THE DEVELOPMENT OF STRUCTURAL ADHESIVE SYSTEMS SUITABLE FOR USE WITH LIQUID OXYGEN

By

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FOREWORD

This report was prepared by Whittaker Corporation, Narmco Research & Development Division, under Contract No. NAS 8-11068, Control No. 1-5-54-01174(1F), entitled "The Development of Structural Adhesive Systems Suitable for Use with Liquid Oxygen," for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the direction of the Propulsion and Vehicle Engineering Division, Engineering Materials Branch, with Dr. W. E. Hill acting as project officer. The research work was conducted in Narmco's laboratory by Dr. Jerome Hollander and Mr. Floyd D. Trischler, Senior Research Chemists, Mr. Edward S. Harrison, Research Chemist and Mr. Robert M. DeBorde, Research Technician. Also contributing to the research were Mr. Richard T. Rafter, Mr. Phillip N. Crabtree, Mrs. Beatrix Y. Sanders, and Mr. Jerry L. Kerkmeyer, Research Chemists. Dr. Jerome Hollander served as program manager. This report covers the period 1 July 1965 to 30 June 1966.

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ABSTRACT

Six new highly halogenated polyurethanes, two new polyethers, two new polycarbonates, and one new polyester have been synthesized. In addition, five polyurethanes prepared previously were synthesized again. Most of these polymers were tested for liquid oxygen (LOX) compatibility.

The results indicate that urethanes based on 1,1-dihydroperfluoroalcohols are stable to impact in LOX if the nitrogen atom is also attached to a 1,1-dihydroperfluoroalkyl chain, but lack LOX stability if attached to a non-fluorinated alkyl chain or a benzyl methylene group.

The results also indicate that the specimen thickness seems to have no effect on the LOX sensitivity of compatible polyurethanes.

A new polyether from chloropentafluoroisopropyl alcohol was LOX compatible. Polycarbonates and nonfluorinated aromatic-based polyesters were shown to be LOX incompatible.

Three interesting polyether systems were synthesized which show real promise of being converted into hydroxyl-terminated prepolymers. These polyethers were prepared from hexafluorobenzene and hexafluoropentanediol, from chloropentafluoroisopropyl alcohol, and from the reaction of a fluoroalkyl polycarbonate with sulfur tetrafluoride.

Preparations and synthetic studies were carried out on a number of additional monomers and intermediates.

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I. SUMMARY

The purpose of this investigation is to develop structural adhesive systems suitable for use in contact with liquid oxygen (LOX). The scope of the work includes the preparation of a variety of highly halogenated polymers, with major emphasis placed on polyurethanes.

The LOX compatibility results obtained on polymers sent to George C. Marshall Space Flight Center (MSFC) show that the urethane linkage flanked on the alcohol side by a 1,1-dihydroperfluoroalkyl chain is stable to impact in LOX if the nitrogen atom is also attached to a 1,1-dihydroperfluoroalkyl chain, but not if it is attached to a nonfluorinated alkyl chain or a benzyl methylene group. Another conclusion drawn from the results is that the thickness of the specimens tested seems to have no effect on the LOX sensitivity of those fluorinated polyurethanes that are truly LOX compatible. A promising new polyether, prepared from chloropentafluoroisopropyl alcohol, is LOX compatible. Two types of polymers have been shown to be LOX incompatible, polycarbonates and nonfluorinated aromatic-based polyesters.

High and low molecular weight, hydroxyl-terminated polyurethanes were synthesized from hexafluoropentamethylene bischloroformate and hexafluoro-1,5-pentanediamine. Polyurethanes were also prepared by reaction of hexafluoropentanediol with tetrafluoro-m-phenylene diisocyanate and tetrachloro-p-xylylene diisocyanates. The reactions of tetrafluoro-p-hydroquinone with tetrafluoro-m-phenylene diisocyanate and of tetrafluoro-p-phenylene bischloroformate with hexafluoro-1,5-pentanediamine yielded the corresponding polyurethanes. Promising new polyurethanes were prepared by reaction of the polyether of chloropentafluoroisopropyl alcohol with tetrafluoro-m- and -p-phenylene diisocyanates.

Polyurethanes, previously prepared during this program by reaction of tetrafluoro-p-phenylene diisocyanate with hexafluoropentanediol, poly(3,3,3-trifluoropropylene oxide), and poly(hexafluoropentamethylene carbonate), were prepared again for LOX testing. Also prepared for additional LOX testing was the polyether of hexamethylene diisocyanate and hexafluoropentanediol.

Two new polycarbonates prepared were poly(tetrafluoro-p-phenylene carbonate) and poly(hexafluoropentamethylene tetrafluoro-p-phenylene carbonate).

High and low molecular weight polyethers were prepared from hexafluorobenzene and hexafluoropentanediol. A considerable amount of work was expended on the preparation of a hydroxyl-terminated prepolymer, and indications are that this polyether system is quite promising.

Attempts to prepare polyethers from hexafluoropentanediol by reaction with perfluorobutadiene and with perfluoro-1,4-pentadiene were unsuccessful. Attempts were also made to prepare poly(hexafluoropentamethylene ether).

The reaction of poly(hexafluoropentamethylene carbonate) with sulfur tetrafluoride seems to have yielded a promising new polyether.

Interesting new polyethers were prepared by reaction of chloropentafluoroisopropyl alcohol with sodium hydroxide and with the monosodium salt of hexafluoropentanediol.

Monomers and intermediates prepared for the first time include tetrafluoro-p-phenylene bischloroformate, tetrafluoro-m-phenylene diisocyanate, 1,5-diiodohexafluoropentane, diethyl-2,2,8,8-tetracarboethoxy-3,7-diketo-4,4,5,5,6,6-hexafluoroazelate, the monoacetal of hexafluoropentanediol and dihydropyran, chloropentafluoroisopropyl alcohol, and N,N'-dipentafluorophenyl-perfluoroglutaramide.

II. INTRODUCTION

The present and proposed use of LOX in space vehicles has created an urgent requirement for materials which are compatible with LOX. This requirement exists in many areas of application including coatings, elastomers, and adhesives. The development of LOX-compatible adhesives which have structural utility at cryogenic temperatures is especially desired to achieve certain critical bonding operations in vehicles using LOX.

The development of such adhesives depends entirely on the availability of suitable polymers which offer resistance to LOX. Prior to this contract, such polymers were not available. Thus, a fundamental program of polymer synthesis was essential to the development of a LOX-compatible adhesive.

The intent of the program is to develop polymers which will be especially suited to the formulation of adhesive systems. The application of these polymers will not be limited to adhesives, however.

The outstanding characteristics of polyurethanes in elastomers and adhesives for cryogenic application have been observed by several investigators. Highly fluorinated polymers, including Teflon, Kel-F, etc., have also demonstrated cryogenic capability. Although these available materials (such as Teflon) form excellent bonds which offer LOX compatibility and good cryogenic performance, the processing conditions required are prohibitive. Polyurethanes show greater utility in that they can be cured under mild conditions, or even of curing at ambient temperature. Coupling this processing requirement with the need for good cryogenic performance and LOX compatibility leads to the highly halogenated polyurethanes as the most logical polymer system.

Thus, it is most likely that the highly halogenated polyurethanes will prove to be the optimum system for use in LOX at cryogenic temperatures. The chance that another polymer having a carbon backbone will offer an improvement over such a system does not appear to be sufficiently favorable to present an immediate solution to the problem. This view is based on an analysis of polymers which have received attention but have not demonstrated any sign of real improvement in cryogenic properties; included are the vinylidene fluoride — tetrafluoroethylene copolymers, nitrosotrifluoromethane-tetrafluoroethylene copolymers, perfluoroamidines, and the whole class of perfluorohydrocarbons. Therefore, major emphasis during this program has been placed on the preparation of highly halogenated polyurethanes and the monomers required for their preparation.

A lesser amount of work has been directed toward the preparation of highly halogenated analogs of other common polymers, such as polyamides, polyimides, and polyureas, which have demonstrated some particular characteristics in adhesive formulations.

From a fundamental standpoint, the research has been carried out to obtain basic information regarding the LOX compatibility of polymers. The information required includes the following.

(1) The type and level of halogen content necessary to impart LOX compatibility to candidate polymers

(2) The effect of different functional groups and other structural features on the LOX compatibility of various polymers with similar halogen content

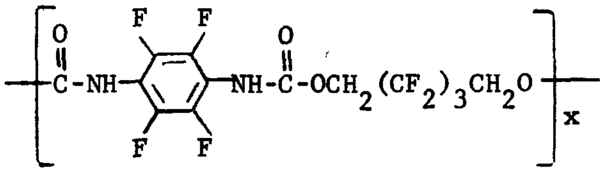
The polymers prepared during this program have been designed to obtain the most basic information of the nature described above. This information will be useful in the design and preparation of an improved LOX-compatible adhesive.

III. DISCUSSION

A. Liquid Oxygen Compatibility

During the current report period, thirteen polymers were prepared and tested for LOX compatibility. The results are shown in tabular form in Section IV.

The three polymers shown below passed the LOX impact test.



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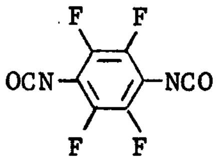
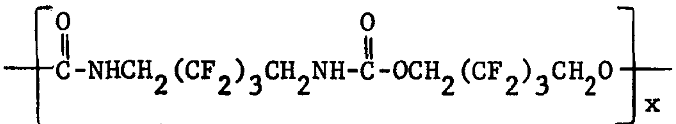
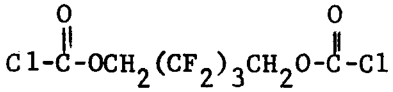


and $HOCH_2(CF_2)_3CH_2OH$

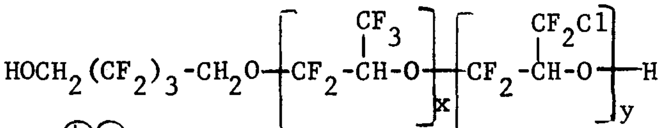


$$-\!\left[\overset{O}{\overset{\|}{C}}-NHCH_2(CF_2)_3CH_2NH-\overset{O}{\overset{\|}{C}}-OCH_2(CF_2)_3CH_2O\right]_x\!-$$

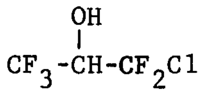
From $H_2NCH_2(CF_2)_3CH_2NH_2$

and 

$$Cl-\overset{O}{\overset{\|}{C}}-OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-Cl$$



$$HOCH_2(CF_2)_3-CH_2O\left[CF_2-\overset{CF_3}{\overset{|}{C}}H-O\right]_x\left[CF_2-\overset{CF_2Cl}{\overset{|}{C}}H-O\right]_y H$$

From 

$$CF_3-\overset{OH}{\overset{|}{C}}H-CF_2Cl$$

and $\overset{\oplus\ominus}{NaO}CH_2(CF_2)_3CH_2OH$

As discussed in Annual Suumary Report II, all of the polyurethane samples tested before this report period that were LOX compatible were 20-30 mils thick. During this report period, four polyurethanes that had been tested previously were prepared again and tested at different thicknesses to determine if those that passed the LOX test were truly LOX compatible or if they had passed only because of specimen thickness.

Last year, poly(hexafluoropentamethylene tetrafluoro-p-phenylene dicarbamate) was LOX compatible at 26 mils. Because this polyurethane was too brittle to press into thinner specimens, it was tested this year as a thin film of powder. It was also LOX compatible in this form.

Poly(hexafluoropentamethylene hexamethylene dicarbamate) was tested again. Because it had been tested at a thickness of 33 mils, and because of its structure, its compatibility was questionable. This year, it was tested at a thickness of 18 mils and shown to be LOX incompatible.

Two polyurethanes, prepared by reaction of tetrafluoro-p-phenylene diisocyanate with poly(3,3,3-trifluoro-1,2-epoxypropane) and with poly(hexafluoropentamethylene carbonate) were LOX incompatible last year when tested at a thickness of 10 mils. When tested again at a thickness of 26 mils, they were both still LOX incompatible.

A new polyurethane prepared this year, poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate), was tested at 16 mils and 50 mils and found to be LOX compatible at both thicknesses.

It therefore appears that if a polymer is truly LOX compatible, thickness has no effect on its LOX performance.

The results on the completely aliphatic polyurethane, poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate), just discussed, extends our knowledge of the stability of various urethane linkages. The urethane linkage, flanked on the alcohol side by a 1,1-dihydroperfluoroalkyl chain, $-NH-\overset{O}{\overset{\parallel}{C}}-O-CH_2-(CF_2)_x-$, is stable to impact in LOX if the nitrogen is also flanked by a 1,1-dihydroperfluoroalkyl chain, $-(CF_2)_x-CH_2-NH-\overset{O}{\overset{\parallel}{C}}-O-$.

The failure of poly(hexafluoropentamethylene tetrachloro-p-xylylene dicarbamate) to pass the compatibility test indicates that a benzyl methylene group imparts LOX sensitivity to a molecule, as poly(hexafluoropentamethylene tetrachloro-p-phenylene dicarbamate), which differs from the above polyurethane only by not having a methylene group between the aromatic ring and the nitrogen atom, has been shown to be LOX compatible (Reference 1).

As discussed above, poly(hexafluoropentamethylene tetrafluoro-p-phenylene dicarbamate) was tested at a thickness of 26 mils, and it was desirable to test thinner specimens. Because the brittleness of this polymer prevented preparation of thinner specimens, 8.5-mil thick specimens of the isomeric poly(hexafluoropentamethylene tetrafluoro-m-phenylene dicarbamate) were prepared and tested. Although this polymer failed the test, it only had 3 reactions in 20 tests. In order to determine if polyurethanes prepared from tetrafluoro-m-phenylene diisocyanate are LOX incompatible whereas those prepared from the isomeric para-diisocyanate are compatible, more of this meta-polyurethane was prepared and submitted for LOX testing as a fine powder.

Last year, poly(hexafluoropentamethylene carbonate) was shown to be LOX incompatible. This year, poly(hexafluoropentamethylene tetrafluoro-p-phenylene carbonate) was also shown to be LOX incompatible. Because the two polyurethanes which have corresponding structures, poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate) and poly(hexafluoropentamethylene tetrafluoro-p-phenylene dicarbamate) are LOX compatible, the indications are that the carbonate linkage itself is the incompatible factor.

Poly(hexafluoropentamethylene perfluoroglutarate) is LOX compatible (Reference 1), while poly(hexafluoropentamethylene adipate) is incompatible.

Our knowledge of polyester compatibility was extended this year by testing another type of polyester of hexafluoropentanediol. Poly(hexafluoropentamethylene isophthalate) was LOX incompatible. The indications are that only polyesters of fluorinated alcohols and fluorinated acids are LOX compatible.

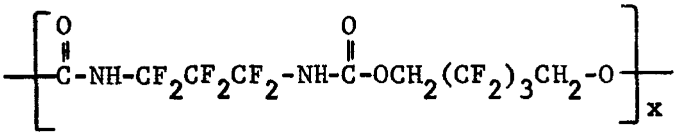
A new polyether prepared from chloropentafluoroisopropyl alcohol, when tested as 12-mil thick disks, appeared to be LOX incompatible. The polyurethanes prepared from this polyether system by reaction with tetrafluoro-m-phenylene and p-phenylene diisocyanates also appeared to be LOX sensitive. The sensitivity of the polyether was shown to be due to trapped solvent; samples prepared with careful drying, after using a LOX compatible solvent, were LOX compatible. The polyurethanes are being prepared again for testing, with special care being taken to remove all traces of solvent.

Another new polyether, prepared from hexafluoropentanediol and hexafluorobenzene, also failed the LOX test. Narmco believes that this failure may also be due to trapped solvent; this polyether will be carefully prepared again and resubmitted to MSFC.

B. Polyurethanes

1. From Hexafluoropentanediol

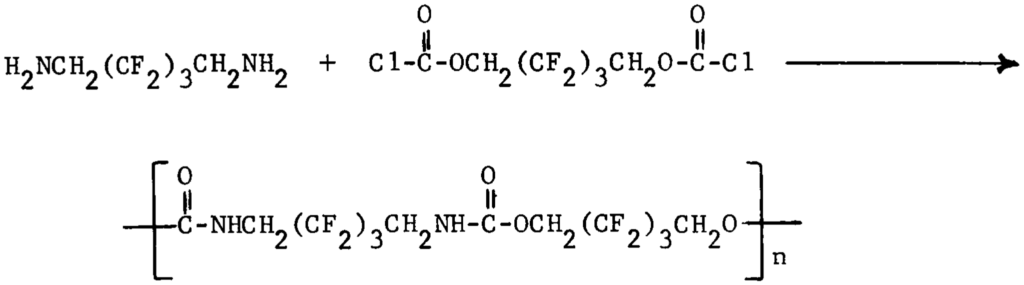
The preparation of a novel highly fluorinated polyurethane, poly(hexafluoropentamethylene perfluorotrimethylene dicarbamate), was reported early in this program (Reference 2).



$$\left[\overset{O}{\overset{\|}{C}}\text{-NH-CF}_2\text{CF}_2\text{CF}_2\text{-NH-}\overset{O}{\overset{\|}{C}}\text{-OCH}_2(\text{CF}_2)_3\text{CH}_2\text{-O}\right]_x$$

This polyurethane was LOX compatible (at the thickness tested) but was hydrolytically unstable. Polyurethanes which are hydrolytically stable while still retaining LOX compatibility have been prepared using tetrafluoro- and tetrachloro-p-phenylene diisocyanates. Another way of introducing hydrolytic stability is to prepare polyurethanes having methylene groups between the difluoromethylenes and the nitrogen atoms of the urethane linkages. Attempts to prepare hexafluoropentamethylene diisocyanate for use in making polyurethanes of this type have not been completely successful.

Poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate) was prepared this year by reaction of hexafluoropentanediamine with hexafluoropentamethylene bischloroformate. This reaction was carried out both in solution and interfacially.

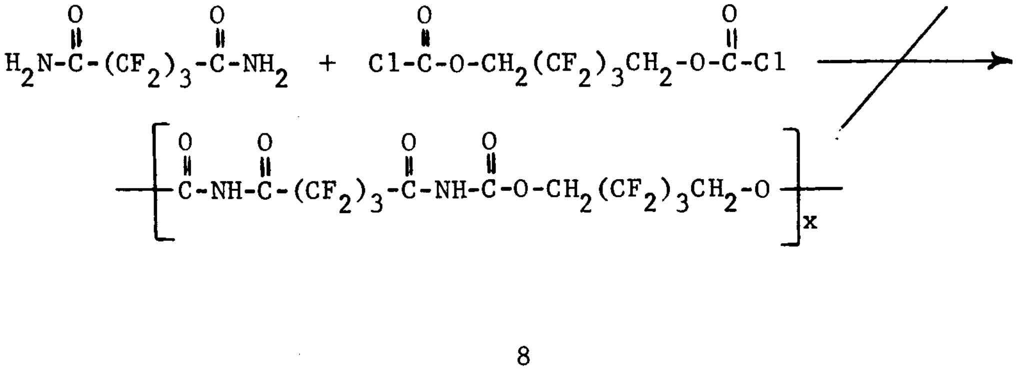


$$H_2NCH_2(CF_2)_3CH_2NH_2 + Cl\text{-}\overset{\overset{O}{\|}}{C}\text{-}OCH_2(CF_2)_3CH_2O\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl \longrightarrow \left[\overset{\overset{O}{\|}}{C}\text{-}NHCH_2(CF_2)_3CH_2NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}OCH_2(CF_2)_3CH_2O\right]_n$$

The first polyurethane prepared interfacially was a semisolid which solidified at or near room temperature. This polyurethane, tested by MSFC at a thickness of approximately 50 mils, had no reactions in the 17 specimens tested. The second sample of this polyurethane was an elastomeric solid which was pressed into a 16-mil thick sheet. The polyurethane was LOX compatible at this thickness, having no reactions in 20 specimens tested.

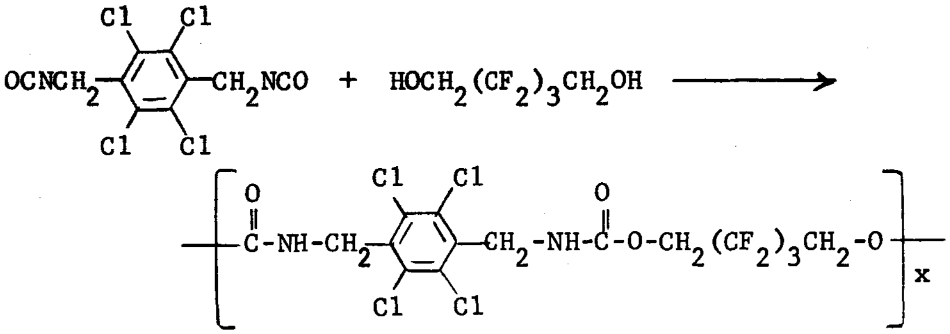
Because of the LOX compatibility and amorphous character of this aliphatic polyurethane system, the possible use of a hydroxyl-terminated polyurethane based on this system is being investigated. A viscous, low molecular weight prepolymer was prepared by reaction of the bischloroformate with the diamine in tetrahydrofuran (THF) solution, followed by hydrolysis of the chloroformate end groups. The reaction of this prepolymer with fluorinated diisocyanates to prepare usable polyurethanes will be studied.

Another type of polyurethane which might be hydrolytically stable is the poly-acylurethane. Previous attempts to prepare perfluoroglutaryl diisocyanate for use in preparing poly(hexafluoropentamethylene perfluoroglutaryl dicarbamate) were unsuccessful (References 1 and 2). During this year, an attempt was made to prepare this polyacylurethane directly by reaction of perfluoroglutaramide with hexafluoropentamethylene-bischloroformate. No reaction took place, indicating that the nitrogen atoms of perfluoroglutaramide are not sufficiently basic to react with the bischloroformate.

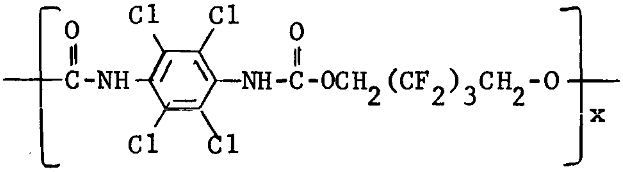


$$H_2N\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CF_2)_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH_2 + Cl\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2(CF_2)_3CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl \not\longrightarrow \left[\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CF_2)_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2(CF_2)_3CH_2\text{-}O\right]_x$$

Another type of halogenated polyurethane which is of interest in the basic study of the relationship of structure and LOX compatibility is represented by poly(hexafluoropentamethylene tetrachloro-p-xylylene dicarbamate). This polyurethane, prepared by reaction of tetrachloro-p-xylylene diisocyanate and hexafluoropentanediol in the melt, was obtained as a brittle solid. The preparation of the diisocyanate is discussed in the monomer section. Twenty-mil thick sample specimens of the polyurethane were prepared by means of a pellet mold and submitted to MSFC for LOX testing. The polyurethane was LOX incompatible, having 7 reactions in 20 specimens tested.



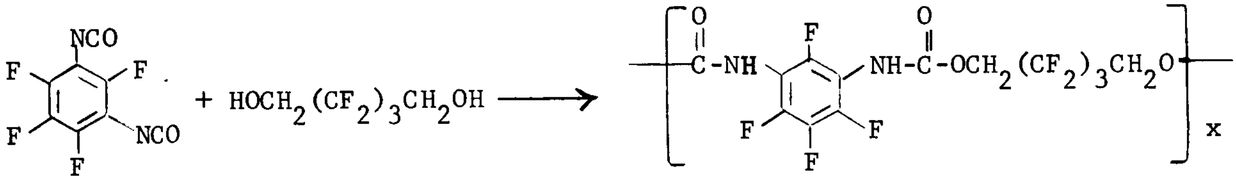
Poly(hexafluoropentamethylene tetrachloro-p-phenylene dicarbamate)



which differs from the above polyurethane only by not having a methylene group between the aromatic ring and the nitrogen atom, has been shown to be LOX compatible. The above LOX result indicates that a benzyl methylene group imparts LOX incompatibility to a molecule.

As discussed in Annual Summary Report II (July 1965), the polyurethanes prepared on this contract that were LOX compatible were all 20-30 mils thick. In order to help determine if the polyurethanes are compatible or if the compatibility is due only to their thickness, it was felt that a representative number of polyurethanes should be tested at 10 mils and also at a thickness of 20-30 mils. One of these polyurethanes poly(hexafluoropentamethylene tetrafluoro-p-phenylene dicarbamate), could not be tested at 10 mils because disks of that thickness were too brittle. Therefore, the corresponding polyurethane from tetrafluoro-m-phenylene diisocyanate was prepared this year.

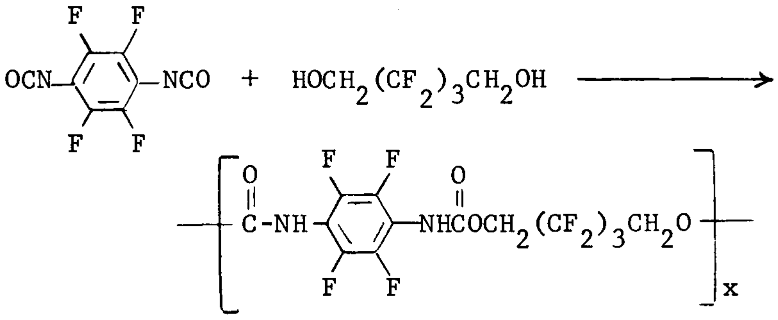
Poly(hexafluoropentamethylene tetrafluoro-m-phenylene dicarbamate) was prepared by reaction of tetrafluoro-m-phenylene diisocyanate with hexafluoropentanediol.



The clear, colorless polymer was pressed into a sheet 8.5 mils thick from which specimens were cut for LOX impact testing. Three specimens of twenty tested reacted with LOX.

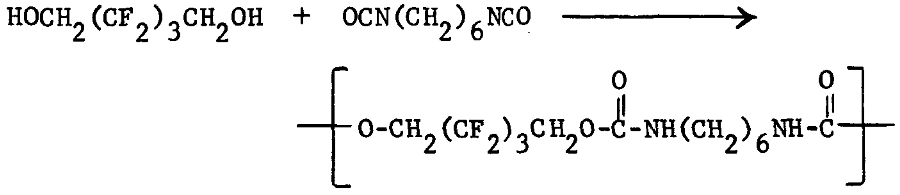
In order to verify these results another sample of poly(hexafluoropentamethylene tetrafluoro-m-phenylene dicarbamate) was prepared and submitted for LOX testing. This sample was submitted in the form of a powder.

Because poly(hexafluoropentamethylene tetrafluoro-p-phenylene dicarbamate) was LOX compatible at a thickness of 26 mils while the corresponding meta dicarbamate was LOX incompatible at a thickness of 8.5 mils, the former polyurethane was prepared this year using the melt polymerization technique.



The strong, brittle polymer was pulverized and the fine powder submitted to MSFC for LOX-compatibility testing. There were no reactions in 20 tests.

In Annual Summary Report I, the preparation of poly(hexafluoropentamethylene hexamethylene dicarbamate) was described. It was prepared in ethyl acetate solution and was a brittle solid. LOX-impact test specimens (33 mils thick) molded in a pellet mold gave no reactions in 20 tests, as reported in Annual Summary Report II. Because of the thickness of these specimens, the stability of the urethane group attached to a methylene chain is questionable. This polyurethane was prepared this month using the melt polymerization technique.



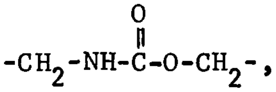
$$HOCH_2(CF_2)_3CH_2OH + OCN(CH_2)_6NCO \longrightarrow \left[O-CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-NH(CH_2)_6NH-\overset{O}{\overset{\|}{C}} \right]$$

The polymer was elastomeric, but had a tendency to crystallize on standing. An 18-mil thick film was pressed and 70 samples from this film were submitted to MSFC for LOX-compatibility testing. These specimens were tested at three energy levels, showing 4 reactions in 20 tests at 10 Kg-M (the required energy level), 1 reaction in 20 tests at 7.6 Kg-M, and 1 reaction in 20 tests at 5.3 Kg-M.

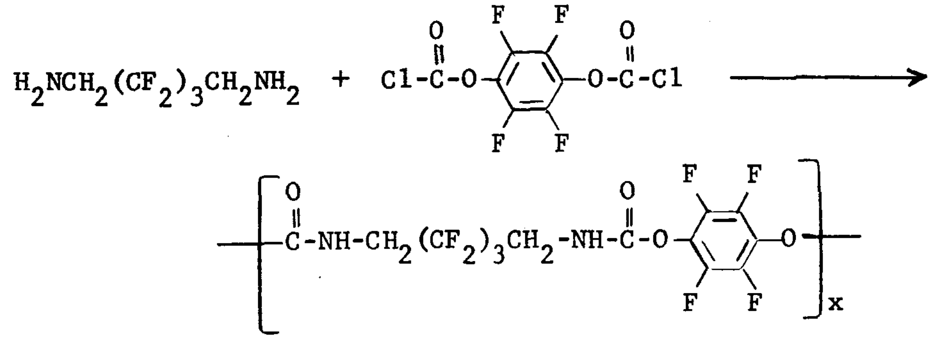
2. From Tetrafluoro-p-hydroquinone

The preparation of poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate) was described earlier in this report.

In view of the possibility that this polyurethane might be sensitive to impact in LOX because of the presence of methylene groups on either side of the urethane linkage,

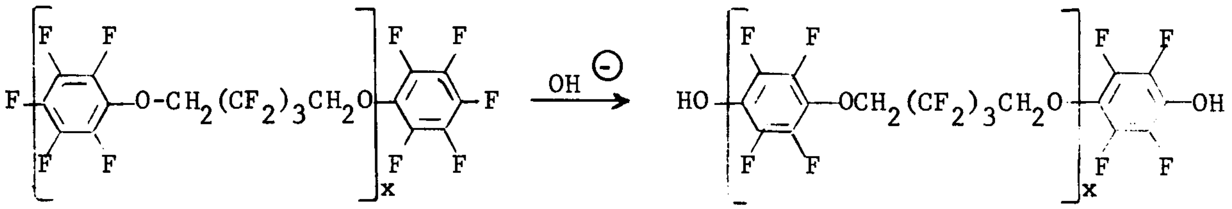


$-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-$, poly(tetrafluoro-p-phenylene hexafluoropentamethylene dicarbamate), was prepared by reacting hexafluoropentanediamine with tetrafluoro-p-phenylene-bischloroformate in solution. The preparation of this new bischloroformate is discussed in the monomer section. The polyurethane was a solid having a softening point of 175°-179°C.

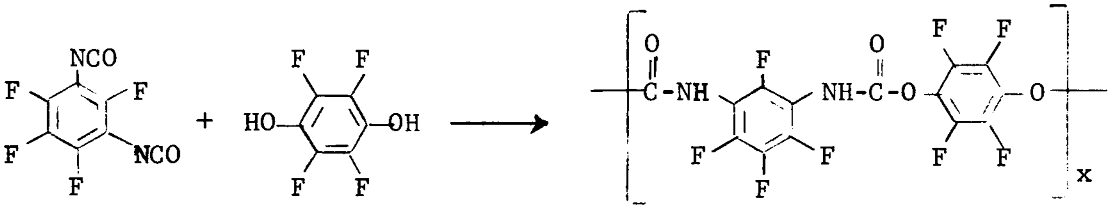


Because attempts to press a film from this polymer were unsuccessful, and the tests on the corresponding all-aliphatic polyurethane showed it to be LOX compatible, this polyurethane was not submitted for LOX testing.

During this report period, a considerable amount of study has been devoted to the preparation of a hydroxyl-terminated prepolymer from the polyether of hexafluorobenzene and hexafluoropentanediol. One of the methods studied was the replacement of one fluorine atom on each of the terminal hexafluorobenzene rings of a completely hexafluorobenzene-terminated polyether by a hydroxyl group.

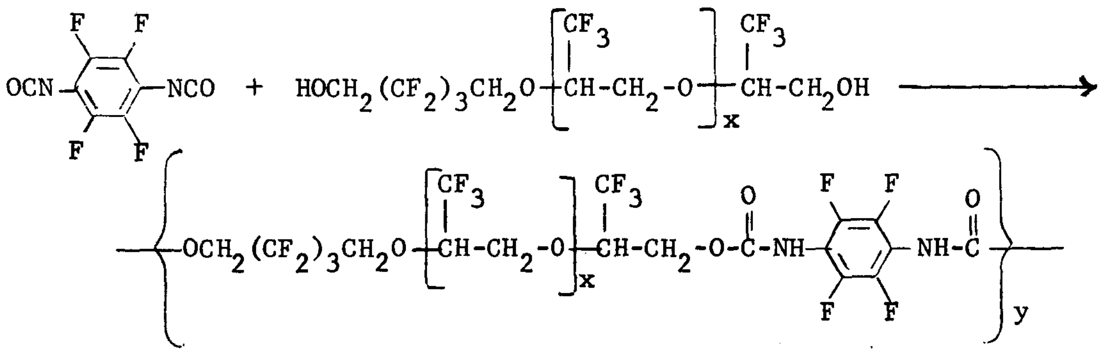


In order to determine the reactivity of the phenolic hydroxyl groups in this prepolymer toward fluorinated diisocyanates, the reaction of a model diol, tetrafluoro-p-hydroquinone, with tetrafluoro-m-phenylene diisocyanate was studied. The expected polyurethane, poly(tetrafluoro-p-phenylene tetrafluoro-m-phenylene dicarbamate), was obtained but the rate of the reaction was extremely slow.



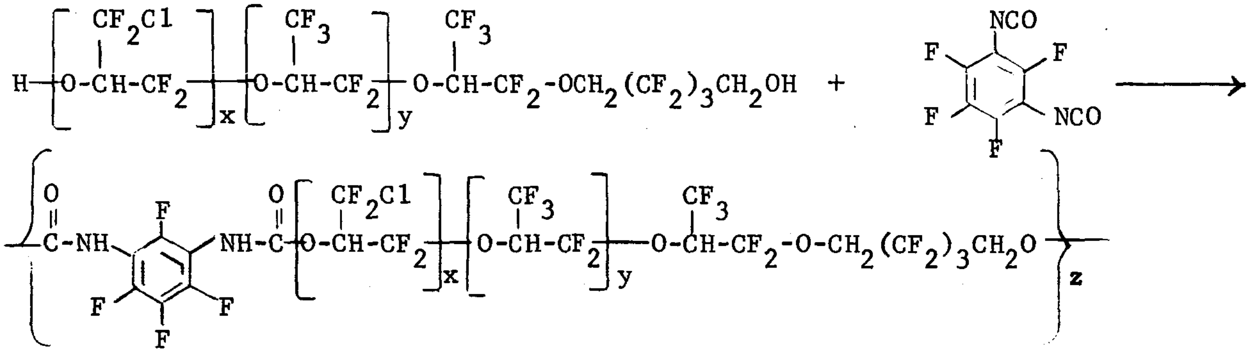
3. From Hydroxyl-terminated Polyethers

The preparation of a very tough, flexible polyurethane from tetrafluoro-p-phenylene diisocyanate and the hydroxyl-terminated polyether of 3,3,3,-trifluoro-1,2-epoxypropane has been reported earlier in this program (Reference 1). Specimens of the polyurethane were not LOX compatible when tested at a thickness of 10 mils. This year the same polymer was again prepared and a 26-mil thick film made from it. Samples punched from this film were also LOX incompatible. There were 17 reactions in 20 specimens tested.

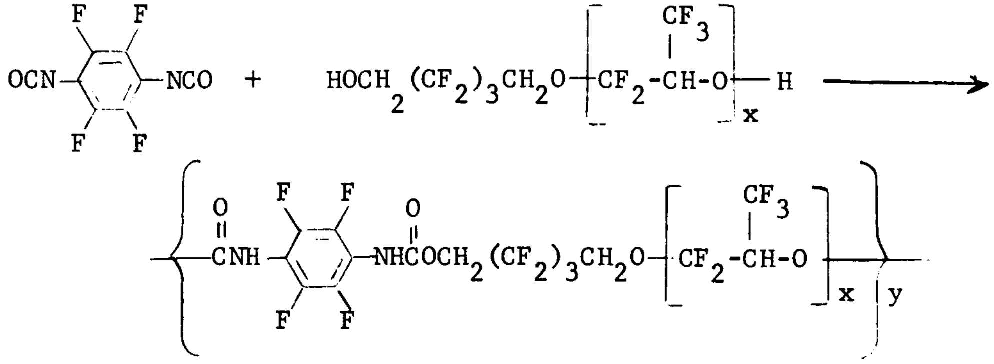


An exciting and significant development which was achieved this year was the successful preparation of a highly fluorinated aliphatic polyether which has the potential of being developed into an isocyanate-terminated prepolymer. The preparation of this polyether, at present believed to be a copolymer of pentafluoropropylene oxide and chlorotetrafluoropropylene oxide, is described in the following section on polyethers. Two polyethers were prepared from chloropentafluoroisopropyl alcohol, one initiated by the sodium salt of hexafluoropentanediol and being completely hydroxyl-terminated, and the other initiated with sodium hydroxide and containing both hydroxyl and acid termination.

The reaction of the sodium salt of hexafluoropentanediol initiated polyether with tetrafluoro-m-phenylene diisocyanate yielded a solid polyurethane which was elastomeric above 65°C and did not melt up to 285°C. Specimens of this polyurethane (12 mils thick) submitted to MSFC for LOX compatibility testing showed 5 reactions in 20 tests.

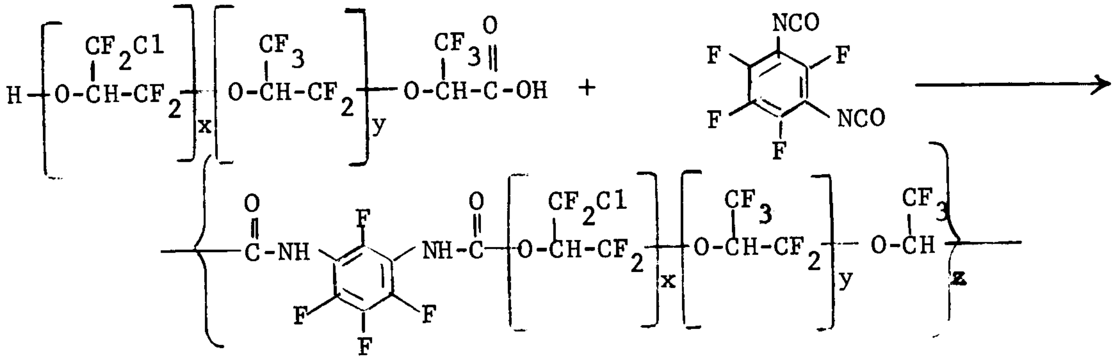


A similar polyurethane was prepared from the same polyether and tetrafluoro-p-phenylene diisocyanate.

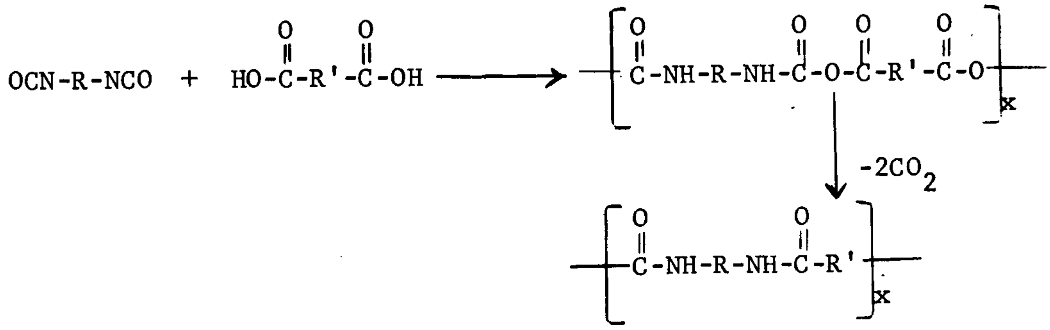


The polymer was a solid, infusible rubber. It was pulverized and the powder submitted to MSFC for LOX-compatibility testing. It had 11 reactions in 20 tests at 10 Kg-M but no reactions out of 20 tests at 7.6 Kg-M. The high molecular weight polyether of chloropentafluoroisopropyl alcohol prepared in THF, which was apparently LOX incompatible, was shown to be compatible when all traces of solvent were removed. Therefore, the LOX sensitivity of these polyurethanes may be the result of the presence of trapped THF.

The sodium hydroxide initiated polyether, however, failed to yield a polymer when reacted with tetrafluoro-m-phenylene diisocyanate.

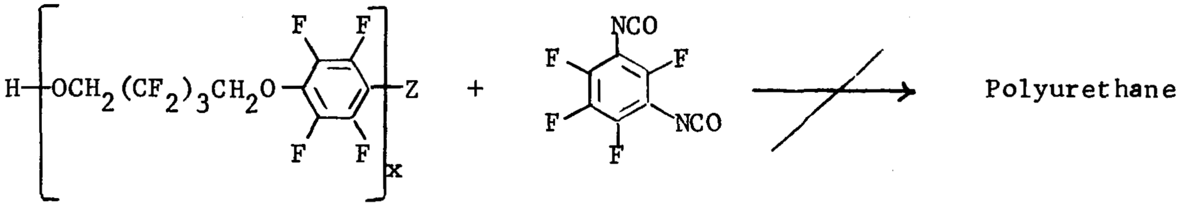


Nonfluorinated diacids react with diisocyanates to yield polyamides by loss of carbon dioxide from the intermediate polyacylurethanes.



Apparently, the fluorinated acid end groups of the polyether are not reactive enough to form a polyacylurethane with the fluorinated diisocyanate.

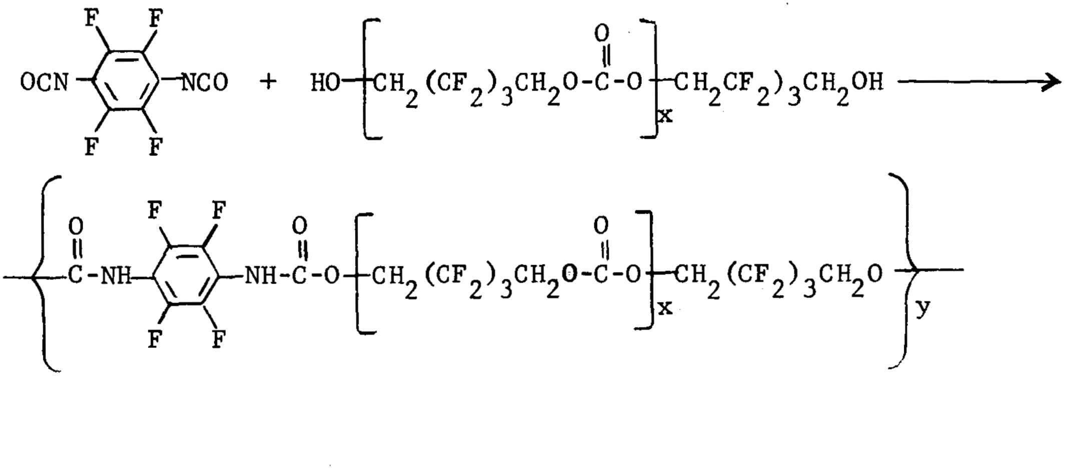
During this report period, considerable study was devoted to the preparation of a hydroxyl-terminated prepolymer from the polyether of hexafluorobenzene and hexafluoropentanediol. A polyether prepolymer which is completely hydroxyl terminated has not yet been obtained. A hexafluorobenzene-hexafluoropentanediol polyether containing a considerable number of hydroxyl end groups was reacted with tetrafluoro-m-phenylene diisocyanate. Although all of the hydroxyl groups reacted (determined by infrared spectroscopy), the reaction mixture remained fluid, indicating that not enough of the polymer chains had hydroxyls on both ends.



(Z = $-OCH_2(CF_2)_3CH_2OH$ or $-F$)

4. From Hydroxyl-terminated Polycarbonates

The preparation of a tough, flexible polyurethane from tetrafluoro-p-phenylene diisocyanate and hydroxyl-terminated poly(hexafluoropentamethylene carbonate) was reported previously (Reference 1). Specimens of this polyurethane were not LOX compatible when tested at a thickness of 10 mils. This year, the same polymer was again prepared and a 26-mil thick film made from it. Samples punched from this film were also LOX incompatible. There were 19 reactions in 20 specimens tested.



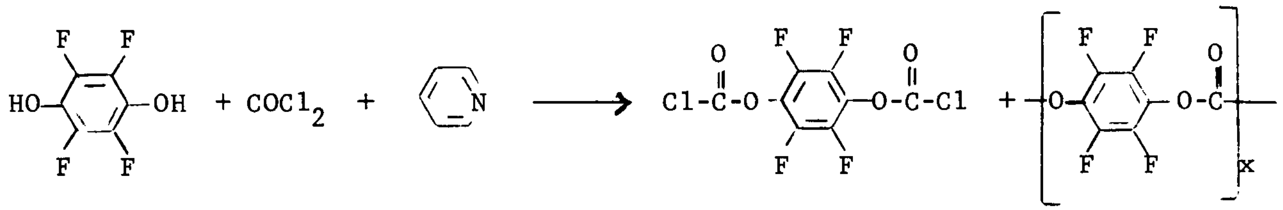
5. Thermal Stability of Polyurethanes

The thermal stabilities of various types of fluorinated polyurethanes are of importance in the preparation, curing, and processing of these polyurethanes. The polyurethane from poly(hexafluoropentamethylene carbonate) and tetrafluoro-p-phenylene diisocyanate was previously subjected to thermogravimetric analysis and its thermogram was presented in Annual Summary Report II (July 1965). Its polymer decomposition temperature was 300°±10°C in helium and 320°±10°C in air. During this report period, three more polyurethanes, poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate), poly(tetrafluoro-p-phenylene hexafluoropentamethylene dicarbamate), and poly(tetrafluoro-p-phenylene tetrafluoro-m-phenylene dicarbamate) were subjected to thermogravimetric analysis. The polymer decomposition temperatures of these polyurethanes are approximately 100 degrees lower than that of the polyurethane previously tested. The thermograms of these polyurethanes are shown in Figures 1 through 6.

