

# Fluorinated Acrylic Polymers: Surface Properties and XPS Investigations

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**ABSTRACT:** A series of polymers based on methylmethacrylate, butylacrylate, and  $\omega$ -perfluorooctylalkylacrylate were prepared by radical polymerization. By changing both the length of the hydrocarbon spacer, between the fluorinated chain and the ester function of the fluorinated monomer, and its concentration, the surface properties of the resulting terpolymers were greatly influenced. Polymers containing small amounts of fluorinated comonomer units had considerably reduced surface energies compared to

the copolymer poly (methylmethacrylate-*co*-butylacrylate) taken as reference. The outermost surface composition has been investigated by the XPS technique, confirming the strong fluorine enrichment. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 821–827, 2006

**Key words:** fluoropolymers; low surface energy; surface modification

## INTRODUCTION

Fluoropolymers are distinguished particularly by their extremely high thermal and chemical resistance, low surface energy, and low refractive index.<sup>1–4</sup> Accordingly, many materials based on fluoropolymers have been designed, prepared, and used in a wide range of applications where these characteristics are required, such as weather resistant paints, oil and water repellents, and antigraffiti coatings.<sup>5–7</sup> Wettability of polymeric films is controlled by the composition of the outermost surface layer. In the case where the said materials contain several constituents of which one component has low surface energy, the outermost layer will be enriched with this one.<sup>8</sup> In fact, according to the Gibbs adsorption law, the surface concentration of the active agent can differ as compared to the one in the bulk. The surface excess  $\Gamma$  of a species  $i$  for two component systems in moles per unit area of surface can be described by the following equation<sup>9–12</sup>:

$$\Gamma_i = -\frac{1}{nRT} \frac{d\gamma}{d \ln C}$$

where  $C$  is the concentration of species  $i$ ,  $R$  is the ideal gas constant,  $T$  is the temperature,  $\gamma$  the surface ten-

sion, and  $n$  the correction factor depending on the nature of the surface active agent considered. If the term is  $d\gamma / d \ln C < 0$ , there will be a surface excess of species  $i$ .

This surface segregation phenomenon could be turned to profit for the preparation of low surface energy coatings via polymer blends,<sup>13</sup> block copolymers,<sup>14</sup> or addition of surface active monomers to a polymerizable system.<sup>15</sup> The low surface properties of the fluorinated polymer depend not only on the coverage of the surface by fluorocarbon chains but also on the degree of ordering of these chains. It was established that a surface formed by close packed trifluoromethyl groups, as that observed for self-assembled monolayers of fluorocarbon tails, allow us to obtain the surface of lowest energy.<sup>16–22</sup>

We have recently reported on the synthesis, characterization, and surface properties of new materials, based on homopoly( $\omega$ -perfluoroalkylalkylacrylate), for water and oil protection of polyethylene terephthalate polymer films.<sup>23</sup> For the purpose of studying the influence of the incorporation of hydrocarbon moieties to this basic system, and to decrease the percentage of the semifluorinated monomers (decrease the polymer cost), we have considered, in the present work, the polymerization and surface properties of new polymers based on methylmethacrylate, butylacrylate, and perfluorooctylalkylacrylate with varying side chain length. Fluorine surface segregation was studied using XPS. The results of our investigations are reported here.

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## EXPERIMENTAL

## Materials

The synthesis of  $\omega$ -perfluorooctylalkylacrylate F(CF<sub>2</sub>)<sub>8</sub>(CH<sub>2</sub>)<sub>n</sub>OC(O)CH=CH<sub>2</sub> labeled F8Hn'A with n' = 2, 4, 6 has been described in a previous report.<sup>23</sup> They were used after distillation into reduced pressure. Butylacrylate and methylmethacrylate were provided from Aldrich and purified by washing with NaOH 5% to remove inhibitor, then with water, dried for several hours with CaCl<sub>2</sub>, and distilled at 25°C under reduced pressure. Azobis(isobutyronitrile) AIBN was purchased from Dupont de Nemours. Acetonitrile was dried and distilled prior to use. Tetrahydrofuran (HPLC grade) and acetone were used as received.

