

# Photopolymerized Low-Surface-Energy Coatings Based on a Novel Fluorinated Ether Acrylate

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**ABSTRACT:** The synthesis, characterization, and polymerization of a perfluoroalkyl ether substituted methacrylic acid (C8F7) were investigated. C8F7 was photopolymerized at different temperatures, higher double-bond conversions being achieved at higher polymerization temperatures. The polymerization rates were fast in comparison with those of typical methacrylate esters. Thermogravimetric analysis of the obtained polymers showed thermal stabilities up to 270–290°C. The initial degradation at 200°C involved the loss of water and the partial loss of the perfluoroalcohol via the

intramolecular formation of anhydride and lactone groups. The surface properties of coatings obtained with C8F7 coatings on various substrates were evaluated with water and hexadecane contact-angle measurements, which confirmed that low-surface-energy polymeric coatings were obtained. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3301–3314, 2004

**Key words:** synthesis; fluoropolymers; coatings; surfaces; photopolymerization

## INTRODUCTION

The development of nonwetable, low-surface-energy polymeric materials with good film-forming characteristics has been under investigation for years.<sup>1</sup> Such polymers are useful in specific commercial applications in aerospace, lithography, clothing, integrated circuits, and wiring insulation<sup>2,3</sup> and as general protective coatings and surface modifiers.<sup>4</sup> One of the most popular strategies for designing films with low surface energy is to incorporate fluorine into the polymers that comprise the coating.<sup>5</sup>

Fluoropolymers<sup>6</sup> and semifluorinated molecules<sup>7</sup> offer many properties desirable in coatings, such as high thermal stability, chemical and oxidative resistance,<sup>8,9</sup> low refractive indices,<sup>10,11</sup> and substantial hydrophobicity. The hydrophobic nature reflects low values of cohesive energy density and surface energy.<sup>12,13</sup> The latter is a key coating property of these polymers. It prevents sticking and adhesion and inhibits attack or solvation by aqueous solutions and most organic solvents.<sup>10</sup> In general, the strength of the C—F bond increases with the extent of adjacent carbon fluorination, and this means that the longer the fluoroalkyl group is, the higher its stability and hydrophobicity are.<sup>11</sup> Moreover, even monolayers of perfluorinated organic molecules possess very low surface free energies because of a highly ordered sur-

face structure with CF<sub>3</sub> groups densely packed above the surface.<sup>14</sup>

In this article, we report the synthesis of a perfluoroalkyl ether substituted methacrylic acid (C8F7). We describe the properties of coatings obtained after its photopolymerization on different supporting substrates, such as stainless steel, glass, and poly(tetrafluoroethylene), and its thermal degradation behavior.

## EXPERIMENTAL

### Materials

*tert*-Butyl  $\alpha$ -(hydroxymethyl)acrylate (TBHMA)<sup>15</sup> and *tert*-butyl  $\alpha$ -(bromomethyl)acrylate (TBBBr)<sup>16</sup> were prepared according to previously published procedures. 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro-1-octanol (Aldrich; 98%), triethylamine (TEA; Aldrich; 99%), and trifluoroacetic acid (Aldrich; 99%) were used as received. Tetrahydrofuran (THF) was freshly distilled over Na(s) and benzophenone. Pentadecafluorooctyl methacrylate (PDFOM) was purchased from Monomer-Polymer and Dajac Laboratories and was used as received. Methacrylic acid (MA; purity = 99%) was purchased from Aldrich and used without further purification. Phenylethyl methacrylate (PEMA) was obtained from Aldrich and used as received.

### Instrumentation

<sup>13</sup>C-NMR solution spectra were recorded on a Bruker AC-300 spectrometer at room temperature with CDCl<sub>3</sub> with tetramethylsilane as an internal reference. Pho-

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topolymerizations were initiated with Irgacure 651 (Ciba–Geigy) with a TA Instruments 930 differential photocalorimeter. The results of the differential scanning photocalorimetry (photo-DSC) experiments were evaluated with Microcal Origin 4.1 and Microsoft Excel. Thermal analyses were performed with a TA Instruments 2960, and DSC experiments were performed with a TA Instruments 2920, both controlled with a Thermal Analyst 2100. The first thermogravimetric analysis (TGA) ramp consisted of heating to 250°C at a rate of 20°C/min for the elimination of any residual monomer. Unexpected side reactions resulting from the heating of C8F7 polymers at temperatures around 200°C also occurred during this stage. Each sample was then cooled to 30°C, and a second heating ramp was applied up to 350°C at a rate of 10°C/min; this provided information on the catastrophic degradation of the polymer. All DSC scans were taken at a heating rate of 10°C/min under nitrogen to a temperature corresponding to 30°C below the temperature at which a 5% weight loss occurred (ca. 250°C) and were then cooled to room temperature and rescanned at the same heating rate. The glass-transition temperature was recorded from the second-scan data for the same sample.

Contact-angle measurements were performed with the sessile drop method. Hexadecane [surface tension ( $\gamma_T$ ) = 27.05 mN m<sup>-1</sup> at 25°C]<sup>17</sup> and water (Aldrich; HPLC-grade;  $\gamma_T$  = 72.75 mN m<sup>-1</sup> at 20°C)<sup>17</sup> were used as the wetting liquids. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were obtained with a Bio-Rad FTS 6000 Digilab FTIR spectrometer equipped with a germanium miracle single-reflection HATR instrument (Pike Technologies, Inc.) at a 4-cm<sup>-1</sup> resolution with 32 coadded scans. Small-angle X-ray diffraction measurements were performed on a Siemens XPD-700P diffractometer with Cu K $\alpha$  radiation in the 2 $\theta$  range of 2–6° at a sample–detector distance of 49 cm.

### Synthesis of monomer 3

Fluoroalkyl ether substituted *tert*-butyl  $\alpha$ -hydroxymethyl acrylate was synthesized according to a literature procedure,<sup>18</sup> which started with *tert*-butyl acrylate. In the final step, 30 mL of dry, freshly distilled THF, pentadecafluorooctanol (23.02 g, 56 mmol), and TBBr (12.45 g, 56 mmol) were mixed in a round-bottom flask. TEA (7.85 mL, 56 mmol) was added dropwise to this stirring mixture with ice-bath cooling (the reaction was slightly exothermic). The reaction mixture was then transferred to an oil bath and held at 70°C with stirring for 24 h. This mixture was diluted with 10 mL of CH<sub>2</sub>Cl<sub>2</sub> and extracted with five 10-mL aliquots of water. The organic layer was separated, dried with anhydrous magnesium sulfate, and fil-

tered, and the solvent was evaporated under reduced pressure to give the monomer in an 88% yield.

