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Journal of Fluorine Chemistry 115 (2002) 107–113

JOURNAL OF FLUORINE CHEMISTRY

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Perfluorinated polymer surfaces comprising SF_5-terminated long-chain perfluoroacrylate

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Received 18 September 2001; accepted 8 January 2002

Abstract

A new perfluorinated acrylate monomer containing the $SF_5(CF_2)_6$-perfluorinated side chain was synthesized and polymerized into films. Bulk monomer characterization is consistent with the molecular structure based on FTIR, mass spectrometry and NMR analyses. The surface properties of polymer coatings were studied with aqueous wetting (contact angle) and X-ray photoelectron spectroscopy (XPS) methods. The surface composition is shown to be highly enriched in the terminal side chain SF_5-chemistry and exhibits properties consistent with a highly apolar, non-wetting perfluorinated polymer surface. Depth-dependent XPS studies using angular-resolved methods (ADXPS) confirmed a non-stoichiometric enrichment of sulfur and fluorine at the film ambient interface, consistent with a surface presence of the terminal SF_5-group and possibly film structural anisotropy in the surface zone. Time-of-flight (TOF) secondary ion mass spectrometry (SIMS) analysis supplements the XPS data by showing the presence of all expected SF_5-acrylate chemistry components in the outer 15 Å of the film surface.

Keywords: Perfluorinated monomer; Pentafluorosulfanyl; Perfluoroacrylate; Polymer film; Surface analysis; XPS; Surface enrichment

1. Introduction

The first SF_5-containing acrylate monomer and bulk polymer system, $SF_5(CF_2)_4CH_2OC(O)CH{=}CH_2$, was reported in 1992 [1,2]; solution deposition of the homopolymer onto a clean microscopic slide resulted in a polymer film exhibiting a contact angle, probed by Nujol oil, of 75° and for glycerol of 119°. Similar experiments were also carried out for the more conventional poly(1,1-dihydroperfluorooctyl methacrylate), which provided similar contact angles of 82 and 117° for Nujol and glycerol, respectively. Both surfaces were roughly equivalent in terms of their solid–air interfacial tension. Calculations of surface energies for the poly-$F_5S(CF_2)_4CH_2OC(O)CH{=}CH_2$ and for poly-$CF_3(CF_2)_6CH_2OC(O)C(CH_3){=}CH_2$ films were found to be 13.1 and 10.7 dyn/cm, respectively. More recently, copolymer films formed from mixing $SF_5(CF_2)_2(CH_2)_2OC(O)CH{=}CH_2$ and 2-hydroxyethyl methacrylate (HEMA) were prepared and characterized [3]. These films exhibited non-stoichiometric surface enrichment of the lower surface energy SF_5-terminated component in the outer surface layer for all binary mixed compositions. This blooming of the SF_5-containing monomer produced surface properties consistent with highly perfluorinated interfaces even at 5 wt.% perfluorinated monomer content. Angle-resolved XPS supported formation of the perfluoro-enriched overlayer. In addition, a new related SF_5-acrylate monomer, $SF_5(CF_2)_2(CH_2)_2OCH_2C(C(O)OCH_2CH_3){=}CH_2$, and its corresponding homopolymer have also been reported [3]. These new materials represent a family of novel, alternative perfluorinated compounds with interesting interfacial properties derived from the SF_5-acrylate chemistry. This paper reports a longer chain SF_5-perfluoroalkylacrylate derivative and its solid-state polymer interfacial chemistry and properties.

2. Results and discussion

A new longer chain SF_5-acrylate, monomer **2** and corresponds polymer **3**, were prepared for surface study by first synthesizing the precursor $SF_5(CF_2)_6(CH_2)_2I$ (**1**); $SF_5(CF_2)_6I$

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PII: S0022-1139(02)00008-8

was added to ethylene using *t*-butyl peroxide and heat (125 °C for over 18 h). Treatment of this new iodide **1** with silver acrylate gave SF_5-acrylate monomer **2** which upon polymerization gave the corresponding homopolymer **3**:

$$SF_5(CF_2)_6I + H_2C{=}CH_2 \rightarrow SF_5(CF_2)_6(CH_2)_2I\ (\mathbf{1})$$

$$SF_5(CF_2)_6(CH_2)_2I + AgOC(O)CH{=}CH_2 \rightarrow SF_5(CF_2)_6(CH_2)_2OC(O)CH{=}CH_2\ (\mathbf{2}) + AgI$$

$$\mathbf{2} + h\nu\ (360\,\text{nm}) \rightarrow \text{poly-}(SF_5(CF_2)_6(CH_2)_2OC(O)CHCH_2)_n\ (\mathbf{3})$$

