ramethylene sulfoxide and benzyl sulfoxide, results of which are summarized in Table I.

Typical Procedure for Deoxygenation of Phenyl Sulfoxide with Tris(dimethylamino)phosphine/Iodine/Sodium Iodide Reagent. Tris(dimethylamino)phosphine/iodine reagent (10 mmol) was prepared as described above in a 50-mL flask equipped with a magnetic stirring bar and reflux condenser, purged with dry nitrogen. To this reagent was slowly added with continuous stirring a solution of phenyl sulfoxide (2.02 g, 10 mmol) in acetonitrile (5 mL). No reaction took place during the addition, and the reaction mixture remained colorless. Powdered sodium iodide (1.5 g, 10 mmol) was then added, which dissolved completely giving a homogeneous solution. Refluxing of the reaction mixture soon resulted in the liberation of iodine, and the reaction was complete in 20 min, as monitored by TLC (benzene as eluent). Workup of the reaction mixture was as described above, giving phenyl sulfide (1.77 g) in 95% yield.

By increasing the molar ratio of tris(dimethylamino)phosphine and sodium iodide as shown in Table I, it was possible to perform the reaction at room temperature.

A similar procedure was used for the deoxygenation of other aromatic sulfoxides, as well as azoxy compounds.

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Registry No.—$[(CH_3)_2N]_3P$, 1608-26-0; I_2, 7553-56-2; NaI, 7681-82-5.

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Synthesis of the Perfluoropoly(ethylene glycol) Ethers by Direct Fluorination

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A new general technique has been developed for the synthesis of perfluorocarbon polyethers by the reaction of elemental fluorine with high molecular weight polyether under conditions selected to promote fragmentation of the ether chain during complete fluorination. A number of new perfluorocarbon ethers of the type $R_fO(CF_2CF_2O)_nR_f$ ($R_f = CF_3, C_2F_5$) have been prepared.

Saturated perfluoro polyethers are of current interest for new material applications due to their unusual properties. Lack of chemical reactivity and thermal stability (>300 °C) is their outstanding feature. They have been described as equally stable in perfluoroalkanes and unaffected by concentrated acids and bases at elevated temperatures over extended periods of time.[1] The only reported reaction of saturated perfluoropolyethers is chain cleavage at the ether linkage by aluminum chloride (at elevated temperatures and autogenous pressure) to produce acyl chloride and trichloromethyl end groups.[2] These remarkable stabilities along with their interesting surface properties, viscosities, and the broad liquid ranges of the low molecular weight compounds make saturated perfluoro polyethers attractive for numerous applications[3] as solvents, hydraulic fluids, heat-transfer agents, lubricants, greases, sealants, elastomers, and plastics.

Synthetic methods have limited the preparation of saturated perfluoro polyethers. The most successful perfluoro polyether synthetic chemistry has been DuPont's anionic polymerization of perfluoro epoxides, particularly hexafluoropropylene oxide and tetrafluoroethylene oxide.[4] Their synthetic procedure is a three-step scheme for saturated perfluoro polyether production involving oxidation of perfluoroolefins to perfluoro epoxides, anionic polymerization to acyl fluoride terminated perfluoro polyethers, and conversion of acyl fluoride end groups to unreactive end groups by decarboxylation reactions or chain coupling photolytic decarboxylative reactions. Other general synthetic methods for perfluoro ether and perfluoro polyether production are the addition reactions of perfluoro hypofluorite, R_fOF, with perfluoroolefins,[5] and the perfluoro peroxide, R_fOOR_f, addition reaction with perfluoroolefins[6] and electrolytic fluorination in anhydrous HF of the corresponding hydrocarbon ethers.[7]

We have developed a useful new synthetic method for the production of saturated perfluoropoly(ethylene glycol) ethers. A one-step reaction, the direct fluorination of poly(ethylene oxide) polymer with reaction conditions chosen to promote fragmentation of the polymer during the fluorination process, has resulted in the synthesis of saturated perfluoro polyethers over a broad range of molecular weights.

$$(CH_2CH_2O)_n \xrightarrow{F_2/He} R_f(OCF_2CF_2)_nOR_f$$
$$R_f = CF_3, C_2F_5$$

