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## Preparation and hydrophobicity failure behavior of two kinds of fluorine-containing acrylic polyurethane coatings

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### Abstract

Two kinds of fluorine-containing acrylic copolymers were prepared with an in-situ radical polymerization fluorine modification method and a post-polymerization fluorine modification route, respectively. And a kind of common acrylic copolymer as a reference was synthesized. Acrylic polyurethane was prepared with the synthesized acrylic copolymer and trimer of hexamethylene diisocyanate curing agent. Different environments including indoor atmospheric environment, hygrothermal environment, different temperature environment, as well as xenon arc aging environment were employed to investigate the failure behavior of the coatings. Fourier transform infrared spectrum (FT-IR) and <sup>19</sup>F NMR were employed to characterize the chemical structure of the copolymer. Glass transition temperature (T<sub>g</sub>) of the copolymer was tested by differential scanning calorimetry (DSC). Water contact angles of the coatings were monitored during the failure process. The difference in hydrophobicity of the coatings was examined. Thermostability of the coatings was explored by thermo gravimetric analysis (TGA). The elemental composition of the coating surface

before and after failure experiment was analyzed by X-ray photoelectron spectrometer (XPS). The results showed that the fluorine-containing copolymers and the corresponding hydrophobic coatings were prepared as expected. Copolymer b coating from the fluorine-containing acrylic copolymer prepared with the in-situ polymerization fluorine modification route exhibited better hydrophobicity in all the above environments compared with the hydrocarbon acrylic copolymer coating (Copolymer a). Copolymer c coating prepared with the fluorine-containing acrylic copolymer via the post-polymerization fluorine modification method performed the best hydrophobicity in moderate conditions and failed fast in hostile environments. The different fluorine modification method resulted in the different failure behavior.

**Keywords:** preparation; failure behavior; hydrophobicity; acrylic polyurethane; coating; fluorine modification

## 1. Introduction

Fluorine-containing polymers have played an important role in coatings due to their peculiar properties, including high thermal-, chemical-, aging- and weather- resistance; low surface energy and fire-retardance; excellent inertness to solvents, acids, alkalies, both water and oil repellency as well as antifouling properties[1-5]. Fluorine-containing acrylic copolymers have been widely used as typical low surface energy materials among fluoropolymers due to their cost effective and the processability advantages[1, 6-8]. Fluorine-containing acrylic copolymers are usually derived from copolymerization of fluorinated monomers with common hydrocarbon acrylic monomers containing reactive vinyl groups[8-10]. Great attention has been paid to the synthesis and properties of the fluorine-containing copolymers. Various fluorinated acrylic monomers, including fluorinated alkyl (meth)acrylates and fluorinated aryl (meth)acrylates, have been employed to prepare fluorine-containing acrylic copolymers via radical polymerization with other common hydrocarbon acrylates[1, 8, 11-14]. In this case, the fluorine segments are grafted onto the side chain of the

random copolymer. Migration behavior of the fluorinated segments during film-forming process of the fluorine-containing copolymers are limited by the molecular structure. Generally, surface energy of the fluorine-containing copolymer film will decrease to a certain limit even if the fluorine content is increasing. To create more hydrophobic films with lower surface energy, a post fluorine modification route of acrylic copolymers was proposed. In this case, a long fluorinated chain with higher migration efficiency is introduced[2]. It shows that the copolymer films exhibited better hydrophobicity with little fluorine content after the modification as compared with the films without post modification. However, further study need to be conducted on the difference between the coatings prepared with the two fluorine modification methods above.

Fluorine-containing acrylic polyurethane coating was prepared by the reaction of fluorine-containing acrylic copolymers containing a certain amount of hydroxyl on side chains with isocyanate curing agent. Consequently, the coating combines the unique corrosion resistance of polyurethane with the weather-proofing ability of acrylic resin, which leads to outstanding mechanical, physical and chemical properties[15, 16]. The properties of the coatings are usually characterized as they are prepared. However, the coatings will fail to work under different service condition including temperature, oxygen, water, pollutants, humidity, salt spray, and photo irradiation, etc.[17, 18] Therefore, it is of high significance to explore failure behavior of the coatings under different condition during their service life.

In this work, two kinds of fluorine-containing acrylic copolymers were prepared with an in-situ radical polymerization fluorine modification method and a post-polymerization fluorine modification route, respectively. And a kind of common acrylic copolymer as a reference was synthesized. Acrylic polyurethane was prepared with the synthesized acrylic copolymer and trimer of hexamethylene diisocyanate curing agent. Different environments including indoor atmospheric environment, hygrothermal environment, high temperature environment, as well as xenon arc aging environment were employed to investigate the failure behavior of the coatings. Fourier transform

infrared spectrum (FT-IR) and  $^{19}\text{F}$  NMR were employed to characterize the chemical structure of the copolymer. Glass transition temperature ( $T_g$ ) of the copolymer was tested by differential scanning calorimetry (DSC). Water contact angles of the coatings were monitored during the failure process. The difference in hydrophobicity of the coatings was examined. Thermostability of the coatings was explored by thermo gravimetric analysis (TGA). The elemental composition of the coating surface before and after failure experiment was analyzed by X-ray photoelectron spectrometer (XPS).

