

Water and Oil Repellency of Polysiloxanes with Highly Fluorinated Alkyl Side Chains

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ABSTRACT: A series of fluorinated polysiloxanes (FLSs) with the 3,3,4,4,5,5,6,6,6-nonafluorohexyl group ($C_4F_9C_2H_4-$), 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl group ($C_8F_{17}C_3H_6-$), 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononanamido) propyl group [HDFNAG; $C_8F_{17}(C=O)NHC_3H_6-$], and 3-(*N*-methyl-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononanamido) propyl group [$C_8F_{17}(C=O)N(CH_3)C_3H_6-$] were synthesized. Their homopolymers (homo-FLSs) and copolymers with dimethylsiloxane (co-FLSs) were included. The polyester fabrics were treated with these FLSs, and their water and oil repellency was evaluated. These fabrics showed a moderate to good level of water repellency but a poor to zero level of oil repellency, except for those fabrics treated with homo-FLSs with HDFNAG. The characterization of the surface chemical composition by X-ray photoelectron spectroscopy showed

that the concentration of fluorine at the surface was not particularly high for poly(ethylene terephthalate) films treated with homo-FLSs with HDFNAG. Differential scanning calorimetry measurements of these FLSs revealed that only homo-FLSs with HDFNAG had a high melting temperature of 75.7°C. These two measurements suggested that the reason the fabrics treated with homo-FLSs with HDFNAG showed good oil repellency was not because the concentration of fluorine at the surface was much higher than for the others but because the reorientation of HDFNAG did not take place for its packing after contact with oil. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1085–1091, 2003

Key words: polysiloxanes; crystallization; differential scanning calorimetry (DSC); X-ray

INTRODUCTION

Many fabrics have been commercially treated with water- and oil-repellent agents such as fluorochemical finishes. These fluorochemical finishes are often fluorinated polymers, including esters or amides of poly(acrylic acid)s.¹ Although these products impart to fabrics good resistance to water and oil, the fabrics treated with them are often stiff to the touch. Therefore, there has been a need to provide a fabric finish that provides water and oil repellency and is not stiff.

The use of polysiloxanes as water-repellent agents has found ever increasing acceptance in the textile industry in the last few years.² Compared with fluorochemical finishes, polysiloxanes are better in that they have a very considerable softening and smoothing effect on textiles. Having an improved fuel- and oil-resistant nature, polysiloxanes with 3,3,3-trifluoropropyl groups have also been proposed³ and are commercially available. However, they have found few applications in the textile industry, for which high oil repellency is required. This has been attributed to their low fluorine content. Moreover, fluorinated polysilox-

anes (FLSs) with the 3,3,4,4,5,5,6,6,6-nonafluorohexyl group (NFHG) have been studied from the viewpoint of surface tension,⁴ but their practical water and oil repellency has not been studied.

Recently, we reported a synthetic method for polysiloxanes with highly fluorinated alkyl side chains (Rf group; $C_nF_{2n+1}-$).⁵ We were able to develop a new class of water- and oil-repellent finishes by introducing long fluorinated alkyl side chains to the polysiloxane backbone.

In this article, we report the water and oil repellency of polysiloxanes with highly fluorinated alkyl side chains and the factor that determines their oil repellency.

EXPERIMENTAL

Materials

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-decene ($C_8F_{17}CH=CH_2$) and AK-225 [a mixture of $CF_3CF_2CHCl_2$ (HCFC-225ca) and $CClF_2CF_2CHClF$ (HCFC-225cb)] were used as obtained from Asahi Glass Co., Ltd. (Tokyo, Japan) 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoro-1-undecene ($C_8F_{17}CH_2CH=CH_2$) was prepared from $C_8F_{17}CH=CH_2$ by the reported procedures.⁶ 1,3,5-Tris(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-1,3,5-

