

## Synthesis of Perfluoropolyethers by Direct Fluorination ; a Novel Preparation for Perfluoro(polypropylene oxide) Ethers and Perfluoro(poly-methylene oxide) Ethers

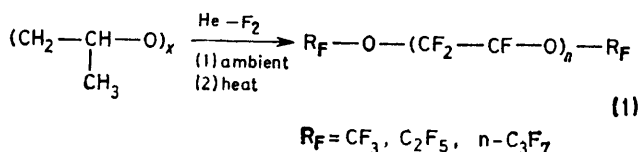
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A new synthetic method has been developed for preparation of perfluoro(polypropylene oxide) ethers and perfluoro(polymethylene oxide) ethers by direct fluorination of polypropylene oxide and polymethylene oxide. A number of new ethers are reported and characterized by  $^{19}\text{F}$  n.m.r., mass spectrometry, and i.r. spectroscopy.

RECENTLY we reported the successful synthesis of perfluoropolyethers from polyethylene oxide by a new direct fluorination process.<sup>1,2</sup> We have now extended this work to include polypropylene oxide ether and polymethylene oxide ether systems.

The properties of perfluoroethers are extremely unusual and are an incentive for further studies. Most perfluoropolyether systems are stable up to 350–360 °C. The only reported reaction of saturated perfluoropolyethers is chain-cleavage at the ether linkage by aluminium chloride (at elevated temperatures and autogenous pressure) to produce acyl chloride and trichloromethyl end-groups.<sup>3</sup> This remarkable stability along with their interesting surface properties, viscosities, and the wide liquid ranges of the low-molecular-weight compounds make saturated perfluoropolyethers attractive for numerous applications<sup>4–6</sup> as solvents, hydraulic fluids, heat-transfer agents, lubricants, greases, sealants, elastomers, and plastics.

The direct fluorination of polypropylene oxide under conditions designed to promote fragmentation has resulted in the synthesis of a number of extremely interesting new ethers [see equation (1)].



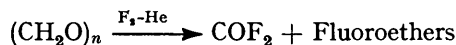
The synthetic strategy for the synthesis of lower-molecular-weight perfluoropolyethers by direct fluorination includes a 'pre-fluorination' period, with reaction conditions chosen so that the structural integrity of the polymer is maintained while a significant number of hydrogens are replaced by fluorine, followed by a 'fragmentation' period, in which higher temperatures promote perfluorination and chain-cleavage; this gives volatile perfluoropolyethers with perfluoroalkyl or possibly acyl fluoride end-groups. This second step is important in the process, since room-temperature fluorination beyond this point will result in a high-molecular-weight polymer.

Current methods for the synthesis of other perfluoroethers are limited to a few specific, and in some cases,

elaborate methods. Synthesis of telomers and polymers of hexafluoropropylene oxide, however, is readily accomplished by the anionic polymerization of hexafluoropropylene oxide monomer.<sup>6,7</sup> DuPont has developed this into a commercial process, and the low- and high-molecular-weight compounds are available as Krytox oils and greases, respectively.<sup>8</sup> The commercialization of the process for hexafluoropropylene oxide, but not for tetrafluoroethylene oxide, may be due in part to the easier handling properties of the hexafluoropropylene oxide monomer and resulting polymers. The more stable<sup>6,9</sup> and higher-boiling ( $\text{CF}_3\text{C}_2\text{F}_3\text{O}$ ,  $-42$  °C;  $\text{C}_2\text{F}_4\text{O}$ ,  $-65$  °C) hexafluoropropylene oxide monomer allows use of conventional glassware with a cryogenic condenser in a continuous polymerization process; the resulting polymers are soluble in all proportions in  $\text{CF}_3\text{-CCl}_3$  (Freon-113). Tetrafluoroethylene oxide polymerizations, however, must be carried out in stainless steel autoclaves, and its polymers are only sparingly soluble in a few solvents. Even though the DuPont process is a very useful method for preparing perfluoropropylene oxide telomers and polymers, the development of direct fluorination as an alternative method for producing the compounds is significant. Its significance lies in that it further extends the generality of direct fluorination as a method for producing perfluoroethers from hydrocarbon polyether polymers, and it is often capable of producing perfluoropolyethers of unique structure, which cannot be produced by polymerization. There is also the possibility of this process being developed into a less expensive source of these compounds.

Perfluoropolyethers with the  $\text{CF}_2\text{O}$  repeating unit have been reported in only two patents by Sianesi and co-workers.<sup>10</sup> Their synthetic scheme involves the ozone-sensitized reaction of oxygen with difluorocarbene (generated *in situ* by the pyrolysis of hexafluoropropene) to give compounds of the formulas  $\text{CF}_3\text{O}(\text{CF}_2\text{O})_n\text{CF}_2\text{-C}(\text{O})\text{F}$  and  $\text{CF}_3(\text{OCF}_2)_n\text{CF}_2\text{C}(\text{O})\text{F}$  and  $\text{CF}_3(\text{OCF}_2)_n\text{OC}(\text{O})\text{F}$ . The direct fluorination of polymethylene oxide,  $(\text{CH}_2\text{O})_n$  [other names for this polymer are polyformaldehyde, polyacetal, and Delrin (DuPont trade name)], was envisaged as an alternate synthetic technique for production of trifluoromethoxy ( $\text{CF}_3\text{O}-$ ) or fluoroformate [ $\text{FC}(\text{O})-\text{O}-$ ] terminated perfluoropolyethers with the  $\text{CF}_2\text{O}$  repeating unit.

