Trichlorosilane Chemisorption on Surface-Modified Poly(tetrafluoroethylene)

Bin Zhao, William J. Brittain,* and Erwin A. Vogler[†]

Department of Polymer Science, The University of Akron, Akron, Ohio 44325

Received July 21, 1998; Revised Manuscript Received November 12, 1998

ABSTRACT: Modification of poly(tetrafluoroethylene) (PTFE) by trichlorosilane chemisorption to hydroxyl-modified (PTFE−OH) and silicate-modified (PTFE/SiO_2) PTFE is reported. PTFE/SiO_2 was prepared by exposure of PTFE−OH to $SiCl_4$ vapor. XPS and contact angle analyses were consistent with the chemical composition of PTFE−OH and PTFE/SiO_2. Chemisorption of trichlorosilanes from solution produced layers on PTFE−OH and PTFE/SiO_2. The FTIR absorption intensity for these layers was consistent with monolayer formation. Monolayers with Br, CF_3, CH_3, CD_3, and $CH{=}CH_2$ terminal groups were prepared. Relative to deuterated hexadecyltrichlorosilane (DHTS) monolayers on PTFE−OH, higher contact angles were observed for DHTS monolayers on PTFE/SiO_2 under a greater variety of deposition conditions. Reflectance FTIR indicated that the monolayers formed on PTFE−OH and PTFE/SiO_2 exhibited crystalline-like order consistent with a well-ordered monolayer. Thermal annealing of the DHTS monolayers for several days at 125 °C did not produce any significant changes in water contact angles.

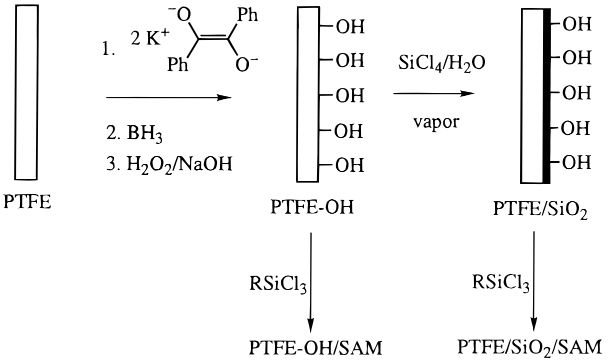
Introduction

Poly(tetrafluoroethylene), PTFE, and related fluoropolymers from one of the most important families of engineering polymers and are known for their mechanical properties, chemical inertness, low coefficients of friction, very low surface energy, and high electrical resistance. These properties recommend fluoropolymers for numerous and diverse applications ranging from low-friction/stick surfaces to medical devices.

A familiar strategy in materials science has been to modify surface properties of a polymer to enhance interfacial properties such as adhesion or biocompatibility while, at the same time, maintaining favorable bulk properties. Consequently, surface modification of PTFE has been the subject of numerous studies. For example, Hubbell and co-workers[1] recently summarized some of the literature methods for PTFE modification. The method of most interest to us is the work of Costello and McCarthy.[2] These workers exposed PTFE to Me_2SO solutions of the potassium salt of benzoin dianion. Electron transfer from the dianion to PTFE leads to loss of fluoride from PTFE and subsequent formation of unsaturated functionality on the surface. Several reactions of the reduced PTFE (PTFE-C) were used to introduce hydroxyl, amino, and carboxylic acid functionalities on the surface.

In general, one of the most precise methods to create a chemically well-defined surface is self-assembly. Normally, this method is applied to the formation of self-assembled monolayers on silicate and gold substrates.[3] The clear advantage of this technique is that telechelic polymethylene chains can be chemically anchored to a surface. The surface chemistry and energy of the resulting monolayer is thus largely defined by the terminal group. The extension of this technology, which has been principally applied to a metallic or oxide surface, to polymers would be useful given the widespread commercial applications. Toward this end, Whitesides and co-workers[4] prepared monolayers on disordered polymer substrates by the self-assembly of trichlorosilanes on surface-modified polyethylene and poly(dimethylsiloxane). For polyethylene, the preparation of self-assembled monolayers (SAMs) involved three basic steps: surface oxidation with an oxygen plasma; formation of a silicate layer anchored to the oxidized surface by reaction with $SiCl_4$; formation of the SAM by chemisorption of a trichlorosilane. We have successfully adopted this method for the surface modification of PTFE with trichlorosilanes.

