Synthesis of fluorosilicone monomer and application in hydrophobic surface of acrylic copolymer

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ABSTRACT: A kind of fluorosilicone monomer with polymerizable vinyl group and fluorine and silicon components has been designed and synthesized. A series of acrylic copolymers were prepared using the monomer and normal acrylic monomers. The effects of the monomer on the surface properties and thermostability of the copolymers were studied. The chemical structure of the monomer and the copolymers were confirmed by FTIR, ^{1}H NMR, and ^{19}F NMR. MALDI-TOF-MS was used to monitor the molecular weight variation during the monomer synthesis process. Thermal properties of the copolymers were analyzed by DSC and TGA. Surface properties of the copolymer films were characterized by static water contact angles, AFM, and XPS. Results showed that the fluorosilicone monomer with the expected structure was synthesized and had been copolymerized into the copolymers. The monomer contributed to a uniform hydrophobic film with no influence on the surface roughness. The thermostability of the copolymers was improved by the monomer. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41926.

INTRODUCTION

Among low surface energy coatings, fluorinated, silicone, and fluorosilicone acrylic coatings play an important role.[1–6] Fluorinated acrylic copolymer coatings have been studied and applied widely due to their outstanding hydrophobic, oleophobic, and antifouling surface behavior.[4,7] Fluorinated acrylic monomers, such as trifluoroethyl methacrylate (TFEMA), hexafluorobutyl acrylate (HFBA), hexafluorobutyl methacrylate (HFMA), dodecafluoroheptyl methacrylate (DFHMA), etc., were mostly used to synthesize fluorinated acrylic copolymers.[4,8] However, these monomers are relatively expensive. To obtain fluorinated copolymers of high performance with lower surface energy, more amount of fluorinated acrylic monomer has to be incorporated. Thus, there inevitably exist other problems about polymerization stability and cost. Therefore, great attention has been paid to the study of synthesis and application of fluorinated monomers with high fluorine content.[1,9–14] Lina *et al.*[9] developed a method to prepare fluorinated acrylic monomers with a perfluoroalkyl group end and a vinyl group end. Zhang *et al.*[10] developed an efficient synthetic approach to fluorinated acrylate containing a sulfonamide group as a space linker

between the fluorinated chain and acrylic group. Moreover, they investigated the reactivity ratios of the monomers in radical copolymerization. Thomas *et al.*[1] prepared polymers by free radical solution polymerization of a variety of hydrocarbon monomers with the (perfluoroalkyl)ethyl methacrylate monomer $CH_2{=}C(CH_3)CO_2(CH_2)_2(CF_2)_nF$, from which water and oil repellent surfaces were created. Huang *et al.*[11] designed and synthesized a series of novel vinylidene fluoride-containing polyacrylates through a five-step process starting from the telomerizations of VDF with perfluoroalkyl iodide.

Meanwhile, silicon-containing polymers, which possess exceptional hydrophobicity, flexibility, excellent resistance to high and low temperature, ultraviolet, and oxidation degradation, have been used as another typical kind of low surface energy material.[5,15] Nevertheless, fluorine-containing polymers usually exhibit poor resistance to low temperature, whereas silicon-containing polymers present poor resistance to chemical media. Therefore, it is valuable to synthesize coatings which combine the excellent properties of fluorine- and silicon-containing polymers.[6,8,16–18] But there existed compatibility problems owing to different polarity of the two components that were added as two different
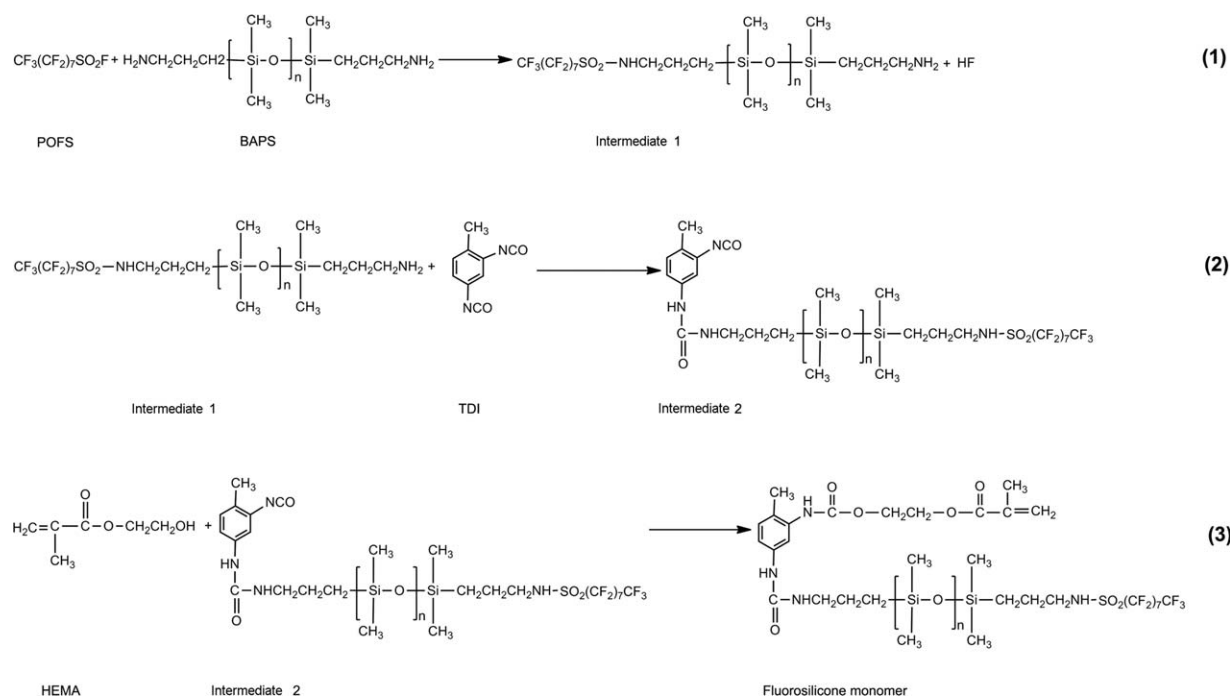
Scheme 1. Synthesis of the fluorosilicone monomer.

reactants.[8] Thus, it is of high significance to develop a new kind of vinyl fluorosilicone monomer, which possesses high fluorine and silicon content in the same molecule, to provide excellent compatibility between the fluorine and silicon components.