The low molecular weight compounds (n = 1–6) which have been isolated are volatile liquids; medium molecular weight compounds are novolatile oils; and the high molecular weight compounds are gellike and powdery solids. Previously we have found that milder fluorination conditions designed to prevent fragmentation lead to an extremely stable high molecular weight perfluoro polyether.[8] Of the perfluoro polyethers reported here, only three have been reported previously by methods other than direct fluorination. Perfluoromonoglyme,[9,10] perfluoroethylene glycol methyl ethyl ether,[9] perfluoroethylene glycol diethyl ether,[11] and perfluorodiethylene glycol diethyl ether[10] have all been prepared by electrolytic fluorination in anhydrous HF in low yield. Direct fluorination has been used previously for the synthesis of specific perfluoro ethers. We have previously reported the successful direct fluorination of monoglyme and diglyme at low temperatures

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Chart I

He flow, cm^3/min	F$_2$ flow, cm^3/min	temp, °C	time, days
40	1.0	amb	6
40	2.0	amb	2
10	2.0	amb	2
10	4.0	amb	2
10	4.0	90	2
10	4.0	110	7

to prepare perfluoroglyme and diglyme:[12]

$$CH_3(OCH_2CH_2)_nOCH_3 \xrightarrow[-78\ ^\circ C]{F_2/He} CF_3(OCF_2CF_2)_nOCF_3 \qquad n = 1, 2$$

The synthesis of the bicyclic perfluoro ether $CF_3C(OCF_2)_3CCF_3$ by low temperature direct fluorination of the corresponding hydrocarbon in the solvent $(C_4F_9)_3N$ has also been reported by Talbott.[13]

For the preparation of new perfluoro ethers, direct fluorination provides a very general, versatile, and powerful capability.

Experimental Section

Our general[14] fluorination procedure involves the reaction of fluorine diluted with helium with a solid substrate. Room-temperature solids serve best as reactants when ground to a finely divided powder; liquids are best fluorinated in their solid state in a cryogenic reactor.[15] The gas mixture, after the reaction, passes through a NaF pellet scrubber to remove the HF byproduct, then volatile products are collected in a −196 °C trap.

Solid poly(ethylene oxide) polymer (Polysciences Inc., Grade 4 000 000) was ground and sieved to a fine powder (150 mesh) and 6.53 g was weighed into nickel boats and placed in a hollow nickel tube reactor. The assembled apparatus was flushed with 100 cm^3/min of He overnight before the fluorine flow was started. The He flow rate was monitored with a Matheson Series 600 Rotameter flowmeter and the fluorine flow rate was controlled with a Monel needle valve and monitored with a Hastings Mass Flow Transducer, Type F-50M. Fluorine was supplied by Allied Chemical Corporation and used without further purification. The reaction was carried out at the gas flow rates and temperatures in Chart I (high temperatures were maintained with a heating tape and insulation). After the fluorine flow was terminated, the apparatus was again flushed with 100 cm^3/min of He overnight.

The volatile products of the reaction were transferred from the collection trap and separated by vacuum line trap-to-trap fractionation into four fractions: −78 °C (dry ice), −131 °C (pentane slush), −160 °C (isopentane slush), and −196 °C. The fractions were analyzed by infrared spectroscopy and GLC, and the separated pure compounds were identified by their infrared, NMR, and mass spectra.

The solid product of the reaction was Soxhlet extracted with diethyl ether for 2 days. A low-volatility, low-viscosity oil separated as a heavier phase from the ether and was analyzed by NMR and infrared spectroscopy and elemental analysis, and its solubility in numerous hydrocarbon and fluorocarbon solvents was tested.

GLC assay of the volatile compounds was done on a 3/8 in. by 7 m column packed with 10% Fluorosilicone QF-1-0065 on Chromosorb P. The gas chromatograph was a Bendix 2300 equipped with an automatic temperature programmer, and the carrier gas (He) flow rate was 150 cm^3/min. The infrared spectra were observed with a Beckman IR-20A infrared spectrometer: the volatile compounds as gases in a 10-cm cell with KBr windows, the nonvolatile liquids as thin films between KBr windows, and the solid product as a KBr pellet. The ^{19}F NMR spectra were recorded on a Varian Associates A-56/60 NMR spectrometer set up for fluorine nuclei. The samples were run as neat liquids with Freon-11, $CFCl_3$, as an external reference. All samples were also checked for hydrogen atoms by ^1H NMR spectroscopy with an A-56/60 set up for protons. The mass spectra of the volatile compounds were run on a Bell and Howell Model 21-491 mass spectrometer with the ion source cooled to room temperature and using the gas inlet system.

