

Synthesis, UV-curing Behavior and Surface Properties of Fluorine-containing Vinyl Ether Polymers^{*}

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Abstract Five fluorine-containing vinyl ether monomers were prepared by the reaction between 2-vinyloxy ethanol, a fluorinated alcohol and hexafluorobenzene in the presence of sodium hydride in dimethylformamide. Two representative properties of these monomers, UV-curing behavior initiated by a cationic photo-initiator PAG 201 and surface free energy of coating films, were investigated. Photo-polymerization proceeded both rapidly and completely with a high double-bond conversion (> 90%) and a fast curing rate (maximum curing time < 21 s) for three monomers. The surface energies of the monomers and the resulting polymer films were then investigated. The minimum surface free energy of the UV-cured homopolymer films reaches 7.1 mJ/m². X-ray photoelectron spectroscopy data show that the low surface tension is influenced by fluorine content in the soft segments and fluorinated chains' migration to the surface. The five monomers exhibit low viscosity, low surface energy, good thermal stability and good photo-polymerization properties, which make them great candidates for UV coating and photoresist applications.

Keywords: Fluorine-containing vinyl ether; Photo-initiated polymerization; Hydrophobic films; Low surface energy.

INTRODUCTION

Fluorinated polymers are well known as low surface energy materials, which have outstanding properties, such as optical and electrical behavior, weathering resistance, chemical and thermal stability, low surface energy, hydrophobicity and oleophobicity^[1]. The introduction of fluorine compounds into UV-curable systems is promising because photo-curing technology possesses the properties of fast curing rate, low energy consumption and environmental protection^[2]. UV-cured fluorinated polymers have been widely applied in different fields such as coatings, photoresists, inks and even many high-tech and electronic applications, such as coatings on optical fibers and microelectronics and the fabrication of printed circuit boards^[3].

Among UV curing cationic systems, the epoxy system is widely used in many industrial applications. However, the vinyl ether system is a good alternative because of its high curing rate and the relatively low viscosities of monomers^[4]. The previous studies have focused mainly on fluorine-containing acrylate (or methacrylate) monomers which go through free-radical photo-polymerization process^[5, 6]. However, cationic UV-initiated photopolymerizations have several advantages over free-radical photopolymerizations. Epoxides and vinyl ethers that are cured using a cationic mechanism have negligible toxicity, are not inhibited by oxygen and have low shrinkage during curing.

In this study, we have incorporated fluorine chains into the UV-curable monomers, which is a combination of cationic photo-polymerization and low surface energy materials. This can make an overall improvement in hydrophobicity of the curing polymers^[7]. According to recent reports in the literature, the reaction of an alcohol

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and hexafluorobenzene represents one of the most facile ways of connecting vinyl ethers with fluorine chains^[8]. Based on this reaction, we designed and synthesized a series of monomers for polymerization. We have also improved the purity and yield of the monomers, and therefore made what we believe to be a novel contribution to the synthesis of fluorine-containing vinyl ether compounds.

Several researchers have investigated the cationic polymerizations of fluorinated vinyl ether monomers: Bongiovanni studied the cationic polymerization of 1H,1H,2H,2H-perfluorooctyl vinyl ether^[9, 10]. This reaction was initiated by the HI/ZnI₂ system leading to living poly(vinyl ether)s bearing fluoroalkyl side groups. Meskini *et al.*^[11] reported the copolymerization of vinylidene cyanide with a fluorinated vinyl ether (1H,1H,2H,2H-perfluorooctyl vinyl ether) for super hydrophobic and highly oleophobic films and their water contact angle was found to be 168 ± 3 (°).

We thus synthesized fluorinated vinyl ethers and their behavior was evaluated. These monomers, together with PAG 201 as a cationic photoinitiator were used to study UV-curing kinetic behavior by real time Fourier transform infrared (RT-FTIR) spectroscopy. The effects of surface fluorine content, thermal properties, and viscosity were also investigated. We also investigated the surface properties of these hydrophobic films.