In this article, we designed a simple but novel method to prepare a kind of fluorosilicone monomer that contains high content of fluorine and silicon and a polymerizable vinyl in the radical polymerization. Consequently, a series of fluorosilicone acrylic copolymers were synthesized via a radical polymerization route using the prepared fluorosilicone monomer and normal acrylic monomers, including hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), and butyl acrylate (BA). Chemical structure of the monomers and the acrylic copolymers were characterized by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (^{1}H NMR and ^{19}F NMR), respectively. Variation of molecular weight during the preparation process of the fluorosilicone monomer was investigated by Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS). Glass transition temperature (T_g) of the copolymers was tested via differential scanning calorimetry (DSC). Surface properties of the copolymer films were studied by water static contact angles, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). Thermostability of the copolymers was explored by thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

Perfluoro-1-octanesulfonyl fluoride (POSF, purity higher than 90%) was obtained from Hubei Hengxin Chemical Co. (Yingcheng, China). Bis-amine propyl polydimethylsiloxane (BAPS, average degree of polymerization n is 10) was supplied by Hangzhou Silong Material Technology Co. (Hangzhou, China). Toluene diisocyanate (TDI, analytical pure) was supplied by Tianjin

Dengke Chemical Reagent Co. (Tianjin, China). HEMA, methyl methacrylate (MMA), and butyl acrylate (BA) were chemically pure and supplied by Dongfang Yakeli Chemicals Corporation (Beijing, China). Butyl acetate (BuA) and N,N-dimethylformamide (DMF) were of analytical pure and purchased from Beijing Chemical Works (Beijing, China). Dibutyl tin dilaurate (DBTDL, purity higher than 90%) was supplied by Beijing Yili Fine Chemical Co. (Beijing, China). Benzoyl peroxide (BPO, analytical pure) was obtained from Xilong Chemicals Corporation (Shantou, China). All the reactants were used as received.

Synthesis of Fluorosilicone Monomer

The reaction procedure consisted of three steps as shown in Scheme 1. At first, BAPS (0.05 mol, 50 g) and BuA (75 g) were added into a four-neck round-bottomed flask equipped with a mechanical stirrer, a thermometer, an addition funnel, and a reflux condenser. After that, POSF (0.05 mol, 25.10 g) was added dropwise under continuous stirring at room temperature. The reaction was performed at 50°C for 3 h to obtain a mixture of intermediate 1 (perfluoro-1-octane sulfonamide propylene aminopropyl polydimethylsiloxane, PFOSAPAPS) and solvent.

Second, TDI (0.05 mol, 8.71 g), BuA (8.71 g), and small amount of DBTDL (0.42 g, as catalyst) were added into another four-neck round-bottomed flask with a mechanical stirrer, a thermometer, an addition funnel, a reflux condenser, and a nitrogen pipe. The mixture was heated to 70°C under continuous stirring. Then, the intermediate 1 (PFOSAPAPS) mixture from step 1 was added dropwise into the flask. The reaction was continued for 2 h after feeding to obtain intermediate 2, which was left in the flask for the next step. The whole process was conducted under nitrogen atmosphere.

In the third step, a mixture of HEMA (0.05 mol, 6.51 g), BuA (6.51 g) as well as DBTDL (0.05 g) was added dropwise into

Table I. Monomer Recipes of the Copolymers (wt %)

Copolymer	MMA	BA	HEMA	FSi
a	60	35	5	0
b	59.9	35	5	0.1
c	59.5	35	5	0.5
d	59.5	34.5	5	1
e	59	33	5	3
f	57.5	32.5	5	5

the above flask containing intermediate 2 at 70°C with continuous stirring under nitrogen atmosphere. The temperature was raised to 80°C and the reaction was continued for 2 h after feeding. Finally, the objective product, i.e., the expected fluorosilicone monomer, was obtained after isolation by vacuum distillation to remove the solvent.

Synthesis of the Fluorosilicone Acrylic Copolymer

The copolymers were synthesized via a solution polymerization route. All the reactions were performed in a four-neck round-bottomed flask equipped with a mechanical stirrer, a thermometer, an addition funnel, and a reflux condenser. DMF was used as the solvent, whereas BPO was used as the initiator. Weight ratio of the solvent DMF with the monomers was 3 : 2, and the initiator BPO account for 1 wt % of the whole monomers. MMA, BA, and HEMA were used as the normal hydrocarbon acrylic comonomers. The above synthesized product was used as the fluorosilicone monomer. At first, 70 wt % DMF and 20 wt % BPO were added into the flask at RT; then, it was heated to 100°C under continuous stirring. Second, all the monomers, 20 wt % DMF, as well as 70 wt % BPO, were added dropwise into the flask over about 2 h. The reaction was performed at 100°C for another 2 h after completion of the addition. After that, the rest 10 wt % DMF and 10 wt % BPO were added dropwise into the flask. The polymerization was continued further for 2 h after feeding to promote the conversion of the residual monomers. At last, the reaction mixture was cooled down to room temperature and the copolymer was prepared.

Various amount of the fluorosilicone monomer (FSi) was used to explore the effect thereof on the properties of the copolymer. The monomer recipes were listed in Table I.

The copolymer were spun on glass slides and then dried at 50°C for 10 h to obtain the copolymer films.

Characterization

FTIR Analysis. The chemical structure of the reactants, intermediate products and the fluorosilicone monomer, as well as the copolymers was characterized by infrared spectra with a Fourier transform infrared spectrum analyzer (FTIR, Thermo Nicolet AVATAR). The reactants were used as received. The intermediate products and the fluorosilicone monomer were distilled under reduced pressure to remove the solvent before test. The vacuum reduced pressure distillation was conducted at a rotary evaporator with an increasing temperature ranging from room temperature to 70°C. Then, a mechanical pump with a cold trap was used to remove the residual solvent directly at room temperature. The copolymer mixtures were dried to

remove the solvent and the remained resin was used for characterization. The analysis was conducted in a transmission mode with a scanning number of 32 per sample.

