

Synthesis and Characterization of Fluorinated Polyacrylate Graft Copolymers Capable as Water and Oil Repellent Finishing Agents

Weiye Tang,¹ Yangen Huang,¹ Feng-Ling Qing^{1,2}

¹College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Songjiang District, Shanghai 201620, China

²Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

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ABSTRACT: A facile method for preparation of fluorinated polyacrylate was developed. Novel multifunctional graft copolymer (**GPF-1**, **2**, **3**) containing short fluoroalkyl side chains and reactive groups were successfully prepared by grafting fluoroalcohols to polyacrylate. The obtained products were characterized by ¹H NMR, ¹⁹F NMR, FTIR, GPC, TGA, and XPS analyses. **GPF-1**, **2**, **3** exhibited very low surface free energy (17.77–25.81 mJ/m²). Cotton fabric treated by **GPF-1** had the highest

water and oil repellency rating which was 100 and 6, respectively (AATCC test methods). The water and oil repellency rating was kept as 90 and 5, respectively, after 10 soaping cycles or 2 h uninterrupted soaping which indicated a very good washing durability. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 84–92, 2011

Key words: graft copolymers; fluoropolymers; surfaces; water and oil repellency

INTRODUCTION

Surface modification of various solid materials continues to be an important research area because surface properties in some cases can be determinant factors for their practical applications. As one important property of a solid surface, the wettability is controlled by the chemical composition and topology of the surface. Usually, hydrophobic and/or oleophobic surfaces are obtained through a combination of low surface-energy species and a peculiar topographic feature based on roughness.^{1–4} Fluoropolymers were widely used as surface modifying agents due to their exceptionally low surface free energy.^{3–8} It is well known that the textile finishing agents containing long perfluoroalkyl pendant chains (R_{fv} , $n \geq 8$) have excellent hydrophobic and oleophobic effects, and the water and oil repellency ratings of the treated textiles were usually 100 and 6 (AATCC test methods), respectively.^{9–14} However, there are increasing evidences that indicate compounds containing long perfluoroalkyl chains (R_{fv} , $n \geq 8$) can accumulate in organism due to their extremely high stabilities and are toxic, especially, perfluorooctanoic acid (PFOA) and its derivatives.^{15–18} Based on the health concern, envi-

ronmentally benign surface modifying reagents containing short fluorocarbon chains (R_{fv} , $n \leq 6$) are highly regarded now. However, usually the hydrophobic and oleophobic effects of textile finishing agents containing short fluorocarbon chains (R_{fv} , $n \leq 6$) had a dramatic decline which make them could not be applied practically. It has been discovered that to provide optimum water and oil repellency the pendant perfluorinated alkyl groups of finishing agents should aligned parallel to each other on the surface. The water and oil repellency of perfluorinated alkyl acrylic resins can be improved by the introduction of urethane groups between acrylic backbone and the perfluorinated groups. The affinity of the urethane groups for one another can keep the entire fluorinated pendant chains substantially in fixed alignment which result in high water and oil repellency.^{19,20} Durability is another important problem for coatings. Fluorinated coatings usually are not stable sufficiently during use since the coatings are achieved only through physical adsorption or adhesion to the solid surfaces. Methods for introducing reactive groups into coating materials which can make the coating firmly adhered on the substrate through covalent bond have been developed.²¹ In this article, we attempted to introduce short fluorocarbon chains and reactive groups into polyacrylate and then investigated the hydrophobicity and oleophobicity of the resulting fluorinated polyacrylates.

Correspondence to: F.-L. Qing (flq@mail.sioc.ac.cn).

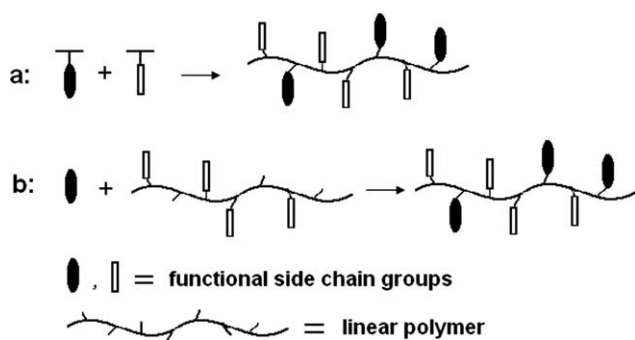


Figure 1 Schematic illustration for the synthesis of copolymer: (a) a “macromonomer” approach; (b) a “graft” approach.

Conventionally, a “macromonomer” approach [Fig. 1(a)] is used for the synthesis of fluorinated polyacrylates. According to this method, fluorinated acrylate “macromonomer” was synthesized firstly and then copolymerized with other acrylate monomers to form random copolymer.^{11,22–26} The main disadvantages of this approach were the low utilization ratio of the expensive fluorinated monomers and low efficiency, as multi steps and careful purification were required during the synthesis of fluorinated acrylate “macromonomers”. Sometimes, the synthesis and purification of the “macromonomer” was very difficult. In addition, “macromonomer” may influence the polymerization and result in low degrees of polymerization.²⁶ In this study, the fluorinated polyacrylate graft copolymers (**GPF-1, 2, 3**) were synthesized through a pseudo one-step “graft-from” procedure [Fig. 1(b)]. The approach was simple, high efficiency, and high utilization ratio of the raw materials (100%). There are two urethane groups between the fluorinated groups and the acrylic backbone in **GPF-1, 2, 3** and in which reactive groups for attachment were also introduced. **GPF-1, 2, 3** were applied to cotton fabrics finishing and the performance as water/oil repellents were investigated.