EXPERIMENTAL

Materials

Sodium hydride (57%–63% dispersed in mineral oil), 2,2,2-trifluoroethanol, 2,2,3,3,4,4,4-heptafluoro-1-butanol, hexafluorobenzene and ethyl vinyl ether were purchased from Alfa Aesar China Ltd (Tianjin, China). These reagents were used without further purification. Dimethylformamide (DMF), tetrahydrofuran (THF) and petroleum ether were provided by Beijing Chemical Reagent Company (Beijing, China). These reagents were distilled and dried over calcium hydride for DMF and sodium for THF. The photo-acid generator (PAG) consisting of a mixture of triphenylhexafluoro-antimonic acid (SbF₆) sulfonium salts ($\lambda_{\max} = 301$ nm) was provided by Power Electronic New Material Co., Ltd. (Changzhou, China) and named PAG 201 as shown in Fig. 1.

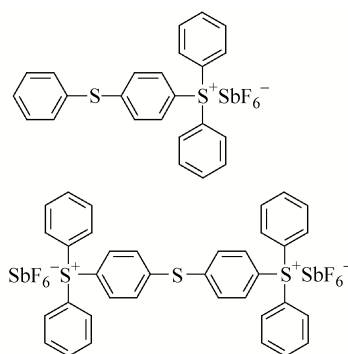
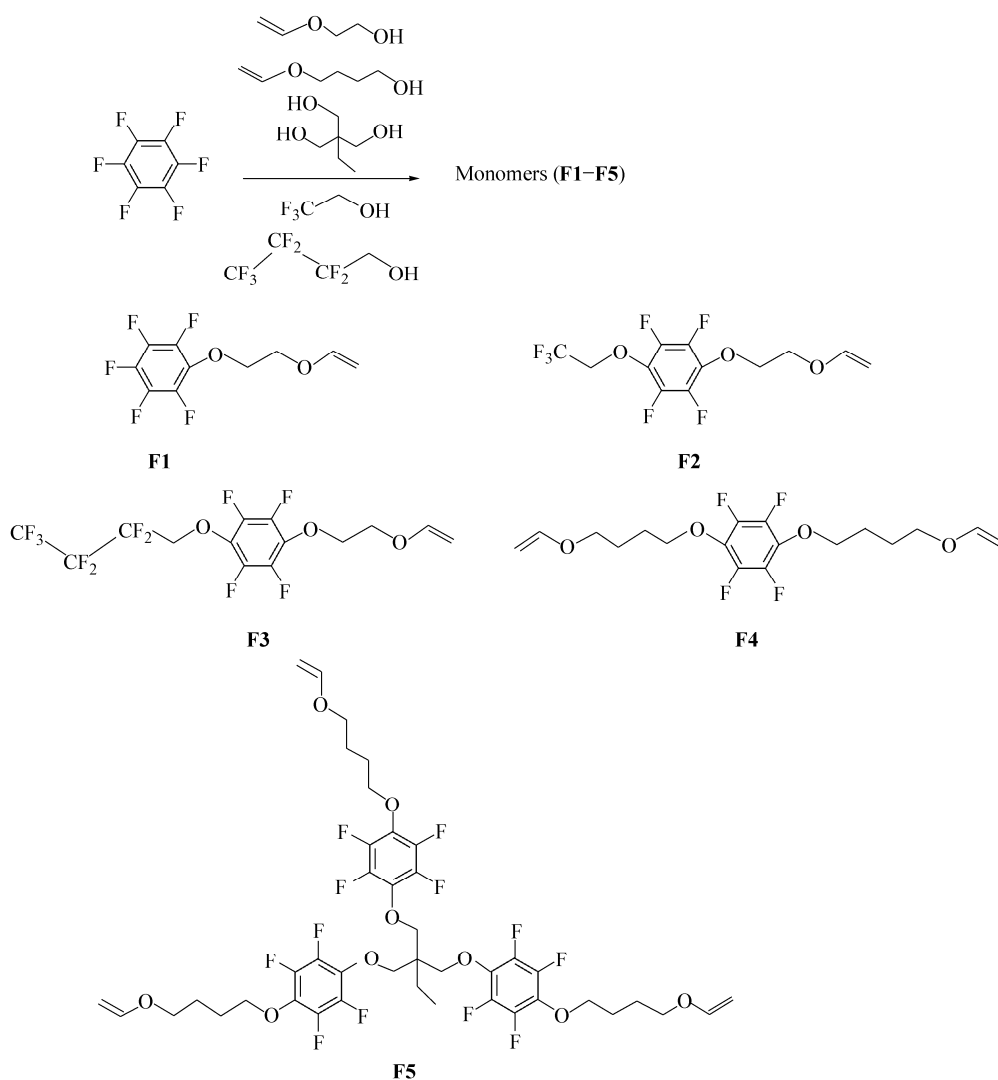