The direct fluorination of polymethylene oxide was undertaken under conditions similar to that of polypropylene oxide. Under the conditions studied, per-



fluoropolyethers are not produced by the direct fluorination of polymethylene oxide. Instead, partially fluorinated ethers and substantial amounts of carbonyl fluoride,  $\text{COF}_2$ , were formed. Complete analysis of the products obtained in a reaction resulted in a reasonable explanation for the absence of perfluoroethers and the isolation and spectral characterization of a number of new, structurally novel, partially fluorinated ethers.

#### EXPERIMENTAL

**Polypropylene Oxide.**—Commercially available polypropylene oxide (Polysciences Inc., M.W. 400) was a viscous oil. The direct fluorination of polypropylene oxide oil, when carried out at ambient temperature, resulted in a more viscous oil with a gel-like surface, and only small amounts of volatile products. The 'pre-fluorinated' oil was mixed to a uniform consistency and then fluorinated at elevated temperatures to produce significant quantities of volatile products and a very viscous red material. Typical reaction conditions for the two-part fluorination process are in Table 1. The volatile products of the reaction were

TABLE 1

He (ml min <sup>-1</sup> )	F <sub>2</sub> (ml min <sup>-1</sup> )	Temperature (°C)	Time (days)
30	1.0	Ambient	4
20	2.0	Ambient	4
20	2.0	70—75	2
20	2.0	90—95	4
20	4.0	90—95	4

trapped at  $-196^\circ\text{C}$  in a glass trap and were separated, by vacuum-line trap-to-trap fractionation, into four fractions:  $-30^\circ\text{C}$  (bromobenzene slush),  $-78^\circ\text{C}$  (solid  $\text{CO}_2$ -acetone),  $-131^\circ\text{C}$  (pentane slush), and  $-196^\circ\text{C}$ . For 2.76 g of polypropylene oxide, the described process yielded 2.61 g of solid residue, 0.821 g of volatile compounds in the  $-30$ ,  $-78$ , and  $-131^\circ\text{C}$  fractions, and an undetermined amount of material in the  $-196^\circ\text{C}$  fraction.

The red, gel-like residue was analysed only by i.r. spectroscopy. A thin film on a KBr window exhibited a strong absorption in the C-H region (*ca.*  $3\,000\text{ cm}^{-1}$ ), weak absorptions in the fluorocarbon C=O region ( $1\,700$ — $1\,890\text{ cm}^{-1}$ ), and strong absorptions in the C-F-ether C-O ( $1\,300$ — $1\,110\text{ cm}^{-1}$ ) and 'fingerprint' ( $1\,000$ — $600\text{ cm}^{-1}$ ) regions. The residue was not analysed further because volatile perfluoroethers were the desired compounds.

The  $-196^\circ\text{C}$  fraction of the volatile products contained small amounts of  $\text{CF}_4$ ,  $\text{COF}_2$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ,  $\text{SF}_6$ ,  $\text{SiF}_4$ , and possibly  $\text{C}_4\text{F}_{10}$ .

The g.l.c. separation of the  $-30$ ,  $-78$ , and  $-131^\circ\text{C}$  fractions resulted in further separation of the more interesting, higher molecular-weight volatile products. The g.l.c. separations were characterized by relatively broad peaks, and a significant amount of peak tailing and overlap, implying that the g.l.c. separation was not providing pure compounds, but probably mixtures rich in one compound with small amounts of one or more compounds as impurities. In an attempt to increase the purity of the separated components, only the centres of the g.l.c. peaks were collected as each fraction (the possible reasons for relatively poor

separation by g.l.c. are given in the Discussion section). The g.l.c. fractions obtained are listed in Table 2.

The i.r. spectra of the fractions were all similar in showing no C-H absorptions, strong broad absorptions in the C-F-ether C-O region ( $1\,300$ — $1\,100\text{ cm}^{-1}$ ), and medium to strong absorptions in the 'fingerprint' region ( $1\,000$ — $600\text{ cm}^{-1}$ ).

TABLE 2

Temperature of vacuum-line trap (°C)	G.l.c. retention time/min <sup>a</sup>	Yield/mg	Yield (%)
$-131$	3 <sup>b</sup>	44	5.4
$-131$	7	140	17.1
$-78$	2		
$-131$	9	Trace <sup>c</sup>	
$-131$	18	Trace <sup>c</sup>	
$-131$	23	Trace <sup>c</sup>	
$-78$	8		
$-78$	6	Trace <sup>c</sup>	
$-78$	12	Trace <sup>c</sup>	
$-78$	18	48	5.8
$-87$	38	95	
$-30$	35	51	6.2
$-30$	46	35	4.3
$-30$	58	27	3.3
	Unseparated material	383	46.6
	Total	821	100

<sup>a</sup> G.l.c. temperature programs:  $-131^\circ\text{C}$  fraction,  $-20^\circ\text{C}$  isothermal;  $-78^\circ\text{C}$  fraction:  $0^\circ\text{C}$  for 30 min,  $1^\circ\text{ min}^{-1}$  to  $80^\circ\text{C}$ ;  $-30^\circ\text{C}$  fraction:  $30^\circ\text{C}$  for 10 min,  $1^\circ\text{ min}^{-1}$  to  $90^\circ\text{C}$ . <sup>b</sup> The different fractions are designated *e.g.* 131-3 in the text and subsequent tables. <sup>c</sup> These were obtained in larger amounts from preliminary reactions.

