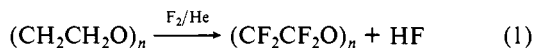# Synthesis of Perfluoropolyethers via Hydrocarbon Polyesters: A New General Method

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Abstract: A new general synthesis for perfluoropolyethers from hydrocarbon polyesters is described. This synthesis is a three-step scheme which involves (1) perfluorination of the hydrocarbon polyester, (2) reaction of SF_4 with the ester carbonyl to produce a CF_2 unit, and (3) high-temperature cleavage to volatile perfluoropolyethers and oligomers. Alternatively, after treatment with nonstoichiometric amounts of SF_4, ester groups remaining in the polymer may be converted by hydrolysis to difunctional perfluoropolyether oligomers. This paper discusses specifically the conversion of the polyesters poly(2,2-dimethyl-1,3-propylene succinate) and poly(1,4-butylene adipate) to branched and linear perfluoropolyether structures, respectively.

As a class the perfluoropolyethers of medium molecular weight are one of the most exotic and important high-performance materials to be developed over the last 10 years. Their stability in many cases exceeds that of poly(tetrafluoroethylene). As high molecular weight polymers, perfluoropolyethers are gaining much importance as perfluorocarbon elastomers, and at slightly lower molecular weights, in the 10 000–24 000 range, they are among the most thermally stable oils known. Important new applications for these materials already have developed as high-performance lubricants in extreme environments and for extraterrestrial applications for which wide liquid ranges and low-temperature lubrication properties are important. Perfluoropolyethers are available commercially now only by the polymerization of hexafluoropropylene oxide by Du Pont[1] and by UV light sensitized random copolymerization of tetrafluoroethylene–oxygen and hexafluoropropylene–oxygen mixtures by Montecatini Edison.[2] Several other perfluoropolyethers are now available by direct fluorination of hydrocarbon polyethers, the simplest process being the fluorination of the hydrocarbon poly(ethylene oxide):[3-6]

$$(CH_2CH_2O)_n \xrightarrow{F_2/He} (CF_2CF_2O)_n + HF \qquad (1)$$

These direct fluorination techniques have markedly increased the number of perfluoropolyether structures available for study, but because there are only 13 commercially available hydrocarbon polyether precursors, they are not generally applicable over the range of attainable structures.

We report here a new synthetic method which we consider to be truly general and which will open synthetic routes to literally hundreds of different perfluoroether and perfluoropolyether structures. This synthetic technique involves the conversion by direct fluorination of hydrocarbon polyesters to perfluoropolyesters followed by treatment with sulfur tetrafluoride to produce new perfluoropolyethers and in some cases perfluoropolyether esters which can be hydrolyzed to produce functional fluorocarbon polyethers.

General Synthetic Scheme
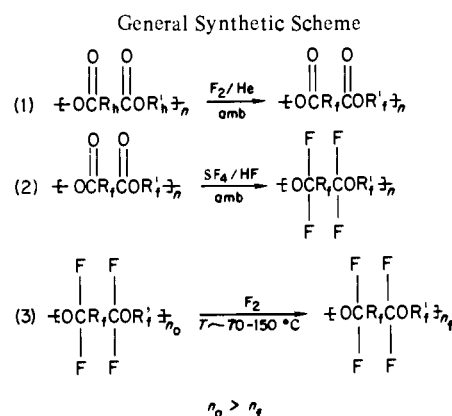
This manuscript reports the conversion in this manner of poly(2,2-dimethyl-1,3-propylene succinate) (I) and poly(1,4-butylene adipate) (II) to novel branched and linear perfluoropolyether structures, respectively:
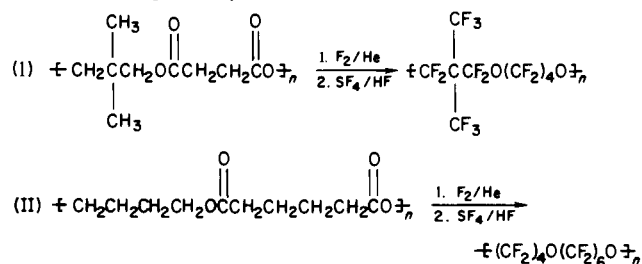
Experimental Section

