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DURABLE FLUOROCARBON-BASED COATINGS FOR AIRCRAFT

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New perfluoroalkyl-branched diols were synthesized. Polyols and polyesters were prepared from the perfluoroalkyl-branched diols. The branching perfluoroalkyl groups are expected to form a protective layer between the polymer backbone and the atmosphere. Thus, the fluorinated polyols and polyesters could be key ingredients for the development of durable for military aircraft.

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1. Introduction

Fluoropolymers, as a class of compounds, are prime candidates to be formulated into extremely durable paints for military aircrafts. Fluorocarbons are known for their excellent chemical and thermal stabilities. Their exceptionally high oxidative stability and UV resistance are the reasons why they can be used as strong barriers against harsh environments for a long period of time. Typical fluoropolymers, developed to date for topcoat applications, can be illustrated as a block polymers (Figure-1) having hydrocarbon segments and fluorocarbon segments.

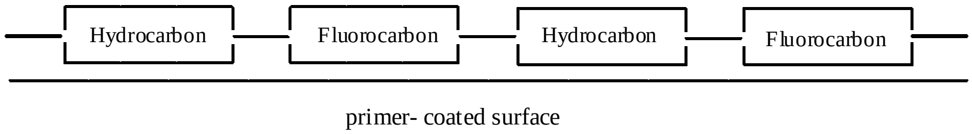


Figure-1 Illustration of typical fluorocarbon polymers

Efforts have been made to increase the fluorocarbon segments to improve performance. When the content of the fluorocarbon segments is increased; however, the adhesion of the polymer to a primer-coated surface (Figure-1) becomes weaker as the interaction between the topcoat and the primer at the interface decreases. In addition, the polymer becomes less and less soluble in organic solvents as the content of the fluorocarbon segments increases. Highly fluorinated polymers are, therefore, difficult to formulate into paints that can be applied by conventional methods.

In order to utilize the fluorocarbon segments as chemical barriers without losing adhesive strength to the primer-coated surface, we designed our fluoropolymers as illustrated in Figure-2.

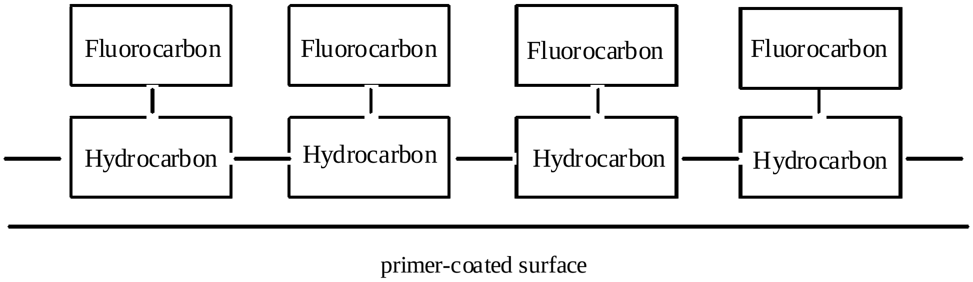


Figure-2 Illustration of Exfluor fluoropolymer

In this design, fluorocarbon segments locate on top of hydrocarbon segments. Our approach was to develop new fluorinated diol monomers that have branching perfluoroalkyl groups. Since fluorine atoms are fully surrounded by electrons, perfluoroalkyl groups generally have a tendency to repel each other. The pendant perfluoroalkyl groups, when present in a polymer made from a perfluoroalkyl-branched diols, are, therefore, likely to arrange themselves in the position vertical to the polymer backbone rather than crisscrossing each other. When the polymers are formulated into paint and applied on a primer-coated surface, the branching perfluoroalkyl groups (fluorocarbon segments) should form a protective layer between the painted surface and atmosphere.

During Phase I, we synthesized two novel monomers, 2-fluoro-2-perfluorooctyl-1,3-propanediol and 2-fluoro-2-perfluoro(2-ethylhexyl)-1,3-propanediol, and demonstrated that polymers containing branching perfluoroalkyl groups can be successfully synthesized. The synthesis of additional 1,3-propanediols, which contain short, long and more highly branched perfluoroalkyl groups, was planned for Phase II to study the steric effect of the perfluoroalkyl groups. All the 1,3-propanediols prepared in Phase II were to be made in sufficient quantities (3 to 5 Kg) to facilitate further studies.

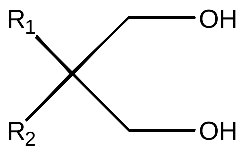
In addition to the 1,3-propanediols, two branched perfluoroalkyl methanols, perfluoro-1H,1H-2-ethylhexanol (pefluoro-1-ethylpentyl methanol) and perfluoro-1H,1H-2,2-dimethylpropanol (perfluoro-t-butyl methanol), were proposed as precursors for new thermosetting acrylic polymers.

Using the above fluorinated monomers, synthesis of three different types of polymers, polyols, polyacrylates and polyesters, were proposed initially. However, some modifications were made to better compliment the ongoing research activities at the Air Force, which were discussed during the mid-term Technical Meeting. The list of fluorinated polyester polymers was expanded to include aliphatic polyesters. Synthesis of the polyacrylate polymers was removed from the task list.

Formulation of the polyol polymers into polyurethane coatings as well as limited performance studies of the formulated polyurethanes were proposed for Phase II. However, the phase II contract was amended near the end of the contract to enable additional time to be spent on the preparation of additional polyol and polyester samples with the Air Force carrying out the performance studies. This shift in effort was considered advantageous to both Exfluor and the Air Force. Exfluor does not have adequate facilities and experience to do formulation and performance studies. Meanwhile, the additional polymer samples are more useful to AFRL/MLBT than the painted panels for the in-house coatings research programs.

2. Synthesis of perfluoroalkyl-branched 1,3-propanediol

Eight perfluoroalkyl-branched 1,3-propanediols, including the two previously prepared diols (EXF-2 and EXF-3), were proposed as shown in Figure-3.



EXF-1 $R_1 = F, R_2 = CF_3CF_2CF_2CF_2-$

EXF-2 $R_1 = F, R_2 = CF_3(CF_2)_6CF_2-$

EXF-3 $R_1 = F, R_2 = CF_3CF_2CF_2CF_2\underset{CF_2CF_3}{\underset{|}{C}}FCF_2-$

EXF-4 $R_1 = F, R_2 = CF_3\underset{CF_3}{\underset{|}{C}}FCF_2CF_2CF_2\underset{CF_3}{\underset{|}{C}}FCF_2CF_2-$

EXF-5 $R_1 = F, R_2 = CF_3(CF_2)_{10}CF_2-$

EXF-6 $R_1 = F, R_2 = CF_3(CF_2)_6CF_2\underset{CF_3(CF_2)_4CF_2}{\underset{|}{C}}FCF_2-$

EXF-7 $R_1 = R_2 = CF_3(CF_2)_6CF_2-$

EXF-8 $R_1 = R_2 = CF_3CF_2CF_2CF_2\underset{CF_2CF_3}{\underset{|}{C}}FCF_2-$

Figure-3 Proposed perfluoroalkyl-branched 1,3-propanediols

A general synthetic procedure was established during Phase I (Figure-4). The procedure was further improved for scale-up during Phase II. First, alcohols were converted to the corresponding bromides by hydrobromic acid in the presence of phase transfer catalysts. The bromides were then reacted with diethyl malonate under phase transfer conditions. The alkyl-substituted diethyl malonates were fluorinated by elemental fluorine to give corresponding perfluorinated malonates. Reduction of the perfluorinated malonates gave the perfluoroalkyl-branched 1,3-propanediols.

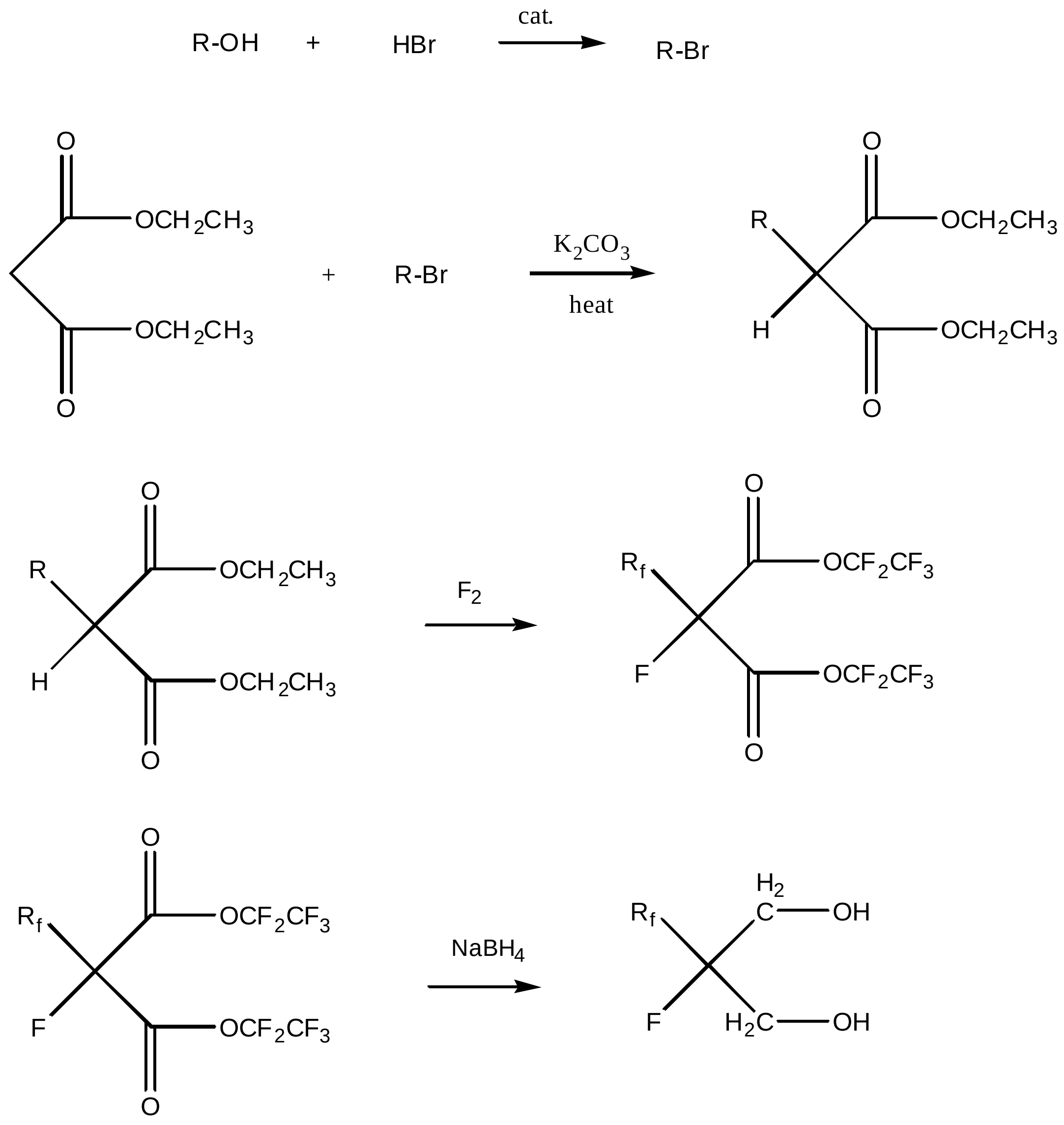


Figure-4 Synthetic procedure for perfluoroalkyl-branched 1,3-propanediols

2.1. Materials

Butanol, octanol, 2-ethylhexanol, 3,7-dimethyloctanol, dodecanol, and 2-hexyldecanol were purchased from various chemical companies and used without further purification. Diethyl malonate and hydrobromic acid were purchased from Penta Manufacturing Company and TemTex Solvents respectively. An extra fine grade potassium carbonate was purchased from Armand Products Company.

2.2. Equipment

2.2.1. Fluorination

One of the most important steps is the fluorination of the alkyl-substituted malonic esters using elemental fluorine, a technology developed by Exfluor. A typical fluorination system is illustrated in U.S.Pat. 5,093,432, 1992 . The process is unique in that there is complete retention of the original hydrocarbon structure. The level of residual hydrogens after fluorination is usually very low.

2.2.2. Reduction of perfluoroesters

During Phase II, we developed a relatively large reactor system for this step. A 30-gallon HDPE reactor, equipped with an explosion-proof stirrer and a drain valve at the bottom, was built as a primary reactor to conduct the sodium borohydride reductions. An internal cooling coil made of ½-inch copper tubing was placed along the reactor wall. Since the crude reduction mixtures need to be washed thoroughly with warm hydrochloric acid to obtain maximum yields, we also built a 30-gallon stainless steel reactor, equipped with an external heating system and a high-speed explosion proof stirrer, as a secondary reactor. With this reaction system, we were capable of reducing up to 30 kg of perfluoroesters in one reaction.

2.3. Synthesis of 2-fluoro-2-perfluorobutyl-1,3-propanediol (EXF-1)

2.3.1. Butyl bromide

Butanol (mw = 74) 3200 g (43.2 mole), 48% hydrobromic acid 15300 g (90.7mole) and tetrabutylammonium bromide 70 g (0.216 mole) were mixed in a 22-liter three-neck flask equipped with a mechanical stirrer and a reflux condenser. The mixture was gently refluxed for 24 hours. After the mixture was cooled to room temperature, the organic layer was separated and washed with a saturated sodium chloride solution. The crude product was distilled under vacuum to give pure butylbromide 5149 g (87% yield). The reaction was repeated once more to get additional 5200 g of the bromide.

2.3.2. Diethyl butylmalonate

In a 22-liter three-neck flask equipped with a powerful mechanical stirrer and a reflux condenser, butylbromide 3014 g (22.0 mole), diethyl malonate 3520 g (22.0 mole) and benzyltriethylammonium chloride (30 g) were mixed and heated to 110 °C. Potassium carbonate (extra fine powder form) 1518 g (11.0 mole) was added to the mixture with vigorous stirring. After 6 hours, additional potassium carbonate 1518 g (11.0 mole) was added to the mixture. The mixture was stirred at 110 °C for another 6 hours. The reaction mixture was cooled to room temperature and inorganic salts were removed by filtration. The filtrate was fractionated to give diethyl butylmalonate 3089 g (65% yield).

2.3.3. 2-Fluoro-2-perfluorobutyl-1,3-propanediol

Diethyl butylmalonate (mw=216) 6000 g (27.8 mole) was fluorinated in a fluorocarbon solvent. Sodium borohydride 2110 g (55.6 mole) and dimethoxyethane (8 gallons) were mixed in the HDPE reactor. The fluorinated mixture was added to the borohydride solution through a metering pump. The reaction temperature was kept between 30 °C and 45 °C during the addition. The mixture was stirred for two additional hours upon completion of the addition. The reduction mixture was removed through a valve located at the bottom of the reactor and carefully added to a stirred mixture of water (14 gallons) and concentrated hydrochloric acid (2 gallons) in the stainless steel reactor. The lower organic phase was isolated and distilled at atmospheric pressure to remove the solvent. The crude product was then distilled under vacuum to give 4850 g (56% yield based on the amount of diethyl butylmalonate) of a slightly yellow product (bp 110 °C at 5 mmHg). The product was allowed to melt in a 5-liter round bottom flask and slowly poured into a vigorously stirred solution of toluene in an ice bath. The mixture was cooled to room temperature and white solids were isolated by vacuum filtration. It was found that the product, obtained after the crystallization in toluene, was better than 98% pure and no longer had the slight yellow color.

2.4. Synthesis of 2-fluoro-2-perfluorooctyl-1,3-propanediol (EXF-2)

2.4.1. Octylbromide

Octanol (mw = 130) 5200 g (40.0 mole), 48% hydrobromic acid 14200 g (84.0mole) and tetrabutylammonium bromide 64 g (0.20 mole) were mixed in a 22-liter three-neck flask equipped with a mechanical stirrer and a reflux condenser. The mixture was gently refluxed for 24 hours. After the mixture was cooled to room temperature, the organic layer was separated and washed with a saturated sodium chloride solution. The crude product was distilled under vacuum to give pure octylbromide 6790 g (88% yield). The reaction was repeated once more to get additional 6500 g of the bromide.

2.4.2. Diethyl octylmalonate

In a 22-liter three-neck flask equipped with a powerful mechanical stirrer and a reflux condenser, octylbromide 4250 g (22.0 mole), diethyl malonate 3520 g (22.0 mole) and benzyltriethylammonium chloride (30 g) were mixed and heated to 110 °C. Potassium carbonate (extra fine powder form) 1520 g (11.0 mole) was added to the mixture with vigorous stirring. After 6 hours, an additional potassium carbonate 1520 g (11.0 mole) was added to the mixture. The mixture was stirred at 110 °C for another 6 hours. The reaction mixture was cooled to room temperature and the inorganic salts were removed by filtration. The filtrate was fractionated to give diethyl octylmalonate 3430 g (60% yield). The distillation residue (858 g) was mainly diethyl dioctylmalonate. The reaction was repeated twice more to get a total of about 10 kg.

2.4.3. 2-Fluoro-2-perfluorooctyl-1,3-propanediol

Diethyl octylmalonate (mw=260) 5000 g (19.2 mole) was fluorinated in a fluorocarbon solvent. Sodium borohydride 1760 g (46.2 mole) and dimethoxyethane (8 gallons) were mixed in the HDPE reactor. The fluorinated mixture was added to the borohydride solution through a metering pump. The reaction temperature was kept between 30 °C and 45 °C during the addition. The mixture was stirred for two additional hours upon completion of the addition. The reduction mixture was removed through the valve located at the bottom of the reactor and carefully added to a stirred mixture of water (14 gallons) and concentrated hydrochloric acid (1.5 gallons) in the stainless steel reactor. The lower organic phase was separated. Solvents were distilled off under atmospheric pressure. The crude product was then distilled under vacuum to give 5700 g (58% yield based on the amount of diethyl octylmalonate) of a slightly yellow product. Bp 165-166 °C at 28 mmHg. The product was purified using the toluene recrystallization method developed for 2-fluoro-2-perfluorobutyl-1,3-propanediol. The mixture was cooled to room temperature and white solids were isolated by vacuum filtration. The pure diol had a melting point of 145-146 °C

2.5. Synthesis of 2-fluoro-2-perfluoro(2-ethylhexyl)-1,3-propanediol (EXF-3)

2.5.1. 2-Ethylhexyl bromide

2-Ethylhexanol (mw = 130) 5200 g (40.0 mole), 48% hydrobromic acid 14200 g (84.0mole) and tetrabutylammonium bromide 64 g (0.20 mole) were mixed in a 22-liter three-neck flask equipped with a mechanical stirrer and a reflux condenser. The mixture was gently refluxed for 24 hours. After the mixture was cooled to room temperature, the organic layer was separated and washed with a saturated sodium chloride solution. The crude product was distilled under vacuum to give pure 2-ethylhexyl bromide 6950 g (90% yield). Boiling point : 75-77 °C/16 mmHg.

2.5.2. Diethyl 2-ethylhexylmalonate

In a 22-liter three-neck flask equipped with a powerful mechanical stirrer and a reflux condenser, 2-ethylhexyl bromide 3470 g (18.0 mole), diethyl malonate 2880 g (18.0 mole) and benzyltriethylammonium chloride (25 g) were mixed and heated to 110 °C. Potassium carbonate (extra fine powder form) 1240 g (9.0 mole) was added to the mixture with vigorous stirring. After 12 hours, an additional potassium carbonate 1240 g (9.0 mole) was added to the mixture. The mixture was stirred at 130 °C for another 12 hours. The reaction mixture was cooled to room temperature and inorganic salts were removed by filtration. The filtrate was fractionated to give diethyl 2-ethylhexylmalonate 2570 g (55% yield). It was found that the reaction was significantly slower than those of butyl and octyl bromides due to the steric hindrance. The reaction was repeated twice more to get a total of about 5 kg. Boiling point : 122 °C/0.5 mmHg.

2.5.3. 2-Fluoro-2-perfluoro(2-ethylhexyl)-1,3-propanediol

Diethyl 2-ethylhexylmalonate (mw=260) 5000 g (19.2 mole) was fluorinated in the usual manner. Sodium borohydride 1760 g (46.2 mole) and dimethoxyethane (8 gallons) were mixed in the HDPE reactor. The fluorinated mixture was added to the borohydride solution through a metering pump. The reaction temperature was kept between 30 °C and 45 °C during the addition. The mixture was stirred for two additional hours upon completion of the addition. The reduction mixture was removed through the valve located at the bottom of the reactor and carefully added to a stirred mixture of water (14 gallons) and concentrated hydrochloric acid (1.5 gallons) in the stainless steel reactor. The lower organic phase was distilled at atmospheric pressure to remove the solvents. The crude product was then distilled under vacuum to give 4920 g (50% yield based on the amount of diethyl 2-ethylhexylmalonate) of a slightly yellow product (bp 120 °C at 0.5 mmHg). Crystallization of the crude product in toluene gave a white solid having a purity of 97% by G.C. and a melting point of 95-98 °C.

2.6. Synthesis of 2-fluoro-2-perfluoro(3,7-dimethyloctyl)-1,3-propanediol (EXF-4)

2.6.1. 3,7-Dimethyloctyl bromide

3,7-Dimethyl-1-octanol ($C_{10}H_{22}O$ = 158) 1632 g (10.3 mole), 48% HBr 3486 g (20.6 mole), tetrabutylammonium bromide (20 g) were mixed and heated to gentle reflux with stirring for 24 hrs. The two phases were separated. The upper organic phase, 2067 g, was dried under vacuum and analyzed with IR (because GC could not resolve the alcohol starting material and the bromide reaction product peaks). A large –OH absorption due to remaining alcohol was seen in the IR spectra. The product was poured back into the reactor. Additional 1181 g (7 mole) of 48% HBr and tetrabutylammonium bromide (10 g) were added to the reactor. The mixture was heated to 110 °C overnight with vigorous stirring. After the mixture was allowed to cool to room temperature, the organic phase was separated and dried under vacuum to give 2758 g of the product. The IR analysis spectra showed very small amount of –OH absorption, meaning that the conversion of the alcohol to the bromide nearly completed. This crude bromide was used for the next step without further purification.

2.6.2. Diethyl (3,7dimethyloctyl)malonate

3,7-Dimethyloctyl bromide (mw = 221) 2758 g (12.5 mole), diethyl malonate (160) 2396 g (15.0 mole), benzyltriethylammonium chloride (≈ 5 g) and potassium carbonate (138) 2067 g (15.0 mole) were mixed and heated to 120 °C with vigorous stirring overnight. The mixture was cooled and filtered to remove solids. The solids were washed with water. The upper organic phase was separated and combined with the filtrate. The combined product was washed with dilute hydrochloric acid. The product was distilled under vacuum using an Oldershaw column to remove excess diethyl malonate (b.p. 50 °C at 0.4 mmHg). The distillation column was then removed and the distillation was continued to give 2188 g (58% yield) of diethyl 3,7-dimethyloctylmalonate. B.p. 125 °C/0.4 mmHg.

2.6.3. 2-Fluoro-2-perfluoro(3,7-dimethyloctyl)-1,3-propanediol

Diethyl 3,7-dimethyloctylmalonate ($C_{17}H_{32}O_4$ = 300) 2170 g (7.23 mole) was fluorinated in a fluorocarbon solvent (5 gallons). The fluorinated mixture was added to a solution containing sodium borohydride 715 g (18.8 mole) and DME (6 gallons) at 30-45 °C. The reduction mixture was carefully poured into water (12 gallons) containing one gallon of concentrated hydrochloric acid. The lower organic phase was separated and washed again with warm water (12 gallons) containing one liter of concentrated hydrochloric acid. The solvents were removed by atmospheric distillation (allowed the bottom temperature to go up to 150 °C). The residue was distilled under vacuum to give

2210 g (50% yield from the hydrocarbon starting material) of the diol. Boiling point : 121-130 °C/0.4 mmHg

2.7. Synthesis of 2-fluoro-2-perfluorododecyl-1,3-propanediol (EXF-5)

2.7.1. Dodecyl bromide

Dodecyl alcohol ($C_{12}H_{26}O = 186$) 3000 g (16.1 mole), 48% HBr 5988 g (35.5 mole, 2.2 eq) and tetrabutylammonium bromide (mw = 322) 32.2 g (0.1 mole) were mixed in a three-neck 12-liter flask equipped with a mechanical stirrer. The mixture was heated to gentle reflux for 24 hrs. The mixture was cooled and the upper layer was separated. The crude product was then dried under vacuum (heated until a gentle reflux was observed). IR analysis of the product showed an –OH absorption due to the starting alcohol, so the product was poured back into the reactor and mixed with 1350 g (8 mole) of 48% HBr and tetrabutylammonium bromide (10 g). The mixture was heated to 100 °C with vigorous stirring overnight. After the completion of the reaction was confirmed by IR analysis, the product layer was separated and heated under vacuum until gentle refluxing was observed to give 3804 g (95% yield) of crude bromide. The crude bromide was used without further purification.

