

Article

Application of Liquid-Phase Direct Fluorination: Novel Synthetic Methods for a Polyfluorinated Coating Material and a Monomer of a Perfluorinated Polymer Electrolyte Membrane

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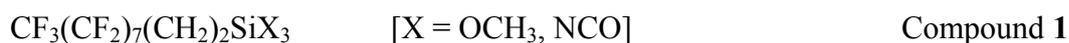
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Abstract: A new polyfluorinated anti-staining coating material $\text{CF}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_x\text{CF}_2\text{-CONHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ has been developed by utilizing the PERFECT method, which employs a liquid-phase direct fluorination reaction with elemental fluorine as a key step. Direct fluorination of a partially-fluorinated ester, which was prepared from a non-fluorinated poly(ethylene glycol) and a perfluorinated acyl fluoride, followed by methanolysis, gave the perfluorinated corresponding compound, which was led to the coating material for surface treating agents, and the methyl ester of the starting perfluorinated acyl fluoride. Application to the synthesis of a new perfluorinated bifunctional sulfonate monomer $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_2\text{SO}_2\text{F})_2$ for polymer electrolyte membranes (PEMs) of fuel cells was also developed.

Keywords: direct fluorination; anti-staining coating; surface treating; polymer electrolyte membrane; fuel cell

1. Introduction

Nowadays, organofluorine compounds are essential materials, especially in recent IT, electronics, and medical applications [1]. For example, the low surface energy of an organofluorine compound leads to water repellent and oil repellent properties, so that it is utilized as surface treating agents for water-and-oil repellent film. Therefore, it is expected that an anti-staining coating material for glass, for example, for automobiles or displays (a liquid crystal display, a CRT display, a projection display, a plasma display, an EL display or the like), could be achieved by an organofluorine compound. One such compound **1** may be a candidate [2,3].



When the compound **1** is applied to the surface of a substrate, the hydrolyzable groups are hydrolyzed by hydroxyl groups of the substrate or moisture on the substrate to form silanol groups. Once the silanol groups are bonded to the substrate, perfluoroalkyl groups will be oriented on the atmosphere side, so that the coating film made of the compound **1** exhibits water repellency [4].

However, as perfluoroalkyl groups are highly crystalline and stiff, the coating film made of the compound **1** does not have enough efficiency for the removal of oil-and-fat stains. To solve the problem, a compound having a perfluoropolyether group **2** was reported [5].



The perfluoropolyether (PFPE) group has a flexible structure, because stiff perfluoroalkyl groups are separated by oxygen atoms and C-O-C bonding have high mobility, so that the coating film made of the compound **2** is excellent in its efficiency in removing oil-and-fat stains, and also has water and oil repellency.

However, the mobility of the PFPE groups in **2** cannot be regarded as sufficient, and the efficiency for removal of oil-and-fat stains is not enough, because the ratio of oxygen atoms to carbon atoms in the PFPE groups is still small. From the viewpoint of molecular design, $-(\text{CF}_2\text{CF}_2\text{O})-$ as a repeating unit is ideal. However, there has not been a synthetic method for creating such a molecule, while it is possible to utilize the industrial intermediate of fluorinated oil to synthesize **2**.

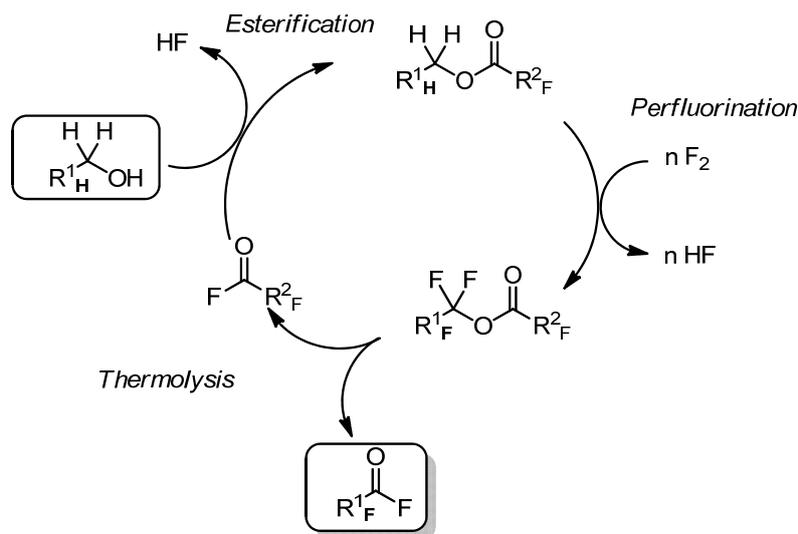
An organofluorine compound also shows chemical and thermal stability, derived from the nature of a C-F bond. Although highly polarized, the C-F bond gains stability from the resultant electrostatic attraction between C and F atoms [6]. Thus, because of their high thermal and chemical stability and conductivity, perfluorinated sulfonic acid ionomers are often used in polymer electrolyte membranes (PEMs) of fuel cells [7]. Their performance is, however, still not enough.

To achieve much higher conductivity, it is necessary to increase the number of sulfonyl groups per unit. On the other hand, PEMs should have a certain mechanical strength to assemble membrane electrode assemblies. In the event that conventional monosulfonated monomers are increasingly used to raise this number, the copolymer obtained will have many branches, and the mechanical strength of the PEM from the copolymer decreases. A bifunctional monomer is expected to overcome this dilemma. However, there has not been a feasible synthetic method to realize such a molecule.

On the other hand, we have reported an entirely new synthetic method for perfluorinated molecules, the PERFECT (PERFluorination of an Esterified Compound then Thermolysis) process [8], which

makes it possible to create new fluorinated compounds because it utilizes organic synthesis in hydrocarbon molecules. For example, a nonfluorinated primary alcohol can be converted to the corresponding perfluorinated acyl fluoride (Scheme 1). PFPE lubricants for hard disk drive (HDD) [9] Afluid[®], PFPE surfactants [10] and perfluoroalkanesulfonyl fluorides for ion-exchange membranes [11] have all been synthesized by employing the PERFECT process. Thus, it was considered to be possible to synthesize the molecules mentioned above by utilizing this process.