### Synthesis of monomer C8F7

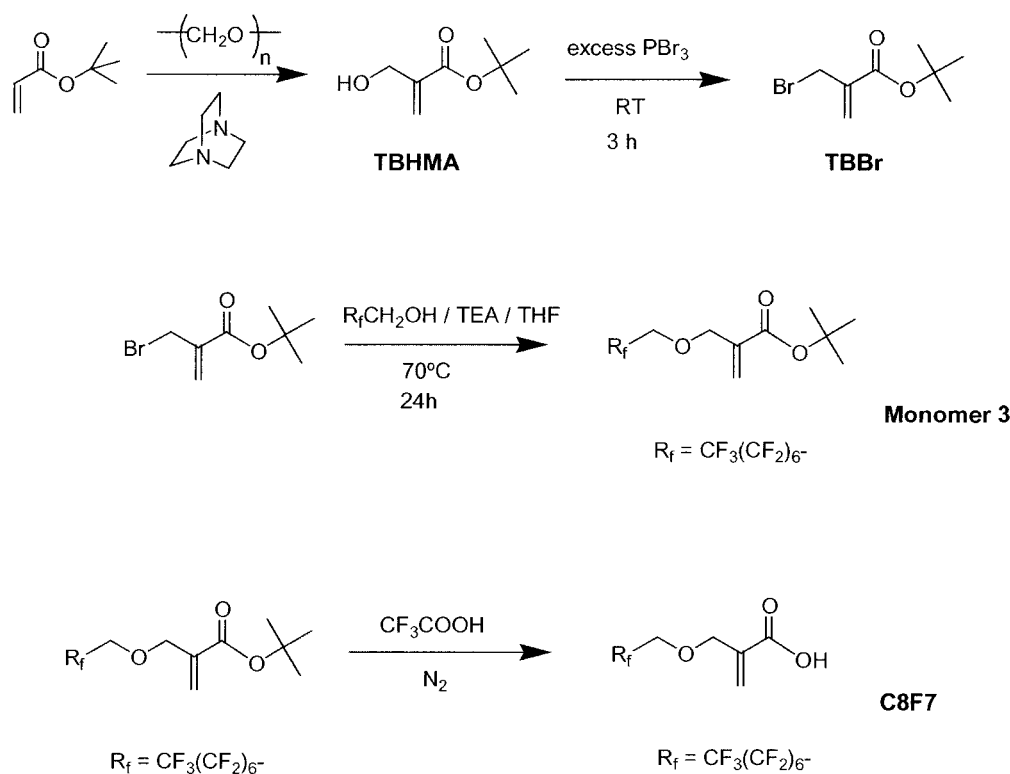
Monomer 3 (9.26 mmol) was placed in a round-bottom flask cooled in an ice bath under a nitrogen flux, and 3.5 mL of trifluoroacetic acid was added dropwise. The mixture was brought to room temperature and allowed to stir overnight. Nitrogen was then bubbled into the flask for 30 min, and CF<sub>3</sub>COOH was evaporated under reduced pressure. The mixture was placed in a refrigerator for 30 min, after which water was added to the flask. The milky solution obtained was extracted with hot hexanes several times. The solid product obtained was recrystallized from hexanes, and this was followed by drying in a vacuum oven overnight to give a highly pure white solid (purity = 99.7% according to gas chromatography; melting point = 45.3–45.7°C according to DSC).

### Bulk free-radical polymerization procedure

In a typical conventional bulk free-radical polymerization procedure, 30 mg of C8F7 and 0.0003 g (1 wt %) of azobisisobutyronitrile (AIBN; previously recrystallized from methanol) were added to a small test tube, and a nitrogen flow was applied for 10 min before polymerization. The tube was placed in an oil bath at 60°C, and polymerization was carried out overnight. The final product was insoluble in common organic solvents and was purified by several washes in boiling chloroform for the elimination of residual monomer; this was followed by drying in a vacuum oven.

### Small-scale photopolymerization procedure (photo-DSC)

In a typical photopolymerization procedure, a sample of approximately 3 mg of C8F7 (or another monomer) was added to an aluminum DSC pan, and a sufficient volume of a solution of Irgacure 651 in CH<sub>2</sub>Cl<sub>2</sub> was added to give a final mixture that was 1 mol % initiator. Several drops of CH<sub>2</sub>Cl<sub>2</sub> were usually added to the mixture to achieve good mixing of the monomer and photoinitiator. The photo-DSC cell was purged with nitrogen for 30 min before the exposure of the sample to the UV light source to remove oxygen and to fully evaporate the solvent. A literature value of  $\Delta H$  of 13.1 kcal/mol for the polymerization of methacrylate double bonds was used.<sup>19</sup> Photopolymerizations were performed at various temperatures, all above the melting point of the monomer. The polymers were then cooled to room temperature. The thermal stabilities of the polymers were evaluated as follows: samples obtained from photo-DSC were placed in the TGA instrument, and two sequential analyses were



**Scheme 1** Synthetic scheme for the production of C8F7.

run. The first consisted of heating each sample up to 250°C at a rate of 20°C/min for the elimination of residual monomer. After the sample cooled to room temperature, the second scan was performed via heating to 350°C at a rate of 10°C/min.

### Coating preparation

A solution of C8F7 (50% w/v) in  $\text{CH}_2\text{Cl}_2$  containing 1 mol % of the photoinitiator Irgacure 651 was prepared. The polymer coatings were obtained in one of two ways. The first consisted of spin-coating 20  $\mu\text{L}$  of the monomer solution onto the substrate at a speed of 2000 rpm for 30 s; this was followed by photopolymerization of the coated supports at 70°C for 10 min under nitrogen. The second method (the drop method) consisted of adding 20  $\mu\text{L}$  of the mixture directly onto the substrate with a syringe. After the addition, the system was subjected to a nitrogen flow for 10 min, and this was followed by photopolymerization at 70°C for 10 min, still under nitrogen. The substrates were sanded stainless steel plates, glass microslides, and Teflon fluorinated ethylene propylene films (DuPont; thickness = 0.125 in).

In a typical photopolymerization procedure, a coated sample was placed on top of a hot plate previously brought to the desired temperature, on which was placed a paper box containing inlet and outlet ports for a nitrogen purge. A clear polyolefin film

(sandwich wrap) was placed on top of the box, through which the UV light traveled to reach the sample. The nitrogen purge was maintained for 10 min before and during the photopolymerization, which was then carried out for 10 min. The part was then placed in an oven at 150°C for 30 min for the removal of trapped volatiles. After it cooled in air, contact-angle measurements were taken. The final contact-angle value reported is the average of at least five different measurements taken on coated substrates prepared under the same conditions.

## RESULTS AND DISCUSSION

The incorporation of fluorinated moieties into a polymer film has been shown to produce nonwetable surfaces with low surface energies.<sup>20</sup> Here we report the synthesis of C8F7, its photopolymerization onto different substrates, and the evaluation of the surface energies of the polymer films formed. The synthesis of the monomer is depicted in Scheme 1. The  $\text{CH}_2\text{OH}$  group of TBHMA was first converted into the more reactive  $\text{CH}_2\text{Br}$  group of TBBr. The next step of the reaction consisted of ether formation involving the reaction of TBBr with a fluoroalcohol. The optimization of the synthetic procedure led to the production of the fluoroalkyl ether acrylate (monomer 3) in a high yield (88%). Finally, the *tert*-butyl group of the intermediate 3 was cleaved with trifluoroacetic acid to

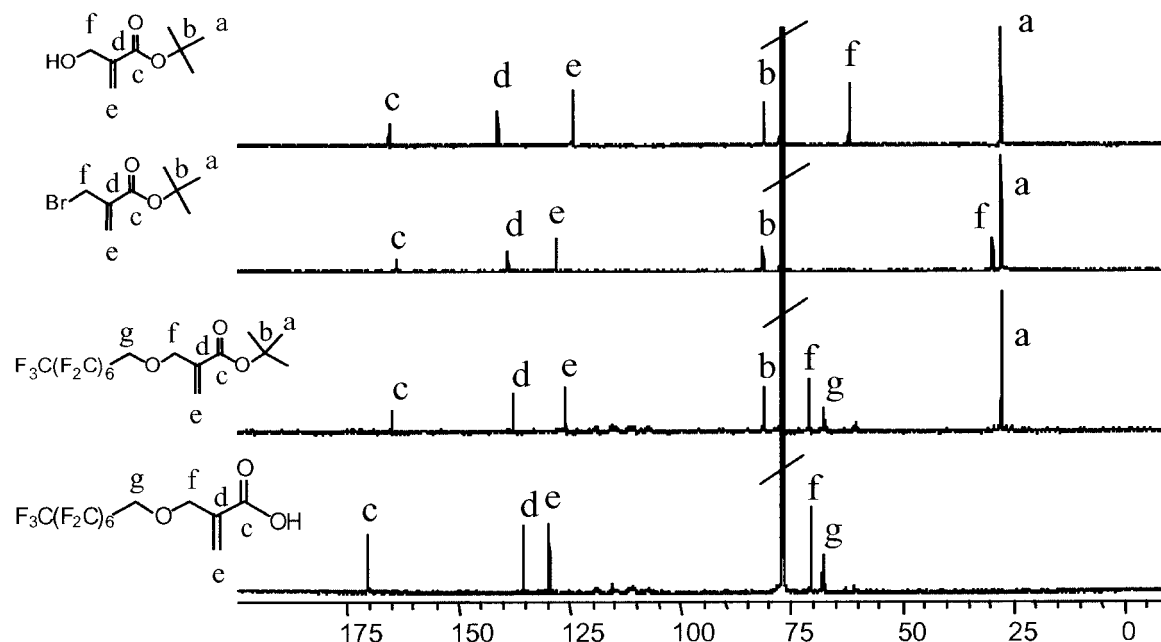


Figure 1  $^{13}\text{C}$  NMR spectra of the products obtained during each step of the C8F7 synthesis.

generate C8F7. Recrystallization from hexanes gave the pure monomer as a white solid (mp = 45.3–45.7°C). C8F7 was prepared in multigram quantities for the coating experiments.