2.7.2. Diethyl dodecylmalonate

Dodecyl bromide (mw = 249) 3804 g (15.3 mole), diethyl malonate (160) 2933 g (18.3 mole), benzyltriethylammonium chloride (≈ 5 g) and potassium carbonate (138) 2553 g (18.5 mole) were mixed in a 22-liter flask. The mixture was heated to 120 °C with vigorous stirring overnight. The mixture was cooled and the solids were removed by filtration. The solids were dissolved in warm (approx. 50 °C) water (16 liters). There was a milky layer between the top organic layer and the bottom aqueous layer. The bottom layer was removed as much as possible. Dilute hydrochloric acid solution was added until the milky layer disappeared. The top organic layer was separated and combined with the filtrate. Fractional distillation gave pure diethyl dodecylmalonate 3260g (65% yield). Boiling point : 135-140 °C/0.5 mmHg.

2.7.3. 2-Fluoro-2-perfluorododecyl-1,3-propanediol

Diethyl dodecylmalonate ($C_{19}H_{36}O_4$ = 328) 2420 g (7.38 mole) was fluorinated in a fluorocarbon solvent (5 gallons) at 30 °C. The fluorinated mixture was added to a mixture of sodium borohydride 1120 g (29 mole) and DME (6 gallons). The reduction mixture was carefully added to water (15 gallons) containing one gallon of concentrated hydrochloric acid. A significant amount of solids precipitated during the hydrolysis. The solid products were isolated by filtration. The lower organic phase was separated and washed again with warm water (15 gallons). More solid products were obtained from the second wash. The solid products were dried in air and then recrystallized twice from isopropanol to give the diol 2360 g (45% yield). The product contained a significant amount (about 10%) of by-product, perfluoro-1H,1H-tetradecanol that was identified by Gas Chromatography using an authentic sample.

2.8. Synthesis of 2-fluoro-2-perfluoro(2-hexyldecyl)-1,3-propanediol (EXF-6)

2.8.1. 2-Hexyldecyl bromide

2-Hexyldecanol ($C_{16}H_{34}O = 242$) 3025 g (12.5 mole), 48% HBr 3164 g (18.65 mole, 1.5 eq) and tetrabutylammonium bromide 20 g were mixed in a 12-liter three-neck flask. The mixture was stirred for overnight at 90 °C and at 115 °C for 3 hrs. A sample was taken and analyzed with IR. The IR spectra showed –OH absorption, which was about 20% of the original intensity. The mixture was heated to 115 °C for 24 more hours. A sample was taken and analyzed again with IR. The –OH absorption was smaller (about 10% of the original intensity). The mixture was cooled and the organic layer was separated. The aqueous phase was discarded. The organic layer was poured back into the reactor and mixed with 48% HBr 1063 g (6.3 mole) and tetrabutylammonium bromide (10 g). The mixture was heated to 100 °C with vigorous stirring for overnight. The IR spectra showed a big improvement showing very small –OH absorption. The product was heated (100 °C) under vacuum to give 3540 g (93% yield) of dry crude bromide. The crude bromide was used without further purification.

2.8.2. Diethyl 2-hexyldecylmalonate

2-Hexyldecylbromide ($C_{16}H_{33}Br = 305$) 3540 g (11.6 mole), diethyl malonate 2231 g (13.9 mole), benzyltriethylammonium chloride (≈ 5 g) were mixed in a 22-liter flask. Potassium carbonate 1932 g (14.0 mole) was added to the mixture, which was then heated to 120 °C with vigorous stirring. Temperature went up to 135 °C due to an exothermic reaction, then after about 1.5 hr, slowly came back down to 124 °C. The reaction was allowed to continue overnight at 124 °C. After the reaction mixture was cooled, the top organic layer was decanted off as much as possible. Water (8 liters) was added to the residual portion to dissolve solids. The top organic layer was separated and combined with the decanted portion. The product was dried over magnesium sulfate and then distilled under vacuum to give 2320 g (52% yield) of the malonate. Boiling point : 158 °C/0.6 mmHg.

2.8.3. 2-Fluoro-2-perfluoro(2-hexyldecyl)-1,3-propanediol

Diethyl 2-hexyldecylmalonate ($C_{23}H_{44}O_4$ = 384) 2320 g (6.05 mole) was fluorinated in a fluorocarbon solvent (5 gallons) at 30 °C. It was observed that the fluorination did not proceed as usual. Since the fluorination did not proceed smoothly, the temperature was raised to 40 °C toward the end to assure complete fluorination. The fluorinated mixture was added to a mixture of sodium borohydride 690 g (18.1 mole) and DME (6 gallons). The reduction mixture was carefully poured into a mixture of water (15 gallons) and concentrated hydrochloric acid (3 liters). The organic phase was separated and washed with warm water (2 gallons). GC analysis of the crude product showed no major peaks. An attempt was made to distill the product under vacuum but it was stopped when the product started to decompose during the distillation. No further effort was made to obtain this highly branched diol.

2.9. Synthesis of 2,2-bis(perfluorooctyl)-1,3-propanediol (EXF-7)

2.9.1. Diethyl dioctylmalonate

Alkylation of malonic esters usually gives a mixture of mono- and di- alkyl substituted malonic esters. It was assumed that the distillation residue obtained from the preparation of diethyl octylmalonate (see section 2.4.2.) should contain some diethyl dioctylmalonate. Since diethyl dioctylmalonate was expected to have very high boiling point, no attempt was made to further purify the compound.

2.9.2. 2,2-Bis(perfluorooctyl)-1,3-propanediol

The crude diethyl dioctylmalonate (2.25 kg) was fluorinated in a fluorocarbon solvent (4 gallons) at 30 °C. The fluorinated mixture was added to a solution containing sodium borohydride 670 g (17.6 mole) and DME (6 gallons) through a metering pump. The rate of the addition was adjusted so that the reaction temperature gradually increased from 30 °C to 45 °C at the end. The reduction mixture was carefully poured into water (15 gallons) containing 3 liters of concentrated hydrochloric acid. Solid products precipitated during the hydrolysis. The solid products were isolated by filtration. The lower organic phase was separated and washed again with warm (50 °C) dilute hydrochloric acid (15 gallons). More solid products were obtained after the second wash. When the organic layer was separated and allowed to cool to room temperature, it turned to a semi-solid. The semi-solid product was mixed with isopropanol (2 liters) and insoluble solids were isolated by filtration. All the solid products were combined and recrystallized from isopropanol to give a compound thought to be 2,2-bis(perfluorooctyl)-1,3-propanediol (500 g). Melting point : 159-160 °C. It was >98% pure by GC analysis. The ^{19}F NMR and mass spectra of the compound, however, did not support the structure (see Analytical Section for details). The ^{19}F NMR spectra was exactly the same as the spectra of EXF-2, while the mass spectra had a base peak at 1025, which indicated that the product was a dimer of EXF-2. More work will be necessary to identify the product.

2.10. Synthesis of 2,2-bis{perfluoro(2-ethylhexyl)}-1,3-propanediol (EXF-8)

2.10.1. Diethyl di(2-ethylhexyl)malonate

As in the case of diethyl dioctylmalonate above, the distillation residue from the preparation of diethyl 2-ethylhexylmalonate was assumed to contain some diethyl di(2-ethylhexyl)malonate and it was used without further purification.

2.10.2. 2,2-Bis{(perfluoro(2-ethylhexyl))-1,3-propanediol

The distillation residue described above, 2740 g, was fluorinated in 4 gallons of a fluorocarbon solvent at 30°C. The fluorinated mixture was added to a mixture of sodium borohydride 650 g (17 mole) and DME (6 gallons) at 30-45 °C. The reduction mixture was then carefully poured into a mixture of water (15 gallons) and concentrated hydrochloric acid (3 liters). The lower organic phase was separated and washed again with dilute hydrochloric acid (15 gallons). The organic phase was separated and the solvents were removed under vacuum to give a dark brown viscous oil. The gas chromatograph of the oily product showed no major peaks. No further attempts were made to synthesize the compound.

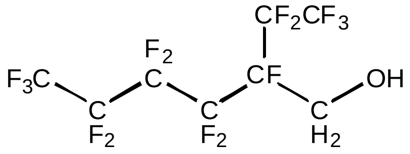
2.11. Discussions

The general procedure that we have developed for the synthesis of the hydrocarbon starting materials is economical and can be easily scaled up. Compared to conventional procedures for the alkylation step, which typically use sodium metal or sodium/potassium alkoxides in strictly anhydrous solvents, the method we chose is also safer because it uses a mild base (potassium carbonate) and it does not require any solvents (anhydrous organic solvents that are used for conventional procedures are usually extremely flammable). The extra-fine grade potassium carbonate by Armand Products had a much higher reactivity than usual reagent grade potassium carbonate.

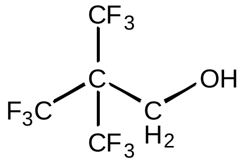
The fluorination and reduction steps gave overall yields of approximately 50%. Both steps need to be optimized to improve the yields. During Phase II we could not synthesize highly sterically hindered diols (EXF-6 and EXF-8). The structure of EXF-7 is also questionable. Since we did not confirm the structures before fluorination, it is possible that the hydrocarbon starting materials for those compounds were not the right compounds. Or, there may be a limit on how sterically hindered perfluoroalkyl group(s) one can introduce at the 2-position of 1,3-propanediol. Introducing one perfluoro-2-hexyldecyl group or two perfluoro-2-ethylhexyl groups into the three-carbon scheme of 1,3-propanediol might have been too difficult due to their steric hindrance.

3. Synthesis of branched perfluoroalkyl methanols

The synthesis of two mono-functional fluorinated alcohols, perfluoro-1H,1H-2-ethylhexanol (pefluoro-1-ethylpentyl methanol) and perfluoro-1H,1H-2,2-dimethylpropanol (perfluoro-t-butyl methanol), was proposed.



Perfluoro-1H,1H-2-ethylhexanol

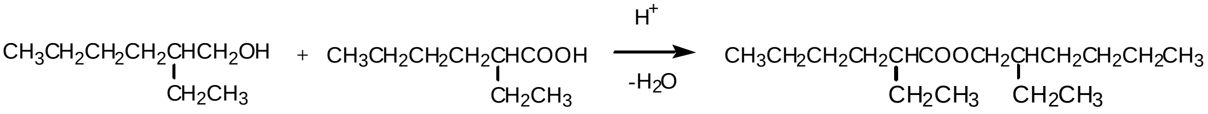


Perfluoro-1H,1H-2,2-dimethylpropanol

These fluorinated branched alcohols were proposed to develop new acrylic polymers. The branched structure was expected to provide chemical and hydrolytic stabilities for acrylic polymers, which are generally less stable than other types of polymers.

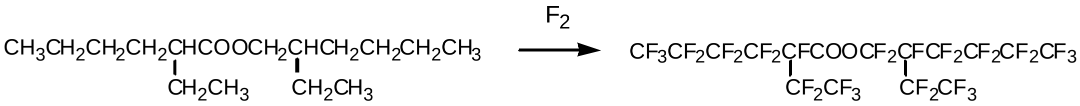
3.1. Synthesis of perfluoro-1H,1H-2-ethylhexanol

We chose 2-ethylhexyl 2-ethylhexanoate as starting hydrocarbon to synthesize perfluoro-1H,1H-2-ethylhexanol.

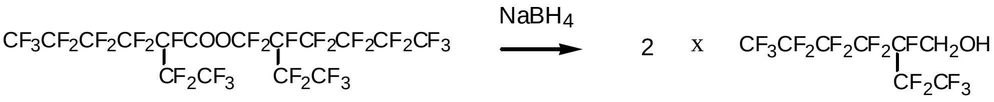


$$CH_3CH_2CH_2CH_2\underset{CH_2CH_3}{\underset{|}{C}}HCH_2OH + CH_3CH_2CH_2CH_2\underset{CH_2CH_3}{\underset{|}{C}}HCOOH \xrightarrow[-H_2O]{H^+} CH_3CH_2CH_2CH_2\underset{CH_2CH_3}{\underset{|}{C}}HCOOCH_2\underset{CH_2CH_3}{\underset{|}{C}}HCH_2CH_2CH_2CH_3$$

Fluorination of the ester followed by reduction with sodium borohydride gave desired branched alcohol in good yield.



$$CH_3CH_2CH_2CH_2\underset{CH_2CH_3}{\underset{|}{C}}HCOOCH_2\underset{CH_2CH_3}{\underset{|}{C}}HCH_2CH_2CH_2CH_3 \xrightarrow{F_2} CF_3CF_2CF_2CF_2\underset{CF_2CF_3}{\underset{|}{C}}FCOOCF_2\underset{CF_2CF_3}{\underset{|}{C}}FCF_2CF_2CF_2CF_3$$



$$CF_3CF_2CF_2CF_2\underset{CF_2CF_3}{\underset{|}{C}}FCOOCF_2\underset{CF_2CF_3}{\underset{|}{C}}FCF_2CF_2CF_2CF_3 \xrightarrow{NaBH_4} 2 \times CF_3CF_2CF_2CF_2\underset{CF_2CF_3}{\underset{|}{C}}FCH_2OH$$

3.1.1. 2-Ethylhexyl 2-ethylhexanoate

In a Typical reaction, 2-ethylhexanol 6500 g (50 mole), 2-ethylhexanoic acid 7200 g (50 mole), toluene (3 liters) and p-toluenesulfonic acid (5 g) were mixed in a 22-liter flask. A water separator was attached to the flask and the mixture was gently refluxed for 24 hours. Water generated was removed continuously during the reaction.

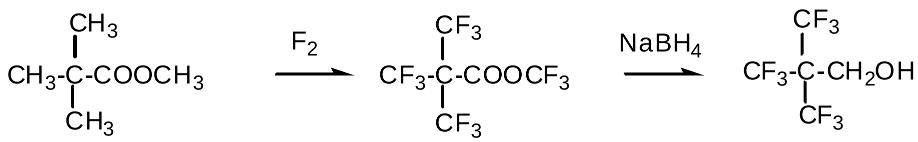
The reaction mixture was cooled to room temperature and neutralized with sodium bicarbonate. Solids were removed by filtration and toluene was removed under vacuum to give a light brown product 12,500 g (98% yield).

3.1.2. Perfluoro-1H,1H-2-ethylhexanol

2-Ethylhexyl 2-ethylhexanoate 7700 g (30 mole) was fluorinated in a fluorocarbon solvent. Sodium borohydride 1540 g (40.6 mole) and dimethoxymethane (8 gallons) were mixed in the 30-gallon HDPE reactor. The fluorinated mixture was slowly added to the hydride mixture using a metering pump. The reaction temperature was controlled between 30°C and 35°C. All of the fluorinated mixture was added within four hours. Upon completion of the addition, the mixture was carefully hydrolyzed with dilute hydrochloric acid. A crude product mixture, which formed at the bottom of the reactor, was separated and transferred to the stainless steel reactor. About 20 gallons of dilute hydrochloric acid was added and the mixture was heated to 50°C. After the mixture was vigorously stirred for 30 minutes, the crude product was separated and fractionated by distillation to give 14,000 g (58% yield from the hydrocarbon ester) of pure perfluoro-1H,1H-2-ethylhexanol. Boiling point : 153 °C

3.2. Synthesis of perfluoro-1H,1H-2,2-dimethylpropanol

Methyl 2,2-dimethylpropionate was purchased from Aldrich and used without further purification. The ester was fluorinated and reduced with sodium borohydride.



$$(CH_3)_3C\text{-}COOCH_3 \xrightarrow{F_2} (CF_3)_3C\text{-}COOCF_3 \xrightarrow{NaBH_4} (CF_3)_3C\text{-}CH_2OH$$

3.2.1. Perfluoro-1H,1H-2,2-dimethylpropanol

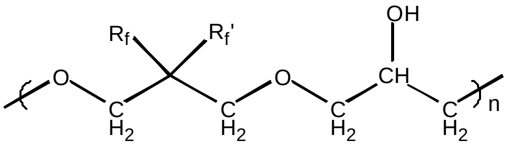
Methyl 2,2-dimethylpropionate ($C_6H_{12}O_2 = 116$) 2000 g (17.2 mole) was fluorinated in a fluorocarbon solvent. The fluorinated mixture was fractionated using a 15-plate Oldershaw column to separate the product from the fluorocarbon solvent. A fraction between 50 °C and 100 °C was collected (1235 g). The crude product was added carefully to a mixture of dimethoxyethane (2 liter) and sodium borohydride 293 g (7.72 mole). The reaction temperature was kept between 40 and 45 °C. After the mixture was stirred for two hours, it was poured into water (2 gallons) containing some ice and concentrated hydrochloric acid (1 liter) with vigorous stirring. The lower organic phase was separated and washed again with dilute hydrochloric acid. The organic layer was dried over magnesium sulfate and fractionated using a 15-plate Oldershaw column to give a semi-solid product, which had a boiling point of 70-75 °C. This product was found to contain some dimethoxyethane as well as other unknown by-products. The purity of the product was only about 85%.

3.3 Discussions

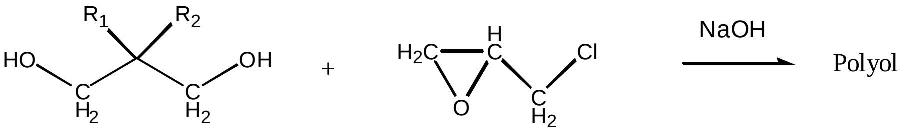
The procedure for Perfluoro-1H,1H-2-ethylhexanol was well established. We are confident that this branched perfluoroalkylmethanol can be prepared in large quantities if the demand arises. On the other hand, the preparation of pure perfluoro-1H,1H-2,2-dimethylpropanol was unsuccessful. We feel that we can synthesize this unique alcohol more successfully in the future by choosing an adequate starting material and by modifying the fluorination conditions.

4.1. Synthesis of fluorinated polyols

Structure of the proposed fluorinated polyols is shown below.

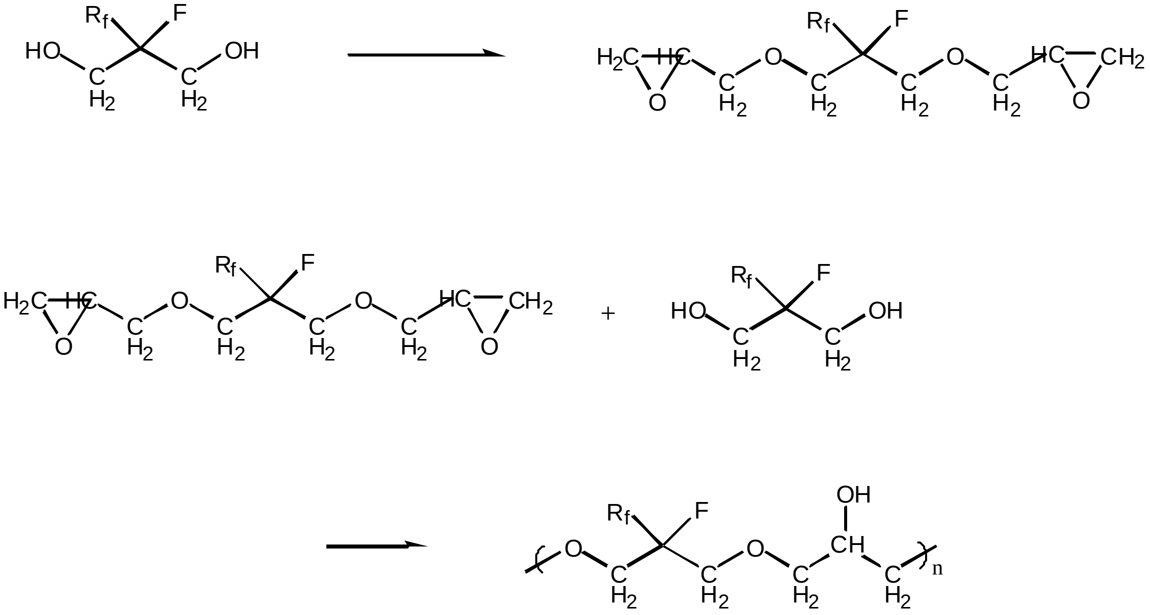


This type of polyol is typically synthesized by reacting a diol with stoicheometric amount of epichlorohydrin and sodium hydroxide.

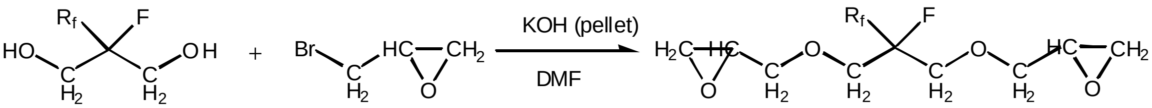


However, this method did not work for the perfluoroalkyl-branched 1,3-propanediols because of their poor reactivity. The fluorinated diols are relatively acidic due to the electron withdrawing perfluoroalkyl groups, hence they are weak nucleophiles. In addition, the bulky perfluoroalkyl groups are expected to keep the reactants away from the diols. As a result, the product was mainly poly(epichlorohydrin) and the majority of the diol did not react. Considering that linear fluorinated diols with the structure $HOCH_2(CF_2)_nCH_2OH$ have similar acidity and can be readily converted to the corresponding polyols in high yields by the above method, the steric hindrance of the branching perfluoroalkyl groups must be the major reason for the poor reactivity.

Our next approach was to first convert the fluorinated 1,3-propanediols to their glycidyl ethers and then react with the diols to prepare the polyols.

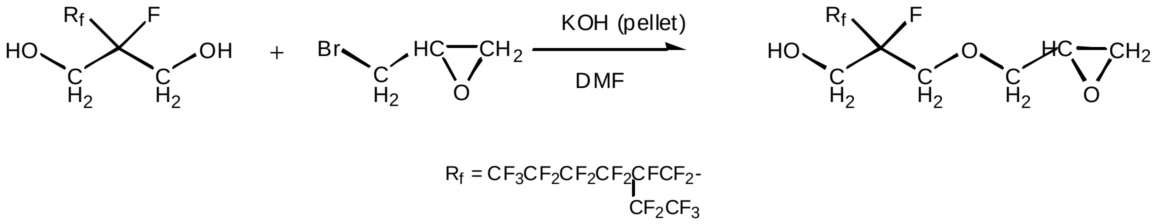


The two-step process should give the same structure of polyols. During Phase I, we found a method to prepare pure diglycidyl ether of 2-fluoro-2-perfluorooctyl-1,3-propanediol by using epibromohydrin and dimethyl formamide (DMF).