Material, Analysis, and Physical Measurement. The polymer poly(2,2-dimethyl-1,3-propylene succinate) was obtained from Aldrich Chemical Co. The polymer poly(1,4-butylene adipate) was obtained from Eastman Organics. Both were sieved to 150-mesh powders. The fluorine was technical grade and was purchased from Air Products & Chemicals. The sulfur tetrafluoride (SF_4) was purchased from Scientific Gas Products. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra were obtained with a Beckman IR-20A spectrometer by using KBr disk samples or gas-phase cells fitted with KBr windows. Fluorine NMR spectra were taken on a Varian EM-390 spectrometer operating at 84.67 MHz. Mass spectra were obtained with a Bell and Howell Model 21-490 mass spectrometer. Gas chromatography was done on a Bendix 2300 programmable gas chromatograph equipped with a cryogenic controller and thermal conductivity detector. The column used for separation was $^3/_8$ in. × 24 ft packed with 10% fluorosilicone (QF-10065) on Chromosorb P (60/30 mesh).

Apparatus. The polymer samples were placed in nickel boats, and fluorine reactors described in a previous publication[7] were used to care-

(1) Moore, E. P.; Milian, A. S.; Eleuterio, H. S., E. I. du Pont de Nemours & Co., U.S. Patent 3 250 808, 1966. Miller, W. T. E. I. du Pont de Nemours & Co., U.S. Patent 3 242 218, 1966.

(2) Sianesi, D.; Bernardi, G.; Moggi, G., Montecatini Edison S. p. A., Pat. Fr. 1 531 902, 1968. Dianesi, D.; Fontanelli, R., Montecatini Edison S. p. A., Brit. Pat. 1 226 566, 1971.

(3) Gerhardt, G. E.; Lagow, R. J. *J. Chem. Soc., Chem. Commun.* **1977**, *8*, 259.

(4) Gerhardt, G. E.; Lagow, R. J. *J. Org. Chem.* **1978**, *43*, 4505.

(5) Gerhardt, G. E.; Dumitru, E. T.; Lagow, R. J. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *18*, 157.

(6) Gerhardt, G. E.; Lagow, R. J. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1321.

(7) Badachhape, R. B.; Hauge, R. H.; Margrave, J. L.; Lagow, R. J. *Kirk-Othmer Encycl. Chem. Technol., 3rd Ed.* **1979**, 1.

Table I. Perfluoroethers Isolated from the Reaction Sequence with Poly(2,2-dimethyl-1,3-propylene succinate)

compound	^{19}F shifts/rel intensity		highest m/e in MS
(1) $(CF_3)_2CFCF_2OCF_2CF_2CF_3$ a b c d e f	a, 73.6/6 b, 189.0/1 c, 76.9/2	d, 86.3 e, 130.1/2 f, 84.3	385 $(C_7F_{15}O)$ P-F
(2) $(CF_3)_3CCF_2OCF_2CF_2CF_3$ a b c d e	a, 66.0/9 b, 69.0/2.2 c, 86.5/1.9	d, 132.3/2.1 e, 84.3/3	435 $(C_8F_{17}O)$ P-F
(3) $(CF_3)_2CFCF_2OCF_2CF_2CF_2CF_3$ a b c d e f	a, 75.6/6 b, 189.2/1 c, 78.0/2	d, 86.7/1.9 e, 128.7/4 f, 84.5/3	435 $(C_8F_{17}O)$ P-F
(4) $CF_3OCF_2C(CF_3)_2CF_2OCF_2CF_2CF_3$ a b c b d e f	a, 57.5/3.1 b, 68.5/3.9 c, 65.5/5.9	d, 86.1/2.1 e, 132.0/2.2 f, 83.6/3	501 $(C_9F_{19}O_2)$ P-F
(5) $CF_3CF_2CF_2OCF_2C(CF_3)_2CF_2OCF_2CF_3$ a b c d e f g h	a, 83.3/3.2 b, 131.3/2.1 c, 85.8/2.0 d, 67.8/2.1	e, 65.1/5.9 f, 67.8/2.1 g, 90.3/1.9 h, 89.3/3.0	551 $(C_{10}F_{21}O_2)$ P-F
(6) $(CF_3)_3CCF_2OCF_2CF_2CF_2CF_2OCF_3$ a b c d e f g	a, 65.2/9.1 b, 68.0/1.9 c, 86.0/2.1 d, 127.8/2.0	e, 127.8/2.0 f, 83.8/2.1 g, 57.4/2.9	551 $(C_{10}F_{21}O_2)$ P-F
(7) $CF_3CF_2CF_2OCF_2C(CF_3)_2CF_2OCF_2CF_2CF_3$ a b c d e d c b a	a, 83.7/6.0 b, 131.7/4.0 c, 86.1/4.0	d, 68.3/4.0 e, 65.5/5.8	601 $(C_{11}F_{23}O_2)$ P-F
(8) $CF_3CF_2CF_2OCF_2CF_2CF_2CF_2OCF_2C(CF_3)_2CF_2OCF_2CF_2CF_3$ a b c d e e d f g f c b a	a, 83.0/6.2 b, 131.0/3.8 c, 84.5/3.9 d, 85.5/3.9	e, 126.7/3.8 f, 67.8/4.0 g, 65.0/6.0	817 $(C_{15}F_{31}O_3)$ P-F
(9) $(CF_3)_2CFCF_2OCF_2CF_2CF_2CF_2OCF_2C(CF_3)_2CF_2OCF_2CF_2CF_3$ a b c d e e d f g f h i j	a, 74.9/6.1 b, 189.0/1.0 c, 76.8/2.1 d, 85.8/3.9 e, 126.9/4.0	f, 67.9/4.1 g, 65.0/5.8 h, 84.6/2.0 i, 131.2/1.9 j, 83.3/2.8	867 $(C_{16}F_{33}O_3)$ P-F

