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XPS Studies of Fluorinated Acrylate Polymers and Block Copolymers with Polystyrene

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ABSTRACT: X-ray photoelectron spectroscopy (XPS) has been used to investigate the surface characteristics of various novel fluorinated acrylate homopolymers [1,1-dihydroperfluorooctyl acrylate (PFOA), 1,1-dihydroperfluorooctyl methacrylate (PFOMA), 1,1,2,2-tetrahydroperfluorooctyl acrylate (PTAN)] as well as diblock copolymers consisting of both a fluorocarbon block of PFOA and a hydrocarbon block of polystyrene (PS). This technique allows nondestructive depth profiling of the top ∼100 Å of a material, providing both elemental composition and chemical state information. Due to the low surface energy of the fluorinated species, its enhanced presence on the surface is of importance in any potential applications. Angle-dependent XPS surface studies were conducted on polymer thick films to monitor surface segregation of the fluorinated component as a function of depth. Fluorine and the fluorine-containing constituents are surface enriched relative to carbon and oxygen from the acrylate portions of the polymers. This effect also occurs in the diblock copolymers, where the PFOA block prefers the polymer−air interface. Furthermore, this surface segregation is enhanced when the samples are thermally annealed. Also, the quantitative XPS data reveal other subtleties in the overall polymer structures, such as extent of chain branching in PFOA, PFOMA, and the diblock copolymers and the slight variations in average fluorine-containing side chain lengths in PTAN.

Introduction

In some polymer systems, the composition of the surface differs, sometimes dramatically, from the composition within the bulk, resulting in a material with distinct surface properties, such as bioadhesion or wettability. Differences in the surface free energy of the components within a polymer or polymer system may dictate the overall surface morphology, whereby the lower surface energy segment resides near the polymer−air interface.[1−5] The surface energies of some conventional polymers are poly(tetrafluoroethylene) (PTFE) = 18.5 dyn/cm,[6] poly(dimethylsiloxane) (PDMS) = 22 dyn/cm,[7] poly(methyl methacrylate) (PMMA) = 39 dyn/cm,[6] and poly(ethylene terephthalate) (PET) = 43 dyn/cm.[6] It has been demonstrated that angle-dependent X-ray photoelectron spectroscopy (ADXPS) is a useful tool to probe the surface composition in such polymer systems, such as in copolymers containing polysiloxane, a low surface energy component.[8−10]

Taking advantage of the low surface energy of fluoropolymers, such as PTFE, makes them useful in a number of applications. For example, fluorochemicals impart resistance to oils, water, and soils and therefore are used prevalently in the textile and carpet industries. Other common uses include nonstick cookware, car finishes, cosmetics, and pharmaceutical applications.[11,12] Furthermore, introducing a fluorinated component, such as PTFE, into a polymer chain is known to reduce both the overall surface free energy and the coefficient of friction of the system.[13] Consequently, the capability to molecularly engineer such heterophase structures has resulted in a variety of additional materials with technological promise. Novel copolymers consisting of both a fluorocarbon and a hydrocarbon block have recently been synthesized in the DeSimone group[14] such that their low surface energy characteristics may be exploited in a number of applications, such as minimally adhesive membrane materials for uses in pervaporation and reverse osmosis to minimize biofouling.

In this study, efforts were first initiated to characterize the surfaces of such materials by investigating the fluorinated homopolymers 1,1-dihydroperfluorooctyl acrylate (PFOA), 1,1-dihydroperfluorooctyl methacrylate (PFOMA), and 1,1,2,2-tetrahydroperfluorooctyl acrylate (PTAN). Surface studies were conducted on thick polymer films, spun cast from solution onto a silicon substrate, and examined by ADXPS. The enrichment of the surface with the fluorine-containing portions of the polymers was anticipated. This surface segregation of the fluorinated component was monitored as a function of depth. Furthermore, it was possible to develop XPS as a tool by which to measure both the overall degree of chain branching in PFOA and PFOMA and the average fluorocarbon chain length in PTAN. Studies were also conducted on block copolymers of PFOA and polystyrene in various molar ratios of the blocks. PFOA, with an exceptionally low overall surface energy of ca. 11 dyn/cm,[15] was expected to strongly segregate at the surface.

Experimental Section

Materials. The monomers for this study were supplied either by 3M (FOA and FOMA) or DuPont (TAN). The fluorinated alcohol used to make FOA and FOMA was prepared by electrochemical fluorination of an octanoic acid starting material.[11] One of the proposed reaction intermediates is a carbocation which can potentially undergo rearrangement. Methyl migrations are prone to occur, which can result in the formation of branching along the fluorocarbon chain, leading to an amorphous polymer. However, the method of preparation of the fluorinated alcohol used to make the TAN monomer is based on the telomerization of tetrafluoroethylene, and as such, the starting materials are derived from straight-chain perfluoroalkyl iodide oligomers which vary in length. Subsequent formation of the TAN acrylate monomers, therefore, results in a material whose fluorocarbon chain lengths are linear but polydisperse;[11] the resulting TAN polymer is semicrystalline. Because of these differences, the monomers

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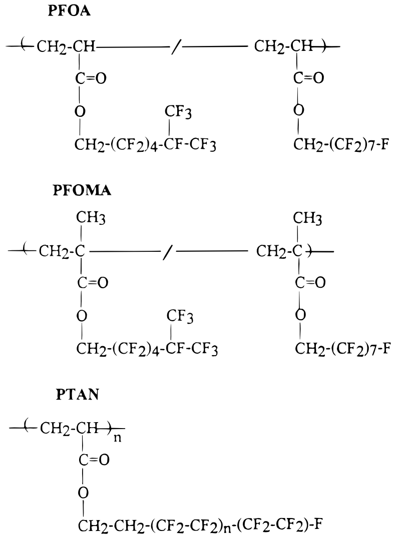

Figure 1. Fluorine-containing acrylate homopolymers.