## 2. Experimental

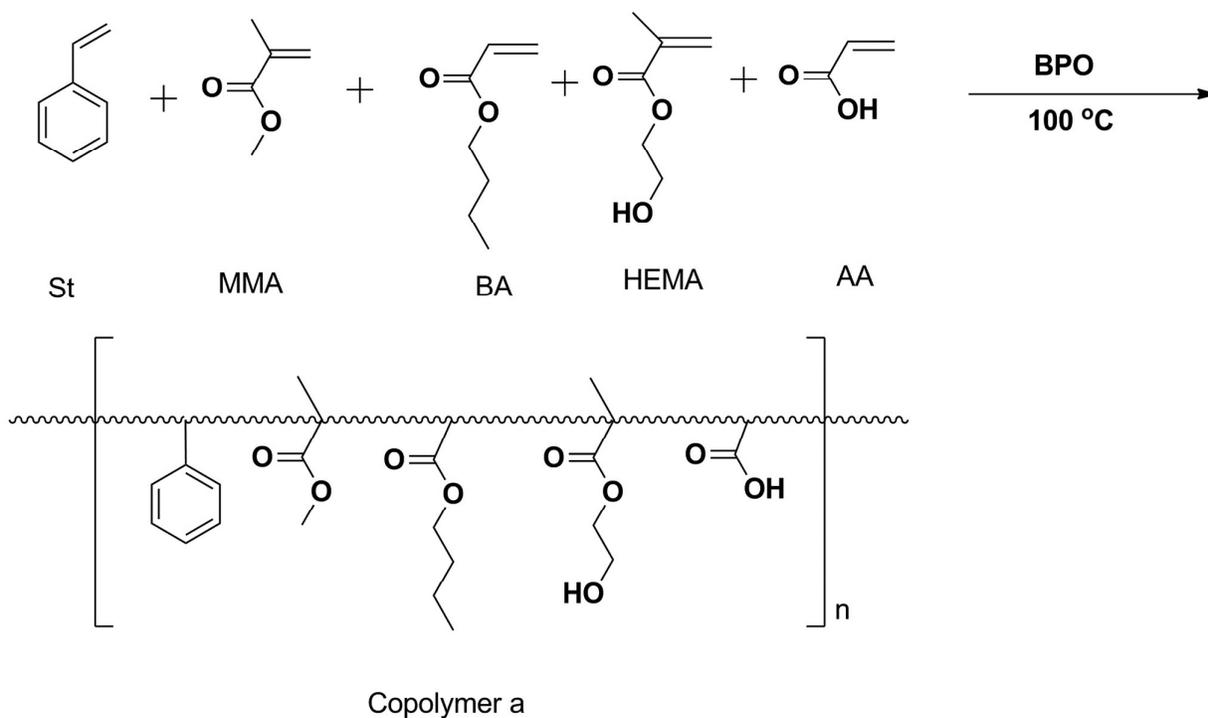
### 2.1 Materials

Methyl methacrylate (MMA), butyl acrylate (BA), styrene (St), hydroxyethyl methacrylate (HEMA), and acrylic acid (AA) were purchased from Dongfang Yakeli Chemicals Limited Corporation (Beijing, China), and used as common monomers. Dodecafluoroheptyl methacrylate (DFHMA, a mixture of  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CF}(\text{CF}_3)\text{CFHCF}(\text{CF}_3)\text{CF}_3$  and  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CF}(\text{CF}_2\text{CF}_3)\text{CH}(\text{CF}_3)\text{CF}_3$ ) was obtained from XEOGIA Fluorine-Silicon Chemical Corporation (Harbin, China), and copolymerized with the common monomers above to in situ prepare fluorine-containing acrylic copolymers. 1H,1H,2H,2H-Perfluoro-1-decanol (FOH) was obtained from Guangzhou Liyuan Industrial Materials CO., LTD (Guangzhou, China). Toluene diisocyanate (TDI) was supplied by Tianjin Dengke Chemical Reagent CO., LTD. (Tianjin, China). Butyl acetate and xylene were purchased from Beijing Chemical Works (Beijing, China) and used as solvents. Benzoyl peroxide (BPO) was used as initiator and obtained from Xilong Chemicals Limited Corporation (Shantou, China). The hexamethylene diisocyanate trimer (N3375, Bayer) was used as curing agent. All the reactants were used as received.

### 2.2 Synthesis of acrylic copolymers and coating preparation

Synthetic route of the common acrylic copolymer (Copolymer a) was shown in Scheme 1. The reaction was conducted in a four-neck round-bottomed flask equipped with a mechanical stirrer, a

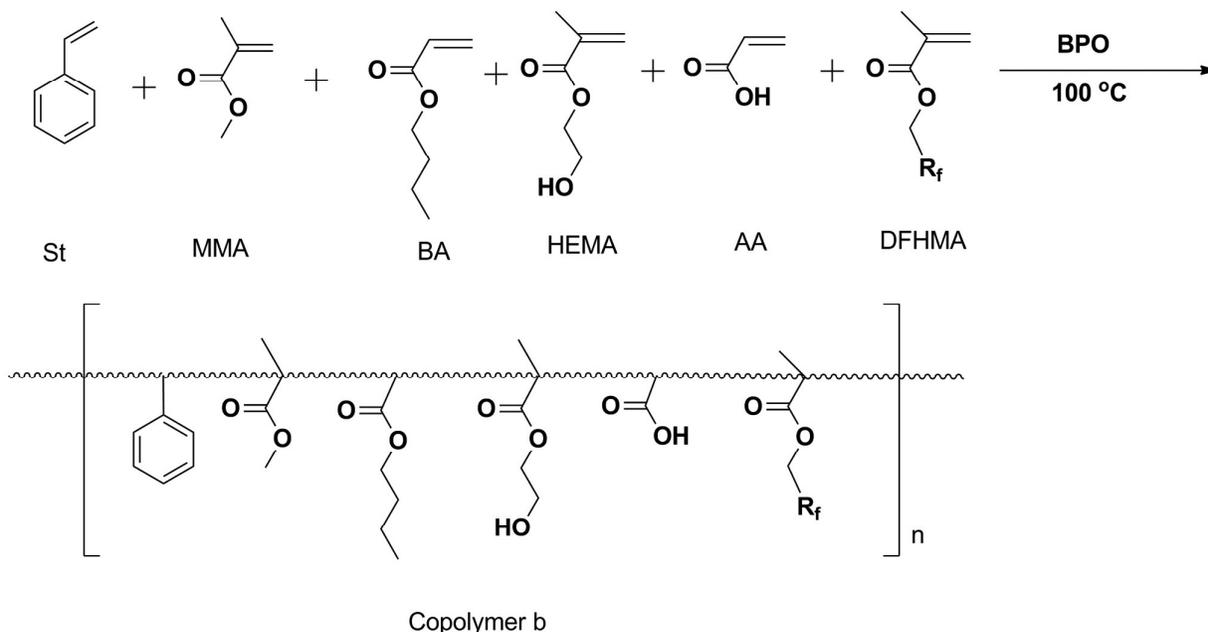
reflux condenser, an addition funnel and a thermometer. A mixture of butyl acetate and xylene with a weight ratio of 2:3 was employed as solvent. St, MMA, BA, HEMA and AA with a weight ratio of 2:2:3.5:2:0.5 were used as the monomers. The amount of initiator BPO accounted for 1 wt.% of the whole monomers. At first, 2/5 of the mixed solvent was added into the flask which was then heated to 100 °C under continuous stirring. All the monomers, 1/2 of the solvent, as well as 9/10 of the BPO solution were added dropwise into the flask for about 3 h. The reaction was maintained at 100 °C for another 2 h at the end of feeding. After that, the residual 1/10 of the solvent and 1/10 of the BPO were added dropwise into the flask for about 0.5 h. The polymerization was continued further for 2 h to promote conversion of the residual monomers. At last, the reaction mixture was cooled down to room temperature to obtain the common acrylic copolymer (Copolymer a) was prepared.



Scheme 1 Synthesis of the common acrylic copolymer (Copolymer a)

The first kind of fluorine-containing acrylic copolymer (Copolymer b) was synthesized with an in-situ radical polymerization fluorine modification method as shown in Scheme 2.

Dodecafluoroheptyl methacrylate (DFHMA) was used as the fluorinated monomer which was copolymerized with styrene and the common hydrocarbon acrylic monomers. Amount of DFHMA was 15 wt.% based on total amount of the whole monomers, and the ratio among other monomers was the same as that in Copolymer a. The synthetic process was the same as that for Copolymer a.

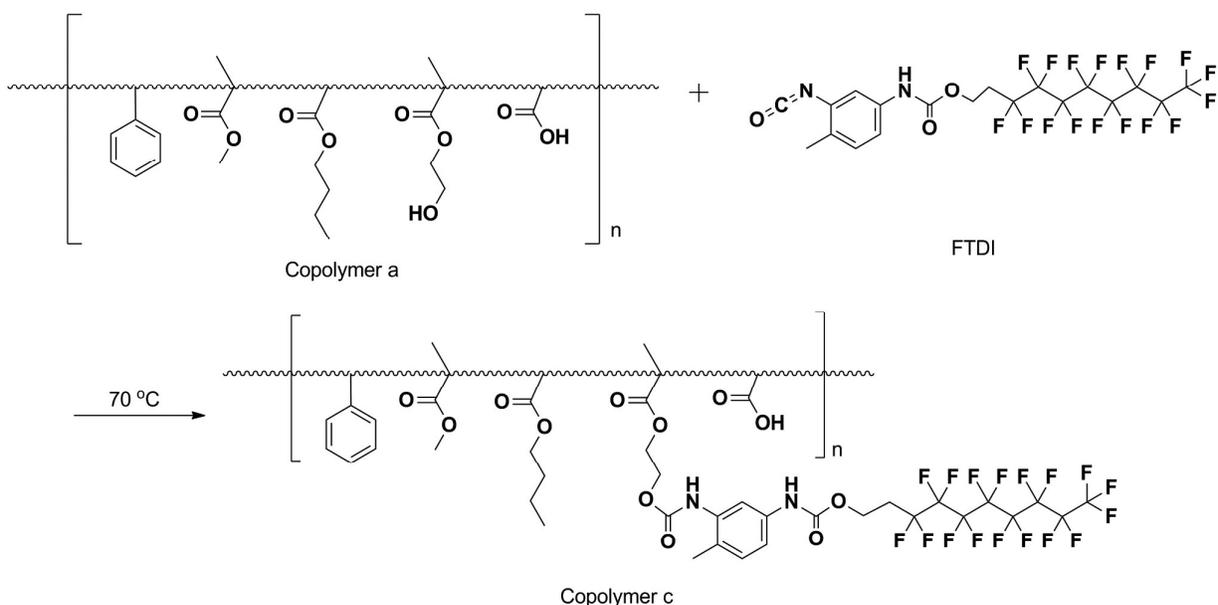


$R_f$ :  $-\text{CF}(\text{CF}_3)\text{CFHCF}(\text{CF}_3)\text{CF}_3$ ,  $-\text{CF}(\text{CF}_2\text{CF}_3)\text{CH}(\text{CF}_3)\text{CF}_3$