Table II. Perfluoroethers Isolated from the Reaction Sequence with Poly(1,4-butylene adipate)

compound	^{19}F shifts/rel intensity		highest m/e in MS
(1) $CF_3CF_2CF_2OCF_2CF_2CF_2CF_3$ a b c c d e f a	a, 84.4/6.0 b, 132.7/2.1 c, 85.6/4.0	d, 128.3/2.1 e, 125.3/2.1 f, 129.0/2.1	435 $(C_8F_{17}O)$ P-F
(2) $CF_3CF_2CF_2OCF_2CF_2CF_2CF_2CF_2CF_3$ a b c c d e e f a	a, 84.3/6.0 b, 132.6/1.7 c, 85.5/4.0	d, 127.8/1.9 e, 125.1/3.5 f, 128.9/1.9	485 $(C_9F_{19}O)$ P-F
(3) $CF_3CF_2CF_2CF_2OCF_2CF_2CF_2CF_2CF_2CF_3$ a b c d d c e e b a	a, 83.9/6.2 b, 127.5/3.8 c, 128.6/3.8	d, 85.3/4.2 e, 124.5/4.0	535 $(C_{10}F_{21}O)$ P-F
(4) $CF_3CF_2OCF_2CF_2CF_2CF_2OCF_2CF_2CF_2CF_2CF_3$ a b c d d e e f g f c	a, 89.8/3.0 b, 90.7/2.0 c, 83.9/4.5 d, 127.8/4.5	e, 85.3/4.5 f, 128.4/4.5 g, 124.9/2.5	601 $(C_{11}F_{23}O_2)$ P-F
(5) $CF_3CF_2CF_2OCF_2CF_2CF_2CF_2OCF_2CF_2CF_2CF_2CF_3$ a b c c d d c c e f e a	a, 84.0/5.6 b, 132.3/1.5 c, 85.1/7.5	d, 127.6/3.5 e, 128.4/3.5 f, 124.4/2.0	651 $(C_{12}F_{25}O_2)$ P-F
(6) $CF_3CF_2CF_2OCF_2CF_2CF_2CF_2OCF_2CF_2CF_2CF_2CF_2CF_3$ a b c c d d c c e f f e a	a, 83.9/5.7 b, 132.4/1.5 c, 85.1/7.6	d, 127.5/4.0 e, 128.4/4.0 f, 124.5/4.5	701 $(C_{13}F_{27}O_2)$ P-F
(7) $CF_3CF_2CF_2OCF_2CF_2CF_2CF_2CF_2CF_2OCF_2CF_2CF_2CF_3$ a b c c d e e d c c f f a	a, 83.9/5.7 b, 132.4/1.5 c, 85.1/7.6	d, 127.5/4.0 e, 124.5/4.5 f, 128.4/4.0	701 $(C_{13}F_{27}O_2)$ P-F

fully react fluorine with the polyesters. The SF$_4$ reaction was done in 30-cm^3 Monel sample cylinders fitted with a Monel valve (the fluorinated sample was handled in an inert atmosphere drybox). A rotating device used to mix and heat the reagents during the SF$_4$ reaction was constructed in our laboratories and was driven with a variable-speed motor.