Fig. 1 Structure of the photo-initiators PAG 201

Synthesis of UV-curable Fluorinated Vinyl Ether Monomers

Five different UV-curable fluorinated vinyl ether monomers (**F1–F5**) were synthesized by the reaction of 2-vinyloxy ethanol with a fluorinated alcohol and hexafluorobenzene in the presence of sodium hydride in DMF, as shown in Scheme 1. Petroleum ether (3×50 mL) was used to extract the product. After washing with water (3×30 mL), the product was dried over anhydrous MgSO₄. The solvent was removed by rotary evaporation, and then the residue was purified under reduced pressure to obtain the final oily product. The yield of the monomers was higher than 80%. IR, ¹H-NMR, and ¹⁹F-NMR were used to characterize the monomer structures. ¹H-NMR spectra and ¹⁹F-NMR spectra were obtained on an Avame PRX500 Bruker-H NMR spectrometer (Bruker Corporation, Germany) with tetramethylsilane as an internal standard in CDCl₃. IR spectra were recorded on a Nicolet 5700 instrument (Thermo Electron Corporation, Waltham, MA, USA) at room temperature.



Scheme 1 Synthesis of the UV-curable fluorinated vinyl ether monomers **F1–F5**

Monomer F1: 2,3,4,5,6-pentafluorophenoxy-ethoxyethylene (80% yield, yellow liquid)

IR (cm⁻¹): 1639.6, 1620.7 (–O–C=C), 1203.3 (C–O–C), ¹H-NMR (400.0 MHz, CDCl₃): 6.41 (m, 1H), 4.33 (t, 2H), 4.13 (dd, 1H), 4.00 (dd, 1H), 3.94 (t, 2H). ¹⁹F-NMR (400.0 MHz, CDCl₃): –156.51 (m, 2F), –163.05 (m, 1F), –163.32 (m, 2F).

Monomer F2: 4-trifluoroethoxy-2,3,5,6-tetrafluorophenoxy-ethoxyethylene (89% yield, yellow liquid)

IR (cm⁻¹): 1639.6, 1618.1 (–O–C=C), 1202.1 (C–O–C), ¹H-NMR (400.0 MHz, CDCl₃): 6.41 (m, 1H), 4.40 (t, 2H), 4.33 (m, 2H), 4.16 (dd, 1H), 4.00 (dd, 1H), 3.96 (t, 2H). ¹⁹F-NMR (400.0 MHz, CDCl₃): –74.8 (s, 3F), –156.9 (d, 2F), –167.5 (d, 2F).

Monomer F3: 1-(perfluorobutylethoxy)-4-vinyloxyethoxy-2,3,5,6-tetrafluorobenzene (85% yield, yellow liquid)

IR (cm⁻¹): 1639.6, 1618.1 (–O–C=C), 1202.1 (C–O–C), ¹H-NMR (400.0 MHz, CDCl₃): 6.41 (m, 1H), 4.50 (t, 2H), 4.39 (m, 2H), 4.13 (dd, 1H), 4.00 (dd, 1H), 3.94 (t, 2H). ¹⁹F-NMR (400.0 MHz, CDCl₃): –80.9 (s, 3F), –122.4 (s, 2F), –127.7 (s, 2F), –156.5 (m, 2F), –167.5 (m, 2F).