Scheme 2 Synthesis of fluorine-containing acrylic copolymer (Copolymer b) via an in-situ method

The second kind of fluorine-containing acrylic copolymer (Copolymer c) was prepared via a post-polymerization fluorine modification route as shown in Scheme 3. In which, a kind of fluorine-containing monomer (FTDI) was synthesized firstly by the reaction of 1H,1H,2H,2H-Perfluoro-1-decanol (FOH) and toluene diisocyanate (TDI). Then a certain amount of FTDI was added into the solution of Copolymer a in above solvent mixture of butyl acetate and xylene under continuous stirring at 70 °C. The mole ratio of  $-\text{NCO}$  to  $-\text{OH}$  was 1:10, wherein the  $-\text{NCO}$  group came from FTDI monomer while  $-\text{OH}$  came from HEMA that copolymerized into

Copolymer a. The reaction was conducted for another 1 h after feeding, and Copolymer c was prepared.



Scheme 3 Synthesis of fluorine-containing acrylic copolymer via a post-polymerization route

Hexamethylene diisocyanate tripolymer (N3375, Bayer) was employed as a curing agent to react with the remaining hydroxyl group in the copolymers and form the corresponding acrylic polyurethane coatings. The acrylic copolymers were mixed with stoichiometric N3375 and spinning-coated on tin plates. The anticipated acrylic polyurethane coatings were dried at 50 °C for 10 h.

### 2.3 Environmental experiments

Different imitating experiments including indoor atmospheric environment, hygrothermal environment, thermal-resistance at different temperature, as well as xenon arc aging were employed to investigate the failure behavior of the coatings.

An indoor atmospheric environment with the temperature ranging from 20 °C to 30 °C and the relative humidity ranging from 20% to 40% was employed to test the failure behavior of the coatings.

A chamber with the temperature of 38 °C and relative humidity of 97% was used for the hygrothermal environment.

50 °C, 100 °C and 150 °C were chosen to test the failure behavior of the coatings at different temperature. The coated samples were put into dry ovens with the setting temperature. The relative humidity ranged from 20% to 40%.

Xenon lamp exposure and weathering equipment (Nanjing Wuhe testing equipment Co. LTD, China) was used to detect the failure behavior of the coatings under artificial weathering environment. The irradiation intensity was 550 W·m<sup>2</sup>. The black-standard temperature was 65±2 °C and the test chamber temperature was 38±3 °C. An alternating wetting/drying cycle composed of 18 min wetting time and 102 min dry period was adopted. The surface of coated samples in the test chamber were sprayed with de-ionized water in wetting period, while the relative humidity was maintained at 60% in the dry period.

#### 2.4 Characterization

Chemical structure of the acrylic copolymer was characterized by infrared spectra with a Fourier transform infrared spectrum analyzer (FT-IR, Thermo Nicolet AVATAR, USA) and <sup>19</sup>F NMR on a 400 MHz AVANCE III Brüker NMR spectrometer using dimethyl sulfoxide-d<sub>6</sub> (CD<sub>3</sub>SOCD<sub>3</sub>) as solvent.

Glass-transition temperature (T<sub>g</sub>) of the copolymers was determined by differential scanning calorimetry (DSC, Mettler Toledo, DSC1, Switzerland). The measurement was conducted under

nitrogen atmosphere with the temperature ranging from  $-20\text{ }^{\circ}\text{C}$  to  $200\text{ }^{\circ}\text{C}$  under a heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$ .

Static water contact angle was measured by sessile drop method using a DSA 20 equipment (KRÜSS, Germany) at  $23 \pm 1\text{ }^{\circ}\text{C}$ . Each sample was tested at three different positions and measured for more than five times to calculate the average value.

Thermostability of the coatings was explored by thermo gravimetric analysis (TGA, TA instruments Q5000, USA). The temperature ranged from  $35\text{ }^{\circ}\text{C}$  to  $500\text{ }^{\circ}\text{C}$  at a heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$  under nitrogen atmosphere. The copolymers were cured with stoichiometric N3375 and dried at  $50\text{ }^{\circ}\text{C}$  to obtain the corresponding coatings before test.

X-ray photoelectron spectrometer (XPS, ESCALAB 250 Xi, Thermo Fisher Scientific, USA) was employed to analyze the elemental composition at surface of the copolymer films.

### 3. Results and discussions

#### 3.1 Synthesis of the acrylic copolymers

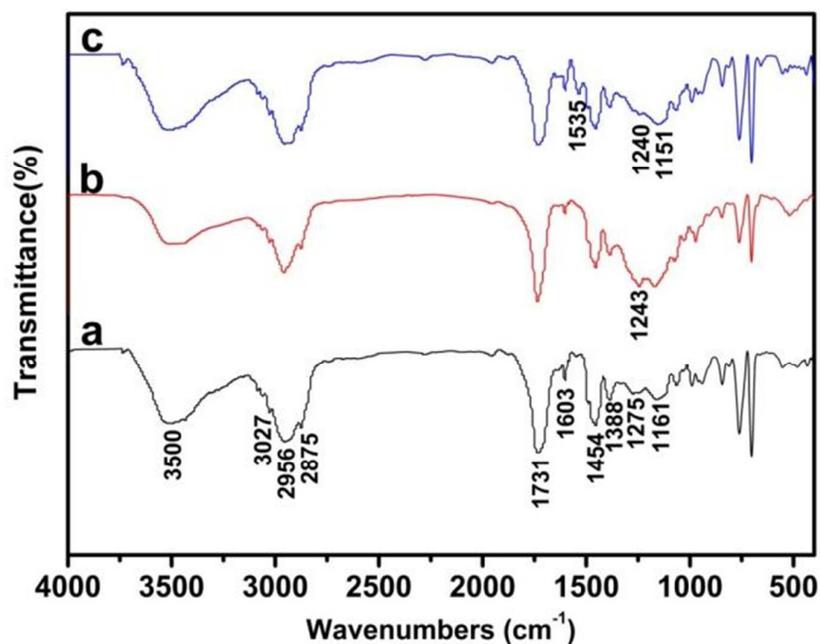


Figure 1 FT-IR spectra of the acrylic copolymers. a, Copolymer a; b, Copolymer b; c, Copolymer c

Chemical structure of the three kinds of copolymers was confirmed by FT-IR and shown in Figure 1. It can be observed that all the copolymers exhibited the characteristic stretching vibration of  $\text{-OH}$  at  $3500\text{ cm}^{-1}$ , stretching vibration of C-H on the benzene ring from St at  $3100\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$ , asymmetrical and symmetrical stretching vibration of  $\text{-CH}_3$  at  $2956\text{ cm}^{-1}$  and  $2875\text{ cm}^{-1}$  respectively, stretching vibration of C=O at  $1731\text{ cm}^{-1}$ , stretching vibration of benzene at  $1603\text{ cm}^{-1}$ , asymmetrical and symmetrical deformation vibration of  $\text{-CH}_3$  at  $1454\text{ cm}^{-1}$  and  $1388\text{ cm}^{-1}$  respectively, as well as the stretching vibration of C-O-C of esters at  $1161\text{ cm}^{-1}$ . The characteristic peak of C=C bond at  $1640\text{ cm}^{-1}$  disappeared which revealed that there was no residual vinyl monomers. Curve a shows the FT-IR spectrum of the common hydrocarbon acrylic copolymer (Copolymer a). As for the fluorine-containing acrylic copolymer synthesized by the in-situ polymerization method (Copolymer b, curve b), the stretching vibration peak of  $\text{-CF}_3$  appeared at  $1243\text{ cm}^{-1}$ . In the FT-IR spectrum of the fluorine-containing copolymer prepared by the post-polymerization route (Copolymer c, curve c), the peak at  $1535\text{ cm}^{-1}$  was assigned to the deformation vibration of N-H from  $\text{-CO-NH-}$ , while the peaks at  $1240\text{ cm}^{-1}$  and  $1151\text{ cm}^{-1}$  were resulted from the characteristic vibration of the C-F bond of perfluoroalkyl group. Shortly, it confirmed that two kinds of fluorine-containing acrylic copolymers were prepared by the two different fluorine modification routes.