C. Polycarbonates

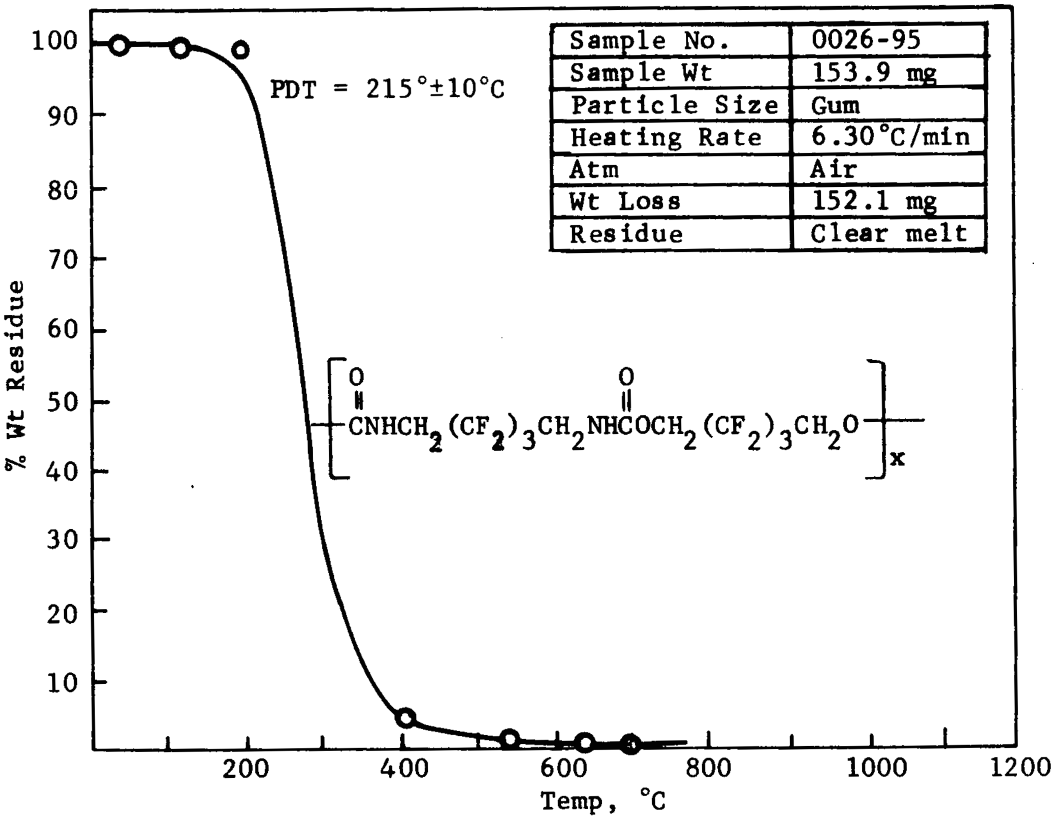
The preparation of a new and interesting fluorinated polycarbonate, poly(hexafluoropentamethylene carbonate), was reported previously (Reference 1). This polycarbonate, however, was LOX incompatible (at a thickness of 10 mils). In order to identify the cause of incompatibility in this polycarbonate and in fluorinated polycarbonates in general, two additional new polycarbonates, poly(tetrafluoro-p-phenylene carbonate), and poly(hexafluoropentamethylene tetrafluoro-p-phenylene carbonate) were prepared.

The fully aromatic polycarbonate was isolated during the preparation of tetrafluoro-p-phenylene-bischloroformate.



It was an infusible solid, and its molecular weight could not be determined by vapor pressure osmometry (VPO) because of its insolubility in suitable solvents.

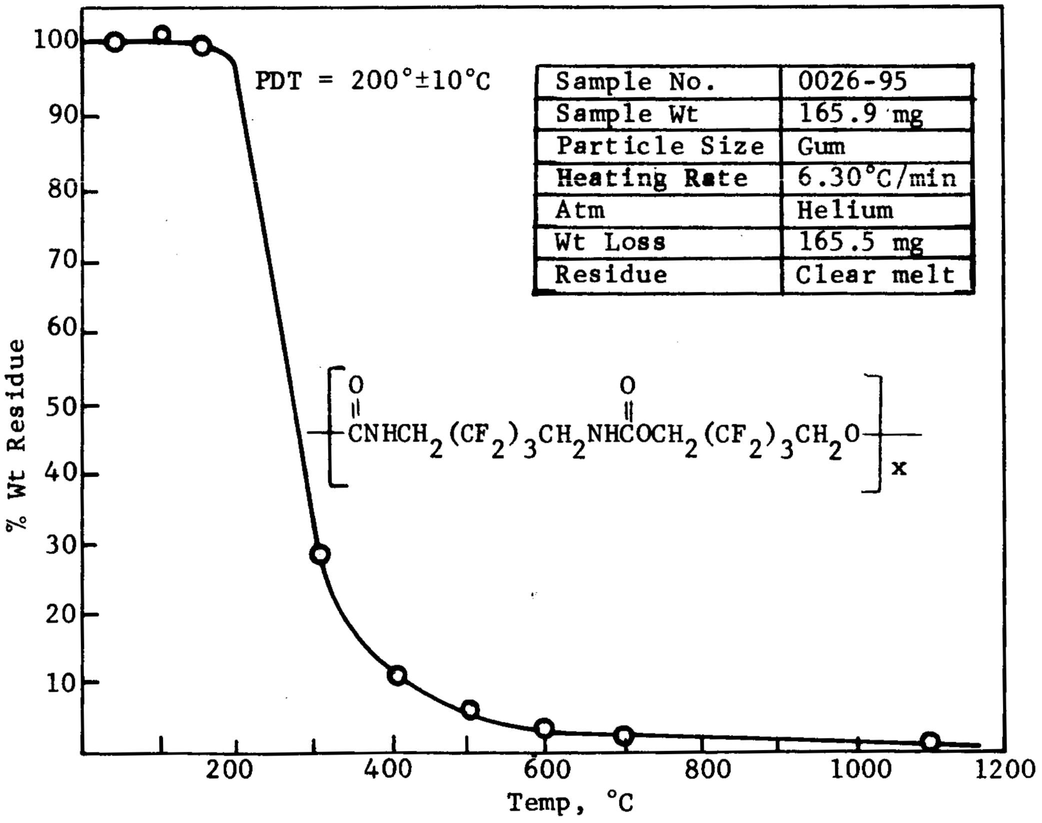
The mixed aliphatic-aromatic polycarbonate was prepared by reaction of hexafluoropentamethylene-bischloroformate with tetrafluorohydroquinone in the presence of pyridine.



Sample No.	0026-95
Sample Wt	153.9 mg
Particle Size	Gum
Heating Rate	6.30°C/min
Atm	Air
Wt Loss	152.1 mg
Residue	Clear melt

$$\left[\overset{O}{\overset{\|}{C}}NHCH_2(CF_2)_3CH_2NH\overset{O}{\overset{\|}{C}}OCH_2(CF_2)_3CH_2O\right]_x$$

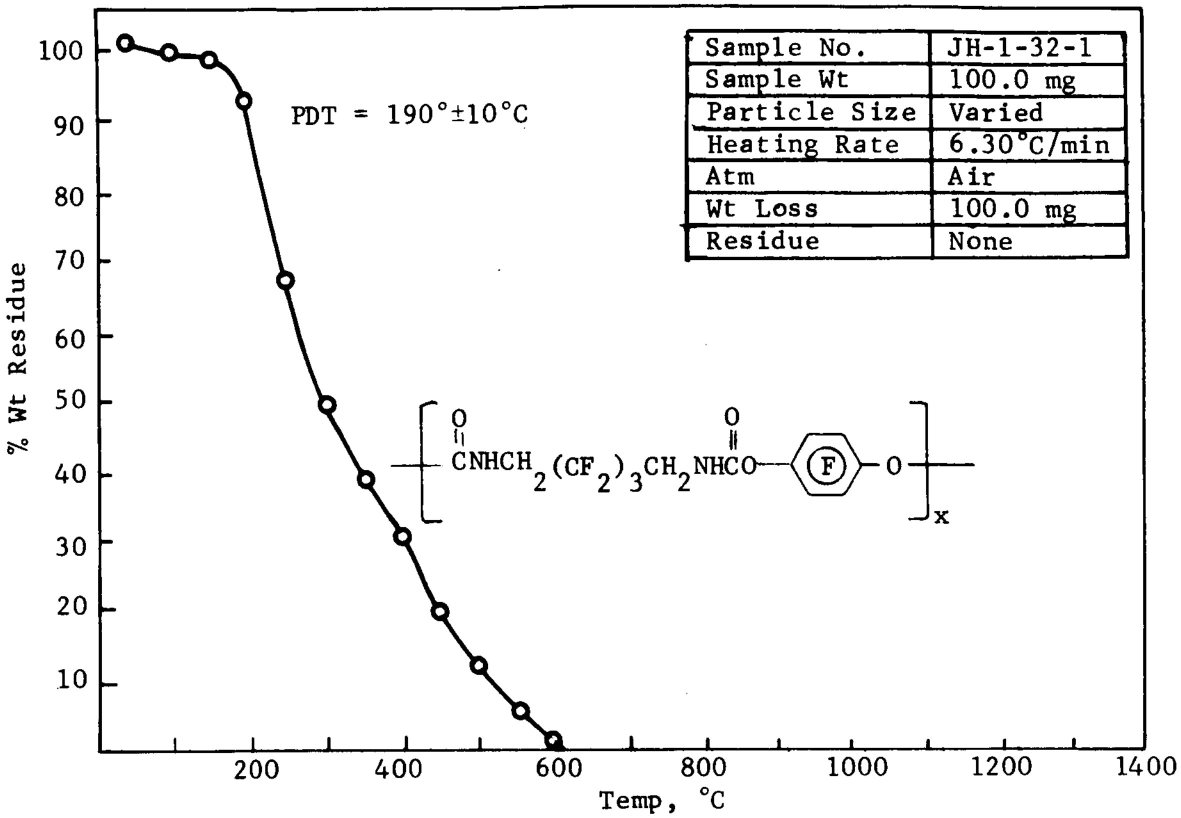
Figure 1. Thermogram of Poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate) in Air



Sample No.	0026-95
Sample Wt	165.9 mg
Particle Size	Gum
Heating Rate	6.30°C/min
Atm	Helium
Wt Loss	165.5 mg
Residue	Clear melt

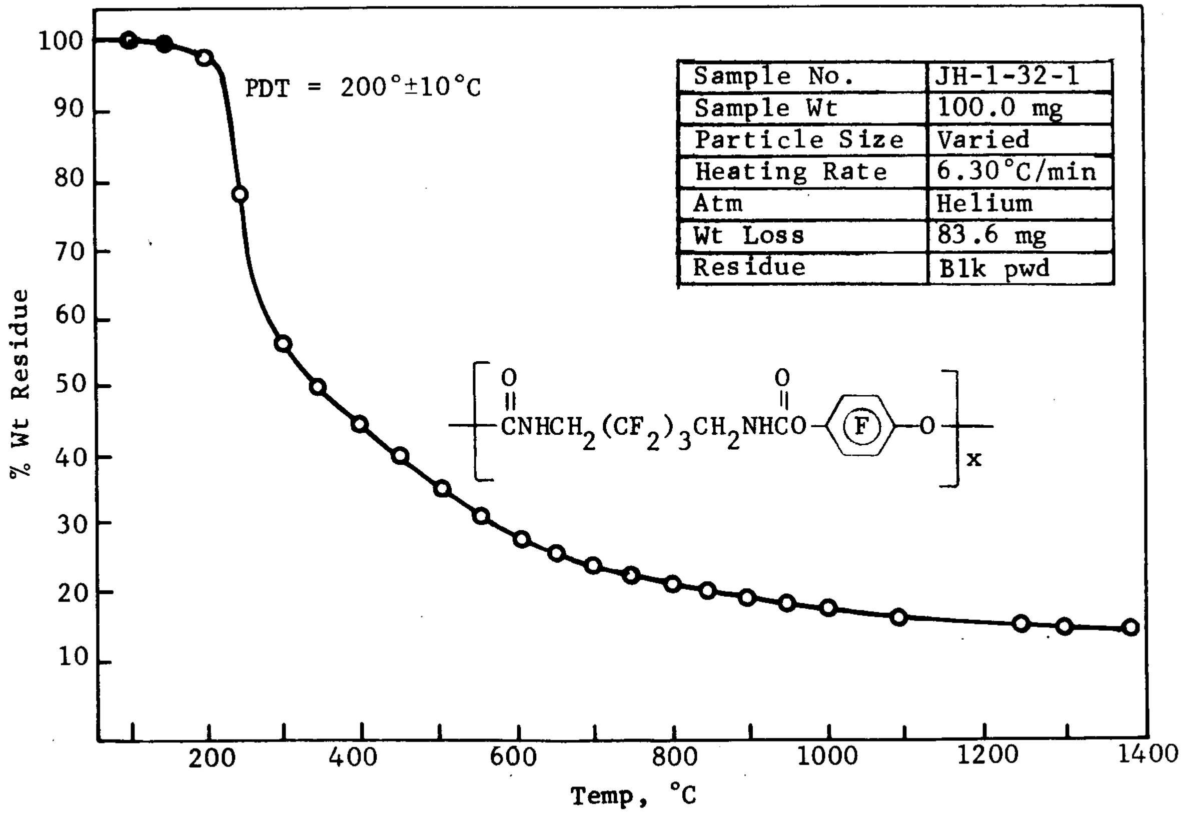
$$\left[\overset{O}{\overset{\|}{C}}NHCH_2(CF_2)_3CH_2NH\overset{O}{\overset{\|}{C}}OCH_2(CF_2)_3CH_2O\right]_x$$

Figure 2. Thermogram of Poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate) in Helium



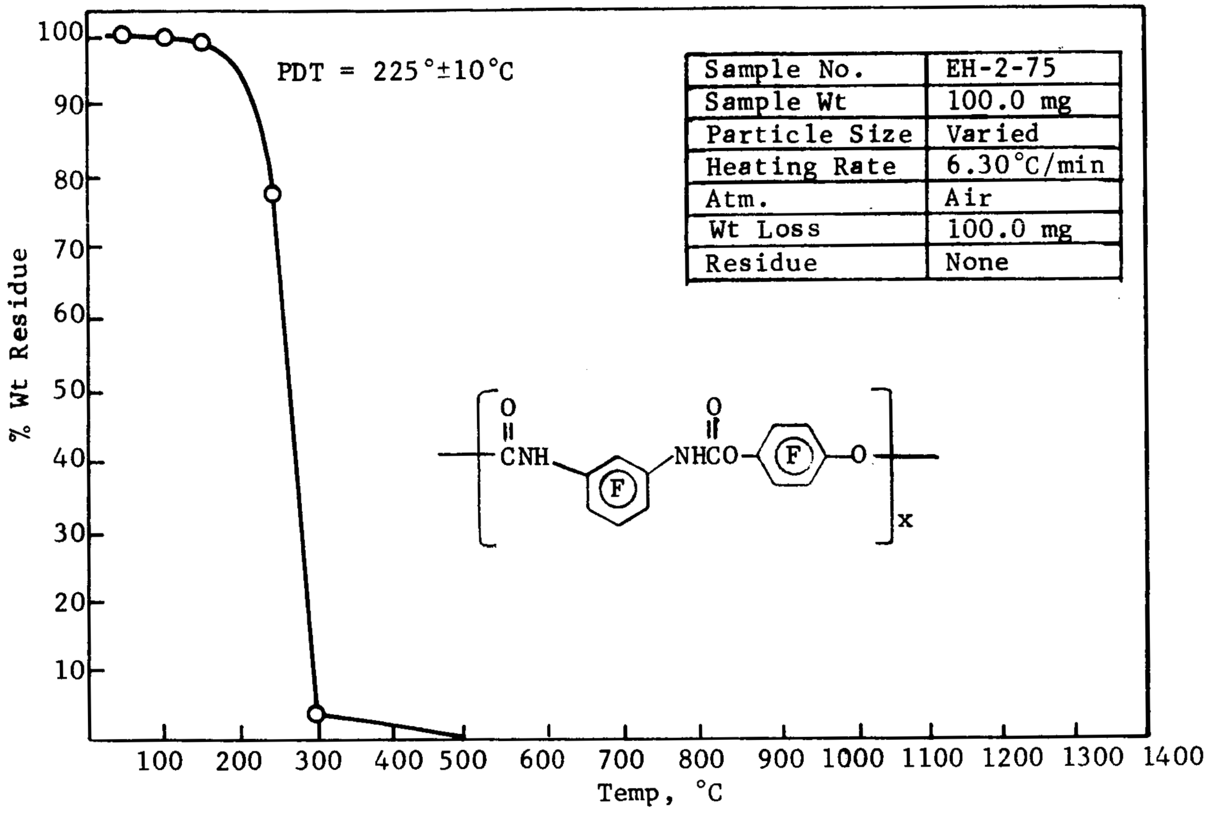
Sample No.	JH-1-32-1
Sample Wt	100.0 mg
Particle Size	Varied
Heating Rate	6.30°C/min
Atm	Air
Wt Loss	100.0 mg
Residue	None

Figure 3. Thermogram of Poly(tetrafluoro-p-phenylene hexafluoropentamethylene dicarbamate) in Air



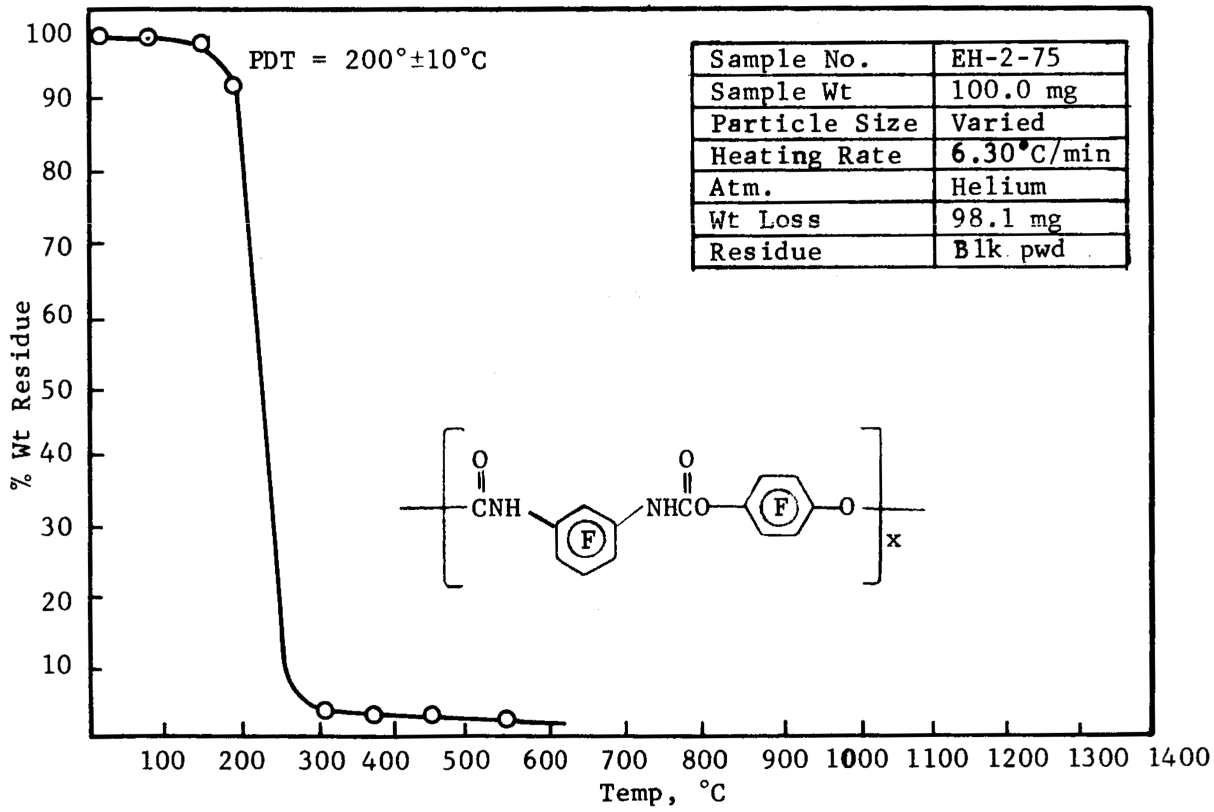
Sample No.	JH-1-32-1
Sample Wt	100.0 mg
Particle Size	Varied
Heating Rate	6.30°C/min
Atm	Helium
Wt Loss	83.6 mg
Residue	Blk pwd

Figure 4. Thermogram of Poly(tetrafluoro-p-phenylene hexafluoropentamethylene dicarbamate) in Helium



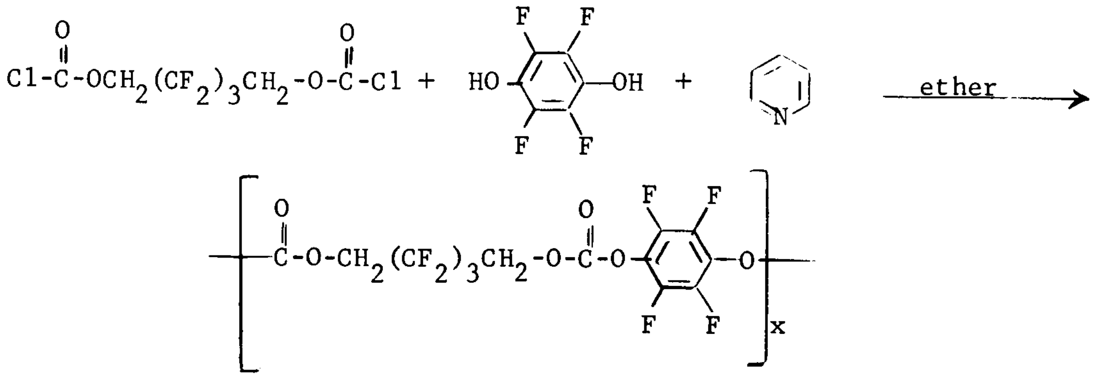
Sample No.	EH-2-75
Sample Wt	100.0 mg
Particle Size	Varied
Heating Rate	6.30°C/min
Atm.	Air
Wt Loss	100.0 mg
Residue	None

Figure 5. Thermogram of Poly(tetrafluoro-p-phenylene tetrafluoro-m-phenylene dicarbamate) in Air



Sample No.	EH-2-75
Sample Wt	100.0 mg
Particle Size	Varied
Heating Rate	6.30°C/min
Atm.	Helium
Wt Loss	98.1 mg
Residue	Blk pwd

Figure 6. Thermogram of Poly(tetrafluoro-p-phenylene tetrafluoro-m-phenylene dicarbamate) in Helium



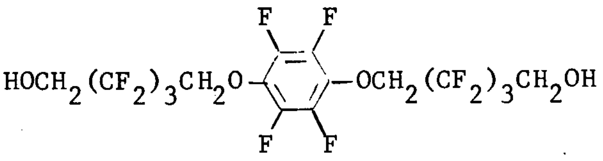
The white powdery polymer had a melting point of 140°-146°C and a molecular weight of 5460 (determined by VPO). It was pressed into a film 7.5 mils thick and samples punched from it were submitted to MSFC for LOX compatibility testing. The results indicated that this polycarbonate was LOX incompatible, having 2 reactions in 20 specimens tested. Since there were only 2 reactions, 20 more 7.5-mil thick specimens of this polycarbonate were submitted for LOX impact testing. The second group gave 5 reactions in 20 tests.

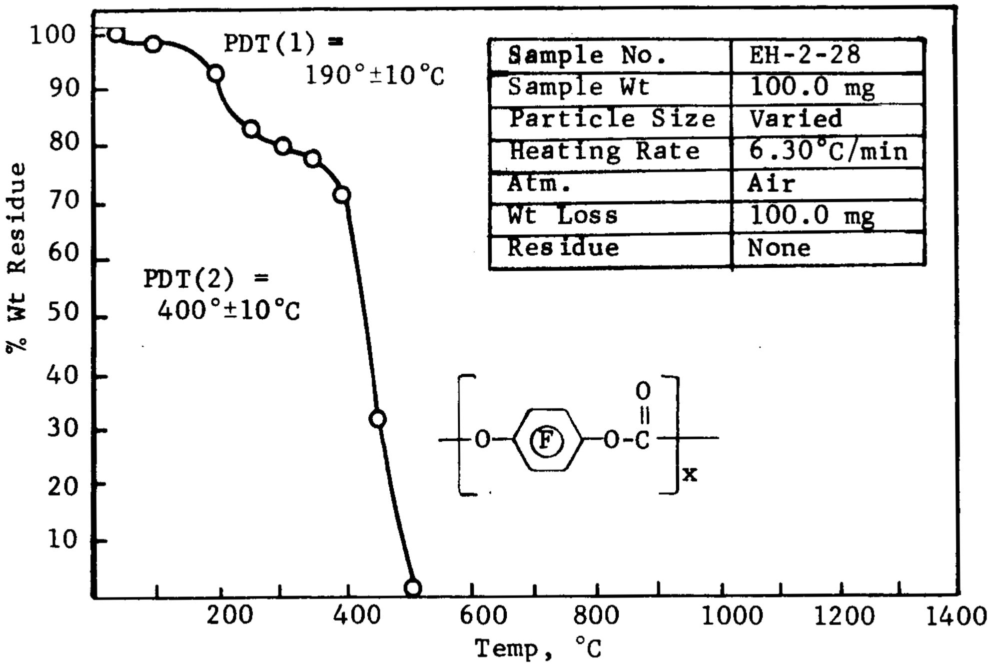
Because of the high degree of thermal stability exhibited by poly(hexafluoropentamethylene carbonate) (Reference 1), these two polycarbonates were subjected to thermogravimetric analysis. The polymer decomposition temperatures of these polycarbonates were lower than that for the completely aliphatic polycarbonate. This indicates that the fluoro-aromatic carbonate linkage is less thermally stable than the 1,1-dihydroperfluoroalkyl carbonate linkage. The thermograms are shown in Figures 7 through 10.

D. Polyethers

1. Polyethers from Hexafluoropentanediol

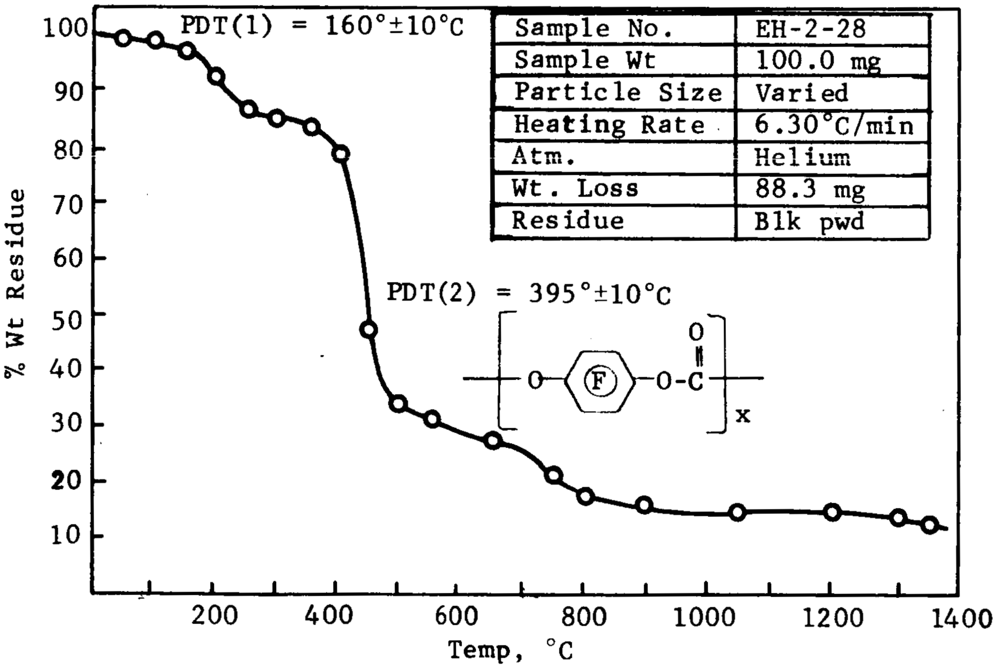
a. Polyethers of Hexafluoropentanediol and Hexafluorobenzene. In Annual Summary Report I (July 1964), the preparation of 1,4-bis(5-hydroxyhexafluoropentoxy)tetrafluorobenzene was described. The yield of product was very low by the two methods used; i.e., the reaction of hexafluorobenzene with hexafluoropentanediol and sodium hydroxide without a solvent, and the reaction of hexafluorobenzene with the sodium salt of hexafluoropentanediol in dibutyl ether. An attempt to improve the yield using N-methylpyrrolidone as the solvent was unsuccessful (Reference 1).





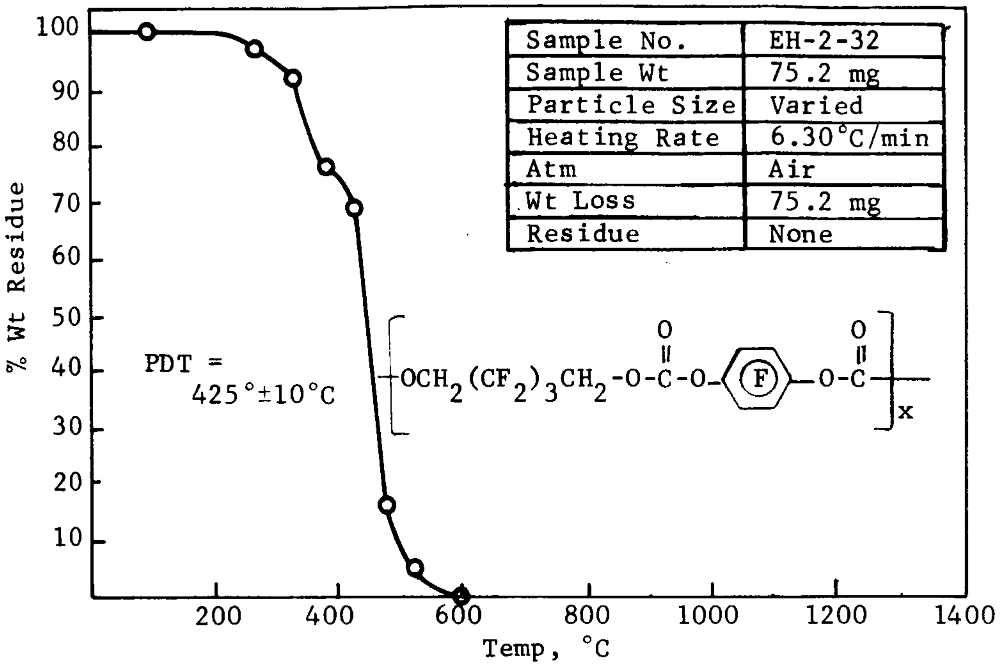
Sample No.	EH-2-28
Sample Wt	100.0 mg
Particle Size	Varied
Heating Rate	6.30°C/min
Atm.	Air
Wt Loss	100.0 mg
Residue	None

Figure 7. Thermogram of Poly(tetrafluoro-p-phenylene carbonate) in Air



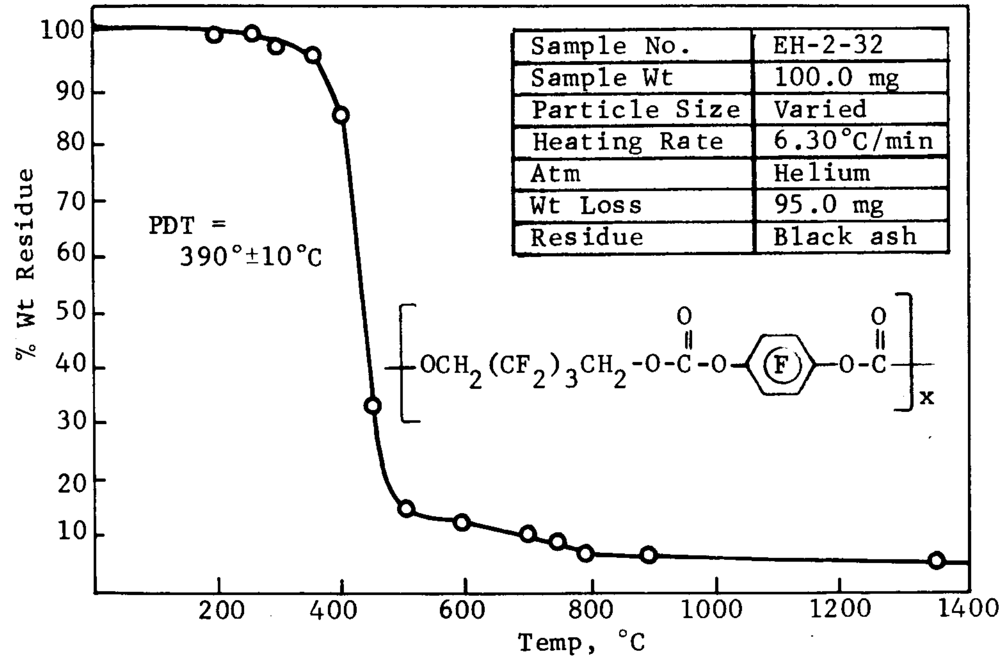
Sample No.	EH-2-28
Sample Wt	100.0 mg
Particle Size	Varied
Heating Rate	6.30°C/min
Atm.	Helium
Wt. Loss	88.3 mg
Residue	Blk pwd

Figure 8. Thermogram of Poly(tetrafluoro-p-phenylene carbonate) in Helium



Sample No.	EH-2-32
Sample Wt	75.2 mg
Particle Size	Varied
Heating Rate	6.30°C/min
Atm	Air
Wt Loss	75.2 mg
Residue	None

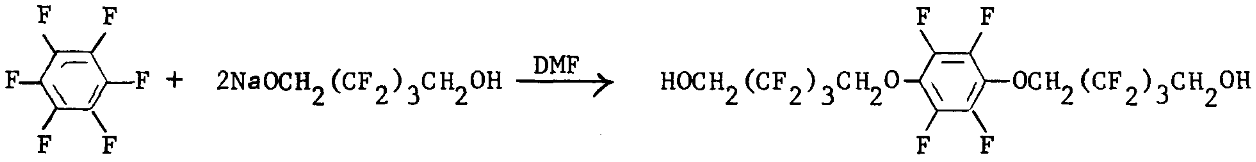
Figure 9. Thermogram of Poly(tetrafluoro-p-phenylene hexafluoropentamethylene carbonate) in Air



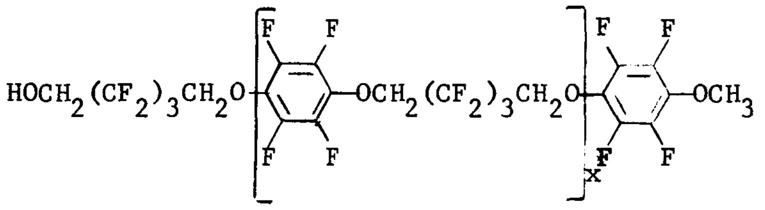
Sample No.	EH-2-32
Sample Wt	100.0 mg
Particle Size	Varied
Heating Rate	6.30°C/min
Atm	Helium
Wt Loss	95.0 mg
Residue	Black ash

Figure 10. Thermogram of Poly(tetrafluoro-p-phenylene hexafluoropentamethylene carbonate) in Helium

This year, in another attempt to prepare this diether, hexafluorobenzene was reacted with the sodium salt of hexafluoropentanediol in N,N-dimethylformamide.

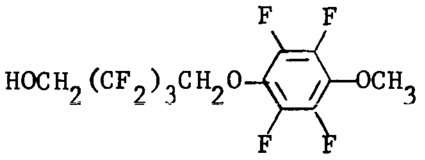


Surprisingly, a polyether of molecular weight 1150 was obtained from this reaction rather than the expected diether. It was identified as the polyether of hexafluoropentanediol and hexafluorobenzene by its molecular weight (determined by VPO), its infrared spectrum, and its elemental analysis. It is believed to possess the following structure:

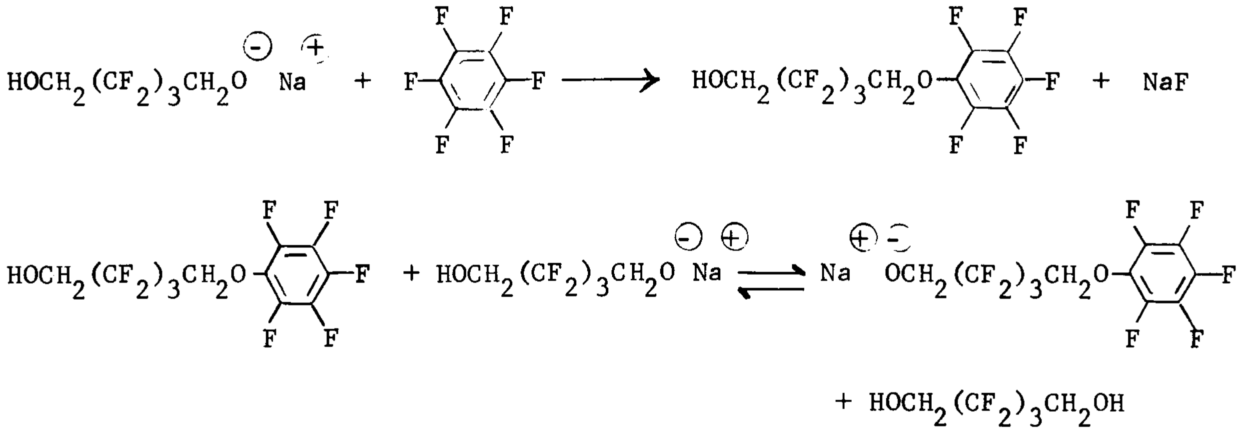


The methoxy group is believed to come from sodium methoxide impurity in the sodium salt of hexafluoropentanediol.

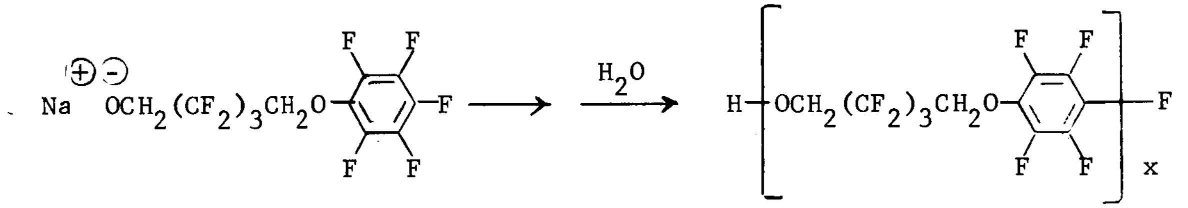
A diether, shown to be 1-methoxy-4-(ε-hydroxyhexafluoropentoxy)-tetrafluorobenzene was also isolated.



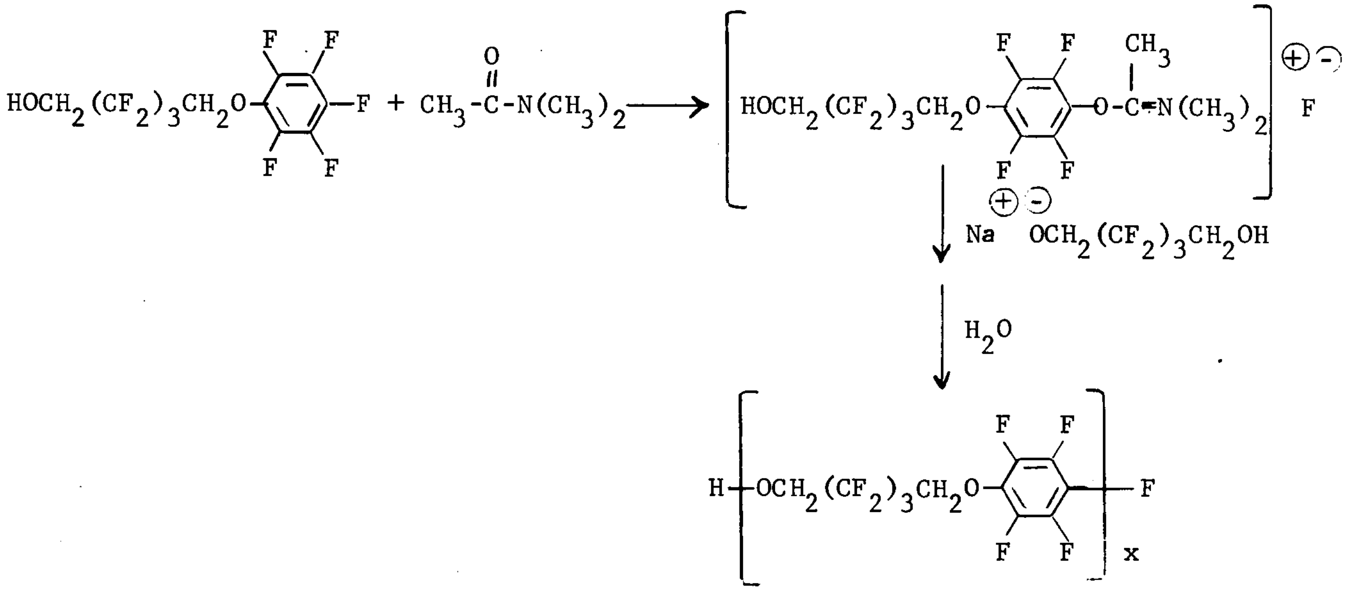
The reaction of hexafluorobenzene with the monosodium salt of hexafluoropentanediol in the ratio of 1:3 was repeated in N,N-dimethylacetamide (DMAC). The same two products were isolated. This unexpected formation of a polyether may be accounted for if a facile equilibrium is considered to occur between the monoether of hexafluorobenzene and hexafluoropentanediol which forms as the initial product and more sodium salt of hexafluoropentanediol.



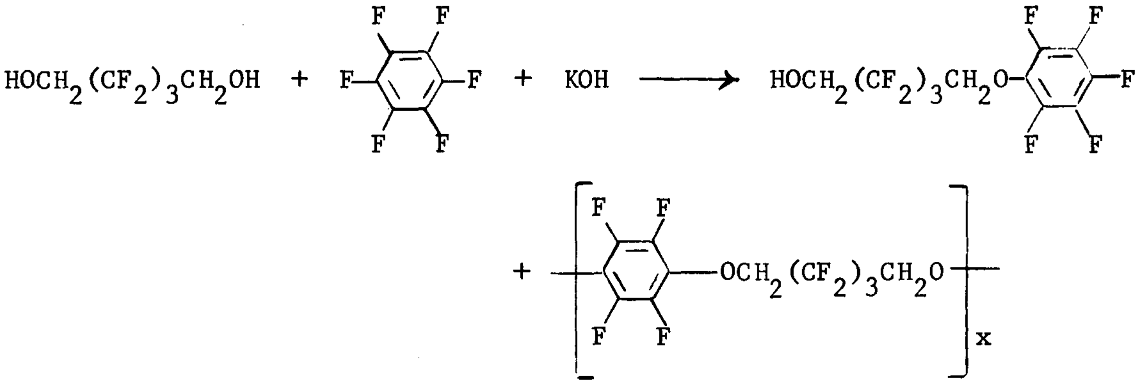
The sodium salt of the monoether can then go on to form polyether.



It is also possible that polyether could result from the reaction of the sodium salt of the monoether with an activated monoether formed by reaction of an aprotic solvent such as DMAC or N,N-dimethylformamide (DMF) with the aromatic ring (Reference 3).

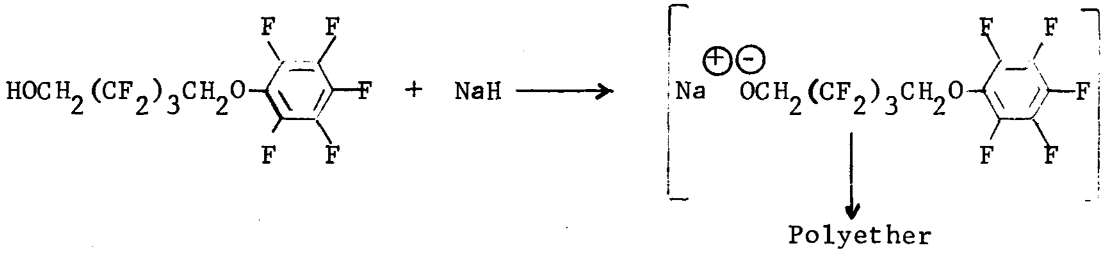


Because the key to preparing these polyethers seems to be the alkali metal salt of the monoether, it was felt that its polymerization would give a good yield of high molecular weight polymer. An attempt was made to prepare the monoether, 5-hydroxyhexafluoropentoxy-hexafluorobenzene, by reaction of hexafluorobenzene, hexafluoropentanediol, and potassium hydroxide in the ratio of 1:1:1 in DMF solution. Some of the desired monoether was obtained along with polyethers of molecular weights ranging up to about 1670. In addition, a small amount of high molecular weight rubber was obtained.

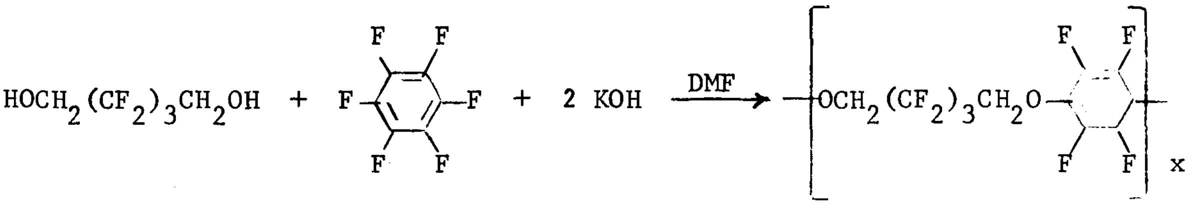


Reaction of the monoether with sodium hydride in ether yielded the same high molecular weight, rubbery polyether.

This method of preparation of the polyether involves the preparation of the AB monomer, the sodium salt of the monoether, which homopolymerizes.



In view of the ease with which alkali metal salts of hexafluoropentanediol and its ethers seem to form in amide solvents, an attempt was made to prepare a high molecular weight polyether by reaction of hexafluorobenzene, hexafluoropentanediol and potassium hydroxide in the ratio of 1:1:2 in DMF solution. Only a small amount of high molecular weight polyether which was insoluble in DMF was obtained. This polymer, however, was a very interesting elastomer.



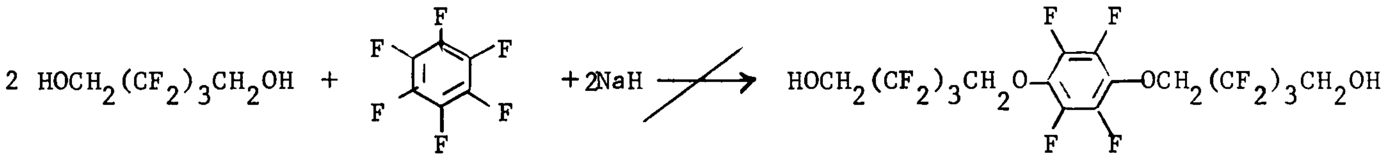
An attempt was then made to prepare a moderate molcular weight, completely hydroxy-terminated polymer. Hexafluorobenzene, hexafluoropentanediol and potassium hydroxide, in the ratio of 2:3:4 were reacted in DMF solution. A good yield of 790 molecular weight liquid polyether was obtained which was shown by VPO and hydroxyl end group determination to have both hydroxyl and hexafluorobenzene termination. In addition, a small amount of high molecular elastomeric material was also isolated.