Monomer F4: 2,3,4,5-tetrafluorophenoxy-1,6-diethoxyethylene (90% yield, white solid)

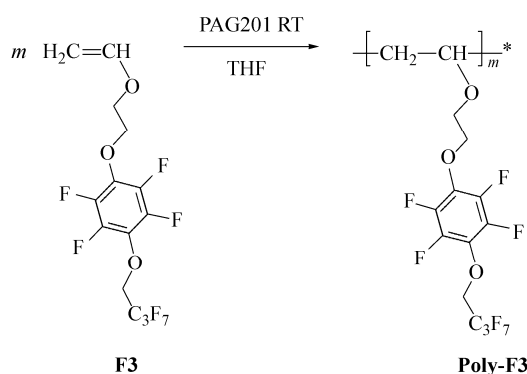
IR (cm⁻¹): 1639.6, 1618.1 (—O—C=C), 1202.1 (C—O—C), ¹H-NMR (400.0 MHz, CDCl₃): 6.39 (m, 2H), 4.12 (t, 2H), 4.10 (d, 2H), 4.00 (dd, 4H), 1.80 (m, 8H). ¹⁹F-NMR (400.0 MHz, CDCl₃): -157.8 (s, 4F).

Monomer F5: tri(2,3,4,5-tetrafluorophenoxy-6-diethoxyethylene-1-oxymethyl)propane (90% yield, yellow solid)

IR (cm⁻¹): 1639.6, 1618.1 (—O—C=C), 1202.1 (C—O—C), ¹H-NMR (400.0 MHz, CDCl₃): 6.39 (m, 3H), 4.12 (t, 3H), 4.10 (d, 3H), 4.00 (dd, 6H), 1.80 (m, 12H), 1.18 (m, 8H), 0.93 (m, 3H). ¹⁹F-NMR (400.0 MHz, CDCl₃): -157.8 (s, 4F).

Polymerization and Film Preparation

These polymers were obtained in the presence of the photo-initiator PAG 201 (2.0 wt% or 3.0 wt%). The UV-curable fluorinated vinyl ether monomer **F3** was polymerized according to the process shown in Scheme 2.



Scheme 2 Cationic polymerization of fluorinated monomer **F3** at room temperature in THF and initiated with PAG 201 (3.0 wt%)

The films were made by coating these mixtures onto glass slides or silicon wafers and the mixtures were prepared by controlling the concentrations of the fluorinated monomers. The photo-initiator PAG 201 (2.0 wt% or 3.0 wt%) was dissolved in THF and added to solutions of the monomers at specific concentrations. The mixtures were spread onto glass plates and after drying the glass plates in an oven at 60 °C for 5 min these dried films were cured using a low-pressure mercury UV lamp (about 30 μW/cm², λ_{max} = 365 nm) over 10 min. The mixtures were cast onto glass plates and dried in an oven at 60 °C for 25 min to prepare the independent film samples for thermogravimetric analysis, X-ray photoelectron spectroscopy (XPS) measurements and static contact angle measurements.

Characterization and Properties

RT-FTIR was used to investigate the kinetics of UV-cured polymerization. The light source was a 200 W high-pressure mercury lamp with a wavelength range of 200–440 nm. The UV light intensity at the sample was 30 mW/cm². The solvent contained in the sample was evaporated over 10 min before UV curing.

Static contact angle measurements were carried out at room temperature using a contact angle analyzer (OCA15-EC, Data Physics Instruments, Germany). The sessile drop technique (each droplet's volume was *ca.* 2 μL) was used together with a video camera and image analyzer. The liquids used for measurements were twice-distilled water and diiodomethane. The temperature and relative humidity were 23 ± 1.5 °C and 55 ± 5%, respectively. At least five measurements were obtained for each film and the deviation from the average was less than 3°.

XPS was performed on the UV-cured films to analyze their surface composition using an X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo Scientific Ltd) and an Al Kα X-ray source (1486.6 eV). Under standard conditions, the X-ray source worked at 100 W, 10 kV, and 10 mA to irradiate the samples and the pass energy was 30 eV. Information was acquired from measurements of electrons escaping from the sample

surface at an angle of 90° resulting in higher resolution spectra for fluorine 1s (F_{1s}), carbon 1s (C_{1s}), and oxygen 1s (O_{1s}). From the peak area, the ratio of the fluorine content on the surface was evaluated.