Two of the fractions, 131-3 and 78-12, exhibited strong acyl fluoride i.r. bands (*ca.*  $1\,880\text{ cm}^{-1}$ ), and most of the other cuts also exhibited weak to very weak absorptions in the fluoro-carbonyl region ( $1\,700$ — $1\,880\text{ cm}^{-1}$ ). This i.r. evidence indicated that fluoroacyl fluorides and fluoroketones were present as impurities in the g.l.c. fractions. However, the main compound of most g.l.c. fractions was thought to be a perfluoroether, as expected. A typical i.r. spectrum of a g.l.c. fraction appears in Figure 1.

Mass spectrometry was the most useful analytical tool for molecular-weight determination. The mass spectra were characterized by extensive fragmentation and rearrangement, and only when the spectra were run with the ion source of the spectrometer cooled to room temperature were informative high-mass peaks observed. The highest mass peaks exhibited by each g.l.c. fraction were as follows: 131-7/78-2, 285 ( $\text{C}_5\text{H}_{11}\text{O}$ )<sup>+</sup>; 131-23/78-8, 351 ( $\text{C}_6\text{F}_{13}\text{O}_2$ )<sup>+</sup>; 78-18, 401 ( $\text{C}_7\text{F}_{15}\text{O}_2$ )<sup>+</sup>; 78-38, 451 ( $\text{C}_8\text{F}_{17}\text{O}_2$ )<sup>+</sup>; 30-35, 617 ( $\text{C}_{11}\text{F}_{23}\text{O}_3$ )<sup>+</sup>; 30-46, 667 ( $\text{C}_{12}\text{F}_{25}\text{O}_3$ )<sup>+</sup>; 30-58, 733 ( $\text{C}_{13}\text{F}_{27}\text{O}_4$ )<sup>+</sup>. Each highest mass peak is attributed to  $M - F$  for the major component of the g.l.c. fraction. The spectra showed decreasing peak intensity with increasing mass, and the highest intensity peak was always 119 ( $\text{C}_2\text{F}_5$ )<sup>+</sup> or 169 ( $\text{C}_3\text{F}_7$ )<sup>+</sup>. The other common low-mass fragment peaks were at  $m/e$  31 ( $\text{CF}$ )<sup>+</sup>, 47 ( $\text{COF}$ )<sup>+</sup>, 50 ( $\text{CF}_2$ )<sup>+</sup>, 69 ( $\text{CF}_3$ )<sup>+</sup>, 81 ( $\text{C}_2\text{F}_3$ )<sup>+</sup>, 97 ( $\text{C}_2\text{F}_5\text{O}$ )<sup>+</sup>, 100 ( $\text{C}_2\text{F}_4$ )<sup>+</sup>, 131 ( $\text{C}_3\text{F}_5$ )<sup>+</sup>, 135 ( $\text{C}_2\text{F}_5\text{O}$ )<sup>+</sup>, 147 ( $\text{C}_3\text{F}_5\text{O}$ )<sup>+</sup>, 150 ( $\text{C}_3\text{F}_6$ )<sup>+</sup>, 181 ( $\text{C}_4\text{F}_7$ )<sup>+</sup>, 185 ( $\text{C}_3\text{F}_7\text{O}$ )<sup>+</sup>, 197 ( $\text{C}_4\text{F}_7\text{O}$ )<sup>+</sup>, 200 ( $\text{C}_4\text{F}_8$ )<sup>+</sup>, 213 ( $\text{C}_4\text{F}_7\text{O}_2$ )<sup>+</sup>, 219 ( $\text{C}_4\text{F}_8$ )<sup>+</sup>, and 235 ( $\text{C}_4\text{F}_9\text{O}$ )<sup>+</sup>. The common high-mass fragment peaks were at values corresponding to the empirical formulae  $\text{C}_n\text{F}_{2n-1}\text{O}_x$  and  $\text{C}_n\text{F}_{2n+1}\text{O}_x$  ( $x = 0$ —3).

Several samples had their molecular weights measured by the ideal gas method. The experimental results were (g.l.c. fraction, gas-phase molecular weight, mass-spectrometric

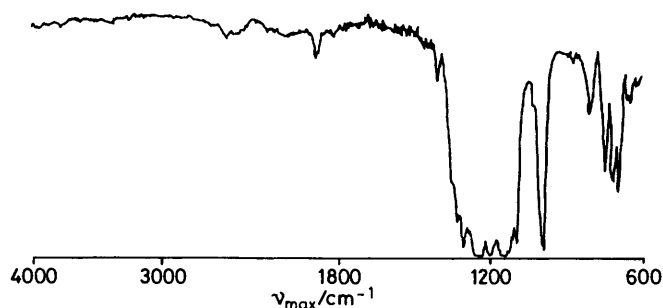


FIGURE 1 I.r. and  $^{19}\text{F}$  n.m.r. spectra of perfluoro-(5-methyl-3,6-dioxanonane)

molecular weight): 131-7/78-2, 307.5, 304; 131-23/78-8, 374, 370; 78-18, 403, 401; 78-38, 466, 470. These results are remarkably consistent, considering that some impurity was present ( $^{19}\text{F}$  n.m.r. spectra).

