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Synthesis of Branched Perfluoro Ethers by Direct Fluorination. Copolymers Based on Hexafluoroacetone

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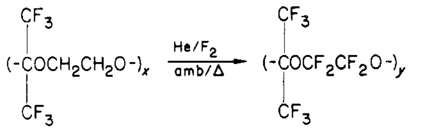
ABSTRACT: The copolymerization of hexafluoroacetone with ethylene oxide, propylene oxide, and trimethylene oxide and subsequent fluorination utilizing elemental fluorine have led to the synthesis of new perfluoro ethers. The syntheses of volatile perfluoro ethers along with perfluoro oligomeric oils from the starting copolymers are reported. Characterization of these new copolymers along with ^{19}F and ^{13}C NMR studies and TGA analyses are discussed.

Introduction

Understanding of the physical properties and structure–property correlations of perfluoro polyethers, one of the most important new classes of materials and high-performance lubricants developed over the last 10 years, is very much limited by the lack of available structures. Most studies have used two commercially available materials: a homopolymer of hexafluoropropylene oxide (Du Pont's Krytox) and the random copolymer of tetrafluoroethylene and oxygen (Montecatini Edison's Fomblin fluids). Montiedison has two types of fluids, a UV scrambled fluid and a more ordered thermal system. Basically the variations in structure are limited to molecular weight distributions.

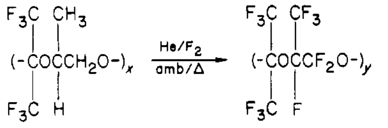
Previously in our laboratory we have produced perfluoro polyether oils, elastomers, and lower molecular weight species by direct fluorination of ethylene oxide,[1] perfluoropropylene oxide,[2] and a few other structures. Recently this laboratory has developed a technique for fluorination of linear hydrocarbon polyesters followed by conversion to polyethers using the selective reagent SF_4, which converts the carbonyl in the ester to a CF_2 group, thus producing a new perfluoro polyether.[3] Special advantages of this technique include synthesis of carbon chains in the polymer backbone longer than two carbon atoms (not possible with vinyl epoxides), synthesis of unsymmetrical copolymers such as AOB alternating perfluoro copolymers, and access to highly branched perfluoro polyether systems. We report here an additional method of value which involves the copolymerization of hexafluoroacetone with oxygen-containing cyclic starting materials. This method is also capable of producing three and four carbon atom linkages between ethers and branched systems after controlled fluorination:

hexafluoroacetone/ethylene oxide copolymer



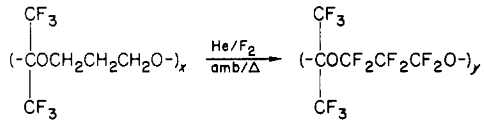
$$(\text{-}\underset{CF_3}{\overset{CF_3}{C}}OCH_2CH_2O\text{-})_x \xrightarrow[\text{amb}/\Delta]{\text{He}/F_2} (\text{-}\underset{CF_3}{\overset{CF_3}{C}}OCF_2CF_2O\text{-})_y \qquad (1)$$

hexafluoroacetone/propylene oxide copolymer



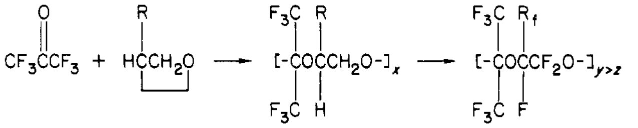
$$(\text{-}\underset{F_3C}{\overset{F_3C}{C}}O\underset{H}{\overset{CH_3}{C}}CH_2O\text{-})_x \xrightarrow[\text{amb}/\Delta]{\text{He}/F_2} (\text{-}\underset{F_3C}{\overset{F_3C}{C}}O\underset{F}{\overset{CF_3}{C}}CF_2O\text{-})_y \qquad (2)$$

hexafluoroacetone/oxetane copolymer



$$(\text{-}\underset{CF_3}{\overset{CF_3}{C}}OCH_2CH_2CH_2O\text{-})_x \xrightarrow[\text{amb}/\Delta]{\text{He}/F_2} (\text{-}\underset{CF_3}{\overset{CF_3}{C}}OCF_2CF_2CF_2O\text{-})_y \qquad (3)$$

