Synthesis of a Novel Perfluorooctylated Polyacrylate and Its Application on Cotton Fabrics

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ABSTRACT: A perfluorooctylated acrylate monomer (FAC) containing a urethane linkage was synthesized, and fluorinated polymers [perfluorooctylated polyacrylate (PFAC)] were obtained from the copolymerization of FAC with other acrylate monomers by emulsion polymerization. The size of the emulsion particles was about 40–60 nm. PFAC was applied to cotton fabrics by a pad–dry–cure process. The treated fabrics that were dried at 100°C after being washed showed good water and oil repellency: the water repellency rating and the oil repellency rating were 100 and 5, respectively. Those dried at room temperature also showed water and oil repellency: the water repellency rating was 70 and the oil repellency rating was 3. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 222–226, 2005

Key words: copolymerization; monomers; TEM

INTRODUCTION

Fluorocarbons have an extremely low surface free energy. Fluorinated coatings are the most important class of water- and oil-repellent finishes for textiles because of their ability to provide optimum performance in terms of both water and oil repellency without impairing the permeability of textiles to air or modifying the hand of the fabric.[1,2] However, conventional fluorocarbon finishing agents have a great shortcoming; that is, fabrics finished by fluorocarbon agents must be dried at a high temperature after being washed, or else the water or oil repellency will be lost.

To provide optimum water and oil repellency, the pendant perfluorinated alkyl groups should be long chains and should be permanently aligned parallel to adjacent pendant groups; thus, a coated substrate will present a surface protected by an array of pendant perfluoroalkyl groups to maximize water and oil repellency. It has been discovered that pendant perfluoroalkyl groups can be modified by the presence of urethane groups.[3,4] The affinity of urethane groups can keep the entire pendant chain substantially in a fixed alignment. In this study, a perfluorooctylated acrylate monomer (FAC) containing a urethane linkage was synthesized, and the fluorinated polymers were obtained from the copolymerization of FAC with other acrylate monomers by emulsion polymerization. They were applied to cotton fabrics, and the water and oil repellency were examined.

EXPERIMENTAL

Materials

1-Iodoperfluorooctane, allyl alcohol, azobisisobutyronitrile (AIBN), tri-*n*-butyl tin hydride, thionyl chloride, chromium (VI) oxide, dibutyltin dilaurate (DBTDL), sulfuric acid, ammonium persulfate, Tx-10 (nonionic surfactant), toluene, sodium azide, sodium lauryl sulfate (SLS), and 2-hydroxylethyl acrylate were used as purchased. Octadecyl acrylate was synthesized according to the literature,[5] and Jones reagent was prepared according to the literature.[6]

Characterization

^{1}H-NMR spectra were recorded on a Bruker AV 400 (400-MHz) spectrometer (Bruker, Faellanden, Switzerland) with Me_4Si as an internal standard. ^{19}F-NMR spectra were obtained on a Bruker AV400 (376 MHz) spectrometer with $CFCl_3$ as an external standard, the downfield shifts being designated as positive. All chemical shifts (δ) are expressed in parts per million, and the coupling constants (J) are in hertz; the following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. The size of the emulsion particles was recorded on a JEOL 200CX electron microscope

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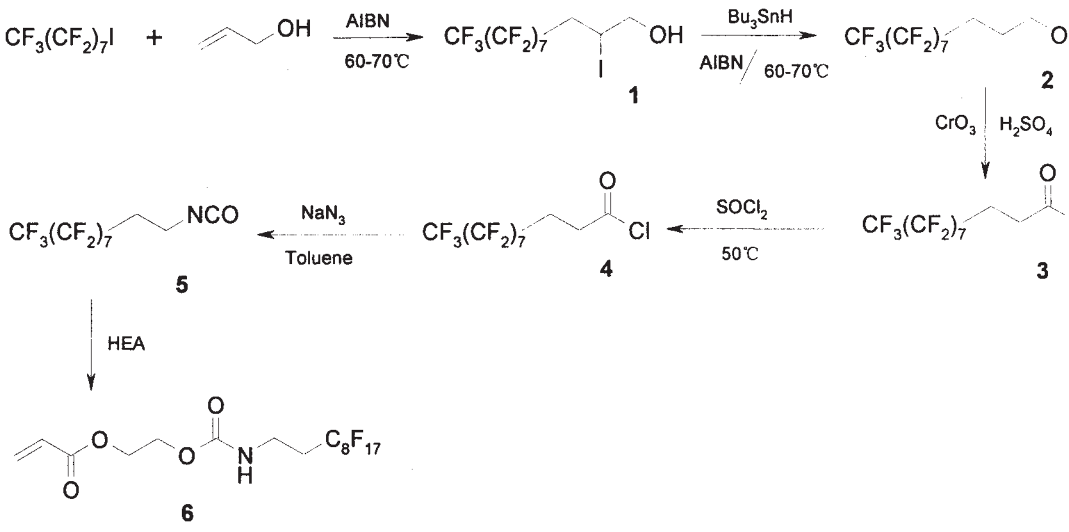