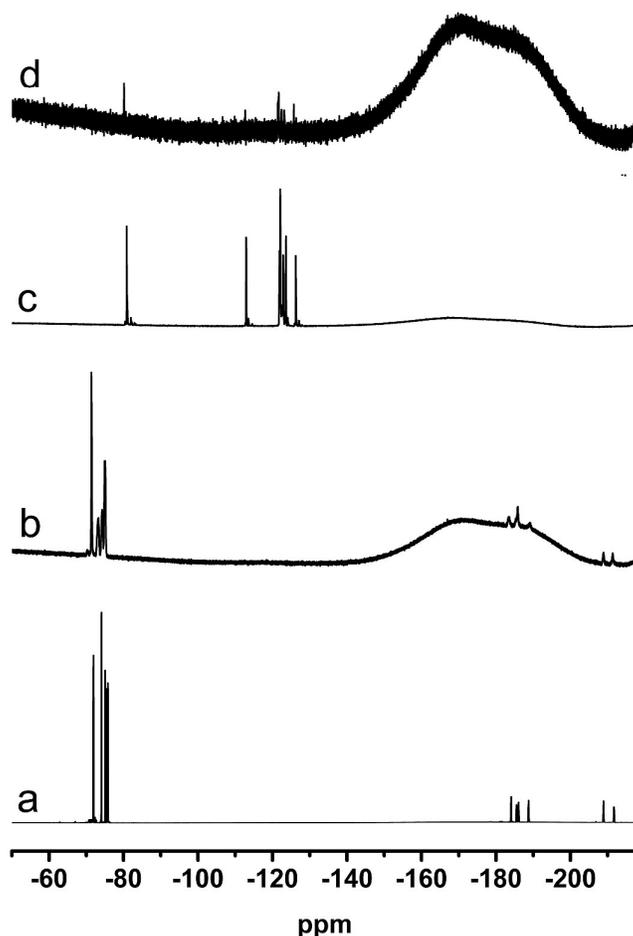


Figure 2  $^{19}\text{F}$  NMR spectra of DFHMA (a), Copolymer b (b), FOH (c), and Copolymer c (d)

Chemical structure of the fluorinated monomers and the fluorine-containing acrylic copolymer was corroborated by  $^{19}\text{F}$  NMR as shown in Figure 2. Figure 2a shows the  $^{19}\text{F}$  NMR spectrum of DFHMA. The chemical shifts ranging from -71 ppm to -76 ppm were assigned to the  $-\text{CF}_3$  group, while the peaks around 185 ppm and 210 ppm were due to the  $-\text{CF}-$  group. In spectrum of FOH (Figure 2c), the chemical shifts at -81 ppm belonged to the  $-\text{CF}_3$  group, the peak at -113 ppm was assigned to the fluorine atoms of  $-\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ , while there existed also characteristic peaks of other  $-\text{CF}_2-$  groups at between -121 ppm to -128 ppm. It is clear that Copolymer b and Copolymer c show almost the same peaks as those of DFHMA and FOH, respectively. In addition, relative less amount of fluorine dissolved in dimethyl sulfoxide- $d_6$  resulted in a rough baseline of the spectra of

the fluorine-containing acrylic copolymers. As a result, it demonstrated that the fluorine-containing acrylic copolymers were prepared via the modification methods as expected.

DSC was employed to test the glass transition temperature ( $T_g$ ) of the copolymers so as to judge the homogeneity of the copolymerization process[19]. One single  $T_g$  for a sample reveals that a copolymer rather than a mixture of at least two polymers is obtained during the reaction. Figure 3 exhibits the DSC curves of the acrylic copolymer and the fluorine-containing copolymers prepared by above mentioned different fluorine modification methods. It is apparent that each copolymer exhibited only one  $T_g$ , indicating that all the monomers had been copolymerized statistically into the expected Copolymers b (curve b) and c (curve c). Furthermore, there was no homopolymer generated during the process of either the in-situ polymerization or the post-polymerization fluorine modification. Besides, it also revealed that incorporation of the fluorinated monomers resulted in higher  $T_g$  than the common hydrocarbon one, namely, 43.9 °C and 48.6 °C for the fluorine-containing copolymers b and c respectively, as compared with 33.3 °C of Copolymer a contained no fluorine.

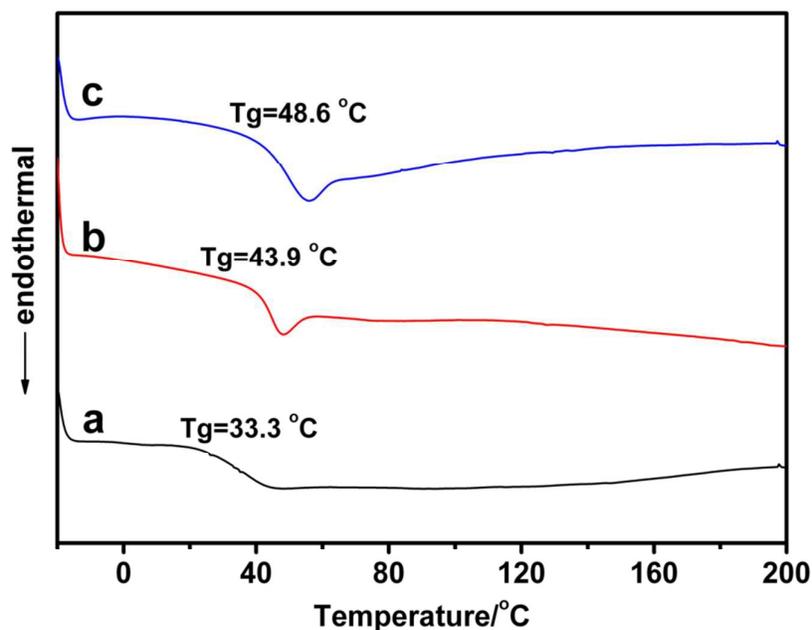


Figure 3 DSC curves of the copolymers. (a) Copolymer a; (b) Copolymer b; (c) Copolymer c

In conclusion, three kinds of predetermined acrylic copolymers were synthesized by a radical random polymerization route. In which, two kinds of fluorine-containing acrylic copolymers were prepared via an in-situ fluorine modification method and a post-polymerization fluorine modification route, respectively.

### 3.2 Hydrophobicity failure behavior of the coatings

To explore the hydrophobicity of the coatings in various environments, the three kinds of acrylic copolymers were cured with stoichiometric N3375 in the solvent mixture followed by spinning coated on tin plates to form corresponding acrylic polyurethane coating films. And the coatings were put into several typical environments. Static water contact angles were tested to investigate the hydrophobicity failure behavior of the coatings.

