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Pentafluoro-λ^6-sulfanyl-Terminated Chlorosilanes: New SF_5-Containing Films and Polysiloxane Materials

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Two new SF_5-terminated perfluoroalkylsilanes—$SF_5(CF_2CF_2)_nCH_2CH_2SiCl_3$ ($n = 1$ and 2)—were synthesized by addition of trichlorosilane to the corresponding synthetic SF_5-terminated perfluoroalkenes by hydrosilylation. Thin films of these SF_5-silanes on clean silicon oxide substrates were characterized by ellipsometry, aqueous contact angle, and X-ray photoelectron spectroscopy (XPS) methods. The shorter SF_5-silane film shows a hydrophobic interface with minimal angle dependence in depth-dependent XPS analysis, suggesting a poorly organized film. The longer SF_5-silane exhibits a high aqueous static contact angle (106°) and angular-dependent XPS compositional variance consistent with improved film assembly (fewer defects and more vertical chain orientation). Bulk SF_5-bearing materials were fabricated by silane hydrolysis, producing SF_5-polymers and cross-linked networks bearing the unique SF_5 perfluoroalkyl chemistry.

Introduction

Functionalized silane coupling agents represent a highly studied body of materials useful for surface modification[1] and sol−gel[2] routes to new materials. Fluoroalkyl organosilanes represent a subset of these chemistries of growing importance due to their well-described capability of reducing surface energy.[3−5] Focus in this regard has been nearly exclusively on perfluorocarbon-based silane systems, terminated in the perfluoromethyl ($-CF_3$) group, because of the desire to produce either low surface energy or low dielectric materials. Little attention has been directed at other possible fluorinated chemistries that might duplicate perfluoroalkyl properties in bulk or interfacially.

In 1975, Berry and Fox[6] reported the first silicon compounds containing the pentafluoro-λ^6-sulfanyl (SF_5) group. These new silanes were prepared by the addition of SF_5Cl and SF_5Br to vinyltrimethylsilane and the addition of SF_5Br to vinyltrichlorosilane. Preparation of polymeric materials or surface coatings from these SF_5-containing silanes has not been reported. Because organo SF_5 derivatives retain much of the unique character of SF_6 (gas), the SF_5 chemistry should prove interesting as an alternative low surface-energy coating comparable to perfluoroalkylsilane analogues. Yet, these materials are not well-studied. Very recently, we have reported synthesis and analysis of films of SF_5-containing polyacrylates.[7] Photopolymerization in mixtures with conventional aliphatic monomers yielded polymer coatings nonstoichiometrically enriched in SF_5 groups at the surface. This stratified polymer surface exhibited low wettability and the highest X-ray photoelectron S2p binding energy recorded to date.

An additional route to produce new apolar SF_5-containing surfaces utilizes SF_5-terminated perfluoroalkylsilanes and resulting polysiloxanes as components for films and coatings. To investigate this alternative, we have prepared two new SF_5-terminated perfluoroalkyl silanes using hydrosilylation methods. Hydrosilylation of olefins can be effected by heating, UV light, peroxide initiators, or transition metal catalysts.[8−12] We report synthesis and surface properties for films fabricated from two new perfluoroalkylated chlorosilanes, $SF_5(CF_2CF_2)_nCH_2CH_2SiCl_3$ (where $n = 1, 2$), created by two hydrosilylation methods: peroxide free-radical initiation and chloroplatinic acid catalysis. These SF_5-terminated materials are predicted to have properties

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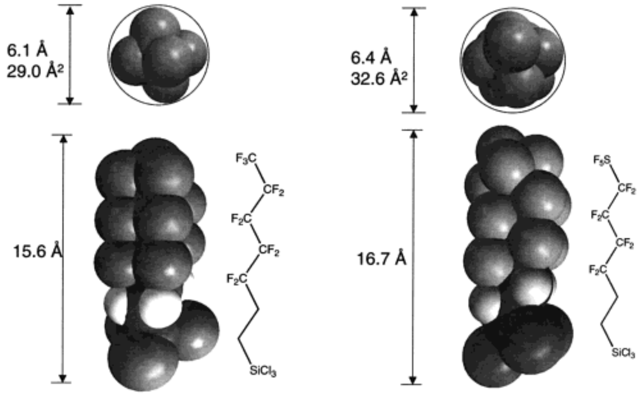