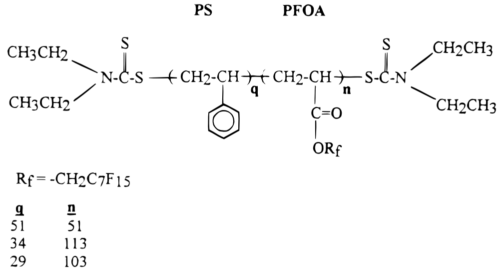

Figure 2. Structure of PS-*b*-PFOA block copolymer with corresponding block lengths (q = number of PS repeat units and n = number of PFOA repeat units).

obtained from 3M (FOA and FOMA) are liquids at room temperature, whereas the monomer obtained from DuPont (TAN) is waxy at room temperature. The synthesis of all three fluoroacrylate homopolymers is based on a homogeneous free-radical solution polymerization in supercritical CO_2, at 59.4 °C, 207 bar, for 48 h, resulting in high molecular weight PFOA, PFOMA, and PTAN (see Figure 1).[16] Three block copolymers of PS-*b*-PFOA (see Figure 2), synthesized by an iniferter process,[14,17,18] were also used in this investigation and varied in the molar ratio of PS/FOA: 1 (M_n = 28 400), 0.30 (M_n = 54 700), and 0.28 (M_n = 49 500).[19]

In preparation for the XPS analyses, films of the various polymers were spun cast at either 500 or 1000 rpm from 1 wt % solutions in 1,1,2-trichlorotrifluoroethane (F-113) onto precleaned silicon substrates. The block copolymer films were annealed at various temperatures, (80, 100, and 140 °C) for various lengths of time (0.5−24 h) in covered Petri dishes in an air atmosphere. Unannealed (homopolymer and copolymer) and annealed (copolymer) films were then studied by XPS.

Instrumentation. All XPS measurements were carried out using a Physical Electronics (PHI) Model 5400 spectrometer equipped with a hemispherical capacitor analyzer. X-rays from a monochromatic Al K$\alpha_{1,2}$ source were used to irradiate a 1 mm diameter spot size of the samples. The binding energy scale of the instrument was calibrated by setting $Au_{4f_{7/2}}$ = 84.0 eV, $Cu_{2p_{3/2}}$ = 932.6 eV, and $Ag_{3d_{5/2}}$ = 368.3 eV. Typical operating conditions for analyses included the following: test chamber pressure 2 × 10^{-8} Torr; 15 kV, 500−600 W, 35−40 mA for the Al X-ray source. Elemental survey scans from 0 to 1000 eV were acquired with a pass energy of 89.5 eV, while high-resolution scans of the C_{1s}, F_{1s}, and O_{1s} regions were acquired with a pass energy of 17.9 or 35.8 eV. Electron flooding was not used to compensate for charging. Data were acquired at take-off angles of 20, 40, and 70° between the sample and analyzer. Based on an estimated inelastic mean free path for a C_{1s} photoelectron of 27 Å[20] originating from organic materials, these angles correspond to the approximate sampling depths of 28, 52, and 76 Å, respectively. The XPS sampling depth is a convolution of the measurement of all components up to that depth, with an exponential attenuation of photoelectrons from subsurface layers due to scattering.[3] The C, O, and F atomic percentages were determined after including the appropriate instrumental sensitivity factors. Furthermore, a more in-depth analysis of the spectra involved use of a least-squares curve fitting program. Peak positions were determined according to previously established binding energies and were thus held relatively constant. The peak parameters that were allowed to vary included peak height, fwhm, and % Gaussian. The program was used to decompose both the C_{1s} and O_{1s} spectra into the various chemical components which correspond to the functional groups of the polymers. Spectra were then charge-corrected to align the hydrocarbon component of the C_{1s} region to 285.0 eV.

Table 1. Binding Energies of C_{1s}, F_{1s}, and O_{1s} Regions of PFOA, PFOMA, and PTAN.

atom	functional group	PFOA (eV)	PFOMA (eV)	PTAN (eV)
C_{1s}	CF_3	293.5 (±0.06)	293.8 (±0.1)	293.7 (±0.09)
	CF_2	291.3 (±0.06)	291.6 (±0.1)	291.6 (±0.1)
	C=O	289.1 (±0.1)	289.4 (±0.1)	289.4 (±0.2)
	*C*OC=O	287.2 (±0.08)	287.6 (±0.1)	286.8 (±0.1)
	*C*HC=O (PFOA, PTAN, PFOMA) *C*CF_2 (PTAN)	285.5 (±0.1)	285.8 (±0.03)	285.7 (±0.09)
	hydrocarbon	285.0	285.0	285.0
F_{1s}	C−F	688.8 (±0.09)	689.5 (±0.1)	689.3 (±0.2)
O_{1s}	C−O	533.9 (±0.04)	534.3 (±0.1)	534.0 (±0.2)
	C=O	532.3 (±0.07)	532.7 (±0.1)	532.6 (±0.1)

Results and Discussion

Homopolymers. To successfully evaluate the surface properties of the various homopolymers studied, it was necessary to first structurally characterize the XPS spectra. Discerning the chemical make-up of the F_{1s} and O_{1s} windows was straightforward. While the F_{1s} window of all fluorinated homopolymers shows a singlet symmetrical peak, the O_{1s} window shows two components of similar areas corresponding to the two different types of oxygen in the ester functional group of these acrylate polymers. The C_{1s} window, however, shows a complex pattern of peaks extending over about a 10 eV range. Although the structure of PFOA consists of eight chemically different types of carbon and PFOMA and PTAN each are made up of nine chemically different types, only six peaks were found necessary to curve fit the data. Peak assignments, given in Table 1, were based on characteristic binding energies and agree well with previously published literature and reference values on fluorinated as well as acrylate polymers.[1,21,22] A typical C_{1s} spectrum of one of the homopolymers, PFOA, is given in Figure 3.