The IR spectrum of **1** exhibited strong S–F stretching modes in the 825–876 cm^{-1} range. The C–F stretching bands are located in the 1070–1226 cm^{-1} range; the C–H vibrations are found in the range, 2982–2967 cm^{-1}. These results agree with those found for other SF_5-fluoroalkyliodides [4]. The ^1H NMR spectrum exhibits proton chemical shifts at 2.72 and 3.24 ppm indicative of CH_2-groups adjacent to the CF_2- and I-groups, respectively. We have found that for the analogous iodide, $SF_5(CF_2)_2(CH_2)_2I$, the proton chemical shifts are located at 2.72 and 3.23 ppm; these proton chemical shift values were originally reported to be located at 1.52 and 2.03 ppm [4]. The ^{19}F NMR spectral data of **1** show an AB_4 pattern for the SF_5-group: A (nine line pattern with each line split into a triplet) at $\varphi = 63.7$ ppm; B (skewed doublet of a pentet) at 44.9 ppm. The chemical shift of the CF_2 fluorines adjacent to the SF_5-group is found at $\varphi = -94.3$ ppm (septet) and the CF_2 fluorines adjacent to the CH_2-group at $\varphi = -115.1$ (multiplet); the four remaining inner CF_2-groups are located as broad singlets at $\varphi = -121.3$ to $\varphi = -123.5$. These results are in excellent agreement with results for similar SF_5-perfluoroalkyl iodides [4,5].

The SF_5-acrylate monomer **2** is a colorless, high boiling (55 °C/55 μm) liquid. The infrared spectrum of **2** exhibited strong S–F stretching modes in the 836–884 cm^{-1} region; similar results have been previously reported for a number of SF_5-perfluoroalkyl compounds [3,4]. The C–F stretching bands are found between 1104 and 1226 cm^{-1}; for a CF_2-group the expected region is 1050–1250 cm^{-1} [6]. The C–H vibrations appear in the range of 2915–2975 cm^{-1}. The vinyl stretching mode in the monomer is located at 1639 cm^{-1}. A significant shift is found for the carbonyl peak; in the monomer this peak is located at 1735 cm^{-1} while for the polymer film it is located at 1742 cm^{-1}.

The IR spectrum of polymer film **3**, cast from solution onto KBr discs, is similar to the bulk monomer spectrum, with the only major difference in spectra between monomer and polymer being the absence of the monomer vinyl stretching mode at 1638 cm^{-1} for the polymer.

Comparing the ^1H NMR spectra for $SF_5(CF_2)_n(CH_2)_2O$-$C(O)CH{=}CH_2$ (where $n = 2$ versus $n = 6$), nearly identical proton chemical shifts indicative of CH_2-groups adjacent to either CF_2 or O sites located at 2.53 and 4.47 ppm for $n = 6$ [3] and at 2.56 and 4.47 ppm for $n = 2$ are found. A similar result is also obtained when comparing the proton chemical shifts for the acrylate group for $n = 2$ and $n = 6$. Integration of the different protons in the NMR spectrum for $n = 6$ gave the relative areas, $CF_2C\underline{H}_2$ (**2**), $C\underline{H}_2O$ (**2**), $C\underline{H}{=}$ (**1**), $=C\underline{H}H$ (**1**) and $=CH\underline{H}$ (**1**). The mass spectrum contained the parent ion and appropriate fragments such as $(CH_2{=}CHC(O)$-$OCH_2CH_2)^+$ and SF_5^+ all consistent with the proposed structure.

X-ray photoelectron spectroscopy (XPS) was also employed to analyze the chemical composition of the polymer film surface. Quantitative XPS analysis is sensitive to elemental composition (sensitivity: ~0.1 at.%) in the outer 90 Å of the surface. The surface depth sensitivity decreases exponentially into the bulk, resulting in an intrinsically sensitive probe of the surface's most outer exposed stoichiometry. Previous reports on a HEMA-SF_5-acrylate copolymer film showed characteristic XPS spectral features consistent with the known bulk polymer chemistry for each copolymer constituent [3]. Specifically, the XPS C 1s high-resolution spectra of photo-cured SF_5-acrylate homopolymer and its copolymer films with the aliphatic comonomer, HEMA, demonstrated prominent CF_2 peaks at all concentrations of the fluorinated SF_5-acrylate monomer. These data were interpreted as consistent with surface enrichment of the SF_5-acrylate monomer at almost all bulk compositions, producing a highly perfluorinated, apolar, non-wetting surface. Additionally, the sulfur S 2p spectrum for this system exhibited a novel doublet peak at approximately 173 eV (highest S 2p XPS binding energy known) assigned to the SF_5-acrylate sulfur. This characteristic XPS chemical signature is also prominent in all copolymer films and provides a convenient diagnostic feature for quantifying the presence of this SF_5-specific sulfur species in the surface region of these polymer films [3].