Figure 1. Space-filling molecular models for the SF_5-$(CF_2)_4$-$(CH_2)_2$-$SiCl_3$ molecule compared to the conventional CF_3-terminated perfluoroalkylsilane. In addition to both side-on perspectives, the top-down molecular view of the terminal $-SF_5$ group is compared to the terminal $-CF_3$ group to contrast the molecular area of occupancy of these perfluorinated silanes in thin films. The molecular structures were energy-minimized with a MMFF94 molecular mechanics model limited to geometrical and conformational predictions. This model does not consider quantum mechanical interactions.

equivalent to perfluoroalkylsilanes but with the important difference of the $-SF_5$ group that has different spatial and chemical properties. A space-filling molecular model for the $SF_5(CF_2)_4$-$(CH_2)_2$-$SiCl_3$ molecule (generated with PC Spartan Pro, Wavefunction, Inc., CA, and energy minimized with MMFF94 molecular mechanics) is shown in Figure 1 and compared in a top-down view to the same length conventional CF_3-terminated perfluoroalkyl chain. A similarly constructed/minimized molecular model of the CF_3-terminated perfluoroalkyltriethoxysilane has been published previously and compares well to this trichloro analogue.[5] The terminal $-SF_5$ umbrella group is seen to occupy 10% larger area compared to the $-CF_3$ terminal group, possibly influencing lateral organization of this chemistry in thin films.

Covalent attachment of silanes via hydrolytic reactions with reactive oxide surfaces (e.g., silicon oxide, TiO_2, or alumina) typically produces modified surfaces bearing this overlayer chemistry.[3−5,13] In this case, we have modified silicon oxide supports with SF_5-bearing silanes as thin film overlayers. Surface analysis of these films by ellipsometry, angle-resolved X-ray photoelectron spectroscopy, and aqueous contact angles distinguishes differences in film quality between the shorter and longer SF_5 silanes. Additionally, bulk polysiloxane materials with SF_5-containing perfluoroalkyl groups are prepared by bulk hydrolysis (sol−gel chemistry)[2] of the SF_5 silanes. These materials are expected to show new, interesting chemical and physical properties including high chemical and thermal stability, high dielectric strength, low refractive index, and low surface energy. These unique chemical and physical properties are derived in part from the similarities of the SF_5 perfluoroalkyl groups to the parent compound, gaseous SF_6. Applications for these new materials include high-performance lubricants and optical materials, water-repellent and oil-resistant sealants, antifoaming agents, and protective surface coatings.

Experimental Methods

Materials. All water was polished Millipore grade (18 MΩ·cm resistivity). Trichlorosilane (99%), *tert*-butyl peroxide (98%), and hexachloroplatinic acid hexahydrate (99.995%) were purchased from Aldrich Chemical Co. and used as received. Methylene chloride (Burdick and Jackson, high-purity grade), hexane (J. T. Baker), diethyl ether (J. T. Baker, anhydrous) and sodium sulfate (EM Science, anhydrous, GR) were used as received. $SF_5(CF_2CF_2)_nCH{=}CH_2$ ($n = 1$ and 2) precursors were prepared as previously described.[14]

General Bulk Characterization Methods. NMR spectra were obtained on a Varian EM-390 spectrometer operating at 84.67 MHz for ^{19}F analysis and a Bruker AMX-400 spectrometer operating at 400 MHz for ^{1}H analysis, 376.5 MHz for ^{19}F analysis, and 100.6 MHz for ^{13}C analysis. $CDCl_3$ was used as the solvent for NMR samples; $(CH_3)_4Si$ and $CFCl_3$ were used as internal standards. Bulk Fourier transform infrared (FTIR) spectra were obtained between potassium bromide plates on a Perkin-Elmer System 2000 FT-IR operating at 2 cm^{-1} resolution. Mass spectra were measured via a Hewlett-Packard HP 5890 series II gas chromatograph (25 m, DB-5 column) with a HP 5970 mass-selective detector operating at 70 eV. Elemental analyses of each product were determined by Beller Mikroanalytisches Laboratorium (Göttingen, Germany).