NMR Analysis

^{1}H NMR and ^{19}F NMR were performed on a 400-MHz AVANCE III Brüker NMR spectrometer using deuterated chloroform (CDCl$_3$) as solvent. POSF, the solvent-free intermediate products, fluorosilicone monomer, and copolymer were dissolved in CDCl$_3$ before test.

MALDI-TOF-MS Analysis. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS, MALDI-TOF AXIMA CFR PLUS mass spectrometer, SHIMADZU Corporation) was applied to determine the molecular weight of the fluorosilicone monomer and the corresponding intermediate products. BAPS, the solvent- free intermediate products, fluorosilicone monomer were analyzed.

DSC Analysis. T_g of the copolymers was determined with differential scanning calorimetry (DSC, Mettler Toledo, DSC1, Switzerland). The temperature ranged from −20°C to 200°C at a heating rate of 10°C/min under nitrogen atmosphere.

Static Water Contact Angle. Static contact angle of water on the copolymer films were measured on a KRÜSS DSA 20 equipment (KRÜSS, German) by a sessile drop method. The measurements were performed at more than five different positions for each sample to report the average value.

AFM Analysis. Atomic Force Microscope (Veeco DI, USA) was used to examine micrograph of the copolymer film surfaces. The instrument was operated in a tapping-mode to obtain the height and phase images. The root-mean-square roughness (R_q) of the films was calculated via specified software.

XPS Studies. X-ray photoelectron spectrometer (XPS, ESCA-LAB 250, Thermo Fisher Scientific, USA) was used to analyze the element composition at the copolymer film surfaces.

TG Analysis. Thermogravimetric analyses (TGA) of the copolymers were conducted on a NETZSCH STA 449F3 instrument (NETZSCH, Germany). The temperature ranged from 35 to 500°C at a heating rate of 10°C/min under argon atmosphere.

RESULTS AND DISCUSSION

Synthesis and Characterization of Fluorosilicone Monomer

FTIR Analysis. Chemical structures of the synthesized fluorosilicone monomer and raw materials thereof as well as the intermediate products were characterized by FTIR as shown in Figure 1. Curve a shows the FTIR spectrum of POSF. The characteristic vibration of 1468 cm^{-1} was attributed to the asymmetrical stretching vibration of −SO$_2$ of −SO$_2$F, whereas 1243 and 1220 cm^{-1} were ascribed to the C–F stretching vibration, 1154 cm^{-1} to the −CF$_2$− symmetrical stretching vibration, and 556 cm^{-1} to the deformation vibration of C–F, respectively. Curve b shows the FTIR spectrum of BAPS. The characteristic vibration of 3306 cm^{-1} was assigned to the symmetrical stretching vibration of −NH$_2$, and 2962 cm^{-1} to the asymmetrical stretching vibration of −CH$_3$, 1581 cm^{-1} to the deformation vibration of −NH$_2$, 1474 cm^{-1} to the C–H vibration,
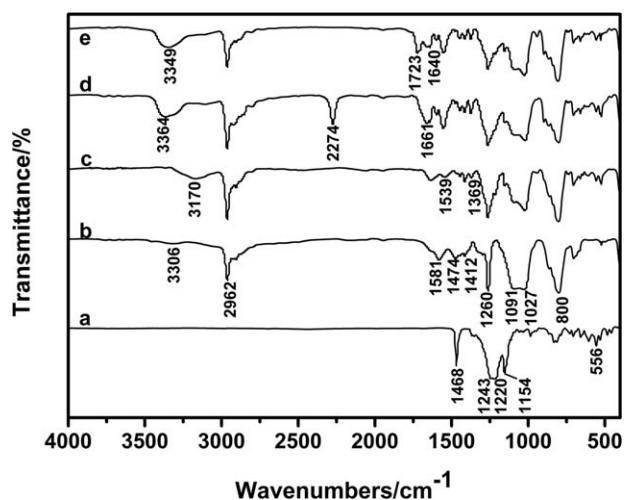
Figure 1. FTIR spectrum of the fluorosilicone monomer as well as the intermediate products compared with the corresponding raw materials. (a) POSF, (b) BAPS, (c) intermediate 1, (d) intermediate 2, (e) the fluorosilicone monomer.

Figure 3. ^{19}FNMR spectra of POSF (a), the fluorosilicone monomer (b), and the copolymer e shown in Table I (c).

1412 cm^{-1} to the –CH$_2$– deformation vibration of Si–CH$_2$–, 1260 cm^{-1} to the symmetrical deformation vibration of –CH$_3$ of Si–CH$_3$, 1027 and 1091 cm^{-1} to the characteristic vibration of –Si(CH$_3$)$_2$O–, and 800 cm^{-1} to the deformation vibration of –CH$_3$ of Si–CH$_3$ and stretching vibration of Si–C, respectively. Curve c shows the FTIR spectrum of intermediate 1, in which the asymmetrical stretching vibration of –SO$_2$ of –SO$_2$F at 1468 cm^{-1} disappeared, instead, the characteristic vibration of –SO$_2$NH– at 1369 cm^{-1} appeared. There also existed the stretching vibration at 3170 cm^{-1} and deformation vibration at 1539 cm^{-1} of –NH–. All the characteristic peaks variation proved that POSF and BAPS had reacted with each other to generate intermediate 1. Curve d shows the FTIR spectrum of intermediate 2. The occurred stretching vibration at 3364 cm^{-1} of N–H and 1661 cm^{-1} of C=O from –NH–CO– revealed that intermediate 1 had reacted with TDI. The asymmetrical stretching vibration of –NCO at 2274 cm^{-1} showed that there existed residual –NCO group. Curve e presents the FTIR spectrum of the final product fluorosilicone monomer. The asymmetrical stretching vibration of –NCO at 2274 cm^{-1} disappeared, whereas the characteristic vibration of C=O of ester at 1723 cm^{-1} and C=C at 1640 cm^{-1} appeared instead. It revealed that the intermediate 2 had reacted with HEMA to
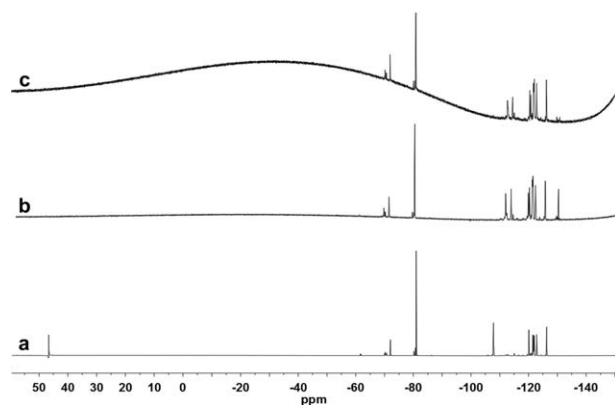
produce the anticipated fluorosilicone monomer. Therefore, it can be concluded that the fluorosilicone monomer was synthesized via the reaction route shown in Scheme 1.