#### 3.2.1 Indoor atmospheric environment

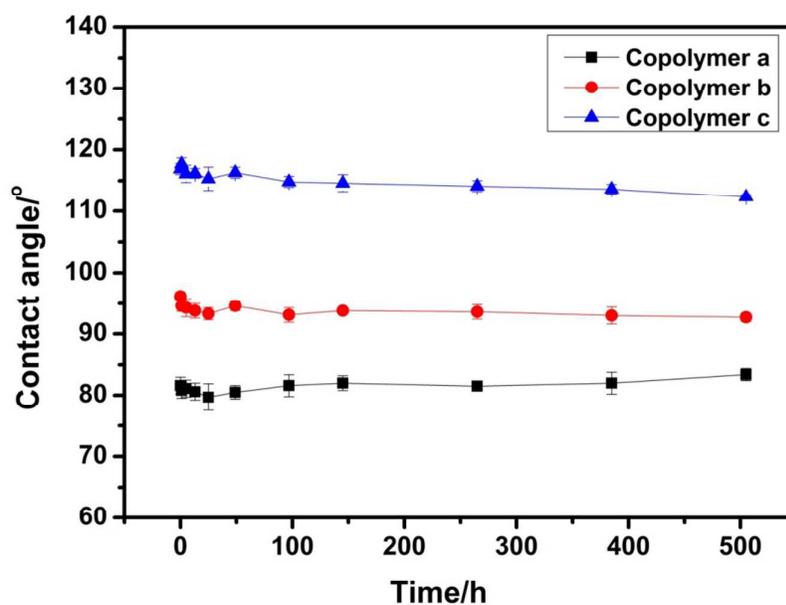


Figure 4 Water contact angles of the coatings in indoor atmospheric environment

Figure 4 shows water contact angles of the coatings as a function of exposure time in indoor atmospheric environment. It can be seen that the three kinds of coatings exhibited a stable hydrophobicity during the test time (500 h). Water contact angle of the common hydrocarbon coating

changed little, which was  $83.4 \pm 1^\circ$  after 500 h test, while those of the two kinds of fluorine-containing acrylic polyurethane coatings dropped from original  $96.2 \pm 0.7^\circ$  and  $116.9 \pm 0.9^\circ$  to  $92.7 \pm 0.7^\circ$  and  $112.3 \pm 0.4^\circ$  over 500 h, respectively. Both the fluorine-containing coatings show better hydrophobicity than the common hydrocarbon one. Moreover, coating film of Copolymer c exhibits substantially higher water contact angle than that of Copolymer b coating, although only small amount of fluorinated monomers were incorporated within the Copolymer c. This might be due to the different fluorine modification route. In the in-situ fluorine modification route, DFHMA was copolymerized with the common hydrocarbon monomers. The fluorine segments distributed randomly in the copolymer molecular chains. Although relatively more fluorine content was incorporated, the shorter fluorine chains containing twelve fluorine atoms in each fluoroalkyl side chain as well as the fluorine-containing segments distribution limit at the coating surface determined the coating hydrophobicity. In the post-polymerization fluorine method, the long perfluoroalkyl chains containing seventeen fluorine atoms in each fluoroalkyl chain reacted with hydroxyl groups of small steric effects. On the other hand, fluorine atoms possess very low surface free energy and self-aggregated property, therefore, the perfluoroalkyl segments behaved preferential orientation toward the film-air surface during film-forming process[20, 21]. Thus as for Copolymer c, the longer perfluoroalkyl segments migrated and distributed at the coating surface more effectively, resulting in a higher water contact angle when compared with that of Copolymer b. The stable water contact angles revealed that the indoor atmospheric environment had little influence on the coatings.

### 3.2.2 Hygrothermal environment

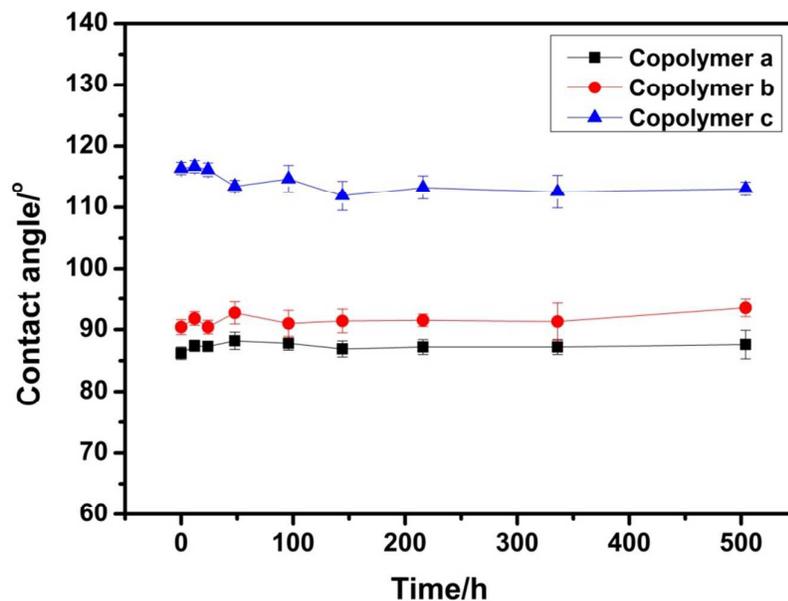


Figure 5 Water contact angles of the coatings in hygrothermal environment

The water contact angles of the coatings as a function of the test time in hygrothermal environment was displayed in Figure 5. Similar trends with the indoor atmospheric environment were observed. The hydrophobicity of the coatings was stable in the hygrothermal environment during the test time (500 h). In fact, although there is hydrophilic monomer of AA was incorporated within the copolymers, segments of polar polyacrylic acid (PAA) would be oriented toward the film-substrate interface during film-forming since the substrate is also comprised of polar material, so that low polar segments were oriented toward the film-air interface which resulted in excellent water resistance. Chemical bonds are stable in the neutral hygrothermal environment at 38 °C over 500 h. In other words, polymeric units of the copolymers cannot be hydrolyzed under the experimental condition of hygrothermal environment. Moreover, hydrophobic fluorinated alkyl groups preferentially migrated to the outmost surface of the film-air interface during film formation. Consequently, water contact angles of the coatings containing fluorinated alkyl groups are higher than that of Copolymer a coating. The hygrothermal environment had little influence on the coatings.

### 3.2.3 Different temperature environments

Different temperature environments were employed to test the failure behavior of the coatings. Table 1 displays the water contact angles of the coatings at different temperatures for 96 h. For the Copolymer a coating, the water contact angle increased as the exposure time at 50 °C and 100 °C, while that increased a little at first 24 h and then decreased as the exposure time extended further over at least 72 h at 150 °C. As for the fluorine-containing coatings, the hydrophobicity was relative stable at 50 °C and 100 °C while the contact angles decreased significantly over the test time at 150 °C, especially for the Copolymer c coating. It is seen clearly that, water contact angle dropped dramatically from 117.7° to 85.1° over 24 h at 150 °C, indicating that the hydrophobic Copolymer c film turned to be hydrophilic in reverse. It suggested that the coatings failed slowly in the relative low temperature environments, while the higher temperature (150 °C) has larger influence on the coatings.

**Table 1 Water contact angles of the coatings under different temperatures**

	Copolymer a coating			Copolymer b coating			Copolymer c coating		
	50 °C	100 °C	150 °C	50 °C	100 °C	150 °C	50 °C	100 °C	150 °C
0h	81.6	82.3	81.4	96.2	95.2	97.2	116.9	118.1	117.7
24h	83.2	87.2	83.9	94.3	94.1	93.8	116.3	114.4	85.1
72h	85.5	88.1	81.8	94.5	96.2	92.0	115.2	112.8	80.5
96h	86.7	89.4	80.6	95.7	98.1	91.0	114.8	112.5	80.0

Figure 6 exhibits the water contact angles of the coatings at 150 °C for 300 h. The water contact angle of Copolymer a coating increased a little during the first 24 h, but decreased slowly as the exposure time extended. The water contact angle of Copolymer b coating also decreased slowly with the test time. Both Copolymer a coating and Copolymer b coating performed relative stable hydrophobicity during the exposed 300 h. As for Copolymer c coating, however, the water contact angle decreased sharply for the first 24 h. Then the water contact angle was similar with that of Copolymer a coating, indicating that the fluorine-containing segments might be destroyed.