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trimethylcyclotrisiloxane (C_4F_9 -D3) was synthesized as reported,⁷ except that cesium hydroxide was used instead of potassium hydroxide for the alkaline catalyst of the cracking process. Ethyl 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononanoate [$C_8F_{17}(C=O)OCH_2CH_3$] was purchased from AZmax Co., Ltd. (Chiba, Japan). The copolymer, consisting of poly(hydromethylsiloxane) and poly(dimethylsiloxane) segments with trimethylsiloxy end groups {[—OSi(H)CH₃—]₈[—OSi(CH₃)₂—]₁₈; **1**}, and the homopolymer consisting of poly(hydromethylsiloxane) with trimethylsiloxy end groups {[—OSi(H)CH₃—]₂₅; **2**}, were also purchased from AZmax and used as delivered. Hexamethyldisiloxane (MM) was purchased from Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan), and used as delivered. Allylamine was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan), and used as delivered. *N*-Methylallylamine was purchased from Sigma-Aldrich (St. Louis, MO) and used as delivered. A platinum catalyst, a 3% toluene solution of a platinum complex with 1,3-divinyl-1,1,3,3-tetramethyldisiloxane [Pt(DVTMDS)], was purchased from Degussa Japan Co., Ltd. (Tokyo, Japan). Activated carbon (FY-2) was purchased from Cataler Corp. (Shizuoka, Japan). The other chemicals and solvents were purchased as reagent-grade materials.

Synthesis

***N*-2-propenyl-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononanamide**
 $[C_8F_{17}(C=O)NHCH_2CH=CH_2]$ or ***N*-methyl-*N*-2-propenyl-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononanamide**
 $[C_8F_{17}(C=O)N(CH_3)CH_2CH=CH_2]$

To an ice-cooled solution of 40 g (813 mmol) of ethyl 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononanoate in 100 mL of diether was added dropwise 894 mmol of allylamine or *N*-methylallylamine. After the completion of the addition, the reaction mixture was allowed to warm to room temperature, and the solvent and excess amine were separated by distillation under reduced pressure and with moderate warming. The residue was distilled to give the title compound.

$C_8F_{17}(C=O)NHCH_2CH=CH_2$. Yield: 98.6%. bp: 86°C (2 mmHg). mp: 60.2–60.4°C. IR: 3330, 2914, 1698, 1645, 1547, 1201, 1146 cm^{-1} . ¹H-NMR ($CDCl_3$, δ): 3.92–4.07 (NCH₂, 2H), 5.16–5.33 (=CH₂, 2H), 5.73–5.92 (CH=CH₂, 1H), 6.36–6.74 (NH, 1H). ¹⁹F-NMR ($CDCl_3$, δ): –80.8 (CF₃, 3F), –119.8 (CF₂CH₂, 2F), –121.7 (6F), –122.5 (4F), –126.0 (CF₃CF₂, 2F).

$C_8F_{17}(C=O)N(CH_3)CH_2CH=CH_2$. Yield: 95.3%. bp: 75–77°C (2 mmHg). IR: 1691, 1412, 1243, 1211, 1151 cm^{-1} . ¹H-NMR ($CDCl_3$, δ): 3.02, 3.11–3.16 (NCH₃, 3H), 4.03–4.10 (NCH₂, 2H), 5.19–5.34 (=CH₂, 2H), 5.69–5.85 (CH=CH₂, 1H). ¹⁹F-NMR ($CDCl_3$, δ): –80.8 (CF₃, 3F), –111.1 (CF₂CH₂, 2F), –120.3 (2F), –120.7 (2F), –121.7 (4F), –122.6 (2F), –125.9 (CF₃CF₂, 2F).

Homo-FLS with NFHG

A 500-mL, three-necked flask equipped with a stirrer and a thermometer was sufficiently filled with nitrogen and was charged with C_4F_9 -D3 (50 g) and MM (1.1 g). After the temperature was raised to 50°C, trifluoromethanesulfonic acid (0.05 g) was added. Five hours later, the extinction of C_4F_9 -D3 was confirmed by gas chromatography, and sodium bicarbonate (0.6 g) was introduced to terminate the reaction. After 1 h of stirring, filtration was carried out at a pressure of 1 kgf/cm² to obtain a transparent oil. The stripping of the volatile siloxanes was done at 180°C under reduced pressure at 3 mmHg for 2 h.

