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Synthesis and cationic photopolymerization of a new fluorinated oxetane monomer

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Abstract

A new fluorinated oxetane monomer (FOX) was prepared using a fluorinated alcohol by phase transfer catalysis in a Williamson ether synthesis. The new fluorinated monomer was used in cationic photopolymerization as comonomer of 3,3′-[oxydi(methylene)]bis(3-ethyloxetane). The presence of the FOX monomer induces a decrease of the glass transition temperature, thermal stabilization and an increase of the final oxetane group conversion. Completely hydrophobic surfaces were obtained with a selective enrichment of the fluorinated comonomer, as confirmed by contact angle and XPS analysis.

Keywords: Fluorinated oxetane; Cationic photopolymerization; Surface properties

1. Introduction

The photoinitiated polymerization process is widely used for rapidly producing highly crosslinked polymer networks [1–5]. Among the advantages of this technology are the high cure speed, the reduced energy consumption and the very low organic solvent emission. In the process, radical or cationic species are generated by the interaction of the UV light with a suitable photoinitiator, which induces the curing reaction of suitable reactive monomers and oligomers: in cationic photopolymerization strong Bronsted acid are generated by UV dissociation of onium salt (iodonium or sulphonium) as reported in Scheme 1 for the generic iodonium salt (Eqs. (1)–(3)). The cationic photoinduced process presents some advantages compared to the radical one [6], in particular lack of inhibition by oxygen, low shrinkage, good mechanical properties of the UV cured materials and good adhesion properties to various substrates. Moreover, the monomers employed are generally characterized by being less toxic and irritating. Different types of monomers and oligomers have been proposed and reported in the literature [7].

Oxetane monomers seem to be a good alternative to epoxy photocurable monomers which are widely used nowadays in many industrial applications. They were introduced in UV curing by Crivello and Sasaki [8]. They observed that oxetane monomers are as reactive as multifunctional epoxy monomers with related structures in photoinitiated cationic polymerization [9], and sometimes their reactivity is even greater [10].

In this work, the synthesis of a new fluorinated monofunctional oxetane is reported; the effects of its presence, on bulk and surface properties of photocured oxetane films based on 3,3′-[oxydi(methylene)]bis(3-ethyloxetane) (DOX), are investigated by changing the ratio of monomers used to form the polymer.

Peculiar characteristics can be imparted to the networks due to the presence of fluorine, such as chemical and thermal stability, weathering resistance, low surface tension, hydrophobicity and oleophobicity, optical and electrical behavior [11].

In previous works, concerning both radical and cationic systems, different copolymers and fluorinated networks were prepared [12–15]; it was also shown that the introduction of fluorinated monomers in low amount in the UV curable formulations is very attractive for the specific surface properties obtained.

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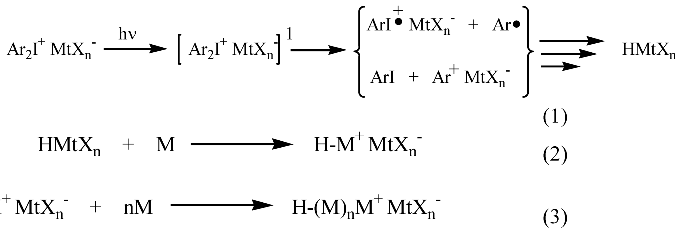


Scheme 1.

The aim of this work is to induce a change of bulk and surface properties of oxetane films starting from a suitable formulation containing an appropriate amount of the synthesized fluorinated nonfunctional oxetane.

2. Experimental

2.1. Materials

The fluorinated oxetane, 3-methyl-3-{[(3,3,4,4,5,5,6,6,6-nonafluorohexyl)oxy]methyl}oxetane (FOX) was synthesized following the procedure reported below and supplied by OMNOVA solutions Inc., (Akron, OH, USA). 3,3,4,4,5,5,6,6,6-Nonafluorohexanol is from Daikin Industries, Ltd (Osaka, Japan). 3-Bromomethyl-3-methyl oxetane is from Chemada Fine Chemicals (Israel). 3,3′-[Oxydi(methylene)]bis(3-ethyloxetane) (DOX) was generously supplied by Toagosei Japan. The structures of the products are reported in Table 1. Triphenylsulfonium hexafluoroantimonate ($Ph_3S^+SbF_6^-$), graciously supplied from DOW, was used as the cationic photoinitiator. It is available in solution of propylene carbonate (50% w/w) and was added to the curable mixtures at a concentration equal to 2 wt%.