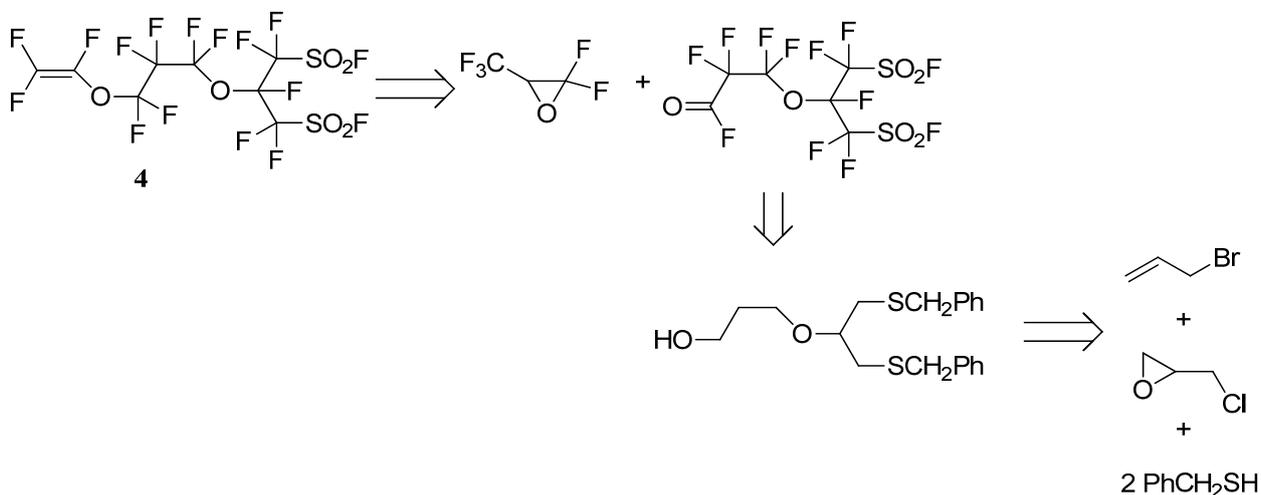
Scheme 1. The PERFECT process.



Here, we report the synthesis of a PFPE derivative, which possesses $-(CF_2CF_2O)-$ as a repeating unit, that is, $CF_3O(CF_2CF_2O)_xCF_2CONHCH_2CH_2CH_2Si(OCH_3)_3$ (**3**), and the synthesis of a perfluorobis(alkanesulfonyl) monomer $CF_2=CFOCF_2CF_2CF_2OCF(CF_2SO_2F)_2$ (**4**). The evaluation of the former on water and oil repellency and anti-staining property is also mentioned.

As for the PFPE derivative **3**, poly(ethylene glycol) monomethyl ether (**5**) is employed as a starting material in Scheme 1. The target, perfluorobis(alkanesulfonyl) monomer **4**, is considered to be synthesized by utilizing the PERFECT process according to the retrosynthesis shown in Scheme 2.

Scheme 2. Retrosynthetic analysis of perfluorobis(alkanesulfonyl) monomer.



2. Experimental Section

2.1. General

All boiling points were not corrected. IR spectra were recorded on a Nicolet Impact 410 spectrometer. NMR spectra were obtained on a JEOL AL-300 or EX-400 (tetramethylsilane as internal standard for ^1H and ^{13}C , and trichlorofluoromethane for ^{19}F). High resolution mass spectra were obtained on a JEOL SX-102A coupled to a HP 5890 with a 60 m capillary column, J&W DB1301.

Average molecular weight (M_n) number and average molecular weight (M_w) weight were measured by gel permeation chromatography (GPC). A solvent mixture of R225 (Dichloropentafluoropropane, ASAHIKLIN[®] AK-225G, available from Asahi Glass Co., Ltd.) and hexafluoroisopropyl alcohol (HFIP) (AK-225G/HFIP=99/1 volume ratio) was used as a mobile phase. As the column for analysis, one having two PL-gel MIXED-E (Polymer Laboratories Ltd.) connected in series was used. As a detector, an evaporation light scattering detector (ELSD, Shimazu Co.) was used, and GPC was measured at a column temperature of 37 °C at a mobile phase flow rate of 1.0 mL/min.

As standard samples for measuring the molecular weight, five types of perfluoropolyethers having molecular weight distributions (M_w/M_n) of less than 1.1 and different molecular weights between 1,300 and 10,000.

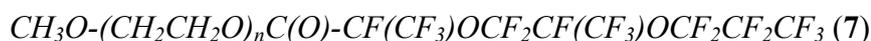
Elemental fluorine was generated by Fluorodec[™] 30, Fluoro Gas (UK). *Elemental fluorine is a highly toxic and corrosive gas, and may cause an explosion on contact with organic compounds in the vapor-phase. Extreme care must be taken when handling! Hydrogen fluoride (bp. 19.5 °C), which evolved in both the liquid and vapor phases during the reaction, are also highly corrosive and cause severe burns on skin contact. Care must be taken! Prior to use, all hydrocarbon greases must be removed and apparatus gradually passivated with elemental fluorine.*

1,1,2-trichlorotrifluoroethane (R113: $\text{CCl}_2\text{FCClF}_2$) was used as a solvent in the fluorination reaction on a small scale. Although the use of R113 is regulated, we give experimental examples with it for convenience, because it is still much more cheaply available (Aldrich) than other solvents. *Care must be taken in order to avoid environment emission!*

Poly(ethylene glycol) monomethyl ether (**5**, Uniox M-400: $\text{CH}_3\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{-H}$ average M_n 400. NOF Co.) was employed as the starting alcohol for the PFPE derivative **3**. Other reagents were obtained from Kanto Chemicals (Japan). Commercially obtained materials were used as received unless otherwise noted. All reactions sensitive to oxygen and/or moisture were conducted under nitrogen atmosphere with magnetic stirring. For large scale column chromatography, a Biotage Flash 150M pre-packed column (KP-Sil silica, 15 cm ID \times 30 cm long) was used.

