THE SYNTHESIS OF FLUOROCARBON MONOMERS AND POLYMERS BY DIRECT FLUORINATION

by

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B.S., Rensselaer Polytechnic Institute

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The Synthesis of Fluorocarbon Monomers and Polymers by Direct Fluorination

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Submitted to the Department of Chemistry in June, 1978 in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

ABSTRACT

The utility of direct fluorination has been expanded to include the successful synthesis of a wide variety of perfluoroethers. Using polymeric ether substrates, an ambient temperature "pre-fluorination" period converts the polymer to a highly fluorinated species while minimizing chain cleavage, and a high temperature "fragmentation" period results in volatile perfluoro products. Poly(ethylene oxide) was used as starting material for the synthesis of fifteen volatile perfluoroethers with the \(-\text{CF}_2\text{CF}_2\text{O}-\) repeating unit, the largest of which contained seven ether linkages. Fluorination of poly-(methylene oxide) yielded mainly the perfluoro monomer, carbonyl fluoride, but nine structurally interesting hydrofluoro mono- and diethers were also obtained. Poly(propylene oxide) was a useful substrate for the synthesis of several volatile perfluoroethers with the branched \(-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-\) repeating unit; the process is an alternative to the commercial method of anionic polymerization of hexafluoropropylene oxide. Radiation copolymerization of ethylene and hexafluoroacetone resulted in an alternating one-to-one copolymer which was used as a precursor for synthesis of perfluoroethers with the \(-\text{CF}_2\text{CF}_2\text{C}(\text{CF}_3)_2\text{O}-\) repeating unit. A synthetic scheme to perfluoroethers from linear hydrocarbon polyesters, i.e. fluorination of the polyester, conversion of fluoroester carbonyls to \(\text{CF}_2\) groups by treatment with \(\text{SF}_4\), and fluorination of the \(\text{SF}_4\) - reaction product, was investigated for poly(butylene adipate), and six volatile perfluoro mono- and diethers were obtained.

"Oxyfluorination", a direct fluorination with oxygen included in the reactant gas mixture, was investigated as a possible method for synthesis of perfluoroacyl fluorides from alkanes. \(n\)-Hexane was the starting material that was extensively studied, but no perfluoroacyl fluorides were obtained.
The General Introduction included a summary of the recent successes for direct fluorination and a literature survey of perfluoroether and perfluoro functional compound chemistry. The General Discussion critically assesses the value and limitations of infrared, NMR and mass spectroscopy, considers various physical states of fluorination starting materials, and makes suggestions for future work.

Thesis Supervisor: Professor Richard J. Lagow
Title: Associate Professor of Chemistry
Acknowledgment

This thesis is dedicated to my loving wife, Sheryl, whose understanding, encouragement, expectations and patience provided my motivation and purpose throughout my graduate career.

I would like to thank Professor Lagow for my financial support, primarily from grants received from the Air Force Office of Scientific Research, during the past three years. The opportunity of working for such a low keyed and optimistic yet demanding professor was a unique learning experience.

I would also like to thank the MIT graduate school for its liberal policies that allowed me to finish my degree "in abstentia" when Professor Lagow moved the research group to the University of Texas.
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Chapter 1

General Introduction
The development of direct fluorination over the last decade has provided fluorocarbon chemists with a new, powerful and versatile synthetic method. Recent experimentation has proven that direct fluorination is a complimentary or often superior technique to the more conventional methods for producing perfluorinated compounds from the corresponding hydrocarbons. To a large extent the chemistry of the more conventional methods, electrolytic fluorination in anhydrous hydrogen fluoride and treatment with a high-valence metal fluoride, particularly cobalt trifluoride, has been developed and documented. Direct fluorination, however, is only beginning to be appreciated for its scope and utility in synthetic fluorocarbon chemistry.

Historical Development of Direct Fluorination

The idea of direct fluorination, combining elemental fluorine with a hydrocarbon substrate to produce a fluorinated compound, is not a new one. Fluorine, the most electronegative element known, is very reactive toward organic compounds because of the weak fluorine–fluorine bond that is broken and the strong carbon–fluorine and hydrogen–fluorine bonds that are formed. The mechanism and thermodynamics of the reaction of fluorine with carbon–hydrogen bonds is presented in Figure 1. The first experiments in direct fluorination generally entailed placing an organic substrate in a highly concentrated fluorine environment and examining the products. This technique led to uncontrolled reaction and heat evolution resulting in substantial substrate decomposition, charring and explosions. The obvious conclusion was that elemental fluorine was not compatible with organic compounds or useful as a fluorinating reagent.
**Figure 1**

**Thermodynamic Data for Steps in Fluorination of CH\textsubscript{4}**

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>$\Delta H_{298^\circ K}$</th>
<th>$\Delta H_{598^\circ K}$</th>
<th>$\Delta G_{298^\circ K}$</th>
<th>$\Delta G_{598^\circ K}$</th>
<th>Kcal/mole</th>
</tr>
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<tbody>
<tr>
<td>Initiation 1a</td>
<td>$F_2 + 2 F^*$</td>
<td>+37.7</td>
<td>+38.5</td>
<td>+29.55</td>
<td>+20.9</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>$F_2 + RH \rightarrow R^* + HF + F^*$</td>
<td>+3.9</td>
<td>+5.1</td>
<td>-5.84</td>
<td>-18.904</td>
<td></td>
</tr>
<tr>
<td>Propagation 2a</td>
<td>$RH + F^* \rightarrow R^* + HF$</td>
<td>-33.8</td>
<td>-33.4</td>
<td>-36.215</td>
<td>-37.51</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>$R^* + F_2 \rightarrow RF + F^*$</td>
<td>-69.1</td>
<td>-69.5</td>
<td>-68.1</td>
<td>-64.15</td>
<td></td>
</tr>
<tr>
<td>Termination 3a</td>
<td>$R^* + F^* \rightarrow RF$</td>
<td>-106.8</td>
<td>-108.0</td>
<td>-97.5</td>
<td>-85.091</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>$R^* + R^* \rightarrow R-R$</td>
<td>-83.8</td>
<td>-83.06</td>
<td>-70.3</td>
<td>-57.5</td>
<td></td>
</tr>
<tr>
<td>Overall Reaction</td>
<td>$R-H + F_2 \rightarrow R-F + HF$</td>
<td>-102.9</td>
<td>-102.9</td>
<td>-103.4</td>
<td>-103.9</td>
<td></td>
</tr>
</tbody>
</table>

(a) Based on JANAF Table for CH\textsubscript{4}
During World War II, interest in fluorocarbon research soared and resulted in significant developments in the electrolytic and high-valence metal fluoride techniques. Many experiments in direct fluorination during this time involved techniques similar to the early ones plus a high surface area of a transition metal (copper, silver or gold) "catalyst" present, but still the results were generally disappointing. The most significant direct fluorination development at this time was by Bigelow and co-workers. Their reactor design was similar to a bensen burner or jet, the fluorine and gaseous organic substrate were injected at high flow rates, and the reaction occurred as a soft blue flame at the jet opening. Although they were able to make some perfluoro compounds from the parent hydrocarbons, their technique is limited to highly volatile organic substrates and by significant amounts of substrate fragmentation and decomposition, which caused low yields.

The lack of success of these pioneering direct fluorination experiments can be attributed to the highly exothermic thermodynamics of the fluorination reaction. By not effectively dissipating or quenching the large amount of heat evolved from the reaction, the partially fluorinated intermediates would be subject to thermal degradation. Skeletal fragmentation and decomposition was the major unsolved problem for the early direct fluorination techniques. Any partial success of the "catalytic" direct fluorinations would be due to heat dissipation by the metal as opposed to a metal-involved catalysis mechanism.

Our innovative concept, that has led to the development of direct fluorination as a useful synthetic technique, is to control the kinetics of the highly exothermic fluorination reaction and to effectively dissipate
the heat of reaction in order to minimize thermal degradation and skeletal fragmentation. The kinetics are controlled by using a mixture of fluorine gas highly diluted with helium (starting fluorine concentrations were generally 1 - 3% fluorine by volume) in a continuous gas flow system over a solid substrate. By limiting the amount of fluorine available for reaction, the reaction is slowed so heat evolution is controlled and effective heat dissipation is possible. Helium is used not only as a convenient diluent gas but also, because of its relatively high heat capacity, as the effective heat dissipator. As the reaction proceeds, the partially fluorinated substrates become resistant to further fluorination by dilute fluorine mixtures, so more fluorine-concentrated gas mixtures are used to promote further reaction. The nature of the partially fluorinated substrates slows the reaction kinetics in the concentrated fluorine environments while efficient heat dissipation is still important for keeping skeletal fragmentation to a minimum. The successful strategy of using diluted fluorine in the initial stages of reaction followed by increasing concentrations of fluorine as the substrate approaches the perfluoro state is depicted graphically in Figure 2. The result of a successful direct fluorination experiment is conversion of a hydrocarbon substrate to a perfluoro compound while completely maintaining the structural integrity of the carbon skeleton.

The first experiments using the LaMar direct fluorination technique were performed by R. J. Lagow and J. L. Margrave at Rice University during the late 1960's. The direct fluorination of various hydrocarbon polymers led to perfluoro polymers of the same carbon skeletal structure, and the fluorination of graphite resulted in an interesting new polymer, poly(car-
FIGURE 2

Fluorine Concentration vs. Time

Volume % Fluorine in Gas Mixture

Start Time Finish

- - - Conceptual Representation
- - - - Experimental Procedure
bonmonofluoride). Prof. Lagow has pursued the promising technique at MIT and more recently at U. of Texas at Austin with gratifying results. A major breakthrough for direct fluorination at MIT was the development of the cryogenic reactor which allowed fluorination of liquids and gases in their solid states at low temperatures.

Perfluoro, highly-branched alkanes are of potential use as blood substitutes due to their ability to dissolve large amounts of oxygen and their emulsion characteristics. The liquid parent hydrocarbons were ideally suited to direct fluorination in a cryogenic reactor and the following reactions can now be performed in yields of 90% or better (principal investigator in parentheses):

\[
\begin{align*}
\text{C(CH}_3\text{)}_4 & \xrightarrow{\text{He} / \text{F}_2 \text{, } -78^\circ \text{C}} \text{C(CF}_3\text{)}_4 \quad \text{(Norma Maraschin)}^9 \\
\text{CH}_3 \text{CH}_3 & \quad \text{CH}_3 \text{-C--C-CH}_3 \quad \text{CH}_3 \text{CH}_3 \\
& \quad \text{CF}_3 \text{CF}_3 \\
\text{He} / \text{F}_2 & \quad \text{CF}_3 \text{-C-C-CF}_3 \quad \text{CF}_3 \text{CF}_3 \\
& \quad \text{CF}_3 \text{CF}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 \text{-C-CH}_2 \text{-C-CH}_3 & \xrightarrow{\text{He} / \text{F}_2 \text{, } -78^\circ \text{C}} \text{CF}_3 \text{-C-CF}_2 \text{-CF}_2 \text{-C-CF}_3 \quad \text{(Larry Shimp)}^11 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 \text{-C-CH}_2 \text{-CH}_2 \text{-C-CH}_3 & \xrightarrow{\text{He} / \text{F}_2 \text{, } -78^\circ \text{C}} \text{CF}_3 \text{-C-CF}_2 \text{-CF}_2 \text{-C-CF}_3 \quad \text{(Edmund Liu)}^12 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

Cyclic, bicyclic and cage-type hydrocarbons have also been fluorinated in the cryogenic reactor for potential use as blood substitutes. Figure 3 shows the specific reactions, and the principal investigators were Norma Maraschin, Jim Adcock and Ed Liu among others. Electrolysis in anhydrous
DIRECT FLUORINATION of CYCLIC HYDROCARBONS

Cyclooctane
\[
\text{Cyclooctane} \quad F\text{-Cyclooctane} + \text{Monohydro-F-cyclooctane}
\]

Norbornane
\[
\text{Norbornane} \quad F\text{-Norbornane} + \text{1-Hydro-F-Norbornane}
\]

Bicyclo[2,2,2]octane
\[
\text{Bicyclo[2,2,2]octane} \quad F\text{-Bicyclo[2,2,2]octane}
\]

Adamantane
\[
\text{Adamantane} \quad \text{1-Hydro-F-adamantane}
\]

\[R = \text{CH}_3, \text{NH}_2; \quad R' = \text{H}\]
\[R = R' = \text{CH}_3\]

R = CF₃, NF₂; \quad R' = F

R = R' = CF₃
HF and CoF$_3$ techniques are not suitable for fluorinations of branched and cyclic hydrocarbons; the major drawbacks are significant skeletal fragmentation and low yields.

A valuable addition to direct fluorination technology was made by Jim Adcock when he successfully fluorinated various oxygen containing hydrocarbons,$^{14}$ see Figure 4. These results suggest that direct fluorination should be a useful synthetic tool for production of a wide range of interesting functional perfluoro compounds. Functional perfluoro compounds are of great interest because of the possible synthetic manipulations of the functional group (which will be discussed later) while nonfunctional perfluoro compounds are some of the most chemically stable compounds known. Of particular interest is the successful perfluorination of ethyl acetate because esters were extensively cleaved when the electrolytic technique was tried,$^{15}$ and no other general synthetic technique for producing perfluoroesters exists.

As our research group has developed the direct fluorination technique, we have come to believe that there is virtually no skeletal structure that cannot be maintained while the compound is perfluorinated. An example of this was the successful fluorination of some organometallic compounds by Ed Liu:$^{16}$

$$\text{Hg(CH}_3\text{)}_2 \xrightarrow{\text{He} / \text{F}_2, -78^\circ} \text{Hg(CF}_3\text{)}_2 \quad (7\%)$$

$$\text{Ge(CH}_3\text{)}_4 \xrightarrow{\text{He} / \text{F}_2, -100^\circ + -20^\circ} \text{Ge(CF}_3\text{)}_4 \quad (63\%)$$

$$\text{OR } \text{Ge(CH}_3\text{)}_w\text{(CH}_2\text{F)}_x\text{(CHF}_2\text{)}_y\text{(CF}_3\text{)}_z$$

$$w + x + y + z = 4$$
FIGURE 4

Direct Fluorination of Oxygen Containing Hydrocarbons

\[
\begin{align*}
\text{CH}_3\text{O-CH}_2\text{CH}_2\text{O-CH}_3 & \xrightarrow{\text{F}_2, -78^\circ\text{C}^*} \text{CF}_3\text{O-CF}_2\text{CF}_2\text{O-CF}_3 + \text{CF}_3\text{O-CF}_2\text{CF}_2\text{O-CF}_2\text{O-CF}_3, \\
\text{1,2-Dimethoxyethane} & \quad \text{E-1,2-Dimethoxyethane} \quad (21\%) \\
\text{CH}_3\text{O-CH}_2\text{CH}_2\text{O-CH}_2\text{CH}_2\text{O-CH}_3 & \xrightarrow{\text{F}_2, -78^\circ\text{C}^*} \text{CF}_3\text{O-CF}_2\text{CF}_2\text{O-CF}_2\text{CF}_2\text{O-CF}_3 \quad (16\%) \\
\text{Bis(2-methoxyethyl) Ether} & \quad \text{E-Bis(2-methoxyethyl) Ether} \\
\text{CH}_3\text{CH}_2\text{O-CH}_2\text{CH}_2\text{O-CH}_2\text{CH}_3 & \xrightarrow{\text{F}_2, -78^\circ\text{C}^*} \text{CF}_3\text{CF}_2\text{O-CF}_2\text{CF}_2\text{O-CF}_2\text{CF}_3 \quad (18\%) \\
\text{1,2-Dioxyethane} & \quad \text{E-1,2-Dioxyethane} \\
\text{CH}_2\text{CH}_2\text{O-CH}_2\text{CH}_2\text{O-CH}_2\text{CH}_2\text{O-CH}_2\text{CH}_3 & \xrightarrow{\text{F}_2, -78^\circ\text{C}^*} \text{CF}_2\text{CF}_2\text{O-CF}_2\text{CF}_2\text{O} \quad (40\%) \\
\text{1,4-Dioxane} & \quad \text{E-1,4-Dioxane} \\
\text{CH}_3\text{C}=\text{O-CH}_2\text{CH}_3 & \xrightarrow{\text{F}_2, -78^\circ\text{C}^*} \text{CF}_3\text{C}=\text{O-CF}_2\text{CF}_3 + \text{CF}_3\text{C}=\text{O-CHF-CF}_3 \\
\text{Ethyl Acetate} & \quad \text{E-Ethyl Acetate} \quad (5\%) \\
\text{CH}_3\text{O} \quad \text{CF}_3\text{C}=\text{O-CF}_2\text{CF}_3 & \xrightarrow{\text{F}_2, -78^\circ\text{C}^*} \text{CF}_3\text{O} \quad \text{HCF}_2\text{O} \\
\text{Pivaloyl Fluoride} & \quad \text{E-Pivaloyl Fluoride} \quad (52\%) \\
\text{CH}_3\text{O} \quad \text{CF}_3\text{C}=\text{O-CF}_2\text{CF}_3 & \xrightarrow{\text{F}_2, -78^\circ\text{C}^*} \text{CF}_3\text{C}=\text{O-CF}_2\text{CF}_3 \quad (14\%) \\
\text{Dimethylmalonyl Difluoride} & \quad \text{E-Dimethylmalonyl Difluoride} \\
\end{align*}
\]

*Coldest Temperature of Gradient
The isolation of the perfluoro mercury and germanium compounds was particularly gratifying, and although the perfluoro silicon compound was not obtained, the fact that any fluoromethyl silicon species were isolated surprised many fluorine and silicon chemists. Silicon is a notorious halogen scavenger and alpha halogen shifts to silicon with elimination of the organic branch is a common mechanism. The successful results of the direct fluorinations of branched, cyclic, ether and functional hydrocarbons and organometallic compounds prove that there is now a fluorination technique in which skeletal fragmentation and rearrangement is minimized.

From this "state of the art" of direct fluorination, we felt additional significant contributions could be made in the areas of functional fluorocarbons and perfluoroethers. Functional fluorocarbons, as mentioned before, are interesting because of the possible synthetic manipulations, and perfluoroethers are interesting because of their unique structure and potential practical uses. Perfluoroethers can be visualized as segments of teflon-like material connected by the oxygen atoms acting as small springs. This interesting structure accounts for the compounds being liquid over a broad temperature range and for their outstanding chemical and thermal stabilities. Perfluoroethers have been described as equally stable as perfluoroalkanes and unaffected by concentrated acids and bases at elevated temperatures over extended periods of time. 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. These properties along with their interesting surface properties and viscosities make perfluoroethers and polyethers attractive for numerous applications as solvents, hydraulic fluids, heat-transfer agents, greases, coatings, sealants, elastomers and resins.

Other Fluorination Techniques

In order to determine the significance of the possible new synthetic uses of direct fluorination, a literature search revealed the capabilities of other fluorination techniques in producing functional perfluoro carbons and perfluoroethers. Of the numerous fluorination techniques available, only two besides direct fluorination are useful in converting hydrocarbons to the corresponding perfluoro compounds; they are electrolytic fluorination in anhydrous hydrogen fluoride and treatment with high-valence metal fluorides. All other techniques are limited to partial or selective fluorination or addition of fluorine to unsaturated sites. These other techniques are outside the scope of this work, and several excellent reviews are available.

High-valence metal fluoride fluorinations have been mainly studied using cobalt trifluoride as the reagent. A fluidized bed of cobalt trifluoride is useful in converting various alkanes, cyclic alkanes and aromatic hydrocarbons to the corresponding saturated perfluoro compound of the same skeletal structure. An attractive feature of the method is that the CoF$_3$ reagent can be regenerated quantitatively by reacting the reduced cobalt species, CoF$_2$, with elemental fluorine. Other high-valence metal fluorides believed to have similar fluorinating capabilities are: silver (II) fluoride, lead (IV) fluoride, manganese (III) fluoride, cerium
(IV) fluoride, bismuth (V) fluoride and uranium (VI) fluoride. The results with these other fluorides are similar to those of CoF$_3$ fluorinations, while the handling procedures are more involved. Although high-valence metal fluoride fluorination is useful for perfluoroalkane production, it seems unlikely that the technique will be successfully applied to functional perfluorocarbon or perfluoroether syntheses.

Electrolytic fluorination in anhydrous hydrogen fluoride was developed by J. H. Simons and co-workers in the 1940’s and is currently the most widely used technique for preparing perfluoro compounds. The organic compound to be fluorinated is dissolved in anhydrous hydrogen fluoride (an excellent solvent for numerous classes of organic compounds) to give a conducting solution and placed in an electrochemical cell with iron cathodes and nickel anodes. An electric current is passed through the solution and the perfluoro product either vaporizes from the solution or separates as a heavier liquid phase as it is formed. This fluorination technique has been successfully applied to numerous hydrocarbon alkanes, ethers, amines, carboxylic acids and acyl halides, but only the ethers and functionalized compounds will be discussed here.

The electrolytic fluorination in anhydrous hydrogen fluoride of carboxylic acids, acyl halides and anhydrides proceeds smoothly to the corresponding perfluoroacetyl fluorides, eg.

\[
\begin{align*}
\text{R}_h^0\text{-C-X} & \xrightarrow{\text{anhyd. HF, electrolysis}} \text{R}_f^0\text{-C-F} \\
X &= \text{OH, F, Cl, Br, I, } -\text{O-C(O)-R}_h \\
\text{R}_f &= \text{CF}_3, \text{C}_2\text{F}_5, \text{C}_3\text{F}_7, \text{C}_4\text{F}_9, \text{C}_5\text{F}_{11}, \text{C}_6\text{F}_{13}, \text{C}_7\text{F}_{15}, \text{C}_9\text{F}_{19}, \text{C}_{13}\text{F}_{27}, \\
& \quad \text{C}_3\text{F}_7, \text{C}_6\text{F}_{11}, \text{C}_6\text{F}_{11}\text{CF}_2 \\
\text{R}_h, \text{R}_f & \text{ have the same carbon skeletal structure}
\end{align*}
\]
Difunctional compounds are equally suitable for this type of fluorination,$^{2,23}$
eg. \[
\begin{array}{c}
\text{X-}R_h-\text{C-X} \\
\text{anhyd. HF} \\
\text{electrolysis}
\end{array}
\rightarrow
\begin{array}{c}
\text{F-}R_f-\text{C-F}
\end{array}
\]

\(X = \text{OH, F, Cl} ; \quad R_f = (\text{CF}_2)_2, (\text{CF}_2)_3, (\text{CF}_2)_4, \text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2, \text{c-C}_6\text{F}_{10}\)

The results indicate that acyl fluoride starting compounds are best. This is reasonable because no chemical transformation of the functional group is necessary. Another significant observation is that as the size of the alkyl chain increases, fragmentation increases causing decreased yields; \(\text{CF}_3\text{COF}\) is produced in 85% yield from \(\text{CH}_3\text{COF}\), while \(\text{C}_7\text{F}_{15}\) is produced in only 4% yield from \(\text{C}_7\text{H}_{15}\text{COF}\).$^2$

An interesting competing reaction in the electrolytic fluorination of carboxylic acids containing six or more carbon atoms is cyclization resulting in perfluoro cyclic ethers,$^{2,24}$ ie. \[
\begin{array}{c}
\text{R}_h-\text{C-OH} \\
\text{anhyd. HF} \\
\text{electrolysis}
\end{array}
\rightarrow
\begin{array}{c}
\text{CF}_3(\text{CF}_2)_{n-3} \quad \text{and} \quad \text{CF}_3(\text{CF}_2)_{n-4}
\end{array}
\]

\(n = \# \text{carbon atoms in alkyl chain (5 or more)}\)

The ratios of five-membered ring compound to six-membered ring compound seems to vary with starting material, and there seems to be disagreement in the literature as to which size of ring is favored. These interesting perfluoro ethers are produced in yields of ca. 40% of the starting acid, but the pathway is minimized when acyl fluoride starting compounds are used.

A wide variety of other perfluoro ethers, polyethers and cyclic ethers can be synthesized using the electrolytic method. Most are conveniently prepared from their parent hydrocarbons,$^{2,25}$ eg. \(\text{CF}_3\text{OCF}_3\), \(\text{C}_2\text{F}_5\text{OCF}_2\text{F}_5\), \(\text{C}_3\text{F}_7\text{OCF}_3\text{F}_7\), \(\text{C}_4\text{F}_9\text{OCF}_4\text{F}_9\), \(\text{C}_5\text{F}_{11}\text{OCF}_5\text{F}_{11}\), \(\text{C}_6\text{F}_{13}\text{OCF}_6\text{F}_{13}\), \(\text{C}_2\text{F}_5\text{OCF}_4\text{F}_9\),
Classes of compounds that cannot be fluorinated successfully by the electrolytic technique are aldehydes, ketones and esters. Only one report of attempted electrolytic fluorination of esters exists,\textsuperscript{15} and their results indicate that cleavage of the ester and formation of perfluoroacyl fluorides is the exclusive pathway, ie.

\[
\begin{align*}
R_h\text{C}-\text{O}-\text{CH}_2-R'_h & \rightarrow R_f\text{C}-\text{F} + R'_f\text{C}-\text{F} \\
0 \quad 0
\end{align*}
\]

This fact enhances the significance of the successful direct fluorination of ethyl acetate. The literature on electrolytic fluorination tends to emphasize the broad utility and successes of the technique while minimizing the limitations. The most notable limitations are: 1) as the size and complexity of the skeletal structure increases, fragmentation becomes more prevalent causing much lower yields and 2) the technique is limited to compounds that are soluble in anhydrous hydrogen fluoride thereby excluding most high molecular weight compounds and polymers.

**Small Molecule Fluorocarbon Synthetic Reactions**

An equally valid strategy for synthesizing perfluoro compounds is the chemical manipulation and combination of small reactive fluorocarbons.
A number of excellent reviews that cover this broad topic are available.\textsuperscript{20,26} The reactions presented here are a survey of those that may be useful in the syntheses and transformations of perfluorofunctional compounds, perfluoroethers and perfluoroesters.

The most successful perfluoropolyether synthetic chemistry has been DuPont's anionic polymerization of perfluoroepoxides. Perfluoroepoxides can be synthesized by combining a perfluoroolefin with oxygen at elevated temperatures\textsuperscript{27} or more easily by treating the perfluoroolefin with 30\% H\textsubscript{2}O\textsubscript{2} in the presence of a base such as NaOH, Na\textsubscript{2}CO\textsubscript{3}, KOH or BaO.\textsuperscript{28} The polymerization reactions of tetrafluoroethylene oxide (c-C\textsubscript{2}F\textsubscript{4}O), hexafluoropropylene oxide (CF\textsubscript{3}-c-C\textsubscript{2}F\textsubscript{3}O) and octafluoroisobutylene oxide (1,1-(CF\textsubscript{3})\textsubscript{2}-c-C\textsubscript{2}F\textsubscript{2}O) have been extensively developed, patented and reviewed.\textsuperscript{29} This work is summarized in Figure 5. Another interesting reaction of per-epoxides is the isomerization by Lewis acids (Al\textsubscript{2}O\textsubscript{3}, AlCl\textsubscript{3}, W(CO)\textsubscript{6}, Fe(CO)\textsubscript{5} and SbF\textsubscript{5}) or Lewis bases (CsF, Et\textsubscript{3}N, PhNMe\textsubscript{2}, pyridine, DMF and BzNEt\textsubscript{2}) to the corresponding perfluoroacyl fluorides and ketones.\textsuperscript{30} The complete synthetic and reaction chemistry of perfluoroepoxides has been reviewed by Tarrant, et al.\textsuperscript{31} Other perfluoroether synthetic schemes have been reported but are less general than the previously mentioned method. Specific perfluoropolyether polymers can be produced by photolytic coupling reactions of perfluoroether diacyl fluorides\textsuperscript{32} or of perfluoroether diiodides in the presence of mercury.\textsuperscript{33} Perfluoroether polymers of the formulas CF\textsubscript{3}(OCF\textsubscript{2})\textsubscript{n}OC(O)F and CF\textsubscript{3}(OCF\textsubscript{2})\textsubscript{n}OCF\textsubscript{2}C(O)F are formed by the pyrolysis reaction of hexafluoropropene in the presence of oxygen and ozone.\textsuperscript{34} Small molecule perfluoroethers can be produced by the addition reactions
Polymerization of Perfluoroepoxides

\[
\begin{align*}
\text{CF}_2^{-2} \text{CF}_2 & \rightarrow \text{CF}_3\text{CF}_2\text{O}((\text{CF}_2\text{CF}_2\text{O})_n\text{CF}_2\text{C}-\text{F}) \quad (A) + \\
\text{F}_2\text{R}^{-}\text{F}_2\text{C}^{-}\text{O}((\text{CF}_2\text{CF}_2\text{O})_n\text{CF}_2\text{C}-\text{F}) \quad (B) + \text{F}_2^{-}\text{R}_2\text{C}^{-}\text{F}_2\text{O}((\text{CF}_2\text{CF}_2\text{O})_n\text{CF}_2\text{C}-\text{F}) \quad (C) \\
\text{F}_2\text{C}^{-}\text{F}_2\text{O}((\text{OCF}_2 \text{CF}_2\text{O})_n\text{OCF}_2\text{F}_2\text{C}\text{C}_2\text{F}_2\text{R}.\text{C}^{-}\text{F}_2\text{O}((\text{CF}_2\text{CF}_2\text{O})_n\text{CF}_2\text{C}-\text{F}) \quad (D) \\
\text{CF}_3\text{C}^{-}\text{CF}_2 \rightarrow \text{CF}_3\text{CF}_2\text{C}^{-}\text{O}((\text{CF}_3\text{C}^{-}\text{CF}_2\text{O})\text{CF}_2\text{C}-\text{F}) \quad (A) + \\
\text{F}_2^{-}\text{R}_2\text{C}^{-}\text{O}((\text{CF}_3\text{C}^{-}\text{CF}_2\text{O})\text{CF}_2\text{C}-\text{F}) \quad (B), (C), (D) \text{ type compounds} \\
\text{CF}_3\text{CF}_2\text{C}^{-}\text{O}((\text{OCF}_2 \text{CF}_2\text{O})_n\text{OCF}_2\text{C}^{-}\text{F}_2\text{C}\text{C}_2\text{F}_2\text{R}.\text{C}^{-}\text{F}_2\text{O}((\text{CF}_3\text{C}^{-}\text{CF}_2\text{O})\text{CF}_2\text{C}-\text{F}) \quad (D) \\
\text{CF}_3\text{CF}_2\text{C}^{-}\text{O}((\text{OCF}_2 \text{CF}_2\text{O})_n\text{OCF}_2\text{C}^{-}\text{F}_2\text{C}\text{C}_2\text{F}_2\text{R}.\text{C}^{-}\text{F}_2\text{O}((\text{CF}_3\text{C}^{-}\text{CF}_2\text{O})\text{CF}_2\text{C}-\text{F}) \quad (D) \\
\end{align*}
\]

Reaction Solvents: Tetraglyme or diglyme is best; others are glyme, EtCN,
(MeO)\text{CH}, MeOAc, CF\text{3}CO\text{2}CH\text{3}, \text{CH}_2\text{R-CHR-CH}_2\text{R} \\
(R = \text{OCH}_2\text{CH}_2\text{OCH}_3)

Product Solvents: CF\text{Cl}_2\text{CF}_2\text{Cl} (Freon-113), perfluoro-2-butyl-tetrahydrofuran,
1,2-(\text{CF}_3)_2-c-C_4\text{F}_6
Polymerization of Perfluoroepoxides

Catalysts:

1) CsF, RbF, KF, Darco charcoal, AgF, R₄NF, Et₄NCN, R₃N, Me₄NI, Me₄NCl, R₄P⁺X⁻, R₄As⁺X⁻, Van de Graaff generator (approximately in order of utility)

2) A wide variety of preformed perfluoroalkoxide catalysts are used in producing (B), (C) and (D) type compounds:

\[
\begin{align*}
\text{R}_f\text{C-F (or } & \text{R}_f\text{-C-R}'_f\text{) + CsF } \xrightarrow{\text{tetraglyme}} \text{R}_f\text{CF}_2\text{O}^-\text{Cs}^+ \\
\text{R}_f = & \text{F, CF}_3, \text{C}_2\text{F}_5, \text{C}_3\text{F}_7, \text{C}_4\text{F}_9, \text{C}_5\text{F}_{11}, \text{C}_6\text{F}_{13}, \text{C}_7\text{F}_{15}, \text{C}_{11}\text{F}_{23}, \\
& \text{CF}_2\text{Cl, CF}_2\text{Br, CF}_2\text{I, I(CF}_2\text{)}_3, \text{FSO}_2\text{CF}_2, \text{FSO}_2\text{CF(CF}_3\text{)}
\end{align*}
\]

Ketones: \( R_f = R'_f = CF_3; \ R_f = R'_f = CF_2H; \ R_f = CF_3, R'_f = C_3F_7; \)

perfluorocyclobutanone; perfluorocyclopentanone

\[
\begin{align*}
\text{F-C-R}_f\text{-C-F + CsF } \xrightarrow{\text{tetraglyme}} \text{Cs}^+\text{OCF}_2\text{R}_f\text{CF}_2\text{O}^-\text{Cs}^+ \\
\text{R}_f = & \text{nothing, CF}_2, (\text{CF}_2)_2, (\text{CF}_2)_3, (\text{CF}_2)_5, \text{CF}_2\text{OFC}_2
\end{align*}
\]
of perfluorohypofluorites and perfluoroperoxides to perfloroolefins,\textsuperscript{35} eg.

\[
\begin{align*}
\text{CF}_3\text{OF} & \quad + \quad \begin{array}{c}
\text{F} \\
\end{array} \\ 
\text{CF}_3\text{OCF}_3 & \quad + \quad \begin{array}{c}
\text{F} \\
\end{array}
\end{align*} \quad \rightarrow \quad \begin{array}{c}
\text{CF}_3\text{OF} \\
\text{CF}_3\text{OCF}_3
\end{array}
\]

The perfluorohypofluorites are usually synthesized by the direct fluorination of suitable alcohols\textsuperscript{36} and by the fluorination of carbonyl compounds in the presence of CsF,\textsuperscript{37} while perfluoroperoxide syntheses are tailored to the specific compound. Use of these hypofluorites and peroxides, however, has been limited due to their relative instability and explosive nature.