EXPERIMENTAL

Materials

2,2,3,3,3-pentafluoro-1-propanol (ABCR, 98%), 2,2,3,4,4,4-hexafluorobutanol (XEOGIA, Harbin, China, 96%), 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol and hexamethylene diisocyanate (HDI) (Alfa Aesar, 98%). n-Octadecyl alcohol, acrylic acid, hydroquinone, paratoluenesulfonic acid (P-TSA), cyclohexane, 2-chloroethanol, sodium hydroxide (NaOH), triethylene glycol, azo-bis-isobutyronitrile (AIBN), 1,4-dioxane, methyl ethyl ketoxime (MEKO) and ethanol were purchased from Shanghai Chemical Reagent Company (Shanghai, China). 1,4-dioxane was puri-

fied by distillation with sodium. All of other reagents were used as received.

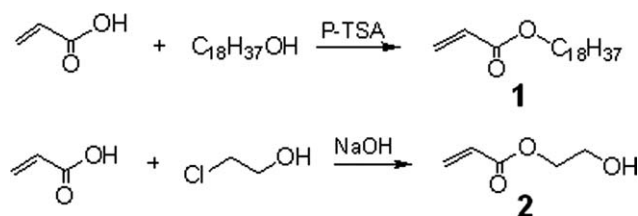
Characterization

¹H NMR spectra were recorded on a Bruker AV 400 (400 MHz) (Bruker, Faellanden, Switzerland) spectrometer with Me₄Si as an internal standard and ¹⁹F NMR spectra were obtained on Bruker AV 400 (376 MHz) spectrometer using CFCl₃ as an external standard. Downfield shifts are designated as positive. All chemical shifts (δ) are expressed in ppm and coupling constants (J) are in Hz. The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet AT-380 (Thermo Electro) spectrometer. Waters 1515 gel permeation chromatography (GPC) with refractive index detector was used to measure the molecular weight (MW). Linear polystyrene was used as standards and THF as solvent. Thermogravimetric analyses (TGA) of polymers was conducted on a Netzsch TG 209 F1 instruments. The surface chemical composition of the treated fabrics was carried out by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) with a power of 150 W and a monochromatic Al K α X-ray source (1486.6 eV). The surface morphology was determined by scanning electron microscopy (SEM, JSM-5600 LV, JEOL, and Japan). The contact angles (CAs) were measured using an automatic video contact angle testing apparatus OCA 40 (DataPhysics, Germany) and the values were averages from measurements on at least five different positions for each sample. The melting point was determined by WRS-2A melting point apparatus (Shengguang, China).

Synthesis of monomers (Scheme 1)

Octadecyl acrylate (1)

To a stirred solution of hydroquinone (0.3 g, 3 mmol) in cyclohexane (40 mL), n-octadecyl alcohol (27.0 g, 100 mmol) was added at room temperature. The mixture was stirred at 60°C for several minutes and then acrylic acid (8.6 g, 120 mmol) and P-TSA (3.0 wt % of reaction mass fed) were charged in. The reaction mixture was heated to reflux and stirred for 12 h, during which the water was removed by Dean and Stark apparatus. After the reaction was completed, the solvent and small quantity of acrylic acid was removed *in vacuo*. The residue was poured into ethyl acetate (100 mL) and washed with deionized water (100 mL \times 3). The combined organic layer was dried with anhydrous MgSO₄, then filtered and evaporated *in vacuo* to afford monomer **1** as white waxy solid (30.4 g, 93.7% yield). m.p. 29.2–29.4°C



Scheme 1 Syntheses of octadecyl acrylate (1) and 2-hydroxyethyl acrylate (2).

(lit. 29.2–31.3 °C); IR ν_{\max} (cm⁻¹, film): 1729, 1637, 1271, no absorption bands > 3100; ¹H NMR (400 MHz, CDCl₃, δ): 6.33 (dd, $J = 1.5, 17.3$ Hz, 1H), 6.04 (dd, $J = 10.4, 17.4$ Hz, 1H), 5.74 (dd, $J = 1.5, 10.4$ Hz, 1H), 4.05 (t, $J = 13.5$ Hz, 2H), 1.50–1.63 (m, 2H), 1.18–1.30 (m, 30H), 0.81 (t, $J = 6.7$ Hz, 3H).

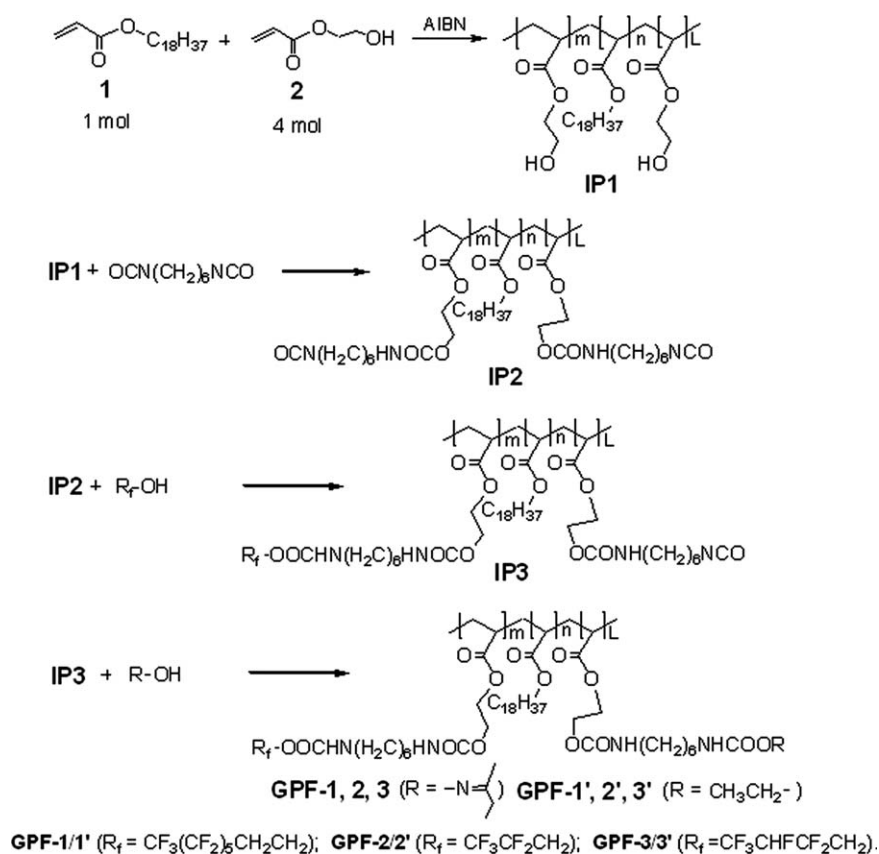
2-Hydroxyethyl acrylate (2)