Preparation of  $\omega$ -perfluorooctylalkylacrylate-co-methylmethacrylate-co-butylacrylate polymers

A typical polymerization experiment for the preparation of **1a** terpolymer is described as follows. The same procedure is used to obtain the other terpolymers, **2a**, **3a**, **3b**, and **3c**, by using the required portion of F8Hn'A monomer. 1.6 mL of dried acetonitrile was introduced in a vessel blanketing with nitrogen, then heated to 80°C. 0.85 g (6.64 mmol) of butylacrylate and 2 g (20 mmol) of methylmethacrylate were added drop-wise during 40 min. Simultaneously, 0.1723g (0.105mmol) of azobis(isobutyronitrile) (AIBN) dissolved in 2.5 mL of acetonitrile were added during 45min. Five min before the end of the monomer addition, 1.11g (2.66 mmol) of fluorinated monomer F8H2A dissolved in 0.1 mL of acetonitrile was added. An additional 0.66 mL of acetonitrile was added, and the reaction mixture was kept at 80°C for another 2 hours. The solution was then allowed to cool at room temperature and was then poured into methanol. The solid was filtered, dissolved in acetonitrile, and reprecipitated into methanol. This procedure was repeated twice before drying the polymer at 60°C under vacuum. A total of 3.56 g, yield = 90% was obtained.  $\overline{Mn}$  = 46.000 (determined by gel permeation chromatography calibrated with standard polystyrene and using THF as eluant). The resulting polymer had a composition of methylmethacrylate (MMA), butylacrylate (BA), and F8H2A in the following mol percentages 68/22/10, respectively. This polymer showed the following spectral data:

<sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  in ppm): 4.27 (C<sub>8</sub>H<sub>17</sub>-CH<sub>2</sub>CH<sub>2</sub>), 3.97 (CO<sub>2</sub>CH<sub>2BA</sub>), 3.57 (CO<sub>2</sub>CH<sub>3MMA</sub>), 2.47 (C<sub>8</sub>H<sub>17</sub>-CH<sub>2</sub>), 1.87 (CH<sub>2</sub>-CH<sub>BA,F8H2A</sub>, CH<sub>2MMA</sub>), 1.57 (CHCH<sub>2BA,F8H2A</sub>, CO<sub>2</sub>CH<sub>2CH2BA</sub>), 1.36 (CH<sub>2BA</sub>), 1.36 (CH<sub>3BA,MMA</sub>); <sup>19</sup>F NMR (CDCl<sub>3</sub>,  $\delta$  in ppm): -81.15 (3F, CF<sub>3</sub>), -114.02 (2F, CF<sub>2 $\alpha$</sub> ), -122.34 (6F, (CF<sub>2 $\beta$</sub> )<sub>3</sub>), -122.97 (2F, CF<sub>2 $\gamma$</sub> ), -123.17 (2F, CF<sub>2 $\delta$</sub> ), -126.57 (2F, CF<sub>2 $\omega$</sub> ).

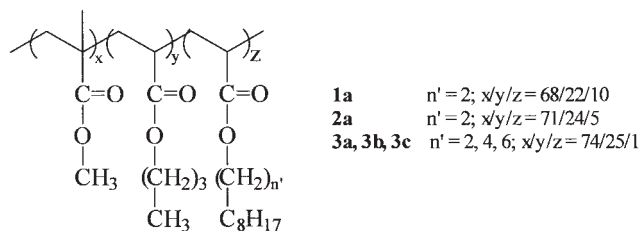


Figure 1 Molecular structures of synthesized polymers.

## Methods

<sup>1</sup>H NMR and <sup>19</sup>F NMR spectra were recorded with a Bruker AC-200 MHz. Tetramethylsilane and CFCl<sub>3</sub> were used as internal references for chemical shifts, respectively. GPC analysis was carried out with an Agilent 1100 liquid chromatography equipped with PL gel 5 Mixed D column, an Agilent G1362A refractive index, and an Agilent G1315A U.V. detector. Molecular weights were referred to monodisperse polystyrenes. Tetrahydrofuran was used as eluant at a 1 mL·min<sup>-1</sup> flux. DSC measurements were performed on a Seiko DSC 220C calorimeter equipped with a liquid-nitrogen system allowing cooling to be carried out. The DSC cell was purged with 50 mL min<sup>-1</sup> of nitrogen. Rates of 10°C min<sup>-1</sup> (heating) and 30°C min<sup>-1</sup> (cooling) were used. The method consisted first in cooling the samples prior to heating and cooling cycles. For a given polymer, two or three independent samples have been studied using the previously described temperature treatment. Data analysis was carried out during the second and third heating ramps. Optical-microscopy observations were performed with a Leica DMRXP microscope equipped with a heating/cooling stage Linkam LTS-350. Measurements and image analysis were performed on a Macintosh PowerPC 7300/166 computer using the public domain NIH Image program. Thermogravimetric analysis was conducted by means of an ATG system from Setaram TGA-92. Measurements were performed under air atmosphere from 20 to 700°C at a rate of 10°C/min. Initial decomposition temperature, IDT, was taken as the temperature at which the onset for a change in dm/dT arose (m = mass sample, T = temperature). Contact angle measurements were performed using the sessile drop method on a Krüss DSA10 contact angle goniometer. The angles reported here are the averages of five measurements. They are recorded at 22°C ± 1 using distilled water, diiodomethane, and hexadecane as wetting liquids. Surface energies were evaluated using the Owens-Wendt-Fowkes concept. According to this approach, the surface energy of a solid,  $\gamma_s$ , can be resolved into dispersion and polar components<sup>24,25</sup>:

