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High resolution XPS investigation of photocured films containing perfluoropolyether acrylates

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Abstract

The paper reports an XPS investigation on films obtained by photopolymerising new perfluoropolyether methacrylates as pure products or added in low amounts to a typical UV-curable resin (Bisphenol A bis-ethylether diacrylate). The structure of the fluorinated monomers is Rf–Rh type, where Rh = $-CH_2O-CO-NH-CH_2-CH_2-OCOC(CH_3)=CH_2$ while Rf = $CF_3-CF_2O-(CF_2O)_n(CF_2-CF_2O)_m-CF_2-$ for monomer **1** (PM 890, $m/n = 1.68$), and Rf = $Cl-CF_2-CF(CF_3)-O-(CF_2CF(CF_3)-O)_2-CF_2-$ for monomer **2**. Quantitative evaluation of the different atomic ratios was performed using take-off angles of 45 and 10° (very surface region) on both film sides, the one in contact with the glass substrate and the one exposed to air. The results obtained indicate strong fluorine enrichment on the air side of the films and a concentration gradient at the surface, while the glass side has a composition similar to the bulk. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The surface properties of polymers are of crucial importance in many applications, due to their strong influence on the wetting, the coating, the frictional behaviour, and adhesion characteristics of the materials. It is often desirable to combine the bulk properties of the polymers with specific surface properties. This effect can be obtained by different surface modification techniques, which modify the structure of a thin layer of the material without affecting the bulk. A method for achieving such results, especially in the case of films, is the addition of surface-active monomers to the polymerisable systems. In fact, a new surface layer is rapidly formed due to the fast diffusion of the monomers through the bulk of the film: when the polymerisation process takes place, the monomers are chemically bonded and the surface is permanently modified. The surface activity of the monomers is dependent on their amphiphilic structure and in particular on the balance of hydrophobic–hydrophilic groups. The type, the dimension and the morphology of these groups influence the monomer behaviour. This feature is very important when the monomeric surfactants contain fluorinated structural units. In fact, for these systems the segregation is often so dramatic that the surface composition is completely different from the bulk, even at very low concentration [1].

In order to have a direct evaluation of the surface activity of the different monomers, one of the most suitable techniques is the X-ray photoelectron spectroscopy, which is widely employed for the characterisation of polymeric surfaces [2].

In previous papers we reported interesting XPS results, investigating acrylic polymeric films obtained by means of the UV-curing technique, modified by acrylic monomers containing perfluoroalkyl chains [3]. The monomer performance is enhanced by the replacement of the perfluoroalkyl group by a perfluoropolyether (PFPE) structure, due to the suppression of crystallisation and to the increase of the chain flexibility [4]. In another work we evaluated the behaviour of a linear PFPE chain of the type—$(CF_2O)_n(CF_2CF_2O)_m$—functionalised by two urethane methacrylic end groups [5].

Pursuing this research line, we investigated here two new fluorinated monomers (monomers **1** and **2**), which are characterised by a PFPE chain linked to one reactive group [6].

Monomer **1**, patented in 1997 [7], was selected in order to compare its behaviour with the homologous one having two

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Table 1
Samples composition of the prepared films (%w/w)

Sample	Monomer **1**	Monomer **2**	Monomer **3**	Photoinitiator
A	96.2			3.8
B		96.2		3.8
C	0.77		95.4	3.8
D		0.77	95.4	3.8

methacrylic functionalities; its structure is

$$\mathrm{CF_3–CF_2O–(CF_2O)_{\mathit{n}}(CF_2CF_2O)_{\mathit{m}}–CF_2– CH_2O–CO–NH–CH_2–CH_2–O–CO–C(CH_3)=CH_2} \quad (1)$$

Monomer **2** is derived from an oligoperfluoropropylenoxide, which ends with a urethane methacrylic group on one side and by a chlorine atom on the other side. The chemical structure is

$$\mathrm{Cl–CF_2–CF(CF_3)–O–(CF_2CF(CF_3)–O)_2–CF_2–CH_2O–CO– NH–CH_2CH_2–O–CO–C(CH_3)=CH_2} \quad (2)$$

The presence of the chlorine could give indications on the disposition of the end group in the polymeric surface. Moreover this monomer is becoming very interesting from an industrial point of view as the process has a very high yield and selectivity [8].