*Polymethylene Oxide.*—Polymethylene oxide polymer was

had previously been successful for polyethylene oxide entailed a 'pre-fluorination' period (ambient temperature) in which fragmentation was minimized while the polymer was being fluorinated, followed by a high-temperature fragmentation period.<sup>2</sup> A similar strategy for polymethylene oxide fluorination required the use of temperatures below ambient for the 'pre-fluorination' period, because the polymer was fragmenting at ambient temperature. A solid- $\text{CO}_2$ -cooled reactor was employed and  $-78^\circ\text{C}$  was selected as the 'pre-fluorination' temperature. Ambient temperature was subsequently used for promotion of fragmentation and volatile product formation. Reaction conditions typically used are in Table 3.

The volatile products of reaction were separated on a vacuum line into  $-196$ ,  $-131$ , and  $-78^\circ\text{C}$  fractions; pure

TABLE 3

He (ml min <sup>-1</sup> )	F <sub>2</sub> (ml min <sup>-1</sup> )	Temperature (°C)	Time (days)
40	0.5	-78	1
40	1.0	-78	1.5
40	1.0	Ambient	5

compounds were isolated from the  $-131$  and  $-78^\circ\text{C}$  fractions by gas chromatography; and pure compounds were spectrally analysed and identified by i.r., n.m.r., and mass spectroscopy.

The  $-196^\circ\text{C}$  fraction was analysed by i.r. spectroscopy and contained only  $\text{COF}_2$ , with traces of  $\text{CF}_4$ ,  $\text{SiF}_4$  (from HF or  $\text{F}_2$  attack on glass), and  $\text{SF}_6$  (an impurity in the fluorine). Quantitatively, the  $-196^\circ\text{C}$  fraction contained a relatively large proportion of the reaction products. In a typical reaction, 2.17 g of starting polymer produced a  $-196^\circ\text{C}$  fraction weighing 1.85 g which is, assuming the whole fraction is  $\text{COF}_2$ , ca. 40 mol% of the starting material.

The partially fluorinated ethers from the reaction were components of the  $-131^\circ\text{C}$  vacuum-line fraction. The

TABLE 4

Hydrofluoroethers from the fluorination of  $(\text{CH}_2\text{O})_n$

Compound	Retention time <sup>a</sup> /min	Yield/mg	Wt. % of volatile products
$\text{CF}_3\text{-O-CF}_2\text{H}$	8	10.5	1.67
$\text{CF}_3\text{-O-CFH-O-CF}_3$	20	25.1	3.99
$\text{CF}_3\text{-O-CF}_2\text{-O-CF}_2\text{H}$	26 <sup>b</sup>	24.0	3.81
$\text{CF}_3\text{-O-CFH}_2$	26 <sup>b</sup>		
$\text{CF}_2\text{H-O-CF}_2\text{H}$	32 <sup>b</sup>	108.6	17.25
$\text{CF}_2\text{H-O-C(O)F}$	32 <sup>b</sup>		
$\text{CF}_3\text{-O-CFH-O-CF}_2\text{H}$	43	57.9 <sup>c</sup>	9.20
$\text{CF}_2\text{H-O-CFH}_2$	46 <sup>b</sup>	78.5 <sup>c</sup>	12.47
$\text{CF}_2\text{H-O-CF}_2\text{-O-CF}_2\text{H}$	47 <sup>b</sup>		
Other separated <sup>d</sup>		107.7	17.11
Unseparated <sup>e</sup>		217.1	34.49
Totals		629.4	99.99

<sup>a</sup> Temperature program:  $-40^\circ\text{C}$  for 10 min;  $2^\circ\text{min}^{-1}$  up to  $40^\circ\text{C}$ . <sup>b</sup> Compounds with the same (or very close) retention times were collected together in the g.l.c. See text for details of further structural analysis. <sup>c</sup> Combined weight of compound from both the  $-131$  and  $-78^\circ\text{C}$  fractions. <sup>d</sup> Separated from the  $-78^\circ\text{C}$  fraction but not identified (explosive compounds). <sup>e</sup> Unseparated material from the  $-131^\circ\text{C}$  and  $-78^\circ\text{C}$  fractions.

obtained from Monomer-Polymer Laboratories in the form of small pellets. To achieve the high surface area per unit weight that is desirable for a direct fluorination, the polymer was recrystallized and sieved to a fine powder, or the pellets were pressed into very thin, clear discs. Both forms of starting polymer were equally useful and gave similar results.

The first fluorination of polymethylene oxide was conducted at room temperature, and volatile products were observed condensing in the glass trap. The strategy that

compounds were separated by g.l.c. and are listed along with their g.l.c. retention times and yields (from 2.17 g of starting polymer) in Table 4. The  $-78^\circ\text{C}$  fraction contained several of the least volatile components of the  $-131^\circ\text{C}$  fraction as its most volatile components. These compounds were routinely separated by g.l.c. of the  $-78^\circ\text{C}$  fraction and combined with the corresponding material from the  $-131^\circ\text{C}$  fraction. The  $-78^\circ\text{C}$  fraction also contained up to eight other compounds that could be cleanly separated

by gas chromatography. However, these compounds, when stored in sealed 4-mm glass tubes at room temperature, evolved gases and formed white solids (they were initially clear liquids); they were also likely to explode. The compounds, therefore, could not be completely characterised, so will only be discussed briefly.