$$0.5 (1 + \cos\Theta) \cdot \frac{\gamma_l}{\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^d} \cdot \sqrt{\frac{\gamma_l^d}{\gamma_l}} + \sqrt{\gamma_s^p} \quad (1)$$

TABLE I  
Glass Transition Temperatures (°C) of Fluorinated  
Polymers

| Polymer    | Mol % of F8Hn'A | T <sub>g</sub> |
|------------|-----------------|----------------|
| MMA-co- BA | 0               | 53             |
| 1a         | 10              | 42             |
| 2a         | 5               | 49             |
| 3a         | 1               | 49             |
| 3b         | 1               | 56             |
| 3c         | 1               | 50             |

If the contact angles formed on a solid surface with two liquids, for which the surface tension and the dispersion and polar components are known and measured, one can calculate the surface free energy of the solid via eq. (1).

The surface tension, dispersion, and polar components of water ( $\gamma_l = 72.8 \text{ mN.m}^{-1}$ ,  $\gamma_l^d = 21.8 \text{ mN.m}^{-1}$ , and  $\gamma_l^p = 51.0 \text{ mN.m}^{-1}$ ) and diiodomethane ( $\gamma_l = 50.8 \text{ mN.m}^{-1}$ ,  $\gamma_l^d = 49.5 \text{ mN.m}^{-1}$ , and  $\gamma_l^p = 1.3 \text{ mN.m}^{-1}$ )<sup>26</sup> were employed for the calculation of the surface energy of modified surfaces. Samples were prepared by coating a 16 wt % solution of acetone onto cleaned polyethylene terephthalate (P.E.T.) substrates. The films were dried at 100°C for 12 h. XPS analyses were performed with a Surface Science Instrument (SSI) spectrometer using a monochromatic and focused (spot diameter of 600  $\mu\text{m}$ , 100 W) Al K $\alpha$  radiation (1486.6 eV) under a residual pressure of  $10^{-7}$  Pa. The hemispherical analyzer worked in constant pass energy

mode, 50 eV for high resolution spectra and 150 eV for quantitative analyses. The latter were performed with a nonlinear Shirley-type baseline<sup>27</sup> using the appropriate Scofield factors.<sup>28</sup> Charge effects were compensated for by the use of a flood gun (5 eV).

The spectra are expressed as a.u., on the y-axis—an arbitrary unit to describe the number of photo-electrons arriving on the detector during a given time—versus binding energy measured in eV, on the x-axis. The C<sub>1s</sub> band at 284.6 eV for aliphatic and adventitious carbon was used as internal standard. Peaks were fitted with theoretical bands (80% Gaussian, 20% Lorentzian), via a least squares algorithm also using Shirley-type baselines.

## RESULTS AND DISCUSSION

### Polymerization and characterization of copolymers

Statistical polymers containing 1, 5, or 10% mol. of w-perfluorooctylalkylacrylate monomers (F8Hn'A), in reference to the molar concentration of the hydrocarbon monomers MMA and BA, were prepared by radical polymerization at 80°C in acetonitrile using AIBN as initiator. The reaction proceeded in high yield (80–92%). All the terpolymers prepared were analyzed satisfactorily by <sup>1</sup>H and <sup>19</sup>F NMR. Size exclusion chromatography in tetrahydrofuran yielded  $\overline{M}_n$  values around 45,000–50,000 according to polystyrene calibration and polydispersities  $\overline{M}_w/\overline{M}_n \approx 3.67$ . In Figure 1 are shown the characteristics of the polymers synthesized.