A potential general synthetic route to perfluoroethers lies in the ability of sulfur tetrafluoride to convert carbonyl groups to \(-\text{CF}_2-\) moieties. W. C. Smith and co-workers\textsuperscript{38} were the originators of the technique, but W. A. Sheppard was the principal developer with his investigations of hydrocarbon, aromatic and partially fluorinated aldehydes, ketones, acids, esters, carbonates and fluoroformates.\textsuperscript{39} His conclusion was that the reaction worked best for carbonyl compounds with electron withdrawing substituents, particularly aromatic and halogenated groups. Specific perfluoroethers were produced from the \(\text{SF}_4\) reaction on suitable perfluoroketone-ethers and perfluoroaromatic-ester-ethers,\textsuperscript{40} but the route to the ketone and ester precursors is long and involved. R. J. DePasquale applied the reaction to a wide range of highly fluorinated esters in his synthesis of highly fluorinated ethers in yields of greater than 80\%.\textsuperscript{41} He was limited, however, to ester precursors with hydrogens on the \(\alpha\)-carbon of the alkoxy part of the ester (or alkoxy \(\alpha\)-carbons bonded to three other
carbon atoms) because of the lack of existence of the primary and secondary perfluoroalcohols (see below) needed for the synthesis of the perfluoroesters. Although DePasquale's results are not strictly applicable to perfluoroesters, they do suggest that if a general perfluoroester synthesis can be developed, the $SF_4$ reaction should be useful in converting these esters and polyesters to perfluoroethers.

As mentioned previously, no general synthetic method for the production of perfluoroesters exists. The primary reason for this is that perfluoro primary and secondary alcohols are practically nonexistent, so the usual ester synthetic methods of combining an alcohol and acyl halide or alcohol, carboxylic acid and mineral acid catalyst cannot be applied.

One perfluoro primary alcohol, $CF_3OH$, has been recently isolated, and the hydrogen halide adducts of perfluorocyclobutanone are stable compounds, but all other primary and secondary perfluoroalcohols are unstable to HF elimination with acyl fluoride or ketone formation. Tertiary perfluoroalcohols can be synthesized and are stable because of their inability to dehydrohalogenate. These tertiary perfluoroalcohols are usually incorporated into perfluoroesters by first forming an alkali $^3^0$ alkoxide and then reacting it with a perfluoroacyl halide. A route to perfluoroesters whose alkoxy part corresponds to a secondary perfluoroalcohol has been partially developed. It utilizes the ability of perfluoroketones to form adducts with fluoride salts of low lattice energy (usually CsF) followed by the condensation reaction of an acyl halide with the perfluoro $^2^0$ alkoxide salt. The scheme has been used almost exclusively and very successfully for hexafluoracetone but probably will not be developed further because of the produced esters' instabilities toward the "$in
situ" fluoride ion. A similar synthetic route can be devised for perfluoroesters whose alkoxy part corresponds to a primary perfluoroalcohol by starting with a perfluoroacetyl fluoride - alkali metal fluoride adduct. There are, however, no reports in the literature utilizing perfluoroalkoxides as ester precursors, and the scheme would probably again be limited by fluoride ion decomposition of the formed perfluoroesters. The development of a general synthetic method for perfluoroesters would fill a significant void in the capabilities of fluorocarbon synthetic methods, as well as enhance interest in using the $\text{SF}_4$ reaction for producing perfluoroethers from perfluoroesters.

Since perfluoroalkanes and perfluoroethers are among the most stable compounds known, chemical manipulations of perfluorocompounds can be done only with the perfluorocarboxylic acids, acid derivatives and perfluoroolefins. The possible reactions of perfluorocarboxylic acids and derivatives are summarized in Figure 6. (The figure is similar to the one in review text by R. E. Banks, p. 73, with some appropriate additions and deletions.) The reactions are illustrated with perfluorobutyric acid as the starting compound, but all of the reactions are general for any perfluoroacid and most are similar to those of hydrocarbon carboxylic acids. Several of the most important reactions of perfluoroolefins are included; the most common mechanistic pathways being free radical and nucleophilic attack.

**Fluorocarbon Polymers**

Most of the current interest in new fluorocarbon compounds is directed toward higher molecular weight polymeric species as oils, greases, coatings, elastomers and resins. To date, the fluorocarbon polymers that have achieved
FIGURE 6
Reactions of Perfluorocarboxylic Acids and Derivatives

\[ \begin{align*}
C_3F_7CO_2H & \xrightarrow{KMnO_4, H_2O} C_3F_7(C_2F_4)_nI \\
C_3F_7C=CH & \xrightarrow{HC≡CH, u.v., Mg} C_3F_7(NgI) \\
C_3F_7NO & \xrightarrow{u.v.} 125^\circ \\
C_3F_7Cl & \xrightarrow{NO, u.v.} 125^\circ \\
C_3F_7NO_2 & \xrightarrow{O_2, 70^\circ} \\
C_3F_7CO_2Ag & \xrightarrow{Ag_2CO_3} \\
C_3F_7CO_2Na & \xrightarrow{NaOH} KCl \\
C_3F_7CO_2K & \xrightarrow{NaOH} KCl \\
C_3F_7CO_2H & \xrightarrow{PCl_5} \\
C_3F_7COCl & \xrightarrow{H_2, Pd/C} C_3F_7CHO \\
C_3F_7COBr & \xrightarrow{CuI_2} \\
C_3F_7COI & \xrightarrow{[C_3F_7CON_3]} in situ \\
[C_3F_7CON_3] & \xrightarrow{110^\circ} C_3F_7NCO \\
C_2H_5OH & \xrightarrow{20^\circ} C_3F_7NHCO_2C_2H_5
\end{align*} \]
practical applications are generally homo- or copolymers of fluoroolefins or copolymers of fluoroolefins with hydrocarbon monomers, usually produced by free radical polymerizations. The polymers discussed here will be perfluorinated or highly fluorinated polyethers and polymers from functional fluorocarbons.

The perfluoropolyethers formed by the anionic polymerizations of the simplest perfluoroepoxides, tetrafluoroethylene oxide, hexafluoropropylene oxide and octafluoroisobutylene oxide, have been discussed in detail, see Figure 5. More complicated perfluoroepoxides of cyclic olefins have also been anionically homopolymerized or copolymerized with hexafluoropropylene oxide. These perfluoropolyethers are terminated by acyl fluoride groups, and two important pathways exist for polymerization manipulations of the acyl fluoride end-groups. One reaction is chain coupling by ultraviolet photolytic decarboxylation; the other is decarboxylative pyrolysis over a solid metal oxide to produce vinyl ether end-groups. Perfluoro-vinyl polyethers can be homopolymerized or copolymerized with fluoroolefins to pendant perfluoropolyether polymers. Other fluoropolyethers with oxygen in the backbone have been produced by utilizing the ability of hexafluoroacetone to polymerize like an olefin through the carbonyl. Hexafluoroacetone has been copolymerized with numerous hydrocarbon olefins, fluoroolefins and hydrocarbon epoxides.

The classic condensation polymerization reactions have been useful in preparing polymers of various difunctional fluorocarbons. Fluorocarbon diacids, diacyl halides and diesters may be condensed with diols and diamines to produce polyesters and polyamides. Fluorocarbon diols and diamines \( \text{HOCH}_2\text{R}_f\text{CH}_2\text{OH} \) and \( \text{H}_2\text{NCH}_2\text{R}_f\text{CH}_2\text{NH}_2 \) have also been condensed to
polyesters and polyamides. The polyesters and polyamides so formed are characterized by rather low thermal stabilities and enhanced chemical reactivities of the ester and amide linkages. These facts have led to investigations of various heterocyclic structures as stable crosslinking species. The heterocyclic structures that may be formed from functional fluorocarbons and that have been investigated are:

s-triazines,

\[ N \equiv C \equiv N \]

1,2,4-oxadiazoles,

\[ \text{N-C-C} \]

1,3,4-oxadiaoles,

\[ \text{C-\(\bigcap\)C} \]

and isocyanurates,

\[ \text{C-N\(\bigcap\)N-C} \]

Summary

The significance of further developing direct fluorination as a synthetic technique lies in the limitations of the other techniques for producing perfluoro compounds. Small molecule combination schemes can be useful, but multiple reactions and purifications are necessary for precursor then desired compound synthesis. The method also suffers from the necessity of handling the fluorocarbon small molecules, many of which are very toxic, reactive, unstable and even explosive. Hexafluoroacetone is a good example of a toxicity complication; just recently, DuPont has claimed that hexafluoroacetone has serious, toxic, cumulative effects and, consequently, they no longer commercially distribute the compound. The limitations of the other fluorination techniques that convert hydrocarbons to the corresponding perfluoro compounds, ie. \(\text{CoF}_3\) treatment and electrolysis in anhydrous HF, are: low yields for large structures due to significant fragmentation, the techniques are not useful for all types of organic substrates (particularly potentially interesting polymers) and the tech-
Techniques have been developed to the extent of their capabilities, so no additional breakthroughs are expected. The utility of modern direct fluorination lies in the one-step process, the minimization of skeletal fragmentation so high yields are possible, the applicability to all organic substrates, solid, liquid or gaseous, and the potential scope of the technique. The development of direct fluorination as an alternative high yield technique for production of perfluorofunctional compounds and perfluoroethers and as the only technique for production of structurally unique perfluoroethers and perfluorofunctional polymers would be a valuable addition to fluorocarbon technology.
Chapter 2

General Experimental
Most of the experiments undertaken in this field of fluorocarbon chemistry involved manipulation of very toxic, reactive and air or water-unstable reagents, substrates or products. The majority of experiments were direct fluorinations, and the appropriate apparatus, procedures and precautions for handling elemental fluorine are described in detail in this section. For other experiments involving hazardous materials such as anhydrous HF, SF₄, SbF₅, etc., appropriate care and consideration was devoted to apparatus design and safety precautions. (Specialized apparatus will be described with the particular experiment in the Results sections.) Many of the products were new or unusual compounds whose physiological effects have not been established, so again, personal safety in product handling and analysis was a foremost consideration.

**Direct Fluorination Apparatus**

Considering the great chemical reactivity and high toxicity of elemental fluorine, appropriate safety precautions are mandatory. The cylinders of fluorine gas were stored in asbestos walled enclosures equipped with ventilation fans. The entire fluorination apparatus was housed in an 8' by 6' by 3' hood with sliding safety glass doors on both sides. The fluorination apparatus was supplied with fluorine through a brass manifold connected by copper tubing to the fluorine storage cylinder. This manifold was equipped with a release valve that led to an aluminum oxide trap, so in case of emergency, the fluorine could be shut off at the cylinder head and the pressure in the manifold quickly vented. Items available for personal safety were: an oxygen mask, asbestos coveralls, plastic face shields, leather gloves and a leather vest.

Careful consideration of what materials the apparatus is to be con-
structured of is also necessary. The materials most suitable to continuous exposure to fluorine in a permanent apparatus are monel, nickel and teflon, but all are very expensive. Other useful materials are copper and brass, which may become brittle over extended periods of time in fluorine, but their lower costs justify their use. Metal apparatus can be used with elemental fluorine because initial exposure of the metal parts to fluorine causes a protective metal fluoride coating to be formed; most metal fluoride coatings are unaffected by fluorine at temperatures below $300^\circ C$, with nickel fluoride, the most fluorine-inert protective coating, being stable well above $1000^\circ C$ in fluorine. All of the connecting tubing in the fluorination apparatus was 1/4 inch O. D. copper tubing, and all of the manifolds, mixing chambers and connecting swagelok and pipe-thread fittings were made of brass. All brass pipe fittings were wrapped with Teflon tape to assure a gas-tight fit. The valves, which needed additional durability because of continuous manipulation, were made of monel; the O-ring seals for flanges were made of Teflon; and the reactors and sample boats were made of nickel. Glass is also compatible with elemental fluorine, but precautions must be taken to assure that no hydrogen fluoride (which etches glass) is present. This, of course, means the system must be kept water-free in addition to removing HF as it is formed during the fluorination processes. The glass - copper tubing connections were made with Cajon Ultra-torr fittings which form gas-tight connections by deforming with pressure a rubber (Viton) O-ring around the glass tubing where it slides into the brass fitting.

A schematic of the direct fluorination apparatus is shown in Figure 7. The fluorine was supplied by Allied Chemical Corp. and was used without
Fig. 7 Schematic of Direct Fluorination Apparatus
further purification. (Approximately 1% oxygen is the major impurity in commercial fluorine.) The regulator on the fluorine cylinder was a Matheson single stage regulator, Model B15F-679. The fluorine passed through copper tubing from the supply tank to a one inch O. D. brass manifold (A). The fluorine flow rate from the manifold was controlled by Monel needle valves, Whitey M-31RS4 (B). The fluorine flow rate was monitored by a Hastings-Raydist Mass Flow Transducer, type F-50M (C), connected by a cable to a Hastings-Raydist Mass Flowmeter, Model LF-50X. The Mass Flow Transducers and Mass Flowmeters were matched and calibrated by the manufacturer, and flow rates could be controlled to within 0.25 cc/min.

A second brass manifold (D) was connected to a tank of helium gas. A Hoke monel throttling valve, Model 2215F4M (E) controlled the helium gas flow rate which was monitored by a glass rotamer type flowmeter, Matheson Series 600 (F). The glass helium flowmeters were connected by short sections of 5/16 inch rubber tubing with hose clamps, to short sections of copper tubing which were fitted to the helium manifold and helium control valves.

If an "oxyfluorination" were to be performed, an additional connection for oxygen could be made at the fluorine-helium junction. The flow rates of oxygen needed were very small, generally 1/2 to 1/10 cc/min, less than what can accurately be measured by practical, inexpensive, commercially available flowmeters. The oxygen flowmeter must also be able to withstand elemental flourine because the low oxygen flow rate would allow back-diffusion of fluorine to the flowmeter. The method devised to control the oxygen flow rate consisted simply of a short piece
of thick-walled (6 mm) capillary tubing (G) as a section of the supply line. The capillary tube had been melted and drawn until the tube was almost closed off, so the free flow of gas through the tube was restricted by the very small orifice. The oxygen flow rate, therefore could be controlled by the pressure of the gas being forced through the orifice, and this pressure was controlled by the regulator of the oxygen tank. This setup also effectively eliminated any back-diffusion of fluorine into the oxygen tank because the velocity of the oxygen molecules through the thinnest section of the capillary would be very high.

The fluorine, oxygen and helium gases mixed thoroughly as they passed through a copper turnings packed brass chamber (H). The gas mixture passed through the reactor (reactor designs and uses described below) and then a small brass chamber (I) packed with sodium fluoride pellets. The sodium fluoride acted as a Lewis base in trapping the hydrogen fluoride by-product of the reaction according to the equation:

NaF + HF $\overset{\Delta}{\longrightarrow}$ NaHF$_2$.

(The sodium fluoride pellets could be regenerated by heating them to $\approx$400°C in a stream of dry nitrogen.) If the desired reaction products were volatile compounds, a glass trap (J) was placed downstream from the sodium fluoride scrubber, and the condensible gases were trapped at -78°C or -196°C.

The resultant gas mixture had to be treated to remove unreacted fluorine before it could be vented into the atmosphere. Alumina, Al$_2$O$_3$, was packed in a large brass chamber (K), and it reacted with any elemental fluorine to form oxygen and aluminum fluoride, as follows:

Al$_2$O$_3$ + 3 F$_2$ $\longrightarrow$ 2 AlF$_3$ + 3/2 O$_2$. 
A nitrogen inlet just before the alumina scrubber was included for two reasons: to act as a heat dissipator for the highly exothermic alumina-fluorine reaction and to inhibit the back-diffusion of alumina produced oxygen to the reactor that would be possible when low helium and fluorine flow rates were used. Nitrogen was supplied to a one inch O.D. brass pipe manifold (L), regulated by a brass throttling valve, Hoke R306A (M), and thoroughly mixed with the gases from the reactor in the small brass chamber (N). The gas mixture after passing through the alumina scrubber contained only helium, oxygen and nitrogen and was vented to the atmosphere through a glass bubbler containing mineral oil (O). The bubbler served the dual purpose of maintaining the pressure of the entire reaction line at atmospheric pressure and preventing the back-diffusion of atmospheric gases into the system.

If volatile reaction products were not trapped at low temperatures in the glass trap (J), they too would pass through the alumina scrubber. Polar molecules would be adsorbed on the activated polar surface of the alumina while the nonpolar molecules were routinely vented through the bubbler. Only when a specific reaction had been previously shown to produce only small amounts of common, low-toxicity, fragment molecules were the volatile products uncollected and vented through the alumina scrubber and bubbler.

**Fluorination Reactors**

Three reactor designs were commonly used for direct fluorination experiments. The choice of reactors depended primarily on the physical properties of the substrate because the available data indicates that direct fluorination is most successful when a finely divided, crystalline
solid starting material is used.

Substrates that are crystalline solids at room temperature were usually fluorinated at ambient temperatures after being sieved to a finely divided powder, less than 100 mesh. The starting material was contained in a small nickel boat, and the boat was placed in the room temperature reactor. The reactor is simply a 1½ inch O. D. nickel pipe 18 inches long with teflon O-rings and flanges for closing the ends, Figure 8A. The flanges were either connected directly to copper tubing or, if the fluorinated product was air sensitive and glove box handling was necessary, monel throttling valves, Hoke 3212M4M, were included. This reactor design was also used in high temperature fluorinations where the nickel pipe was wrapped with a heating tape and fiberglass insulation. The upper temperature limit for the reactor was ~120°C because the teflon O-rings at the flanges would be significantly attacked by fluorine at higher temperatures.

Occasionally, a compound that was a crystalline solid at room temperature would be fluorinated at low temperatures. Reasons for this included: the starting compound or the partly fluorinated intermediates had a significant vapor pressure, so the substrate would be blown out of the reactor before reaction was complete; the starting compound was extremely attacked and decomposed by ambient temperature fluorination; and the partly fluorinated intermediates had melting points or glass transition temperatures lower than room temperature, so if the reaction temperature was not lowered to maintain the finely divided crystalline state, the substrate would "collapse" to a grease or oil with low surface area per unit weight.

The low temperature reactor used consisted of a room temperature reactor inserted through a standard urethane ice bucket with the bucket made solvent-
A. Room temperature reactor

F₂ + He

B. Bucket reactor

F₂ + He

C. Cryogenic reactor

Entry Port

F₂ + He

Fig. 8 Schematic of Reactors
tight with rubber cement, Figure 8B. Low temperatures of 0°C and -78°C were easily maintained with ice and dry ice - solvent, respectively. Other sub-ambient temperatures were maintained with a cryogenic liquid nitrogen setup. The liquid nitrogen was supplied from a Union Carbide Model LS-160 liquid nitrogen cylinder through jacketed copper tubing to the reactor. The liquid nitrogen flow was controlled by a solenoid valve connected to a cryogenic temperature controller, Cryogenic Control Co. Model 123-000, that monitored temperature with a copper-constantan thermocouple.

If a room temperature liquid or gas material was to be fluorinated, a cryogenic reactor, Figure 8C, was used. It consisted of a length of 1½ inch O. D. nickel pipe with teflon O-rings and flanges and packed with copper turnings. The pipe was encased in a 6 inch wide, 9 inch high stainless steel outer chamber with 4 inch diameter, 8 inch high cylindrical stainless steel inner chambers (zones) spaced evenly along the pipe. The outer and inner chambers were separated and insulated by urethane foam, and the outer chamber was further insulated by styrofoam and cork sheets. Three lengths of cryogenic reactors were available: 24 inch, 4 - zone reactors; 36 inch, 6 - zone reactors; and 48 inch, 8 - zone reactors. A swagelok "T"-connector was included as a sample entry port just upstream of the reactor.

Starting materials were introduced to the cryogenic reactor by first cooling the second zone of the reactor to below the melting point of the compound and starting a high flow rate of helium. (The first zone was not directly cooled because the inlet copper tubing could get sufficiently cold to condense starting material.) Gas reactants were slowly vented through the entry port into the helium stream; volatile liquids were evap-
orated from a reservoir connected to the entry port; or the liquid reactants were syringed in small aliquots through a rubber septum fixed to the entry port and evaporated from a copper tubing coil as the helium blew through. As the vapor laden helium stream passed through the cold reactor, the condensible molecules could "snow out" if they crystallized from the gas phase, or they would condense and freeze on the high surface area of the copper turnings. Whichever condensing mechanism operates, a crystalline solid with high surface area would result.

The advantage of having multiple zones for the cryogenic reactor is that as the reaction proceeds, successive zones of the reactor can be cooled and previous zones warmed, thereby establishing a thermal gradient and moving it down the reactor. Since highly fluorinated compounds are generally more volatile than partially fluorinated ones, they would vaporize and move to the colder sections of the reactor leaving a fresh surface of partially fluorinated and non-fluorinated molecules for reaction. This reactor and technique has produced high yields of perfluoro compounds. Cooling of the zones was accomplished as with the bucket reactor: ice for 0°C, dry ice - solvent for -78°C and liquid nitrogen with a cryogenic temperature controller for any other sub-ambient temperature.

**General Procedures and Equipment**

The general procedure for performing a direct fluorination experiment involved mainly adjusting and monitoring the gas flow rates and temperature of the reactor. First, the appropriate reactor was connected to the fluorination apparatus and the starting material introduced. Powdered solids were sieved into nickel boats and placed in the reactor, and liquids or gases were blown in as vapors and condensed, as discussed previously.
high helium flow rate of 100 - 150 cc/min was passed through the apparatus for a minimum of 8 hours in order to completely flush atmospheric gases and adventitious moisture or solvents from the system. The helium, fluorine and oxygen flow rates along with the reactor temperature were adjusted in a step-wise manner throughout the reaction. The initial conditions of the reaction were the most gentle with a low percentage of fluorine in the gas mixture and low temperatures, whereas the final stages of the reaction involved more vigorous conditions with more concentrated mixtures of fluorine / helium and higher temperatures. The specific conditions and times were determined arbitrarily at first but adjusted as the results dictated. To terminate the reaction, the fluorine and oxygen flows were stopped and the reaction line was again flushed with 100 - 150 cc/min of helium. The apparatus could then be safely disassembled and the products removed, separated and analyzed.

A major concern throughout the reaction was the quick and safe detection and elimination of leaks in the reaction line. A leak resulted not only in the dangerous escape of fluorine gas into the lab but also in the diffusion of atmospheric gases and moisture into the apparatus causing non-reproducible conditions and problems in the fluorination. The safest, most convenient method for pin-pointing fluorine leaks involved wetting a cotton swab or "Kimwipe" with aqueous potassium iodide and placing it near the suspect connection. The presence of fluorine was indicated by a color change of the swab to dark orange-brown caused by the fluorine oxidation of iodide to iodine. Although the KI detection method is good for location the leaks, the existence of fluorine leaks was usually first established by smell. Fluorine has a characteristic pungent, biting
odor, and even the smallest leaks, ones barely detectable by the KI method, are apparent to the trained nose. The strong odor of fluorine is ironically fortunate in that it serves as a personal warning in dangerous situations and as an unpleasant reminder as to the dangers of elemental fluorine.

When replacement monel, nickel, copper or brass parts are used for the first time, the reaction line is pretreated with fluorine. The fresh metallic surfaces of the new parts are passivated by fluorine to high-valence metal fluoride protective coatings. The alumina scrubbers were recharged when fluorine was detected at the bubbler by reaction and discoloration of the mineral oil. The sodium fluoride scrubbers were recharged following every reaction because of potential caking of the pellets and line blockage.

Volatile products of the reactions were transferred from the collection trap and first separated by vacuum line, low temperature, trap-to-trap fractionation. Common slush baths used were (prepared by mixing liquid nitrogen with a solvent until a thick mixture of solid solvent and liquid solvent results): bromobenzene (-30°C), chlorobenzene (-45°C), dry ice-isopropanol (-78°C), toluene (-95°C), pentane (-131°C) and isopentane (-160°C). Pure compounds were isolated by gas-liquid chromatographic (GlC) assay of the vacuum line fractions. The gas chromatograph was a Bendix 2300 equipped with an automatic temperature programmer. The most efficient column used was a 3/8 inch by 7 meter coiled copper tube packed with 10% Fluorosilicone QF-1-0065 on Chromosorb P, and the carrier gas (He) flow rate was 150 cc/min.

Separations and purifications of solid fluorocarbon products were
difficult due to the nature of the polymeric, highly fluorinated compounds. Extreme lack of solubility in almost any solvent rendered recrystallization, extraction and preparatory high-pressure liquid chromatography methods useless. Occasionally useful techniques included sublimation, prolonged Soxhlet extraction and hydrolysis reactions. Handling of air or hydrolytically sensitive solids was done either in a glove bag or a glove box kept water and oxygen free by Sodium / Potassium alloy.

The common analytical spectroscopic methods, infrared, NMR and mass spectroscopy, were used as appropriate for solid, liquid and gaseous mixture analyses, as well as for pure compound structural determination. The infrared spectra were run on a Beckman IR-20A infrared spectrometer, the volatile compounds as gases in a 10 cm cell with KBr windows, the low volatility liquids as thin films between KBr windows and the solid products as KBr pellets or films cast from solution on KBr windows. $^{19}$F and $^{1}$H NMR spectra were recorded on a Perkin-Elmer R20-B spectrometer (at MIT) and Varian Associates A-56/60 spectrometers (at U. Tex.); excitation r. f. frequencies were 60 MHz for protons and 56.4 MHz for fluorine nuclei. Samples were run as neat liquids when possible with TMS as an external proton reference and Freon-11, CFC$_3$, or trifluoroacetic acid (TFA) as an external fluorine reference. Mass spectra were measured on a Hitachi RMU 6D mass spectrometer (at MIT) and a Bell and Howell Model 21-491 mass spectrometer (at U. of Tex.). Better mass spectra, i.e. less fragmentation and rearrangement, were usually obtained when the ion source was cooled to room temperature.

Physical analytical methods included boiling point and melting point determinations and elemental analyses. Elemental analyses were performed
commercially by Schwarzkopf Microanalytical Laboratories of New York City. High temperature melting points of solid samples in sealed capillary tubes were routinely measured on a Mel-Temp. Low temperature melting points were measured by freezing sealed capillary tube samples of the liquids 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 compound was 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.
Chapter 3

Fluorination of Poly(ethylene oxide)
Fluorination of Poly(ethylene oxide)

\[
(CH_2-CH_2-O)_x \xrightarrow{\text{He} / F_2} R-F-(CF_2-CF_2-O)_n-R_f
\]

1) \( T = \text{amb.} \)
2) \( \Delta \)

\( R_f = \text{CF}_3, \text{C}_2\text{F}_5 \)

Introduction

As discussed in the general introduction, saturated perfluoropolyethers are of current interest for new material applications due to their unusual properties. Their outstanding features are lack of chemical reactivity, high thermal stability (>300°C), interesting surface properties and broad liquid ranges of the low molecular weight compounds.

Synthesis of saturated perfluoropolyethers in general has been limited by the few general synthetic methods available (see General Introduction), and synthesis of perfluoropolyethers with the \((\text{CF}_2-\text{CF}_2-0)\) repeating unit is limited to two methods. One method, electrolytic fluorination in anhydrous HF, is useful only for synthesis of several low molecular weight species from suitable hydrocarbon precursors. The method is limited to low molecular weight compounds because the hydrocarbon precursor and partially fluorinated intermediates must be soluble in anhydrous HF. The highest tetrafluoroethylene oxide telomer that has been synthesized by HF electrolytic fluorination is \( \text{C}_2\text{F}_50(\text{CF}_2\text{CF}_20)_2\text{C}_2\text{F}_5 \), in only 4% yield.

The other method for producing \((\text{CF}_2-\text{CF}_2-0)_n\) ethers is DuPont's synthesis then polymerization of tetrafluoroethylene oxide. Synthesis of tetrafluoroethylene oxide involves synthesis of tetrafluoroethylene, then oxidation of the olefin to the epoxide. Anionic polymerization of the tetrafluoroethylene oxide results in acyl fluoride-terminated telomers.
and polymers over a wide range of molecular weights. (See Figure 5 for an extensive outline of anionic perfluoroepoxide polymerizations.) Although numerous chemical manipulations of the acyl fluoride terminus are possible, unreactive perfluoroethers were usually desired, so decarboxylation reactions for transformation of the functional end-groups to chemically stable end-groups were applied. The common decarboxylation reactions were: \(^{29,52,63}\) pyrolysis in the presence of a hydrogen source to form hydrogen-capped chains; fluorination with elemental fluorine at elevated temperatures in a solvent to form fluorine-capped chains; and photo-lytic decarboxylative chain coupling by u. v. light. The overall scheme, therefore, is a four-step process involving two steps for monomer synthesis, a polymerization step and an end-capping step. The multi-step method is also complicated by the necessary handling procedures for the tetrafluoroethylene oxide monomer which is toxic, explosive and readily isomerizes to trifluoroacetyl fluoride, \(\text{CF}_3\text{COF}\), above its boiling point. \(^{31}\)

We have developed direct fluorination as a useful, new, one-step synthetic method for the production of saturated perfluoropolyethylene glycol ethers. The reaction of high molecular weight polyethylene oxide polymer with elemental fluorine, with reaction conditions chosen to promote fragmentation of the polymer during the fluorination process, has resulted in the synthesis of saturated perfluoropolyethers over a broad range of molecular weights. The low molecular weight compounds \((n = 1 - 6)\) which have been isolated are volatile liquids; medium molecular weight compounds are nonvolatile oils; and the high molecular weight compounds are gel-like and powdery solids. Previously, we have found that milder fluorination conditions designed to prevent fragmentation led to an ex-
tremely stable high molecular weight perfluoropolyether. Of the specific perfluoropolyethers synthesized, only four have been previously reported in the literature when methods other than direct fluorination were used. Perfluoromonoglyme\[^{64,65}\] (CF\(_3\)OCF\(_2\)CF\(_2\)OCF\(_3\)), perfluoroethylene glycol methyl ethyl ether\[^{64}\] (CF\(_3\)OCF\(_2\)CF\(_2\)OCF\(_2\)CF\(_3\)), perfluoroethylene glycol diethyl ether\[^{66}\] (CF\(_3\)CF\(_2\)OCF\(_2\)CF\(_2\)OCF\(_2\)CF\(_3\)), and perfluorodiethylene glycol diethyl ether\[^{65}\] (CF\(_3\)CF\(_2\)OCF\(_2\)CF\(_2\)OCF\(_2\)CF\(_2\)OCF\(_2\)CF\(_3\)) have all been prepared by electrolytic fluorination in anhydrous HF in low yield. Two of the compounds, perfluoromonoglyme (CF\(_3\)OCF\(_2\)CF\(_2\)OCF\(_3\)) and perfluorodiglyme (CF\(_3\)OCF\(_2\)CF\(_2\)OCF\(_2\)CF\(_2\)OCF\(_3\)), had been previously synthesized by Jim Adcock of our research group\[^{14}\] by low temperature direct fluorination of the parent hydrocarbons. The development of direct fluorination as a one-step synthetic technique for synthesis of a wide range of saturated perfluoropolyethylene glycol ethers is a significant breakthrough in fluorocarbon technology.