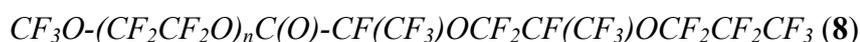
2.2. Typical Procedure for the Anti-staining Coating Material

2.2.1. Synthesis of the Anti-staining Coating Material (Scheme 3)



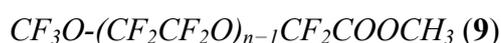
Prior to use, all glass flasks were oven dried at 120 °C. A mixture of **5** (25.0 g, 62.5 mmol), R225 (20.0 g, 98.5 mmol), NaF (1.20 g, 28.6 mmol) and pyridine (1.60 g, 20.2 mmol) was vigorously stirred

in a flask at under 10 °C. Subsequently, perfluoro(2,5-dimethyl-3,6-dioxanonanoyl) fluoride (**6**, 46.6 g, 93.5 mmol) was added to the flask over a period of 3.0 h while maintaining the internal temperature to be no higher than 5 °C. After completion of the addition, the mixture was stirred at 50 °C for 12 h and at room temperature for 24 h. The crude liquid was filtered under reduced pressure and dried for 12 h in a vacuum drier at 50 °C. The crude liquid was then dissolved in R225 (100 mL) and washed three times with a saturated sodium hydrogen carbonate aqueous solution (1,000 mL). To the organic phase, magnesium sulfate (1.0 g) was added, followed by stirring for 12 h, and removed by filtration under pressure. From the recovered liquid, R225 was evaporated to obtain **7** (56.1 g, 62.0 mmol, 99.0%, average value of *n*: 7.3) which was liquid at room temperature; ¹H-NMR (300.4 MHz, CDCl₃) δ (ppm): 3.50 (m, 3H, CH₃), 3.60–3.80 (m, 2H, OCH₂), 4.50–4.65 (m, 2H, CH₂CH₂OCO); ¹⁹F-NMR (282.7 MHz, CDCl₃) δ (ppm): –79.5 (3F, CF₃), –80.0 (5F, CF₂CF₂CF₃), –82.5 to –85.0 (5F, OCF₂, CF₃), –129.2 (2F, CF₂CF₂CF₃), –131.5 (1F, OCOCF), –144.5 (1F, CFO).



Prior to use, all hydrocarbon greases must be removed and the apparatus must be gradually passivated with elemental fluorine. Into a 3,000 mL hastelloy autoclave, R113 (1,560 g, 8.32 mol) was stirred at 25 °C. At a gas outlet of the autoclave, a condenser held at 20 °C, a NaF pellet-packed layer and a condenser held at –20 °C were connected in series. Further, a liquid-returning line was installed to return a liquid condensed by the condenser held at –20 °C to the autoclave.

Nitrogen gas was supplied for 1.0 h into the autoclave, and then fluorine gas, diluted to 10% by nitrogen gas, (hereafter referred to as 10% fluorine in nitrogen) was supplied for one hour at a flow rate of 24.8 L/h. Then, a solution of **7** (27.5 g, 31.3 mmol), dissolved in R113 (1,350 g, 7.20 mol), was injected over a period of 30 h into the autoclave, while supplying 10% fluorine in nitrogen at the same flow rate. Then, R113 (12 mL) was injected at 40 °C into the autoclave, while supplying 10% fluorine in nitrogen at the same flow rate. Then, 1% benzene in R113 (6 mL) was injected. Further, 10% fluorine in nitrogen was supplied for 1.0 h and then, nitrogen gas was supplied for 1.0 h. Then, the solvent was removed by vacuum drying at 60 °C for 6.0 h to obtain liquid **8** (45.4 g, 29.6 mmol, 94.6%). From the results of the NMR analysis of the compound, it was confirmed that 99.9% of the total number of hydrogen atoms in **7** were substituted by fluorine atoms, that is, **8** was the main component (average value of *n*: 7.1); ¹⁹F-NMR (282.7 MHz, R113, internal standard for quantitative determination: hexafluorobenzene) δ (ppm) : –54.9 (3F, CF₃O), –79.5 (3F, CF₃), –80.0 (5F, CF₂CF₂CF₃), –82.5 to –85.0 (5F, OCF₂, CF₃), –87.5 (2F, OCF₂), –89.7 (2F, CF₃OCF₂), –91.5 (2F, CF₂OCOCF), –129.2 (2F, CF₂CF₂CF₃), –131.5 (1F, CF₂OCOCF), –144.5 (1F, CFO).



In a 300 mL egg-plant type PTFE flask, methanol (40.0 g, 1.25 mmol), NaF (5.60 g, 133 mmol) and R225 (50.0 g, 246 mmol) were stirred in nitrogen. Compound **8** (43.5g, 28.3mmol) was added, followed by vigorous stirring while bubbling nitrogen at room temperature for 8 h. The excess methanol and CH₃OC(O)-CF(CF₃)OCF₂CF(CF₃)OCF₂CF₂CF₃ that formed were distilled off by a vacuum pump installed at the condenser tube. After 24 h, liquid **9** (26.8 g, 25.5 mmol, 90.3%) was obtained. ¹H-NMR (300.4 MHz, R-113, internal standard for quantitative determination: nitrobenzene)

δ (ppm): 3.88 (m, 3H, $\text{CF}_2\text{COOCH}_3$); ^{19}F -NMR (282.7 MHz, R113, internal standard for quantitative determination: hexafluorobenzene) δ (ppm) : -54.9 (3F, CF_3O), -77.4 (2F, $\text{CF}_2\text{COOCH}_3$), -87.5 (2F, OCF_2), -89.7 (2F, CF_3OCF_2).

The molecular weight (Mn) of obtained **9** was 1718, and the molecular weight distribution was 1.11.