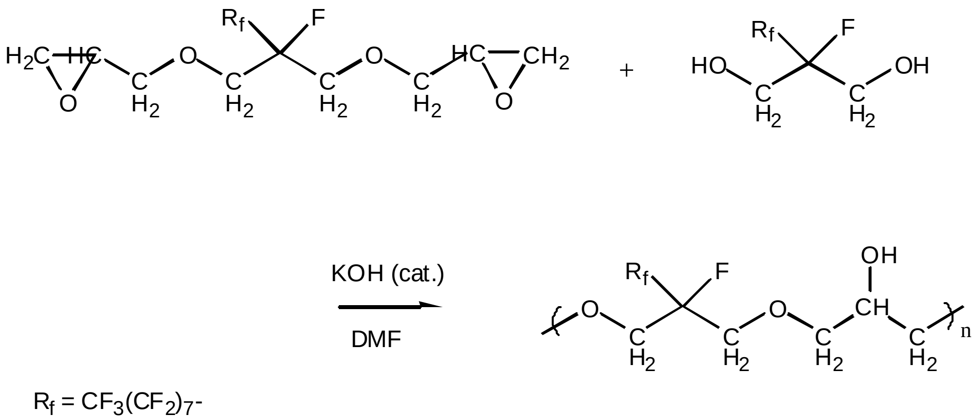


$R_f = CF_3(CF_2)_7$-

In case of more sterically hindered 2-fluoro-2-perfluoro(2-ethylhexyl)-1,3-propanediol, however, the reaction gave only monoglycidyl ether.

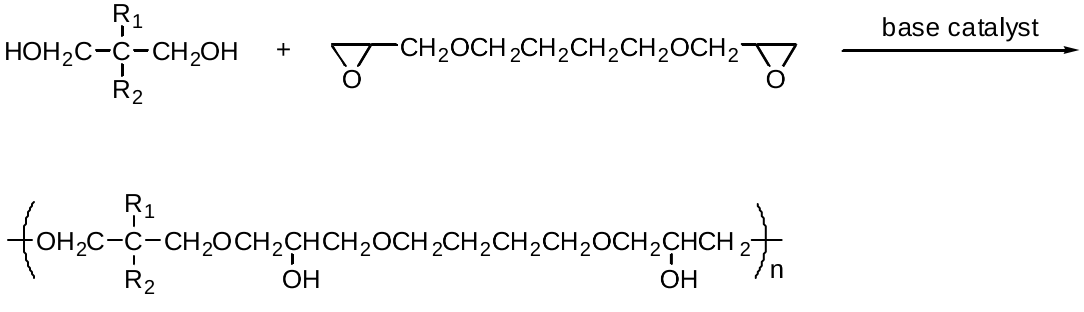


The reaction of 2-fluoro-2-perfluorooctyl-1,3-propanediol with its diglycidyl ether was investigated.



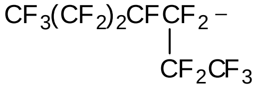
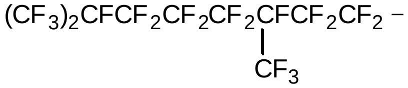
The polymerization did not proceed very well even in polar solvents such as dimethyl formamide or dimethyl sulfoxide. It was observed that the diglycidyl ether slowly decomposed into polymeric compounds and the diol remained unreacted.

We decided to modify the reaction scheme to ease the steric effect by using a commercially available hydrocarbon diglycidyl ether, 1,4-butanediol diglycidyl ether. In this case, the reaction proceeded smoothly to give polyol polymers in quantitative yield.



Using the six fluorinated diols, six different polyols were prepared. Lot numbers were assigned for each polyol and their physical appearances were summarized in Table-1.

Table-1 Fluorinated polyols

Lot #	**R_1**	**R_2**	**Physical Property**
AF1017	F-	$CF_3(CF_2)_2CF_2-$	Brown viscous oil
AF1018	F-	$CF_3(CF_2)_6CF_2-$	Yellow semi-solid
AF1019	F-	 $CF_3(CF_2)_2CF\underset{CF_2CF_3}{\underset{\vert}{C}}F_2-$	Dark brown viscous oil
AF1020	$CF_3(CF_2)_6CF_2-$	$CF_3(CF_2)_6CF_2-$	Light yellow semi-solid
AF1021	F-	 $(CF_3)_2CFCF_2CF_2CF_2\underset{CF_3}{\underset{\vert}{C}}FCF_2CF_2-$	Amber viscous oil
AF1022	F-	$CF_3(CF_2)_{10}CF_2-$	Light yellow solid

4.2. Experimental Section

Polyol AF1017. In a typical reaction, 1,4-butanediol diglycidyl ether (95% from Aldrich) 68g (0.32 mol), 2-fluoro-2-perfluorobutyl-1,3-propanediol 100g (0.32 mol) and 300 ml CTFE 0.8™ (obtained from Holocarbon, Inc.) solvent were stirred until solution turned homogeneous. Potassium hydroxide (45%) solution (2.7 g; 0.022 mol) was then added and the mixture was refluxed under nitrogen for three days. The product solution was cooled to room temperature. A small amount of solids were removed by filtration. The solvent was removed under vacuum to give a brown viscous product in quantitative yield.

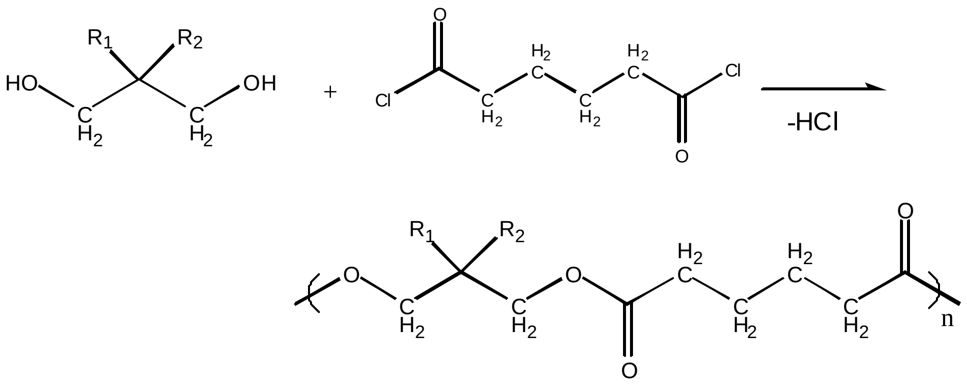
Polyols AF1018 ~ ***AF1022*** were prepared similarly.

4.3. Discussions

The steric effect of the branching perfluoroalkyl groups was unexpectedly large. We were able to prepare polyol polymers by using 1,4-butanediol diglycidyl ether, which was available from Aldrich Chemical Co. in 95% pure form. If required, it is possible to increase the fluorine content by using diglycidyl ether of fluorinated 1,4-butanediol, $HOCH_2CF_2CF_2CH_2OH$, which is available from Exfluor.

5. 1. Preparation of polyesters

Originally, we proposed to synthesize only aromatic polyesters. At the mid-term Technical Meeting, we agreed to synthesize both aliphatic and aromatic polyesters using adipoyl chloride and telephthaloyl chloride respectively.



Typical procedures used to synthesize polyesters did not work for the above polyesters. Since the fluorinated branched diols were much less reactive than typical hydrocarbon diols due to their steric hindrance and their acidity, the polymerization proceeded very slowly. We established a general procedure that works well for all the fluorinated branched diols. The procedure involved the use of fluorocarbon solvents having boiling points between 130 and 140 °C. The reaction proceeded in a well-controlled manner to completion within about five days at reflux for both aliphatic and aromatic polyesters. The results were summarized in Table-2.

Table-2 Fluorinated Polyesters

	EXF-diol	R	Dianhydride	Appearance at room temperature
AF1009	EXF-2	-C_6H_4-		White powder
AF1010	EXF-3	-C_6H_4-		Slightly yellow, very viscous oil
AF1011	EXF-2	-C_6H_4-	Added	White powder
AF1012	EXF-3	-C_6H_4-	Added	Slightly yellow, very viscous oil
AF1013	EXF-2	-$(CH_2)_4$-		Yellow semi-solid
AF1014	EXF-3	-$(CH_2)_4$-		Brown oil
AF1015	EXF-7	-C_6H_4-		White powder
AF1016	EXF-1	-C_6H_4-		Slightly yellow semi-solid

Pyromellitic dianhydride was added for the preparation of AF1011 and AF1012 to include some carboxylic acid functional groups as cross-linking sites.

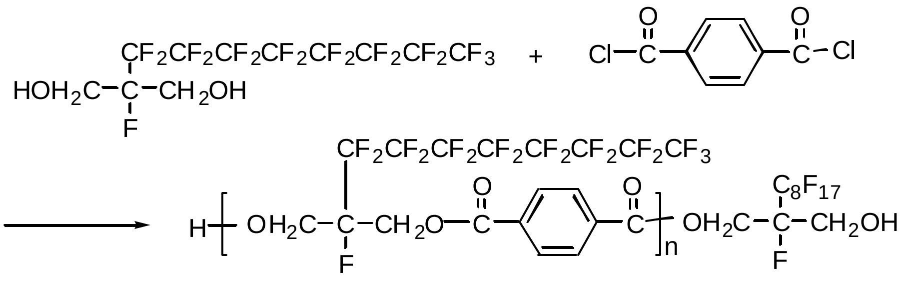
When the contract was amended, we synthesized more polyesters including both aliphatic and aromatic polyesters from 2-fluoro-2-perfluorododecyl-1,3-propanediol and 2-fluoro-2-perfluoro(3,7-dimethyloctyl)-1,3-propanediol along with aliphatic polyesters from 2-fluoro-2-perfluorobutyl-1,3-propanediol and 2,2-bis(perfluorooctyl)-1,3-propanediol. The results were summarized in Table-3.

Table-3 Additional Polyesters

	EXF-diol	R	Appearance at room temperature
AF1023	EXF-4	$-(CH_2)_4-$	Amber viscous oil
AF1024	EXF-4	$-C_6H_4-$	Light yellow semi-solid
AF1025	EXF-5	$-(CH_2)_4-$	Light brown powder
AF1026	EXF-5	$-C_6H_4-$	White powder
AF1027	EXF-1	$-(CH_2)_4-$	Amber viscous oil
AF1028	EXF-7	$-(CH_2)_4-$	Light gray powder

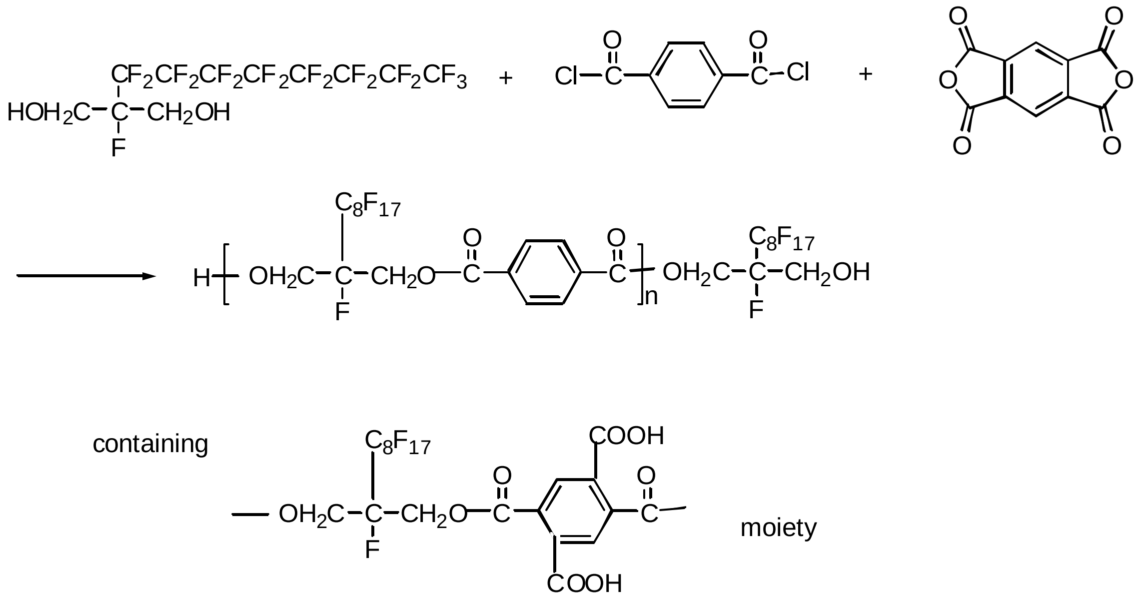
5.2. Experimental

<ins>Synthesis of Polyester of AF 1009.</ins>



Terephthaloyl chloride (36 g, 0.177 mol), 2-fluoro-2-perfluorooctyl-1,3-propanediol (100 g, 0.195 mol) and 300 ml of a fluorocarbon solvent were stirred at 140 °C for 5 days. During the reaction, an evolution of hydrogen chloride gas was observed. The reaction mixture was then cooled to room temperature (approximately 25 °C). Upon cooling, a precipitation of very fine white powder was observed. The white powder was isolated by filtration to give 130 g of the product. The yield was almost quantitative. The IR spectra of the product contained intense carbonyl absorption at 1738 cm^{-1}, which is characteristic for a fluorinated ester functional group.

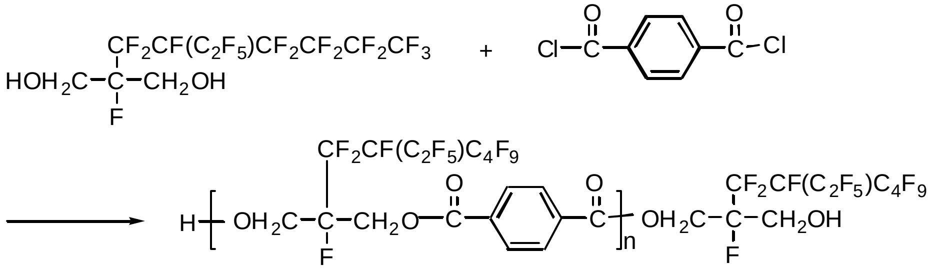
Synthesis of Polyester of AF 1011.



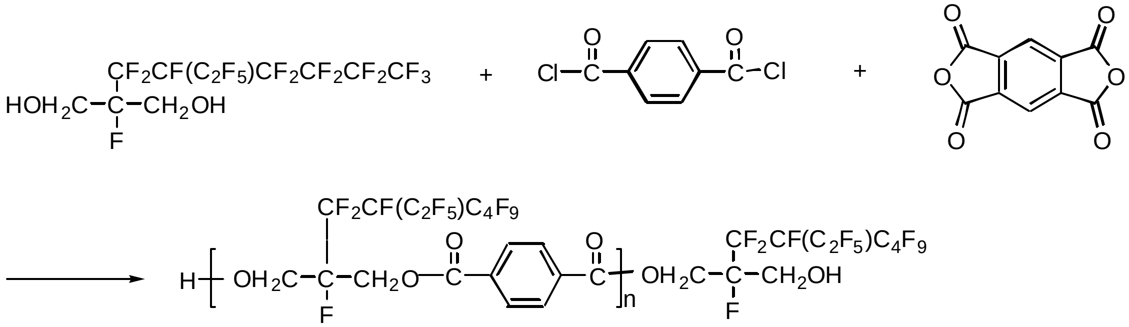
Terephthaloyl chloride (36 g, 0.177 mol), pyromellitic dianhydride (400 mg, 1 mol %), 2-fluoro-2-perfluorooctyl-1,3-propanediol (100 g, 0.195 mol) and 300 ml of a fluorocarbon solvent were stirred at 140 ^{o}C for 5 days. The reaction mixture was then cooled to room temperature. The product polymer (fine white powder, 132 g) was isolated by filtration and dried under vacuum. The addition of the dianhydride was to introduce some cross-linking sites.

Polyesters AF1010, AF 1012, AF 1013, AF 1014, AF 1015, AF 1016, AF1023, AF1024, AF1025, AF1026, AF1027 and AF1028 were prepared similarly by using the corresponding fluorinated branched diols. Liquid polymer samples were obtained by removing the fluorocarbon solvent under vacuum.

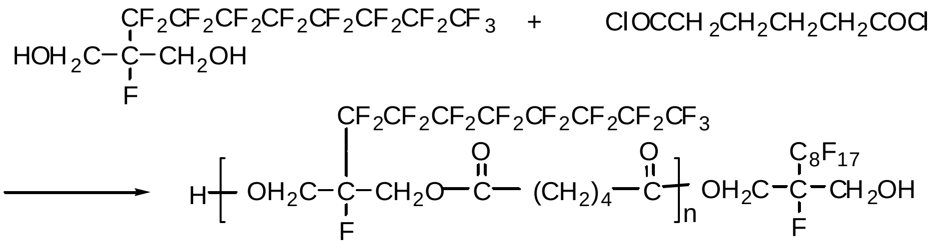
AF1010



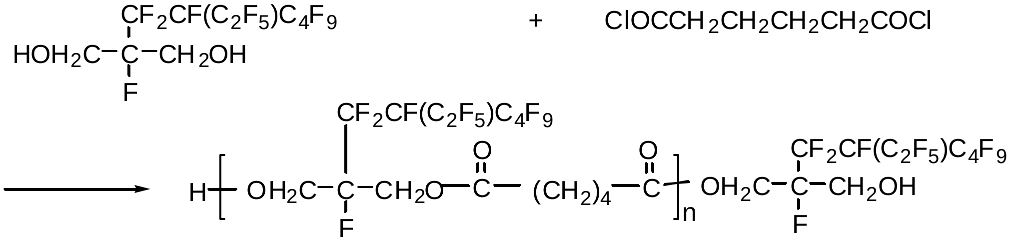
AF1012



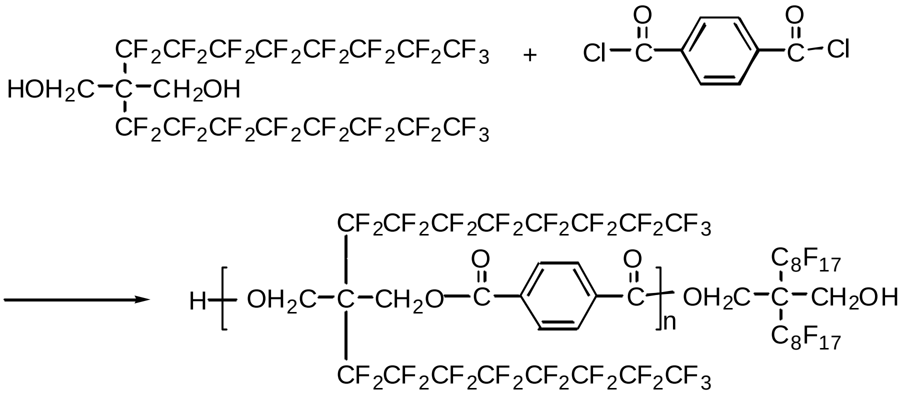
AF1013



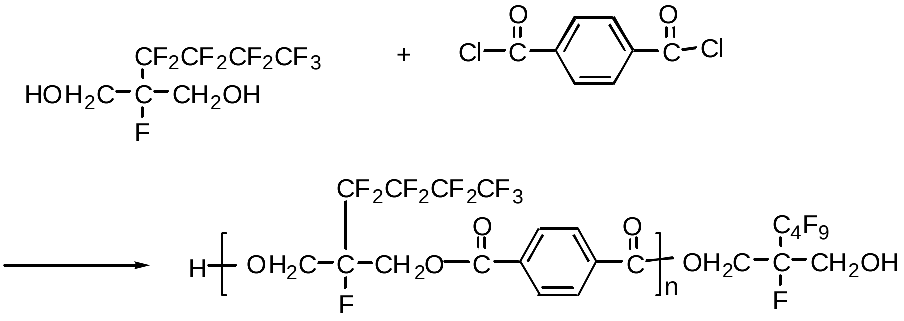
AF 1014



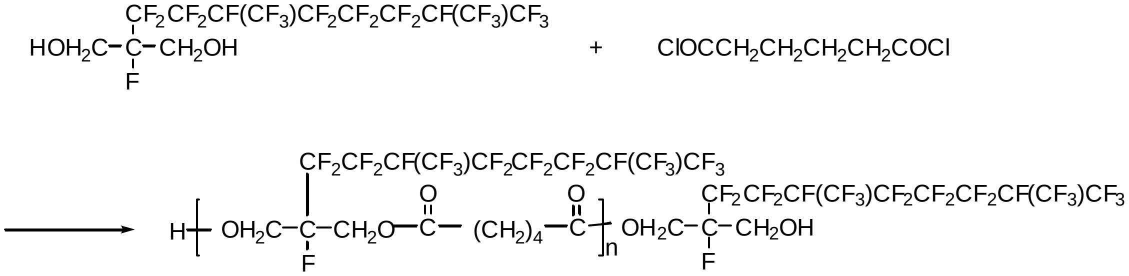
AF 1015



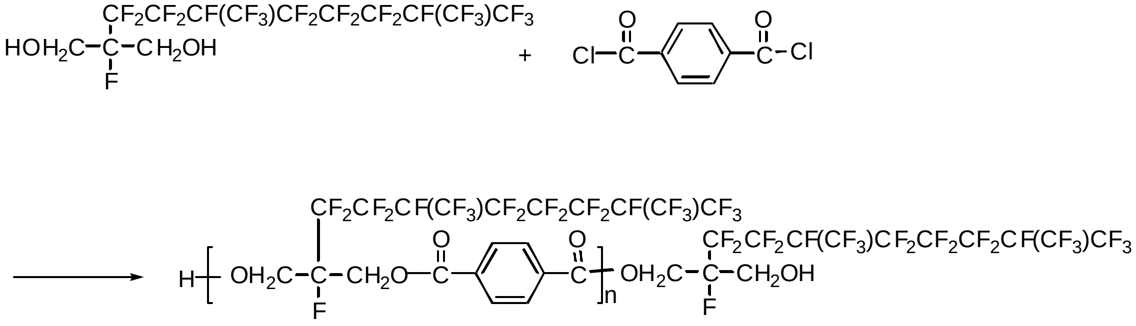
AF 1016



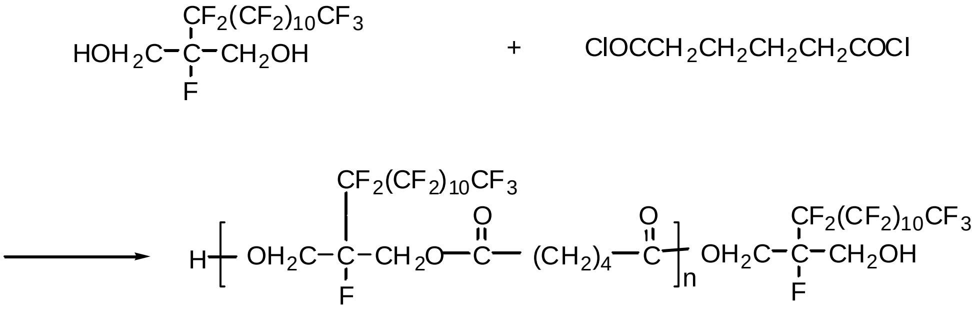
AF 1023



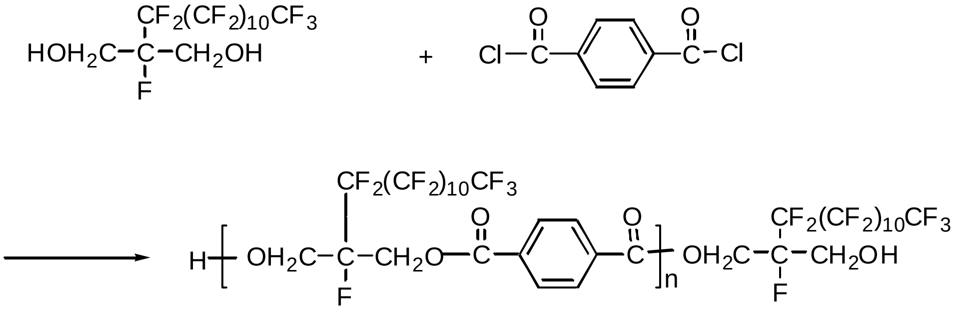
AF 1024



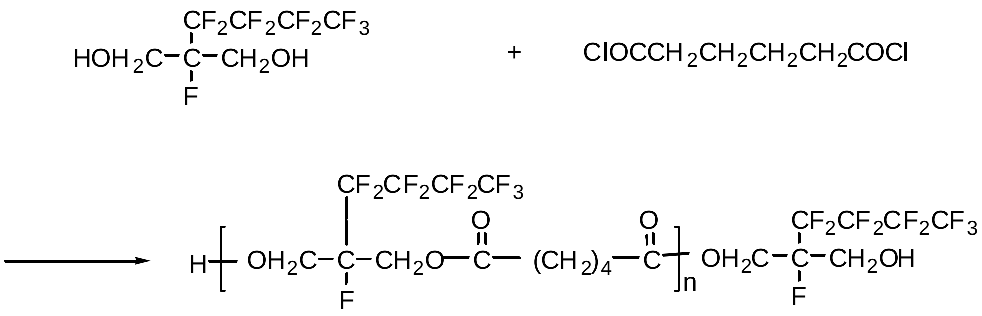
AF 1025



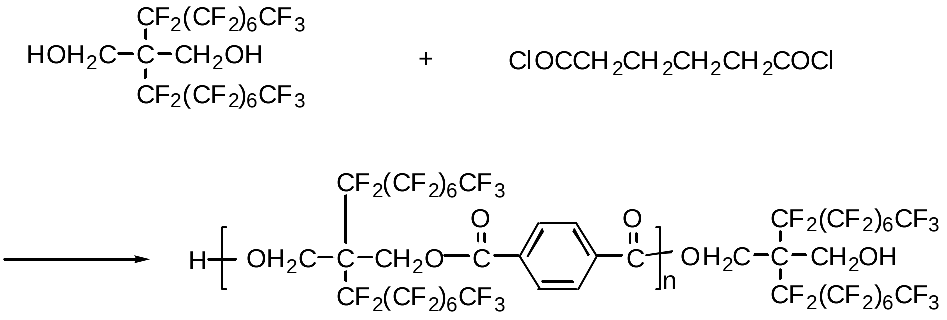
AF 1026



AF 1027



AF 1028

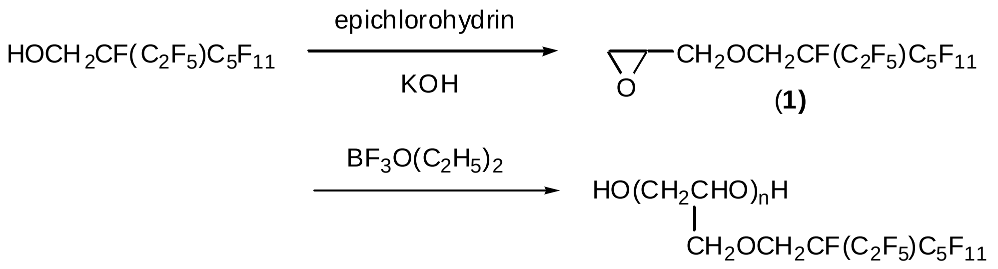


5.3. Discussion

Adipoyl chloride and terephthaloyl chloride are commonly used monomers to prepare polyesters. Since a wide variety of perfluoro dicarboxylic acids are available at Exfluor, we can prepare more highly fluorinated polyesters. Although highly fluorinated esters are hydrolytically unstable, the branching perfluoroalkyl groups may greatly enhance the stability of the polyesters.