Experimental

The direct fluorination of solid polyethylene oxide polymer (Poly-sciences Inc., Grade 4,000,000), which had been ground and sieved to a fine powder (<150 mesh), was performed in a room temperature reactor. The results reported here were from a reaction of 6.53 g of polyethylene oxide polymer using the following gas flow rates, temperatures and times (high temperatures were maintained with a heating tape and insulation):

<table>
<thead>
<tr>
<th>He (cc/min)</th>
<th>F(_2) (cc/min)</th>
<th>Temp. ((^{\circ})C)</th>
<th>Time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1.0</td>
<td>amb.</td>
<td>6</td>
</tr>
<tr>
<td>40</td>
<td>2.0</td>
<td>amb.</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>2.0</td>
<td>amb.</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>4.0</td>
<td>amb.</td>
<td>2</td>
</tr>
</tbody>
</table>
The volatile products of the reaction were trapped at -196°C in a glass 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 assay, and the separated pure compounds were identified by their infrared, $^{19}$F NMR and mass spectra.

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$_6$ (an impurity in the fluorine), COF$_2$, C$_2$F$_6$ and SiF$_4$ were also detected by infrared. 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$^{67}$, the isolated yield of CF$_4$ was 2.268 g or 8.7 mole % 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$_2$O 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$^{67}$, is 1.83 g or 9.3 mole % of the starting...
polymer. The water-stable gases of the fraction were separated further
by Glc at -50°C isothermal. Only several milligrams of one compound, per-
fluoromonoglyme (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 predominately SF₆ with
traces of C₂F₆ and perhaps C₃F₈ or CF₃OCF₃.

It was the Glc assay of the -131°C and -78°C fractions that resulted
in isolation of significant amounts of fifteen volatile perfluoroethylene
glycol ethers:

\[
\begin{align*}
\text{CF}_3-O-(\text{CF}_2-\text{CF}_2-O)_a-\text{CF}_3, & \quad a = 1 - 6 \\
\text{CF}_3-O-(\text{CF}_2-\text{CF}_2-U)_b-\text{C}_2\text{F}_5, & \quad b = 1 - 6 \\
\text{C}_2\text{F}_5-O-(\text{CF}_2-\text{CF}_2-O)_c-\text{C}_2\text{F}_5, & \quad c = 1 - 3
\end{align*}
\]

The Glc assays were characterized by excellent peak sharpness and separa-
tion which facilitated isolation of highly pure compounds. The amounts
and yields of the isolated pure perfluoroethers are listed in Table 1.
(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 pre-
liminary reactions.) The mole % yields in Table 1 were calculated as
follows: \( g \) compound \( \div \) MW compound = moles compound, \( (\text{moles compound}) \times (# \text{ carbon atoms in structure}) = \text{moles carbon atoms, } (\text{moles carbon atoms in compound}) \div (\text{moles carbon atoms in starting polymer}) \times 100\% = \text{mole \% of starting polymer.} \) The material left unseparated by the Glc assay of
the fractions was examined by infrared and showed carbon - hydrogen and
acyl fluoride stretching absorptions was well as the strong carbon - fluorine
stretching absorption. This inseparable mixture contained the numerous
branched, partially fluorinated and acyl fluoride - terminated volatile
<table>
<thead>
<tr>
<th>Compound</th>
<th>Milligrams (mg)</th>
<th>Wt. % of -78° &amp; -131° fractions</th>
<th>Mole % of Starting Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>a = 1</td>
<td>86</td>
<td>7.1</td>
<td>.43</td>
</tr>
<tr>
<td>b = 1</td>
<td>27</td>
<td>2.2</td>
<td>.14</td>
</tr>
<tr>
<td>c = 1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>a = 2</td>
<td>110</td>
<td>9.1</td>
<td>.58</td>
</tr>
<tr>
<td>b = 2</td>
<td>46</td>
<td>3.8</td>
<td>.25</td>
</tr>
<tr>
<td>c = 2</td>
<td>4.5</td>
<td>0.4</td>
<td>.02</td>
</tr>
<tr>
<td>a = 3</td>
<td>123</td>
<td>10.2</td>
<td>.66</td>
</tr>
<tr>
<td>b = 3</td>
<td>48</td>
<td>4.0</td>
<td>.26</td>
</tr>
<tr>
<td>c = 3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>a = 4</td>
<td>122</td>
<td>10.1</td>
<td>.66</td>
</tr>
<tr>
<td>b = 4</td>
<td>51</td>
<td>4.2</td>
<td>.28</td>
</tr>
<tr>
<td>a = 5</td>
<td>123</td>
<td>10.2</td>
<td>.68</td>
</tr>
<tr>
<td>b = 5</td>
<td>83</td>
<td>6.9</td>
<td>.46</td>
</tr>
<tr>
<td>a = 6</td>
<td>85</td>
<td>7.1</td>
<td>.47</td>
</tr>
<tr>
<td>b = 6</td>
<td>39</td>
<td>3.2</td>
<td>.22</td>
</tr>
<tr>
<td>Unseparated material</td>
<td>256</td>
<td>21.3</td>
<td>1.38 *</td>
</tr>
<tr>
<td>Totals</td>
<td>1.2045 g</td>
<td>100%</td>
<td>6.49 %</td>
</tr>
</tbody>
</table>

* Calculated assuming an average MW of 500 and an average # of carbon atoms per molecule of 8
fluoroethers 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 fifteen volatile perfluoroethers were all similar in showing strong, broad absorptions in the carbon-fluorine stretching region, 1300 - 1100 cm$^{-1}$. (The infrared spectrum of perfluorotriglyme is included as representative of the spectra obtained, see Figure 9.) The spectra also exhibited weaker absorptions in the "fingerprint" region, 1000 - 600 cm$^{-1}$, which are listed for each compound in Table 2. No other infrared absorptions are observed except for the carbon-fluorine overtone near 2400 cm$^{-1}$ when high gas concentrations are used.

The $^{19}$F NMR data was the most useful information for structure determination. The following signal assignments were deduced from the spectra interpretation ($^{19}$F NMR reference - neat external CFCl$_3$):

- CF$_3$-O: 59.4 - 58.9 ppm (triplet)  
  J = 9 - 10 Hz
- CF$_3$-O-CF$_2$CF$_2$: 94.0 - 93.5 ppm (quartet)
- CF$_3$-CF$_2$-O: 90.7 - 90.3 ppm (singlet)
- Internal CF$_2$-O: 91.9 - 91.4 ppm (singlet)

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 is listed in Table 3.

The mass spectra of the fifteen perfluoroethers were characterized by extensive chain degradation and rearrangement. In fact, with the ion source of the mass spectrometer at normal operating temperatures, the
Figure 9

Perfluorotriglyme

3000 cm⁻¹  1800 cm⁻¹  1200 cm⁻¹  600 cm⁻¹
TABLE 2

Infrared Absorptions in the Fingerprint Region
of Volatile Perfluoroethylene Glycol Ethers

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption Frequency (cm(^{-1})) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>a = 1</td>
<td>925(w), 890(m), 865(w), 820(m), 690(m)</td>
</tr>
<tr>
<td>b = 1</td>
<td>910(w), 800(w), 730(m), 685(w)</td>
</tr>
<tr>
<td>c = 1</td>
<td>905(w), 845(w), 795(w), 740(m), 710(m), 695(sh)</td>
</tr>
<tr>
<td>a = 2</td>
<td>920(sh), 905(m), 765(m), 690(w), 675(w,sh)</td>
</tr>
<tr>
<td>b = 2</td>
<td>910(w), 765(w), 740(sh), 720(m), 690(w)</td>
</tr>
<tr>
<td>c = 2</td>
<td>765(w), 725(m), 705(w), 690(w)</td>
</tr>
<tr>
<td>a = 3</td>
<td>905(m), 790(w), 738(m), 685(w)</td>
</tr>
<tr>
<td>b = 3</td>
<td>910(m), 785(w), 745(m), 710(m), 695(sh), 685(sh)</td>
</tr>
<tr>
<td>c = 3</td>
<td>1000(w), 910(w), 785(w), 750(sh), 720(m), 710(sh), 695(m)</td>
</tr>
<tr>
<td>a = 4</td>
<td>910(m), 765(w), 725(w), 685(w)</td>
</tr>
<tr>
<td>b = 4</td>
<td>955(w), 910(w), 765(w), 735(m), 710(w), 695(w)</td>
</tr>
<tr>
<td>a = 5</td>
<td>910(w), 740(w), 720(sh), 705(sh), 685(w)</td>
</tr>
<tr>
<td>b = 5</td>
<td>905(w), 730(m), 690(w)</td>
</tr>
<tr>
<td>a = 6**</td>
<td>1000(w), 905(m), 765(w), 730(sh), 685(m)</td>
</tr>
<tr>
<td>b = 6**</td>
<td>995(w), 905(m), 765(w), 735(sh), 690(m)</td>
</tr>
</tbody>
</table>

* Letters in parentheses indicate strength of absorption: w - weak, m - medium, sh - shoulder

** Not volatile enough to be run as a gas and have the fingerprint absorptions appear; run as a liquid film between KBr windows.
TABLE 3

$^{19}$F NMR Signals of Volatile Perfluoroethylene Glycol Ethers
(Shift in ppm vs. CFCI$_3$ ext.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>CF$_3$-O (t)</th>
<th>CF$_3$-O-CF$_2$ (q)</th>
<th>Internal -CF$_2$-O- (s)</th>
<th>CF$_3$-CF$_2$-O (s)</th>
<th>$^3$J$_{CF_3-O-CF_2}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a=1</td>
<td>59.4</td>
<td>94.0</td>
<td>-</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>b=1</td>
<td>59.4</td>
<td>93.9</td>
<td>91.9 (4)</td>
<td>90.7</td>
<td>10</td>
</tr>
<tr>
<td>c=1</td>
<td>-</td>
<td>-</td>
<td>91.7 (4)</td>
<td>90.5</td>
<td>-</td>
</tr>
<tr>
<td>a=2</td>
<td>59.3</td>
<td>93.8</td>
<td>91.8 (2)</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>b=2</td>
<td>59.2</td>
<td>93.7</td>
<td>91.7 (8)</td>
<td>90.5</td>
<td>9</td>
</tr>
<tr>
<td>c=2</td>
<td>-</td>
<td>-</td>
<td>91.6 (6)</td>
<td>90.4</td>
<td>-</td>
</tr>
<tr>
<td>a=3</td>
<td>59.1</td>
<td>93.8</td>
<td>91.7 (4)</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>b=3</td>
<td>59.0</td>
<td>93.7</td>
<td>91.6 (12)</td>
<td>90.4</td>
<td>9</td>
</tr>
<tr>
<td>c=3 *</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>a=4</td>
<td>59.1</td>
<td>93.7</td>
<td>91.6 (6)</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>b=4</td>
<td>58.9</td>
<td>93.5</td>
<td>91.5 (16)</td>
<td>90.3</td>
<td>10</td>
</tr>
<tr>
<td>a=5</td>
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<td>93.5</td>
<td>91.5 (8)</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>b=5</td>
<td>59.0</td>
<td>93.6</td>
<td>91.5 (20)</td>
<td>90.3</td>
<td>10</td>
</tr>
<tr>
<td>a=6</td>
<td>59.0</td>
<td>93.6</td>
<td>91.4 (10)</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>b=6</td>
<td>59.1</td>
<td>93.7</td>
<td>91.6 (24)</td>
<td>90.4</td>
<td>9</td>
</tr>
</tbody>
</table>

* Insufficient compound isolated to obtain an NMR spectrum.

$^t$ = triplet, $^q$ = quartet, $^s$ = singlet

Relative Intensities:  
\[
\begin{align*}
\text{CF}_3\text{-O} & = 3 \\
\text{CF}_3\text{-O-CF}_2 & = 2 \\
\text{CF}_3\text{-CF}_2\text{-O} & = 3 \\
\text{Internal -CF}_2\text{-O-} & = \text{as indicated in parentheses}
\end{align*}
\]
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 was 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.

Other common low-mass fragments observed were: 31 (\( CF \)), 47 (\( COF \)), 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 high 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 perfluoroethers, boiling points, melting points and Glc retention times, are listed in Table 4. A graph of the boiling points versus compound mass produces a smooth curve, as can be seen in Figure 10. 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
<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. (°C)</th>
<th>B.P. (°C)</th>
<th>Glc Retention Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a = 1</td>
<td>-</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>b = 1</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>c = 1</td>
<td>-</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>a = 2</td>
<td>-</td>
<td>66 → 66.5</td>
<td>11</td>
</tr>
<tr>
<td>b = 2</td>
<td>-</td>
<td>81.5 → 82</td>
<td>22</td>
</tr>
<tr>
<td>c = 2</td>
<td>-78.5 → -77</td>
<td>*</td>
<td>34</td>
</tr>
<tr>
<td>a = 3</td>
<td>-82 → -80.5</td>
<td>104.5 → 105</td>
<td>44</td>
</tr>
<tr>
<td>b = 3</td>
<td>-80 → -78</td>
<td>117.5 → 118.5</td>
<td>58</td>
</tr>
<tr>
<td>c = 3</td>
<td>**</td>
<td>*</td>
<td>66</td>
</tr>
<tr>
<td>a = 4</td>
<td>-71 → -69.5</td>
<td>133 → 138.5</td>
<td>74</td>
</tr>
<tr>
<td>b = 4</td>
<td>-60.5 → -60</td>
<td>145.5 → 148</td>
<td>84</td>
</tr>
<tr>
<td>a = 5</td>
<td>-47 → -46</td>
<td>164 → 164.5</td>
<td>102</td>
</tr>
<tr>
<td>b = 5</td>
<td>-47 → -46</td>
<td>173.5 → 174</td>
<td>114</td>
</tr>
<tr>
<td>a = 6</td>
<td>-43.5 → -43</td>
<td>186 → 186.5</td>
<td>129</td>
</tr>
<tr>
<td>b = 6</td>
<td>-35 → -34</td>
<td>193 → 194</td>
<td>142</td>
</tr>
</tbody>
</table>

Temp. Prog. A: 0° for 20 min; 1°/min → 60°; 60° for 20 min; 1°/min → 120°

Temp. Prog. B: 30° for 30 min; 1°/min → 120°

* Insufficient compound isolated to obtain a B.P.

** Insufficient compound isolated to obtain a M.P.
FIGURE 10

VOLATILE PERFLUOROPOLYETHERS

B.p. vs. COMPOUND MASS
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 crystallization 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 fifteen perfluoroethers was 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 $a = 4$, Calc.: $C = 19.42\%$, $F = 67.64\%$, $O = 12.94\%$; Found: $C = 19.23\%$, $F = 68.48\%$; for $b = 4$, Calc.: $C = 19.76\%$, $F = 63.26\%$, $O = 11.93\%$; Found: $C = 19.92\%$, $F = 69.32\%$.

Gas liquid chromatography (Glc) was used for separation of the volatile perfluoroethers because it has been proven to be the best method for separation of fluorocarbons produced on an experimental scale. Clearly, Glc is impractical for large scale separations, so fractional distillation was examined as an alternative separatory method. Several milliliters of volatile perfluoroether 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 listed below:
Boiling Range of Distillate (°C) Compounds and Relative Amounts in Distillate (by Glc)

<table>
<thead>
<tr>
<th>Range</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 - 30</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>47 - 60</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>60 - 65</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>67 - 77</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>88 - 93</td>
<td>4</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>100 - 105</td>
<td>5</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

It can be seen from this 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 an adequate and the preferred technique.

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 (~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 a six hour period at one micron 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 one micron pressure. The combined material had a weight of 0.86 g and a density of 1.79 g/cc.

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 - 1100 (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 perfluoroethers. The $^{19}$F NMR spectrum showed signals at 58.7 ppm (t) $J = 9$ Hz, 93.3 ppm (q) $J = 9$ Hz, 91.3 ppm (s), 90.0 ppm (s), (the signals exhibited by the volatile straight-chain perfluoroethylene glycol ethers), and much weaker, broad signals at 128.1 ppm 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 crosslinked 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 perfluoroethers, 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 $M_{av}$ = 1080 , the average degree of polymerization is 8 and the average number of carbon atoms per molecule is 18 . The yield of nonvolatile perfluoroether oil (calculated as in Table 1) was 4.9 mole % 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, gel-like 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 perfluoroethers and the nonvolatile oil. The bands observed were (in cm\(^{-1}\)): 1300 - 1100 (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 mole% 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 fluoro-carbon solvents tested, only two, perfluoro-2-butylltetrahydrofuran and 1,1,2-trichlorotrifluoroethane, showed slight solvation ability. Solvents were tested with heating and stirring over two to three 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\(_3\)-O- signal near 59 ppm upfield. For the two successful solvents, the CF\(_3\)-O- signal was barely detectable,
and the -CF₂-O- 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 ~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 by-products, CF₄ and COF₂, account for 8.7% and 9.3% of the starting material respectively. The unaccounted for 13.8% of starting material would be comprised of unisolated CF₄, 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 (CF₄, COF₂ and C₂F₆) 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 perfluoroethers by decreasing impurity peaks and peak overlaps in the Glc assay.

Discussion

The results of the reaction show that the direct fluorination of polyethylene 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 volatile liquid, nonvolatile oil and solid product that are formed. Fluorination of polyethylene oxide polymer at just ambient temperature results in conversion to perfluorinated polymer with only small amounts of volatile products formed by fragmentation. Fluorinations at ambient temperature then high temperatures, as in the discussed 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 perfluoroethers and extractable nonvolatile oil. Larger amounts of volatile perfluoroethers and nonvolatile oil may be simply produced by fluorinating and fragmenting the perfluoropolymer for longer times at the high temperatures. Higher temperatures than those used should also promote faster more extensive fragmentation, but the reactor was not designed for use at very high temperatures. (The teflon O-ring seals at the reactor flanges would have been significantly attacked at higher temperatures in the fluorine atmosphere unless a cooling system were installed; this is easy to do. Teflon should be good to \( \approx 250^\circ \text{C} \) then the reactor should be constructed of nickel or monel.) 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 perfluoropolyethylene 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 \( \text{CF}_3\text{-O-} \) end-groups are formed than \( \text{CF}_3\text{-CF}_2\text{-O-} \) end-groups. Chain cleavage at carbon - carbon bonds of the perfluoropolymer must,
therefore, predominate, ie.

\[ -\text{O-CF}_2\text{-CF}_2\text{-O-} + 2 \text{F}^\cdot \rightarrow 2 \text{-O-CF}_3 \]

Chain cleavage at carbon-oxygen bonds must also occur in order to account for the \( \text{CF}_3\text{-CF}_2\text{-O-} \) end-groups. The result of backbone cleavage at the carbon-oxygen bond would be one \( \text{CF}_3\text{-CF}_2\text{-O-} \) end-group, one \( \text{CF}_3\text{-O-} \) end-group and one molecule of carbonyl fluoride as follows:

\[ \begin{align*}
-\text{O-CF}_2\text{-CF}_2\text{-O-} + & \rightarrow -\text{O-CF}_2\text{-CF}_2\text{F}^\cdot + \text{\textbf{O-CF}_2\text{-CF}_2\text{-O-}} \\
-\text{O-CF}_2\text{-CF}_2\text{F}^\cdot + & \rightarrow -\text{O-CF}_2\text{-CF}_3 \\
-\text{O-CF}_2\text{-CF}_2\text{-O}^\cdot + & \rightarrow \text{COF}_2 + -\text{O-CF}_2\text{F}^\cdot + \rightarrow -\text{O-CF}_3
\end{align*} \]

Chain cleavage occurring predominately at the carbon-carbon bonds is consistent with the calculated bond strengths in perfluoroethers: \( \text{C-C} = 80 - 90 \text{ kcal}, \text{C-O} = > 100 \text{ kcal} \).

Acyl fluoride terminated compounds did not constitute a significant fraction of the reaction products. At temperatures above \( 100^\circ \text{C} \) in a fluorine atmosphere perfluoroether acyl fluorides are relatively unstable, so any acyl fluoride end-groups that had been formed at lower temperatures would be subject to decomposition and further fluorination, ie.

\[ \begin{align*}
-\text{-CF}_2\text{-C(O)F} + & \rightarrow \text{COF}_2 + \text{CF}_3\text{-O-}
\end{align*} \]

This pathway would further account for the observation of more \( \text{CF}_3\text{-O-} \) end-groups than \( \text{CF}_3\text{-CF}_2\text{-O-} \) end-groups. If an experimental technique that promotes fragmentation of the perfluoroethylene oxide polymer at temperatures below \( 100^\circ \text{C} \) can be developed, the acyl fluoride terminated compounds may be attained. Such a development would be a valuable extension of the scope and utility of direct fluorination for perfluoroethylene glycol ether synthesis.
Chapter 4

Fluorination of Poly(methylene oxide)
Fluorination of Poly(methylene oxide)

\[(CH_2-O)_n \xrightarrow{F_2/He} COF_2 + \text{Fluoroethers}\]

Introduction

The outstanding success of direct fluorination in producing perfluoropolyethylene glycol ethers from polyethylene oxide encouraged us to develop direct fluorination as a general method for producing perfluoropolyethers from hydrocarbon polyether polymers.

Perfluoropolyethers with the CF\(_2\)O repeating unit have been reported in only two patents by some Italian chemists, Sianesi and co-workers.\(^{34}\) 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 CF\(_3\)O(CF\(_2\)O\(_n\))\(_n\)CF\(_2\)C(O)F and CF\(_3\)(OCF\(_2\))\(_n\)OC(O)F. The direct fluorination of polymethylene oxide, (CH\(_2\)O)\(_n\) (other names for this polymer are polyformaldehyde, polyacetal and "Delrin", the DuPont tradename), was hypothesized as an alternate synthetic technique for production of trifluoromethoxy (CF\(_3\)O-) or fluoroformate (FC(O)-O-) terminated perfluoropolyethers with the CF\(_2\)O repeating unit.

After only several experiments, it appeared evident that perfluoropolyethers would not be produced by the direct fluorination of polymethylene oxide. Instead, hydro-fluoroethers and large quantities of carbonyl fluoride, 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 hydro-fluoroethers.
Experimental

Polymethylene oxide polymer was obtained from Monomer-Polymer Laboratories as 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 run in a room temperature reactor, and volatile products were observed condensing in the glass trap from the beginning. The strategy that was so 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. A similar strategy for polymethylene oxide fluorination required the use of sub-ambient temperatures for the "pre-fluorination" period because the polymer was fragmenting at ambient temperature. A bucket reactor allowed use of dry ice (-78°C) as the "pre-fluorination" temperature, and ambient temperature was subsequently used for promotion of fragmentation and volatile product formation. Reaction conditions typically used were:

<table>
<thead>
<tr>
<th>He (cc/min)</th>
<th>F₂ (cc/min)</th>
<th>Temp. (°C)</th>
<th>Time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.5</td>
<td>-78</td>
<td>1</td>
</tr>
<tr>
<td>40</td>
<td>1.0</td>
<td>-78</td>
<td>1½</td>
</tr>
<tr>
<td>40</td>
<td>1.0</td>
<td>amb.</td>
<td>5</td>
</tr>
</tbody>
</table>

The volatile products of a reaction were fractionated on a vacuum line into -196°C, -131°C and -78°C fractions; pure compounds were isolated from the -131°C and -78°C fractions by gas chromatography; and pure compounds
were spectrally analyzed and identified by infrared, NMR and mass spectroscopy.

The -196° fraction was analyzed only by infrared spectroscopy. The fraction contained almost pure carbonyl fluoride, COF₂, with traces of CF₄, SiF₄ (from HF or F₂ attack on glass) and SF₆ (an impurity in the fluorine). Quantitatively, the -196° fraction contained a relatively large proportion of the reaction products. In a typical reaction, 2.17 g of starting polymer produced a -196° fraction weighing 1.85 g which is, assuming the whole fraction is COF₂, approximately 40 mole % of the starting material. (The weight of the -196° fraction was determined by condensing the highly volatile compounds in a heavy-walled glass tube, sealing the tube, allowing the tube to warm and weighing it. This procedure is very dangerous because of the high pressure established in the sealed tube and should only be performed with the appropriate safety shields and caution.) This high yield of carbonyl fluoride is consistent with the deduced fragmentation mechanism which is discussed below.

The structurally-unique hydro-fluoroethers isolated and identified from the reaction were components of the -131° vacuum line fraction. The compounds were separated by Glc assay of the fraction and are listed along with their Glc retention times and yields (from 2.17 g of starting polymer) in Table 5. The -78° fraction contained several of the least volatile components of the -131° fraction as its most volatile components. These compounds were routinely separated by Glc assay of the -78° fraction and combined with the respective material from the -131° fraction. The -78° fraction also contained up to eight other compounds that could be cleanly separated by gas chromatography. However, these compounds, when
TABLE 5
Hydrofluoroethers from the Fluorination of \((\text{CH}_2\text{O})_n\):
Glc Retention Times and Yields

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention Time * (min)</th>
<th>Yield (mg)</th>
<th>Wt. % of Volatile Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CF}_3\text{-O-CF}_2\text{H})</td>
<td>8</td>
<td>10.5</td>
<td>1.67</td>
</tr>
<tr>
<td>(\text{CF}_3\text{-O-CFH-0-CF}_3)</td>
<td>20</td>
<td>25.1</td>
<td>3.99</td>
</tr>
<tr>
<td>(\text{CF}_3\text{-O-CF}_2\text{-O-CF}_2\text{H})</td>
<td>26 †</td>
<td>24.0</td>
<td>3.81</td>
</tr>
<tr>
<td>(\text{CF}_3\text{-O-CFH}_2)</td>
<td>26 †</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{CF}_2\text{H-0-CF}_2\text{H})</td>
<td>32 †</td>
<td>108.6</td>
<td>17.25</td>
</tr>
<tr>
<td>(\text{CF}_3\text{H-0-C(OF)})</td>
<td>32 †</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{CF}_3\text{-O-CFH-0-CF}_2\text{H})</td>
<td>43</td>
<td>57.9 ‡</td>
<td>9.20</td>
</tr>
<tr>
<td>(\text{CF}_2\text{H-0-CFH}_2)</td>
<td>46 †</td>
<td>78.5 ‡</td>
<td>12.47</td>
</tr>
<tr>
<td>(\text{CF}_2\text{H-0-CF}_2\text{-O-CF}_2\text{H})</td>
<td>47 †</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Other compounds separated from -78 fraction but not identified (explosive compounds)

<table>
<thead>
<tr>
<th>Other Compounds</th>
<th>Wt. %</th>
<th>Yield (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>107.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.11</td>
</tr>
</tbody>
</table>

Unseparated material from the -131 & -78 fractions

<table>
<thead>
<tr>
<th>Unseparated Material</th>
<th>Wt. %</th>
<th>Yield (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>217.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>34.49</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Totals</th>
<th>Wt. %</th>
<th>Yield (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>629.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>99.99 %</td>
</tr>
</tbody>
</table>

* Temperature Program: -40° for 10 min; 2°/min + 40°

† Compounds with the same (or very close) retention times were collected together in the Glc assay. See text as to how the mixtures were analyzed so both structures could be determined.

‡ Combined weight of compound from both the -131° and -78° fractions.
stored in sealed 4 mm glass tubes at room temperature, exhibited bubbling, formation of white solids (they are clear liquids initially) and the inconsiderate tendency to explode. The compounds, therefore, could not be completely characterized and identified, so they will only be discussed briefly and generally.

The bands of the infrared spectra of the stable hydro-fluoroethers of the -131° fraction are listed in Table 6. The spectra were useful only for qualitative bond type identification. Two distinct bands in the carbon-hydrogen region (~3000 cm⁻¹) were observed, and after the structures had been deduced, the following assignments could be made: around 3050 cm⁻¹ indicates -CF₂H or -CFH⁻ and 2960 - 2970 cm⁻¹ indicates -CFH₂. The other bond types indicated by infrared were fluoroformate (-O-C(O)F) at 1875 cm⁻¹ (the same position as usual acyl fluorides, R_fC(O)F) and carbon-fluorine at 1300 - 1100 cm⁻¹. The carbon-oxygen stretch is in the same area as the carbon-fluorine 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 cm⁻¹. The infrared spectra of the unstable, explosive compounds of the -78° fraction were also recorded. They were rather similar to the spectra of the stable hydrofluoroethers except that all of them exhibited strong bands in the fluoroformate / acyl fluoride region. Two representative infrared spectra, one of the stable ether CF₃-O-CFH-O-CF₂H, the other of an unstable compound, are shown in Figure 11.

The ¹⁹F NMR, ¹H NMR and mass spectral data was the definitive information which led to structure determination of the stable hydrofluoroethers. The complete ¹⁹F and ¹H NMR data, including nuclei assignments, experi-
Infrared Absorptions of the Hydrofluoroethers from the Fluorination of \((\text{CH}_2\text{O})_n\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption Frequencies ((\text{cm}^{-1})) †</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CF}_3\text{-O- CF}_2\text{H})</td>
<td>3050(w), 1375(w), 1310(s), 1235(s,br), 1170(s), 1125(s), 920(m), 740(w)</td>
</tr>
<tr>
<td>(\text{CF}_3\text{-O-CFH-0-CF}_3)</td>
<td>3050(w), 1330 - 1200(s,br), 1125(s,br), 1015(w), 1000(sh), 955(w), 890(m), 740(w), 670(w)</td>
</tr>
<tr>
<td>(\text{CF}_3\text{-O-CF}_2\text{-O-CF}_2\text{H} / \cdot \text{CF}_3\text{-O-CFH}_2) *</td>
<td>3045(w), 2970(w), 1380(m), 1320(s,br), 1250(s,br) 1165(s,br), 1000(s), 980(m), 965(sh), 885(w), 870(w), 855(w), 800(w), 740(w), 705(w)</td>
</tr>
<tr>
<td>(\text{CF}_2\text{H}-0-CF}_2\text{H} / \cdot \text{CF}_2\text{H}-0-C(0)F) *</td>
<td>3050(w), 1875(s), 1380(m), 1315(w), 1275(s), 1250(s,br), 1095(s), 1015(s), 790(m), 740(w), 705(w)</td>
</tr>
<tr>
<td>(\text{CF}_3\text{-O-CFH-0-CF}_2\text{H})</td>
<td>3065(w), 1370(m,br), 1310(s), 1265(s,br), 1140(s,br) 1075(sh), 1040(sh), 1020(m), 920(m), 790(w), 740(w), 675(w)</td>
</tr>
<tr>
<td>(\text{CF}_2\text{H}-0-CF}_2\text{H} / \cdot \text{CF}_2\text{H}-0-CF}_2-0-CF}_2\text{H} *</td>
<td>3045(w), 2960(w), 1830(w), 1410(sh), 1375(m), 1285(s), 1245(s), 1165(s,br), 1075(s), 940(sh), 920(w), 780(w), 765(w), 695(w), 645(w)</td>
</tr>
</tbody>
</table>

* Two compound mixture because we could not separate the two compounds by Glc.