Low-temperature melting points were determined by freezing the samples in a cold solvent in a transparent dewar, allowing the solvent to warm with stirring, and monitoring the temperature with an iron–constantan thermocouple connected to a Leeds and Northrup Model 8690-2 millivolt potentiometer. Boiling points were measured with a micro-boiling-point apparatus as follows: several drops of compounds were placed in a 4-mm tube attached to a thermometer at the bulb; a capillary tube was sealed 3 to 4 mm from the open end and placed open end down in the sample tube; the apparatus was immersed in an oil bath to above the sample level and heated until a steady stream of bubbles was established at the capillary tube; the setup was allowed to cool, and the temperature at which the bubbles stop and sample rises in the capillary tube is the boiling point of the compound. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories of New York, N.Y.

Volatile Products. Infrared analysis of the −196 °C fraction of the volatile products indicated almost all of the sample was CF_4. Traces of SF_6 (presumably an impurity in the fluorine), COF_2, C_2F_6, and SiF_4 were also detected by infrared spectroscopy. The liquid volume of the fraction was estimated to be 1.2 mL, and assuming all of the material was CF_4, density 1.89 g/mL at −183 °C,[16] the isolated yield of CF_4 was 2.268 g or 8.7 mol % of the starting polymer. This isolated yield is probably lower than the actual yield because CF_4 has a vapor pressure at −196 °C, and a significant amount could be pumped away during the vacuum line fractionation of the volatile products. CF_4 would also be lost by passing through the −196 °C volatile product trap during the fluorination.

Infrared analysis of the −160 °C fraction indicated COF_2 and SF_6 as the major components. The fraction was hydrolyzed to convert the COF_2 to CO_2, and the resulting gases were passed through a −131 °C trap on a vacuum line to remove CO_2 and H_2O from the water-stable gases of the fraction. The measured liquid volume of the fraction before hydrolysis was 1.8 mL and after hydrolysis was 0.2 mL. The 1.6-mL yield of COF_2, density 1.139 g/mL at −114 °C,[16] is 1.83 g or 9.3 mol % of the starting polymer. The water-stable gases were separated further by GLC at −50 °C.

Several milligrams of one compound, perfluoromonoglyme (which was combined with the perfluoromonoglyme from the −131 °C fraction), was separated cleanly from the mixture. The rest of the mixture was analyzed by infrared which indicated predominantly SF_6 with traces of C_2F_6 and perhaps C_3F_8 or $(CF_3)_2O$.

It was the GLC assay of the −131 and −78 °C fractions that resulted in isolation of significant amounts of 15 volatile perfluoroethylene glycol ethers:

$$CF_3O(CF_2CF_2O)_aCF_3 \qquad a = 1\text{–}6$$

$$CF_3O(CF_2CF_2O)_bC_2F_5 \qquad b = 1\text{–}6$$

$$C_2F_5O(CF_2CF_2O)_cC_2F_5 \qquad c = 1\text{–}3$$

The amounts and yields of the isolated pure perfluoro ethers are listed in Table I. (The compounds $c = 1$ and $c = 3$ were not isolated from the products of this particular reaction but were found in low yields in the products of preliminary reactions.) The material left unseparated by the GLC assay of the fractions was examined by infrared spectroscopy and showed C–H and COF absorptions as well as the strong C–F absorption. This inseparable mixture contained the numerous branched, partially fluorinated, and acyl fluoride terminated volatile fluoro ethers that may be produced by the free-radical fluorination reaction.

The isolated compounds were characterized by ^{19}F NMR and mass spectral analysis. The infrared spectra of the 15 volatile perfluoro ethers were all similar in showing strong, broad absorptions in the C–F stretching region, 1300–1100 cm^{-1}. (The infrared spectrum of perfluorotriglyme is [Figure 1 available on microfilm, see supplementary material paragraph] included as representative of the C–F region.) The spectra also exhibited weaker absorptions in the "fingerprint" region, 1000–600 cm^{-1}, which are useful for compound identification. These weaker fingerprint absorptions are listed for each compound in Table II. No other infrared absorptions are observed except for the C–F overtone near 2400 cm^{-1} when high gas concentrations are used.

