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XPS Study on Surface Segregation in Poly(ethylene-iso/terephthalate)−Perfluoropolyether Block Copolymers

F. A. Bottino, G. Di Pasquale, and A. Pollicino*

Istituto Chimico, Facoltà di Ingegneria, Università di Catania, Viale A. Doria 6-95125 Catania, Italy

F. Pilati

Dipartimento di Chimica, Facoltà di Ingegneria, Università di Modena,
Via Campi 183, 41100 Modena, Italy

M. Toselli

Dipartimento di Chimica Applicata e Scienza dei Materiali, Facoltà di Ingegneria, Università di Bologna, Viale Risorgimento 2, 40136 Bologna, Italy

C. Tonelli

R and D Center, Ausimont Spa, Via S. Pietro 50/A, Bollate, 20021 Milano, Italy

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ABSTRACT: Samples of poly(ethylene-iso/terephthalate)-perfluoro polyether multiblock copolymers with perfluoropolyether (PFPE) segments of different lengths have been characterized for surface composition by XPS and angular dependent XPS in order to determine the influence of the length of the PFPE blocks on the surface segregation of fluorine moieties. The results indicated that there was a high surface excess of PFPE when the PFPE blocks had molecular weight (MW) of 2200; for a bulk content of PFPE of about 8%, the amount of PFPE at the surface was 94 wt %. When the MW of PFPE blocks was 3400 or 1200, for the same bulk content of PFPE of about 8%, the surface showed a more limited excess of PFPE (about 46 and 30 wt % for MW 3400 and 1200 respectively). The segregation capability of PFPE blocks was also influenced by the length of polyester segments to which the PFPE blocks are bonded. So, when the fraction of PFPE bonded to very short segments of polyesters was extracted, the surface enrichment was reduced, and for a bulk composition of PFPE of about 6%, the surface amount of PFPE was of 15, 45, and 29% for PFPE with MW of 1200, 2200, and 3400, respectively. These data suggest that surface segregation depends on the MW of the initial PFPE and of the polyester segments bonded to PFPE after polymerization and that there is an optimum MW for PFPE surface segregation; the most favorable conditions are met for PFPE with MW 2200.

Introduction

The composition and the structure of the surface play an important role in those applications where properties such as adhesion, wettability, and biocompatibility are concerned. In such applications the modulation of the surface composition, in some cases specific and distinct from that of the bulk, is of paramount importance and its control is achieved through various means. The techniques used for this goal are plasma or flame treatment, chemical reactions, coating deposition, or incorporation of small molecules or additives.[1,2]

An alternative approach could be the preferential segregation at the polymer surface that is achieved when there are differences in the surface free energy of the components within a polymer or a polymer system. In this case, the lower surface energy segment resides near the polymer−air interface.[3−7]

Fluoropolymers have low surface energy (as an example, poly(tetrafluoroethylene) has a surface energy of 18.5 dyn/cm)[8] and therefore their presence in a polymer blend, or the introduction of a fluorinated segment in a block copolymer, will influence surface composition. Fluoropolymers also exhibit high thermal and thermal oxidative stability, chemical resistance, and low coefficient of friction.

The study of the surface composition, as a function of parameters such as bulk composition or structure and length of fluorinated segments, gives fundamental information to be used to control segregation processes.

In previous papers we have reported studies on polymeric products obtained using telechelic perfluoropolyethers (PFPE) in the polymerization of PET or PBT[9,10] with the aim of modifying some surface properties of these materials exploiting some specific characteristics of fluorinated products. In particular, the final aim of the introduction of PFPE in polyester chains was to take advantage of the spontaneous PFPE surface segregation for the enhancement of PET or PBT performances in all the applications where low coefficient of friction, low wettability, and superior chemical resistance are required. Predictable applications are in those fields, such as biomedical or in electric industry, where the surface properties play a leading role.