The thermal stability of these photo-crosslinked copolymers was measured by conducting thermogravimetric analysis (Mettler-Toledo TGA/DSC 1/1100 instrument). The weight of the copolymers was 5 mg and the specimens were placed in an aluminum pan and heated at a heating rate of 10 K/min from room temperature to 600 °C in air.

RESULTS AND DISCUSSION

Analysis of Monomer Properties

From the data in Table 1, we can summarize that the introduction of aromatic rings can increase the viscosity and thermal stability of monomers. These physical properties of low viscosity and thermal stability satisfied the material requirements for UV imaging materials.

Table 1. The fluorine content (FC), decomposition temperature (DT) and viscosity (mm²/s, 25 °C)

Monomers	FC (wt%)	Viscosity	DT (°C)
F1	37.4	2.61	156.8
F2	39.8	5.60	172.5
F3	48.2	9.79	191.0
F4	20.1	–	246.2
F5	24.8	–	281.5

Photo-polymerization Kinetics

The UV-curing kinetics of fluorinated vinyl ether monomers was measured by using RT-FTIR, and the UV light intensity was 30 mW/cm². Conversion data could be obtained by monitoring the decay of $\nu_{C=C}$ peak around 1620 cm⁻¹. Upon irradiation, the decrease of the absorption peak area accurately reflects the extent of polymerization; the decrease of the absorption peak area was directly proportional to the number of double bond functionalities that had been polymerized. The degree of conversion (DC) of the function groups could be calculated by measuring the peak area at each time of the reaction and determined using the following equation:

$$DC(\%) = (A_0 - A_t) / A_0 \times 100 \quad (1)$$

where DC is the conversion at time t , and A_0 and A_t are the peak area of the functional group before irradiation and at time t .

The concentration of PAG201 is one of the important factors that affect the UV-curing process (Figs. 2 and 3). Proper concentration of PAG201 can promote the UV-curing system to obtain faster polymerization rate and higher conversion, but it doesn't mean that increase higher concentration is always a proper choice.

The polymerization proceeded quickly, 80% of the vinyl ether double bonds were consumed after 27 s irradiation for most monomers. Moreover, we find that the photo-initiator concentration can influence the curing reaction, the conversion with 3 wt% PAG201 is higher than the conversion with 2 wt% PAG201.

The most important parameters, including the maximum curing time and the final conversion, characterize the curing kinetics of these cationic UV-cured systems are shown in Table 2.

Table 2. The maximum curing time and final conversion of the UV-curable fluorinated monomers with 3.0 wt% and 2.0 wt% PAG201

	Monomers with 3.0 wt% PAG201		Monomers with 2.0 wt% PAG201	
	Maximum curing time (s)	Final conversion (%)	Maximum curing time (s)	Final conversion (%)
F1	20.9	99.9	26.8	96.0
F2	14.9	98.1	20.9	95.9
F3	17.9	89.3	17.9	82.0
F4	188.0	88.6	188.0	62.3
F5	89.5	100.0	109.9	80.3

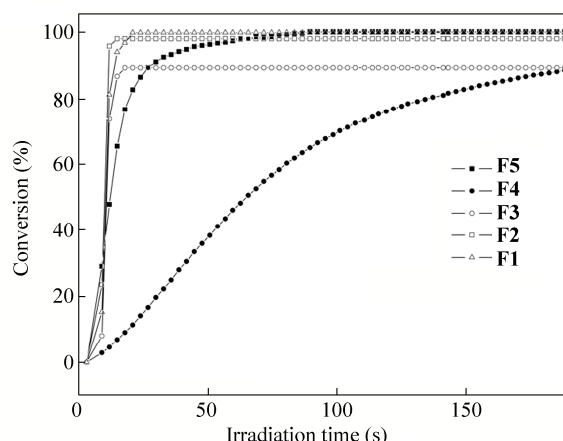


Fig. 2 Conversion-time curves with 3.0 wt% PAG201 before and after 3 min of curing