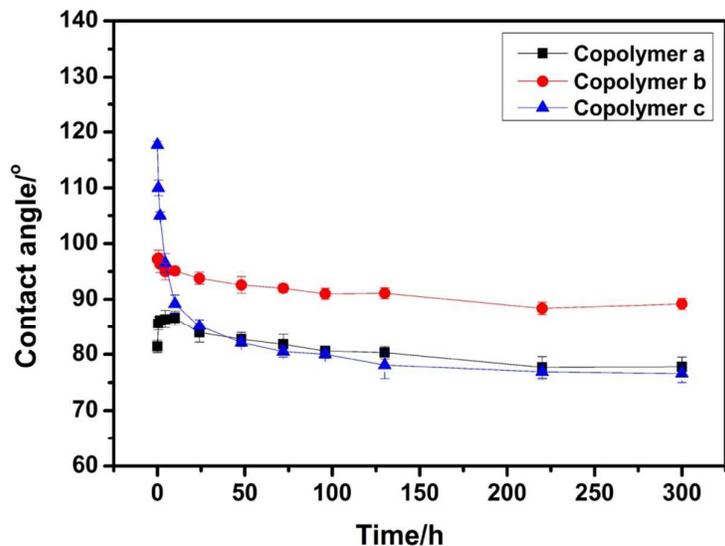


Figure 6 Water contact angles of the coatings at 150 °C

TGA test was employed to explore the thermostability of the fluorine-containing copolymer coatings and the results are included in Figure 7. It can be seen that only 0.7 wt.% of the Copolymer b coating degraded at 150 °C, while that for the Copolymer c coating was 2.3 wt.%. And 10 wt.% of the coating degraded at 272.5 °C for Copolymer b coating, while that at 206.8 °C for Copolymer c coating. It is clear that the Copolymer b coating performed better thermostability than the Copolymer c coating.

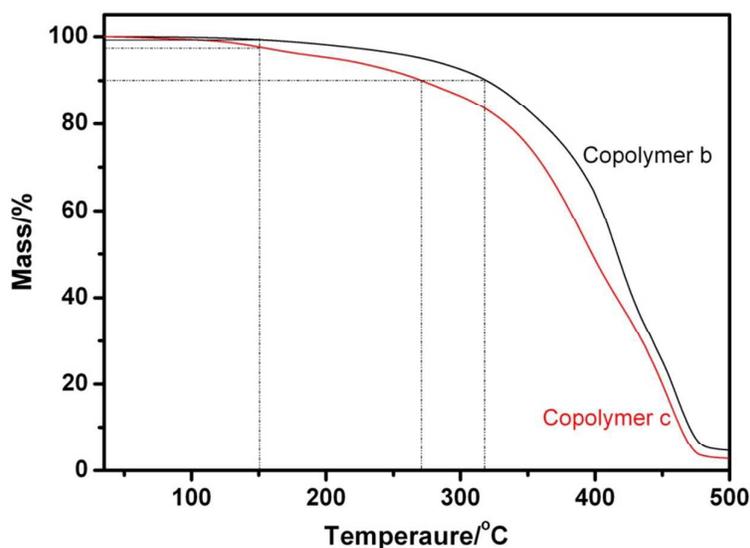


Figure 7 TGA curves of Copolymer b and c coatings

The presence of fluorine chains and their migration and degradation behavior can be quantified by surface characterization of XPS. The surface compositions of the coatings before and after the failure experiments at 150 °C with different depth resolution were studied. The maximum depth resolution for XPS is determined by the mean free path of the X-ray photon and is no more than 10 nm. In this characterization, the test depth can be varied by changing the angle between the coating surface in normal direction and the detector of the instrument. The test depth will decrease when the angle increases. When the angle is 0°, the test depth reaches the maximum value (no more than 10 nm), while the outmost of the film surface is detected at the maximum angle value of 55° in the employed instrument.

Figure 8 displays the XPS spectra of the two kinds of fluorine-containing coatings before and after failure experiment at 150 °C. Table 2 shows the atomic ratio data of the films. It can be seen that there was more fluorine content being detected when the test angle was 55°, suggesting that more fluorine-containing segments migrated toward the film-air interface and distributed on the coating surface. For Copolymer b coating, the F/C ratio was 0.136 at 0° and 0.160 at 55°. After the environment test at 150 °C, the F/C ratio increased to 0.141 at 0° and 0.182 at 55°, indicating that the fluorine-containing segments were stable and the high temperature was helpful to the migration of the fluorine-containing segments. However, the O/C ratio increased from 0.037 at 0° and 0.026 at 55° to 0.042 at 0° and 0.034 at 55°, suggesting that the oxygen content on the coating surface increased after the environment test at 150 °C for 96 h. This might result in the little decrease of the Copolymer b water contact angle. As for Copolymer c coating, although less fluorine-containing monomer was incorporated, there was more fluorine content detected on the coating surface. The F/C ratio was 0.620 at 0° and 0.943 at 55° before failure test, which were much higher than those of the Copolymer b coating. It reveals that the long perfluoroalkyl side chains can migrate more to the coating surface. So the coating performed better hydrophobicity. However, the fluorine content decreased sharply

after the environment test at 150 °C. The F/C ratio decreased to 0.047 at 0° and 0.075 at 55°, resulting in the dramatic decrease of the coating hydrophobicity.