The high molecular weight material obtained here and in the previous reactions was an extremely thermally stable elastomer, which showed no signs of softening or decomposition up to 300°C. A larger sample of this rubbery polyether was prepared. It was pressed into a 17-mil thick sheet, and specimens punched from it were submitted to MSFC for LOX impact testing. It had 2 reactions in 20 tests. It is very possible that this polyether could have contained trapped solvent, which caused the two reactions.

Since this polyether seemed to be an extremely thermally stable material, it was subjected to thermogravimetric analysis. The polymer decomposition temperature was 340°±10°C in both helium and air. The thermograms are shown as Figures 11 and 12.

A moderate molecular weight (720) polyether, completely terminated by hexafluorobenzene, was prepared by reaction of hexafluorobenzene, hexafluoropentanediol, and potassium hydroxide in the ratio of 3:2:6 in DMF solution.

In view of the successful polymerization of the monoether with sodium hydride, an attempt was made to prepare the diether by reaction of hexafluoropentanediol, hexafluorobenzene, and sodium hydride in ether.



None of the desired product was isolated.

The various reactions carried out with hexafluoropentanediol or its alkali metal salts with hexafluorobenzene give considerable insight into the reactivity of the fluoroaromatic ring toward nucleophilic attack by the anion of hexafluoropentanediol. The fact that the disodium salt of hexafluoropentanediol, formed in situ by reaction of the diol with sodium hydride, does not react with hexafluorobenzene in ether solution indicates that the attack of the first anion on the fluoroaromatic ring is a very slow reaction. This reaction occurs at an appreciable rate only if the ring is activated by

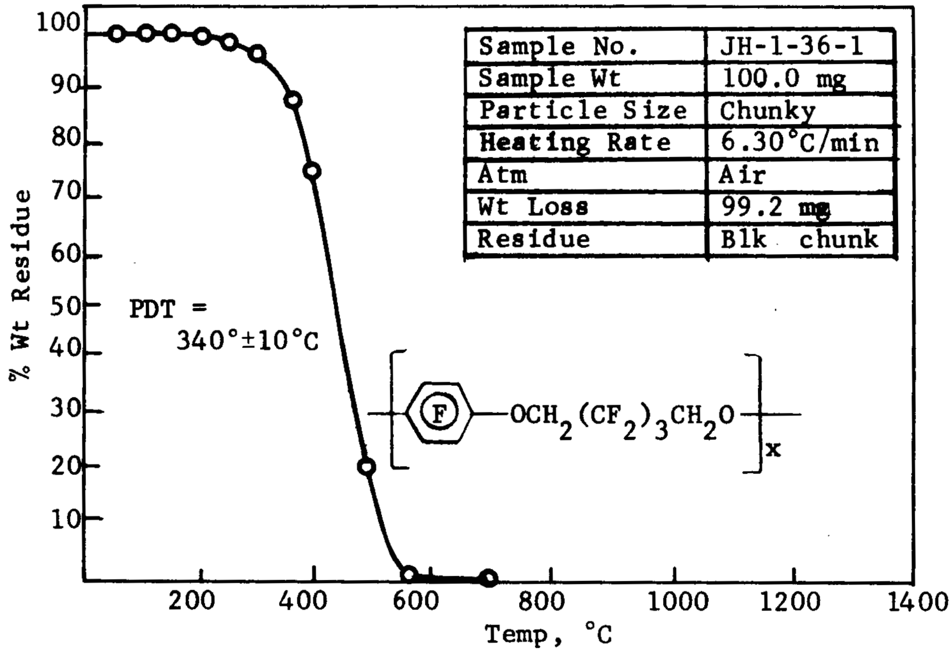


Figure 11. Thermogram of Polyether of Hexafluoropentanediol and Hexafluorobenzene in Air

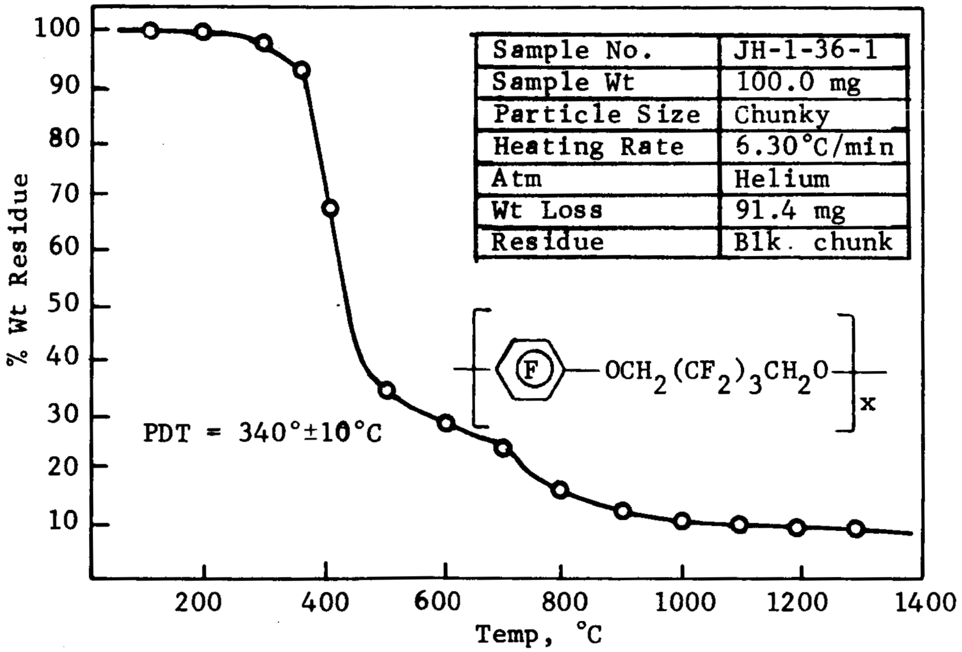
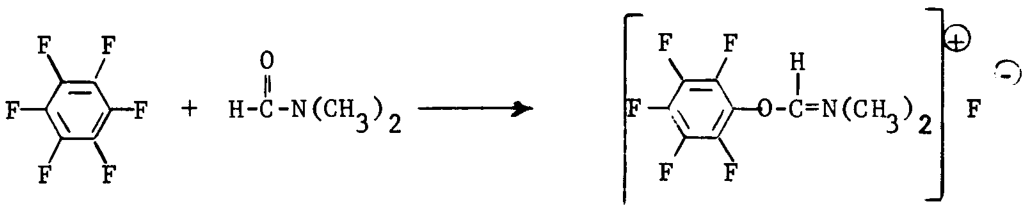
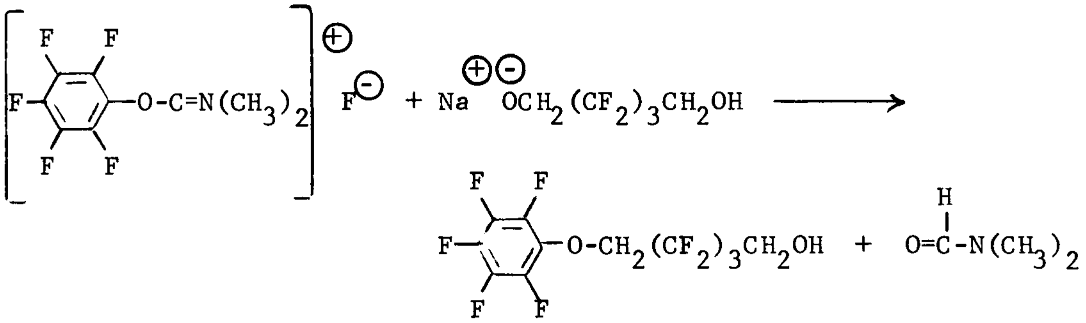


Figure 12. Thermogram of Polyether of Hexafluoropentanediol and Hexafluorobenzene in Helium

a basic solvent such as DMF. This activation is observed in the apparently rapid reaction of the mono- and di- potassium salts of the diol, formed in the reaction medium from the diol and potassium hydroxide, with hexafluorobenzene to yield monoether and polyether when the reactions were run in DMF or similar solvent. It is possible that this activation of the aromatic ring is due to the formation of a salt by reaction of hexafluorobenzene with DMF.

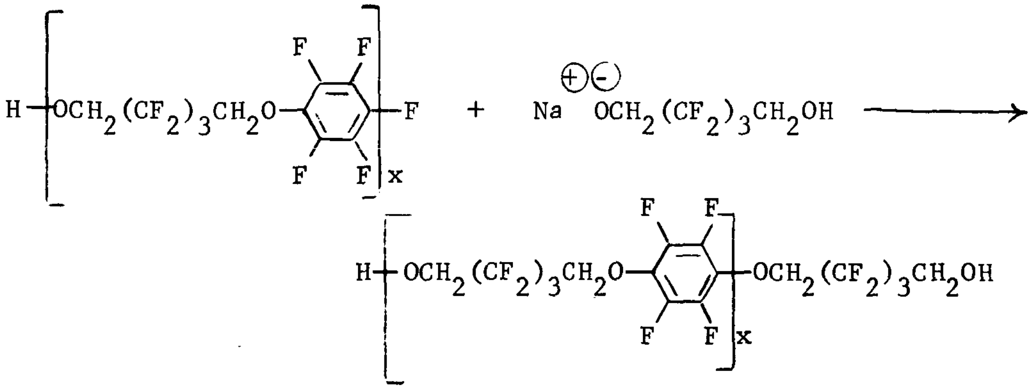


This type of salt has been suggested as an intermediate in the reaction of alkyl or aryl halides with various anions in DMF (Reference 3). A facile nucleophilic displacement by the anion of hexafluoropentanediol would yield the monoether.



Once the monomether is formed, the position para to the substitution is so reactive toward further nucelophilic attack that substitution occurs without activation by DMF. This is shown by the homopolymerization of the sodium salt of the monoether. When the reaction is carried out using the sodium salt of hexafluoropentanediol, the attacking nucleophile is most likely either the sodium salt of the monoether or the sodium salt of the diether, both formed by an equilibrium with the monosodium salt of hexafluoropentanediol. When the reaction involves hexafluoropentanediol and potassium hydroxide, the attacking reagent probably is the dipotassium salt of hexafluoropentanediol or the potassium salt of the monoether.

As described above, reaction of hexafluorobenzene with excess hexafluoro-pentanediol in the presence of base yields polyethers with both hexafluoropentanediol and hexafluorobenzene termination. An attempt was made to convert this type of polyether to a completely hydroxyl-terminated one by reaction with the monosodium salt of hexafluoropentanediol.



Based on the VPO and hydroxyl number results, only a portion of the perfluorophenyl end groups reacted. The possibility that some of the end groups in the original polyether were fluorinated phenols was discounted by further analytical investigation. Tetrafluoro-p-hydroquinone, which could not be picked up by the standard hydroxyl end-group determination, could be directly titrated potentiometrically with base. The polyethers showed no reactive acid groups by this method.

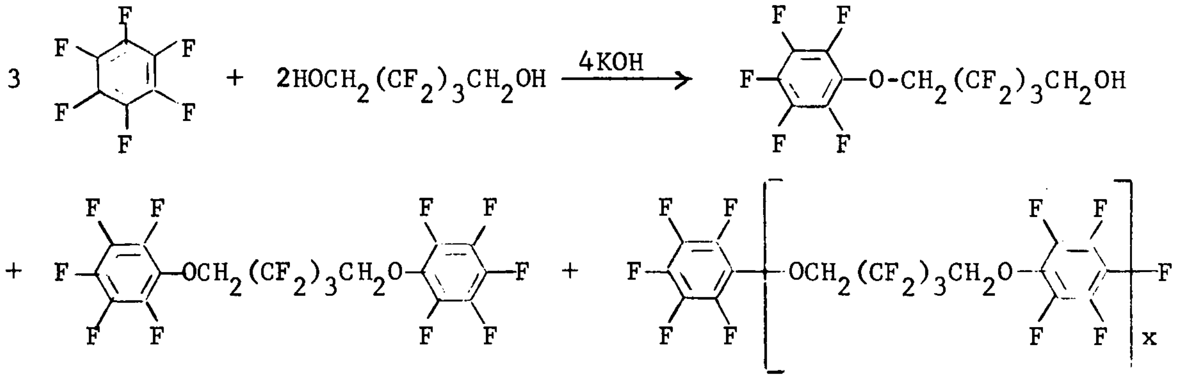
An attempt was also made to prepare a completely hydroxyl-terminated polyether by reaction of hexafluorobenzene, hexafluoropentanediol, and potassium hydroxide in DMF; followed by reaction of the polyether formed with more hexafluoropentanediol and potassium hydroxide; followed again by reaction of this polyether product with more hexafluoropentanediol and potassium hydroxide. According to the molecular weight [determined by VPO] and the hydroxyl end-group analysis, approximately five of every six chain ends are hydroxyl terminated.

Another possible way to convert the polyether to a completely hydroxyl-terminated one, is by blockage of the hydroxyl groups (to prevent further polymerization) and reaction with more hexafluoropentanediol and base or more sodium salt of hexafluoropentanediol. An attempt to block the hydroxyl groups by reaction with p-toluenesulfonyl chloride was unsuccessful. During this work, a brief study of the hydrolysis of the ditosylate of hexafluoropentanediol was carried out using potassium hydroxide in water, in ethanol, and in acetone. This hydrolysis study indicated that the ditosylate was very difficult to hydrolyze with base.

The use of dihydropyran as a blocking agent with the polyether and subsequent reaction to form completely hydroxyl-terminated material is currently being investigated and seems to be quite promising.

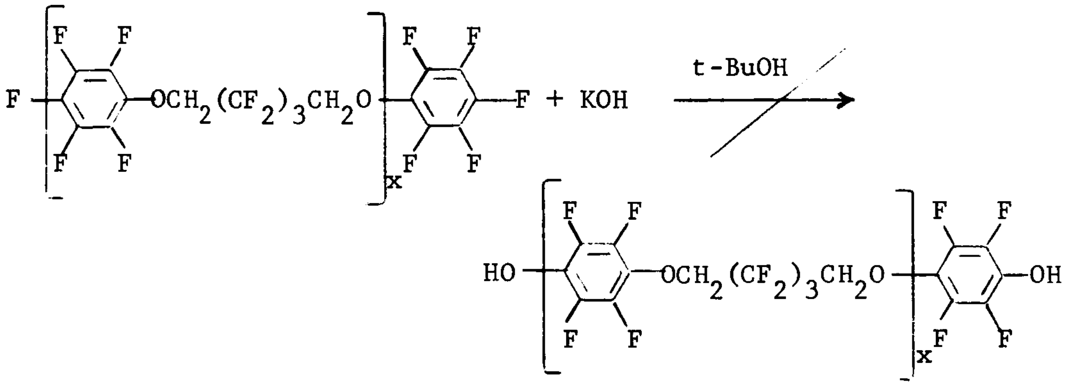
As attempts to convert the polyether terminated by both hexafluorobenzene and hexafluoropentanediol to a completely hydroxyl-terminated polyether were unsuccessful, reaction conditions, including ratios, times and temperatures, were investigated to see if the hydroxyl-terminated material can be obtained in a one-step operation. The results indicated that in the preparation of the initial polyether prepolymer by reaction of hexafluorobenzene, hexafluoropentanediol and potassium hydroxide, hydroxyl-termination cannot be ensured simply by using an excess of hexafluoropentanediol. Thus, emphasis was shifted to the conversion of the completely hexafluorobenzene-terminated polyether to a completely hydroxyl-terminated polyether.

During one of the preparations of hexafluorobenzene-terminated polyether, a new compound, the di-pentafluorophenyl ether of hexafluoropentanediol, was isolated from the monoether of hexafluorobenzene and hexafluoropentanediol by fractional distillation of the polyether.

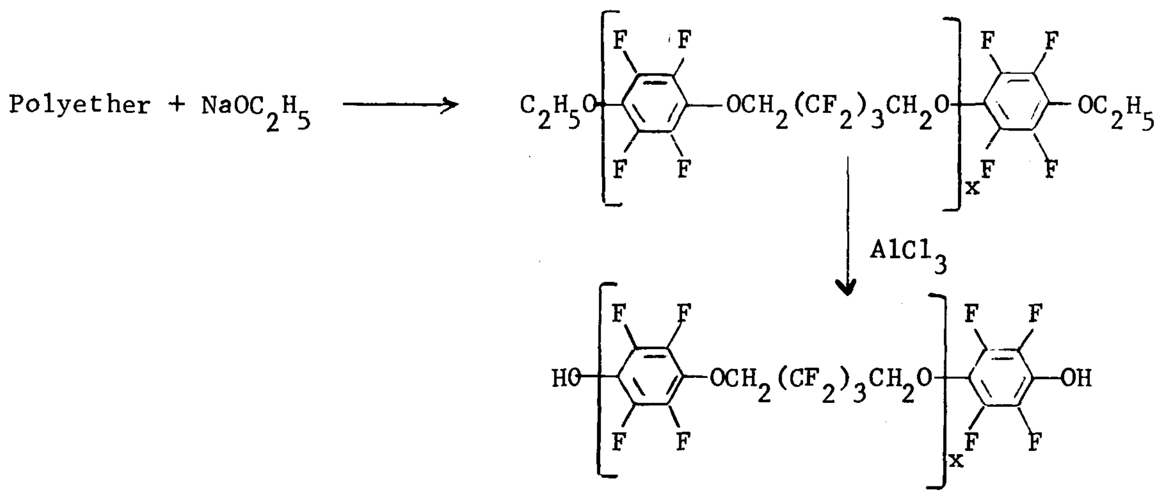


Attempts were made to "cap" the polyether with -OH, $-OC_2H_5$, $-OC_2H_4OH$ and $-OCH_2(CF_2)_3CH_2OH$ groups. These reactions would provide hydroxyl-terminated prepolymers, either directly or by a subsequent cleavage reaction, which would be suitable for further reaction with tetrafluoro-m-phenylene diisocyanate to provide a desirable polyurethane.

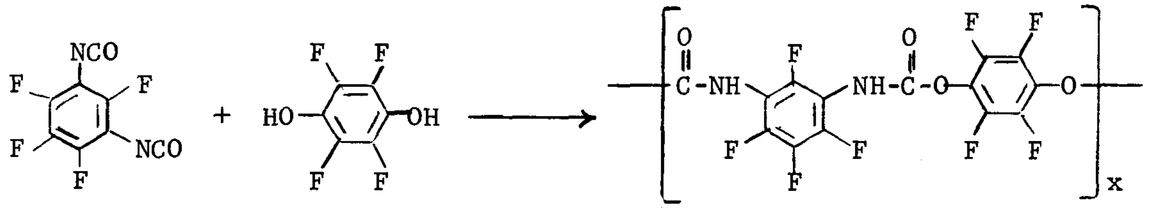
The attempt to cap the polyether with hydroxyl groups by reaction with potassium hydroxide in tert-butyl alcohol was unsuccessful. No hydroxyl groups were introduced into the polyether.



The reaction of the polyether with sodium ethoxide apparently proceeded as expected. The cleavage of the product by aluminum chloride would probably yield the hydroxyl-terminated polyether.

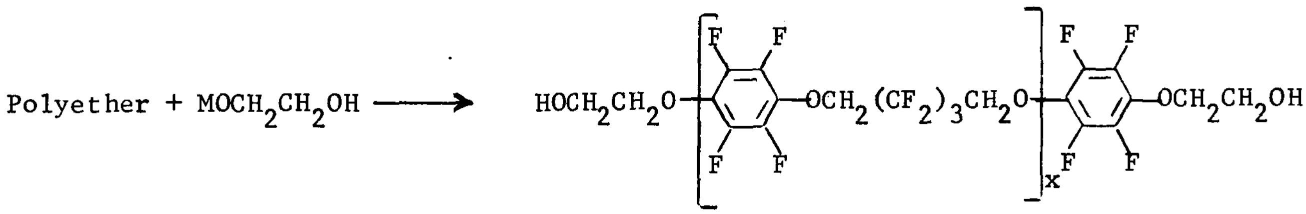


The phenolic hydroxyl group would probably provide a LOX-compatible polymer; however, when the model polyurethane was prepared from tetrafluoro-m-phenylene diisocyanate and tetrafluoro-p-hydroquinone, the reaction rate was found to be extremely slow. The low reactivity can most easily be attributed to the very low basicity of the perfluoro phenolic group.



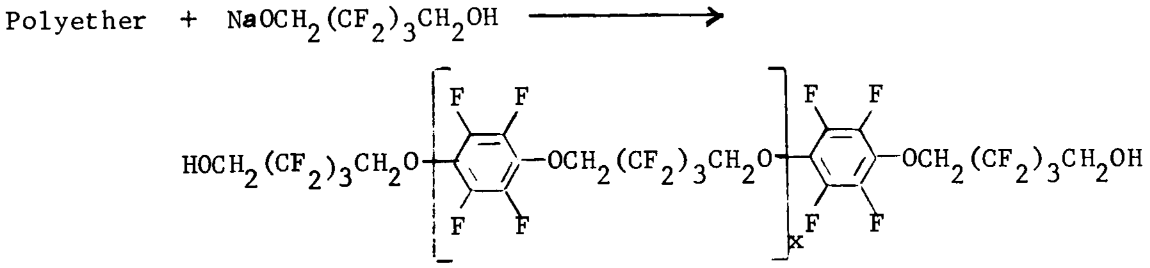
Owing to the sluggishness of the polymerization reaction, efforts to prepare the phenolic-terminated polyether are temporarily discontinued.

The hydroxylethyl ether end group in the product of the reaction of the polyether with the alkali metal salt of ethylene glycol may provide a suitable candidate for termination, providing that the two adjacent methylene units are compatible with LOX.

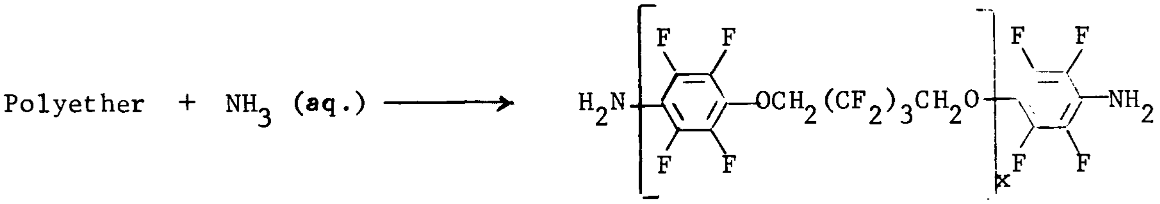


The reaction of the polyether with (1) the sodium salt of ethylene glycol, (2) ethylene glycol and potassium hydroxide in ethylene glycol, and (3) ethylene glycol and potassium hydroxide in DMF yielded the same product. The structure of this product is questionable, because analytical results indicate that there is termination with an acidic functionality.

The most promising structure is, of course, the ω-hydroxy-hexafluoropentoxy ether. This termination would be present in the product from the reaction of the hexafluorobenzene-terminated polyether with the sodium salt of hexafluoropentanediol. Results thus far are promising, as about two-thirds of the ends have been hydroxyl terminated. Further efforts are being directed toward achieving complete termination with the desired end group.



Another terminal group of interest is the amine. Completely amine-terminated polyethers could be used as prepolymers to give polyureas by reaction with diisocyanates. This amine-terminated polyether might also be converted by phosgenation to an isocyanate-terminated polyether which might be a valuable liquid diisocyanate. One attempt was made this year to prepare this amine-terminated polyether by reaction of the polyether with aqueous ammonia in a sealed metal tube at 500°F. The reaction conditions were apparently too severe and only carbonaceous material was obtained.

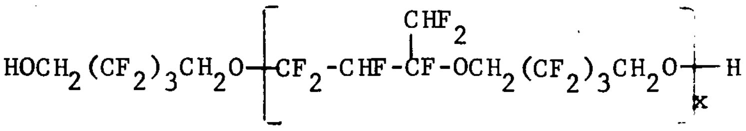


b. Polyethers of Hexafluoropentanediol and Perfluorinated Dienes. — The addition of alcohols to fluorinated olefins in the presence of base to yield ethers has been known for some time (Reference 4). The addition of diols to fluorinated dienes to yield polyethers has also been reported (Reference 5). It was believed that a useful hydroxyl-terminated polyether might be obtained by reaction of the available perfluorobutadiene with hexafluoropentanediol and potassium hydroxide.

$$HOCH_2(CF_2)_3CH_2OH + CF_2{=}CF{-}CF{=}CF_2 \xrightarrow{KOH}$$

$$HOCH_2(CF_2)_3CH_2O\left[CF_2\text{-}CHF\text{-}CHF\text{-}CF_2\text{-}O\text{-}CH_2(CF_2)_3CH_2O\right]_x H$$

or



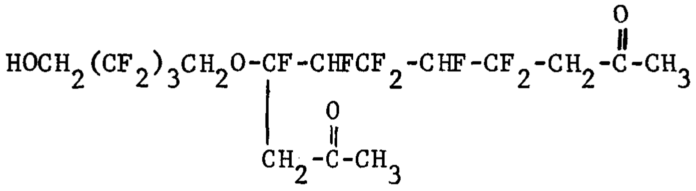
$$HOCH_2(CF_2)_3CH_2O\left[CF_2\text{-}CHF\text{-}\overset{\overset{CHF_2}{|}}{C}F\text{-}OCH_2(CF_2)_3CH_2O\right]_x H$$

A hydroxyl-terminated polyether was formed, but it contained some unsaturation due to base-catalyzed dehydrofluorination. This type of dehydrofluorination is reported (Reference 6) to occur in the reaction of perfluorobutadiene with sodium ethoxide in ethanol. In addition to the unsaturation, there are possibly some ester groups in the polyether. These esters could arise from hydrolysis of the difluoromethylene groups alpha to the oxygen atoms. Thus, attention was turned to the use of nonconjugated dienes. A similar reaction was carried out using a nonconjugated perfluorinated diene, perfluoropenta-1,4-diene to prepare a similar polyether.

$$\mathrm{CF_2{=}CF{-}CF_2{-}CF{=}CF_2 + HOCH_2(CF_2)_3CH_2OH \xrightarrow{KOH}}$$

$$\mathrm{-\!\!\left[OCH_2(CF_2)_3CH_2O{-}CF_2CHFCF_2CHFCF_2\right]_x\!\!-}$$

Reaction of this diene with hexafluoropentanediol yielded a viscous, light yellow oil. This oil was identified by its molecular weight, infrared spectrum, and elemental analysis as a condensation product of one mole of hexafluoropentanediol, one mole of perfluoropentadiene, and two moles of acetone. A suggested structure for this material is shown below.



$$\mathrm{HOCH_2(CF_2)_3CH_2O{-}\underset{\displaystyle |\atop CH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3}{CF}{-}CHFCF_2{-}CHF{-}CF_2{-}CH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3}$$

Work is being carried out on the reaction of hexafluoropentanediol with perfluoropentadiene in solvents other than acetone.

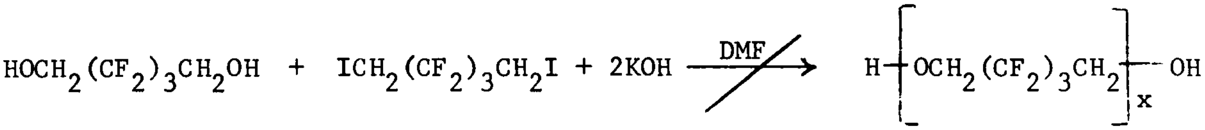
c. Tri-hexafluoropentylene Glycol. — Unsuccessful attempts to prepare tri-hexafluoropentylene glycol by reaction of 1,5-dichlorohexafluoropentane and the ditosylate of hexafluoropentanediol with the monosodium salt of hexafluoropentanediol were described previously (Reference 2). Since 1,5-diiodohexafluoropentane has now been prepared, the preparation of this diether was attempted by reaction of the diiodide with the sodium salt of hexafluoropentanediol in both DMF and ethanol. Tri-hexafluoropentylene glycol could be used as a diol for the preparation of polyurethanes or might be capable of forming a higher molecular weight polyether by dehydration. None of the desired product was obtained.

$$\mathrm{ICH_2(CF_2)_3CH_2I + 2\ \overset{\oplus}{Na}\ \overset{\ominus}{O}CH_2(CF_2)_3CH_2OH \not\longrightarrow}$$

$$\mathrm{HOCH_2(CF_2)_3CH_2O{-}CH_2(CF_2)_3CH_2{-}OCH_2(CF_2)_3CH_2OH}$$

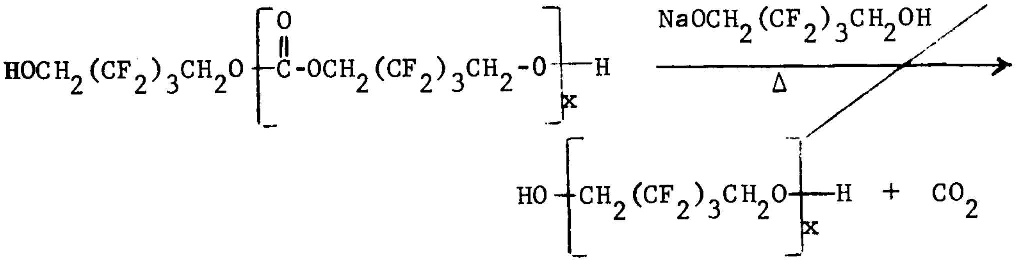
The same reaction was attempted by addition of the 1,5-diiodohexafluoropentane in DMF to the monosodium salt of hexafluoropentanediol which had been prepared in situ from hexafluoropentanediol and sodium methoxide in dioxane. No identifiable products were isolated.

d. Poly(hexafluoropentamethylene ether). — A considerable amount of work on the preparation of polyethers from hexafluoropentanediol and hexafluorobenzene has been described. In view of the facile reaction of hexafluoropentanediol with hexafluorobenzene, an attempt was made to prepare poly(hexafluoropentamethylene ether) by reaction of hexafluoropentanediol with 1,5-diiodohexafluoropentane in the presence of potassium hydroxide in DMF. No reaction occurred.



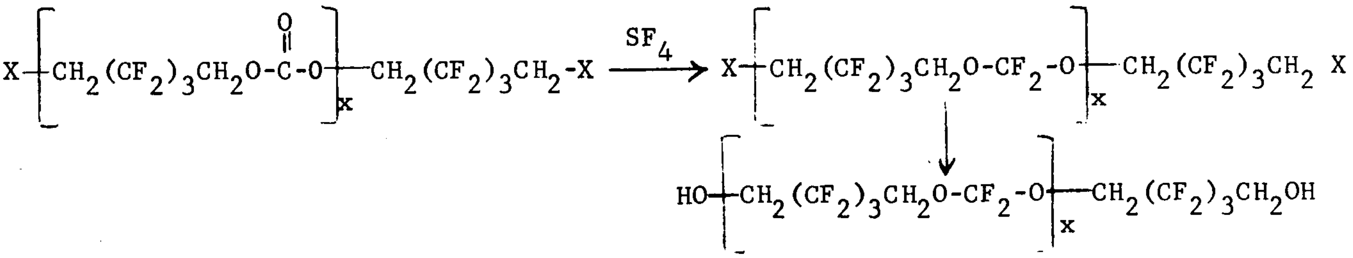
$$HOCH_2(CF_2)_3CH_2OH + ICH_2(CF_2)_3CH_2I + 2KOH \cancel{\xrightarrow{DMF}} H\left[OCH_2(CF_2)_3CH_2\right]_x OH$$

Annual Summary Report II describes an unsuccessful attempt to convert a hydroxyl-terminated poly(hexafluoropentamethylene carbonate) to a polyether by thermal decarboxylation. Reference 7 describes the conversion of alkyl aryl polycarbonates to the corresponding alkyl aryl polyethers. The conversion was achieved by heating the polycarbonate with an alkoxide or phenoxide salt in the absence of solvent. In view of this work, an attempt was made this quarter to decarboxylate hydroxyl-terminated poly(hexafluoropentamethylene carbonate) by heating it with a small amount of the monosodium salt of hexafluoropentanediol. No decarboxylation occurred.



$$HOCH_2(CF_2)_3CH_2O\left[\overset{O}{\overset{\|}{C}}\text{-}OCH_2(CF_2)_3CH_2\text{-}O\right]_x H \cancel{\xrightarrow[\Delta]{NaOCH_2(CF_2)_3CH_2OH}} HO\left[CH_2(CF_2)_3CH_2O\right]_x H + CO_2$$

e. Poly(1,1-difluoroformals) from Polycarbonates and Sulfur Tetrafluoride. — The reaction of 1,1-dihydroperfluoroalkyl carbonates with sulfur tetrafluoride has been reported (Reference 8) to yield 1,1-difluoroformals, a class of α-fluorinated esters. Extension of this reaction to fluoroalkyl polycarbonates such as those prepared under this program might yield the desired hydroxyl-terminated polyether precursors to polyurethanes.



$$X\left[CH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\right]_x CH_2(CF_2)_3CH_2\text{-}X \xrightarrow{SF_4} X\left[CH_2(CF_2)_3CH_2O\text{-}CF_2\text{-}O\right]_x CH_2(CF_2)_3CH_2\ X$$

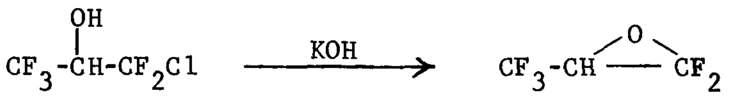
$$\downarrow$$

$$HO\left[CH_2(CF_2)_3CH_2O\text{-}CF_2\text{-}O\right]_x CH_2(CF_2)_3CH_2OH$$

Poly(hexafluoropentamethylene carbonate) was reacted with sulfur tetrafluoride using boron trifluoride as a catalyst.* A viscous liquid was obtained. The reaction apparently proceeded as expected, since the product was a liquid whose elemental analysis checked very closely for the desired product. This reaction is currently being investigated more fully.

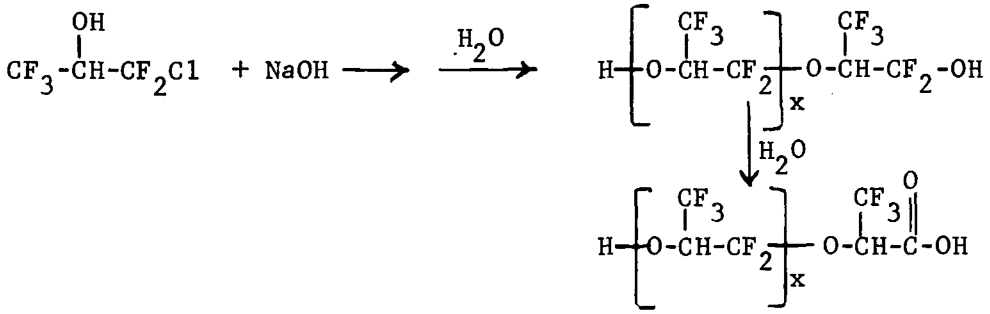
2. Polyethers from Chloropentafluoroisopropyl Alcohol

The preparation of a LOX-incompatible polyurethane from the polyether of 3,3,3-trifluoro-1,2-epoxypropane was discussed earlier in this report. Polyurethanes prepared from more highly fluorinated polyethers, such as the polyether from 2-hydroperfluoro-1,2-epoxypropane, would have a greater possibility of being LOX compatible. During this report period, attempts were made to prepare this epoxide by dehydrohalogenation of chloropentafluoroisopropyl alcohol.



The attempted dehydrohalogenation was first carried out in an aqueous medium, the method used successfully for the preparation of 3,3,3-trifluoroepoxypropane (Reference 1). As no epoxide or starting alcohol were isolated, hydrolysis of the epoxide was suspected. The reaction was then run in a nonaqueous medium. Instead of the epoxide, a low molecular weight polyether was obtained. In this reaction, the base apparently dehydrochlorinated the α-chloroalcohol and then immediately initiated polymerization of the epoxide formed. The epoxide must polymerize as rapidly as it is formed, as none of its hydrolysis product, the 1,2-glycol, was found.

The reaction of chloropentafluoroisopropyl alcohol with a 10% excess of sodium hydroxide in THF yielded a very viscous liquid polyether whose molecular weight was 2210 (determined by VPO). The infrared spectrum of this polyether indicated that it was terminated by both hydroxyl groups and acid groups, as would be expected in hydroxide catalysis.



$$CF_3\text{-}\overset{OH}{\overset{|}{CH}}\text{-}CF_2Cl + NaOH \longrightarrow \xrightarrow{H_2O} H\left[O\text{-}\overset{CF_3}{\overset{|}{CH}}\text{-}CF_2\right]_x O\text{-}\overset{CF_3}{\overset{|}{CH}}\text{-}CF_2\text{-}OH \xrightarrow{H_2O} H\left[O\text{-}\overset{CF_3}{\overset{|}{CH}}\text{-}CF_2\right]_x O\text{-}\overset{CF_3}{\overset{|}{CH}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH$$

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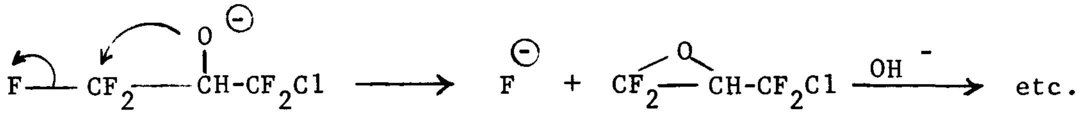
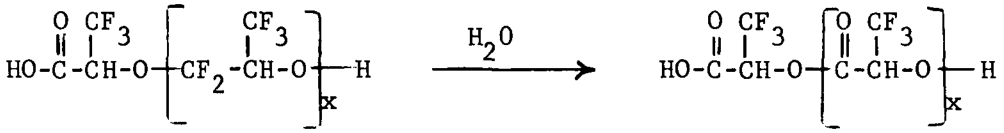
* Boron trifluoride has been shown to be an effective catalyst for the reaction of sulfur tetrafluoride with esters; [Reference W. R. Hasek et al., J. Am. Chem. Soc., 82, 543-51 (1960)].

An attempt to prepare a high molecular weight polyether by reaction of the alcohol with an equivalent amount of sodium hydroxide resulted in a viscous liquid polymer of 4240 molecular weight (determined by VPO). The elemental analysis of the polymer did not correspond to the expected structure, the percentage of fluorine being particularly low. In addition, the polymer contained a considerable amount of chloride.

It appears that the anion formed by reaction of the alcohol with base may have displaced some fluoride ions rather than all chloride ions, which eventually yielded a chlorine-containing polyether.

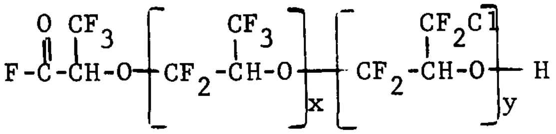


The method of workup of the polymer included pouring into water. The water, being basic from excess sodium hydroxide, may have caused some hydrolysis of difluoromethylene groups, resulting in the very low fluorine content.



$$\mathrm{HO{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{CF_3}{|}}{C}H{-}O{-}\left[CF_2{-}\overset{\overset{CF_3}{|}}{C}H{-}O\right]_x{-}H} \xrightarrow{H_2O} \mathrm{HO{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{CF_3}{|}}{C}H{-}O{-}\left[\overset{\overset{O}{\|}}{C}{-}\overset{\overset{CF_3}{|}}{C}H{-}O\right]_x{-}H}$$

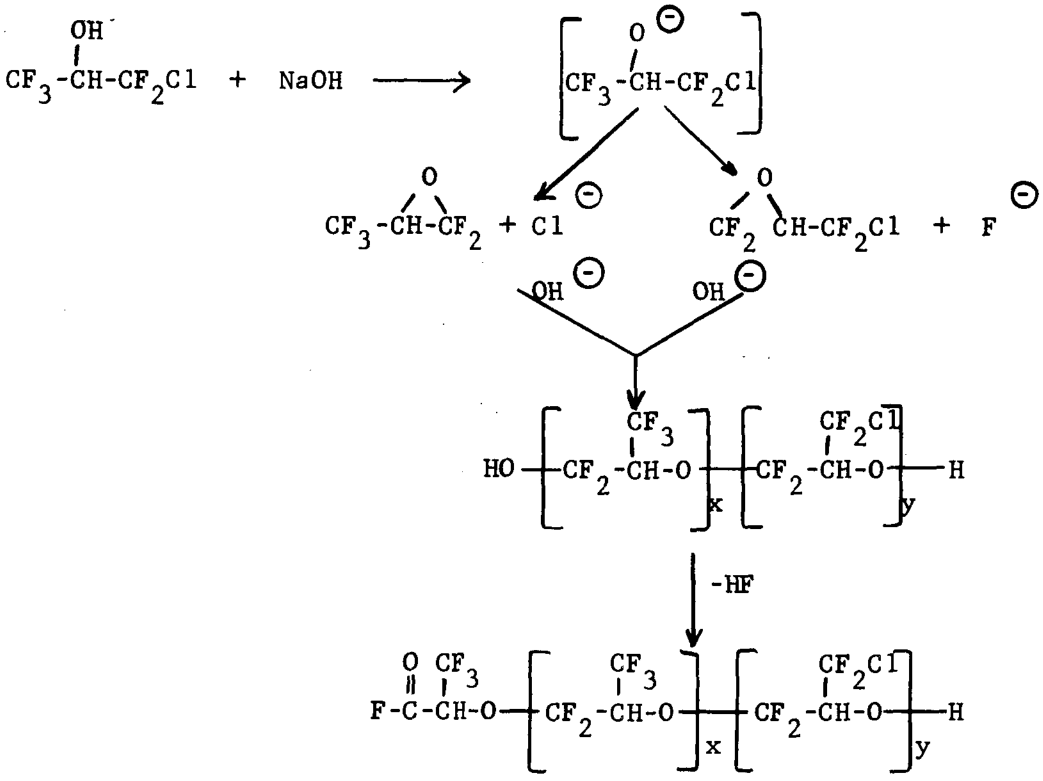
This polymerization was repeated. The reaction was run in diethyl ether instead of THF, and the polyether worked up without using water, to avoid hydrolysis. The molecular weight of the polymer was 5700±100 (determined by VPO). The elemental analysis of the polyether obtained checked quite closely for the mixed polyether of the following structure.



$$\mathrm{F{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{CF_3}{|}}{C}H{-}O{-}\left[CF_2{-}\overset{\overset{CF_3}{|}}{C}H{-}O\right]_x\left[CF_2{-}\overset{\overset{CF_2Cl}{|}}{C}H{-}O\right]_y{-}H}$$

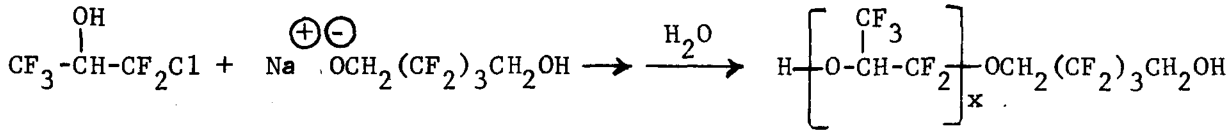
where the ratio of x to y is between 3:1 and 4:1. It thus appears that the displacement of halide ion by the anion of chloropentafluoroisopropanol is random, displacing three or four fluoride ions for every one chloride ion. The suggested overall path for the polymerization is shown below.

This is the first highly fluorinated aliphatic polyether which has the potential of being developed into an isocyanate-terminated prepolymer. This polyether contains over 57% fluorine. The preparation and identification of this polyether is a significant advance in the development of a LOX-compatible adhesive system.



The ratio of the reactants in the above reaction, from which a polyether of molecular weight 5700 was obtained,was 1:1. The polymerization was repeated using different ratios of reactants. When the ratio of sodium hydroxide to alcohol was increased to 1.2:1, the molecular weight of the product increased to 7850. When the ratio was reduced to 0.8:1, a product of 2400 molecular weight was obtained. In the latter polymerization the yield of polymer was also reduced. A large sample of a 3680 molecular weight polyether was prepared and used in the attempt to prepare a polyurethane by reaction with tetrafluoro-m-phenylene diisocyanate.

A high molecular weight polyether was prepared by reaction of equimolar amounts of chloropentafluoroisopropyl alcohol and pure monosodium salt of hexafluoropentanediol in THF. The product was an elastic gum which was insoluble in all solvents tested. Because of its insolubility, its molecular weight could not be determined. As would be expected from catalysis by a monosodium salt of a diol, the polyether is proably terminated by hydroxyl groups only. It exhibited unexpected thermal stability, and did not discolor even when heated to 300°C.

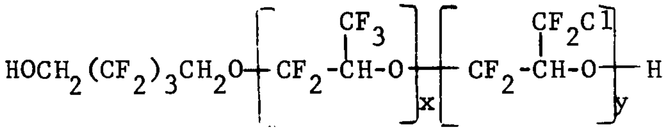


$$CF_3\text{-}\overset{OH}{\overset{|}{C}}H\text{-}CF_2Cl + Na^{\oplus}\,{}^{\ominus}OCH_2(CF_2)_3CH_2OH \longrightarrow \xrightarrow{H_2O} H\left[O\text{-}\overset{CF_3}{\overset{|}{C}}H\text{-}CF_2\right]_x OCH_2(CF_2)_3CH_2OH$$

This polyether was subjected to thermogravimetric analysis. Its polymer decomposition temperature was 250°±10°C both in air and in helium. The thermograms are shown in Figures 13 and 14.

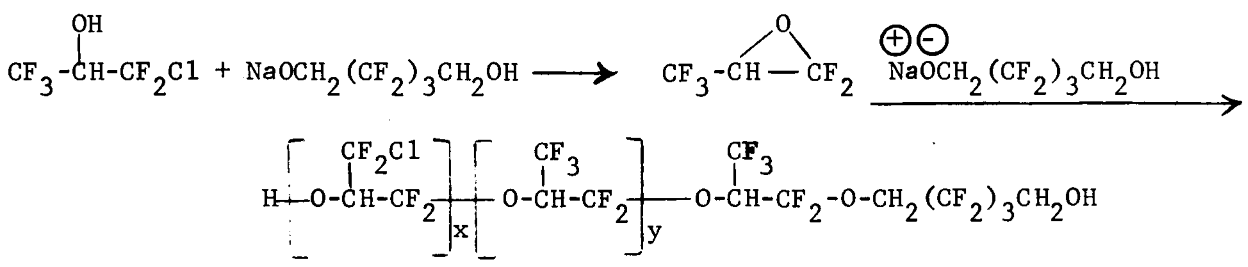
Samples of this polyether (12 mils thick) were submitted to MSFC for LOX-compatibility testing. It had 2 reactions in 20 tests. Because Narmco believed that this incompatibility was due to residual solvent, the polyether was again prepared. One sample was synthesized in THF solution and the product extensively dried. A second sample was prepared in a LOX-compatible solvent, perfluorotributylamine. Neither of the polyethers obtained could be pressed into sheets, and both samples were pulverized and sent as powders to MSFC for LOX-impact testing. Neither sample reacted in 20 tests, proving that the incompatibility of the first sample tested was indeed due to solvent, and this polyether is LOX compatible.