The recent availability of telechelic perfluoropolyethers with hydroxyl terminal groups (HO-R_H-PFPE-R_H-OH, where R_H stands for a hydrogenated ethylene oxide segment [$-CH_2CH_2O-$]) makes possible the preparation of fluorine-modified polyesters containing PFPE blocks. The HO-R_H-PFPE-R_H-OHs, which are characterized by a very low glass transition temperature (it ranges from −115 to −90 °C, according to the internal fluorinated chain length) can react, completely or in part, with the other comonomers and, depending on the extent of reaction and on the starting molecular weight,

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can segregate fluorinated blocks on the surface and allow a significant modification of the surface properties also to be obtained with a relatively small amount of PFPE in the bulk.

The study of polymer surfaces has been given considerable impetus by the use of "X-ray photoelectron spectroscopy" (XPS),[11,12] and we have reported[13,14] some results from studies by XPS and secondary ion mass spectrometry (SIMS) on series of PET polymers containing various amounts of a PFPE having M_n 2200 either simply blended, as a block in multiblock copolymers, or in a multiblock copolymer blended with PFPE. In all cases we observed a higher fluorine percentage on the surface with respect to the bulk composition. The results also showed that there was a decrease in the fluorine surface composition by decreasing the overall F wt % in the bulk, but for the same overall fluorine wight percent, there was an higher fluorine content on the surface when "free" PFPE was present.

To determine the influence of PFPE chain length on the surface composition, we have studied by XPS the surface of copolyesters having PFPE's blocks of different lengths, and the results are reported here. As the segregation effects previously observed for PET could have been affected by the crystallization of the PET segments, we prepared multiblock copolymers containing polyester segments consisting of iso/terephthalates random copolymers and PFPEs blocks in order to avoid effects of crystallization on the surface segregation of PFPE.

Experimental Section

Materials. Dimethyl terephthalate (DMT), dimethyl isophthalate (DMI), ethylene glycol (EG), and titanium tetrabutylate $Ti(OBu)_4$ were reagent-grade products used as supplied. The fluorinated macromers HO-R_H-PFPE-R_H-OH used to prepare the various samples were supplied by Ausimont (registered name Fomblin Z-DOL TX); they are liquids with the formula $H(OCH_2CH_2)_nOCH_2CF_2O(C_2F_4O)_p(CF_2O)_qCF_2CH_2O(CH_2CH_2O)_nH$, in which the copolymeric units $-(C_2F_4O)-$ and $-(CF_2O)-$, randomly distributed along the fluorinated chain, constitute the PFPE internal body where $p/q = 0.7-0.9$, while the short poly(ethylene oxide) chain (schematically R_H) is the end-capping segment containing the functional hydroxy groups; the average n value is close to 1.5 and $M_w/M_n = 1.8$. The number average molecular weight (by NMR) of the three fluorinated macromers used is 1200, 2200, and 3400.

The solvents, chloroform ($CHCl_3$) and 1,1,2-trichloro-1,2,2-trifluoroethane (TCTFE, supplied by Ausimont) were distilled before use and completely recovered.

Polymerization. The polymerizations were carried out by the usual two-stage process in a stainless steel reactor, equipped with a paddle agitator. DMT (200 g), DMI (200 g), and EG (281 g) and Fomblin Z-DOL TX (44.8 g) were reacted in the presence of $Ti(OBu)_4$ (0.4 g, 0.1 % wt/wt with respect to (DMT + DMI)) as catalyst. The first stage (esterinterchange) was carried out at atmospheric pressure with the temperature maintained at 193−197 °C; during the second stage (polycondensation), the temperature was raised and maintained at 255−257 °C, under reduced pressure (about 1 mbar). Polymerizations were carried out using Fomblin Z-DOL TX of different molecular weights under the conditions reported in Table 1. Fomblin Z-DOL TX was added before starting the first stage, when both the temperature and viscosity of the medium were low.

A copolyester control sample was obtained by polymerization of ethylene glycol and DMT and DMI under the same conditions in the absence of HO-R_H-PFPE-R_H-OH.

Crude products obtained after polymerization were submitted to extractions both for preparing new samples for XPS measurements and for a better characterization of the chemical nature of PFPE after polymerization.