Since the composition of the surface is a critical feature of these homopolymers, an attempt was made to evaluate the extent of surface segregation of the fluorinated regions. Analyses performed at the various take-off angles of 20, 40, and 70° provided a means to probe both the surface and bulk features of these materials. Given in Figure 4 are the carbon, oxygen, and fluorine atomic concentrations of PFOA, PFOMA, and PTAN as a function of take-off angle. It can be seen that in all three cases, the fluorine signal is enhanced

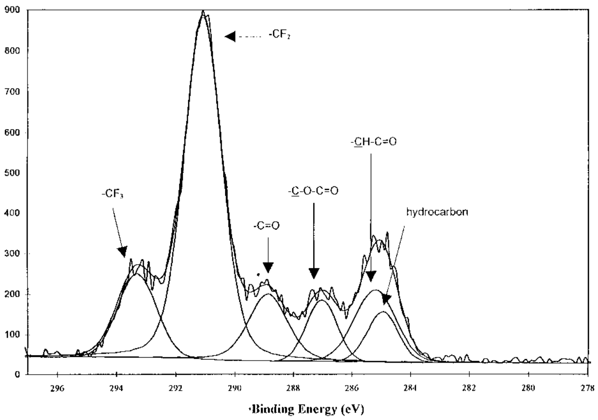

Figure 3. Raw and curve-fit data of C_{1s} spectrum of PFOA with carbon components assigned.

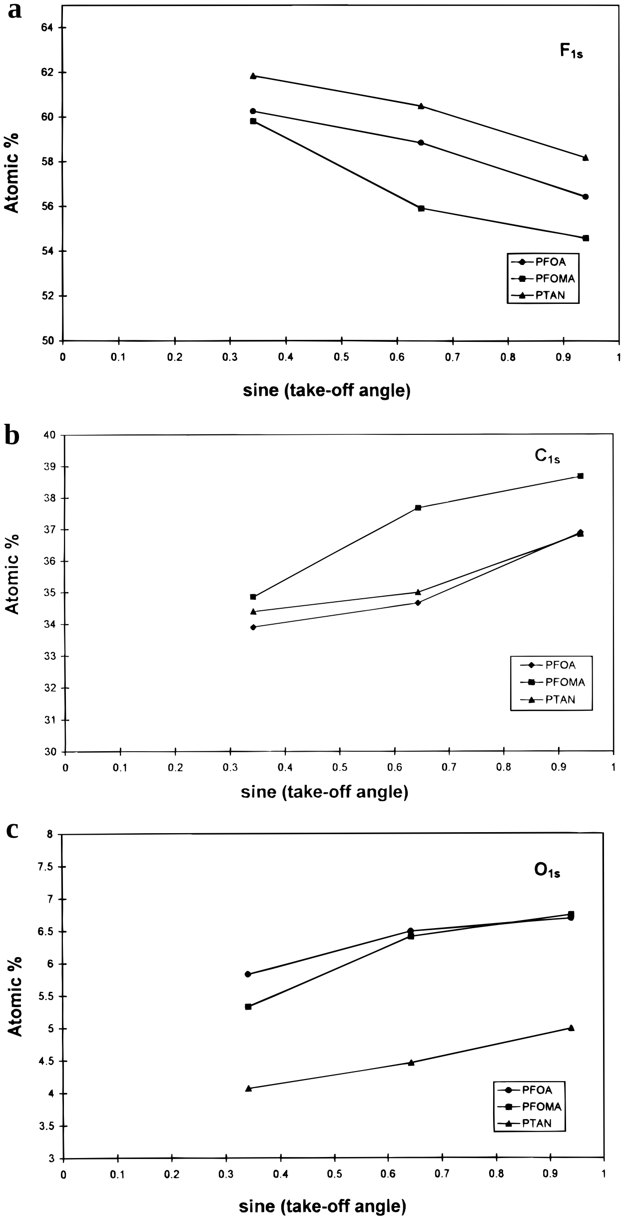

Figure 4. Concentrations versus sine(take-off angle) of fluorine (a), carbon (b), and oxygen (c) for PFOA, PFOMA, and PTAN.

Table 2. Ratio of (CF_3 + CF_2)/(total carbon) for PFOA, PFOMA, and PTAN as a Function of Take-off Angle

	(CF_3 + CF_2)/(total carbon)		
angle (deg)	PFOA	PFOMA	PTAN
20	1.99 (±0.02)	1.73 (±0.01)	1.98 (±0.12)
40	1.83 (±0.03)	1.55 (±0.01)	1.85 (±0.04)
70	1.73 (±0.01)	1.46 (±0.02)	1.70 (±0.03)