Synthesis of $SF_5CF_2CF_2CH_2CH_2SiCl_3$. *Procedure A—tert-Butyl Peroxide Initiator*. To a 25 mL Pyrex glass Carius tube equipped with a Kontes Teflon stopcock and a Teflon coated stirring bar were added 2.06 g (8.1 mmol) of $SF_5CF_2CF_2CH{=}CH_2$, 0.20 g (17 mol %) of *tert*-butyl peroxide, and 3.37 g (25.0 mmol) of trichlorosilane. The reaction vessel was cooled to −196 °C and evacuated. After heating at 110−130 °C for 22 h, distillation of the reaction mixture at reduced pressure provided 2.07 g of $SF_5CF_2CF_2CH_2CH_2SiCl_3$ (boiling point 58−59 °C at 8 mmHg) in 66% yield.

Procedure B—Chloroplatinic Acid Catalysis. To a 50 mL Pyrex glass Carius tube equipped with a Kontes Teflon stopcock and a Teflon coated stirring bar were added 2.04 g (8.0 mmol) of $SF_5CF_2CF_2CH{=}CH_2$, 5 mL of methylene chloride, 1.36 g (10.1 mmol) of trichlorosilane, and approximately 700 ppm of chloroplatinic acid (relative to the amount of olefin). The reaction vessel was cooled to −196 °C and evacuated. After heating at 90 °C for 22 h, the reaction mixture was distilled at reduced pressure to give 1.50 g of $SF_5CF_2CF_2CH_2CH_2SiCl_3$ in 48% yield. Substitution of hexane for methylene chloride as reaction solvent and heating at 90 °C for 49 h resulted in a 54% yield. Elemental analysis calcd for $C_4H_4F_9Cl_3SSi$: C, 12.33; H, 1.04; S, 8.23; F, 43.9. Found: C, 12.54; H, 1.05; S, 8.35; F, 43.4.

Synthesis of $SF_5(CF_2CF_2)_2CH_2CH_2SiCl_3$. Preparation of $SF_5(CF_2CF_2)_2CH_2CH_2SiCl_3$ is similar to procedure B described above. Approximately 400 ppm of chloroplatinic acid, 1.96 g (5.5 mmol) of $SF_5(CF_2CF_2)_2CH{=}CH_2$, 5 mL of hexane, and 1.05 g (7.8 mmol) of trichlorosilane were mixed together. The reaction vessel was cooled to −196 °C, evacuated, and heated at 85−100 °C for 45 h. Distillation of the product at reduced pressure provided 1.94 g of $SF_5(CF_2CF_2)_2CH_2CH_2SiCl_3$ (bp 86.2−86.8 °C at 5 mmHg) in 72% yield. Elemental analysis calcd for $C_6H_4F_{13}Cl_3SSi$: C, 14.72; H, 0.83; F, 50.45. Found: C, 14.79; H, 0.85; F, 49.60.

Bulk Hydrolysis of $SF_5CF_2CF_2CH_2CH_2SiCl_3$. To a 50 mL Pyrex glass Carius tube equipped with a Kontes Teflon stopcock and a Teflon coated stirring bar was added 6 mL of deionized water. A mixture of 0.47 g (1.21 mmol) of SF_5CF_2-$CF_2CH_2CH_2SiCl_3$ and 5 mL of diethyl ether was added dropwise to the water with vigorous stirring over a 10 min period and the reaction mixture was heated at 90−100 °C for 23 h. The mixture was extracted with three 5 mL portions of ether, and the ether extract was dried with anhydrous sodium sulfate. The ether solvent was removed in vacuo, resulting in 0.30 g of a clear, colorless, viscous solid. A portion of the final product (0.24 g) was placed on a watch glass and heated under

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a nitrogen atmosphere to 160 °C for 1.5 h and 250 °C for 1 h, resulting in 0.17 g of a tan, tacky polymerized solid.

The infrared spectrum exhibited the following bands (cm^{-1}): 3716 (w), 3372 (br, vw), 2987 (w), 2960 (w), 2920 (w), 1446 (w), 1424 (w), 1374 (vw), 1320 (m), 1285 (w), 1270 (w), 1199 (s), 1117 (s), 1082 (m), 1021 (m), 959 (w), 875 (vs), 838 (s), 824 (s), 735 (m), 700 (m), 682 (m), 643 (w), 605 (s), 574 (m), 533 (w), 495 (w).