Scheme 1



Results and Discussion

Our experimental strategy for surface modification of PTFE can be summarized by the following sequence: reduction of PTFE with benzoin dianion; oxidation with diborane; reaction with $SiCl_4$ (this step may be optional); trichlorosilane chemisorption (Scheme 1). We have used FTIR, XPS, and contact angles to characterize the chemistry of these surface modifications.

Formation of PTFE−OH. The first surface−synthetic step is formation of PTFE with hydroxyl chemical groups on the surface. This was done according to the method of Costello and McCarthy.[2] We obtained results in reasonable agreement with those of Costello and McCarthy. We treated PTFE with a Me_2SO solution of the potassium salt of benzoin dianion. Subsequent treatment of the gold-colored films (PTFE-C) with a

---

[†] Present address: Becton Dickinson Research Center, Research Triangle Park, NC 27709.

10.1021/ma9811526 CCC: $18.00

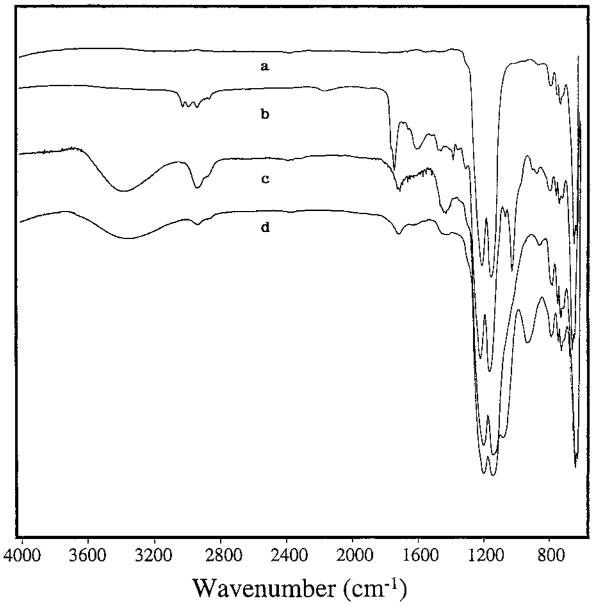


Figure 1. Reflectance FTIR of PTFE (a), PTFE-C (b), PTFE−OH (c), and PTFE/SiO_2 (d).

THF solution of BH_3 (20 h) and oxidation with a basic solution of peroxide produced film samples (PTFE−OH). XPS analysis was similar to the published results; for example, McCarthy reported an atomic composition ratio for C/O of 3.4/1 while we observed a C/O ratio of 2.9/1. ATR-IR analysis of PTFE−OH supports hydroxyl introduction (Figure 1); absorbances at 3500 and 1020 cm^{-1} are due to ν(O−H) and ν(C−O). Water contact angles for PTFE−OH were $\theta_a = 64 \pm 4°$ and $\theta_r = 44 \pm 3°$. Costello and McCarthy reported a similar advancing angle but a much lower receding angle ($\theta_r = 0°$). We cannot account for the difference in receding angles for our samples compared to the literature; however, it is worthwhile to note in this connection that contact angles depend on several important experimental factors including roughness of the sample, methods of analysis, purity of water, and quality of starting materials which can vary from experimentalist to experimentalist.