^{1}H NMR. Figure 2 displays the ^{1}H NMR spectra of intermediate 1, intermediate 2, and the fluorosilicone monomer. In spectrum of the intermediate 1, the chemical shifts at 4.06 ppm (peak a) were assigned to the –SO$_2$NH– group, whereas the peaks between 3.10 and 3.35 ppm (peak b) were due to the –NH$_2$ group. In spectrum of the intermediate 2, the chemical shifts between 3.10 and 3.40 ppm (peak g) were assigned to the imino group of –C$_3$H$_6$–NH–CO–. The characteristic chemical shifts of –NH–CO– and –CH$_3$ on the benzene ring appeared at 4.16 ppm (peak h) and 2.20 ppm (peak f), respectively. In spectrum of the fluorosilicone monomer, the enhancement of peak k, appearance of peak i and j suggested that intermediate 2 reacted with HEMA to generate the fluorosilicone monomer. Chemical shifts of the double bonds at 5.60 and 6.15 ppm (peak i) revealed that the vinyl group kept intact after the synthetic reaction of the fluorosilicone monomer. In combination of the FTIR results, it can be concluded that the reaction was conducted according to the synthetic route in Scheme 1, so that the anticipated fluorosilicone monomer was prepared.

^{19}F NMR. The chemical structure of POSF and the fluorosilicone monomer were corroborated by ^{19}F-NMR as shown in Figure 3. Curve a shows the ^{19}F NMR spectrum of POSF. The peaks between 46.6 and 46.7 ppm were assigned to the –SO$_2$F
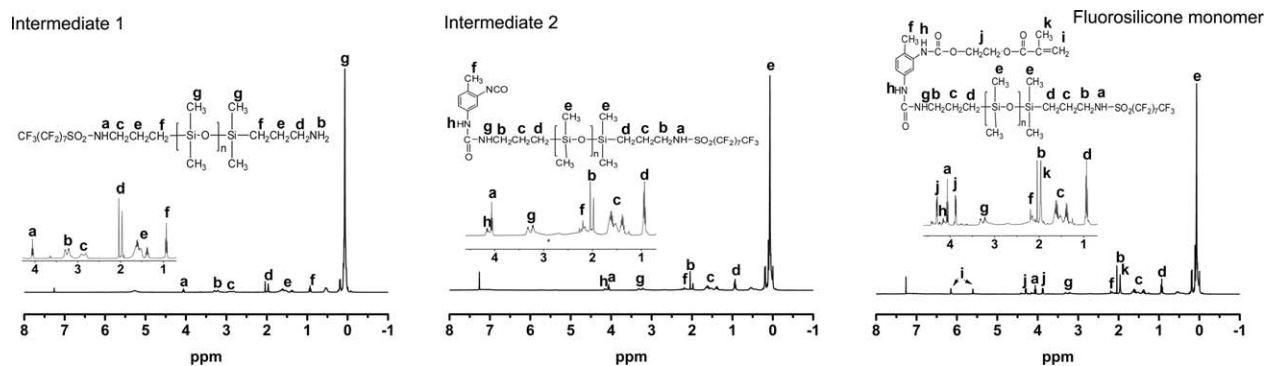