To a stirred mixture of acrylic acid (14.4 g, 200 mmol) and 2-chloroethanol (48.3 g, 600 mmol), hydroquinone (3.0 g, 27 mmol) and NaOH (8 g, 200 mmol) were added at room temperature. The reaction mixture was heated to reflux and stirred for 4 h. After cooling to room temperature, the precipitate was filtered off, and then triethylene glycol (45 g

and hydroquinone (1.0 g, 9.1 mmol) were added into the filtrate and distilled under reduced pressure. The fraction of 80–82 °C per 5 mmHg was collected to afford monomer 2 as colorless liquid (18.1 g, 78% yield). ¹H NMR (400 MHz, CDCl₃, δ): 6.36 (dd, $J = 1.2, 17.4$ Hz, 1H), 6.07 (dd, $J = 10.5, 17.4$ Hz, 1H), 5.78 (dd, $J = 1.1, 10.4$ Hz, 1H), 4.21 (t, $J = 4.6$ Hz, 2H), 3.78 (t, $J = 4.8$ Hz, 2H), 2.54 (br, 1H). IR ν_{\max} (cm⁻¹, film): 3399, 2953, 1721, 1637, 1619.

Synthesis of fluorinated polyacrylate graft copolymer (GPF-1, 2, 3/GPF-1', 2', 3')

The syntheses of GPF-1, 2, 3 were outlined in Scheme 2. To a stirred solvent (1, 4-dioxane, 4 mL), the mixture of 1 (0.49 g, 1.5 mmol), 2 (0.70 g, 6 mmol), and AIBN (0.01 g) in 1,4-dioxane (1 mL) was added slowly within 10 min under nitrogen atmosphere at 75 °C. The temperature was raised to 80 °C and then proper quantity of AIBN was refilled every three hours for two times. The reaction mixture was stirred at 80 °C for further 14 h to give the solution of intermediate product IP1 (percent conversion, 97.7%). The pure product of IP1 was precipitated by adding deionized water (100 mL) into the solution and collected by filtration, washed with deionized water (100 mL) and dried under vacuum at 50 °C for 48 h to afford IP1 as white solid (1.01 g, 84.9% yield; M_w ,



Scheme 2 Syntheses of GPF-1, 2, 3/GPF-1', 2', 3'.

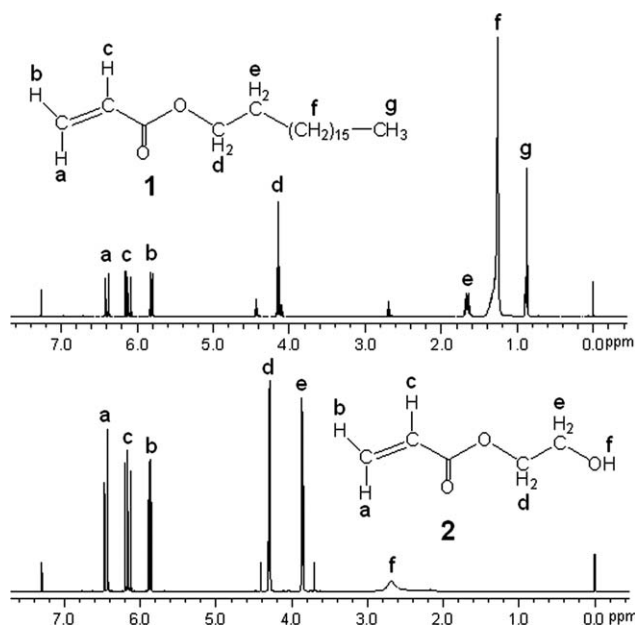


Figure 2 ^1H NMR spectra of monomer 1 and monomer 2 in CDCl_3 .

46,500). Theoretically, crosslinking would occur during the preparation of **IP2** starting from **IP1** and hexamethylene diisocyanate. To avoid crosslinking during the reaction, special feeding process of starting materials has been taken that 5 mL of the above resulting solution of **IP1** (20 wt %) was diluted in 29 mL of 1,4-dioxane and added dropwise to a stirred solution of HDI (1.09 g, 6.5 mmol) in 6 mL of 1,4-dioxane at 100°C . The reaction mixture was stirred for 3 h to give the solution of intermediate product **IP2**. Then 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol (2.0 g, 5.4 mmol) was added to the solution of **IP2**. The reaction mixture was stirred for further 6 h at 100°C to give the solution of intermediate product **IP3**. After cooling to 55°C , MEKO (0.27 g, 3.2 mmol) was added to the solution of **IP3** and stirred for another hour until the absorption band (2273 cm^{-1}) of $-\text{NCO}$ group in infrared spectrum was disappeared. Ethanol (29.5 mL) was charged in and stirred for several minutes to give a clear solution of **GPF-1** (6.5%, concentration of % weight of bath and supposed the conversion of reactant was completed). The pure product can be obtained by adding deionized water (300 mL) into the solution and collecting the precipitation by filtration which was then washed with deionized water (500 mL) and dried under vacuum at 80°C for 24 h to afford pure **GPF-1** as white solid (3.83 g, 85.8% yield; M_w , 103,800). When 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol was substituted by equimolar amounts of 2,2,3,3,3-hentafluoro-1-propanol or 2,2,3,4,4,4-hexafluorobutanol, **GPF-2** (2.80 g, 80.2% yield; M_w , 66,400) or **GPF-3** (2.78 g, 82.1% yield; M_w , 90,800) was obtained, respectively. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ), **GPF-1**: 7.19 (s), 4.24 (t), 3.00 (m), 2.60 (d), 2.26 (d),