The i.r. bands of the stable partially fluorinated ethers of the  $-131^{\circ}\text{C}$  fraction have been deposited with NAPS.\* Two distinct bands in the C-H region ( $3000\text{ cm}^{-1}$ ) were observed, and after the structures had been deduced, the following assignments could be made: peaks around  $3050\text{ cm}^{-1}$  indicate  $-\text{CF}_2\text{H}$  or  $-\text{CFH}-$ , and at  $2960-2970\text{ cm}^{-1}$  indicate  $-\text{CFH}_2$ . The other bond types indicated by i.r. were fluoroformate  $[-\text{O}-\text{C}(\text{O})\text{F}]$  at  $1875\text{ cm}^{-1}$  [the same position as for acyl fluorides,  $\text{R}_x\text{C}(\text{O})\text{F}$ ] and C-F at  $1300-1100\text{ cm}^{-1}$ . The C-O stretch is in the same area as the C-F stretch, and this serves to broaden and intensify the bands in that region. Other bands characteristic of the individual compounds were observed in the 'fingerprint' region,  $1000-600\text{ cm}^{-1}$ . The i.r. spectra of the unstable, explosive compounds of the  $-78^{\circ}\text{C}$  fraction were also recorded. They were rather similar to those of the stable partially fluorinated

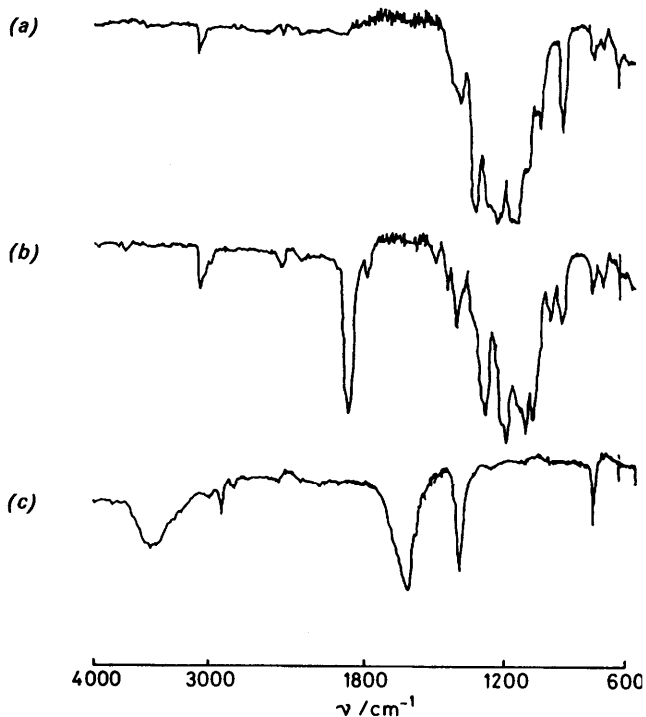


FIGURE 2 I.r. spectra of some products from the fluorination of  $(\text{CH}_2\text{O})_n$ : (a)  $\text{CF}_3\text{-O-CFH-CF}_2\text{H}$ ; (b) an unstable fluoroether; (c) potassium formate  $\text{HCO}_2^- \text{K}^+$

ethers except that all of them exhibited strong bands in the fluoroformate-acyl fluoride region. Two representative i.r. spectra, one of the stable ether,  $\text{CF}_3\text{-O-CFH-O-CF}_2\text{H}$ , the other of an unstable compound, are shown in Figure 2.

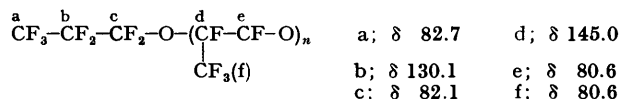
## RESULTS

**Polypropylene Oxide.**—The  $^{19}\text{F}$  n.m.r. spectra was very crucial in determining the structure of the main compound of each g.l.c. fraction. The  $^{19}\text{F}$  n.m.r. spectra for fluoroethers with the  $\text{CF}(\text{CF}_3)\text{-CF}_2\text{-O}$  repeating unit are second

\* The Table of i.r. and mass spectral data has been deposited as NAPS Document No. 03780 (2pp.).

order. Fluorine-fluorine coupling can occur for fluorine nuclei separated by as much as six or seven bonds; thus the fluorine nuclei in the products are coupled to many different fluorine nuclei, so broad unresolved n.m.r. signals and second-order spectra result.

The most useful and reliable information from the  $^{19}\text{F}$  n.m.r. spectra, therefore, was the chemical shift. Interpretation of the spectra was begun by assigning specific structures to the chemical shifts similar to the work of Hill.<sup>7</sup> The  $^{19}\text{F}$  n.m.r. signal assignments for the second-order spectra of the hexamer and heptamer were included. The applicable assignments were as follows (reference external  $\text{CFCl}_3$ ):



These values are 2–3 p.p.m. lower than the calculated chemical shifts for what are considered to be the same signals of the products. A 2–3 p.p.m. discrepancy is not unusual in  $^{19}\text{F}$  n.m.r. spectroscopy and results from instrumental differences. The spectra were run as neat samples in thinner coaxial tubes inside the n.m.r. tube.

The data from the  $^{19}\text{F}$  n.m.r. spectra of the g.l.c. fractions and the structural assignments for the various chemical shifts are compiled in Table 5. No signals were observed in  $^1\text{H}$  n.m.r. scans for any of the g.l.c. fractions. Because the integrated intensities were unreliable, the molecular weights of the compounds were necessary for structure elucidation.