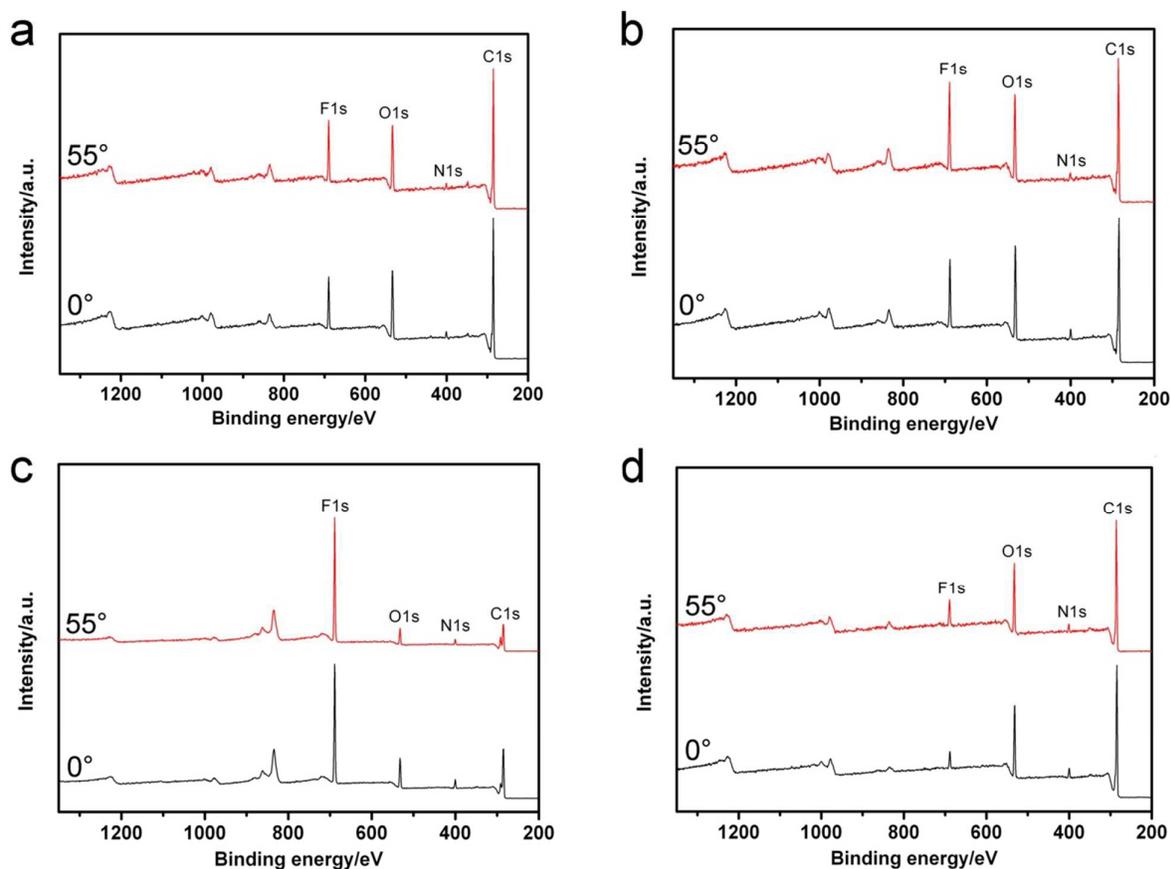


Figure 8 XPS spectra of Copolymer b and Copolymer c coating before and after failure experiment at 150 °C. a, original Copolymer b coating before test; b, Copolymer b coating after failure test; c, original Copolymer c coating before test; d, Copolymer c coating after failure test. 0° and 55° were the angle between film surface the sample in normal direction and the detector of the XPS instrument

**Table 2 XPS data of Copolymer b and Copolymer c coating before and after failure experiment at 150 °C**

Atomic%	Copolymer b coating before test		Copolymer b coating after test		Copolymer c coating before test		Copolymer c coating after test	
	0°	55°	0°	55°	0°	55°	0°	55°
	<b>C1s</b>	71.66	71.49	69.02	67.87	51.87	45.13	73.91
<b>N1s</b>	2.62	1.83	2.93	2.28	5.04	4.14	4.14	2.79
<b>O1s</b>	16.01	15.22	18.3	17.52	10.9	8.2	18.47	17.75
<b>F1s</b>	9.71	11.45	9.74	12.33	32.18	42.54	3.48	5.51

0° and 55° were the angle between film surface the sample in normal direction and the detector of the XPS instrument.

Combined with the TGA and the XPS results, it can be inferred that the Copolymer c coating began to degrade at 150 °C, resulting in the sharp decrease of the coating hydrophobicity. This was relevant to the fluorine modification method. In the copolymer coatings prepared by post-polymerization fluorine modification method (Copolymer c), the fluorine-containing side chains mostly distribute at the coating surface. When the segments are damaged, the fluorine content at the coating surface will decrease, resulting in the decrease of the coating hydrophobicity. It has been reported that the degradation of the acrylic urethane coating mostly proceeds through a direct or radical induced scission of the urethane linkage[22, 23]. Since the fluorinated alkyl side group was incorporated into the copolymer via a linker of toluene diisocyanate (TDI), in which, urethane linkage was produced during the synthesis of Copolymer c. The urethane linkage got ruptured when exposed to heating at 150 °C for 24 h. So that the fluorine-containing alkyl chains with extremely low surface free energy were isolated, resulting in substantial dropping of water contact angle of Copolymer c. Therefore, water contact angle of the Copolymer c decreased to almost the same as that of the Copolymer a coating. On the other hand, however, in the fluorine-containing alkyl chain of Copolymer b prepared via in-situ copolymerization route, the fluorine-containing segments were incorporated by acrylic ester linkage and distributed randomly in the copolymer molecules. The ester bonds are more stable than the urethane linkage at high temperature, thus the fluorine-containing segments were more difficult to be isolated than Copolymer c. Moreover, the XPS results showed

that more fluorine content was detected after the failure test at 150 °C, indicating that the high temperature was helpful to the migration of the low surface energy chains. Even if the coating surface were destroyed due to the broken of the urethane linkage, the fluorine-containing chains will not get ruptured from the main chains of the coatings. Consequently, Copolymer b coating exhibited good thermal resistance and kept still hydrophobic after exposure to heat at 150 °C for at least 300h.

### 3.2.4 Xenon arc aging environment

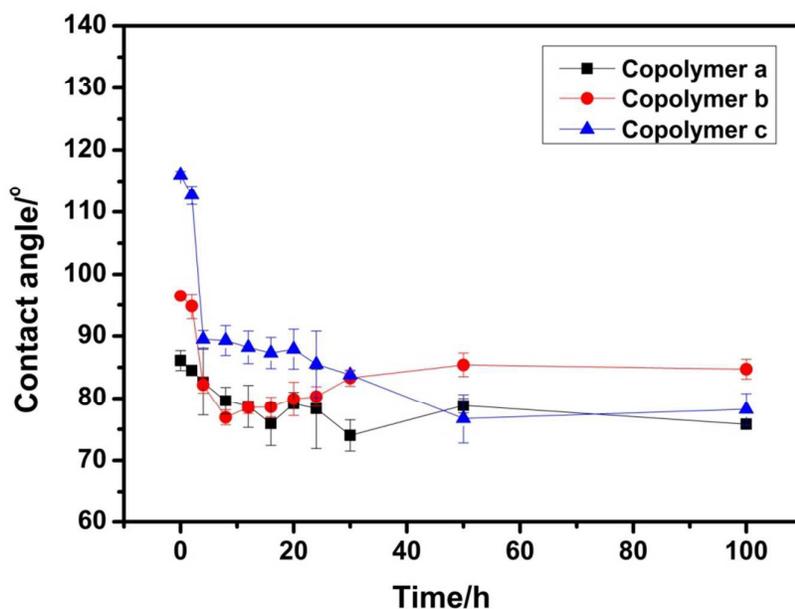


Figure 9 Water contact angles of the coatings in xenon arc aging environment

To explore the failure behavior of the coatings in comprehensive environments, a xenon lamp exposure and weathering equipment was used to provide artificial weathering environment. Figure 9 displays the water contact angles of the coatings under xenon arc aging environment. All the three kinds of coatings failed more quickly compared with the other individual conditions as stated herein above. As in the 150 °C environment, the contact angle of Copolymer c coating was similar with that of Copolymer a coating after exposing 50 h. Copolymer b coating performed better hydrophobicity than the other two kinds of coating.

It has been proved that the photo irradiation aging play a significant role in the degradation of the acrylic urethane coating than the other climatic conditions[22-24]. And the photo cleavage of the urethane linkage controls the loss of physical properties of the acrylic urethane coating[24]. The xenon test caused more severe damage on the coating surface, including the thickness loss[25]. Therefore, the hydrophobicity of the three kinds of coatings failed more serious than that in the other individual conditions. Compared with the 150 °C environment, more severe damage occurred at the coating surface and more components including the fluorine-containing segments in the Copolymer b were lost. Therefore, the Copolymer b coating failed to be hydrophilic as the other two kinds of coatings shortly after the beginning of the xenon test.