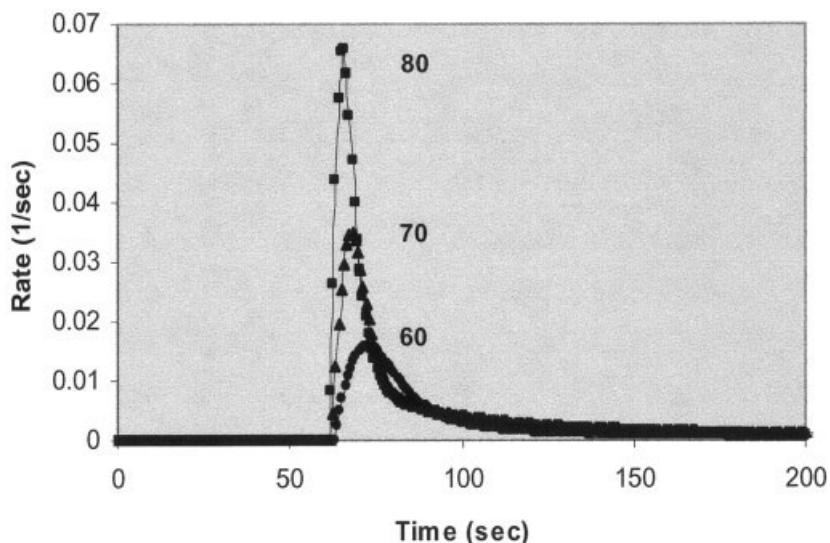
Intermediates in the synthesis of C8F7 were characterized with NMR spectroscopy (Fig. 1). The  $^{13}\text{C}$ -NMR spectra of the monomers showed the shift of the methylene carbon ( $\text{CH}_2\text{OH}$ ) from 61.7 to 29.6 ppm ( $\text{CH}_2\text{Br}$ ), indicating the formation of TBBr. The same methylene carbon moved downfield and shifted to 67.2 ppm after the reaction of TBBr with the fluoroalcohol. Moreover, peaks in the 106–120 ppm region ( $\text{CF}_2$  and  $\text{CF}_3$  groups), a triplet at 67.2 ppm ( $\text{OCH}_2\text{R}_f$ ), and a singlet at 70.6 ppm ( $=\text{CCH}_2\text{O}$ ) appeared in the spectrum, demonstrating the formation of the fluoroalkyl ether acrylate intermediate. The disappearance of the methyl peak at 27.4 ppm and the methine peak at 81.0 ppm clearly showed the cleavage of the *tert*-butyl group of intermediate 3 in the final step generating C8F7. In addition, peaks were seen at 129.4 and 135.3 ppm for the monomer double-bond carbons, whereas the  $-\text{CH}_2\text{O}-$  groups of the fluoroalkyl and allylic carbons were seen at 70.4 and 67.8 ppm, respectively.

The photopolymerization of the perfluoroalkyl monomer C8F7 was carried out at different temperatures, ranging from 60 to 90°C, to ensure that the reaction temperature was sufficiently above the melting point of the monomer ( $45.5 \pm 0.2^\circ\text{C}$ , as estimated by DSC) for maximum rates. The instantaneous rates of polymerization ( $\text{Rate}_{\text{pol}}$ ) were determined from the heat flux measured by the DSC according to the following equation:<sup>21</sup>

$$\text{Rate}_{\text{pol}} = [(Q/s) * M] / (n * \Delta H_{\text{pol}} * \text{Mass}) \quad (1)$$

where  $Q/s$  is the heat flow per second,  $M$  is the molar mass of the monomer C8F7,  $n$  is the number of double bonds per monomer molecule,  $\Delta H_{\text{pol}}$  is the heat released per mole of double bonds reacted, and mass is the mass of the monomer present in the sample pan. The theoretical value of 13.1 kcal/mol was used as the heat evolved per methacrylate bond ( $\Delta H_{\text{pol}}$ ) for the calculations.<sup>19</sup> The normalized rates of C8F7 polymerization were then followed over time, as shown in Figure 2. The double-bond conversion achieved at each polymerization temperature was then calculated by the integration of the area under the curve of the polymerization rate as a function of time. Figure 3 shows the conversions reached at each temperature. The rates of polymerization and the conversions increased at higher polymerization temperatures, as expected.

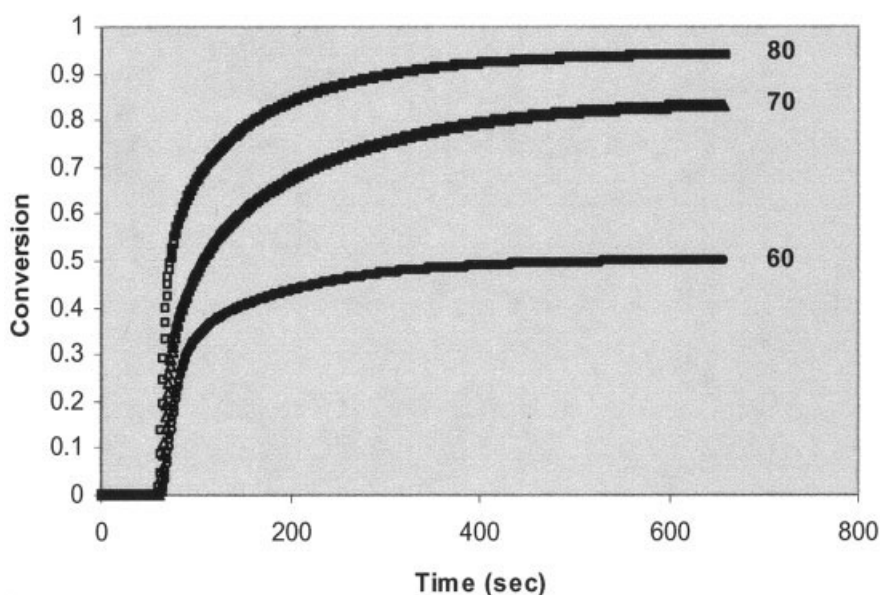
The rates and conversions in photopolymerizations of C8F7 were compared to those of MA and PDFOM at a polymerization temperature of 70°C (Fig. 4). The rate of C8F7 polymerization was much faster, with a higher overall conversion being achieved and no evidence of autoacceleration. The higher rates for the fluoroalkyl ether substituted methacrylic acid could be due to several factors. Electronic effects (caused by substitution with an oxygen atom  $\beta$  to the double bond) have been previously shown to compete with steric effects (caused by the fluoroalkyl groups), resulting in faster polymerizations of derivatives of  $\alpha$ -(hydroxymethyl)acrylates.<sup>11,22</sup> Preorganization of the monomer through acid/hydrogen-bond interactions could contribute to the rate enhancement observed.<sup>23</sup>