The patent literature contains several methods for synthesis of hexafluoroacetone (HFA)–epoxide copolymers.[4] The best technique for our purposes was to utilize bulk polymerization with an anionic catalyst. It was hoped that a method could be developed which would make it possible to place varying amounts (10–50%) of the HFA species in the precursor backbone. However, for reasons involving the nature of the monomers, only a 1:1 alternating polymer was attainable. The general reaction scheme is outlined as follows:



$$CF_3\overset{O}{\overset{\|}{C}}CF_3 + H\overset{R}{C}CH_2O \longrightarrow [\text{-}\underset{F_3C}{\overset{F_3C}{C}}O\underset{H}{\overset{R}{C}}CH_2O\text{-}]_x \longrightarrow [\text{-}\underset{F_3C}{\overset{F_3C}{C}}O\underset{F}{\overset{R_f}{C}}CF_2O\text{-}]_{y>z}$$

Perfluoro polyethers are highly regarded in the specialty lubricant field because of their long liquid range, low vapor pressure, and high thermal and oxidative stability.[5] Presently Du Pont's anionic polymerization of perfluoropropylene oxide (Krytox)[6] and Montecatini Edison's photoinduced polymerization of perfluoro olefins, using oxygen and ozone (Fomblin),[7] are currently the only sources of commercially attainable perfluoro polyethers.

Two very interesting analytical themes seem to be developing in the analysis of lubrication properties and thermal stabilities of perfluoro polyethers. Many researchers feel that the unusual liquid properties of the random Fomblin Z copolymer is a direct result of the inclusion of difluoromethylene oxide (CF_2O) linkages in the polyether which provide hinglike flexibility. Another view is that the higher thermal stability of the perfluoropropylene oxide polymers results in some way from the branching (trifluoromethyl group) in the polymer. Studies in our laboratory[2] and discussions with others in this field[8] have led to an emerging view that it is the difluoromethylene unit that results in the lower thermal stability of the Fomblin Z material with respect to the Krytox structure. Certainly the homopolymer[2a] of difluoromethylene oxide is subject to depolymerization and readily forms the very stable molecule carbonyl fluoride.

One should note that these new systems provide a combination of both effects. It is quite clear then that consecutive methylene oxide linkages in a copolymer would provide much greater thermal instability problems than observed in these fluids. It should be noted that the systems reported here contain branched (trifluoromethyl-substituted) methylene units in a regular copolymer sequence so they are actually very much a hybrid of the two systems.

Experimental Section

All gaseous reactants were measured by using vacuum line techniques and assuming ideal behavior. The reactants were

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degassed at liquid-nitrogen temperatures and expanded into a 2.07-L Pyrex bulb connected to a mercury manometer. A Pyrex tube which had been charged, under nitrogen, with the selected catalyst, was used as the reaction container. The reactants were condensed into the Pyrex tube at −196 °C and degassed again, and the tube was sealed. The tube was then brought to −78 °C in a dry ice/acetone slush and slowly warmed to ambient. The reactants were agitated at ambient for 6 h and then the temperature was raised to 65 °C for 36 h. When the reaction was complete, the resulting product was held under vacuum to remove any unreacted monomer.

The fluorination apparatus has been described previously.[9] The reaction conditions to preserve each polymer structure varied significantly. Optimized conditions are given under each synthetic subheading. Volatile products from the reaction were collected in a glass trap maintained at dry ice temperature. These products were washed with a KOH/H_2O mixture to remove any functional components, dried on molecular sieves, and separated by gas chromatography to obtain pure compounds for analysis.

The resultant nonvolatile oils from the reaction were dissolved in Freon 113 ($CF_2ClCFCl_2$) and filtered through a Celite/Norit bed to remove any foreign matter. The solvent was then removed under vacuum at 80 °C for 24 h.

