Photopolymerized Acrylate Copolymer Films with Surfaces Enriched in Sulfur Pentafluoride (−SF_5) Chemistry

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Acrylate monomers bearing side chains terminated in sulfur pentafluoride (−SF_5) groups have been synthesized. These monomers have been copolymerized into films with the conventional aliphatic acrylic monomer 2-hydroxyethyl methacrylate (HEMA) using neat cast mixed monomer films and photoinitiation. Depth-dependent surface analysis of these photocured films using X-ray photoelectron spectroscopy shows that surfaces are enriched nonstoichiometrically in the −SF_5 functionality, even when compositions of the binary mixed film heavily favor the HEMA component. All polymer films containing the SF_5−acrylate have a surface composition corresponding to an enriched overlayer of pure SF_5−acrylate. The thickness of the surface-enriched overlayer decreases as the bulk concentration of SF_5−acrylate monomer decreases. At the lowest bulk concentration examined, 1 wt % SF_5−acrylate monomer, the overlayer thickness was approximately 20 Å. Results mirror previous surface enrichment observed for fluorinated/aliphatic epoxide monomer mixed films prepared using an analogous strategy. (Schnurer, A. U.; et al. *Chem. Mater.* **1996**, *8*, 1475−1481). This suggests that such a route to inexpensive, high-performance perfluorinated coatings using small amounts of perfluorinated monomers might be generalized to many other classes of monomers.

Introduction

Fluorinated polymer surfaces have high industrial interest and relevance due to the valuable properties of perfluorinated surfaces, specifically their chemical inertness, nonwetting, tribological, nonadhesive, and corrosion-resistant properties. However, many fluorinated polymers suffer from poor solvent processing and coating application methods in addition to their significant expense. High-value-added films with significant technological potential are desired from either new perfluorinated polymer formulations or alternative methods to place perfluorinated species in the surface zone.

We have previously reported a strategy to fabricate polymeric coatings with surfaces highly enriched in perfluorinated components by mixing liquid epoxide-based hydrocarbon and perfluorocarbon monomers and photopolymerizing these mixtures as cast films in situ.[1] We were able to utilize unique fluorinated epoxides bearing −SO_2F terminal groups for this study.[2−4] High degrees of nonstoichiometric surface enrichment of the perfluorinated monomer were observed in the upper 50 Å of these UV-cured films even at bulk film compositions that comprised up to 99 wt % aliphatic hydrocarbon diepoxide monomer.[1] Blooming of low-energy perfluorinated chemistries to surfaces, using both their intrinsic immiscibility with many hydrocarbon chemistries and their low solid-state interfacial tension in air, could form the basis for placing specific desirable chemistries on surfaces of coatings.

In this current paper, we have extended this spontaneous perfluorinated overlayer fabrication process to new acrylate monomers bearing sulfur pentafluoride (−SF_5) terminal groups. Very little has been reported regarding SF_5-containing materials, particularly any surface or interfacial properties. Synthetic polymers appear as attractive options to introduce this chemistry into practical materials. The first acrylate monomer bearing an SF_5 group was reported in l995.[5] Most of the fluoroacrylate monomers found in the literature are prepared by esterification of a fluoro alcohol with

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acryloyl chloride;[6] another approach using perfluoro ketones was also successful.[7,8] The use of silver acrylate with alkyl bromides has also been reported.[9] More recently, a new synthetic approach to preparing substituted methacrylates involving the use of ethyl α-(chloromethyl)acrylate (ECMA) has been reported.[10] Monomers prepared from it are readily polymerized using free radicals to give homopolymers and copolymers.[10] Our goal in pursuing these new SF_5-containing fluorinated materials is 2-fold: (1) to extend a general approach for providing fluorine-enriched polymer surfaces from cast, neat monomer mixtures and (2) to explore the interfacial properties for SF_5-containing polymer surfaces, a chemistry that remains relatively unexplored.

Experimental Section

Materials. The alcohol $SF_5(CF_2)_2(CH_2)_2OH$ (**1**), ethyl α-(chloromethyl)acrylate (**2**), and $SF_5(CF_2)_2(CH_2)_2I$ (**3**) were prepared according to the literature methods.[11,12] Triethylamine (Et_3N), tetrahydrofuran (THF), methylal, acrylic acid, $Ag_2(0)$, 2-hydroxyethyl methacrylate (HEMA), and 2,2′-azobis(isobutyronitrile) (AIBN) from Aldrich were used as received. Acetonitrile and acetone (J.T. Baker) were used as received.

General Monomer Characterization Procedures. Bulk infrared spectra for the monomers were obtained using a Perkin-Elmer System 2000 FTIR operating at 1.0 cm^{-1} resolution using KBr cells. Mass spectra were measured on a HP 5970 gas chromatograph coupled to a mass spectrometer (GC−MS) operated at 70 eV. NMR spectra were obtained on a Varian EM-390 spectrometer operating at 90.00 MHz for ^1H and 84.67 MHz for ^{19}F. Elemental analyses were determined by Beller Mikroanalytisches Laboratorium (Göttingen, Germany).