2.2. Synthesis of fluorinated oxetane

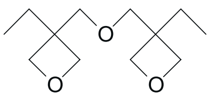
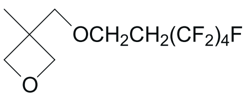
3,3,4,4,5,5,6,6,6-Nonafluorohexanol (3.5 kg, 13.2 mol), 3-bromomethyl-3 methyl oxetane (2.40 kg, 14.6 mol) and tetrabutyl ammonium bromide (106.81 g) are added to a 10 l jacketed reaction vessel equipped with a mechanical stirrer, temperature probe, reflux condenser, addition funnel, and a temperature controlled ethylene glycol water bath. The reaction temperature is set to 85 °C, and the mixture is allowed to equilibrate. Forty-five percent potassium hydroxide is added at over 2 h and 50 min. A maximum temperature of 91.3 °C was reached. An off-white precipitate is observed immediately upon the start of addition. Following the end of addition, conversion was determined with gas chromatography. Additional potassium hydroxide, or 3-bromomethyl-3 methyl oxetane are added as necessary until a conversion of 95% or higher is observed based on nonafluorohexanol. The reaction mixture was filtered to remove potassium bromide precipitate and 5% ammonium hydroxide (2.15 kg) is added and allowed to stir for 5 min. A phase separation is performed and the organic layer is washed with water (2.06 kg). Three hundred and fifty grams of heptane was added, then the heptane was removed under rotary evaporation along with water. A distillation was then performed and product was collected from 85–115 °C at 28.5 in Hg, followed by 3,3,4,4,5,5,6,6,6-nonafluorohexanol monomer between 125 and 130 °C at 28.5 in Hg. A total of 3.85 kg of 3-methyl-3-{[(3,3,4,4,5,5,6,6,6-nonafluorohexyl)oxy]methyl}oxetane were isolated resulting in an 83.4% yield. The product was characterized by ^1H, ^{13}C and ^{19}F NMR analyses. Chemical shifts are reported against internal tetramethylsilane for ^1H and ^{13}C and hexafluorobenzene (-162.5 ppm vs δ $CFCl_3 = 0$) for ^{19}F.

^1H NMR ($CDCl_3$) δ 1.31 ($-CH_3$, s, 3H), 2.34–2.49 ($-CH_2CF_2-$, t of t, 2H), 3.52 ($-CH_2O-$, s, 2H), 3.77 (OCH_2-, s, 2H), 4.33–4.51 (ring $-CH_2-$, AB q, 4H); ^{13}C NMR ($CDCl_3$) δ 21.2, 31.4, 39.9, 63.3, 76.5, 80.8; ^{19}F NMR ($CDCl_3$) δ -81.4, -113.81, -124.8, -126.5.

2.3. Film preparation

The films were obtained by coating the photopolymerizable mixtures on glass slides. The mixtures were spread on a glass slide with a calibrated wire-wound applicator to obtain a thickness of about 100 μm. The solvent was evaporated in air. The curing reaction was performed by UV irradiation using a Fusion lamp with radiation intensity on the surface of the sample of 280 mW/cm^2 and a belt speed of 8 m/min.

Table 1
Structure of the monomers

	
3,3′-[Oxydi(methylene)]bis(3-ethyloxetane) (DOX)	3-Methyl-3-{[(3,3,4,4,5,5,6,6,6-nonafluorohexyl)oxy]methyl}oxetane (FOX)

2.4. Film characterization

NMR spectroscopy was performed using a Varian Unity 400 spectrometer with a probe frequency of 399.945, 100.575 and 376.282 MHz for ^{1}H, ^{13}C and ^{19}F observation, respectively.

The oxetane group conversion during the photopolymerization was determined by FT-IR spectrometry by coating the photocurable mixture on a KBr disk and measuring the decrease of the oxetane absorption band at 830 cm^{-1}. The instrument used was a Genesis Series ATI Mattson (USA) Spectrometer. The gel content of the films was determined by measuring the weight loss after 20 h extraction at room temperature with different solvents, i.e. chloroform and trichlorotrifluoroethane.