2.09 (s), 1.91 (d), 1.32 (d), 1.23 (s), 1.04 (q). **GPF-2**: 7.63 (s), 7.19 (s), 4.71 (t), 4.01 (q), 3.00 (m), 2.26 (t), 2.09 (s), 1.91 (d), 1.35 (q), 1.23 (s), 1.06 (m), 0.82 (d). **GPF-3**: 7.51 (s), 7.10 (t), 6.26 (s), 5.96 (q), 5.72 (s), 4.81 (s), 4.52 (t), 4.11 (s), 2.95 (m), 2.26 (t), 2.08 (s), 1.90 (s), 1.37 (s), 1.23 (s), 1.06 (d), 0.85 (s). ^{19}F NMR (376 MHz, cyclohexanone, δ), **GPF-1**: -81.53 (t, $J = 8.0$ Hz, 3F), -114.01 (s, 2F), -122.47 (s, 2F), -123.45 (s, 2F), -124.19 (s, 2F), -126.75 (s, 2F). **GPF-2**: -83.98 (t, $J = 13.8$ Hz, 3F), -123.83 (q, $J = 13.2$ Hz, 2F). **GPF-3**: -74.37 (d, $J = 7.5$ Hz, 3F), -116.13 to -120.83 (m, 2F), -213.50 (m, 1F). During the last stage of the reaction, if ethanol was added into the solution of **IP3** instead of MEKO and reacted for 6 h at 75°C , **GPF-1'**, **2'**, **3'** were obtained. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ), **GPF-1'**: 7.20 (s), 7.01 (s), 4.92 (s), 4.24 (s), 3.95 (d), 3.57 (s), 3.45 (d), 2.94 (s), 2.33 (q), 2.08 (s), 1.36 (s), 1.23 (s), 1.14 (d), 0.83 (s). **GPF-2'**: 7.63 (s), 7.01 (s), 5.71 (t), 4.74 (t), 3.56 (s), 3.95 (m), 2.95 (m), 2.09 (s), 1.37 (t), 1.22 (s), 1.11 (m), 0.80 (s). **GPF-3'**: 7.50 (d), 7.02 (s), 6.16 (s), 5.96 (s), 4.52 (t), 4.01 (m), 3.57 (s), 2.96 (m), 2.08 (s), 1.38 (s), 1.22 (s), 1.08 (m), 0.81 (s). ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$, δ), **GPF-1'**: -80.27 (t, $J = 13.0$ Hz, 3F), -112.61 (q, $J = 13.2$ Hz, 2F), -121.71 (s, 2F), -122.65 (s, 2F), -123.25 (s, 2F), -125.76 (s, 2F). **GPF-2'**: -83.12 (t, $J = 11.3$ Hz, 3F), -122.76 (q, $J = 13.2$ Hz, 2F). **GPF-3'**: -73.36 (d, $J = 9.4$ Hz, 3F), -116.58 to -120.24 (m, 2F), -214.55 (m, 1F).

Fabric treatments and preparation of films on glass slides

Clean, plain weave 20 cm \times 20 cm cotton fabric weighed 146 g/m^2 was used. Fabric samples were firstly immersed in the solution of **GPF-1**, **2**, **3**/**GPF-1'**, **2'**, **3'** for 4–5 min and then padded through two dips and two nips to reach a wet pickup of 80–85%. The samples were dried at 80°C for 3 min and cured at 170°C for 3 min. The resulting solution of **GPF-1**, **2**, **3** (6.5% owb) was spread equably on the glass

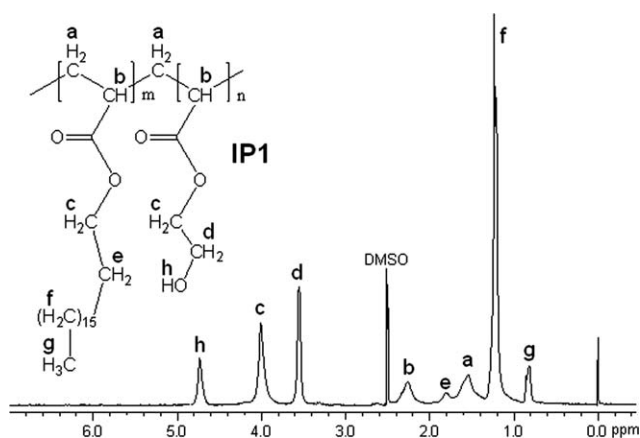


Figure 3 ^1H NMR spectrum of **IP1** in $\text{DMSO}-d_6$.

TABLE I
The Composition of Copolymer IP1

	($S_e/2$)	($S_f/30$)	($S_g/3$)	($S_d/2$)	(S_h)	In theory
Monomer 1 ^a	1.05	1.00	1.11	–	–	1
Monomer 2 ^a	–	–	–	4.11	4.00	4

^a The mole ratio of octadecyl acrylate (1)/2-Hydroxyethyl acrylate (2) in IP1 backbone calculated by different hydrogen atomic integration in ¹H NMR spectrum.

slide and dried at 70°C for 30 min then 110°C for 20 min to afford flat GPF-1, 2, 3 cast films.