Table 1. Reactants Used for Polymerization[a]

			polymerization conditions			
			first stage		second stage	
	Fomblin Z-DOL TX					
sample	MW	G (wt %)	time (min)	T (°C)	time (min)	T (°C)
1	1200	44.8 (10)	78	193	128	255
2	2200	44.5 (10)	93	195	103	257
3	3400	44.6 (10)	89	197	122	255

[a] $Ti(OBu)_4$ (0.4 g) was used as catalyst (0.1% wt/wt with respect to DMT + DMI).

Characterization. All products before and after extraction were characterized by FTIR and ^1H NMR spectroscopy, intrinsic viscosity, SEC, DSC, and fluorine elemental analysis.

Extractions. A fraction of PFPE unreacted or bonded to very short segments of polyester ("free" PFPE) can be present in the crude samples and it may behave in a different way than PFPE blocks bonded to long polyester segments, with respect to surface segregation. For this reason extraction of the free PFPE was carried out by exploiting the different solubility of PFPE and polyester. The extraction of free PFPE was carried out by dissolving at room temperature 2 g of the samples in 30 mL of dry $CHCl_3$ and adding the resulting solution to about 150 mL of TCTFE. The precipitate was separated by filtration and was again dissolved with $CHCl_3$ and reprecipitated with TCTFE; fractions recovered after this treatment by filtration and by evaporating the solvent from the solution are hereinafter called first precipitate and first extract, respectively.

For a better characterization of the chemical nature of PFPE extracted with the procedure described above, a further extraction was carried out on the first extract. About 100 mg was stirred with TCTFE (4 mL) and a second extract was obtained by evaporating the solvent from the liquid recovered after filtration.

Measurements. FTIR spectra were recorded with a Brucker IFS 48.

^1H NMR spectra were recorded on a 300 MHz Variant instrument usually from TCTFE/$CDCl_3$ solutions, due to the poor solubility of PFPE in the presence of the common deuterated solvents.

DSC curves were recorded with a DSC Perkin-Elmer Series 7 instrument on about 12 mg of sample. The value of glass transition was obtained from curves recorded at 20 °C/min as the midpoint in the second run. Some annealing tests were carried out at 90 °C for 8 h on films, from samples before and after extraction, cast with the same procedure used to prepare films for XPS measurements.

SEC was carried out using three PLGel columns (10^4, 10^3, and 500 Å), $CHCl_3$ as solvent (eluted at 0.6 mL/min), and UV detection. Curves were recorded for crude products and the first precipitate and extract.

Intrinsic viscosity was calculated on the basis of viscosity measurements of diluted solutions by Ubbelhode viscometers from $CHCl_3$ solutions at 30 °C.

XPS measurements. All specimens used for surface analysis were prepared by casting films from chloroform solutions (1 wt %) onto aluminum foil.

The XPS measurements were carried out on the air-side surface with a VG Instrument electron spectrometer using a Mg $K\alpha_{1,2}$ X-ray source (1253.6 eV). The X-ray source in the standard conditions had been working at 100 W, 10 kV, and 10 mA. The base pressure of the instrument was 5×10^{-10} Torr, and an operating pressure of 2×10^{-8} Torr was typically used. A pass energy of 100, 50, and 20 eV was used for wide scans, narrow scans, and curve fitting, respectively. All data analyses (linear background subtraction, peak integration, and curve fitting) were accomplished using the Peakfit 4 (Jandel Scientific) software. Binding energies were referenced to the C−H level at 285.0 eV. The electron takeoff angle with respect

Table 2. Surface Composition of Samples 1−3 Before and After Extraction

			F_{1S}/C_{1S}	
sample	wt % PFPE[a] (bulk)	bulk F/C	90° [wt % PFPE]	30° [wt % PFPE]
1	7.9	0.044	0.096 [16]	0.20 [30]
2	8.0	0.049	0.92 [78]	1.44 [94]
3	7.8	0.049	0.25 [33]	0.40 [46]
1a[b]	6.6	0.037	0.066 [11]	0.090 [15]
2a[b]	6.2	0.037	0.21[29]	0.37 [45]
3a[b]	6.0	0.037	0.16 [23]	0.21 [29]

[a] Evaluated by elemental analysis of fluorine. [b] Residual after extraction of nonbonded PFPE from the parent samples.

to the sample surface was 90°. Angular dependent studies were also performed, in which the electron takeoff angle was 30°.