The ^{19}F NMR data were the most useful information for structure determination. The following signal assignments were deduced from the spectra interpretation (^{19}F NMR reference–neat $CFCl_3$ external):

$\mathbf{CF_3}O$	59.4–58.9 ppm (triplet), J = 9–10 Hz
$CF_3O\mathbf{CF_2}CF_2$	94.0–93.5 ppm (quartet), J = 9–10 Hz
$\mathbf{CF_3}CF_2O$	90.7–90.3 ppm (singlet)
internal CF_2O	91.9–91.4 ppm (singlet)
$CF_3\mathbf{CF_2}O$	magnetically equivalent to internal CF_2O

Table I. Yields of Volatile Perfluoroethylene Glycol Ethers

compd	registry no.	yield, mg	wt % of −78 and −131 °C fractions	mol % of starting polymer[a]
$a = 1$	378-11-0	86	7.1	0.43
$b = 1$	55135-02-9	27	2.2	0.14
$c = 1$	356-70-7			
$a = 2$	40891-99-4	110	9.1	0.58
$b = 2$	64028-03-1	46	3.8	0.25
$c = 2$	7621-49-0	4.5	0.4	0.02
$a = 3$	64028-04-2	123	10.2	0.66
$b = 3$	64028-05-3	48	4.0	0.26
$c = 3$	67584-23-0			
$a = 4$	64028-06-4	122	10.1	0.66
$b = 4$	64028-07-5	51	4.2	0.28
$a = 5$	64028-08-6	123	10.2	0.68
$b = 5$	64028-09-7	83	6.9	0.46
$a = 6$	67584-24-1	85	7.1	0.47
$b = 6$	67584-25-2	39	3.2	0.22
unseparated material		256	21.3	1.38[b]
totals		1.2045 g	100%	6.49%

[a] Calculation: g compd/mol wt compd = mol compd, (mol compd) × (no. of carbon atoms in structure) = mol carbon atoms, (mol carbon atoms in compd)/(mol carbon atoms in starting polymer) × 100% = mol % of starting polymer. [b] Calculated assuming an average molecular weight of 500 and an average number of carbon atoms per molecule of 8.

Table II. Infrared Absorptions in the Fingerprint Region of Volatile Perfluoroethylene Glycol Ethers

compd	absorption freq, cm^{-1} [a]
$a = 1$	925 (w), 890 (m), 865 (w), 820 (m), 690 (m)
$b = 1$	910 (w), 800 (w), 730 (m), 685 (w)
$c = 1$	905 (w), 845 (w), 795 (w), 740 (m), 710 (m), 695 (sh)
$a = 2$	920 (sh), 905 (m), 765 (m), 690 (w), 675 (w, sh)
$b = 2$	910 (w), 765 (w), 740 (sh), 720 (m), 690 (w)
$c = 2$	765 (w), 725 (m), 705 (w), 690 (w)
$a = 3$	905 (m), 790 (w), 738 (m), 685 (w)
$b = 3$	910 (m), 785 (w), 745 (m), 710 (m), 695 (sh), 685 (sh)
$c = 3$	1000 (w), 910 (w), 785 (w), 750 (sh), 720 (m), 710 (sh), 695 (m)
$a = 4$	910 (m), 765 (w), 725 (w), 685 (w)
$b = 4$	955 (w), 910 (w), 765 (w), 735 (m), 710 (w), 695 (w)
$a = 5$	910 (w), 740 (w), 720 (sh), 705 (sh), 685 (w)
$b = 5$	905 (w), 730 (m), 690 (w)
$a = 6$[b]	1000 (w), 905 (m), 765 (w), 730 (sh), 685 (m)
$b = 6$[b]	995 (w), 905 (m), 765 (w), 735 (sh), 690 (m)

[a] Letters in parentheses indicate strength of absorption: w, weak; m, medium; sh, shoulder. [b] Not volatile enough to be run as a gas and have the fingerprint absorptions appear; run as a liquid film between KBr windows.

Table III. ^{19}F NMR Signals of Volatile Perfluoroethylene Glycol Ethers Shift in ppm vs. External Reference $CFCl_3$

compd	CF_3O (t)	$CF_3O\mathbf{CF_2}$ (q)	internal CF_2O (s)	$\mathbf{CF_3}CF_2O$ (s)	$J_{CF_3OCF_2}$, Hz
$a = 1$	59.4	94.0			10
$b = 1$	59.4	93.9	91.9 (4)	90.7	10
$c = 1$			91.7 (4)	90.5	
$a = 2$	59.3	93.8	91.8 (2)		9
$b = 2$	59.2	93.7	91.7 (8)	90.5	9
$c = 2$			91.6 (6)	90.4	
$a = 3$	59.1	93.8	91.7 (4)		9
$b = 3$	59.0	93.7	91.6 (12)	90.4	9
$c = 3$[a]					
$a = 4$	59.1	93.7	91.6 (6)		9
$b = 4$	58.9	93.5	91.5 (16)	90.3	10
$a = 5$	58.9	93.5	91.5 (8)		10
$b = 5$	59.0	93.6	91.5 (20)	90.3	10
$a = 6$	59.0	93.6	91.4 (10)		9
$b = 6$	59.1	93.7	91.6 (24)	90.4	9