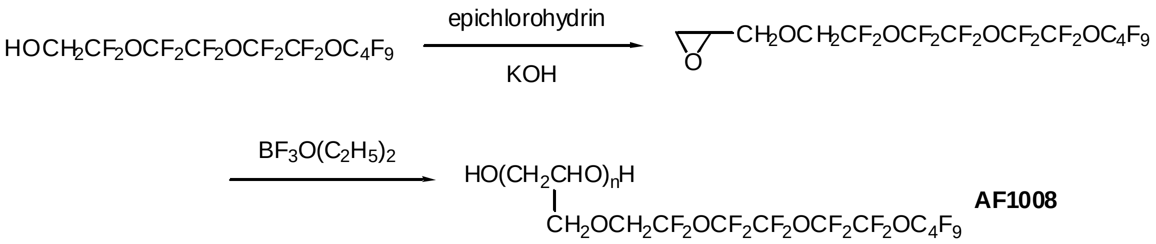
6.1. Preparation of fluorinated polyether diols

Upon request by the Air Force at the mid-term Technical Meeting, two additional samples, AF1007 and AF1008, were prepared from perfluoro-1H,1H-2-ethylhexanol glycidyl ether and perfluoro-1H,1H-triethlene glycol mono-butyl ether glycidyl ether respectively. Perfluoro-1H,1H-2-ethylhexanol was converted to its glycidyl ether (1) by the reaction with epichlorohydrin and potassium hydroxide. The epoxide was found to polymerize in the presence of boron trifluoride etherate catalyst. The polyether (AF1007) was a clear viscous liquid.


(1)

AF1007

Similarly, polyether AF1008 was prepared from perfluoro-1H,1H-triethylene glycol mono-butyl ether.


AF1008

6.2. Experimental

Synthesis of AF1007.

Perfluoro-1H,1H-2-ethylhexanol (0.5 mol), epichlorohydrin (2.66 mol) and isopropanol (500 mL) were mixed and vigorously stirred in a water bath. Potassium hydroxide pellets (85 %, 0.55 mol) were added to the above solution over a three-hour period. The reaction temperature was kept between 25 and 30 °C during the addition. Upon completion of the addition, the reaction mixture was stirred overnight at room temperature. The mixture was then washed with one liter of ice/water and purified by vacuum distillation. The glycidyl ether (**1**) having a boiling point of 85-88 °C/40 mmHg was obtained in 52 % yield.

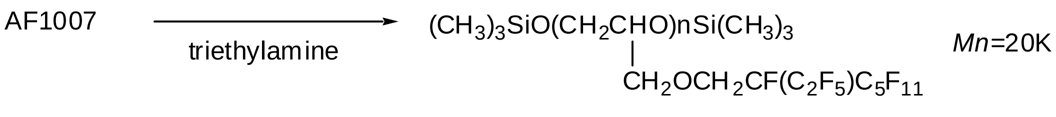
Glycidyl ether (**1**) (114 g) was placed in a round bottom flask under nitrogen. Boron trifluoride etherate (0.7 ml) was slowly added to glycidyl ether (**1**). After the addition, the mixture was stirred for 24 hours at room temperature to give a viscous liquid. Water (100 ml) and concentrated hydrochloric acid (10 ml) were added to the viscous polymer liquid and stirred at 80 °C for 3 days to completely decompose the catalyst. The polymer was separated and dried under vacuum overnight.

Synthesis of AF1008

AF1008 was synthesized under the same conditions. A clear, highly viscous polymer was obtained.

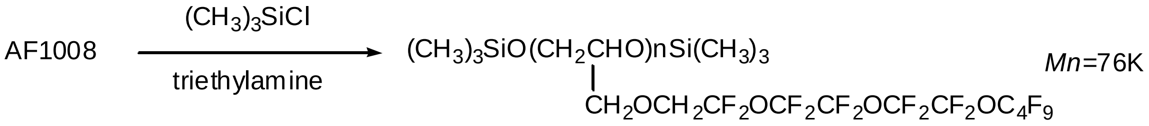
6.3. Determination of molecular weight

The number average molecular weight (*Mn*) of AF 1007 was determined by modifying the hydroxyl end-group to trimethylsilyl group.



$$\text{AF1007} \xrightarrow[\text{triethylamine}]{(CH_3)_3SiCl} (CH_3)_3SiO(CH_2\underset{\displaystyle CH_2OCH_2CF(C_2F_5)C_5F_{11}}{\underset{|}{C}}HO)nSi(CH_3)_3 \qquad Mn\text{=20K}$$

By means of ^{1}H NMR, *Mn* of AF 1007 was calculated to be approximately 20,000. The calculation was made by comparing the signal intensities of the trimethylsilyl group and the methylene group next to the perfluoroalkyl group. Similarly, the number average molecular weight of AF1008 was determined to be approximately 76,000.



$$\text{AF1008} \xrightarrow[\text{triethylamine}]{(CH_3)_3SiCl} (CH_3)_3SiO(CH_2\underset{\displaystyle |\atop \displaystyle CH_2OCH_2CF_2OCF_2CF_2OCF_2CF_2OC_4F_9}{C}HO)nSi(CH_3)_3 \qquad Mn\text{=76K}$$

6.4. Discussion

The two polyether diols were prepared to be used as highly fluorinated polymer blocks. These polymer blocks should exhibit excellent hydrophobic property and chemical resistance due to the branching perfluoroalkyl groups. Since AF1007 contains rigid perfluoroalkyl groups and AF1008 contains flexible perfluoro polyalkylether groups, the two polymer blocks may contribute to give quite different surface properties.

As in the case of the preparation of polyols and polyesters, other perfluoroalkyl methanols, R_f-CH_2OH, are available that can be used to synthesize other polyether-based polymer blocks if needed.

7.1. Analytical Data for EXF Diols

Purity of the EXF diols was determined by Gas Chromatography (HP 5790A with TCD). A stainless steel (1/8 in. x 6 ft.) column, packed with 6% OV-210 and 4% SE-30 on chromosorb AW, was used. Low-resolution mass spectroscopic analysis was performed on a MAT TSQ-80 spectrometer. High-resolution mass spectra were obtained from a VG analytical ZAB2-E mass spectrometer. Methane was used as the reagent gas for the chemical ionization mass spectra. The ^{1}H and ^{19}F NMR spectra were taken on a Varian *Unity plus*-300 NMR spectrometer. The ^{1}H NMR were recorded at 300 MHz using d^6-acetone as the lock solvent and internal reference. The ^{19}F NMR were recorded at 282 MHz using d^6-acetone as the lock solvent and $CFCl_3$ as the internal standard. ^{19}F NMR Chemical shifts are given in ppm with negative values indicating resonance at higher frequencies.

7.1.1. Mass Spectroscopy

In all cases, the base peak obtained was the (M^+ + 32) peak. Interestingly, the (M+1) peak was much smaller. It was confirmed that the (M^+ + 32) peak was "the parent plus oxygen (O_2)" peak by high-resolution mass spectroscopy. The only exception was EXF-7, which did not contain either peak. The mass spectrum of EXF-7 indicates as if it is a mixture of EXF-2 (F.W. 512) and dimer of EXF-2 (F.W. 1024).

EXF-1. 2-Fluoro-2-perfluorobutyl-1,3-propanediol. $C_7F_{10}H_6O_2$. F.W.: 312. *m/z*(identification, intensity) 313(M^+ + 1, 18), 345(M^+ + 32, 100).

EXF-2. 2-Fluoro-2-perfluorooctyl-1,3-propanediol. $C_{11}F_{18}H_6O_2$. F.W.: 512. *m/z*(identification, intensity) 513(M^+ + 1, 15), 545(M^+ + 32, 100), 577(M^+ + 64, 14). High resolution mass : 513.0146 (Found) and 513.0159 (Calcd.) for $C_{11}F_{18}H_7O_2$ (M^+ + 1). ; 545.0039(Found) and 545.0057(Calc.) for $C_{11}F_{18}H_7O_4$(M^+ + 32).

EXF-3. 2-Fluoro-2-perfluoro(2-ethylhexyl)-1,3-propanediol. $C_{11}F_{18}H_6O_2$. F.W.: 512. *m/z*(identification, intensity) 513(M^+ + 1, 10), 545(M^+ + 32, 55), 577(M^+ + 64, 10). High resolution mass : 513.0151 (Found) and 513.0159 (Calcd.) for $C_{11}F_{18}H_7O_2$ (M^+ + 1).

EXF-4. 2-Fluoro-2-perfluoro(3,7-dimethyloctyl)-1,3-propanediol. $C_{13}F_{22}H_6O_2$. F.W.: 612. *m/z*(identification, intensity) 613(M^+ + 1, 15), 645(M^+ + 32, 100), 677(M^+ + 64, 30).

EXF-5. 2-Fluoro-2-perfluorododecyl-1,3-propanediol. $C_{15}F_{26}H_6O_2$. F.W.: 712. *m/z*(identification, intensity) 713(M^+ + 1, 18), 745(M^+ + 32, 100), 777(M^+ + 64, 33).

EXF-7. 2,2 Bis(perfluorooctyl)-1,3-propanediol. $C_{19}F_{34}H_6O_2$. F.W.: 912. *m/z*(identification, intensity) 513 (22), 545 (42), 577 (76), 1025 (100), 1053 (10).

7.1.2. ^{19}F NMR analysis

The ^{19}F NMR spectra supported the structures of EXF diols. The only exception was EXF-7, which showed almost exactly the same pattern of spectra as that of EXF-2.

EXF-1. 2-Fluoro-2-perfluorobutyl-1,3-propanediol. ^{19}F NMR δ −81(3F, $-CF_3$), −119(2F, $-CF_2$), −121.5(2F, $-CF_2$), −126(2F, $-CF_2$) and −184(1F, −CF) ppm.

EXF-2. 2-Fluoro-2-perfluorooctyl-1,3-propanediol. ^{19}F NMR δ −81(3F, $-CF_3$), −119(2F, $-CF_2$), −120.5(2F, $-CF_2$), −121(6F, $-CF_2$), −122(2F, $-CF_2$), −126(2F, $-CF_2$) and −184(1F, -−CF) ppm.

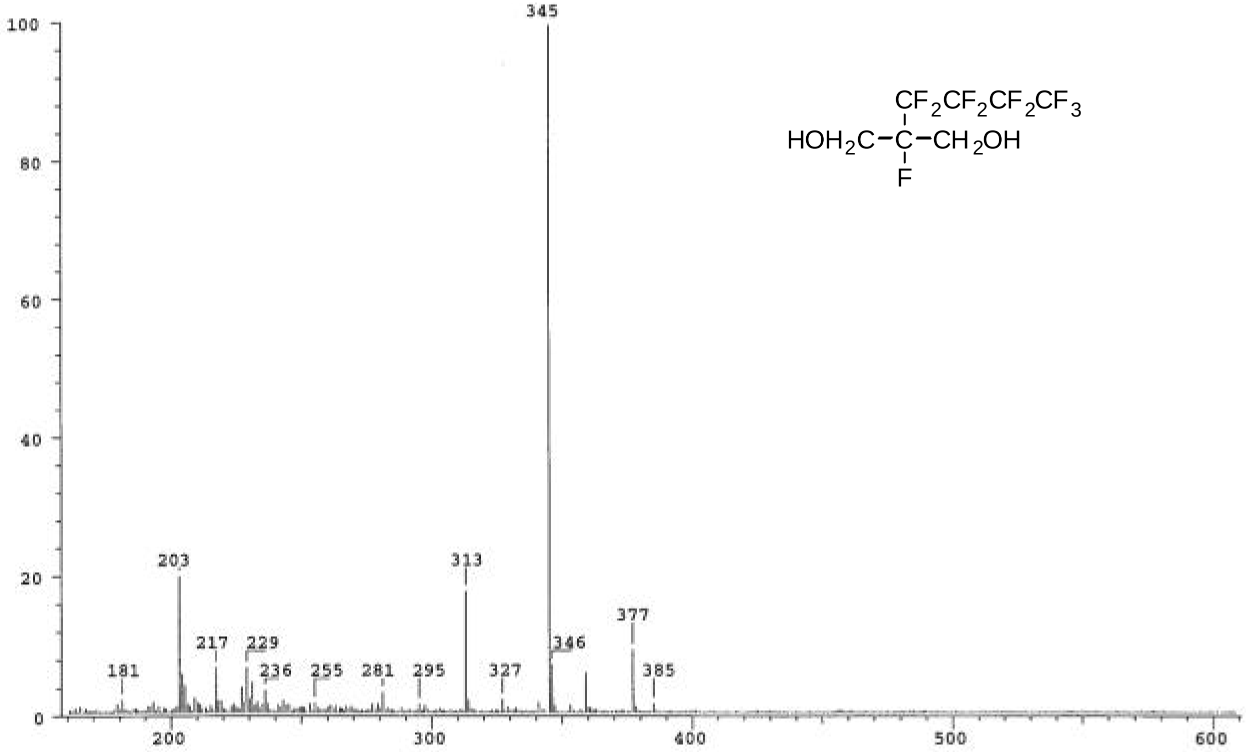
EXF-3. 2-Fluoro-2-perfluoro(2-ethylhexyl)-1,3-propanediol. ^{19}F NMR δ −79(3F, $-CF_3$), −81(3F, $-CF_3$), −106(2F, $-CF_2$), −108.5(2F, $-CF_2$), −112(2F, $-CF_2$), −118.5(2F, $-CF_2$), −126(2F, $-CF_2$), −181.5(1F, −CF), and −182.5(1F, −CF) ppm.

EXF-4. 2-Fluoro-2-perfluoro(3,7-dimethyloctyl)-1,3-propanediol. ^{19}F NMR δ −70(3F, $-CF_3$), −72(3F, $-CF_3$), −110.5(2F, $-CF_2$), −111(2F, $-CF_2$), −114(2F, $-CF_2$), −117(2F, $-CF_2$), −118(2F, $-CF_2$), −184(1F, −CF), −185(1F, −CF), and −186(1F, −CF) ppm.

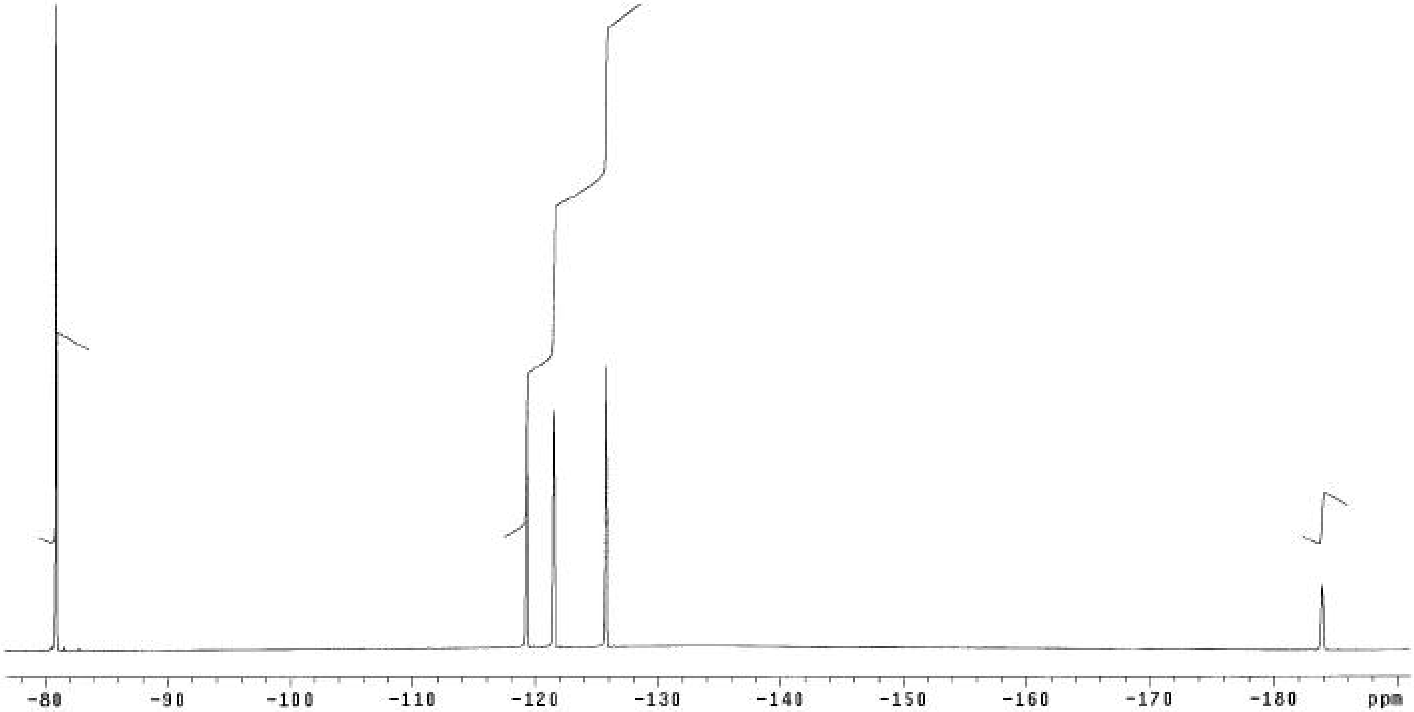
EXF-5. 2-Fluoro-2-perfluorododecyl-1,3-propanediol. ^{19}F NMR δ −81(3F, $-CF_3$), −119 ~ −126(22F, $-CF_2$) and −184(1F, −CF) ppm.

EXF-7. 2,2 Bis(perfluorooctyl)-1,3-propanediol. ^{19}F NMR δ −81(3F, $-CF_3$), −119(2F, $-CF_2$), −120.5(2F, $-CF_2$), −121(6F, $-CF_2$), −122(2F, $-CF_2$), −126(2F, $-CF_2$) and −184(1F, −CF) ppm.