With the mass-spectral molecular weights and the assignments for the observed n.m.r. signals, structures could be elucidated for the main component of several g.l.c. fractions. The compounds were identified by  $^{19}\text{F}$  n.m.r. analysis, and the structures, molecular weights, and assigned n.m.r. data are listed in Table 6. An example of a typical  $^{19}\text{F}$  n.m.r. spectrum observed is the interpreted spectrum of  $\text{CF}_3\text{CF}_2\text{-CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}_2\text{CF}_3$  in Figure 1.

The  $^{19}\text{F}$  signals for  $\text{CF}_3\text{O}$  and  $\text{CF}_3\text{CF}_2\text{O}$  end-groups, the middle  $\text{CF}_2$  of perfluoro-n-propyl end-groups, and the tertiary  $\text{CF}$  of the repeating unit usually had accurate integrated intensities. The signals of the other  $\text{CF}_2$  and  $\text{CF}_3$  groups of the structure were all close together at  $\delta$  83–86, and the integrated intensities were always higher than expected (resulting from small amounts of impurity of similar molecular wt.).

Comparing the spectra for our perfluoroethers, particularly  $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}_2\text{CF}_3$  and  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_2\text{CF}_2\text{CF}_3$ , we can see which of the four signals in the region  $\delta$  83–86 increase in intensity, and which remain constant, as the number of repeating units increases. The better signal assignments are:  $\text{CF}_3$  of the repeating unit, ca.  $\delta$  83.5;  $\text{CF}_2$  of the repeating unit, ca.  $\delta$  85.0; and  $\text{CF}_2$   $\alpha$  to the oxygen of the  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}$  end-group, ca.  $\delta$  86.0 (the assignments for the  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}$  end-group were distinguished by integrated intensity.)

When the n.m.r. spectra were interpreted with reliable molecular weights, integrated intensities, and improved signal assignments for signals of  $\delta < 80$ , still only four perfluoroether structures could be definitely deduced, due to impurities in other g.l.c. fractions.

Physical characterization of the four identified perfluoroethers included m.p. and b.p. determinations; however, it was discovered that the materials solidified as glasses instead of crystalline powders, and therefore the values

obtained were glass transition temperatures. Boiling points were determined for two of the compounds, but the other two were so volatile that they vaporized before values could be obtained. The observed physical constants were [compound, m.p. (°C), b.p. (°C)]:  $C_3F_7OC_2F_5$ , -122;  $C_3F_7OCF(CF_3)CF_2OC_2F_5$ , -115, 93-94;  $CF_3OCF(CF_3)CF_2OC_2F_5$ , -120;  $C_3F_7[OCF(CF_3)CF_2]_2OC_2F_5$ , -108, 144-145.

*Polymethylene Oxide.*—The  $^{19}F$  n.m.r.,  $^1H$  n.m.r., and mass spectral data provided information which led to

For the stable partially fluorinated ethers, first-order n.m.r. analysis was an invaluable analytical tool. The only n.m.r. observation that could not be explained by first-order analysis was the 13-Hz coupling of the doublet of doublet of doublets for the fluorines of the  $-O-CF_2H$  in  $CF_3-O-CFH-O-CF_2H$ . This is thought to be due to a favoured molecular conformation leading to an AB quartet for the  $-O-CF_2H$  fluorine nuclei.

The mass spectra of the stable partially fluorinated ethers were useful in that they confirmed the molecular weights of

TABLE 5  
 $^{19}F$  N.m.r. data of the g.l.c. fractions of the polypropylene oxide volatile products \*  
Signal assignment

G.l.c. fraction	Signal assignment									
	$CF_3O$	$CF_3R_F$	Internal $CF_3$	Internal $CF_2O/CF_3CF_2CF_2O$	$CF_3CF_2CF_2O$	$CF_3CF_2O$	$CF_3CF_2O$	$R_FCF_2R_F$	$CF_3CF_2CF_2O$	Internal $\geq CF-O$
131-3	59.2 [t(11)]		84.2 (8)	85.1 [t(16)]	86.9 [t(25)], 89.6 [quintet(8)]	87.1 [dt(45)],	91.8 (6)	124.9 [dq(30)] 125.7 [quintet(15)]	133.3 (6)	
131-7/ 78-2 131-9	59.1 [d(2)] 59.1 [t(10)]	78.0 (4) 76.9 (7)	84.2 (17)	84.9 (28)	87.5 (18)	90.7 (27)	91.7 (15)	129.4 (2)	133.2 (16)	
131-18		76.7 (3)		84.8 (12)	87.1 (4)	90.5 (5)	91.6 (6)	129.2 (4)	132.9 (5)	
131-23/ 78-8 78-6	57.2 [dq(10)]		83.4 (11)	86.0 (10)		90.6 (10)	91.7 (7)			149.0 (trace)
78-12		77.3 (5)	84.3 (12)	85.1 (15)	87.3 [quintet(4)]	90.7 [q(2)]	91.5 (5)		132.9 (3)	133.2 (4.5)
78-18	59.2 [t(2)]		83.7 (25)	85.1 (25)		90.7 (12)	91.9 (12)	126.2 (9), 129.5 (12)	133.2 (7)	
78-38			83.4	84.9 (58)	86.1	90.6 (15)	91.7 (10)		132.8 (10)	148.0 (4)
30-35			83.2	84.9 (63)	86.0	90.5 (11)	91.4 (7)		132.7 (7)	147.9 (6)
30-46			83.2	84.8 (65)	85.8	90.3 (12)	91.4		132.8 (5)	147.9 (5)
30-58			83.3	85.0 (80)	86.0	90.6 (25)	91.8		133.0 (3)	148.1 (3)