[a] Insufficient compound isolated to obtain NMR spectrum: t, triplet; q, quartet; s, singlet. Relative intensities: CF_3O = 3; $CF_3O\mathbf{CF_2}$ = 2; $\mathbf{CF_3}CF_2O$ = 3; internal $-CF_2O-$ = as indicated in parentheses.

For all compounds, the experimental relative intensities of the signals correspond exactly to the calculated relative intensities. No signals were observed for any of the compounds in ^{1}H NMR scans. The ^{19}F NMR data are listed in Table III.

The mass spectra of the 15 perfluoro ethers were characterized by extensive chain cleavage and rearrangement. In fact, with the ion source of the mass spectrometer at normal operating temperatures, the highest mass peak observed for any of the compounds was *m/e* 300. When the spectra were run with the ion source cooled to room temperature, higher mass peaks up to the parent minus fluorine peak were observed for each compound as follows: $a = 1$, 251 ($C_4F_9O_2^+$); $b = 1$, 301 ($C_5F_{11}O_2^+$); $c = 1$, 351 ($C_6F_{13}O_2^+$); $a = 2$, 367 ($C_6F_{13}O_3^+$); $b = 2$, 417 ($C_7F_{15}O_3^+$); $c = 2$, 467 ($C_8F_{17}O_3^+$); $a = 3$, 483 ($C_8F_{17}O_4^+$); $b = 3$, 533 ($C_9F_{19}O_4^+$); $c = 3$, 583 ($C_{10}F_{21}O_4^+$); $a = 4$, 599 ($C_{10}F_{21}O_5^+$); $b = 4$, 649 ($C_{11}F_{23}O_5^+$); $a = 5$, 715 ($C_{12}F_{25}O_6^+$); $b = 5$, 765 ($C_{13}F_{27}O_6^+$); $a = 6$, 831 ($C_{14}F_{29}O_7^+$); $b = 6$, 881 ($C_{15}F_{31}O_7^+$). Chain fragmentation and rearrangement still persisted with the cooled ion source, and for the higher molecular weight compounds, the low *m/e* peaks had to be expanded off scale in order to observe the parent minus fluorine peaks. By far the most intense peaks of the mass spectra for all compounds were *m/e* 69 (CF_3^+) and 119 ($C_2F_5^+$), with higher mass peaks decreasing in intensity with increasing mass, a characteristic of many fluorocarbons.[17] Other common low-mass fragments observed were: 31 (CF); 47 (CFO); 50 (CF_2); 97 (C_2F_3O); 100 (C_2F_4); 135 (C_2F_5O); 163 ($C_3F_5O_2$); 169 (C_3F_7); and 185 (C_3F_7O). The common higher mass fragments observed for the higher molecular weight compounds were of the general formulas $C_nF_{2n+1}O_x$ and $C_nF_{2n-1}O_x$.

The physical constants of the volatile perfluoro ethers, boiling points, melting points, and GLC retention times are listed in Table IV. A graph of the boiling points vs. compound mass is available on microfilm (see supplementary material paragraph). Boiling points were precisely measured with the micro-boiling-point apparatus. No boiling points are reported for the compounds a, b, $c = 1$ because they are so volatile that the several drops of sample would evaporate from the micro-boiling-point apparatus before a boiling point could be determined. No melting points are reported for the compounds a, b, $c = 1$ and a, $b = 2$ because either a supercooling problem may have arisen, that prevented cystallization of the compounds even at temperatures much below the predicted melting points, or because the compounds froze as glasses which made visual distinction between the solid and liquid states impossible.