Results and Discussion

Product Characterization. Three different samples of poly(ethylene-iso/terephthalate)perfluoro polyether multiblock copolymers were prepared having the PFPE blocks with M_n of about 1200 (sample **1**), 2200 (sample **2**) and 3400 (sample **3**), respectively. The polymerizations were carried out (see the Experimental Section) by a two-stage process, using $Ti(BuO)_4$ as catalyst and feeding the reaction with a 10 wt % of PFPE (Table 1). The average molecular weight of the products obtained was quite high, as attested by values of intrinsic viscosity ranging from 0.64 to 0.72 dL/g.

As $Ti(BuO)_4$ is a very efficient catalyst toward ester−ester exchange reactions, it was expected that terephthalate and isophthalate units were randomly distributed along the polyester segments and that the most probable molecular weight distribution was approached. Indeed, NMR spectra, SEC curves, and DSC traces were consistent with this expectation.

The overall amount of PFPE present in the resulting products was evaluated by fluorine elemental analysis. The results showed a lower PFPE content in the bulk with respect to the one that could be forecast from feeding (Tables 1 and 2); the loss of about 20% of the initial amount of PFPE during polymerization is in agreement with previous results.[9,10]

As HO-R_H-PFPE-R_H-OHs have only a limited solubility in the reaction medium, during polymerization a large part of the fluorinated macromers stays in fluorine-rich domains where they can react with monomers soluble in that phase and less probably with polyester chains at the interface. Therefore in the crude products obtained, PFPE can be unreacted or bonded to very short segments of polyester (just few monomeric units, as previously observed for PET and PBT)[9,10] or to long polyester segments.

The fraction unreacted or bonded to very short polyester segments ("free" PFPE) is expected to have higher mobility and lower solubility than the PFPE blocks bonded to long polyester segments. To achieve information about the contribution of free PFPE to the PFPE surface enrichment, we extracted it by exploiting the very different solubility of PFPE and polyesters in TCTFE.

For all samples about 90−95 wt % of the crude product was recovered after reprecipitation in TCTFE from a chloroform solution (see the Experimental Section).

From ^1H NMR spectroscopy, about 80 wt % of the extracted fraction was attributable to polyester moieties (with a molar ratio of terephthalate to isophthalate units 1:1, as in the feed); the remaining 20 wt % of the extracted fraction was PFPE (about 20−25 wt % of the amount of PFPE present in the crude product, see Table 2, F content in samples **1**−**3** and **1a**−**3a**).

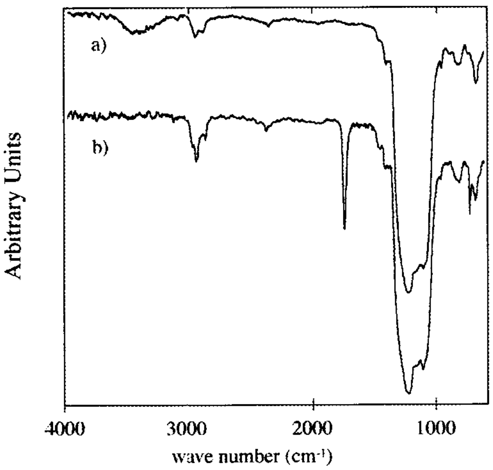

Figure 1. FTIR spectra of (a) Fomblin ZDOLTX 2200, (b) sample **2**, second extract.