Physical analysis of the isolated compounds and the oligomeric oils was obtained in the following manner. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY, and Galbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were obtained with a Perkin-Elmer 467 spectrometer utilizing a gas cell with KBr windows, or by casting a film (oils) from Freon 113 onto KBr plates. ^{19}F NMR spectra were run on a Varian EM-390 spectrometer operating at 84.67 MHz. $^{13}C\{^{19}F\}$ (^{19}F decoupled) NMR spectra were run on Bruker WH-100 spectrometer. Mass spectra were obtained with a Bell and Howell 21-490 mass spectrometer with the ion source cooled to ambient. Gas chromatography was done on a Bendix 2300 programmable chromatograph equipped with a cryogenic controller and a thermal conductivity detector. The column used for sample separation was $^3/_8$ in. × 24 ft packed with 10% Fomblin Z-25 on Chromosorb P (60/30 mesh), with a helium flow of 100 cm^3/min. GPC analyses were done by using a Waters Associates Inc. system equipped with a R-401 differential refractometer and an IBM 10-μm GPC/SEC column. TGA analyses were obtained on a Du Pont Model 990 thermal analyzer equipped with a Du Pont Model 951 thermogravimetric analyzer.

Hexafluoroacetone/Ethylene Oxide Copolymer (HFA/EO). A 5-mg sample of Et_4NCl was added to 4.65×10^{-2} mol each of HFA and EO. The resultant polymer weighed 8.6 g and this corresponds to a yield of 88%. The white crystalline powder had a melting range of 182–184 °C (lit. mp 188–192 °C;[2] elemental analysis gave C, 28.65; F, 54.50; H, 1.96 (theor C, 28.57; F, 54.29; H, 1.90), confirming a 1:1 copolymer.

Because of the crystalline nature of the polymer, ambient conditions were first studied for the fluorination procedure. These conditions proved to be unsatisfactory as significant cleavage to hydrogen-containing volatile products occurred before pure fluorine conditions could be reached. Subsequently low temperatures were found to be necessary early in the reaction to assure perfluorinated volatile products as well as a higher amount of the desired perfluorinated oil. Initial conditions were therefore set at −78 °C and the total sequence of reaction conditions can be seen in Table I. These conditions proved to be advantageous as degradation yielding extremely volatile products (those which are volatile at −78 °C) was kept to an acceptable level and a reasonable amount of nonvolatile perfluoro polyether oil was also obtained. After each temperature increment the volatile products were weighed and analyzed by gas chromatography. The relative amount of volatile products at each temperature was the same, indicating that the same fragmentation processes were responsible for the volatile species over the entire temperature range. There was also no threshold temperature (up to 70 °C) above which all of the polymer degraded to volatile species. Infrared analysis of the nonvolatile oil proved it contained functional end groups, as would be expected by the cleavage route (see Discussion section). To obtain a nonfunctional product the oil was allowed to air hydrolyze, thus allowing the carbonyl fluoride end groups to be hydrolyzed to carboxylic acid end groups. These acid groups were then removed by further reaction with elemental fluorine which causes decarboxylation leaving behind perfluoro nonfunctional end groups. Infrared analysis of the volatile byproducts revealed that they also contained a substantial quantity of functionality. The volatile fractions were washed with a KOH/H_2O solution, leaving behind the nonfunctional polyethers. These were subsequently separated and characterized. The results are shown in Table II.

Table I
Copolymer Fluorination Conditions

time, h	He, cm^3/min	F_2, cm^3/min	temp, °C
	HFA/EO		
24	50	1.0	−78
24	0	2.0	−78
24	0	2.0	amb
12	0	2.0	35
12	0	2.0	45
12	0	2.0	55
12	0	2.0	65
12	0	2.0	70
12	0	2.0	70
12	60	0	70
	HFA/PO and HFA/TMO		
60	100	1.0	amb
24	0	1.0	amb
24	0	1.0	35
24	0	1.0	45
12	0	1.0	50
12	0	1.0	50

The infrared spectra for the seven isolated compounds were all similar and contained a strong broad absorption in the carbon–fluorine and ether carbon–oxygen region (1350–1050 cm^{-1}) as well as strong, sharp characteristic absorptions in the region at 1000–980 and 730–660 cm^{-1}. Additionally, a peak at 890–870 cm^{-1} can be found in all molecules containing a perfluoromethoxy end group. The infrared spectrum of the resultant oil contains the same basic features with no trace of functional end groups.