Elemental analyses of all 15 perfluoro ethers were deemed unnecessary and prohibitively expensive, but the accuracy of the elemental analyses of a couple of compounds should be representative of the results that would be obtained for the other compounds. The compounds chosen for elemental analysis were $a = 4$, perfluorotetraglyme, and $b = 4$, perfluorotetraethylene glycol methyl ethyl ether. The results were: for $a = 4$, Calcd: C, 19.42; F, 67.64; O, 12.94. Found: C, 19.23; F, 68.48. For $b = 4$, Calcd: C, 19.76; F, 68.26, O, 11.98. Found: C, 19.92; F, 69.32.

Gas-liquid chromatography (GLC) was used for separation of the volatile perfluoro ethers because it has been proven to be the best method for separation of fluorocarbons produced on an experimental scale.[18] Clearly, GLC is impractical for large-scale separations, so fractional distillation was examined as an alternative separator method. Several milliliters of volatile perfluoro ether product mixture (from a previous reaction) was subject to fractional distillation, and the cuts of distillate were analyzed for composition by GLC. The boiling ranges of the fractions and the compounds that comprise each fraction are available on microfilm (see the supplementary material paragraph). It can be seen from these data that the fractions are relatively poorly separated mixtures and distillation, as would be expected, is much less efficient than GLC for separation of pure compounds on an experimental scale. On a larger scale, where a larger, more efficient fractionation column could be used, distillation should be adequate and the preferred technique.

Table IV. Physical Constants of Volatile Perfluoroethylene Glycol Ethers

compd	mp, °C	bp, °C	GLC retention time, min temp prog A[c]	 temp prog B[d]
a = 1			2	
b = 1			4	
c = 1			6	
a = 2		66 to 66.5	11	4
b = 2		81.5 to 82	22	6
c = 2	−78.5 to −77	*a*	34	8
a = 3	−82 to −80.5	104.5 to 105	44	11
b = 3	−80 to −78	117.5 to 118.5	58	18
c = 3	*b*	*a*	66	28
a = 4	−71 to −69.5	138 to 138.5	74	43
b = 4	−60.5 to −60	146.5 to 148	84	56
a = 5	−47 to −46	164 to 164.5	102	74
b = 5	−47 to −46	173.5 to 174	114	83
a = 6	−43.5 to −43	186 to 186.5	129	96
b = 6	−35 to −34	193 to 194	142	103

[a] Insufficient compound isolated to obtain a boiling point. [b] Insufficient compound isolated to obtain a melting point. [c] Temperature program A: 0 °C for 20 min; 1 °C/min to 60 °C; 60 °C for 20 min; 1 °C/min to 120 °C. [d] Temperature program B: 30 °C for 30 min; 1 °C/min to 120 °C.

Solid Products. The solid product of the reaction, material remaining in the nickel boats in the reaction chamber, was first subject to Soxhlet extraction with diethyl ether for several days. A low-viscosity oil separated as a heavier phase from the ether. The 0.32 g of oil was removed, the ether (ca. 100 mL) was concentrated by distillation, and an additional 0.27 g of oil was obtained. The extracted oil had a very low volatility; only a trace of material could be pumped into a vacuum line over 6 at 1 μm pressure. The extracted oil was combined with 0.27 g of liquid that remained in the volatile product trap after pumping on the trap for several hours at 1 μm pressure. The combined material had a weight of 0.86 g and a density of 1.79 g/cm^3.

The nonvolatile oil was analyzed by infrared of a thin liquid film and by ^{19}F NMR. The infrared spectrum showed bands at (absorptions in cm^{-1}) 1300–1000 (s, broad), 1000 (w), 955 (w), 910 (m), 810 (sh), and 685 (m), a spectrum almost identical to those of the higher molecular weight volatile perfluoro ethers. The ^{19}F NMR spectrum showed signals at 58.7 (t, J = 9 Hz), 93.3 (q, J = 9 Hz), 91.3 (s), 90.0 ppm (s) (the signals exhibited by the volatile straight-chain perfluoroethylene glycol ethers), and much weaker, broad signals at 128.1 and 125.8 ppm and 89.5 through 82.5 ppm. The ^{19}F NMR spectrum was unchanged after washing the sample with concentrated aqueous base, and no ^{1}H NMR signals were detected. The weak, broad signals observed are believed due to fluorine nuclei at chain-branching or cross-linking sites from cross-linked species which are present in extremely low yield in the mixture. Integration of the NMR signals indicates the weak signals represent a small, insignificant amount of the sample. Ignoring these weak signals and using the integrated intensities of the major signals due to the straight-chain perfluoro ethers, an average molecular weight of the mixture may be determined by NMR end-group analysis. Such analysis indicates 8.2 CF_2 groups per CF_3 group, or MW_{av} = 1080, the average degree of polymerization is 8, and the average number of carbon atoms per molecule is 18. The yield of nonvolatile perfluoro ether oil (calculated as in Table I) was 4.9 mol % of the starting polymer.