Measurements

The water and oil repellency of the finished fabrics were measured according to AATCC test methods 22–2001 and 118–2002,²⁷ respectively. Washing durability was tested using a soaping tester according to AATCC test method 61–2003.²⁸ Soaping temperature was 50°C.

RESULTS AND DISCUSSION

¹H NMR and ¹⁹F NMR studies

¹H NMR spectra of the monomers (1 and 2) are shown in Figure 2. Resonance assignments (δ ppm) are as follows: octadecyl acrylate (1), 6.33 and 6.05 (CH₂=CH–), 5.74 (CH₂=CHCOO–), 4.06 (–COOCH₂–), 1.50–1.63 (–COOCH₂CH₂–), 1.18–1.30 (–COOCH₂CH₂(CH₂)₁₅–), 0.81 (–CH₃). 2-Hydroxyethyl acrylate (2), 6.36 and 6.07 (CH₂=CH–), 5.78 (CH₂=CHCOO–), 4.21 (–COOCH₂–), 3.78 (–CH₂OH), 2.54 (–CH₂OH).

¹H NMR spectrum and resonance assignments (δ ppm) of IP1 are shown in Figure 3. The mole ratio of octadecyl acrylate (1)/2-Hydroxyethyl acrylate (2)

in copolymer backbone was controlled to be 1 : 4 by monomer feed (Scheme 2). According to the ¹H NMR spectrum, the actual mole ratio of the monomers in copolymer IP1 can be calculated by the integration of different peaks. For example, the integration of peak e divided by 2 ($S_e/2$) or the integration of peak f divided by 30 ($S_f/30$) is the relative mole number of monomer 1 (octadecyl acrylate) in the backbone of copolymer IP1. The relative mole number of monomer 2 in the backbone of copolymer IP1 was obtained by the integration of peak d divided by 2 ($S_d/2$). The results are shown in Table I and the actual mole ratio of the monomers was about 1 : 4 which is in well agreement with the monomer feed.

The fluorinated polyacrylate copolymers were confirmed by ¹⁹F NMR spectra (Fig. 4). As fluoroalcohols used here are liquid, the characteristic signals came from solid GPF-1, 2, 3/GPF-1', 2', 3' samples in the ¹⁹F NMR spectra indicated that the fluoroalkyl chains have been introduced to the copolymer successfully.

FTIR analysis

The syntheses of GPF-1, 2, 3 were monitored and further confirmed by FTIR analysis as shown in Figure 5, the characteristic absorptions of O–H stretch (3422 cm^{–1}), C=O (1727 cm^{–1}), aliphatic C–H stretch (2851–2920 cm^{–1}) in the spectrum of IP1

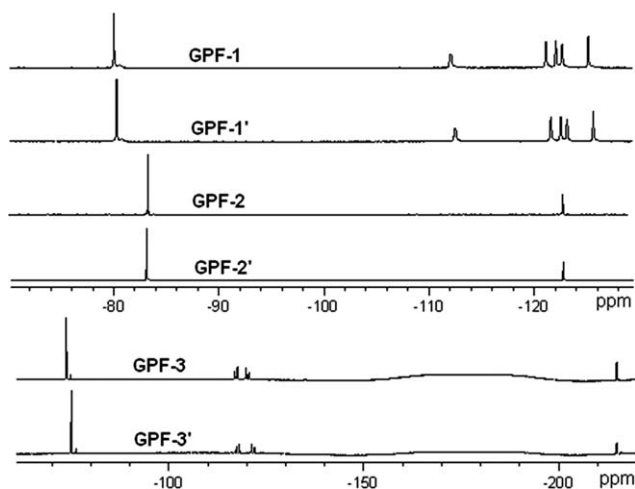


Figure 4 ¹⁹F NMR spectra of GPF-1, 2, 3/GPF-1', 2', 3' in DMSO-d₆.

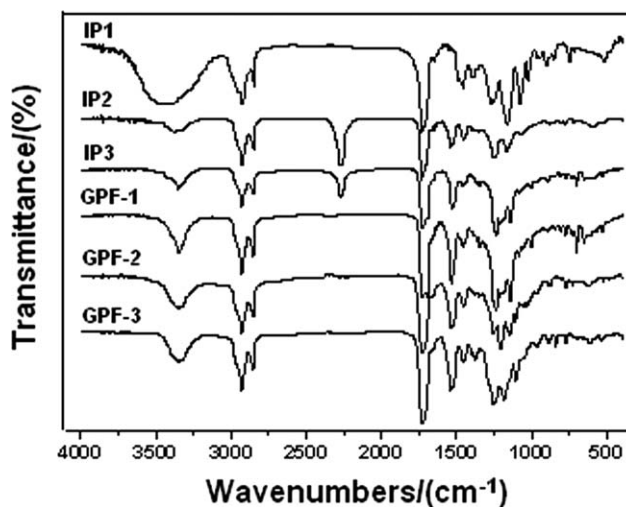


Figure 5 FTIR spectra of IP1, IP2, IP3, and GPF-1, 2, 3.

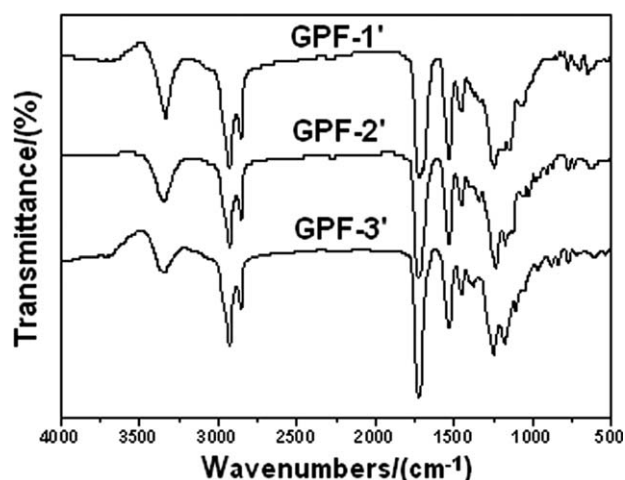


Figure 6 FTIR spectra of GPF-1', 2', 3'.