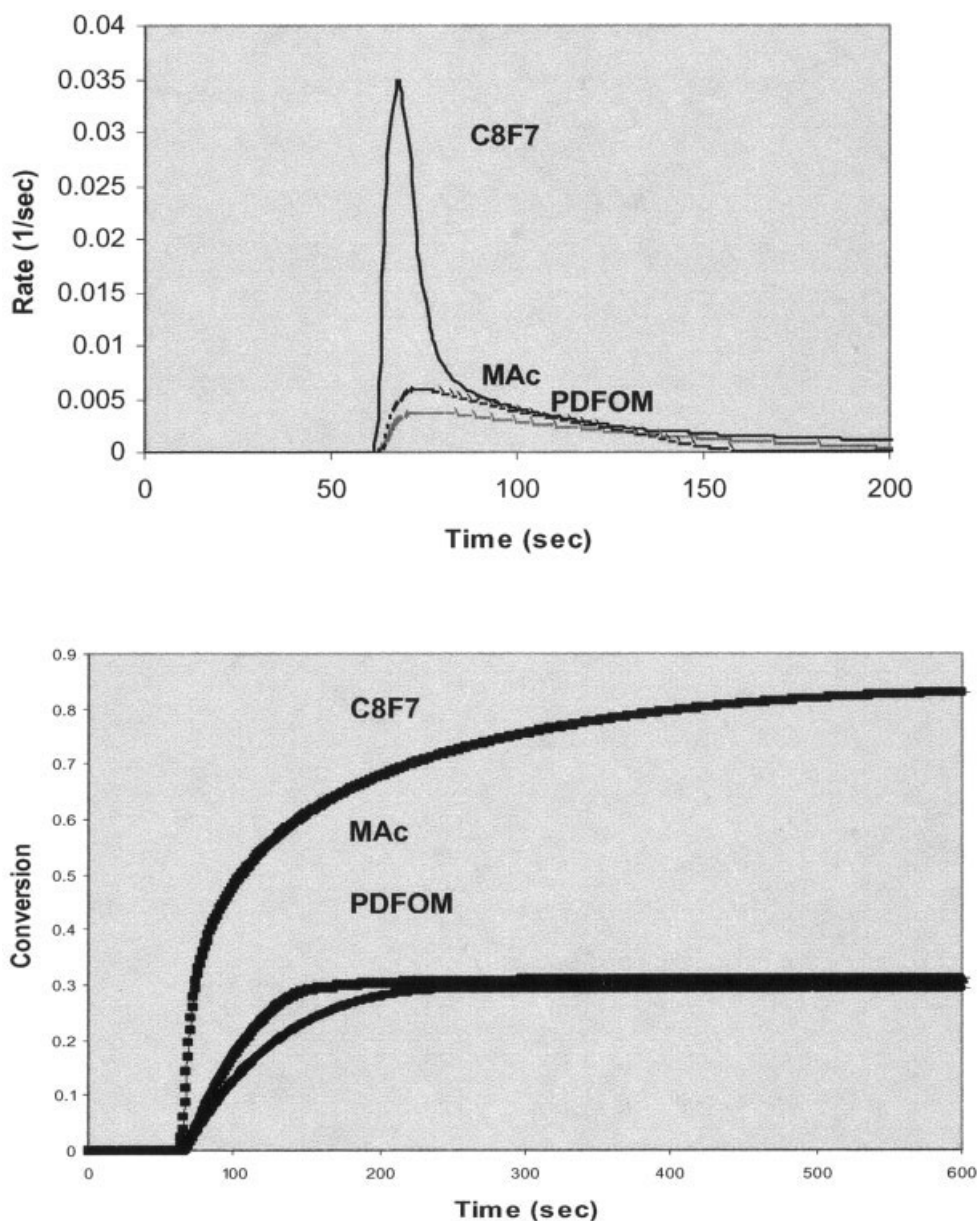
**Figure 2** Instantaneous rates of the photopolymerization of C8F7 carried out at different temperatures and followed over time, with the onset of light exposure set at 60 s.

As shown by TGA of a sample of the C8F7 polymer (Fig. 5) synthesized with conventional AIBN free-radical polymerization in bulk, some weight loss was evident around 200°C. This weight loss was maximum at this temperature and did not exceed 15% even under isothermal conditions for 5 h. This weight loss was determined to involve the elimination of penta-decafluoro-1-octanol, as observed by gas chromatography/mass spectrometry analysis, and the formation of a six-member ring lactone, detected as a shoulder around 1722  $\text{cm}^{-1}$  in the FTIR spectrum [Fig. 6(A)]. The elimination of the fluorinated alcohol was assumed to be caused by an attack of the OH group of

the pendant acid functionality on the methylene carbon of the fluoroalkyl ether closer to the polymer backbone. This reaction was possibly due to the proximity of the pendant groups in the polymer molecule on both sides of each pendant carboxylic acid group. Cyclic anhydride formation, involving pairs of neighboring carboxylic acid pendant groups, also occurred in this temperature region, as shown by the two bands at 1807 and 1763  $\text{cm}^{-1}$  in Figure 6(A). The mechanism was similar to that observed for polymers containing MA units.<sup>24</sup> When the coated substrates were heated in an oven at 150°C for 30 min, these side reactions were also detected by ATR-FTIR, as shown in Figure 6(B).



**Figure 3** Conversion of the photopolymerization of C8F7 carried out at different temperatures.



**Figure 4** Comparative rates of polymerization and conversion plots for the photopolymerizations of C8F7, PDFOM, and MA at 70°C.

The polymers of C8F7 obtained by photo-DSC polymerizations were characterized by TGA in two stages (Fig. 7). The first TGA ramp consisted of heating to 250°C at a rate of 20°C/min (Fig. 7, top) for the elimination of any residual monomer. The side reactions resulting from the heating of C8F7 polymers at temperatures around 200°C also occurred during this stage. The samples were then cooled to 30°C, and a second heating ramp was applied up to 350°C at a rate of 10°C/min (Fig. 7, bottom), which provided further information on the degradation of the polymer. Once we elucidated the degradation reactions that occurred during the heating process by FTIR, we were able to interpret the

TGA curves of Figure 7. In the first stage, the polymers that were synthesized at 70 and 80°C underwent mainly the side reactions mentioned previously. The polymer synthesized at 60°C, however, showed a more pronounced weight loss due to both side reactions and the loss of unreacted monomer present in this sample due to a lower polymerization conversion. Considering that these side reactions were completed after the first heating stage, we reported the temperature at which a 5% weight loss occurred during the second stage as the actual degradation temperature of the polymer, as shown in Table I. Thermal stabilities up to 270–290°C were observed for these annealed polymers.