Analogously, in the new SF_5-acrylate homopolymer film system reported here, the XPS C 1s high-resolution spectrum shown in Fig. 1 (sampling depth: ~50 Å; take-off angle: 55°) exhibits similar expected chemical features:

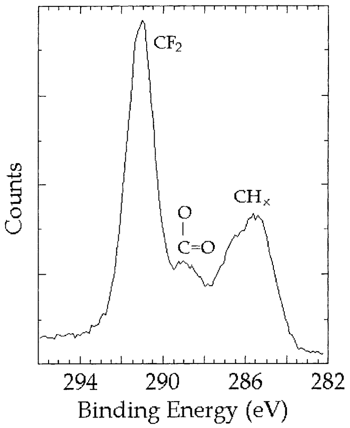

Fig. 1. XPS high-resolution C 1s spectrum of the cast homopolymer film of the SF_5-acrylate monomer **3** taken at a take-off angle of 55° (50 Å sampling depth).

presence of aliphatic (C–C, C–H) carbon at 285.0 eV and oxidized carbon (C–O, O=C–O) assigned to the acrylate backbone, and CF_2 side chain peak (292 eV). The important difference in this new polymer coating is the relative XPS contribution of these carbon peaks proportional to their relative surface concentrations. In theory, an isotropic homopolymer film of the long-chain perfluorinated SF_5-acrylate **2** would yield an elemental composition (both bulk and surface) of 35.5 at.% carbon, 54.8 at.% fluorine, 3.2 at.% sulfur and 6.5 at.% oxygen. Except for the higher oxygen concentrations detected, the experimental XPS data are consistent with theory: carbon content is 33.0 at.% (±0.5%), fluorine is 53.9 at.% (±0.3%), sulfur is 3.7 at.% (±0.3%) and oxygen is 9.1 at.% (±0.3%). From peak fitting, the C 1s spectrum in Fig. 1, it was determined that the contribution of the CH_x, O–C=O, and CF_2 species to the total carbon spectrum were 35.7% (±0.5%), 9.1% (±0.2%) and 55.2% (±0.6%), respectively. These measured carbon percentages compare well with expected theoretical carbon percentages for the bulk polymer (36.4% CH_x, 9.1% O–C=O and 54.5% CF_2). Both the XPS elemental composition and C 1s spectrum at the take-off angle of 55° are consistent with isotropic film composition and surface density of all monomer chemistry. For this long-chain perfluorinated acrylate, the relative abundance of the C 1s perfluorocarbon peak (55.2 at.%) is substantially higher, due to its longer chain length, than that observed previously for the shorter chain SF_5-acrylate film system (19 at.%) [3].

The sulfur S 2p spectrum shown in Fig. 2 (sampling depth: ∼50 Å; take-off angle: 55°) is essentially identical to that reported earlier for analogous polymer films [3] and new SF_5-terminated perfluoroalkylthiol monolayer films on gold [7]. Its high binding energy (172.7 eV) is derived from inductive effects of the five fluorine atoms of the SF_5-group and is characteristic of this unique sulfur functional group. The XPS determined sulfur concentration (3.7 at.%) is slightly higher than the expected theoretical value (3.2 at.%), one piece of supporting data for film compositional anisotropy.

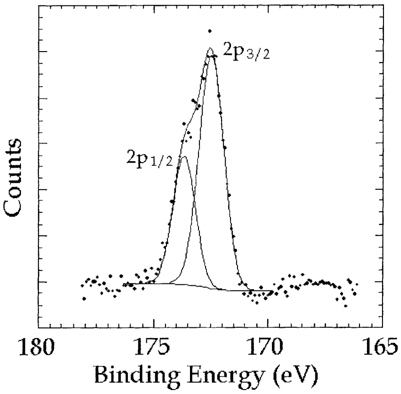

Fig. 2. XPS high-resolution S 2p spectrum of the cast homopolymer film of the SF_5-acrylate monomer **3** taken at a take-off angle of 55° (50 Å sampling depth).

Angle-dependent XPS results provide further support for surface enrichment of the SF_5-perfluoroalkyl polymer side chains to surface concentrations above that noted for bulk composition in these cast films. Film composition at XPS take-off angle of 0° (sampling depth: ≈100 Å) was identical, within experimental error, to the 55° film composition, as expected for a homopolymer film of isotropic composition throughout this film depth. However, at a sampling angle of 80° (sampling depth: ≈20 Å), a detectable, non-stoichiometric increase in both F and S concentrations above the bulk concentration is noted, corresponding to a noted decrease in the C and O concentrations. The XPS composition at the 80° photoelectron take-off angle (20 Å sampling depth) yields 58.1 at.% fluorine, 30.0 at.% carbon, 7.8 at.% oxygen and 4.2 at.% sulfur. Noted increases in both fluorine and sulfur signals observed with this shallower XPS sampling depth support higher amounts of sulfur and perfluorinated groups exposed at the outer surface of the film. Additionally, hydrocarbon (C 1s) and oxygen (O 1s) XPS signals largely associated with the polymer backbone are both reduced at this shallower sampling angle, supporting this surface enrichment interpretation for the SF_5-containing side chains. Enrichment of F and S over C and O is seen at the most extreme XPS sampling angle and shallowest sampling depth, consistent with a compositional gradient within the polymer film where sulfur (SF_5) and associated perfluoroalkyl side chain groups are enriched near the film-ambient surface over bulk theoretical stoichiometry. Because, this result is observed at the 20 Å sampling depth and not obvious at the deeper 50 Å sampling depth, the compositional gradient from theoretical bulk to enriched anisotropy is seemingly quite steep across this thickness profile within the film surface zone. This result is consistent with the rather abrupt, increased presence of perfluorinated side chains in the outer atomic layers of this film over that reported previously [3], enhancing the properties associated with this particular chemistry in the interfacial region. Enrichment of S and F at the expense of C and O could only occur across this small thickness profile if the side chains were anisotropically ordered (layered or vertical) away from the polymer backbone in this surface.