were clearly presented. The disappearance of the characteristic absorption of O—H (3422 cm^{-1}) and the appearance of new characteristic absorptions of N—H (3352 cm^{-1}) and —NCO (2273 cm^{-1}) indicated the formation of IP2 (Scheme 2). Strong absorption bands around 1240 cm^{-1} and 1143 cm^{-1} which were assigned to C—F stretch in the spectrum of IP3 (Scheme 2) indicated that the fluoroalkyl chains have been grafted onto the copolymer. The remaining absorption band at 2273 cm^{-1} indicated the remaining of —NCO in IP3 and which was disappeared completely (Figs. 5 and 6) after blocking with MEKO or ethanol.

GPC analysis

GPC is one of the most widely used techniques for the determination of molecular weight (MW) and polydispersity index (PDI) of polymers. GPC with refractive index detector was used to measure the MW and PDI of IP1 and GPF-1, 2, 3. Molecular weights of IP1 and GPF-1, 2, 3 were listed in Table II. MW (M_w) of IP1 was about 4.65×10^4 , and MW (M_w) of GPF-1, 2, 3 were about 10.38, 6.64 and 9.08×10^4 , respectively. The MW of GPF-1, 2, 3 were in the normal ranges according to the MW of IP1. These indicated that there were few crosslinking in IP2 and the measure to avoid crosslinking was efficacious.

TABLE II
Molecular Weights of IP1 and GPF-1, 2, 3

Samples	GPC		PDI ^a (M_w/M_n)
	M_n	M_w	
IP1	29300	46500	1.59
GPF-1	59000	103800	1.76
GPF-2	54500	66400	1.22
GPF-3	55900	90800	1.63

^a Polydispersity index.

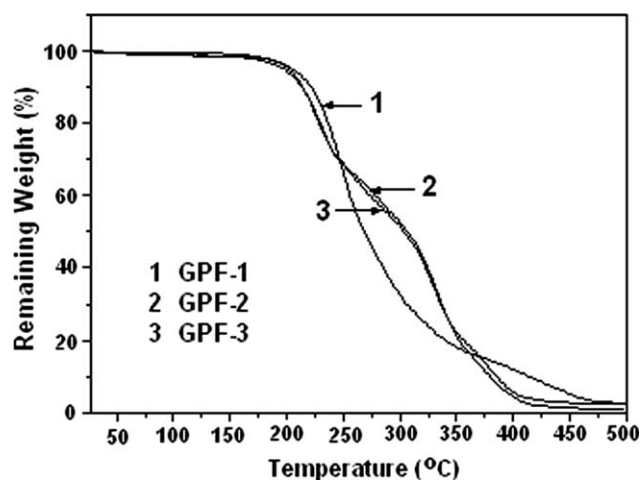


Figure 7 TG ($10^\circ\text{C}/\text{min}$) curves of GPF-1, 2, 3 under nitrogen.

Thermal degradation property

The thermal stabilities of the graft copolymers were studied by TGA from 25 to 500°C at a heating rate of $10^\circ\text{C}/\text{min}$ (Fig. 7). TGA shows that the onset decomposition temperatures of GPF-1, 2, 3 are in the range of 212 to 221°C . GPF-1, 2, 3 exhibited temperatures of 50% weight loss ranging from 250 to 310°C under nitrogen. The final weight losses of the fluorinated graft copolymers are nearly 97% at about 500°C .

Surface elemental characterization

The X-ray photoelectron spectroscopy (XPS) spectrum of the cotton fabric surface treated by GPF-1, 2, 3 was shown in Figure 8. In the XPS spectra, it is clear that the surface layer is mainly composed of C, F, O, and N. The peak for GPF-1 at about 688.71 eV ,

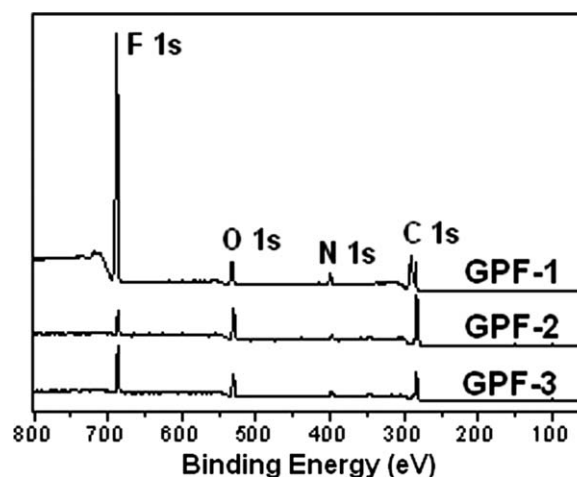


Figure 8 XPS spectra of cotton fabric surfaces treated by GPF-1, 2, 3.

TABLE III
Static CAs of GPF-1, 2, 3 Smooth Films/The Treated Fabrics for Different Wetting Liquids and The Surface Free Energy

Samples	CAs (°)								Surface free energy (mJ/m ²)
	Water		C14 ^a		C12 ^a		C10 ^a		
	S.F. ^b	T.F. ^b	S.F.	T.F.	S.F.	T.F.	S.F.	T.F.	
GPF-1	110	138	71	96	64	91	59	83	17.77
GPF-2	98	135	47	–	44	–	37	–	25.09
GPF-3	97	134	48	–	43	–	33	–	25.81

^a C14 = n-tetradecane; C12= n-dodecane; C10 = n-decane.

