboxylic acid groups at the solid/water interface.

Discussion

PE[ox]/SiO$_2$: A "Barrier Film" of Silica on Polyethylene. Several characteristics of the surface of
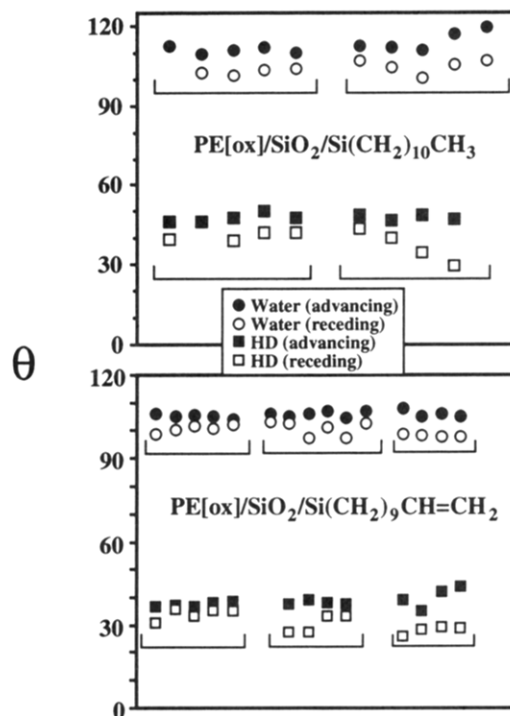
Individual Drops

Figure 3. Contact angles of water and of hexadecane on SAMs prepared by adsorption of Cl$_3$Si(CH$_2$)$_{10}$CH$_3$ (top) and Cl$_3$Si(CH$_2$)$_9$-CH=CH$_2$ (bottom) onto PE[ox]/SiO$_2$ through the vapor phase. The *groups* of points in each plot represent single samples: two methyl-terminated samples and three vinyl-terminated samples. Each point represents the average of measurements taken on two sides of a single drop of liquid. The horizontal axis has no geometric significance: each point is simply a drop taken at an arbitrarily chosen point on the surface. Lower contact angles than those shown and swelling by hexadecane were taken as evidence for an incomplete silicate layer; such samples were disregarded and new samples prepared.
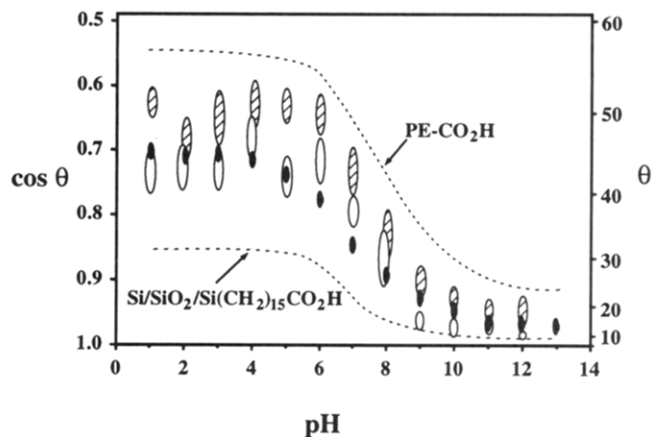

Figure 4. Advancing contact angles of water on SAMs bearing terminal carboxylic groups as a function of the pH of the contacting drop. The open and striped ovals represent two samples prepared in the same way, by oxidation of PE[ox]/SiO$_2$/O$_3$Si(CH$_2$)$_9$CH=CH$_2$. The solid ovals represent a sample prepared by oxidation of PDMS[ox]/O$_3$Si(CH$_2$)$_9$CH=CH$_2$. The sizes of the ovals indicate the average deviation in the measurements at a given pH. The dashed lines provide similar data from the following reference systems: a surface prepared by permanganate/periodate oxidation of an analogous monolayer on Si/SiO$_2$ (Si/SiO$_2$/Si(CH$_2$)$_{15}$CO$_2$H); and chromic acid-etched polyethylene (PE-CO$_2$H).