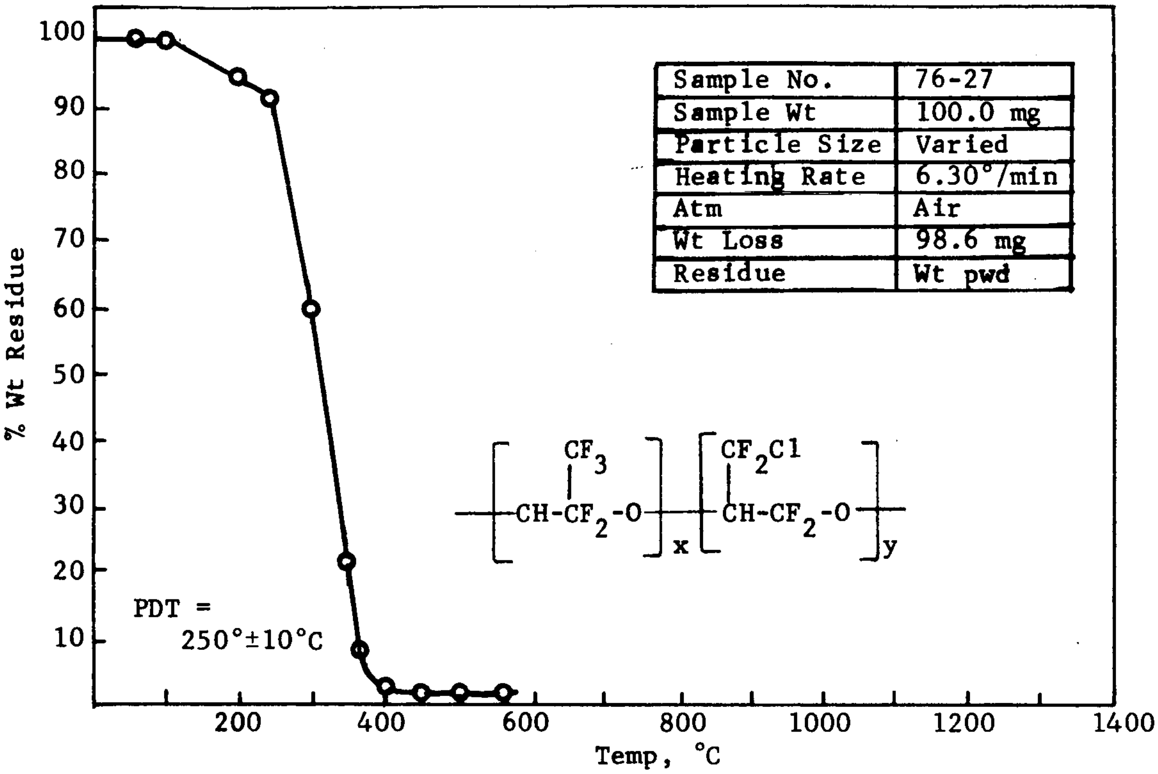
Previously, polyethers of chloropentafluoroisopropyl alcohol that were prepared using the monosodium salt of hexafluoropentanediol failed to give elemental analyses that agreed with the calculated values for the expected products. In each preparation, the polymers were washed repeatedly with water. The high molecular weight polyether prepared in THF solution and worked up without water washing gave an elemental analysis that agrees fairly well with the calculated values for the polyether of the following structure, in which only a small amount of the "y" moiety is present.



$$HOCH_2(CF_2)_3CH_2O\left[CF_2\text{-}\overset{CF_3}{\overset{|}{C}}H\text{-}O\right]_x\left[CF_2\text{-}\overset{CF_2Cl}{\overset{|}{C}}H\text{-}O\right]_y H$$

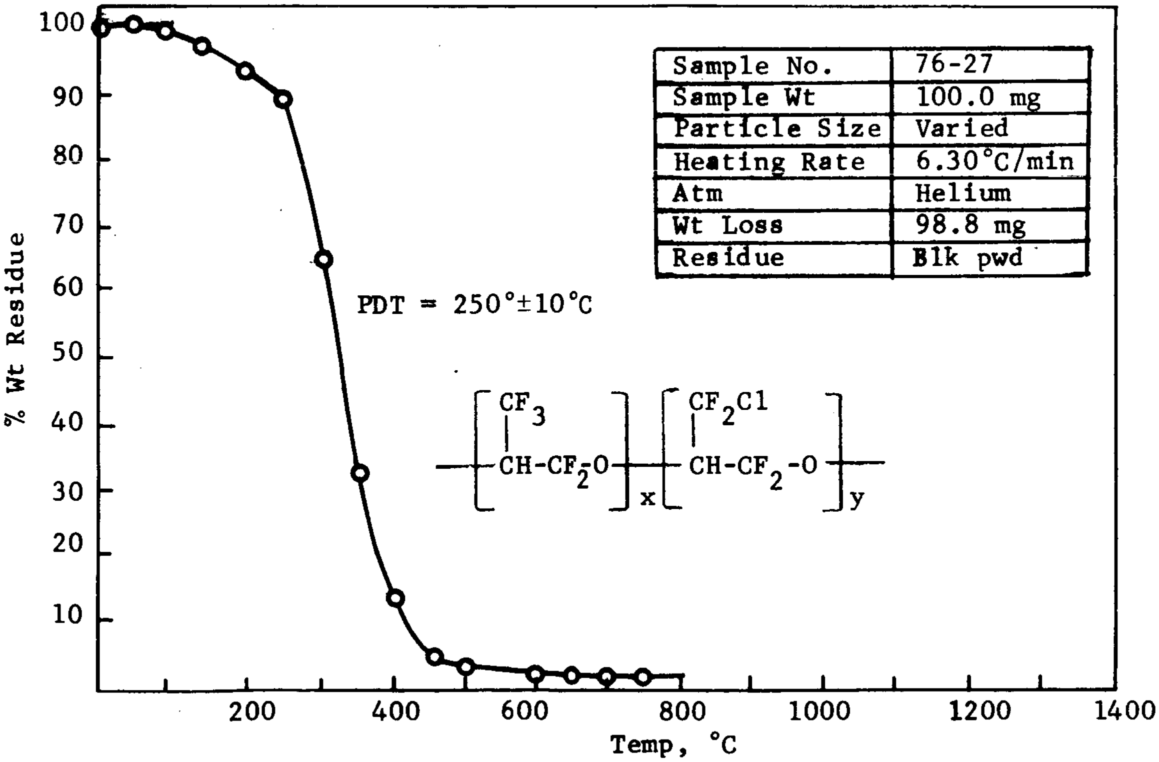
When the polymerization was carried out using equimolar amounts of chloropentafluoroisopropyl alcohol and extremely pure sodium salt of hexafluoropentanediol in THF solution, a high molecular weight, elastomeric polyether was obtained. When the same ratio of reactants but less pure sodium salt was used, a polyether of 1960 molecular weight was isolated. The hydroxyl number was 1900, indicating that the product was terminated on one end with hexafluoropentanediol. The secondary group on the other end is not identified by the method used for alcohol determination. This was established by the failure to determine the presence of any hydroxyl groups in chloropentafluoroisopropyl alcohol. The infrared spectrum and direct titration of the polymer indicated that there were no acid groups present. This evidence indicates that the structure of the polyether is most probably that shown below, and establishes for the first time that the attack of the initiating anion on the intermediate epoxide occurs at the primary (CF_2) carbon rather than the secondary (-CH-) carbon.





Sample No.	76-27
Sample Wt	100.0 mg
Particle Size	Varied
Heating Rate	6.30°/min
Atm	Air
Wt Loss	98.6 mg
Residue	Wt pwd

Figure 13. Thermogram of Polyether from Chloropentafluoroisopropyl Alcohol (Sodium Salt of Hexafluoropentanediol Initiated) in Air



Sample No.	76-27
Sample Wt	100.0 mg
Particle Size	Varied
Heating Rate	6.30°C/min
Atm	Helium
Wt Loss	98.8 mg
Residue	Blk pwd

Figure 14. Thermogram of Polyether from Chloropentafluoroisopropyl Alcohol (Sodium Salt of Hexafluoropentanediol Initiated) in Helium

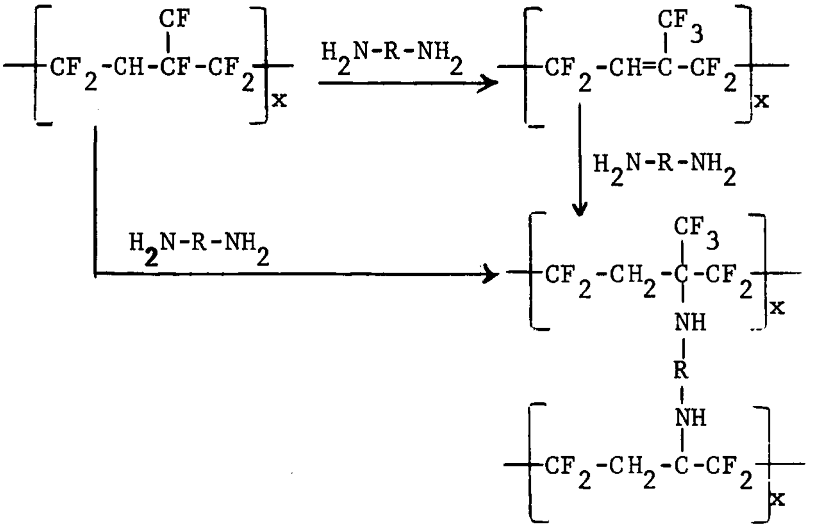
A polyurethane was prepared by reaction of this polyether with tetrafluoro-m-phenylene diisocyanate.

This polymerization was repeated using different ratios of reactants. When the ratio of sodium salt of hexafluoropentanediol to chloropentafluoroisopropyl alcohol was increased to 1.2:1, the molecular weight of the product decreased to 1000. When the ratio was decreased to 0.8:1, a product of 2640 molecular weight was obtained.

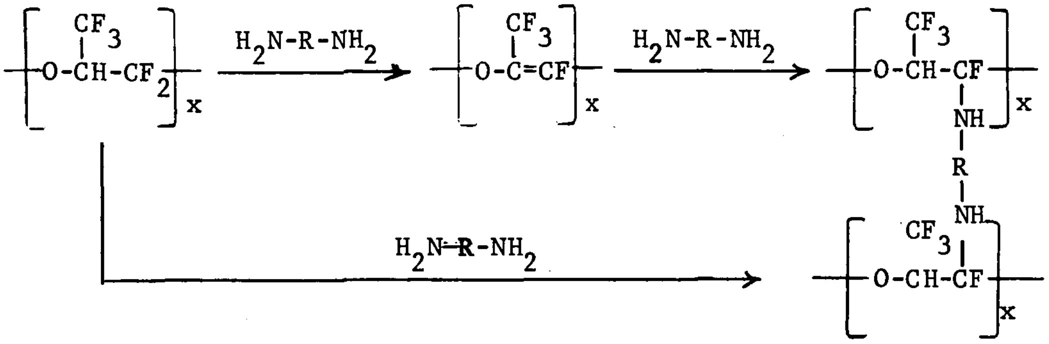
Since the polyurethane prepared from tetrafluoro-m-phenylene diisocyanate and a 1960 molecular weight polyether was elastomeric only above 65°C, an attempt was made to prepare a large amount of higher molecular weight polyether. A ratio of 0.8 mole of sodium salt to 1 mole of chloropentafluoroisopropyl alcohol was again used. This time, however, a polyether of 1790 molecular weight was obtained. Work is currently being conducted to prepare higher molecular weight polyether in order to prepare a more flexible polyurethane.

The structures of these polymers prepared from chloropentafluoroisopropyl alcohol still have not been positively established. Although Narmco believes that the structure of these polymers is that proposed during this discussion, some doubt still exists, especially since the elemental analysis of various samples of these polymers show considerable variation. These structures are still under investigation.

The high molecular weight polyether from chloropentafluoroisopropyl alcohol, mentioned above, could show promise as an elastomer, especially if it could be crosslinked. One of the methods of curing Viton A, a copolymer of perfluoropropylene and vinylidene fluoride, is reaction with a diamine or triamine. The crosslinking most likely occurs either by elimination of HF from the copolymer followed by addition of the amine group to the double bond formed or by displacement of the tertiary fluoride ion by the amine.



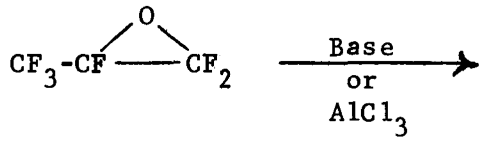
The chloropentafluoroisopropyl alcohol polyether is believed to have a structure which could eliminate HF or undergo a displacement reaction. Therefore, a curing experiment was conducted on this polyether.



A sample of the polyether of 7850 molecular weight prepared by sodium hydroxide initiation was successfully cured at room temperature with triethylenetriamine. The cured polymer was a tough elastomer which did not melt.

3. Poly(perfluoropropylene oxide)

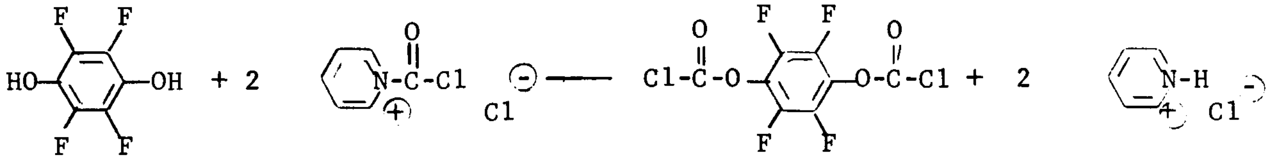
An attempted synthesis of poly(perfluoropropylene oxide) was described in Annual Summary Report II (July 1965). The published procedure (Reference 9) for the preparation of perfluoro-1,2-epoxypropane was followed and an attempt was made to polymerize it without isolation using an anionic initiator, the monosodium salt of hexafluoropentanediol. No polyether was obtained. This year, the polyether was isolated and attempts were made to polymerize it with potassium hydroxide and with a solution of sodium cyanide in DMAC. An attempt was also made to initiate the polymerization using aluminum chloride, a powerful cationic initiator. There was no indication of polymerization in any of the attempts.



E. Monomers

1. Tetrafluoro-p-phenylene Bischloroformate

Tetrafluoro-p-phenylene bischloroformate was prepared using the method developed and used successfully for the preparation of hexafluoropentamethylene bischloroformate, the addition of the diol to a suspension of chlorocarbonyl pyridinium chloride in ether.

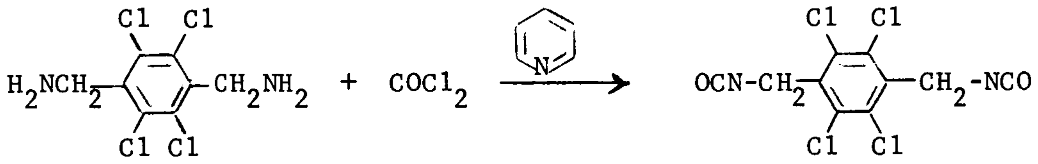


The product was identified by its infrared spectrum, elemental analysis, and conversion to its di-N-methylanilino derivative.

The yield of the aromatic bischloroformate was somewhat low and was accompanied by the formation of a considerable amount of polycarbonate. This is in contrast to the excellent yield of bischloroformate from hexafluoropentanediol.

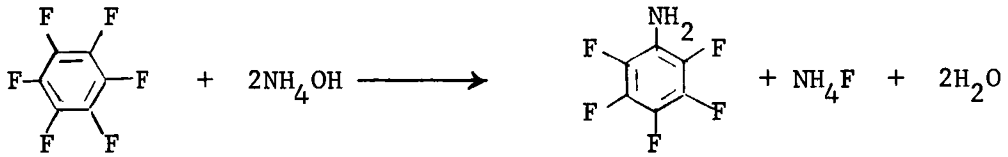
2. Tetrachloro-p-xylylene α,α'-Diisocyanate

The preparation of tetrachloro-p-xylylene α,α'-diisocyanate was described previously (Reference 1). Neither the elemental analysis nor the isocyanate equivalent was close enough to the theoretical values to consider this compound pure. The synthesis of the diisocyanate was again carried out using Narmco's usual phosgenation procedure. As it was believed that the product obtained previously contained some carbamyl chloride, the intermediate product obtained was heated for a long period of time in refluxing o-dichlorobenzene to convert any carbamyl chloride to isocyanate. The product obtained was pure tetrachloro-p-xylylene α,α'-diisocyanate, identified by its elemental analysis and isocyanate equivalent.



3. Pentafluoroaniline

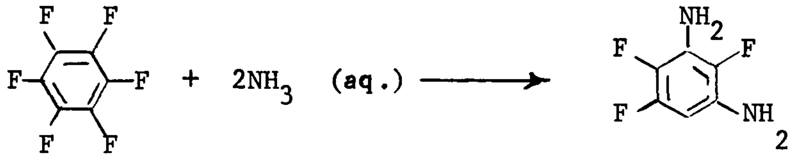
During this report period, the preparation of pentafluoroaniline and tetrafluoro-m-phenylenediamine was investigated using a recently reported Russian procedure (Reference 10). Pure pentafluoroaniline was prepared in 54% yield by reaction of hexafluorobenzene with aqueous ammonia.



4. Tetrafluoro-m-phenylenediamine

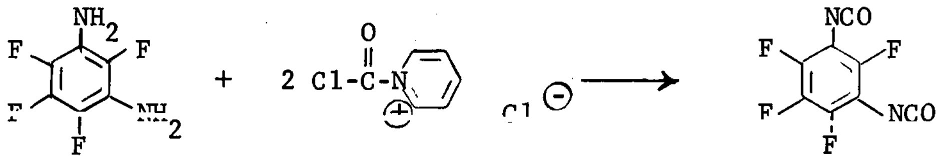
Several polyurethanes have been prepared during this program using tetrafluoro-p-phenylene diisocyanate. As more flexibility might be obtained by using tetrafluoro-m-phenylene diisocyanate, its precursor, tetrafluoro-m-phenylenediamine, was prepared and phosgenated. The preparation of tetrafluoro-m-phenylenediamine by reaction of pentafluoroaniline and potassium phthalimide was previously reported (Reference 2).

Tetrafluoro-m-phenylenediamine was prepared in 48% yield by reaction of hexafluorobenzene with aqueous ammonia using a modification of the Russian procedure (Reference 10).



5. Tetrafluoro-m-phenylene Diisocyanate

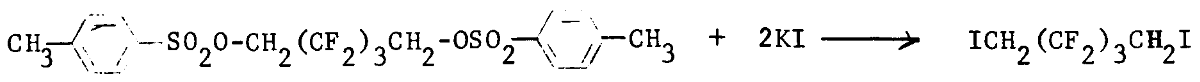
Tetrafluoro-m-phenylene diisocyanate was prepared in 56% yield by the reaction of tetrafluoro-m-phenylenediamine with chlorocarbonyl pyridinium chloride using the same procedure used for the preparation of the para diisocyanate.



The starting diamine contained about 5% of the para diamine. This mixture was used because it was believed that polyurethanes prepared from the mixed diisocyanate might be less crystalline. The diisocyanate prepared contained the same ratio of meta to para materials, 95% meta diisocyanate and 5% para diisocyanate. The identity of this liquid diisocyanate was confirmed by its infrared spectrum, elemental analysis, and the preparation of a derivative. Although the elemental analysis of the N-methylaniline derivative checked, it had a broad melting point. By fractional precipitation of the derivative, a small amount of a high-melting substance was obtained which was identified as the diurea of tetrafluoro-p-phenylene diisocyanate. The isolation of this diurea further substantiates that the impurity is the para diisocyanate.

6. 1,5-Diiodohexafluoropentane

1,5-Diiodohexafluoropentane was prepared in good yield by reaction of the ditosylate of hexafluoropentanediol with potassium iodide in refluxing ethylene glycol solution. It was identified by elemental analysis.



$$CH_3C_6H_4SO_2O\text{-}CH_2(CF_2)_3CH_2\text{-}OSO_2C_6H_4CH_3 + 2KI \longrightarrow ICH_2(CF_2)_3CH_2I$$

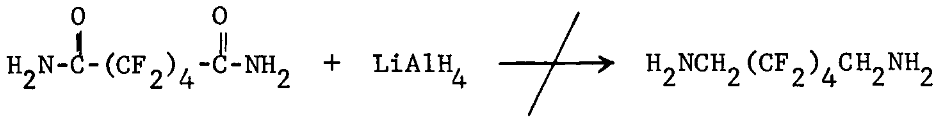
7. Attempted Preparation of Hexafluoropentamethylene Diisocyanate

The attempted preparation of hexafluoropentamethylene diisocyanate by reaction of the ditosylate of hexafluoropentanediol with potassium isocyanate was reported previously (Reference 1). This year two more attempts were made to prepare this diisocyanate: by reaction of 1,5-diiodohexafluoropentane with potassium isocyanate, and with silver cyanate. Neither of these methods was successful.

$$\begin{array}{lll} ICH_2(CF_2)_3CH_2I & + \ 2KNCO \ \not\longrightarrow & OCNCH_2(CF_2)_3CH_2NCO \\ & + \ 2AgOCN \ \not\longrightarrow & \end{array}$$

8. Attempted Preparation of Octafluorohexanediamine

As discussed previously (Reference 1), octafluorohexanediamine might be converted to the corresponding diisocyanate by phosgenation more conveniently than hexafluoropentanediamine. An attempt was made to prepare octafluorohexanediamine by lithium aluminum hydride (LAH) reduction of the previously prepared (Reference 1) perfluoroadipamide. Only unreacted starting material was recovered.



$$H_2N\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CF_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 + LiAlH_4 \not\longrightarrow H_2NCH_2(CF_2)_4CH_2NH_2$$

9. Attempted Preparation of Hexafluoropimelic Acid

The hydrolytic instability of polyesters prepared from perfluorinated acids was discussed previously (Reference 2). Consideration has been given to the possibility that polyesters of 1,1-dihydroperfluoro acids, such as hexafluoropimelic acid, might be hydrolytically stable and still be LOX compatible (Reference 1). One of Narmco's approaches involved the conversion of 1,5-diiodohexafluoropentane to hexafluoropimelonitrile, followed by hydrolysis to hexafluoropimelic acid.

$$I\ CH_2(CF_2)_3CH_2I + 2M\ CN \longrightarrow NCCH_2(CF_2)_3CH_2\ CN \xrightarrow{\text{Hydrolysis}} HOOC\text{-}CH_2(CF_2)_3\ CH_2\text{-}COOH$$

Several attempts to prepare 3,3,4,4,5,5-hexafluoropimelonitrile and pimelic acid have been described previously (Reference 1). Additional attempts were made to prepare these compounds by reaction of 1,5-diiodohexafluoropentane with sodium cyanide and copper (I) cyanide in aqueous methanol, sodium cyanide in ethylene glycol, and the copper (I) cyanide in N-methylpyrrolidone (NMP) and in DMF. No appreciable amount of product was obtained in any of these reactions.

$$ICH_2(CF_2)_3CH_2I \quad + \quad 2NaCN \;\not\xrightarrow{CH_3OH,\ H_2O}\; HOOCCH_2(CF_2)_3CH_2COOH$$

$$ICH_2(CF_2)_3CH_2I \quad + \quad 2NaCN \;\not\xrightarrow{HOCH_2CH_2OH}\; NCCH_2(CF_2)_3CH_2CN$$

$$ICH_2(CF_2)_3CH_2I \quad + \quad 2CuCN \;\not\xrightarrow{DMF}\; NCCH_2(CF_2)_3CH_2CN$$

$$ICH_2(CF_2)_3CH_2I \quad + \quad 2CuCN \;\not\xrightarrow{NMP}\; NCCH_2(CF_2)_3CH_2CN$$

10. Attempted Preparation of 4,4,5,5,6,6-Hexafluoronona-1,8-diyne

Another approach to the preparation of hexafluoropimelic acid involves the oxidation of 4,4,5,5,6,6-hexafluoro-nona-1,8-diyne.

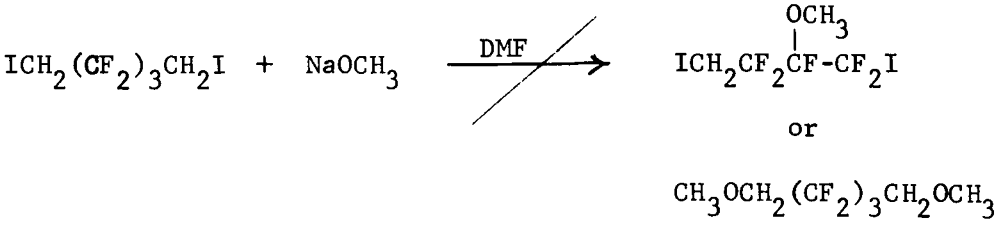
$$HC{\equiv}C\text{-}CH_2(CF_2)_3CH_2\text{-}C{\equiv}CH \xrightarrow{\text{Oxidation}} HOOC\text{-}CH_2(CF_2)_3CH_2\text{-}COOH$$

An attempt was made to prepare this diacetylene compound by reaction of diiodohexafluoropentane with sodium acetylide in a mixed solvent of xylene and DMF following the procedure of Rutledge (Reference 11). Only unreacted diiodide was recovered.

$$ICH_2(CF_2)_3CH_2I + 2\ NaC{\equiv}CH \;\not\xrightarrow[DMF]{Xylene-}\; HC{\equiv}C\text{-}CH_2(CF_2)_3CH_2\text{-}C{\equiv}CH \quad + \quad 2\ NaI$$

11. Attempted Reaction of 1,5-Diiodohexafluoropentane with Sodium Methoxide

Various reactions in which derivatives of hexafluoropentanediol have been reacted with the sodium salt of hexafluoropentanediol made from sodium methoxide have yielded small amounts of product containing methoxy groups. Since the sodium salt had been prepared using sodium methoxide, it might have contained sodium methoxide as an impurity. It was speculated that the products isolated probably resulted from the reaction of this sodium methoxide with either the derivative or the sodium salt. In order to shed some light on the structure and the origin of this compound, diiodohexafluoropentane was reacted with sodium methoxide in DMF. Only unreacted starting material was isolated.



$$ICH_2(CF_2)_3CH_2I \;+\; NaOCH_3 \;\cancel{\xrightarrow{\text{DMF}}}\; ICH_2CF_2\overset{OCH_3}{\overset{|}{C}}F\text{-}CF_2I$$

or

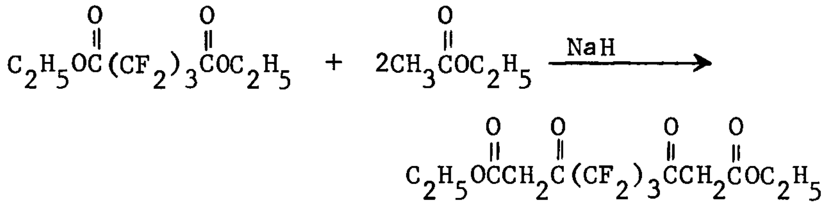
$$CH_3OCH_2(CF_2)_3CH_2OCH_3$$

12. <u>Attempted Preparation of 3,3,4,4,5,5,6,6,7,7-Decafluoroazelaic Acid</u>

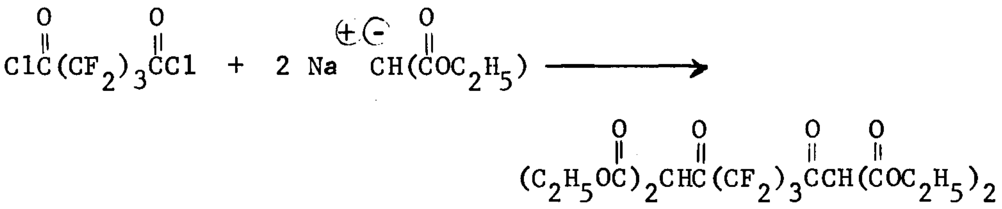
Various unsuccessful attempts to prepare hexafluoropimelic acid have been reported during this program. This diacid would be used to prepare hydroxyl-terminated polyesters. Three attempts were made to prepare an acid of similar structure, 3,3,4,4,5,5,6,6,7,7-decafluoroazelaic acid, for use in the preparation of polyesters.

$$HOOCCH_2(CF_2)_5CH_2COOH$$

The preparations of diethyl-3,7-diketo-4,4,5,5,6,6-hexafluoroazelate and diethyl-2,8-dicarbethoxy-3,7-diketo-4,4,5,5,6,6-hexafluoroazelate were reported by McBee (Reference 12).

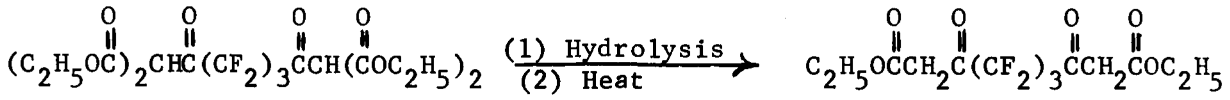


$$C_2H_5O\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}OC_2H_5 \;+\; 2CH_3\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow{\text{NaH}} C_2H_5O\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$$



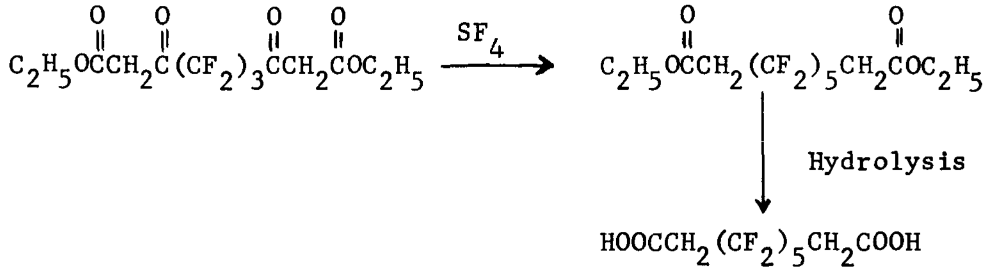
$$Cl\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}Cl \;+\; 2\;\overset{\oplus}{Na}\;\overset{\ominus}{C}H(\overset{O}{\overset{\|}{C}}OC_2H_5) \longrightarrow (C_2H_5O\overset{O}{\overset{\|}{C}})_2CH\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}CH(\overset{O}{\overset{\|}{C}}OC_2H_5)_2$$

The latter compound should be capable of conversion into the former compound by hydrolysis and decarboxylation.



$$(C_2H_5O\overset{O}{\overset{\|}{C}})_2CH\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}CH(\overset{O}{\overset{\|}{C}}OC_2H_5)_2 \xrightarrow[\text{(2) Heat}]{\text{(1) Hydrolysis}} C_2H_5O\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$$

This diester might be converted to decafluoroazelaic acid by reaction with sulfur tetrafluoride, followed by hydrolysis.



$$C_2H_5O\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow{SF_4} C_2H_5O\overset{O}{\overset{\|}{C}}CH_2(CF_2)_5CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$$

$$\Big\downarrow \text{Hydrolysis}$$

$$HOOCCH_2(CF_2)_5CH_2COOH$$

The attempts to repeat the preparations of these two diketoazelates, however, were unsuccessful.

A similar line of approach would involve the preparation of diethyl-2,2,-8,8-tetracarbethoxy-3,7-diketo-4,4,5,5,6,6-hexafluoroazelate.

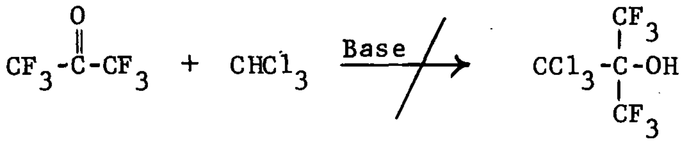
$$Cl\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}Cl + Na^{\oplus}\ {}^{\ominus}C(\overset{O}{\overset{\|}{C}}OC_2H_5)_3 \longrightarrow (C_2H_5O\overset{O}{\overset{\|}{C}})_3C\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}C(\overset{O}{\overset{\|}{C}}OC_2H_5)_3$$

This compound should also be capable of being converted to decafluoroazelaic acid by partial hydrolysis and decarboxylation followed by reaction with sulfur tetrafluoride and hydrolysis.

The reaction of perfluoroglutaryl chloride with the sodio salt of tricarbethoxy methane apparently proceeded as expected since a product was isolated whose elemental analysis checked reasonably well for the desired product. This product,however, was very susceptible to hydrolysis and/or decarboxylation. On shaking with distilled water, the product loses practically all of its fluorine atoms.

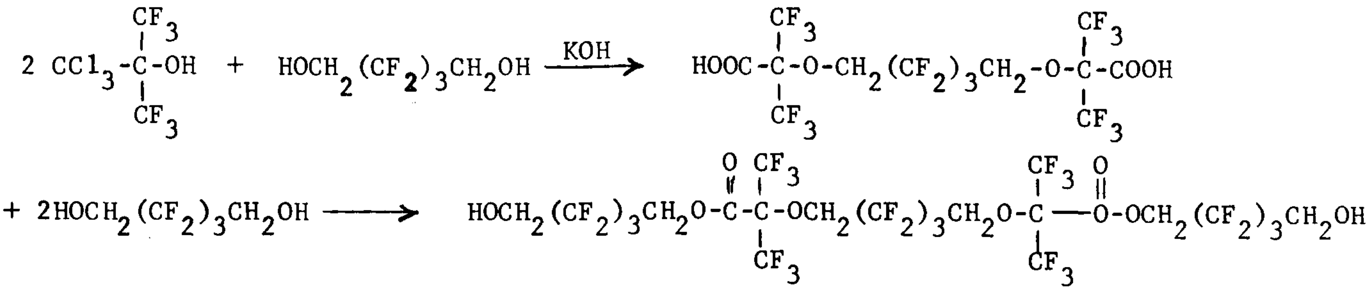
13. Attempted Preparation of Hexafluorochloretone

Two unsuccessful attempts were made to prepare hexafluorochloretone by the reaction of hexafluoroacetone and chloroform in the presence of a base.



$$CF_3-\overset{O}{\overset{\|}{C}}-CF_3 + CHCl_3 \not\xrightarrow{\text{Base}} CCl_3-\underset{CF_3}{\overset{CF_3}{C}}-OH$$

This compound was of interest because there is a possiblity of converting it to an interesting diacid by reaction with hexafluoropentanediol. This acid could then be used to prepare a highly fluorinated, hydroxyl-terminated polyester. A similar series of reactions starting with acetone has been described by Weizmann and coworkers (References 13 and 14).

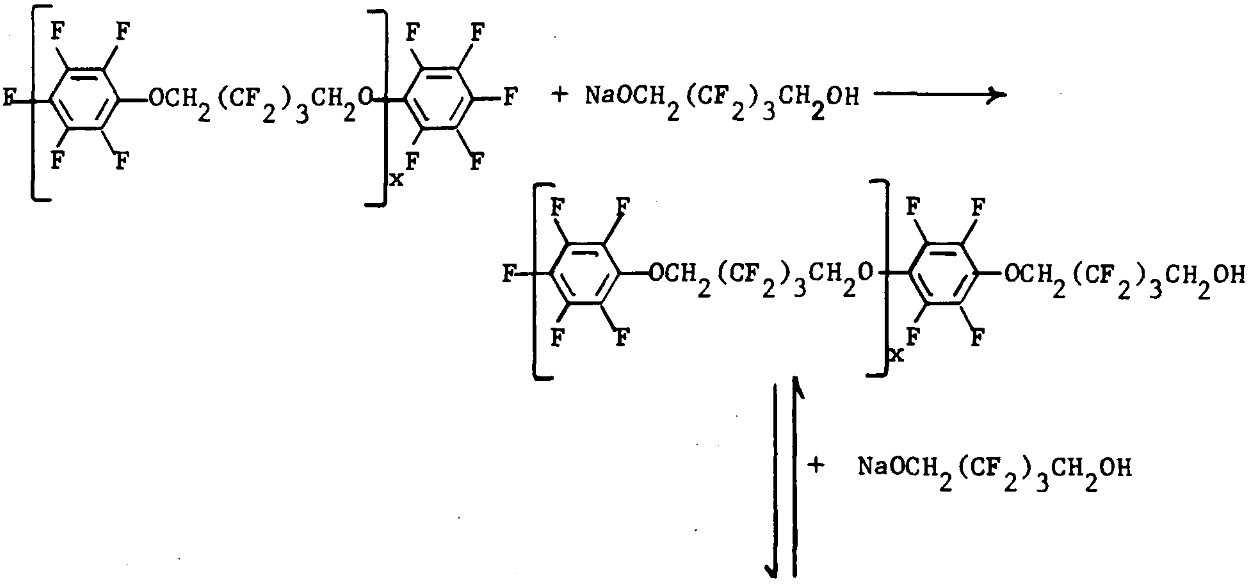


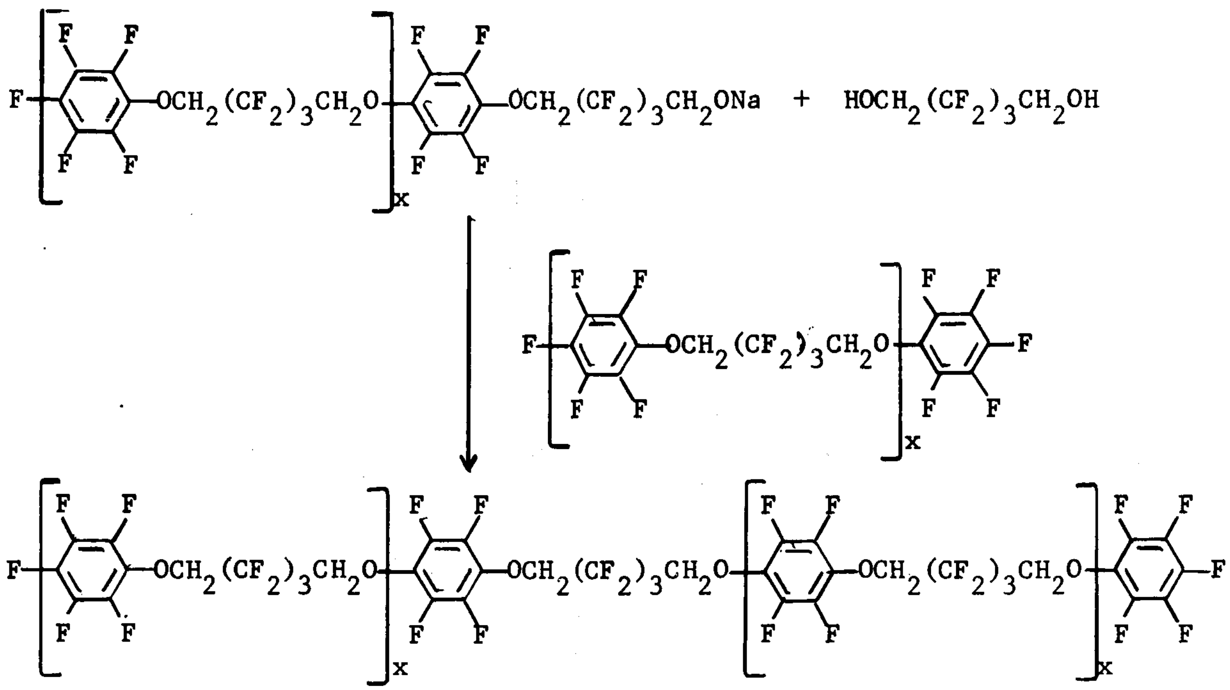
$$2\ CCl_3\text{-}\overset{CF_3}{\underset{CF_3}{C}}\text{-}OH + HOCH_2(CF_2)_3CH_2OH \xrightarrow{KOH} HOOC\text{-}\overset{CF_3}{\underset{CF_3}{C}}\text{-}O\text{-}CH_2(CF_2)_3CH_2\text{-}O\text{-}\overset{CF_3}{\underset{CF_3}{C}}\text{-}COOH$$

$$+\ 2HOCH_2(CF_2)_3CH_2OH \longrightarrow HOCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{CF_3}{\underset{CF_3}{C}}\text{-}OCH_2(CF_2)_3CH_2O\text{-}\overset{CF_3}{\underset{CF_3}{C}}\text{—}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}OCH_2(CF_2)_3CH_2OH$$

14. Monoacetal of Hexafluoropentanediol and Dihydropyran

As described in an earlier section of this report on polyethers, considerable effort is being expended to produce hydroxyl-terminated prepolymers by reaction of the hexafluorobenzene-terminated polyether of hexafluorobenzene and hexafluoropentanediol with various anions including the sodium salt of hexafluoropentanediol. One of the reasons this has not been completely successful may be that an equilibrium between added sodium salt and the alcohol end of a capped polyether leads to further polymerization.





One method of avoiding this additional polymerization and obtaining a completely hydroxyl-terminated polyether might be to block all hydroxyl groups on the mixed end group polyether followed by reaction with the sodium salt of hexafluoropentanediol. One of the most widely used methods of blocking hydroxyl groups is the formation of an acetal by reaction with dihydropyran. This type of acetal is very stable to basic conditions, but is easily removed with acid. In order to determine the reactivity of the polyether alcohol end groups with dihydropyran and the ease of hydrolysis of the resulting acetals, hexafluoropentanediol was reacted with dihydropyran in THF solvent. Even with a 100% excess of dihydropyran at reflux temperature of the solvent, only a monoacetal formed.

The reaction was run again using excess dihydropyran as solvent. The reaction was conducted at reflux temperature for 32 hours. Even under these drastic conditions, only the monoacetal was obtained.

15. Attempted Preparation of Octafluoro-1,5-dibromopentane

The preparation of a polyether by reaction of perfluorobutadiene with hexafluoropentanediol and potassium hydroxide was described earlier in this report. Since this polyether contained unsaturation due to base-catalyzed dehydrofluorination, work was begun on the preparation of perfluoro-1,4-pentadiene. The polyether from this diene should have considerably less tendency to lose hydrogen fluoride. Following the procedure of Paciorek (Reference 5), an attempt was made to prepare octafluoro-1,5-dibromopentane by reaction of trifluoroethylene with dibromodifluoromethane, in the presence of benzoyl peroxide in a shaking Aminco pressure vessel at 120°C.

$$CF_2Br_2 + CHF{=}CF_2 \cancel{\xrightarrow{\text{Benzoyl Peroxide}}} BrCF_2CHFCF_2CHFCF_2Br$$

Dehydrobromination of this dibromopentane would yield the desired diene. None of the desired dibromopentane was obtained, however. The reaction was carried out in a pressure vessel without a glass liner and it is possible that the metal walls of the vessel could have inhibited the reaction. This reaction was repeated using a glass liner in the pressure vessel. Only a small amount of fairly high molecular weight telomer was obtained.

$$CF_2Br_2 + CHF{=}CF_2 \xrightarrow{\text{Benzoyl Peroxide}} BrCF_2\left[CHFCF_2\right]_x Br$$

Since preparation of this diene could be accomplished more conveniently from an available starting material, Kel-F acid 683, no further work was done on this telomerization reaction.

16. Perfluoropenta-1,4-diene

The preparation of perfluoropentadiene from Kel-F acid 683 (Reference 15) has been reported recently. This preparation involves pyrolysis of the sodium salt of the acid, followed by dechlorination of the monolefin.

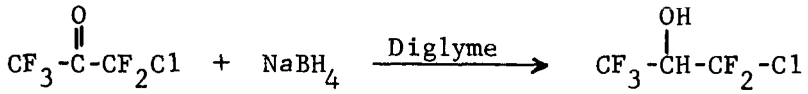
$$\begin{tikzcd}
CF_2Cl(CFCl\text{-}CF_2)_2\text{-}COOH \arrow[r, "NaOH"] & CF_2Cl(CFCl\text{-}CF_2)_2\text{-}COO^{-}\ Na^{+} \arrow[dd, "\Delta"] \\
\text{Kel-F Acid 683} & \\
CF_2{=}CF\text{-}CF_2\text{-}CF{=}CF_2 & CF_2Cl\text{-}CFCl\text{-}CF_2\text{-}CF{=}CF_2 \arrow[l, "Zn"']
\end{tikzcd}$$

The monolefin, 4,5-dichloroperfluoropentene-1, was successfully prepared and dechlorinated to yield perfluoropenta-1,4-diene in good yield.

17. Chloropentafluoroisopropyl Alcohol

In the recent preparation of chloropentafluoroisopropyl alcohol (Reference 1), the isolation of pure material was made difficult because monohydropentafluoroisopropyl alcohol was also formed in the reduction using LAH.

By using sodium borohydride, pure chloropentafluoroisopropyl alcohol was prepared in 63% yield. The purity was established by vapor phase chromatography and elemental analysis.



$$CF_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CF_2Cl + NaBH_4 \xrightarrow{\text{Diglyme}} CF_3\text{-}\overset{OH}{\overset{|}{C}}H\text{-}CF_2\text{-}Cl$$

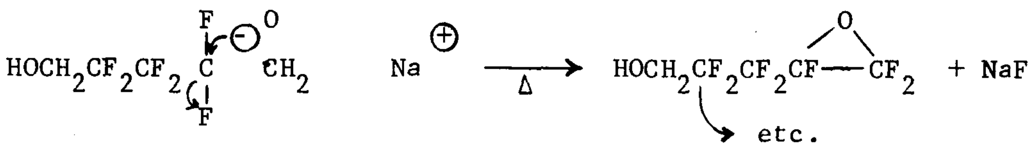
18. Monosodium Salt of Hexafluoropentanediol

The preparation of the monosodium salt of hexafluoropentanediol using metallic sodium (Reference 1) and using sodium hydride (Reference 1) have been described. The monosodium salt was prepared this year using sodium methoxide.

$$HOCH_2(CF_2)_3CH_2OH + NaOCH_3 \longrightarrow NaOCH_2(CF_2)_3CH_2OH + CH_3OH$$

There is good evidence that polymers prepared by initiation with the sodium salt of hexafluoropentanediol prepared from sodium methoxide are methoxy ($-OCH_3$) terminated. Thus the purity of the sodium salt becomes suspect.