General. Many highly branched or otherwise unusual perfluoropolyether systems are under study in our laboratory. Hydrocarbon polyester systems which have gone through the reaction sequence with excellent results are the symmetrically branched poly(2,2-dimethyl-1,3-propylene succinate) (Table I) and the linear alkyl poly(1,4-butylene adipate) (Table II). We report here in both instances lower molecular weight polyethers which have been prepared from the high molecular weight perfluoroether by using step 3 of the general reaction scheme. This procedure is designed to fragment the polyether chain and produce oligomers which are GLC separable. The corresponding high molecular weight oils have also been prepared and characterized by ^{19}F and ^{13}C NMR studies. The synthesis of perfluoropolyether diacid systems, which

is of great importance since the diacids can be used in further copolymer chemistry, will be treated elsewhere.[8] We include Tables I and II to list individual perfluoropolyethers. These tables list the ^{19}F NMR spectra of characterized perfluoropolyethers resulting from the high-temperature fragmentation step (step 3). These materials have been purified by gas chromatography and characterized by infrared spectra, NMR, mass spectra (usually P$^+$ or P$^+$-19 ions are observed), and in some cases elemental analysis.

Fluorination of Poly(2,2-dimethyl-1,3-propylene succinate) (PDPS). The hydrocarbon polyester was fluorinated initially at room temperature using dilute fluorine (diluted with helium gas) followed by a stepwise increase in fluorine concentration until pure fluorine conditions were achieved. The reaction conditions used to produce the highly fluorinated polyester are shown in Table III.

(8) Persico, D. F.; Lagow, R. J., manuscript in preparation.

Synthesis of Perfluoropolyethers

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Table III. Poly(2,2-dimethyl-1,3-propylene succinate) Fluorination Conditions

He, cm^3/min	F$_2$, cm^3/min	time, days
100	0	1
50	0.5	1
50	1.0	1
20	1.5	4
20	2.0	1
10	3.0	1
5	3.0	1
0	3.0	3

Table IV. Poly(2,2-dimethyl-1,3-propylene succinate) Polymer Fragmentation Conditions

He, cm^2/min	F$_2$, cm^3/min	temp, °C	time, h
20	2.0	amb	24
5	2.0	50	12
5	4.0	50	12
5	4.0	65–70	48

When 2.520 g of PDPS powder was fluorinated by using the above conditions, 5.621 g of fluoropolymer was obtained. Elemental analysis indicated that per repeating unit of polymer, 12.5–13 of the 14 hydrogens had been replaced by fluorine (C, 25.92%; F, 58.60%; H 1.27%) in the initial stages of this reaction. Oxygen cannot be analyzed in a highly fluorinated sample; however, calculations proved that the balance, 14.21%, coincided with the expected amount of oxygen.

Reaction with SF$_4$. The next step involves conversion of the carbonyls to difluoromethylenes by reacting the highly fluorinated polyester with SF$_4$. Handling of the easily air-hydrolyzed hydrofluoropolyester outside of the reactor was done in an argon glovebox equipped with a drying train to purge H$_2$O, O$_2$, and solvents from the box.

In a typical SF$_4$ reaction, 2.0 g (4.18 mmol of repeating unit) of the hydrofluoropolyester was placed in a 75-cm^3 Monel sample cylinder. When a metal Kel-F vacuum line extension was used, anhydrous HF (20 cm^3) and SF$_4$ (4.1 g, 38 mmol) were distilled into the evacuated cooled (−196 °C) sample cylinder. The loaded cylinder was heated (∼185 °C), and the reaction was run for a period of 20–24 h in the rotating apparatus. Before analysis took place on the volatile products from the SF$_4$ reaction, they were first transferred by vacuum distillation through a metal NaF trap to consume any HF by formation of NaHF$_2$. The volatile species remaining were later combined with lower volatility, higher molecular weight fragments, which were slightly volatile and were obtained only after several hours on the vacuum line. These combined products later were separated on the vacuum line into −78, −131, and −196 °C fractions.

The nonvolatile oil remaining in the cylinder was of primary interest. This oily product was removed from the reaction cylinder with several 20-cm^3 aliquots of a 20% v/v acetone/Freon 113 (CFCl$_2$CF$_2$Cl) solvent mixture. The resulting solution was filtered through a diatomaceous earth (Celite) and activated charcoal bed in a frit which aided in clearing up the solution. The acetone/Freon 113 solvent mixture was vacuum-distilled from the filtered solution (60–80 cm^3) at room temperature to leave behind a viscous gold oil. From 2.0 g of starting fluoropolyester, approximately 1.3 g of oil was produced.