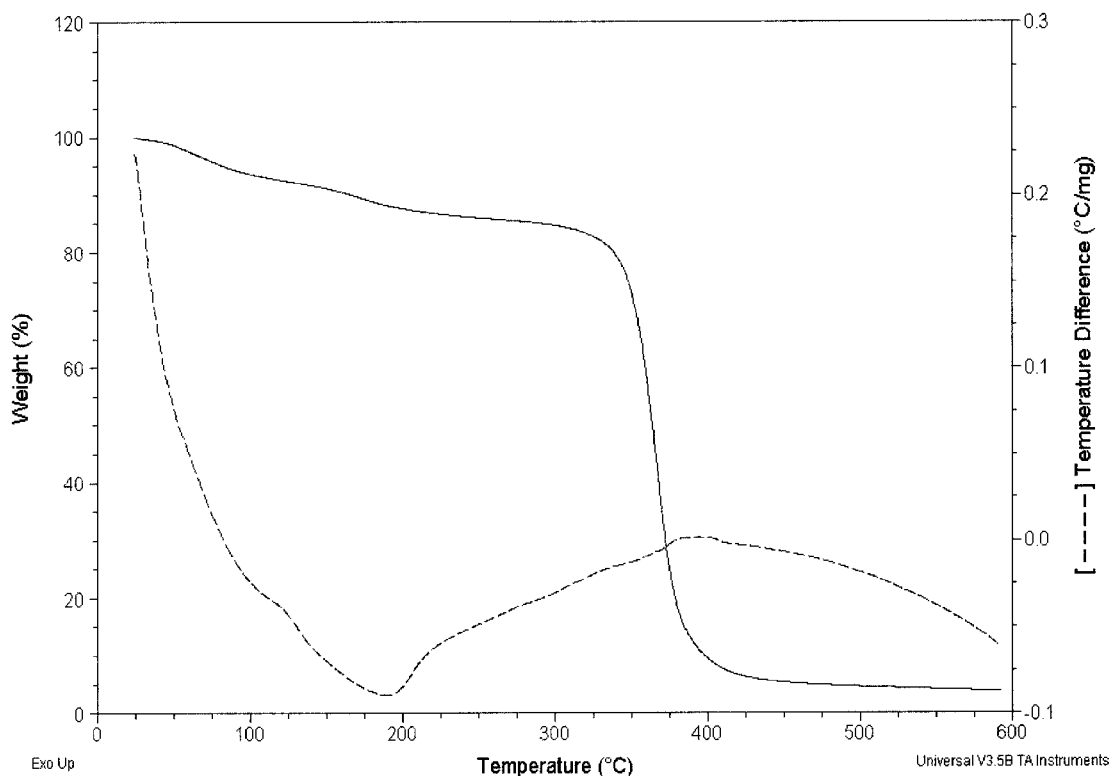


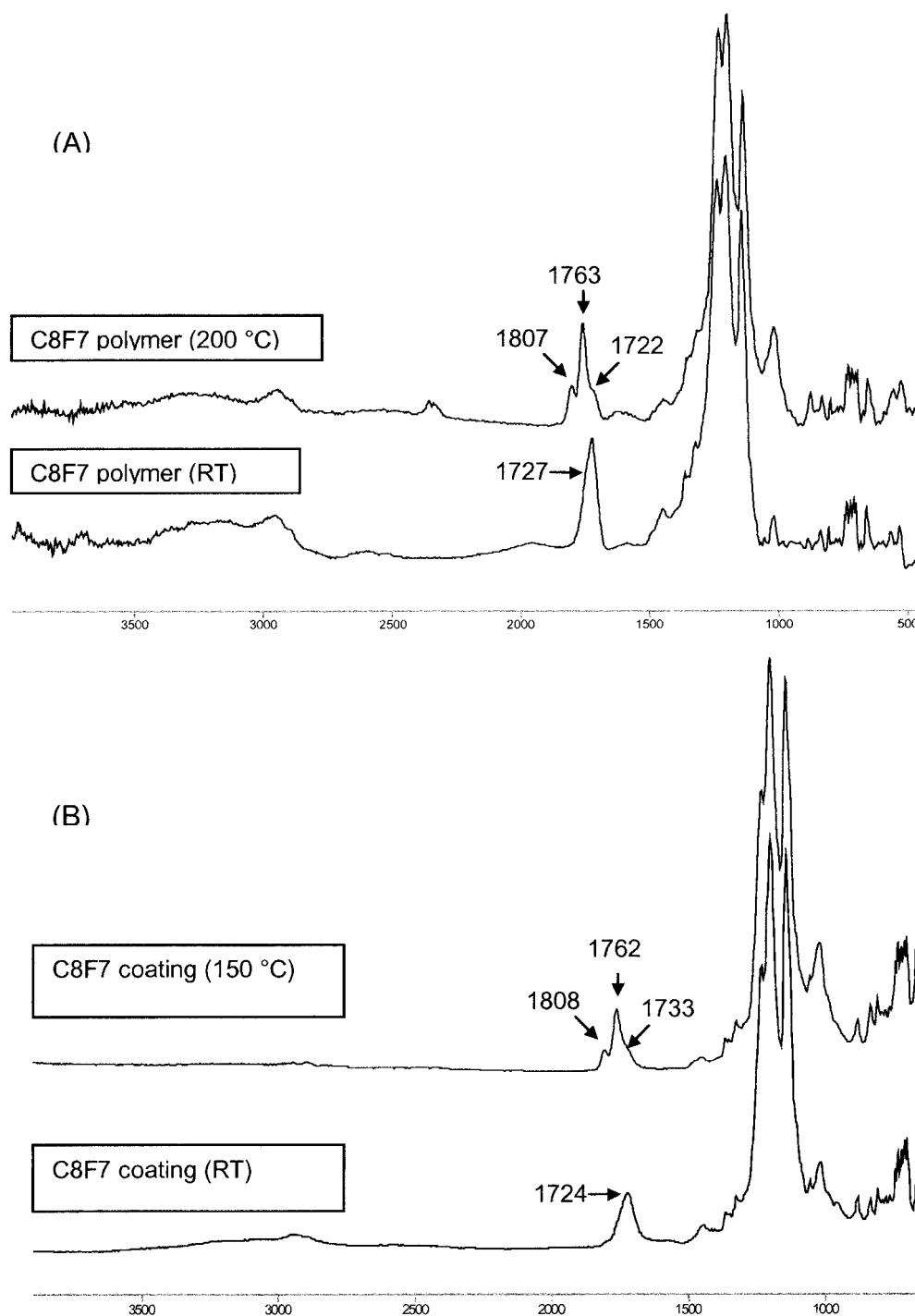
Figure 5 TGA of the C8F7 polymer obtained by free-radical bulk polymerization.

Differential scanning calorimetry (DSC) was also used to investigate the thermal transitions of the polymers obtained. Once side reactions were identified under the thermal treatment of the C8F7 polymers, two different procedures were used for DSC analysis. In the first procedure, C8F7 polymers, synthesized either by bulk free-radical polymerization or photopolymerization, were not subjected to thermal treatment and were characterized by DSC as synthesized, via heating to 150°C at a rate of 10°C/min. In this case, no thermal transitions were seen. In the second procedure, the polymers were annealed via heating to 250°C at a rate of 20°C/min in the TGA instrument to eliminate unreacted monomer and drive side reactions to completion, and then they were characterized by DSC analysis accomplished by the heating of the samples to 250°C at a rate of 10°C/min. In this case, however, a thermal transition at 120°C was observed. This transition may correspond to the melting of crystalline domains formed because of side-chain crystallization of the polymer as a result of side reactions occurring at 200°C. Evidence for side-chain crystallization was obtained with X-ray analysis. No Bragg diffraction peak was noticed for the polymer of C8F7 as synthesized, whereas after the thermal treatment (150°C for 1 h), two sharp reflections were observed at 3.0 and 5.87° corresponding to lamellar thicknesses of approximately 29 and 15 Å, respectively. This was consistent with well-ordered packing of the fluorocar-

bon side chains, which were approximately 15 Å long, as estimated by computer modeling. The distance of 29 Å suggested head-to-head stacking of the side chains in the crystalline domains.

### Surface properties

The polymer surface energies were calculated from contact angles with the Girifalco–Good–Fowkes–Young method. Films of C8F7 polymers were prepared by one of two methods, as described in the Experimental section. By syringe, a single droplet (20 μL) of the monomer mixture was placed on the support and photocured. The obtained films were homogeneous, and the contact-angle data were reproducible. Spin coating did not provide a uniform distribution of the material on the parts, and the contact-angle data were not reproducible. Figure 8 shows the contact angles for water obtained after polymerizations on the different supports. These values correspond to the surfaces of the multilayer coating obtained rather than a monolayer model. The values of the contact angles obtained for steel parts and for glass supports increased after the coating treatment, and a second coating treatment on the already coated steel substrate led to a further slight increase in the contact angle measured. However, when a Teflon sheet was used as a substrate, the contact angle in water decreased after the coating treatment, and this was indicative of an