DSC measurements were performed with a Mettler DSC30 (Switzerland) instrument, equipped with a low temperature probe. Contact angle measurements were performed with a Krüss DSA10 instrument, equipped with a video camera. Analyses were made at room temperature by means of the sessile drop technique. Three to five measurements were performed on every sample and the values averaged. The measuring liquid was doubly distilled water ($\gamma = 72.1$ mN/m).

XPS analyses were carried out with a Physical Electronics 5802 Multitechnique instrument using a probe beam of focused, monochromatic Al K_{α} X-rays (4 μA) with charge neutralization using a 1 eV electron flood gun. On each sample, data were acquired at a take-off angle (t.o.a.) in the order 25° (near-grazing), 45°, then 85° (near normal). Due to the 90° source-analyzer geometry, it was not possible to acquire data from a 90° take-off angle, so 85° was substituted instead. At each take-off angle a fresh location on the film ~1.5 cm from the previous acquisition was analyzed to minimize the effects of beam damage. The X-rays generate photoelectrons that are energy analyzed and counted to reveal the atomic composition and chemistry of the sample surface. The escape depth of the photoelectrons limits the depth of analysis to the outer ~50 Å. The data presented include low-resolution survey scans, which give the full spectrum between 0 and 700 eV binding energy. The spectra are used to obtain surface composition by integrating the areas under the photoelectron peaks and applying empirical sensitivity factors. The detection limits for most elements are on the order of 0.1 at.%.

The thermal stability of the photocured films was assessed by thermogravimetric analysis (TGA Leco TGA/601). Experiments were performed in air on samples of about 10 mg at a heating rate of 2 C/min from 25 to 600 °C.

3. Results and discussion

3.1. UV curing and bulk properties

Different coatings were obtained by introducing into the DOX resin the fluorinated monomers at a concentration ranging from 5 to 15 wt%. In this range, homogeneous and transparent formulations were obtained. The highest concentration of the fluorinated monomer in the reference resin DOX, as assessed by visual inspection, corresponds to the solubility limit. The mixtures were coated on glass slides and, upon UV irradiation, gave rise to transparent films of about 100 μm thick.

The polymerization process was monitored by FT-IR. In Fig. 1 the FT-IR spectra of the DOX/FOX 85:15 wt/wt mixture before (a) and after (b) curing are reported as an example. The complete disappearance of the oxetane IR

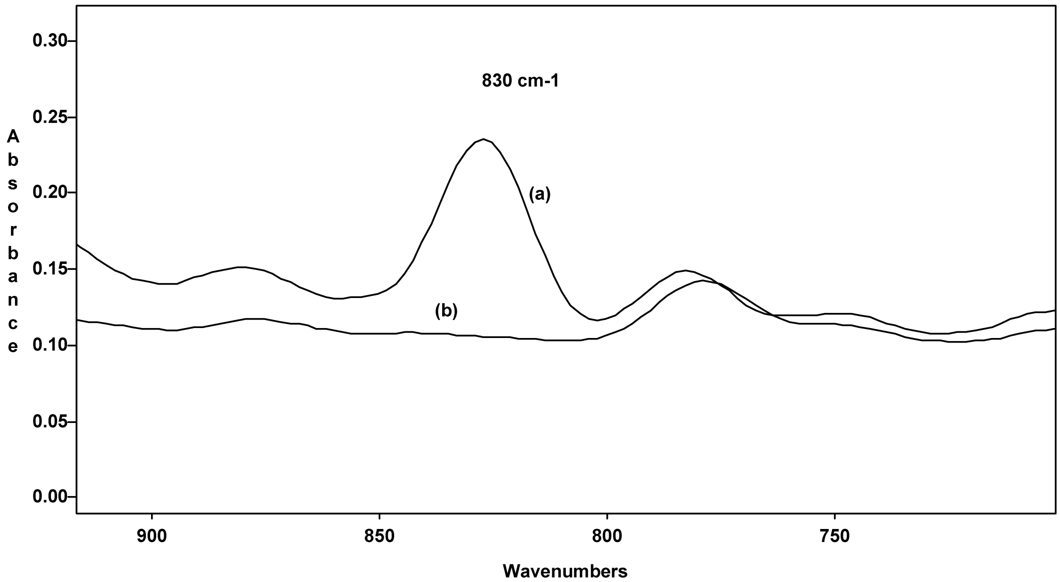


Fig. 1. FT-IR spectra of the DOX/FOX 85:15 wt/wt mixture before (a) and after (b) UV-curing.