† Letters in parentheses indicate the strength and shape of the absorption band: s = strong, m = medium, w = weak, br = broad, sh = shoulder
Figure 11: Infrared Spectra of some Products from the Fluorination of (CH\textsubscript{2}O)
mental relative intensities, theoretical relative intensities and the most informative high mass peaks of the mass spectra are compiled in Table 7. The experimental relative intensities of the signals were invaluable for structure determination and corresponded almost exactly to the values that would be expected for the elucidated structures. The unquestionable nuclei assignments were made by considering all of the NMR spectra together; individual structure determination logically followed the general signal assignments. A summary of the average chemical shifts for the various nuclei follows (number of chemical shift values used in computing the averages are in parentheses; values for CF₂H-O- in CF₂H-O-C(0)F were excluded from the averages):

<table>
<thead>
<tr>
<th></th>
<th>Chemical Shift (ppm)</th>
<th>Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃-O-</td>
<td>62.5</td>
<td>5</td>
</tr>
<tr>
<td>CFH₂-O-</td>
<td>158.3</td>
<td>1</td>
</tr>
<tr>
<td>-O-CF₂-O-</td>
<td>59.4</td>
<td>2</td>
</tr>
<tr>
<td>CF₂H-O-</td>
<td>6.05</td>
<td>6</td>
</tr>
<tr>
<td>-O-CFH-O-</td>
<td>6.15</td>
<td>2</td>
</tr>
<tr>
<td>CF₂H-0-</td>
<td>88.8</td>
<td>6</td>
</tr>
<tr>
<td>FC(0)-O-</td>
<td>20.1</td>
<td>1</td>
</tr>
<tr>
<td>-O-CFH-0-</td>
<td>93.2</td>
<td>2</td>
</tr>
<tr>
<td>CFH₂-0-</td>
<td>5.10</td>
<td>1</td>
</tr>
</tbody>
</table>

From the observed signal multiplets, generalizations about homonuclear and heteronuclear coupling could be made and average coupling constants computed. Heteronuclear coupling was observed only for geminal hydrogen and fluorine nuclei; no heteronuclear coupling "across on oxygen" was observed. The average geminal heteronuclear coupling constants were: for -O-CF₂H, 70 Hz (average of 7 values); for -O-CFH-O-, 66.5 Hz (average of 2 values); and for -O-CFH₂, 51.5 Hz (average of 2 values). Homonuclear fluorine coupling was observed in all compounds, but no homonuclear hydrogen coupling was evident. A fluorine nucleus would always couple "across one oxygen" to the fluorine nucleus/nuclei of the next
### TABLE 7

NMR and Mass Spectral Data of the Hydrofluoroethers from the Fluorination of \((\text{CH}_2\text{O})_n\)

<table>
<thead>
<tr>
<th>Compound / Mass Spec.</th>
<th>Highest m/e</th>
<th>F: ppm from CFCl₃</th>
<th>H: ppm from TMS (J in Hz)</th>
<th>Rel. Intensity*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃-O-CF₂H</td>
<td>135 (C₂F₅HO) P-H</td>
<td>Fa: 62.6, t (4.5)</td>
<td>57</td>
<td>3</td>
</tr>
<tr>
<td>a b c</td>
<td>117 (C₂F₄HO) P-F</td>
<td>Fb: 89.9, d of quar. (69, 4.5)</td>
<td>36</td>
<td>2</td>
</tr>
<tr>
<td>201 (C₃F₇O₂) P-H</td>
<td>Hc: 6.05, t (69)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>183 (C₃F₆HO₂) P-F</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF₃-O-CFH-O-CF₃</td>
<td>201 (C₃F₇O₂) P-H</td>
<td>Fa: 62.9, d (5.0)</td>
<td>118</td>
<td>6</td>
</tr>
<tr>
<td>a b c</td>
<td>183 (C₃F₆HO₂) P-F</td>
<td>Fb: 93.7, d of septet (66, 5.0)</td>
<td>19</td>
<td>1</td>
</tr>
<tr>
<td>201 (C₃F₇O₂) P-H</td>
<td>Hc: 6.15, d (66)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>183 (C₃F₆HO₂) P-F</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF₃-O-CF₂-O-CF₂H</td>
<td>201 (C₃F₇O₂) P-H</td>
<td>Fa: 60.7, t (9.0)</td>
<td>79</td>
<td>3</td>
</tr>
<tr>
<td>a b c d</td>
<td>183 (C₃F₆HO₂) P-F</td>
<td>Fb: 59.5, m</td>
<td>55</td>
<td>2</td>
</tr>
<tr>
<td>201 (C₃F₇O₂) P-H</td>
<td>Fc: 89.4, d of t (69, 4.5)</td>
<td>54</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>183 (C₃F₆HO₂) P-F</td>
<td>Hd: 6.05, t (69)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF₃-O-CFH₂</td>
<td>117 (C₂F₄HO) P-H</td>
<td>Fa: 64.3, d (5.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a b c</td>
<td>Hc: 4.95, d (51)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>117 (C₂F₄HO) P-H</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF₂H-O-CF₂H</td>
<td>117 (C₂F₄HO) P-H</td>
<td>Fa: 88.4, d (70)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a b</td>
<td>Hb: 6.05, d (70)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>99 (C₂F₃H₂O) P-F</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 7 (cont.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass Spec.</th>
<th>NMR Data</th>
<th>Rel. Intensity*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CF₂H-O-C-F</td>
<td>Fₐ: 93.8, d of d (69, 7.5)</td>
<td>72 2</td>
</tr>
<tr>
<td></td>
<td>a c b</td>
<td>Fₑₜ: 20.1, t (7.5)</td>
<td>36 1</td>
</tr>
<tr>
<td>113 (C₂F₃O₂) P-H</td>
<td>Hₜ: 6.48, t (69)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF₃-O-CFH-O-CF₂H</td>
<td>Fₐ: 62.0, d (5.0)</td>
<td>63 3</td>
<td></td>
</tr>
<tr>
<td>a bd c e</td>
<td>Fₖ: 92.6, d of mₖ (67)</td>
<td>40 2</td>
<td></td>
</tr>
<tr>
<td>183 (C₃F₆H₂O₂) P-H</td>
<td>Fₖ: 88.5, d of d of d (70, 13, 4.5)</td>
<td>21 1</td>
<td></td>
</tr>
<tr>
<td>165 (C₃F₅H₂O₂) P-F</td>
<td>Hₖ: 6.15, d (67)</td>
<td>76 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hₙ: 6.00, d (70)</td>
<td>83 1</td>
<td></td>
</tr>
<tr>
<td>CF₂H-O-CFH₂</td>
<td>Fₐ: 88.0, d of d (73, 6.0)</td>
<td>58 2</td>
<td></td>
</tr>
<tr>
<td>a c bd</td>
<td>Fₖ: 158.3, t of t (52, 6.0)</td>
<td>28 1</td>
<td></td>
</tr>
<tr>
<td>99 (C₂F₃H₂O) P-H</td>
<td>Hₙ: 5.95, t (73)</td>
<td>27 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hₖ: 5.10, d (52)</td>
<td>56 2</td>
<td></td>
</tr>
<tr>
<td>CF₂H-O-CF₂-O-CF₂H</td>
<td>Fₐ: 88.9, d of t (70, 4.5)</td>
<td>54 2</td>
<td></td>
</tr>
<tr>
<td>a c b</td>
<td>Fₖ: 59.2, pentet (4.5)</td>
<td>26 1</td>
<td></td>
</tr>
<tr>
<td>183 (C₃F₆H₂O₂) P-H</td>
<td>Hₙ: 6.20, t (70)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The observed relative intensities of the ¹⁹F NMR signals cannot be compared to the observed relative intensities of the ¹H NMR signals; two spectrometers with different power and amplitude characteristics were used.
nearest carbon atom (4-bond coupling), but no homonuclear fluorine coupling "across two oxygens" (6-bond coupling) was observed. The average value for all 4-bond, fluorine-fluorine, homonuclear coupling was 5.55 Hz (average of 10 values).

For the stable hydrofluoroethers, first-order NMR analysis was an invaluable analytical tool. The only NMR 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 $-O\text{-CF}_2\text{H}$ in $\text{CF}_3\text{-O-CF}_2\text{H}$.

This is thought to be due to a favored molecular conformation and an "AB" type pattern for the $-O\text{-CF}_2\text{H}$ fluorine nuclei. The NMR spectra for the hydrofluoroethers separated from the -780 fraction could not be obtained because of the instability and explosive nature of the compounds when in their liquid states. If the spectra had been obtained, similar first-order analysis and structure determination would have been possible.

The mass spectra of the stable hydrofluoroethers were useful in that they confirmed the molecular weights of the deduced structures. All of the compounds exhibited peaks at the "parent minus hydrogen" mass values and most of them also exhibited the "parent minus fluorine" peak (see Table 7). Like the mass spectra of the volatile compounds from the polyethylene oxide fluorination, the hydrofluoroethers' mass spectra were characterized by extensive fragmentation and rearrangement, and the informative high mass peaks were observed only when the spectra were run with the ion source of the mass spectrometer cooled to room temperature. The common fragment and rearrangement peaks observed were at m/e 31 (CF), 47 (COF), 51 (CF$_2$H), 67 (CF$_2$HO), 69 (CF$_3$), 71 (CF$_3$H$_2$?), 81 (C$_2$F$_3$), 83 (C$_2$F$_3$H$_2$), 85 (CF$_3$O), 95 (C$_2$F$_2$HO$_2$), 99 (C$_2$F$_3$H$_2$O), 100 (C$_2$F$_4$), 117 (C$_2$F$_4$HO), 131 (C$_3$F$_5$).
and 135 (C₃F₅O), with m/e 51 (CF₂H) usually as the largest peak. Complex rearrangement must be an important process for these compounds because of the relative high abundance of the multi-carbon / no-oxygen peaks at m/e 81 (C₂F₃), 100 (C₂F₄) and 131 (C₃F₅). The mass spectra of the unstable, -78⁰ fraction compounds were not recorded because of the experimental complications that would have resulted from their self-decomposition in the mass spectrometer.

Six of the identified compounds were from three, two-compound mixtures that could not be cleanly separated by simple Glc assay, see Table 5. The mixture with the 46/47 minute 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 analyzed by its NMR and mass spectra which exhibited strong signals attributable to CF₂H-O-CF₂H with only weak signals from CF₂H-O-CF₂-O-CF₂H. Similarly, the "last-third" was analyzed as mainly CF₂H-O-CF₂-O-CF₂H with only a trace of CF₂H-O-CF₂H. This peak splitting separation method was useful only for this one mixture.

The mixture with the 32 minute retention time was resolved by hydrolysis. NMR and mass spectral analysis of the water-insoluble portion of the mixture indicated pure CF₂H-O-CF₂H. The spectral signals present in the mixture but absent from the pure CF₂H-O-CF₂H sample logically corresponded to the water-reactive compound CF₂H-O-C(O)F. This hydrolysis method was suggested by the infrared fluoroformate stretch at 1875 cm⁻¹ of the mixture.

The mixture with the 26 minute retention time could not be further
resolved. The presence of two compounds was inferred by a $^{19}$F NMR signal (64.3 ppm, d, 5 Hz) and a $^1$H NMR signal (4.95 ppm, d, 51 Hz) with small integrated intensities that were not integral multiples of the other signals' integrated intensities. Ignoring those two signals, all of the other signals logically implied $\text{CF}_3\text{-O-CF}_2\text{-O-CF}_2\text{H}$ as the structure of the major component of the mixture. When the two unaccounted for signals were considered alone, the $^{19}$F NMR signal suggested a $\text{CF}_3\text{-O-}$ moiety, and the $^1$H NMR signal suggested $\text{CFH}_2\text{-O-}$ (compare with the $^1$H NMR signals of $\text{CFH}_2\text{-O-CF}_2\text{H}$). The structure $\text{CF}_3\text{-O-CFH}_2$ for the minor component is reasonable on volatility grounds, and the only other expected NMR signal would be from the fluorine of the $-\text{O-CFH}_2$. 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 would further broaden the signal into the background noise.

When the $-78^0$ fraction, which contained the unstable, fluoroformate terminated hydrofluoroethers, was hydrolyzed with aqueous KOH, carbon dioxide and potassium formate ($\text{H-C(O)-O^- K^+}$) were the only detected products. The recorded infrared spectrum of potassium formate (KBr pellet) is included in Figure 11. This result is consistent with an anionic attack and depolymerization mechanism which will be discussed below.

**Discussion**

The production of large amounts of carbonyl fluoride from the direct fluorination of polymethylene oxide was a predicted rather than unexpected result. The polyethylene oxide project indicated that when a perfluoro
chain is cleaved at the carbon – oxygen bond, the resulting alkoxide radical is subject to carbonyl fluoride elimination, ie.

\[ R_fOCF_2CF_2\text{-}OCF_2CF_2OR_f \rightarrow R_fOCF_2CF_2^* + R_fOCF_2CF_2O^* \]

\[ R_fOCF_2CF_2O^* \rightarrow COF_2 + R_fOCF_2^* \]

\[ R_fOCF_2^* + R_fOCF_2CF_2^* \rightarrow \text{F}_2 \rightarrow R_fOCF_3 + R_fOCF_2CF_3 \]

If fluorination of polymethylene oxide had resulted in the perfluoropolymer, fragmentation and the same carbonyl fluoride elimination mechanism would have resulted in depolymerization and production of nearly quantitative amounts of carbonyl fluoride, ie.

\[ R_fOCF_2\text{-}OCF_2OCF_2OCF_2OR_f \rightarrow R_fOCF_2^* + R_fOCF_2OCF_2OCF_2O^* \]

\[ R_fOCF_2OCF_2OCF_2O^* \rightarrow COF_2 + R_fOCF_2OCF_2O^* \]

\[ R_fOCF_2OCF_2O^* \rightarrow COF_2 + R_fOCF_2O^* \rightarrow \text{etc.} \]

A perfluromethylene oxide ether would result only if both ends of a perfluoro chain segment were fluoroalkyl radicals after chain cleavage, both fluoroalkyl radical end-groups were routinely fluorinated to CF_3-O-end-groups and no further chain cleavage of the segment occurred.

The production of workable quantities of hydrofluoroethers from the actual reactions is an indication that polymer fragmentation was occurring before perfluorination had been achieved. The alkyl radicals formed by chain cleavage should be routinely fluorinated. The degree of fluorination of the resulting methoxy end-group would simply depend on the degree of fluorination of the carbon atom of the carbon – oxygen bond that was cleaved.

The alkoxide radical, formed by chain cleavage of the partially fluorinated polymer, would be free to unzip with carbonyl fluoride production until a carbon bonded to a hydrogen was encountered. The alkoxide would then
be transformed to a fluoroformate end-group or to a methoxy end-group. The end-group possibilities and viable mechanisms for a fragmented partially fluorinated polymethylene oxide chain are:

\[
\begin{align*}
\text{CR}_1\text{R}_2\text{OR}_f & \quad \xrightarrow{+R_fOCF_1\text{R}_2} \quad \text{R}_f\text{OCCR}_1\text{R}_2 \quad (R_1=R_2=H; \ R_1=H, \ R_2=F; \ R_1=R_2=F) \\
\text{OCF}_2\text{OCF}_2\text{OCHR}_3\text{OCR}_1\text{R}_2\text{OR}_f & \quad \xrightarrow{2+\text{COF}_2} \quad 2\ \text{COF}_2 + \text{R}_f\text{OCCR}_1\text{R}_2\text{OCHR}_3\text{O}' \\
\text{R}_f\text{OCCR}_1\text{R}_2\text{OCHR}_3\text{O}' \quad (\text{for } R_3=F) & \quad \xrightarrow{+\text{F}_2} \quad \text{R}_f\text{OCCR}_1\text{R}_2\text{OCHFOF} \quad \xrightarrow{-\text{HF}} \quad \text{R}_f\text{OCCR}_1\text{R}_2\text{O-C-F} \\
\text{(for } R_3=H) & \quad \xrightarrow{+\text{F}_2} \quad \text{R}_f\text{OCCR}_1\text{R}_2\text{OCH}_2\text{OF} \quad \xrightarrow{-\text{HF}} \quad \text{R}_f\text{OCCR}_1\text{R}_2\text{O-C-H} \\
& \quad \xrightarrow{-\text{HF}} \quad \text{HF} + \text{CO}_2 + \text{R}_f\text{OCCR}_1\text{R}_2\text{F}
\end{align*}
\]

Other more intricate mechanisms may be operating on the radical end-groups formed by chain cleavage, but the important point is that residual hydrogens on the polymer chain stop the carbonyl fluoride "unzipping" mechanism so significant amounts of hydrofluoroethers may be formed.

Aqueous KOH hydrolysis of the fluoroformate-terminated unstable ethers of the -78° fraction to produce only \( \text{CO}_2 \) and \( K^+ \text{HCO}_2^- \) is consistent with an anionic depolymerization process. The envisaged mechanism is:

\[
\begin{align*}
\text{FC(O)OCF}_2\text{OCHFOR}_f & \quad \xrightarrow{\text{KOH}} \quad \text{OC(O)OCF}_2\text{OCHFOR}_f \quad \xrightarrow{-\text{CO}_2} \\
\text{OCF}_2\text{OCHFOR}_f & \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{HOCEF}_2\text{OCHFOR}_f \quad \xrightarrow{-\text{HF}} \\
\text{FC(O)OCHFOR}_f & \quad \xrightarrow{\text{KOH}} \quad \text{HC(O)OH} + \text{OR}_f \quad \xrightarrow{\text{KOH}} \quad \text{HCO}_2^- \quad \text{K}^+ \text{etc.}
\end{align*}
\]

The fact that these ethers are unstable by themselves could be due to: the fluoroformate end-group reacting inter- or intramolecularly with re-
residual hydrogens, other interesting HF elimination and depolymerization mechanisms or the presence of the notoriously unstable hypofluorite group, \(-\text{C-O-F}\).

The direct fluorination of polymethylene oxide does not result in the production of volatile perfluoroethers. This conclusion is substantiated by the carbonyl fluoride producing "unzipping" mechanism 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 fragmentation of polymethylene oxide polymer in fluorine before it has been perfluorinated. (A possible synthetic route to the corresponding perfluoro compounds would be recycling of the isolated hydrofluoroethers in a cryogenic fluorination reactor.) The successful separation, spectral characterization and structure determination of these interesting hydrofluoroethers stands alone as a significant achievement.
Chapter 5

Fluorination of Poly(propylene oxide)
Fluorination of Poly(propylene oxide)

$$(\text{CH}_2-\text{CH-O})_x \xrightarrow{\text{He} / \text{F}_2, \text{amb.}} \text{CF}_3 \xrightarrow{\Delta} R_f-\text{O-}-(\text{CF}_2-\text{CF-O})_n-R_f$$

$R_f = \text{CF}_3, \ C_2\text{F}_5, \ n-\text{C}_3\text{F}_7$

Introduction

The successful fluorination of polyethylene oxide to perfluoroethylene oxide telomers and the isolation of stable hydrofluoropolyethers from the fluorination of polymethylene oxide naturally led to direct fluorination experimentation on other hydrocarbon polyethers. Polypropylene oxide was the logical choice for the third hydrocarbon polyether substrate for three reasons: 1) the branched structure of the repeating unit is the simplest complication of the linear polyethylene oxide structure, 2) any complications due to pendant methyl groups (chain branching) and methine hydrogens (-C-H) on the backbone would be observed and 3) polypropylene oxide is commercially available. The working hypothesis and synthetic strategy remained; 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, will result in volatile perfluoropolyethers with perfluoro alkyl or possibly acyl fluoride end-groups.

The significance of producing perfluoroethers with the hexafluoropropylene oxide repeating unit by direct fluorination is not as great as the significance of producing other perfluoroethers by direct fluorination. Synthesis of other perfluoroethers is limited to a few specific or involved methods. Synthesis of telomers and polymers of hexafluoropropylene oxide,
however, is readily accomplished by the anionic polymerization of hexafluoropropylene oxide monomer (see General Introduction). DuPont has extensively developed this technology into a commercial process, and the low and high molecular weight compounds are available as "Krytox" oils and greases, respectively. The commercialization of the process for hexafluoropropylene oxide but not tetrafluoroethylene oxide is a reflection of the easier handling properties of the hexafluoropropylene oxide monomer and resulting polymers. The more stable and higher boiling (hexafluoropropylene oxide, CF₃-c-C₂F₃O, -42°C; tetrafluoroethylene oxide, c-C₂F₄O, -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 CFCl₂CF₂Cl (Freon-113). (Tetrafluoroethylene oxide polymerizations 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 alternate 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. There is also the possibility of this process developing into a less expensive source of these compounds.

**Experimental**

The direct fluorination of polypropylene oxide was approached with a bit of reluctance because the commercially available material (Poly-science, Inc., MW 4000) was a viscous oil. All previous successful direct fluorination experiments had utilized crystalline solid polymers or liquids
that had been frozen to a crystalline solid state as the starting materials. A finely divided crystalline solid is desirable as a fluorination substrate because of the high surface area per unit weight that favors the gas-solid heterogeneous reaction. An oil has a low surface area per unit weight, so successful direct fluorination would depend on the ability of fluorine to diffuse into the oil and the ability of HF by-product to diffuse out. Since the polymer chains of an oil are free to move about, crosslinking would also be a potential complication because of possible chain-radical to chain-radical coupling. Fluorination of the oil below its glass transition temperature was considered, but abandoned without trial because the glassy state would still have a low surface area per unit weight. Finally, it was decided to fluorinate the polypropylene oxide oil "as is" at ambient temperatures in a room temperature reactor and worry about crosslinking and diffusion problems only if they developed. (The physical state of the fluorination substrate and fluorine diffusion are very important experimental considerations which will be further elaborated on in the General Discussion section.)

The direct fluorination of polypropylene oxide oil, when carried out in a room temperature reactor 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, tacky, gel-like, blood-red residue. Typical reaction conditions for the two-part fluorination process were:
The volatile products of the reaction were trapped throughout the reaction at -196°C in a glass trap and were separated by vacuum line trap-to-trap fractionation into four fractions: -30°C (bromobenzene slush), -78°C (dry ice), -131°C (pentane slush) and -196°C. For 2.76 g of polypropylene oxide starting material, the described process yielded 2.61 g of solid residue, 0.821 g of volatile compounds in the -30°C, -78°C and -131°C fractions and an undetermined amount of small fragment molecules in the -196°C fraction.

The blood-red, gel-like, solid residue was analyzed only by infrared spectroscopy. A thin film of the material on a KBr window exhibited a strong absorption in the carbon-hydrogen region (~3000 cm⁻¹), weak absorptions in the fluorocarbon carbonyl region (1700 - 1890 cm⁻¹) and strong absorptions in the carbon-fluorine/ether carbon-oxygen (1300 - 1100 cm⁻¹) and "fingerprint" (1000 - 600 cm⁻¹) regions. The residue was not analyzed further because volatile perfluoroethers were the desired compounds, and the many residual hydrogens, carbonyl groups, crosslinking (inferred by the gel-like nature of the residue) and polymeric nature of the residue implied an unresolvable, complicated mixture.

The -196°C fraction of the volatile products was also analyzed only by infrared spectroscopy. Comparison of the obtained spectra with literature infrared spectra indicated the presence of large amounts of CF₄.
and COF$_2$ and small amounts of CO$_2$, C$_2$F$_6$, C$_3$F$_8$, SF$_6$, SiF$_4$ and possibly C$_4$F$_{10}$. The estimated quantity of the fraction was several hundred milligrams, and this fraction of trivial, small, fragment molecules was routinely discarded.

The Glc assay of the -30$^\circ$, -78$^\circ$ and -131$^\circ$ fractions resulted in further separation of the more interesting, higher molecular weight volatile products. The Glc separations were characterized by relatively broad peaks, frequently with shoulder peaks or humps, and a significant amount of peak tailing and overlap. These observations implied that the Glc separation was not providing pure compounds but probably mixtures rich in one compound with small amounts of one or more other compounds as impurities. In the attempt to minimize the amount of impurity compounds with the main compound of a Glc "peak", only the centers of the Glc "peaks" were "collected" as each Glc "cut". (The possible reasons for relatively poor separation by Glc are dealt with in the Discussion section.) The Glc "cuts" of the volatile products (vacuum line fraction - retention time) are listed with their produced weights and % yields in Table 8.

Since only the centers of the Glc peaks were collected, each cut of isolated material was assumed to be a fairly pure compound, and structure determination was attempted, as usual, through infrared, NMR and mass spectral analysis. The infrared spectra of the cuts were all similar in showing no carbon-hydrogen absorptions (~3000 cm$^{-1}$), strong and broad absorptions in the carbon-fluorine / ether carbon-oxygen region (1300 - 1100 cm$^{-1}$) and medium to strong absorptions in the "fingerprint" region (1000 - 600 cm$^{-1}$). Two of the cuts, 131-3 and 78-12, exhibited strong acyl fluoride infrared bands (~1880 cm$^{-1}$), and most of the other cuts also
### TABLE 8

**Glc "Cuts" of the -131°, -78° and -30° Vacuum Line Fractions of the Polypropylene Oxide Volatile Products**

<table>
<thead>
<tr>
<th>Glc &quot;Cut&quot; (Vacuum line fraction - Glc retention time (min)*)</th>
<th>Weight Produced (mg)</th>
<th>Weight % Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>131 - 3</td>
<td>44</td>
<td>5.4</td>
</tr>
<tr>
<td>131 - 7 / 78 - 2</td>
<td>140</td>
<td>17.1</td>
</tr>
<tr>
<td>131 - 9</td>
<td>trace†</td>
<td>-</td>
</tr>
<tr>
<td>131 - 13</td>
<td>trace†</td>
<td>-</td>
</tr>
<tr>
<td>131 - 23 / 78 - 3</td>
<td>trace†</td>
<td>-</td>
</tr>
<tr>
<td>78 - 6</td>
<td>trace†</td>
<td>-</td>
</tr>
<tr>
<td>78 - 12</td>
<td>trace†</td>
<td>-</td>
</tr>
<tr>
<td>78 - 18</td>
<td>48</td>
<td>5.8</td>
</tr>
<tr>
<td>78 - 38</td>
<td>93</td>
<td>11.3</td>
</tr>
<tr>
<td>30 - 35</td>
<td>51</td>
<td>6.2</td>
</tr>
<tr>
<td>30 - 46</td>
<td>35</td>
<td>4.3</td>
</tr>
<tr>
<td>30 - 58</td>
<td>27</td>
<td>3.3</td>
</tr>
<tr>
<td>Unseparated material</td>
<td>383</td>
<td>46.6</td>
</tr>
<tr>
<td>Total</td>
<td>821 mg</td>
<td>100 %</td>
</tr>
</tbody>
</table>

* Glc Temperature Programs:

- **-131° Fraction:** -20° isothermal
- **-78° Fraction:** 0° for 30 min; 1° / min + 90°
- **-30° Fraction:** 30° for 10 min; 1° / min + 80°

† These "cuts" obtained in larger amounts from preliminary reactions.
exhibited weak to very weak absorptions in the fluorocarbonyl region (1700 - 1880 cm\(^{-1}\)). The weak carbonyl absorptions were interpreted as evidence of fluoroacetyl fluorides and fluoroketones being present as the impurities of the Glc cuts. Considering the strong bands of the infrared spectra, the main compound of most Glc cuts was thought to be a perfluoroether, as expected. An example of a typical infrared spectrum of a Glc cut appears in Figure 12, p. 102.

Since \(^{19}\)F NMR analysis had been so useful for structure determination in the other fluoroether projects, we had hoped to rely heavily on the \(^{19}\)F NMR spectra for structure determination of the main compound of each Glc cut. NMR analysis, however, was extremely complicated for a couple of reasons. Most important, the \(^{19}\)F NMR spectra for fluoroethers with the \(\text{CF(CF}_3)\text{-CF}_2\text{-O}\) repeating unit are second order, ie. the usual multiplet splitting patterns with measurable coupling constants that are so useful for relative position and signal assignments are not observed. The reason for this is the fact that fluorine - fluorine coupling can occur for fluorine nuclei separated by as much as six or seven bonds. The fluorine nuclei in the produced compounds are coupled to many different fluorine nuclei, so broad unresolved NMR signals and second-order spectra resulted. The other complication in NMR interpretation was due to the signals of the impurities. Since all of the compounds produced in the reaction should be of the same general structure, the impurity compounds probably differ in structure from the main compound of the Glc cut only at the end-groups. The impurity compounds would, therefore, exhibit some of the same NMR signals as the main compound and would contribute to the integrated relative intensities of these signals.
The only useful unquestionable information from the $^{19}$F NMR spectra, therefore, was the chemical shifts of the signals. Interpretation of the spectra was begun by assigning specific structures to the chemical shifts. A review article of DuPont's anionic polymerization of hexafluoropropylene oxide by J. T. Hill$^7$ was unearthed in the literature, and the $^{19}$F NMR signal assignments for the second-order spectra of the hexamer and heptamer were included. The applicable assignments were (reference - CFCl$_3$):

$$CF_3-CF_2-CF_2-O-(CF-CF_2-O)_n$$

$$\begin{align*}
  a & = 82.7 \text{ ppm} \\
  b & = 130.1 \text{ ppm} \\
  c & = 82.1 \text{ ppm} \\
  d & = 145.0 \text{ ppm} \\
  e & = 80.6 \text{ ppm} \\
  f & = 80.6 \text{ ppm}
\end{align*}$$

These reported values are 2 - 3 ppm lower than the calculated chemical shifts for what is considered to be the same signals of the produced compounds. A 2 - 3 ppm discrepancy is not large in $^{19}$F NMR and can often be explained by the way the spectra were recorded and referenced. Our experimental spectra were run with "neat" samples in thinner coaxial tubes inside the NMR tube and referenced by "neat" CFCl$_3$ in a substitute NMR tube. (The thinner tubes "stretched" small samples so $^{19}$F NMR spectra could be obtained, and the additional glass in the field may alter the overall diamagnetic susceptibility of the sample.) With these signal assignments, chemical shift values for the nuclei of the $CF_3-CF_2-O$ and $CF_3-O$ end-groups (from the polyethylene oxide project) and knowledge of approximate chemical shifts of other types of fluorine nuclei, most of the observed signals could be accounted for by fluorine nuclei of perfluoroethers.