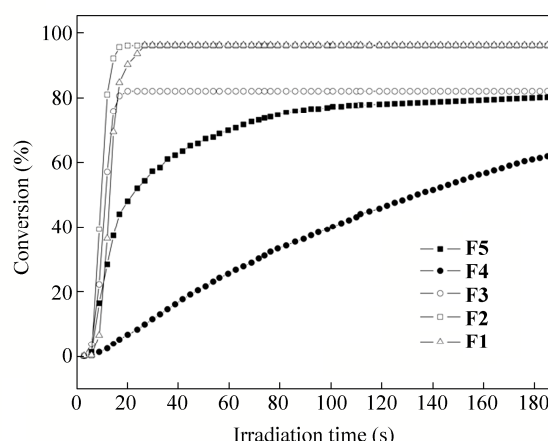


Fig. 3 Conversion-time curves with 2.0 wt% PAG201 before and after 3 min of curing

On the basis of these findings, we could conclude that the conversion of vinyl ether double bonds changed sharply by the introduction of different PAG201 concentrations in such small amounts. The photopolymerization proceeds efficiently with a high double-bond conversion ($> 89\%$) and a fast curing rate (< 21 s) for **F1**, **F2** and **F3** with 3.0 wt% PAG201. With the increase of fluorine content, the final conversion of these three monomers decrease. For the solid monomers **F4** and **F5**, the activity is so low that they need more time to cure completely. Especially for monomer **F4**, this monomer does not have good compatibility with the photo-initiator, which results in the lowest final conversion. The impact of PAG201 concentration for solid monomers **F4** and **F5** is larger than that for liquid monomers **F1**, **F2** and **F3**. Therefore, 3.0 wt% PAG201 is a better choice for the whole cationic UV-cured system.

Surface Properties

Contact-angle measurements were performed, with twice distilled water and diiodomethane, on all the UV-cured films. The typical water contact angle of the pure vinyl ether monomer was 77° ^[9]. But for a fluorinated monomer, the surface energy greatly changed, as shown in Table 3. For the system containing **F3**, a value of 119° was obtained; this result means that the surface was hydrophobic.

Table 3. Contact angle and surface free energy of the UV-cured films

Samples	Fluorine content (wt%)	Contact angle ($^\circ$)		Surface free energy (mJ/m^2)		
		θ_w^a	θ_{dim}^b	γ^d	γ^p	γ^e
F1	37.4	102.9 ± 1.5	80.2 ± 1.9	-0.8	17.6	16.8
F2	39.8	104.9 ± 2.2	83.5 ± 1.6	-0.5	16.1	15.6
F3	48.2	119.1 ± 2.4	100.4 ± 2.1	-1.7	8.8	7.1
F4	20.1	95.2 ± 2.7	58.8 ± 3.2	-4.0	30.3	26.3
F5	24.8	96.8 ± 2.0	61.4 ± 1.7	-3.3	28.6	25.3
GLASS	—	21.8 ± 1.4	47.4 ± 2.6	36.6	18.3	54.9

^a Contact angle by water; ^b Contact angle by diiodomethane; ^c γ^d = dispersion force component;

^d γ^p = polar force component; ^e γ = surface free energy

Indeed, as in previous studies, the higher the fluorine content of the monomer, the higher the contact angle^[10]. These data indicate that there was a dependence on the fluorine content of monomers, the higher the fluorine content in the monomer, the more evident the effect induced on the surface properties. Similar behavior was observed in a previous work reporting the photo-polymerization of diacrylate with fluoroacrylates^[11].

XPS shows this difference by providing direct information about the relative concentrations of different atoms. This method is crucial for determination of the composition of the outermost layer of the coating under

high vacuum.

The XPS spectrum of the UV-cured **F1** film is shown in Fig. 4. The photoemission peaks of the F_{1s}, O_{1s}, C_{1s}, and N_{1s} core levels were observed with bonding energies of 688, 532, 285, and 400 eV, respectively. The element content of the film-air surface is shown in Table 4.