Preparation of $SF_5CF_2CF_2CH_2^aCH_2^bOCH_2^cC(COOCH_2^dCH_3^e)=CH_2^{f,g}$ (Monomer 4). To a mixture of **1** (1.45 g, 5.33 mmol) and **2** (0.80 g, 5.39 mmol) in 5.0 mL of tetrahydrofuran was added 0.55 g (5.43 mmol) of triethylamine with swirling in a dropwise fashion. The reaction temperature was maintained at room temperature by a water bath during the slow addition of the triethylamine (10 min), and the concentration of **1** was continuously monitored via gas chromatography−mass spectrometry (GC−MS). To minimize any possible polymerization, heating was avoided and the reaction was carried out over a 10 day period (during this time several drops of ECMA and triethylamine were added due to side reactions), after which the GC−MS showed that all of **1** was consumed; a single GC−MS peak was observed at 10.1 min (DB5, 12 m, 50 °C/4 min and then 18 °C/min up to 280 °C). Water (15.0 mL) was added, and after mixing the clear top aqueous layer was removed. This procedure was repeated. The remaining bottom layer, the crude product, was transferred to a distillation flask. To this crude product was added the chloroform extract (2 × 2.0 mL) of the second washing. Distillation of the crude product gave a clear, colorless liquid, 1.23 g, bp at 55 °C/28 μm, in 60% yield.

The infrared spectrum for **4** shows the following peaks (cm^{-1}): 2988 (wm); 2942 (vw, sh); 2909 (w, sh); 2880 (w); 2828 (vw); 1716 (s); 1646 (w); 1484 (w); 1469 (w); 1448 (wm); 1404 (wm, sh); 1383 (m); 1329 (m); 1309 (ms); 1224 (ms); 1248 (m, sh); 1195 (s); 1149 (s, sh); 1124 (s); 1061 (wm, sh); 1033 (ms); 955 (m); 921 (m); 881 (vs); 835 (s); 807 (ms); 760 (vw, sh); 745 (m); 722 (wm); 684 (m); 647 (vw); 604 (ms); 575 (wm); 571 (vw). ^1H NMR ($CDCl_3$, internal $Si(CH_3)_4$): δ (ppm) **a**, 2.51 (tt); **b**, 3.87 (t); **c** and **d**, 4.30 (overlap s, q); **e**, 1.33 (t); **f**, 5.94 (s, cis to **c**); **g**, 6.42 (s, trans to **c**). Integration **a, b, c** + **d, e, f, g**:1.9:2.0:4.0:3.0:1.0:1.0. Couplings: $J_{CH_2-CH_2} = 6.75$; $J_{CH_2CH_3} = 7.35$ Hz. ^{19}F NMR ($CDCl_3$, internal $CFCl_3$): δ (ppm) SF_5, 66.8 (nine lines) and 46.5 (skewed d); $SF_5\mathbf{CF_2}CF_2$, −97.1 (br, sept); $SF_5CF_2\mathbf{CF_2}$, −116.7 (m). Integration $SF_5CF_2CF_2$: 1.0:4.0:1.98:2.0. Couplings: $J_{F-SF_4} = 151.0$ Hz; $J_{SF_4-CF_2} \approx 15$ Hz; $J_{CF_2-CF_2} = 17.0$ Hz; $J_{CF_2-CH_2} = 18.8$ Hz. MS (*m/e*, rel abund, species): 384 (0.4, M^+); 129 (50, $(M - SF_5CF_2CF_2CH_2CH_2)^+$); 127 (13, SF_5^+); 113 (25, $M^+ - SF_5CF_2CF_2CH_2CH_2O$). Anal. Calcd for $C_{10}H_{13}F_9SO_3$: C, 31.26; H, 3.41; F, 44.5; S, 8.34. Found: C, 31.42; H, 3.29; F, 44.4; S, 8.56.

Bulk Polymerization of SF_5−Acrylate Monomer 4. To a 50.0 mL round-bottom flask equipped with a Kontes Teflon valve were 0.15 g of **4** and 11.4 mg of AIBN. The vessel was cooled to −196 °C and evacuated. Through three freeze−thaw−evacuation cycles all of the air was removed. The reaction mixture was heated for 3 days at 60 °C. The colorless oil that was formed was removed from the vessel with 1.0 mL of Freon-113; to this solution was added ice-cold hexane. After 15 h, decanting, and removing any residual solvent by pumping through a trap cooled to −196 °C, a white, brittle solid was found (0.08 g). Evaporation of the decanted solution left behind an oil. The infrared spectrum of the oil was similar to that found for the solid; a weak band at 1650 cm^{-1} suggests the presence of unsaturation in the oil. This band is absent in the solid. The melting range of the solid was 126−150 °C.