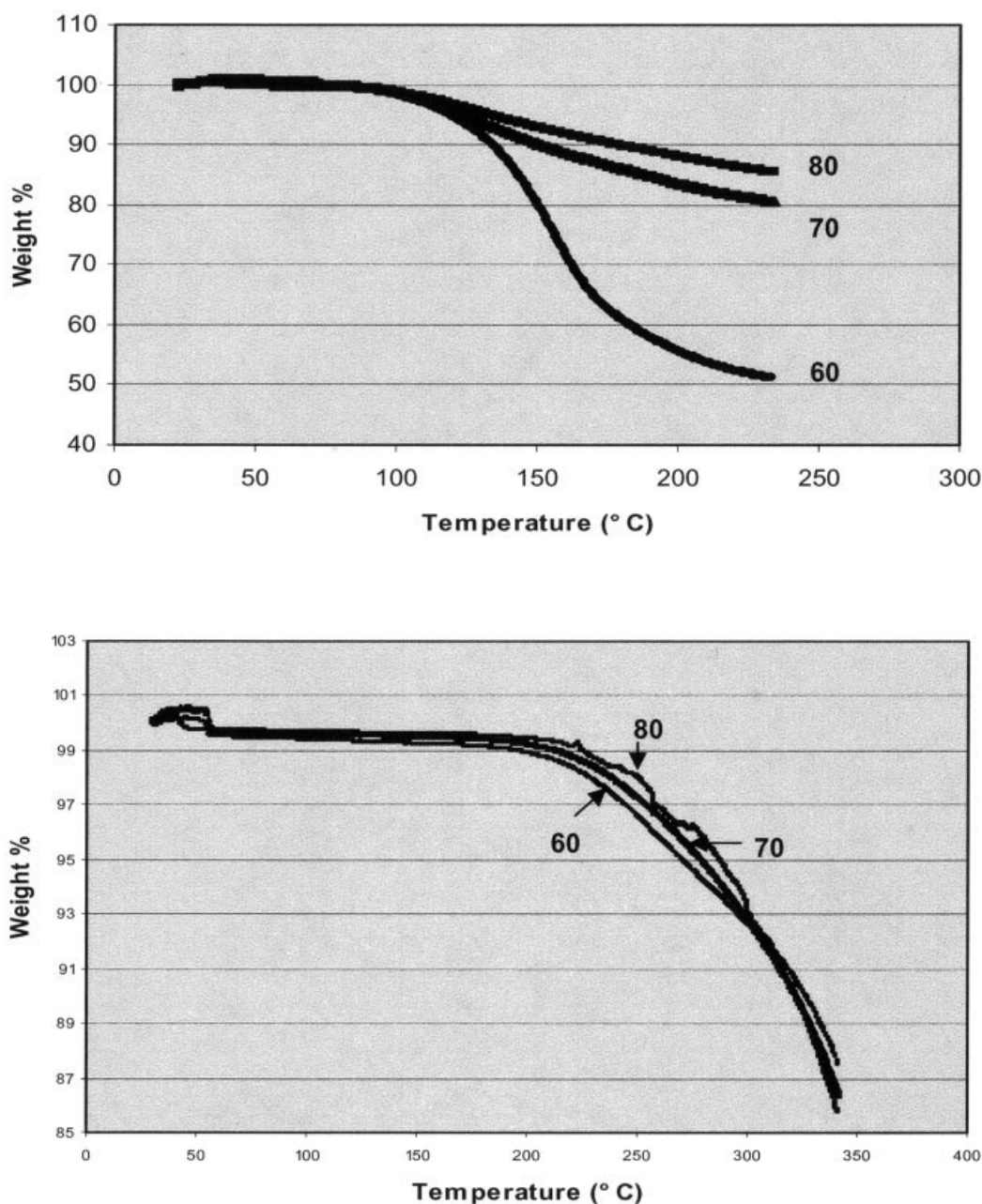
**Figure 6** (A) FTIR spectra of the homopolymer of C8F7 (synthesized by conventional free-radical polymerization) at room temperature and after exposure to 200°C *in vacuo* and (B) ATR-FTIR spectra of the surface of the C8F7 polymer coating (synthesized by photopolymerization) at room temperature and after exposure to 150°C.

organization of the polymer molecules in which the hydrophobic side chains of C8F7 aligned toward the fluorinated surface during polymerization, whereas the polar carboxylic acid groups oriented toward the air interface. The results on glass and steel agreed with previously reported data showing that fluorinated groups could migrate to the air–monomer surface and

could form highly oriented layers with low surface energy.<sup>25</sup> However, the orientation of the fluorinated moieties was strongly influenced by the substrate used, with maximum effects for those that interacted strongly with the carboxylic acid groups.

It has also been shown that low-surface-energy values obtained for coatings based on fluorinated poly-





**Figure 7** TGA of polymers obtained at different polymerization temperatures: first heating stage (top) and second heating stage (bottom).

mers are caused not only by the hydrophobic nature of the coating but also by a synergistic effect of the hydrophobic nature combined with the oleophobic nature.<sup>1</sup> Therefore, the contact angles of the prepared coatings were also evaluated with *n*-hexadecane as the wetting liquid to evaluate their oleophobicity index. The results obtained for steel parts and glass microslides coated with the C8F7 polymer are summarized in Figure 9. The oleophobicity of the former increased significantly, whereas for glass only a slight change (5°) was observed. These results were consistent with the surface hydrophilicity and hydrophobicity of the

substrates used influencing the behavior of the monomer layers and polymer coating formed.

#### Copolymerization studies

It has been demonstrated that large weight fractions of fluorinated materials are not needed to produce non-wettable surfaces with low surface tensions.<sup>5</sup> To evaluate such behavior here, we carried out the copolymerization of PEMA in the presence of low fractions of fluorinated moieties, and we investigated the surface properties of the coatings obtained. Because the C8F7

**TABLE I**  
**Double-Bond Conversions and TGA Degradation**  
**Temperatures of the C8F7 Polymers Obtained After**  
**Photopolymerization at Different Temperatures**  
**in photo-DSC**

| Polymerization temperature (°C) | Monomer conversion <sup>a</sup> | Weight (%) remaining at 200°C <sup>b</sup> | Degradation temperature (°C) <sup>c</sup> |
|---------------------------------|---------------------------------|--|---|
| 60                              | 49.8                            | 55.7                                       | 271                                       |
| 70                              | 83.1                            | 83.6                                       | 279                                       |
| 80                              | 93.9                            | 88.0                                       | 288                                       |

<sup>a</sup> Obtained through integration of the area under the curve of the rate versus time.

<sup>b</sup> Obtained on ramp to 250°C at 20°C/min.

<sup>c</sup> Observed in the TGA curve on ramp to 350°C at 10°C/min.

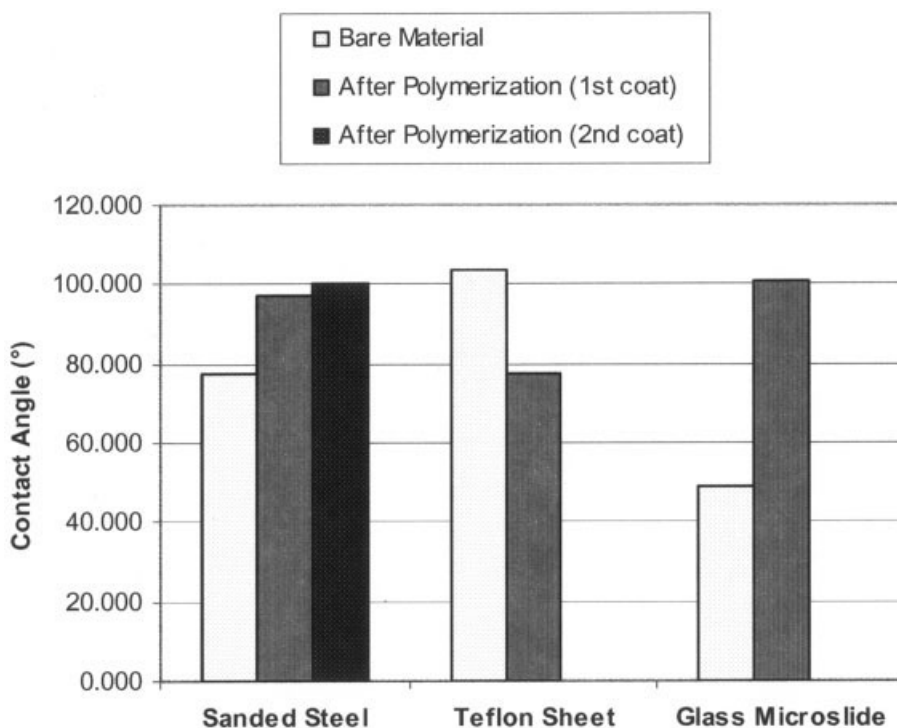
monomer possesses carboxylic acid groups and fluorinated segments, its presence in a copolymerization system containing PEMA would force some of the molecules to stick to the surface, through the COOH groups, and some of the molecules to migrate to the surface–air interface, because of the fluorinated segments. In some cases, bonding to the surface may be disrupted by this behavior, and delamination of the coating may occur. Thus, the copolymerization system used was composed of PEMA and different weight fractions of monomer 3, the *tert*-butyl ester intermediate of C8F7 synthesis (Scheme 1). The copolymerization systems consisted of PEMA with 2 or 10 wt % of