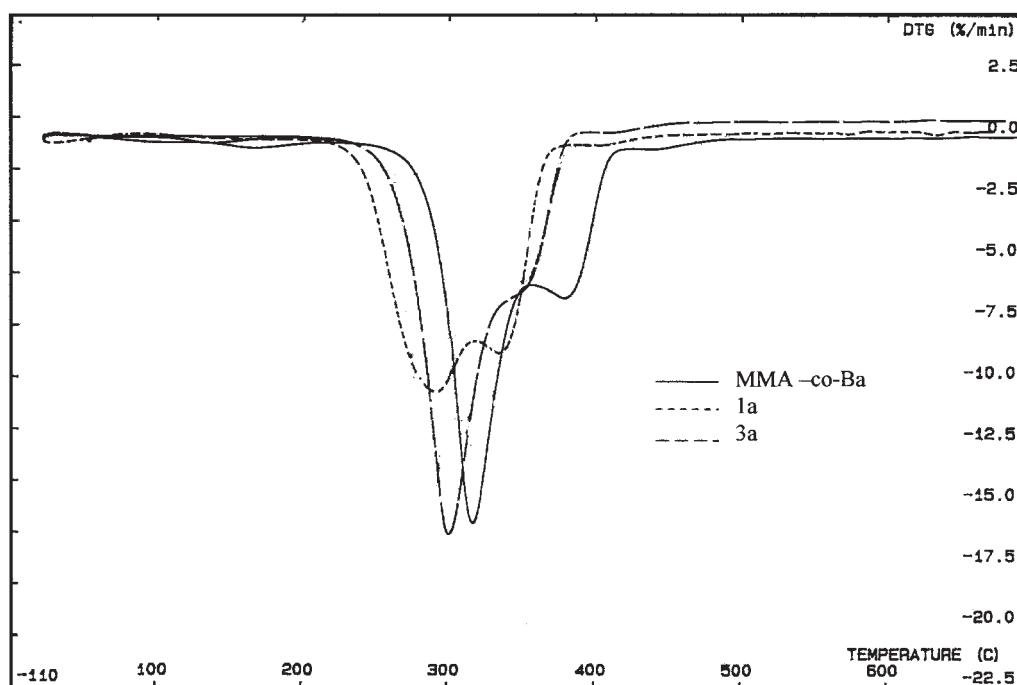


Figure 2 DTG curves of fluorinated polymers.

TABLE II  
Thermal Degradation Characteristics of Fluorinated Polymers

| Polymer    | Mol % of F8Hn'A | IDT <sup>a</sup> | T <sub>10%</sub> <sup>b</sup> | T <sub>50%</sub> <sup>b</sup> | T <sub>70%</sub> <sup>b</sup> | T <sub>100%</sub> <sup>b</sup> | T <sub>max</sub> (Δm) <sup>c</sup> |
|------------|-----------------|------------------|-------------------------------|-------------------------------|-------------------------------|--------------------------------|------------------------------------|
| MMA-co- BA | 0               | 207              | 268                           | 297                           | 323                           | 425                            | 323 (70%); 390 (99%)               |
| 1a         | 10              | 218              | 268                           | 308                           | 330                           | 428                            | 295 (37%); 341 (80%)               |
| 2a         | 5               | 212              | 266                           | 307                           | 334                           | 437                            | 280 (26%); 347 (81%)               |
| 3a         | 1               | 220              | 280                           | 309                           | 327                           | 442                            | 301 (37%); 354 (89%)               |
| 3b         | 1               | 223              | 279                           | 313                           | 334                           | 444                            | 305 (39%); 358 (88%)               |
| 3c         | 1               | 214              | 278                           | 309                           | 329                           | 451                            | 304 (41%); 353 (87%)               |

<sup>a</sup> Initial decomposition temperature (°C).

<sup>b</sup> Temperatures corresponding, respectively, to a weight loss of 10, 50, 70, and 100%, compared to the initial weight.

<sup>c</sup> Temperature noted in DTG curve and corresponding to the temperature where the decomposition rate is maximum (DTG minimum).

### Thermal properties

Thermal properties of the synthesized polymers were studied by differential scanning calorimetry and thermogravimetric analysis.