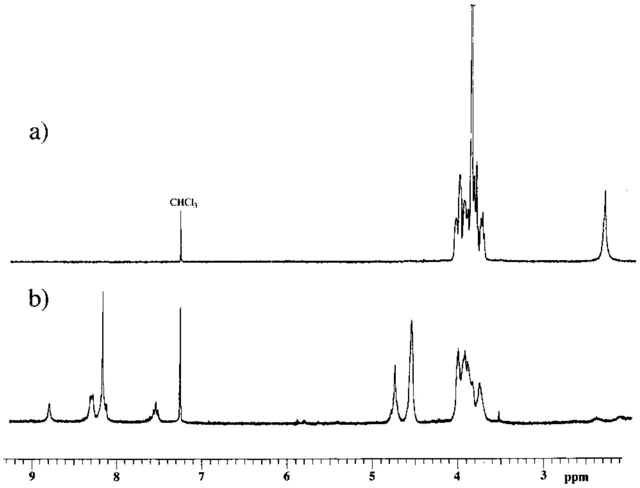

Figure 2. ^1H NMR spectra of (a) Fomblin Z-DOL TX, (b) sample **2**, second extract.

Polyester moieties in the extracted fraction can belong to oligomers or to polyester segments which became soluble in TCTFE being linked to PFPE segments. On the other hand, PFPE in the extracted fraction can derive from unreacted PFPE or PFPE bonded to short polyester segments. To achieve more information about the chemical nature of the polyester and PFPE extracted from the crude products, a second extraction with TCTFE was carried out (see the Experimental Section). Almost all PFPE present in the first extract was contained in the fraction soluble in TCTFE, as revealed by IR and ^1H NMR analysis of the fractions collected after this second extraction.

The IR spectra typical of the starting PFPE macromers (a) and of the corresponding products recovered as fraction soluble in TCTFE after the second extraction (b) are shown in Figure 1; the main features of spectrum b are the absence of the OH band at 3400 cm^{-1} and the presence of the carbonyl−ester band at 1724 cm^{-1}. Typical ^1H NMR spectra of the same products are shown in Figure 2 (a and b); from the intensity ratio of the peak at 4.5 ppm (−CH_2− of PFPE adjacent to an ester group)

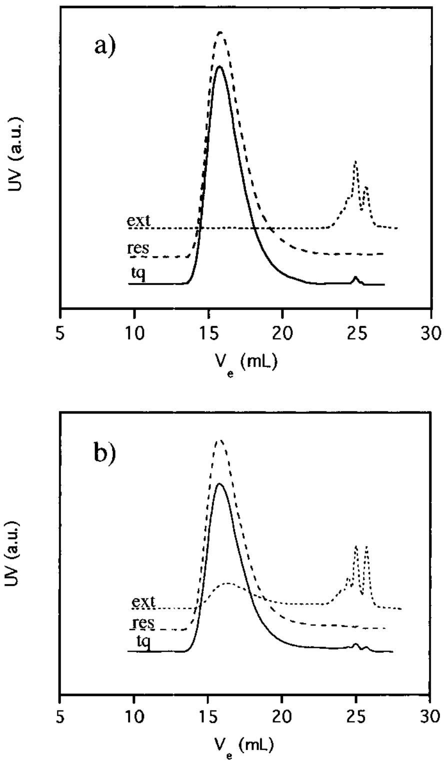

Figure 3. (a) SEC curves obtained from a copolyester prepared as control: (tq) crude copolyester, (res) first precipitate, and (ext) first extract. (b) SEC curves obtained from samples **2**: (tq) crude copolyester, (res) first precipitate (sample 2a), and (ext) first extract.

with the complex signals of the hydrogenated moieties of PFPE (peaks at 3.7−4.0 ppm) it can be concluded that all the −OH terminal groups of PFPE have reacted. Furthermore, assuming that all aromatic and ethylene glycol moieties of this fraction are bonded to PFPE blocks, from the intensity ratios of peaks typical of PFPE and of aromatic (7.5−8.9 ppm) and ethylene glycol (4.7 ppm) units it is possible to derive information about the average number of aromatic units per block of PFPE. It appears that the average length of the polyester segments bonded to PFPE blocks is about 1.5. By considering that all OH terminal groups of HO-R_H-PFPE-R_H-OH have reacted and that the OH band is not detectable in the IR spectrum, we can conclude that most PFPE is present in the extracted fraction as macrocycles, with aromatic units joining terminal groups of PFPE.