Enrichment of lower-energy perfluorinated species on the film's outer surface is thermodynamically favored [3,7,8]. Given the observation that no hint of non-stoichiometric enrichment is observed at any other angle than the most sensitive surface angle (80°, 20 Å sampling depth), the surface enrichment of polymer side chains must be limited to only a few molecular layers. In fact, our previous work on SF_5-terminated perfluoroalkyl monolayers immobilized on silicon [8] and gold [7] indicated that these thin film layers are both less than 20 Å thick for chain structures analogous to the SF_5-terminated side chains studied here. Taken together with XPS data, this would support claims to roughly monolayer enrichment of side chains for these polymer films at their outer surface, imparting a SF_5-enriched surface with some side chain anisotropy and film structuring.

Angle-dependent (depth resolved) XPS analysis of the SF_5-acrylate-HEMA copolymer films [3] previously showed surface 'blooming' of low surface energy SF_5-acrylate components preferentially to the film surface for all bulk copolymer film compositions. The current longer chain SF_5-acrylate perfluorinated monomers would be presumed to increase this surface active 'blooming' tendency when mixed with aliphatic comonomers under equilibrium conditions, increasing the perfluorinated surface enrichment stoichiometry. These important studies are now underway.

Aqueous wetting of surfaces with aqueous static drops were determined by static contact angle measurements. Contact angles with liquid probes are sensitive to both surface composition and surface topology. Low magnification optical microscopy showed that the homopolymer films were featureless at the micron level. Surface roughness was assumed to be a negligible factor since probe drops were symmetrical and reproducible. Aqueous contact angles for non-annealed photopolymerized SF_5-acrylate films were $106 \pm 2.4°$. After annealing under a nitrogen environment for 24 h, aqueous contact angles were $112 \pm 3.6°$. This result reflects the relative inability of the polymer surface to either significantly relax or undergo rearrangement after photopolymerization. The high water contact angle (non-wetting) is consistent with a highly perfluorinated apolar surface chemistry—for comparison, the contact angle for poly(fluorinated ethylene propylene) is reported to be 108° [9] and for polytetrafluoroethylene is reported to be 112° [10]. Self-assembled monolayers of long-chain SF_5-terminated perfluoroalkylthiol monolayers on gold exhibit similar hydrophobic, non-wetting water contact angles [7]. Therefore, this SF_5-terminated polymer surface exhibits molecular density and organization similar to that observed for the templated SF_5-terminated perfluoroalkylthiol monolayer, and is also consistent with the known, highly fluorinated polymer: the acrylate polymer backbone is not surface-exposed but likely resides under a layer of long perfluoroalkyl side chains. This is distinct from previous results using SF_5-fluoroalkyl systems with shorter chains [3,8] where surface organization of the low-energy perfluoroalkyl components was reduced by short chain packing problems and defects.

Table 1
Negative ion peaks derived from TOF-SIMS data characteristic of the polymer perfluorinated side chain

m/z	Species
1.008	H
13.008	CH
18.997	F
25.008	C_2H
34.970	Cl
36.967	Cl
37.996	F_2
39.005	F_2H
43.002	C_2F
50.974	SF
68.999	CF_3
69.970	SF_2
88.971	SF_3
107.971	SF_4
126.962	SF_5

TOF-SIMS surface analytical results from both the negative and positive ion spectra showed the presence of characteristic peaks for both the acrylate polymer backbone and the polymer perfluorinated side chain. Since TOF-SIMS methods extract mass spectral information from the outermost 15 Å of a surface, these ions are characteristic of the polymer composition exclusively in the top-most atomic levels of the SF_5-polymer surface [11]. The negative ion spectrum shown in Fig. 3 is dominated by the F^- peak and several SF_x^- peaks from the polymer side chain. Tables 1 and 2 list other characteristic fragments present in the negative ion spectrum of this surface, divided by fragments associated with perfluorinated side chain (Table 1) versus hydrocarbon backbone (Table 2). The positive ion spectrum shown in Fig. 4 exhibits many fragments from hydrocarbon, fluorocarbon and several SF_x^+-groups, attributable to either the polymer backbone or the side chain. Tables 3 and 4 summarize the characteristic peaks from the polymer sample in the positive ion spectral regions for perfluorinated side