For all prepared polymers, the thermograms obtained show the existence of one transition temperature between 42°C and 56°C according to the nature and the concentration of the fluorinated monomer used for the polymerization. These values are close to those calculated from the Fox law for statistic polymers. One can see, for example, that the estimated value  $T_g \sim 44^\circ\text{C}$  for **3a** is close to the experimental observation  $T_g \sim 49^\circ\text{C}$ .

We thought, however, that the existence of only one transition temperature is closely tied to the homogeneity of the investigated phase. A superposition of the fluorinated moiety glass transition temperature with that of the hydrocarbon one is more probable.

Glass transitions temperatures values are summarized in Table I. Except for **3b** polymer, the incorporation of low concentration of  $\omega$ -perfluorooctylacrylate segments into the polymer structure leads to a slight decrease on the  $T_g$  value compared to the pure MMA-co-BA hydrocarbon polymer reference.

Polymer thermostability was examined via thermogravimetric analysis in air atmosphere. Some DTG curves are presented in Figure 2. Data are collected in Table II. We noted that the decomposition of all poly-

mers occurs three times between two main temperatures,  $T_{max}$ , noted in the DTG curves where the polymer decomposition rates are maximum.

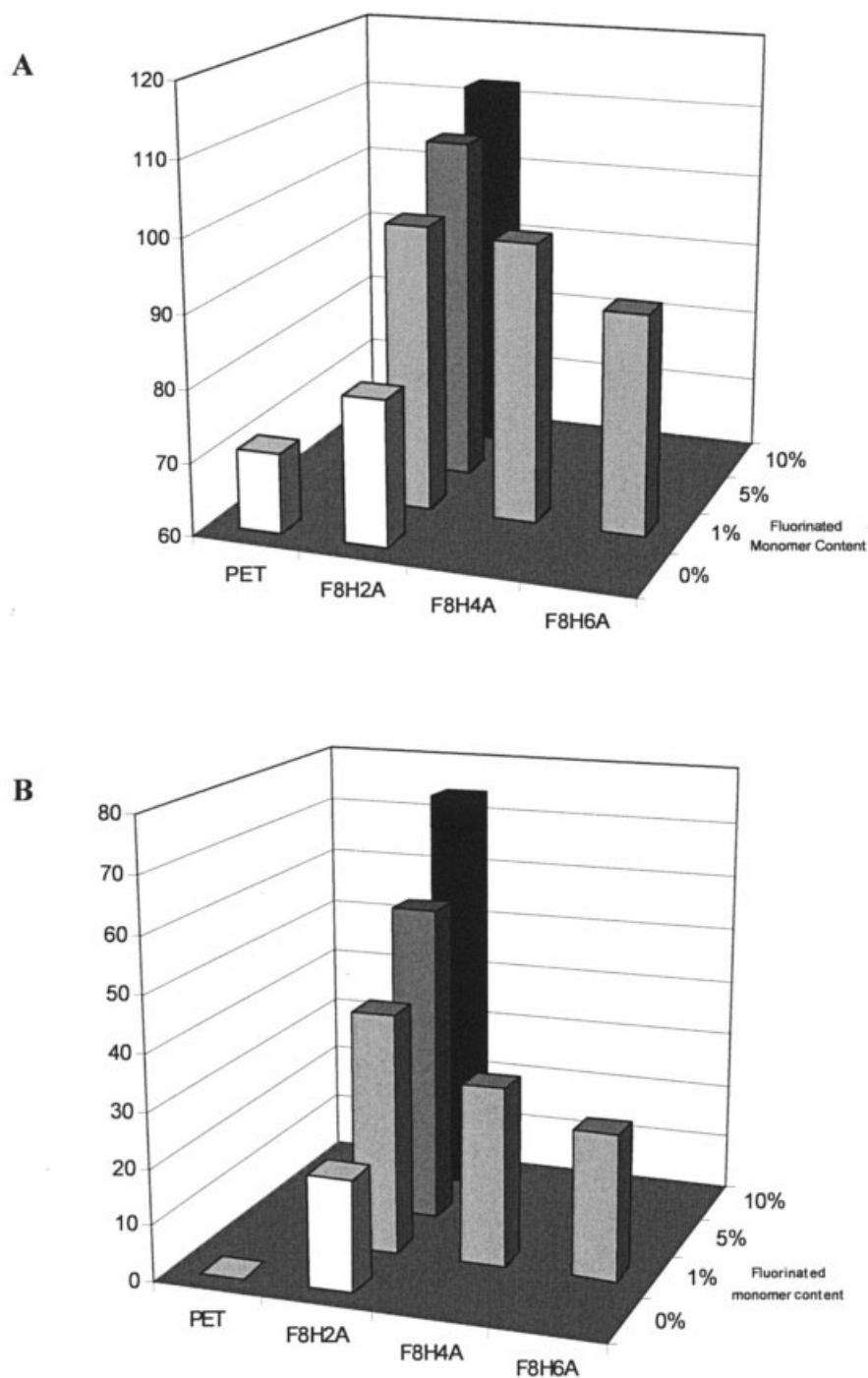
The MMA-co-BA DTG curve exhibits a typical endotherm, with peaks at 320 and 390°C associated with the depolymerization of the methylmethacrylate moieties by unzipping reactions and the decomposition of butylacrylate components.<sup>29</sup> When the fluorinated monomer is added, these temperatures shift to lower values. The broad endotherm noted at  $T > 340^\circ\text{C}$  (second  $T_{max}$ ) is associated to the decomposition of the butylacrylate component and the depolymerization of the fluorine acrylate part. This feature is not affected by increasing the hydrocarbon spacer length between the fluorinated chain and the acrylate moiety.