Perfluorination and Fragmentation Step. To obtain the perfluoropolyesters, the oil obtained previously was subjected to additional direct fluorination. Ambient reaction conditions at this stage yielded nonvolatile, high molecular weight perfluoroethers. Separation and characterization of volatile compounds are much easier than that of corresponding nonvolatile compounds, and fragmentation fluorination using elevated temperatures was incorporated as shown in Table IV and was done on several samples to produce such easily characterizable volatile species.

The volatile products resulting from this fragmentation scheme were first separated on the vacuum line into −78, −131, and −196 °C fractions. The ratio of volatile products to nonvolatile products (oil left behind in reaction vessel) is dependent upon the length and severity of the fragmentation conditions.

From 1.30 g of nonvolatile oil at the onset of the fragmentation reaction, yield of 420 mg of nonvolatile perfluoropolyether oil remained.

The higher molecular weight volatile species which stopped in the −78 °C fraction were separated by gas chromatography. The isolated compounds are listed by GC retention time in Table V along with their yields and highest m/e in the mass spectra.

The isolated compounds with full characterization and identification are listed in Table I along with their ^{19}F NMR Chemical shifts. The −78 °C fraction contained 234 mg of volatile products.

Infrared analysis of the highly fluorinated polyester powder, using a fluorocarbon mull between two KBr plates, showed a very strong, broad carbonyl stretch at 1820 cm^{-1} due to the ester carbonyl linkages and fluorocarbon acid remaining in the polyester. When allowed to air-hydrolyze, the peak at 1820 cm^{-1} yielded new peaks at 1760 and 1630 cm^{-1} (due to the free acid carbonyl group and carboxylate anion formation). Also upon hydrolysis new very broad absorptions appeared in the 3000-cm^{-1} region due to the unassociated acid OH group.

Infrared and mass spectral analyses on the volatile products showed that the −196 and −131 °C fractions primarily contained unreacted SF$_4$, SOF$_2$ (byproduct of carbonyl oxidation to CF$_2$), and SiF$_4$ (due to glass etching from incomplete HF removal by NaF or from HF producing hydrofluoro products). Small amounts of acyl fluorides were also detected. The −78 °C fraction contained hydrofluoroacyl fluorides.

An infrared analysis of the nonvolatile oil from the SF$_4$ reaction gave carbon–fluorine features at ∼1100–1300-cm^{-1} and carbonyl at 1820-cm^{-1} absorptions.

The −78 °C fraction from the fragmentation step contained a significant amount of higher molecular weight compounds which were separated by gas chromatography. The isolated compounds were characterized by infrared, ^{19}F NMR, and mass spectral analysis. The infrared spectra were similar to each other with only minor differences. They exhibited the usual broad, strong carbon–fluorine and carbon–oxygen absorptions in the 1350–1100-cm^{-1} region. They all also exhibited the similar characteristic absorptions at 1000 (m), 900 (m), and 760–700 cm^{-1} (m, br).

The ^{19}F NMR's were run in capillary tubes inserted into a 5 mm o.d. NMR tube containing CFCl$_3$ as an external standard.

Elemental analysis of the perfluorinated polyether oil gave the following results. Theoretical: C, 22.41; F, 70.95. Found: C, 22.33; F, 71.10.

Fluorination of Poly(1,4-butylene adipate) (PBA). The polymer poly(1,4-butylene adipate) was sieved to a fine powder (<150 mesh) to give the large surface area necessary for fluorination. Reaction conditions for fluorination are shown in Table VI. When 2.48 g of the polyester was fluorinated under these conditions, 4.97 g of fluoropolymer was obtained. Elemental analysis indicated C 27.12% and F 49.42;, thus giving an empirical formula of C$_{10}$F$_{11.5}$. Assuming that hydrogen and oxygen make up the balance of the compound, this implied that out of the 16 hydrogens in the repeating unit of the original polymer, between 11 and 12 of them had been replaced by fluorine. Additional ambient temperature experiments using pressurized (up to 40 psi) pure fluorine in the last fluorination step and longer times were investigated. However,

Table V. Yields of Volatile Compounds Isolated from the −78 °C Fraction of the Poly(2,2-dimethyl-1,3-propylene succinate) Fragmentation Reaction

compd (GC retention time^a)	yield, mg	wt % of −78 °C frac.	mp, °C	highest m/e in MS
22	23.3	10.0	−115	385 (C$_7$F$_{15}$O)
43	5.6	2.4	−110	435 (C$_8$F$_{17}$O)
45	10.4	4.4	−110	435 (C$_8$F$_{17}$O)
63	15.2	6.5	−95	501 (C$_9$F$_{19}$O$_2$)
75	10.5	4.5	−85	551 (C$_{10}$F$_{21}$O$_2$)
77	8.2	3.5	−85	551 (C$_{10}$F$_{21}$O$_2$)
86	63.7	27.2	−60	601 (C$_{11}$F$_{23}$O$_2$)
97	20.2	8.6	−70	817 (C$_{15}$F$_{31}$O$_3$)
100	28.3	12.1	−65	867 (C$_{16}$F$_{33}$O$_3$)
unseparated material	48.6	20.8		
total	234.0	100.0%		