Table 3. Predicted Bulk Values and Observed Area Percents of CF_3, CF_2, and C=O Peaks (as a Function of Total Carbon) for PFOA and PFOMA at 70° Take-off Angle

carbon	PFOA		PFOMA	
moiety	pred bulk	obsd	pred bulk	obsd
CF_3	9.09	11.8 (±0.4)	8.33	10.7 (±0.2)
CF_2	54.5	52.0 (±0.8)	50.0	45.9 (±0.7)
C=O	9.09	10.5 (±0.3)	8.33	9.44 (±0.5)

at the shallow angles, while carbon and oxygen are bulk segregated. This observation suggests that the fluorocarbon side chain is preferentially found at the surface compared to the acrylate backbone. This behavior is consistent with such low surface energy materials. To further investigate this trend, the relative areas of the individual carbon components were monitored with increasing depth. Table 2 shows the ratio of the fluorinated carbon species (% CF_3 and % CF_2) to total atomic carbon. As further evidence for surface segregation of the fluorinated tails, this ratio is highest at the shallowest angle for the three homopolymers and decreases with higher take-off angles. In comparison to bulk values calculated from the stoichiometric area percents (1.62 for PFOA, 1.41 for PFOMA, and 1.52 for PTAN), all experimental values are greater than bulk values, even at the deepest depth probed.

While it has been shown that the fluorinated components of PFOA, PFOMA, and PTAN do preferentially segregate at the surface, one may expect that as the take-off angle approaches 70°, stoichiometric values closer to the bulk values would be approximated. However, this does not entirely appear to be the case. For example, the predicted bulk F/C ratios for PFOA, PFOMA, and PTAN are 1.62, 1.41, and 1.52, respectively, while the observed F/C ratios are 1.73, 1.46, and 1.70, respectively. To examine a potential source of such inconsistencies, some of the individual carbon components themselves were examined. Table 3 lists the observed area percents (of the total carbon signal) for the CF_3 and CF_2 components at 70° for PFOA and PFOMA along with the stoichiometric area percents. There are discrepancies between these values and the predicted bulk values. The % CF_3 is higher than would be expected, while the % CF_2 is lower. Furthermore, the area percent of the C=O peak is also higher than would be expected. Noting that bulk values for these ratios were calculated assuming a straight-chain fluorocarbon tail, all of these observations are consistent with chain branching, as described below.

As mentioned previously, preparation of the FOA and FOMA monomers is such that chain branching can occur. A typical branch results in the conversion of a CF_2 moiety in the fluorocarbon tail to a CF with a fluorinated methyl branch. However, the overall fluorine to carbon ratio is maintained. Consequently, assuming a single branch results in an additional CF_3 and CF group and a loss of two CF_2 groups, one can then estimate the degree of branching independently from each of the area percentages of the CF_3 and CF_2 peaks (as a function of total carbon). One can also use the area of the C=O peak as an independent estimate of chain branching since the binding energy of any CF groups (ca. 289.6 eV) would essentially be indistinguishable from that of C=O (289.2 eV), resulting in peak

Table 4. Percent Branching for PFOA and PFOMA As Calculated from the Area Percents of CF_3, CF_2, and C=O Peaks (as a Function of Total Carbon) at 70° Take-off Angle

	% branching	
carbon moiety	PFOA	PFOMA
CF_3	29.8 (±3.9)	28.4 (±2.5)
CF_2	14.0 (±4.2)	24.6 (±4.0)
C=O + CF	15.5 (±3.7)	13.3 (±6.1)
ave	19.8	22.1

overlap. Equations were derived to calculate the percent chain branching from each of these three individual carbon peaks. The calculation for all peaks was based on a simple ratio relating the number of carbons of a particular type (e.g., CF_3 type carbons) to the total number of carbons in a single chain of the polymer. Determination of the number of carbons of a specific type, such as CF_3, includes those from the fraction of unbranched chains (1 per chain) as well as those from branched chains (2 per chain). The ratio for % CF_3 is as follows:

$$\% \text{ CF}_3 = \frac{[(1-x)1 + 2x] \times 100}{11}$$

$$\% \text{ CF}_3 = \frac{100 + 100x}{11} \tag{1}$$

where x is the percent branching and 11 is the number of carbons in a FOA monomer unit (12 for FOMA). For the calculation of the percent branching based on the CF_2 peak, the total number of carbons of type CF_2 is determined from the fraction of unbranched chains (6 per chain) as well as those from the branched chains (loss of 2 per chain, leaving only 4). The ratio for % CF_2 is set up as follows:

$$\% \text{ CF}_2 = \frac{[(1-x)6 + 4x] \times 100}{11}$$

$$\% \text{ CF}_2 = \frac{600 - 200x}{11} \tag{2}$$

where x is the percent branching and 11 is the number of carbons in a FOA monomer. The calculation of the percent chain branching based on the C=O and CF peak is analogous to that of the CF_3 peak (i.e., for every branch, one CF group is added). Therefore, the equation is as follows:

$$\% \text{ CF} + \% \text{ C=O} = \frac{100 + 100x}{11} \tag{3}$$

The data, given in Table 4, show that the overall percentage of chain branching as calculated from each of the 3 peaks (% CF_3, % CF_2, and % C=O) does differ, possibly due to surface segregation effects or errors in curve-fitting (for example, a 5% RSD in the peak area for CF_3 can result in a 20% error in chain branching), yet the average for both homopolymers is consistent with each other at about 20% as well as consistent with the estimates provided by the manufacturer of 20–25%.[23]