In an attempt to evaluate the conditions necessary for the isolation of pure monosodium salt, the preparation was carried out using sodium methoxide in various solvents. In general, the preparation was carried out by adding an excess of the diol to a slurry of sodium methoxide in a particular solvent. The reaction was then heated and the methanol formed distilled off, theoretically forcing the reaction equilibrium toward the desired products. Results of the reaction run in nonpolar solvents indicate some unexpected side products and reactions. In no case was the theoretical amount of methanol recovered. The implication is that there is a relatively stable molecular complex formed either between sodium methoxide and hexafluoropentanediol or the fluorinated alkoxide and methanol. Further evidence indicates that some polymerization with consequent degradation may occur when the sodium salt is heated to temperatures above 110°C in solution or to a temperature of 190°C in air. One possible route to polymerization would be through the epoxide which subsequently reacts with more anion.



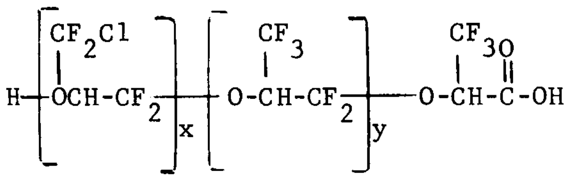
The considerable heat generated is sufficient to degrade the resulting polymer to the point where no identifiable products were found in the reaction mass. However, the sublimate from the reaction was determined to be hexafluoropentanediol.

When the reaction of hexafluoropentanediol with sodium methoxide was carried out in a polar solvent, such as dioxane, results were more consistent with the expected reaction. The insoluble salt had to be washed free of dioxane and other contaminants with copious quantities of diethyl ether. The overall yield was low, indicating incomplete reaction, but the product isolated appears to be of high purity. Possibly, solvation of the anion prevents the formation of the molecular complex with methanol.

Because of the difficulties encountered in the preparation of pure sodium salt using sodium hydride or sodium methoxide, most of the sodium salt was prepared this year by reaction of hexafluoropentanediol with sodium metal in di-n-butyl ether, a method used earlier (Reference 2) in this program. The sodium salt obtained was very pure, as indicated by its elemental analysis.

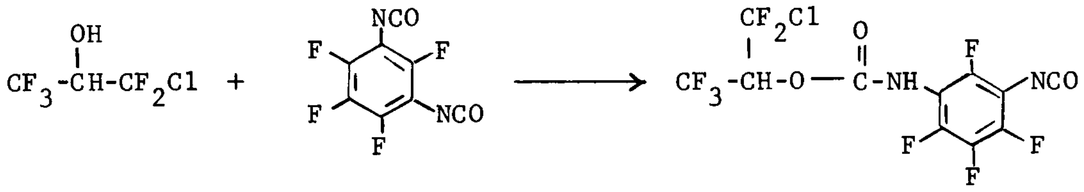
19. Chloropentafluoroisopropyl-3-isocyanato-tetrafluorophenyl Carbamate

Earlier in this report, the failure of the sodium hydroxide initiated polyether of chloropentafluoroisopropyl alcohol to react with tetrafluoro-m-phenylene diisocyanate was reported. As discussed in that section, it is believed the structure of the polyether is a co-polyether having both acid and secondary alcohol end groups, and that the fluorinated acid groups are unreactive toward the fluorinated diisocyanate.



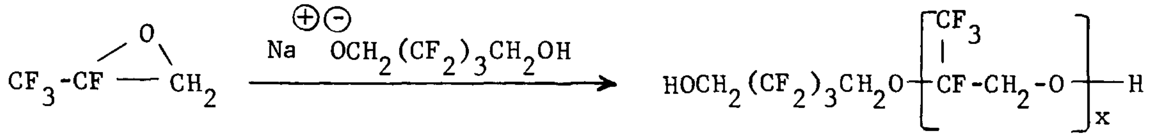
$$H\left[O\overset{CF_2Cl}{\overset{|}{C}}H\text{-}CF_2\right]_x\left[O\text{-}\overset{CF_3}{\overset{|}{C}}H\text{-}CF_2\right]_y O\text{-}\overset{CF_3}{\overset{|}{C}}H\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH$$

This month,chloropentafluoroisopropyl alcohol was successfuly reacted with tetrafluoro-m-phenylene diisocyanate to confirm that the alcohol end groups of the above polyethers do react with the fluorinated diisocyanate.



20. 2,3,3,3-Tetrafluoropropene

A fluorinated polyether which would have some fluorine in the polyether backbone and yet have primary alcohol end groups on both ends is that from 2,3,3,3-tetrafluoro-1,2-epoxypropane. Polymerization with the sodium salt of hexafluoropentanediol should give a polyether with the desirable primary end groups.



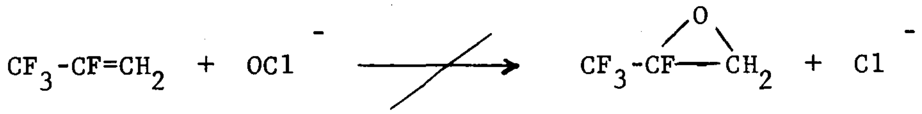
The precursor to this epoxide, 2,3,3,3-tetrafluoropropene, was prepared in 92% yield by deiodofluorination of pentafluoropropyl iodide with zinc.

$$CF_3CF_2CH_2I + Zn \longrightarrow CF_3CF{=}CH_2 + ZnIF$$

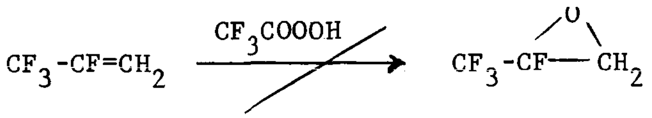
The product was identified by its infrared spectrum and shown to be better than 99% pure by vapor phase chromatography.

21. Attempted Preparation of 2,3,3,3-Tetrafluoro-1,2-epoxypropane

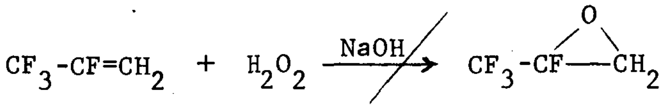
Three methods were used in an attempt to epoxidize 2,3,3,3-tetrafluoropropene. A recent direct method (Reference 16) has been used successfully for the epoxidation of olefins substituted with electronegative groups. This method, which involves the reaction of hypochlorite ion with the olefin, was unsuccessful with 2,3,3,3-tetrafluoropropene.



An attempt was made to epoxidize this olefin using peroxytrifluoroacetic acid. None of the desired epoxide was obtained.

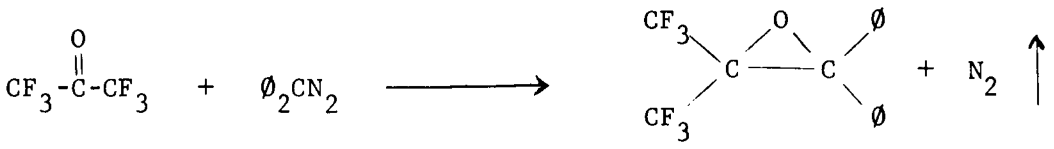


An attempt was also made to epoxidize this olefin with 30% hydrogen peroxide and potassium hydroxide in methanol-water solution. Again none of the desired epoxide was obtained.

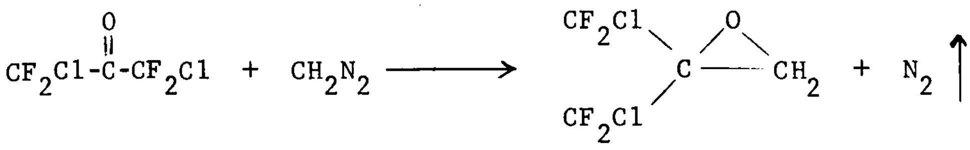


22. Attempted Preparation of 3,3,3-Trifluoro-2-(trifluoromethyl)-1,2-epoxypropane

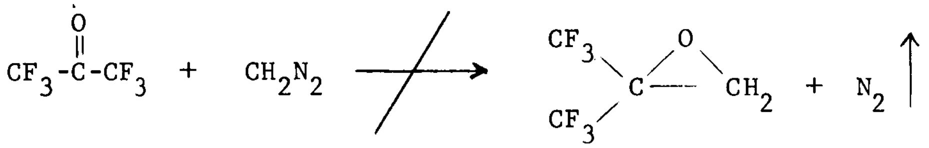
Knunyants has reported (Reference 17) the preparation of 1,1-diphenyl-2-(trifluoromethyl)-3,3,3-trifluoro-1,2-epoxypropane from hexafluoroacetone and diphenyl diazomethane.



Simmons and Wiley have reported (Reference 18) the preparation of 3-chloro-3,3-difluoro-2-(trifluoromethyl)-1,2-epoxypropane from dichlorotetrafluoroacetone and diazomethane.

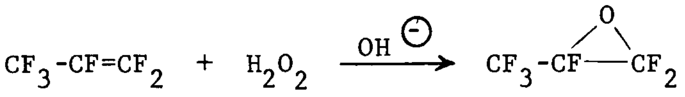


An attempt was made to prepare a similar epoxide, 3,3,3-trifluoro-2-(trifluoromethyl)-1,2-epoxypropane by reaction of hexafluoroacetone with diazomethane. None of the desired epoxide was isolated.



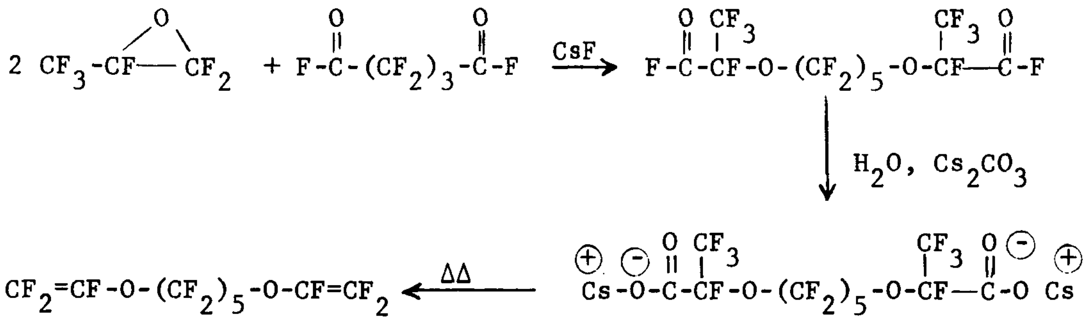
23. Perfluoro-1,2-epoxypropane

Following a published procedure (Reference 9) perfluoro-1,2-epoxypropane was prepared by reaction of perfluoropropylene with hydrogen peroxide in basic solution. The product obtained contained about equal amounts of epoxide and unreacted olefin. The majority of the olefin was removed by passing the mixture through an acetic acid solution of iodine monobromide.



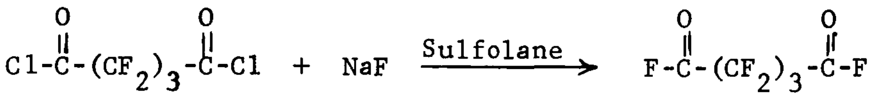
24. Attempted Preparation of Perfluoro-2,10-dimethyl-3,9-dioxaundecanedioyl Fluoride

The preparation of divinyl ethers by reaction of perfluoropropylene oxide with acid fluorides followed by pyrolysis of the resulting acid fluorides or corresponding acid salts was reported recently (Reference 19). One of the ethers reported was perfluoropentamethylenebis(perfluorovinyl ether) from perfluoropropylene oxide and perfluoroglutaryl fluoride.



A stable, hydroxyl-terminated polyether might be prepared by reaction of this diether with hexafluoropentanediol.

The first step in the preparation of this polyether, the preparation of perfluoroglutaryl fluoride was carried out in good yield using an exchange reaction between the acid chloride and sodium fluoride.

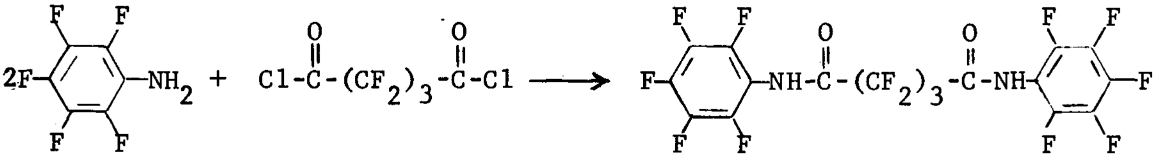


$$\mathrm{Cl{-}\overset{O}{\overset{\|}{C}}{-}(CF_2)_3{-}\overset{O}{\overset{\|}{C}}{-}Cl} + \mathrm{NaF} \xrightarrow{\text{Sulfolane}} \mathrm{F{-}\overset{O}{\overset{\|}{C}}{-}(CF_2)_3{-}\overset{O}{\overset{\|}{C}}{-}F}$$

The reaction of perfluoroglutaryl fluoride with perfluoropropylene oxide was run as reported in the patent, but none of the desired product could be isolated.

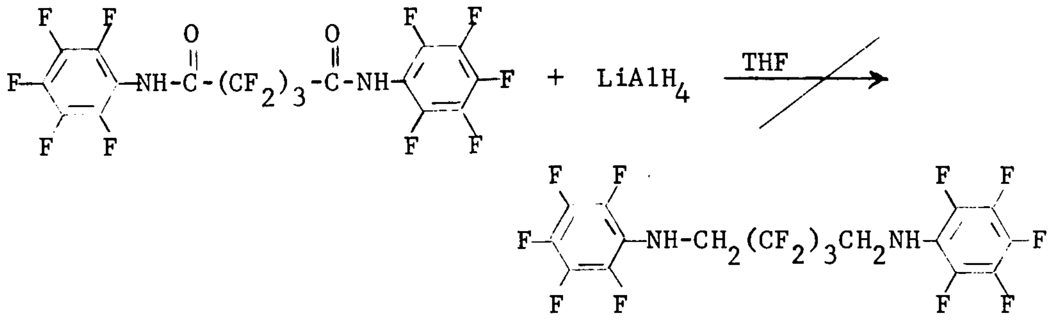
25. N,N'-Di-pentafluorophenyl Perfluoroglutaramide

In a search for a very unreactive curing agent, work was begun on the preparation of a di-secondary amine, N,N'-di pentafluorophenyl-hexafluoropentanediamine. In the first route chosen to this diamine, N,N'-di-pentafluorophenyl perfluoroglutaramide will be reduced to the desired product. N,N'-di-pentafluorophenyl perfluoroglutaramide was prepared in 89% yield by reaction of perfluoroglutaryl chloride with pentafluoroaniline in benzene solution.

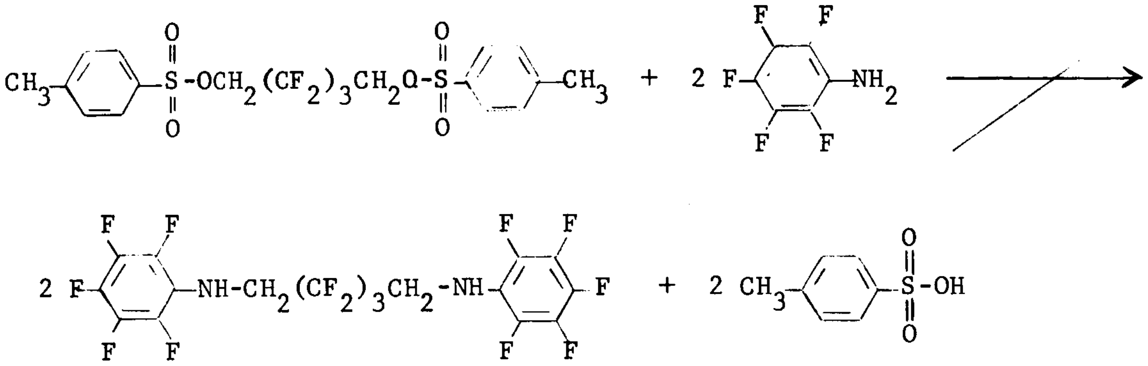


26. Attempted Preparation of N,N'-Di-pentafluorophenyl Hexafluoropentanediamine

The reduction of N,N'-di-pentafluorophenyl perfluoroglutaramide to N,N'-di-pentafluorophenyl hexafluoropentanediamine was attempted using LAH. The reduction did not proceed, and 94% of the starting diamine was recovered.

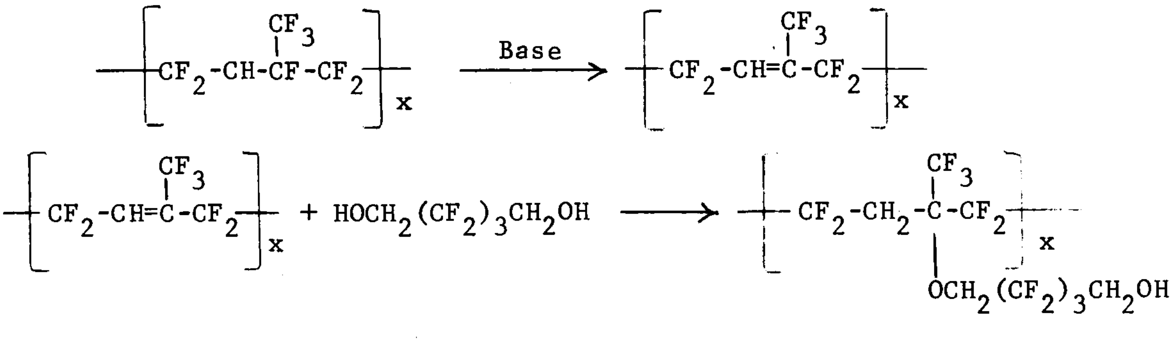


In another attempt to prepare this diamine, hexafluoropentamethylene ditosylate was reacted with pentafluoroaniline. None of the desired product was isolated.



27. Attempted Dehydrofluorination of Viton LM

Viton A, a copolymer of perfluoropropylene and vinylidene fluoride is an interesting LOX-compatible polymer which has found many uses. This polymer, if modified to contain hydroxyl groups, might be a useful backbone for polyurethane adhesives. One possible route to this type of hydroxyl-containing prepolymer would be by grafting hexafluoropentanediol units onto the Viton polymer. The partial dehydrofluorination of Viton by base would yield olefin groups to which hexafluoropentanediol should add.



$$\left[-CF_2-CH-\overset{CF_3}{\overset{|}{C}}F-CF_2-\right]_x \xrightarrow{\text{Base}} \left[-CF_2-CH=\overset{CF_3}{\overset{|}{C}}-CF_2-\right]_x$$

$$\left[-CF_2-CH=\overset{CF_3}{\overset{|}{C}}-CF_2-\right]_x + HOCH_2(CF_2)_3CH_2OH \longrightarrow \left[-CF_2-CH_2-\underset{OCH_2(CF_2)_3CH_2OH}{\underset{|}{\overset{CF_3}{\overset{|}{C}}}}-CF_2-\right]_x$$

Viton LM (a low molecular weight polymer) was treated with sodium hydroxide and with tributylamine to see if dehydrofluorination could be induced. In neither case were there any signs of hydrogen fluoride elimination.

IV. EXPERIMENTAL

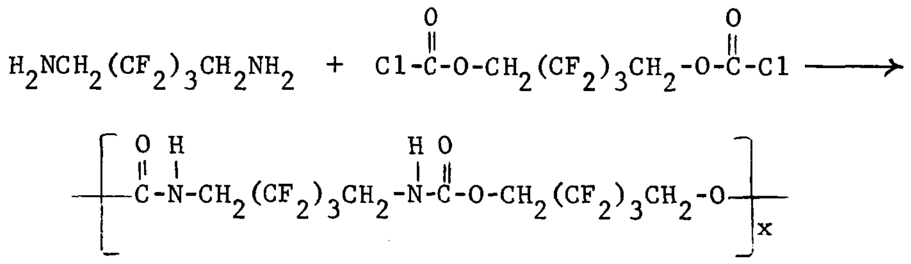
A. LOX Compatibility Results

The results of all LOX compatibility tests completed this year are presented in Table 1.

B. Polyurethanes

1. From Hexafluoropentanediol

a. Preparation of Poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate)



$$H_2NCH_2(CF_2)_3CH_2NH_2 + Cl-\overset{O}{\overset{\|}{C}}-O-CH_2(CF_2)_3CH_2-O-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow$$

$$\left[\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-CH_2(CF_2)_3CH_2-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-CH_2(CF_2)_3CH_2-O \right]_x$$

(1) Solution Polymerization

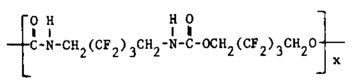
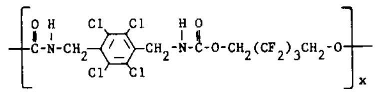
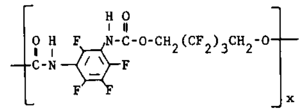
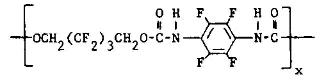
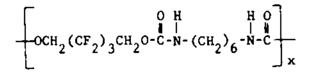
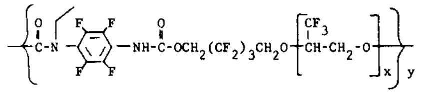
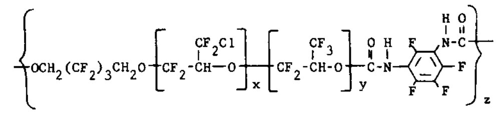
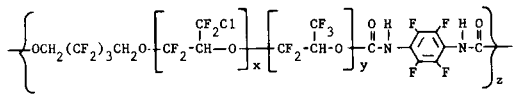
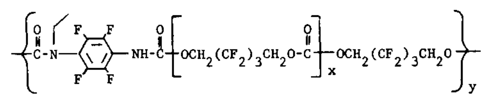
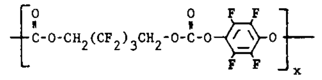
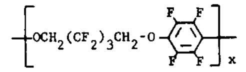
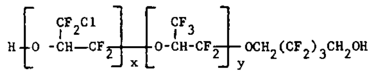
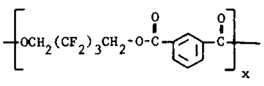
Hexafluoropentamethylene bischloroformate (10.1 g, 0.03 mole) was added slowly with stirring to hexafluoropentanediamine (6.3 g, 0.03 mole), pyridine (5.2 g, 0.066 mole), and dry ethyl acetate (50 ml) at 22°-50°C under nitrogen. After all the bischloroformate had been added, the slurry was a blood red. It was mixed for 1-3/4 hours at 30°-50°C, followed by 4 hours at 80°C, at which time the slurry had turned a dark green. When the reaction mixture was poured into 1 liter of rapidly stirred water, a black oil settled. The water was decanted and the black oil dried in a vacuum oven overnight at 90°C. A brown, brittle solid, 11.9 g (84.0% yield), was obtained.

(2) Interfacial Polymerization

Hexafluoropentamethylene bischloroformate (23.6, 0.07 mole) in methylene chloride (100 ml) was rapidly added to hexafluoropentanediamine (14.7 g, 0.07 mole) and sodium carbomate (14.9 g, 0.14 mole) in 250 ml of distilled water at 0°-5°C with vigorous stirring. The slurry was then stirred for 2½ hours at 0°-5°C. The water and methylene chloride were decanted and the oily residue dried overnight at 80°-100°C in a vacuum oven. A white opaque elastomeric polyurethane, weighing 21.4 g (64.5% yield), was obtained. Twenty specimens of the polymer, 16 mils in thickness, were submitted to MSFC for LOX-compatibility testing and no reaction occurred. The infrared spectrum is shown as Figure 15.

TABLE I

LOX COMPATABILITY RESULTS

Name of Polymer	Polymer Structure	% Fluorine	Film Thickness, mils	LOX Results,* No. Reactions
Poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate)		50.7	50 16	0/17 0/20
Poly(hexafluoropentamethylene tetrachloro-p-xylylene dicarbamate)		47.6**	20	7/20
Poly(hexafluoropentamethylene tetrafluoro-m-phenylene dicarbamate)		42.8	8.5	3/20
Poly(hexafluoropentamethylene tetrafluoro-p-phenylene dicarbamate)		42.8	Powder 26	0/20 0/20***
Poly(hexafluoropentamethylene hexamethylene dicarbamate)		32.4	18 33	4/20 1/20 (7.6 kg) 1/20 (5.3 kg) 0/20***
Polyurethane of tetrafluoro-p-phenylene diisocyanate and poly(3,3,3-trifluoro-1,2-epoxypropane)		46.2	26 10	17/20 9/20***
Polyurethane of tetrafluoro-m-phenylene diisocyanate and polyether of chloropentafluoroisopropanol		53.8	12	5/20†
Polyurethane of tetrafluoro-p-phenylene diisocyanate and polyether of chloropentafluoroisopropanol		53.8	Powder	11/20† 0/20 (7.6 kg)
Polyurethane of tetrafluoro-p-phenylene diisocyanate and poly(hexafluoropentamethylene carbonate)		45.6	10 26	19/20*** 20/20 (7.6 kg-m)*** 14/20 (5.3 kg-m)*** 19/20
Poly(hexafluoropentamethylene tetrafluoro-p-phenylene carbonate)		41.7	7.5 7.5	2/20 5/20 (Repeat)
Polyether of hexafluorobenzene and hexafluoropentanediol		52.8	17	2/20†
Polyether of chloropentafluoroisopropyl alcohol (Na salt of hexafluoropentanediol initiated)		57.7	12 Powder Powder	2/20†,†† 0/20†† 0/20†††
Poly(hexafluoropentamethylene-isophthalate)		33.4	15.5-20	11/20

* Energy Level = 10 kg-m unless otherwise designated.

** Fluorine plus chlorine.

*** Reported in Annual Summary Report II, July 1965.

† LOX sensitivity may be due to trapped solvent.

†† Polymer prepared in THF.

††† Polymer prepared in perfluorotributylamine.

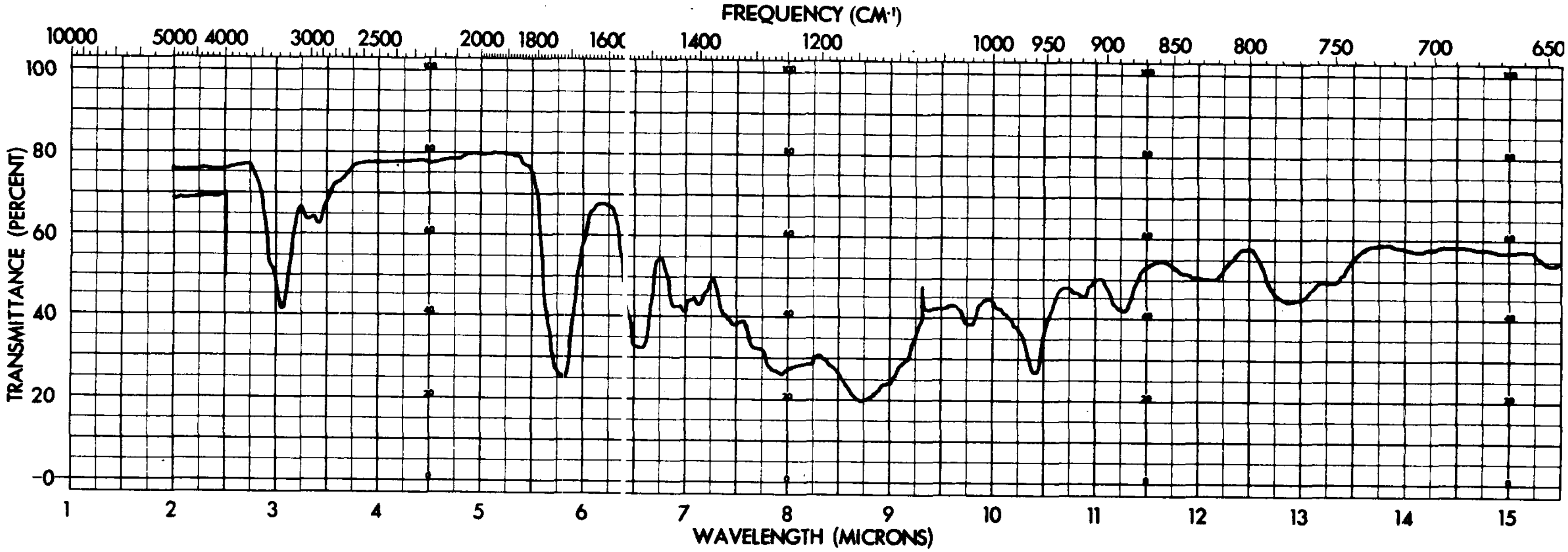
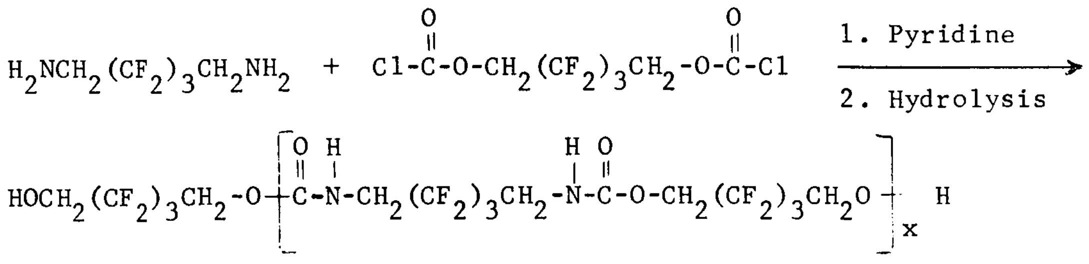


Figure 15. Poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate) II. Film

The above described polymer was a semisolid when prepared at 5°-10°C. Samples of this polymer had no reactions in 17 specimens at approximately 50 mils thick when tested for LOX compatibility by MSFC.

b. Preparation of the Prepolymer of Poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate)

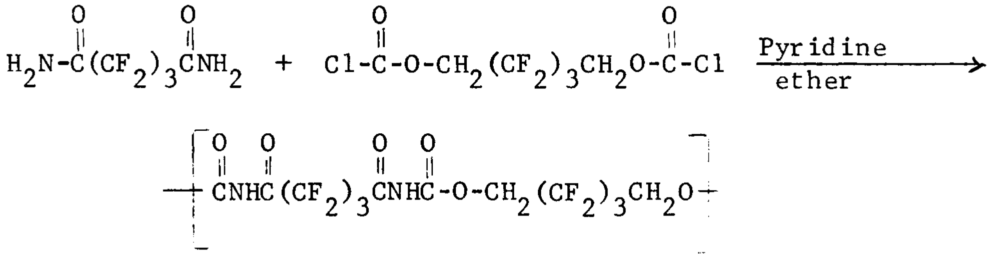


$$H_2NCH_2(CF_2)_3CH_2NH_2 + Cl\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2(CF_2)_3CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl \xrightarrow[\text{2. Hydrolysis}]{\text{1. Pyridine}}$$

$$HOCH_2(CF_2)_3CH_2\text{-}O\left[\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{\overset{|}{N}}\text{-}CH_2(CF_2)_3CH_2\text{-}\overset{H}{\overset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2(CF_2)_3CH_2O\right]_x H$$

Hexafluoropentanediamine (10.5 g, 0.05 mole) and pyridine (7.9 g, 0.10 mole) in 30 ml of THF were added to hexafluoropentamethylene bischloroformate (20.2 g, 0.06 mole) in 70 ml of THF over a 1-hour period at 15°-25°C with stirring. The slurry was mixed for an additional 2 hours at 20°-25°C, filtered and the THF removed from the filtrate. The residue was extracted thrice with boiling water and dried in a vacuum oven at 80°-100°C for 8 hours to yield 20.7 g (80.5%) of a viscous prepolymer. The hydroxyl equivalent weight was 645±15.

c. Attempted Preparation of Poly(hexafluoropentamethylene perfluoroglutaryl dicarbamate)

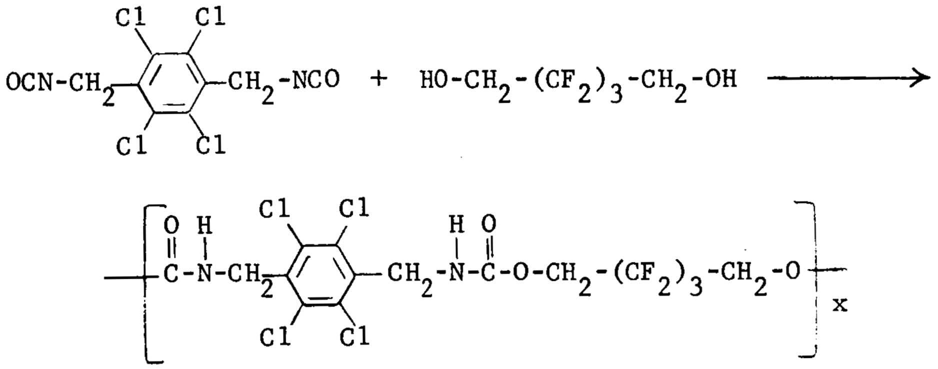


$$H_2N\text{-}\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}NH_2 + Cl\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl \xrightarrow[\text{ether}]{\text{Pyridine}}$$

$$\left[\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2(CF_2)_3CH_2O\right]$$

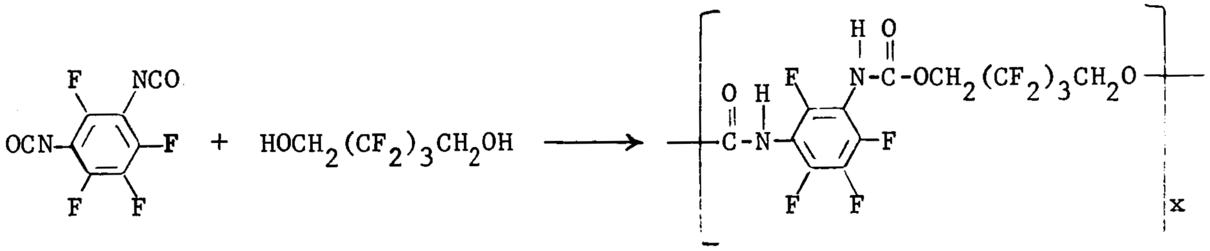
Hexafluoropentamethylene bischloroformate (16.8 g, 0.05 mole) was added over a 2-hour period to perfluoroglutaramide (11.9 g, 0.05 mole) and pyridine (7.9 g, 0.10 mole) in 300 ml of anhydrous THF with vigorous stirring. A greenish-white precipitate formed on addition. The slurry was stirred 3 hours at room temperature and then allowed to stand overnight. The solids were filtered off and the solvent stripped from the filtrate, yielding perfluoroglutaramide (11.8 g, 99% starting material). There was no apparent reaction.

d. Preparation of Poly(hexafluoropentamethylene tetrachloro-p-xylylene dicarbamate)



To a stirred melt of tetrachloro-p-xylylene-α,α'-diisocyanate (8.7 g, 0.0267 mole) was added hexafluoropentanediol (5.65 g, 0.0267 mole) under a nitrogen atmosphere. Stirring was continued for 50 minutes while the mixture was maintained at 130°-140°C. The mixture began to gel and was placed in a press at 325°F for 1 hour at 5000-lb pressure. The polyurethane hardened to a brittle sheet and could not be processed. Samples approximately 20 mils thick were prepared by means of a pellet mold at 25,000-lb pressure and submitted for LOX-compatibility testing. The polymer had 7 chars in 20 specimens. The infrared spectrum is shown as Figure 16.

e. Preparation of Poly(hexafluoropentamethylene tetrafluoro-m-phenylene dicarbamate)



Tetrafluoro-m-phenylene diisocyanate (2.90 g, 0.0125 mole) and hexafluoropentanediol (2.65 g, 0.0125 mole) were mixed and warmed to 40°C; at this temperature, a clear solution was obtained. After stirring a few minutes, the stirrer was removed and the temperature raised to 90°C. After 1 hour at 90°C, the now solid polymeric mass was transferred to Teflon caul sheets and molded into a 8.5 mil thick film by pressing at 200°F and holding for 15 minutes. The resulting clear brittle polymer was broken into squares and submitted to MSFC for LOX impact testing. These 8.5 mil thick specimens had 3 reactions in 20 tests.

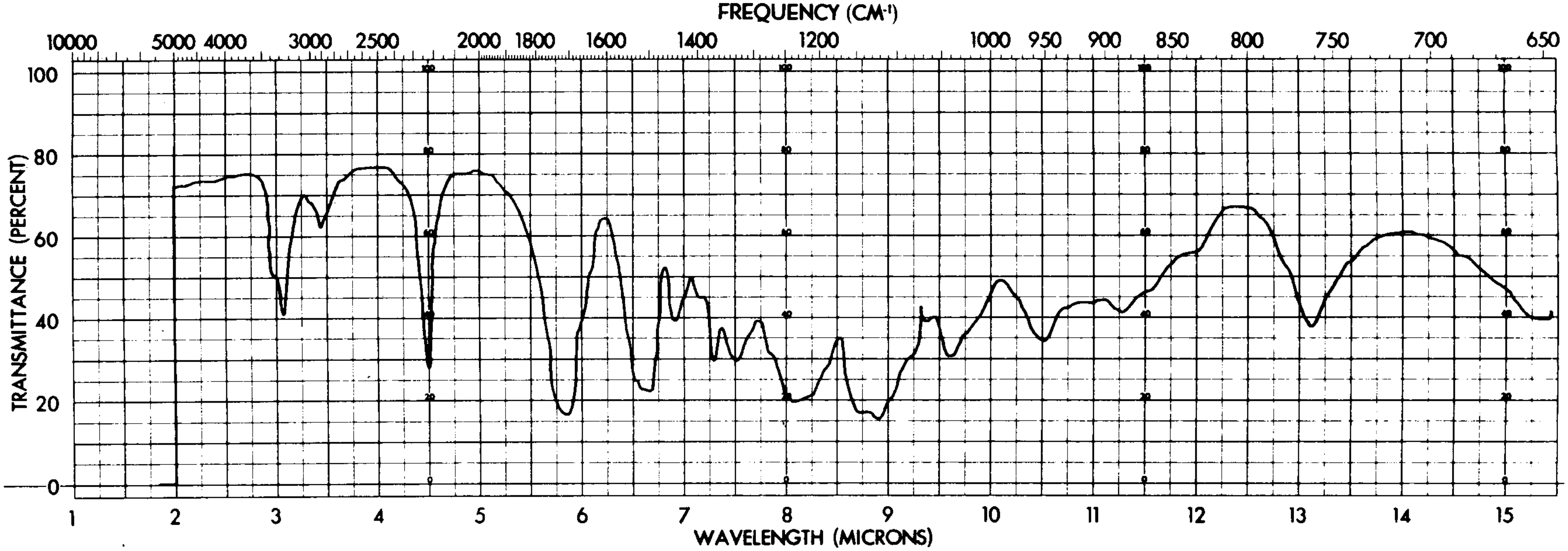
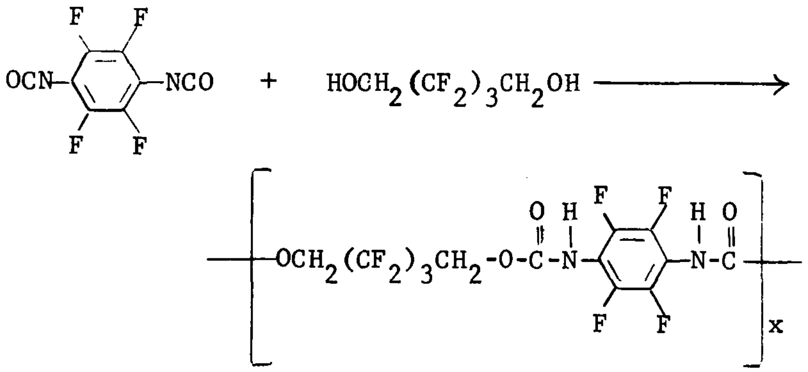


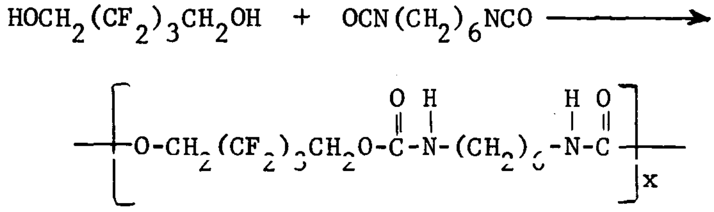
Figure 16. Poly(hexafluoropentamethylene tetrachloro-p-xylylene dicarbamate) V. Potassium Bromide Pellet

f. Preparation of Poly(hexafluoropentamethylene tetrafluoro-p-phenylene dicarbamate)



Tetrafluoro-p-phenylene diisocyanate (16.2 g, 0.07 mole) and hexafluoropentanediol (14.8 g, 0.07 mole) were heated to 140°C, at which time the temperature of the mixture increased to 205°C and solidification occurred. The polymer was a strong brittle solid. It was finely pulverized and submitted to MSFC for LOX-compatibility testing. The polymer had no reactions in 20 specimens.

g. Preparation of Poly(hexafluoropentamethylene hexamethylene dicarbamate)



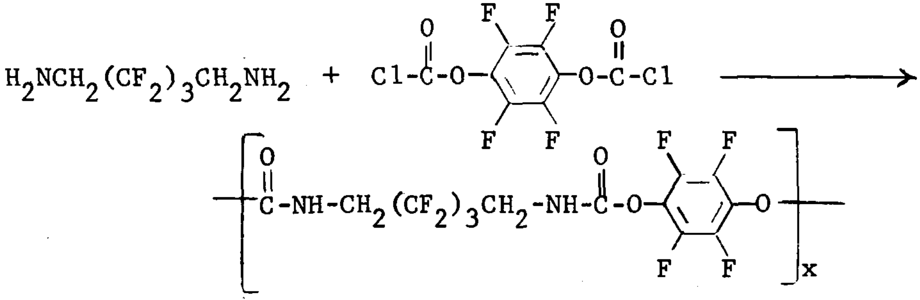
$$HOCH_2(CF_2)_3CH_2OH + OCN(CH_2)_6NCO \longrightarrow$$

$$\left[-O-CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}- \right]_x$$

Hexamethylene diisocyanate (33.6 g, 0.2 mole) was added to hexafluoropentanediol (42.4 g, 0.2 mole) at 75°C over a 20-minute period under nitrogen. The mixture was heated from 100°-180°C in ½ hour, followed by 1-1/4 hours at 180°-190°C, after which there was no apparent increase in viscosity. The polymer was cooled and a film pressed at 120°C. Seventy samples (18-mils thick) were punched and submitted to MSFC for LOX-compatibility testing. The polymer had 4 reactions in 20 specimens at 10 Kg-M; 1 reaction in 20 at 7.6 Kg-M; and 1 reaction in 20 at 5.3 Kg-M.

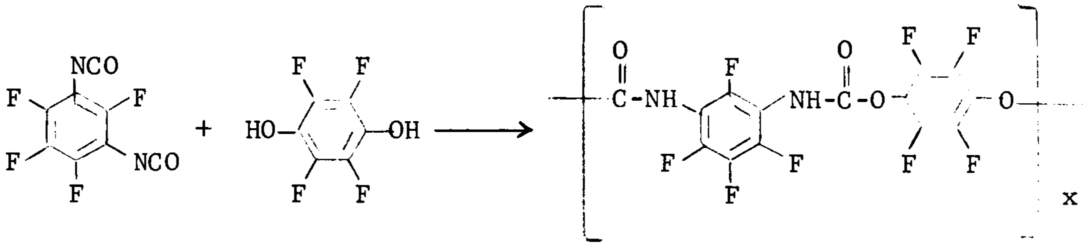
2. From Tetrafluorohydroquinone

a. Preparation of Poly(tetrafluoro-p-phenylene hexafluoropentamethylene dicarbamate)



Tetrafluoro-p-phenylene bischloroformate (4.8 g, 0.016 mole) in THF (25 ml) was slowly added to hexafluoropentanediamine (3.4 g, 0.016 mole) and pyridine (2.7 g, 0.034 mole) in THF (75 ml) with rapid stirring. Pyridine hydrochloride precipitated as the bischloroformate was added. After the addition was completed, the mixture was stirred at 60°C for 1 hour, then at room temperature overnight. It was then poured into dilute hydrochloric acid and boiled for ½ hour. The orange-brown solid obtained was suspended in water, boiled for an additional ½ hour, filtered, washed with additional water, and dried overnight in a vacuum oven at 60°C. The orange-brown product weighed 4.9 g (69% yield) and had a softening point of 175°-196°C (with darkening). An attempt to make a film in a press at 350°F was unsuccessful. The infrared spectrum is shown as Figure 17.

b. Preparation of Poly(tetrafluoro-p-phenylene tetrafluoro-m-phenylene dicarbamate)



Tetrafluoro-p-hydroquinone (1.8 g, 0.01 mole) was added to tetrafluoro-m-phenylene diisocyanate (2.3 g, 0.01 mole) in dry xylene (20 ml). The mixture was refluxed for 24 hours. Because the infrared spectrum of the solution showed a strong absorption at 4.5 μ, indicating excess isocyanate, an additional 0.5 g of tetrafluoro-p-hydroquinone was added and reflux continued for 6 hours. The resulting suspension was cooled to room temperature, filtered, and the solids washed with ether. After drying in a vacuum oven, the resultant white powder (4.0 g) was found to be infusible below its decomposition point of 225°C.