Table 2
FT-IR conversion, glass transition temperature and gel content

Mixture	Oxetane conversion (%)	T_g (°C) DSC	Gel content (wt%)
Pure DOX	86	65	85
DOX/FOX 95:5 wt/wt	90	58	92
DOX/FOX 90:10 wt/wt	96	46	95
DOX/FOX 85:15 wt/wt	100	38	90

peak at 830 cm^{-1} is evident. In Table 2, final oxetane conversions are reported.

These results indicate that, by increasing the amount of the FOX monomer in the photocurable mixture, an increase of the final conversion to poly(oxetane) is achieved, reaching complete conversion in the presence of 15 wt% of FOX monomer.

At the same time, an increase of the gel content in the presence of the fluorinated additive is evidenced which reaches 90% in the case of the highest FOX/DOX ratio.

It is possible to explain these results by taking into account that the FOX monomer, being a monofunctional additive, induces a decrease of the crosslinking density of the network. As a consequence, the network structure is more flexible and the mobility of the reactive species is retained so that the polymerization can be completed. In other words, the decrease of the functionality of the reactive system delays the vitrification effect.

This is confirmed by the trend of the T_g values of the films as a function of the composition. The results of the DSC, reported in Table 2, show a decrease of the glass transition temperature as FOX content increases.

3.2. Thermal stability

Thermal stability of the photocured films was investigated by TGA analysis. The weight loss percentage in the temperature interval between 25 and 600 °C is reported in Fig. 2 for the pure photocured DOX film and for the film containing 10 and 15 wt% of FOX monomer.

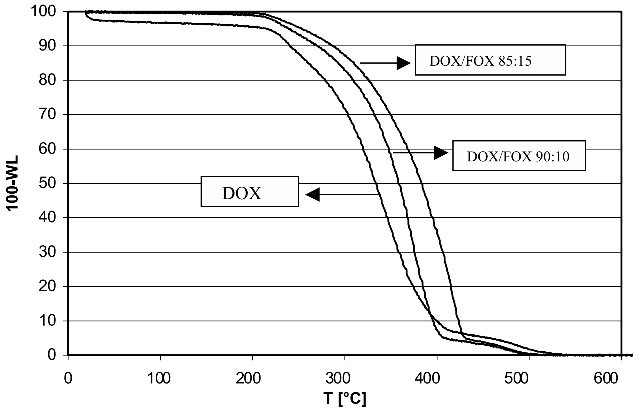


Fig. 2. Thermogravimetrical analyses of the photocured DOX and DOX/FOX films.

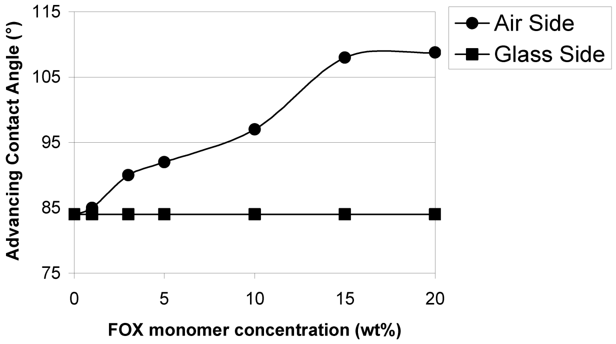


Fig. 3. Advancing contact angle measurements with water for photocured films.

All the films start to degrade at around 225 °C, but while the DOX photocured film yields a 10 wt% loss around 235 °C, the same loss is achieved only around 270 °C and around 300 °C for the films containing 10 and 15 wt%, respectively, of the FOX monomer in the photocurable mixture. Comparing the T_{50} data, the results have the same trend. While a DOX homopolymer 50% weight loss is reached at around 320 °C, for the DOX/FOX 90:10 sample at around 360 °C and for the DOX/FOX 85:15 specimen at around 400 °C. As expected, in the presence of the fluorinated additive, an increase of the thermal stability of the photocured films is observed.