In a 100 mL round-bottomed flask, a mixture of **9** (33.1 g, 31.6 mmol) and 3-trimethoxysilylpropylamine (**10**, 5.80 g, 32.3 mmol) were stirred at room temperature for 2 h. Then, unreacted **10** and by-product methanol were distilled off under reduced pressure to obtain **3** (32.3 g, 27.0 mmol) which was liquid at room temperature. From the results of the NMR analysis of the compound, it was confirmed that 98.0 mol% of $-\text{CF}_2\text{C}(\text{O})\text{OCH}_3$ in **9** was converted to $-\text{CF}_2\text{C}(\text{O})\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$.

^1H -NMR (300.4 MHz, R113) δ (ppm) : 0.51 (m, 2H, CH_2Si), 1.60 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.41 (2H, $\text{CF}_2\text{CONHCH}_2$), 3.67 (m, 3H, OCH_3), 7.20 (m, 1H, NH); ^{19}F -NMR (282.65 MHz, R113) δ (ppm) : -54.9 (3F, CF_3O), -77.4 (2F, $\text{CF}_2\text{COOCH}_3$), -87.5 (2F, OCF_2), -89.7 (2F, CF_3OCF_2).

The molecular weight (Mn) of **3** was 1072, and the molecular weight distribution was 1.33.

2.2.2. Evaluation of Anti-staining Performance

After synthesis, **3** was carried out to assess anti-staining performance compared with a conventional anti-staining material $\text{C}_6\text{F}_{13}\text{C}_2\text{H}_4\text{Si}(\text{OCH}_3)_3$ (**1a**). Both **3** and **1a** were applied on glass by dip coating in a dilute solution, as described below.

Glass substrate was cleaned in acetone with ultrasound for 10 minutes and dried at 60 °C for 10 min. It was dipped in a 0.05% solution of the material at room temperature for 10 min. ASAHIKLIN[®] AC6000 ($\text{C}_6\text{F}_{13}\text{C}_2\text{H}_5$, available from Asahi Glass Co., Ltd.) was used as a dilute solvent. Finally, the glass was cured at room temperature under a relative humidity between 40% and 60% for 24 h. After coating, contact angle, friction coefficient and the abrasion resistance were evaluated.

An abrasion test on the surface of a coating film of an article with a flannel cloth was carried out according to Japanese Industrial Standards JIS L0849 under conditions of a load of 1 kg and abrasion times of 1,000 reciprocations. The water contact angle was measured after various intervals to obtain the relationship with abrasion cycles.

2.3. Typical Procedure for the Synthesis of the Perfluorobis(alkanesulfonyl) Monomer (Scheme 4)

2.3.1. 1,3-Bis(phenylmethylthio)propan-2-ol (**11**)

α -toluenethiol (507 g, 4.08 mol) was added dropwise for 1 h to a stirred solution of NaOH (163.3 g, 4.08 mol) in methanol (2 L) under 10 °C. Epichlorohydrin (189 g, 2.04 mol) was further added dropwise for 1 h. The mixture was stirred for 3.5 h at 20 °C and poured into 5 L of water. The mixture was separated and the aqueous phase was extracted with methyl *tert*-butyl ether (MTBE, 3 \times 1,000 mL). The combined organic phase was washed with saturated aqueous NH_4Cl (3 \times 200 mL), dried over MgSO_4 and filtered, and the solvent was evaporated to afford 604 g

(1.98 mol, 97%) of **11**; ^1H NMR (300.4 MHz, CDCl_3) δ (ppm): 2.47 (dd, $J = 7.5, 13.9$ Hz, 2H), 2.58 (dd, $J = 4.7, 13.9$ Hz, 2H), 2.75 (d, $J = 3.2$ Hz, 1H), 3.63~3.73 (m, 1H), 3.68 (s, 4H), 7.18~7.33 (m, 10H); IR (neat): 3445.8, 3060.2, 3026.9, 2913.4, 1493.6, 1452.8, 1239.7, 1071.2, 1028.2, 767.6, 700.5 cm^{-1} .

The obtained crude **11** was used for the next step without carrying out purification.

2.3.2. 2-Allyloxy-1,3-Bis(phenylmethylthio)propane (**12**)

To a stirred suspension of 60% NaH (84.6 g, 2.12 mol) in anhydrous THF (2L) under $5\text{ }^\circ\text{C}$ was added a solution of **11** (604 g, 1.98 mol) in anhydrous THF (400 mL) dropwise for 40 min. After stirring under $5\text{ }^\circ\text{C}$ for one hour, allyl bromide (252 g, 2.08 mol) was further added dropwise for 45 min. The mixture was stirred for 19 h at $20\text{ }^\circ\text{C}$, and poured into water (5 L). The mixture was separated and the aqueous phase was extracted with MTBE (3×1000 mL). The combined organic phase was washed with saturated aqueous NH_4Cl (3×200 mL), dried over MgSO_4 and filtered, and the solvent was evaporated. The large scale column chromatography on silica gel using a Biotage Flash 150M pre-packed column (KP-Sil silica, 15 cm ID \times 30 cm long) with hexane-ethyl acetate (7:1) as the eluent provided 643 g (1.86 mol, 94%) of **12**; ^1H NMR (300.4 MHz, CDCl_3) δ (ppm): 2.59 (dd, $J = 5.8, 13.7$ Hz, 2H), 2.64 (dd, $J = 5.8, 13.7$ Hz, 2H), 3.47 (qui, $J = 5.8$ Hz, 1H), 3.70 (s, 4H), 3.95 (dm, $J = 5.8$ Hz, 2H), 5.14 (dm, $J = 10.3$ Hz, 1H), 5.23 (dm, $J = 17.1$ Hz, 1H), 5.87 (ddt, $J = 10.3, 17.1, 5.8$ Hz, 1H), 7.18~7.34 (m, 10H); ^{13}C NMR (75.45 MHz, CDCl_3) δ (ppm): 34.45, 36.98, 70.81, 78.38, 116.98, 126.95, 128.39, 128.91, 134.79, 138.31; IR (neat): 3061.0, 3027.3, 2918.3, 1493.7, 1452.9, 1071.6, 923.1, 767.4, 700.5 cm^{-1} .