Formation of PTFE/SiO_2. We reacted PTFE−OH with $SiCl_4$ vapor to create a surface layer of silicate. The experimental method of Whitesides and co-workers[4] was used. The PTFE−OH samples were held at a distance of 1 cm over liquid $SiCl_4$ for 30 s; no effort was made to control ambient humidity. This procedure was repeated until the sample was fully wettable. XPS analysis of PTFE-SiO_2 revealed atom % surface composition (excluding hydrogen) of 23.6% Si, 23.0% C, and 47.4% O, with the remaining 6 atom % comprised of trace quantities (<4% each) of P, Cl, Ca, and N in decreasing order of surface concentration. In particular, the O(1s) line appeared at 532.4 eV (corrected to C(1s) binding energy at 284.6 eV) with a 2.1 eV full width at half-maximum, consistent with the 532.8 eV peak associated with SiO_2 gel.[5] After silicate deposition, the samples were fully wettable ($\theta_a = \theta_r = 0$). Two relevant FTIR absorptions were observed at 1080 cm^{-1}, ν(Si−O−Si) and 3400 cm^{-1}, ν(O−H). We performed a similar $SiCl_4$ deposition on a silicon wafer and used ellipsometry to determine that the thickness of the newly formed layer of SiO_2 was 28 ± 9 nm. The thickness of SiO_2 layer varied with exposure time (1.5−3 min) and ambient humidity. We use this result on silicon as an extremely rough estimate of the analogous SiO_2 layer formed on PTFE−OH.

While we do not have spectroscopic evidence of a covalent SiO_2 bond to PTFE−OH, we observed a profound difference in SiO_2 deposited on unmodified PTFE vs PTFE−OH. We observed $SiCl_4$ deposition on unmodified PTFE as deduced by water contact angle changes, but the silicate layer was not adherent and could easily be removed by rubbing. Similar mechanical abrasion experiments with PTFE/SiO_2 did not lead to silicate removal as evidenced by wettability and physical inspection.

Monolayer Formation on Surface-Modified PTFE. Chemisorption of trichlorosilanes to samples of PTFE−OH and PTFE/SiO_2 was performed. We prepared a series of layers on surface-modified PTFE and silicon wafers at the same time. Layers on silicon wafers were used as analytical standards by which to judge our results on PTFE−OH and PTFE/SiO_2.

We formed layers by trichlorosilane absorption onto PTFE/SiO_2 in the same manner that we formed monolayers on silicon semiconductor wafers of silicon ATR crystals. In both types of experiments, the silicate overlayer was hydrated (by soaking in water, followed by surface drying with a stream of nitrogen), and thus, we expect that the trichlorosilane deposition should be similar for both substrata. Tripp and Hair[6] have discussed the importance of hydrated silicate for successful monolayer formation in trichlorosilane chemisorption. On the basis of the mechanism of monolayer formation elucidated by Tripp and Hair and internal consistency of experimental procedures applied to silicon control and PTFE/SiO_2 samples, we propose that SAMs were formed on both surfaces.

Whitesides and co-workers[4] observed solvent swelling of some poly(ethylene)/SiO_2 samples. Thus, they obtained better coatings using a vapor deposition method; this method avoided surface reconstruction by the deposition solvent (hexadecane or chlorocarbons). We did not observe swelling of any PTFE/SiO_2 samples in this work, and therefore, we performed depositions of silanes from hexadecane solutions.

Experimental evidence for the formation of monolayers is based on FTIR absorption intensities. Reflectance FTIR was used to analyze monolayers on silicon and surface-modified PTFE. For SAMs on silicon, the monolayer was prepared on a silicon attenuated-total-reflectance (ATR) crystal. For PTFE layers, the surface-modified PTFE was pressed against the surface of a KRS ATR crystal for analysis. For reflectance FTIR of very thin films, absorption intensity is proportional to chemisorbed molecule concentration. FTIR analysis of a deuterated hexadecyltrichlorosilane (DHTS) layer on PTFE/SiO_2 reveals $A = 0.0038$ for the $\nu_a(CD_2)$ band at 2196 cm^{-1}. For the DHTS monolayer directly bonded to the ATR crystal (which we use as the standard model for a monolayer), $A = 0.013$ for the same band. One factor must be considered in comparing the absorption intensities. We do not believe that we were able to produce a conformal interface between the PTFE and ATR crystal. If any gaps between the surface-modified PTFE and ATR crystal exceeded the penetration depth of the evanescent field, then the absorption intensity of the DHTS layer would be affected. The optical difference between Si−ATR/SiO_2/DHTS/air and KRS−ATR/SiO_2// DHTS/SiO_2/PTFE (where "//" represents the press-on interface) may be a more a significant factor in accounting for the difference in absorption intensities. Also, the inherent roughness of the PTFE would be a factor.