\* Data presented as follows: chemical shift in p.p.m. [multiplicity (integrated intensity)]. All signals are broad unresolved multiplets unless otherwise noted; d = doublet, t = triplet, q = quartet. Referenced to neat external  $CFCl_3$ .

structure determination of the stable partially fluorinated ethers. A summary of the average chemical shifts for the various nuclei is in Table 7 [number of chemical-shift values used in computing the averages are in parentheses; values for  $CF_2H-O-$  in  $CF_2H-O-C(O)F$  were excluded from the averages].

From the observed multiplicities, generalizations about homo- and hetero-nuclear coupling could be made, and average coupling constants computed. Heteronuclear coupling was observed only for geminal hydrogen and fluorine nuclei; no heteronuclear coupling 'across one oxygen' was observed. The average geminal heteronuclear coupling constants were: for  $-O-CF_2H$ , 70 Hz (average of seven values); for  $-O-CFH-O-$ , 66.5 Hz (average of two values); and for  $-O-CFH_2$ , 51.5 Hz (average of two values). Homonuclear fluorine coupling was observed in all compounds, but no homonuclear hydrogen coupling was evident. Fluorine nuclei on carbons separated by an ether linkage were always coupled (four-bond coupling). The average value for all four-bond, F-F coupling was 5.55 Hz (average of ten values).

the deduced structures. All the compounds exhibited peaks due to  $M-H$  and most of them also exhibited a peak due to  $M-F$ .

Six of the identified compounds were from three two-component mixtures that could not be cleanly separated by g.l.c. (see Table 4). The mixture with the 46/47-min retention time was partially separated by a second passage through the gas chromatograph. The first-eluted one-third of the mixture was collected, the second one-third was discarded, and the last-eluted one-third of the mixture was collected separately. The first third was analysed by its n.m.r. and mass spectra which exhibited strong signals attributable to  $CFH_2-O-CF_2H$  with only weak signals from  $CF_2H-O-CF_2-O-CF_2H$ . Similarly, the last third was analysed as mainly  $CF_2H-O-CF_2-O-CF_2H$  with only a trace of  $CFH_2-O-CF_2H$ . This separation method was useful only for this one mixture.

The mixture with the 32-min retention time was separated by hydrolysis. N.m.r. and mass spectral analysis of the water-insoluble portion of the mixture indicated pure  $CF_2H-O-CF_2H$ . The spectral signals from the mixture which

were absent from the pure  $\text{CF}_3\text{H}-\text{O}-\text{CF}_2\text{H}$  sample logically correspond to the water-reactive compound  $\text{CF}_2\text{H}-\text{O}-\text{C}(\text{O})\text{F}$ .

The mixture with the 26-min retention time could not be further separated. The presence of two compounds was

signals were considered alone, the  $^{19}\text{F}$  n.m.r. signal suggested a  $\text{CF}_3-\text{O}$  moiety, and the  $^1\text{H}$  n.m.r. signal suggested  $\text{CFH}_2-\text{O}-$  (compared with the  $^1\text{H}$  n.m.r. signals of  $\text{CFH}_2-\text{O}-\text{CF}_2\text{H}$ ). The structure  $\text{CF}_3-\text{O}-\text{CFH}_2$  for the minor component is

TABLE 6

Volatile compounds identified from the fluorination of polypropylene oxide with assigned  $^{19}\text{F}$  n.m.r. data

G.l.c. fraction	Highest $m/e$ in mass spectrum	Molecular weight (gas-phase)	Compound, $^{19}\text{F}$ n.m.r. data *	Multiplicity (coupling constants)	Observed relative intensity	Theoretical relative intensity
131-3		166	$\text{CF}_3-\text{CF}_2-\text{C}(\text{O})\text{F}$ a b e c a = 87.1 b = 124.9 c = -19.2	dt ( $J$ 5.5, 1.5 Hz) dq ( $J$ 9.0, 1.0 Hz) m	45 30 15	3 2 1
131-7/ 78-2	$m/e$ 285 ( $\text{C}_6\text{F}_{11}\text{O}$ ), $M - \text{F}$ $M = 304$	307.5	$\text{CF}_3-\text{CF}_2-\text{CF}_2-\text{O}-\text{CF}_2-\text{CF}_3$ a e b d c a = 84.9 b = 87.5 c = 90.7 d = 91.7 e = 133.2		28 18 27 15 16	3 2 3 2 2
131-23/ 78-8	$m/e$ 351 ( $\text{C}_6\text{F}_{13}\text{O}_2$ ), $M - \text{F}$ $M = 370$	374	$\text{CF}_3-\text{O}-\text{CF}_2-\text{CF}_2-\text{O}-\text{CF}_2-\text{CF}_3$ e b f   $\text{CF}_3$ (a) d c			
			a = 83.4 b = 86.0 c = 90.6 d = 91.7 e = 149.0 f = 57.2		11 10 10 7 Trace 10	3 2 3 2 1 3
				dq ( $J$ 15, 4 Hz)		
78-38	$m/e$ 451 ( $\text{C}_8\text{F}_{17}\text{O}$ ), $M - \text{F}$ $M = 470$		$\text{CF}_3-\text{CF}_2-\text{CF}_2-\text{O}-\text{CF}(\text{CF}_3)-\text{CF}_2-\text{O}-\text{CF}_2-\text{CF}_3$ c g d h b f e   $\text{CF}_3$ (a)			
			a = 83.4 b = 84.4 c = 85.0 d = 86.1 e = 90.6 f = 91.7 g = 132.8 h = 148.0		58 15 10 10 4	10 3 2 2 1
30-35	$m/e$ 617 ( $\text{C}_{11}\text{F}_{23}\text{O}_3$ ), $M - \text{F}$ $M = 636$		$\text{CF}_3-\text{CF}_2-\text{CF}_2-\text{O}-\text{CF}(\text{CF}_3)-\text{CF}_2-\text{O}-\text{CF}_2-\text{CF}_3$ c g d h b f e   $\text{CF}_3$ (a)			
			a = 83.2 b = 84.3 c = 84.9 d = 86.0 e = 90.5 f = 91.4 g = 132.7 h = 147.9		63 11 7 7 6	15 3 2 2 2