^{a} GC program 0 °C for 20 min, 1 °C/min → 100 °C, 10 °C/min → 185 °C.

Table VI. Poly(1,4-butylene adipate) Fluorination Conditions

He, cm³/min	Fe₂, cm³/min	time, days
50	1.0	3
20	2.0	1
8	2.0	1
5	4.0	1
0	4.0	3

Table VII. Poly(1,4-butylene adipate) Polymer Fragmentation Conditions

He, cm³/min	Fe₂, cm³/min	temp, °C	time, h
18	2.0	amb	8
5	4.0	amb	24
5	4.0	50	18
5	4.0	65–70	36

hydrogen remained possibly in the form of associated hydrogen fluoride.

The hydrofluoropolyester was weighed and placed in the 30-cm³ reaction cylinders in an argon filled drybox. When an all-metal (brass, Monel, and stainless steel) extension of a vacuum line was used, the appropriate amount of anhydrous HF was drained from a translucent, graduated Kel-F cylinder into the cooled (0 °C) sample cylinder. The required amount (usually a 4- to 5-fold excess) of SF₄ was measured in a standard volume by the ideal gas method and transferred by vacuum distillation into the cooled (−196 °C) polyester/HF-containing sample cylinder. In a typical reaction, 0.80 g (2.0 mmol of repeating unit; average molecular weight of the fluorinated polyester repeating unit ~400) of fluoropolyester and 1.77 g (16.3 mmol of SF₄) and ~8 mL of anhydrous HF were used in the 30-cm³ sample cylinder. The charged cylinder was heated and shaken throughout the reaction. The most successfuly reaction temperatures were 180–188 °C, and all reaction times were 22 ± 2 h.

If the volatile products from the SF₄ reaction were to be analyzed, they were first transferred by vacuum distillation (all-metal system) into a cooled (−196 °C) stainless steel cylinder charged with dry NaF pellets. The cylinder was warmed and shaken for several hours so that all anhydrous HF would be consumed by NaHF₂ formation. The remaining volatile species were pumped from the NaF cylinder into the vacuum line and combined with low-volatility, higher molecular weight products from the SF₄ reaction cylinder that did not distill into the NaF cylinder but would transfer from the reaction cylinder when subjected to a dynamic vacuum for several hours. The combined volatile products were vacuum line fractionated into −78, −131, and −196 °C fractions.

The −196 and −131 °C fractions were shown by infrared analysis to contain mainly unreacted SF₄, SOF₂, and SiF₄. SOF₂ is the sulfur-containing byproduct of carbonyl to CF₂ conversion by SF₄, and SiF₄ is due to glass etching by inefficient HF removal or HF-producing decomposition of metastable hydrofluoro products. Infrared analysis also indicated the presence of small amounts of fluoroacyl fluorides in the −131 °C fraction, but separation of these low yield products from the large amount of toxic sulfur-containing species in the fraction would have been difficult and dangerous and of little consequence. The −78 °C fraction contained (by IR) hydrofluoroacyl fluorides, but gas chromatographic analysis indicated that it was a many-component inseparable mixture. From 800 mg of starting fluoropolyester, 163 mg (average of two reactions) of the −78 °C fraction of inseparable hydrofluoroacyl fluorides was produced.

The nonvolatile only product of the SF₄ reaction was removed from the reaction cylinder by extraction with several 20-mL aliquots of Freon 113 (CFCl₂CF₂Cl). The solution was filtered and concentrated to approximately one-quarter of its volume by distillation, with a small amount of some yellow needlelike crystals being filtered out. The remaining solution was further concentrated by vacuum distillation. A viscous gold oil resulted. For 800 mg of starting fluoropolyester, an average of 500 mg of this oil was produced.

The yellow crystals were analyzed by melting point (117–119 °C) and solubilities (benzene and carbon disulfide) and found to be elemental sulfur. Sulfur was obtained in amounts of 50–100 mg from the reactions.