EXF-1 Spectra

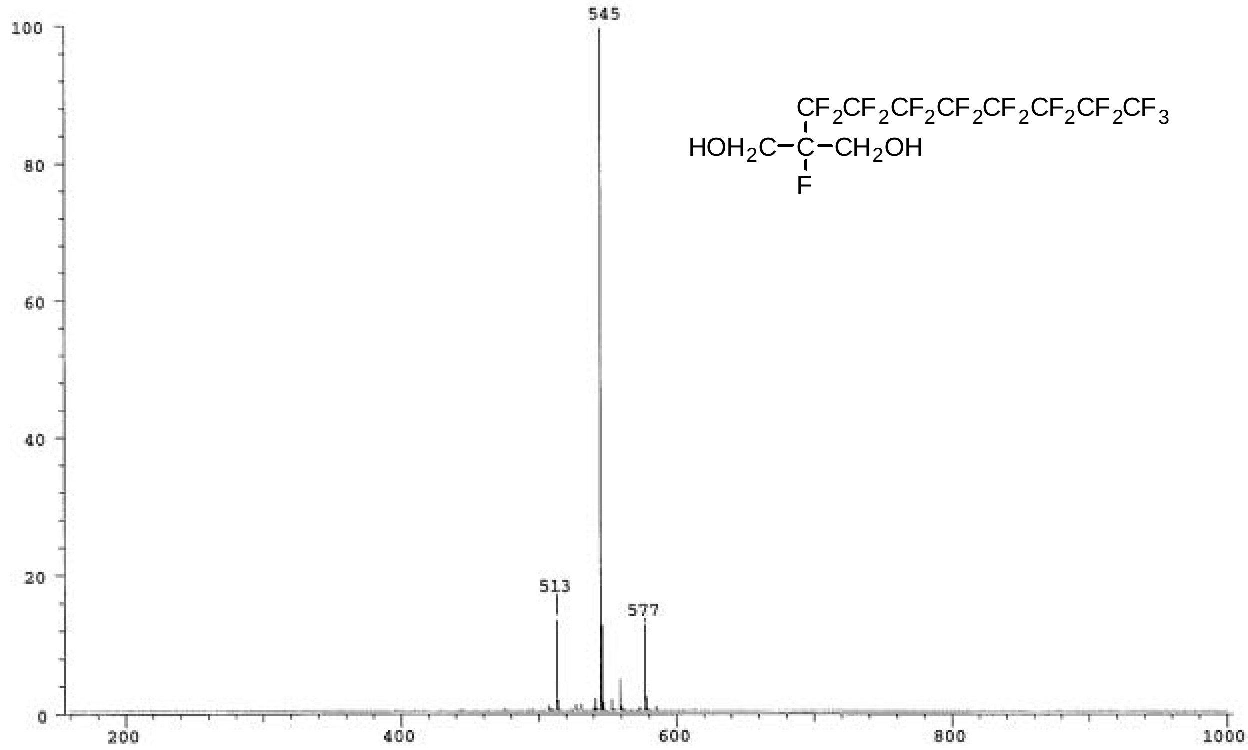


Mass Spectrum



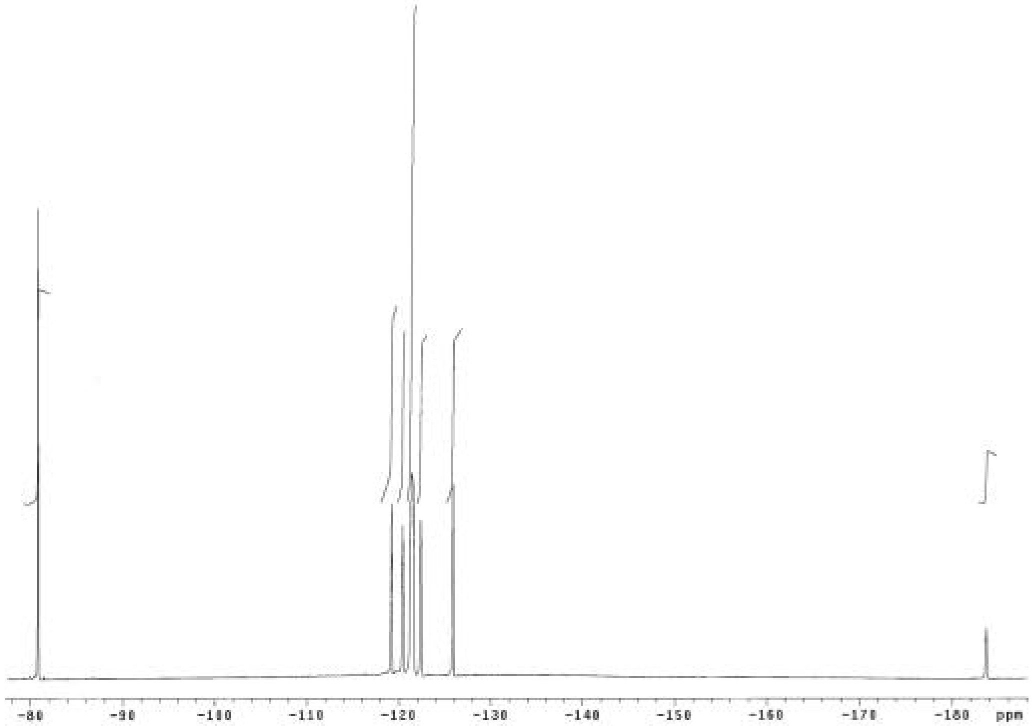
^{19}F NMR Spectrum

EXF-2 Spectra



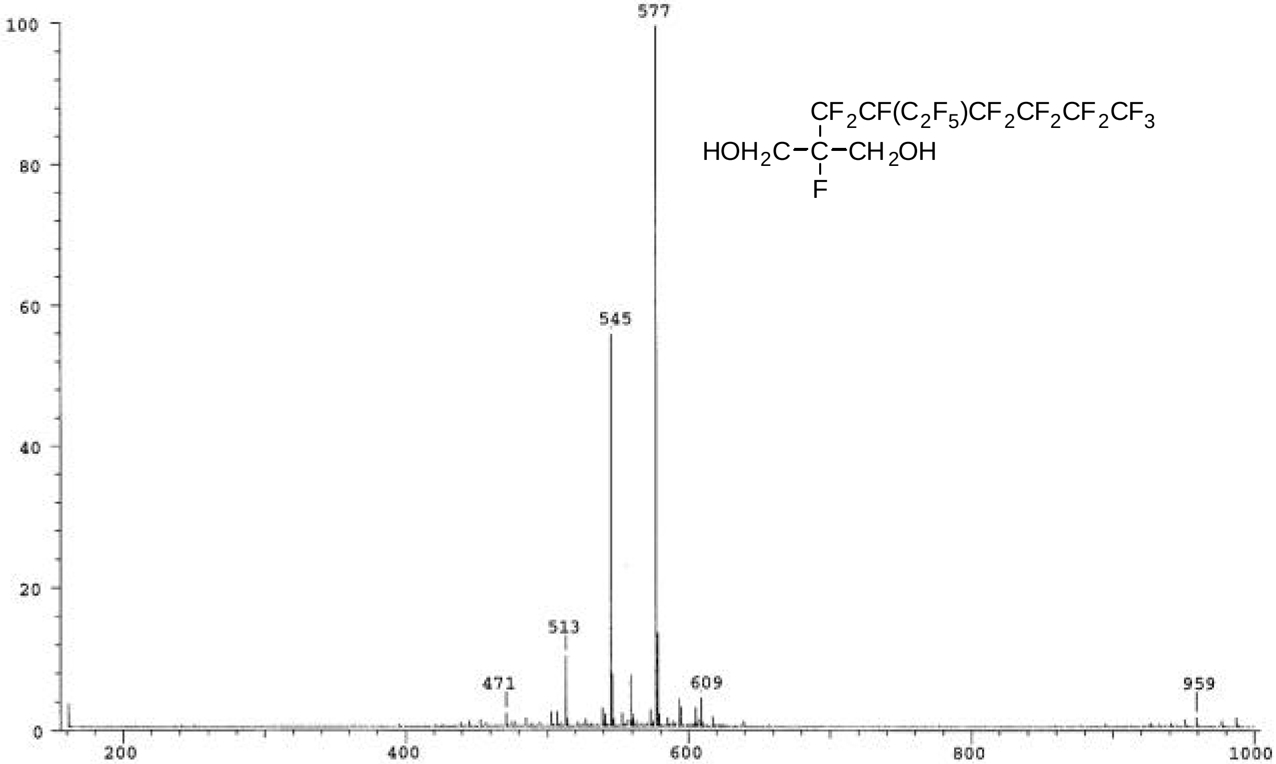
$$\mathrm{HOH_2C{-}\overset{CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_3}{\underset{F}{C}}{-}CH_2OH}$$

Mass Spectrum



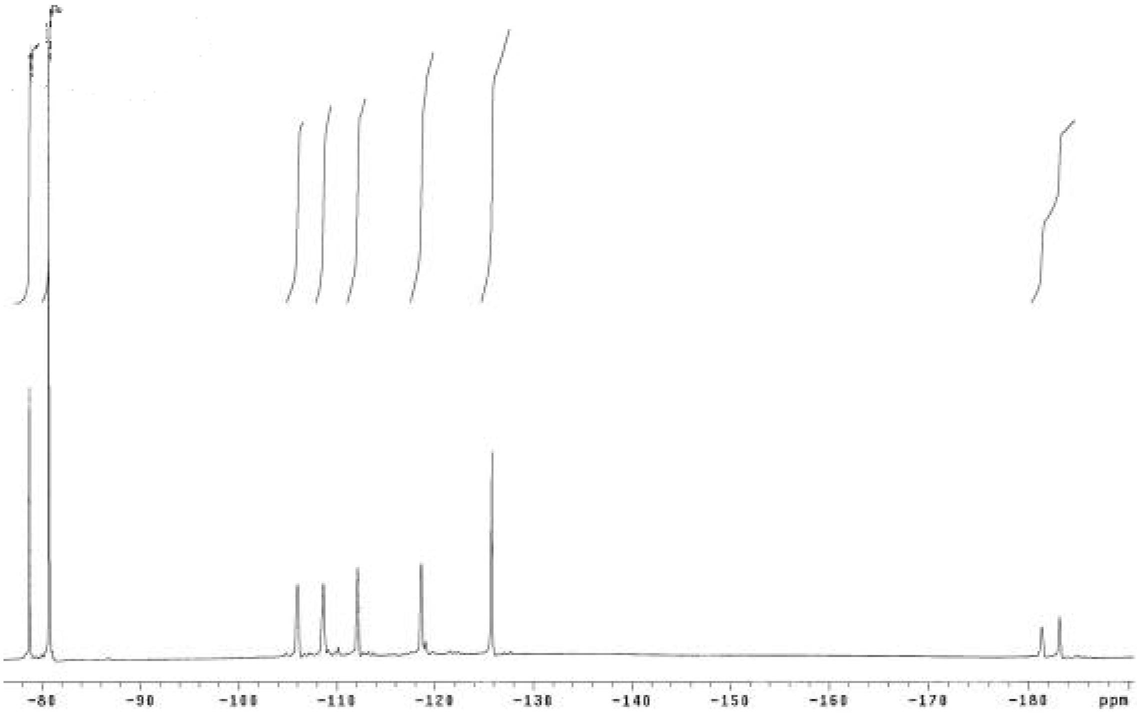
^{19}F NMR Spectrum

EXF-3 Spectra



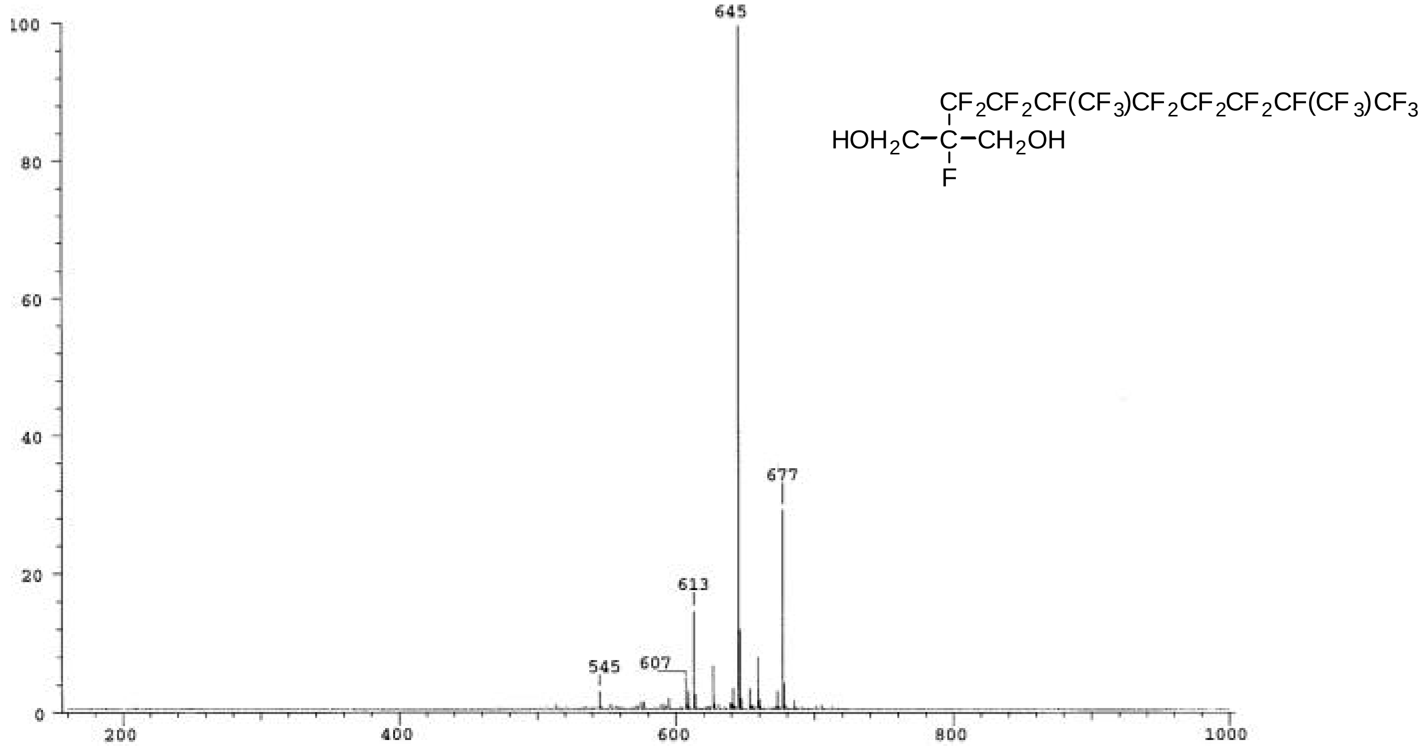
$$\mathrm{HOH_2C{-}\underset{\displaystyle F}{\overset{\displaystyle CF_2CF(C_2F_5)CF_2CF_2CF_2CF_3}{C}}{-}CH_2OH}$$

Mass Spectrum

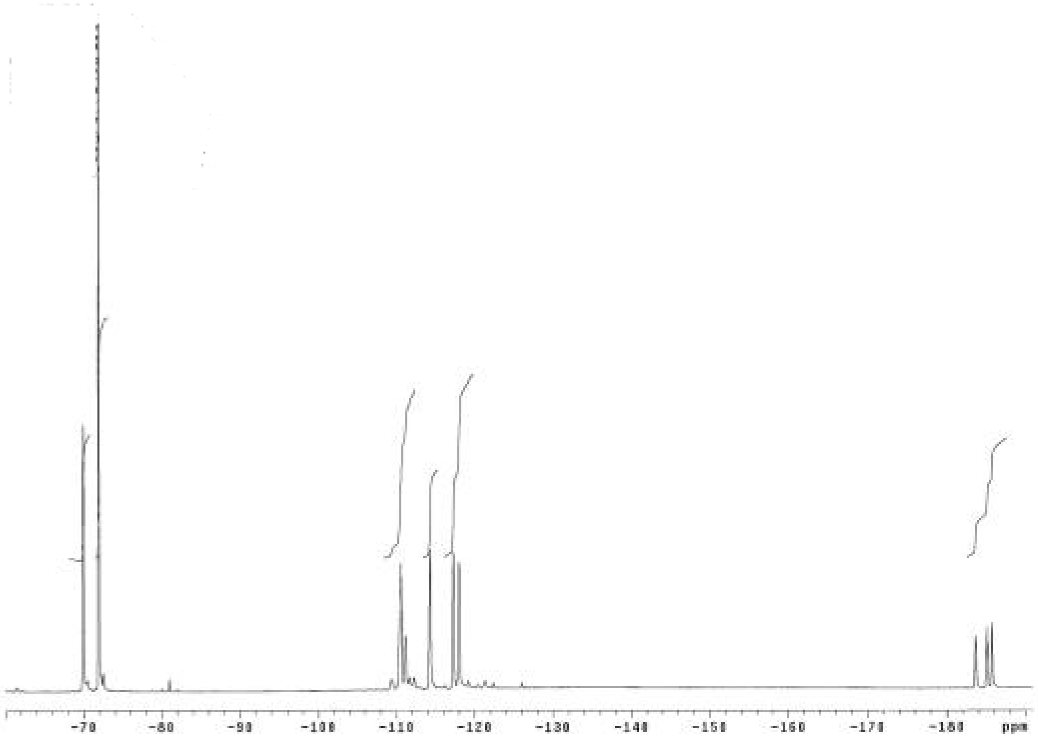


^{19}F NMR Spectrum

EXF-4 Spectra

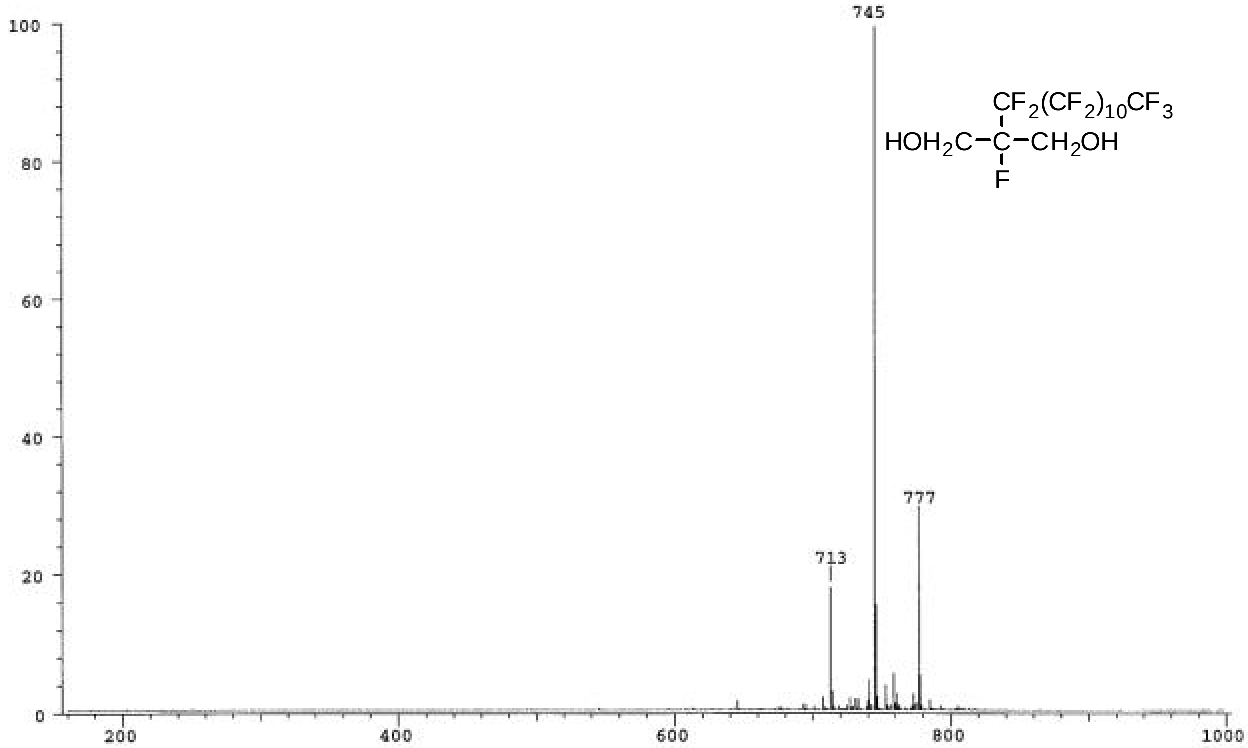


Mass Spectrum

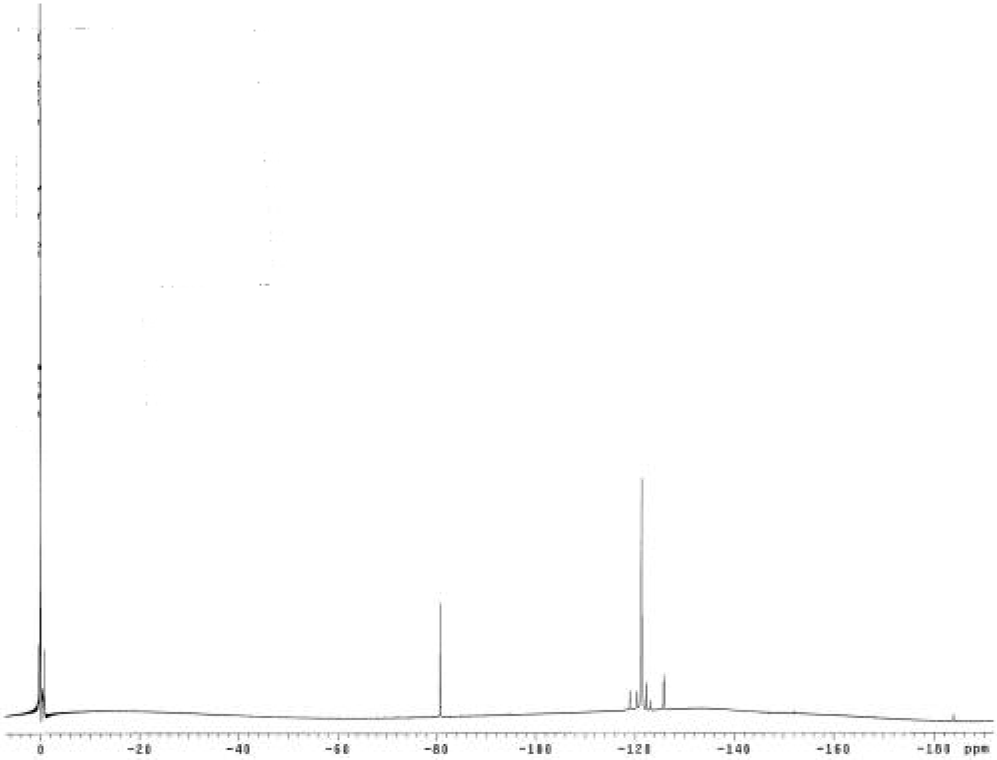


^{19}F NMR Spectrum

EXF-5 Spectra

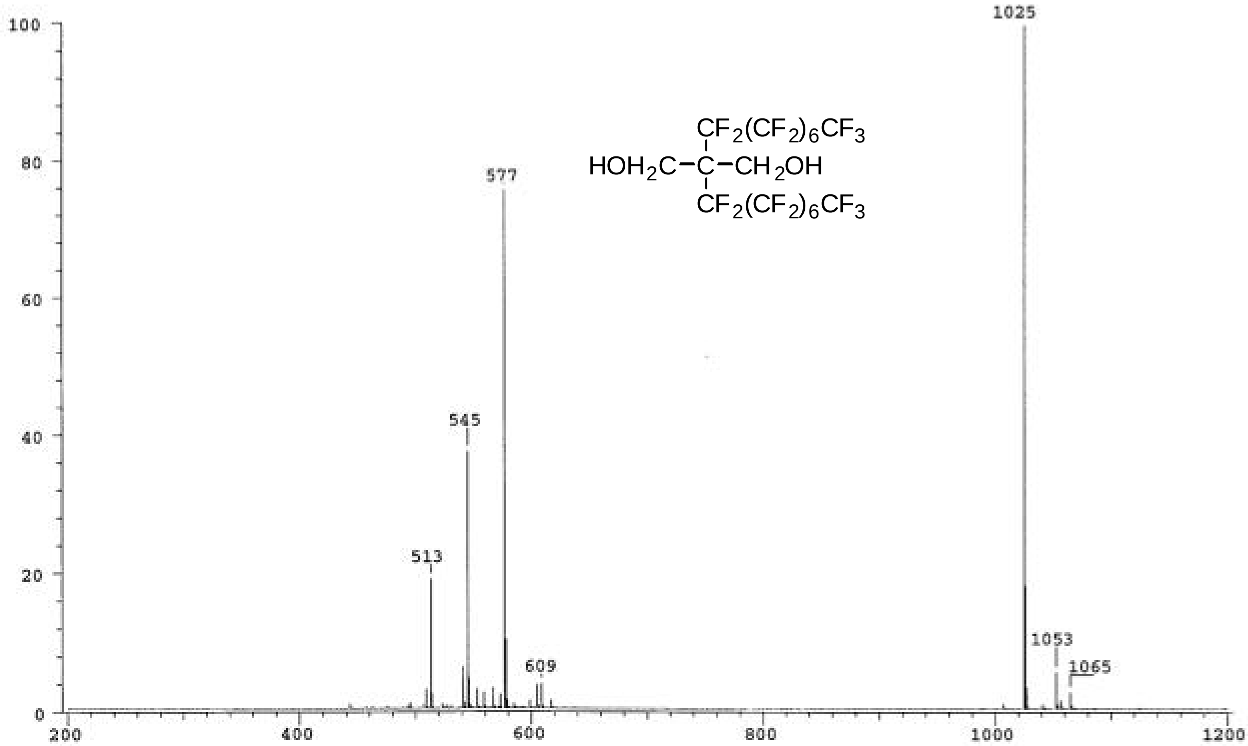


Mass Spectrum

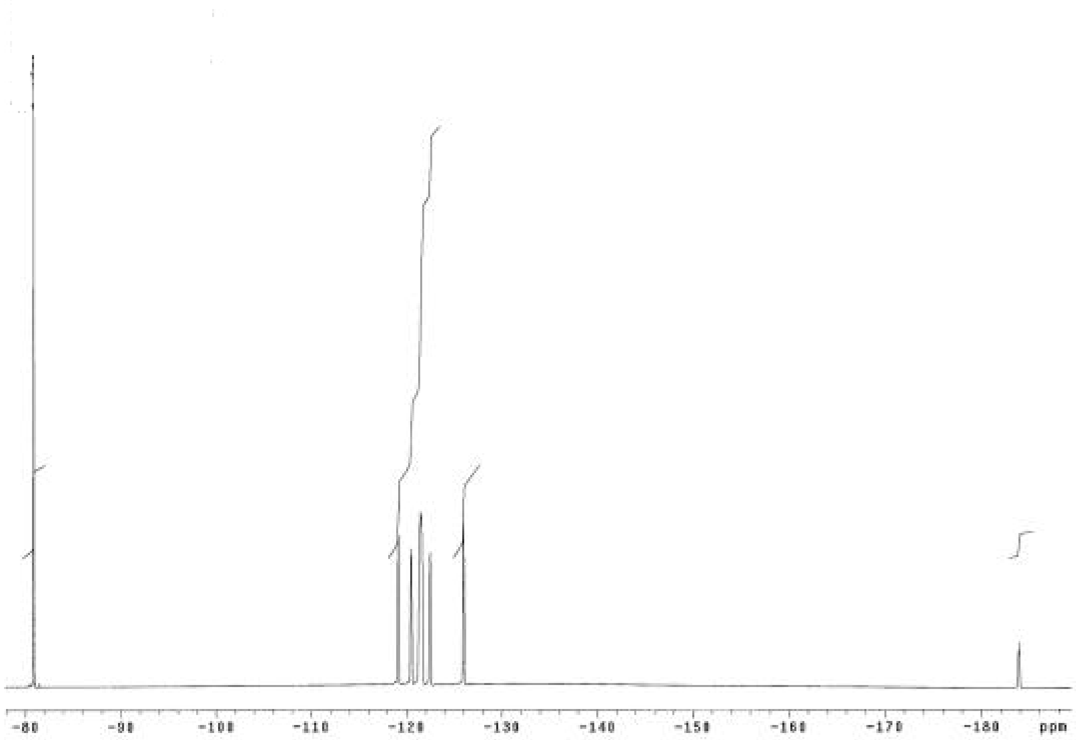


^{19}F NMR Spectrum

EXF-7 Spectra



Mass Spectrum



^{19}F NMR Spectrum

7.2. Analytical Data of Polyols

The ^1H NMR spectra of the polyols contained various peaks in the region of 2.0 ppm ~ 4.7 ppm. The ^{19}F NMR spectra of the polyols were nearly identical to those of the corresponding EXF diols. The spectra are shown from page 51 to 56.