Scheme 1

(JEOL, Tokyo, Japan), and the accelerating voltage of the electron beam was 100 kV. A transmission electron microscopy (TEM) image of the sample was obtained as follows. A 1.0% (w/w) sample emulsion was placed on a Formvar film-coated TEM grid and dried at room temperature. The molecular weight of the sample was recorded on a Waters 105C gel permeation chromatograph (Waters Corp., Milford, MA) with tetrahydrofuran (THF) as the mobile phase. Mass spectra were recorded on a Finnigan MAT-8430 instrument (Finnigan Co., Waltham, MA) with electron-impact ionization at 70 eV. IR spectra were recorded on a Shimadzu IR-440 spectrometer (Shimadzu, Kyoto, Japan).

Synthesis of the monomers

The synthesis of FAC was carried out as shown in Scheme 1.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecan-1-ol (**2**)[7]

Allyl alcohol (3.73 g, 64.2 mmol) was added dropwise to a mixture of perfluorooctyl iodide (27.1 g, 49.7 mmol) and AIBN (0.166 g, 1.01 mmol) at 95°C. The reaction mixture was stirred for 24 h at 95°C. Then, the excessive allyl alcohol was removed *in vacuo*. The purification of the yellowish residue by column chromatography on silica gel (petroleum ether/ethyl acetate = 10 : 1) gave compound **1** (22.5 g, 75% yield) as a white solid.

Tributyl tin hydride (10.6 g, 36.5 mmol) was added dropwise to a mixture of **1** (22.0 g, 36.5 mmol) and AIBN (0.041 g, 0.24 mmol) at 100°C for 4 h under a nitrogen atmosphere. The reaction mixture was stirred at 80°C for 24 h. Phase separation occurred. The lower liquid phase was collected and purified on silica gel (petroleum ether/ethyl acetate = 10 : 3) to afford compound **2** as a white solid (12.2 g, 70% yield).

^{1}H-NMR (400 MHz, CDCl$_3$, δ): 3.70 (t, J = 6.0 Hz, 2H), 2.20 (m, 2H), 1.88 (m, 2H), 1.50 (s, 1H). ^{19}F-NMR (376 MHz, CDCl$_3$, δ): −80.72 (t, J = 9.9 Hz, 3F), −114.24 (m, 2F), −121.66 to −121.87 (m, 6F), −122.65 (s, 2F), −123.46 (s, 2F), −126.06 (s, 2F).

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanoic acid (**3**)[8]

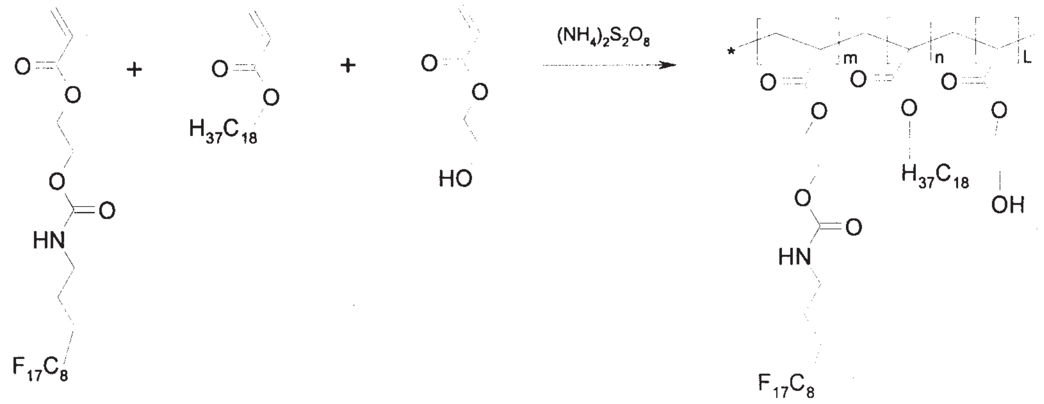
Alcohol **2** (8.10 g,16.9 mmol) was dissolved in a mixture solution of ether (25 mL) and acetone (25 mL); then, a solution of Jones reagent was added slowly at 0–5°C, and the reaction was followed by thin-layer chromatography. The purification of the residue by column chromatography on silica gel (petroleum ether/ethyl acetate = 2 : 1) gave compound **3** (7.9 g, 95% yield) as a white solid.