3.3. Surface properties

Contact angle measurements were performed, with doubly-distilled water, on all the UV cured films, by peeling them off the glass substrate, then labeling the side in contact with the substrate as the glass side and the other one as the air side. The contact angle of the pure DOX photocured film is around 84° on both sides. When the fluorinated monomer is added to the curable product and the mixture coated on a glass substrate, the wettability of the air side of the films changes, as evidenced from the values reported in Fig. 3. Comparing the two sides of the films, the data clearly show that FOX additive is effective only at the air side, while the side in contact with the substrate keeps the same properties of the pure DOX monomer. The contact angle values on the air side depend on the additive concentration and increase by increasing the amount of the fluorinated additive.

The contact angle for the film containing 15 wt% of the fluoromonomer is very high (108°) and similar to that exhibited by a fully fluorinated polymer. This high

Table 3
Surface properties

Mixtures	$C_{16}H_{34}$ θ_{adv} (air side)	Surface tension (mN/m)
Pure DOX	0	36
DOX/FOX 95:5 wt/wt	15	32
DOX/FOX 90:10 wt/wt	27	29
DOX/FOX 85:15 wt/wt	35	24

Table 4
XPS surface concentrations (at.%)

FOX % (t.o.a. °)	C	O	F	C (calculated values)	O (calculated values)	F (calculated values)
0% (25)	78.9	20.6	0.1			
0% (45)	77.6	21.1	0.3	79.9	19.8	0.2
0% (85)	78.4	21.0	0.2			
5% (25)	69.3	19.5	11.0			
5% (45)	71.6	20.6	7.7	78.4	19.3	2.2
5% (85)	72.1	21.2	6.6			
10% (25)	66.6	18.5	14.7			
10% (45)	69.2	19.5	11.2	77.1	18.9	3.9
10% (85)	69.8	20.2	9.9			
15% (25)	57.2	15.0	27.5			
15% (45)	61.1	16.6	22.0	75.5	18.4	6.1
15% (85)	63.4	17.8	18.4			

hydrophobicity surface is a consequence of the segregation effect of the fluorinated oxetane which, due to its low surface energy, migrates towards the air interface and concentrates in the outermost layer.

This behavior has been discussed at length in the literature for polymer blends [16,17], copolymers [18,19] and polymeric solutions [20]. Similar segregation results have already been observed in photopolymerized systems which contained low amounts of acrylic monomers having perfluoroalkyl branches [21,22] or perfluoroalkylether chains [23].

The wettability of the films with hexadecane was also measured as reported in Table 3. There is an increase in the oil repellency in the presence of the fluorinated momomer judging by the increasing hexadecane contact angle with increasing FOX monomer in the copolymer. From the contact angle measurements with water and hexadecane by means of the harmonic mean method [24], the surface tension of the films was calculated. A decrease of the surface tension by increasing the fluorinated monomer concentration can be observed.

3.4. X-ray photoelectron spectroscopic analyses

The contact angles on the UV cure films suggest that the composition of the air/polymer interface is different from the bulk. The surface segregation of the low free energy component of the DOX/FOX copolymer (i.e., FOX) at the air side of the film, as suggested above, can be checked by surface spectroscopic analysis.

In Fig. 4, typical XPS spectra at different t.o.a. are reported. Shown are data for the air side of DOX films, with the typical signals due to C1s and F1s being present. High resolution C1s and F1s shown in Fig. 5 display the appearance of fluorine signals at 690 eV when the FOX is at 5 wt% and the signal strongly increases when the concentration goes up to 10 and 15 wt%. At the same time, near the main C1s signals at 285 eV, two weak peaks appear at higher energy due to the C–F bonds. As the 45° spectra have been collected at high resolution, peak deconvolution has been performed, as shown in Fig. 6. The peak at 285 eV is due to the main bonds, C–H or C–C and to the C–O ether bonds present in the oxetane system. The peaks at 295 eV are due to C–F bonds with a different degree of substitution i.e. CF_2 and CF_3.

Carbon, oxygen and fluorine atomic compositions were determined at take-off angles (t.o.a.) 25, 45 and 85°. The results are collected in Table 4, together with the atomic percentage of the elements calculated on the basis of the mixture composition. The most interesting features concern the fluorine content. In the pure DOX film, the amount found corresponds to the concentration of the photoinitiator counterion (SbF_6^-). For the copolymers, the calculated and the experimental data are very different and the amount is three to five time larger than the calculated one.