The infrared spectrum of the solid shows the following peaks (cm^{-1}): 2915 (w), 2848 (vw), 1734 (m), 1480 (vw), 1450 (vw), 1382 (w), 1250 (w), 1195 (m), 1120 (m), 1021 (w), 978 (vw), 932 (vw), 878 (s), 834 (m), 803 (wm), 740 (wm), 681 (m), 604 (ms). The infrared spectrum of the oil contains the following bands (cm^{-1}): 2992 (w), 2918 (w, br), 1732 (ms), 1650 (vw), 1480 (vw), 1450 (vw), 1382 (w), 1250 (wm), 1194 (ms), 1126 (ms), 1028 (wm), 978 (w), 932 (w), 878 (s), 834 (ms), 806 (ms), 742 (wm), 680 (w), 604 (ms), 576 (w).

Preparation of $SF_5(CF_2)_2CH_2^aCH_2^bOCOCH^c=CH_2^{d,e}$ (Monomer 5). In a stoppered and aluminum foil-wrapped flask (100 mL), 0.63 g of acrylic acid (8.75 mmol) and 1.00 g Ag_2O (4.3 mmol) were stirred with 50 mL of CH_3CN. Within an hour, a gray, voluminous precipitate appeared. After the mixture was stirred for 22 h, 2.89 g of $SF_5CF_2CF_2CH_2CH_2$ I (7.6 mmol) was added and the mixture brought to reflux with stirring for 27 h, at which time all $SF_5CF_2CF_2CH_2CH_2I$ was consumed (as monitored by GC). The mixture was centrifuged for 1 h. The supernatant was distilled through a 12 cm Vigreux column at 100 Torr to remove the solvent (−196 °C trap); the pressure was then lowered to 17 μm (under dynamic vacuum), and a clear liquid (0.56 g) was collected at 32 °C. The product contained two olefins, (evidenced by infrared spectroscopy, $\nu = 1638$ and 1622 cm^{-1} and by GC−MS an unknown product (10%) and $SF_5(CF_2)_2(CH_2)_2OC(O)CH=CH_2$ (90%). The final overall recovered yield of compound **5** was ∼20% as considerable losses of the product occurred via codistillation with the solvent.

The IR spectrum contains the following characteristic bands (cm^{-1}): 2978 (w, C−H); 1730 (s, C=O); 1638 (w, C=C); 1299−1121 (ms, CF_2); 879, 836, 807 (s, S−F); 605 (s, S−F). ^1H NMR: δ (ppm) **a**, 2.56 (tt); **b**, 4.47 (t); **c**, 6.13 (dd); **d**, 5.89 (dd); **e**, 6.48 (dd). Integration **a, b, c, d, e:** 2.0:1.96:0.98:1.0:1.0. Couplings: $J_{a-b} = 6.47$; $J_{CF_2-a} = 18.19$; $J_{c-e} = 17.33$; $J_{d-e} = 0.93$; $J_{c-d} = 10.50$ Hz. ^{19}F NMR: δ (ppm) SF_5, 65.0 (nine lines) and 43.8 (d); $SF_5\mathbf{CF_2}CF_2$, −96.3 (∼p); $SF_5CF_2\mathbf{CF_2}$, −116.0 (∼sept). Integration $SF_5CF_2CF_2$; 1.0:4.0:1.90:1.95. Coupling: $J_{F-SF_4} = 150.6$ Hz. Gas Chromatography: retention time for monomer **5**, 6.48 min (DB-5 column, 12 m, held at 50 °C/5 min, temperature raised to 280 °C at 18 °C/min). MS (*m/e*, rel abund, species): 326 (5.3, M^+); 127 (4.3, SF_5^+); 113 (1.5, $C_3F_4H^+$); 100 (2.8, C_2F_4+, $C_5H_7O_2H^+$); 99 (13.5, $C_5H_7O_2^+$); 95 (2.0, $CF_2CF_2CH_2CH_2OH^+$); 89 (6.2, SF_3^+); 77 (13.0, $C_3H_3F_2^+$);

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72 (4.6, $C_3H_4O_2^+$); 70 (1.3, SF_2^+); 69 (3.7, $C_3HO_2^+$); 65 (3.3, $CF_2CH_2H^+$); 64 (3.5, $CF_2CH_2^+$); 56 (5.0, C_2S^+, $C_3H_3OH^+$); 55 (100, $C_3H_3O^+$); 53 (1.6, C_3HO^+); 51 (4.1, SF^+).

Bulk Polymerization of SF_5−Acrylate Monomer 5. In a dry 100 mL Carius tube, 20 mL of methylal, 1.50 g of acrylic acid (21 mmol), and 2.50 g of Ag_2O (10.8 mmol) were stirred for 2 days (the tube was wrapped in aluminum foil); a gray, voluminous mass was formed. Then, 5.02 g (13.1 mmol) of $SF_5CF_2CF_2CH_2CH_2I$ was added and the mixture shaken for 1 week without any noticeable reaction. It was then heated at 45−55 °C for 7 days in a sand bath. Analysis of the reaction mixture (GC−MS) showed that all $SF_5(CF_2)_2(CH_2)_2I$ was consumed and that monomer **5** and $SF_5(CF_2)_2(CH_2)_2OH$ were present. The reaction mixture was filtered with suction and the filter cake washed with methylal; the filtrate that remained was a viscous liquid (2.49 g). An attempt to distill this material failed and yielded a tannish viscous liquid in the distillation pot (1.59 g). This residue was dissolved in 10 mL of F-113, 80% of which was transferred to a column (50 g of silica gel, 5 cm i.d. tube). A minor band was first eluted with CH_2Cl_2. The second fraction, polymer **5**, was then eluted with acetone (elution was monitored by evaporating the eluent on a glass plate). The eluted polymer was freed of solvent and vacuum-dried; 1.03 g of a nearly colorless tacky solid was obtained (yield 30%).