The TAN monomer is derived from fluorinated alcohols made by the telomerization of tetrafluoroethylene and as such are linear but contain a distribution of overall lengths. The carbon to fluorine atom ratio in the side group can vary from C_8F_{17} to $C_{10}F_{21}$ or to $C_{12}F_{25}$. Again, if one examines the % CF_3 and % CF_2 at the 70° take-off angle, we see that % CF_3 is slightly lower and % CF_2 is slightly higher than expected for an eight carbon long side chain, both cases indicating a longer chain (predicted values for % CF_3 and % CF_2 are 7.7 and 53.8, respectively; observed values for % CF_3 and % CF_2 are 7.4 and 54.4, respectively). Thus, based on these values, ratios can be derived to calculate the average number of carbons in the tail. For every chain irregardless of fluorocarbon chain length, there will always be 1 CF_3 group and one less CF_2 group than the total number of carbons in the side chain. Equations based on the number of CF_3 groups over the total number of carbons and the total number of CF_2 groups over the total number of carbons can be calculated as follows:

$$\% \text{ CF}_3 = \frac{1(100)}{5 + x} \tag{4}$$

$$\% \text{ CF}_2 = \frac{(x-1)100}{5 + x} \tag{5}$$

where x is the number of carbons in the fluorocarbon chain and 5 is the number of carbons in the acrylate portion of the monomer unit. From these equations, the fluorocarbon side chain length was calculated to be 8.5 as determined by the % CF_3 and 8.2 as determined by the % CF_2, thus leading to an overall average of 8.4. XPS then confirms that the PTAN fluorocarbon side chains are not monodisperse, but rather a distribution of lengths are observed as is also seen by GCMS. However, the overall average chain length as determined by XPS is lower than predicted from both GCMS and NMR (8.9 in both cases) due to both errors in curve-fitting (±5%) as well as surface segregation effects. For the latter case, it has been shown that PTAN is a semicrystalline polymer whose linear side chains would be expected to pack closely, possibly exhibiting a higher enhancement of the fluorine signal than the branched homopolymers, which cannot achieve such a close packing density due to steric effects.[11] Furthermore, because PTAN is a semicrystalline material, its density is expected to be greater than those of PFOA and PFOMA, which are amorphous. Consequently, the inelastic mean free path of a C_{1s} electron of PTAN would be shorter than that of PFOA and PFOMA, resulting in lower effective sampling depths probed for PTAN at the three take-off angles. Therefore, at 70° less "bulk" PTAN would be sampled than that of the other two homopolymers at an equivalent angle, which in turn leads to a greater contribution of the fluorinated side chain in the overall ratio (CF_3 + CF_2)/(total carbon). This would result in a slight decrease in the apparent average chain lengths observed by XPS, thus helping to explain the systematic differences compared to bulk values derived from GCMS or NMR.

Block Copolymers. As discussed in the previous section, the surface compositions of PFOA, PFOMA, and PTAN were highly enriched with the fluorine-containing side groups. On the basis of these results, we examined the surface characteristics of block copolymers of PFOA and polystyrene (PS) to determine the extent of segregation upon addition of another component. Three block copolymers, which vary in the molar ratio of polystyrene (PS) to PFOA, were examined. As with the homopolymers, the initial goal was to first structurally interpret the XPS spectra. Though the F_{1s} and O_{1s} windows were

Table 5. Binding Energies of C_{1s} Components of PFOA, PS, and PS-*b*-PFOA

carbon moiety	PFOA (eV)	PS (eV)	PS-*b*-PFOA (eV)
CF_3	293.5 (±0.06)		293.6 (±0.1)
CF_2	291.3 (±0.06)		291.4 (±0.1)
C=O	289.1 (±0.1)		289.3 (±0.1)
*C*OC=O	287.2 (±0.08)		287.3 (±0.1)
*C*HC=O	285.5 (±0.1)		285.4 (±0.09)
hydrocarbon from FOA	285.0		285.0
hydrocarbon from PS		285.0	284.1 (±0.08)[a]
$\pi \rightarrow \pi^*$ (PS)		291.6[20]	*b*

[a] We presume that the signal at 284.1 eV is due to PS and does not overlap the 285.0 eV component of PFOA. [b] Since the $\pi \rightarrow \pi^*$ in PS is only 10% of the total C_{1s} signal in 100% PS[20] and the PS in these spectra is already small, the shake-up peak was too weak to be seen in the block copolymers.

qualitatively the same as the previous polymers as expected, there were slight differences in the C_{1s} region. Based on the previously established binding energies of the carbon components in PFOA and the binding energies of the carbon components in PS, as listed in Table 5, the C_{1s} window of the block copolymers should look qualitatively identical to that of the PFOA homopolymer since the hydrocarbon components at 285.0 eV would overlap.[24] However, this was not found to be the case.

The C_{1s} region was evaluated by first assigning the C_{1s} components of PFOA based on the previously established binding energies. However, there was an additional component ca. 0.8−1 eV lower in energy than the 285.0 eV component of PFOA. To verify that this lower binding energy peak was not an artifact and attributable to PS, spectra were acquired using electron charge compensation as well as collecting data on another instrument. Possible reasons for the lower apparent binding energy may include some beam damage effect, though spectra have been acquired over time and this has not been noticed to be a significant problem, or differential charging, though there is no change in the peak position relative to the other C_{1s} peaks or peak line shapes with charge neutralization. Other possibilities include charge referencing errors of the hydrocarbon components of both PFOA and PS due to the uncertainities in the literature values (±0.3 eV). There also may be the possibility of an effect on the PS due to the chemical environment being predominantly PFOA. In light of all possible causes, there is still no reason to assume that this peak is not due to PS.