3. From Hydroxyl-Terminated Polyethers

a. Polyurethane from Tetrafluoro-p-phenylene Diisocyanate and the Polyether of 3,3,3-Trifluoro-1,2-epoxypropane

This polyurethane was prepared as described previously in Annual Summary Report II (Reference 1). Specimens 26 mils thick showed 17 reactions in 20 LOX tests.

b. From the Polyether of Chloropentafluoroisopropanol (Sodium Salt of Hexafluoropentanediol Initiated)

(1) Polyurethane of Tetrafluoro-m-phenylene Diisocyanate

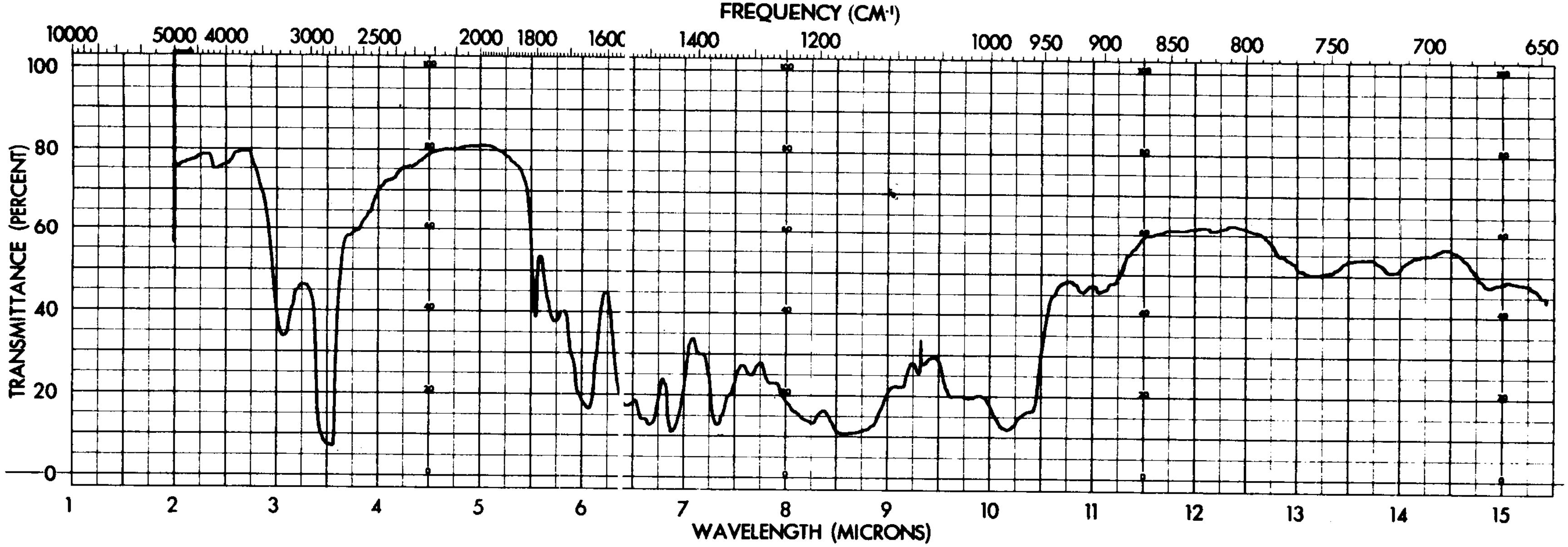
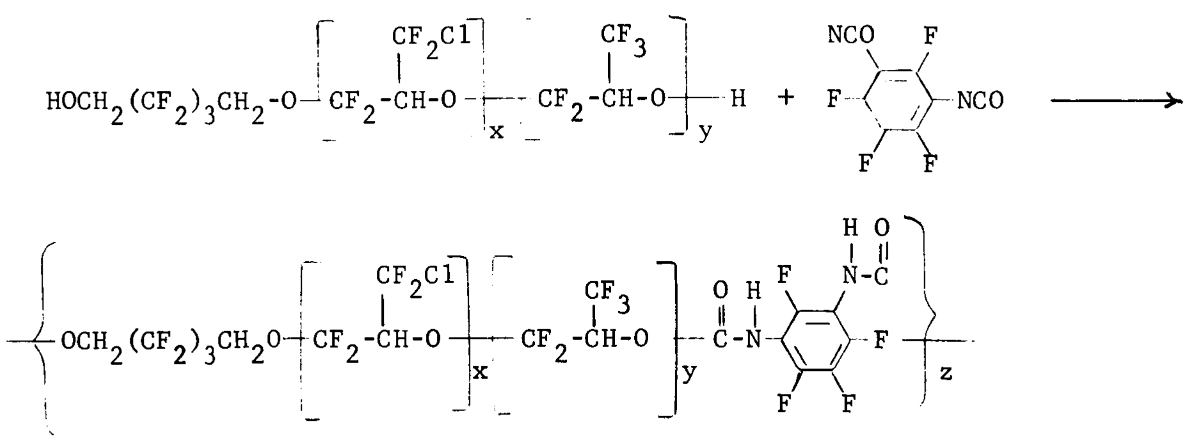


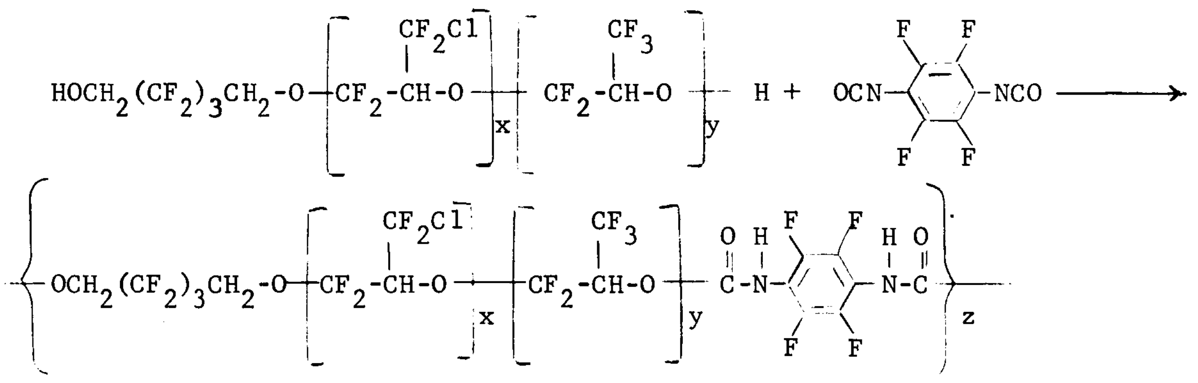
Figure 17. Poly(tetrafluoro-p-phenylene hexafluoropentamethylene dicarbamate) Nujol Mull



The polyether of chloropentafluoroisopropanol having a molecular weight of 1900 (initiated with sodium salt of hexafluoropentanediol (9.5 g, 0.005 mole) and tetrafluoro-m-phenylene diisocyanate (1.8 g, 0.0075 mole) were mixed at 90°C. The polymer gelled in a matter of minutes. The polymer was then cured in a press at 177°C for ½ hour to yield a product which was elastomeric above 65°C but did not melt below 285°C.

The above experiment was repeated at an NCO-to-OH ratio of 1:1 and 12-mil thick specimens sent to MSFC for LOX compatibility testing. This polymer had 5 reactions in 20 specimens, possibly due to trapped volatiles.

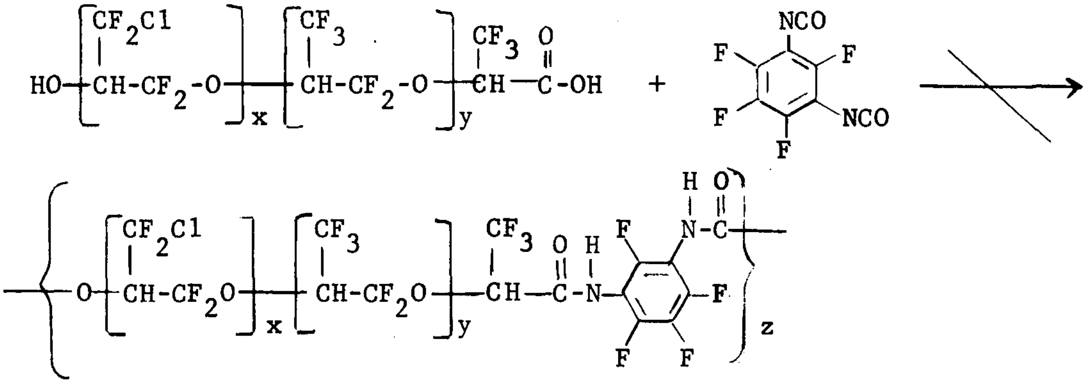
(2) Polyurethane of Tetrafluoro-p-phenylene Diisocyanate



Tetrafluoro-p-phenylene diisocyanate (2.7 g, 0.0117 mole) was added to the polyether of chloropentafluoroisopropanol of 1790 molecular weight (17.2 g, 0.0096 mole) at 90°C. The mass gelled immediately. The polymer was then cured in a press at 177°C for ½ hour to yield a solid, infusible rubber which was pulverized and submitted to MSFC for LOX compatibility testing. It had 11 reactions in 20 specimens at 10 Kg-M, and no reactions in 20 specimens at 7.6 Kg-M. The LOX sensitivity may be due to trapped THF in the polyether.

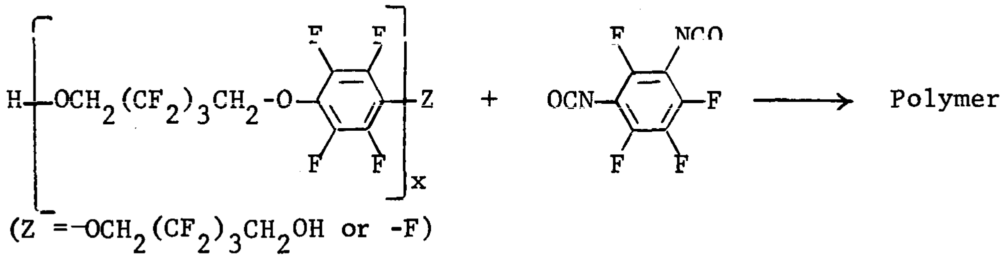
c. From the Polyether of Chloropentafluoroisopropanol (Sodium Hydroxide Initiated)

(1) Attempted Preparation of Polyurethane of Tetrafluoro-m-phenylene Diisocyanate



The sodium hydroxide initiated polyether of chloropentafluoroisopropanol (MW 366) (.2 g, 0.0025 mole) and tetrafluoro-m-phenylene diisocyanate (0.9 g, 0.00375 mole) were mixed at 80°C to 90°C for 72 hours. There was no apparent reaction. Apparently one end of the polyether failed to react with the diisocyanate.

d. Attempted Preparation of Polyurethane of Tetrafluoro-m-phenylene Diisocyanate and the Polyether of Hexafluoropentanediol and Hexafluorobenzene



The polyether of hexafluoropentanediol and hexafluorobenzene of 1260 MW (by VPO) (990 hydroxyl equivalency) (12.6 g, 0.01 mole) and tetrafluoro-m-phenylene diisocyanate (2.9 g, 0.0125 mole) were mixed at 80°-130°C for 3 hours, during which time the viscosity increased slightly. Based on the infrared spectra, all of the OH groups had reacted. Two drops of stannous octoate were added and the mixture stirred for 2½ hours at 120°-130°C. The mixture remained very fluid at 130°C. Apparently only a few of the polyethers contain hydroxyl groups on both ends of the chain.

4. From Hydroxyl-Terminated Polycarbonates

a. Polyurethane from Tetrafluoro-p-phenylene Diisocyanate and Poly(hexafluoropentamethylene carbonate)

This polyurethane was prepared as described previously in Annual Summary Report II (Reference 1). LOX-impact specimens, 26 mils thick, had 19 reactions in 20 tests.

C. Polycarbonates

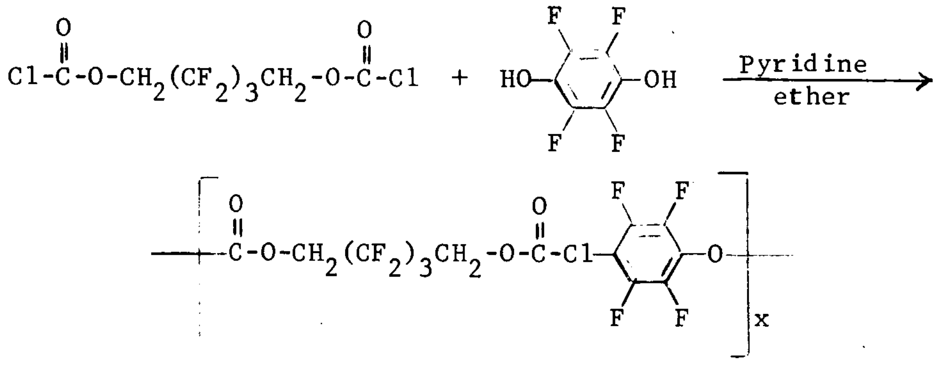
1. Isolation and Characterization of Poly(tetrafluoro-p-phenylene carbonate)

The solid residue from the filtration step in the preparation of tetrafluoro-p-phenylene-bischloroformate (described in the Monomer Section) was boiled for 20 minutes in 500 ml of distilled water which had been acidified with 20 ml of concentrated hydrochloric acid. The polymer was filtered off and washed several times with distilled water, followed by two washings with hexane. The product was dried overnight in the vacuum oven at 80°C and 10-mm Hg. The polymer did not melt below 400°C, but some volatile material was evolved at 200°C. This subliming ceased after continued heating to 240°C. The material simply darkened on further heating, until at 400°F the color had become a tobacco tan. The molecular weight by VPO could not be determined due to insolubility. The infrared spectrum is shown as Figure 18.

Analysis:

	% C	% F
Calculated for $C_7F_4O_3$:	40.40	36.52
Found:	39.96	36.52

2. Preparation of Poly(hexafluoropentamethylene tetrafluoro-p-phenylene carbonate)



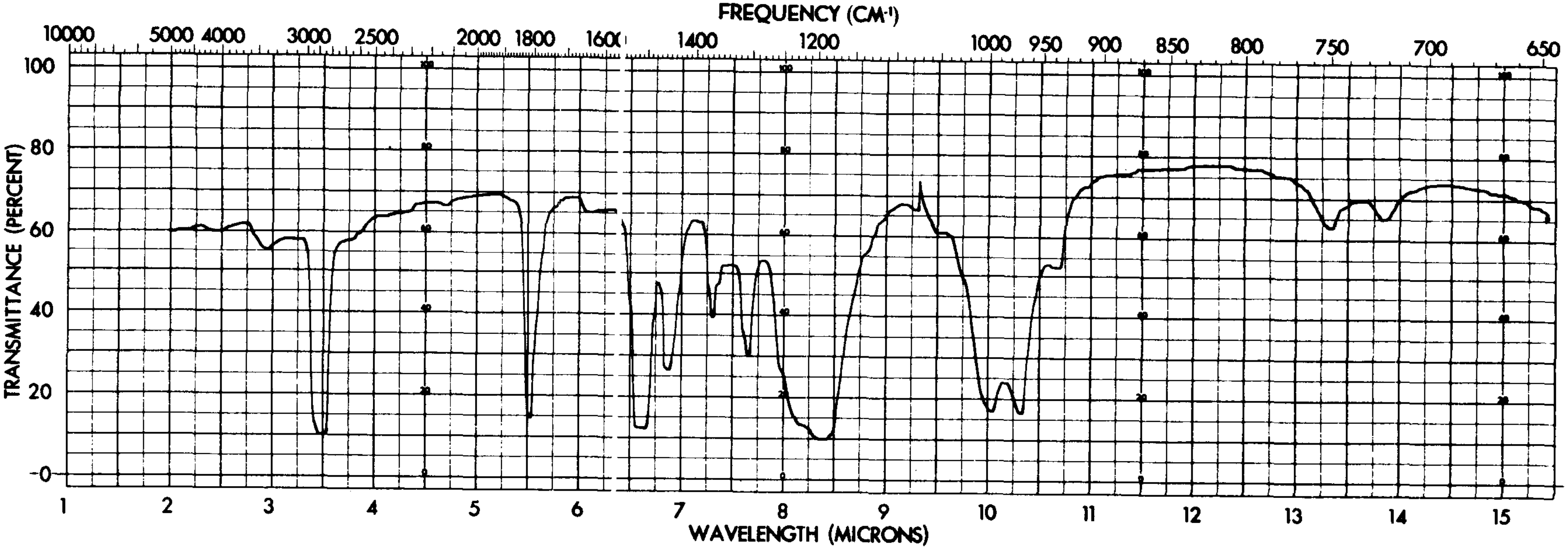


Figure 18. Poly(tetrafluoro-p-phenylene carbonate). Nujol Mull

Hexafluoropentamethylene bischloroformate (16.8 g, 0.05 mole) was added over a 2-hour period to a stirred solution of tetrafluorohydroquinone (9.1 g, 0.05 mole) and pyridine (7.9 g, 0.10 mole) in 300 ml of anhydrous ether; a white precipitate formed on addition. Stirring was continued for 3 hours at room temperature. After standing overnight, the solids were filtered off and the ether stripped from the filtrate, yielding 1 g of low molecular weight polymer. The residue, which consisted of pyridinium chloride and higher molecular weight polymer, was boiled for 30 minutes in 1 liter of distilled water and acidified with 20 ml of concentrated hydrochloric acid. The solid polymer was filtered off and again boiled (30 minutes) in 1 liter of distilled water. The polymer was filtered, washed several times with water, and dried in the vacuum oven for 3 hours at 90°C and 5-mm Hg. A slight amount of tetrafluorohydroquinone sublimed out of the polymer. The weight of polycarbonate obtained was 20 g (90% yield). The melting range of the polymer was 140°-146°C and the molecular weight as determined by VPO, in methyl ethyl ketone, was 5460±170. A portion of the polymer was pressed into a 7.5-mil thick transparent film at 290°F and 500-psi pressure. Samples were punched from this film and submitted to MSFC for LOX-compatibility testing. There were 2 reactions out of 20 specimens tested.

This reaction was repeated and samples 7.5 mils thick were tested for LOX compatibility. There were 5 reactions in 20 specimens. The infrared spectrum is shown in Figure 19.

Analysis:

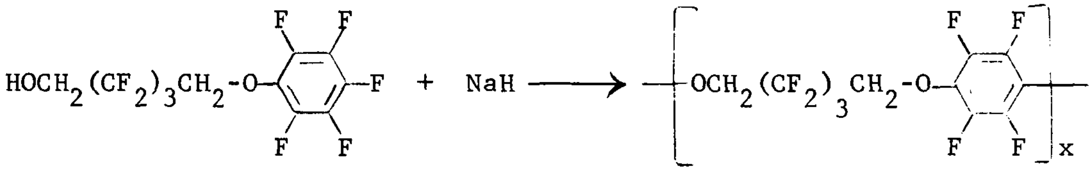
	% C	% H	% F
Calculated for $C_{13}H_4F_{10}O_6$:	34.99	0.89	42.59
Found:	34.64	1.04	41.66

D. Polyethers

1. Polyethers from Hexafluoropentanediol

a. Preparation of High Molecular Weight Polyether of Hexafluorobenzene and Hexafluoropentanediol

(1) From 5-Hydroxyhexafluoropentoxy-pentafluorobenzene



Sodium hydride (1.4 g of 53½% dispersion in mineral oil, 0.03 mole) was slurried in 20 ml of ether. 5-Hydroxyhexafluoropentoxy-pentafluorobenzene (11.3 g, 0.03 mole) was added over a period of 10 minutes and

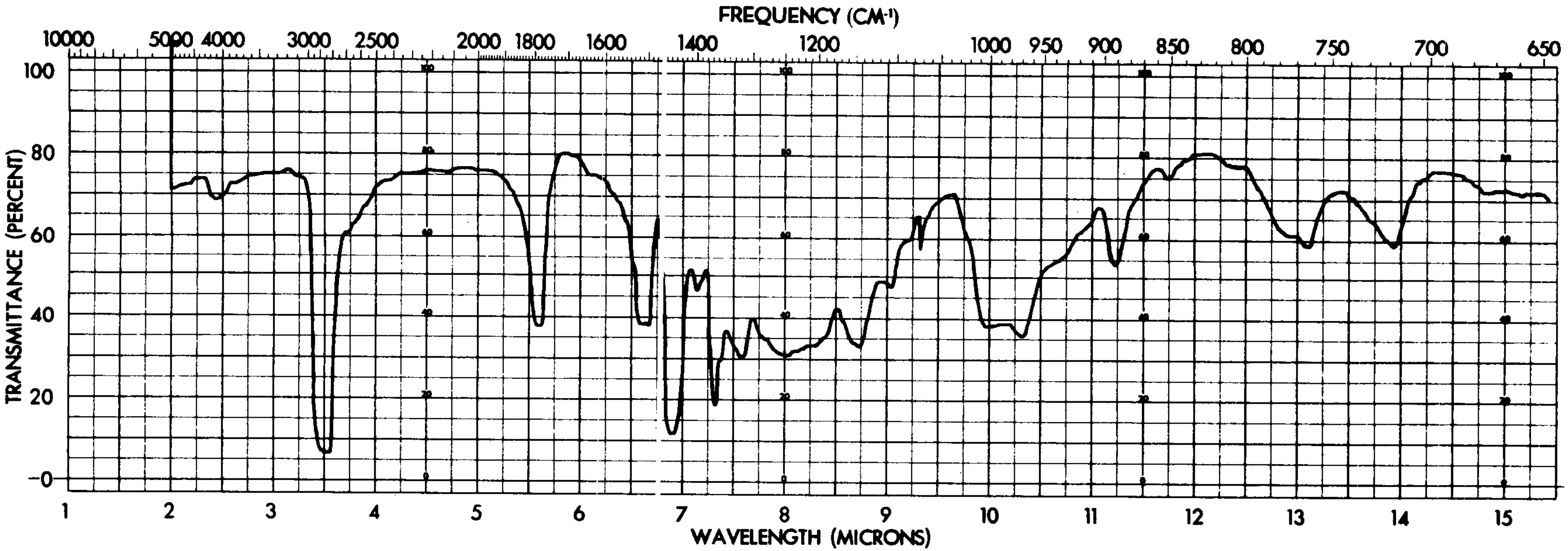
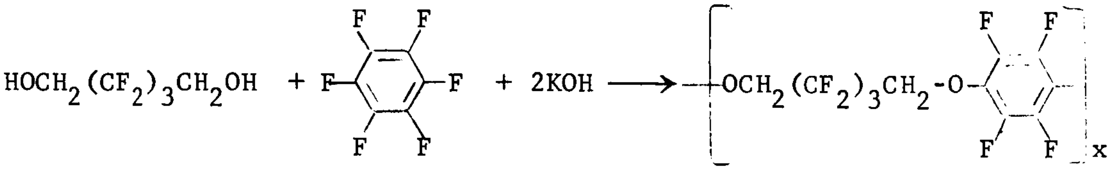


Figure 19. Poly(hexafluoropentamethylene tetrafluoro-p-phenylene carbonate). Nujol Mull

the mixture stirred for an additional ½ hour at room temperature. The ether was removed and the residue heated for 18 hours at 100°-110°C. The polymer was extracted twice with boiling water, twice with THF, and finally once with boiling water. The residue was dried in a vacuum oven at 100°-110°C for 1½ hours to yield 1.5 g (10.7%) of a rubbery, brown solid resembling crepe rubber. This polymer failed to flow in a heated press at 200°C.

The above experiment was repeated. The polymer was washed with ligroine instead of THF to give a brown semisolid polymer in 86% yield.

(2) From Hexafluorobenzene and Hexafluoropentanediol

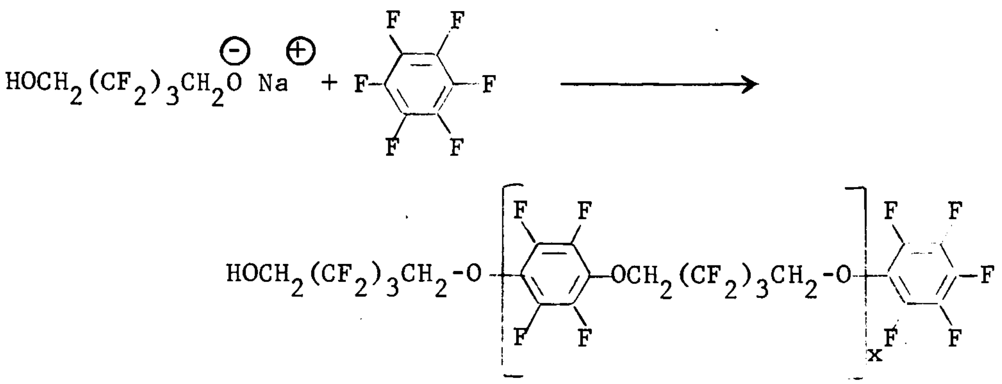


Hexafluorobenzene (18.6 g, 0.1 mole), hexafluoropentanediol (21.2 g, 0.1 mole), sodium hydroxide (8.0 g, 0.2 mole) and 150 ml of DMF were heated to 100°C over a 15-minute period, at 100°-120°C for 10 minutes, 120°-138°C for 20 minutes, and 138°-142°C for 18 hours. The slurry was cooled and filtered. The residue was washed twice with hot water and dried for 4 hours at 80°C in a vacuum oven to yield 0.2 g of rubbery, insoluble polymer. The polymer did not soften to 300°C, and was rubbery throughout the entire temperature range.

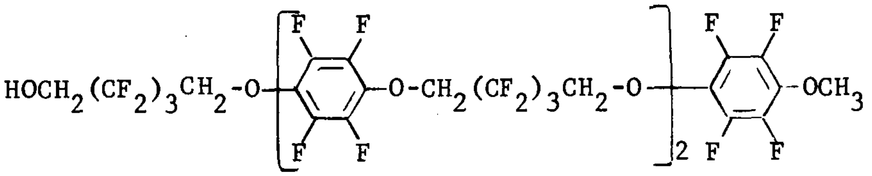
The above experiment was repeated using 0.29 mole of potassium hydroxide. There was no high molecular polymer formed.

b. Preparation of Low Molecular Weight Polyether of Hexafluorobenzene and Hexafluoropentanediol

(1) From Monosodium Salt of Hexafluoropentanediol



Hexafluorobenzene (7.44 g, 0.04 mole), the monosodium salt of hexafluoropentanediol (18.72 g, 0.08 mole) and DMF (100 ml) were mixed and the mass exothermed from 25°C to 50°C with thickening. After the initial exotherm subsided, the mass became less viscous. It was stirred under nitrogen for 20 minutes at 45°-50°C, 20 minutes at 50°-80°C, 1 hour at 80°-125°C, 20 minutes at 125°-150°C and 2 hours at 150°-155°C. After cooling, the slurry was poured into water and the water decanted. The oily residue was dissolved in ether, dried with magnesium sulfate, and the ether removed to yield 11.3 g of polymeric material. Distillation of volatile material (pot temperature raised to 180°C and head temperature rose to 120°C) yielded a residue, 9.5 g, tentatively identified as a polyether of the structure

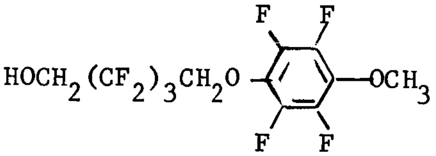


The molecular weight by VPO was 1150±50; (theoretical MW = 1106).

Analysis:

	% C	% H	% F
Calculated for $C_{34}H_{16}F_{30}O_7$:	36.9	1.45	51.5
Found:	36.90	1.42	50.86

The distillate (bp 102°-130°C/1 mm) is believed to have the following structure:



The hydroxyl equivalent weight was 381.5±10, theory = 390.

Analysis:

	% C	% H	% F
Calculated for $C_{12}H_8F_{10}O_3$:	37.0	2.05	48.8
Found:	38.81	2.01	48.92

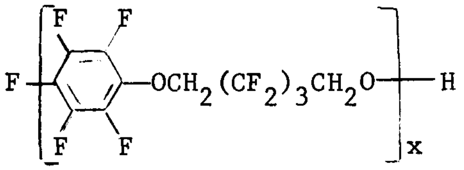
The methoxy compounds are believed to have been formed from sodium methoxide impurties in the sodium salt of hexafluoropentanediol.

(2) From Hexafluoropentanediol

Hexafluoropentanediol (106.0 g, 0.5 mole), hexafluorobenzene (93.0 g, 0.5 mole), sodium hydroxide (20.0 g, 0.5 mole) and DMF (300 ml) were mixed at 120°-130°C for 6 hours. After cooling, the slurry was filtered and poured into 1 ℓ of water. The water was decanted and the residue dissolved in ether and dried with magnesium sulfate. The ether was removed and the crude product distilled at 1-mm pressure.

Cut No.	bp @ 1 mm	Wt, g	OH Equiv Wt	MW by VPO	Remarks
1	--	--	--	--	DMF
2	--	--	--	--	DMF
3	110°-130°C	20.2	480	395±10	377 = theory
4	130°-145°C	23.3	510	--	--
5	145°-160°C	8.0	1020	--	--
6	160°-200°C	13.0	1670	660	--
7	Residue	27.3	1230	--	--

Cut No. 3 was identified by its molecular weight and infrared spectrum (shown as Figure 20), and 5-hydroxypentafluoropentoxy pentafluorobenzene. Cuts Nos. 4 through 7 were apparently polyethers of the following structure with varying degrees of X.



The insoluble, high molecular weight polymer weighed 3.0 g.

In order to obtain higher molecular weight polyether, the reaction was repeated. Hexafluoropentanediol (114.5 g, 0.54 mole), hexafluorobenzene (67.0 g, 0.36 mole), potassium hydroxide (59.5 g, 1.08 mole) and 480 ml of DMF were refluxed for 18 hours. The product mixture was poured into 2 liters of distilled water, the aqueous solvent decanted from the precipitated material, and extracted with ether. The extracts were combined, dried over anhydrous magnesium sulfate, filtered, and stripped of solvent, yielding 56.4 g of a tan viscous oil whose molecular weight was 1120±50 vy VPO. Its hydroxyl equivalency was 1500. The residual solvent was stripped from the precipitated material and the residue was shaken with 1 liter of ether. The supernatant ethereal solution was siphoned off, dried over anhydrous magnesium sulfate, filtered, and stripped under reduced pressure yielding 42.5 g of a very viscous brown liquid whose molecular weight was 1020±50 by VPO. Its hydroxyl

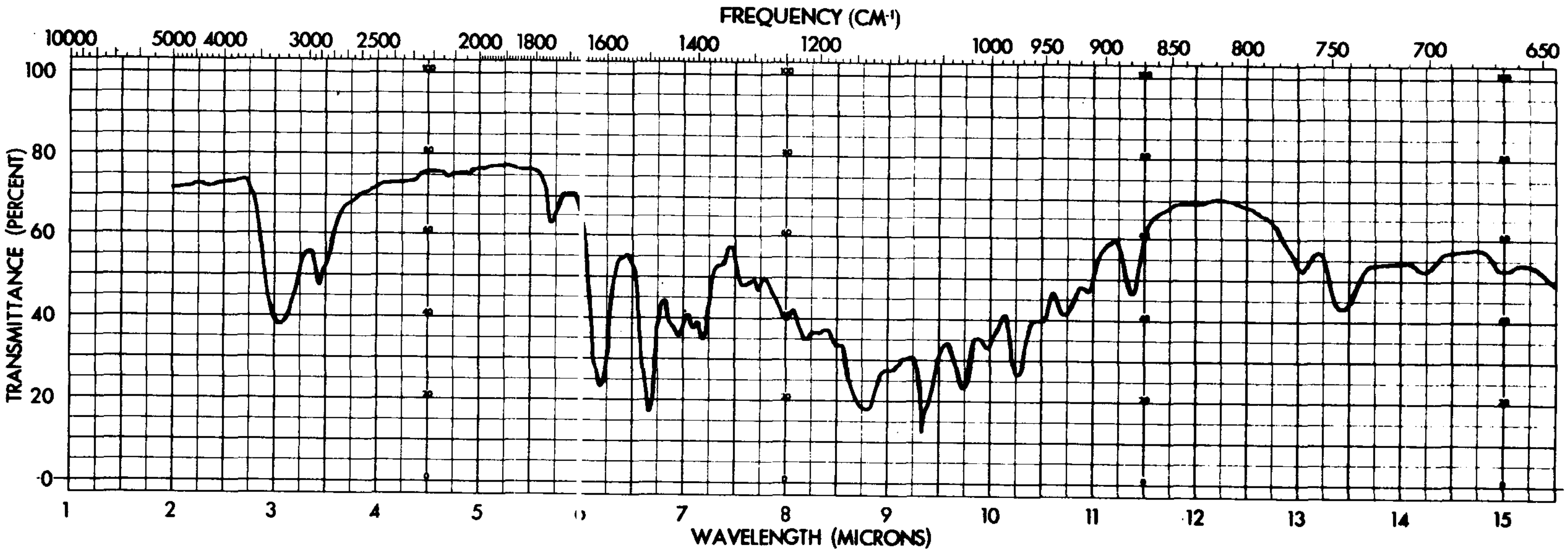


Figure 20. 5-Hydroxy-hexafluoropentoxy Pentafluorobenzene

equivalency was 1650. The insoluble solids were stripped free of solvent, yielding 15.5 g of brown rubbery polymer. This elastomeric material was boiled in 500 ml of distilled water, filtered hot, and washed with an additional 500 ml of water. It was then dried in a vacuum oven at 60°C for 1 hour.

Analysis:

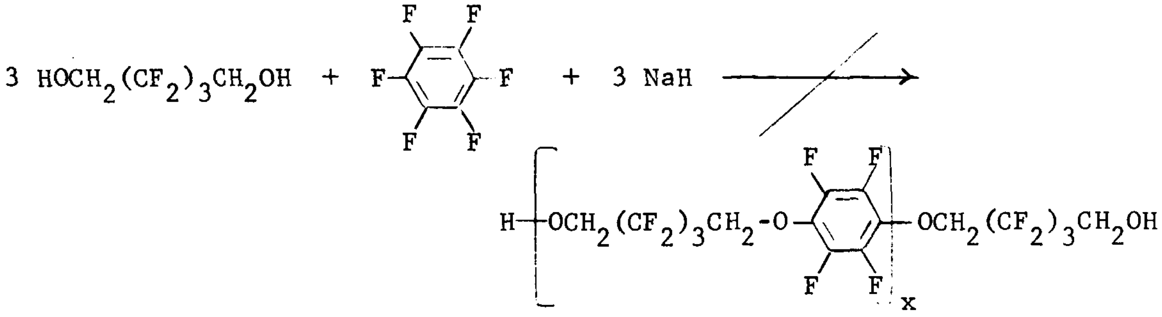
	% C	% H	% F
Calculated for $(C_{11}H_4F_{10}O_2)_x$:	36.87	1.12	53.07
Found:	36.84	1.26	52.81

The material was formed into a sheet by pressing at 200°F and 8000-lb pressure (approximately 200 psi). Samples 17 mils thick were punched from this sheet and submitted to MSFC for LOX-impact testing.

This polymer had 2 reactions in 20 specimens, probably due to trapped solvent.

There was no reaction when hexafluorobenzene and hexafluoropentanediol were mixed in DMF at 150°C for 2 hours in the absence of base.

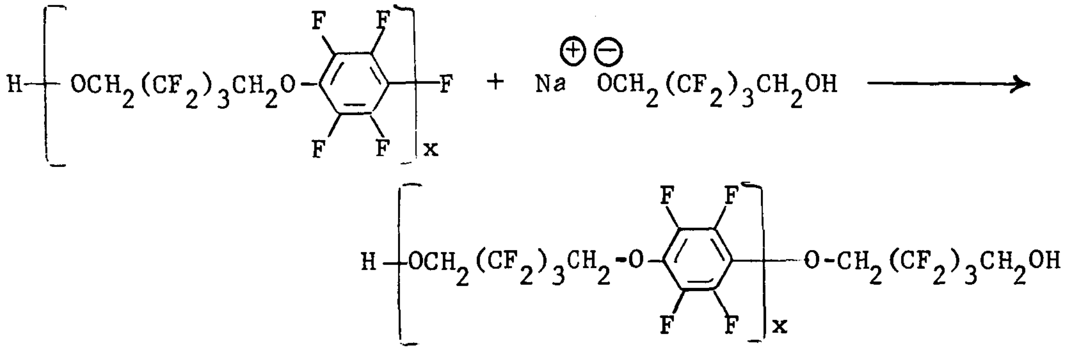
c. Attempted Preparation of Polyether Using Sodium Hydride



Sodium hydride (13.5 g of a 53½% dispersion in mineral oil, 0.3 mole) was suspended in 100 ml of ether. Hexafluoropentanediol (63.6 g, 0.3 mole) in 100 ml of ether was added and the slurry mixed for 24 hours at room temperature. Hexafluorobenzene (18.6 g, 0.1 mole) in 100 ml of ether was added and the slurry stirred for 8 hours at room temperature. There was no reaction.

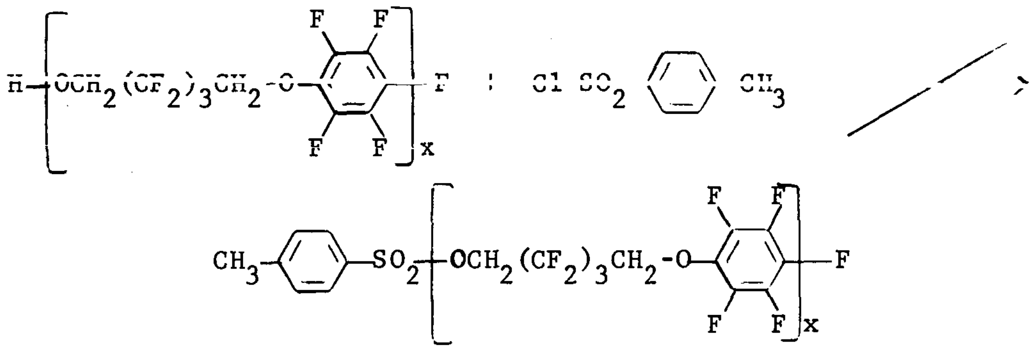
d. Reaction of Low Molecular Weight Polyether of Hexafluorobenzene and Hexafluoropentanediol

(1) Attempted Preparation of Completely Hydroxyl-Terminated Polyether of Hexafluorobenzene and Hexafluoropentanediol



Sodium hydride (0.9 g of a 53½% dispersion in mineral oil, 0.02 mole) was suspended in 15 ml of ether. Hexafluoropentanediol (42. g, 0.02 mole) was added and the reaction stirred for 17 hours at room temperature to form the mono-sodio salt. The mixed polymer of hexafluorobenzene and hexafluoropentanediol (containing some end groups other than hydroxyl, MW = 790, hydroxyl No. = 1010) (7.9 g, 0.01 mole) in 20 ml of ether was added and the slurry stirred for 8 hours. The ether was then removed, the residue slurried in water and neutralized. The oil was redissolved in ether, the ether dried with magnesium sulfate and the ether removed to yield 4.9 g of a viscous oil. The molecular weight by VPO was 885±50, and the hydroxyl number was 810. Apparently only some of the perfluorophenyl end groups were converted to hydroxyl end groups.

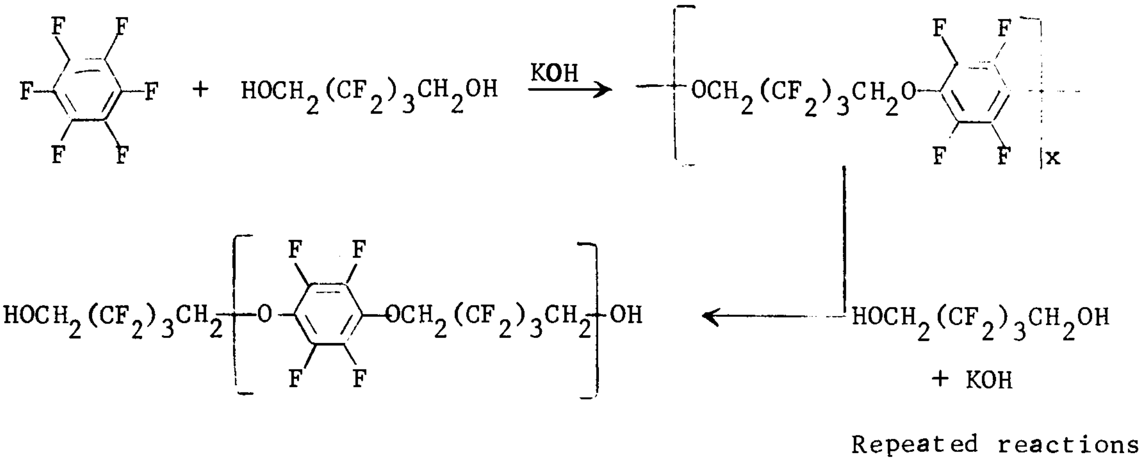
(2) Attempted Preparation of Tosyl Ester of Hydroxyl-Terminated Polyether of Hexafluorobenzene and Hexafluoropentanediol



The polyether of hexafluorobenzene and hexafluoropentanediol (MW = 1020, OH No. = 1615) (15.3 g, 0.015 mole) was dissolved in 50 ml of pyridine. Para-toluenesulfonyl chloride (3.3 g, 0.017 mole) in 30 ml of pyridine was added to the polyether solution at 0°-10°C over a period of 15 minutes. The solution was allowed to warm to room temperature and mixed at room temperature for 5 hours. The solution was poured into water, neutralized, and decanted. The residue was dissolved in ether, dried with anhydrous magnesium sulfate, and the ether removed to yield 11.6 g of a viscous oil. Based on the infrared spectrum, there was no reaction.

e. Preparation of Moderate Molecular Weight Polyethers

(1) Preparation of Hydroxyl-Terminated Polyether of Hexafluorobenzene and Hexafluoropentanediol



Hexafluorobenzene (67.0 g, 0.36 mole), hexafluoropentanediol (114.5 g, 0.54 mole) and potassium hydroxide (60.5 g, 1.08 mole) were allowed to react in refluxing DMF (500 ml) for 2 hours. The mixture was then poured into 1 liter of distilled water, stirred vigorously, and the aqueous layer separated and extracted with ether. The precipitated organic portion was extracted with THF. There was 1.2 g of THF-insoluble high molecular weight polyether recovered in this fashion. The ethereal extract was dried and stripped yielding low molecular weight polymer (20.3 g). The THF extract was dried and stripped yielding a very viscous brown liquid (96.5 g) (A). The infrared spectrum of this hydroxyl- and hexafluorobenzene-terminated polyether is shown in Figure 21.

Polymer (A) (96.5 g) was again reacted with hexafluoropentanediol and potassium hydroxide (in the ratio of 2:3:6) in DMF (300 ml) as above. Isolation was again accomplished by pouring into water, taking up the insoluble material in THF, boiling the THF solution with decolorizing charcoal and filtering. The THF solution was then poured into water (1 liter), boiled, and cooled. The water was decanted, more water added, and the mixture reboiled. After cooling, the water was decanted and the residual water removed by drying in a vacuum oven at 5-mm Hg and 70°C. The yield of glassy polymer (compound B) was 47 g.

Polymer (B) was again reacted with hexafluoropentanediol and potassium hydroxide (2:3:6) in DMF (300 ml) as above. Subsequent workup yielded 25.3 g of glassy dark brown polymer. Molecular weight by VPO was 2010±20. Equivalent weight by hydroxy end groups was 1218. Hence, approximately five of every six chain ends are hydroxyl terminated.

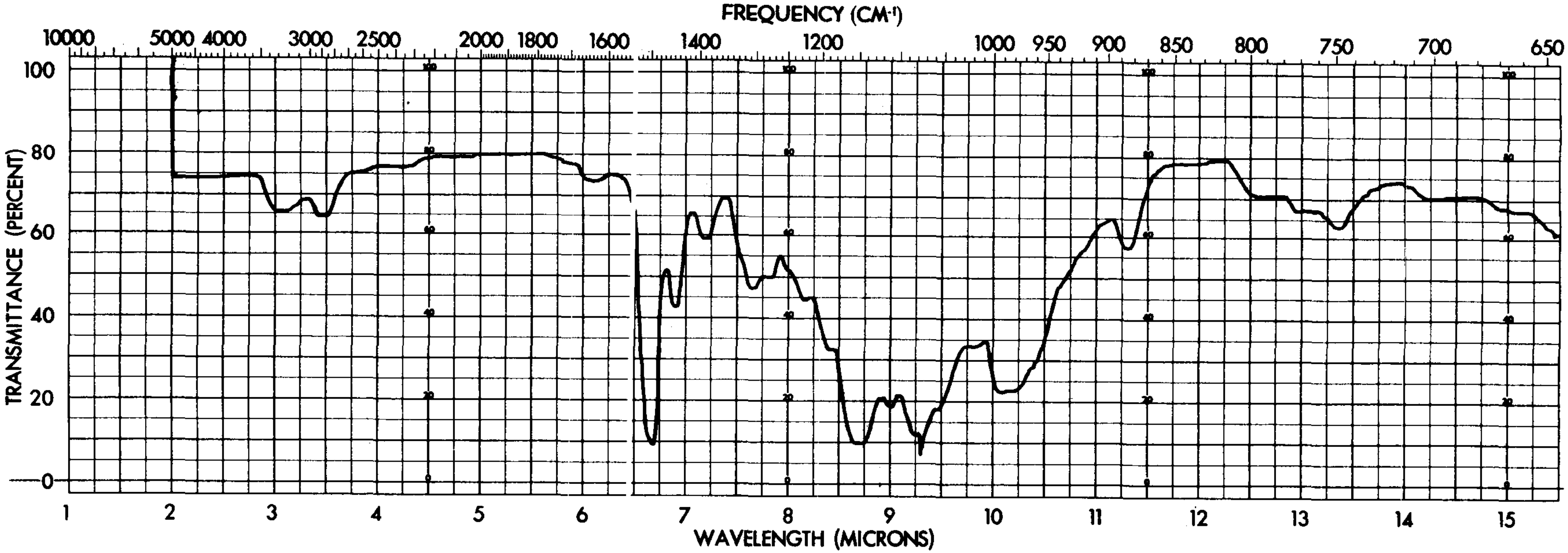
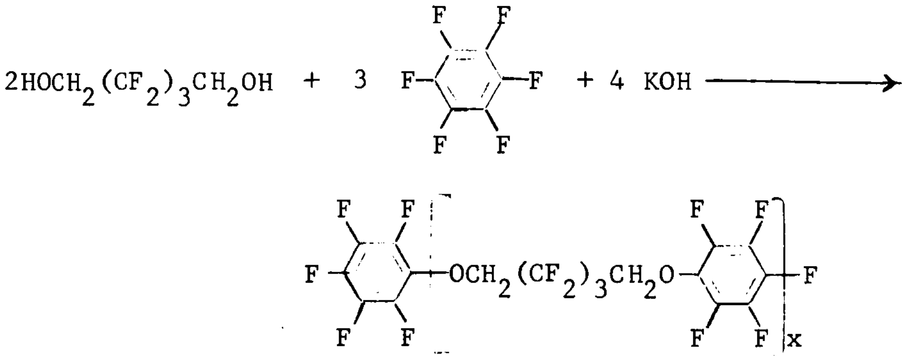


Figure 21. Polyether of Hexafluoropentanediol and Hexafluorobenzene Containing both Hexafluoropentanediol and Hexafluorobenzene End Groups

(2) Preparation of Pentafluorophenyl-Terminated Polyether

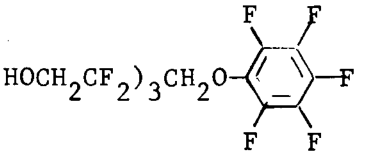


Hexafluorobenzene (55.8 g, 0.30 mole), hexafluoropentanediol (42.4 g, 0.20 mole), potassium hydroxide (22.4 g, 0.4 mole) and DMF (500 ml) were combined. The reaction was exothermic (temperature rose to 54°C). Stirring was continued overnight at ambient temperature. The reaction solution was poured into 2 liters of distilled water (pH of the resulting solution was 7). The mixture was acidified and extracted with 2 liters of diethyl ether. The ethereal extracts were combined and dried over magnesium sulfate. After stripping the solvent under reduced pressure, a slightly viscous, pale tan liquid was recovered (89.3 g). Infrared spectroscopy indicated solvent (DMF) contamination. The material was then boiled twice in distilled water. After the water was decanted, the remaining mobile liquid was taken up in ether and dried over anhydrous magnesium sulfate. Stripping the solvent under reduced pressure yielded 81.4 g (90.3%) of product, MW 625±20 (by VPO). Infrared spectroscopy indicated only very slight hydroxyl termination.