The data from the $^{19}$F NMR spectra of the Glc cuts and the structural assignments for the various chemical shifts is compiled in Table 9. No
TABLE 9

$^{19}$F NMR Data of the Glc "Cuts" of the Polypropylene Oxide Volatile Products

<table>
<thead>
<tr>
<th>Glc &quot;Cut&quot;</th>
<th>CF$_3$O</th>
<th>CF$_3$R$_f$</th>
<th>CF$_3$</th>
<th>Internal</th>
<th>CF$_2$O</th>
<th>CF$_3$CF$_2$CF$_2$O</th>
<th>CF$_3$CF$_2$O</th>
<th>CF$_3$CF$_2$O</th>
<th>R$_f$CF$_2$R$_f$</th>
<th>CF$_3$CF$_2$CF$_2$O</th>
<th>Internal</th>
</tr>
</thead>
<tbody>
<tr>
<td>131 - 3</td>
<td>59.2 t(11)</td>
<td>84.2 (8)</td>
<td>85.1 t(16)</td>
<td>86.9,87.1,89.6,90.7</td>
<td>91.8</td>
<td>124.9,125.7</td>
<td>133.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>131 - 7 / 78 - 2</td>
<td>59.1 d(2)</td>
<td>78.0 (4)</td>
<td>84.9 (28)</td>
<td>37.5 (18)</td>
<td>90.7 (27)</td>
<td>91.7</td>
<td>129.4</td>
<td>133.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>131 - 9</td>
<td>59.1 t(10)</td>
<td>76.9 (7)</td>
<td>84.2 (17)</td>
<td>89.4 (6)</td>
<td>90.5 (6)</td>
<td>91.6</td>
<td>129.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>131 - 18</td>
<td>76.7 t(10)</td>
<td>34.8 (12)</td>
<td>37.1 (4)</td>
<td>90.5 (5)</td>
<td>91.6</td>
<td>129.2</td>
<td>132.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>131 - 23 / 78 - 8</td>
<td>57.2 d/quar(10)</td>
<td>83.4 (11)</td>
<td>96.0 (10)</td>
<td>149.0 (trace)</td>
<td>90.6 (10)</td>
<td>132.9,133.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>78 - 6</td>
<td>84.3 (12)</td>
<td>85.1 (15)</td>
<td>37.3 (4)</td>
<td>90.7 (15)</td>
<td>pen(4)</td>
<td>quar(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>78 - 12</td>
<td>77.3 (5)</td>
<td>84.9,85.6 (15)</td>
<td>90.5</td>
<td>132.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>78 - 18</td>
<td>59.2 t(2)</td>
<td>83.7 (25)</td>
<td>35.1 (25)</td>
<td>90.7</td>
<td>133.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glc &quot;Cut&quot;</td>
<td>CF$_3$O</td>
<td>CF$_3$R$_f$</td>
<td>Internal Pendant</td>
<td>Internal CF$_2$O / CF$_3$CF$_2$CF$_2$O</td>
<td>CF$_3$CF$_2$O</td>
<td>CF$_3$CF$_2$O</td>
<td>R$_f$CF$_2$R$_f$</td>
<td>CF$_3$CF$_2$CF$_2$O</td>
<td>Internal -CF-O</td>
<td></td>
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</tr>
<tr>
<td>78 - 38</td>
<td>83.4</td>
<td>84.9</td>
<td>86.1</td>
<td>90.6</td>
<td>91.7</td>
<td>132.8</td>
<td>148.0</td>
<td>(58)</td>
<td>(15)</td>
<td>(10)</td>
<td></td>
</tr>
<tr>
<td>30 - 35</td>
<td>83.2</td>
<td>84.9</td>
<td>86.0</td>
<td>90.5</td>
<td>91.4</td>
<td>132.7</td>
<td>147.9</td>
<td>(63)</td>
<td>(11)</td>
<td>(7)</td>
<td></td>
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<td>30 - 46</td>
<td>83.2</td>
<td>84.8</td>
<td>85.8</td>
<td>90.3</td>
<td>91.4</td>
<td>132.3</td>
<td>147.9</td>
<td>(65)</td>
<td>(12)</td>
<td>(5)</td>
<td></td>
</tr>
<tr>
<td>30 - 58</td>
<td>83.3</td>
<td>85.0</td>
<td>86.0</td>
<td>90.6</td>
<td>91.3</td>
<td>133.0</td>
<td>148.1</td>
<td>(80)</td>
<td>(25)</td>
<td>(3)</td>
<td></td>
</tr>
</tbody>
</table>

Data presented as follows: Chemical Shift in ppm
Multiplicity (Integrated Intensity)

Reference: neat external CFCl$_3$

All signals are broad unresolved multiplets unless otherwise noted;
d - doublet, t - triplet, quar - quartet, pen - pentet
signals were observed in $^1$H NMR scans for any of the Glc cuts. With the structure assignments of the signals but unreliable integrated intensities, overall molecular weights of the compounds were necessary for structure elucidation.

Mass spectrometry was the analytical tool that was useful 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 peak exhibited by each Glc "cut" was as follows:

- 131-7 / 78-2 , 285 (C$_5$F$_{11}$O)
- 78-18 , 401 (C$_7$F$_{15}$O$_2$)
- 30-35 , 617 (C$_{11}$F$_{23}$O$_3$)
- 30-58 , 733 (C$_{13}$F$_{27}$O$_4$)

(the lowest yield "cuts" 131-9, 131-18, 78-6, 78-12 obtained mainly from preliminary experiments were not analyzed by mass spectrometry).

Each highest mass peak is attributed to the parent minus fluorine formula for the major component of the Glc cut. The spectra showed decreasing peak intensity with increasing mass, and the highest intensity peak was always 119 (C$_2$F$_5$) or 169 (C$_3$F$_7$). The other common low-mass fragment peaks were at m/e 31 (CF), 47 (COF), 50 (CF$_2$), 69 (CF$_3$), 81 (C$_2$F$_3$), 97 (C$_2$F$_3$O), 100 (C$_2$F$_4$), 131 (C$_3$F$_5$), 135 (C$_2$F$_5$O), 147 (C$_3$F$_5$O), 150 (C$_3$F$_6$), 181 (C$_4$F$_7$), 185 (C$_3$F$_7$O), 197 (C$_4$F$_7$O), 200 (C$_4$F$_8$), 213 (C$_4$F$_7$O$_2$), 219 (C$_4$F$_9$) and 235 (C$_4$F$_9$O). The common high-mass fragment peaks were at values corresponding to the empirical formulas C$_n$F$_{2n-1}$O$_x$ and C$_n$F$_{2n+1}$O$_x$ (x = 0 - 3). High-mass peaks with fewer oxygen atoms than expected for
a polypropylene oxide fragment, such as 435 (C₈F₁₇O) and 551 (C₁₀F₂₁O₂), was a direct indication of a rearrangement process. The mass spectra were also useful in conclusively establishing the absence of hydrogen in the compounds; none of the peaks always observed for hydrogen-containing fluorocarbons, particularly 51 (CF₂H), were observed.

In order to test the validity of assigning the highest mass peaks of the mass spectra to parent minus fluorine formulas, several samples were analyzed for molecular weights by the ideal gas method. The experimental results were (Glc cut, gas phase molecular weight, molecular weight implied by mass spectrometry): 131-7 / 78-2, 307.5, 304; 131-23 / 78-8, 374, 370; 78-18, 403, 401; 78-38, 466, 470. These confirming values are remarkably accurate considering the Glc cuts were mixtures rich in one compound but with impurities present, and the small analytical samples that were isolated provided only small pressure differences in the standard volume that was used. The three highest molecular weight Glc cuts could not be analyzed for gas phase molecular weights because their vapor pressures at room temperature were too low.

With the mass spectrally-determined molecular weights and the structure assignments for the observed NMR signals, structures could be elucidated for the main compound of several Glc cuts. The compounds were identified by rigorous ¹⁹F NMR analysis, and the structures, parent minus fluorine peaks of the mass spectra and assigned NMR data is listed in Table 10. An example of a typical ¹⁹F NMR spectrum observed is the interpreted spectrum of CF₃CF₂CF₂OCF(CF₃)CF₂OCF₂CF₃ in Figure 12.

In interpreting the NMR spectra, critical evaluation of the experimental integrated intensities of the signals was possible by knowing the
<table>
<thead>
<tr>
<th>Glc &quot;Cut&quot; / Highest m/e in Mass Spec. / Mol. Wt. of Structure</th>
<th>Identified Compound / Assigned (^{19}\text{F} \text{NMR Data}</th>
<th>Observed Relative Intensity</th>
<th>Theoretical Relative Intensity</th>
</tr>
</thead>
</table>
| 131 - 3<br>(no Mass Spec.)<br>MW = 166 | \(0\)
\(\text{CF}_3\text{-CF}_2\text{-C-F}\)
\(a \quad b \quad c\)
\(a = 87.1 \text{ ppm} \quad d \text{ of } \text{t} \quad (J = 5.5, 1.5)\)
\(b = 124.9 \text{ ppm} \quad d \text{ of } \text{quart.} \quad (J = 9.0, 1.9)\)
\(c = -19.2 \text{ ppm} \quad \text{multiplet} \quad 15 \quad 1\) | | |
| 131 - 7, 78 - 2 | \(\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-O-CF}_2\text{-CF}_3\)
\(a \quad e \quad b \quad d \quad c\)
\(a = 84.9 \text{ ppm} \quad \) | 28 | 3 |
\(b = 87.5 \text{ ppm} \quad \) | 18 | 2 |
\(c = 90.7 \text{ ppm} \quad \) | 27 | 3 |
\(d = 91.7 \text{ ppm} \quad \) | 15 | 2 |
\(e = 133.2 \text{ ppm} \quad \) | 16 | 2 |
| 131 - 23, 78 - 8 | \(\text{CF}_3\text{-O-CF-CF}_2\text{-O-CF}_2\text{-CF}_3\)
\(a \quad \text{f} \quad d \quad c \quad \text{e}\)
\(a = 83.4 \text{ ppm} \quad \) | 11 | 3 |
\(b = 86.0 \text{ ppm} \quad \) | 10 | 2 |
\(c = 90.6 \text{ ppm} \quad \) | 10 | 3 |

Identified Volatile Compounds from the Fluorination of Polypropylene Oxide with Assigned \(^{19}\text{F} \text{NMR Data} \)
TABLE 10 (cont.)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>78 - 33</td>
<td>$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-O}\text{-CF}\text{-CF}_2\text{-O}\text{-CF}_2\text{-CF}_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m/e: 451 ($\text{C}<em>8\text{F}</em>{17}\text{O}$), P-F</td>
<td>$d = 91.7$ ppm</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>$e = 149.0$ ppm</td>
<td>trace</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$f = 57.2$ ppm d of quart. (J = 15', 4)</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-O}\text{-CF}\text{-CF}_2\text{-O}\text{-CF}_2\text{-CF}_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a = 83.4$ ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$b = 84.4$ ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c = 85.0$ ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d = 86.1$ ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$e = 90.6$ ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$f = 91.7$ ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$g = 132.8$ ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$h = 148.0$ ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-O}\text{-CF}\text{-CF}_2\text{-O}\text{-CF}_2\text{-CF}_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a = 83.2$ ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$b = 84.3$ ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c = 84.9$ ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d = 86.0$ ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$e = 90.5$ ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$f = 91.4$ ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$g = 132.7$ ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$h = 147.9$ ppm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 12: Infrared and $^{19}\text{F}$ NMR Spectra of Perfluoro-4-methyl-3,6-dioxanonane

$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-O-CF-CF}_2\text{-O-CF}_2\text{-CF}_3$

c
g
d
\text{CF}_3

e
f

$\beta = 83.4 \text{ ppm}$

$\beta = 84.4 \text{ ppm}$

$\beta = 85.0 \text{ ppm}$

$\beta = 86.1 \text{ ppm}$

$\epsilon = 90.6 \text{ ppm}$

$\epsilon = 91.7 \text{ ppm}$

$\epsilon = 132.8 \text{ ppm}$

$\epsilon = 148.0 \text{ ppm}$
molecular weight of the structure. The signals for CF₃O and CF₃CF₂O end-groups, the middle CF₂ of perfluoro-n-propyl end-groups and the tertiary CF of the repeating unit usually had accurate experimental integrated intensities. The signals for the other CF₂'s and CF₃'s of the structure were all close together in the 83 - 86 ppm region, and the experimental integrated intensities were always higher than expected. The higher values are attributed to signals in the same region from the impurity compounds of the same general structure. Knowing the molecular weight of the structure also assisted in establishing how many signals should be observed, so other weak signals were more easily identified as signals from impurity compounds and excluded from consideration.

The NMR spectra could not be successfully interpreted until some signal assignments by Hill in the low - 80 ppm region were changed. Comparing the spectra for our perfluoroethers, particularly CF₃CF₂CF₂O(CF(CF₃)CF₂O)₂CF₂CF₃ and CF₃CF₂CF₂O(CF(CF₃)CF₂O)₂CF₂CF₃, we can see which of the four signals in the region increase in intensity and which remain constant as the number of repeating units increases. The better signal assignments are: CF₃ of the repeating unit, 83.5 ppm; CF₂ of the repeating unit, 84.5 ppm; CF₃ of the CF₃CF₂CF₂O end-group, 85.0 ppm; and CF₂ α to the oxygen of the CF₃CF₂CF₂O end-group, 86.0 ppm. (The assignments for the CF₃CF₂CF₂O end-group were distinguished by integrated intensity.) The questioning of Hill's signal assignments occurred because his published spectra were characterized by wide sweep widths causing sharp signals, so signal assignments for the low - 80 ppm region with its numerous overlapping signals would be very difficult. Our spectra were run over narrower sweep widths, so broader signals were obtained. Broad-
ening the low - 80 ppm region allowed easier observance of the differences in the region for different compounds and more accurate signal assignments for the region.

Even when the NMR spectra were interpreted with reliable molecular weights, critically evaluated integrated intensities and improved signal assignments in the low - 80 ppm region, only four perfluoroether structures could be deduced. The success for those compounds is because their respective Glc cuts probably contained only minor amounts of impurity compounds. The other Glc cuts probably contained larger amounts of impurity compounds with the main compound (or several compounds in equal amounts), so the NMR spectra were too complicated and could not be resolved.

Physical characterization of the four identified perfluoroethers included melting point and boiling point determinations. When the low temperature melting points were measured, it was discovered that the materials solified as glasses instead of crystalline powders when frozen. (This could be due to the presence of impurities or due to the method of quickly freezing the samples by placing them in liquid nitrogen.) The melting points obtained, therefore, were actually glass transition temperatures. Boiling points were determined for the two higher molecular weight perfluoroethers that were identified, but the other two identified perfluoroethers were so volatile that they vaporized from the 4 mm tube of the micro boiling point apparatus before values could be obtained. The observed physical constants were (compound, m.p. (°C), b.p. (°C)):

\[ \begin{align*}
C_3F_7OC_2F_5 & , -122 , - ; \\
C_3F_7OCF(CF_3)CF_2OC_2F_5 & , -115 , 93 - 94 ; \\
CF_3OCF(CF_3)CF_2OC_2F_5 & , -120 , - ; \\
C_3F_7(OCF(CF_3)CF_2)_2OC_2F_5 & , -108 , 144 - 145 .
\end{align*} \]
Discussion

Infrared, $^{19}$F NMR and mass spectral analysis of the Glc-separated volatile products indicates that perfluoroethers can, indeed, be produced by the direct fluorination of polypropylene oxide. The particular ethers obtained, for which the structures were determined, were:

$$R_f-0-(CF-CF_2-0)_n-CF_2CF_3$$

for $R_f = n-C_3F_7$, $n = 0, 1, 2$

$$CF_3$$

for $R_f = CF_3$, $n = 1$.

The major problem in the project was poor separation of the products by Glc. Since pure compounds were not obtained by Glc separation, structure determination through spectral analysis was complicated or impossible. The reason for poor separation by Glc assay was the large number of perfluoroether structures that could be produced by the direct fluorination reaction. The possible perfluoro end-groups that may result from fluorination and fragmentation of polypropylene oxide are: $CF_3O$, $CF_3CF_2O$, $CF_3CF_2CF_2O$, $(CF_3)_2CF_2O$, $F(0)CCF(CF_3)O$ and $CF_3C(0)CF_2O$. Fragmentation of the pendant methyl groups from the internal repeating units is also a possibility. Since saturated perfluoroethers should not be actively adsorbed on the stationary liquid phase of the gas chromatography column, separation would be by molecular weight (i.e. volatility), so isomeric compounds would not be separated. Perfluorocarbonyl compounds should be actively adsorbed on the column, so smaller perfluorocarbonyl compounds could have the same Glc retention times as larger saturated perfluoroethers. For these reasons, i.e. many possible compounds, non-separable isomeric compounds and the complicating presence of carbonyl compounds, Glc assay was not a useful method for the separation of pure compounds for this reaction.
Another complication for this reaction is the fact that the starting material is a low molecular weight polymer, an oil. Visual observation of a gel-like skin on the surface of the substrate after the "pre-fluorination" period indicated more extensive reaction was occurring at the oil's surface. This was expected because of the problem of fluorine diffusion into the oil and resulted in non-uniform fluorination of the whole sample. A possible method for maximizing an oil's surface area for fluorination is adsorption of the oil on a fluorine-inert solid support with a high surface area, such as fluorinated alumina. If a higher molecular weight, solid, polypropylene oxide polymer would have been available, the higher surface area of the finely-ground polymer would have allowed uniform reaction. The reaction of the oil was successful in producing only perfluoro volatile ethers because the fragmentation process also occurred predominately at the surface where the highly fluorinated polymer would be. The "fragmenting away" of the perfluoro surface exposed additional polymer to fluorination and fragmentation.

Conclusions about the fragmentation process could be made by the type of end-groups that were observed. The following homolytic fragmentation mechanisms account for the observed end-groups:

\[
\begin{align*}
R_f-O-CF_2-CF_2-O-R_f & \xrightarrow{F_2} R_f-O-CF_2-CF_3 + R_f-O-CF_3 \\
R_f-O-CF_2-CF_2-O-R_f & \xrightarrow{F_2} R_f-O-CF_2-CF_2-CF_3 + (R_f-O-CF-CF_2-0') \\
(R_f-O-CF-CF_2-0') & \xrightarrow{OR} COF_2 + R_f-O-CF_2-CF_3 \\
\end{align*}
\]

OR \[ F' + R-O-CF-C-F \]
The presence of only trace amounts of fluoroketone end-groups (by IR) and no detection of perfluoroisopropyl end-groups indicated backbone cleavage at the CF₂-O bond was not a favored fragmentation mechanism.

The direct fluorination of polypropylene oxide to produce perfluoropropylene glycol ethers proves the generality of direct fluorination as a technique for preparing perfluoropolyethers. Although DuPont's commercial process for producing hexafluoropropylene oxide ethers is a well developed method, and alternative method now exists.
Chapter 6

Fluorination of Hexafluoroacetone-Ethylene Copolymer
Fluorination of Hexafluoroacetone-Ethylene Copolymer

\[(CH_2CH_2OC(CF_3)2)_n \xrightarrow{F_2} \text{Perfluoroethers}\]

Introduction

Direct fluorination has been shown to be a useful synthetic method for the production of perfluoroethers from polyethylene oxide and polypropylene oxide polymers. These compounds and other perfluoroethers with a two carbon - one oxygen backbone repeating unit can also be synthesized by DuPont's established method, the anionic polymerization of perfluoroepoxides. A significant extension of the utility and importance of the direct fluorination technique would be the successful synthesis of perfluoroethers that cannot be synthesized by the polymerization of perfluoroepoxides or any other available technique. Perfluoroethers with more than two backbone carbon atoms between successive oxygen atoms are examples of potentially interesting compounds that are currently unobtainable.

Use of hydrocarbon polymers with the desired more than two carbon atom - one oxygen backbone repeating unit as fluorination substrates was limited by the lack of availability of such polymers. Hydrocarbon polyethers are also usually produced by polymerization of the suitable epoxides, so hydrocarbon polyethers with the two carbon - one oxygen backbone repeating units, particularly polyethylene oxide and polypropylene oxide, are most common. Tabata and co-workers\(^7\) have synthesized a polymer with a three carbon atom - one oxygen backbone repeating unit by the \(^{60}\text{Co}\) radiation induced, low temperature copolymerization of ethylene and hexa-acetone, ie.

\[
\text{CH}_2\text{=CH}_2 + \text{CF}_3\text{-C-CF}_3 \xrightarrow{^{60}\text{Co \gamma-rays}} \left(\text{CH}_2\text{CH}_2\text{OC(CF}_3\text{)}_2\right)_n \quad T < -90^\circ\text{C}
\]
Their polymer is strictly a one to one alternating copolymer as indicated by the x-ray diffraction data for the crystalline polymer, the NMR data and the one to one consumption of monomers during polymerization that is independent of the ratio of monomers used. (The high temperature, radical induced polymerization of the same monomers does not result in a one to one alternating copolymer.74) The successful direct fluorination of Tabata's polymer would result in the synthesis of perfluoroethers with the \(-\text{CF}_2\text{CF}_2\text{OC(CF}_3\text{)}_2\)- repeating unit. These perfluoroethers cannot be synthesized by a perfluoroepoxide polymerization scheme or any other method; the copolymerization of tetrafluoroethylene and hexafluoroacetone does not result in the perfluoro one to one alternating copolymer.74 The successful use of direct fluorination for production of these otherwise unobtainable perfluoroethers would be a significant achievement for the technique in the perfluoroether area.

Experimental

Synthesis of Hexafluoroacetone-Ethylene Alternating Copolymer:
Tabata's copolymerization reaction entailed charging a 10 cc stainless steel autoclave with the monomers and irradiating with \(^{60}\text{Co}\) \(\gamma\)-rays. His investigation included thorough examination of the variables time, temperature and various additives. Although the publication of interest did not explicitly state the strength of his \(^{60}\text{Co}\) source, examination of several other publications of his indicated a very strong \(^{60}\text{Co}\) source of at least \(500,000\) rads/hr. The reported melting point of the copolymer was \(100^\circ\text{C}\).

The strongest available \(^{60}\text{Co}\) source to us was only \(35,000\) rads/hr, so longer reaction times were deemed necessary. The available \(^{60}\text{Co}\)
source was also immersed in a large water tank, so the only practical
less than \(-9^\circ C\) temperature was \(-78^\circ C\) at which a doubly insulated pack
of dry ice was used as the cooling agent. Interpretation of Tabata's
results indicated bulk copolymerization or copolymerization with a chlor-
inated solvent as an additive was best. Two preliminary \(-78^0\), two-day
reactions, one bulk reaction and one reaction with methylene chloride,
were run to determine the effect of an additive. The bulk reaction re-
sulted in 16\% conversion to polymer, m.p. 99.5 - 101\(^0\), and the methylene
chloride reaction resulted in 7\% conversion to polymer, m.p. 95 - 97\(^0\),
with a small amount of oily by-product. (\% conversions are based on monomer
consumption) The lower conversion and oily by-product of the methylene
chloride additive reaction was contrary to Tabata's results but not in-
vestigated further.

The better bulk reaction was tripled in scale and a useful amount
of copolymer was produced. Equimolar amounts of ethylene and hexafluoro-
acetone, 0.120 moles of each, were charged into a 30 cc stainless
steel autoclave and then irradiated with the 35,000 rads/hr \(60^{\text{Co}}\) source
for three days at \(-78^0\). After the reaction, the unreacted monomers were
separated and quantitatively analyzed; a 22.4 mole \% conversion to polymer
was calculated. The white powder copolymer was dissolved in Freon-113
\((\text{CFCl}_2\text{CF}_2\text{Cl})\), filtered and recrystallized by addition of an equal volume
of hexane. 4.25 g of fluffy, white, crystalline copolymer was obtained,
which is a 18.2 \% yield. The melting point determined with a Mel-Temp
was 99.5 - 101\(^0\)\(^{\circ}\); the physical constants determined by Differential
Scanning Calorimetry (DSC) were \(T_g = -23.4^\circ C\) (\(T_g\) is the glass transition
temperature) and \(T_{m.p.} = 96.5^\circ C\). The infrared spectrum of the copolymer
(polymer film cast from Freon-113 solution) corresponded exactly to Tabata's reported spectrum and is included in Figure 13. NMR end-group analysis, by the integrated intensities of the internal pendant CF$_3$ at 73.4 ppm and the end-group pendant CF$_3$ at 78.4 ppm, indicated the average degree of polymerization was 360 which corresponds to $\text{MW}_{\text{av.}} = 70,000$.

Fluorination of Hexafluoroacetone-Ethylene Copolymer: The direct fluorination of the copolymer was approached with the same strategy that was successful for the other hydrocarbon polyether polymers, i.e., a "pre-fluorination" period that would highly fluorinate the polymer while maintaining its structural integrity, followed by a higher temperature fragmentation period that would produce volatile perfluoroethers.

Since the copolymer was a finely-divided crystalline powder at room temperature, ambient temperatures were expected to be useful for the "pre-fluorination" period. Such a reaction, however, resulted in conversion of the crystalline polymer to a clear, viscous grease. Infrared analysis of the grease indicated a significant number of residual hydrogens and the presence of acyl fluoride and carboxylic acid end-groups. (Acid end-groups would be due to acyl fluoride hydrolysis by atmospheric moisture while the material was being handled.) Infrared analysis of the volatile products obtained indicated large amounts of CF$_4$ and COF$_2$ and small amounts of partially fluorinated acyl fluorides. These physical and infrared observations indicated that polymer fragmentation with carbon by carbon end-group degradation was the primary process with only a minor amount of the expected hydrogen-replacing fluorination reaction.

Failure of ambient temperatures for the "pre-fluorination" period
led to investigations of sub-ambient temperatures for the "pre-fluorination" conditions. Fluorinations of the copolymer at \(0^\circ\)C and \(-25^\circ\)C gave similar results to the ambient temperature fluorination. The obtained greases were less dense and viscous, but their infrared spectra again indicated a large amount of functionalization and residual hydrogens. Volatile products were obtained in smaller amounts but were qualitatively similar to those of the ambient temperature reaction. Fluorination of the copolymer at \(-78^\circ\)C had very little effect; the infrared spectrum of the powdery solid product was very similar to that of the starting copolymer, and only traces of the usual volatile products were obtained. Fluorination of the copolymer at \(-50^\circ\)C produced a powdery solid product whose infrared spectrum indicated more reaction than for the \(-78^\circ\)C trial but less functionalization than for the \(0^\circ\) and \(-25^\circ\) trials; volatile product formation was also of an intermediate nature. The infrared spectra of the solid products (films cast from Freon-113 solution) are included in Figure 13 to emphasize the low temperature fluorination trends. The inescapable conclusion is that the onset of reaction in the direct fluorination of hexafluoroacetone-ethylene copolymer results in chain cleavage at the branched-carbon-oxygen bond and acyl fluoride formation, ie.

\[
\text{-CH}_2\text{CH}_2\text{O-C(CF}_3\text{)}_2^- + \text{F}_2 \rightarrow \text{-CF(CF}_3\text{)}_2^\circ + \text{-CH}_2\text{-C-F}
\]

This result was totally unexpected in light of the structural maintenance of the other polyether polymers when subjected to low or ambient temperature direct fluorination.

The most interesting "pre-fluorination" result was obtained when the powdery product of the \(-50^\circ\)C reaction was further fluorinated at \(-50^\circ\), then at step-wise increased temperatures until ambient temperature was
Figure 13

Starting copolymer

\((-\text{CH}_2-\text{CH}_2-\text{O-C(CF}_3)_2-)\_n\)

Fluorinated at \(T = \text{amb.}\)

Fluorinated at \(T = -78^\circ\text{C}\)

Infrared Spectra of \((\text{CH}_2\text{CH}_2\text{OC(CF}_3)_2)\_n\) and the Solid Products from "Pre-fluorination" Experiments
Figure 13 (cont.)

Fluorinated at $T = -25^\circ C$

Fluorinated at $T = -50^\circ C$

Fluorinated at $T = -50^\circ C + \text{amb.}$
reached. The solid product obtained was somewhat sticky but still a powder, and infrared analysis indicated about the same amount of functionalization but a greatly reduced amount of residual hydrogens. (The IR spectrum is included in Figure 13.) A similar experiment with the powdery product of the -78⁰ reaction resulted in a similar powder containing (by IR) few hydrogens and a relatively small amount of functional groups. These reactions also produced larger amounts of the usual volatile products (CF₄, COF₂ and partially fluorinated acyl fluorides), presumably by a carbon by carbon or segment by segment degradation of the polymer chain ends. These results indicate that careful control of the reaction conditions, temperature and % fluorine in the reactant gas mixture, allows normal fluorination of the hexafluoroacetone-ethylene copolymer after the fluorination has been begun by an unavoidable chain cleavage / acyl fluoride producing process. The useful "pre-fluorination" conditions were determined to be:

<table>
<thead>
<tr>
<th>He (cc/min)</th>
<th>F₂ (cc/min)</th>
<th>Temp. (⁰C)</th>
<th>Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.0</td>
<td>-50</td>
<td>25</td>
</tr>
<tr>
<td>18</td>
<td>2.0</td>
<td>-50</td>
<td>8</td>
</tr>
<tr>
<td>8</td>
<td>2.0</td>
<td>-50</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>4.0</td>
<td>-50</td>
<td>12</td>
</tr>
<tr>
<td>0</td>
<td>4.0</td>
<td>-50</td>
<td>18</td>
</tr>
<tr>
<td>0</td>
<td>4.0</td>
<td>-25</td>
<td>8</td>
</tr>
<tr>
<td>0</td>
<td>4.0</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>0</td>
<td>4.0</td>
<td>amb.</td>
<td>12</td>
</tr>
</tbody>
</table>

The powdery products with few residual hydrogens were further fluorinated in the attempt to produce the perfluoroacyl fluoride - terminated
polymers. At ambient temperatures with pure fluorine, longer reaction times were used and high-pressure experiments were tried, but no perfluoro solid products were obtained. All that was obtained was more of the usual volatile products from chain end degradation. (Reasons for the lack of perfluoro solid products will be proposed in the Discussion section.)

When useful "pre-fluorination" conditions were finally worked out and an intermediate polymer of relatively high fluorine content was obtained, a fragmentation period was added to the experiment in the attempt to produce volatile perfluoroethers. Fragmentation was promoted, as usual, by the use of elevated temperatures. From the results of the first couple of fragmentation trials, the importance of precise temperature control for fragmentation-fluorination reaction was demonstrated. Fragmentation-fluorination was performed at 75°C in one reaction and at 65°C, 67°C, then 69°C in another. The specific reaction conditions were as follows:

<table>
<thead>
<tr>
<th>Trial #</th>
<th>He (cc/min)</th>
<th>F₂ (cc/min)</th>
<th>Temp. (°C)</th>
<th>Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td># 1</td>
<td>5</td>
<td>4.0</td>
<td>amb.</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.0</td>
<td>55</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.0</td>
<td>75</td>
<td>48</td>
</tr>
<tr>
<td># 2</td>
<td>5</td>
<td>4.0</td>
<td>amb.</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.0</td>
<td>65</td>
<td>24</td>
</tr>
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<td>5</td>
<td>4.0</td>
<td>67</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.0</td>
<td>69</td>
<td>36</td>
</tr>
</tbody>
</table>

The volatile products from the reactions were first separated by vacuum line trap-to-trap fractionation into -196°, -131° and -78° fractions. The -196° fractions from both reactions were very similar and were qual-
itatively examined only by infrared spectroscopy. Such analysis indicated the fraction contained mostly COF$_2$, and a significant amount of CF$_4$ and small amounts of C$_2$F$_6$, SF$_6$ and SiF$_4$. The fraction was relatively large in quantity, and quantitative analysis (of the -196$^\circ$ fraction of the 65$^\circ$ - 67$^\circ$ - 69$^\circ$ reaction) by the ideal gas method indicated 6.9 millimoles of compounds. Since the fraction was mostly COF$_2$ and CF$_4$, a reasonable approximation was that the average number of carbon atoms per molecule was one, so 6.9 millimoles of compounds equals 6.9 millimoles of carbon atoms. 0.744 g of starting hexafluoroacetone-ethylene copolymer was used (for the 65$^\circ$ - 67$^\circ$ - 69$^\circ$ reaction) which corresponds to 3.84 millimoles of repeating units or 19.2 millimoles of carbon atoms. The mole % yield based on carbon of the -196$^\circ$ fraction is, therefore, 35.9 %.

The -131$^\circ$ and -78$^\circ$ fractions contained the more interesting, higher molecular weight, perfluoro fragments. Analysis of these fractions obtained from each fragmentation reaction by Glc assay showed that striking differences in the composition of the fractions had resulted; comparison of the Glc printouts for the -78$^\circ$ fractions of the reactions illustrates the differences, see Figure 14. The yields, weight percents and mole percents of the compounds isolated from the -131$^\circ$ and -78$^\circ$ fractions from both reactions are listed in Table 11.