The infared spectrum of the polymer contains the following peaks (cm^{-1}): 2971 (w), 2937 (w), 2877 (vw), 1746 (s), 1457 (w), 1434 (vw), 1380 (w), 1339 (w), 1308 (w), 1249 (m), 1196 (s), 1166 (s), 1120 (s), 1079 (wm), 1046 (w), 1016 (w), 876 (vs), 834 (s), 807 (s), 741 (wm), 712 (w), 682 (wm), 605 (s), 574 (wm), 529 (w). ^{19}F NMR ($CDCl_3$, internal $CFCl_3$): δ (ppm) SF_5, 65.9 (nine lines) and 45.0 (d); $SF_5\mathbf{CF_2}CF_2$, −96.8 (b); $SF_5CF_2\mathbf{CF_2}$, −115.3 (m). Integration $SF_5CF_2CF_2$: 1.0:4.0:1.9:1.9. Coupling: J_{F-SF_4} = 147.8 Hz. Anal. Calcd for $C_7H_7F_9SO_2$: C, 25.78; H, 2.16; F, 52.42. Found: C, 25.81; H, 2.31; F, 51.20.

Cast Photoinitiated Polymer Films from Perfluorocarbon/Hydrocarbon Acrylate Monomer Binary Mixtures. HEMA and SF_5−acrylate monomer **5** were weighed directly into glass vials to precalculated weight percent mixtures (±0.1 mg). Irgacure 261 photoinitiator (Union Carbide) solution in acetone (4 mg/mL) was added dropwise 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 glass slides or fresh gold mirrors evaporated onto acid-cleaned silicon wafers by dropping the solution onto the slide surface using a Pasteur pipet. Solvent (acetone) was allowed to evaporate under a nitrogen atmosphere at room temperature for 0.5−1 h. A short arc mercury lamp (HBO100, 150 W) was used to photopolymerize these films at a distance of 18 cm at room temperature under nitrogen atmosphere for 10−12 h. A 10 cm diameter water-cooled quartz heat filter was used between the lamp and film-coated slides to eliminate sample heating.

Characterization of Photopolymerized Fluorinated Acrylate Films. *Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR).* Attenuated total reflectance FTIR spectra of cast polymer films were collected on a Nicolet Magna instrument with a liquid N_2-cooled MCT detector using a Spectratech variable angle grazing incidence reflection accessory at normal incident angle onto a KRS-5 crystal (50 mm × 10 mm, face angles of 45°). Bare substrates were used as references. Films on substrates or clean bare substrates as references were pressed against the ATR prism to maximize interfacial contact. Spectra were taken at 4 cm^{-1} resolution with 1024 scans. Reference subtraction and spectral flattening were achieved using OMNIC software (Nicolet Instruments), but no curve smoothing or other alterations were used.

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 K_α source, hemispherical analyzer, and multichannel detector. Typically, spectra were collected with the analyzer at 55° 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 compositions, the analyzer transmission function was assumed not to vary with photoelectron kinetic energy (KE),[13] the photoelectron escape depth was assumed to vary as $KE^{0.7}$,[13] and Scofield's photoionization cross sections were used.[14] From analysis of replicates, the typical XPS uncertainties were observed to be less than ±1.5 atom % for carbon, fluorine, and oxygen and less than ±0.5 atom % for sulfur.

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. Using mean free paths calculated from the equations given by Seah and Dench,[15] the sampling depth (3 times the mean free path) for C 1s photoelectrons should decrease from 90 to 15 Å as takeoff angle increases from 0° to 80°. The regularization method of Tyler and co-workers[16] was used to generate compositional depth profiles (CDPs) from the angle-dependent XPS data.

Contact Angle Analysis. Sessile drop contact angle analysis (Ramè-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% RH). Measurements were taken on both sides of the water drops at ambient temperature 30−40 s after the drops were applied to the surfaces. Contact angle data report the average of three drops at different surface locations.