2.3.3. 4-Oxa-8-Phenyl-5-(Phenylmethylthiomethyl)-7-Thiaoctan-1-ol (**13**)

To 1.01 M solution of borane-THF complex in THF (1,880 mL, 1.90 mol) under $10\text{ }^\circ\text{C}$ was added cyclohexene (312 g, 3.80 mol) dropwise for 1.5 h. After stirring under $5\text{ }^\circ\text{C}$ for 3 h, **12** (643 g, 1.98 mol) was further added dropwise for 1 h. The mixture was stirred for 17 h at $10\text{ }^\circ\text{C}$. To the mixture was added a solution of NaOH (84.3 g, 2.11 mol) in water (700 mL) dropwise under $10\text{ }^\circ\text{C}$ for 45 min. The mixture was stirred for 15 min at the same temperature, and 30% H_2O_2 (700 mL, 8.12 mol) was further added dropwise for 3.5 h. The temperature was maintained under $20\text{ }^\circ\text{C}$. The mixture was poured to a solution of K_2CO_3 (3 kg) in water (3 L), separated, and the aqueous phase was extracted with MTBE (3×800 mL). The combined organic phase was dried over MgSO_4 , filtered and freed of solvent *in vacuo*. The large scale column chromatography on silica gel using a Biotage Flash 150M pre-packed column (KP-Sil silica, 15 cm ID \times 30 cm long) with hexane-ethyl acetate (3:1) as the eluent produced **13** (569 g, 1.57 mol, 84%) and recovered **12** (46.0 g, 0.13 mol, 7%).

13: ^1H NMR (300.4 MHz, CDCl_3) δ (ppm): 1.75 (qui, $J = 5.7$ Hz, 2H), 2.46 (t, $J = 5.7$ Hz, 1H), 2.56 (dd, $J = 6.2, 13.7$ Hz, 2H), 2.62 (dd, $J = 5.8, 13.7$ Hz, 2H), 3.34 (qui, $J = 5.8$ Hz, 1H), 3.55 (t, $J = 5.8$ Hz, 2H), 3.69 (s, 4H), 3.74 (q, $J = 5.4$ Hz, 2H), 7.20~7.35 (m, 10H); ^{13}C NMR (75.45 MHz, CDCl_3) δ (ppm): 32.09, 34.63, 36.87, 60.95, 68.32, 78.55, 127.04, 128.45, 128.87, 138.14; IR (neat): 3439.8, 3026.9, 2917.3, 2870.8, 1493.7, 1452.9, 1239.7, 1088.5, 1072.0, 768.9, 701.2 cm^{-1} .

2.3.4. 4-Oxa-8-Phenyl-5-(Phenylmethylthiomethyl)-7-Thiaoctyl Perfluoro(2,5-Dimethyl-3,6-Dioxanonanoate) (**14**)

To a stirred solution of **13** (596 g, 1.57 mol) and triethylamine (175 g, 1.73 mol) in dichloromethane (2.5 L) under 5 °C was added **6** (822 g, 1.65 mol) dropwise for 2 h. The mixture was stirred for 3 h at 20 °C. The mixture was washed with saturated aqueous NaHCO₃ (2 × 800 mL), 2 N-HCl (2 × 900 mL) and saturated aqueous NH₄Cl (500 mL). The organic phase was dried over MgSO₄, filtered, and freed of solvent *in vacuo* to afford **14** (1,323 g, 1.57 mol, >98%); ¹H NMR (300.4 MHz, CDCl₃) δ (ppm): 1.91 (qui, *J* = 6.1 Hz, 2H), 2.55 (dd, *J* = 6.1, 13.5 Hz, 1H), 2.61 (dd, *J* = 5.8, 13.5 Hz, 2H), 3.31 (qui, *J* = 6.0 Hz, 1H), 3.44 (t, *J* = 6.0 Hz, 2H), 3.68 (s, 4H), 4.49 (m, 2H), 7.20~7.35 (m, 10H); ¹⁹F NMR (282.7 MHz, CDCl₃) δ (ppm): -78.98~-85.55 (m, 4F), -80.48 (m, 3F), -81.82 (q, *J* = 7.0 Hz, 3F), -82.65 (m, 3F), -130.06 (s, 2F), -131.93 (dm, *J* = 21.1 Hz, 1F), -145.65 (m, 1F); IR (neat): 3029.3, 2916.5, 1782.6, 1240.7, 1148.4, 1037.2, 993.5, 701.2 cm⁻¹.

The obtained crude **14** was used for the next step without carrying out purification.

2.3.5. 6-Fluorosulfonyl-5-(Fluorosulfonylmethyl)-4-Oxahexyl Perfluoro(2,5-Dimethyl-3,6-Dioxanonanoate) (**16**)

A flask-equipped dry ice condenser was charged with **14** (642 g, 764 mmol), acetic acid (1,350 mL) and water (150 mL). Chlorine was bubbled in the stirred mixture at a flow rate of 600 mL/min for 2.5 h and 75 mL/min for 3.5 h at 20 °C. The mixture was cooled by water so that the reaction temperature did not exceed 30 °C. After bubbling, the mixture was purged with nitrogen, and water was added (1.5 L). The mixture was extracted with MTBE (3 × 500 mL). The combined organic phase was washed with water (500 mL), dried over MgSO₄, filtered, and the solvent was evaporated to afford 800 g of crude 6-Chlorosulfonyl-5-(chlorosulfonylmethyl)-4-oxahexyl perfluoro(2,5-dimethyl-3,6-dioxanonanoate) (**15**); ¹H NMR (300.4 MHz, CDCl₃) δ (ppm): 2.05 (m, 2H), 3.79 (t, *J* = 5.8 Hz, 2H), 4.11 (d, *J* = 6.0 Hz, 4H), 4.43~4.58 (m, 2H), 4.64 (m, 1H); ¹⁹F NMR (282.7 MHz, CDCl₃) δ (ppm): -78.97~-85.64 (m, 4F), -80.48 (m, 3F), -81.82 (m, 3F), -82.63 (m, 3F), -130.06 (s, 2F), -132.01 (dm, *J* = 20.0 Hz, 1F), -145.65 (m, 1F).