^b S.F.= smooth film; T.F.= treated fabric.

corresponding to F 1s, was stronger markedly than that of **GPF-2, 3**. The peaks at about 533.42 and 291.27 eV were assigned for O 1s and C 1s, respectively. The peak at about 399.97 eV which was assigned for N 1s also confirmed the existence of fluorinated hyperbranched polymer coating on the surface of the treated cotton fabric because there are only peaks corresponding to C and O for untreated cotton textile.²⁹ A preliminary quantitative analysis about the treated fabrics indicates that the atomic ratio of C/O/N/F for **GPF-1, 2, 3** was 10.3:1.9:1:13.5, 19.8:5.8:1:3.2, and 10.7:3.5:1:4.8, respectively. The F content of **GPF-1** was significantly higher than those of **GPF-2, 3** due to the longer perfluoroalkyl chain.

Low surface free energy properties of GPF-1, 2, 3

Fluorocarbons are famous and have many important applications for their particularly low surface free energy. The low surface energy property can be investigated and characterized through measuring of

liquid contact angles on a solid surface. The surface free energy properties on smooth cast films of **GPF-1, 2, 3** were examined by using a homologous series of n-alkanes (decane, dodecane, tetradecane) and water as wetting liquids. Corresponding contact angles and surface free energy (calculated by the method Wu³⁰) were summarized in Table III. The surface free energy of **GPF-1** (17.77 mJ/m²) which has the longest fluorocarbon chain is apparently lower than those of **GPF-2, 3** (25.09, 25.81 mJ/m², respectively). The cause may be the longer fluorocarbon chains can lay over the surface better and result in a lower surface free energy in the homologous fluorinated polyacrylate.

Surface morphology and wettabilities of the treated fabrics

The surface morphology and roughness were investigated by SEM. The typical top views of the smooth

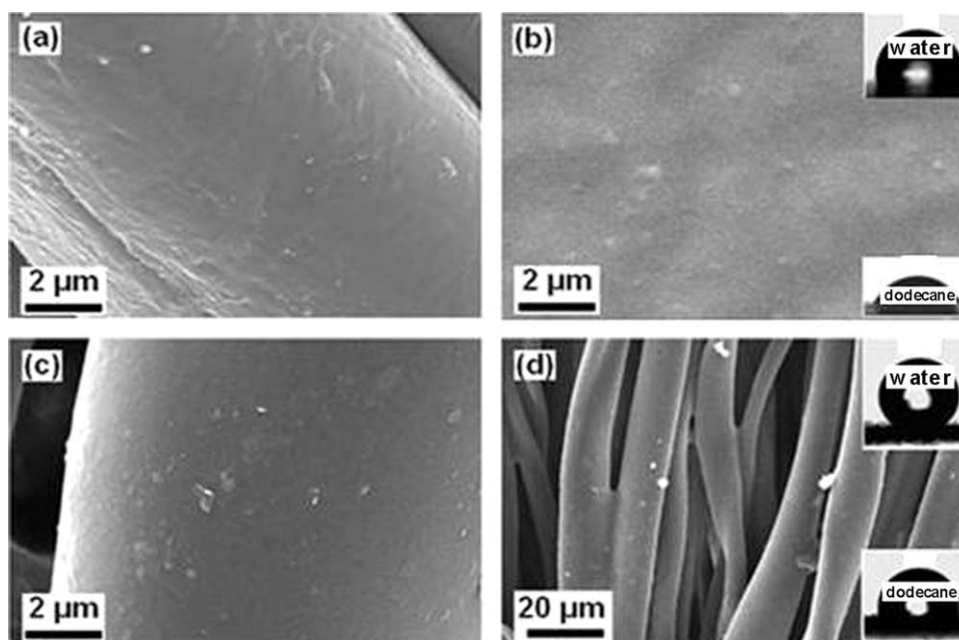


Figure 9 SEM images of (a) the native cotton fiber, (b) the GPF-1 smooth cast film, (c, d) the GPF-1 modified cotton fiber. Shown in the insets are the images of static droplets (4μL) on the smooth cast film and treated fabric.

TABLE IV
Wettabilities/Durability of the Treated and Untreated Cotton Fabrics

	GPF-1/GPF-1'		GPF-2/GPF-2'		GPF-3/GPF-3'		Untreated fabrics
	U.E. ^a	S.E. ^a	U.E. ^a	S.E. ^a	U.E. ^a	S.E. ^a	
C.A. ^{b(c)}	138/137	124/0	135/134	112/0	134/134	115/0	0
W.R.R. ^b	100/100	70/0	70/70	50/0	70/70	50/0	0
O.R.R. ^b	6/6	0/0	0/0	0/0	0/0	0/0	0

^a U.E. = Unextracted; S.E. = Soxhlet-extracted with THF for 48 h. (the fabrics treated by **GPF-1, 2, 3/GPF-1', 2', 3'**).

^b C.A. = Contact angle; W.R.R. = Water repellency rating; O.R.R. = Oil repellency rating.

cast film, untreated cotton fabric, and treated cotton fabric were shown in Figure 9. The native cotton fiber presented a comparatively smooth surface [Fig. 9(a)]. A coat of resin was observed on the treated microfibril surface [Fig. 9(c,d)], which was almost as smooth as the flat cast film of **GPF-1** [Fig. 9(b)]. The micro- and/or nanoscale rough structures which have been proven to be vital in generating superhydrophobic property did not increase markedly on the microfibril surface after finishing. So, we believe that the roughness of the treated fabric surfaces is mainly originated from the woven structure of the diameter 8–15 μm cotton fibers.