Results and Discussion

A facile reaction occurs between ECMA and $SF_5CF_2CF_2(CH_2)_2OH$ in the presence of Et_3N involving the displacement of the chloro group and the formation of a more stable ether linkage:

$$ClCH_2C(C(O)OCH_2CH_3)=CH_2 + SF_5CF_2CF_2(CH_2)_2OH \xrightarrow[THF]{N(Et)_3} SF_5CF_2CF_2(CH_2)_2OCH_2C(C(O)OCH_2CH_3)=CH_2 \quad \mathbf{4}$$

Using silver acrylate and $SF_5CF_2CF_2CH_2CH_2I$, with solvent CH_3CN or methylal, the following monomer synthetic reaction occurred:

$$AgOC(O)CH=CH_2 + SF_5CF_2CF_2(CH_2)_2I \xrightarrow{-AgI} SF_5CF_2CF_2(CH_2)_2OC(O)CH=CH_2 \quad \mathbf{5}$$

The new acrylate monomer **4** is a colorless, clear liquid that has a faint pleasant odor. The infrared spectra of the bulk monomer, solid polymer film, and oligomeric oil exhibit strong S−F stretching modes in the region of 834−881 cm^{-1} and one of the SF deformation modes at 604 cm^{-1}; similar results have been reported for a number of SF_5 fluoroalkyl compounds.[17] The C−F stretching frequencies are found between 1120 and 1250 cm^{-1}. The C−H vibrations appear in the range 2915−2988 cm^{-1}. The vinyl stretching mode in the

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monomer is located at 1646 cm^{-1}; this band is also found as a very weak absorption in the polymeric oil fraction and is nearly absent in the solid polymer of **4**. A significant shift is found for the carbonyl peak: in the monomer this peak is found at 1716 cm^{-1}, while for the oligomeric oil and the polymer film it is located at l732−1734 cm^{-1}. It is interesting to note that similar results for both the vinyl and carbonyl peaks in R_f—CH_2-$OCH_2C(COOCH_2CH_3)$=CH_2 were found.[10] The ^{19}F NMR spectrum for monomer **4** shows an AB4 pattern for the SF_5 group: **A** (a nine line pattern) at δ 66.8 ppm and **B** (skewed doublet) at δ 46.5 ppm. The chemical shifts of the $-CF_2$ fluorines adjacent to the SF_5 group are located at δ −97.1 ppm; the other $-CF_2$ signals are found at δ −116.7 ppm. These results are in excellent agreement with those for similar molecular systems such as SF_5-$CF_2CF_2(CH_2)_2I$.[18] The proton chemical shifts adjacent to the $-CF_2$ and to the ether linkage are located at 2.51 and 3.87 ppm, respectively; these results are in good agreement with those reported for $SF_5CF_2CF_2(CH_2)_2$-OH.[10] The assignment for the vinylic hydrogens that are cis and trans to the $-CH_2OCH_2CH_2CF_2CF_2SF_5$ group was based on the literature.[19]

The second acrylate monomer **5** is a colorless liquid which forms a tacky solid homopolymer. The infared spectrum of the polymer contains strong S−F stretching modes in the region 807−876 cm^{-1} and one SF_5 deformation mode at 605 cm^{-1}. The C−F stretching frequencies are located between 1120 and 1249 cm^{-1}. The C−H vibrations appear in the range 2877−2971 cm^{-1}. The vinyl stretching band in the monomer at 1638 cm^{-1} is missing in the polymer while the carbonyl peak is shifted from 1730 cm^{-1} in the monomer to 1746 cm^{-1} in the polymer. The ^{19}F NMR for the polymer of **5** is similar to that reported for the polymer of **4**.

FTIR spectral features from the solvent cast polymer and copolymer films from the two monomers are consistent with their composition and their respective monomer neat IR spectra (see the Experimental Section). Figure 1 shows overlayed FTIR spectra for pure poly(HEMA) and various bulk polymerized copolymers of HEMA with SF_5-containing monomer **4**, all cast on NaCl plates from $CHCl_3$ and desiccated. The most prominent change in the spectral features is the loss of the monomer C=C absorption at 1635 cm^{-1} upon polymerization. Other spectral features in copolymer films with monomer **4** include carbonyl stretching at 1731 cm^{-1}, $-CF_2$ and $-CF_3$ stretching bands in the region of 1250−1121 cm^{-1}, and SF_5 modes at 883, 836, and 808 cm^{-1}. The spectral features of the polymeric HEMA include the broad hydroxyl −OH stretch at 3435 cm^{-1}, hydrocarbon asymmetric and symmetric stretching bands at 2917 and 2850 cm^{-1} (neither shown), and aliphatic $-CH_3$ and $-CH_2$ bending modes at 1454 and 1379 cm^{-1}. These film spectra are consistent with bulk neat spectra for both monomers **4** and **5**, their respective bulk polymers (vida supra), and pure poly (HEMA).[20]