This conclusion seems also supported by SEC curves (Figure 3 a and b). Figure 3a shows the SEC curves of the copolyester used as control (tq) and of the fraction (ext) extracted from it by the same procedure used to extract free PFPE. Figure 3b shows the SEC curves of sample **2**: the crude products from polymerization (tq), the first precipitate (res), and first extract (ext). It appears that, for the copolyester alone, the extracted fraction consists only of oligomers, while for sample **2** in the first extract a second peak at higher molecular weight is present along with a peak similar to that of oligoesters extracted from the control. It has also to be noted that the molecular weight distributions of the samples before (tq) and after extraction (res) are almost identical.

Therefore, we can conclude that after the samples were submitted to extraction treatment the new samples (**1a**−**3a**) have a composition which is different from that of the crude products because free PFPE (about 25 wt % of the PFPE in the crude samples) and oligoesters (about 4−5 wt % of the crude sample) were extracted.

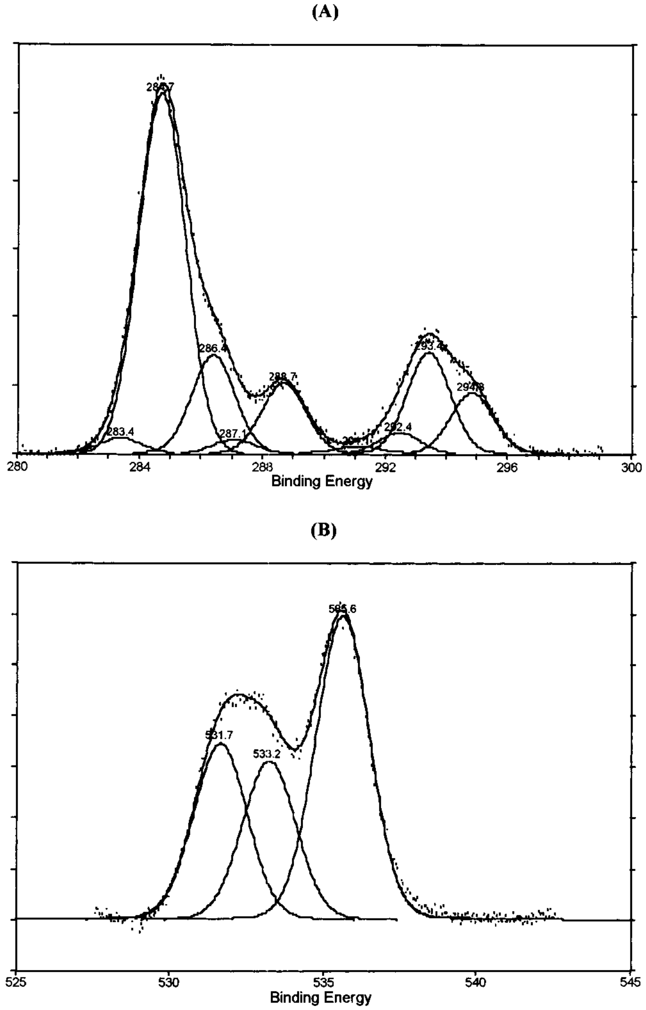

Figure 4. C_{1s} (A) and O_{1s} (B) envelopes of sample **2**.

XPS Measurements. Due to the good solubility in chloroform of the obtained copolymers, films for XPS analysis were cast from solution. After casting, all resulting samples were amorphous by the DSC analysis, with the same glass transition temperature of 68 ± 1 °C for all samples before and after extraction, in good agreement with the value expected for random copolyester containing a 1:1 molar ratio of terephthalate and isophthalate units from the literature values[15] of T_gs for PET and poly(ethylene isophthalate) (PEI). No crystallization was observed, even after long annealing times at 100 °C.

To determine the effect of length of PFPE block on surface segregation, we studied the air-side surface composition by XPS. The quantitative XPS analysis of the samples was carried out by the determination of F_{1s} and C_{1s} areas obtained by multiplying the experimental values with the appropriate sensitivity factor.