7.3. Analytical Data of Polyesters

The ^1H NMR spectra of the polyesters are summarized below. It was noticed that the ^{19}F NMR spectra of the polyesters became much more complicated than those of the EXF diols. The spectra are shown from page 57 to 64.

AF1009. Polyester made from 2-Fluoro-2-perfluorooctyl-1,3-propanediol (EXF-2) and Terephthaloyl chloride. ^1H NMR δ 2.82(–OH), 4.15 ~ 5.25($-C\underline{H}_2OH$), 4.9 ~ 5.2 ($-O\underline{H}_2C-CR_f(F)-$) and 8.1 ~ 8.22(aromatic) ppm.

AF1010. Polyester made from 2-Fluoro-2-perfluoro(2-ethylhexyl)-1,3-propanediol (EXF-3) and Terephthaloyl chloride. ^1H NMR δ 2.82(–OH), 4.2($-C\underline{H}_2OH$), 4.9 ~ 5.2 ($-O\underline{H}_2C-CR_f(F)-$) and 8.1 ~ 8.2(aromatic) ppm.

AF1011. Polyester made from 2-Fluoro-2-perfluorooctyl-1,3-propanediol (EXF-2), Terephthaloyl chloride 99(%) and Pyromellitic dianhydride(1%). ^1H NMR δ 2.75(–OH), 5.0 ~ 5.2($-O\underline{H}_2C-CR_f(F)-$) and 8.1 ~ 8.2(aromatic) ppm.

AF1012. Polyester made from 2-Fluoro-2-perfluoro(2-ethylhexyl)-1,3-propanediol (EXF-3), Terephthaloyl chloride 99(%) and Pyromellitic dianhydride(1%). ^1H NMR δ 2.82(–OH), 4.2($-C\underline{H}_2OH$), 4.9 ~ 5.2($-O\underline{H}_2C-CR_f(F)-$) and 8.1 ~ 8.25(aromatic) ppm.

AF1013. Polyester made from 2-Fluoro-2-perfluorooctyl-1,3-propanediol (EXF-2) and Adipoyl chloride. ^1H NMR δ 1.4($-CH_2$), 2.5(–OH), 4.1($-C\underline{H}_2OH$) and 4.6 ~ 4.8($-O\underline{H}_2C-CR_f(F)-$) ppm.

AF1014. Polyester made from 2-Fluoro-2-perfluoro(2-ethylhexyl)-1,3-propanediol (EXF-3) and Adipoyl chloride. ^1H NMR δ 1.65($-CH_2$), 2.45(–OH), 4.1($-C\underline{H}_2OH$) and 4.6 ~ 4.7($-O\underline{H}_2C-CR_f(F)-$) ppm.

AF1015. Polyester made from 2,2-Bis(perfluorooctyl)-1,3-propanediol (EXF-7) and Terephthaloyl chloride. ^{1}H NMR δ 2.8(−OH), 4.0 ~ 5.2(−O$\underline{H}_2$C−CR_f(F)−) and 8.4(aromatic) ppm.

AF1016. Polyester made from 2-Fluoro-2-perfluorobutyl-1,3-propanediol (EXF-1) and Terephthaloyl chloride. ^{1}H NMR δ 2.8(−OH), 4.1(−C$\underline{H}_2$OH), 5.0 ~ 5.2 (−O$\underline{H}_2$C−CR_f(F)−) and 8.4 (aromatic) ppm.

Spectral data of the following polyesters, which were made as additional samples, are not available.

AF1023. Polyester made from 2-Fluoro-2-perfluoro(3,7-dimethyloctyl)-1,3-propanediol and Adipoyl chloide.

AF1024. Polyester made from 2-Fluoro-2-perfluoro(3,7-dimethyloctyl)-1,3-propanediol and Terephthaloyl chloride.

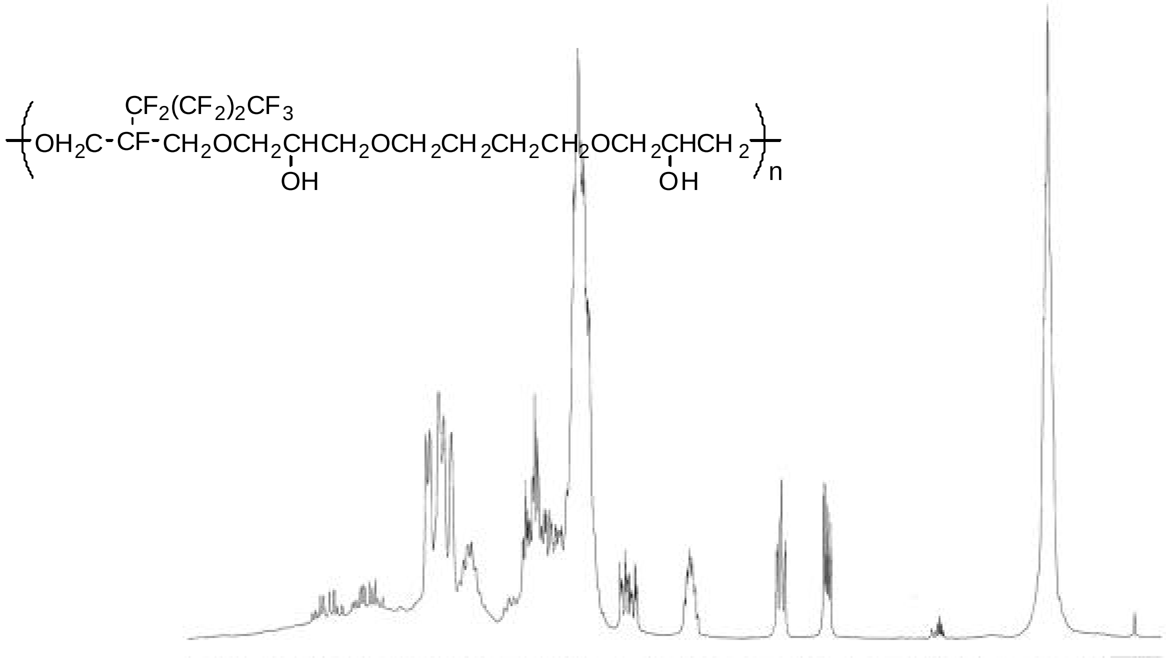
AF1025. Polyester made form 2-Fluoro-2-perfluorododecyl-1,3-propanediol and Adipoyl chloride.

AF1026. Polyester made from 2-Fluoro-2-perfluorododecyl-1,3-propanediol and Terephthaloyl chloride.

AF1027. Polyester made from 2-Fluoro-2-perfluorobutyl-1,3-propanediol and Adipoyl chloride.

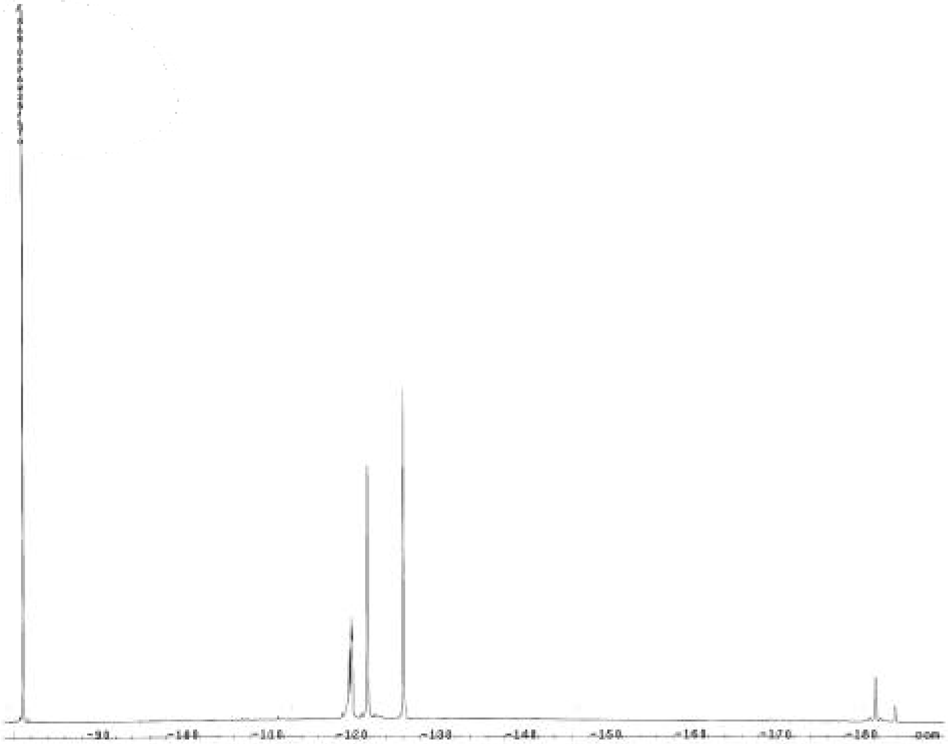
AF1028. Polyester made from 2,2-Bis(perfluorooctyl)-1,3-propanediol and Adipoyl chloride.

AF1017 Spectra



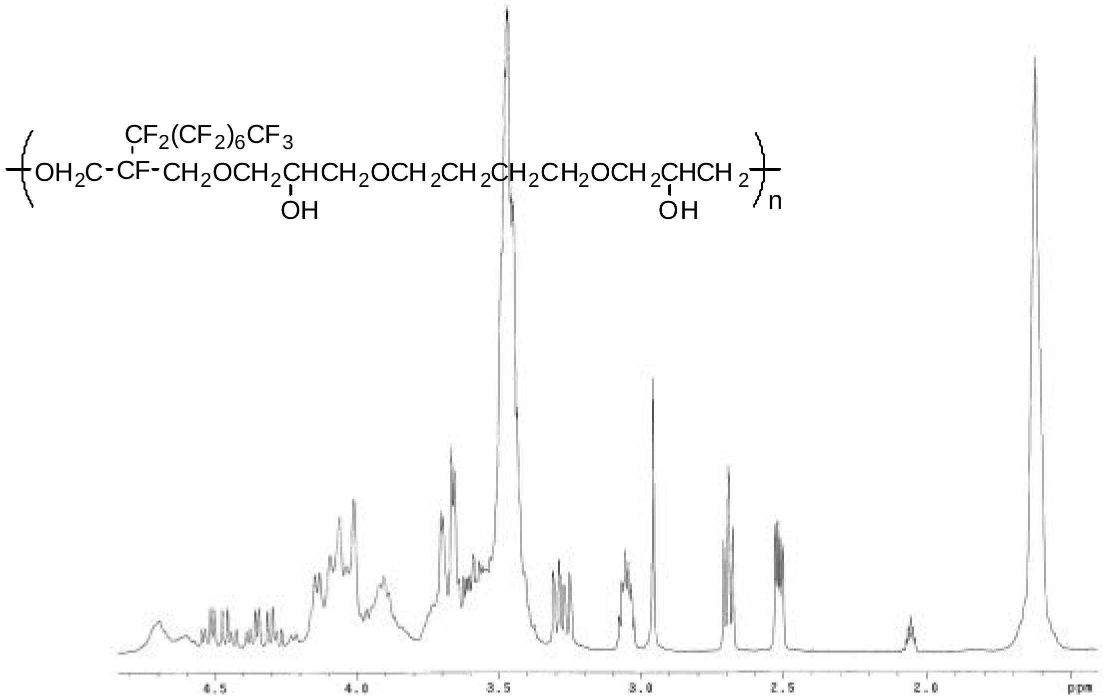
$$\left[\mathrm{OH_2C-\overset{CF_2(CF_2)_2CF_3}{CF}-CH_2OCH_2\underset{OH}{CH}CH_2OCH_2CH_2CH_2CH_2OCH_2\underset{OH}{CH}CH_2}\right]_n$$

^{1}H Spectrum

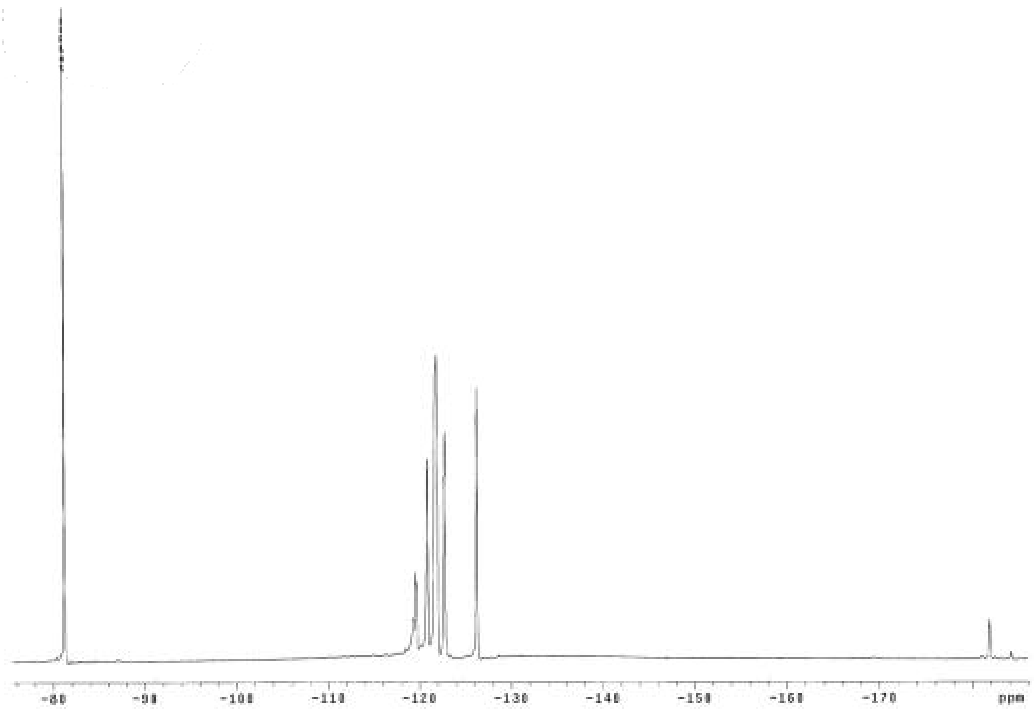


^{19}F NMR Spectrum

AF1018 Spectra

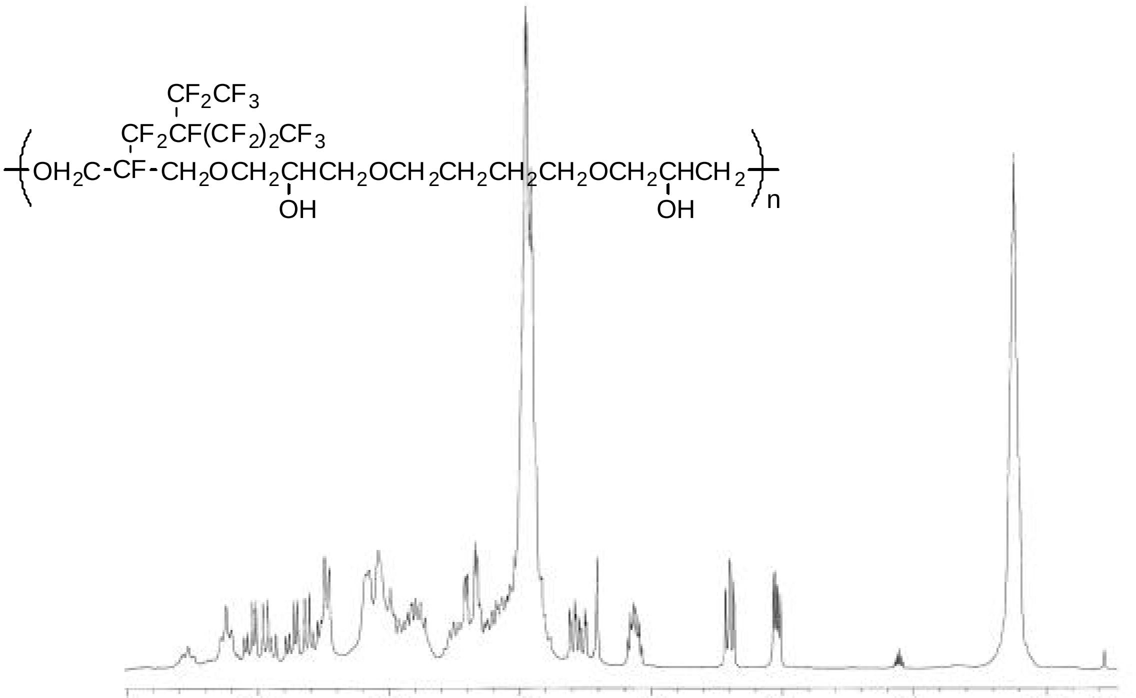

$$\left(OH_2C\text{-}\overset{CF_2(CF_2)_6CF_3}{CF}\text{-}CH_2OCH_2\underset{OH}{C}HCH_2OCH_2CH_2CH_2CH_2OCH_2\underset{OH}{C}HCH_2 \right)_n$$

^{1}H Spectrum



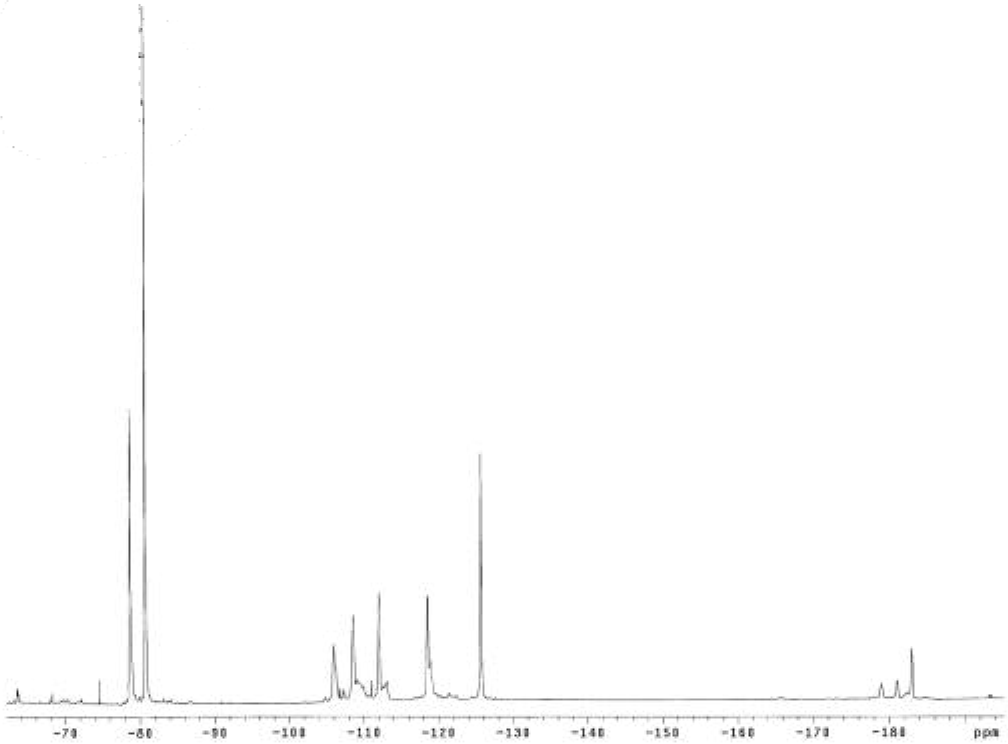
^{19}F NMR Spectrum

AF1019 Spectra



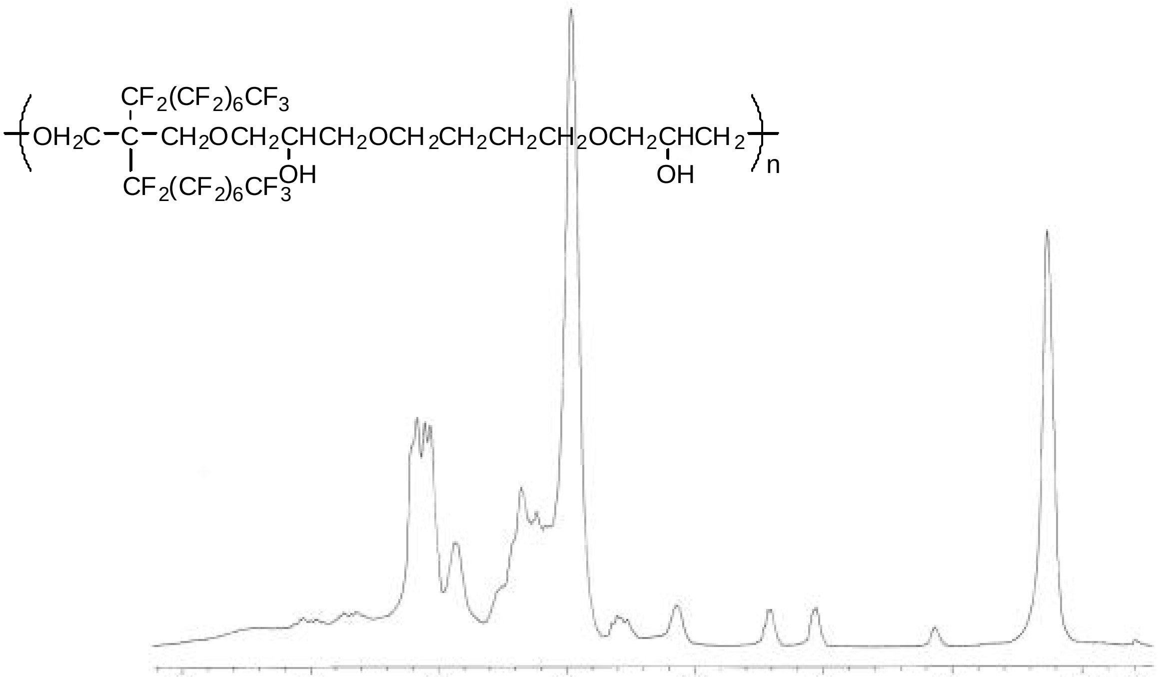
$$\left(\mathrm{OH_2C-\overset{\substack{CF_2CF_3\\ |\\ CF_2CF(CF_2)_2CF_3\\ |}}{CF}-CH_2OCH_2\underset{\substack{|\\ OH}}{CH}CH_2OCH_2CH_2CH_2CH_2OCH_2\underset{\substack{|\\ OH}}{CH}CH_2}\right)_n$$