IR (neat): 1354, 1220, 1134, 1073, 881, 844, 809, 735 cm^{-1} . ¹H-NMR [$CDCl_3$ /1,1,2-trichloro-1,2,2-trifluoroethane (R-113), δ]: 0.12–0.32 (18H + 3H \times *n*, SiCH₃), 0.77–0.97 (2H \times *n*, SiCH₂), 2.00–2.24 (2H \times *n*, CH₂CF₂). ¹⁹F-NMR ($CDCl_3$ /R-113, δ): –80.6 to –81.4 (CF₃, 3F \times *n*), –115.6 to –116.3 (CF₂CH₂, 2F \times *n*), –123.2 to –124.0 (CF₂CF₂CF₂, 2F \times *n*), –125.1 to –125.9 (CF₃CF₂, 2F \times *n*).

n is the number-average degree of polymerization.

Homo-FLS or co-FLS with the 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl group (HDFUG)

Poly(hydromethylsiloxane) (**1** or **2**) was charged into a flask equipped with a stirrer, a dropping funnel, and a thermometer and heated to 90°C under a nitrogen blanket. A mixture of fluorinated olefins with the 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-heptadecafluoroundecyl group [$C_8F_{17}CH_2CH=CH_2$, 1.05 molar equiv to H—Si, and Pt(DVTMDS), 5 ppm Pt based on the total reagent weight] was added with the dropping funnel, with the temperature kept below 100°C. After 4 h of stirring at 90°C, an IR analysis revealed the disappearance of the peak based on H—Si. After the mixture was cooled to room temperature, the activated carbon (0.1 wt % based on the total reagent weight) was added, and the reaction mixture was stirred at room temperature for 1 h, this being followed by filtration through a 1.0- μ m-porosity PTFE filter pad. The stripping was performed at 180°C under reduced pressure at 3 mmHg for 1 h to give the title product. Homo-FLS or co-FLS with the 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononanamido) propyl group (HDFNAG) or the 3-(*N*-methyl-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononanamido) propyl group (NMHDFNAG) was prepared with the same procedure except that tetrahydrofuran (weight equivalent to the fluorinated olefin) was used as a solvent.

Homo-FLS with HDFUG. IR (neat): 1242, 1207, 1097, 1023, 804 cm^{-1} . ¹H-NMR ($CDCl_3$ /R-113, δ): 0.12–0.33 (18H + 3H \times *n*, SiCH₃), 0.61–0.79 (2H \times *n*, SiCH₂), 1.67–1.86 (2H \times *n*, SiCH₂CH₂), 2.01–2.26 (2H \times *n*,

CH_2CF_2). ^{19}F -NMR ($\text{CDCl}_3/\text{R-113}$, δ): -80.8 to -81.7 (CF_3 , $3\text{F} \times n$), -114.2 to -115.1 (CF_2CH_2 , $2\text{F} \times n$), -121.1 to -122.2 ($6\text{F} \times n$), -122.4 to -123.0 ($2\text{F} \times n$), -123.2 to -123.8 ($2\text{F} \times n$), -125.8 to -126.5 (CF_3CF_2 , $2\text{F} \times n$).

Homo-FLS with HDFNAG. IR (KBr pellets): 3315, 1712, 1545, 1201, 1071 cm^{-1} . ^1H -NMR ($\text{CDCl}_3/\text{R-113}$, δ): -0.02 – 0.33 ($18\text{H} + 3\text{H} \times n$, SiCH_3), 0.47 – 0.79 ($2\text{H} \times n$, SiCH_2), 1.58 – 1.86 ($2\text{H} \times n$, SiCH_2CH_2), 3.21 – 3.59 ($2\text{H} \times n$, $\text{CH}_2\text{NH}(\text{C}=\text{O})$), 8.27 – 8.98 ($1\text{H} \times n$, NH). ^{19}F -NMR ($\text{CDCl}_3/\text{R-113}$, δ): -80.6 to -81.7 (CF_3 , $3\text{F} \times n$), -119.5 to -120.6 (CF_2CH_2 , $2\text{F} \times n$), -121.3 to -123.8 ($10\text{F} \times n$), -125.7 to -127.1 (CF_3CF_2 , $2\text{F} \times n$).