Fifteen grams of the polyether was fractionally distilled under reduced pressure through an 18-in. helices-packed, vacuum-jacketed column.

Fraction	Boiling Range @ 3 mm Hg	MW by VPO	g Collected	Wt % Starting Polyether
1	105	387±5	6.7	44.6
2	162-165	541±5	3.2	21.3
3	166-168	550±10	2.1	14.0
4	Pot Residue	710±20	1.4	9.3

Fraction 1, which was a mobile clear liquid, showed a large hydroxy peak, as would the simple ether below:



($C_{11}F_{11}H_5O_2$)

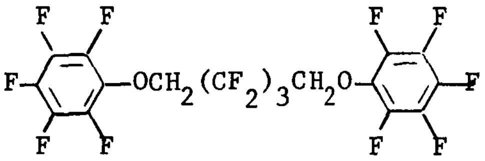
MW 378

Analysis:

	% C	% H	% F	% N
Calculated for $C_{11}H_5F_{11}O_2$:	34.9	1.32	55.4	0
Found:	35.29	1.25	54.77	1.37

The nitrogen found was unexpected, but can be attributed to solvent (DMF) contamination.

Fractions 2 and 3 are the same material since the elemental analyses and infrared spectra are virtually identical. They appear to be the simple diether below.



MW 544

Analysis:

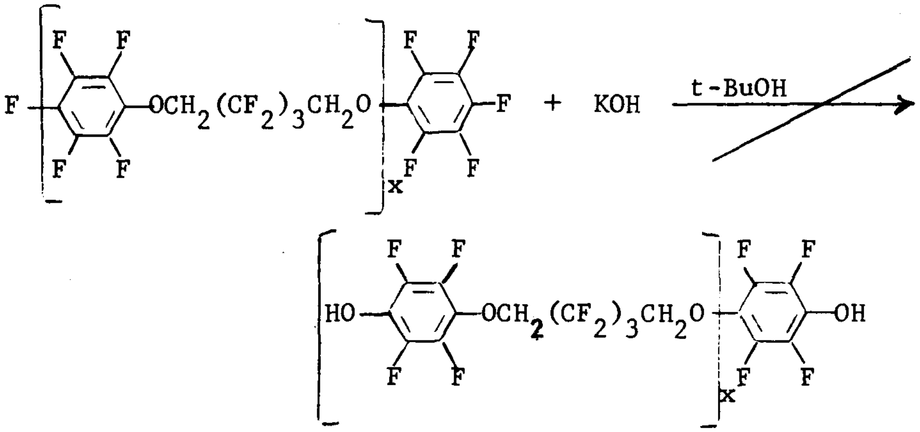
	% C	% H	% F
Calculated for $C_{17}H_4F_{16}O_2$:	37.5	0.74	56.1
Found Fraction 2:	36.5	0.80	56.40
Found Fraction 3:	37.15	0.90	55.12

Fraction 4 (pot residue) was the polyether of average molecular weight 710.

The infrared spectrum of this pentafluorophenyl-terminated polyether is shown in Figure 22.

f. Reactions of Pentafluorophenyl-Terminated Polyether of Hexafluorobenzene and Hexafluoropentanediol

(1) With Potassium Hydroxide



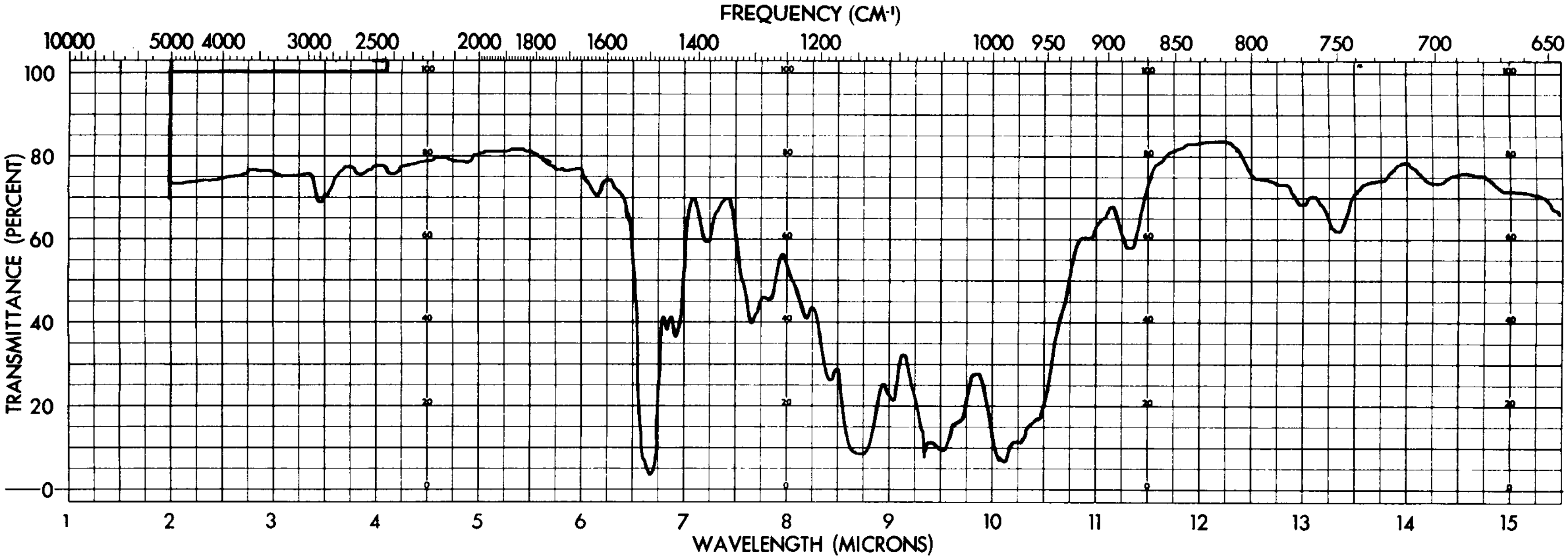
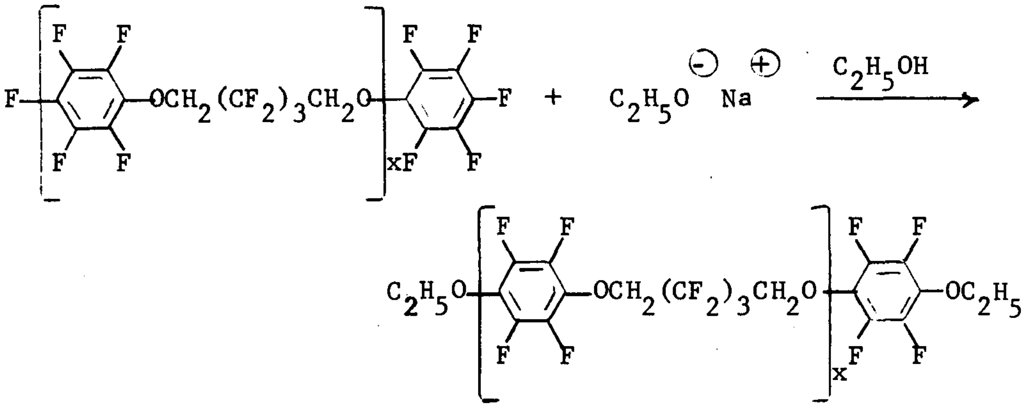


Figure 22. Pentafluorophenyl-Terminated Polyether of Hexafluoropentanediol and Hexafluorobenzene

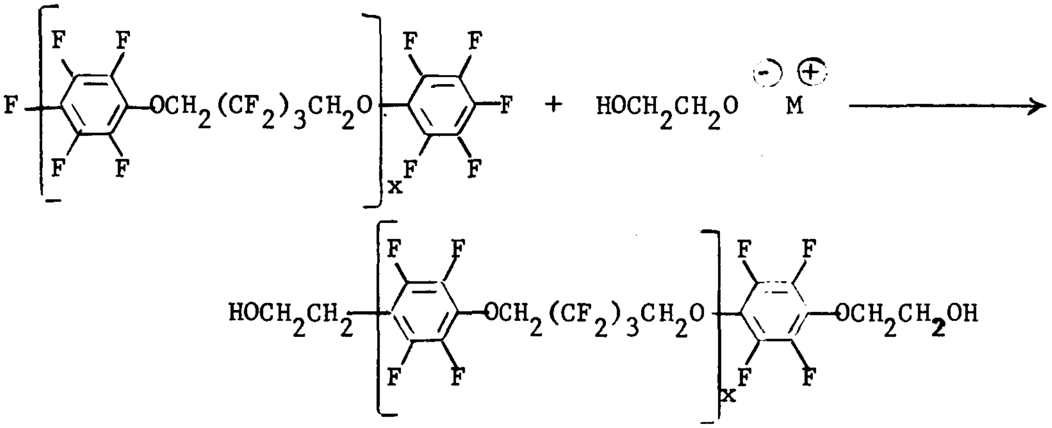
The pentafluorophenyl terminated polyether of hexafluorobenzene and hexafluoropentanediol (6.0 g, 0.01 mole) and potassium hydroxide (2.5 g, 0.044 mole) in 100 ml of dry t-butyl alcohol were mixed for 1 hour at 82°C. After cooling, the reaction mixture was poured into distilled water,acidified, and extracted with ether. The ether extracts were combined, dried, and stripped, yielding 4.2 g of starting material. Infrared spectroscopy indicated no hydroxyl termination. There was no apparent reaction.

(2) With Sodium Ethoxide



Sodium ethoxide was prepared by adding sodium metal (1.4 g, 0.06 mole) to anhydrous ethyl alcohol (100 ml). This ethanolic solution and the polyether (6.0 g, 0.01 mole) were refluxed (78°C)for 32 hours. When the cooled solution was poured into distilled water (800 ml), an emulsion was formed. After acidifying with aqueous hydrochloric acid,the solution was extracted with ether, using sodium chloride to salt out the organic material. The ether extracts were combined, dried, and stripped under reduced pressure to yield 5.2 g of polymer. Infrared spectroscopy showed a considerable increase in carbon-hydrogen content, indicating that the desired product was formed.

(3) With Alkali Metal Salt of Ethylene Glycol



(a) The monosodium salt of ethylene glycol was prepared by reacting sodium metal(1.4 g, 0.061 mole) with dry ethylene glycol (100 ml) at 60°C. The polyether (6.0 g, 0.01 mole) was added and the mixture heated to reflux (176°C). Upon cooling, higher molecular weight starting material precipitated (1.8 g). The solution was filtered and the glycol solution was poured into distilled water (500 ml). After acidification, the aqueous solution was extracted with ether, dried, and stripped, yielding 4.7 g of brown polymeric material. Infrared spectroscopy indicated hydroxyl termination with a consequent increase in carbon-hydrogen content. Functional group analysis indicates two acidic groups per molecule.

(b) The polyether (7.1 g, 0.01 mole) and potassium hydroxide (1.40 g, 0.025 mole) were added to ethylene glycol (150 ml). The solution was heated to reflux (considerable darkening) and maintained for 18 hours. After cooling, the dark brown solution was poured into 1 liter of distilled water. The pH of the aqueous mixture at this point was 5. The mixture was stirred vigorously and the water was decanted from the precipitated solids. The dark brown polymeric material was taken up in THF, refluxed with charcoal and filtered hot. Precipitation was again accomplished by pouring into water with rapid stirring. After decanting the water, the oily product was redissolved in THF, dried, filtered and stripped. The yield of pale brown solid was 2.3 g.

Molecular Weight (By VPO) = 632

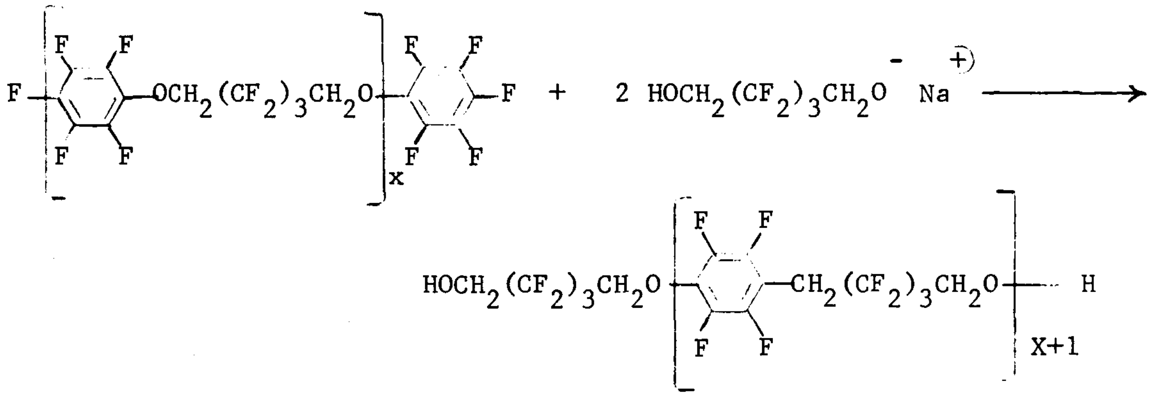
Hydroxyl Number = 446±10

(c) The polyether (7.1 g, 0.01 mole), potassium hydroxide (1.40 g, 0.025 mole) and ethylene glycol (3.1 g, 0.02 mole) were dissolved in 150 ml of DMF and refluxed 6 hours. The workup of the resultant pale tan solution was the same as outlined above. The yield of pale brown solid was 5.8 g.

Molecular Weight (By VPO) = 853

Hydroxyl Number = 595±10

(4) With Sodium Salt of Hexafluoropentanediol



Run No. 1. – The polyether (6.0 g, 0.01 mole) was dissolved in n-butyl ether (250 ml) in a reaction flask. Monosodium salt of hexafluoropentanediol (7.0 g, 0.03 mole) was added and the stirred mixture heated (on a steam bath) and maintained at 94°C for 18 hours. After cooling, the reaction mixture was poured into 1 liter of water and acidified. The n-butyl ether layer was separated and the aqueous solution extracted with diethyl ether. The ethereal solutions were combined, dried, and stripped of solvent under reduced pressure, yielding 3.7 g of starting material.

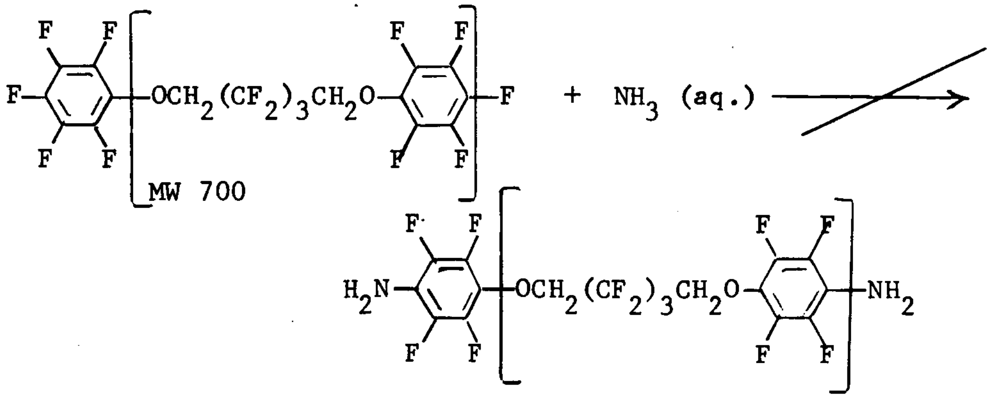
Run No. 2. – Reaction 1 above was repeated using the identical procedure and quantities with the exception of a change in solvent. In this experiment a mixture of equal parts by volume of n-butyl ether and DMF was utilized. Following the work-up, the resultant polymer was twice boiled in distilled water to remove entrapped DMF solvent. After the second water boil, the polymer material was again dissolved in diethyl ether, dried and stripped of solvent, yielding 6.4 g of a brown viscous material.

Molecular weight (By VPO) = 780±20
Equivalent weight by hydroxyl determination = 1290±20

Run No. 3. – The polyether (7.1 g, 0.01 mole) and the monosodium salt of hexafluoropentanediol (23.4 g, 0.1 mole) was added to 250 ml of DMF. The reaction mixture was heated with stirring to 115°C for 18 hours. Dimethylformamide (200 ml) was distilled off and the remaining dark brown solution was poured into boiling water. The precipitated solids were filtered off and dissolved in THF. The THF solution was poured into boiling water, the water decanted off and the solids taken up in diethyl ether, dried, and stripped under reduced pressure at 80°C. A brown, glassy polymeric material (6.7 g) was obtained.

Molecular weight (By VPO) = 1440±20
Hydroxyl number (With acetic anhydride) = 940

(5) With Ammonia



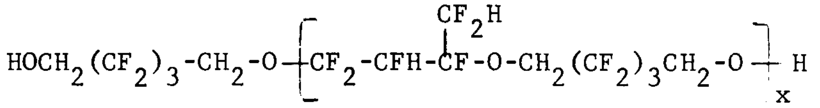
The polyether (14.0 g, 0.02 mole) was charged to a metal tube (2-in. ID x 10-in. length). Concentrated ammonium hydroxide (30 ml, 0.45 mole NH_3) was added and the tube and its contents frozen in liquid nitrogen during sealing (by welding). The sealed tube was heated to 500°F for 18 hours. Upon opening the tube, only carbonaceous material was found.

g. Preparation of Fluorinated Polyether of Perfluorobutadiene and Hexafluoropentanediol

$$CF_2{=}CF{-}CF{=}CF_2 \; + \; HOCH_2(CF_2)_3CH_2OH \xrightarrow{KOH}$$

$$HOCH_2(CF_2)_3CH_2{-}O{+}\left[CF_2{-}CHF{-}CHF{-}CF_2{-}O{-}CH_2(CF_2)_3CH_2{-}O\right]_x{-}H$$

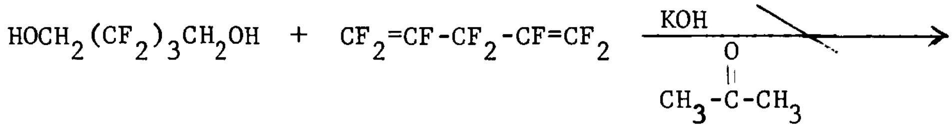
or



$$HOCH_2(CF_2)_3{-}CH_2{-}O{+}\left[CF_2{-}CFH{-}\overset{\overset{\displaystyle CF_2H}{|}}{C}F{-}O{-}CH_2(CF_2)_3CH_2{-}O\right]_x{-}H$$

Hexafluoropentanediol (14.1 g, 0.066 mole) was dissolved in 30 ml of acetone, then potassium hydroxide (1.1 g, 0.02 mole) was added. The solution was cooled to -20°C and perfluorobutadiene (8.1 g, 0.05 mole) was added over a 10-minute period. The mixture was then warmed to 20°C over a 35-minute period and stirred for an additional 66 hours. It was then poured into water, whereupon an oil separated which was dissolved in ether. The water had a pH of 4, indicating some loss of hydrogen fluoride. The ether was dried over anhydrous magnesium sulfate, then removed to yield 13.1 g of an opaque oil. The infrared spectrum (Figure 23) indicated that the product contained hydroxyl groups, unsaturation and possibly ester or acid groups. The molecular weight by VPO was 635±20. The iodine number was 60, indicating an average of 1½ double bonds per mole.

h. Attempted Preparation of the Polyether of Hexafluoropentanediol and Perfluoropenta-1,4-diene



$$HOCH_2(CF_2)_3CH_2OH \; + \; CF_2{=}CF{-}CF_2{-}CF{=}CF_2 \; \xrightarrow[CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3]{KOH} \!\!\!\!\!\!\!\!\!\!\!\!\backslash$$

$$-\!\!\left[OCH_2(CF_2)_3CH_2{-}O{-}CF_2CFHCF_2CFHCF_2\right]_x\!\!-$$

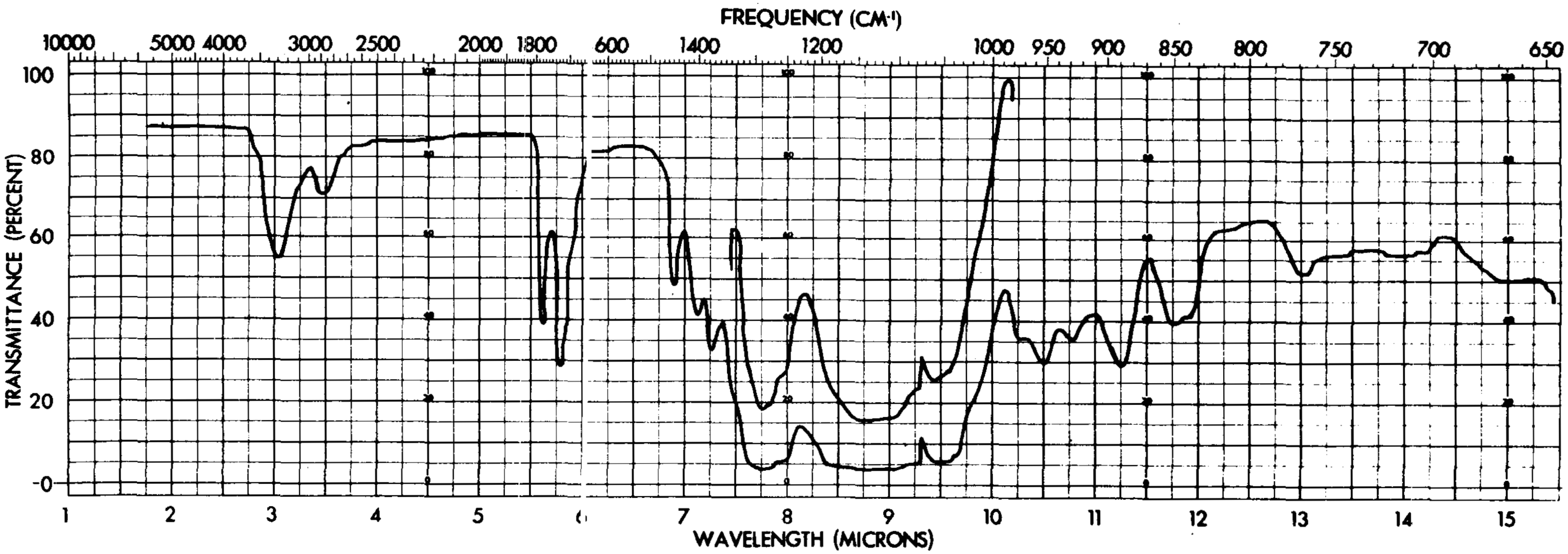


Figure 23. Polyether of Hexafluoropentanediol and Perfluorobutadiene

Potassium hydroxide (1.1 g, 0.02 mole) was dissolved in acetone (20 ml), hexafluoropentanediol (4.9 g, 0.023 mole) added, and the solution cooled to -10°C. Perfluoropentanediene (4.2 g, 0.02 mole) at 0°C was then added and the temperature of the solution rose to 20°C. The solution was then mixed for ½ hour at -10°C to 20°C, ½ hour at 20°C to reflux, then refluxed for ½ hour. It was then stirred overnight at room temperature and filtered. The insoluble polymer was washed with water and dried to yield 0.7 g of tan elastomer. The acetone was removed from the filtrate to yield 7.7 g of a light yellow viscous oil.

The molecular weight (by VPO) was 497, calculated for $C_{16}H_{17}F_{13}O_4$ = 520.

The infrared spectrum attached as Figure 24 confirmed the presence of the carbonyl and OH groups.

Analysis:	% C	% H	% F
Calculated for $C_{16}H_{17}F_{13}O_4$:	36.9	3.27	47.5
Found:	37.74	3.34	47.24

i. Attempted Preparation of Tri-hexafluoropentylene Glycol

$$2\ HOCH_2(CF_2)_3CH_2\overset{\ominus}{O}\ \overset{\oplus}{Na} + ICH_2(CF_3)CH_2I \ \cancel{\xrightarrow{\qquad}}$$

$$HOCH_2(CF_2)_3CH_2OCH_2(CF_2)_3CH_2OCH_2(CF_2)_3CH_2OH \ + \ 2\ NaI$$

Method 1. — The monosodium salt of hexafluoropentanediol (11.7 g, 0.05 mole) and 1,5-diiodohexafluoropentane (10.3 g, 0.025 mole) in 150 ml of DMF were mixed and refluxed for 64 hours. None of the desired product was isolated.

The above reaction was repeated in refluxing ethanol for 18 hours. There was no reaction.

Method 2. — Sodium methoxide (2.7 g, 0.05 mole) was suspended in 100 ml of dry dioxane. Hexafluoropentanediol (10.6 g, 0.05 mole) was added and the solution was distilled through a 30-cm glass helix-packed, vacuum jacketed column. The distillate began coming over at 64°C. A total of 8 ml of distillate was collected, at which time the head temperature was 101°C. 1,5-Diiodohexafluoropentane (10.3 g, 0.025 mole) in 150 ml of DMF was added and the solution was refluxed for 64 hours. The dark brown solution was cooled and the solvent stripped under reduced pressure. Aqueous potassium hydroxide, (2N 100 ml) was added and the mixture extracted three times with 50 ml portions of carbon tetrachloride. Only a dark brown oil (4.2 g) of indeterminate structure was recovered. Vacuum distillation yield no desired material.

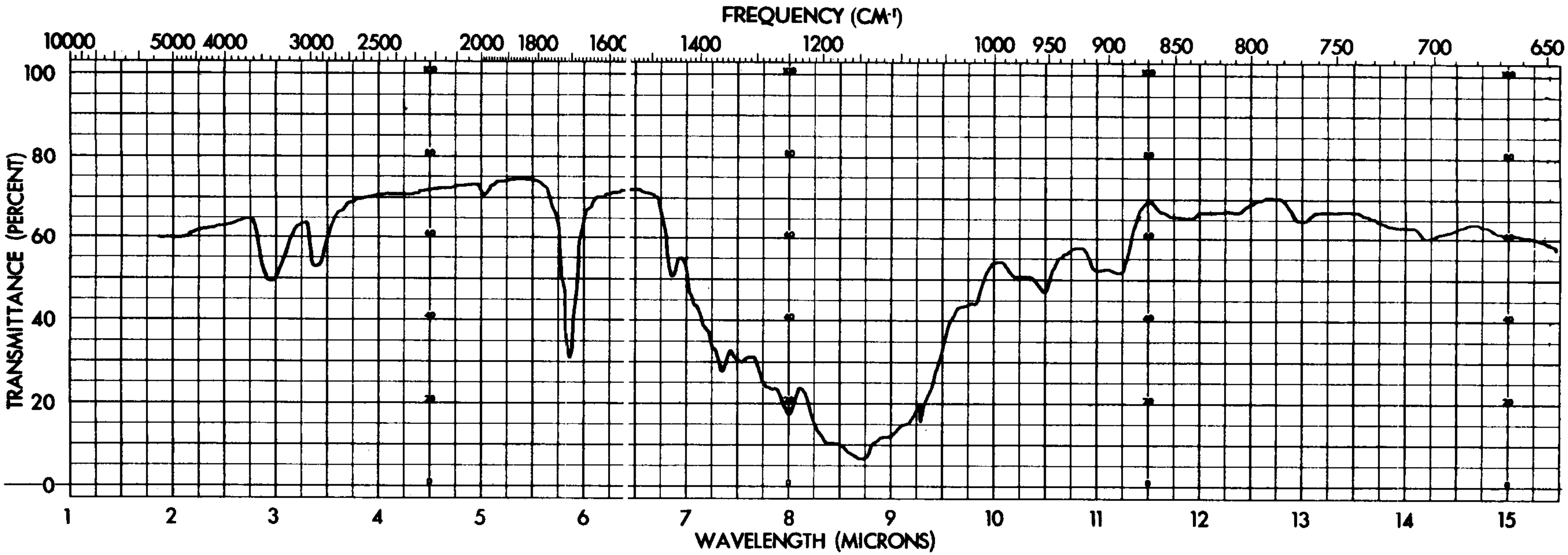


Figure 24. Ether of Hexafluoropentanediol and Perfluoropentadiene

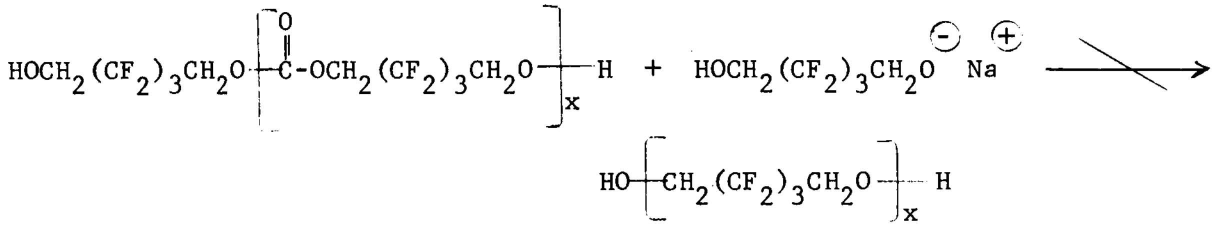
j. Attempted Preparation of Poly(hexafluoropentamethylene ether)

(1) From 1,5-Diiodohexafluoropentane

$$HOCH_2(CF_2)_3CH_2OH + ICH_2(CF_2)_3CH_2I + 2KOH \xrightarrow{DMF} H\left[OCH_2(CF_2)_3CH_2\right]_x OH$$

Hexafluoropentanediol (5.3 g, 0.025 mole), 1,5-diidohexafluoropentane (10.8 g, 0.025 mole) and potassium hydroxide (2.8 g, 0.05 mole) were refluxed in 30 ml of DMF for 20 hours. After cooling, the reaction mixture was poured into 500 ml of distilled water. The brown oil which settled was extracted with ether and the ether solution dried over anhydrous magnesium sulfate. Evaporation of the ether yielded 10.6 g of a viscous brown oil, which was identified by its infrared spectrum and iodine analysis as unreacted 1,5-diiodohexafluoropentane.

(2) From Poly(hexafluoropentamethylene carbonate)

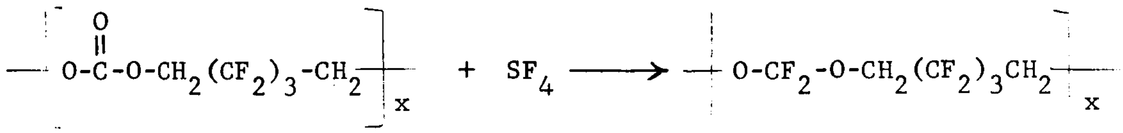


$$HOCH_2(CF_2)_3CH_2O\left[\overset{\overset{O}{\|}}{C}-OCH_2(CF_2)_3CH_2O\right]_x H + HOCH_2(CF_2)_3CH_2O^{\ominus}\ Na^{\oplus} \not\longrightarrow HO\left[CH_2(CF_2)_3CH_2O\right]_x H$$

The monosodium salt of hexafluoropentanediol was prepared by reaction of hexafluoropentanediol with sodium metal in refluxing di-n-butyl ether for 2 hours. The sodium salt thus formed was used, without further purification, to catalyze the attempted decarboxylation of the polycarbonate.

Poly(hexafluoropentamethylene carbonate) (1.854 g, MW 700) was dissolved in 20 ml of refluxing di-n-butyl ether, and freshly prepared monosodium salt (0.23 g, 0.001 mole) was added. Refluxing was continued for 6 hours. After cooling, the ethereal solution was extracted with two 200-ml portions of distilled water. The nonaqueous layer was separated and dried over anhydrous magnesium sulfate. The infrared spectrum of the product was identical with that of the starting material. A drying tube filled with Ascarite showed no increase in weight due to carbon dioxide absorption.

k. Preparation of Poly(difluoromethylene hexafluoropentamethylene ether)



$$-\left[O-\overset{\overset{O}{\|}}{C}-O-CH_2(CF_2)_3-CH_2\right]_x- + SF_4 \longrightarrow -\left[O-CF_2-O-CH_2(CF_2)_3CH_2\right]_x-$$

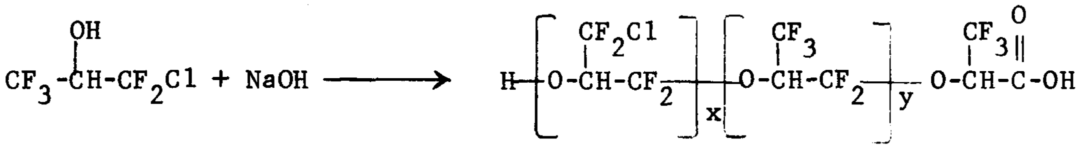
(1) A stainless steel pressure vessel with 75-ml capacity was charged with 10 g of poly(hexafluoropentamethylene carbonate) having a molecular weight of 1550. The vessel was evacuated, cooled in liquid nitrogen, and 9.1 g of sulfur tetrafluoride and 0.2 g of boron trifluoride were introduced. The reactants were heated in a rocker for 16 hours at 150°C. The vessel was cooled and the excess sulfur tetrafluoride and boron trifluoride were vented to the air. The reaction product was washed three times with water, dissolved in ether and the ether solution dried and evaporated. The viscous liquid recovered weighed 7.3 g and had an infrared spectrum similar to that of the starting material. Its elemental analysis, however, checked for the desired polyether. The molecular weight (by VPO) was 794.

Analysis:

	% C	% H	% F
Calculated for $C_6H_4F_8O_2$:	27.8	1.54	58.4
Found:	27.7	1.56	59.6

2. Polymerization of Chloropentafluoroisopropanol

a. Sodium Hydroxide Initiated



$$CF_3-\overset{OH}{\overset{|}{C}}H-CF_2Cl + NaOH \longrightarrow H\left[O-\overset{CF_2Cl}{\overset{|}{C}}H-CF_2\right]_x\left[O-\overset{CF_3}{\overset{|}{C}}H-CF_2\right]_y O-\overset{CF_3}{\overset{|}{C}}H-\overset{O}{\overset{\|}{C}}-OH$$

(1) In Tetrahydrofuran

Chloropentafluoroisopropanol (18.5 g, 0.1 mole) was dissolved in 50 ml of THF. Sodium hydroxide (4.0 g, 0.1 mole) was added over a 15-minute period with mixing, the temperature being kept at 20°-40°C. The slurry was mixed at 20°-25°C for 1½ hours, heated to 55°C over a ½-hour period, then cooled. The slurry was filtered to recover 5.3 g of sodium chloride (77.0% yield). The filtrate was poured into 300 ml of water. The water was decanted and the resinous oil dissolved in ether and dried with magnesium sulfate. The aqueous layer contained no fluoride ion. The ether was removed to yield 10.2 g of pale yellow, opaque, viscous polymer. The molecular weight by VPO was 4240±50. The hydroxyl equivalent was >7700; the neutralization equivalent was 520±15. The elemental analysis was: % C = 27.94, % H = 1.84, % Cl = 3.34 and % F = 53.78. The infrared spectrum (Figure 25) indicated that product probably was an acid terminated polyether.

(2) In Ether

Run No. 1. — Sodium hydroxide (2.0 g, 0.05 mole) was slurried in 20 ml of ether. Chloropentafluoroisopropanol (> 97% pure; 9.3 g, 0.05 mole) was dissolved in 15 ml of ether. On dissolution, there was an exotherm, indicating that the alcohol apparently forms a complex with the ether. The

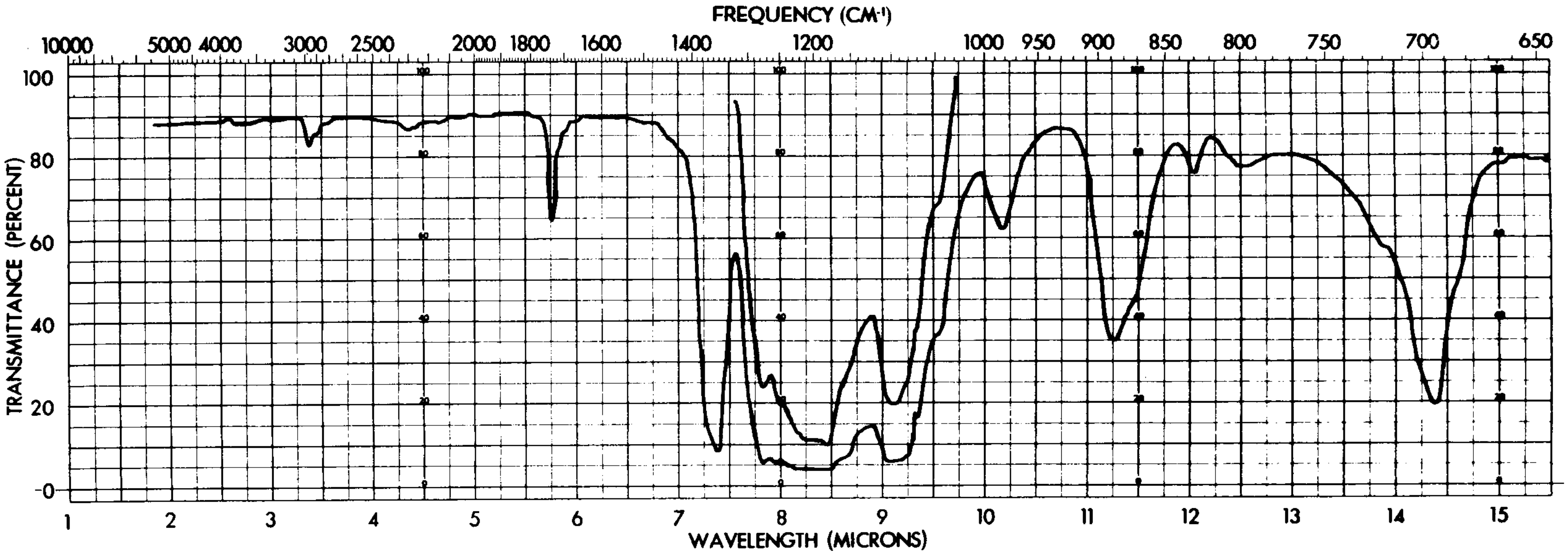


Figure 25. Polyether from Chloropentafluoroisopropyl Alcohol•Sodium Hydroxide Initiated

alcohol solution was added to the base over a 10-minute period with mixing at 27°-35°C. The slurry was stirred for 16 hours at 25°-30°C, during which time it became clear, then turned turbid. The slurry was then filtered, the solution dried with anhydrous magnesium sulfate, and the ether removed to yield 4.9 g (66.2%) of polymer. The molecular weight (determined by VPO) was 5700±100. Analysis:

	% C	% H	% F	% Cl
Calculated for copolymer of C_3HF_5O and C_3HF_4ClO				
in ratio of 4:1:	23.8	0.66	60.5	4.3
in ratio of 3:1:	23.7	0.66	59.7	5.4
Found:	24.0	0.89	57.21	4.69

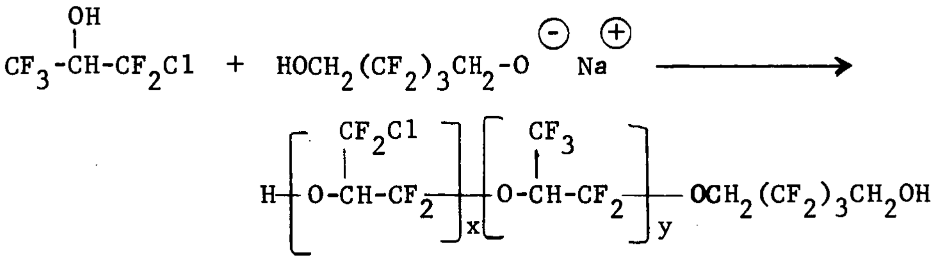
Additional Runs (General Procedure). — Chloropentafluoroisopropanol was added over a 10-minute period to the powdered sodium hydroxide in ether. The slurry was mixed for 19 hours at 25°-35°C, then filtered and the ether removed to yield the polymer. Table 2 contains the results of the polymerization at three different stoichiometric levels.

TABLE 2

EFFECT OF STOICHIOMETRY ON THE MOLECULAR WEIGHT OF POLYETHER OF CHLOROPENTAFLUOROISOPROPANOL — SODIUM HYDROXIDE INITIATED

Chloropentafluoro-isopropanol — Equivalents	Sodium Hydroxide — Equivalents	Yield, g	MW by VPO
1.0	1.2	61.0	7850
1.0	1.0	66.2	5700
1.0	0.8	27.0	2400

b. Monosodium Salt of Hexafluoropentanediol Initiated



$$CF_3\text{-}\overset{OH}{\overset{|}{CH}}\text{-}CF_2Cl + HOCH_2(CF_2)_3CH_2\text{-}O^{\ominus}\ Na^{\oplus} \longrightarrow$$

$$H\left[O\text{-}\overset{CF_2Cl}{\overset{|}{CH}}\text{-}CF_2\right]_x\left[O\text{-}\overset{CF_3}{\overset{|}{CH}}\text{-}CF_2\right]_y OCH_2(CF_2)_3CH_2OH$$

(1) Preparation of High Molecular Weight Polyether in Tetrahydrofuran

Chloropentafluoroisopropanol (13.0 g, 0.07 mole) and the monosodium salt of hexafluoropentanediol (16.4 g, 0.07 mole) in THF (50 ml) were mixed for 1 hour at room temperature, then 12 hours at reflux. The THF was removed and the residue washed repeatedly with hot water, then dried at 100°C for 3 hours in a vacuum oven to yield 7.0 g (67.5%) of polymer. Samples of this polymer, 12 mils thick, were punched and submitted to MSFC for LOX compatibility testing. The polymer had 2 reactions out of 20 specimens tested, probably caused by trapped THF.

In order to recheck the LOX data obtained above, additional polyether was prepared as follows:

Chloropentafluoroisopropanol (37.0 g, 0.2 mole) was added to the monosodium salt of hexafluoropentanediol (46.8 g, 0.2 mole) in THF (150 ml) over a 15-minute period. The slurry was mixed for 18 hours at 70°-80°C, then filtered. The THF was removed from the filtrate and the residue extracted thrice with boiling benzene. The residue was then dried in a vacuum oven at 140°-150°C for 24 hours to yield 13.9 g (47%) of an insoluble rubber which did not melt or dissolve when heated to 300°C.

Analysis:

	% C	% H	% F	% Cl
Calculated for Copolymer of C_3HF_5O and C_3HF_4ClO ratio of 14:1:	24.1	0.7	62.9	1.6
Found:	25.5	1.0	57.7	1.5

The hard rubber was ground into a powder and had no reactions in 20 specimens when tested by MSFC for LOX compatibility.

(2) Preparation of High Molecular Weight Polyether in Perfluorotributylamine

Chloropentafluoroisopropanol (61.0 g, 0.33 mole) was added to a slurry of the monosodium salt of hexafluoropentanediol (77.0 g, 0.33 mole) in 200 ml of perfluorotributylamine over a 5-minute period. The slurry agglomerated, then dispersed with rapid agitation. The mixture was stirred for 18 hours at 75°-85°C. It was then cooled, the solvent decanted, and the residue washed thrice with hot water. The residue was dried in a vacuum oven at 80°-100°C for 8 hours, followed by 16 hours at 120°-130°C to yield 6.3 g (13.7%) of an infusible insoluble polymer. This polymer was pulverized and the powder had no reactions in 20 specimens when tested for LOX compatibility by MSFC.

(3) Preparation of Moderate Molecular Weight Polyethers

Chloropentafluoroisopropanol (13.0 g, 0.07 mole), the sodium salt of hexafluoropentanediol and THF (50 ml) were mixed at 65°C to 70°C for 24 hours, followed by 24 hours at 25°C. The THF was removed and the residue washed thrice with boiling water. The residue was then dissolved in ether, dried with magnesium sulfate, and the ether removed. The results are shown in Table 3. The infrared spectrum is shown in Figure 26.

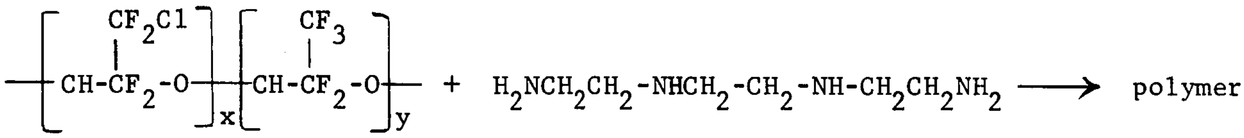
TABLE 3

EFFECT OF STOICHIOMETRY ON THE MOLECULAR WEIGHT OF POLYETHER OF CHLOROPENTAFLUOROISOPROPANOL — MONOSODIUM SALT OF HEXAFLUOROPENTANEDIOL INITIATED

Chloropentafluoro-isopropanol — Equivalents	Monosodium Salt of Hexafluoropentanediol — Equivalents	Yield, g	MW by VPO
1.0	1.2	30.8	1000
1.0	1.0	62.0	1900
1.0	0.8	30.7	2640

When diethyl ether was used as a replacement for THF as the solvent, no reaction occurred.

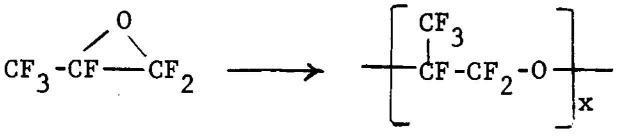
c. Crosslinking of Polyether of Chloropentafluoroisopropyl Alcohol



$$\left[\overset{CF_2Cl}{\overset{|}{CH}}-CF_2-O\right]_x\left[\overset{CF_3}{\overset{|}{CH}}-CF_2-O\right]_y + H_2NCH_2CH_2\text{-}NHCH_2\text{-}CH_2\text{-}NH\text{-}CH_2CH_2NH_2 \longrightarrow \text{polymer}$$

The polyether of chloropentafluoroisopropyl alcohol (2.0 g) MW 7850 (prepared by NaOH initiation) was dissolved in ether (20 ml) and 3 drops of triethylenetetramine was added. The entire solution gelled immediately. The ether was removed in a vacuum oven at 40°-50°C to yield an elastomer which did not melt.