Table 1. Water Contact Angles (deg) for Monolayers Prepared on Silicon Wafers and PTFE/SiO$_2$

trichlorosilane used for SAM formation	PTFE−SiO$_2$ θ_a	PTFE−SiO$_2$ θ_r	silicon wafer θ_a	silicon wafer θ_r
$Cl_3Si(CH_2)_{15}CH_3$	117 ± 2	91 ± 2	111 ± 1	94 ± 1
$Cl_3Si(CH_2)_6CH{=}CH_2$	101 ± 2	84 ± 3	99 ± 1	85 ± 1
$Cl_3Si(CH_2)_{11}Br$	91 ± 3	69 ± 2	91 ± 1	77 ± 1
$Cl_3Si(CH_2)_2(CF_2)_7CF_3$	116 ± 4	95 ± 2	117 ± 1	98 ± 1
$Cl_3Si(CD_2)_{15}CD_3$	117 ± 2	92 ± 2	112 ± 1	93 ± 2

Table 2. Water Contact Angles[a] (deg) for DHTS Monolayers Prepared on PTFE−OH and PTFE/SiO$_2$

reduction time,[b] h	SAMs on PTFE/SiO$_2$ θ_a	SAMs on PTFE/SiO$_2$ θ_r	SAMs on PTFE−OH θ_a	SAMs on PTFE−OH θ_r
0.5	119	96	113	91
2	119	93	110	90
120	117	92	118	95

[a] Experimental error in contact angle measurements = ±3°. [b] Time of PTFE exposure to potassium benzoin dianion solution.

Therefore, we cannot draw quantitative conclusions from absorption intensity comparison of the DHTS layer on silicon vs PTFE/SiO$_2$. However, we can *qualitatively* conclude that the DHTS layer formed on PTFE/SiO$_2$ is *not* a multilayer and may represent a monolayer. In addition, on the basis of the FTIR peak position analysis (to follow in a later section of this article), we have concluded that monolayers formed on surface-modified PTFE are structurally ordered.

It should be emphasized that the chemical etching process using to reduce PTFE has the potential to create pitting and porosity. We studied changes in surface morphology using scanning electron microscopy and did not observe gross changes in surface morphology. Our conclusion that we have produced monolayers says nothing about the possibility of silane deposition within pits and pores formed from the chemical reduction step. The comparison of IR absorption intensities indicates that we have not formed a large proportion of multilayers at the PTFE surface; this statement also applies to silanes deposited within pores.

Table 1 contains contact angle data. On the basis of contact angles, the SAMs on PTFE-SiO$_2$ were comparable to SAMs on silicon. We also measured hexadecane contact angles for the SAMs obtained by HTS (hexadecyltrichlorosilane) chemisorption; for PTFE/SiO$_2$/HTS $\theta_a = 50 \pm 2°$ and $\theta_r = 27 \pm 3°$ and for silicon/HTS, $\theta_a = 48 \pm 2°$ and $\theta_r = 40 \pm 2°$. As with results for water contact angles, the similarity of contact angles using hexadecane as a probe fluid suggest comparable surface energy for the SAMs on silicon and PTFE/SiO$_2$.

We studied the influence of reduction time (the exposure time of PTFE to benzoin dianion solution) on the contact angle of monolayers formed from deposition of DHTS (DHTS was chosen for study in order to facilitate FTIR analysis), see Table 2. Longer reduction times lead to increased amounts of carbonaceous product (a complex mixture of single, double, and triple bonds, extended conjugation, and condensed aromatic-like cross-links); longer reduction times influence not only the extent of reduction but also the depth of the reduced layer.[2] Therefore, we expect that longer reduction times would lead to a higher concentration of surface hydroxyl groups; this higher hydroxyl concentration should facilitate more robust monolayer formation (greater number of chemical attachment sites) but not necessarily chemically different monolayers. Consistent with this, inspection of Table 2 indicates that the influence of reduction time on DHTS monolayers prepared on PTFE/SiO$_2$ is small, if not statistically insignificant.