Homo-FLS with NMHDFNAG. IR (KBr pellets): 1690, 1212, 1151, 805 cm^{-1} . ^1H -NMR ($\text{CDCl}_3/\text{R-113}$, δ): -0.03 – 0.38 ($18\text{H} + 3\text{H} \times n$, SiCH_3), 0.48 – 0.75 ($2\text{H} \times n$, SiCH_2), 1.60 – 1.89 ($2\text{H} \times n$, SiCH_2CH_2), 2.94 – 3.34 ($3\text{H} \times n$, NCH_3), 3.36 – 3.62 [$2\text{H} \times n$, $\text{CH}_2\text{N}(\text{CH}_3)(\text{C}=\text{O})$]. ^{19}F -NMR ($\text{CDCl}_3/\text{R-113}$, δ): -80.6 to -81.6 (CF_3 , $3\text{F} \times n$), -109.6 to -111.4 (CF_2CH_2 , $2\text{F} \times n$), -119.4 to -120.8 ($4\text{F} \times n$), -120.9 to -121.9 ($4\text{F} \times n$), -121.9 to -122.7 ($2\text{F} \times n$), -125.4 to -126.3 (CF_3CF_2 , $2\text{F} \times n$).

Measurements

^1H -NMR spectra were recorded on a JEOL JNM-AL300 instrument (Tokyo, Japan) with CDCl_3 or mixtures of CDCl_3 and R-113 as a solvent with the solvent peak as a reference (CDCl_3). ^{19}F -NMR spectra were also recorded on a JEOL JNM-AL300 with CDCl_3 or mixtures of CDCl_3 and R-113 as a solvent and with CFCl_3 as an internal reference. IR spectra were obtained on a Nicolet IR Impact 410 spectrometer (Madison, WI). Gas chromatography analyses were performed on a Shimadzu GC-15A (Kyoto, Japan) equipped with a thermal conductivity detector (TCD). Gel permeation chromatography (GPC) was carried out in 1,3-dichloro-1,1,2,2,3-pentafluoropropane/hexafluoroisopropanol (1 vol %) on a Tosoh HLC-8020 chromatograph (Tokyo, Japan) equipped with two polystyrene gel columns (PLgel mixed-C columns) and a refractive-index detector. The molecular weights of the polymers were calibrated with perfluoropolyether standards. The melting point was determined on a Buchi 530 model (Buchi Laboratoriums Technik AG,

Flawil, Switzerland). Differential scanning calorimetry (DSC) data were obtained with a MACScience DSC 3100 (Yokohama, Japan). A heating rate of $10^\circ\text{C}/\text{min}$ was used for a sample of 15 mg. Before the DSC measurements, the samples were preheated up to 200°C to eliminate the effect of the thermal history. Subsequently, they were cooled to -100°C and measured from -100 to 120°C . X-ray photoelectron spectroscopy (XPS) was performed on a PHI Quantum 2000 (ULVAC-PHI, Inc., Yokohama, Japan) with an Al $\text{K}\alpha$ X-ray source. Spectra were recorded at 45° takeoff angles. The analyzer chamber pressure was 10^{-6} to 10^{-7} Pa.

Treatment of polyester fabrics by FLSs

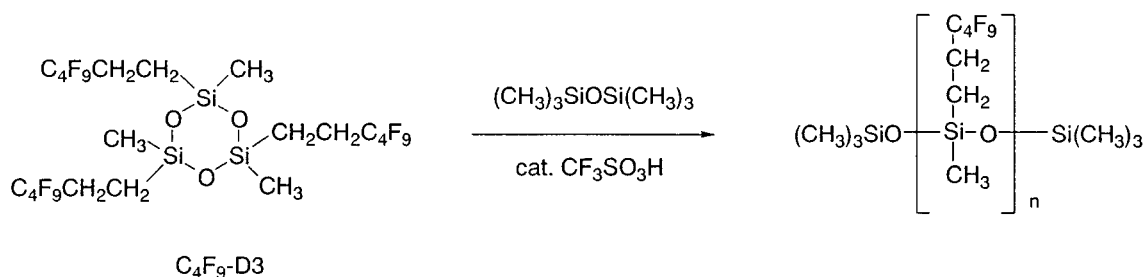
An FLS (1g) was dissolved in 100 g of AK-225. The pad bath mixture was charged into a V-shaped metal dipping trough, and a polyester fabric swatch was immersed completely in the trough, removed, and wrung through a roll press operating at $3 \text{ kgf}/\text{cm}^2$. The treated fabric was immediately dried at room temperature.