In this paper high resolution XPS technique is employed for characterising the surfaces of the films obtained by copolymerising a typical hydrogenated resin with a low amount of monomers **1** and **2**. The surface composition of the films is reported and the influence of the monomer structure on such composition is discussed.

2. Experimental

2.1. Materials

The fluorinated monomers were synthesised by reaction of the corresponding perfluoropolyetheralcohols with isocyanateethylmethacrylate.

The molecular weight of monomer **1** is 1076 and $m/n = 1.68$. Monomer **2** contains 20% of the following isomer:

$$\mathrm{CF_3–CFCl–CF_2–O–(CF_2CF(CF_3)–O)_2–CF_2–CH_2O–CO– NH–CH_2–CH_2–O–CO–C(CH_3)=CH_2}$$

Details of the synthesis and characterisation are reported elsewhere [6–8].

As a hydrogenated resin, a typical UV-curable product was used, i.e. bisphenol A bis ethyletherdiacrylate, kindly supplied by UCB, Belgium, referred to as monomer **3**.

2,2-Dimethoxy-2-phenylacetophenone, used as photoinitiator, was added to the oligomers at a concentration of 3.8%w/w.

2.2. Film preparation

Four films (A–D) were prepared by radical photopolymerisation, initiated by UV irradiation. The composition of the films is reported in Table 1. The curable mixtures were coated on glass slides by using a calibrated wire-wound applicator. The glass substrates were carefully cleaned before being used. The cleaning procedure was the following: washing with nitric acid, rinsing with water, finally washing with acetone. The surface wettability after the washing cycle was always less than 10°.

The curing reaction was performed in a small box equipped with a quartz window under nitrogen atmosphere by UV irradiation with a 500 W medium pressure Hg lamp. The light intensity at the film surface was 12 mW cm^{-2}. The IR radiation was screened by water, flowing in a quartz jacket by which the lamp is protected. The UV exposure time was 45″ and was controlled by means of a camera shutter.

The curing reaction was monitored by FTIR analysis, controlling the disappearance of the methacrylic double bond ($\nu = 1650\ \mathrm{cm}^{-1}$).

Films A and B were not detachable from the substrate. Films C and D were gently peeled off the glass slide: the side in contact with the substrate is labelled as the glass side; the opposite one as the air side.

2.3. XPS characterisation

XPS spectra were recorded using a SCIENTIA ESCA 300 spectrometer. This combines a high-power rotating anode and a monochromatised $\mathrm{AlK_\alpha}$ X-ray source ($h\nu = 1486.6$) with high transmission electron optics and a multichannel detector [9,10]. Efficient pumping by liquid nitrogen trapped diffusion pumps on the sample analysis chamber, electrostatic lens column and hemispherical analyses/detector were available. Charge compensation for insulating samples was achieved with a low energy electron flood gun. The adjustment of flood gun settings for optimum charge compensation and examples of the resulting high resolution polymer spectra which can be obtained with an ESCA 300 Spectrometer have been already described [10].

The survey and core line spectra were recorded for each sample at an X-ray source power of 2.8 kW. Survey Spectra were acquired at 300 eV pass energy and 1.9 mm slitwidth, core lines at 150 eV pass energy, 0.5 slitwidth. Under these conditions the instrument resolution is 1.0 and 0.32, respectively [11]. For core lines a step internal of 0.05 eV was used. Typical acquisition times were around 40 min for a set of survey, $\mathrm{C_{1s}}$, $\mathrm{O_{1s}}$, $\mathrm{N_{1s}}$, and $\mathrm{F_{1s}}$ regions. The electron take-off angles (t.o.a) selected for the analyses were 45 and 10° relative to the sample surface. With typical flood gun settings charging was minimal and spectra were referenced to the main $\mathrm{C_{1s}}$ component at 285 eV.

Table 2
Surface composition of the UV-cured films (air side)

Sample	O_{1s}/C_{1s}	N_{1s}/C_{1s}	F_{1s}/C_{1s}	Cl_{2p}/C_{1s}
A[a]	0.60	0.037	1.43	–
A[b]	0.53	0.050	1.37	–
A[c]	0.54	0.030	1.78	–
B[a]	0.33	0.055	1.11	0.055
B[b]	0.39	0.066	1.05	0.038
B[c]	0.35	0.024	1.26	0.040
C[a]	0.24	0.0003	0.012	–
C[b]	0.49	0.020	1.11	–
C[c]	0.54	0.013	1.70	–
D[a]	0.24	0.0003	0.0066	0.0003
D[b]	0.34	0.016	0.39	0.008
D[c]	0.34	0.012	0.94	0.021

[a] Calculated values.