The data indicates that reaction at 75$^\circ$ produced primarily two volatile perfluoro species with only traces of other products, while the 65$^\circ$ - 67$^\circ$ - 69$^\circ$ reaction produced larger, isolable quantities of other interesting volatile species along with the two high-yield products. An important observation for the 65$^\circ$ - 67$^\circ$ - 69$^\circ$ reaction was that very
Figure 14

Glc Printouts of the -78°C Fractions of Volatile Products from the Fluorinations of (CH₂CH₂OC(CF₃)₂)ₙ
<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield Weight % of 131° (mg) and -78 Fractions - Starting Polymer†</th>
<th>75° Reaction</th>
<th>65° - 67° - 69° Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>131 - 10 *</td>
<td>258 - 40.2 - 16.8</td>
<td>201 - 41.3 - 17.6</td>
<td></td>
</tr>
<tr>
<td>131 - 22 *</td>
<td>24 - 3.7 - 1.7</td>
<td>19 - 3.9 - 1.9</td>
<td></td>
</tr>
<tr>
<td>78 - 30 **</td>
<td>7 - 1.1 - 0.5</td>
<td>15 - 3.1 - 1.4</td>
<td></td>
</tr>
<tr>
<td>78 - 56 **</td>
<td>191 - 29.8 - 13.2</td>
<td>123 - 25.3 - 11.5</td>
<td></td>
</tr>
<tr>
<td>78 - 64 **</td>
<td>13 - 2.0 - 0.9</td>
<td>13 - 2.6 - 1.3</td>
<td></td>
</tr>
<tr>
<td>78 - 92 **</td>
<td>trace</td>
<td>12 - 2.4 - 1.2</td>
<td></td>
</tr>
<tr>
<td>78 - 104 **</td>
<td>trace</td>
<td>47 - 9.7 - 4.5</td>
<td></td>
</tr>
<tr>
<td>Unseparated Material</td>
<td>148 - 23.1</td>
<td>57 - 11.7</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>641 100%</td>
<td>487 100%</td>
<td></td>
</tr>
</tbody>
</table>

* Glc Temperature Program: -50° for 12 min; 10° / min → 100°

** Glc Temperature Program: 0° for 10 min; 1° / min → 100°

† Calculation: (g compound) ÷ (MW compound) x (# carbon atoms in compound) = Moles of carbon atoms in compound

(Moles of carbon atoms in compound) ÷ (Moles of carbon atoms in starting polymer) = Mole % Yield

For 75° reaction - 1.003 g starting polymer = 25.85 millimoles carbon

For 69° reaction - 0.744 g starting polymer = 19.2 millimoles carbon
small quantities of volatile products were produced at the 65⁰ and 67⁰ temperatures; only when 69⁰ was reached did significant fragmentation and volatile product formation occur. Also noted was the fact that the 75⁰ reaction caused complete fragmentation of the substrate to volatile products and left essentially no solid residue, while from the 65⁰ - 67⁰ - 69⁰ reaction, 196 mg of solid product was obtained (which is described later). All of these observations indicate that a fragmentation threshold temperature exists between 65⁰C and 75⁰C, and careful control of the fragmentation temperature allows control over the types and amounts of volatile products that are produced.

The structures of the two compounds isolated from the -131⁰ fraction were readily determined by spectral analysis. The reactions' highest-yield compound, 131-10, was identified as perfluoroisobutane, (CF₃)₃CF, by a peak to peak match of the experimental infrared spectrum with a literature infrared spectrum. The identifying infrared absorption bands were (cm⁻¹): 1330 - 1260 (broad, strong, 3-peak pattern), 1200 (w), 1170 (m), 995 (s) and 730 (m). The ¹⁹F NMR spectrum of the compound confirmed the structure: CF₃ region - 76.3 ppm, doublet (J = 6 Hz); CF region - 190.1 ppm, dectet expected but only eight peaks clearly evident (J = 6 Hz); relative integrated intensities - 9 to 1.

The compound 131-22 was identified as (CF₃)₂CF₂C(O)F, perfluoroisovaleryl fluoride. Its infrared spectrum exhibited strong acyl fluoride (1890 cm⁻¹) and carbon-fluorine (1240 - 1330 cm⁻¹) stretches. The mass spectrum showed a parent minus fluorine peak at m/e 247 (C₅F₉O). The ¹⁹F NMR data was the most useful information for structure determination; the observed signals and their assignments were:
The acyl fluoride fluorine nucleus was not observed in the $^{19}F$ NMR spectrum, so the infrared spectrum was rerun for reaffirmation of the acyl fluoride group. No acyl fluoride absorption was observed, but an OH stretch (3580 cm$^{-1}$), two carbonyl stretches (1820 and 1780 cm$^{-1}$, assigned to the monomeric and associated forms of a carboxylic acid, respectively) and the same carbon-fluorine and "fingerprint" absorptions were observed. The rationalization is that poor vacuum line technique was used allowing water to be condensed with the sample which caused hydrolysis to $(CF_3)_2CFCF_2COOH$. The doublet splitting ($J = 5$ Hz) of the CF$_2$ is thought due to coupling with the CF. The CF was, therefore, coupled almost equally to the CF$_3$ groups ($J = 6$ Hz) and CF$_2$ group ($J = 5$ Hz), so a nonet with broad peaks would be expected; the peaks of the CF envelope were indeed broad but only the middle seven of the expected nine were clearly evident.

The five compounds isolated from the -78$^0$ fraction were spectrally identified as the structurally-novel, branched perfluoroethers expected from the reaction. Their infrared spectra were all similar in showing a strong, broad absorption in the carbon-fluorine and ether carbon-oxygen region (1350 - 1100 cm$^{-1}$) and the same strong, sharp absorptions in the "fingerprint" region at 1000 - 990 cm$^{-1}$, 900 - 890 cm$^{-1}$, 760 cm$^{-1}$ and 735 cm$^{-1}$. Each spectrum also exhibited other, weaker,
non-general signals on the fingerprint region. The infrared spectra were very similar to those obtained for the perfluoroethers produced from polyethylene oxide and polypropylene oxide polymers.

Mass spectrometry, as for the other perfluoroether projects, was useful for determining the molecular weights of the isolated compounds. The spectra were characterized, as usual, by extensive fragmentation, rearrangement and decreasing peak intensity with increasing mass. Only when the spectra were run with the ion source of the mass spectrometer cooled to room temperature were the informative high mass peaks up to and including the parent minus fluorine peak observed; the parent minus fluorine peaks for the five perfluoroethers are listed in Table 12. The common low-mass peaks were at m/e 31 (CF), 44 (CO₂), 47 (COF), 50 (CF₂), 69 (CF₃), 81 (C₂F₃), 93 (C₃F₃), 97 (C₂F₅O), 100 (C₂F₄), 119 (C₂F₅), 131 (C₃F₅), 150 (C₃F₆), 169 (C₃F₇), 181 (C₄F₇), 197 (C₄F₇O), 200 (C₄F₈), 219 (C₄F₉), 231 (C₅F₉), 235 (C₄F₉O), 247 (C₅F₉O), 269 (C₅F₁₁) and 285 (C₅F₁₁O). The common high-mass peaks from the higher molecular weight compounds were at m/e values corresponding to the empirical formulas \(C_nF_{2n-1}O_x\), \(C_nF_{2n}O_x\) and \(C_nF_{2n+1}O_x\) (x = 1 - 3). The presence of low intensity "two oxygen peaks" in the spectra of the monoethers and "three oxygen peaks" in the spectra of the diethers is evidence of a complicated rearrangement process. Again, the lack of peaks at m/e 51 (CF₂H) and 101 (C₂F₄H), the peaks always observed for highly fluorinated, hydrogen-containing compounds, proved the compounds were perfluoro.

\(^{19}\text{F}\) NMR analysis was, again, the most useful spectral method for structure determination. The perfluoroethers' \(^{19}\text{F}\) NMR signals, their assignments, observed relative intensities and theoretical relative inten-
TABLE 12

$^{19}$F NMR Data and Structures of Perfluoroethers from the Fluorination of Hexafluoroacetone-Ethylene Copolymer

<table>
<thead>
<tr>
<th>Compound / Glc Retention Time / Highest m/e in Mass Spec.</th>
<th>Assigned $^{19}$F NMR Data</th>
<th>Relative Intensities (Obs. to Theor.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CF}_3)_2\text{CFOC}_2\text{CF}_2\text{CF(CF}_3)_2$</td>
<td>a: 75.2 ppm octet ($J=8.5$)</td>
<td>16 to 6</td>
</tr>
<tr>
<td>b: 83.4 ppm $t$ ($J=5$)</td>
<td>16 to 6</td>
<td></td>
</tr>
<tr>
<td>c: 82.5 ppm $m$</td>
<td>6 to 2</td>
<td></td>
</tr>
<tr>
<td>d: 120.1 ppm septet ($J=11.5$)</td>
<td>5 to 2</td>
<td></td>
</tr>
<tr>
<td>e: 147.0 ppm $t$ ($J=22$)</td>
<td>3 to 1</td>
<td></td>
</tr>
<tr>
<td>f: 187.9 ppm $m$</td>
<td>2.5 to 1</td>
<td></td>
</tr>
<tr>
<td>Glc r. t.: 30</td>
<td>m/e: 435 ($\text{C}<em>8\text{F}</em>{17}0$), P-F</td>
<td></td>
</tr>
<tr>
<td>$(\text{CF}_3)_3\text{COCF}_2\text{CF}_2\text{CF(CF}_3)_2$</td>
<td>a: 72.9 ppm $t$ ($J=9.5$)</td>
<td>165 to 9</td>
</tr>
<tr>
<td>b: 75.2 ppm octet ($J=5.8$)</td>
<td>106 to 6</td>
<td></td>
</tr>
<tr>
<td>c: 81.8 ppm $m$</td>
<td>34 to 2</td>
<td></td>
</tr>
<tr>
<td>d: 119.7 ppm septet ($J=11.5$)</td>
<td>34 to 2</td>
<td></td>
</tr>
<tr>
<td>e: 188.0 ppm $m$</td>
<td>17 to 1</td>
<td></td>
</tr>
<tr>
<td>Glc r. t.: 56</td>
<td>m/e: 485 ($\text{C}<em>9\text{F}</em>{19}0$), P-F</td>
<td></td>
</tr>
<tr>
<td>$(\text{CF}_3)_2\text{CFOC}_2\text{CF}_2\text{C(CF}_3)_2\text{OCF}_2\text{CF}_3$</td>
<td>a: 72.3 ppm $m$</td>
<td>10 to 6</td>
</tr>
<tr>
<td>b: 84.0 ppm $t$ ($J=5$)</td>
<td>9 to 6</td>
<td></td>
</tr>
<tr>
<td>c: 88.1 ppm $m$</td>
<td>4 to 3</td>
<td></td>
</tr>
<tr>
<td>d: 73.6 ppm $m$</td>
<td>3 to 2</td>
<td></td>
</tr>
<tr>
<td>e: 89.0 ppm $m$</td>
<td>2.5 to 2</td>
<td></td>
</tr>
<tr>
<td>f: 118.9 ppm $m$</td>
<td>3 to 2</td>
<td></td>
</tr>
<tr>
<td>g: 146.5 ppm $t$ ($J=20$)</td>
<td>1.5 to 1</td>
<td></td>
</tr>
<tr>
<td>Glc r. t.: 64</td>
<td>m/e: 551 ($\text{C}<em>{10}\text{F}</em>{21}0_2$), P-F</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 12 (cont.)

<table>
<thead>
<tr>
<th>Compound / Glc Retention Time /</th>
<th>Highest m/e in Mass Spec.</th>
<th>Assigned $^{19}F$ NMR Data</th>
<th>Relative Intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$^{19}F$ NMR Data</td>
<td>Obs.</td>
</tr>
<tr>
<td>(CF$_3$)$_2$CFOCF$_2$CF$_2$C(CF$_3$)$_2$OCF$_2$CF$_2$CF(CF$_3$)$_2$</td>
<td>a: 69.7 ppm m</td>
<td>7.5</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>b: 74.8 ppm octet (J=5.8)</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>c: 82.9 ppm m</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>d: 71.9 ppm m</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>e: 80.3 ppm m</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>f: 116.3 ppm m</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>g: 118.7 ppm septet (J=11.5)</td>
<td>2.5</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>h: 147.0 ppm t (J=20)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>i: 187.7 ppm m</td>
<td>1.5</td>
<td>1</td>
</tr>
<tr>
<td>(CF$_3$)$_3$COCF$_2$CF$_2$C(CF$_3$)$_2$OCF$_2$CF$_2$CF(CF$_3$)$_2$</td>
<td>a: 69.8 ppm m</td>
<td>24</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>b: 72.3 ppm t (J=9.5)</td>
<td>35</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>c: 74.8 ppm octet (J=5.8)</td>
<td>25</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>d: 79.3 ppm m</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>e: 80.8 ppm m</td>
<td>7.5</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>f: 115.7 ppm m</td>
<td>7.5</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>g: 118.8 ppm septet (J=11.5)</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>h: 187.8 ppm m</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>
sities are listed in Table 12. The average chemical shifts of the various fluorine nuclei were as follows (in ppm from neat external CFCl$_3$):

- CF$_3$ of isopropyl end-groups 83.4
- CF$_3$ of t-butyl end-groups 72.6
- CF$_3$ of isoamyl end-groups 75.0
- Internal pendant CF$_3$ 70.6
- All CF$_2$-0 79.9
- All internal CF$_2$ 118.3
- CF of isopropyl end-groups 146.8
- CF of isoamyl end-groups 187.8

The fluorine-fluorine coupling patterns observed are good examples of the unpredictable and unusual coupling characteristics in $^{19}$F NMR spectroscopy. The CF$_3$ groups and CF of isopropyl end-groups do not couple to one another, but each couples to the nearest CF$_2$ "across" the oxygen with average coupling constants of 21 Hz and 5 Hz, respectively. The CF$_3$ groups of the tertiary-butyl groups also couple "across" the oxygen to the nearest CF$_2$ with a coupling constant of 9.5 Hz. The coupling observed for the signals of the isoamyl end-group was the most interesting; the internal CF$_2$ is always a septet with $J \approx 11.5$ Hz, and the CF$_3$ groups always appear as octets with $J \approx 5.8$ Hz. The explanation is that the six fluorines of the two CF$_3$ units couple to the internal CF$_2$ with $J \approx 11.5$ Hz (the internal CF$_2$ is coupled to no other nuclei, so it is a septet), and they also couple to the other three fluorines of the end-group equally and with exactly half the coupling constant of the internal CF$_2$ coupling, ie. $\approx 5.8$ Hz. The result for the CF$_3$ groups is a triplet ($J \approx 11.5$ Hz) of quartets ($J \approx 5.8$ Hz) which is indistinguishable from a 5.8 Hz octet. The signals for the other three fluorines of the isoamyl end-group and for all the fluorines of the internal $\text{-CF}_2\text{CF}_2\text{C(CF}_3\text{)}_2\text{O}$-groups appeared as broad unresolved multiplets, so no additional conclusions as to coupling trends can be made.
Physical characterization of the isolated perfluoroethers involved melting point and boiling point determinations. In attempts to measure melting points, the problem of freezing to glasses instead of crystalline powders occurred again for several of the samples. Therefore, the solid to liquid phase change temperatures for those samples are actually glass transition temperatures ($T_g$) instead of crystalline melting points. Boiling points could only be measured for two of the perfluoroethers because the others were not obtained in sufficient yields. The measured physical constants were:

<table>
<thead>
<tr>
<th>Compound</th>
<th>M. P.</th>
<th>B. P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(CF_3)_2COCF_2CF_2CF(CF_3)_2$</td>
<td>-120 ($T_g$)</td>
<td>-</td>
</tr>
<tr>
<td>$(CF_3)_3COCF_2CF_2CF(CF_3)_2$</td>
<td>-56 to -57.5</td>
<td>118.5 - 119.5</td>
</tr>
<tr>
<td>$(CF_3)_2CFOCF_2CF_2C(CF_3)_2OCF_2CF_3$</td>
<td>-110 ($T_g$)</td>
<td>-</td>
</tr>
<tr>
<td>$(CF_3)_2CFOUCF_2CF_2C(CF_3)_2OCF_2CF_2CF(CF_3)_2$</td>
<td>-95 ($T_g$)</td>
<td>-</td>
</tr>
<tr>
<td>$(CF_3)_3COCF_2CF_2C(CF_3)_2OCF_2CF_2CF(CF_3)_2$</td>
<td>-61 to -63</td>
<td>190.5 - 191.5</td>
</tr>
</tbody>
</table>

As stated previously, the fragmentation period of the 65° - 67° - 69° reaction did not convert all of the polymeric substrate to volatile products. A small amount (196 mg) of sticky, white powder remained in the reaction boat. Infrared analysis (KBr pellet) of the solid showed the usual strong broad carbon - fluorine and ether carbon - oxygen stretches at 1350 - 1100 cm⁻¹ with only very weak absorptions in the carbon - hydrogen (3000 cm⁻¹) and fluorocarbon acid (1800 cm⁻¹) regions. This suggests that the residue is more highly fluorinated than the product of the "pre-fluorination" phase of the reaction, but the perfluoro polymer still has not been obtained. $^{19}$F NMR end-group analysis was attempted in order to determine an average molecular weight for the material, but the solid was only very slightly soluble in the best solvent (CFCI₂CF₂Cl), and only very weak signals
attributable to the fluorines of the -CF₂CF₂C(CF₃)₂O- repeating unit were observed.

Discussion

Extensive experimentation for the "pre-fluorination" period indicated a highly fluorinated, functional polymer could be obtained, but perfluorination was not possible for the conditions used. Experimentation with other acyl fluoride (and other carbonyl group) containing substrates (see subsequent experimental sections) also indicated that perfluorination was not possible when the usual range of experimental conditions were applied. Hypotheses explaining these observations have been made and will be presented in later sections. In direct fluorination experiments on branched alkanes, Liu and Shimp have observed that hydrogens of -CH₂- moieties alpha to a carbon with pendant methyl groups are the most difficult hydrogens to replace with fluorine by direct fluorination. These other observations and the fact that the partially fluorinated hexafluoroacetone-ethylene copolymer contains both acyl fluoride groups and pendant methyl groups suggest that the residual hydrogens on this copolymer should be very difficult to replace with fluorine by direct fluorination.

The presence of large amounts of just three compounds, perfluoroisobutane, perfluoro-t-butyl-isoamyl ether and (CF₃)₂COCF₂CF₂C(CF₃)₂OCF₂CF₂CF(CF₃)₂ in the -131⁰ and -78⁰ fractions of the volatile products of the fragmentation reactions is consistent with a favored fragmentation mechanism. As stated earlier, acyl fluoride formation early on in the fluorination of the copolymer suggests chain cleavage at the branched-carbon - oxygen bond, ie.

\[ -\text{C(CF}_3\text{)}_2\text{O-CH}_2\text{-CH}_2\text{-} \xrightarrow{F_2} -\text{CF(CF}_3\text{)}_2 + \text{F-C-CH}_2\text{-} \]
Fragmentation at the same position in a perfluoro segment combined with carbonyl fluoride elimination would result in perfluoro-t-butyl and perfluoroisoamyl end-groups, ie.

\[-\text{O-CF}_2\text{-CF}_2\text{-C}([\text{CF}_3])_2\rightarrow\text{-O-CF}_2\text{-CF}_2\text{-C}([\text{CF}_3])_2\text{-O-} + \text{F}_2\rightarrow\]

\[-\text{O-CF}_2\text{-CF}_2\text{-CF}([\text{CF}_3])_2 + (\text{CF}_3)_2\text{C-O-} + \text{COF}_2\]

Therefore, fragmentation at every branched-carbon - oxygen bond would result in large amounts of perfluoroisobutane, fragmentation at every other branched-carbon - oxygen bond would result in large amounts of perfluoro-t-butyl-isoamyl ether, and fragmentation at every third branched-carbon - oxygen bond would result in \((\text{CF}_3)_3\text{COCF}_2\text{CF}_2\text{C}([\text{CF}_3])_2\text{OCF}_2\text{CF}_2\text{CF}([\text{CF}_3])_2\).

Another route to perfluoro-t-butyl end-groups would be decarboxylative fluorination of acyl fluoride terminated chains, ie.

\[-\text{OC}([\text{CF}_3])_2\text{CF}_2\text{C(O)F} \rightarrow \text{F}_2\rightarrow \text{-OC}([\text{CF}_3])_3 + \text{COF}_2\]

The small amounts of products with perfluoroisopropyl end-groups and the one compound with the perfluoroethyl end-group indicates a less favored fragmentation mechanism, cleavage at the branched-carbon - carbon bond, also occurs to a small extent, ie.

\[-\text{OC}([\text{CF}_3])_2\text{CF}_2\text{CF}_2\text{O} \rightarrow \text{F}_2\rightarrow \text{-OC}([\text{CF}_3])_2 + \text{CF}_3\text{CF}_2\text{O}^{-}\]

The absence of larger telomer polyethers from the volatile products is because the higher molecular weight compounds would not be volatile enough to pass from the reactor to the volatile product trap; further fragmentation would occur producing the smaller more volatile perfluoro fragments.

The fact that greases were obtained when the fluorination was started at higher than -50°C temperatures, indicated that extensive chain cleavage was occurring. Extensive chain cleavage resulted in shorter telomer mole-
cules which are expected to be oils or greases. Another factor exists that would cause "collapse" of a crystalline solid to a grease or amorphous solid even when the polymer chain is not cleaved. Chemical transformation through fluorination may disrupt the crystalline packing of the polymer substrate, so if a new crystalline form is not attained, the polymer would revert to an amorphous solid (if the temperature was below the material's glass transition temperature) or a grease. (See the General Discussion for additional elaboration on the crystalline state in direct fluorination.)

The synthesis of five new perfluoroethers, perfluoroisopropyl-isooamyl ether, perfluoro-t-butyl-isoamyl ether, perfluoro-2,6,6-trimethyl-3,7-dioxanonane, perfluoro-2,6,6,10-tetramethyl-3,7-dioxaundecane and perfluoro-2,2,6,6,10-pentamethyl-3,7-dioxaundecane, by the direct fluorination of hexafluoroacetone-ethylene copolymer proves that the method is useful for the production of otherwise unobtainable perfluoroethers. The reaction also further generalizes direct fluorination as a useful synthetic method for the production of perfluoroethers from hydrogen-containing polyether polymers.
Chapter 7

"Oxyfluorination" of Hexane
"Oxyfluorination" of Hexane

\[
\begin{align*}
\text{CH}_3-(\text{CH}_2)_4-\text{CH}_3 & \xrightarrow{\text{He} / \text{F}_2 / \text{O}_2} \text{Cryogenic Reactor} \quad \text{U} \quad \text{F-C-(CF}_2)_4-C-F \\
& + \quad \text{CF}_3-(\text{CF}_2)_4-C-F \\
& \xrightarrow{?} \quad \text{?}
\end{align*}
\]

Introduction

The development of direct fluorination as an alternative method for production of perfluorofunctional compounds would be a valuable addition to fluorocarbon technology. The combination of direct fluorination's utility in fluorinating complex structural skeletons and its potential for perfluorofunctional compounds makes the technique potentially useful for synthesis of perfluoro, structurally-complex, functional compounds that have never before been produced.

The successful fluorination by J. L. Adcock of pivaloyl fluoride and dimethylmalonyl difluoride, see Figure 4, show that further direct fluorination experiments with functional compounds are warranted. Other hydrocarbon acyl fluorides may be useful precursors for perfluorofunctional compounds by direct fluorination, but the applicability of direct fluorination to hydrocarbon substrates with other functional groups would be a better test of the generality of the technique. Unpublished results suggest that hydrocarbon carboxylic acids are not useful substrates for production of perfluorofunctional compounds by direct fluorination. The major problem with carboxylic acids is decarboxylation and perfluoroalkane production.

The suggested decarboxylation mechanism is:

\[
\text{R-C(O)OH} + \text{F}^* \rightarrow \text{HF} + \text{R-CO}_2^* \rightarrow \text{R}^* + \text{CO}_2
\]

Instead of investigating substrates with many different functional groups, other unpublished observations suggested a unique and general synthetic
route to perfluorofunctional compounds.

Direct fluorination of various alkanes has occasionally resulted in the production of minor amounts of compounds containing acyl fluoride groups. The presence of oxygen in the reaction apparatus and products could be due to any of three reasons: the presence of oxygen in the commercial-grade fluorine (<1%), a leak in the apparatus or back-diffusion of oxygen from the alumina scrubber to the reactor. A possible mechanism for acyl fluoride formation would be as follows:

\[
\begin{align*}
R-CH_3 & \overset{F^-}{\longrightarrow} R-CH_2^+ + HF \overset{F_2}{\longrightarrow} R-CH_2F + F^- \\
R-CH_2F & \overset{F^+}{\longrightarrow} R-CHF^+ + HF \\
R-CHF^+ & \overset{(0)}{\longrightarrow} R-CHFO^+ \\
R-CHFO^+ & \overset{F^+}{\longrightarrow} HF + (R-CFO^+) \rightarrow 0 R-C-F \\
OR & \overset{F^+}{\longrightarrow} (R-CHFOF) \overset{-HF}{\longrightarrow} R-C-F
\end{align*}
\]

Fluoroketones have not been observed along with the acyl fluoride compounds. Their absence is probably due to the instability of hypofluorites (a probable intermediate) in elemental fluorine or to ketone - carbonyl instability in fluorine.

The preceding observations have been developed to establish that in branched polymer systems "oxyfluorination", a direct fluorination with oxygen in the reaction gas mixture, results in the production of fluorocarbon polymers functionalized with pendant acyl fluoride groups. For the three types of carbon - hydrogen bonds in alkanes, methyl (-CH₃, primary), methylene (-CH₂-, secondary) and methine (-C-H, tertiary), the oxyfluorination reaction should result in acyl fluoride (-C(0)-F), difluoromethylene (-CF₂-) and fluoromethylene (-C-F) groups, respectively. A conclusive proof of this hypothesis would provide fluorocarbon chemists with a useful, new
technique for production of a wide range of structurally interesting per-
fluorofunctional compounds from the alkane of the same skeletal structure.

Although the greatest potential of oxyfluorination lies in the syn-
thesis of structurally unique perfluorofunctional compounds, proof of the
hypothesis by successfully oxyfluorinating any alkane would be a significant
development. In order to minimize any potential for structural fragmen-
tation or rearrangement and simplify product separation and analysis, the
simple alkane n-hexane was chosen for the first investigations of oxyfluor-
ination. The desired products were the perfluoro 6-carbon monoacyl fluoride,
perfluorocaproyl fluoride (CF$_3$-(CF$_2$)$_4$-COF), and the diacyl fluoride,
perfluoroadipoyl difluoride (FC(0)-(CF$_2$)$_4$-COF).

Experimental

The oxyfluorinations of n-hexane were performed in a 6-zone cryogenic
reactor. The volatile products were collected in a glass trap cooled by
liquid nitrogen, fractionated by trap-to-trap vacuum line techniques, and
pure compounds separated by Glc assay of the vacuum line fractions. The
separated compounds were analyzed by infrared, NMR and mass spectroscopy.

Numerous oxyfluorinations of n-hexane were performed. The project
was the first of my graduate career, and the results of the first several
experiments reflected my degree of experience. The first reactions were
run at temperatures of -130$^\circ$C and -120$^\circ$C which have been determined
to be too low for extensive fluorination to occur. Product analysis for
the first reaction did show, however, that acyl fluoride formation had
extensively occurred (IR: COF = 1880 - 1890 cm$^{-1}$) although the degree of
fluorination for the rest of the molecule was small.

When a couple of the first reactions inadvertently warmed to $\sim$-50$^\circ$C
when the liquid nitrogen coolant ran out, more extensive fluorination was observed. This fact suggested that temperature control was an important variable of the reaction, and more extensive fluorination could be achieved by use of higher temperatures. The useful temperatures were dictated by the physical properties of the starting compound, n-hexane, and the partially fluorinated intermediate compounds. The melting point of n-hexane is \(-95^\circ\text{C}\), so the highest starting temperature used was \(-105^\circ\text{C}\) which assured the crystalline state of the substrate. A useful technique for promoting further fluorination was to gradually increase the temperature as the reaction progressed. At significantly increased temperatures, however, the intermediate compounds would start to vaporize and pass out of the reactor, so the highest useful temperature was determined to be \(-50^\circ\text{C}\).

Since the first reactions showed that acyl fluoride formation was extensively occurring, and molecular oxygen is known to be a free-radical scavenger and, therefore, a possible inhibitor of direct fluorination, oxygen concentration in the reaction gas mixture is also an important variable. When only trace amounts of oxygen were used (as little as 1/10 cc/min or \(~2\%\) of the fluorine flow rate) acyl fluoride formation still extensively occurred, but perfluorination was still a problem. The strategy of using alternating periods of fluorine and oxygen, then only fluorine was less successful. Several experiments showed that acyl fluoride formation was minimal, and the end-carbons were fully fluorinated to \(-\text{CF}_3\) groups during the "only fluorine" periods.

A dozen oxyfluorination reactions of n-hexane were run using the improved conditions of only a trace of oxygen, the \(-105^\circ\text{C}\) starting temperature with step-wise increase as the reaction progressed, higher %
concentrations and flow rates of fluorine and longer total reaction times than for the first reactions. The results of the reactions were similar in showing more highly fluorinated acyl fluoride compounds, but the perfluoroacyl fluoride target compounds were not obtained. The specific conditions of each reaction were chosen so that the important variables, the rate of fluorine concentration increase and the rate of temperature increase, were systematically studied. The differences in reaction conditions were not reflected by differences in products, in fact, the products of all of these reactions were very similar in amount and composition. The reaction conditions listed below are representative of the conditions used in the experiments that resulted in the most highly fluorinated functional compounds obtained.

<table>
<thead>
<tr>
<th>He (cc/min)</th>
<th>F&lt;sub&gt;2&lt;/sub&gt; (cc/min)</th>
<th>O&lt;sub&gt;2&lt;/sub&gt; (cc/min)</th>
<th>Temp. (°C)</th>
<th>Time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.0</td>
<td>0.1</td>
<td>-105</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>2.0</td>
<td>0.1</td>
<td>-105</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td>0.1</td>
<td>-105</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>3.0</td>
<td>0.1</td>
<td>-95</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>3.0</td>
<td>0.1</td>
<td>-85</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>4.0</td>
<td>0.1</td>
<td>-75</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>5.0</td>
<td>0.1</td>
<td>-65</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>5.0</td>
<td>0.1</td>
<td>-55</td>
<td>1</td>
</tr>
</tbody>
</table>

The volatile products of the reactions were first separated by trap-to-trap fractionation on a vacuum line into three fractions, -196°, -95° (toluene slush) and -45° (chlorobenzene slush). The -196° fraction generally contained small amounts of small, trivial fluorocarbons formed by
minor fragmentation processes. The fraction was usually analyzed by infrared spectroscopy, then discarded. Compounds identified by their infrared spectra in the -196\(^{\circ}\) fraction were: \(\text{CF}_4\), \(\text{CF}_3\text{H}\), \(\text{COF}_2\), \(\text{CO}_2\), \(\text{CF}_3\text{OF}\), \(\text{C}_2\text{F}_6\), \(\text{C}_2\text{F}_5\text{H}\), \(\text{SiF}_4\) (from HF or \(\text{F}_2\) attack on the glass trap) and \(\text{SF}_6\) (an impurity in the fluorine). Three other compounds were isolated from several -196\(^{\circ}\) fractions by Glc assay of the higher molecular weight species that could be trapped at -131\(^{\circ}\) (pentane slush) in the vacuum line. The compounds, identified by their infrared and mass spectra, were \(\text{C}_3\text{F}_7\text{COF}\) and two isomers of \(\text{C}_2\text{F}_4\text{HCOF}\).