The viscous, nonvolatile oil was analyzed by infrared spectroscopy of a thin oil film cast on a KBr window from the CFCl₂CF₂Cl solution. During its workup, no provision for the exclusion of atmospheric moisture was made, thus allowing any acyl fluoride end groups or remaining fluoroester linkages to be hydrolyzed to acid end groups. It was clearly evident from comparison of the relative intensities of the carbon–fluorine (~1200 cm⁻¹) and fluorocarbon acid (~1780 cm⁻¹) absorptions that the SF₄ treated material was much lower in functional group content than the starting fluoropolyester.

Samples of SF₄-produced, functional, hydrofluoro oil were fluorinated in a room temperature–high temperature reaction, according to the conditions outlined in Table VII. The volatile products were first separated by vacuum line trap-to-trap fractionation into −196, −131, and −78 °C fractions. The relatively large −196 °C fraction contained (by IR) mainly COF₂ from decarboxylation and CF₄ from chain end degradation. The very small −131 °C fraction contained fluoroacyl fluorides.

Significant amounts of higher molecular weight volatile compounds in the −78 °C fraction were separated by gas chromatography. The isolated compounds are listed by their GC retention times in Table VIII along with their yields, melting points, and highest m/e peaks in the mass spectra.

The isolated compounds were characterized and identified by infrared, ¹⁹F NMR, and mass spectral analyses. All infrared spectra were very similar to each other and to the infrared spectra of other perfluoroethers. They exhibited the usual strong, broad carbon–fluorine and ether carbon–oxygen absorptions at 1350–1100 cm⁻¹ and, also, all showed the same characteristic absorptions at 1000 (m), 900 (m), and 750–700 cm⁻¹ (m, br).

The ¹⁹F NMR signals for the isolated compounds were broad unresolved multiplets, but their chemical shifts and normalized integrated intensities were useful for structure assignment. The ¹⁹F NMR data are listed in Table II with the signal assignments and deduced structures. For the largest perfluorocompound isolated, $C_{13}F_{28}O_2$ by its mass spectrum, the NMR signal at 132.4 ppm implies an *n*-propyl end group, but the two possible structures $C_3F_7O(CF_2)_4OC_6F_{13}$ and $C_3F_7O(CF_2)_6$-OC_4F_9 cannot be distinguished by NMR analysis.

The fragmentation fluorination of the SF₄ reaction product was of short duration so that all the substrate was not fragmented to volatile species. Along with the volatile products just described, a nonvolatile, nonfunctional, viscous perfluoro oil was obtained. Its infrared spectrum (a thin oil film) was almost identical, even the sharp "fingerprint" absorptions, with those of the volatile perfluoroethers. The ¹⁹F NMR spectrum of the oil, "neat" or in CFCl₂CF₂Cl solution, was characterized by very broad signals at the same chemical shift values as the NMR signals for the isolated volatile perfluoroethers.

Results and Discussion

These new methods offer a number of extremely significant and important advantages. The first advantage with this technique is that it is possible to prepare perfluoropolyethers containing more than two sequential carbon atoms in the perfluoropolyether backbone between adjacent oxygen sites. In the tetrafluoroethylene oxide and hexafluoropropylene oxide technology (i.e., polymerization of vinyl monomers and vinyl epoxides), one is limited to repeating two carbon–ether chains. A second important advantage is that perfluoropolyethers with unsymmetrical repeating units (alternating copolymers) are available (AOBOAOB) whereas with vinyl epoxides, other than random copolymers, one must have repeating AOA structures. A third advantage is that this technique also is capable of producing highly branched ethers

Table VIII. Yields of Volatile Compounds Isolated from the −78 °C Fraction of the Poly(1,4-butylene adipate) Fragmentation Reaction

compd (GC retention time[a]	yield, mg	wt % of −78 °C frac.	mp, °C	highest m/e in MS
33	50	16.3	−115	435 ($C_8F_{17}O$)
51	64	20.9	−110	485 ($C_9F_{19}O$)
64	36	11.8	−100	535 ($C_{10}F_{21}O$)
77	32	10.5	−100	601 ($C_{11}F_{23}O_2$)
90	42	13.7	−95	651 ($C_{12}F_{25}O_2$)
100	20	6.5	−90	701 ($C_{13}F_{27}O_2$)
unseparated material	62	20.3		
total	306	100.0%		