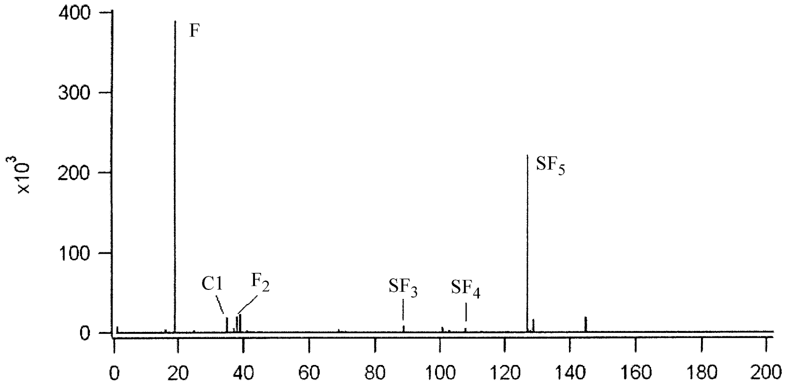

Fig. 3. Time-of-flight secondary ion mass spectrometry negative ion spectrum of SF_5-acrylate polymer film cast onto brass supports. Only the major peaks are labeled on the spectra to maintain clarity.

Table 2
Negative ion peaks derived from TOF-SIMS data characteristic of the polymer hydrocarbon backbone

m/z	Species
15.994	O
41.004	C_2HO
42.004	C_2H_2O
45.002	CHO_2
60.994	CHO_3

Table 3
Positive ion peaks derived from TOF-SIMS data characteristic of the polymer perfluorinated side chain

m/z	Species
1.008	H
12.001	C
18.999	F
22.989	Na
27.023	C_2H_3
30.997	CF
47.031	C_2H_4F
51.004	CHF_2
68.992	CF_3
69.996	SF_2
88.959	SF_3
118.988	C_2F_5
126.957	SF_5
130.987	C_3F_5
168.998	C_3F_7
180.996	C_4F_7

Table 4
Positive ion peaks derived from TOF-SIMS data characteristic of the polymer hydrocarbon backbone

m/z	Species
29.003	CHO
29.040	C_2H_5
31.020	CH_3O
41.040	C_3H_5
44.997	CHO_2
55.018	C_3H_3O
71.013	$C_3H_3O_2$
85.028	$C_4H_5O_2$

chain (Table 3) and hydrocarbon backbone (Table 4). The presence of the SF_5 and other SF_x fragments, along with the many fluorocarbon fragments, in the TOF-SIMS spectra provide chemically specific verification of the polymer composition and film structure in the outermost surface zone. This chemical evidence for both side chain and polymer backbone presence in the surface is complementary to that provided by XPS and asserts the enrichment of the fluorinated side chain chemistry hinted at by XPS analysis. Also, to our knowledge, mass spectrometry of any perfluoroalkyl SF_5-terminated surfaces has not been reported to-date. Direct quantitation of peak intensities and correlation with relative abundance of film chemistry, however, is not possible due to film matrix effects; TOF-SIMS data are currently not quantifiable. Small levels of surface contamination are evident as contaminant peaks, e.g. Na^+ and Cl^- ions are present. This level of contamination is not detected in the XPS analysis (species below 0.1 at.% are not seen).

3. Experimental

3.1. Materials

The starting iodide, $SF_5(CF_2)_6I$, was prepared in our laboratory [5]. Silver oxide and acrylic acid were obtained from Aldrich and were used as received.

3.2. General monomer characterization procedures

The infrared spectra for **1–3** were obtained using a Perkin-Elmer System 2000 FTIR operating at 1.0 cm^{-1} resolution using KBr discs. Mass spectra were measured on a HP 5970 gas chromatograph coupled to a mass spectrometer (GC–

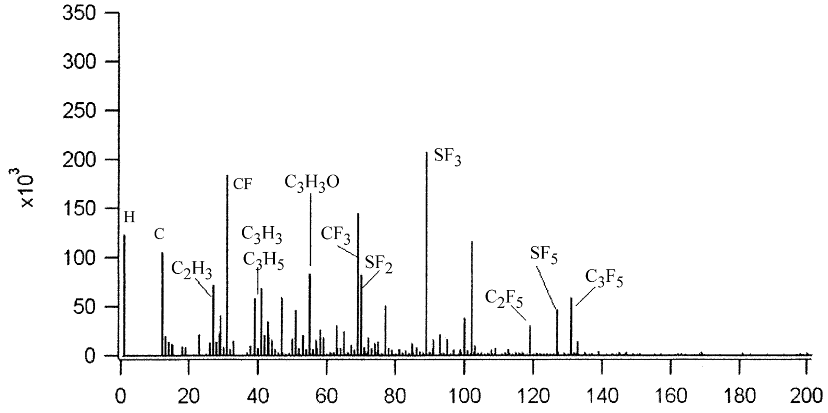

Fig. 4. Time-of-flight secondary ion mass spectrometry positive ion spectrum of SF_5-acrylate polymer film cast onto brass supports. Only the major peaks are labeled on the spectra to maintain clarity.