### Surface properties

Contact angles were measured by the sessile drop method and are listed in Table III. Water and hexadecane contact angles are taken as the index of hydrophobicity and oleophobicity, respectively. Contact angles were measured for the surfaces of terpolymer films consisting of MMA, BA, and F8H2A by varying the molar concentration of F8H2A with respect to MMA and BA. The results for water and hexadecane contact angles are shown in Figure 3(a,b). It is noticeable that the addition of even a small amount (1 mol

TABLE III  
Water, Diiodomethane, and Hexadecane Contact Angles and Surface Energies of Various Acrylic Polymer Formulations

| Polymer    | Mol % of F8Hn'A | Contact angles ( $\theta$ , °) |                                  |                              | Surface energy ( $\gamma$ , mJ.m <sup>-2</sup> ) |            |            |
|------------|-----------------|--------------------------------|----------------------------------|------------------------------|--|------------|------------|
|            |                 | $\theta_{\text{water}}$        | $\theta_{\text{CH}_2\text{I}_2}$ | $\theta_{\text{Hexadecane}}$ | $\gamma$   | $\gamma^d$ | $\gamma^p$ |
| P.E.T.     | 0               | 71                             | 40                               | <15                          | 43.1   | 34.9       | 8.2        |
| MMA-co- BA | 0               | 80                             | 49                               | 20                           | 36.6   | 31.7       | 4.9        |
| 1a         | 10              | 112                            | 97                               | 74                           | 10.2   | 8.6        | 1.6        |
| 2a         | 5               | 107                            | 94                               | 57                           | 12.0   | 9.5        | 2.5        |
| 3a         | 1               | 99                             | 64                               | 43                           | 26.4   | 25.5       | 0.9        |
| 3b         | 1               | 98                             | 63                               | 32                           | 26.9   | 25.0       | 1.9        |
| 3c         | 1               | 90                             | 61                               | 26                           | 28.8   | 28.0       | 0.8        |



**Figure 3** Water (a) and hexadecane (b) contact angles of perfluorooctylalkylacrylate modified polymers against F8Hn'A monomer content (mol %).

%) of F8H2A to hydrocarbon monomers can increase significantly the contact angles compared to MMA-co-BA and P.E.T. reference films. In fact, a hydrophobicity gain of  $19^\circ$  and of oleophobicity of  $23^\circ$  in relation to the hydrocarbon reference was reached. Surface energies of these polymers were calculated from water and diiodomethane contact angles using eq. (1). For perfluorooctylethylacrylate modified acrylic poly-

mers (1a, 2a, and 3a), the surface energies decrease drastically, compared with those of MMA-co-BA, as the F8H2A concentration increases. Surface energy of the polymer containing 10 mol % of F8H2A was found to be  $10.2 \text{ mJ}\cdot\text{m}^{-2}$ , which is very close to the corresponding fluorohomopolymer (poly-2-F-octylethylacrylate), previously reported, having a surface energy of  $9.4 \text{ mJ}\cdot\text{m}^{-2}$ .<sup>23</sup> This result indicates that most of the