To correctly fit this component, the spectrum of the block copolymer was used with the highest percentage of PS (1.0 = PS/PFOA) at 70°. Subsequently, it served as a template to fit the rest of the C_{1s} windows. A typical C_{1s} spectrum of a block copolymer of PS-*b*-PFOA is shown in Figure 5. Once it was established that the peak at the lowest binding energy was due solely to the presence of PS, the degree of surface segregation of the fluorinated component was quantified by examining the area of the PS peak as a function of angle. The PS shake-up peak (ca. 10% of the total carbon signal in the case of a 100% PS sample),[24] which is 6.7 eV higher binding energy than the main PS photopeak, was not considered in the calculations. Since the main PS peak is relatively weak in these spectra, the shake-up peak will be negligible. The contribution from any adventitious carbon was also considered negligible.

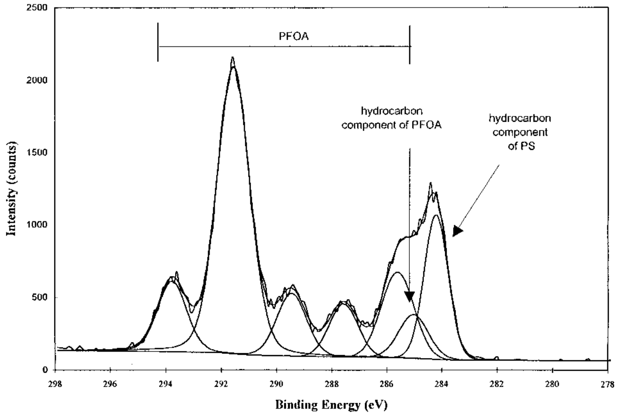

Figure 5. Raw and curve-fit data of C_{1s} spectrum of PS-*b*-PFOA indicating hydrocarbon components corresponding to PFOA and PS.

Table 6. % PS Monomer for Unannealed Diblock Copolymers of PS-*b*-PFOA as a Function of Take-off Angle

	% PS monomer		
angle (deg)	PS-*b*-PFOA (PS/PFOA = 1.0)	PS-*b*-PFOA (PS/PFOA = 0.30)	PS-*b*-PFOA (PS/PFOA = 0.28)
20	7.0 (±0.4)	1.7 (±0.5)	3.1 (±0.4)
40	15 (±0.3)	4.1 (±0.1)	5.1 (±0.6)
70	20 (±0.3)	5.7 (±0.7)	11 (±0.4)

The area of the PS peak (relative to total carbon) for each of the block copolymers at each of the three take-off angles was determined from the curve fits generated. By assuming that all of the carbons of PS were equally accessible, the percent of PS monomer was calculated:

$$\text{exp det area} = \frac{(\%\ \text{PS} \times 8) \times 100}{(\%\ \text{PS} \times 8) + [(1 - \%\ \text{PS}) \times 11]} \tag{6}$$

where % PS is the percent monomer units sampled, 8 is the number of equivalent PS carbons, 11 is the number of nonequivalent FOA carbons, and exp det area is the area of peak 7 (284.1 eV) as determined by curve-fitting. The values for % PS monomer are listed in Table 6. As anticipated in all three cases, the PFOA blocks were strongly surface segregated. Even in the case where the PS/PFOA ratio is 1.0, only 20% of the PS monomer is sampled within an effective sampling depth of 76 Å. As for the block copolymers with PS/PFOA = 0.30 and PS/PFOA = 0.28, there is significantly less PS sampled as expected. However, in the case of PS/PFOA = 0.28, there is almost twice as much PS sampled at the 70° take-off angle than that of PS/PFOA = 0.30. Though this does not appear to correlate with the molar ratio of the PS available, it is possible that it could be related to the differences in their molecular weights (54 700 vs 49 500) or a function of chain organization in an unannealed film.

Temperature has been shown to be a key variable in affecting the surface morphology and composition in many systems. Annealing materials above their glass transition temperature, T_g, can result in a situation where the chains can relax, migrate, and reorganize, thus allowing all components to reach a state of thermodynamic equilibrium.[3] Although the T_g of PFOA is well below room temperature (ca. −15 °C), the T_g of PS is about 95 °C as determined from differential scanning calorimetry (DSC). Changes in the overall copolymer surface composition upon heating were expected, particularly in consideration of the differences in the surface energy of these two components: PFOA (ca. 11 dyn/cm)[15] and PS (40 dyn/cm).[25] Thus, all samples were annealed at various temperatures and times to inves-