To get information on the presence of a concentration gradient of the PFPE blocks in the outer layers, angular dependent measurements were also carried out. The takeoff angles of the analyzed photoelectrons were 90° and 30°. Since the higher the takeoff angle is, the deeper the layer analyzed, by comparing the results it is possible to estimate the depth profile of the PFPE.

The XPS measurements showed the photoionization peaks of carbon, oxygen, and fluorine in the wide scans.

No peak attributable to the aluminum substrate was detected, indicating that the film thickness was higher than the probing depth. As expected, the C_{1s} envelope had three prominent photoionization peaks. The first is attributable to the CH plus CO functionalities and a variable amount of hydrocarbon contamination, the second arises from the carboxylate functionality, and the third is indicative of the CF_2 and C_2F_4 functionalities (Figure 4). In particular, the curve-fitting analysis evidenced the presence of seven main peaks centered respectively at 284.7 eV (aromatic hydrocarbons), 286.4 eV ($-\mathit{C}H_2OC(O)-$), 288.7 eV ($-CH_2O\mathit{C}(O)-$), 291.1 eV ($\pi \rightarrow \pi^*$), 292.4 eV ($OCH_2\mathit{C}F_2O$), 293.4 eV ($-OC_2F_4-$), and 294.8 eV ($-OCF_2-$). The O_{1s} envelope was roughly fitted with three main peaks centered respectively at 531.7 eV ($OC{=}\mathit{O}$), 533.2 eV ($\mathit{O}C{=}O$), and 535.6 eV ($\mathit{O}CF_2$), while the photoelectrons arising from the F_{1s} level showed a peak centered at 689 eV.

The comparison of the area deriving from the component centered at 288.7 eV with that of the large C_{1s} contribution due to hydrocarbon functionalities (284.7 eV) showed that in all cases a variable amount of hydrocarbon contamination was present. This contamination is frequently observed in studying polymer surfaces by XPS. It almost certainly comes from the X-ray gun windows or casing being in close proximity to the sample,[12] and routinely working with polymers increases the problem because the spectrometer working pressure is usually significantly greater than base pressure. It affects quantification and the C_{1s} profile directly unless its contribution is eliminated. The procedure used was based on the theoretical area ratio between the contribution centered at 284.7 eV and that centered at 288.7 eV. In the absence of contamination, the area ratio would have been 3:1. Therefore, to have the area of the C_{1s} envelope due to the original samples only, the experimental C_{1s} area was then corrected in accord with the following formula:

$$\mathrm{CA} = A_{\mathrm{tot}} - [A_{\mathrm{H}} - (3A_{\mathrm{C}})]$$

where CA is the corrected C_{1s} area, A_{tot} is the experimental C_{1s} area, A_{H} is the experimental contribution of the peak centered at 284.7 eV, and A_{C} is the experimental contribution of the peak centered at 288.7 eV.

We have already reported[13,14] that in analogous systems a surface enrichment of fluorine blocks was observed and that the surface composition was dependent on the overall amount of PFPE and on the amount of free PFPE, extractable by a dissolution−reprecipitation treatment. For this reason, XPS measurements were carried out on samples before (samples **1**−**3**) and after (samples **1a**−**3a**) extraction.

The results (Table 2) showed that samples **2** and **3** (M_n 2200 and 3400, respectively) had actual surface F_{1s}/C_{1s} area ratios much higher than expected from the bulk composition while sample **1** had surface area ratio closer to the stoichiometric value.