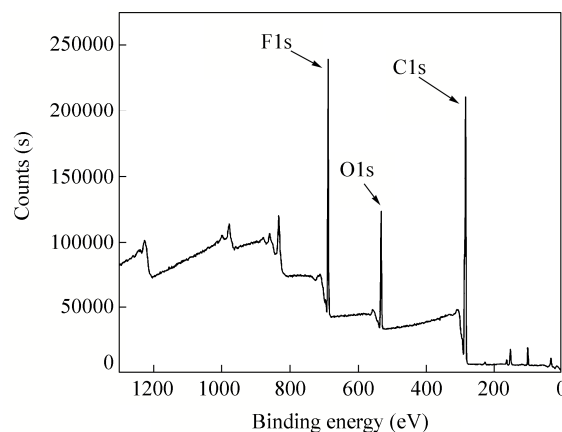


Fig. 4 XPS spectrum of the UV-cured **F1** film

Table 4. Element content of the film-air surface

Element	Estimated atomic% in the films	Atomic% measured by XPS
F 1s	29.17	34.19
O 1s	8.33	5.32
C 1s	37.50	35.48

The samples containing fluorine gave higher fluorine content than that estimated in the bulk, indicating that the fluorinated groups migrated to the extreme surface of the film. For this reason, the fluorinated films have lower surface energy.

CONCLUSIONS

Five different UV-curable vinyl ether monomers with perfluorinated aromatic units were designed and synthesized. The synthetic method has advantages of high yield and mild situation. With the introduction of aromatic rings, the viscosity and thermal stability of monomers increase. The figure regarding UV-curing kinetics exhibits a high double-bond conversion ($> 80\%$) and fast curing rate (maximum curing time < 27 s) for most monomers. Compared with the concentration of 2.0 wt% PAG201, 3.0 wt% is a better choice for the whole cationic UV-cured system. An increase in hydrophobic fluorine content had a strong effect on the UV-curing reaction. Upon the addition of a fluorinated monomer to the curable resin and the mixture coated on the glass substrate, the surface energy changed significantly. The water contact angle can reach 119.1 ± 2.4 ($^\circ$) indicating that hydrophobic surfaces were obtained. The minimum surface free energy of these films is less than $10 \text{ mJ} \cdot \text{m}^{-2}$. Low surface tension of these films is not only the influence of high fluorine content in the soft segments, but also the effect fluorine migration ability to the surface. The polymers also exhibit good thermal stability.

REFERENCES

- 1 Dreher, W.R., William, L.J. and Urban, M.W., *Macromolecules*, 2005, 38(6): 2205
- 2 Sha, X.Z., Pang, Y.L. and Zou, Y.Q., *Chin. Sci. Bull.*, 2013, 58(13): 1536
- 3 Xie, K.L., Hou, A.Q. and Shi, Y.Q., *J. Appl. Polym. Sci.*, 2008, 108(3): 1778

- 4 Golaz, B., Michaud, V., Leterrier, Y. and Manson, J., *Polymer*, 2012, 53(10): 2038
- 5 Xiao, S.Z. and Zou, Y.Q., *Chem. J. Chinese U.*, 2011, 32(2): 383
- 6 Fang, Y. and Zou, Y.Q., *Polym. Int.*, 2013, 62(11): 1624
- 7 Bongiovanni, R., Medici, A., Zompatori, A., Garavaglia, S. and Tonelli, C., *Polym. Int.*, 2012, 61(1): 65
- 8 Song, B.J., Park, J.K. and Kim, H.K., *J. Polym. Sci. Part A: Polym. Chem.*, 2004, 42(7): 6375
- 9 Bongiovanni, R., Malucelli, G., Sangermano, M. and Priola, A., *J. Fluorine Chem.*, 2004, 125(2004): 345
- 10 Bongiovanni, R., Sangermano, M. and Malucelli, G., *J. Polym. Sci. Part A: Polym. Chem.*, 2003, 41(18): 2890
- 11 Ahmed, M., Mustapha, R. and Bruno, A., *Macromolecules*, 2009, 42(10): 3532