Bulk Hydrolysis of $SF_5(CF_2CF_2)_2CH_2CH_2SiCl_3$. The hydrolysis of $SF_5(CF_2CF_2)_2CH_2CH_2SiCl_3$ was similar to the hydrolysis of $SF_5CF_2CF_2CH_2CH_2SiCl_3$ above. A mixture of 0.51 g (1.04 mmol) of $SF_5(CF_2CF_2)_2CH_2CH_2SiCl_3$ and 6 mL of diethyl ether was added dropwise to 6 mL of water over a 5-min period and the reaction mixture was heated at 60−70 °C for 24 h. The mixture was extracted with three 5 mL portions of ether, and the ether solvent was removed in vacuo. The resulting polymer was dried for 2 days in vacuo. The polymer (0.44 g) was a clear, waxy solid.

The infrared spectrum exhibited the following bands (cm^{-1}): 3717 (vw), 3419 (w, br), 2989 (vw), 2955 (vw), 2925 (vw), 1446 (m), 1423 (w), 1373 (w), 1317 (m), 1220 (vs), 1168 (s), 1147 (vs), 1074 (m), 962 (m), 930 (m), 881 (vs), 815 (m), 789 (m), 765 (m), 749 (m), 719 (m), 706 (m), 686 (m), 636 (w), 603 (m), 584 (m), 537 (w), 454 (m), and 418 (m).

Substrate Silanization. Silicon wafers (Wacker Siltronic, Portland, OR) were cleaned by 24-h immersion in a Pirhana solution (1:1 mix of concentrated sulfuric acid and 30% H_2O_2) etch (*caution*: *this solution contains reactive peroxides*), followed by copious rinsing in pure water, then anhydrous ethanol, and dry nitrogen gas. Silicon wafer pieces were cut by scoring with a diamond scribe. Each SF_5-containing silane was dissolved to approximately 2 mM concentration in hexanes. Cleaned wafer pieces were immersed into these silane solutions for 24 h, then rinsed copiously with pure hexanes, dried under N_2 gas, and heated in a dry vacuum oven at 105 °C for 24 h.

Surface Analysis of SF_5-Perfluoroalkylsilane Thin Films. *Ellipsometry*. Film thicknesses were measured on a Gaertner L117 ellipsometer with a wavelength of 6328 Å (He−Ne laser) at an incident angle of 70°. Each underivatized, bare silicon wafer was used as its own internal reference, and 3−4 measurements were made on each sample. Thicknesses were calculated with the assumption of a refractive index of 1.36 for the adsorbed SF_5 film on SiO_2.

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) experiments were performed on a Surface Science SSX-100 spectrometer (Mountain View, CA) equipped with a monochromatic Al Kα source, hemispherical analyzer, and a multichannel detector.[7] 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 with a 1000 μm spot size. Both survey spectra and data for quantitative analysis were collected at a pass energy of 150 eV and a spot size of 1000 μm. The binding energy (BE) scales for all spectra were referenced to the C1s C−H peak at 285.00 eV. Peak fitting of the high-resolution spectra was done with Gaussian peak shapes by use of 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),[15] the photoelectron escape depth was assumed to vary as $KE^{0.7}$,[15] and Scofield's photoionization cross sections were used.[16]

Angle-dependent XPS data were collected at nominal photoelectron takeoff angles of 0°, 55°, and 80°. The takeoff angle was defined as the angle between the surface normal and the axis of the analyzer lens system. With mean free paths calculated from the equations given by Seah and Dench,[17] the sampling depth (three times the mean free path) for C1s photoelectrons should decrease from 90 to 15 Å as the takeoff angle increases from 0° to 80°.[18] From analysis of replicates, the typical XPS uncertainties were observed to be less than ±1.0 atom % for carbon, oxygen, silicon, and fluorine, and less than ±0.5 atom % for sulfur.

Static Contact Angle Analysis. Sessile drop contact angle analysis (Ramé-Hart 100 apparatus) used purified (Millipore 18 MΩ·cm resistivity) water drops (2 μL) on three separate spots on each film surface in a controlled environment (100% relative humidity). Measurements were taken on both sides of water drops at ambient temperature 30−40 s after drops were applied to surfaces. Contact angle data report the average of three drops at different surface locations.