XPS analysis of the SAMs on PTFE/SiO$_2$ gave complicated results. For example, XPS analysis revealed an atomic composition ratio for Si/O of 2.0/1 which is consistent with silicate overlayer. However, there is an abundance of other elements which include (listed in order of decreasing contribution) C, F, Ca, Cl, and N. We obtained variable XPS results that were often at odds with expectation; therefore, we found it difficult to make quantitative conclusions. However, some qualitative conclusions could be deduced. With the exception of the SAM obtained by $Cl_3Si(CH_2)_2(CF_2)_7CF_3$ chemisorption, the XPS peaks for F were small or nonexistent. This result is consistent with a thick (>10 nm) overlayer of silicate/monolayer on PTFE. This is consistent with our previous estimate of the SiO$_2$ layer thickness. The XPS of SAMs all show an increase in C relative to the PTFE/SiO$_2$.

Reflectance FTIR Analysis of Monolayers on PTFE/SiO$_2$. For SAMs prepared on flat substrates, reflectance and grazing angle FTIR has been an indispensable technique for characterizing the structural order in the monolayers. For example, the dichroic ratio can provide information about the average tilt of chains normal to the substrate surface. Allara and Swalen[7] performed early work on the grazing angle FTIR spectroscopy of monolayers. Porter and co-workers[8] studied the grazing angle FTIR of alkanethiol monolayers on gold. They studied the peak positions and intensities of the C−H stretching modes for $CH_3(CH_2)_n$-SH in the crystalline and liquid states and adsorbed on gold. For the SAM prepared from $CH_3(CH_2)_{21}SH$, $\nu_a(CH_2) = 2918$ cm^{-1} and $\nu_s(CH_2) = 2850$ cm^{-1}. These peak positions were similar to those for the crystalline state, 2918 and 2851 cm^{-1}, but different from the liquid state, 2924 and 2855 cm^{-1}. In going from the crystalline state (in KBr) to the liquid state, there are shifts of +6 and +4 cm^{-1} for the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ modes. The peak frequencies for the 21-carbon thiol adsorbed on gold were crystalline-like and suggested the alkyl chains were fully extended in the all-trans conformation. In addition, the peak positions varied as a function of chain length; for the SAM prepared from $CH_3(CH_2)_5SH$, $\nu_a(CH_2) = 2921$ cm^{-1} and $\nu_s(CH_2) = 2852$ cm^{-1}, indicating a less crystalline-like order in the SAM. These results were analogous to results reported by Synder and co-workers[9] for crystalline and liquid polymethylene chains.

The application of reflectance FTIR to monolayers on PTFE/SiO$_2$ must take into account the inherently disordered surface of the underlying PTFE. However, if it is assumed that SAMs are conformal with the surface morphology of the underlying PTFE, we can probe the local order of the chains comprising the SAM. We have used the positions of the asymmetric (ν_a) and symmetric (ν_s) C−D stretching modes of the CD$_2$ group in monolayers prepared from DHTS. We chose DHTS so that we could unambiguously attribute the absorptions of interest to the SAM and not to adventitious contamination of the surface by hydrocarbon contaminants from the local environment. When we studied HTS layers on modifed-PTFE, the intensity of CH$_2$ absorptions was not reproducible.