monomer 3 and 1 mol % of Irgacure 651. Polymerizations were carried out with the same procedure used for homopolymerizations on glass microslides at 70°C.

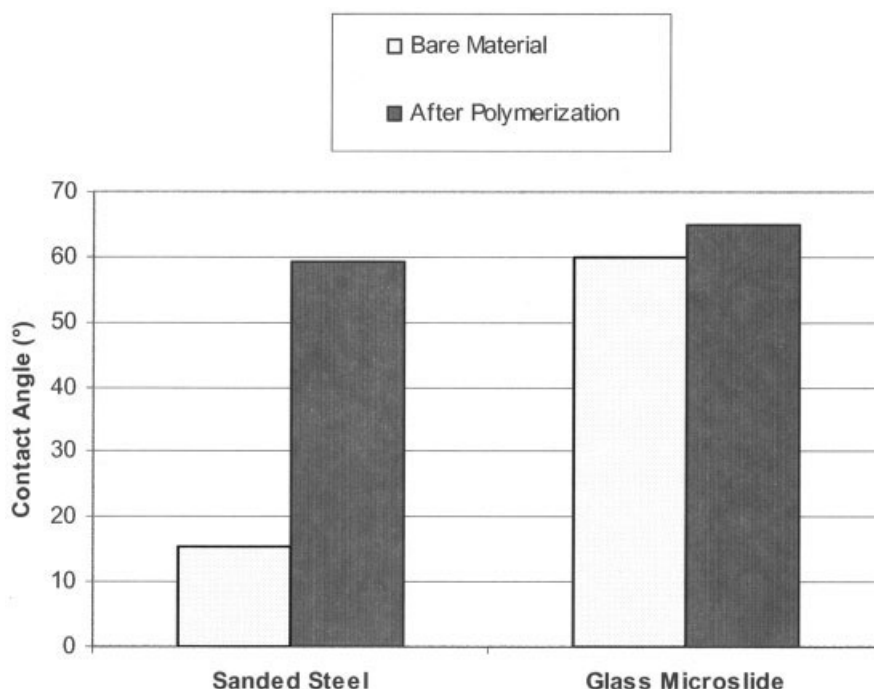
Figure 10 shows the contact angles of the surfaces obtained in these experiments; the contact angle of a surface coated with PEMA homopolymerized in the absence of monomer 3 is also included. The coating formed after the photopolymerization of PEMA onto glass microslides gave a relatively high contact angle (79.3°) and a low surface energy (25.5 dyn/cm) because of the hydrophobic nature of the pendent groups. However, the presence of only 10 wt % of the fluorinated component in the mixture led to a coating with an even higher contact angle of 87.5°, an increase of 8.2°, and a surface energy of 19.8 dyn/cm.

Copolymerizations of PEMA with 2 or 10 wt % C8F7 were also carried out for comparison, and the results are presented in Figure 11. The contact angles of these surfaces were consistent with those obtained for the copolymers of PEMA with the *tert*-butyl ester intermediate of C8F7 (monomer 3) and confirmed the formation of low-surface-energy polymeric coatings.

The effect of low amounts of C8F7 was also investigated in a second copolymerization system with methyl acrylate along with 10 wt % hexane diol diacrylate (HDDA) as a crosslinker. These mixtures were polymerized onto glass substrates according to the procedure previously mentioned but at a temperature of 50°C. The contact angles of the coatings obtained with C8F7 at low fractions, along with that of the



**Figure 8** Water contact-angle measurements of C8F7 polymer coatings polymerized at 70°C.



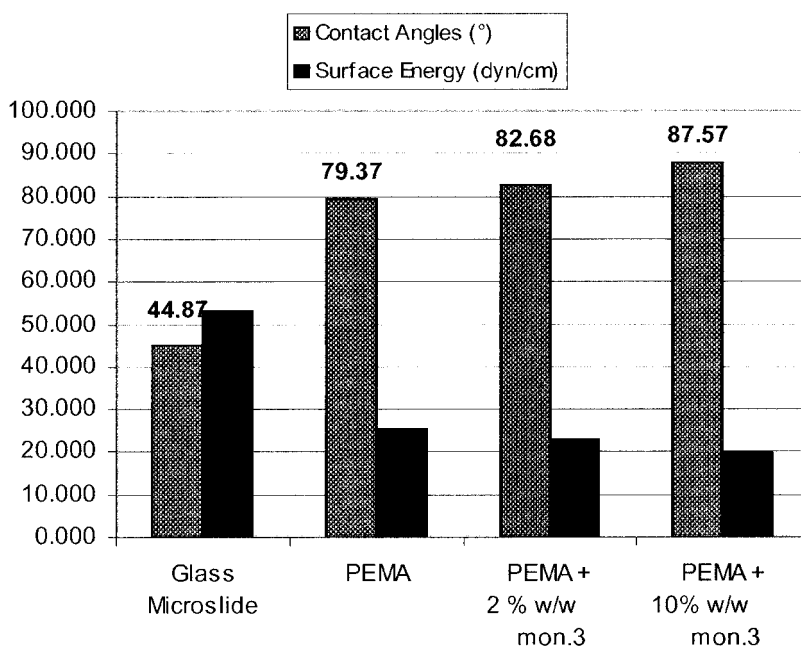
**Figure 9** *n*-Hexadecane contact-angle measurements of C8F7 polymer coatings obtained after photopolymerization at 70°C.

control coating prepared without the fluorinated material, are shown in Figure 12. The presence of 10 wt % C8F7 as a comonomer led to the formation of a low-surface-energy coating with a water contact angle of 99.3°.

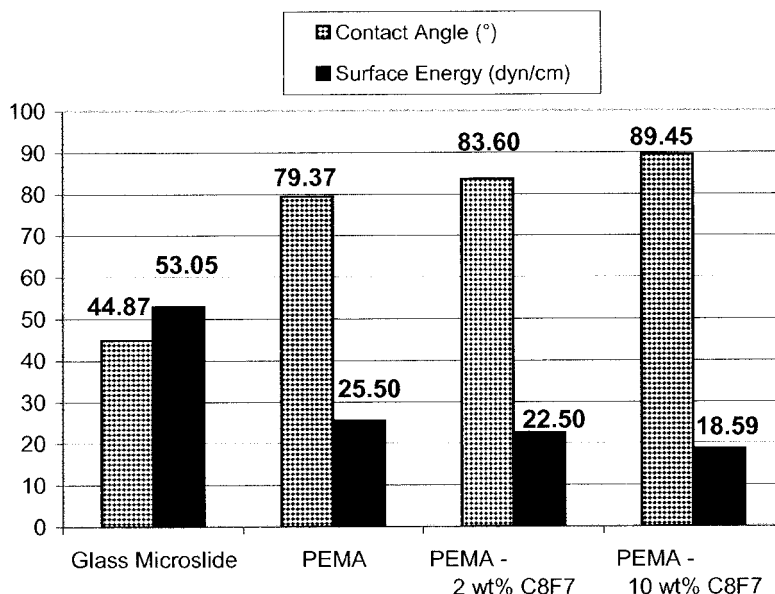
**Surface analysis**

ATR-FTIR spectroscopy was used to provide qualitative information about the surfaces of the coatings.