Mass spectrometry was extremely useful for determining the molecular weights of the volatile components. By running the ion source of the spectrometer at ambient the extensive fragmentation and rearrangements inherent in mass spectra of fluorocarbons was kept to a minimum. This method resulted in the observation of parent minus fluorine ions for most of the volatile compounds (Table II) along with the characteristic fragmentation pattern.

The most useful method for structural identification proved to be ^{19}F NMR. The perfluoro ether ^{19}F NMR signals, assignments, and relative intensities are listed in Table II. The average chemical shifts of the various fluorine nuclei were as follows (in ppm from external $CFCl_3$): CF_3 of methoxy end groups, −56.9; internal pendant groups, −78.5; CF_3 of isopropyl end groups, −83.2; all CF_2O groups, −88.5; CF of isopropyl end groups, −147.3. The observed coupling patterns are good examples of the unusual coupling characteristics often observed in ^{19}F NMR spectroscopy. The CF_3 and CF groups of the isopropyl group do not couple with one another; however, they both couple with the CF_2 "across" the oxygen linkage yielding average coupling constants of 5 and 21 Hz, respectively. All other coupling characteristics were routine.

The $^{13}C\{^{19}F\}$ NMR data are in agreement with the assigned structure and are listed in Table III. The average chemical shifts of the various carbon nuclei were as follows (in ppm downfield from Me_4Si): carbon of methoxy end groups, 119.8; carbon of pendant internal methyl groups, 118.8; carbon of isopropyl methyl groups, 118.0; carbon of CF_2O groups, 115.2; tertiary carbon of isopropyl groups, 102.5; quaternary carbon, 96.0.

The physical characterization involving melting point determination was complicated by the problem of the liquids freezing to glasses rather than crystalline powders. Repeated analysis, however, gave reproducible results and these are found in Table III along with the boiling points of the two perfluoro ethers which were obtained in sufficient amounts.

Table IV lists the yields of volatile products and oil obtained from a typical reaction relative to 1.0 g of starting materials. From ^{19}F NMR and group analysis the average molecular weight of the

Table II
Perfluoro Ethers Isolated from Hexafluoroacetone/Ethylene Oxide Polymer Fluorination

compd	^{19}F shift (ppm)/rel intensity	highest *m/e* in mass spec
(1) $(CF_3)_2CFOCF_3$ a b c	(a) 83.3/6, (b) 148.2/1, (c) 56.6/3	235 (C_4F_9O), P − F
(2) $CF_3OC(CF_3)_2OCF_3$ a b a	(a) 57.3/1, (b) 78.7/1	301 ($C_5F_{11}O_2$), P − F
(3) $(CF_3)_2CFOCF_2CF_2OCF(CF_3)_2$ a b c c b a	(a) 83.3/6, (b) 146.9/1, (c) 88.5/2	451 ($C_8F_{17}O_2$), P − F
(4) $CF_3OC(CF_3)_2OCF_2CF_2OCF(CF_3)_2$ a b c d e f	(a) 56.7/3, (b) 78.4/6, (c) 89.7/2, (d) 87.7/2, (e) 147.1/1, (f) 83.2/6	467 ($C_8F_{17}O_3$), P − CF_3
(5) $CF_3OC(CF_3)_2OCF_2CF_2OC(CF_3)_2OCF_3$ a b c c b a	(a) 57.1/3, (b) 78.7/6, (c) 89.7/2	545 ($C_{10}F_{19}O_4$), P − F_3
(6) $(CF_3)_2CFOCF_2CF_2OC(CF_3)_2OCF_2CF_2OCF(CF_3)_2$ a b c d e d c b a	(a) 83.2/6, (b) 147.1/1, (c) 87.7/2, (d) 88.1/2, (e) 78.3/3	733 ($C_{13}F_{27}O_4$), P − F
(7) $CF_3OC(CF_3)_2OCF_2CF_2OC(CF_3)_2OCF_2CF_2OCF(CF_3)_2$ a b c c b c d e f	(a) 56.6/3.1, (b) 78.3/11.6, (c) 89.0/5.9, (d) 87.6/2.0, (e) 147.1/1.0, (f) 83.2/6.0	799 ($C_{14}F_{29}O_5$), P − F
(8) $(CF_3)_2CFO[CF_2CF_2OC(CF_3)O]_xOCF_3$ a b c c d e	(a) −81.3, (b) −145.7, (c) −87.7, (d) −76.6, (e) −54.9	