The XPS-determined elemental composition of polymer **4** cast onto a gold-coated Si wafer was 35.8 ± 1.2 atom % F, 48.1 ± 0.8 atom % C, 12.2 ± 0.9 atom % O, and 3.9 ± 0.2 atom % S. Small amounts (ca. 1 atom %) of Au and Cl were detected on some of the replicates, but were excluded when the polymer composition was calculated. The XPS composition is in good agreement with the expected stoichiometric composition of polymer **4** (39.1 atom % F, 43.5 atom % C, 13.0 atom % O, and 4.4 atom % S). In particular, the XPS measured F/S of 9.2 is in excellent agreement with the expected theoretical stoichiometric value of 9. The slightly higher carbon concentration measured by XPS is likely due to the presence of some adsorbed adventitious hydrocarbon contaminant. The high-resolution XPS C 1s spectrum of polymer **4**, shown in Figure 2, presents a series of carbon peaks due to hydrocarbon (38%), ether (32%), ester (11%), and fluorocarbon (19%) species. The percentages of carbon species determined from peak fitting are in excellent agreement with the expected stoichiometric values. The high-resolution XPS S 2p spectrum of polymer **4** shown in Figure 3 has two characteristic overlapping peaks due the S $2p_{3/2}$ and S $2p_{1/2}$ spin−orbit doublet arising from one sulfur species, $-SF_5$. The measured S $2p_{3/2}$ binding energy (BE) was 172.7 eV, significantly higher than the BE from $-SO_2F$ polymer chemistry[1] and other sulfur species[20] (*in fact, likely the highest S 2p binding energy known*). This high sulfur

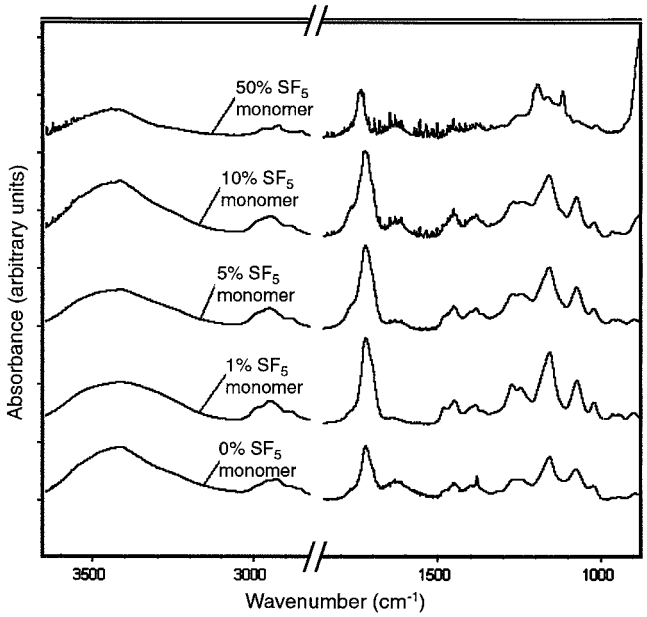

Figure 1. Transmission FTIR spectra of photocured SF_5−acrylate monomer **5**−HEMA copolymer films.

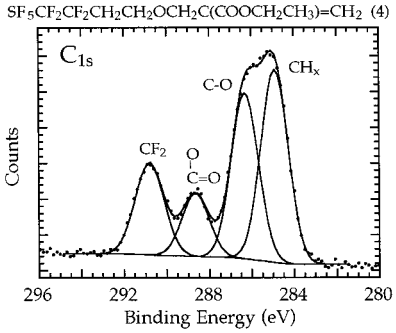

Figure 2. XPS C 1s spectrum of a photocured homopolymer cast from monomer **4**.

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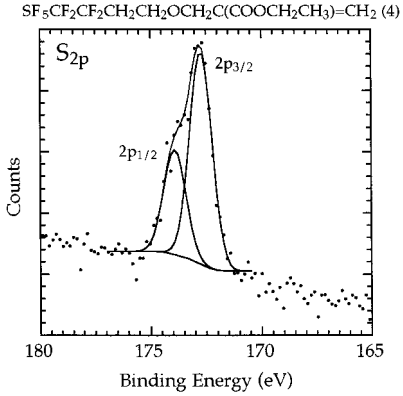

Figure 3. XPS S2p spectrum of photocured homopolymer cast from monomer **4**.

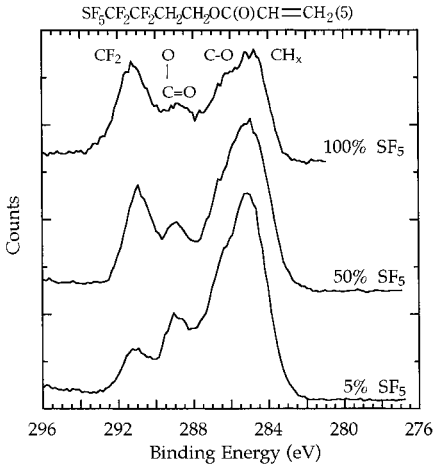

Figure 4. Composition-dependent XPS C 1s spectra showing surface perfluorinated enrichment for photocured copolymer films comprising SF_5−acrylate monomer **5** (100%) (upper spectrum) with 50 wt % HEMA (middle spectrum) and 95 wt % HEMA (lower spectrum). XPS data were acquired at a photoelectron takeoff angle of 55° corresponding to a sampling depth of approximately 50 Å.

BE is due to the five electron-withdrawing fluorine atoms bound to the sulfur atom.