The molecular structure of the homopolymer of C8F7 obtained on glass was compared to copolymers of PEMA and methyl acrylate with low fractions of C8F7 (Fig. 13). Curve A (homopolymer of C8F7) shows C—F stretching bands at 1235, 1203, and 1146 cm<sup>-1</sup> and CF<sub>2</sub> and CF<sub>3</sub> bands in the 660-cm<sup>-1</sup> region. Spectra of the copolymers of PEMA with 10 and 2 wt % C8F7 are shown in curves B and C, respectively, whereas the spectrum of a homopolymer of PEMA is



**Figure 10** Water contact-angle and surface-energy measurements of copolymer coatings of PEMA and monomer 3 obtained by photopolymerization at 70°C.



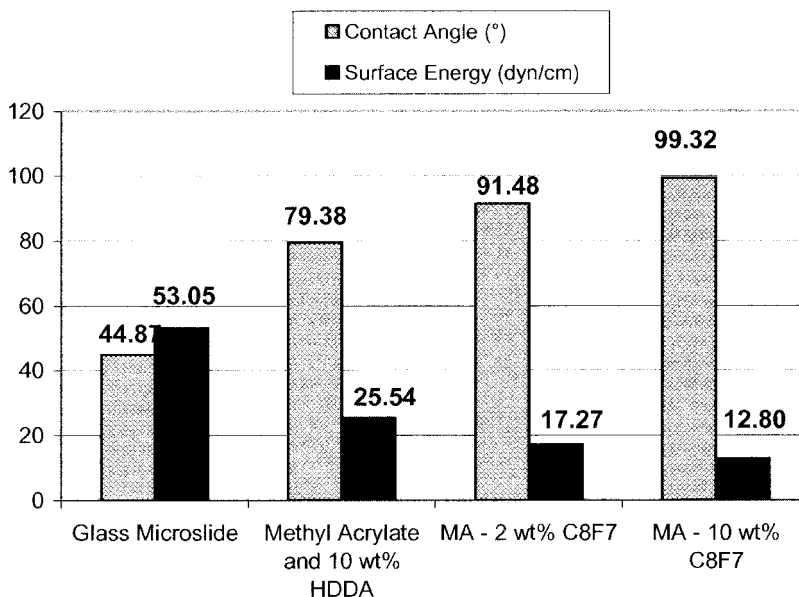
**Figure 11** Water contact-angle and surface-energy measurements of copolymer coatings of PEMA with C8F7 obtained by photopolymerization at 70°C.

shown in curve D. Curves E and F represent copolymers of methyl acrylate with 10 wt % HDDA and 10 or 2 wt % C8F7, respectively. The cured mixture of methyl acrylate with 10 wt % HDDA without C8F7 is shown in curve G. Small shoulders can be observed in the CF stretching band regions of curves C and F, confirming the presence of small amounts of the fluorinated component on the surfaces of these coatings. However, when larger amounts of the fluorinated comonomer (10 wt %) were present (curves B and E),

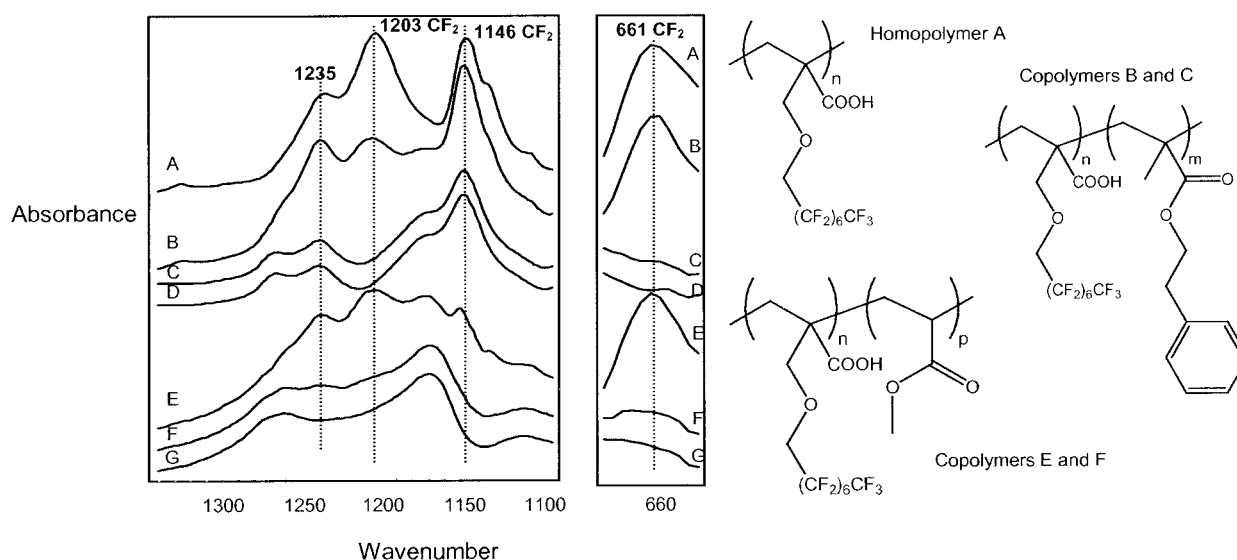
the peaks of fluorinated groups were more pronounced; this indicated preferential migration to the air-liquid interface.

## CONCLUSIONS

We have reported that the synthesis of C8F7 provides higher yields and allows the synthesis of larger quantities for coating applications. The coatings obtained after the photopolymerization of this



**Figure 12** Water contact-angle and surface-energy measurements of copolymers of methyl acrylate with 10 wt % HDDA or 0–10 wt % C8F7 obtained by photopolymerization at 50°C.



**Figure 13** ATR-FTIR spectra of (A) a homopolymer of C8F7, (B) a copolymer of PEMA with 10 wt % C8F7, (C) a copolymer of PEMA with 2 wt % C8F7, (D) a homopolymer of PEMA, (E) a copolymer of methyl acrylate with 10 wt % C8F7, (F) a copolymer of methyl acrylate with 2 wt % C8F7, and (G) a polymer mixture of methyl acrylate with 10 wt % HDDA.

monomer onto different substrates gave high contact angles and low-surface-energy values. The surfaces of the coatings obtained were found to be both hydrophobic and oleophobic; this indicated the selective concentration of the fluorinated segments at the surface–air interface. However, surface reorganization was observed in contact with water for coatings on Teflon because of changes in the orientation of the fluoroalkyl chains. In addition, even low weight fractions of the fluorinated monomer in a copolymer led to a lower surface energy of the coatings, which produced nonwettable surfaces. Typical values of the surface energy obtained for the C8F7 homopolymer coated onto stainless steel, Teflon, and glass microslides were 14.0, 27.05, and 12.03 dyn/cm, respectively. Qualitative information about the molecular environment at the surface of the polymer coatings was obtained by ATR-FTIR, which showed the presence of the fluorinated functional groups and confirmed the orientation of the fluorinated segments toward the air interface.

The coatings obtained also proved to be thermally stable, up to 270–290°C, after a weight loss around 200°C due to partial elimination of pentadecafluoro-1-octanol and the formation of a six-member lactone. This was possibly due to the proximity of the pendant groups in the polymer molecule on both sides of each carboxylic acid group. Cyclic anhydride formation, involving pairs of neighboring carboxylic acid pendant groups, was also possible in this temperature region. These results confirmed that a low-surface-energy polymeric material was obtained in excellent conversions through the photopolymerization of C8F7 on different substrates.

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