Results and Discussion

New perfluoroalkylchlorosilanes, $SF_5(CF_2CF_2)_nCH_2CH_2SiCl_3$ ($n = 1$ and 2), were prepared by the addition of trichlorosilane to the corresponding SF_5-containing perfluoroalkylolefins, with either *tert*-butyl peroxide as the radical initiator or chloroplatinic acid as the transition metal catalyst. The four carbon adduct was prepared in 66% yield with *tert*-butyl peroxide initiator (compared to 48−53% yield with the transition metal catalyst). Changing the solvent from methylene chloride to hexane in the chloroplatinic acid method showed little effect on product yield. The six-carbon trichlorosilane was prepared in 72% yield by the chloroplatinic acid method with hexane as the solvent:

$$SF_5CF_2CF_2CH{=}CH_2 + HSiCl_3 \xrightarrow[110-130\ °C]{(t\text{-}BuO)_2} SF_5CF_2CF_2CH_2CH_2SiCl_3 \tag{1}$$

$$SF_5(CF_2CF_2)_nCH{=}CH_2 + HSiCl_3 \xrightarrow[90\ °C]{H_2PtCl_6} SF_5(CF_2CF_2)_nCH_2CH_2SiCl_3 \tag{2}$$

The bulk infrared spectra of the new SF_5-containing chlorosilanes show several characteristic absorption bands attributable to the SF_5 group:[7,19,20] SF_5 stretching modes are strong between 840 and 880 cm^{-1} with deformation modes appearing as medium to strong bands at 417−418 and 574−605 cm^{-1}. These frequencies overlap with weaker asymmetric Si−Cl bands assigned previously at 605 and 582 cm^{-1},[21] confounding distinct interpretation. Both compounds contain strong bands between 1117 and 1221 cm^{-1}, corresponding to CF_2 stretching vibrations, and weak methylene stretching vibrations between 2870 and 2987 cm^{-1}. The symmetric bulk $SiCl_3$ stretching band observed at 464 cm^{-1} for both compounds is in general agreement with a previous report.[21]

Detailed ^{1}H, ^{19}F, and ^{13}C NMR spectral assignments for both of these silane products are available as Supporting Information (available free of charge via the Internet at http://pubs.acs.org). Chemical shifts and multiplicities in the ^{1}H NMR spectrum agree with data for similar β-(perfluoroalkyl)ethylsilanes. The SF_5 group

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appears as a distinct AB_4 pattern in the ^{19}F spectrum with the axial fluorine (A) at 66.2 ppm and the equatorial fluorines (B) at 44.4 ppm. The axial fluorine appears as a distorted pentet (9-line pattern) and the equatorial fluorines appear as doublets of pentets. The ^{19}F NMR chemical shifts, multiplicities, and coupling constants are in good agreement with values for similar perfluoroalkyl silanes, SF_5-containing perfluoroalkyl iodides and dibromides.[12,22,23]

The mass spectrum of the $SF_5CF_2CF_2CH_2CH_2SiCl_3$ synthetic product showed mass fragments typical of alkyl trichlorosilanes and SF_5-containing perfluoroalkyl compounds. The base peak occurs at *m*/*e* 135 but no parent ion was observed in the spectrum. The $Cl_3SiCH_2CH_2^+$ fragment appears at *m*/*e* 165, 163, and 161; Cl_3Si^+ at *m*/*e* 137, 135, and 133; and $ClSi^+$ at *m*/*e* 65 and 63. All of the fragments in this series show relative intensities typical for trichlorosilanes.[24] The presence of the SF_5 group is indicated by fragments at *m*/*e* 127 (SF_5^+), 89 (SF_3^+), and 51 (SF^+).

Bulk hydrolysis of the two new trichlorosilanes resulted in polymeric products. The polymer formed from $SF_5CF_2CF_2CH_2CH_2SiCl_3$ was a viscous liquid after heating at 90−100 °C in an ether/water mixture, while $SF_5(CF_2CF_2)_2CH_2CH_2SiCl_3$ was converted to a waxy solid following a similar treatment. The hydrolysis product of the shorter $SF_5CF_2CF_2CH_2CH_2SiCl_3$ was further heated to 160 and then 250 °C in attempts to increase the degree of polymerization or cross-linking in the material. The material became a waxy solid following this temperature treatment. Both polymers contained residual free (3716 cm^{-1}) and associated (3372−3419 cm^{-1}) silanol groups as shown by the infrared spectrum. The symmetric Si−O−Si vibration appears in the spectra of both polymers as two strong broad bands between 1074 and 1116 cm^{-1}.