PE[ox] or PE-CH$_2$OH prevent their usefulness as substrates for the formation of SAMs (of alkylsiloxanes) directly. One important difference between the surface

of PE-H (and its oxidized derivatives) and that of Si/SiO_2 is their relative structural mobility. The methylene chains at the surface of polyethylene are conformationally mobile, and the surface of PE-X can reconstruct on gentle heating, on mechanical deformation, or on contact with organic solvents;[22,23] the surface of Si/SiO_2 is stable at the temperatures used in these experiments.

In particular, most solvents reported for the preparation of SAMs of alkylsiloxanes on Si/SiO_2—hydrocarbons and chlorinated hydrocarbons and mixtures of both—swell the interfacial region of polyethylene.[3,18,19] Swelling causes reconstruction of the polymer surface and would probably disrupt formation of a packed, oriented array of the alkyl groups of the adsorbates.[22,23] Most published methods for the preparation of these SAMs also deposit excess oligomeric alkylsiloxane during the adsorptions. On silica, gentle wiping or sonication is sufficient to remove the alkylsiloxane gel particles.[3,18,19] On polyethylene, these procedures could cause reconstruction of the interfacial region.

The functional groups introduced into the interfacial region of polyethylene by treatment with an oxygen plasma probably included alcohols, ketones and aldehydes, carboxylic acids, and hydroperoxy species.[11,12] The hydroxyl groups and adsorbed water at the surface of PE[ox] served as a "primer"—by their reaction with $SiCl_4$—for coverage of the polymer surface by SiO_2. Others have described the formation of oxide (e.g., SiO_2, TiO_2, In_2O_3) layers on the surfaces of other polymers.[24]

The layer of SiO_2 served several purposes. First, it allowed us to apply known methods for the preparation of SAMs of alkylsiloxanes on silica to the formation of SAMs supported on polyethylene. Second, it acted as a "barrier film" that protected the polymer surface from contacting solvents that swelled and reconstructed that surface.[2] Third, its surface was smoother than that of the PE[ox] on which it was supported (and much smoother than chromic acid-oxidized $PE-CO_2H$[15,20] and its derivatives): this difference reduced the contribution of roughness to hydrophobicity and hysteresis in studies of the wettability of these functionalized interfaces.[25]

The layer of silica in PE[ox]/SiO_2 was a barrier film that provided limited but useful protection to the surface from hexadecane (a solvent that otherwise swells the polymer) and allowed us to use the liquid in measuring contact angles. Upon standing for several minutes, drops of hexadecane did occasionally (i.e., on approximately 20% of our samples) swell these interfaces, and although we have not studied the parameters that determine the effectiveness of protection, the most important of these is probably the completeness and integrity of the silica layer. When swelling did occur, it only became apparent after several minutes and thus did not prevent measurement of contact angles. We infer that the slow onset of swelling indicates that this process is mediated by defects in the SiO_2 layer, either from incomplete formation of the layer or from defects introduced in handling the film. Samples with incomplete layers of SiO_2 (*vide supra*) were quickly swollen by hexadecane.

SAMs of Alkylsiloxanes on PE[ox]/SiO_2 and PDMS[ox]: Comparison with SAMs on Si/SiO_2. In order to avoid swelling the polymer substrates by their exposure to solvent, SAMs were formed through the vapor phase.[4-7,26,27] In a separate paper, we describe the adsorption from the vapor phase of alkyltrichlorosilanes onto silicon/silicon dioxide and of alkanethiols onto gold—that is, onto substrates that are smooth relative to polyethylene—to give SAMs we inferred to be ordered: the

thickness and wettability of these SAMs were indistinguishable from those prepared in solution.[4]

For both the methyl- and vinyl-terminated SAMs on PE[ox]/SiO_2 and on PDMS[ox], the contact angles of water and hexadecane were very close to those on SAMs of alkanethiols on gold and of alkylsiloxanes on Si/SiO_2 (Table I). Some of the apparent hydrophobicity of these SAMs may be due to differences in roughness between these films and those on silicon wafers—behavior expected according to Wenzel's equation[25]—but the values of hysteresis of the polymer-supported surfaces are to SAMs formed on Si/SiO_2.