[b] Experimental values obtained for the spectra carried out using a take-off angle of 45°.

[c] Experimental values obtained for the spectra carried out using a take-off angle of 10°.

3. Results and discussion

The XPS spectra were performed on the two sides of the films (air side and glass side), when it was possible to detach them from the substrate. The results obtained are reported below and discussed separately for each surface.

The quantitative evaluation of the spectra was carried out by determining the areas of the C_{1s}, F_{1s}, O_{1s}, N_{1s} and Cl_{2p} peaks and multiplying them for the appropriate sensitivity factors: the results, presented in Tables 2 and 3, are reported in terms of the atomic ratios and compared with the calculated values.

The curve fitting of the C_{1s} envelope was also performed, resolving the contributions of the different bond and calculating the integrated areas under each peak (Table 4). The integrated intensity ratios identify the amounts of the carbon atoms having different chemical environment. In fact the intensity of the core-electrons photoemission spectrum is proportional to the number of atoms per unit sample volume and to the sensitivity factor, which is approximately identical for the carbon atoms in the different chemical environments.

Table 3
Deconvolution contributions of the spectra of the UV-cured films (air side)

Sample	C_{1s} (%)				
	C	O	F	N	Cl
A[a]	29.2	28.5	39.8	2.4	
A[b]	33.8	18.1	46.4	1.7	
A[c]	29.8	16.2	53.2	0.9	
B[a]	38.6	21.0	35.0	3.5	1.7
B[b]	39.3	15.2	41.4	2.6	1.5
B[c]	37.0	12.9	46.6	1.9	1.5
C[a]	85.6	13.9	0.004	0.0003	
C[b]	38.2	18.6	42.4	0.8	
C[c]	30.7	16.7	52.2	0.4	
D[a]	83.3	16.4	0.003	0.0003	0.0002
D[b]	57.0	19.3	22.2	0.9	0.5
D[c]	43.2	14.5	40.5	0.9	0.9

[a] Calculated values.

[b] Experimental values obtained for the spectra carried out using a take-off angle of 45°.

[c] Experimental values obtained for the spectra carried out using a take-off angle of 10°.

3.1. Air side

The survey ESCA spectra of the films unremoved from the glass plate, obtained with the two different take-off angles of 45 and 10°, reveal, as expected, the photoelectronic peaks of carbon, nitrogen, oxygen and fluorine for samples A and C as well as the presence of an additional chlorine peak for samples B and D.

As an example, the ESCA spectrum of sample A, reported in Figs. 1 and 2, reveals the typical C_{1s}, O_{1s}, N_{1s} and F_{1s} core levels both in the cases of a take-off angle of 45° (surface) and 10° (very surface), respectively.

The quantitative data obtained from the spectrum of sample A at the highest take-off angle, i.e. analysing the deeper layers (Table 2), are very similar to the calculated ones. The composition at that depth corresponds to the bulk composition.

At a take-off angle of 10°, i.e. in the very external surface, the F_{1s}/C_{1s} ratio is higher than the bulk one, showing an increase of the fluorine content at the very surface of the film.

The shoulder at high binding energy of the CF_2 peak (Figs. 1 and 2) represents the CF_3. It increases on going from 45 to 10° take-off-angle because the PFPE side chains are oriented towards the surface. The CF_3 group is the uppermost group, i.e. the closest to the surface and above the CF_2 groups. Hence CF_3 increases relative to CF_2 on going to low take-off-angles. This effect is well known in oriented perfluoro chains [12]. Any possible surface roughness would have the effect of reducing the surface sensitivity of the low take-off-angle measurements. However, polymer films as we have prepared, are expected to be sufficiently smooth to give good angle dependent data. The data for sample B reveal similar features as sample A.