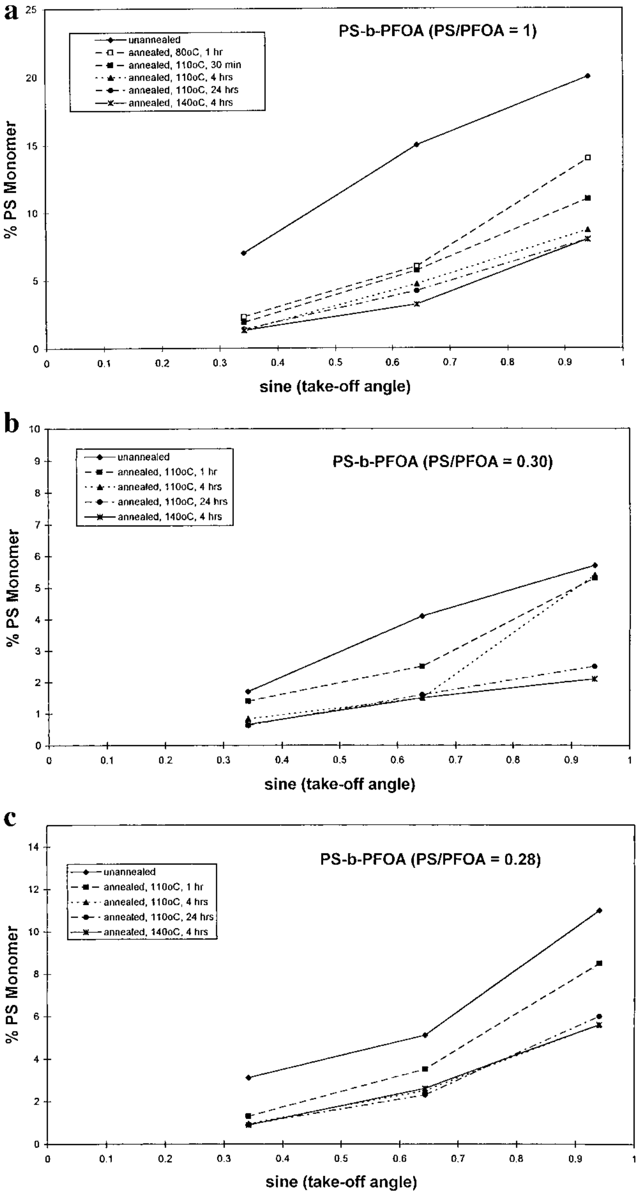

Figure 6. % PS monomer vs sine(take-off angle) for unannealed and annealed diblock copolymers where PS/PFOA = 1 (a), PS/PFOA = 0.30 (b), and PS/PFOA = 0.28 (c).

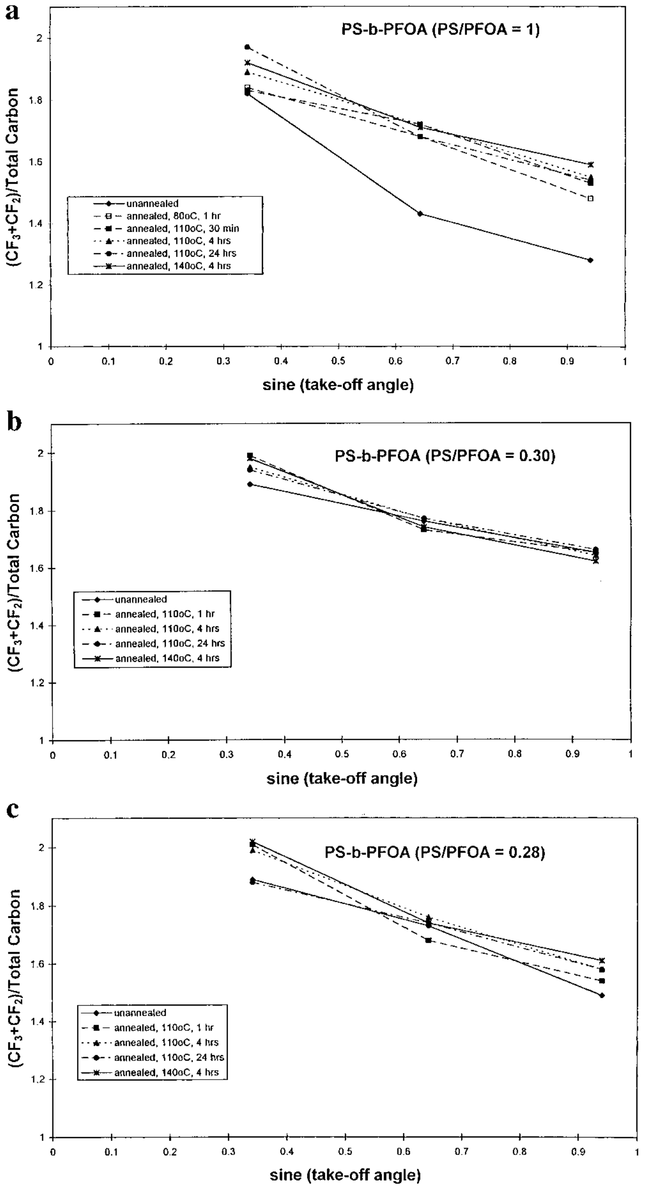

Figure 7. (CF_3 + CF_2)/(total carbon) vs sine(take-off angle) for unannealed and annealed diblock copolymers where PS/PFOA = 1 (a), PS/PFOA = 0.30 (b), and PS/PFOA = 0.28 (c).

tigate the possibility of enhancement of the surface segregation. Since the block copolymer with the highest percentage of PS would be anticipated to show the most dramatic decreases in PS at the surface, this sample was annealed at temperatures both above and below the T_g of PS. The PS-*b*-PFOA copolymer with a 1.0 molar ratio of PS/PFOA was annealed at 80 °C (1 h), 110 °C (0.5, 4, and 24 h), and 140 °C (4 h) to determine if there were any differences in the spectra. In Figure 6a, data of the spectra from the annealed case at 80 °C show that there is a decrease in the % PS at all angles compared to the unannealed case. However, it does not appear to be fully annealed when compared to the higher temperature cases, as is consistent with the fact that 80 °C is below the T_g of PS. This is further substantiated by examination of the ratio of the areas of the fluorinated carbon species (CF_3 and CF_2) to total carbon for the unannealed case and the 80 °C case (see Figure 7a). The ratios show an increase of fluorine at the surface upon heating and heating to higher temperatures does further enhance this effect. Annealed samples of the other two block copolymers (PS/PFOA = 0.3 and PS/PFOA = 0.28) at both 110 °C (1, 4, and 24 h) and 140 °C (4 h) show additional decreases in % PS at all angles (see Figure 6b,c). The percent change in PS monomer sampled in the unannealed case compared to the cases annealed at the various temperatures does show the most significant change for the copolymer with the highest initial molar ratio (1.0) of PS. However, the case with the least amount of initial PS (PS/PFOA = 0.28) surprisingly shows the next largest percent decrease, though the % PS monomer sampled is still greater than the case that has the slightly higher initial bulk concentration of PS (PS/PFOA = 0.30). It may be that the PS/PFOA = 0.28 case was not annealed long enough at a sufficiently high temperature.