MS) which operated at 70 eV. The proton and fluorine NMR spectra were obtained on a Bruker AMX-400 spectrometer operating at 400 MHz for ^{1}H and 376.5 MHz for ^{19}F. Also, proton spectra were obtained using a GE 500 MHz instrument. The elemental analyses determinations were performed by Mikroanalytisches Laboratorium Beller in Göttingen, Germany. The precise molecular weight determination for compound **2** was obtained on a Kratos MS 50TC; chemical ionization with methane.

3.3. General polymer characterization procedures

3.3.1. X-ray photoelectron spectroscopy (XPS)

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 multi-channel detector [3]. 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 C 1s C–H peak at 285.00 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), the photoelectron escape depth was assumed to vary as $KE^{0.7}$ [12], and Scofield's photoionization cross-sections were used [13].

3.3.2. Angular dependent XPS: compositional depth analysis

Angle-dependent XPS experiments were also conducted on polymer samples cast onto clean flat brass supports from methylene chloride solutions and dried under nitrogen and then under vacuum. Three different sampling depths were analyzed at three distinct instrument take-off angles of 0, 55, and 90°. These take-off angles correspond to film sampling depths of approximately 100, 50, and 20 Å, respectively [3].

3.3.3. 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 microsyringe-deposited spots on each polymer film surface in a controlled environment (100% relative humidity). Photopolymerized surfaces were always rinsed in 100% ethanol, dried under nitrogen flow and placed in a closed quartz cell for analysis. Measurements were taken on both sides of applied water drops at ambient temperature 30–40 s after drops were applied to surfaces. Contact angle data reported the average of three drops at different surface locations. Contact angles were measured on the same photopolymerized surface samples both before and after thermal annealing at 70 °C for 24 h.

3.4. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) surface analysis

TOF-SIMS spectra on polymer surfaces were acquired using a Physical Electronics PHI 7200 TOF spectrometer with an 8 keV Cs^+ ion source in the pulsed mode. Spectra were acquired for both positive and negative secondary ions over a mass range of $m/z = 0$ to $m/z = 1000$. The ion source was operated with a pulse width of 1.2 ns and current of 1.5 pA. Secondary ions of a given polarity were extracted into a two-stage reflectron TOF mass analyzer and detected using a pair of stacked micro-channel plates equipped with a time to digital converter. Spectra were acquired using an analysis area of 0.04 mm^2 and the total ion dose was maintained below 2×10^{12} ions/cm^2, an ion flux sufficiently diffuse so that surface damage might be considered minimal or negligible at any given sampling location. An electron flood gun was used to prevent sample charging during the analysis. Negative spectra were calibrated using the F^-, $F_2{}^-$, and $SF_5{}^-$ peaks. Positive spectra were calibrated using the CF^+, $SF_3{}^+$, and $SF_5{}^+$ peaks. Calibration errors were kept below 20 ppm. Mass resolution ($m/\Delta m$) for a typical spectrum was between 4000 and 6000. Spectra were acquired from polymer films on glass and brass substrates. The polymer films were thick enough that the underlying substrates had minimal impact on the TOF-SIMS spectra.

*3.4.1. Preparation of $SF_5(CF_2)_6C_2H_4I$ (**1**)*

Into a 50 ml Hoke stainless-steel metal vessel equipped with a Whitey stainless-steel valve, 4.91 g (0.0089 mol) of **3** and 0.17 g (0.00116 mol) *t*-butyl peroxide were added. The vessel was cooled to −196 °C and evacuated; C_2H_4 (0.64 g, 0.023 mol) was transferred under vacuum into the vessel. The mixture was gradually heated (from −196 to 125 °C, 4 h) and then held at 125 °C for an additional 18 h. The vessel was cooled to room temperature and vented. A white solid was recovered from the reaction vessel. Sublimation (50–60 °C) of this material at reduced pressure gave 1.45 g (0.0025 mol) of white solid **9**; mp 50–55 °C, in 28% yield.

The IR spectrum shows the following bands (cm^{-1}): 2982 (w), 2967 (vw), 1445 (w), 1365 (w), 1346 (vw), 1308 (w), 1276 (vw), 1226 (vs, b), 1196 (m–s), 1177 (vs, b), 1151 (vs), 1131 (m), 1107 (w), 1070 (w–m), 994 (w), 903 (m), 876 (vs), 825 (m), 792 (w), 774 (w), 752 (w), 697 (w–m), 663 (w–m), 607 (m), 561 (m), 524 (w).