The composition of sample C is very different from the calculated one: there is an increase of the oxygen and nitrogen content and a dramatic enrichment of fluorine, as the F_{1s}/C_{1s} ratio is two order of magnitudes higher than the bulk value. Moreover varying the take-off angle a clear gradient in the concentration of oxygen, nitrogen and fluorine elements is observed: going from a take-off angle of 45 to 10°, the fluorine concentration increases, while the nitrogen amount decreases. Since the sample C has a copolymeric structure containing the monomer **1**, an interesting result comes from the comparison of its outermost layers with that of sample A. Since the experimental O_{1s}/C_{1s} and F_{1s}/C_{1s} ratios of sample C are very similar to those of sample

Table 4
Surface composition of the UV-cured films (glass side)

Sample	O_{1s}/C_{1s}	N_{1s}/C_{1s}	F_{1s}/C_{1s}	Cl_{2p}/C_{1s}
C[a]	0.24	0.0003	0.012	
C[b]	0.32	0.010	0.17	–
C[c]	0.30	0.014	0.27	–
D[a]	0.24	0.0003	0.0066	0.0003
D[b]	0.29	0.011	0.08	0.0042
D[c]	0.28	0.013	0.12	0.0042

[a] Calculated values.

[b] Experimental values obtained for the spectra carried out using a take-off angle of 45°.

[c] Experimental values obtained for the spectra carried out using a take-off angle of 10°.

A, the surface of the copolymeric network is mainly composed of the fluorinated monomer.

Another comparison can be made with the acrylic films containing a PFPE chain identical to monomer **1** both in structure and in molecular weight, but having two reactive end groups. As described in Ref. [5], the presence of the difunctional oligomer gives rise on the air side of the film to the same segregation phenomenon observed with monomer **1**. However, considering the same bulk concentration of the fluorinated molecule and comparing the ESCA spectra recorded in similar conditions, the F_{1s}/C_{1s} ratio obtained in the presence of the difunctional oligomer is lower than in the case of the monofunctional monomer. Similar results are obtained by using a difunctional oligomer with a longer PFPE chain. This confirms that when the fluorinated chain is freely dangling from the polymeric network it is more surface active than when is inserted in the main polymeric backbone.

The analysis of sample D also shows a surface segregation of the fluorinated comonomer, but the comparison of the atomic ratios with the homologous data of the homopolymer B suggests that at the film surface the hydrogenated and the fluorinated structures coexist. At the very surface of the film there is also a concentration of chlorine higher than expected: as the chlorine atom is bound to the carbon of the methyl end group of monomer **2**, we can supposed that its PFPE chain is extended toward the exterior.

The surface composition was also determined by curve fitting the various spectra. In all the cases the C_{1s} peak results from three main components, corresponding to aliphatic carbon atoms, to the α-carbon atoms and to the CF_2 and CF_3 groups. The C_{1s} deconvolution components are reported in Table 4.

It can be observed that the C–O bonds evaluation in the films A and B gives lower values than expected: it could be due to the peculiar characteristics of the C–O bond in the perfluoropolyether structures, in which the ether character is