Table 3 contains the peak position data for SAMs prepared from DHTS. Figure 2 displays the CD$_2$ region

Table 3. Peak Positions for $CD_3(CD_2)_{15}SiCl_3$ (DHTS) C−D Stretching Modes in Liquid and Adsorbed on Silicate Surfaces[a]

	C−D peak position, cm^{-1}	
sample	$\nu_a(CD_2)$	$\nu_s(CD_2)$
liquid DHTS (neat)	2198	2096
$PTFE/SiO_2/DHTS$	2196	2092
PTFE−OH/DHTS	2196	2092
$ATR/SiO_2/DHTS$[b]	2196	2091

[a] Experimental error in assigning peak positions = ±2 cm^{-1}. [b] $ATR/SiO_2/DHTS$: SAM prepared on ATR silicon crystal using DHTS.

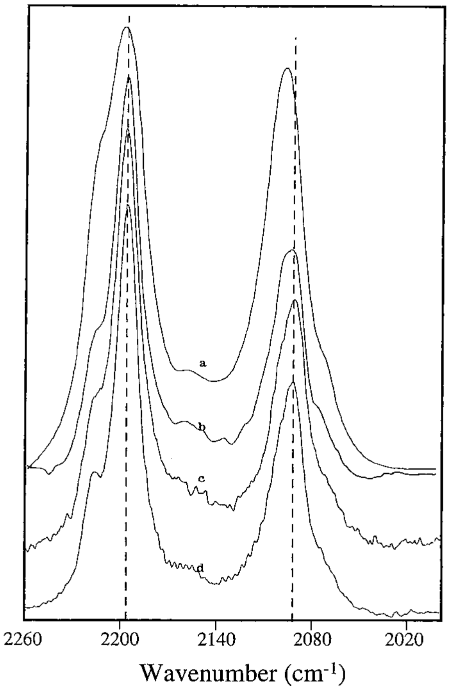


Figure 2. Transmission FTIR of liquid DHTS (a); reflectance FTIR of DHTS monolayers on $PTFE/SiO_2$ (b), PTFE−OH (c), and silicon ATR crystal (d). Absorption intensities have been normalized to facilitate comparison.

Table 4. Effect of Thermal Annealing on Water Contact Angles (deg) of Surface-Modified PTFE[a]

time at 125 °C, h	PTFE−OH		PTFE−OH/DHTS		$PTFE/SiO_2/DHTS$	
	θ_a	θ_r	θ_a	θ_r	θ_a	θ_r
Samples Prepared Using a 2 h Reduction Time						
0	62	44	110	90	119	93
17	65	47	111	90	118	93
43	64	47	109	87	118	95
68	66	52	109	89	119	94
Samples Prepared Using a 0.5 h Reduction Time						
0	67	49	113	91	119	96
24	77	61	111	89	120	95

[a] Experimental error in contact angle measurements = ±3°.

of the FTIR spectrum for the samples in Table 3. The absorption intensities have normalized to facilitate comparison. The peak positions of the monolayers prepared on $PTFE/SiO_2$ and PTFE−OH are similar to those for the monolayer prepared on a silicon ATR crystal. We assume that the SAM prepared on the ATR crystal represents a well-ordered monolayer system based on literature reports on similar systems.[10] Therefore, we conclude the monolayers on the $PTFE/SiO_2$ or PTFE−OH have similar structural order compared to the well-ordered monolayer prepared on the silicon ATR crystal. The peak positions are comparable to those for monolayers of perdeuterated stearic acid, $\nu_a(CD_2)$ = 2195 cm^{-1} and $\nu_s(CD_2)$ = 2090 cm^{-1}.[11] For $CD_3(CD_2)_{16}COOH$ in CCl_4, $\nu_a(CD_2)$ = 2200 cm^{-1} and $\nu_s(CD_2)$ = 2095 cm^{-1}.

One of the CD_3 modes appears at 2216 cm^{-1} in the reflectance FTIR of DHTS monolayers on $PTFE/SiO_2$ (Figure 2); it appears as a shoulder on the $\nu_a(CD_2)$ peak. The ratio of intensities for the CD_3 mode and the $\nu_a(CD_2)$ peak (A_{CD_2}/A_{CD_3}) are 2.7 ($PTFE/SiO_2/DHTS$), 3.0 ($ATR/SiO_2/DHTS$) and 2.6 (PTFE−OH/DHTS) for the monolayers. For liquid DHTS, A_{CD_2}/A_{CD_3} = 1.3. As in foregoing discussion on peak positions, this ratio indicates that DHTS chemisorbed to modified PTFE leads to a monolayer with similar structural order compared to a SAM prepared on silicon.