Table III
Perfluoro Ethers Isolated from Hexafluoroacetone/Ethylene Oxide Polymer Fluorination

compd	$^{13}C\{^{19}F\}$ shift, ppm	mp, °C
(1) $(CF_3)_2CFOCF_3$ a b c	(a) 118.0, (b) 102.5, (c) 119.3	−123
(2) $CF_3OC(CF_3)_2OCF_3$ a b c a	(a) 119.3, (b) 95.5, (c) 118.9	−60
(3) $(CF_3)_2CFOCF_2CF_2OCF(CF_3)_2$ a b c c b a	(a) 118.0, (b) 102.4, (c) 115.1	−100 (bp 115 °C)
(4) $CF_3OC(CF_3)_2OCF_2CF_2OCF(CF_3)_2$ a b c d d e f	(a) 120.2, (b) 95.9, (c) 118.7, (d) 115.2, (e) 102.6, (f) 118.0	−98 (bp 144 °C)
(5) $CF_3OC(CF_3)_2OCF_2CF_2OC(CF_3)_2OCF_3$ a b c d d b c a	(a) 120.3, (b) 96.0, (c) 118.8, (d) 115.3	0
(6) $(CF_3)_2CFOCF_2CF_2OC(CF_3)_2OCF_2CF_2OCF(CF_3)_2$ a b c c d e c c b a	(a) 118.0, (b) 102.6, (c) 115.1, (d) 96.6, (e) 118.8	−74
(7) $CF_3OC(CF_3)_2OCF_2CF_2OC(CF_3)_2OCF_2CF_2OCF(CF_3)_2$ a b c d d b c d d e f	(a) 120.1, (b) 95.8, (c) 118.8, (d) 115.2, (e) 102.6, (f) 118.1	−58
(8) $(CF_3)_2CFO[CF_2CF_2OC(CF_3)_2O]_xOCF_3$ a b c d e f	(a) 118.2, (b) 102.7, (c) 115.3, (e) 118.9	

perfluoro polyether oil was found to be 2800.

Hexafluoroacetone/Propylene Oxide Copolymer (HFA/PO). Added to 4.8 mg of Et_4NCl were 4.5×10^{-2} mol of HFA and 4.5×10^{-2} mol (3.15 cm^3) of PO. The polymer produced was a slightly yellow, amorphous solid with a melting point of ~45–50 °C. The resultant polymer weighed 5.2 g, which corresponded to a yield of 52%.

Previous experience with oils and waxy solids has shown that such materials would be fluorinated best if they were coated on a support, thus increasing the surface area available for fluorination. The polymer was dissolved in Freon 113 and Teflon powder was added. The solution was evaporated, leaving behind a free running powder, much like the HFA/EO copolymer.

The structural similarity to the HFA/EO copolymer led to use of the previous conditions. It was found, however, that when the temperature was elevated to ambient, much of the polymer readily degraded to volatile products, some of which were partially fluorinated, and that when the temperature reached 35 °C, extensive fragmentation occurred. The subsequent fluorination conditions selected are listed in Table I.

As with the HFA/EO copolymer the volatile products were collected and analyzed prior to each temperature change. It was found that if a nonvolatile product was desired, it was essential that the temperature be maintained no higher than 50 °C. The oil was allowed to hydrolyze prior to each elevation in temperature, thus assuring nonfunctional products.

The volatile products showed some functionalization by infrared analysis and the functionalization was removed in the same manner as for the HFA/EO copolymer. The resultant nonfunctional volatile portion differed only in quantity from fraction to fraction to be composed of predominately one compound with extremely small amounts of other components.