**TABLE IV**  
Binding Energies of  $C_{1s}$ ,  $F_{1s}$ , and  $O_{1s}$  Regions  
of Polymer 1a

| Atoms    | Functional group    | $E^{35^\circ}$ (eV) |
|----------|---------------------|---------------------|
| $C_{1s}$ | $CF_3$              | 292.9               |
|          | $CF_2$              | 291.2               |
|          | $O-C=O$             | 288.3               |
|          | $\underline{C}H_2O$ | 286.0               |
|          | $C_{hydrocarbon}$   | 284.6 (ref.)        |
| $F_{1s}$ | $C-F$               | 687.8               |
| $O_{1s}$ | $C-O$               | 532.6               |
|          | $O-C=O$             | 531.4               |

fluorinated moiety introduced in the polymer structure must be located in the outermost layer of the polymer system. The differences in surface energies are in fact linked to variations in the nature of the chemical groups on the solid state. Among the numerous molecular structures investigated, a close packed uniform  $CF_3$  surface was found to possess the lowest surface energy ever measured ( $6\text{mJ}\cdot\text{m}^{-2}$ ), much lower than the one of polytetrafluoroethylene ( $20\text{mJ}\cdot\text{m}^{-2}$ ).<sup>30</sup>

To study the relationship between surface properties and the hydrocarbon spacer length, contact angles of samples, with fixed fluorinated monomer concentration and variable hydrocarbon spacer length (two, four, or six methylene groups between the perfluorinated chain and the ester function of F8Hn'A monomer), were examined. It was previously reported that molecular design of the monomer structure has a great effect on the final properties of the corresponding polymer film. It was established that the general structural requirement for low surface energy polymers is the existence of a flexible linear backbone attached to sufficient pendant groups, based on fluorocarbon or hydrocarbon, by linking groups that introduce no additional factors.<sup>1,31</sup> These entities must be stable and have no undesirable interactions. The influence of the  $n'$  value on surface energy does not strongly stand out as compared to the one obtained from the fluorinated monomer concentration. Nevertheless, shorter spacers seem to generate more oleophobic films ( $\Theta_{3a} = \Theta_{3c} + 17^\circ$ ).

### XPS studies

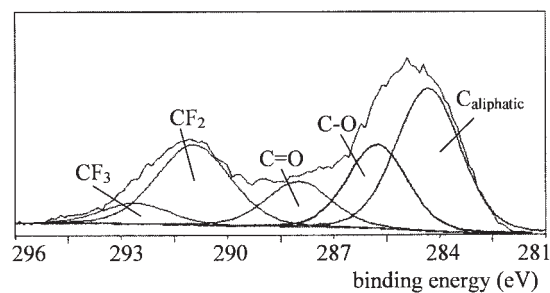
XPS spectra of the partly fluorinated polyacrylate films obtained with the two different take-off angles of  $35^\circ$  and  $70^\circ$  reveal, as expected, the photoelectronic peaks of carbon, oxygen, and fluorine. Discerning the chemical make-up of  $F_{1s}$  shows a singlet symmetrical peak, while the  $O_{1s}$  window shows two components of similar areas corresponding to the two different types of oxygen in the ester functional group of the acrylate moiety. The  $C_{1s}$  window, however, presents more a complex pattern of peaks. Five chemically different

**TABLE V**  
Predicted Bulk Values and Observed Area Percents of  
Elements at Fluorinated Acrylic Copolymer Surfaces

| Polymer | Exit angle ( $^\circ$ ) | Experimental<br>atom % |    |    | Theoretical<br>atom % |    |    |
|---------|-------------------------|------------------------|----|----|-----------------------|----|----|
|         |                         | C                      | O  | F  | C                     | O  | F  |
| 1a      | 35                      | 56                     | 11 | 33 | 63                    | 20 | 17 |
|         | 70                      | 58                     | 12 | 30 |                       |    |    |
| 2a      | 35                      | 63                     | 16 | 21 | 67                    | 23 | 10 |
|         | 70                      | 62                     | 18 | 20 |                       |    |    |
| 3a      | 35                      | 70                     | 22 | 8  | 72                    | 26 | 2  |
|         | 70                      | 74                     | 21 | 5  |                       |    |    |
| 3b      | 35                      | 71                     | 20 | 9  | 72                    | 26 | 2  |
|         | 70                      | 72                     | 23 | 5  |                       |    |    |
| 3c      | 35                      | 72                     | 21 | 7  | 72                    | 26 | 2  |
|         | 70                      | 72                     | 22 | 6  |                       |    |    |

types of carbons were found necessary to curve fit the data. Maximum binding energies found in the deconvolution of the  $C_{1s}$ ,  $O_{1s}$ , and  $F_{1s}$  spectra are given in Table IV and are comparable to the reported literature values.<sup>32</sup>