From the corrected F_{1s}/C_{1s} area ratio it was possible to calculate the surface weight percent of PFPE blocks using the following equation:

$$\frac{I_{\mathrm{F1s}}}{I_{\mathrm{C1s}}} = \frac{\dfrac{FW}{M_{\mathrm{F}}}}{\dfrac{C_{\mathrm{F}}W}{M_{\mathrm{F}}} + \dfrac{C_{\mathrm{P}}(100 - \mathrm{W})}{M_{\mathrm{P}}}}$$

where F is the average number of fluorine atoms present in one block of PFPE (33.7, 66.3, and 105.5 for Fomblin 1200, 2200, and 3400, respectively), W is the surface weight percent of PFPE, C_{F} is the average number of carbon atoms present in one block of PFPE (22.9, 39.2, and 58.7 for Fomblin 1200, 2200, and 3400 respectively), C_{P} is the number of carbon atoms present in the repeat unit of PET/PEI (10), M_{F} and M_{P} are the starting PFPE molecular weight and the PET/PEI repeat-unit molecular weight, respectively ($M_{\mathrm{F}} = 1200$, 2200, 3400 and $M_{\mathrm{P}} = 192$).

Moreover a depth profiling of the PFPE abundance was calculated, considering that the sampling depth depends on the takeoff angle of emitted photoelectrons as $d_{\mathrm{i}} = 3\lambda \sin \theta$ where d_{i} is the sampling depth, λ is the inelastic mean free path (IMFP) of emitted photoelectrons, and θ is the takeoff angle. In this way, taking into account the IMFP reported in the literature[16] for the F_{1s} photoelectrons ($\lambda = 1$ nm), the calculations gave information on the mean composition of layers of 3 nm for takeoff angle of 90° and 1.5 nm for takeoff angle of 30°.

From the calculations it was found that in the crude copolymer **2** the amount of PFPE was 78% by weight in the 3 nm thick layer and it reached 94% by weight moving toward the outermost layers. An excess of PFPE was detected also in the outer layers of the crude copolymer **3** (from 33 wt % in the 3 nm layer to 46 wt % in the outermost layer). In the copolymer **1**, having the PFPE blocks with lower MW, an excess of fluorine moieties is still present at the surface, but at a lower extent (from 16 to 30 wt %).

The crude samples obtained from polymerization contain macromolecules that are different for MW, the relative weight of polyester segments, and the length of the PFPE segments. As a consequence, a fraction of macromolecules having a high content of PFPE (free PFPE, bonded to very short polyester segments or unreacted) exists and can be responsible of the observed high concentration of fluorine on the surface. To eliminate the surface fluorine enrichment due to this fraction, we performed additional measurements on samples after extraction of free PFPE. The resulting samples (indicated with **a** in Table 2) showed a surface fluorine concentration lower with respect to the crude ones than expected from the decrease of the overall fluorine concentration. In particular, the amount of PFPE calculated in sample **3a** at takeoff angle of 90° is 23 wt %, while at 30° is 29%. In sample **2a**, the PFPE amount is 29% and 45% at 90° and 30°, respectively. As the concentration of fluorine on the surface decreased after the extraction treatment, we have to conclude that a significant contribution to the surface segregation in the crude samples derived from the free PFPE. However, both samples **2a** and **3a** still had a much higher surface fluorine concentration with respect to the bulk composition and angular dependent XPS data indicate that a significant excess of PFPE is commonly present within 1.5 nm of the surface and the presence of a concentration gradient suggests that the iso/terephthalate segments are largely, if not completely, excluded from outermost layers. Sample **1a** showed a PFPE amount calculated to be 11% at 90° and 15% at 30°, closer to that of the bulk composition than observed for samples **2a** and **3a**, suggesting that a PFPE block with a M_n of 1200 has a chain length close to a critical value that reduce the driving force for surface segregation of PFPE blocks. It is also interesting to note that the fluorine concentration on the surface in the case of samples **3** and **3a** is lower than for sample **2** and **2a**. This suggests that under the conditions of film formation used in this study there is an optimum molecular weight of the PFPE blocks for segregation. The low tendency to migration onto the surface observed for PFPE 1200 can be explained by its higher solubility with the polyester segments that reduces the driving force for migration, but it is quite strange that PFPE with M_n 3400 migrate onto the surface less easily than PFPE with M_n 2200. We can speculate that as the average length of the PFPE blocks becomes higher, there is a decrease of the number of blocks (for the same PFPE weight %) and an easier segregation of the PFPE segments in distinct PFPE domains in the bulk which limit the mobility of the PFPE blocks with respect to diffusion onto the surface.

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