Mass-spectral results and ^{19}F NMR results were again very useful in ascertaining the structure of the volatile compound, a perfluoro diether containing two isopropyl end groups and the internal branched propyl group. The mass spectrum gave a large parent minus fluorine peak while ^{19}F NMR analysis was not so straightforward owing to the extent of coupling and the proximity of the CF_3 and CF_2 resonances which were broadened and unresolved. Also, since the propylene group is unsymmetrical, the tertiary fluorines on the isopropyl groups are unequivalent and

Table IV
Yields of Compounds Produced by Fluorination of Hexafluoroacetone/Ethylene Oxide Copolymer[a]

compd	GC retentn time, min	yield, mg	−78 frac, wt %	starting polymer, mol %
1	1	57	10.9	3.8
2	3	69	13.2	4.5
3	11	122	23.2	8.7
4	21	149	28.3	10.5
5	29	45	8.6	3.1
6	40	54	10.4	3.9
7	52	24	4.5	1.7
unseparated material		5	0.9	0.4[b]
total		525	100	36.6

[a] Yield of nonvolatile oil, 0.450 g; starting polymer, 33.8 mol%. Calculations based on 1.00 g of starting polymer. GC temperature program: 50 °C for 5 min; 75 °C for 20 min; 100 °C for 40 min. [b] Assumes average molecule is a seven-carbon ether.

Table V
Products Isolated from Hexafluoroacetone/Propylene Oxide Fluorination[a]

compd	^{19}F shift (ppm)/rel intensity	mp/bp, °C
(9) $(CF_3)_2CFOCF(CF_3)CF_2OCF(CF_3)_2$ a b c d d b e	(a) −82.2/6, (b) −141.7/2, (c) −146.4/1, (d) −81.3/5, (e) −82.5/6	−107/134
(10) $(CF_3)_2CF[OC(CF_3)_2OCF(CF_3)CF_2O]_x$ a b c d e e	(a) −80.4, (b) −145.7, (c) −77.1, (d) −144.3, (e) −81.1	

	$^{13}C\{^{19}F\}$ shift, ppm	elem anal.
(9) $(CF_3)_2CFOCF(CF_3)CF_2OCF(CF_3)_2$ a b c d e b a	(a) 118.2, (b) 103.1, (c) 103.7, (d) 118.0, (e) 116.8, (f) 102.7	Actual: C, 20.86; F, 73.02.
(10) $(CF_3)_2CF[OCF(CF_3)CF_2OC(CF_3)_2]_x$ a b c d e f g	(a) 118.3, (b) 103.0, (c) 103.8, (d) 118.0, (e) 116.8, (f) 96.8, (g) 118.0	Actual: C, 21.78; F, 69.02. Theory: C, 21.56; F, 69.30.

[a] Yield of volatile component = 520 mg = 87.5 wt % of volatile components. This is equivalent to 34.6 mol % of starting polymer based on 1.00 g. Yield of nonvolatile oil = 175 mg − 12.2 mol % of starting polymer.

Table VI
Volatile Perfluoro Ethers Isolated from Hexafluoroacetone/Oxetane Polymer Fluorination

compd	^{19}F shift (ppm)/rel intensity	highest *m/e* in mass spec
(11) $(CF_3)_2CFOCF_2CF_2CF_2OCF(CF_3)_2$ a b a c a b a	(a) 83.0/8, (b) 143.4/1, (c) 130.6/1	501 ($C_9F_{19}O_2$), P − F
(12) $CF_3OC(CF_3)_2OCF_2CF_2CF_2OCF(CF_3)_2$ a b c d c e f	(a) 57.3/3, (b) 78.7/6, (c) 84.9/4, (d) 130.8/2, (e) 147.0/1, (f) 83.6/6	529 ($C_{10}F_{19}O_3$), P − F_3
(13) $(CF_3)_2CFOCF_2CF_2CF_2OC(CF_3)_2OCF_2CF_3$ a b c d c e f f	(a) 83.0/6, (b) 146.3/1, (c) 83.8/4, (d) 130.4/2, (e) 78.2/6, (f) 89.4/5	617 ($C_{11}F_{23}O_3$), P − F
(14) $(CF_3)_2CF[OCF_2CF_2CF_2OC(CF_3)_2]_xOCF_2CF_3$ a b c d c e f f	(a) −81.1, (b) −145.0, (c) −82.5, (d) −129.7, (e) −76.4, (f) −87.2	