Evaluation of the water and oil repellency

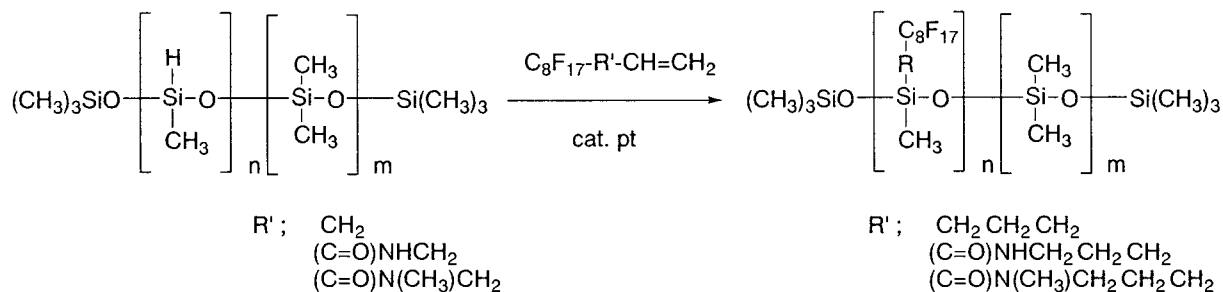
The water and oil repellency of the textile fabrics treated with FLSs was evaluated according to the technical manual of the American Association of Textile Chemists and Colorists (AATCC Test Method 22-1996 for water repellency and AATCC Test Method 118-1997 for oil repellency). The water-repellency grade was given over a range of 0–100, and the oil-repellency grade over a range of 0–8.

Preparation of the thin polymer coatings

By the dipping method, a poly(ethylene terephthalate) (PET) film (Mitsubishi Polyester Film Corp., Tokyo, Japan, O301-E188-U42, $20 \text{ mm} \times 100 \text{ mm} \times 0.188 \text{ mm}$) was coated with an FLS dissolved in AK-225 (concentration = 1 wt %). The dipping speed was $0.5 \text{ mm}/\text{s}$.



Scheme 1 Synthesis of FLS with NFHG.



Scheme 2 Synthesis of FLS by the hydrosilylation of poly(hydromethylsiloxane)s with the fluorinated olefins.

RESULTS AND DISCUSSION

Preparation of the FLSs

FLSs with NFHG, HDFUG, HDFNAG, and NMHD-FNAG were synthesized. Their homo-FLSs and co-FLSs were included.

An FLS with NFHG was synthesized by the ring-opening polymerization of $\text{C}_4\text{F}_9\text{-D3}$ (Scheme 1).⁸ FLSs with other Rf-containing side-chain groups were synthesized by the hydrosilylation of poly(hydromethylsiloxane)s with the corresponding fluorinated olefins (Scheme 2). The synthesized FLSs were characterized by ^1H - and ^{19}F -NMR spectra and GPC (Table I).

Water and oil repellency of the FLSs

Polyester fabrics were treated with FLS finishes, as described in the Experimental section, and their water and oil repellency was evaluated. Table II shows the results.

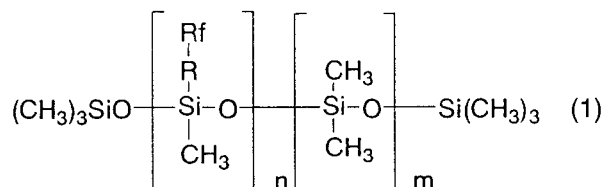
These fabrics showed a moderate to good level of water repellency (Table II, 1–7), as nominal water repellency is considered to be a water-repellency rating of 50 or higher. It was an appropriate result that the

water repellency was the same regardless of the fluorine content, the side-chain length of the Rf group, the orientation of the Rf group, and so forth because siloxane polymers and fluorinated polymers are representative water-repellent agents. However, the oil repellency of these fabrics was at a low level or the poorest level, except for those fabrics treated with homo-FLSs with HDFNAG. It was very surprising that the fabrics treated with homo-FLSs with HDFUG showed only 2 ratings (Table II, 3) because a fluorinated acrylate polymer with C_8F_{17} groups as side chains, being a representative water- and oil-repellent agent, showed an oil repellency of 6–7.