Annealing time appears to have some impact on the PS surface composition for all copolymer samples as well. There are distinct differences between the spectra of the 110 °C annealing for 0.5 or 1 h and the annealing at 4 h. However, the differences between spectra taken after the 110 °C annealing for 4 h and 24 h are less dramatic. Furthermore, there appears to be even less of a change at 24 h between 110 and 140 °C. The similar

Table 7. Predicted Bulk Values and Observed Area Percents of CF_3, CF_2, and $C{=}O$ Peaks (as a Function of Total Carbon) for PS-*b*-PFOA Diblock Copolymers at 70° Take-off Angle

		obsd		
carbon moiety	pred bulk	PS-*b*-PFOA (PS/PFOA = 1.0)	PS-*b*-PFOA (PS/PFOA = 0.30)	PS-*b*-PFOA (PS/PFOA = 0.28)
CF_3	9.09	11.1 (±0.4)	11.3 (±0.5)	10.4 (±0.5)
CF_2	54.5	50.1 (±1.1)	51.6 (±1.5)	51.3 (±1.2)
$C{=}O$	9.09	10.2 (±0.5)	10.7 (±0.9)	12.4 (±1.3)

ratio of the % CF_3 and % CF_2 to total carbon for these temperatures and times indicates that the degree of surface enrichment of fluorine appears to quickly reach a state of thermodynamic equilibrium (see Figure 7a–c).

It is apparent from the data that the surfaces of both the unannealed and the annealed copolymers are highly enriched with the PFOA block. Because there is the presence of PS at all angles, if there is a relatively homogeneous overlayer of PFOA, its thickness is less than that of the XPS sampling depth even at 20°. If the polymer blocks were such that they were organized into horizontally aligned lamellar structures whereby a PFOA layer would be followed by a PS layer, which in turn would be followed by another layer of PFOA and so on, the thickness of the first two layers would be greater than the XPS sampling depth. If this thickness was less than the XPS sampling depth, one may predict the % PS to decrease at high take-off angles (e.g., probing the third layer, PFOA) while conversely, the $(CF_3 + CF_2)$/(total carbon) ratio would increase. Based on the XPS results that the % PS monomer increases with increasing depth and the fraction of fluorinated carbons decreases with increasing depth, a likely morphology (at least of the top 80 Å) would be one where the PFOA, the continuous phase, makes up predominantly the surface regions and within the subsurface are embedded PS domains. At present, transmission electron microscopic (TEM) studies are underway to further investigate the surface morphology of these materials.

As in the case of the PFOA homopolymer, the C_{1s} window of the XPS spectra of these polymers should show evidence of chain branching since the copolymerization process involved use of the same FOA monomer. To determine the extent of chain branching for the three copolymers, the XPS data of the C_{1s} region at 70° for the unannealed cases were used, which as mentioned before would most closely approximate bulk values. To be able to compare the percent chain branching of these copolymers with the PFOA homopolymer, the % CF_3, % CF_2, and % $C{=}O$ were determined based only on the contribution of the FOA block (did not take into account the percentages as determined of the total carbon signal since those would include polystyrene). Once again, the % CF_3 and % $C{=}O$ were higher than predicted values while the % CF_2 was lower, as indicative of chain branching. The values we calculated are listed in Table 7. As expected, it can be seen that the average degree of chain branching for the fluorinated side chains in all three copolymers agrees well with that of the PFOA homopolymer as well as the manufacturer's estimates (see Table 8).

Conclusions

It has been demonstrated that XPS is a powerful tool for the quantitative surface characterization of various fluorine-containing acrylate homopolymers and diblock copolymers. The data are consistent with the behavior of low surface energy fluorinated materials and their tendency to orient themselves in a thermodynamically favorable morphology at the polymer–air interface. It can be clearly seen that the fluorine side chains in both the homopolymers and copolymers exhibit surface segregation. This idea of surface segregation was further demonstrated in the block copolymers whereby the FOA block was oriented at the surface and the PS was oriented more toward the bulk. Furthermore, this effect was enhanced with the addition of heat to anneal the system. These XPS studies have also allowed the subsequent development and application of this technique to determine as well as corroborate manufacturer's estimates on the degree of chain branching in PFOA, PFOMA, and the PS-*b*-PFOA copolymers as well to confirm GCMS and NMR data which show that there is a distribution of side chain lengths in PTAN. From the work reported, the capability of angular-dependent XPS to both qualitatively and quantitatively investigate both homopolymer and block copolymer systems has been shown.

Table 8. Percent Branching for PS-*b*-PFOA Diblock Copolymers As Calculated from Area Percents of CF_3, CF_2, and $C{=}O$ Peaks (as a Function of Total Carbon) at 70° Take-off Angle

	% branching		
carbon moiety	PS-*b*-PFOA (PS/PFOA = 1.0)	PS-*b*-PFOA (PS/PFOA = 0.30)	PS-*b*-PFOA (PS/PFOA = 0.28)
CF_3	22.1 (±4.5)	24.3 (±5.9)	14.4 (±5.1)
CF_2	24.6 (±5.9)	16.2 (±8.1)	17.9 (±6.7)
$C{=}O + CF$	12.2 (±5.5)	17.7 (±9.4)	36.4 (±14.0)
ave	19.6	19.4	22.9

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