The -45\(^{\circ}\) fractions from all reactions were characterized by poor gas chromatographic separation and a significant amount of unreacted alkyl hydrogens as evidenced by infrared and mass spectra. The species that comprise the fraction were expected to be the highest in hydrogen content due to volatility considerations. If a series of compounds of the same carbon skeletal structure but varying degrees of fluorination are plotted with boiling point vs. compound mass, a boiling point maximum (or volatility minimum) is usually observed in the average mass area with the perhydro and perfluoro compounds exhibiting boiling point minimums.\(^75\) This observation is readily explained by the classical van der Waals and polar interaction considerations. All compounds obtained by the oxyfluorination of hexane would correspond to the higher than average and highest mass compounds of such a graph. The least fluorinated compounds obtained, therefore, would be the least volatile and trapped in the highest temperature slush bath used in the vacuum line fractionation. Quantitatively, the -45\(^{\circ}\) fractions usually contained approximately \(1/3\) of the volatile products of a reaction.
The -95°C fractions contained the most highly fluorinized products of the reactions and would have contained the perfluoroacyl fluoride target compounds if they had been formed. The fraction was extensively analyzed by Glc assay and infrared and mass spectral analysis of the separated compounds. The compounds are conveniently labeled by their Glc retention times and the spectral results of the commonly isolated compounds are summarized in Table 13. The Glc retention times and mass spectral results together provide experimental evidence of the concept that a more highly fluorinated compound exhibits a higher volatility.

Discussion

The fact that the target perfluoroacyl fluoride compounds were not produced was very disappointing. Success for these model compounds would have led to oxyfluorination experimentation on more interesting skeletal structures. Several reasons for the lack of success may be hypothesized with inductive electron withdrawal as the important concept.

In a highly fluorinated acyl fluoride compound with only one or several hydrogens remaining, those hydrogens would be rather electropositive due to inductive electron withdrawal by the rest of the fluorocarbon chain and the acyl fluoride group. The electropositive hydrogens would increase the required activation energy for the fluorination process as a consequence of the decreased local density and availability of the hydrogen electron. The electropositive hydrogen may also result in a favored conformation for the molecule. Ball and stick models show that for a linear monohydrofluoroacyl fluoride of six or more carbon atoms, conformations exist in which the remaining hydrogen is completely surrounded by the perfluoro sections of the molecule. Such a conformation may effectively shield the
TABLE 13

Compounds in the -95° Vacuum Line Fraction of Volatile Products from the Oxyfluorination of Hexane

<table>
<thead>
<tr>
<th>Gas Chromatograph Retention Time (min) *</th>
<th>Infrared Assignments **</th>
<th>Highest Mass Peak(s) of the Mass Spec. and Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>n-C₆F₁₄ (peak for peak match with lit. IR)</td>
<td>-</td>
</tr>
<tr>
<td>16.5</td>
<td>COF, -CO-, CF</td>
<td>219 - C₄F₉, 247 - C₅F₉O</td>
</tr>
<tr>
<td>24</td>
<td>COF, CF</td>
<td>201 - C₄F₇H</td>
</tr>
<tr>
<td>28.5</td>
<td>COF, CF</td>
<td>251 - C₅F₁₀H</td>
</tr>
<tr>
<td>44</td>
<td>COF, CF, CH</td>
<td>259 - C₆F₁₀O, 279 - C₆F₁₀HO</td>
</tr>
<tr>
<td>72</td>
<td>COF, CF, CH</td>
<td>130 - C₃F₄H₂O</td>
</tr>
<tr>
<td>75</td>
<td>COF, CF</td>
<td>183 - C₄F₇H</td>
</tr>
<tr>
<td>80</td>
<td>COF, CF, CH</td>
<td>233 - C₅F₉H</td>
</tr>
<tr>
<td>82</td>
<td>COF, CF, CH</td>
<td>195 - C₅F₇H</td>
</tr>
<tr>
<td>94</td>
<td>COF, CF, CH</td>
<td>233 - C₅F₉H₂, 245 - C₆F₉H₂</td>
</tr>
<tr>
<td>103</td>
<td>COF, CF, CH</td>
<td>197 - C₅F₇H₄ (C₄F₇O)</td>
</tr>
<tr>
<td>110</td>
<td>COF, CF, CH</td>
<td>215 - C₅F₆H₃, 227 - C₆F₉H₃</td>
</tr>
<tr>
<td>133</td>
<td>COF, CF, CH</td>
<td>143 - C₄F₄H₃O, 183 - C₄F₇H₂</td>
</tr>
</tbody>
</table>

* Temperature Program: 0° for 60 min; 1° / min → 30°; 30° for 60 min

** The CH absorption is very weak compared to the COF and CF absorptions. It sometimes is not observed in the infrared spectra of highly fluorinated acyl fluorides.
remaining hydrogen from fluorine molecules and radicals, thus prohibiting perfluorination.

Electropositive hydrogens in the presence of acyl fluoride groups raises the possibility of stabilization of the hydrogens toward fluorine through hydrogen bonding. Inter- and intramolecular hydrogen bonding may be visualized, ie.

\[
\begin{align*}
0 & \cdots \cdot - H & CF-R_f' \\
R_f-C-F & \cdots \cdot & R_f-C-F
\end{align*}
\]

and

\[
\begin{align*}
\cdots \cdot & CF \cdots \cdot \cdot - H & CF
\end{align*}
\]

Intramolecular hydrogen bonding between an acyl fluoride and a hydrogen on a carbon atom alpha to that acyl fluoride suggests that possible enol type resonance may account for hydrogen stabilization, ie.

\[
\begin{align*}
0 & \cdots \cdot - H & - O \\
R_f-CF-H-C-F & \cdots \cdot & R_f-CF-C-F
\end{align*}
\]

These hydrogen bonding possibilities further enhance the electropositive character of remaining hydrogens by stabilizing the partial-positive hydrogen nucleus which allows increased inductive withdrawal of the hydrogen electrons by the fluorocarbon chain. Again, as the positive character of the hydrogen increases, local electron density and availability decreases which may decrease the susceptibility to attack by fluorine.

The argument of an electropositive nature for the few remaining hydrogens may be supported by a curious experimental observation. Most of the highly fluorinated acyl fluorides, when handled by the usual vacuum transfer techniques, left a small amount of nonvolatile, white fluorocarbon solid on the walls of the vessel from which the compound was transferred. This is perhaps due to a self-condensation polymerization reaction in which the electropositive (or acidic) hydrogens react with the acyl
fluoride functionality to give a fluoropolyketone and a molecule of HF.

The gas chromatographic assay of the volatile products was characterized by a very large number of peaks and a significant amount of peak overlap. This can easily be explained by considering, first, the number of compounds possible due to varying degrees of fluorination and then, by considering the number of possible isomers for each empirical formula. For example, the empirical formula for the six-carbon, mono-hydro, mono-acyl fluoride (C₅F₁₀HCOF) accounts for five isomers, i.e. α-hydro, β-hydro, γ-hydro, etc.; the six-carbon, di-hydro, mono-acyl fluoride empirical formula accounts for fifteen more isomers, i.e. α,α-dihydro, α,β-, α,γ-, β,β-, etc.; the more remaining hydrogens, the more possible isomers. When it is then realized that each isomer may differ slightly in volatility and polar character (which effects the strength of adsorption to the stationary liquid phase of the column), the large number of peaks and significant peak overlap in the Glc assay is readily understood. Pure compounds were isolated by collecting only the tops of the peaks during Glc assay in order to minimize contamination due to peak overlap.

Structural identification through spectral analysis of the separated highly fluorinated acyl fluoride compounds would have been a significant achievement in itself. Exact structures, however, could not be elucidated because of complications that arose when the common spectral methods were applied to the produced fluorocarbons.

Infrared spectra were useful only for determination of the types of bonds present. Carbon - hydrogen (3000 - 2900 cm⁻¹), acyl fluoride (F-C- , 1880 - 1890 cm⁻¹) and carbon - fluorine (1300 - 1100 cm⁻¹) bonds along with the "fingerprint" absorptions (1000 - 600 cm⁻¹) were commonly observed.
Other absorptions noted were the carbon-fluorine overtone (near 2400 cm\(^{-1}\)) and an infrequent fluoroketone (∼1800 cm\(^{-1}\)). The infrared spectra of two highly fluorinated acyl fluorides are included in Figure 15 as representative of the many spectra that were recorded. The most important point to remember in interpreting infrared spectra of fluoroacyl fluorides is that the absence of alkyl hydrogens is not conclusively established by the absence of an absorption in the carbon-hydrogen stretching region (see General Discussion for further elaboration).

Little structural information could be obtained from the mass spectra of the fluoroacyl fluorides. Structural fragmentation and rearrangement was predominate which is common for many fluorocarbons. Extensive rearrangement prevented the piecing together of the fragment peaks for parent identification. An example of typical patterns observed, that emphasized rearrangement, was an acyl fluoride that exhibited peaks at m/e 219 (C\(_4\)F\(_9\)), 201 (C\(_4\)F\(_8\)H) and 183 (C\(_4\)F\(_7\)H\(_2\)). Clearly, these three peaks could not come from the same six-carbon acyl fluoride unless a rearrangement mechanism was operating. The most common m/e peaks observed for the highly fluorinated acyl fluorides were: 31 (CF), 32 (CFH), 33 (CH\(_2\)F), 47 (COF), 51 (CF\(_2\)H), 65 (C\(_2\)H\(_3\)F\(_2\)), 69 (CF\(_3\)), 82 (C\(_2\)HF\(_3\)), 83 (C\(_2\)H\(_2\)F\(_3\)), 95 (C\(_3\)H\(_2\)F\(_3\)), 97 (C\(_2\)F\(_3\)O), 100 (C\(_2\)F\(_4\)), 101 (C\(_2\)F\(_4\)H), 113 (C\(_2\)HF\(_4\)), 115 (C\(_3\)H\(_3\)F\(_4\)), 119 (C\(_2\)F\(_5\)), 127 (C\(_4\)H\(_3\)F\(_4\)), 131 (C\(_3\)F\(_5\)), 133 (C\(_3\)H\(_2\)F\(_5\)), 151 (C\(_3\)HF\(_6\)), 163 (C\(_4\)HF\(_6\)), 169 (C\(_3\)F\(_7\)), 181 (C\(_4\)F\(_7\)), 183 (C\(_4\)H\(_2\)F\(_7\)), 195 (C\(_5\)H\(_2\)F\(_7\)), 197 (C\(_5\)H\(_4\)F\(_7\) or C\(_4\)F\(_7\)O), 201 (C\(_4\)HF\(_8\)), 213 (C\(_5\)HF\(_8\)), 215 (C\(_5\)H\(_3\)F\(_8\)), 233 (C\(_5\)H\(_2\)F\(_9\)), 245 (C\(_6\)H\(_2\)F\(_9\)), 251 (C\(_5\)HF\(_{10}\)) and 263 (C\(_6\)HF\(_{10}\)). One piece of information conclusively established by the mass spectra was the presence or absence of hydrogens. The monohydro peaks 51 (CF\(_2\)H) and 101 (C\(_2\)F\(_4\)H) were always observed for hydrogen.
Figure 15

Infrared Spectra of Two Products from the "Oxyfluorination" of Hexane
containing species no matter what the structure or total number of hydrogens in the molecule.

\(^{19}\text{F}\) and \(^1\text{H}\) NMR was not at all applicable to structure determination of the produced compounds. \(^{19}\text{F}\) NMR, for fluoroorganic compounds in general, is characterized by fluorine-fluorine coupling over many bonds (up to seven) and, consequently, complicated multiplets and unresolved broad bands are commonly observed. The \(^{19}\text{F}\) NMR spectra of the rather simple fluorocarbons perfluoro-n-hexane and the target compound, octafluoroadipoyl difluoride, are included as examples in Figure 16. Similarly, extensive hydrogen-fluorine heteronuclear coupling complicates the \(^1\text{H}\) and \(^{19}\text{F}\) NMR spectra. For these reasons, the NMR spectra of the produced fluoroacyl fluorides were generally uninterpretable, so the relative positions of the fluorine and hydrogen nuclei and the exact molecular structures could not be determined. Two structures could be inferred from relatively simple NMR spectra and supporting mass spectral data; they were (\(^{19}\text{F}\) NMR reference - ext. \(\text{CF}_3\text{COOH}\) ):

- \(\text{CF}_3\text{CH}_2\text{COF}\)
  - Mass Spec.: 130 (P), 111 (P-H)
  - \(^1\text{H}\) NMR: \(= 3.2 \text{ (q)}\) \(J = 10 \text{ Hz}\)
  - \(^{19}\text{F}\) NMR: \(= -8.8 \text{ ppm (t)}\) \(J = 10 \text{ Hz}\)
    \(-121.2 \text{ ppm (m)}\)

- \(\text{CF}_3\text{CF}_2\text{-C}-\text{CF}_2\text{COF}\)
  - Mass Spec.: 251 (P-COF)
  - \(^1\text{H}\) NMR: not observed
  - \(^{19}\text{F}\) NMR: \(= 8.1 , 10.8 , 52.0 , 54.0 \text{ ppm (t)}\) \(J = 7\)
    \(-14\) \(\text{(m)}\) \(\text{(m)}\)
  - Rel. Int. 3 : 3 : 2 : 2
Typical $^{19}$F NMR Spectra for Perfluoro Organic Compounds

**Perfluorohexane**

$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$

- $a = 84.3$ ppm
- $b = 128.9$ ppm
- $c = 125.4$ ppm

**Octafluoro-adipoyl difluoride**

$\text{F-C-CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{-C-F}$

- $a = -20.6$ ppm
- $b = 121.3$ ppm
- $c = 125.3$ ppm
The branched structure may be questioned because spectro-quality n-hexane was used as the starting material and the acyl fluoride fluorine nucleus was not observed in the $^{19}\text{F}$ NMR spectrum.

The fact that the perfluoroacyl fluoride target compounds were not produced by the experimental conditions used does not preclude development of the "oxyfluorination" technique as a method for producing perfluoroacyl fluorides. The partially fluorinated acyl fluorides obtained could be recycled through the cryogenic reactor for complete fluorination. Other experimental conditions may be tried, and the continuing refinement of the experimental techniques and apparatus may eventually lead to a breakthrough.
Chapter 8

The Synthesis of Perfluoroethers from Hydrocarbon Polyesters
The Synthesis of Perfluoroethers from Hydrocarbon Polyesters

Introduction

Linear hydrocarbon polyesters are potential precursors for perfluoropolyethers through the use of direct fluorination and sulfur tetrafluoride reactions. Jim Adcock's successful perfluorination of ethyl acetate by direct fluorination\(^4\) suggests that other perfluoroesters and polyesters may be synthesized by direct fluorination. Reaction of perfluoroesters with \(SF_4\) should result in formation of perfluoroethers. The use of \(SF_4\) to convert carbonyls to \(CF_2\) was first reported by Smith\(^{38}\) and has been extensively studied by Sheppard.\(^{39}\) DePasquale\(^{41}\) has shown that reaction of \(SF_4\) with numerous low molecular weight, highly fluorinated monoesters produces high yields of the corresponding monoethers. The synthetic scheme which we sought to explore to perfluoropolyethers from hydrocarbon polyesters is, therefore:

\[
\begin{align*}
(-C(0)-R_h-C(0)-O-R_h-0-)_n & \xrightarrow{F_2} (-C(0)-R_f-C(0)-O-R_f-0-)_n \\
(-C(0)-R_f-C(0)-O-R_f-0-)_n & \xrightarrow{SF_4} (-CF_2-R_f-CF_2-O-R_f-0-)_n
\end{align*}
\]

Perfluoroesters are interesting compounds in their own right, and production by direct fluorination, isolation and characterization of such compounds would be a significant achievement for the technique and the experimentalist. The significance of this work is seen clearly in view of the current absence of any general method for producing perfluoroesters (see General Introduction). Perfluoroesters, however, are not of great interest for practical applications; the electron withdrawing perfluoro substituents cause the ester linkage to be extremely susceptible to hy-
drolysis, even by atmospheric moisture. Each perfluoroester linkage would be hydrolyzed by two molecules of water to two carboxylic acid end-groups as follows:

\[
-R_f^1-C(O)-O-CF_2-R_f^1 + H_2O \rightarrow R_f^1-COOH + (R_f^1-CF_2-OH)
\]

Our current interest in fluorinated esters lies in using them as intermediates for the syntheses of practically applicable perfluoroethers. We have shown that perfluoroethers and perfluoropolyethers can be produced by direct fluorination of hydrocarbon polyether polymers, but the method's generality is limited by the relatively few polyether polymers that are readily available. In order to produce many perfluoropolyethers with a wide variety of repeating units, numerous hydrocarbon polymer precursors with various repeating units must be available. Numerous hydrocarbon polyesters are, indeed, available. Successful development of the direct fluorination - SF₄ reaction scheme would allow production of perfluoropolyethers with any desired repeating unit, through proper choice of a hydrocarbon polyester starting material.

The first experiments for the project involved attempts to produce perfluoroesters from hydrocarbon esters by direct fluorination. Three linear polyesters, polybutylene adipate \((-C(O)-(CH_2)_4-C(O)-O-(CH_2)_4-O-)_n\), polyethylene succinate \((-C(O)-(CH_2)_2-C(O)-O-(CH_2)_2-O-)_n\) and polybutylene terephthalate \((-C(O)-C_6H_4-C(O)-O-(CH_2)_4-O-)_n\), were investigated. It was soon evident that direct fluorination of the polyesters in a room temperature reactor using, first, dilute fluorine, then step-wise increased concentrations of fluorine, and, finally, pure fluorine was not producing the desired perfluoropolyester polymers, but highly fluorinated, hydrogen-
containing polyesters. (The most useful reaction conditions for fluorinating polyesters are included in the experimental section.) Numerous additional experiments (see the table, next page) using pure fluorine for long times, pressurized pure fluorine and elevated temperatures were performed, but there was not a substantial increase in the degree of fluorination achieved. (Elevated temperature fluorinations generally resulted in chain fragmentation and volatile product formation.) This was disappointing because DePasquale’s very successful SF₄ reactions with highly fluorinated esters compared with Sheppard’s poor success with hydrocarbon esters, suggests that the more highly fluorinated the polyester substrate (perfluoroesters should be best), the better the SF₄ reaction will work.

The fact that perfluoroesters are not produced by direct fluorination of hydrocarbon polyesters using common reaction conditions may be explained by the same hypotheses advanced to explain the production of hydrofluoroacetyl fluorides in the Oxyfluorination project. The residual hydrogens would be electropositive due to electron withdrawing by the fluoro segments. The electropositive (or acidic) hydrogens may be stabilized by inter- and intramolecular hydrogen bonding to the ester carbonyls and possibly by enol tautomer structures. These hypotheses are at present only conjecture, and no conclusively supporting experimental evidence exists. A related experiment, the synthesis by direct fluorination of perfluoroethyl acetate (5% yield) and α-hydro tetrafluoroethyl trifluoroacetate (20% yield) from ethyl acetate,

Instead of abandoning the project because perfluoropolyesters were not produced in the first fluorination step, the overall synthetic scheme to perfluoroethers from hydrocarbon polyesters was altered. It was decided that the highly fluorinated polyesters that could be produced by direct fluorination would be useful substrates for the SF₄ reaction. Hydrofluoropolyethers should result, and perfluoroethers may be obtained by further direct fluorination of the SF₄ reaction product.

For the investigations of the SF₄ reaction and direct fluorination
of the SF$_4$ reaction product, one fluorinated polyester, polybutylene adipate was chosen. Successful results for this substrate would be a significant achievement, and the process could later be applied to other fluorinated polyesters. Fluorinated polybutylene adipate was chosen for the following reasons: 1) polybutylene adipate can be highly fluorinated at ambient temperatures while chain cleavage is minimal; 2) polybutylene adipate has a simple, nonbranched, alkyl backbone (no cyclic segments as in polybutylene terephthalate), so product analysis should be rather straightforward; and 3) polybutylene adipate best retains the finely-divided powdery state after "pre-fluorination" (a physical indication of minimal chain cleavage; polyethylene succinate is fluorinated to a tacky powder or viscous grease indicating significant chain cleavage), so fluorination should be uniform throughout the sample and its handling quite simple and without loss.

An important synthetic aspect of the SF$_4$ reaction is that DePasquale determined in his work with highly fluorinated esters that the reaction works best when anhydrous hydrogen fluoride is used in large amounts as a solvent and catalyst, and the reaction temperature is just below the critical temperature for HF, 188°C. Another relevant observation of his was that a low yield side reaction, ester cleavage to acyl fluorides also occurs. For example, C$_7$F$_{15}$CO$_2$CH$_2$C$_2$F$_5$ when treated with SF$_4$ gave C$_7$F$_{15}$CF$_2$OCH$_2$C$_2$F$_5$ in 92% yield and C$_7$F$_{15}$COF in <1% yield. In general his isolated products were ethers in >80% yield and acyl fluorides in <1% yield by weight. This side reaction is important when using a polymer substrate because shorter chain, acyl fluoride - terminated polyethers would result. (Further SF$_4$ reaction with the carbonyl of the
acyl fluoride terminus would result in \( \text{CF}_3 \) end-groups.) The hypothesized overall, three-step, synthetic scheme for producing perfluoropolyethers from polybutylene adipate is, therefore:

\[
(-\text{C}(\text{O})-(\text{CH}_2)_4-\text{C}(\text{O})-\text{O}-(\text{CH}_2)_4-\text{O}-)_x \xrightarrow{\text{F}_2, \text{amb.}} (-\text{C}(\text{O})-\text{C}_4\text{H}_m\text{F}_n-\text{C}(\text{O})-\text{O}-\text{C}_4\text{H}_p\text{F}_q-\text{O}-)_x
\]

\[m + n + p + q = 16, \quad n + q = 11\]

\[
(-\text{C}(\text{O})-\text{C}_4\text{H}_m\text{F}_n-\text{C}(\text{O})-\text{O}-\text{C}_4\text{H}_p\text{F}_q-\text{O}-)_x \xrightarrow{\text{SF}_4, \text{HF}, T = 185^\circ} (-\text{CF}_2-\text{C}_4\text{H}_m\text{F}_n-\text{CF}_2-\text{O}-\text{C}_4\text{H}_p\text{F}_q-\text{O}-)_y
\]

\[x > y, \quad \text{end-groups} = -\text{COF}, -\text{CF}_3\]

\[
(-\text{CF}_2-\text{C}_4\text{H}_m\text{F}_n-\text{CF}_2-\text{O}-\text{C}_4\text{H}_p\text{F}_q-\text{O}-)_y \xrightarrow{\text{F}_2, T > \text{amb.}} (-\text{(CF}_2)_6-\text{O}-(\text{CF}_2)_4-\text{O}-)_y
\]

**Experimental**

The first step of the scheme, fluorination of hydrocarbon polybutylene adipate (purchased from Eastman and sieved to a fine powder, <150 mesh) to highly fluorinated polyester, was performed in a room temperature reactor using the usual conditions of dilute fluorine followed by step-wise increased concentrations until pure fluorine conditions were reached. The most highly fluorinated polymer that could be obtained by ambient temperature fluorination had an average (by weight increase and elemental analysis) of 11 to 11.5 of the 16 hydrogens per repeating unit replaced with fluorine. Additional ambient temperature experiments using pressurized (up to 40 psi) pure fluorine as the last step and longer times were investigated, but the degree of polymer fluorination was not increased. The ambient temperature reaction conditions used to produce the highly fluorinated polyester were:

<table>
<thead>
<tr>
<th>( \text{He (cc/min)} )</th>
<th>( \text{F}_2 (\text{cc/min}) )</th>
<th>( \text{Time (days)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.0</td>
<td>3</td>
</tr>
</tbody>
</table>
When 2.482 g of polybutylene adipate was fluorinated at these conditions, 4.97 g of fluoropolymer was obtained. Elemental analysis indicated C - 27.12 % and F - 49.42 % (C_{10}F_{11.5}); the elemental analysis values for hydrogen and oxygen (oxygen not analyzed directly but assumed to be the balance of the compound, i.e. Oxygen % = 100% - C% - F% - H%) were unreasonably high, but since the product is hydrophilic and hydrolyzed by atmospheric moisture, and the samples were sent away for commercial analysis, the high values are not surprising. All handling of the hydrolytically sensitive hydrofluoropolyester product as done in the Na/K alloy-dried, Argon glove box.

The SF$_4$ reactions were performed in 25 and 30 cc stainless steel sampling cylinders with monel throttling valves, Hoke 3212M4M. The hydrofluoropolyester was weighed out and placed in the cylinder in the glove box. Using an all metal (brass, monel and stainless steel) extension of a vacuum line, the appropriate amount of anhydrous HF was drained from a translucent, graduated Kel-F cylinder into the cooled (0°C) sample cylinder. The required amount (usually a four to five-fold excess) of SF$_4$ was measured out in a standard volume by the ideal gas method and then, transferred by vacuum distillation into the cooled (-196°C) polyester / HF - containing sample cylinder. In a typical reaction, 0.80 g (2.0 millimoles of repeating unit; average molecular weight of the fluorinated polyester repeating unit ~400) of fluoropolyester, 1.77 g (16.3 milli-
moles) of SF₄ and \( n \sim 8 \text{ ml} \) of anhydrous HF were used in a 30 cc sample cylinder. The charged cylinder was heated and shaken throughout the reaction. The most successful reaction temperatures were 180 - 188°C, and all reaction times were 22 ± 2 hours.

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

The -196°C and -131°C fractions were shown by infrared analysis to contain mainly unreacted SF₄, SOF₂ and SiF₄. SOF₂ is the sulfur-containing by-product of carbonyl to CF₂ conversion by SF₄, and SiF₄ is due to glass etching by inefficient HF removal or HF-producing decomposition of metastable hydrofluoro products. Infrared analysis also indicated the presence of small amounts of fluoroacyl fluorides in the -131°C fraction, but separation of these low yield products from the large amount of toxic sulfur-containing species in the fraction would have been difficult, dangerous and of little consequence. The -78°C fraction contained (by IR) hydrofluoroacyl fluorides, but gas chromatographic analysis indicated it was a many component inseparable mixture. From 800 mg of
starting fluoropolyester, 163 mg (average of two reactions) of the -78\(^{\circ}\)C fraction of inseparable hydrofluoroacyl fluorides were produced. The volatile products of the SF\(_4\) reactions were analyzed only for two reactions because: separation and analysis of the fluoroorganic species would have been very difficult; the fluoroorganic species were hydrofluoroacyl fluorides from the competing ester-cleavage SF\(_4\) side reaction; and the reactions' higher yield, nonvolatile oil residue proved to be of considerably greater interest.

The nonvolatile oily product of the SF\(_4\) reaction was removed from the reaction cylinder by heating and shaking the cylinder with several 20 ml aliquots of Freon-113 (CFCl\(_2\)CF\(_2\)Cl). The obtained solution was filtered to remove scraps of pipe-thread-sealing teflon tape and some unusual small yellow spheres. The filtered solution was concentrated to approximately 1/4 its volume by distillation, and a small amount of some yellow needle-like crystals was filtered out. The remaining solution was further concentrated by distillation and the last bit of CFCl\(_2\)CF\(_2\)Cl solvent was removed by evaporation. A viscous gold-colored oil resulted. For 800 mg of starting fluoropolyester, and average of 500 mg of this oil was produced.

The unusual yellow balls and the yellow needle-like crystals each were analyzed by their melting points of 117 - 119\(^{\circ}\)C and solubilities in benzene and carbon disulfide to be elemental sulfur. Sulfur was obtained in amounts of 50 - 100 mg from the reactions. The production of elemental sulfur by the SF\(_4\) reaction has very interesting implications which will be dealt with in the Discussion section.

The viscous, nonvolatile oil was analyzed by infrared spectroscopy.
of a thin oil film cast on a KBr window from CFCl₂CF₂Cl solution. During its workup, no provision for the exclusion of atmospheric moisture was made, so any produced acyl fluoride end-groups or remaining fluoroester linkages would have been hydrolyzed to acid end-groups; see the hydrolysis reaction of perfluoroesters in the Introduction, p. 149. The infrared spectrum of an SF₄ produced oil is compared to the infrared spectrum of a hydrolyzed sample of starting fluoropolyester in Figure 17. (Starting fluoropolyester was hydrolyzed by making a THF slurry and exposing it to atmospheric moisture overnight; infrared samples were oil films cast from the resulting solution.) It is clearly evident from comparison of the relative intensities of the carbon-fluorine (~1200 cm⁻¹) and fluorocarbon acid (~1780 cm⁻¹) absorptions that the SF₄ treated material is lower in functional group content than the starting fluoropolyester. The SF₄ reaction, therefore, must have been successful in converting a significant number of ester linkages to ether linkages, i.e. carbonyl to CF₂, as expected. In the 3000 cm⁻¹ region, the broad unassociated acid OH absorption and the sharper carbon-hydrogen stretching absorption due to remaining hydrogens is observed; the weak carbonyl absorptions at 1600 - 1650 cm⁻¹ would be due to carboxylate anion end-groups. The SF₄ produced non-volatile oil, therefore, was concluded to be a mixture of functional, hydrofluoropolyethers. The lack of volatility and viscous, oily nature infers a relatively high molecular weight, and we were not able to develop a procedure to separate the mixture into discrete compounds. The practical value of these particular compounds would be limited because of their ability to dehydrofluorinate; their real value is that they are the immediate precursors to perfluoroethers and polyethers.
Figure 17

Fluorinated Polyester (hydrolyzed)

SF₄ - Treated Fluorinated Polyester

Infrared Spectra of Fluorinated Polybutylene Adipate and its Product from Reaction with SF₄
In order to obtain the desired perfluoroethers, the SF₄ - produced, functional, hydrofluoro, viscous oil was subject to additional fluorination. Nonvolatile, high molecular weight, functional (acyl fluoride) perfluoroethers should result from ambient temperature fluorination, but since conclusive proof of ether formation was desired and volatile compounds are more easily separated by gas chromatography and structurally identified by spectroscopic methods, high temperature, fragmentation fluorination was performed. High temperature fragmentation fluorination would be expected, according to the results of some other high temperature fluorination experiments, to be accompanied by decarboxylation and inert CF₃ end-group formation.

A sample of SF₄ - produced, functional, hydrofluoro oil was fluorinated in a room temperature - high temperature reactor, see General Experimental p. 41, at the following conditions:

<table>
<thead>
<tr>
<th>He (cc/min)</th>
<th>F₂ (cc/min)</th>
<th>Temp. (°C)</th>
<th>Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>2.0</td>
<td>amb.</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>4.0</td>
<td>amb.</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>4.0</td>
<td>50</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>4.0</td>
<td>65 - 70</td>
<td>36</td>
</tr>
</tbody>
</table>

The volatile products were first separated by vacuum line trap-to-trap fractionation into -196°, -131° and -78° fractions. The relatively large -196° fraction contained (by IR) mainly COF₂ and CF₄ from decarboxylation and chain end degradation, respectively. The very small -131° fraction contained (by IR) fluoroacyl fluorides.

The significant amount of higher molecular weight volatile compounds in the -78° fraction were separated by Glc assay. The isolated compounds
are listed by their Glc retention times in Table 14 along with their yields, melting points and highest m/e peaks in the mass spectra.

The isolated compounds were characterized and identified by infrared, $^{19}$F NMR and mass spectral analysis. All infrared spectra were very similar to each other and to the infrared spectra of other perfluoroethers, an example is included in Figure 18. They exhibited the usual strong, broad carbon - fluorine and ether carbon - oxygen absorptions at $1350 - 1100 \text{ cm}^{-1}$ and, also, all showed the same "fingerprint" region absorptions at $1000 \text{ cm}^{-1}$ (m), $900 \text{ cm}^{-1}$ (m) and $750 - 700 \text{ cm}^{-1}$ (m,broad). The $750 - 700 \text{ cm}^{-1}$ band is reminiscent of the broad band observed at $740 - 700 \text{ cm}^{-1}$ for hydrocarbon alkanes with four sequential methylene, $\text{CH}_2^-$, units.