The difference between the wettability by water (Table I) of PE[ox]/SiO_2/$O_3Si(CH_2)_{10}CH_3$ and that of PE-$CO_2(CH_2)_{11}CH_3$ is striking, despite the similarity in the "outermost" functionality on these two surfaces. Although the advancing contact angle of water on PE-$CO_2(CH_2)_{11}$-CH_3 is significantly higher than that on PE[ox]/SiO_2/O_3-$Si(CH_2)_{10}CH_3$, the hysteresis on the two surfaces differs enormously. We infer—again, by comparison to studies of wetting on well-defined SAMs of alkanethiolates on gold[28]—that this disparity reflects a difference in the composition and roughness of these two interfaces. A second striking difference between the two surfaces is their wettability by hexadecane: the contact angles of hexadecane on PE[ox]/SiO_2/$Si(CH_2)_{10}CH_3$ are comparable to those on SAMs of alkanethiols on gold and of alkylsiloxanes on Si/SiO_2, while hexadecane wets and swells the surface of PE-$CO_2(CH_2)_{11}CH_3$. This difference argues for greater uniformity of the interface between solvent and functionality on the surface of the polymer–supported SAM than on the surface of PE-$CO_2(CH_2)_{11}CH_3$.

Contact angle titrations provide information (although not always easily interpretable information) about the local environment of ionizable functionality in the interfacial region of a solid.[17,20,29-33] We have reported the pH dependence of wetting by water on several surfaces: PE-CO_2H[20] (and its derivatives[29-31]), SAMs of ω-mercapto carboxylic acids on gold,[33] and SAMs bearing terminal carboxylic acid moieties on Si/SiO_2.[17] One aspect in the interpretation of these curves is clear: at low pH, the contact angle of a drop of water reflects the hydrophilicity of the protonated form of the acid groups in that part of the interface sensed by contact angles (the "θ interphase"[23]);[3,29] at high pH, it reflects (at least in part) the increased hydrophilicity of the charged carboxylate ions.

The shapes of the contact angle titration curves for PE-[ox]/SiO_2/$O_3Si(CH_2)_9CO_2H$ and PDMS[ox]/$O_3Si(CH_2)_9$-CO_2H in Figure 4 were qualitatively similar to one another, although the average deviations in contact angles at a given pH were typically larger on polyethylene. The shapes of these curves were also similar to that reported for a SAM formed in an analogous way on Si/SiO_2. This similarity suggests that the carboxylic acid groups in these interfaces have similar local environments. The shapes of the curves in Figure 4 were different, however, from that reported for SAMs containing ω-mercapto carboxylic acids on gold. This difference is probably due to differences in the density and distribution of the carboxylic acid groups in the interfacial region.[31] In addition, the shapes of the curves in Figure 4 may be artifactual in the region of high pH ($\geq$9), since 0° is the lowest possible value of the contact angle.

The wetting of the surface of modified polyethylene can be controlled to a high degree using the techniques described here. An uncertainty about the interfacial systems generated using these techniques is the degree of order in the SAMs on PE[ox]/SiO_2 and PDMS[ox]. The

analysis of structure and order in the SAMs on gold and on Si/SiO$_2$ has been aided by the use of external reflectance FTIR and optical ellipsometry—techniques that are not applicable on these nonreflective polymer surfaces. We believe that contact angles provide a useful, qualitative measure of the uniformity and composition of solid/liquid interfaces, and infer, from these data, that the systems described here provide excellent control over these properties of these modified polymers.

Conclusions

Treatment of the surface of polyethylene films with an oxygen plasma and then with SiCl$_4$ and water in the vapor phase produces an overlayer of silicon dioxide. The surface of this layer is smoother and more densely and uniformly functionalized than that of unmodified polyethylene and provides functional groups at the solid/air interface that can be used in the formation of SAMs of alkylsiloxanes. Plasma oxidation of poly(dimethylsiloxane) produces a silicate layer on that polymer directly. Adsorption of alkyltrichlorosilanes at the surfaces of PE[ox]/SiO$_2$ and PDMS[ox] produces monolayers whose wetting behavior is similar to those of well-characterized, highly ordered SAMs on Si/SiO$_2$ and on gold.

References and Notes

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