Surface Analysis of SF_5 Silane Films on Silicon Oxide Substrates. SF_5-containing silane films on silicon oxide supports were characterized by ellipsometry, aqueous wetting, and angle-resolved XPS. Ellipsometry provided film thicknesses of 12 Å for the shorter silane and 14 Å for the longer silane on SiO_2. These values are based on a two-layer calculation with the assumption of an average refractive index of $n = 1.36$ for the chemisorbed overlayer and a 13 Å thickness for the native oxide on silicon. Variance of Δ and ψ associated with varying the assumed model film refractive index from 1.35 (equivalent to pure perfluorocarbon) to 1.45 (equivalent to pure hydrocarbon) were negligible for a two-layer model and also negligibly different for a three-layer model based on a 7 Å pure perfluorocarbon top layer, 7 Å pure hydrocarbon middle layer, and 13 Å SiO_2 bottom layer. These film thickness values are consistent with monolayers of the perfluorinated silanes expected from surface coupling.[5,25] Aqueous static contact angles for these same films are 95° and 106°, respectively, indicating that these SF_5-silane film surfaces are substantially more hydrophobic than alkylsilane monolayers[1,13,25,26] and comparable to wetting data reported for SF_5-terminated polyacrylate films shown to be highly enriched in $-SF_5$ chemistry at their outer surface[7] and perfluoroalkylsilane films on SiO_2.[3−5,23,25−29] Reduced contact angles for the shorter SF_5 silane are similar to those reported for short CF_5-terminated silanes[5] and indicate reduced chain order or poor lateral organization with defects likely contributing to exposure of more polar chemistry (i.e., SiO_2 substrate). This is intuitive, based on the spatial mismatch of the bulky SF_5-terminal group and the short mixed perfluoroalkyl/alkyl underlying chain above the silane anchor group, supported by the space-filling alkylsilane molecular model comparison in Figure 1.[5,25] These models show the difference in spatial occupancy anticipated for the well-studied terminal $-CF_3$ group and the terminal $-SF_5$ group. Previously published experimental data support the validity of these models, yielding molecular areas of 31 Å^2 for organized, highly compressed CF_3-terminated perfluoroalkylsilane Langmuir−Blodgett films[30] identical to that in the Figure 1 model and 33.2 Å^2 for the cross-sectional area of a perfluorocarbon chain.[31,32]

Table 1. XPS Data for SF_5-Terminated Perfluoroalkylsilane Films on Silicon Oxide[a]

thin film sample	XPS elemental atomic percent F	C	S	O	Si
SF_5-CF_2-CF_2-CH_2CH_2-$SiCl_3$					
all elements (film)	24.1	20.9	2.0	24.6	28.4
without Si or O[b]	51.3	44.5	4.3		
theory w/o Si or O	64.3	28.6	7.1		
SF_5-CF_2-CF_2-CF_2-CF_2-CH_2-CH_2-$SiCl_3$					
all elements in film	38.5	17.7	2.1	22.7	19.0
without Si or O[b]	66.0	30.4	3.7		
theory w/o Si or O	65.0	30.0	5.0		

[a] Fixed sampling depth of ∼45 Å. [b] Si and O compositional weighting removed to eliminate confusion with SiO_2 substrate contribution.

Table 2. Angular Resolved XPS Data (Depth Dependence) for Films of $SF_5(CF_2)_4(CH_2)_2SiCl_3$ on Silicon Oxide Subtrates

depth dependence angle (deg)	depth (Å)	XPS elemental atomic percent F	S	C	O	Si
0	90	32.3	1.8	15.0	24.4	26.6
55	50	39.0	2.4	18.6	21.5	18.5
80	15	50.2	3.8	24.2	13.0	8.8
		Without Si or O				
80	15	64.2	4.9	30.9		
		Theory without Si or O				
		65.0	5.0	30.0		

Film XPS data are summarized in Tables 1 and 2. High-resolution spectra show features very similar to that from surfaces of SF_5-perfluoroalkylacrylate films.[7] Specifically, the carbon C1s spectrum exhibits compo-

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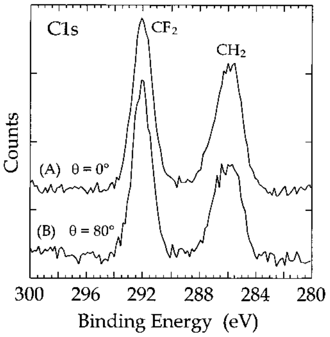