The solid product, after ether extraction, was dried and visual examination indicated it was a mixture of two types of material. Most of the solid was a fluffy, sticky, white, amorphous powder, but a significant number of small chunks of translucent, gellike material exhibiting rudimentary elastomeric properties was also observed. Infrared analysis of the powder (KBr pellet) produced another spectrum almost identical to the spectra of the higher molecular weight volatile perfluoro ethers and the nonvolatile oil. The bands observed were: 1300–110 (s, broad), 1000 (sh), 950 (w), 910 (w), 895 (sh), 760 (sh), and 690 (m). Elemental analyses were performed on samples of both powder and gel. The results for the powder were C, 20.82; F, 66.37; O, 12.52, and the results for the gel were C, 20.79; F, 66.46; O, 12.20 (fluorine values reported as ±0.6% and oxygen values as ±1.0%). These results show no difference in the two types of solid product, and both sets of results are within experimental error of the calculated analysis of the $(CF_2CF_2O)_n$ structure. Thermal analysis of the gel on a DuPont 990 thermal gravimetric analyzer indicates the material shows no melting point and is stable up to 300 °C. At 370 °C a minor mode of decomposition occurs, major thermal decomposition begins at 400 °C, and by 550 °C all of the sample had decomposed except for a small residue. The amount of solid product from the reaction was 9.78 g which is, based on the $(CF_2CF_2O)_n$ structure, 56.8 mol % of the starting polymer.

Further analysis and separation of the solid product was limited by its lack of solubility. Of the numerous organic hydrocarbon and fluorocarbon solvents tested, only two, perfluoro-2-butyltetrahydrofuran and 1,1,2-trichlorotrifluoroethane, showed slight solvation ability. Solvents were tested with heating and stirring over 2 to 3 day periods. Solubility was tested by centrifuging the mixture and examining the solution by ^{19}F NMR, looking for the internal $-CF_2O-$ signal near 91 ppm upfield from $CFCl_3$ and the CF_3O- signal near 59 ppm upfield. For the two successful solvents, the CF_3O- signal was barely detectable, and the $-CF_2O-$ signal was clearly evident but very weak compared to the solvent signals. Product solubility in both solvents was approximately the same and was calculated, by NMR integrated intensities, to be ca. 2.5 wt %. Such limited solubility prevented average molecular weight determination of the solid product by NMR end-group analysis and the use of high-pressure liquid chromatography for preparative separation.

In summary, the complete mass balance for the reaction is presented. Low molecular weight, volatile, liquid ethers are produced in 6.5% yield; medium molecular weight, nonvolatile, liquid ethers are produced in 4.9% yield; and high molecular weight solids are produced in 56.8% yield of the starting polymer. The major low molecular weight byproducts, CF_4 and COF_2, account for 8.7 and 9.3% of the starting material, respectively. The unaccounted for 13.8% of starting material would be comprized of unisolated CF_4, as discussed previously, and volatile products produced in the initial stages of the reaction which were not collected. These uncollected products were shown by previous experiments to be mainly small fragment molecules (CF_4, COF_2, and C_2F_6) and a complex mixture of partially fluorinated volatile ethers. Elimination of the partially fluorinated volatile ethers formed in the first part of the reaction from the collected volatile product mixture simplified separation of the desired perfluoro ethers by decreasing impurity peaks and peak overlaps in the GLC assay.

Discussion

The results of the reaction show that the direct fluorination of poly(ethylene oxide) polymer is a useful synthetic method for production of perfluoroethylene glycol ethers of low to very high molecular weights. An important feature of the method is that the reaction conditions employed govern the relative amounts of voalitle liquid, nonvolatile oil, and solid product that are formed. Fluorination of poly(ethylene oxide) polymer at just ambient temperature results in conversion to prefluorinated polymer with only small amounts of volatile products formed by fragmentation. Fluorinations at ambient temperature then high temperatures, as in the reported reaction, results in perfluorination of the polymer at the ambient temperatures then fragmentation of the perfluoropolymer at the high temperatures to produce significant amounts of volatile perfluoro ethers and extractable nonvolatile oil. Larger amounts of volatile perfluoro ethers and nonvolatile oil may be simply produced by fluorinating and fragmenting the perfluoro polymer for longer times at the high temperatures. Higher temperatures then those used should also promote faster more extensive fragmentation, but the reactor was not designed for use at higher temperatures. (The teflon O-ring seals at the reactor flanges would have been attacked significantly at higher temperatures in the fluorine atmosphere unless a cooling system were installed.) It is the additional thermal activation energy available at the higher temperatures that makes fragmentation a significant process in the free-radical direct fluorination reaction.