^{1}H Spectrum



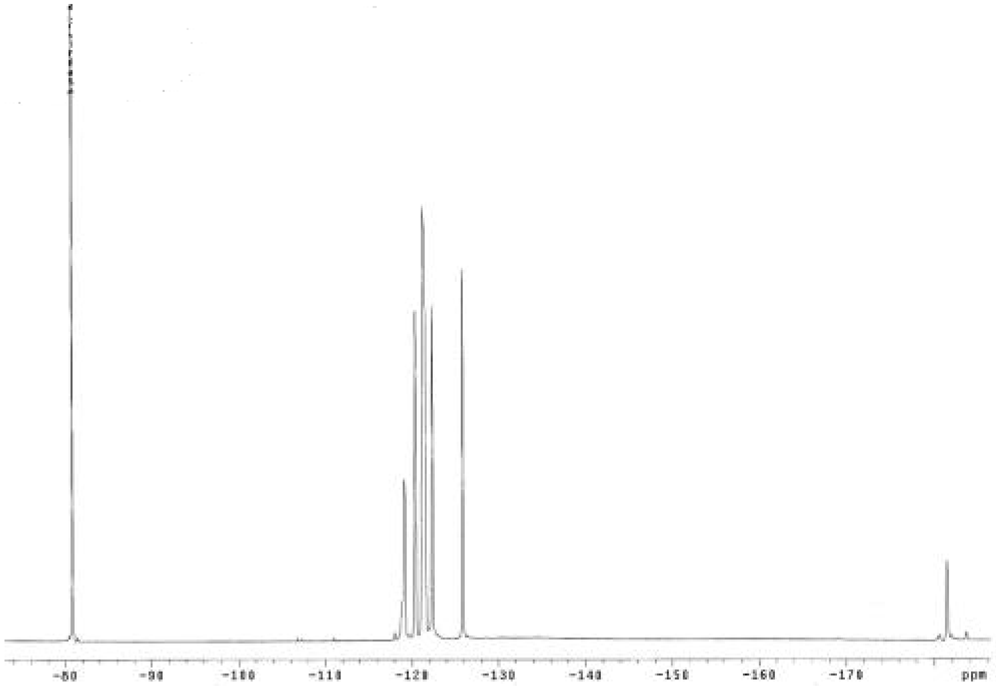
^{19}F NMR Spectrum

AF1020 Spectra



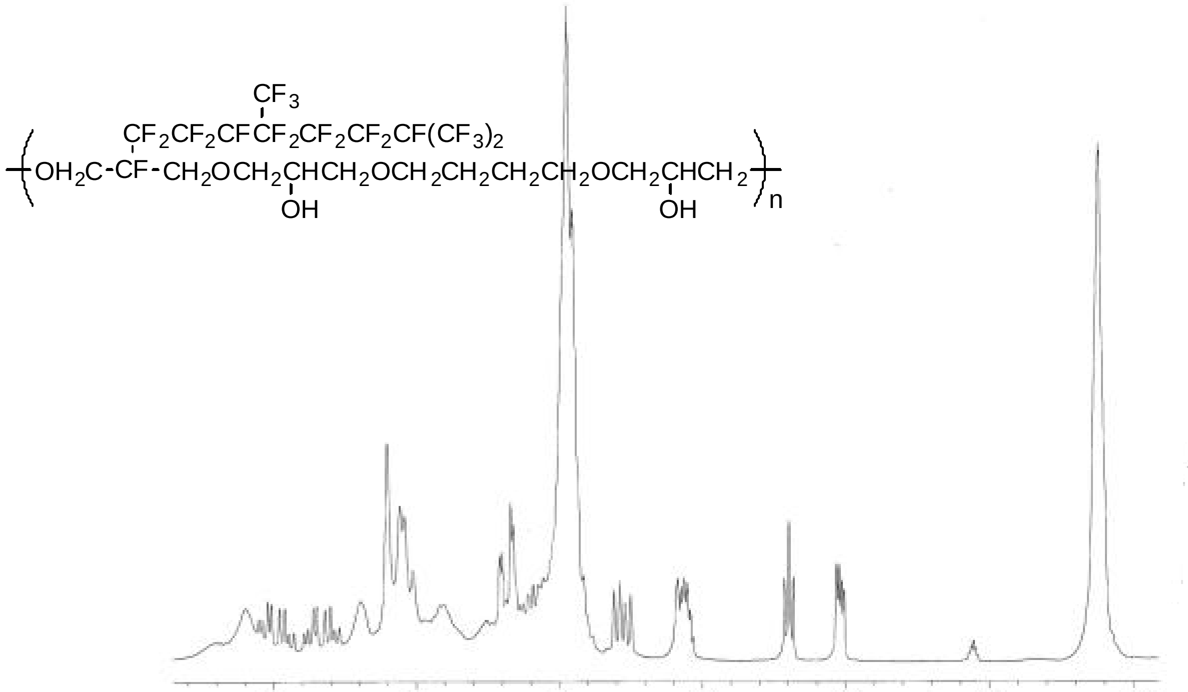
$$\left(OH_2C-\overset{CF_2(CF_2)_6CF_3}{\underset{CF_2(CF_2)_6CF_3}{C}}-CH_2OCH_2\underset{OH}{C}HCH_2OCH_2CH_2CH_2CH_2OCH_2\underset{OH}{C}HCH_2\right)_n$$

^{1}H Spectrum



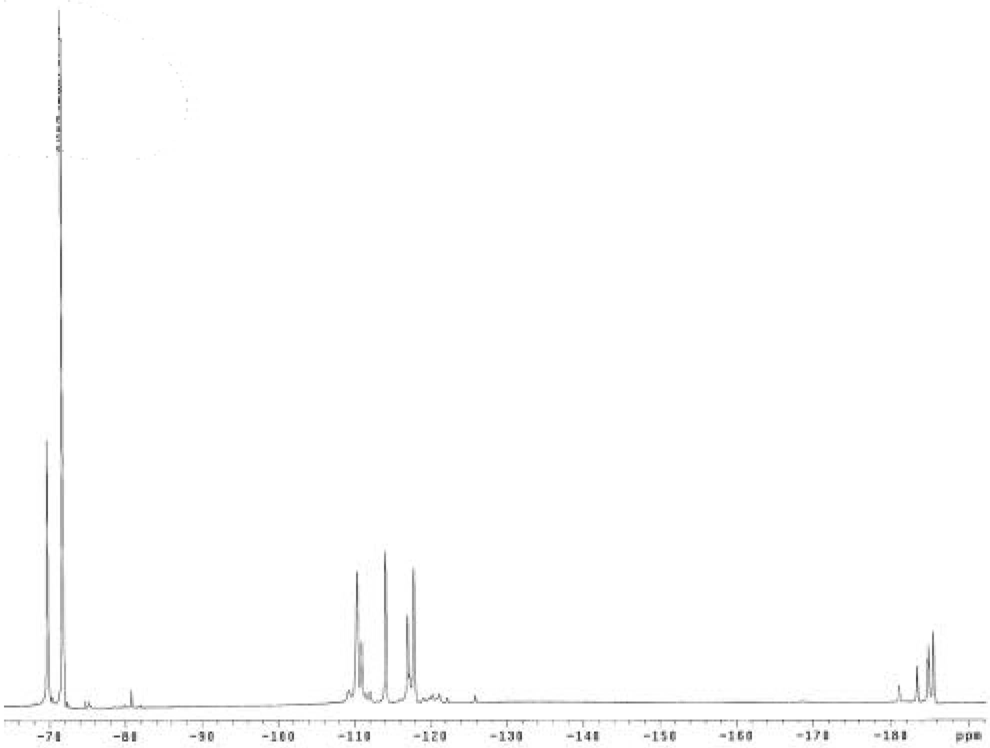
^{19}F NMR Spectrum

AF1021 Spectra



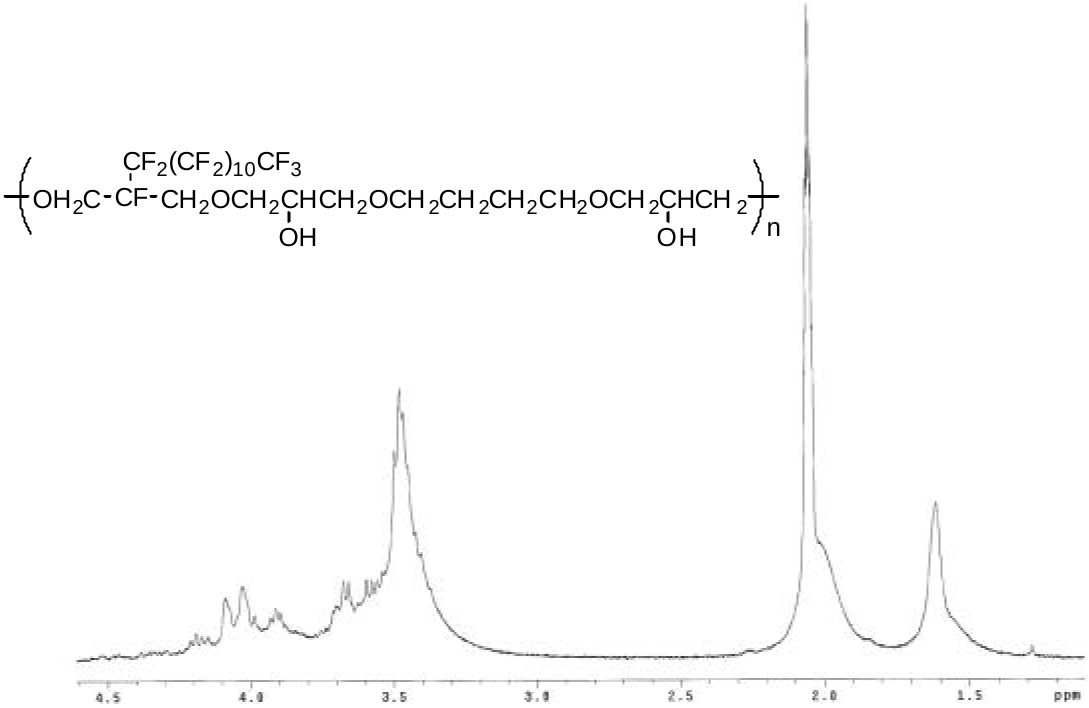
$$-\!\left(OH_2C-\overset{CF_2CF_2CF(CF_3)CF_2CF_2CF_2CF(CF_3)_2}{CF}-CH_2OCH_2\underset{OH}{CH}CH_2OCH_2CH_2CH_2CH_2OCH_2\underset{OH}{CH}CH_2\right)_n\!-$$

^1H Spectrum



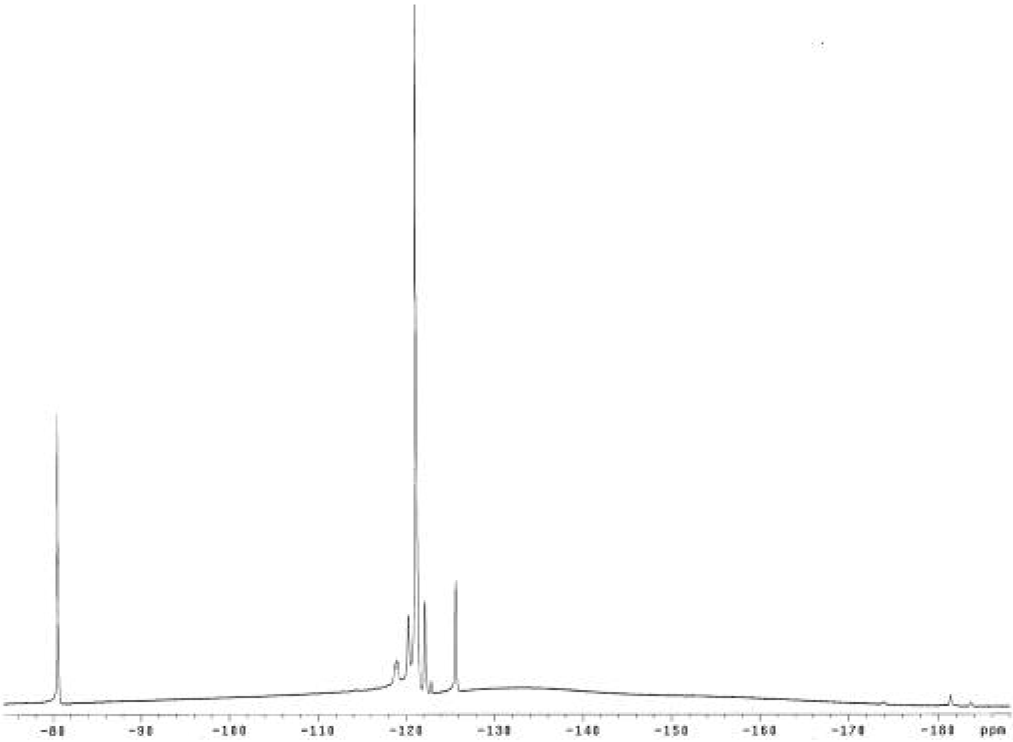
^{19}F NMR Spectrum

AF1022 Spectra



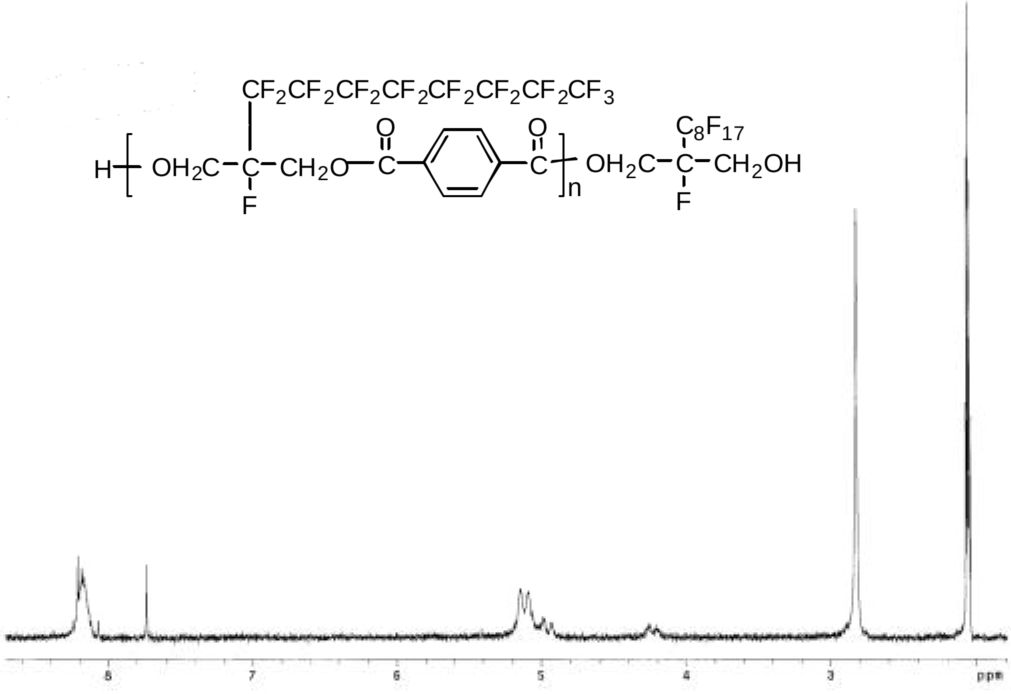
$$\left(OH_2C-\overset{CF_2(CF_2)_{10}CF_3}{CF}-CH_2OCH_2\underset{OH}{CH}CH_2OCH_2CH_2CH_2CH_2OCH_2\underset{OH}{CH}CH_2 \right)_n$$