Quantitative evaluation of the spectra was carried out by determining the area of  $O_{1s}$ ,  $C_{1s}$ , and  $F_{1s}$  peaks and multiplying them by the appropriate sensitivity factors. The results, presented in Table V, are reported in terms of the atomic composition and compared with theoretical bulk concentrations. For typical polymer systems,  $35^\circ$  and  $70^\circ$  exit angles correspond, respectively, to an integrate depth of sensitivity of about 5 and 8 nm. Surface analysis of the acrylate polymers demonstrates clearly that the surface is enriched in fluorine above the bulk level. The fluorine composition in the bulk polymers ranged from 2 to 17%, whereas that at  $35^\circ$  changes from 7 to 33%. Fluorine content decreases with increasing the exit angle from  $35^\circ$  to  $70^\circ$ . At the opposite, both carbon and oxygen contents increase or remain constant at higher exit angles. These results indicate clearly that fluorinated side chains are preferentially arranged and concentrated at the polymer-air interface and that a gradient of fluorine must exist normal to the surface into the bulk of the polymer films. The magnitude of this



**Figure 4**  $C_{1s}$  spectrum of polymer 1a.

TABLE VI  
Ratios of  $(CF_3 + CF_2)/C_{total}$  for Polymers as a Function of Take-Off Angle and the Theoretical Values

| Polymer | Exit angle (°) | $(CF_3 + CF_2)/C_{total}$ % |             |
|---------|----------------|-----------------------------|-------------|
|         |                | Experimental                | Theoretical |
| 1a      | 35             | 29.8                        | 12.8        |
|         | 70             | 24.6                        |             |
| 2a      | 35             | 12.7                        | 6.8         |
|         | 70             | 9.3                         |             |
| 3a      | 35             | 2.0                         | 1.4         |
|         | 70             | 1.5                         |             |
| 3b      | 35             | 1.0                         | 1.4         |
|         | 70             | 0.4                         |             |
| 3c      | 35             | 1.5                         | 1.4         |
|         | 70             | 1.3                         |             |

gradient and its spatial dependence will have important effects on coating properties, such as repellency and durability.

The fluorine contents presented here increase with increasing the fluorine monomer concentrations; however, they are still lower than fluorine content value of about 41–54% of polymer films constituted only of fluorinated homopolymer derived from F8Hn'A monomers.<sup>23</sup> The coexistence of hydrocarbon and fluorinated structures is necessary. As for contact angle measurements, the observed surface concentration of fluorine appears to provide only slight indication that hydrocarbon side chain length has an influence on polymer film surface properties.

A high resolution  $C_{1s}$  spectrum typical of one kind of fluorine containing polymers, **1a**, is shown in Figure 4. Discrete peaks assignable to  $CF_3$  and  $CF_2$  functional groups show clearly the fluorotelomer end group  $-(CF_2)_7CF_3$  at the air polymer interface. Table VI shows the ratio of fluorinated carbon elements (%  $CF_3$  and %  $CF_2$ ) to the total atomic carbon. The ratios obtained are higher at the shallowest angle for all samples as compared to the higher take-off angle. The trifluoromethyl groups are the uppermost group, that is, the closest to the surface (e.g., for polymer **1a**:  $CF_2 / CF_3$  (theoretical) = 7.0;  $CF_2 / CF_3$  (35°) = 4.2,  $CF_2 / CF_3$  (70°) = 7.8). Since the lowest surface energies are obtained from coatings containing perfluoroalkyl groups that are oriented to yield exposed trifluoromethyl groups, the surface organization phenomena for these polymers are consistent with the trends of the surface energies obtained previously.

## CONCLUSIONS

A series of novel polymers have been prepared by radical polymerization of methylmethacrylate, butylacrylate, and perfluorooctylalkylacrylate monomers. The effect of the chemical structure on surface properties was evaluated by varying the relative length of

the hydrocarbon units in the side group. The resulting polymers were shown to be quite surface active in the solid state. Surface and bulk organizations were investigated by XPS analysis. A strong correlation between bulk organization and surface properties of the polymers could be established. We have shown that fluorinated chains surface segregate to the outermost layer. This surface enrichment can be useful to design a coating system that combines the best bulk properties and the optimized surface composition.

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