Figure 2. H^{1}NMR spectra of intermediate 1, intermediate 2, and the fluorosilicone monomer.
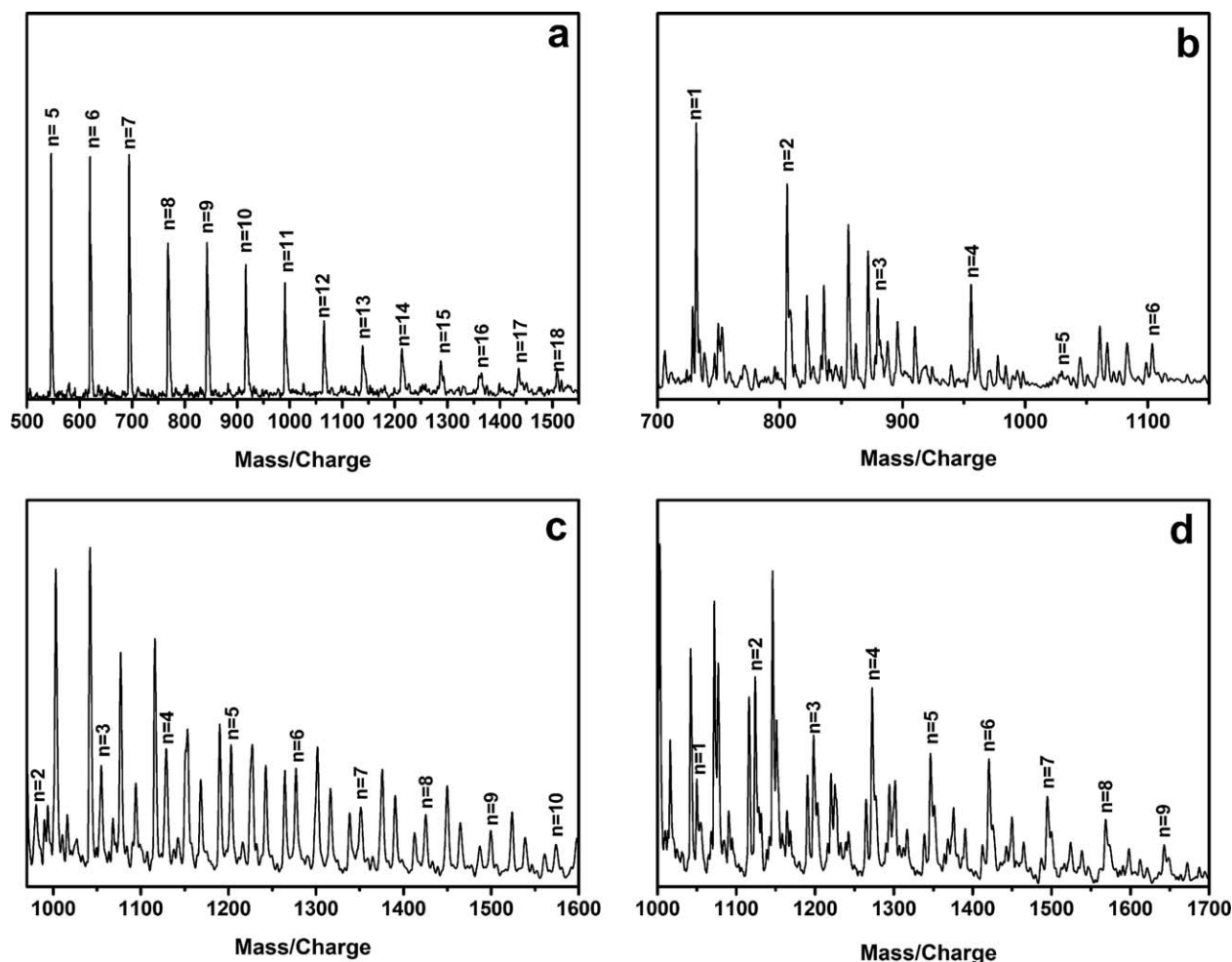
Figure 4. The MALDI-TOF-MS images of BAPS (a), intermediate 1 (b), intermediate 2 (c), and the fluorosilicone monomer (d).

group, the peak between -80.9 and -81.1 ppm to the $-CF_3$ group, whereas the peaks between -107.8 and -126.3 ppm to the $-CF_2-$ group. It is obvious that the $-SO_2F$ group peaks disappeared in the ^{19}F-NMR spectrum of the fluorosilicone monomer (curve b); however, the $-CF_3$ group and the $-CF_2-$ group still showed their characteristic peaks. As a result, it demonstrated that POSF had participated in the reaction and the fluorosilicone monomer contained the perfluorooctane segment.

MALDI-TOF-MS Analysis. Figure 4 shows the MALDI-TOF-MS images of BAPS, the intermediated products, and the synthesized fluorosilicone monomer, in which, **n** represented number of the $-Si(CH_3)_2O-$ structural unit. Molecular weights of the reactants, the intermediate products, and the fluorosilicone monomer were presented. It is seen clearly that molecular weights fit very well with the molecular structure of the intermediates and the newly designed monomer, respectively. Consequently, it is concluded that the target fluorosilicone monomer is exactly the one shown in Scheme 1. The other peaks might be originated from small amount of some impurities.

Synthesis and Characterization of Acrylic Copolymer
Chemical structure of the copolymers was confirmed by FTIR as shown in Figure 5. It is clear that both the copolymers exhib-

ited the characteristic stretching vibration of $-OH$ at 3436 cm^{-1}, asymmetrical stretching vibration and symmetrical stretching vibration of $-CH_3$ at 2955 and 2875 cm^{-1} respectively, asymmetrical stretching vibration of $-CH_2-$ at 2923 cm^{-1}, stretching vibration of $C=O$ at 1733 cm^{-1},
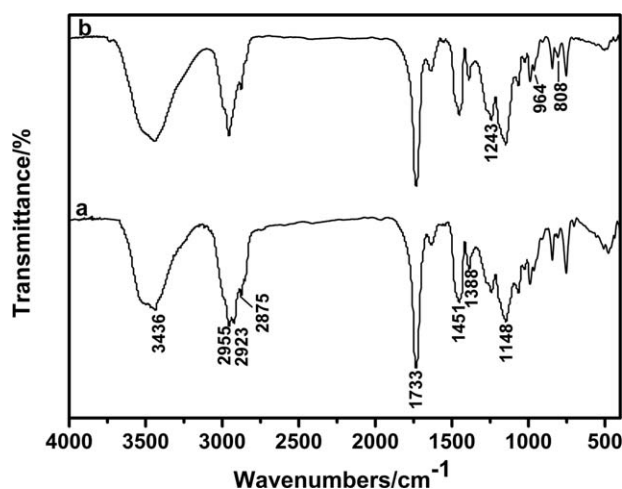

Figure 5. FTIR spectra of the copolymers. (a) Copolymer a; (b) Copolymer e.
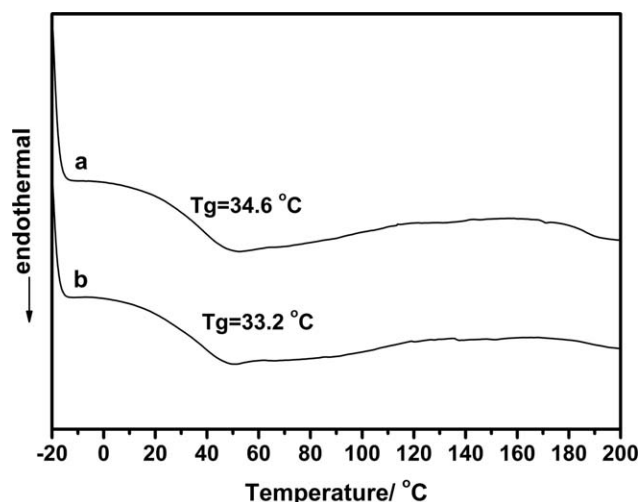
Figure 6. DSC curves of the copolymers. (a) Copolymer a; (b) Copolymer e.