The fluorine concentration also increases as the t.o.a. decreases, indicating that the fluorine is more concentrated at the air/film interface than in the bulk and there is a concentration gradient from the inner (higher t.o.a.) to the

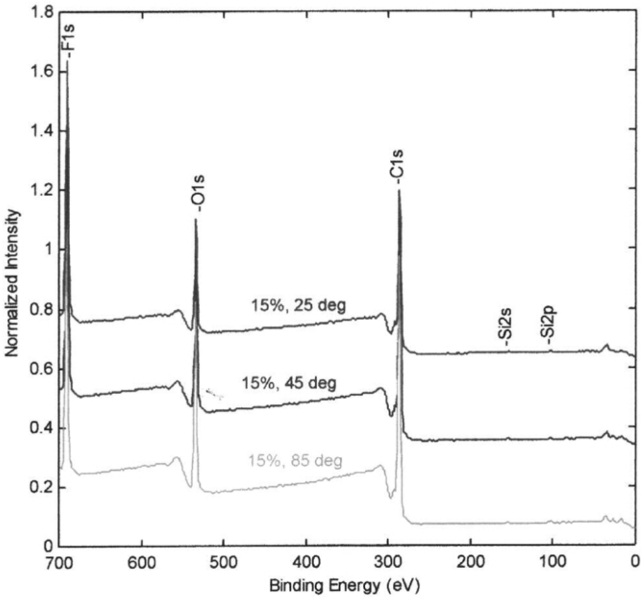


Fig. 4. Typical XPS survey spectra for the 15 wt% FOX copolymer.

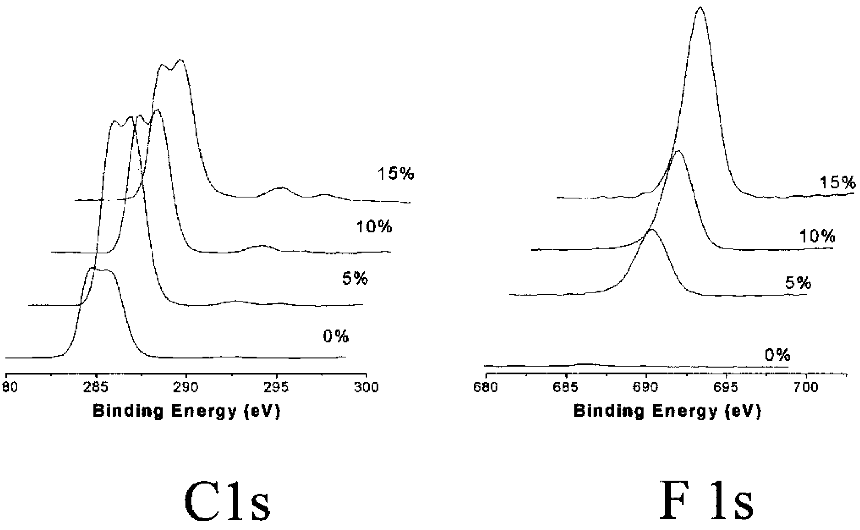


Fig. 5. High resolution C1s and F1s XPS spectra collected at a take-off angle of 45°.

very external surface (lower t.o.a.). It is interesting to observe that in the copolymer, the fluorine concentration increases as the oxygen amount decreases at the surface. There, the oxygen concentration is lower than the calculated one. This is a further evidence of the FOX surface migration; moreover, a selective segregation of the fluorinated chain could be seen.

The monomer surface concentration can be calculated on the basis of the fluorine atom results and values are reported in Table 5. The FOX monomer nearly saturates the surface