\* Chemical shifts in p.p.m.

inferred from a  $^{19}\text{F}$  n.m.r. signal ( $\delta$  64.3, d,  $J$  5 Hz) and a  $^1\text{H}$  n.m.r. signal ( $\delta$  4.95, d,  $J$  51 Hz) with small integrated intensities. Ignoring those two signals, all the other sig-

TABLE 7

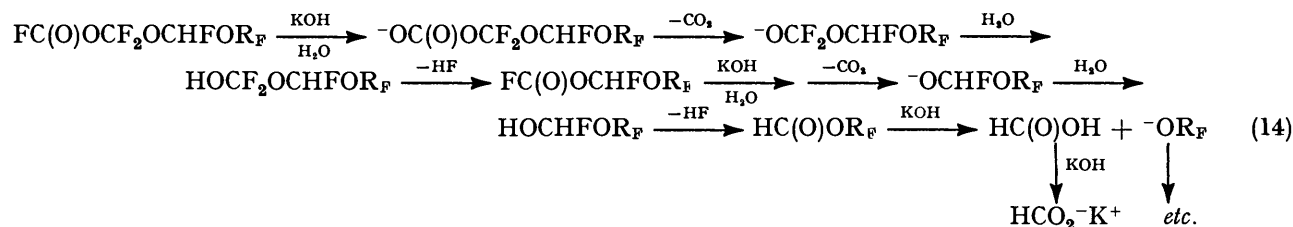
$\text{CF}_3-\text{O}-$	62.5(5)	$\text{CF}_2\text{H}-\text{O}-$	88.8(6)
$\text{CFH}_2-\text{O}-$	158.3(1)	$\text{FC}(\text{O})-\text{O}-$	20.1(1)
$-\text{O}-\text{CF}_2-\text{O}-$	59.4(2)	$-\text{O}-\text{CFH}-\text{O}-$	93.2(2)
$\text{CF}_2\text{H}-\text{O}-$	6.05(6)	$\text{CFH}_2-\text{O}-$	5.10(1)
$-\text{O}-\text{CFH}-\text{O}-$	6.16(2)		

nals indicated  $\text{CF}_3-\text{O}-\text{CF}_2-\text{O}-\text{CF}_2\text{H}$  as the structure of the major component of the mixture. When the two impurity

reasonable on volatility grounds, and the only other expected n.m.r. signal would be from the fluorine of the  $-\text{O}-\text{CFH}_2$ . Lack of detection of the other expected signal is not unreasonable for two reasons: (1) the minor component was of low concentration, so the signal would be weak; and (2) the weak signal, based on the coupling observed for the other signals, should be a triplet of quartets ( $J$  51, 5 Hz) which could further broaden the signal into the background noise.

When the  $-78^\circ\text{C}$  fraction, which contained the unstable fluoroformate-terminated partially fluorinated ethers, was hydrolysed with aqueous KOH, carbon dioxide and potassium formate were the only detected products. The i.r.





so that significant amounts of hydrofluoroether may be formed.

Aqueous KOH hydrolysis of the fluoroformate-terminated unstable ethers of the  $-78^\circ\text{C}$  fraction to produce only  $\text{CO}_2$  and  $\text{HCO}_2\text{K}$  is consistent with an anionic depolymerization process. The envisaged mechanism is shown in equation (14). The fact that these ethers are unstable by themselves could be due to: (a) the fluoroformate end-group reacting inter- or intra-molecularly with residual hydrogen; (b) other interesting HF elimination and depolymerization mechanisms; or (c) the presence of the notoriously unstable hypofluorite group C-O-F.

The direct fluorination of polymethylene oxide does not result in the production of volatile perfluoroethers. This conclusion is substantiated by carbonyl fluoride depolymerization and by the experimental observation that use of higher concentrations of fluorine in a reaction only increases carbonyl fluoride yield while decreasing hydrofluoroether yield. Useful quantities of some novel hydrofluoroethers have been obtained by promoting the fragmentation of an oxide polymer in fluorine before it has been perfluorinated. [A possible synthetic route to the corresponding perfluoro-compounds would be re-

cycling of the isolated hydrofluoroethers in a cryogenic ( $-78^\circ\text{C}$  or below) fluorination reactor.<sup>11,12</sup>

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