asymmetrical deformation vibration and symmetrical deformation vibration of –CH$_3$ at 1451 and 1388 cm^{-1} respectively, as well as the stretching vibration of C–O–C of acrylic esters at around 1148 cm^{-1}. As 3 wt % of the acrylic monomers were replaced by the same amount of the fluorosilicone monomer (curve b), the enhancement of the peak at 1243 cm^{-1} was assigned to the C–F stretching vibration, whereas the enhancement of the peaks at 964 and 808 cm^{-1} were resulted from the stretching vibration of Si–C and deformation vibration of –CH$_3$ of Si–CH$_3$, respectively. Therefore, the fluorosilicone monomer was copolymerized into the copolymers.

The ^{19}F NMR spectra of copolymer e shown in Figure 3 provided further evidence. It can be seen from Figure 3 that copolymer e [Figure 3(c)] displayed the same peaks as the fluorosilicone monomer [Figure 3(b)], which verified again that the fluorosilicone monomer had participated in the copolymerization. The fluctuant baseline of Figure 3(c) was due to the low fluorine content in the copolymers.

The glass transition temperature (T_g) of the copolymers were tested by DSC. It is absolutely not trivial to prepare a homogene-
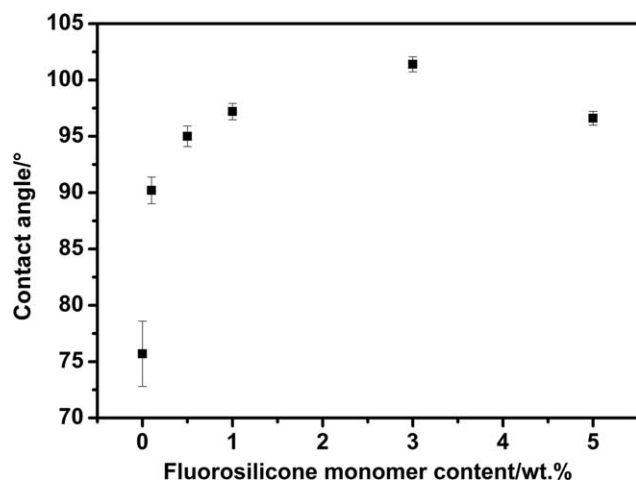

Figure 7. Water contact angle of the copolymer films containing different amount of fluorosilicone monomer.

ous fluorinated or fluorosilicone dispersion by classical radical polymerization. Although DSC is suited to judge the homogeneity of the copolymerization process.[3] One single T_g is undoubtedly an indication of a statistical copolymerization. Figure 6 displays the DSC curves of Copolymer a and Copolymer e. Each copolymer exhibited only one T_g, indicating that all the monomers had copolymerized to produce the expected copolymers. It is obvious that there was no homopolymer generated during the polymerization. The little difference between T_g of the hydrocarbon acrylic copolymer (Copolymer a, 34.6°C) and the fluorosilicone acrylic copolymer (Copolymer e, 33.2°C) suggested that the rigid fluorinated segments and the soft silicone segments were incorporated within the F-Si copolymer based on their good compatibility. Meanwhile, the introduction of small amount (no more than 5 wt % based on the total monomers) of the fluorosilicone monomer affected little on the T_g of the copolymers.

Surface Properties of the Copolymer Films

Contact Angles. Water contact angle has been used to reflect the hydrophobicity of the copolymer films and higher contact angle suggests better hydrophobicity.[19,20] Figure 7 exhibits the static water contact angle of the copolymer films containing different amount of the fluorosilicone monomer. When the copolymer did not contain fluorosilicone monomer, average value of water contact angle was only 75.7° ± 2.9° (Copolymer a in Table I), indicating a hydrophilic film.[15] However, water contact angle value of the copolymer film increased sharply to 90.2° ± 1.2° when only 0.1 wt % of the fluorosilicone monomer was incorporated within the copolymer (Copolymer b). Film of the copolymer turned into a hydrophobic one, suggesting that the monomer could improve the hydrophobicity of the copolymers substantially. For the Copolymer c, d, e, and f, the water contact values of the films were 95° ± 0.9°, 97.2° ± 0.7°, 101.4° ± 0.7°, and 96.6° ± 0.6°, respectively. It is clear that the hydrophobicity of the copolymers increase as the increase amount of the fluorosilicone monomer, when the monomer was no more than 3 wt %. As the fluorosilicone amount was increased further to 5 wt % (Copolymer f), water contact angle decreased to 96.6° ± 0.6°, which was smaller even than that of copolymer e. This might be due to the little fluctuation of polymerization stability and film forming behavior. As is well known that there exist significant difference of polarity among the fluorinated components, silicone components and the normal hydrocarbon acrylic (co)polymer, consequently, compatibility of the new fluorosilicone monomer with the hydrocarbon acrylic monomers became poorer as amount of the former increased, which resulted in certain reaction unstability during the copolymerization.