A flask was charged with **15**, KHF₂ (239 g, 3.06 mol), acetonitrile (1.5 L) and water (1.5 L). The mixture was stirred at 20 °C for 24 h, and organic phase was separated from aqueous phase. The aqueous phase was extracted with MTBE (200 mL). The combined organic phase was washed with water (2 × 200 mL), dried over MgSO₄, filtered, and freed of solvent *in vacuo*. The residue separated into two layers and the upper one (mainly α-chlorotoluene) was removed. A crude mixture (373 g), including **16**, was obtained. The large scale column chromatography on silica gel using a Biotage Flash 150M pre-packed column (KP-Sil silica, 15 cm ID × 30 cm long) with hexane-ethyl acetate (3:1) as the eluent furnished **16** (269 g, 354 mmol, 46% from **14**), which was directly used for the next liquid phase fluorination reaction; ¹H NMR (300.4 MHz, CDCl₃) δ (ppm): 2.06 (qui, *J* = 6.0 Hz, 2H), 3.77 (t, *J* = 5.9 Hz, 2H), 3.79 (dd, *J* = 3.2, 5.7 Hz, 4H), 4.42~4.58 (m, 3H); ¹⁹F NMR (282.7 MHz, CDCl₃) δ (ppm): 61.56 (s, 2F), -79.01~-85.62 (m, 4F), -80.51 (m, 3F), -81.86 (m, 3F), -82.69 (m, 3F), -130.09 (s, 2F), -132.03 (dm, *J* = 18.8 Hz, 1F), -145.65 (m, 1F); IR (neat): 3003.9, 2953.8, 1781.6, 1420.6, 1239.5, 1149.8, 1038.7, 993.8, 804.2, 744.8 cm⁻¹.

2.3.6. Perfluoro[6-Fluorosulfonyl-5-(Fluorosulfonylmethyl)-4-Oxahexanoyl] Fluoride (**18**)

In a 3 L autoclave made of stainless steel, equipped with a condenser maintained at 25 °C, an NaF pellet packed layer and a condenser maintained at -10 °C in series at its gas outlet, as well as a liquid returning line in order to return the condensed liquid from the condenser maintained at -10 °C, **6** (4,520 g) was stirred at 25 °C. Nitrogen was blown into the system for 1 hr, and then 20% F₂/N₂ for 0.5 h at a flow rate of 93.4 L/h. While blowing 20% F₂/N₂ at the same rate, the internal pressure of the reactor was raised to 0.1 MPa, and a solution of **16** (404 g, 532 mmol) in R113 (1,640 mL) was injected over a period of 31.5 h. After the injection, 20% F₂/N₂ was further blown at the same rate for 8 h. The reactor was cooled to room temperature and purged with nitrogen. The removal of the solvent afforded the crude mixture (643 g), including the perfluorinated ester **17**; ¹⁹F NMR (282.7 MHz, CDCl₃) δ (ppm): 46.59 (2F), -78.62 ~ -80.46 (4F), -82.15 (8F), -84.23 ~ -87.36 (5F), -104.54 (4F), -128.40 (2F), -130.16 (2F), -132.26 (1F), -133.78 (1F), -145.96 (1F).

A flask was charged 623 g of the mixture above and KF (3.16 g, 54.3 mmol). The mixture was heated at 90 °C for 1.5 h. The distillation *in vacuo* provided **18** (99.5 g, 216 mmol, 36% from **16**); bp 77 ~ 78 °C/40 mmHg; ¹⁹F NMR (282.7 MHz, CDCl₃) δ (ppm): 46.65 (s, 2F), 25.29 (tt, *J* = 4.6, 9.2 Hz, 1F), -81.37 (d, *J* = 13.7 Hz, 2F), -104.60 (m, 4F), -120.53 (m, 2F), -133.72 (t, *J* = 19.8 Hz, 1F).

2.3.7. Perfluoro[9-Fluorosulfonyl-8-(Fluorosulfonylmethyl)-2-Methyl-3,7-Dioxanonanoyl] Fluoride (**19**)

18 (82.7 g, 180 mmol), CsF (2.33 g, 15.3 mmol) and monoglyme (18.0 g) were charged into a 200 mL vacuumed autoclave. The mixture was stirred and hexafluoropropene oxide (HFPO, 33.0 g, 199 mmol) was introduced at 5 °C. Internal pressure was raised to 1.4 atm. The mixture was further stirred for 1 h. The distillation *in vacuo* provided **19** (38.9 g, 62.0 mmol) and recovered **18** (35.9 g, 78.0 mmol) (conversion = 57%, yield of **19**: 60%); bp 79~80 °C/5 mmHg; ¹⁹F NMR (282.7 MHz, CDCl₃) δ (ppm): 46.65 (s, 2F), 26.66 (q, *J* = 4.6 Hz, 1F), -78.95 (ddt, *J* = 18.3, 149.5, 7.6 Hz, 1F), -79.32 (m, 2F), -82.08 (s, 3F), -86.35 (dm, *J* = 149.5 Hz, 1F), -104.46 (m, 4F), -128.20 (s, 2F), -130.87 (d, *J* = 16.8 Hz, 1F), -133.73 (m, 1F).

2.3.8. Perfluoro[2-(Fluorosulfonylmethyl)-3,7-Dioxa-8-Nonene]Sulfonyl Fluoride (**4**)

To a suspension of KHCO₃ (6.03 g, 60.2 mmol) in monoglyme (59 mL) was added **19** (35.6 g, 52.6 mmol) dropwise for 30 min at 4 °C. The mixture was stirred for 30 min and freed of solvent *in vacuo* at 95 °C for 8 days and 120 °C for 2 days. Crude potassium perfluoro[9-fluorosulfonyl-8-(fluorosulfonylmethyl)-2-methyl-3,7-dioxanonanoate] (21.1 g, 29.7 mmol) was obtained. The potassium salt was heated to 200 °C under reduced pressure (3 mmHg). Gas generated was corrected in a liquid nitrogen trap. Condensed liquid in the trap was washed with water (10 mL) to afford **4** (8.35 g, 13 mmol, 25%); ¹⁹F NMR (282.7 MHz, CDCl₃) δ (ppm): 46.62 (s, 2F), -79.45 (m, 2F), -85.56 (m, 2F), -103.14 ~ -105.38 (m, 4F), -113.27 (dd, *J* = 65.6, 82.4 Hz, 1F), -121.66 (ddt, *J* = 82.4, 112.9, 6.1 Hz, 1F), -128.27 (s, 2F), -133.65 (m, 1F), -135.67 (ddt, *J* = 65.6, 112.9, 6.1 Hz, 1F); IR (neat): 1839.4, 1777.6, 1468.6, 1340.6, 1286.4, 1213.6, 1167.1, 999.0, 812.2 cm⁻¹; HRMS (CI) *m/z* (M-F⁺, C₈F₁₅O₆S₂⁺) calculated 540.8897, found 540.8898.