Water and oil repellent effects of the cotton fabrics treated with **GPF-1, 2, 3** were examined. The results were summarized in Table V. Fabrics treated by **GPF-1** showed excellent hydrophobic and oleophobic properties: the water and oil repellency ratings were 100 and 6, respectively. Fabrics treated with **GPF-2, 3** have hydrophobicity but water repellent ratings are relatively low and have no oil repellent property. These results reflected that the longer fluorocarbon chain ($\text{CF}_3(\text{CF}_2)_5-$) could cover the outermost layer of the treated fabrics more efficiently than the shorter fluorocarbon chains (CF_3CF_2- , CF_3CHF_2-) and resulted in a lower surface free energy in the homologous fluorinated polyacrylate. In addition, it also can be found that the increasing of surface roughness can enhance the liquid contact angle markedly. For example, when the wetting liquids were water, tetradecane, dodecane, and decane, the contact angles for **GPF-1** smooth cast films were 110, 71, 64, and 59°, respectively. However, the contact angles increased to 138, 96, 91, and 83°, respectively, for **GPF-1** (Table III) treated cotton fabrics due to the rough woven structure of textiles.

Durability studies

Traditional fluorinated finishing agents do not always show sufficient stability during the use because the coating materials were only attached on the top of the fabrics through physical adsorption or adhesion and no permanent chemical bonds were formed between the coatings and the textile substrate. Isocyanate groups blocked with MEKO in

GPF-1, 2, 3 were reactive through release of MEKO under heating and then reacted with hydroxyl groups of cellulose at the same time. As a result, **GPF-1, 2, 3** were permanently grafted to the cotton fabric surface by O—C covalent bonds as demonstrated in Figure 10. This was confirmed by the control experiments of the cotton fabrics treated by **GPF-1, 2, 3** and **GPF-1', 2', 3'** (analogous material without reactive ends, i.e., where the end isocyanate groups in **IP3** have been permanently blocked by quantitative reaction with ethanol.) as follows: (a) The treated cotton fabrics were subsequently Soxhlet-extracted with tetrahydrofuran (THF) for 48 h (**GPF-1, 2, 3** had a good solubility in THF). (b) Washing durability test according to the AATCC test method. The results are summarized in Tables IV and V. From Table IV, we can find that cotton fabrics treated with **GPF-1/1', 2/2', and 3/3'** almost presented the same water and oil repellency before Soxhlet-extraction. After being Soxhlet-extracted with THF, the water repellencies of the cotton fabrics treated with **GPF-1, 2, 3** decreased greatly and oil repellencies were lost completely. The contact angle and water repellent ratings changed from 138° and 100° to 124° and 70°, respectively, for the cotton fabric treated by **GPF-1**. However, the cotton fabrics treated with **GPF-1', 2', 3'** lost both the water and oil repellency entirely, which indicated that **GPF-1', 2', 3'** has been removed absolutely

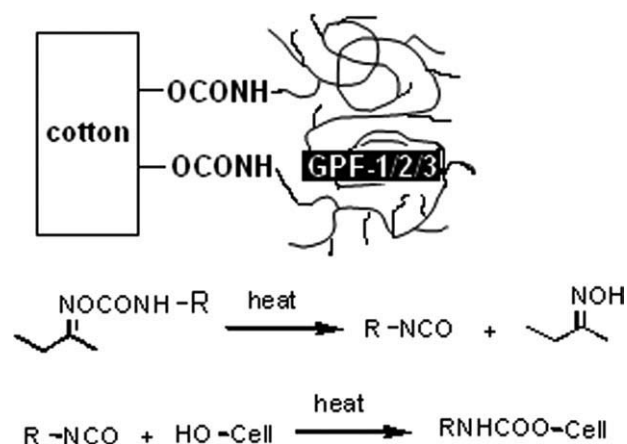


Figure 10 Schematic illustrations of **GPF-1/2/3** covalently grafted to the cotton fabric surfaces.

TABLE V
Wettabilities/Washing Durability of the Treated and Untreated Cotton Fabrics

	GPF-1/GPF-1'		GPF-2/GPF-2'		GPF-3/GPF-3'		Untreated fabrics
	1 ^a	10 ^a	1 ^a	10 ^a	1 ^a	10 ^a	
C.A. ^{b(c)}	138/137	135/0	135/134	132/0	134/134	132/0	0
W.R.R. ^b	100/100	90/0	70/70	70/0	70/70	70/0	0
O.R.R. ^b	6/6	5/0	0/0	0/0	0/0	0/0	0

^a Number of soaping cycles before testing (the fabrics treated by **GPF-1, 2, 3/GPF-1', 2', 3'**).

^b C.A. = Contact angle; W.R.R.= Water repellency rating; O.R.R.= Oil repellency rating.

from the treated cotton fabric surfaces and part of **GPF-1, 2, 3** have been covalently combined to the cotton fabric surfaces. The covalent bonds between **GPF-1, 2, 3** and the fabrics were also confirmed by washing durability test. As shown in Table V, the water and oil repellency of the cotton fabrics treated with **GPF-1, 2, 3** only descended slightly after 10 soaping cycles at 50°C. For example, the contact angle, water, and oil repellent ratings changed from 138°, 100° and 6° to 135°, 90°, and 5°, respectively, for the cotton fabric treated by **GPF-1**. However, the water and oil repellency of cotton fabrics treated with **GPF-1', 2', 3'** were lost completely after 10 soaping cycles at 50°C.

CONCLUSIONS

A series of novel multifunctional polyacrylate graft copolymer containing short fluoroalkyl chains and reactive groups (**GPF-1, 2, 3**) have been prepared and their surface wettabilities were also investigated. The cotton fabrics treated by **GPF-1** showed the best water and oil repellency and the water and oil repellency ratings were 100 and 6, respectively. The cotton fabrics treated by **GPF-2/3** exhibited relatively low water repellency and had no oil repellency, which indicated that fluorocarbon chains (CF₃CF₂—, CF₃CHF₂—) were too short to induce oil repellency. Cotton fabrics treated by **GPF-1, 2, 3** presented very good washing durability due to the covalent bonding between the coating and substrate which was confirmed by control experiments.

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