^{1}H NMR spectrum, [$CDCl_3$, $(CH_3)_4Si$], 500 MHz: $\delta_{CF_2CH_2} = 2.72$ ppm (d, d, t), 2H, $J_{CF_2\underline{CH_2}} = 17.0$ Hz, $J_{CH_2CH_{a,b}} = 8.2$ and 8.6 Hz; $\delta_{\underline{CH_2}I} = 3.24$ ppm (d, d), 2H, $J = 8.2$ and 8.6.

^{19}F NMR spectrum, ($CDCl_3$, $CFCl_3$), 376.5 MHz: AB_4 (SF_5), $\varphi_A = 63.7$ ppm (t, nine-line pattern), 1F, $J_{ACF_2} = 4$ Hz; $\varphi_B = 44.9$ ppm (skewed d, p), $J_{AB} = 146.6$ Hz; $\varphi_{SF_5\underline{CF_2}} = -94.3$ ppm (septet), 2F, $J = 16.5$ Hz; $\varphi_{\underline{CF_2}CH_2} =$

-115.1 ppm (multiplet), 2F; $\varphi_{\mathrm{int(CF_2)_4}} = -121.3$ to -123.5 ppm (four broad singlet), 8F.

The GC–MS analysis shows a molecular ion peak and appropriate fragments. A number of significant peaks include (*m/z*, ion, %): 582, $(M)^+$, 87; 455, $(M-\mathrm{F})^+$, 8; 435, $(M-\mathrm{HF}{-}\mathrm{SF_5}$ or I$)^+$; 327, $(\mathrm{SF_5(CF_2)_4})^+$, 29; 281, $((\mathrm{CF_2})_5\mathrm{CF})^+$, 13; 263, $(\mathrm{SF_5C_5F_4})^+$, $((\mathrm{CF_2})_5\mathrm{CH})^+$, 14; 257, $(\mathrm{C_2H_2(CF_2)_4CF})^+$, 12; 213, $(\mathrm{CH(CF_2)_4})^+$, 14; 205, $(\mathrm{IC_2H_4CF_2})^+$, 18; 181, $((\mathrm{CF_2})_3\mathrm{CF})^+$, 12; 169, $(\mathrm{C_2H_2(CF_2)_2C_2F})^+$, 16; 155, $(\mathrm{IC_2H_4})^+$, $(\mathrm{C_5F_5})^+$, 40; 145, $(\mathrm{CH_2(CF_2)_2CF})^+$, 12; 139, $(\mathrm{C_2H_3(CF_2)_2C})^+$, $(\mathrm{SF_5C})^+$, 10; 127, $(\mathrm{I})^+$, $(\mathrm{SF_5})^+$, $(\mathrm{C_2H_3CF_2CF_2})^+$, 53; 113, $((\mathrm{CF})_2\mathrm{CH})^+$, 10; 109, $((\mathrm{CH_2})_2\mathrm{CF_2CF})^+$, 16; 108, $(\mathrm{C_2H_3{-}CF_2CF})^+$, $(\mathrm{SF_4})^+$, 11; 100, $(\mathrm{C_2F_4})^+$, 22; 95, $(\mathrm{C_3H_2F_3})^+$, 13; 89, $(\mathrm{C_2H_3CF_2C})^+$, $(\mathrm{SF_3})^+$, 43; 77, $(\mathrm{CF_2CH_2CH})^+$, 100; 51, $(\mathrm{SF})^+$, 43.

Elemental analysis: Calculated for $\mathrm{SF_5(CF_2)_6CH_2CH_2I}$: C, 16.51; H, 0.69; S, 5.51; F, 55.49; I, 21.80; found: C, 16.51; H, 0.71; S, 5.30; F, 55.24; I, 21.65%.

3.4.2. *Preparation of $\mathrm{SF_5(CF_2)_6(CH_2)_2OC(O)CH{=}CH_2}$ (**2**)*

A suspension of silver acrylate was obtained by stirring 1.51 g $\mathrm{Ag_2O}$ and 1.11 g of acrylic acid (in the dark) in a 250 ml flask for 4 days. Into the stirred amber mixture was added 2.00 g of $\mathrm{SF_5(CF_2)_6(CH_2)_2I}$; after 4 h of heating (in the dark) in a water bath at 43 °C, the GC–MS showed the absence of the iodide **1**. The main band (>90% of total area) represented the new acrylate **2**. After standing at room temperature overnight, the mixture was poured into 400 ml of water and extracted with ether (1× 100 ml, 3× 40 ml), the combined extracts were washed with water (1× 100 ml), the washing solution was back-extracted with ether (30 ml), the combined ether extracts were filtered and the ether was partially removed under vacuum, at 10 Torr, into a -196 °C trap to a final volume of about 10 ml. The remaining ether solution was fractionally distilled yielding two fractions: (1) 55–57 °C/55 μm, 0.22 g; and (2) 55–41 °C/55–45 μm, 0.16 g. Fraction (1) contained substantial amounts of impurities (GC–MS), while fraction (2) was >96% pure.