coefficient than the conventional anti-staining material **1a**. This is because **3** has more fluorine contents in a molecule and a higher degree of molecular mobility, due more to an ether bond than **1a**. Higher hydrophobic and oleophobic properties will give a better anti-staining performance. Moreover, a lower friction coefficient predicts that **3** will have both better stay-clean and easy-to-clean characteristics.

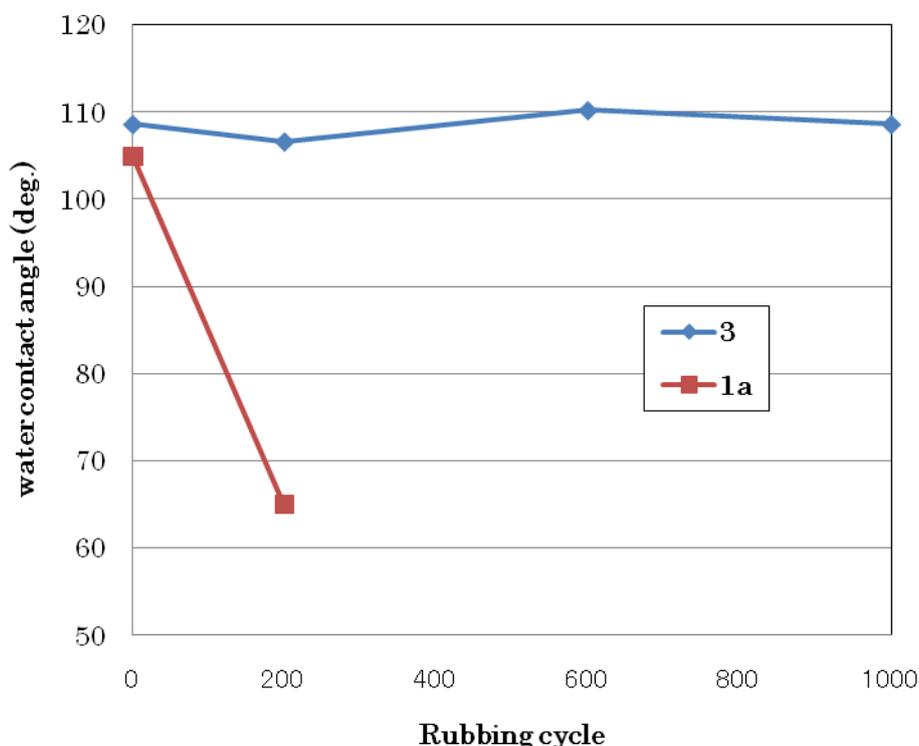
Table 1. Contact angle and friction coefficient of coating glass.

Material	Water (deg.)	n-Hexadecane (deg.)	friction coefficient
3	108	71	0.159
1a	105	65	0.184

3.1.3. Abrasion Resistance Test

The effect of the abrasion resistance is also a key parameter when considering the use of **3** coating on surfaces subjected to physical wear. An abrasion test of the treated surface is a method commonly used to predict the effective life of the surface modification. The results are shown in Figure 1. As can be seen from Figure 1, there was a significant difference in the resistance to abrasion as measured by water contact angle. After 200 cycles the conventional **1a** material had a drastic reduction in water contact angle, while **3** maintained high contact angle even after 1,000 cycles. It is considered that both longer molecular chain and lower friction coefficient of **3** contribute to this higher abrasion property.

Figure 1. Abrasion Resistance Test.