XPS C 1s and S 2p spectra for surfaces of photocured polymer films comprising pure SF_5−acrylate monomer **5** are qualitatively quite similar to those shown for films of monomer **4** in Figures 2 and 3 (data not shown). Photopolymerized mixed films of HEMA and **5** show significant surface enrichment features, evidenced by XPS data shown in Figure 4. Two photocured polymer films comprising two substantially different ratios of SF_5−acrylate monomer **5** and HEMA show similar surface compositional trends. XPS C 1s data in Figure 4, acquired at a fixed photoelectron takeoff angle of 55° (sampling depth ∼50 Å),[22] exhibit both the hydrocarbon (285 eV) and ester carbon (289 eV) features of both acrylates and the higher binding energy signals characteristic of the perfluorinated species in SF_5−acrylate **5**. Comparison of the upper spectrum in Figure 4 (50 wt % HEMA) with the lower spectrum (95 wt % HEMA) supports a significant surface enrichment of the SF_5−acrylate **5**, even at 5 wt %. A substantial nonstoichiometric $-CF_2-$ signal at 291 eV is observed at 50 Å depth at this film composition. This surface enrichment trend can be better followed through the more complete compositional profile of the various monomer mixtures. The XPS-determined elemental compositions of the photopolymerized films prepared from pure monomer **5** and a series of mixtures of monomer **5** with HEMA are listed in Table 1. The XPS results in Table 1 were all acquired at a photoelectron takeoff angle of 55°, corresponding to a sampling depth of approximately 50 Å.[22] Also included in Table 1 are the expected calculated stoichiometric values for films comprising pure monomer **5** and pure HEMA, respectively. All mixed polymer films exhibit significant surface enrichment of **5**. The XPS compositions of the 40% and 50% films are within experimental error of compositions observed for films of pure monomer **5**. Moreover, these values are close to that calculated for pure monomer **5** films (Table 1). Thus, at least the outer 50 Å of these polymer films comprise nearly pure monomer **5**. As the percent of **5** in the film drops below 40%, the XPS fluorine and sulfur concentrations also decrease. However, the observed decrease in the XPS fluorine and sulfur concentrations was smaller than the decrease in the bulk concentration of monomer **5** in the film. For example, comparing the 50 wt % and 1 wt % monomer **5** mixed photocured films, a 50-fold decrease in the bulk concentration of monomer **5** resulted in less than a 2-fold decrease in the XPS surface fluorine concentration. Thus, relative *surface* enrichment of monomer **5** actually increases as the *bulk* concentration of **5** decreases.

Table 1. XPS-Determined Surface Elemental Compositions of Photocured HEMA− SF_5 Monomer 5 Mixed Films as a Function of Bulk Film Composition[a]

wt % SF_5 monomer **5**	atom %					
	F	S	C	O	Si	Cl
1	25.8	2.4	51.6	20.2		
5	27.7	2.8	49.9	19.5	trace	trace
10	30.5	3.3	48.2	18.1		
20	27.7	2.6	49.7	19.3	trace	0.8
30	33.6	4.0	46.0	16.5		
40	40.7	4.9	40.3	12.7	0.7	0.7
50	42.2	5.3	41.1	11.1	trace	
100[b]	41.7	5.1	38.5	12.5	1.5	
100% monomer **5** (theory)	47.4	5.3	36.8	10.5		
100% HEMA (theory)			66.7	33.3		

[a] XPS data acquired at a photoelectron takeoff angle of 55° corresponding to a sampling depth of approximately 50 Å. [b] Trace Na (0.5 atom %), Ca (0.4 atom %), and Si (1.5 atom %) are contaminants.

Previous data reported for films of an epoxide mixed monomer series have shown that nonstoichiometric surface "blooming" of perfluorinated monomer persists to very low bulk perfluorinated monomer levels.[1] Angle-dependent XPS results for a photocured polymer film containing only 1 wt % of SF_5−acrylate **5** in the majority HEMA matrix are shown in Figure 5. These C 1s spectra, taken at two different sampling depths (angle 80°, ∼15 Å depth upper spectrum; angle 0°, ∼90 Å depth, lower spectrum) also support high nonstoichio-

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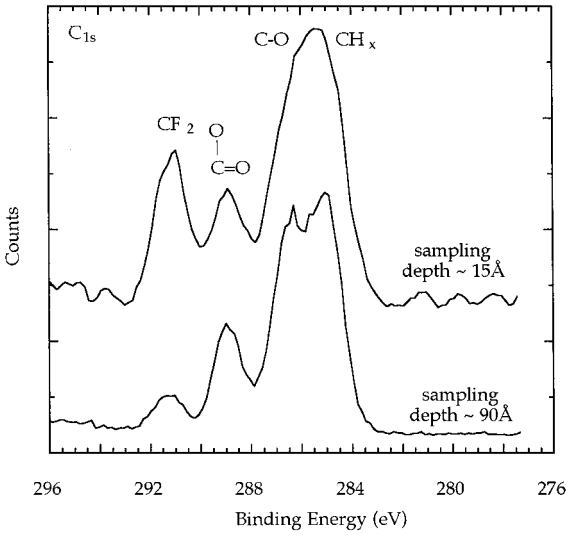

Figure 5. Angular-dependent XPS C 1s spectra at two surface sampling depths (angle 80°, ~15 Å depth; angle 0°, ~90 Å depth) for the SF_5−acrylate monomer **5**−HEMA copolymer film photocured with 1 wt % monomer **5** (see Table 2).