AFM. It is believed that the hydrophobicity of the films is determined by the film surface composition and the surface roughness.[21,22] The fluorine and silicon components distributed on the film surface are naturally helpful to improve the hydrophobicity of the films. It is generally believed that in case of hydrophobic film, surface roughness is helpful to increase the water contact angle.[23] Figure 8 shows the AFM phase and height images of the copolymers and the root-mean-square roughness of the films were also recorded. In the phase images, the brighter contrast was assigned to the stiffer domains, whereas the dark contrast to the soft domains. In this system, the stiffer regions were the fluorinated segments, whereas the soft regions
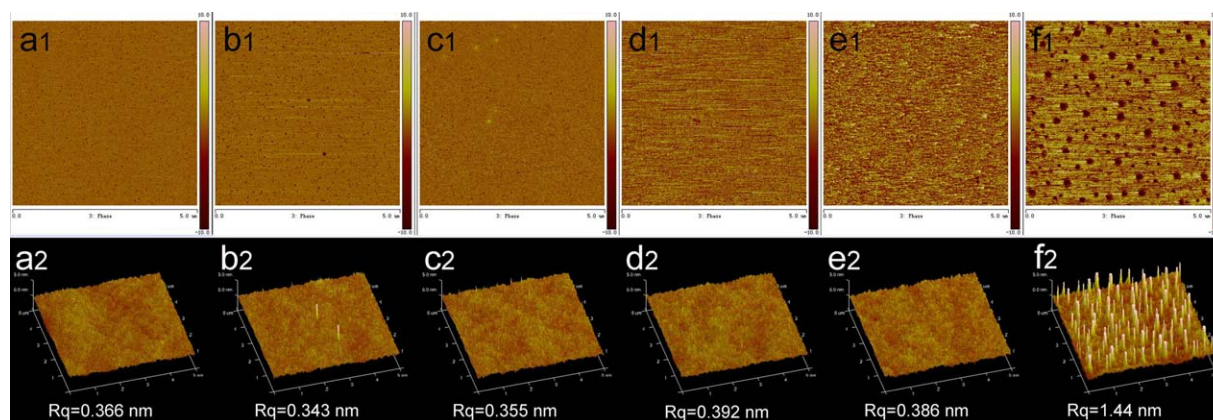
Figure 8. AFM images of the copolymer films. a1-f1, phase images of Copolymer a-f; a2-f2, height images of Copolymer a-f. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

belonged to the silicon-containing and hydrocarbon segments. Compared with the phase images [Figure 8(a1–f1)], it is clear that when the fluorosilicone monomer content was no more than 3 wt % (Copolymer a-e), the fluorinated, silicon-containing, and hydrocarbon segments were in good compatibility, whereas there existed distinct phase separation as the monomer increased to 5 wt % (Copolymer f). Through the height images [Figure 8(a2–f2)], it is easily found that when the monomer content was no more than 3 wt % (Copolymer a-e), the films were plat so that roughness thereof were almost the same. But as the monomer amount increased to 5 wt %, the film became rough with an R_q of 1.44 nm. In combination with the phase image [Figure 8(f1)], the silicon segments might be in bad compatibility with the other compositions. These might be due to the unstable polymerization and resulted in the phase separation during the film formation. When the fluorosilicone monomer was no more than 3 wt %, the copolymer film was uniform with the same roughness, but the fluorine- and silicon-containing components distributed more on the film surface with the increase of the monomer content. Therefore, water contact angle increased with the increasing content of the fluorosilicone monomer. As for Copolymer f, although more fluorosilicone monomer was introduced, the copolymerization was unstable, thus the film was not so hydrophobic as Copolymer e. It can be concluded that a uniform hydrophobic film can be prepared by adding the fluorosilicone monomer (no more than 3 wt %) during the copolymerization. Moreover, compared with the fluorosilicone copolymer film prepared by us with the separated fluorinated acrylic monomer and vinyl triethoxysilane,[8] the hydrophobic copolymer film in this work was platter and more uniform with less fluorosilicone monomer.

XPS. Table II shows the atomic ratio of the elements in different copolymers through the XPS characterization. For Copolymer a, there was no fluorosilicone monomer incorporated; therefore, only C and O elements were detected. As 0.1 wt % fluorosilicone monomer was copolymerized with other acrylic monomers, there were F and Si elements distributed on the film surface, and the C/F ratio was 131.52, whereas the C/Si ratio was 18.50. Because of the low surface energy composition on the film surface, the corresponding water contact angle increased substantially from

$75.7° \pm 2.9°$ to $90.2° \pm 1.2°$. When the fluorosilicone monomer content increased to 3 wt %, the C/F ratio decreased strikingly to 10.75 and the C/Si ratio decreased to 5.08, indicating that the fluorine and silicon segments distributed on the film surface increased significantly. Therefore, the water contact angle increased further to $101.4° \pm 0.7°$. Similar phenomena has been observed in related research work about copolymers of fluorinated monomer(s) with other hydrocarbon acrylic monomers, and fluorinated groups with lower surface free energy which contain at least 12 fluorine atoms in the monomer molecule preferentially migrated to the outmost surface of film during the film formation.[17,24] On the other hand, however, although the fluorosilicone monomer increased 30 times in Copolymer e than that in Copolymer b, the C/F and C/Si ratios were not in this multiple. These were due to the characteristic of the low surface energy segments. The low surface energy segments tend to migrate to the surface and distribute on the film–air interface. When the monomer content was only 0.1 wt %, the low surface energy segments were absolutely fewer and easier to distribute on the film-air surface. But when the monomer content increased to 3 wt %, the low surface energy segments on the film surface were almost in saturated, thus the water contact reached the maximum value.

Thermostability of the Copolymers
TGA experiment was used to evaluate the heat resistance of the copolymers. Mass loss versus temperature of Copolymer a and Copolymer e were displayed in Figure 9. Copolymer a began to decomposition at 303.3°C, whereas Copolymer e at 321.7°C. The degraded speed

Table II. Atomic Ratio of the Elements in Different Copolymers

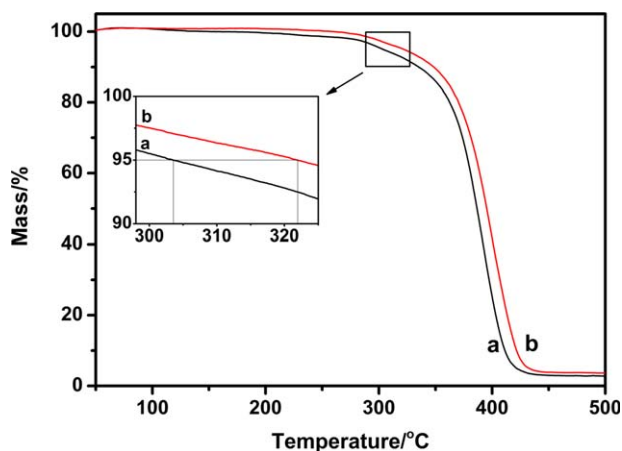| Elements	Atomic/%		
	Copolymer a	Copolymer b	Copolymer e
C1s	74.54	71.02	58.7
O1s	25.46	24.17	21.38
F1s		0.54	5.46
Si2p		3.84	11.55
N1s		0.43	2.17
S2p			0.74

Figure 9. TGA curves of the copolymers. (a), Copolymer a; (b), Copolymer e. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the hydrocarbon copolymer (Copolymer a) was faster than the fluorosilicone one (Copolymer e), suggesting that incorporation of the newly fluorosilicone monomer improved the thermostability of the copolymers distinctly, though only a small amount (as low as 3 wt %) of the newly monomer was incorporated.