The mass spectra were again very useful for determining the molecular weights and formulas; the highest mass peak in each spectrum corresponded to the parent minus fluorine fragment. The mass spectra were very similar to those of other perfluoroethers in showing extensive fragmentation and rearrangement and in exhibiting the informative high mass peaks only when the spectra were run with the ion source of the spectrometer cooled to ambient temperature. The mass spectra also showed the usual decreasing peak intensity with increasing mass. The common fragment peaks observed were at m/e values corresponding to the following empirical formulas: $C_nF_{2n+1}$ , $C_nF_{2n-1}$ , $C_nF_{2n+1}O$ and $C_nF_{2n-1}O$ for all compounds ($n = 1$ to # of carbon atoms in the compound) and $C_nF_{2n+1}O_2$ and $C_nF_{2n-1}O_2$ ($n > 10$) for the three diethers.

The $^{19}$F NMR signals for the isolated compounds were broad unresolved multiplets, but their chemical shifts and normalized integrated intensities were useful for structure elucidation. A representative $^{19}$F NMR spectrum
TABLE 14

Compounds Isolated from the -78° Fraction of the
Volatile Products from the Fluorination of the SF₄ Reaction Product

<table>
<thead>
<tr>
<th>Compound (Glc Retention Time*)</th>
<th>Yield (mg)</th>
<th>Wt. % of -78° Frac.</th>
<th>M. P. (°C)</th>
<th>Highest m/e in Mass Spec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>25</td>
<td>16.3</td>
<td>-115</td>
<td>435 (C₈F₁₇O)</td>
</tr>
<tr>
<td>51</td>
<td>32</td>
<td>20.9</td>
<td>-110</td>
<td>485 (C₉F₁₉O)</td>
</tr>
<tr>
<td>64</td>
<td>18</td>
<td>11.8</td>
<td>-100</td>
<td>535 (C₁₀F₂₁O)</td>
</tr>
<tr>
<td>77</td>
<td>16</td>
<td>10.5</td>
<td>-100</td>
<td>601 (C₁₁F₂₃O₂)</td>
</tr>
<tr>
<td>90</td>
<td>21</td>
<td>13.7</td>
<td>-95</td>
<td>651 (C₁₂F₂₅O₂)</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>6.5</td>
<td>-90</td>
<td>701 (C₁₃F₂₇O₂)</td>
</tr>
</tbody>
</table>

Unseparated Material 31 20.3
Total 153 100%

* Glc Temp. Program: 0° for 20 min, 1°/min → 100°, 10°/min → 185°
Figure 18: Typical Infrared and $^{19}$F NMR Spectra for the Perfluoroethers from Polybutylene Adipate

Infrared Spectrum of $C_3F_7OC_6F_{13}$

$^{19}$F NMR Spectrum of Nonvolatile Perfluoroether Mixture (shows all signals)
is included in Figure 18. The $^{19}$F NMR data is listed in Table 15 with
the deduced structures and signal assignments. The key to structure de-
termination was to conclusively establish the identity of one end-group
by a characteristic $^{19}$F NMR signal. CF$_3$CF$_2$CF$_2$O end-groups are definitely
indicated by a relatively sharp signal at ~133 ppm due to the internal
CF$_2$ (see the fluorinated Polypropylene Oxide NMR data) and CF$_3$CF$_2$O
end-groups by signals at ~90 ppm and ~91 ppm (relative intensities
3:2) for the CF$_3$ and CF$_2$ nuclei, respectively. No CF$_3$O end-groups,
characteristic shift of ~59 ppm, were observed. With an end-group estab-
lished, the mass spectrally - determined molecular formula and the struc-
ture of the starting material in mind, the structures were quickly eluci-
dated. For C$_3$F$_7$OC$_5$F$_{11}$, the NMR signal at 132.7 ppm implies an n-propyl
end-group, and the mass spectrum indicates a 9 carbon monoether. For
C$_4$F$_9$OC$_6$F$_{13}$, no end-group is readily identified by the $^{19}$F NMR spectrum,
but the mass spectrum indicates a 10 carbon monoether and this is the
only possible 10 carbon monoether from polybutylene adipate starting
material. For CF$_3$CF$_2$O(CF$_2$)$_4$OCF$_2$CF$_2$CF$_2$CF$_3$, the ethyl end-group is
indicated by the NMR signals at 89.8 ppm and 90.7 ppm and the mass
spectrum indicates an 11 carbon diether; it was distinguished from the
other possible 11 carbon, ethyl end-group, diether structure CF$_3$CF$_2$O-
-(CF$_2$)$_6$OCF$_2$CF$_2$CF$_3$ by the absence of a signal at 133 ppm for the internal
CF$_2$ of the n-propyl group. For C$_3$F$_7$O(CF$_2$)$_4$OC$_5$F$_{11}$, the NMR signal at
132.3 ppm indicates an n-propyl end-group and the mass spectrum indicates
a 12 carbon diether; it was distinguished from the possible C$_3$F$_7$O(CF$_2$)$_6$-
-OC$_3$F$_7$ structure because the relative intensity of the 132.3 ppm signal
was not great enough to account for two n-propyl end-groups. For the
**TABLE 15**

19\text{F} NMR Data and Structures for the Volatile Perfluoroethers from Polybutylene Adipate

<table>
<thead>
<tr>
<th>Compound</th>
<th>Assigned 19\text{F} NMR Data (Shift vs. ext. CFCl₃)</th>
<th>Relative Intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Obs.</td>
</tr>
<tr>
<td>CF₃CF₂CF₂OCF₂CF₂CF₂CF₂CF₂CF₃</td>
<td>a = 84.4, 85.6 ppm</td>
<td>14</td>
</tr>
<tr>
<td>a d a a a b c b a</td>
<td>b = 128.3, 129.0 ppm</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>c = 125.3 ppm</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>d = 132.7 ppm</td>
<td>2.5</td>
</tr>
<tr>
<td>(33)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF₃CF₂CF₂OCF₂CF₂CF₂CF₂CF₂CF₃</td>
<td>a = 84.3, 85.5 ppm</td>
<td>30</td>
</tr>
<tr>
<td>a d a a a b c c c a</td>
<td>b = 127.8, 128.9 ppm</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>c = 125.1 ppm</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>d = 132.6 ppm</td>
<td>4.5</td>
</tr>
<tr>
<td>(51)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF₃CF₂CF₂CF₂OCF₂CF₂CF₂CF₂CF₂CF₃</td>
<td>a = 83.9, 85.3 ppm</td>
<td>14.5</td>
</tr>
<tr>
<td>a b b a a b c c c b a</td>
<td>b = 127.5, 128.6 ppm</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>c = 124.5 ppm</td>
<td>5</td>
</tr>
<tr>
<td>(64)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF₃CF₂OCF₂CF₂CF₂OCF₂CF₂CF₂CF₂CF₂CF₃</td>
<td>a = 83.9, 85.3 ppm</td>
<td>12</td>
</tr>
<tr>
<td>d e a b b a a b c b a</td>
<td>b = 127.8, 128.4 ppm</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>c = 124.9 ppm</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>d = 89.8 ppm</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>e = 90.7 ppm</td>
<td>2</td>
</tr>
<tr>
<td>Compound</td>
<td>Assigned $^{19}$F NMR Data Relative Intensities</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>(Glc retention time)</td>
<td>(Shift vs. ext. CFCl$_3$)</td>
<td>Obs.</td>
</tr>
<tr>
<td>CF$_3$CF$_2$CF$_2$OCF$_2$CF$_2$CF$_2$OCF$_2$CF$_2$CF$_2$CF$_2$CF$_3$</td>
<td>a d a a b b a a b c b a</td>
<td>a = 84.0, 85.1 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b = 127.6, 128.4 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 124.4 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>d = 132.3 ppm</td>
</tr>
<tr>
<td>OR CF$_3$CF$_2$CF$_2$OCF$_2$CF$_2$CF$_2$OCF$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_3$</td>
<td>a d a a b b a a b c c b a</td>
<td>a = 83.9, 85.1 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b = 127.5, 128.4 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 124.5 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>d = 132.4 ppm</td>
</tr>
</tbody>
</table>
largest perfluoro compound isolated, \( \text{C}_{13}\text{F}_{28}\text{O}_2 \) by its mass spectrum, the NMR signal at 132.4 ppm implies an n-propyl end-group, but the two possible structures, \( \text{C}_3\text{F}_7\text{O} (\text{CF}_2)_4\text{OC}_6\text{F}_{13} \) and \( \text{C}_3\text{F}_7\text{O} (\text{CF}_2)_6\text{OC}_4\text{F}_9 \), cannot be distinguished by NMR analysis.

The structures, deduced by NMR end-group analysis and "building" the structure according to the mass spectral information and starting material structure, are confirmed by considering the assignments and integrated relative intensities of all of the \(^{19}\text{F} \) NMR signals. The observed relative intensities of the \( \text{CF}_3 \) and \( \text{CF}_2\text{O} \) signals, the signals due to \( \text{CF}_2 \) groups adjacent to \( \text{CF}_3 \) or \( \text{CF}_2\text{O} \) groups and the signals due to \( \text{CF}_2 \) groups one \( \text{CF}_2 \) removed from any \( \text{CF}_3 \) and \( \text{CF}_2\text{O} \) groups all closely correspond to the theoretical relative intensities for the deduced structures. More precise signal assignments for the two signals in the 84 - 86 ppm (\( \text{CF}_3 \) and \( \text{CF}_2\text{O} \)) region and the two signals in the 127 - 129 ppm (\( \text{CF}_2 \) adjacent to \( \text{CF}_3 \) or \( \text{CF}_2\text{O} \)) region were not attempted because they were not needed for structure determination. Precise assignments in those regions cannot be made with any degree of certainty because there is no other information such as resolvable coupling constants that would distinguish the various nuclei.

The fragmentation fluorination of the \( \text{SF}_4 \) reaction product was purposely of short duration so that all of the substrate was not fragmented to volatile species. Along with the volatile products just described, a nonvolatile, nonfunctional, viscous perfluoro oil was obtained. Its infrared spectrum (a thin oil film) was almost identical, even the sharp "fingerprint" absorptions, to those of the volatile perfluoroethers. The \(^{19}\text{F} \) NMR spectrum of the oil, "neat" or in \( \text{CFCl}_2\text{CF}_2\text{Cl} \) solution, was char-
acterized by very broad signals, and the observed signals were at the same
chemical shift values as the NMR signals for the isolated volatile per-
fluoroethers. These spectral results indicate the oil is also a mixture
of saturated perfluoropolyethers. The mixture's lack of volatility and
relatively high viscosity implies the compounds are simply of higher molec-
ular weight than the isolated volatile perfluoroethers. If pure compounds
were separated from this oily mixture, they would probably be perfluoro
tri-, tetra- and pentaethers.

Discussion
The results clearly show that perfluoroethers and perfluoropolyethers
can be synthesized by the three-step process, direct fluorination, reaction
with $\text{SF}_4$ and direct fluorination, using hydrocarbon polybutylene adipate
as the starting material. The success of the synthetic scheme is very
significant because if it is applied to other hydrocarbon polyesters, many
otherwise unobtainable perfluoropolyethers may be produced.

The production of elemental sulfur from the reaction of $\text{SF}_4$ with
the hydrofluoropolyester was completely unexpected. When $\text{SF}_4$ reacts with
a carbonyl to produce $\text{CF}_2$, the by-product sulfur-containing species is
$\text{SOF}_2$. Production of elemental sulfur from $\text{SF}_4$ requires a four electron
reduction. The only reducing species for $\text{SF}_4$ in the $\text{HF} - \text{SF}_4$ - hydro-
fluoropolyester system is the remaining hydrogens on the polyester. Our
proposed process for $\text{SF}_4$ reduction is $\text{SF}_4$ fluorination of carbon-
hydrogen bonds, ie.

$$R_f\text{-CHF-}R'_f + \text{SF}_4 \rightarrow R_f\text{-CF}_2\text{-}R'_f + \text{HF} + (\text{SF}_2),$$

with complete reduction of the unstable "$\text{SF}_2$" species to elemental sulfur.
through oxidation of additional SF$_4$, ie.

\[(SF_2) + SF_4 \rightarrow SF_6 + S^0\]

The proposed two electron reduction of "SF$_2" to $S^0$ through oxidation of SF$_4$ to SF$_6$ is substantiated by detection (by IR) of a small amount of SF$_6$ in the -196$^\circ$ fraction of the NaF - scrubbed volatile products of the SF$_4$ reaction. Further conclusions about the nature of the polyester's remaining hydrogens are suggested by this proposed fluorination process and the fact that a sample of monohydro-undecafluoro-neopentane was not perfluorinated by treatment with SF$_4$. (A steric problem could also occur for the neopentane compound.) The implication is that alkyl hydrogens must be actively acidic to be fluorinated by SF$_4$. Actively acidic hydrogens are accounted for by the hypotheses advanced for alkyl hydrogen stabilization to elemental fluorine in hydrofluorofunctional compounds, ie. inter- and intramolecular hydrogen bonding to carbonyl oxygens and enol tautomers. The net result of SF$_4$ reaction of hydrofluoropolysteres is a significant amount of ester carbonyl to CF$_2$ conversion and there appears to be an unexpected bonus of additional fluorination of some remaining alkyl hydrogens.

The production of predominately perfluoro n-propyl, n-butyl, n-pentyl and n-hexyl end-groups from the fragmentation - perfluorination step is consistent with the expected decarboxylation and ether fragmentation mechanisms. Decarboxylation of perfluoroacid - terminated species (any unreacted ester linkages and the acyl fluoride end-groups produced by the
SF₄ cleavage reaction were hydrolyzed in the workup) through fluorination would yield a molecule of carbon dioxide and the respective perfluoro n-propyl or n-pentyl end-group, ie.

\[ R_f-O-(CF_2)_n-CF_2-COOH \xrightarrow{F^+} HF + \left( R_f-CO_2^+ \right) \rightarrow R_f-O-(CF_2)_n-CF_3 \]
\[ \text{n} = 2 \text{ or } 4 + \text{CO}_2 \]

Fragmentation of the perfluoroether chains at the carbon-oxygen ether bonds would produce all four commonly observed end-groups and carbonyl fluoride as a by-product, ie.

\[ -OCF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_3O^- \xrightarrow{\Delta^2} -O-(CF_2)_3-CF_3 \]
\[ \text{COF}_2^- + CF_3-(CF_2)_4-O^- \]
\[ -OCF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_3O^- \xrightarrow{\Delta^2} -O-(CF_2)_2-CF_3 \]
\[ \text{COF}_2^- + CF_3-(CF_2)_5-O^- \]

Perfluoro n-butyl and n-hexyl end-groups could also be formed during the SF₄ reaction through cleavage of the ester linkage to acyl fluoride end-groups and SF₄ transformation of the acyl fluorides to CF₃ groups. Any C₂F₅O end-groups and C₃F₇O end-groups adjacent to -O(CF₂)₄O- segments must be attributed to chain cleavage at carbon-carbon bonds either during the initial fluorination of the polyester or during the final fragmentation - perfluorination step.

The most important future development for the process would be the ability to perfluorinate the polyester during the first fluorination step. A perfluoroester would be a far superior substrate for the SF₄ reaction. DePasquale obtained outstanding conversions to ethers by the SF₄ reaction of his very highly fluorinated monoesters. An SF₄ experiment using less fluorinated polybutylene adipate produced less nonvolatile oil and larger amounts of volatile fragment species, presumably by increased SF₄ cleavage
of the ester linkages. If perfluoropolyesters can be produced, high ester to ether conversion by $\text{SF}_4$ should be possible, thereby producing the target perfluoropolyethers with only a two-step process. The unavoidable amount of chain cleavage that would occur during $\text{SF}_4$ reaction, would result in the highly desirable acyl fluoride-terminated perfluoropolyethers as the main products. (Chemical manipulations of the functional perfluoropolyethers would be possible through the functional end-groups, so the materials may be useful as reactive monomers in extensive copolymer chemistry.) The third step, direct fluorination of the $\text{SF}_4$ product, would not be necessary for production of perfluoro products, but third-step direct fluorination would be useful as a decarboxylation method if inert end-groups were desired or as a fragmentation method if lower molecular weight polyethers were desired.
Chapter 9

General Discussion
General Discussion

All of the pertinent fluorination and fragmentation implications have been discussed where appropriate in the Discussion sections of the particular projects. This was done to simplify the necessary reference to the relevant experimental data. The subjects presented here will be a review of the utility and problems associated with the spectral methods, the processes and consequences due to the physical states of the fluorination substrates and suggestions for future work.

Spectral Methods

The infrared spectra were very useful for determining the types of bonding present in a sample. The common stretching absorptions observed (bond type and wavenumber in cm\(^{-1}\)) for the produced compounds were: associated OH, \(\sim3600\); unassociated OH, 3400 - 2900; carbon - hydrogen, 3000 - 2900; fluoroacyl fluoride carbonyl, 1890 - 1880; fluorocarboxylic acid carbonyl, \(\sim1780\); fluorocarboxylate carbonyl, 1650 - 1600; and carbon - fluorine and ether carbon - oxygen, 1300 - 1100. The common overtone absorptions observed were the fluoroacyl fluoride carbonyl overtone at 3800 - 3750 cm\(^{-1}\) and the carbon - fluorine overtone at 2500 - 2300 cm\(^{-1}\). Carbon - fluorine absorptions are always broad and intense, and since the carbon - oxygen ether absorption is in the same region, the absorptions in the 1300 - 1100 cm\(^{-1}\) region for the many fluoroethers synthesized were extremely broad and intense. The important factor to keep in mind concerning the carbon - hydrogen absorption region is that although the presence of carbon - hydrogen bonds is conclusively established by the presence of sharp absorptions at \(\sim3000\) cm\(^{-1}\), the absence
of absorption bands in the area is not conclusive proof of the absence of carbon-hydrogen bonds in fluorocarbon samples. The infrared stretching force constants for carbon-fluorine and acyl fluoride carbonyl bonds are much larger than the infrared stretching force constants for carbon-hydrogen bonds. If the strong carbon-fluorine and acyl fluoride absorptions are kept on scale, the weaker carbon-hydrogen absorptions are frequently not discernible. Therefore, the absence of carbon-hydrogen bonds, i.e. a perfluoro structure, must be proven by a different analytical method.

The best fluorocarbon infrared spectra are obtained from gaseous and liquid (thin films) samples; solid fluorocarbons do not give good spectra. Solid fluorocarbons are generally opaque, white materials, and they do not mix well when ground with KBr powder. When infrared samples of solids are prepared, opaque films and opaque KBr pellets are usually obtained. Opaque samples do not give good infrared spectra because they cut off light transmission at the high wavenumber end of the spectrum, and the infrared baseline becomes slanted. Good infrared spectra are usually obtained for gaseous and liquid samples, in fact, very small fluorocarbon molecules such as CF₄, COF₂ and C₂F₆ are routinely identified by their characteristic infrared spectra. The only problem with gaseous samples is that occasionally a sample is obtained that is unstable and decomposes with HF elimination. The evolved HF etches and clouds the gas cell walls and KBr windows which necessitates cleaning of the cell and repolishing of the KBr windows.

Mass spectrometry of the produced fluorocarbons was always characterized by extensive fragmentation and rearrangement. See the experimental sections.
for further elaboration and some unusual formulas that must be assigned
to peaks that are commonly observed. The probable reason for the observed
extensive fragmentation and rearrangement is that fluorocarbon cations are
generated which are very unstable species. The mass spectra were always
run with the ion source of the mass spectrometer cooled to ambient temper-
ature in the attempt to minimize the fragmentation and rearrangement pro-
cesses of the unstable fluorocarbon cations. Negative ion mass spectrom-
etry might have been a more applicable analytical method and would have
been investigated had it been available.

Since atom scrambling was so common for the mass spectra of fluoro-
carbons, structures could not be "pieced together" by consideration of the
successive fragment peaks. Fortunately, for all of the produced perfluoro-
ether compounds and most of the other perfluoro compounds, parent minus
fluorine peaks were observed as the highest mass peaks of the spectra which,
with the $^{19}$F NMR spectral data, were invaluable for structure elucidation.
The other useful information obtainable from the mass spectra was conclusive
proof as to the presence or absence of carbon - hydrogen bonds in the sample.
For all fluorocarbon compounds containing alkyl hydrogens, an intense peak
at m/e 51 ($\text{CF}_2\text{H}$) was observed in the mass spectrum, irrespective of the
actual structure of the compound.

$^{19}$F NMR spectroscopy was a useful analytical tool, but it has some
significant limitations. Its utility lies in the broad range of frequencies
over which signals are observed. The broad frequency range causes signals
of nuclei with similar magnetic environments to be well separated, so the
chemical shift values are very informative as to the exact structure of
the group causing the signal. Compilations of fluoro groups and their
chemical shift values\textsuperscript{77,79} are very useful for assigning specific structures to observed signals through their chemical shift values. With the accurate integrated intensities that can be obtained and the structural information from the chemical shift values, structure elucidation is usually possible without consideration of the signals' splitting patterns and coupling constants.

The most confusing aspect of \textsuperscript{19}F NMR is that fluorine - fluorine coupling is unpredictable, and the usual trends observed in \textsuperscript{1}H NMR coupling do not apply. A fluorine nucleus can couple to any, all or none of the fluorine nuclei that are anywhere from three to seven chemical bonds away. An excellent example is the end-groups of the perfluoroethers produced by the fluorination of polyethylene oxide; for CF\textsubscript{3}-O-CF\textsubscript{2}-, the CF\textsubscript{3} and CF\textsubscript{2} couple with a coupling constant of 9 - 10 Hz; for CF\textsubscript{3}-CF\textsubscript{2}-O-, no CF\textsubscript{3} - CF\textsubscript{2} coupling is observed. Another better example is the confusing but interpreted coupling observed in (CF\textsubscript{3})\textsubscript{2}CFCF\textsubscript{2}CF\textsubscript{2}0- end-groups of the volatile ethers formed by the fluorination of hexafluoroacetone-ethylene copolymer (see Chapter 6, Fluorination of Hexafluoroacetone-Ethylene Copolymer, p. 108). For most highly fluorinated organic compounds, each fluorine nucleus is coupled to many others with many different coupling constants, so broad, unresolved, second-order signals result. Whether the signals are broad, unresolved humps or well-resolved multiplets, assignment of adjacent groups through observed coupling is not possible in \textsuperscript{19}F NMR as it is in \textsuperscript{1}H NMR. Heteronuclear hydrogen - fluorine coupling is common in hydrofluoro compounds and is better behaved with geminal coupling being very large and coupling quickly decreasing with increasing separation. This additional coupling, however, usually serves to further complicate
the NMR spectra. The confusing coupling usually observed in $^{19}$F NMR spectra increases the significance of the precise structural information obtainable from the chemical shift values.

The type of sample used in $^{19}$F NMR analysis is very important; "neat" liquids are best. Solutions can be used but must be very concentrated in order to obtain good spectra. To this end, when the $^{19}$F NMR spectrum of a very small liquid sample was desired, the neat sample was condensed in a capillary, 3 mm or 4 mm tube in order to "stretch" the sample instead of preparing a solution. The thinner tubes were placed in regular thin-walled NMR tubes and the spectra were run. This usually caused the signals to be at slightly higher chemical shifts (probably caused by a change in the overall magnetic susceptibility due to more glass in the field), but the signals were always better resolved than those observed when using solutions. Since concentrated solutions are required for good $^{19}$F NMR spectra, a major problem exists for solid fluorocarbon samples. Organic fluorocarbon solids, particularly polymers, are notoriously insoluble in most any solvent. Sufficiently concentrated solutions for $^{19}$F NMR analysis, therefore, frequently cannot be prepared. This unsolved solubility problem causes difficulties not only for $^{19}$F NMR analysis, but also for separation and purification of organic fluorocarbon solids.

Physical States of Fluorination Substrates

In the direct fluorination of a hydrocarbon substrate, the fluorine molecules must diffuse into the substrate, react with the carbon-hydrogen bonds and the HF produced must diffuse out. The relative success of any fluorination, therefore, is somewhat related to the ease with which the gases diffuse through the substrate.
Most of the successful direct fluorinations have utilized solid substrates, either room temperature solids or room temperature liquids that have been frozen to solids at cryogenic temperatures, as the starting materials. On a macroscopic level, gas diffusion is made easier by using the starting material in its finely-divided powder form. Solids can be recrystallized or ground and sieved to a fine powder; liquids can be frozen as fine powders if their highly diluted vapors are "blown" into an area whose temperature is much lower than the liquids' melting point and the vapors "snow" out. Use of a finely-divided powder maximizes the surface area per unit weight which would favor the heterogeneous gas-solid reaction.

A more important consideration for the heterogeneous gas-solid reaction is the microscopic level, i.e., the molecular packing of the substrate. Although small particle size increases gas-solid contact, each particle is made up of a massive network of molecules, and extensive and uniform reaction is dependent upon gas diffusion into the particles. Basically, two types of molecular packing exist, crystalline and amorphous, and therein lies the relevant gas-solid contact and diffusion considerations and differences.

For an amorphous solid material, the molecules or polymer chains are "arranged" in a haphazard manner, so packing is inefficient, and numerous spaces and channels with no solid molecules exist. Gas molecules would easily diffuse through those spaces and channels, so high gas mobility and gas-solid contact would exist on a microscopic level. Such a situation would be extremely favorable for heterogeneous gas-solid reaction, and extensive and uniform reaction should occur.

For crystalline solid small molecules (crystalline polymers are con-
sidered below), the crystal is a group of molecules with each molecule in a favored orientation with respect to its neighbors. Such an arrangement favors a high packing density and leaves no room for gas molecule diffusion. Gas-solid contact and heterogeneous reaction would, therefore, be at first limited to the molecules on the surfaces of each crystal. For uniform and extensive reaction to occur, surface reaction must disrupt the crystalline packing around each reacted molecule producing amorphous material and allowing gas diffusion to previously unexposed substrate molecules. The new crystal surfaces must continue to react and "decrystallize" to amorphous material so all substrate molecules could experience gas contact and reaction. If crystalline packing is not disrupted for the surface molecules after reaction, gas diffusion to and reaction with the crystals' interior molecules would be prevented by a crystal surface of reacted molecules. For direct fluorination, a very unusual compound and crystal structure would be required for reaction not to disrupt the crystalline structure, so crystalline material would become amorphous through reaction. Therefore, all starting solids, amorphous and crystalline, are expected to be reacted uniformly and extensively by direct fluorination.

The term "crystalline polymer" actually is a bit of a misnomer because such a material is in reality comprised of amorphous and crystalline sections. In the crystalline sections, the polymer chains are aligned and oriented in a favored packing conformation. The chains, however, do not end at the edge of the crystal but continue into a region of no alignment and orientation, the amorphous section. For any given polymer chain, its segments may be included in many different crystalline and amorphous sections including doublebacks that would include the same chain in the same crys-
talline section two or more tomes. Gas diffusion and heterogeneous gas-solid reaction for the amorphous regions would be straightforward, and the same arguments that were advanced for reaction of crystalline small molecules would apply to the crystalline sections of polymers. A physical observation that supports the suggestion of disruption of crystals to amorphous material by reaction is when "crystalline polymers" are fluorinated, the sample boats always appeared much fuller after reaction than before. This is simply explained by the fact that crystalline material is more dense than amorphous material.

For an oil substrate, as in the Polypropylene Oxide fluorination, the material is amorphous, so gas diffusion into the substrate is possible. The major problem for oils is extensive gas contact to substrate is limited due to the low surface area per unit weight. Another important problem for oils is the mobility of the molecules; this allows substrate radical combination so polymer crosslinking and network polymer formation can occur.

Another possible fluorination starting material is a solution of substrate in a solvent that is inert to elemental fluorine. A solution is amorphous, and since it is generally less viscous than an oil, gas diffusion into the solution should be appreciable. The problems due to low surface area and substrate mobility allowing radical combination would still exist. New problems that could occur would be solvent grafting onto the substrate if the solvent is not completely inert to fluorine, and as the substrate becomes highly fluorinated, solvation of the hydrofluoro intermediates may be decreased. The major problem for fluorination of solutions is that few solvents that are completely inert to elemental fluorine exist, and the solvent characteristics of those solvents are
very poor.

Future Work

From the very successful results of the direct fluorinations of hydrocarbon polyether polymers, it is clear that a general method for the production of perfluoropolyethers has been established. Further fluorinations of hydrocarbon polyether polymers are necessary only if specific perfluoroether structures are desired, and suitable hydrocarbon precursors can be prepared.

The production of perfluoroethers from polybutylene adipate by the three-step scheme, direct fluorination, reaction with SF\(_4\) and further direct fluorination, opens a new area for direct fluorination that should prove very fruitful for the production of perfluoroethers. Other linear hydrocarbon polyesters should be investigated to prove the expected generality of the scheme. The scheme should also be investigated for hydrocarbon pendant polyester starting materials as precursors for perfluoro pendant ether polymers. A potential bonus from the SF\(_4\) reaction step is the SF\(_4\) side-reaction, cleavage of a small percentage of ester groups to acyl fluorides. Additional experimentation may lead to use of the scheme for production of perfluoroether functional compounds, linear and pendant. The perfluoroether functional compounds are highly desirable because of the possible subsequent chemical manipulations through the functional group; nonfunctional perfluoroethers are chemically very inert.

Since functional perfluoroethers are highly desirable and most claims concerning the outstanding chemical stability of the perfluoroether linkage were made 25 - 30 years ago, several reactions that could have led to perfluoroether cleavage with functional group formation were investigated.
The fluorination of polyethylene oxide produces not only volatile perfluoroethylene glycol ethers, but also a high yield of perfluoroethylene oxide polymer; this perfluoroether polymer was used as the substrate for the potential ether cleavage - functional group forming reactions. Since the perfluoroalkoxide ion should be a good leaving group, reflux in ethanol-olic sodium ethoxide overnight may cleave a perfluoroether linkage; there was no effect. In preparing the fluoropolymer by direct fluorination, a very very small number of alkyl hydrogens may have been left intact; reflux with ethanolic KOH or ethanol / THF / KOH should dehydrofluorinate the polymer at the residual hydrogen, producing an olefin, which could be cleaved by KMnO₄ to produce functional polyethers; there was no effect, so the polymer was indeed completely fluorinated. Hydrocarbon ethers are classically cleaved by refluxing in aqueous hydrogen halide acids; the perfluoropolyether was not effected. An anhydrous hydrogen halide with a Lewis acid catalyst, such as HBr / AlBr₃, could have been the stronger acid system needed to cleave the perfluoroether linkage; there was no effect. Even the superacid system SbF₅ / anhydrous HF had no effect on the perfluoropolyether. These result confirm the outstanding chemical stability of perfluoroether linkages, and no additional experimentation is warranted. The stability is undoubtedly due to the high bond strengths in perfluoroethers and effective stereochemical shielding by the fluorine atoms.

The most significant future development for direct fluorination in organic chemistry would be the ability to produce perfluorofunctional compounds through oxyfluorination or fluorination of suitable functional hydrocarbons. Recent experimentation along those lines, using reaction
conditions similar to those suitable for synthesis of perfluoroalkanes and perfluoroethers, has not been successful. Adcock was successful in producing several specific perfluorofunctional compounds by direct fluorination, and generalization of the method is a reasonable expectation. Further experimentation may lead to an innovative experimental concept or design that will allow a breakthrough in the area. The use of polymeric substrates and high temperature - chain cleavage fluorination in this work can be considered an innovative concept, and other new ideas for direct fluorination are limited only by the creativity of the experimentalists.

The most unfortunate aspect of elemental fluorine as a chemical reagent is that too many chemists prefer to work "without recourse to elemental fluorine." Their ideas have been prejudiced by those before them, and they fail to realize that elemental fluorine, when properly handled, is no more dangerous or difficult to work with than any other toxic gas. The point that must be stressed is the great utility of elemental fluorine and direct fluorination. Direct fluorination is useful for preparing many types of compounds, from high-valence metal fluorides (SbF$_5$ was prepared from SbF$_3$ and SeF$_4$ from elemental Se in nearly quantitative yields during the course of this work) to fluoroorganometallics to perfluoroethers and perfluoroalkanes, straight-chain, branched or cyclic. The method is especially suited for polymer and materials research. Significant progress has been made with direct fluorination in the past decade, and its limitations have yet to be established.
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