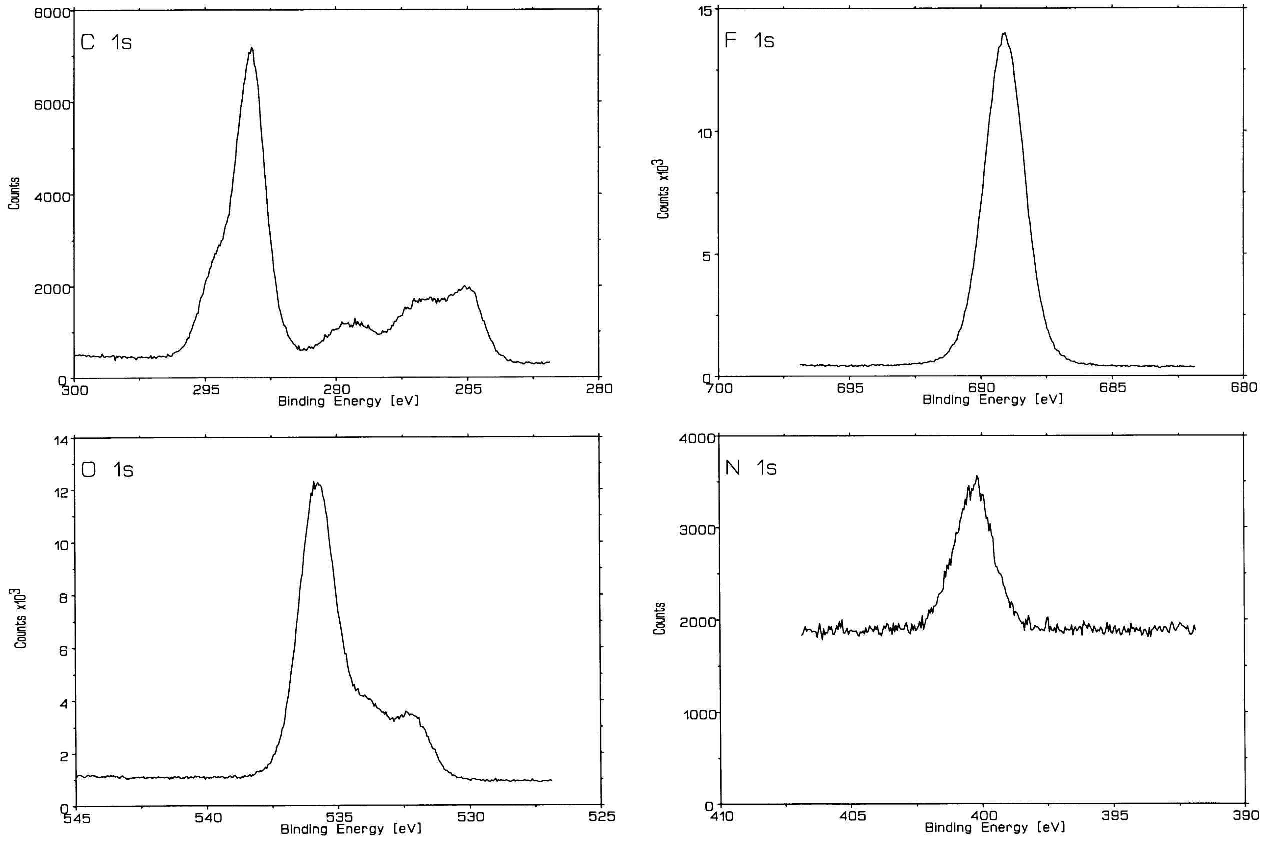

Fig. 1. The ESCA spectrum of sample A, obtained with a take-off angle of 45°.