Table VII
Volatile Perfluoro Ethers Isolated from Hexafluoroacetone/Oxetane Polymer Fluorination

compd	$^{13}C\{^{19}F\}$ shift, ppm	mp, °C
(11) $(CF_3)_2CFOCF_2CF_2CF_2OCF(CF_3)_2$ a b c d c b a	(a) 118.0, (b) 102.6, (c) 116.3, (d) 107.5	−105
(12) not enough material to obtain spectra		
(13) $(CF_3)_2CFOCF_2CF_2CF_2OC(CF_3)_2OCF_2CF_3$ a b c d c e f g f	(a) 118.0, (b) 102.6, (c) 116.4, (d) 107.6, (e) 96.0, (f) 118.7, (g) 114.7	−95
(14) $(CF_3)_2CF[OCF_2CF_2CF_2OC(CF_3)_2]_x$ a b c d c e f	(a) 118.0, (b) 102.6, (c) 116.5, (d) 107.8, (e) 96.1, (f) 118.6	−85

emerge as a sextet while the propylene tertiary fluorine appears as a broadened triplet. The assignment of the CF_3 and CF_2 groups was based on chemical shift information and coupling.

Infrared analyses of the volatile and nonvolatile components were very similar. The volatile product showed a strong, broad absorption in the carbon–fluorine and COC region (1375–1025 cm^{-1}). Also, there was a strong, sharp absorption in the region from 980 to 960 cm^{-1} and a medium, broad peak in the 720–650-cm^{-1} region. The nonvolatile component showed a strong, broad absorption (1350–1030 cm^{-1}) in the CF, COC region as well as a medium-intensity sharp peak from 980 to 960 cm^{-1} and a weak, broad absorption in the region 730–670 cm^{-1}.

Complete analysis of both the volatile and nonvolatile products is given in Table V. The average molecular weight of the perfluoro polyether oil was determined to be 3000 by ^{19}F NMR end group analysis.

Hexafluoroacetone/Trimethylene Oxide Copolymer (HFA/TMO). To 5 mg of Et_4NCl were added 3.21 × 10^{-2} mol of HFA and 3.21 × 10^{-2} mol (2.1 cm^3) of TMO. The resultant white powdered polymer weighed 5.4 g (75% yield) and had a melting point of 118–121 °C.

Considering the crystalline nature of the polymer, it was decided that conditions similar to those used for the HFA/EO copolymer would be used. Later it was found that conditions more similar to those used for the HFA/PO polymer produced better results. Finally, it was found advantageous to combine the two techniques; once the polymer turned to a gel early in the fluorination process, it was dissolved in Freon 113 and coated on a Teflon powder support.

The infrared analyses of the volatile and nonvolatile products were very similar and corresponded closely to those of the two previous polymers. The carbon–fluorine and ether linkages showed a strong absorption at 1350–1030 cm^{-1}. In addition, a sharp absorption of medium intensity was seen in the region 990–960 cm^{-1} as well as a weak, broad characteristic absorption in the 730–680-cm^{-1} region.

Table VIII
Yields of Products Isolated from Fluorination of Hexafluoroacetone/Trimethylene Oxide Copolymer[a]

compd	GC retentn time, min	yield, mg	−78 frac, wt %	starting polymer, mol %
1	15	100	28.9	6.7
2	26	47	13.6	3.1
3	30	112	32.4	7.6
unseparated material		87	25.1	5.7[b]
total		346	100	23.1

[a] Yield of nonvolatile oil = 150 mg = 10.5 mol % of starting polymer. [b] Assumes average molecule to be a 10-carbon ether.