Figure 2. Angle-dependent XPS high-resolution C1s spectra for SF_5-$(CF_2)_4$-$(CH_2)_2$-$SiCl_3$ on SiO_2 substrate. (A) Zero-degree takeoff angle (sampling depth ~90 Å); (B) glancing angle (sampling depth ~15 Å).

nents characteristic of both perfluoroalkyl and hydrocarbon chemistry in the silane. Additionally, the sulfur S2p spectrum (data not shown) is essentially identical to that published previously for SF_5-containing polyacrylate films[7] and shows the characteristic overlapping spin doublets for sulfur[33] shifted to extremely high binding energy due to the fluorine electron-withdrawing influence at high stoichiometry in $-SF_5$. For the fixed 55° XPS takeoff angle (Table 1, sampling depth ~45 Å), both samples show the presence of the underlying O and Si substrate signals. When elemental film composition is normalized to the less ambiguous chemistry characteristic of the silane alone, differences between the XPS analysis of these two films are evident. The shorter SF_5 silane chemistry shows actual film elemental composition containing less F and S than predicted from calculated theoretical composition of this surface (Table 1). This together with the increased C1s content support the creation of a poorly organized, perhaps defect-ridden, chemisorbed layer, consistent with somewhat reduced contact angles seen on this surface. Again, this might be expected from films comprising short underlying alkyl chains precluded from high lateral packing density by a large $-SF_5$ terminal umbrella like structure. The longer SF_5 silane exhibits improved monolayer quality. Table 1 XPS data at ~45 Å sampling depth for this film elemental composition are equivalent to those expected for a theoretical bulk SF_5 silane composition. This supports a more uniform, organized film structure consistent with observed ellipsometry and film wetting data.

Additional insight is gained from depth-dependent XPS data for this longer silane film (Figure 2 and Table 2). While the shorter silane film showed no angular (depth) dependence in compositional analysis (data not shown), Figure 2 shows high-resolution C1s spectra at the two extreme angles that support depth-dependent differences in this film chemistry. The top spectrum (Figure 2A) samples the entire film depth and shows equal amounts of C1s perfluorocarbon and hydrocarbon constituent chemistry. At glancing angles, the 15 Å sampling depth (Figure 2B) shows 58% perfluorocarbon and 42% hydrocarbon Cls weighting, suggesting moderate perfluorinated chemistry enrichment of the outer surface of this monolayer, consistent with known attachment chemistry and predicted orientation. Table 2 data show some additional trends in film composition for the longer silane that support improved film organization. As sampling depth moves from deep within the film (takeoff angle of 0°) to very shallow 15 Å depths (takeoff angle of 80 Å), fluorine, sulfur, and carbon compositions all increase substantially, consistent with more regular, upright orientation of SF_5 perfluoroalkylsilanes on this support. Silicon and oxygen signals from the substrate decrease proportionally. Because the XPS sampling depth at glancing angle (15 Å) still penetrates to the SiO_2 substrate, film analysis without substrate contributions cannot be experimentally probed. Normalization of 15 Å depth film composition to F, S, and C elements alone (Table 2) shows nearly stoichiometric agreement of actual with theoretical SF_5 silane film composition.

These data strongly support formation of organized SF_5 silane monolayer films from this longer silane, despite anticipated steric and structural problems from the large SF_5 terminal cap (see Figure 1) within these layers. Stronger surface enrichment to nonstoichiometric levels might be expected in the XPS angle-resolved data for fluorine and sulfur if these films were consistently organized laterally over large length scales.[7,34-36] Absence of nonstoichiometric enrichment trends in these SF_5 systems at shallow depth suggests either tilted layers[36] (not supported by ellipsometry) or some degree of film lateral heterogeneity that limits consistent layer formation and high degrees of organization, possibly due to the bulky $-SF_5$ terminal group. Geometric constraints of the bulky $-SF_5$ terminal group with underlying alkylsilane chain lateral packing must be reconciled before these materials can produce consistent low-energy apolar surface chemistry comparable to other known perfluoroalkylsilane materials.

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Supporting Information Available: Detailed assignments of the ^{19}F, ^{1}H, and ^{13}C NMR and FTIR and mass spectra for both SF_5-$(CF_2)_4$-$(CH_2)_2$-$SiCl_3$ and SF_5-$(CF_2)_4$-$(CH_2)_2$-$SiCl_3$ molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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