#### 4. Conclusion

Two kinds of fluorine-containing acrylic copolymers were prepared with an in-situ radical polymerization fluorine modification method and a post-polymerization fluorine modification route, respectively. And a kind of common acrylic copolymer as a reference was synthesized. Corresponding acrylic polyurethane coatings were prepared with the acrylic copolymers with stoichiometric isocyanate curing agent. The hydrophobicity failure behaviors of the coatings were explored in different environments, including indoor atmospheric environment, hygrothermal environment, different temperature environments, as well as xenon arc aging environment. FT-IR,  $^{19}\text{F}$  NMR and DSC confirmed that the fluorine-containing acrylic copolymers were prepared as expected. The Copolymer b coating prepared with the fluorine-containing acrylic copolymer using the in-situ polymerization fluorine modification route exhibited better hydrophobicity in all the above environments compared with the hydrocarbon acrylic copolymer coating (Copolymer a coating). In common environments including indoor atmosphere, hygrothermal and low temperature conditions, Copolymer c coating prepared with the fluorine-containing acrylic copolymer via the post-polymerization fluorine method performed the best hydrophobicity. However, the hydrophobicity of Copolymer c coating failed fast in hostile environments, such as high temperature

condition and xenon arc aging environment. This was due to the different fluorine modification route. The in-situ fluorine modification method produced random copolymer, and the corresponding coating performed lower water contact angle than that prepared with the post-polymerization fluorine route. But the coating failed more slowly. The post-polymerization fluorine modification route resulted in a more hydrophobic coating. The fluorine-containing segments distributed at the coating surface, and the fluorine content in the bulk was much less. However, when the coating was used in hostile environments, the coating surface might be destroyed, which was confirmed by the TGA and XPS characterization. Therefore, once the fluorine-containing segments decreased, the hydrophobicity of the coating failed quickly.

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### References

- [1] W. Yao, Y. Li, X. Huang, Fluorinated poly(meth)acrylate: Synthesis and properties, *Polymer*, 55 (2014) 6197-6211.
- [2] D. Han, L. Zhu, Y. Chen, W. Li, X. Wang, L. Ning, Synthesis of fluorinated monomer and formation of hydrophobic surface therefrom, *RSC Adv.*, 5 (2015) 22847-22855.
- [3] X. Yang, L. Zhu, Y. Zhang, Y. Chen, B. Bao, J. Xu, W. Zhou, Surface properties and self-cleaning ability of the fluorinated acrylate coatings modified with dodecafluoroheptyl methacrylate through two adding ways, *Appl. Surf. Sci.*, 295 (2014) 44-49.
- [4] K.A. Pollack, P.M. Imbesi, J.E. Raymond, K.L. Wooley, Hyperbranched Fluoropolymer-Polydimethylsiloxane-Poly(ethylene glycol) Cross-Linked Terpolymer Networks Designed for Marine and Biomedical Applications: Heterogeneous Nontoxic Antibiofouling Surfaces, *Acs Appl Mater Interfaces*, 6 (2014) 19265-19274.
- [5] R.A. Iezzi, S. Gaboury, K. Wood, Acrylic-fluoropolymer mixtures and their use in coatings, *Prog. Org. Coat.*, 40 (2000) 55-60.
- [6] W. Xu, Q.F. An, L.F. Hao, D. Zhang, M. Zhang, Synthesis and characterization of self-crosslinking fluorinated polyacrylate soap-free latices with core-shell structure, *Appl. Surf. Sci.*, 268 (2013) 373-380.
- [7] J.Z. Gao, X.M. Wang, Y.X. Wei, W. Yang, Synthesis and characterization of a novel fluorine-containing polymer emulsion with core/shell structure, *J. Fluorine Chem.*, 127 (2006) 282-286.
- [8] Q.H. Zhang, Q.Y. Wang, X.L. Zhan, F.Q. Chen, Synthesis and Performance of Novel Fluorinated Acrylate Polymers: Preparation and Reactivity of Short Perfluoroalkyl Group Containing Monomers, *Ind Eng Chem Res*, 53 (2014) 8026-8034.

- [9] W. Yang, Y. Chen, D. Han, L. Zhu, Synthesis and characterization of the fluorinated acrylic latex: Effect of fluorine-containing surfactant on properties of the latex film, *J. Fluorine Chem.*, 149 (2013) 8-12.
- [10] D.X. Han, L.Q. Zhu, Y.C. Chen, W.P. Li, L.L. Feng, Synthesis and characterization of acrylic latex: Effects of fluorine and silicon components on properties of the latex copolymers, *J. Fluorine Chem.*, 156 (2013) 38-44.
- [11] S. Ito, S. Kaneko, C.M. Yun, K. Kobayashi, M. Nakagawa, Investigation of Fluorinated (Meth)Acrylate Monomers and Macromonomers Suitable for a Hydroxy-Containing Acrylate Monomer in UV Nanoimprinting, *Langmuir*, 30 (2014) 7127-7133.
- [12] C. Benbayer, S. Saidi-Besbes, E.T. de Givenchy, S. Amigoni, F. Guittard, A. Derdour, Copolymerization of novel reactive fluorinated acrylic monomers with styrene: reactivity ratio determination, *Colloid. Polym. Sci.*, 292 (2014) 1711-1717.
- [13] J.-Q. Huang, W.-D. Meng, F.-L. Qing, Synthesis and repellent properties of vinylidene fluoride-containing polyacrylates, *J. Fluorine Chem.*, 128 (2007) 1469-1477.
- [14] R.R. Thomas, D.R. Anton, W.F. Graham, M.J. Darmon, B.B. Sauer, K.M. Stika, D.G. Swartzfager, Preparation and Surface Properties of Acrylic Polymers Containing Fluorinated Monomers, *Macromolecules*, 30 (1997) 2883-2890.
- [15] V.V. Gite, P.P. Mahulikar, D.G. Hundiwale, Preparation and properties of polyurethane coatings based on acrylic polyols and trimer of isophorone diisocyanate, *Prog. Org. Coat.*, 68 (2010) 307-312.
- [16] Y.F. Zhu, J.P. Xiong, Y.M. Tang, Y. Zuo, EIS study on failure process of two polyurethane composite coatings, *Prog. Org. Coat.*, 69 (2010) 7-11.
- [17] S. Saha, D. Kocaefe, C. Krause, T. Larouche, Effect of titania and zinc oxide particles on acrylic polyurethane coating performance, *Prog. Org. Coat.*, 70 (2011) 170-177.
- [18] Y. He, J.P. Yuan, H. Cao, R. Zhang, Y.C. Jean, T.C. Sandreczki, Characterization of photo-degradation of a polyurethane coating system by electron spin resonance, *Prog. Org. Coat.*, 42 (2001) 75-81.
- [19] K. Landfester, R. Rothe, M. Antonietti, Convenient synthesis of fluorinated latexes and core-shell structures by miniemulsion polymerization, *Macromolecules*, 35 (2002) 1658-1662.
- [20] W.R. Dreher, A. Singh, M.W. Urban, Effect of perfluoroalkyl chain length on synthesis and film formation of fluorine-containing colloidal dispersions, *Macromolecules*, 38 (2005) 4666-4672.
- [21] M. Bertolucci, G. Galli, E. Chiellini, Wetting Behavior of Films of New Fluorinated Styrene-Siloxane Block Copolymers, *Macromolecules*, 37 (2004) 3666-3672.
- [22] F.X. Perrin, M. Irigoyen, E. Aragon, J.L. Vernet, Artificial aging of acrylurethane and alkyd paints: a micro-ATR spectroscopic study, *Polym. Degrad. Stab.*, 70 (2000) 469-475.
- [23] C. Merlatti, F. Perrin, E. Aragon, A. Margaillan, Natural and artificial weathering characteristics of stabilized acrylic-urethane paints, *Polym. Degrad. Stab.*, 93 (2008) 896-903.
- [24] F. Perrin, M. Irigoyen, E. Aragon, J. Vernet, Evaluation of accelerated weathering tests for three paint systems: a comparative study of their aging behaviour, *Polym. Degrad. Stab.*, 72 (2001) 115-124.
- [25] J. Hu, X. Li, J. Gao, Q. Zhao, Ageing behavior of acrylic polyurethane varnish coating in artificial weathering environments, *Prog. Org. Coat.*, 65 (2009) 504-509.