Surface analysis by XPS

XPS measurements were conducted to obtain information on the surface chemical compositions. As the XPS measurements of the fabrics treated with FLSs were affected by the roughness of the fabrics, PET films treated with FLSs were analyzed. Table III shows the chemical compositions of the surfaces. The $\text{F}_{1s}/\text{C}_{1s}$ and $\text{F}_{1s}/\text{Si}_{2p}$ values represent the relative magnitude of fluorine at the surface.

TABLE I
GPC Measurement of FLSs



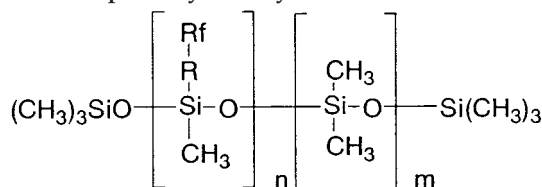
Sample	Rf-R	<i>n</i>	<i>m</i>	$M_{n,th}^a \times 10^{-3}$	$M_{n,GPC}^b \times 10^{-3}$	M_w/M_n^b
1	$\text{C}_4\text{F}_9\text{C}_2\text{H}_4$	25	0	7.8	5.9	2.5
2	$\text{C}_8\text{F}_{17}\text{C}_3\text{H}_6$	8	18	5.7	5.8	1.8
3	$\text{C}_8\text{F}_{17}\text{C}_3\text{H}_6$	25	0	13.2	12.2	2.2
4	$\text{C}_8\text{F}_{17}(\text{C}=\text{O})\text{NHC}_3\text{H}_6$	8	18	6.0	6.4	2.4
5	$\text{C}_8\text{F}_{17}(\text{C}=\text{O})\text{NHC}_3\text{H}_6$	25	0	14.2	13.9	2.1
6	$\text{C}_8\text{F}_{17}(\text{C}=\text{O})\text{N}(\text{CH}_3)\text{C}_3\text{H}_6$	8	18	6.1	6.5	2.0
7	$\text{C}_8\text{F}_{17}(\text{C}=\text{O})\text{N}(\text{CH}_3)\text{C}_3\text{H}_6$	25	0	14.6	14.9	1.7

M_n = number-average molecular weight; M_w = weight-average molecular weight.

^a Calculated according to eq. (1).

^b Estimated by GPC (perfluoropolyether calibration).

TABLE II
Water and Oil Repellency of Polyester Fabrics Treated with FLSs



Sample	Rf-R	<i>n</i>	<i>m</i>	Water repellency ^a	Oil repellency ^b
1	C ₄ F ₉ C ₂ H ₄	25	0	50	0
2	C ₈ F ₁₇ C ₃ H ₆	8	18	50	0
3	C ₈ F ₁₇ C ₃ H ₆	25	0	80	2
4	C ₈ F ₁₇ (C=O)NHC ₃ H ₆	8	18	60	0
5	C ₈ F ₁₇ (C=O)NHC ₃ H ₆	25	0	90	7
6	C ₈ F ₁₇ (C=O)N(CH ₃)C ₃ H ₆	8	18	50	0
7	C ₈ F ₁₇ (C=O)N(CH ₃)C ₃ H ₆	25	0	60	2

^a Water repellency ratings on a scale in which 100 is the best and 0 is the poorest.

^b Oil repellency ratings on a scale in which 8 is the best and 0 is the poorest.

These values were expected to be high for the films treated with FLSs that showed high oil repellency, but the significant difference in these values was not observed for the PET films treated with homo-FLSs with HDFUG or HDFNAG. Figure 1 shows XPS spectra for a homo-FLS with HDFUG and a homo-FLS with HDFNAG. The ratio of the peak intensity of CF₃ to that of CF₂ was also almost the same for both FLSs. These results suggest that the reason homo-FLS with HDFNAG showed high oil repellency was not simply because its fluorine concentration at the surface was high.