The mechanism of fragmentation of the perfluoropoly(ethylene oxide) polymer chains may be deduced by determination of the number and types of the end groups of the low molecular weight compounds. Approximately six times more CF_3O- end groups are formed than CF_3CF_2O- end groups. Chain cleavage at carbon–carbon bonds of the perfluoropolymer must, therefore, predominate.

$$-OCF_2 \wr CF_2O- \xrightarrow{2F\cdot} 2(-OCF_3)$$

Chain cleavage at carbon–oxygen bonds must also occur in order to account for the CF_3CF_2O- end groups. The result of backbone cleavage at the carbon–oxygen bond would be one CF_3CF_2O- end group, one CF_3O- end group, and one molecule of carbonyl fluoride as follows:

$$-OCF_2CF_2 \wr OCF_2CF_2O- \rightarrow -OCF_2CF_2\cdot + \cdot OCF_2CF_2O-$$

$$-OCF_2CF_2\cdot \xrightarrow{F\cdot} -OCF_2CF_3$$

$$-OCF_2CF_2O\cdot \xrightarrow{-COF_2} -OCF_2\cdot \xrightarrow{F\cdot} -OCF_3$$

Chain cleavage occurring predominately at the carbon–carbon bonds is consistent with the calculated bond strengths in perfluoro ethers: C–C = 80–90 kcal, C–O = >100 kcal.

Acyl fluoride terminated compounds did not constitute a significant fraction of the reaction products. At temperatures above 100 °C in a fluorine atmosphere perfluoro ether acyl fluorides are relatively unstable. Functionalized perfluoro ethers are also desirable compounds due to the chemical versatility of the acyl fluoride terminus of the otherwise unreactive structure. Further experimentation in the direct fluorination of polyether polymers is underway with acyl fluoride terminated perfluoro polyethers as target compounds.

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Registry No.—α-Trifluoromethyl-ω-trifluoromethoxypoly[oxy(1,1,2,2-tetrafluoro-1,2-ethanediyl)], 67584-21-8; α-hydro-ω-hydroxypoly[oxy(1,1,2,2-tetrafluoro-1,2-ethanediyl)], 67584-22-9; poly(ethylene oxide) polymer, 25322-68-3.

Supplementary Material Available: Infrared spectrum of perfluorotriglyme (Figure 1); boiling point vs. compound mass graph for all perfluoropolyethers produced (Figure 2); and range of boiling temperatures for distillation of product vs. the relative amount of each compound in the fraction (Table V) (3 pages). Ordering information can be found on any current masthead page.

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Reactions of 5-Halogeno-2*H*,3*H*-benzo[*b*]thiophene-2,3-diones with Nucleophiles. An Electron Spin Resonance Investigation on Carbon–Halogen Bond Reactivity

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The reactions of the 5-halogeno-2*H*,3*H*-benzo[*b*]thiophene-2,3-diones (5-X-BTD: X = F, Cl, Br, I) with several nucleophiles (t-BuO$^-$, MeO$^-$, OH$^-$, PhO$^-$, MeS$^-$, PhS$^-$) have been studied by ESR spectroscopy. The observed halogenated radical anions 5-X-BTD$^{-\cdot}$ are intermediates of a nucleophilic substitution in the presence of PhS$^-$ and of a reductive dehalogenation with the other nucleophiles.

Many examples of reactions of aryl halides with nucleophiles proceeding through a radical pathway have been reported[1] in the last 10 years. A general feature of these processes is an electron transfer to the aromatic substrates to give radical anions which decompose by loss of halide ions thus generating aryl radicals. The fate of the last species determines the overall process which may be a nucleophilic substitution and/or a reductive dehalogenation. The first occurs in Bunnett's $S_{RN}1$ mechanism[1b] characterized by coupling of the aryl radical with a nucleophile; in the second the neutral radical abstracts a hydrogen atom from a suitable donor.[1a]

In these reactions, however, there is no direct physical ev-

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