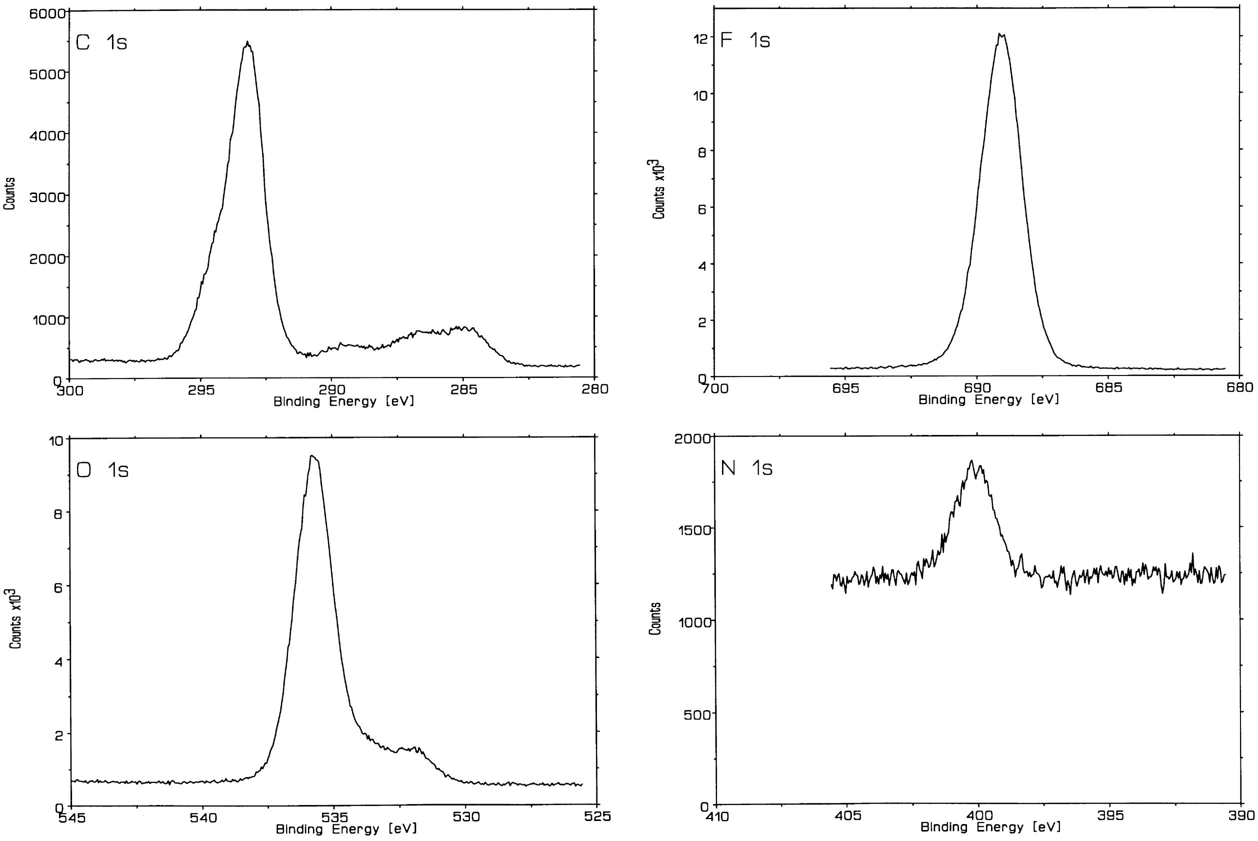

Fig. 2. The ESCA spectrum of sample A, obtained with a take-off angle of 10°.

strongly decreased by the electron attracting effect of the perfluoroalkylenic groups [13].

For sample C the composition is very close to that of the homopolymeric film A, as reported before when considering the spectrum at take-off angle = 10°.

In the case of sample D the data are in agreement with the atomic ratios previously discussed and are consistent with a composition which is the average of the calculated one and the composition of the pure fluorinated monomer. Therefore the surface is made of the hydrogenated resin with a high percentage of the fluorinated additive. This can be calculated on the basis of the CF contribution and corresponds to 54%w/w at take-off angle of 45° and to 87%w/w at take-off angle = 10°.

It is interesting to note the difference between the spectra taken with a take-off angle of 45° (surface) and the spectra recorded at a take-off angle of 10° (very surface). In fact, it is evident that in the second ones there is an increase of the CF_2 and CF_3 contributions in the C_{1s} peak, indicating an enrichment of fluorine in the very surface of the material.

3.2. Glass side

Samples C and D were gently removed from the glass substrate and the hidden surface was analysed. The data are reported in Table 3. There is a small enrichment of fluorine and nitrogen in the most external layer. In the case of sample D there is also an increase of the chlorine content.

This enrichment is negligible compared to the air side. This behaviour was already found in other systems containing fluorinated monomers: it confirms that the surface composition of films coated onto a polar substrate as glass is different from the air side composition, as a consequence of the interfacial energy minimisation [4–6]. The enrichment that is however observed could be due to the molecular rearrangement of the surface once exposed to the air after the film was removed from the substrate.

We can exclude that such results are caused by a removal of some contamination from the glass surface because if the polymer surface peeled from the polymer glass interface was heavily contaminated with an overlayer of material picked from the glass surface the F/C ratio would be expected to decrease on going from 45 to 10° take-off angle. On the contrary, the F_{1s}/C_{1s} ratio increases showing that the surface is not seriously contaminated.

4. Conclusions

The experimental O_{1s}/C_{1s}, N_{1s}/C_{1s} and, particularly the F_{1s}/C_{1s} area ratios of the XPS spectra of the samples investigated are higher than the calculated values, indicating a greater concentration of the fluorinated moiety in the surface of the materials. The different values of the area ratios (take-off angles of 45 or 10°) indicate that the outer 50 Å are not homogeneous, with a greater concentration of the fluorinated block in the very surface region (20 Å). This surface segregation is dramatic when the film is copolymeric (samples C and D): in this case the fluorinated moiety is by far the most abundant on the surface even when its percentage in the bulk is very low.

The confirmation of such a real surface segregation is that the XPS data on samples A and B at 45° take-off angle are very close to the expected composition by considering the amount of materials used in the reactive mixture.

It is evident that monomers **1** and **2** behave as surfactants and tend to concentrate at the polymer–air interface, lowering the polymer surface energy. Their relative surface activity is in agreement with the length of the fluorinated chain and its structure.

The composition of the surface in contact with the glass substrate is very similar to the bulk composition, confirming the absence of the monomer enrichment on polar substrates.

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