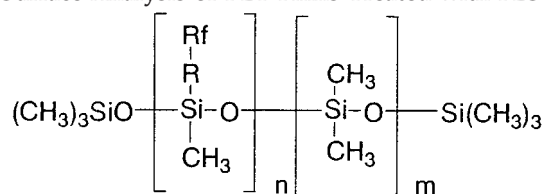
Crystallization of the side-chain Rf groups

Some research groups have pointed out that the crystallization of side-chain Rf groups is important in determining polymer surface properties, including the surface free energy and the water and oil repellency.⁹ DSC measurements were made to study a correlation

between the crystallization of Rf groups and the oil repellency. Table IV shows the result of the DSC measurements.

A homo-FLS with HDFNAG had a melting temperature (*T_m*) of 75.7°C. This showed that this FLS was in a crystalline state and had low mobility. However, a homo-FLS with HDFUG as the side chain had a *T_m* value of 20.5°C. This indicated that this FLS was in a rubbery state and had high mobility. The fact that the FLS with HDFUG showed poor oil repellency can be explained if we assume that the flexible siloxane backbone prevented the orientation of Rf groups, and the fact that the FLS with HDFNAG showed good oil repellency can be explained if we assume that the hydrogen bonding of the NH moiety helped the orientation of the Rf groups. This is supported by the fact that the homo-FLS with NMHDFNAG, for which no hydrogen bonding existed, showed poor oil repellency (Table II, 7).

TABLE III
Surface Analysis of PET Films Treated with FLSs



Sample	Rf-R	<i>n</i>	<i>m</i>	C	O	F	Si	N	F _{1s} /C _{1s}	F _{1s} /Si _{2p}
1	C ₄ F ₉ C ₂ H ₄	25	0	35.8	7.6	51.0	5.6	0	1.42	9.1
2	C ₈ F ₁₇ C ₃ H ₆	8	18	38.8	10.6	43.3	7.4	0	1.12	5.9
3	C ₈ F ₁₇ C ₃ H ₆	25	0	35.7	4.9	56.1	3.4	0	1.57	16.5
4	C ₈ F ₁₇ (C=O)NHC ₃ H ₆	8	18	37.3	12.0	40.7	7.9	2.1	1.09	5.2
5	C ₈ F ₁₇ (C=O)NHC ₃ H ₆	25	0	35.6	6.6	52.2	3.1	2.6	1.47	16.8
6	C ₈ F ₁₇ (C=O)N(CH ₃)C ₃ H ₆	8	18	38.7	12.1	39.3	7.6	2.3	1.02	5.2
7	C ₈ F ₁₇ (C=O)N(CH ₃)C ₃ H ₆	25	0	36.9	7.0	50.7	3.1	2.3	1.37	16.4