[a] GC program 0 °C for 20 min, 1 °C/min → 100 °C, 10 °C/min → 185 °C.
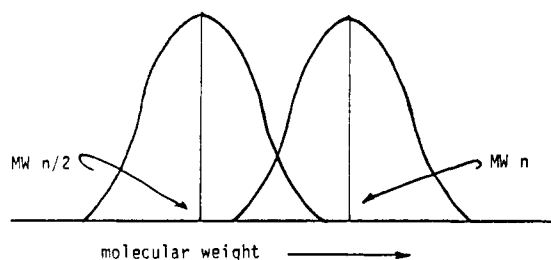
Figure 1. Gaussian distribution of difunctional perfluoropolyether molecular weights produced with n and $n/2$ mol of SF_4. Both samples are hydrolyzed to produce the diacids after treatment with SF_4.

which have elastomeric properties and fluids of higher thermal stability.

It is clear that if one considers as a class vinyl epoxides of the form of structure **2** where **R** groups are large, such as more than two trifluoromethyls or structures much more exotic, polymerization would be hampered markedly by the steric bulk of certain R groups, leading to a low molecular weight material. In many

2
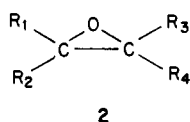
cases the synthesis of certain vinyl-substituted epoxide monomers would be extremely difficult or impossible even if polymerization was not a problem. A fourth and very important advantage with this method is the ease with which one can leave ester units in the high polymer and subsequently base hydrolyze to produce difunctional fluorocarbon polyesters of lower molecular weight.

3
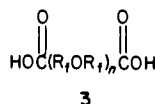
Functionalization of fluorocarbon polyethers is exceedingly difficult with conventional technology and often involves many steps and extremely high costs. An important effect observed when nonstoichiometric amounts of SF_4 are used is illustrated in Figure 1. Normally a 2-fold excess of SF_4 is necessary to obtain the high molecular weight nonfunctional polymer. As illustrated, if less than stoichiometric amounts of SF_4 are used, one obtains different Gaussian distributions of molecular weights, indicative of the average distance between the ester units left in the macromolecule. By varying the SF_4 used, it is possible to shift the average molecular weight distribution at will. This technology

makes available a very low-cost route to important new fluorocarbon surfactants and intermediates.

There are some 350 commercially obtainable linear hydrocarbon polyesters; thus the sulfur tetrafluoride-to-ether conversion technique is very broadly applicable to produce many novel perfluoroether structures. There are also over 750 hydrocarbon polyester structures prepared and characterized in the literature, allowing this technique almost total structural flexibility.

The reaction of sulfur tetrafluoride with carbonyls is a well-known reaction[9] and has been used widely in the pharmaceutical industry to produce selective fluorination sites on steriod and other drugs.[10] De Pasquale[11] and Griffin[12] have demonstrated the conversion of small and oligomeric, highly fluorinated esters to fluorinated ethers. Their starting materials were made by polymerization of perfluorocarbon diacids and fluorine containing diols. Because perfluoroalcohols are thermally unstable (α fluorine leads to HF elimination above -60 °C), it is not possible to prepare perfluoropolyester materials by this technique. In their studies it was necessary to have hydrogen remaining on both α sites of the diol, which was used to prepare the highly fluorinated polyester. There are also severe limitations on the number and type of structures of branched fluorodiols available. Due to the versatility of direct fluorination, one would be forced to prepare many of the fluorodiol structures with this technology.[13]

The individual fluorocarbons reported in this manuscript are light oils useful in certain lubrication applications, prosthetic fluids in biomedical applications, oxygen carriers, and solvents. The higher molecular weight materials have a myriad of applications. This technique opens the path for synthesis of an unlimited number of new materials and broadens this new class of perfluoro compounds, the synthesis of which could be among the most important materials developments in recent times.

(9) (a) Hasek, W. R.; Smith, W. C.; Englehardt, V. A. *J. Am. Chem. Soc.* **1960**, *82*, 543. (b) Smith, W. C. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 467.

(10) (a) Sheppard, W. A. *J. Org. Chem.* **1964**, *29*, 1. (b) Aldrich, P. E.; Sheppard, W. A. *J. Org. Chem.* **1964**, *29*, 11. (c) Sheppard, W. A. *Org. Synth.* **1964**, *44*, 39.

(11) De Pasquale, R. J. *J. Org. Chem.* **1973**, *38*, 3025.

(12) Griffin, W. R. U.S. Patent 4 201 876, 1980; U.S. Patent 4 238 602, 1980.

(13) Lagow, R. J.; Margrave, J. L. *Proc. Natl. Acad. Sci. U.S.A.* **1970**, *67*, 4, 8A.