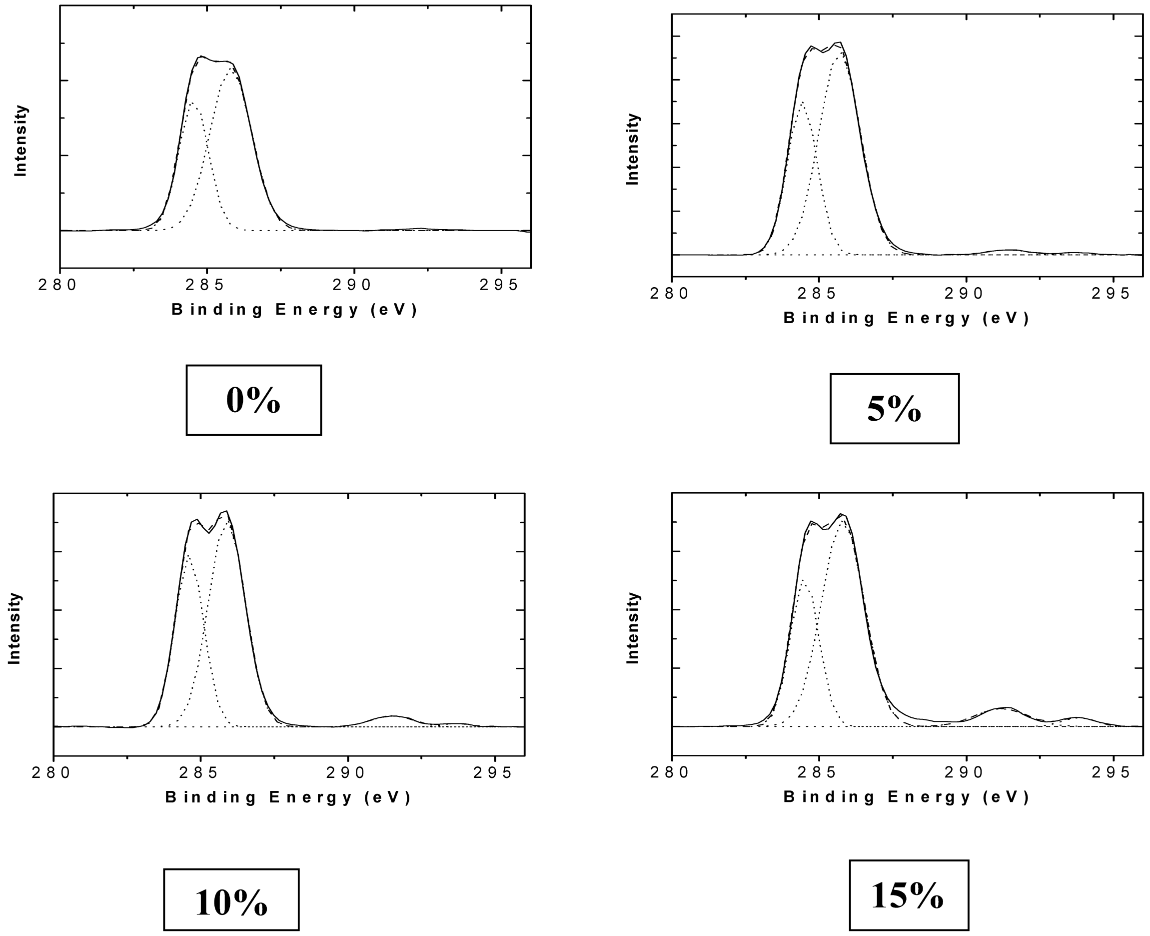


Fig. 6. Deconvolution of the C1s region of the high resolution data collected at a take-off angle of 45 °C for different weight fractions of FOX in the copolymer.

Table 5
Monomer surface concentration

% FOX	25°	45°	85°
5 wt%	39	27	23
10 wt%	52	40	35
15 wt%	97	78	64

when its bulk concentration is 15 wt% and that is in agreement with the contact angle results.

4. Conclusions

A new fluorinated oxetane monomer was prepared using a fluorinated alcohol assisted by phase transfer catalysis (PTC) in a Williamson ether synthesis. The fluorinated monomer (FOX) was used as comonomer at different concentration (between 1 and 15 wt%) in cationic photopolymerization in the presence of a difunctional oxetane.

The presence of the FOX monomer introduced a modification of the bulk properties, namely a decrease of the glass transition temperature a thermal stabilization and an increase of the final oxetane group conversion. The photocured film became highly hydrophobic in the presence of the fluorinated oxetane. A selective enrichment of FOX was observed at the air side of the film while the opposite side, in contact with glass, was not modified. Surface segregation of the low free energy component, the fluorinated oxetane, was confirmed by XPS analysis. Atomic compositions at different t.o.a. showed a fluorine concentration profile normal to the surface.

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