^{1}H-NMR (400 MHz, dimethyl sulfoxide-d_6, δ): 2.20–2.51 (m, 4H), 12.50 (s, 1H). ^{19}F-NMR (376 MHz, CDCl$_3$, δ): −80.75 (t, J = 9.9 Hz, 3F), −114.43 (m, 2F), −121.90 to −121.94 (m, 6F), −122.69 (s, 2F), −123.46 (s, 2F), −126.08 (s, 2F).

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanoyl chloride (**4**)

To a 100-mL, two-necked flask with a dropping funnel and a reflux condenser connected at the top to a gas absorption trap, acid **3** (7.9 g, 16 mmol) and thionyl chloride (3.0 g, 24 mmol) were added. The reaction mixture was stirred for 3 h at 50°C. Acyl chloride **4** was obtained by distillation, and the fraction at 125–126°C and 60 mmHg was collected (7.35 g, 90% yield).

^{1}H-NMR (400 MHz, CDCl$_3$, δ): 2.45–2.71 (m, 2H), 3.22–3.26 (m, 2H). ^{19}F-NMR (376 MHz, CDCl$_3$, δ):



Scheme 2

−80.75 (t, *J* = 9.9 Hz, 3F), −114.43 (m, 2F), −121.90 to −121.94 (m, 6F), −122.69 (s, 2F), −123.46 (s, 2F), −126.08 (s, 2F).

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-isocyanato-decane (**5**)[9]

Under a nitrogen atmosphere, sodium azide (13 g, 20 mmol) and anhydrous toluene (20 mL) were added to a 100-mL, three-necked flask with a dropping funnel and a reflux condenser. A solution of compound **4** (7.7 g, 15 mmol) in 20 mL of anhydrous toluene was added slowly. The reaction mixture was stirred for 6 h at 60°C. The crude isocyanate **5** was collected as a fraction at 117–120°C and 40 mmHg (4.93 g, 70% yield)

^{1}H-NMR (400 MHz, CDCl$_3$, δ): 2.37–2.49 (m, 2H), 3.67–3.70 (m, 2H). ^{19}F-NMR (376 MHz, CDCl$_3$, δ): −80.75 (t, *J* = 9.9 Hz, 3F), −114.40 (m, 2F), −121.91 to −121.94 (m, 6F), −122.68 (s, 2F), −123.44 (s, 2F), −126.07 (s, 2F).

Acrylic acid 2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylcarbmoyloxy)-ethyl ester (**6**; fac)

Compound **5** (7.3 g, 15 mmol) was charged into a 100-mL, three-necked, round-bottom flask, and then 20 mL of anhydrous THF was added with two drops of DBTDL. A solution of 2-hydroxylethyl acrylate (2.2 g, 20 mmol) in anhydrous THF (10 mL) was added slowly. The reaction mixture was refluxed under nitrogen with magnetic stirring for 3 h. The solution was poured into distilled water (100 mL) with stirring in a beaker. The white precipitate (5.18 g, 85% yield) was filtered and vacuum-dried overnight at room temperature.

^{1}H-NMR (400 MHz, CDCl$_3$, δ): 6.44 (d, 1H, $^{3}J_{\mathrm{HH}}$ = 17.2 Hz), 6.14 [dd, 1H, $^{3}J_{\mathrm{HH}}$ = 17.2 Hz (trans), $^{3}J_{\mathrm{HH}}$ = 10.4 Hz (cis)], 5.86 (d, 1H, $^{3}J_{\mathrm{HH}}$ = 10.4 Hz), 5.01 (s, 1H), 4.34 (m,4H), 3.54 (m, 1H), 2.36 (m,2H). ^{19}F-NMR (376 MHz, CDCl$_3$, δ): −80.1 (s, 3F), −112.1 (s, 2F), −121.3 (m, 6F), −122.2 (s, 2F), −122.9 (s, 2F), −125.5 (s, 2F). IR (υ_{max}, cm^{-1}, KBr): 3324, 3070, 2361, 1719, 1685, 1285. Electron-impact mass spectrometry (70 eV) *m*/*z*: 605 (M^{+}, 0.12), 55 (100), 99 (68.27), 44 (25.08), 56 (17.53), 73 (14.90), 69 (11.42). ANAL. Calcd for $C_{16}H_{12}F_{17}NO_4$: C, 31.78%; H, 1.998%; N, 2.31%. Found: C, 31.85%; H, 2.13%; N, 2.23%.