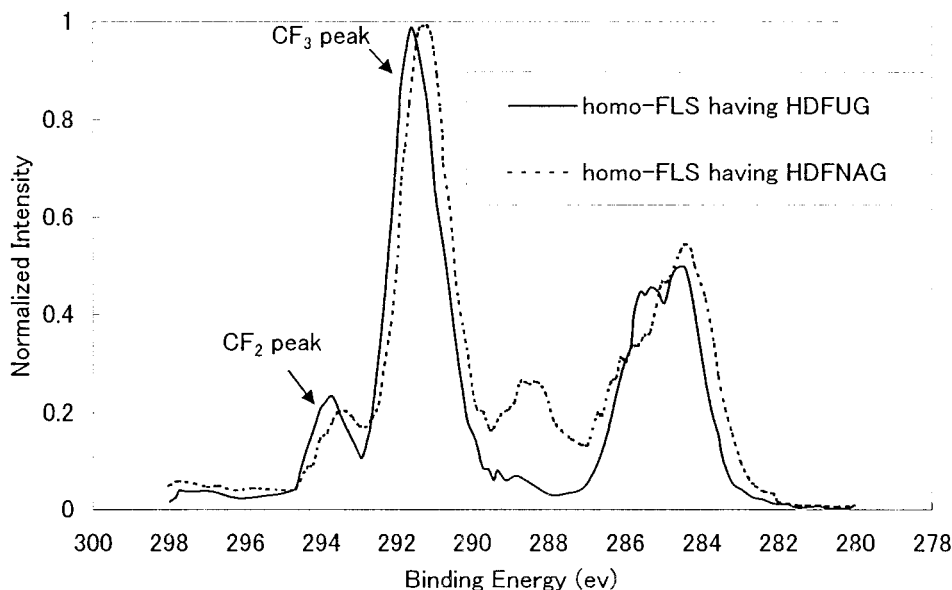


Figure 1 XPS spectra of the PET films treated (—) with homo-FLS with HDFUG and (---) with homo-FLS with HDFNAG.

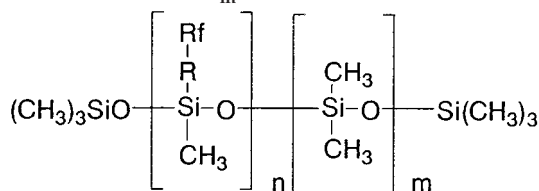
Therefore, it was shown that the performance of oil repellency could be related to the degree of the crystallization of the side-chain Rf groups. The fluorine concentration at the surface was almost equal in air, independent of the Rf-containing side-chain groups. However, the reorientation and regression of Rf groups occurred after the contact of test oils for FLSs that showed poor oil repellency. The reorientation did not occur for FLSs with HDFNAG during the contact of test oils because they had the strong packing of Rf groups due to the hydrogen bonding of the NH moiety. The other noteworthy point is that this reorientation of Rf groups perhaps occurred on the order of seconds at the most because the test of the oil repellency was conducted in 30 s.

CONCLUSIONS

The water and oil repellency of polysiloxanes with highly fluorinated alkyl side chains was studied. The conclusions from this study can be summarized as follows:

1. Polyester fabrics were treated with FLSs with NFHG, HDFUG, HDFNAG, and NMHDFNAG, and their water and oil repellency was evaluated. These fabrics showed a moderate to good level of water repellency but a poor to zero level of oil repellency, except for those fabrics treated with homo-FLSs with HDFNAG.
2. XPS measurements of PET films treated with FLSs showed that the concentration of fluorine at the surface was not particularly high for homo-FLSs with HDFNAG.
3. DSC measurements of FLSs showed that homo-FLSs with HDFNAG had a high T_m value of 75.7°C.
4. These facts suggest that the crystallization of HDFNAG, which was attributed to the effect of the hydrogen bonding of the NH moiety, played an important role in the performance of oil repellency. This was also supported by the fact that FLSs with NMHDFNAG, for which hydrogen bonding did not work, showed poor oil repellency. Therefore, the reason the fabrics treated with homo-FLSs with HDFNAG showed good oil repellency was not because the concentration of fluorine at the surface was higher than those of others but because the reorientation of HDFNAG did not take place for its packing after contact with oil.

TABLE IV
 T_m 's of FLSs



Sample	Rf-R	n	m	T_m (°C)
1	$\text{C}_4\text{F}_9\text{C}_2\text{H}_4$	25	0	— ^a
2	$\text{C}_8\text{F}_{17}\text{C}_3\text{H}_6$	8	18	-35.5
3	$\text{C}_8\text{F}_{17}\text{C}_3\text{H}_6$	25	0	20.5
4	$\text{C}_8\text{F}_{17}(\text{C}=\text{O})\text{NHC}_3\text{H}_6$	8	18	33.8
5	$\text{C}_8\text{F}_{17}(\text{C}=\text{O})\text{NHC}_3\text{H}_6$	25	0	75.7
6	$\text{C}_8\text{F}_{17}(\text{C}=\text{O})\text{N}(\text{CH}_3)\text{C}_3\text{H}_6$	8	18	— ^b
7	$\text{C}_8\text{F}_{17}(\text{C}=\text{O})\text{N}(\text{CH}_3)\text{C}_3\text{H}_6$	25	0	— ^b

^a T_m was not observed in the range of measurement.

^b A clear T_m was not observed.

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