The spectral data for fraction (2) are: ^{1}H NMR spectrum, [$\mathrm{CDCl_3}$, $\mathrm{(CH_3)_4Si}$], 500 MHz: $\delta_{\mathrm{CF_2\underline{CH_2}}} = 2.53$ ppm (t, t), 2H, $J_{\mathrm{CF_2CH_2}} = 18.36$ Hz, $J_{\mathrm{CH_2CH_2}} = 6.64$ Hz; $\delta_{\mathrm{\underline{CH_2O}}} = 4.47$ ppm (t), 2H, $J_{\mathrm{CH_2CH_2}} = 6.64$ Hz.

For the acrylate group, [$\mathrm{OC(O)CH_c{=}CH_aH_b}$, a *trans* to c]: $\delta_a = 6.44$ ppm (d–d) $J_{ac} = 17.29$ Hz; $J_{ab} = 1.17$ Hz, 1H; $\delta_b = 5.89$ ppm (d–d) $J_{ab} = 1.17$ Hz, $J_{bc} = 10.45$ Hz, 1H; $\delta_c = 6.13$ ppm (d–d) $J_{ac} = 17.29$ Hz; $J_{bc} = 10.45$ Hz, 1H.

^{19}F NMR spectrum, ($\mathrm{CDCl_3}$, $\mathrm{CFCl_3}$), 84.7 MHz: $\mathrm{AB_4}$ ($\mathrm{SF_5}$), $\varphi_A = 64.7$ ppm (t, nine-line pattern), 1F; $\varphi_B = 47.7$ ppm (skewed d), $J_{AB} = 151.0$ Hz; $\varphi_{\mathrm{SF_5\underline{CF_2}}} = -95.9$ ppm (d, p), 2F, $J_{\mathrm{BCF_2}} = 12$ Hz, $J_{\mathrm{ACF_2}} = 4.5$ Hz; $\varphi_{\mathrm{\underline{CF_2}CH_2}} = -116.2$ ppm (broad pentet), 2F, $J = 13$ Hz; $\varphi_{\mathrm{int(CF_2)_4}} = -124.0$ to -126.5 ppm (three broad singlet), 8F.

The IR spectrum, for **2** shows the following bands (cm^{-1}, KBr): 2975 (w–vw, br), 2927 (vw), 2915 (vw), 1735 (s), 1639 (w), 1627 (vw), 1492 (vw), 1413 (m–w), 1402 (m–w), 1346 (vw), 1299 (w–m), 1273 (w–m), 1226 (s–vs), 1190 (s–vs), 1155 (vs), 1133 (m–s), 1104 (m), 1073 (m), 1011 (vw), 986 (w), 973 (w–vw), 884 (vs), 836 (w–m), 810 (w–m), 785 (w), 761 (vw), 744 (w–m), 704 (vw), 694 (m), 653 (w).

GC–MS analysis (DB5, 12 m, 50 °C, 4 min; then, 18 °C/min to 280 °C), $R_t = 8.9$ min (*m/z*, ion, %): 526, $(M)^+$, 4; 127, $(\mathrm{SF_5})^+$, 2; 99, $(\mathrm{CH_2{=}CHCOOC_2H_4})^+$, 10; 89, $(\mathrm{SF_3})^+$, 6; 77, $(\mathrm{CF_2CH_2CH})^+$, 8; 55, $(\mathrm{CH_2{=}CHCO})^+$ 100.

High-resolution mass spectrum: $m^+ = 525.98977$. Calculated for $^{12}\mathrm{C}_{11}{}^{1}\mathrm{H}_7{}^{16}\mathrm{O}_2{}^{32}\mathrm{S}^{19}\mathrm{F}_{17}$; $m = 525.98953$.

3.4.3. *Cast photoinitiated polymer film (**3**)*

The $\mathrm{SF_5}$-acrylate monomer **2** was weighed directly into a glass vial. Irgracure 261 photoinitiator (Union Carbide) solution in acetone (4 mg/ml) was added to make an initiator concentration of 0.4 wt.% to total monomer. Additional acetone was added to make the total monomer concentration 25% (w/v). This solution was cast onto acid-cleaned slides or acid-cleaned silicon wafers by dropping the solution onto the slide surface using a Pasteur pipet. The solvent was allowed to evaporate under a nitrogen atmosphere at room temperature for 0.5–1 h. A Hanovia high-pressure quartz mercury lamp (S654A, 200 W), placed inside a water-cooled quartz finger, was used to photopolymerize the monomer at a distance of 16.5 cm at room temperature under a flushed nitrogen atmosphere for 8–10 h.

Acknowledgements

We are grateful to the National Science Foundation (CHE-9904316, GLG, DMR 9596023, DWG), the Petroleum Research Fund (ACS-PRF 34624-AC7, GLG), National Institute of Health RR01296 (DGC), a 3M Faculty Fellowship (DWG), and a Dupont Research Fellowship (DWG) for partial support of this work.

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