Synthesis of perfluorooctylated polyacrylate (PFAC)

The synthesis of PFAC is outlined in Scheme 2. Under a nitrogen atmosphere, a mixture of distilled water (35 mL), Tx-10 (Tx-10/monomers = 0.02 w/w), and SLS (SLS/monomers = 0.01 w/w) was charged into a 100-mL, three-necked flask and was stirred for 0.5 h at 50°C; then, the temperature was raised to 60°C, and a 10-mL acetone solution of FAC **6** (78 wt %), octadecyl acrylate (16 wt %), and 2-hydroxylethyl acrylate (6 wt %) was added slowly within 0.5 h. The reaction mixture was stirred at 70°C for 14 h to give PFAC.

Fabric and treatment

The desized, scoured, bleached, and mercerized plain-weave 40 × 40 cotton weighed 108.6 g/cm^2.

Fabric samples were first immersed in an aqueous solution containing PFAC and the crosslinking agent Ciba Hydrophobol XAN (Ciba, Ltd., Basel, Switzerland); they were then padded through two dips and two nips to reach a wet pickup of 95–100%. The samples were dried at 80°C for 3 min and cured at 150°C for 3 min.

Test method

The water and oil repellency of the finished fabrics was measured according to AATCC test methods 22-2001 and 118-2002, respectively.[10] The samples were

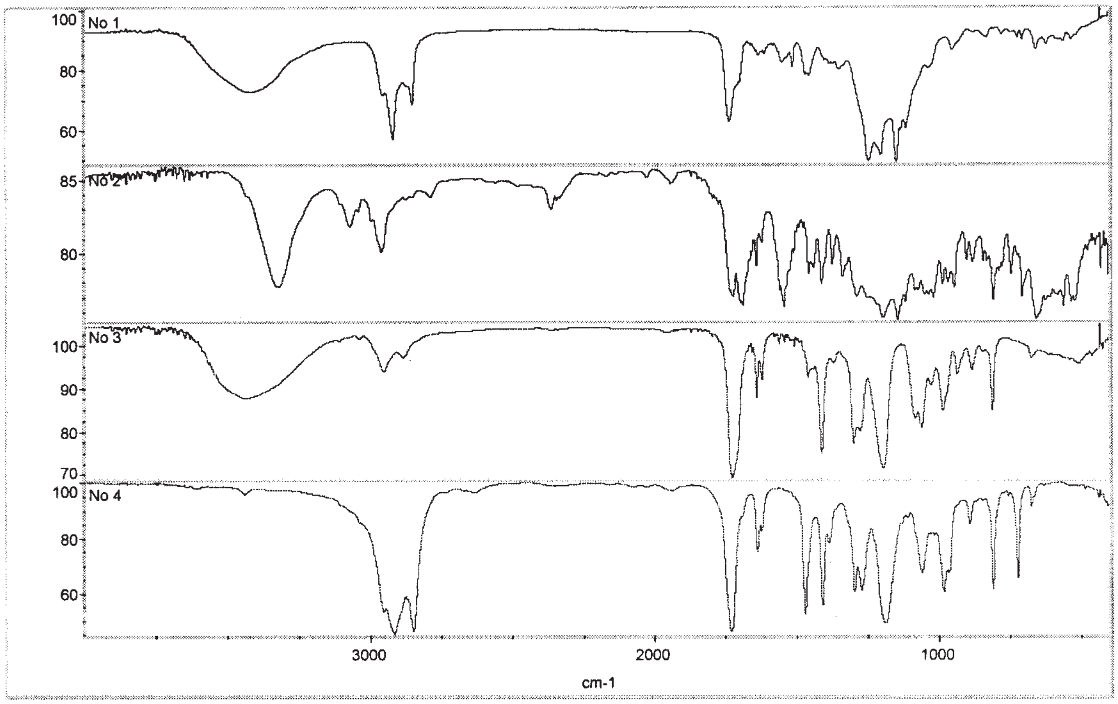


Figure 1 FTIR spectra of samples 1–4.

conditioned for 24 ± 4 h at 65 ± 2% relative humidity and 21 ± 1°C before the measurements.

RESULTS AND DISCUSSION

Characterization of PFAC

The synthesis of PFAC was confirmed by Fourier transform infrared (FTIR) analysis. The results are shown in Figure 1. Samples 1–4 showed IR spectra of PFAC, FAC, 2-hydroxylethyl acrylate, and octadecyl acrylate. In spectrum 1, there are characteristic absorptions of O—H stretch (3424 cm^{-1}), C═O (1735 cm^{-1}), aliphatic C—H stretch (2850–2920 cm^{-1}), and C—F stretch (1204 and 1245 cm^{-1}). The disappearance of the characteristic absorption of C═C (1630 cm^{-1}) indicates that all the acrylate monomers completed the transformation to the polymer.