Table 2. XPS-Determined Surface Elemental Compositions of the 99% HEMA−1% SF_5 Monomer 5 (w/w) Mixed Polymer Film as a Function of XPS Sampling Depth

takeoff angle (deg)	sampling depth (Å)	atom % F	S	C	O
0	90	20.0	1.7	53.4	24.9
55	50	25.8	2.4	51.6	20.2
80	20	42.0	5.1	40.4	12.6
100% monomer **5** (theory)	47.4	5.3	36.8	10.5	
100% HEMA (theory)			66.7	33.3	

metric surface enrichment of perfluorinated chemistry even at this low bulk level of perfluorinated monomer.[1] The upper spectrum in Figure 5 shows a prominent $-CF_2$ peak at 291 eV characteristic of a surface presence of monomer **5** far exceeding its bulk 1 wt % value if compared to the same XPS peak for the 5 wt or 50 wt % films shown in Figure 4. Comparison of the higher relative integrated XPS C 1s peak areas from fluorinated carbon (291 eV) versus hydrocarbon (285 eV) for the upper and lower spectra in Figure 5 (data not shown) also supports greater depths perfluorinated enrichment at shallower depths (upper spectrum) versus deeper in the film (lower spectrum). Quantitation of the complete, detected elemental compositions of this film as a function of XPS sampling depth is compiled in Table 2, along with theoretical calculated values for films of each pure monomer. Elemental fluorine, sulfur, and carbon compositions approaching that calculated for a 100 wt % monomer **5** film also support high levels of surface enrichment from small amounts of monomer **5** in mixed polymer films.

Used together with the 55° angular XPS data presented in Table 2 for this film, a model-derived compositional depth profile (CDP) can be generated,[16] and is shown graphically in Figure 6. These calculated compositional trends show that, even at a 1 wt % bulk level, the composition of the outermost polymer film surface is pure monomer **5**. Film fluorine and sulfur elemental concentrations decrease rapidly with depth into the surface: by a depth of 50 Å, the CDP in Figure 6

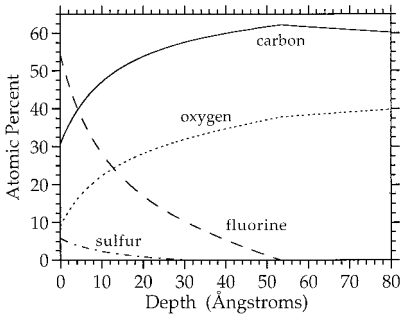

Figure 6. Composition depth profile generated from the angle-dependent XPS compositions of the SF_5−acrylate monomer **5**−HEMA copolymer film photocured with 1 wt % monomer **5** (see Table 2, ref 16).

indicates that the polymer film composition is pure HEMA. Thus, the main difference between the 50 and 1 wt % polymer films of **5** is the thickness of the enriched **5** surface overlayer. The outer surface region of both films is pure monomer **5**, but this region is significantly thinner in the 1 wt % film. These results parallel surface analytical data published previously for mixed monomer photocured epoxide films bearing perfluorinated segments and $-SO_2F$ terminal groups.[1] Both monomer chemistries (acrylate and epoxide) exhibit nonstoichiometric surface enrichment of perfluorinated components that have phase separated, migrated, or bloomed to the film surface. This enrichment results in placement of unique functional groups ($-SF_5$) in the surface region.

Such surface enrichment of perfluorinated chemistry (blooming) has been noted for other polymer film systems 22−25, and is attributed to a combination of the low intrinsic interfacial ($Y_{5/v}$) energy for perfluorinated components, and poor miscibility of such chemistry with hydrocarbon-based polymer segments.

Conclusions

Two new acrylate monomers bearing perfluoralkyl $-SF_5$ side chains have been synthesized and polymerized as homo- and copolymers. Photopolymerized cast films of acrylate monomer mixtures containing the SF_5-perfluorinated acrylate and HEMA show surface enrichment of the SF_5−acrylate as monitored by XPS. The depth profile for the top 80 Å shows high nonstoichiometric levels of fluorine enrichment, even at very low bulk SF_5−perfluoroacrylate levels. Chemistry, specifically the $-SF_5$ functionality, can be imparted to surfaces of polymer coatings using this surface enrichment method. In addition, the highest XPS S 2p sulfur binding energy ever reported is noted for the SF_5 surface. Surface blooming of perfluorinated species bearing specific functional groups or desired chemistry for surface localization should prove a general method to tailor surface properties, particularly using low levels of exotic or expensive perfluorinated materials.[1]

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