^1H Spectrum

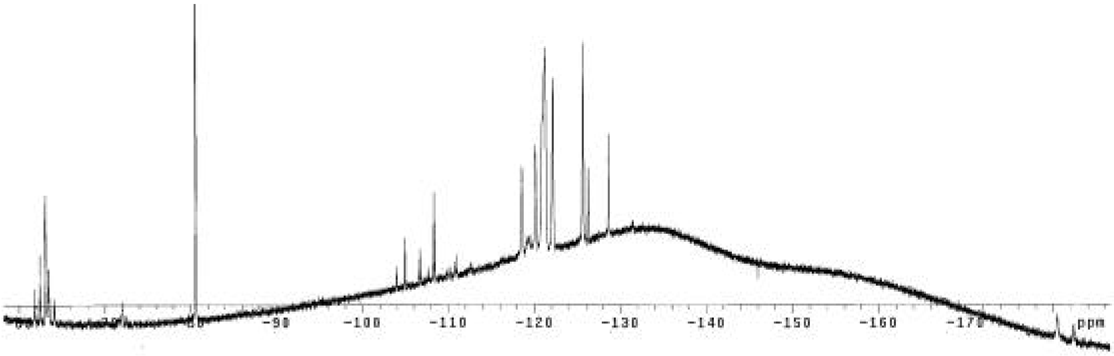


^{19}F NMR Spectrum

AF1009 Spectra

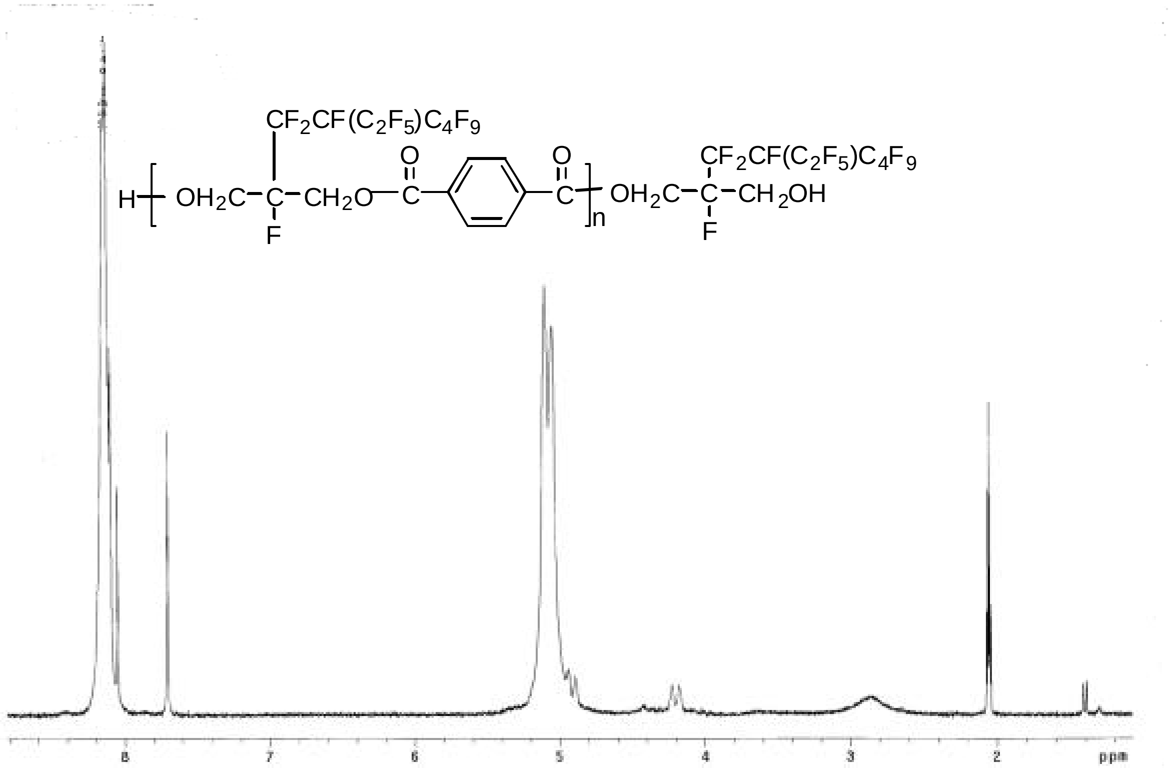


^{1}H Spectrum

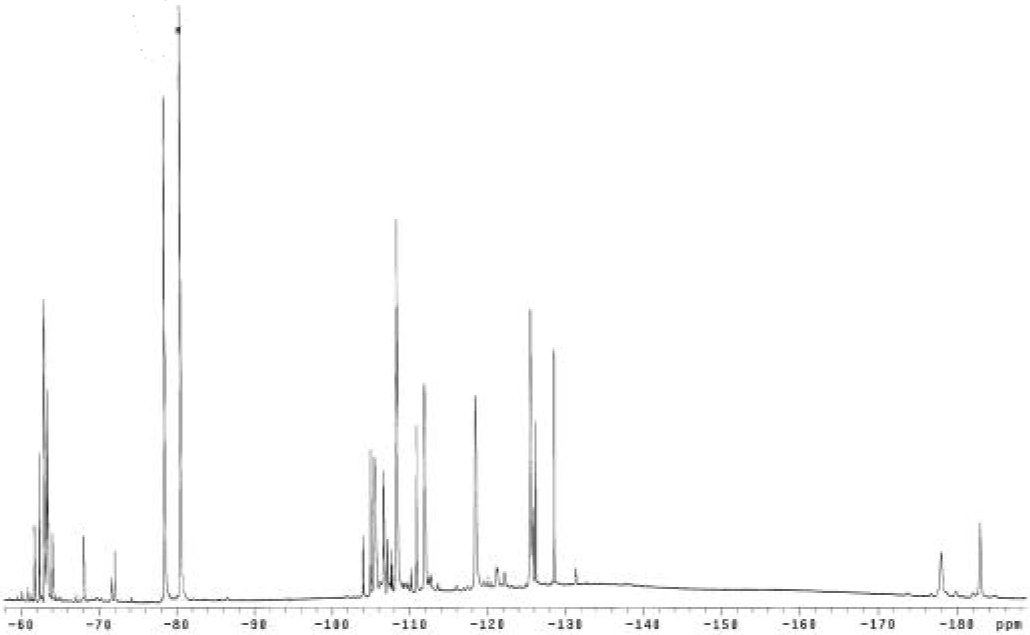


^{19}F NMR Spectrum

AF1010 Spectra

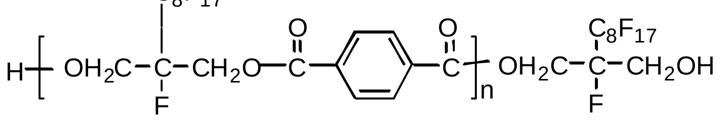


^{1}H Spectrum

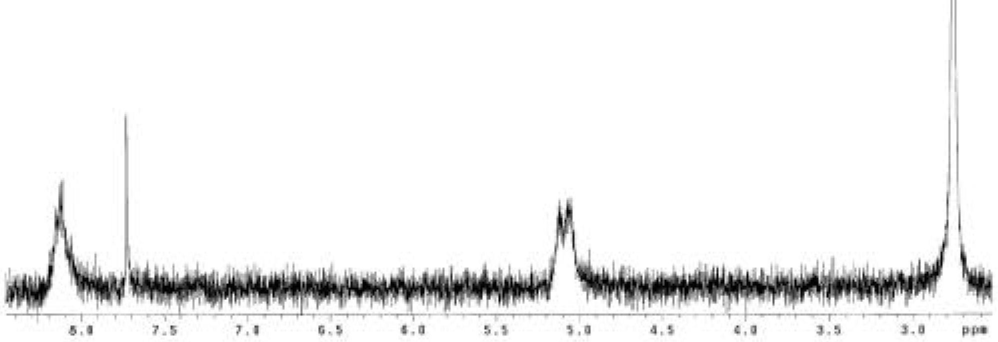


^{19}F NMR Spectrum

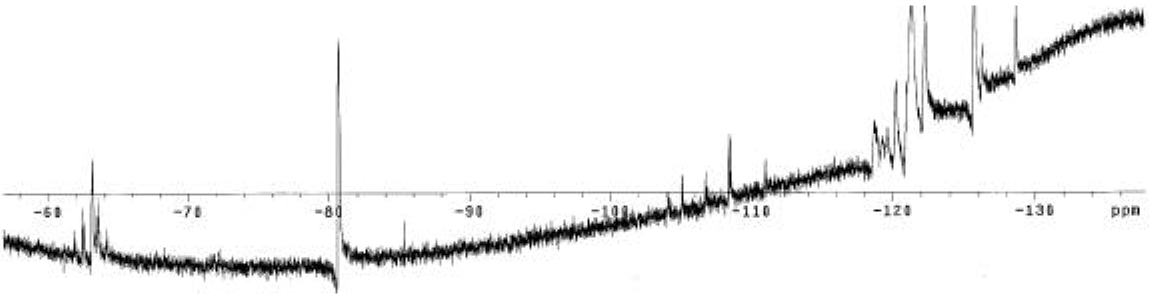
AF1011 Spectra



with 1% pyromellitic dianhydride

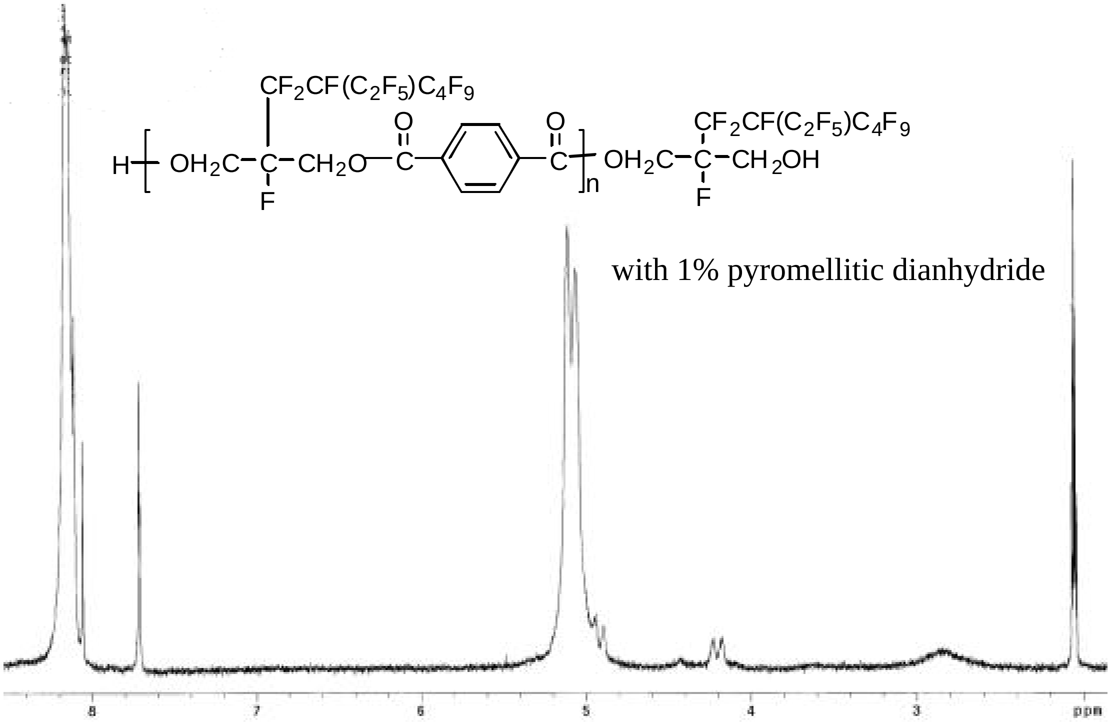


^{1}H Spectrum

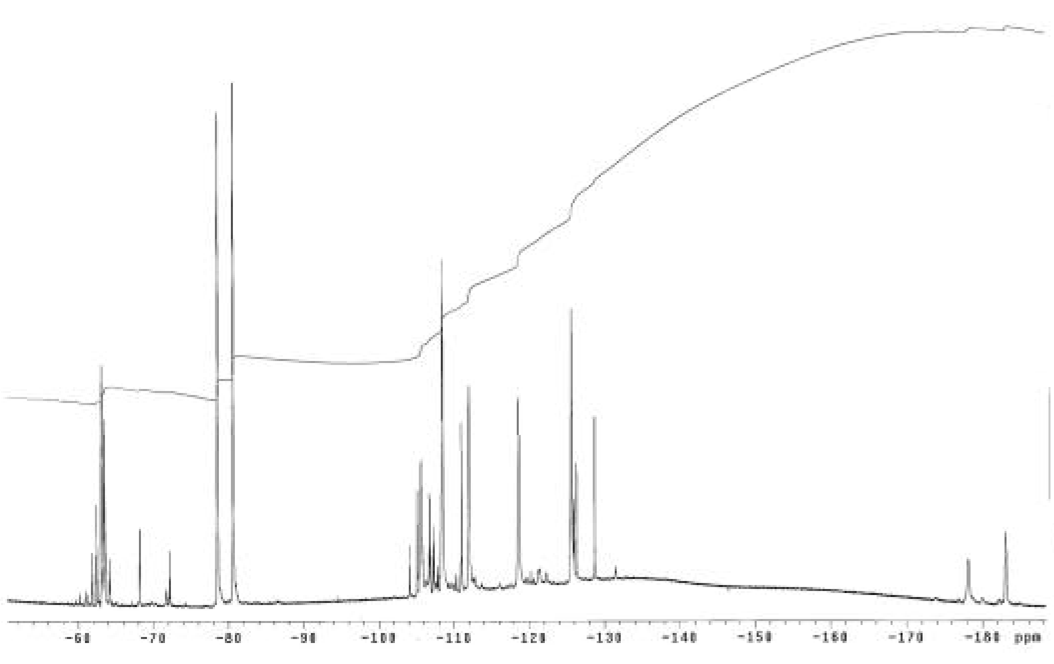


^{19}F NMR Spectrum

AF1012 Spectra

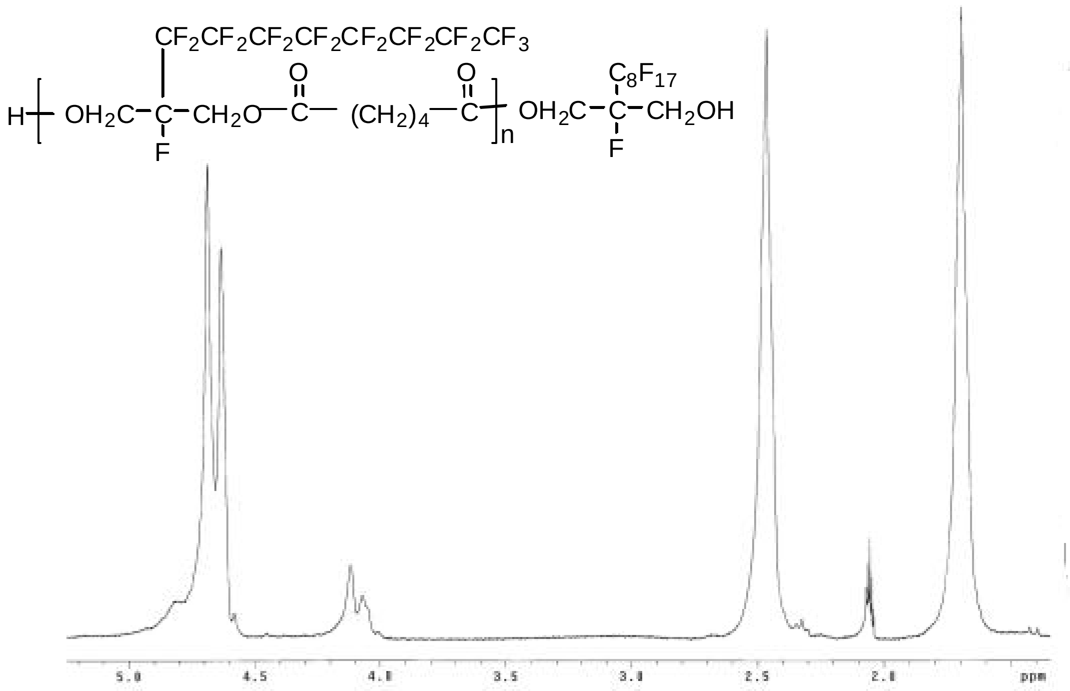


^{1}H Spectrum



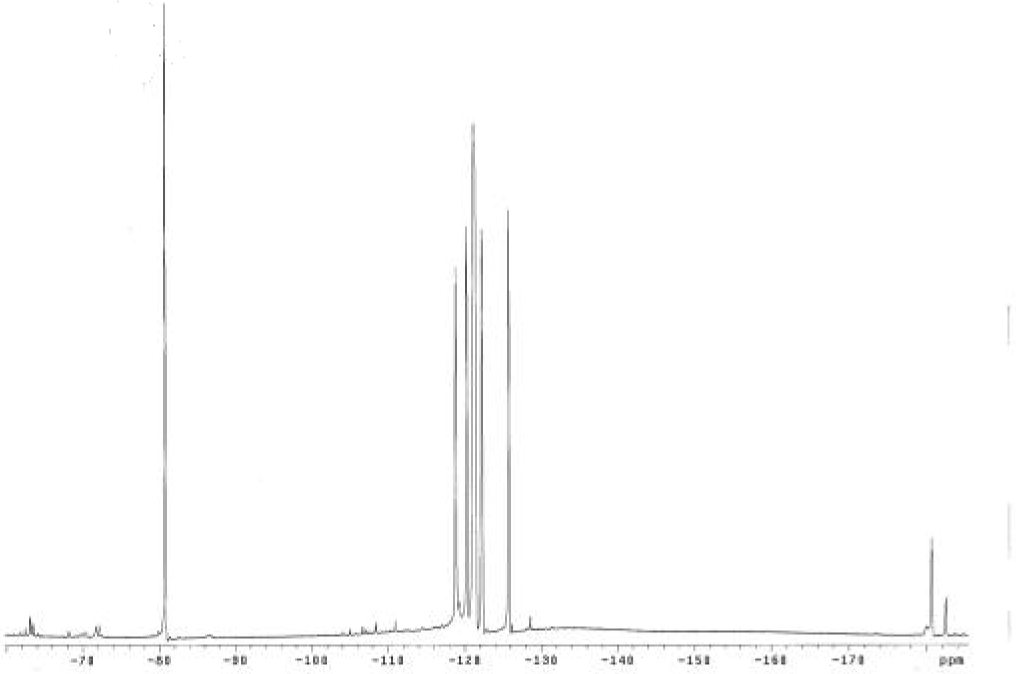
^{19}F NMR Spectrum

AF1013 Spectra



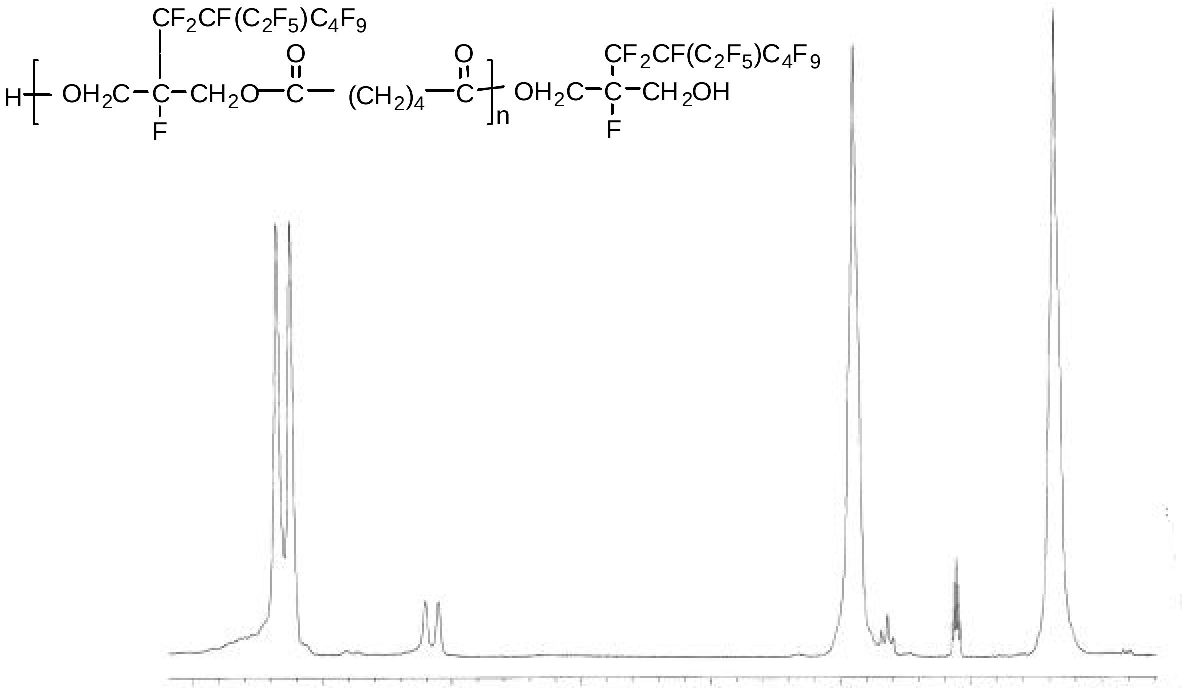
$$\mathrm{H\!\left[OH_2C-\underset{F}{\overset{CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_3}{C}}-CH_2O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n OH_2C-\underset{F}{\overset{C_8F_{17}}{C}}-CH_2OH}$$

^{1}H Spectrum



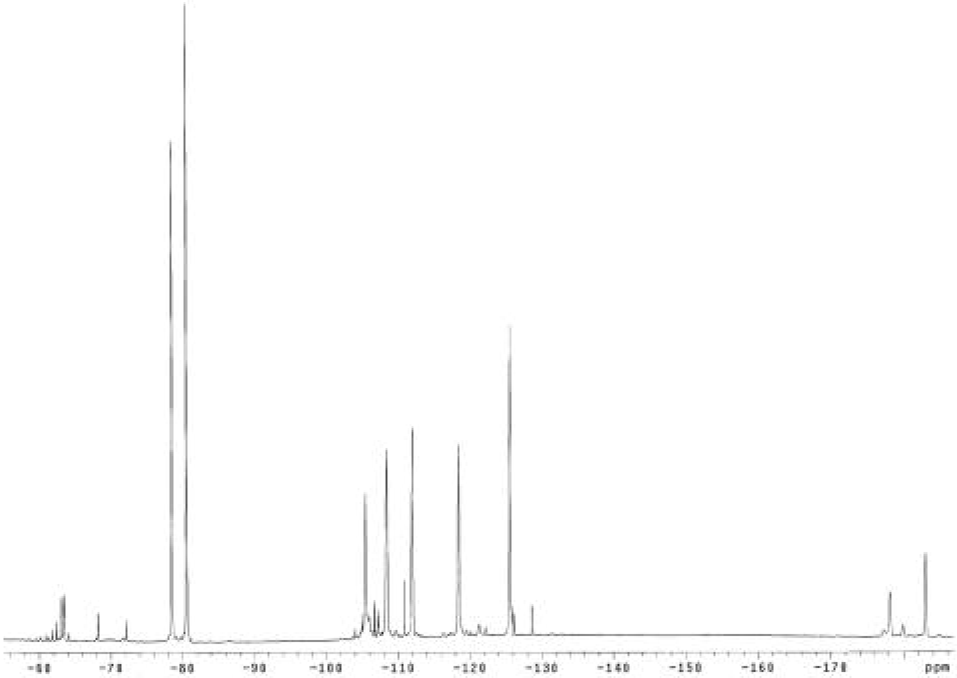
^{19}F NMR Spectrum

AF1014 Spectra



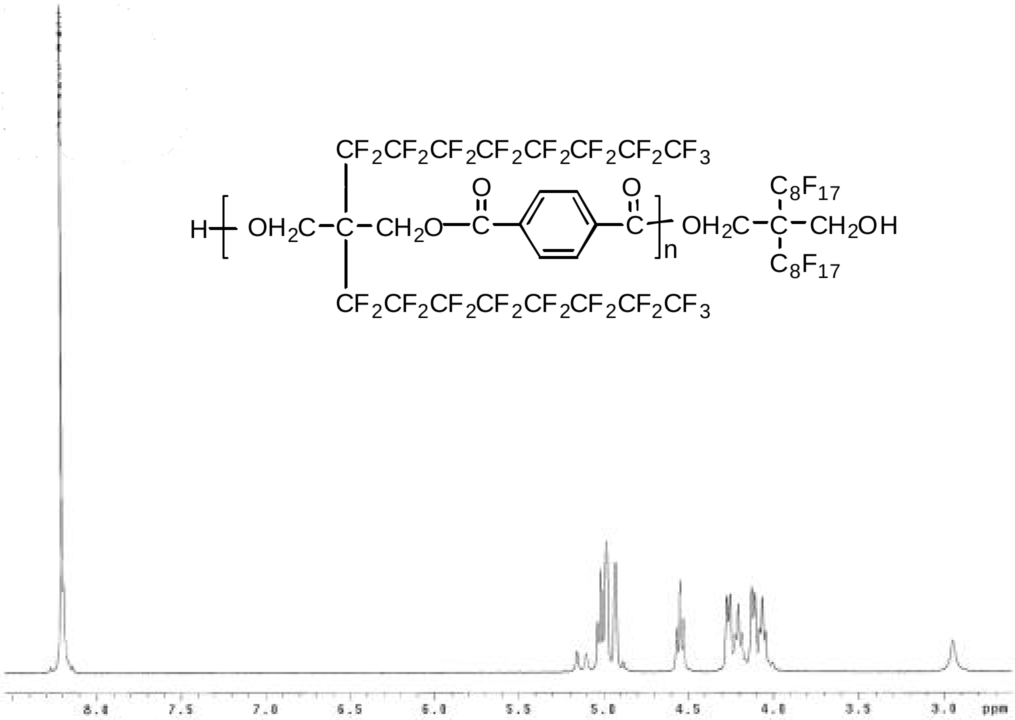
$$\mathrm{H}\left[\mathrm{OH_2C}-\overset{\overset{\textstyle CF_2CF(C_2F_5)C_4F_9}{|}}{\underset{\underset{\textstyle F}{|}}{C}}-\mathrm{CH_2O}-\overset{\overset{\textstyle O}{\|}}{C}-(\mathrm{CH_2})_4-\overset{\overset{\textstyle O}{\|}}{C}\right]_n\mathrm{OH_2C}-\overset{\overset{\textstyle CF_2CF(C_2F_5)C_4F_9}{|}}{\underset{\underset{\textstyle F}{|}}{C}}-\mathrm{CH_2OH}$$

^{1}H Spectrum

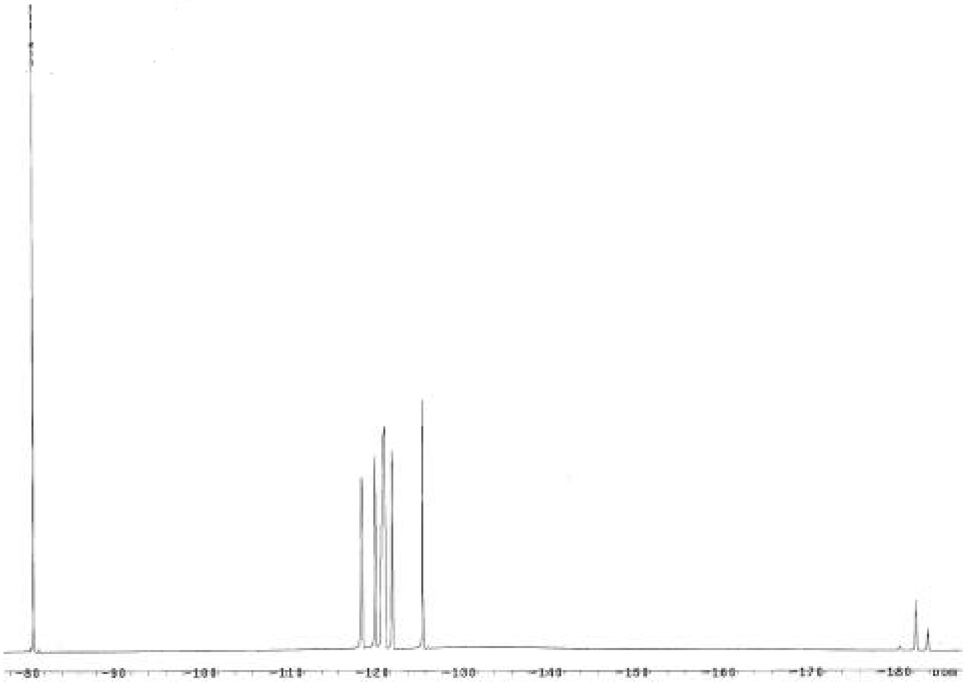


^{19}F NMR Spectrum

AF1015 Spectra

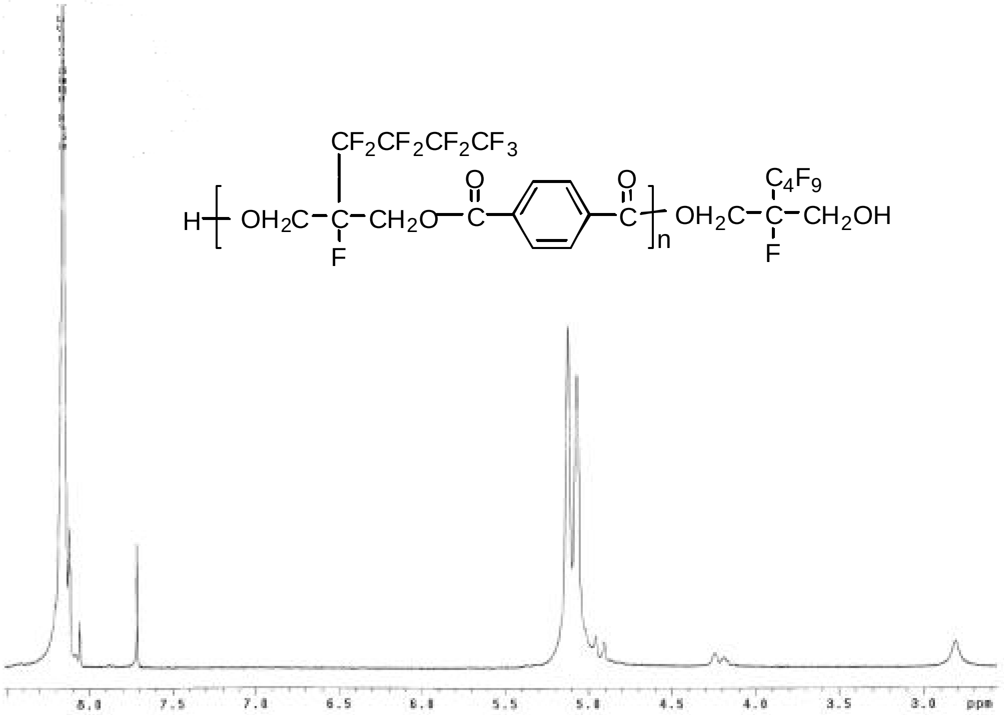


^{1}H Spectrum

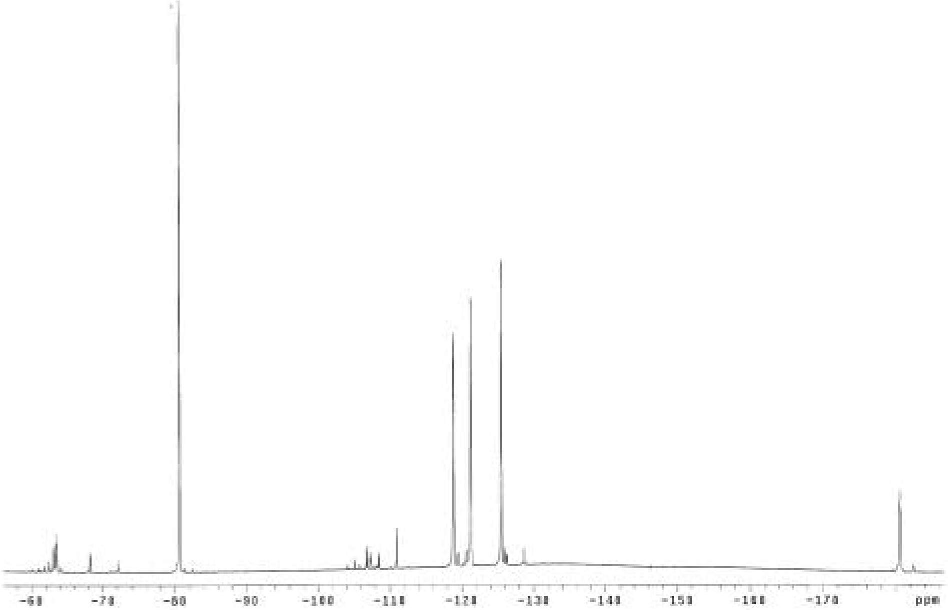


^{19}F NMR Spectrum

AF1016 Spectra



^{1}H Spectrum



^{19}F NMR Spectrum