An emulsifying agent is very important to emulsion polymerization because it affects the stability, particles size, and mechanical properties of the polymers. The specific gravity of perfluorooctyl-containing monomers is heavier than that of other acrylate monomers, and the solubility is lower, so it is difficult to choose the emulsifying agent. In this study, Tx-10 and SLS were chosen as a dual emulsion agent. Tx-10 is a nonionic surfactant, and its stability to electrolytes is very good; SLS is an anionic surfactant, and its stability to electrolytes is not very good, but its emulsifying ability is very good. To improve the solubility of the perfluorooctyl-containing monomers, acetone was used. Figure 2 presents a TEM photograph of emulsion particles, and the sizes were about 40–60 nm. The molecular weights of PFAC were measured by gel permeation chromatography (number-average molecular weight = 22,000, weight-average molecular weight = 28,765).

Finishing of cotton fabrics with PFAC

PFAC was applied to cotton fabrics by a pad–dry–cure process, and the results are shown in Table I. To

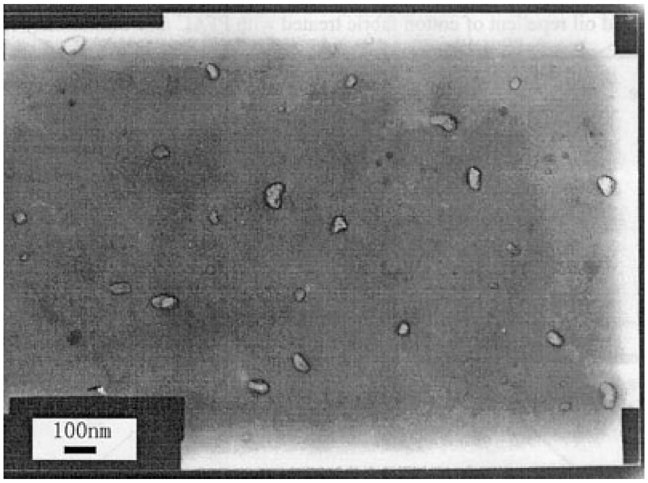


Figure 2 TEM photograph of the emulsion particles.

TABLE I
Water and Oil Repellency of Cotton Fabric Treated with PFAC and Ciba Olephobol C

Sample	Concentration (g/L)	Crosslinking agent (g/L)	Water repellency rating		Oil repellency rating	
			A[a]	B[b]	A[a]	B[b]
Untreated	—	—	0	0	0	0
PFAC	60	10	100	70	5	3
Ciba Olephobol C	60	10	100	70	6	0

[a] Sample was dried at 100°C for 2 min.
[b] Sample was air-dried at room temperature for 24 h.

examine the water and oil repellency of the fabrics finished by PFAC, Ciba Olephobol C, a commonly used water- and oil-repellent agent, was chosen for comparison with PFAC; the results are also shown in Table I. The water and oil repellency ratings of the cotton fabrics finished with PFAC were 100 and 5, respectively, when they were dried at 100°C after washing, and for those finished with Ciba Olephobol C, the ratings were 100 and 6. This indicated that the water and oil repellency of PFAC was comparable to that of Ciba Olephobol C. The reason was probably that the perfluorooctyl group ($\text{—}C_8F_{17}$) was introduced into PFAC. The perfluoroalkyl compounds have extremely low surface free energies, and they are able to lower remarkably the critical surface tension of treated surfaces.

In addition, the results showed that the water and oil repellency ratings of the cotton fabrics finished with PFAC were 70 and 3, respectively, when the treated fabrics were dried at room temperature. However, the water and oil repellency rating of the cotton fabrics finished with Ciba Olephobol C were 70 and 0, respectively. The reason was probably that the introduction of a urethane linkage made the pefluorooctyl group vertical on the surface of the cotton fabrics and arrays closely in the air atmosphere at all times, whether the temperature was high or low.

CONCLUSIONS

In this study, FAC containing a urethane linkage was synthesized successfully, and the fluorinated polymers (PFAC) were obtained from the copolymerization of FAC with other acrylate monomers by emulsion polymerization. Tx-10 and SLS were chosen as the complex emulsion agent, and the size of the emulsion particles was about 40–60 nm. PFAC was applied to cotton fabrics by a pad–dry–cure process. The treated fabrics that were dried at 100°C after being washed showed good water and oil repellency: the water repellency rating and the oil repellency rating were 100 and 5, respectively. Those dried at room temperature also showed water and oil repellency: the water repellency rating was 70, and the oil repellency rating was 3.

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