CONCLUSION

A novel method has been developed for synthesizing fluorosilicone monomer containing low surface energy fluorine and silicon segments and polymerizable vinyl in the radical polymerization. Moreover, the monomer was used to prepare fluorosilicone acrylic copolymers. Effects of the fluorosilicone monomer on the surface properties and thermostability of the copolymers were studied. FTIR, ^{1}H NMR, ^{19}F NMR, and MALDI-TOF-MS analyses exhibited that the fluorosilicone monomer has been synthesized successfully. FTIR, ^{19}F NMR, and DSC results showed the fluorosilicone monomer has copolymerized into the acrylic copolymers and there was no homopolymer generated. Static water contact angle data suggested that the fluorosilicone monomer was significantly helpful to improve the hydrophobicity of the copolymer films. The water contact angle increased greatly from 75.7° ± 2.9° to 90.2° ± 1.2°, although only 0.1 wt % of the fluorosilicone monomer was incorporated within the copolymer, and the film hydrophobicity increased further with the increasing amount of the monomer until 3 wt % of the monomer was incorporated. AFM phase and height images indicated that the fluorine and silicon segments were in good compatibility and the incorporation of the monomer produced no observable influence on the surface roughness, when the monomer content was no more than 3 wt %. XPS studies revealed that the fluorinated and silicon-containing segments distributed more on the film surface with the increase of the monomer, which was in accordance with the water contact angle results. TGA results revealed that incorporation of the monomer contributed to a better thermostability of the copolymers. The monomer synthesis route might be helpful to prepare a series of vinyl fluorosilicone monomers containing different fluorine and silicon segments by varying the reactants. And the synthesized monomers can be used both in solution and emulsion polymerization to prepare copolymers of low surface energy.

REFERENCES

1. Thomas, R. R.; Anton, D. R.; Graham, W. F.; Darmon, M. J.; Sauer, B. B.; Stika, K. M.; Swartzfager, D. G. *Macromolecules* **1997**, *30*, 2883.

2. Cui, X. J.; Zhong, S. L.; Wang, H. Y. *Polymer* **2007**, *48*, 7241.

3. Landfester, K.; Rotheand, R.; Antonietti, M. *Macromolecules* **2002**, *35*, 1658.

4. Xu, W.; An, Q. F.; Hao, L. F.; Zhang, D.; Zhang, M. *Appl. Surf. Sci.* **2013**, *268*, 373.

5. Rodriguez, R.; Alarcon, C. D.; Ekanayake, P.; McDonald, P. J.; Keddie, J. L.; Barandiaran, M. J.; Asua, J. M. *Macromolecules* **2008**, *41*, 8537.

6. Xiong, P. T.; Lu, D. P.; Chen, P. Z.; Huang, H. Z.; Guan, R. *Eur. Polym. J.* **2007**, *43*, 2117.

7. Malshe, V. C.; Sangaj, N. S. *Prog. Org. Coat.* **2005**, *53*, 207.

8. Han, D.; Zhu, L.; Chen, Y.; Li, W.; Feng, L. *J. Fluorine Chem.* **2013**, *156*, 38.

9. Lina, M.-J.; Lune, T. L. D.; Dessaint, A. Fluorinated Acrylic Monomers as Hydrophobic and Oleophobic Agents, U.S.A, 5144056 [P/OL], **1992**.

10. Zhang, Q. H.; Wang, Q. Y.; Zhan, X. L.; Chen, F. Q. *Ind. Eng. Chem. Res.* **2014**, *53*, 8026.

11. Huang, J.-Q.; Meng, W.-D.; Qing, F.-L. *J. Fluorine Chem.* **2007**, *128*, 1469.

12. Ameduri, B.; Boutevin, B. *J. Fluorine Chem.* **2000**, *104*, 53.

13. Borkar, S.; Jankova, K.; Siesler, H. W.; Hvilsted, S. *Macromolecules* **2004**, *37*, 788.

14. Ozbay, S.; Erbil, H. Y. *Colloids Surf. A* **2014**, *452*, 9.

15. Zhang, B. T.; Liu, B. L.; Deng, X. B.; Cao, S. S.; Hou, X. H.; Chen, H. L. *Appl. Surf. Sci.* **2007**, *254*, 452.

16. Mori, H.; Sada, C.; Konno, T.; Yonetake, K. *Polymer* **2011**, *52*, 5452.

17. Xiao, X. Y.; Xu, R. *J. Appl. Polym. Sci.* **2011**, *119*, 1576.

18. Liang, J.; He, L.; Dong, X.; Zhou, T. *J. Colloid Interface Sci.* **2012**, *369*, 435.

19. Ha, J. W.; Park, I. J.; Lee, S. B. *Macromolecules* **2005**, *38*, 736.

20. Bertolucci, M.; Galli, G.; Chiellini, E. *Macromolecules* **2004**, *37*, 3666.

21. Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988.

22. Feng, L.; Li, S. H.; Li, Y. S.; Li, H. J.; Zhang, L. J.; Zhai, J.; Song, Y. L.; Liu, B. Q.; Jiang, L.; Zhu, D. B. *Adv. Mater.* **2002**, *14*, 1857.

23. Cho, K. L.; Liaw, I. I.; Wu, A. H.-F.; Lamb, R. N. *J. Phys. Chem. A* **2010**, *114*, 11228.

24. Zhang, C.; Chen, Y. *Polym. Int.* **2005**, *54*, 1027.