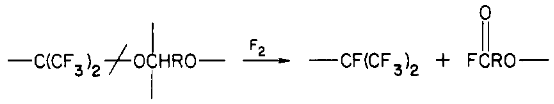
^{19}F NMR and mass-spectral analysis again proved quite useful in establishing the structures of the three isolated compounds. Although only three volatile compounds were isolated, a variety of end groups were present, as seen by the ^{19}F data. Mass-spectral results gave parent minus fluorine or parent minus three fluorines as the highest molecular weight ion. The second is uncommon in perfluoro polyether fragmentation patterns. On the two most abundant volatile compounds and on the oil, $^{13}C\{^{19}F\}$ spectra were obtained. The average molecular weight of the oil was determined by ^{19}F NMR end group analysis and was found to be 2800. Tables VI–VIII show the compiled analytical and spectral data for the products.

Discussion

All systems studied were handled in such a manner that they produced both low molecular weight perfluoro polyethers and high molecular weight oils. If lower temperature fluorination conditions were used, it is felt that solids and elastomers might also be obtained, but it was our goal here to focus upon oils and small fluorocarbon polyethers which can subsequently be used as model systems for structure–property correlations.

Fluorination conditions were adjusted very carefully for each polymer system in a manner to preserve structural integrity; the HFA/EO system was the easiest to handle while the HFA/TMO was the most delicate. When one deals with elemental fluorination, it is very common for yields and reaction techniques to improve significantly upon further development of reaction techniques.

The absence of end groups due to carbon–carbon bond cleavage along with the large relative amount of isopropyl end groups (especially in the HFA/PO system) is noteworthy. A mechanism consistent with chain scission at the branched carbon is illustrated:



$$\text{—C(CF}_3)_2 \not\text{—OCHRO—} \xrightarrow{F_2} \text{—CF(CF}_3)_2 + \text{FC(=O)RO—}$$

Further elimination of carbonyl fluoride would result in methyl end groups, in the case of the HFA/EO polymer:

$$\text{-OCF}_2\text{CF}_2\text{OC(CF}_3)_2\text{O-} \xrightarrow{F_2} \text{-OCF}_3 + \text{CF(CF}_3)_2\text{O-} + \text{COF}_2$$

The fact that an equal number of perfluoroisopropyl end groups and trifluoromethyl end groups was observed in the HFA/EO experiment supports such a view.

After obtaining average molecular weights, the new oils produced in this study were compared with commercial materials. The comparisons were done on a Du Pont thermogravimetric analysis differential scanning calorimeter to obtain values for $R_{1/2}$. Separate runs were done on each sample, one using helium as a pure gas and one using air as a purge gas. The tests with air would provide a measure of the polyether's stability in a moderately oxidative atmosphere. The fluids used for comparison were the Krytox AX ($\bar{M} \sim 4000$) and AA ($\bar{M} \sim 6500$) and the Fomblin Z-25 and Z-45 fluids. Numbers for the Krytox molecular weights were obtained by ^{19}F NMR end group analysis. The variety and type of pendant groups on the Fomblin fluids made it difficult to ascertain $\bar{M}_n$ by this method. Further, the physical property data on the Fomblin fluids are not really comparable to the new copolymers or to the Krytox data since they are of much greater molecular weight (~10000–15000). The average $\bar{M}_n$ of our newly synthesized fluids were also obtained by NMR end group analysis and are as follows: HFA/EO, ~2800; HFA/PO, ~3000; HFA/TMO, ~2800. Analysis by GPC using Freon 113 as the liquid phase also showed the fluids to be approximately the same $\bar{M}_n$. These values correspond to a $\overline{\text{DP}}_n$ of ~8.

Table IX
TGA, $T_{1/2}$ Data

	HFA copolymers			Krytox		Fomblin	
	EO	PO	TMO	AZ	AA	Z-45	Z-25
$T_{1/2}$, °C	198	227	208	212	280	375	473
$T_{1/2}$, °F	388	440	406	414	536	707	883

Extrapolation of the $T_{1/2}$ data (Table IX) indicates that the new fluids may have a lower vapor pressure than commercial fluids of comparable molecular weight and similar stability in oxidizing environments.

The synthesis of these three new perfluoro polyethers, along with the characterization of 11 new volatile perfluoro ethers, extends the range of perfluoro polyether structures available for study. The highly branched nature of these new oils, along with their morphologies, should prove interesting in extending the knowledge of lubrication properties and of many other types of physical properties of perfluoro polyethers. Particularly valuable will be the structure vs. property content of such information.

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