Thermal Reconstruction of Monolayers on Modified PTFE. Cross and McCarthy[12] studied the thermal reconstruction of surface-functionalized poly(chlorotrifluoroethylene) (PCTFE). When samples were heated for days at 80−110 °C, surface-functionalized samples of PCTFE underwent surface reconstruction as evidenced by changes in contact angles and XPS data. For example, the water contact angle of hydroxyl-modified PCTFE increased +20° after annealing a sample for several days at 100 °C. The reconstruction was depth dependent and surface-chemistry dependent.

We have investigated the possibility of the same phenomenon for DHTS monolayers on PTFE. Table 4 contains data for two sets of samples: one prepared by an initial reduction time (the time of treatment of PTFE by potassium benzoin dianion) of 0.5 h and the second set prepared by an initial reduction time of 2 h. Only the PTFE−OH samples showed significant changes in contact angles after annealing at 125 °C in air. The time of reduction presumably affects the depth of chemical modification but should not appreciably alter the subsequent modifications with SiO_2/DHTS. The glass-transition temperature for PTFE is −73 °C.[13] The changes observed for PTFE−OH are considerably smaller than Cross and McCarthy saw for PCTFE-OH although the trends are similar; in addition, the samples with shorter reduction times show the largest effects.

Summary

PTFE has been successfully modified by trichlorosilane chemisorption to hydroxyl-modified (PTFE−OH) and silicate-modified ($PTFE/SiO_2$) PTFE. XPS results and contact angles are consistent with the anticipated surface chemistry. Evidence for monolayer formation is based on absorption intensities in reflectance FTIR analysis. We have used SAMs prepared on silicon substrates as an analytical standard to evaluate our results on surface-modified PTFE. The monolayers form equally well on both PTFE−OH and $PTFE/SiO_2$, although higher contact angles were observed for DHTS monolayers on $PTFE/SiO_2$ under a greater variety of conditions. Peak positions of the C−D stretching modes in DHTS monolayers are consistent with a crystalline-like monolayer suggesting structurally well-ordered monolayers. Thermal annealing of the DHTS monolayers did not produce any significant changes in water contact angles.

The primary value of this surface modification technique is the opportunity to introduce specific functional groups onto the surface of PTFE with the same structural and chemical certainty that is normally associated with the self-assembled monolayers on conventional silicate substrates. This is an avenue of research that we are currently exploring.

Experimental Section

Materials. PTFE was obtained from Bergoff/America as $^1/_{32}$ in. thickness film, extracted with refluxing THF for 24 h and dried (<0.1 mm, 50 °C) for 8 h. THF was distilled from sodium benzophenone dianion. Hexadecane (Aldrich) was dried over 4 Å molecular sieves. Hexadecyltrichlorosilane-d_{33} (DHTS) and 1-bromo-11-(trichlorosilyl)undecane were synthesized by the method of Lander.[14] 1*H*,1*H*,2*H*,2*H*−Perfluorodecyltrichlorosilane (Gelest) and 7-oct-1-enyltrichlorosilane (Gelest) were distilled prior to use. House-distilled water was doubly distilled. Silicon substrates were standard n-type semiconductor grade silicon wafers (Semiconductor Processing, Inc.) and were cut to size using a diamond-tipped glass cutter. Silicon ATR crystals (25 × 5 × 1 mm) and KRS-5 (25 × 10 × 1) (used for PTFE samples analysis) were obtained from Harrick Scientific. The silicon substrates were cleaned prior to use with “piranha” etching.[10a] All other reagents were obtained from Aldrich and used as received.