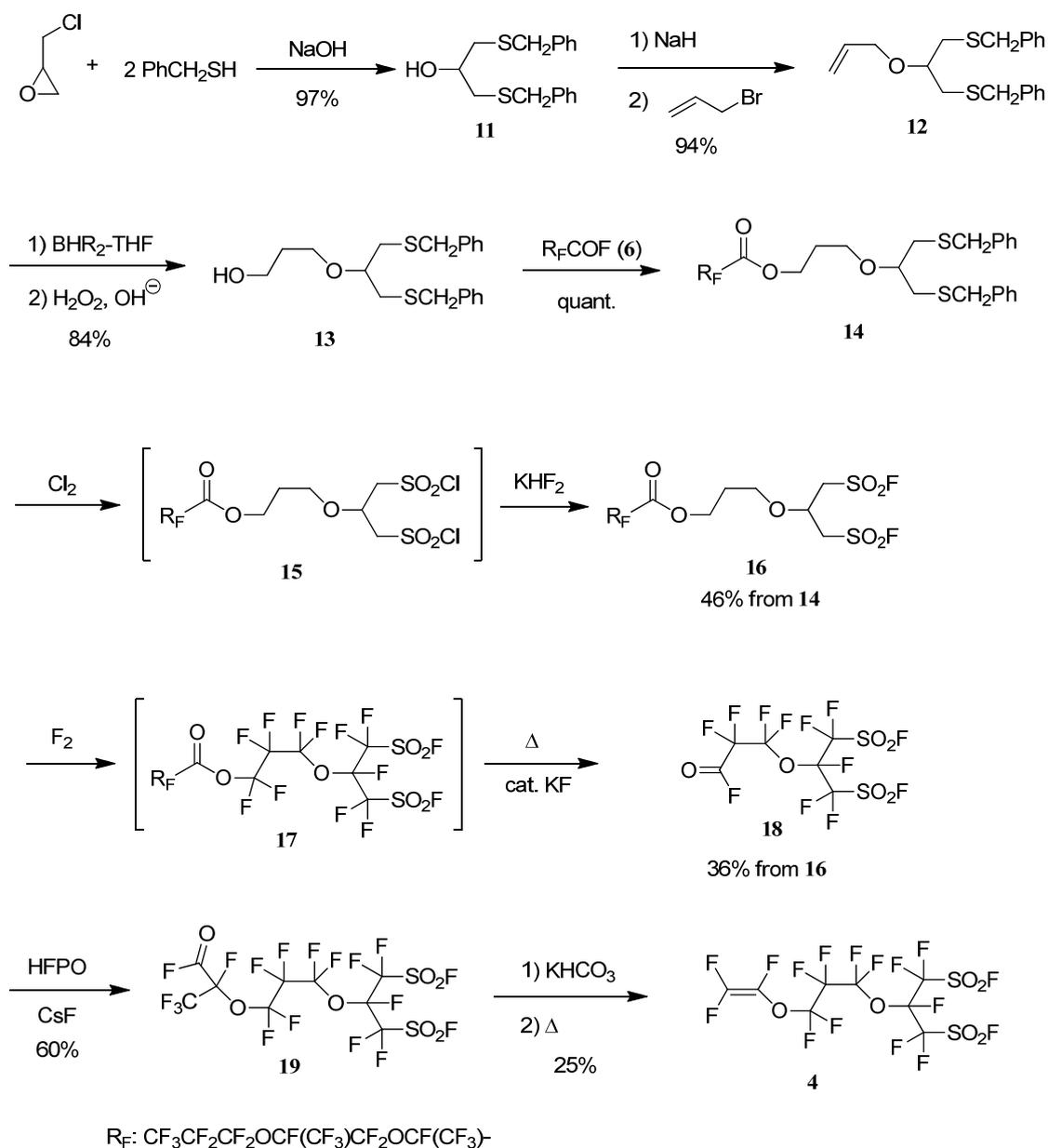


3.2. Synthesis of Perfluorobis(alkanesulfonyl) Monomer (Scheme 4)

To date, the method to prepare perfluorobis(sulfonyl) compounds has been very limited. Forohtar and DesMarteau reported fluorobis(fluorosulfonyl)acetyl fluoride, (FSO₂)₂CFCOF [14]. The yield of

this compound, however, was low, and it easily decarbonylated in the presence of fluoride ions. Instead of employing this method, we adopted a totally different approach, which includes the PERFECT process as a key step. It enabled us to build the perfluorinated backbone structure with two fluorosulfonyl groups and one fluorocarbonyl group from a non-fluorinated sulfonyl compound prepared by organic synthesis. Then, the introduction of a polymerizable trifluorovinyl group was carried out using hexafluoropropene oxide. Our method seemed not to have the problem described above, since the fluorocarbonyl group reacts with hexafluoropropene oxide prior to decarbonylation. The synthetic path to **4** is shown in Scheme 4.

Scheme 4. Synthesis of perfluorobis(alkanesulfonyl) monomer **4**.



Compound **11** was prepared by a nucleophilic attack of α -toluenethiol to epichlorohydrin [15]. Allylation of the hydroxy group (allyl bromide-NaH-THF, 0 °C, 1 h, then 25 °C, 20 h) produced **12** [16]. Hydroboration-oxidation was performed to the double bond of **12** (1. dicyclohexylborane-THF,

0 °C, 19 h; 2. NaOH aq. then 30% H₂O₂) to furnish **13**. When the borane/THF complex was used as the hydroboration reagent, the unwanted secondary alcohol (2°-ol) was formed with the desired **13** (**13**: 2°-ol = 69:31). Using the more sterically hindered dicyclohexylborane as the borane reagent essentially eliminated 2°-ol [17]. The compound **13** was condensed with perfluoro-2,5-dimethyl-3,6-dioxanonanoyl fluoride (**6**) (triethylamine-dichloromethane, 0 °C, 1 h, then 25 °C, 3 h) to afford the ester **14**. Oxidation of **14** by chlorine (acetic acid-water, 25 °C, 16 h) [18], followed by treatment with KHF₂ (acetonitrile-water, 25 °C, 24 h) provided the sulfonyl fluoride **16** [19]. The PERFECT process was applied to **16** (1. 20% F₂/N₂-trichlorotrifluoroethane, 20 °C, 1.5 h; 2. KF, 90 °C, 1.5 h) to furnish **18** [8]. The reaction of **18** with hexafluoropropene oxide (CsF-diglyme, 0 °C, 1 h) proceeded to obtain **19**, which was decarbonylated (1. KHCO₃-glyme, 0 °C, 0.5 h; 2. 120 °C, 3 h, then 200 °C, 1 h) to afford the desired **4** [20].

The overall yield of **4** was as low as 2%, the net result of several low yield steps. The single lowest yield was the fluorination step. C-S bond disconnection occurred as in the case of the fluorination of other C-S bond containing substrates [11]. The typical yields of the fluorination of the substrates with one C-S bond have been 60–70%. The substrate **16**, however, has two C-S bonds so that there is a high chance of the disconnection compared with substrates with one C-S bond. The introduction of sulfur into fluorinated molecules should be reconsidered.

The yields of the steps after the fluorination were also low. They could be improved after optimizing the reaction conditions.

4. Conclusions

Applying the PERFECT process, a perfluoropoly(ethylene glycol) derivative has been synthesized, and proved to be a surface treating agent, which is excellent in water-and-oil repellency and efficiency for the removal of oil-and-fat stains. An industrial application to stain-proof glass is now being studied. Furthermore, the monomer having two sulfonyl groups has been synthesized by utilizing the PERFECT process. Polymerization with it and application to PEMs of fuel cells are items to be studied. The polymer made from the monomer is expected to show good performance and enhanced durability when used for PEMs of electropower systems.

Thus, the PERFECT process provides the synthetic method of entirely new functional fluorinated molecules for leading-edge industries.

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