Methods. Contact angle measurements were performed using a Rame-Hart NRL-100 contact angle goniometer equipped with an environmental chamber and tilting base mounted on a vibrationless table (Newport Corp.). Drop volumes were 10 uL. Details of our tensiometric methods have been published previously.[15] The reported value of contact angles are usually the average of eight measurements. ATR−IR spectra were obtained with a Nicolet System 730 spectrometer using a modified 4XF beam condenser (Harrick Scientific). ATR spectra were run at 4 cm^{-1} resolution, collecting 2000−4000 scans. The sample chamber was purged either with dry air or with nitrogen for at least 60 min. Background spectra were recorded for each ATR crystal and subtracted from the sample spectra. Baselines were adjusted to zero absorbance for measurement of spectra. XPS data was collected using a Surface Science SSX-100 spectrometer. The incidence angle of the X-rays was 35° with respect to the sample normal. Survey spectra were taken for each sample (resolution 4 eV, spot size 1000u, 2 scans). High-resolution scans of silicon, carbon, oxygen, and nitrogen regions were also obtained. Ellipsometric measurements were performed with a Gaertner Model L116C Ellipsometer. ^{1}H and ^{13}C NMR spectra were recorded using a Varian Gemini 200 MHz spectrometer.

Preparation of PTFE/SiO$_2$. PTFE−OH was prepared by the method of Costello and McCarthy.[2] Samples of PTFE−OH 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. No attempt was made to control humidity. The sample was removed from the bottle, soaked in distilled water for 15 min, and dried with a stream of air. The wettability of the sample was checked, and if water spread symmetrically across the surface ($\theta_a \approx 0°$), then the sample was dried with nitrogen and treated again with $SiCl_4$. The thickness of the SiO_2 layer was estimated by the analogous treatment of a silicon wafer; ellipsometry was used to determine the SiO_2 thickness.

Monolayer Deposition. The preparation of SAMs on the silicon substrates followed well-established literature methods.[10] For surface-modified PTFE, the deposition process was similar. Samples of PTFE/SiO_2 or PTFE−OH were immersed in a solution of the trichlorosilane (0.1 mL) in hexadecane (20 mL). Depositions were conducted at either room temperature or 70 °C for 6 h. The samples were washed with CH_2Cl_2 and $CHCl_3$ and brushed gently with a cotton-tipped applicator soaked in CH_2Cl_2. The samples were rinsed one more time with CH_2Cl_2 and dried under a stream of air.

References and Notes

(1) Noh, I.; Chittur, K.; Goodman, S. L.; Hubbell, J. A. *J. Polym. Sci., Polym. Chem.* **1997**, *35*, 1499.
(2) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2819.
(3) Ulman, A. *Ultrathin Organic Films*; Academic Press: San Diego, CA, 1991.
(4) Ferguson, G. S.; Chaudhury, M. K.; Biebuyck, H. A.; Whitesides, G. M. *Macromolecules* **1993**, *26*, 5870.
(5) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F. In *Handbook of X-ray Photoelectron Spectroscopy*; Mullenberg, G. E., Ed., Perkin-Elmer Corp.: Eden Prairie, 1979.
(6) Tripp, C. P.; Hair, M. L. *Langmuir* **1995**, *11*, 1215.
(7) Allara, D. L.; Swalen, J. D. *J. Phys. Chem.* **1982**, *86*, 2700.
(8) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.
(9) Synder, R. G.; Maroncelli, M.; Strauss, H. L.; Hallmark, V. M. *J. Phys. Chem.* **1986**, *90*, 5623.
(10) (a) Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074. (b) Balachander, N.; Sukenik, C. N. *Langmuir* **1990**, *6*, 1621.
(11) Dote, J. L.; Mowery, R. L. *J. Phys. Chem.* **1988**, *92*, 1571.
(12) Cross, E. M.; McCarthy, T. J. *Macromolecules* **1990**, *23*, 3916.
(13) Lau, S.-F.; Suzuki, H.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 379.
(14) Lander, L. M. Ph.D. Dissertation, University of Akron, 1994.
(15) Lander, L. M.; Siewierski, L. M.; Brittain, W. J.; Vogler, E. A. *Langmuir* **1993**, *9*, 2237.

MA9811526