3. Attempted Polymerization of Perfluoro-1,2-epoxypropane



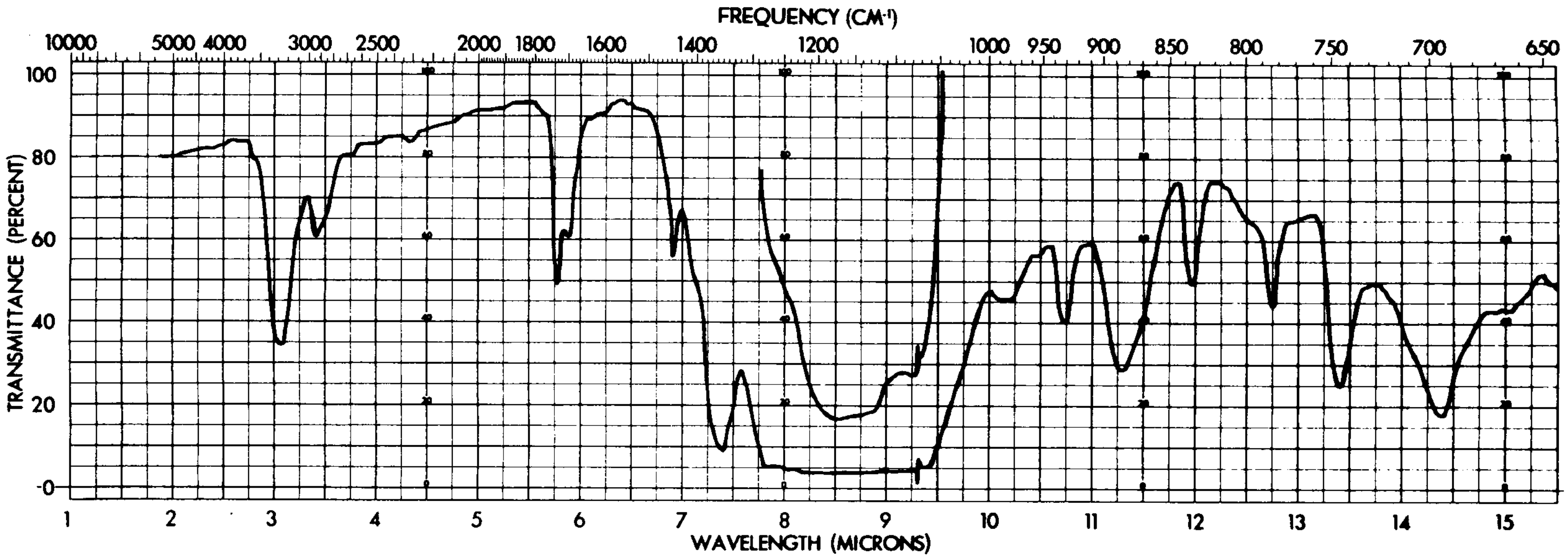


Figure 26. Polyether from Chloropentafluoroisopropanol. Monosodium Salt of Hexafluoropentanediol Initiated

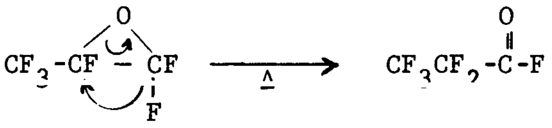
a. With Base

A mixture of perfluoropropylene and perfluoro-1,2-epoxypropane (6.0 g) was transferred to a bomb containing 0.1 g of pulverized potassium hydroxide and was left standing for 4 days. There was no reaction.

Ten grams of the mixture of perfluoropropylene and the epoxide was condensed and cooled to -80°C and 1 ml of a saturated solution of sodium cyanide in DMAC was added. The solution was mixed at -80°C for 3 hours. There was no reaction.

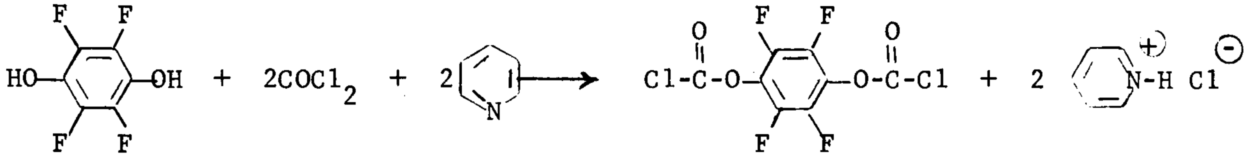
The perfluoropropylene and perfluoro-1,2-epoxypropane mixture (10.0 g) was condensed in a bomb containing 0.1 g of pulverized potassium hydroxide. The bomb was heated for 8 days at 100°-110°C. Based on the infrared spectrum of the off-gases, a substantial amount of the epoxide had rearranged to the acid fluoride. The residue in the bomb was dissolved in ether, washed with water and the ether dried with magnesium sulfate. The ether was removed to yield 1.2 g of crystalline material which was not the desired product.

Perfluoropropylene oxide was prepared by the method described previously. The mixture of perfluoropropylene oxide and perfluoropropylene was passed through an acetic acid solution of iodine monobromide to remove the majority of the olefin. Perfluoropropylene oxide (10.1 g) was condensed into a steel bomb containing aluminum chloride (1.7 g). This mixture was heated for 60 hours at 110°-115°C. The only product was perfluoropropionyl fluoride resulting from rearrangement of the epoxide.



E. Monomers

1. Preparation of Tetrafluoro-p-phenylene-bischloroformate

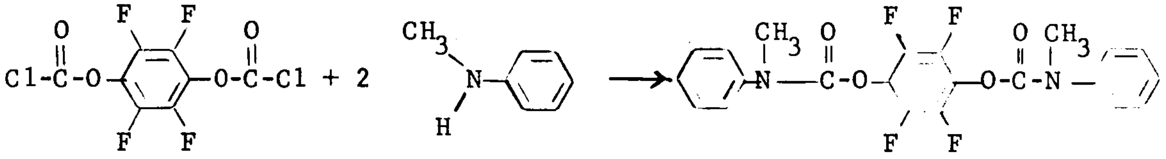


Phosgene (1.05 mole) was condensed into 1000 ml of anhydrous ether at -60°C in the reaction vessel of the phosgenation apparatus. Pyridine (43.4 g, 0.55 mole), in 150 ml of ether, was added to the stirred solution over a 30-minute period. The characteristic yellow precipitate of chlorocarbonyl pyridinium chloride which formed was stirred for an additional 15 minutes to ensure a finely dispersed slurry. Tetrafluorohydroquinone (45.5 g, 0.25 mole) in 250 ml of ether, was added to the stirred slurry at -60°C over a 2-hour period. The reaction mixture was allowed to come to room temperature and the stirring continued for 3 hours. The white precipitate of pyridinium chloride and poly(tetrafluoro-p-phenylene carbonate) was filtered off with the aid of suction. The filtrate stood overnight and then was stripped of volatiles. The residue was transferred to a 250-ml flask and fractionally distilled under reduced pressure, yielding 5.0 g (9.6% yield) of tetrafluoro-p-phenylene bischloroformate, bp 99°-102°C/5 mm, mp 81°-82°C. Its infrared spectrum is shown in Figure 27.

Analysis:

	% C	% Cl	% F
Calculated for $C_8Cl_2F_4O_4$:	31.26	23.12	24.75
Found:	31.22	23.05	24.74

2. Preparation of Tetrafluoro-p-phenylene-bis(N-methylanilino carbamate)

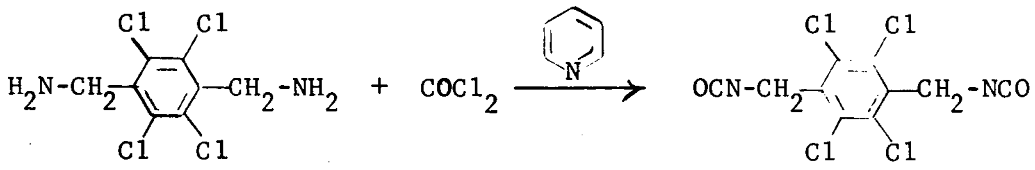


Tetrafluoro-p-phenylene-bischloroformate (0.1 g , 0.003 mole) was dissolved in 3 ml of anhydrous benzene in a micro test tube. N-methylaniline (0.14 g, 0.014 mole) was added dropwise with stirring. The resultant slurry was poured into 10 ml of hexane. The white crystalline solid was filtered off, washed with two 20-ml portions of hexane and two 20-ml portions of water, and dried overnight, yielding the desired derivative, mp 206°-208°C. Its infrared spectrum (Figure 28) is attached.

Analysis:

	% C	% H	% F	% N
Calculated for $C_{22}H_{16}F_4N_2O_4$:	58.94	3.57	16.97	6.25
Found:	59.07	3.35	17.04	6.34

3. Preparation of Tetrachloro-p-xylylene α,α'-Diisocyanate



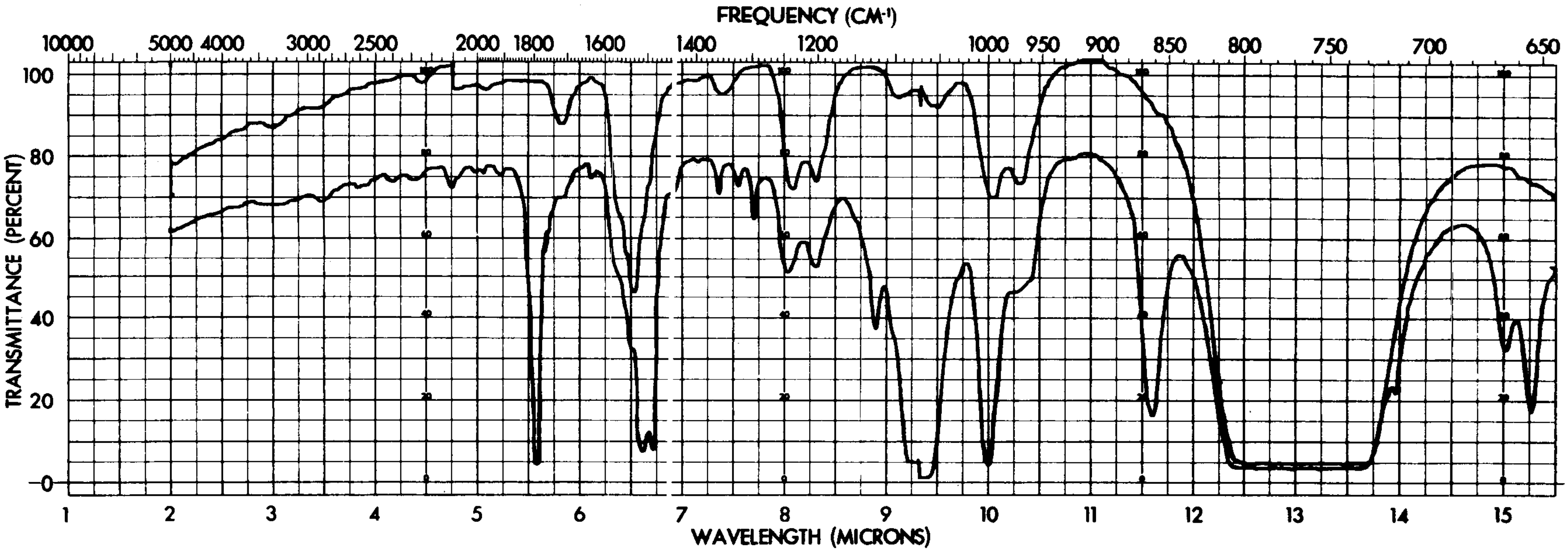


Figure 27. Tetrafluoro-p-phenylene-bischloroformate
in Carbon Tetrachloride

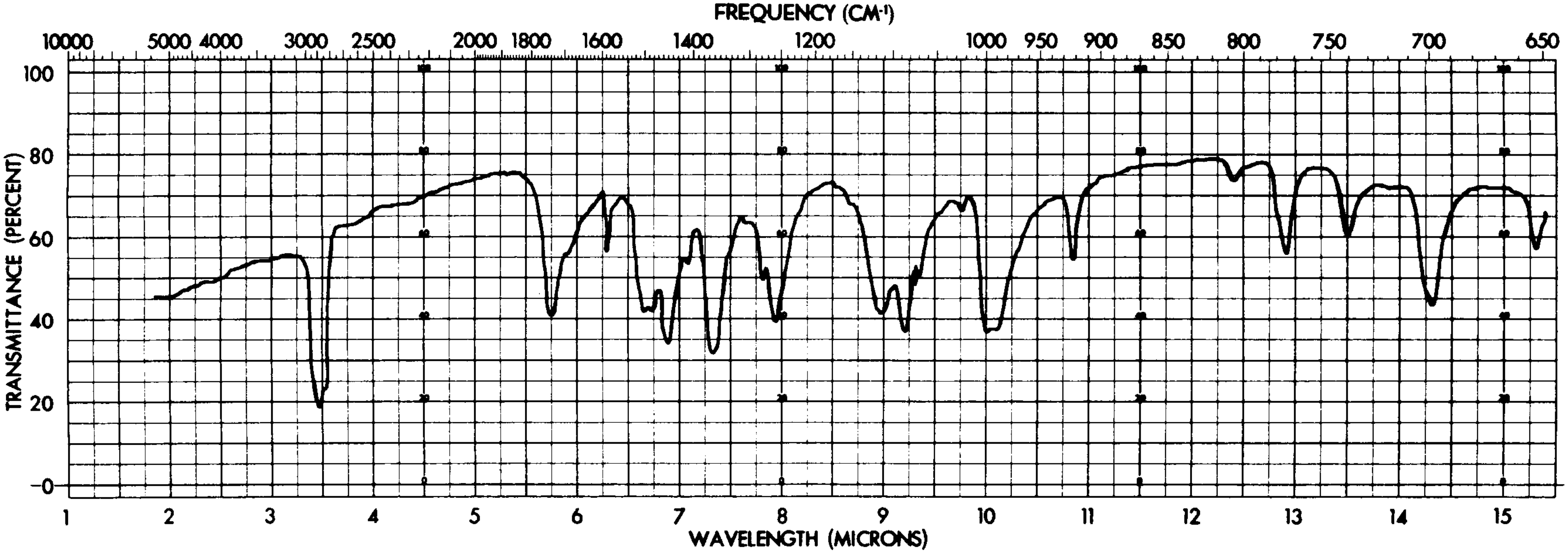


Figure 28. Tetrafluoro-p-phenylene-bis(N-methylanilino carbamate). Nujol Mull

Phosgene (> 0.50 mole) was condensed into 500 ml of dry THF in the usual phosgenation apparatus. Pyridine (31.6 g, 0.40 mole) was added with stirring at -40°C. A suspension of tetrachloro-p-xylylene α,α'-diamine (27.4 g, 0.1 mole) in 250 ml of dry THF was added over a period of 20 minutes, followed by an additional 300 ml of THF. The solution was stirred at room temperature for 28 hours then filtered. The THF filtrate was evaporated, leaving 32.2 g of crude material. To this was added o-dichlorobenzene and the mixture refluxed for 5 hours, hydrogen chloride being evolved. The solvent was stripped off and the residue vacuum distilled to give 10.1 g (30%) of a solid product, mp 116°-117°C, bp 162°-164°C/3 mm. This solid was identified by isocyanate equivalent and elemental analysis as the desired product, tetrachloro-p-xylylene α,α'-diisocyanate. The infrared spectrum is shown as Figure 29.

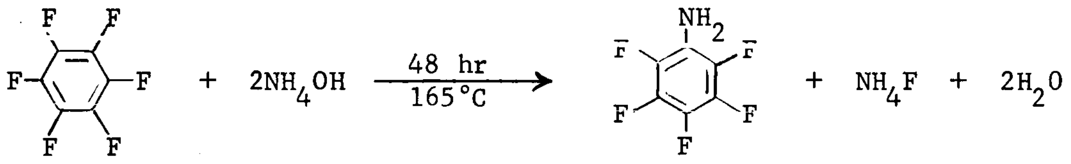
Isocyanate Equivalent:

Calculated for $C_{10}H_4Cl_4N_2O_2$:	163.0
Found:	164.6

Analysis:

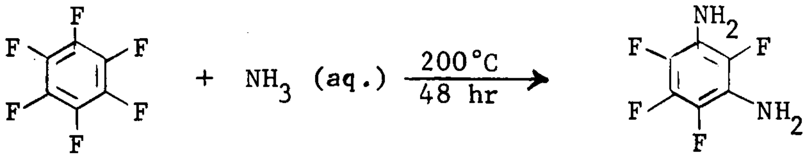
	% C	% H	% Cl	% N
Calculated for $C_{10}H_4Cl_4N_2O_2$:	36.8	1.23	43.6	8.6
Found:	37.43	1.06	43.79	8.47

4. Preparation of Pentafluoroaniline



A thick-walled glass tube (22-mm OD, 17-mm ID) was charged with hexafluorobenzene (5 ml, 0.043 mole) and 30% ammonium hydroxide (9 ml, 0.135 mole). The glass tube was then sealed, wrapped in glass wool, and placed in a rocker bomb. The bomb was heated at 165°C for 48 hours. The glass tube was then cooled to room temperature, opened, and the aqueous layer decanted off; 7 g of a solid brown residue was recovered from the hexafluorobenzene layer. It was steam-distilled, yielding 2.7 g (54% yield) of pentafluoroaniline, mp 36°-37°C.

5. Preparation of Tetrafluoro-m-phenylene



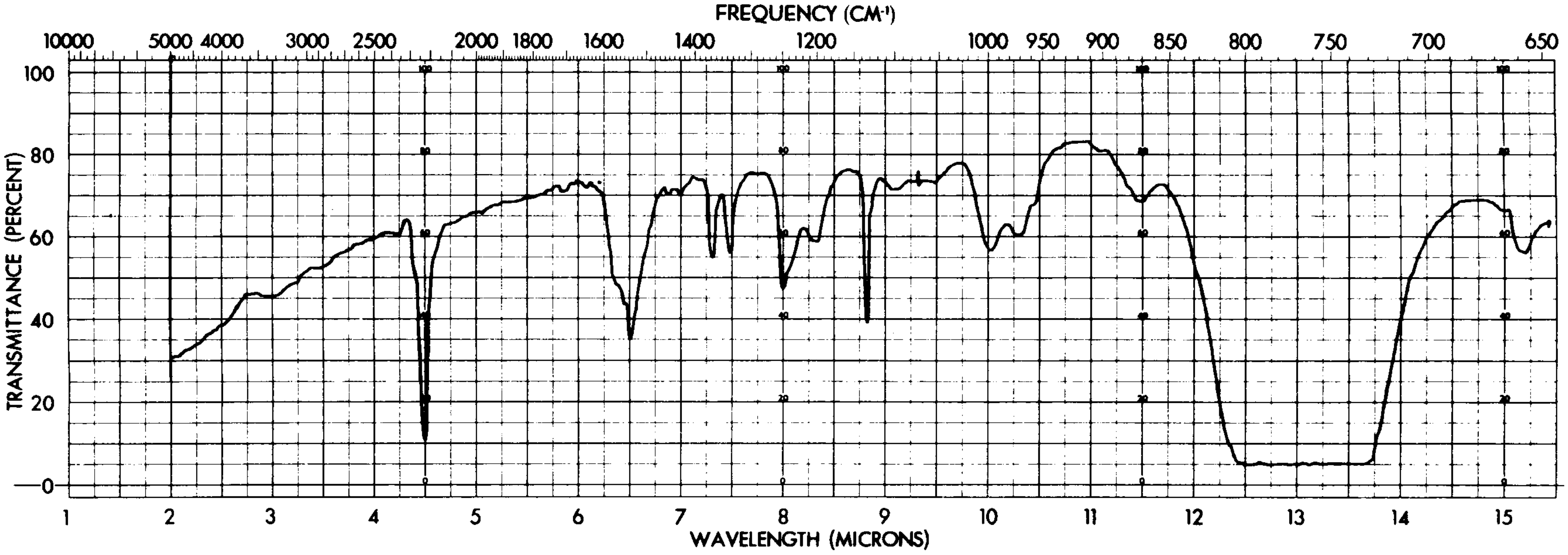
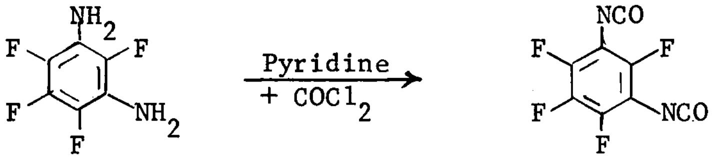


Figure 29. Tetrachloro-p-xylylene α,α'-Diisocyanate — Carbon Tetrachloride Solution

A glass-lined rocker bomb was charged with hexafluorobenzene (5 ml, 0.43 mole) and aqueous ammonia (18 ml, 0.27 mole). The temperature of the bomb was brought to 200°C and the bomb was rocked at that temperature for 48 hours. After cooling, the contents of the bomb were removed, and the solid material filtered. The filtrate, consisting of two layers, was separated. The upper brown aqueous layer was extracted with ether and the ether evaporated leaving a brown solid. The solid materials were combined and steam distilled to yield 2.3 g (48%) of tetrafluoro-m-phenylenediamine as a white solid, mp 128°-130°C.

6. Preparation of Tetrafluoro-m-phenylene Diisocyanate



Tetrafluoro-m-phenylenediamine (10.0 g, 0.055 mole)(approximately 95% meta isomer + 5% para isomer) was dissolved in 250 ml of anhydrous diethyl ether and charged to the addition funnel of the phosgenation apparatus. Phosgene (0.35 mole) was condensed into 750 ml of anhydrous ether, and pyridine (23.9 g, 0.25 mole) dissolved in 150 ml of ether was added to the stirred phosgene solution at -50°C. The characteristic yellow precipitate formed upon addition. The stirring was continued for 15 minutes, which produced a finely dispersed slurry. The diamine solution was then added over a 45-minute period, during which time the reaction mixture was allowed to come to room temperature. Stirring was continued for 3 hours at room temperature. The solids were filtered off and the solvent and excess phosgene stripped under reduced pressure. The residual tan liquid was distilled under reduced pressure through a helices-packed micro-column. The product (7.1 g, 56%) distilled at 70°-76°C at 3-5 mm. Redistillation gave 6.2 g (48.5% yield) of a clear liquid, bp 61.5°-62°C/1 mm. Vapor phase chromatography showed a mixture of approximately 95% meta and 5% para isomers. The infrared spectrum is attached as Figure 30.

Analysis:

	% C	% H	% N	% F
Calculated for $C_8N_2F_4O_2$:	41.39	0.00	12.06	32.75
Found:	41.70	0.03	12.19	32.70

A derivative of the above diisocyanate mixture was prepared by reacting the diisocyanate (0.232 g, 0.01 mole) with N-methylaniline (0.225 g, 0.021 mole) in 5 ml of benzene and warming gently on the steam bath. The resulting clear solution was poured into 10 ml of ligroine. The white solids were removed by filtration and dried. The melting point range was 83°-160°C, indicating highly impure material. The material was fractionally precipitated by dissolving it in a minimum amount of boiling benzene, cooling and filtering the small amount of precipitate formed. After drying, the precipitated

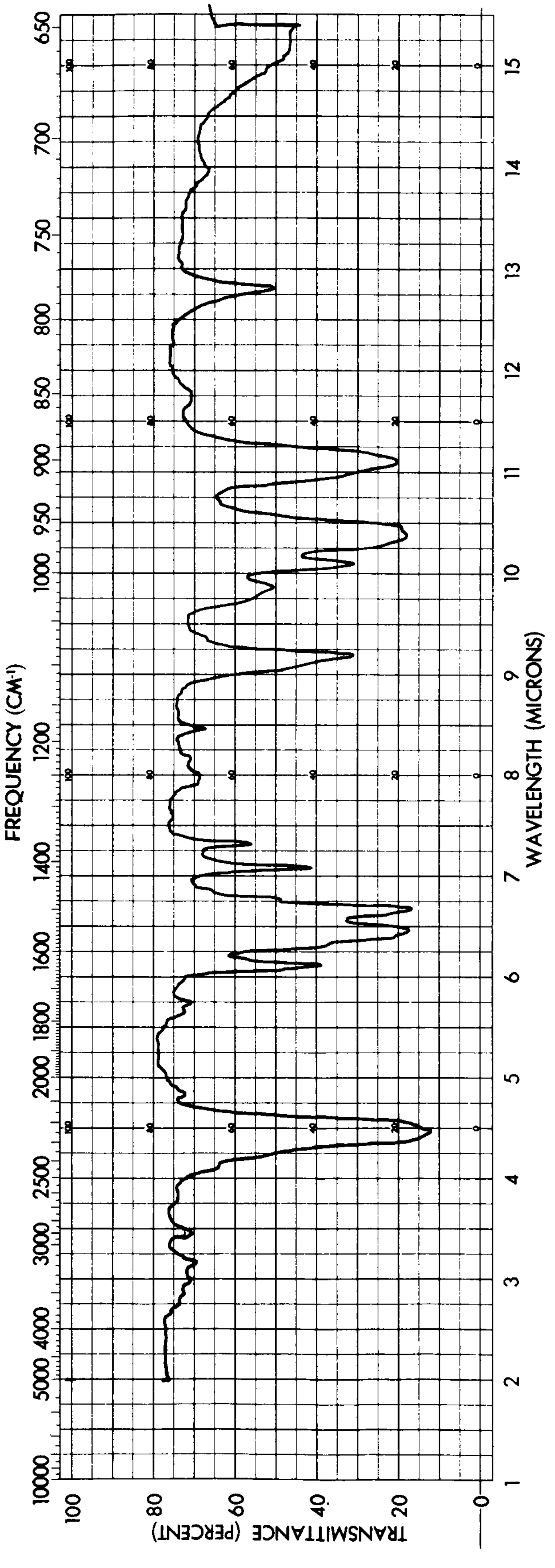


Figure 30. Tetrafluoro-m-phenylene Diisocyanate

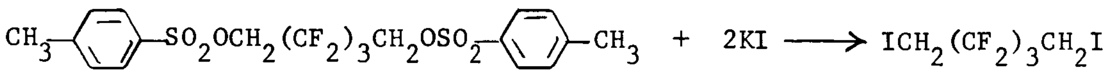
material melted between 210°-218°C (mp of the para derivative 236°-238°C). The benzene soluble portion was precipitated by addition of ligroine. Following filtration and drying, the derivative melted at 65°-105°C.

Analysis:

	% C	% H	% N	% F
Calculated for $C_{22}H_{18}O_2N_4F_4$:	59.11	4.06	12.77	17.02
Found:	58.59	4.37	12.10	16.98

The wide melting point range, coupled with the correct elemental analysis, substantiates the presence of the mixed meta and para isomers.

7. Preparation of 1,5-Diiodohexafluoropentane

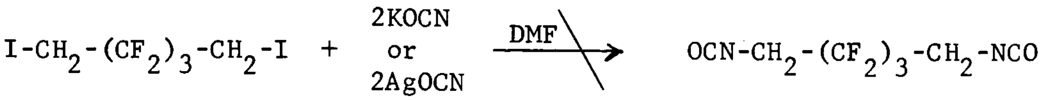


The di-p-toluenesulfonate of hexafluoropentanediol (106 g, 0.2 mole) and potassium iodide (69.7 g, 0.42 mole) in 450 ml of ethylene glycol were heated at reflux for 56 hours. When the solution was poured into water, a dark oil separated. The water and oil mixture was extracted with carbon tetrachloride, giving a purple solution. The carbon tetrachloride solution was decolorized with sodium thiosulfate solution, dried over anhydrous magnesium sulfate, and the solvent evaporated yielding 79.3 g (91.8%) of a yellow oil, which solidified on cooling. The solid was recrystallized from a methanol-water mixture giving 64.8 g (75.0%) of 1,5-diiodohexafluoropentane, mp 48°-49°C. The infrared spectrum is given as Figure 31.

Analysis.

	% C	% H	% F	% I
Calculated for $C_5H_4F_6I_2$:	13.90	0.93	26.40	58.8
Found:	13.88	0.95	26.37	59.00

8. Attempted Preparation of Hexafluoropentamethylene Diisocyanate



$$\text{I-CH}_2\text{-(CF}_2)_3\text{-CH}_2\text{-I} \; + \; \begin{matrix}\text{2KOCN}\\ \text{or}\\ \text{2AgOCN}\end{matrix} \; \cancel{\xrightarrow{\text{DMF}}} \; \text{OCN-CH}_2\text{-(CF}_2)_3\text{-CH}_2\text{-NCO}$$

A mixture of 1,5-diiodohexafluoropentane (17.3 g, 0.04 mole) and potassium isocyanate (6.5 g, 0.08 mole) was stirred into 75 ml of DMF. The resulting suspension was heated with stirring at 140°C for 30 minutes. The solution was filtered, and the filtrate concentrated. There was no apparent reaction.

There was no reaction when the operation was repeated using silver isocyanate.

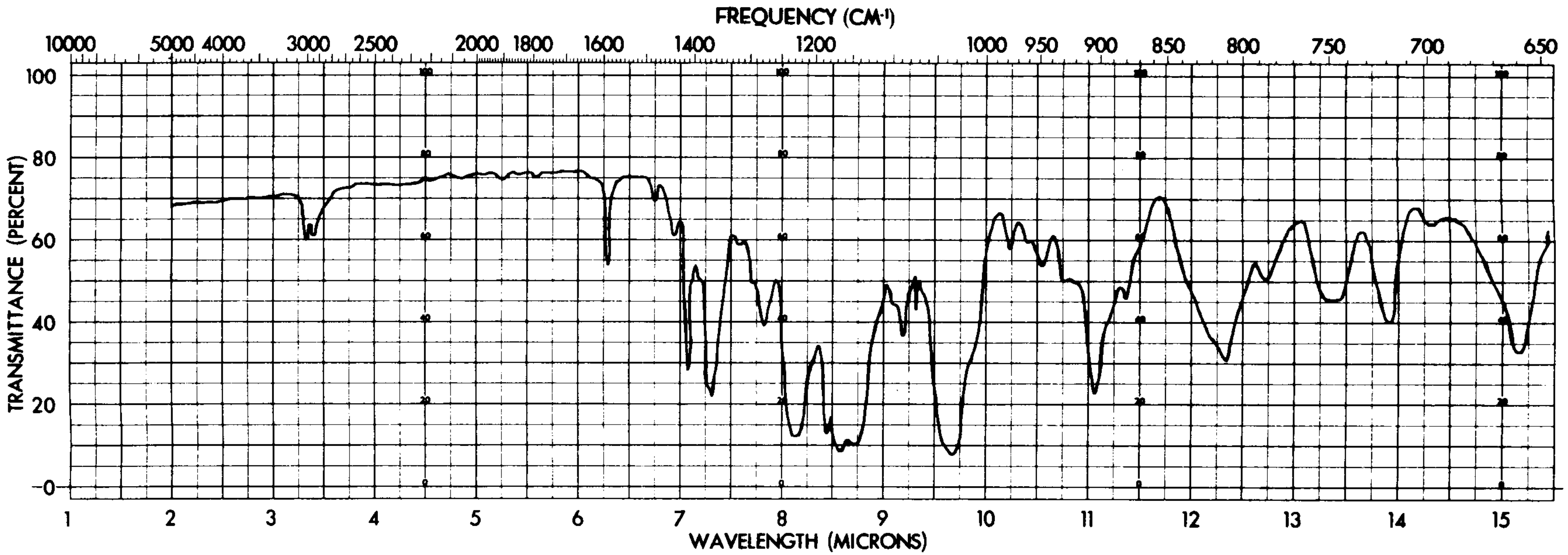
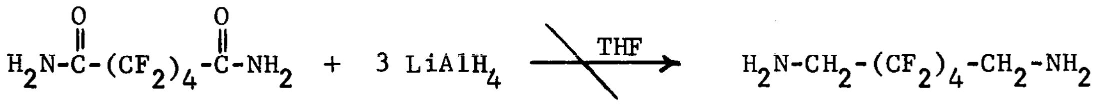


Figure 31. 1,5-Diiodohexafluoropentane — Melt

9. Attempted Reduction of Perfluoroadipamide



$$H_2N\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CF_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 + 3\ LiAlH_4 \xcancel{\xrightarrow{THF}} H_2N\text{-}CH_2\text{-}(CF_2)_4\text{-}CH_2\text{-}NH_2$$

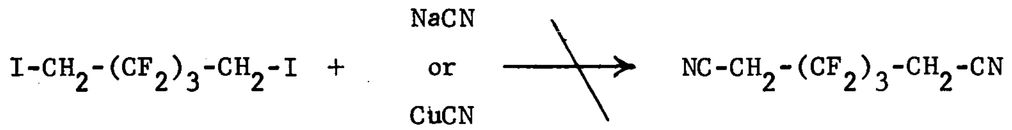
Perfluoroadipamide (16.4 g, 0.057 mole) dissolved in 500 ml of THF was added dropwise into a stirred suspension of LAH (6.5 g, 0.0171 mole) in 200 ml of THF. After the addition was complete, the solution was heated to reflux for 21 hours. The reaction mass was cooled and 5 ml of water was cautiously added to destroy excess LAH. The inorganic solids were filtered off and the filtrate was treated with charcoal and dried over anhydrous magnesium sulfate. The solution was filtered and the solvent removed, leaving a dark brown semi-solid. This was identified by its infrared spectrum as starting material, perfluoroadipamide.

10. Attempted Preparation of Hexafluoropimelic Acid

$$I\text{-}CH_2\text{-}(CF_2)_3\text{-}CH_2\text{-}I + 2\ NaCN \xcancel{\xrightarrow[CH_3OH,\ H_2O]{CuCN,\ \Delta}} HOOC\text{-}CH_2(CF_2)_3\text{-}CH_2\text{-}COOH$$

A steel bomb was charged with 1,5-diiodohexafluoropentane (4.3 g, 0.01 mole), sodium cyanide (1.5 g, 0.003 mole), copper (I) cyanide (0.5 g, 0.003 mole), and 31 ml of methanol in 13 ml of water. The bomb was heated at 180°-200°C for 16 hours. After workup, none of the desired product was isolated.

11. Attempted Preparations of 1,5-Dicyano-2,2,3,3,4,4-hexafluoropentane



$$I\text{-}CH_2\text{-}(CF_2)_3\text{-}CH_2\text{-}I + \begin{matrix} NaCN \\ \text{or} \\ CuCN \end{matrix} \xcancel{\longrightarrow} NC\text{-}CH_2\text{-}(CF_2)_3\text{-}CH_2\text{-}CN$$

a. Method A. — A mixture of 1,5-diiodohexafluoropentane (8.6 g, 0.02 mole) and sodium cyanide (3.0 g, 0.06 mole) in 80 ml of ethylene glycol was stirred and refluxed for 60 hours. The black solution was poured hot into 300 ml of water. A black precipitate was filtered off, and the filtrate extracted with carbon tetrachloride. This layer was separated and concentrated to give 1.5 g of a liquid identified by its infrared spectrum and elemental analysis as essentially unreacted 1,5-diiodohexafluoropentane with a trace of unidentified impurity.

b. Method B. — A mixture of 1,5-diiodohexafluoropentane (8.6 g, 0.02 mole) and copper (I) cyanide (10.7 g, 0.06 mole) in 100 ml of DMF was stirred and refluxed for 60 hours. The hot brown slurry was poured into 300 ml of water and filtered. The solid (10.2 g) was identified as copper (I) cyanide. The filtrate was poured into a solution of 8 g of iron (III) chloride and 2 ml of hydrochloric acid in 100 ml of water and heated to 70°C. On cooling, no separation of organic layer occurred, indicating that no reaction had taken place.

c. Method C. — A mixture of 1,5-diiodohexafluoropentane (8.6 g, 0.02 mole) and copper (I) cyanide (4.3 g, 0.048 mole) dissolved in 20 ml of pyridine and 50 ml of N-methylpyrrolidone was stirred and heated at 110°C for 24 hours. After cooling, attempts to break up any organic cyanide-copper (I) cyanide complex formed with aqueous ammonia, iron (III) chloride and aqueous hydrochloric acid, or sodium cyanide only resulted in isolation of inorganic copper (I) cyanide. In all cases, the infrared spectrum of organic material isolated was similar to the spectrum of 1,5-diiodohexafluoropentane, with no -CN absorption.

d. Method D. — A mixture of 1,5-diiodo-2,2,3,3,4,4-hexafluoropentane (21.6 g, 0.05 mole) and copper (I) cyanide (10.8 g, 0.12 mole) in 30 ml of DMF were stirred and heated under nitrogen to 70°C. Pyridine (10 ml) was added and heating was increased to 135°C and maintained for 4 hours. The hot mixture was then poured into a solution of iron (III) chloride (20 g) in concentrated hydrochloric acid (5 ml) and water (30 ml). This was then heated at 75°C for 20 minutes to decompose any complex formed. After cooling, the inorganic solids were filtered off, and the filtrate was extracted with ether. The ether was dried over anhydrous magnesium sulfate, filtered, and stripped to dryness. An infrared spectrum of the solid was identified as unreacted starting material.

12. Attempted Preparation of 4,4,5,5,6,6-Hexafluoro-nona-1,8-diyne

$$ICH_2(CF_2)_3CH_2I \quad + \quad 2\ NaC\equiv CH \ \not\xrightarrow[DMF]{Xylene} \ HC\equiv C\text{-}CH_2(CF_2)_3CH_2\text{-}C\equiv CH \quad + \ 2NaI$$

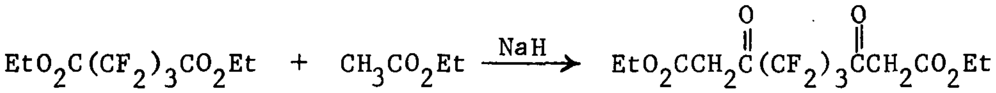
A solution of diiodohexafluoropentane (39.2 g, 0.091 mole) dissolved in 60 ml of dry xylene and 50 ml of dry DMF was added slowly to a stirred suspension of sodium acetylide (10 g, 0.21 mole) in 60 ml of dry xylene and 40 ml of dry DMF which was heated to 90°C. The reaction mixture was stirred for 22 hours at 110°C. When the stirring was stopped, a white, flocculent solid settled out. After cooling, 25 ml of distilled water and a solution of 11.3 g of ammonium chloride in 50 ml of water were added to destroy any unreacted sodium acetylide. All of the white solid dissolved. The lower water-DMF layer which separated gave a positive test for iodide ion. The upper xylene layer was dried over anhydrous magnesium sulfate. Distillation yielded only the unreacted starting diiodide.

13. Attempted Reaction of 1,5-Diiodohexafluoropentane With Sodium Methoxide

$$I\text{-}CH_2(CF_2)_3CH_2\text{-}I \quad + \quad (2)\ \overset{\oplus}{Na}\ \overset{\ominus}{OCH_3} \ \not\longrightarrow \ CH_3O\text{-}CH_2(CF_2)_3CH_2\text{-}OCH_3$$

Sodium methoxide (6.6 g, 0.12 mole) and 1,5-diiodohexafluoropentane (17.3 g, 0.04 mole) were dissolved in DMF (25 ml) and the solution refluxed 18 hours under dry nitrogen. After cooling, the dark brown solution was poured into acidified water (150 ml). The water was then extracted with ether, the extracts combined, and dried over magnesium sulfate. Vacuum distillation yielded 4.9 g of the starting diiodo material. No substituted material was recovered.

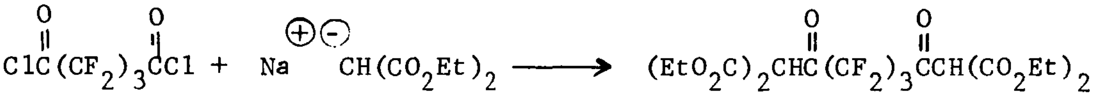
14. Attempted Preparation of Diethyl-3,7-diketo-4,4,5,5,6,6-hexafluoroazelate



$$\mathrm{EtO_2C(CF_2)_3CO_2Et} \;+\; \mathrm{CH_3CO_2Et} \xrightarrow{\mathrm{NaH}} \mathrm{EtO_2CCH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{(CF_2)_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2CO_2Et}$$

Ethyl acetate (13.2 g, 0.5 mole) was added over a 5-hour period to a slurry of diethyl perfluoroglutarate (22.2 g, 0.075 mole) and sodium hydride (3.6 g, 0.15 mole). The brown-black viscous liquid was poured into a sulfuric acid – ice mixture. The aqueous layer was decanted and the organic phase taken up in ether, dried over anhydrous magnesium sulfate, stripped, and distilled under reduced pressure. None of the desired product was isolated.

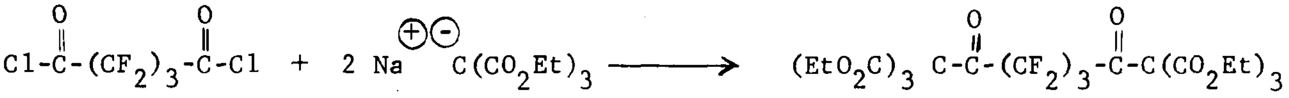
15. Attempted Preparation of Diethyl-2,8-dicarbethoxy-3,7-diketo-4,4,5,5,6,6-hexafluoroazelate



$$\mathrm{Cl}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{(CF_2)_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Cl} \;+\; \overset{\oplus}{\mathrm{Na}}\;\overset{\ominus}{\mathrm{CH}}\mathrm{(CO_2Et)_2} \longrightarrow \mathrm{(EtO_2C)_2CH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{(CF_2)_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH(CO_2Et)_2}$$

Sodium shot (10.6 g, 0.46 mole) and diethyl malonate (74.0 g, 0.46 mole) were added to anhydrous diethyl ether and stirred for 25 hours. At the end of this time, the reaction was complete as indicated by the disappearance of the sodium. Perfluoroglutaryl chloride (55.4 g, 0.20 mole) in ether (100 ml) was added to the well-stirred slurry of the sodio derivative of malonic ester at a rate such that a gentle reflux was maintained. The addition time was 1½ hours. Refluxing on the steam bath was continued for 3 more hours. After cooling, the mixture was poured into water (200 ml), the ether layer separated, and the aqueous portion extracted with ether. The extracts were combined, dried, stripped, and distilled under reduced pressure. None of the desired product was isolated.

16. Preparation of Diethyl-2,2,8,8-tetracarboethoxy-3,7-diketo-4,4,5,5,6,6-hexafluoroazelate



$$\mathrm{Cl}\text{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\mathrm{(CF_2)_3}\text{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\mathrm{Cl} \;+\; 2\;\overset{\oplus}{\mathrm{Na}}\;\overset{\ominus}{\mathrm{C}}\mathrm{(CO_2Et)_3} \longrightarrow \mathrm{(EtO_2C)_3\;C}\text{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\mathrm{(CF_2)_3}\text{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\mathrm{C(CO_2Et)_3}$$

A fine suspension of sodium (2.3 g, 0.1 mole) was prepared by mixing in 50 ml of refluxing dioxane. Triethyl methanetricarboxylate (23.2 g, 0.1 mole) in 50 ml of dioxane was then added and the mixture refluxed overnight. The resulting reddish brown solution was filtered hot to remove the untreated sodium (0.01 g). The clear deep red solution was allowed to cool and the precipitated sodium salt was filtered off and recrystallized from dioxane. Yield 24.6 g (97.2%).

Perfluoroglutaryl chloride (5.7 g, 0.02 mole) in 20 ml of dioxane was then added to the above sodio salt and the slurry refluxed for 3 hours. It was then cooled, filtered, and stripped of solvent. When the crude product was fractionated under reduced pressure, some decomposition apparently took place. The fraction boiling between 97°C and 103°C was isolated (8.5 g).

Analysis:

	% C	% H	% F
Calculated for $C_{25}H_{30}F_6O_{14}$:	44.9	4.5	17.1
Found:	46.24	5.30	15.16

A portion of the above product was shaken in contact with distilled water overnight. The organic material was then separated and dried over magnesium sulfate. Elemental analysis demonstrated hydrolysis of the fluorines.

	% C	% H	% F
Analysis Found after Hydrolysis:	50.04	6.61	5.0

17. Attempted Preparation of 2,2,2-Trichloro-1,1-di(trifluoromethyl) Ethanol (Hexafluorochloretone)

$$CHCl_3 + CF_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CF_3 \xrightarrow{\text{base}} CCl_3\text{-}\underset{\underset{CF_3}{|}}{\overset{\overset{OH}{|}}{C}}\text{-}CF_3$$

a. In Triglyme. — Freshly molten potassium hydroxide (22 g, 0.4 mole) was heated to 150°C in triglyme (100 ml) and slowly cooled to room temperature with vigorous stirring. The resulting fine suspension was further cooled to -5°C, and chloroform (44.3 g, 0.37 mole) was added. Hexafluoroacetone (0.40 mole) was bubbled into the reaction mixture at -5°C over a period of 40 minutes. The solution darkened slightly upon addition. The temperature was held below -5°C, with stirring, for 2 hours. The stirring was discontinued and the slurry allowed to stand overnight at room temperature. The resulting dark suspension was poured into a mixture of dilute sulfuric acid and cracked ice. The aqueous solution was extracted with two 100-ml portions of chloroform. The chloroform layer was separated and dried over anhydrous magnesium sulfate. None of the desired product was obtained.

b. In Acetaldehyde Dibutyl Acetal. – The same ratio of reactants was utilized in the attempt with the following exceptions. Sodium carbonate (0.12 mole/mole chloroform) was used in place of potassium hydroxide and acetaldehyde dibutyl acetal was substituted for triglyme. The addition order and rate of reaction times were the same as above. Again, none of the desired product was obtained.

18. Preparation of the Monoacetal of Hexafluoropentanediol and Dihydropyran

Hexafluoropentanediol (30.0 g, 0.14 mole), dihydropyran (60 ml) and 1 drop of concentrated hydrochloric acid were refluxed (at 94°C) for 16 hours. After allowing the solution to cool, potassium hydroxide pellets (3 g) were added and the mixture was stirred for 1 hour. The solution was then decanted and poured into water, whereupon an oil separated. This oil was washed twice with water, dissolved in ether, and the ether solution dried over anhydrous sodium sulfate. The ether was stripped off and the oil distilled under vacuum. Four fractions, with a total weight of 23 g, distilling from 40°C to 64°C at 0.5 mm, were collected. The infrared spectra of all the fractions indicated that hydroxyl groups were still present, but that there was no hexafluoropentanediol present.

The collected fractions were refluxed for an additional 16 hours, again using an excess of dihydropyran and a drop of concentrated hydrochloric acid. The distilled product which crystallized on standing was identical to the starting oil. The product was identified as the desired monoacetal. The infrared spectrum is shown in Figure 32.

Analysis:

	% C	% H	% F
Calculated for $C_{10}H_{14}F_6O_3$:	40.5	4.8	38.5
Found:	40.78	5.15	36.59

19. Attempted Preparation of 1,5-Dibromo-1,1,2,3,3,4,5,5-octafluoropentane

$$2CF_2{=}CFH + CF_2Br_2 \xrightarrow{BZP} CF_2BrCHFCF_2CHFCF_2Br$$

Benzoyl peroxide (0.1 g) was placed in a glass-lined, stainless steel pressure reactor of 125-ml capacity. The evacuated bomb was cooled to -75°C and dibromodifluoromethane (23.1 g, 0111 mole) was condensed in. Trifluoroethylene (17.0 g, 0.21 mole) was then added in a similar fashion. The sealed bomb was heated to 110°C and held at that temperature for 4 hours.

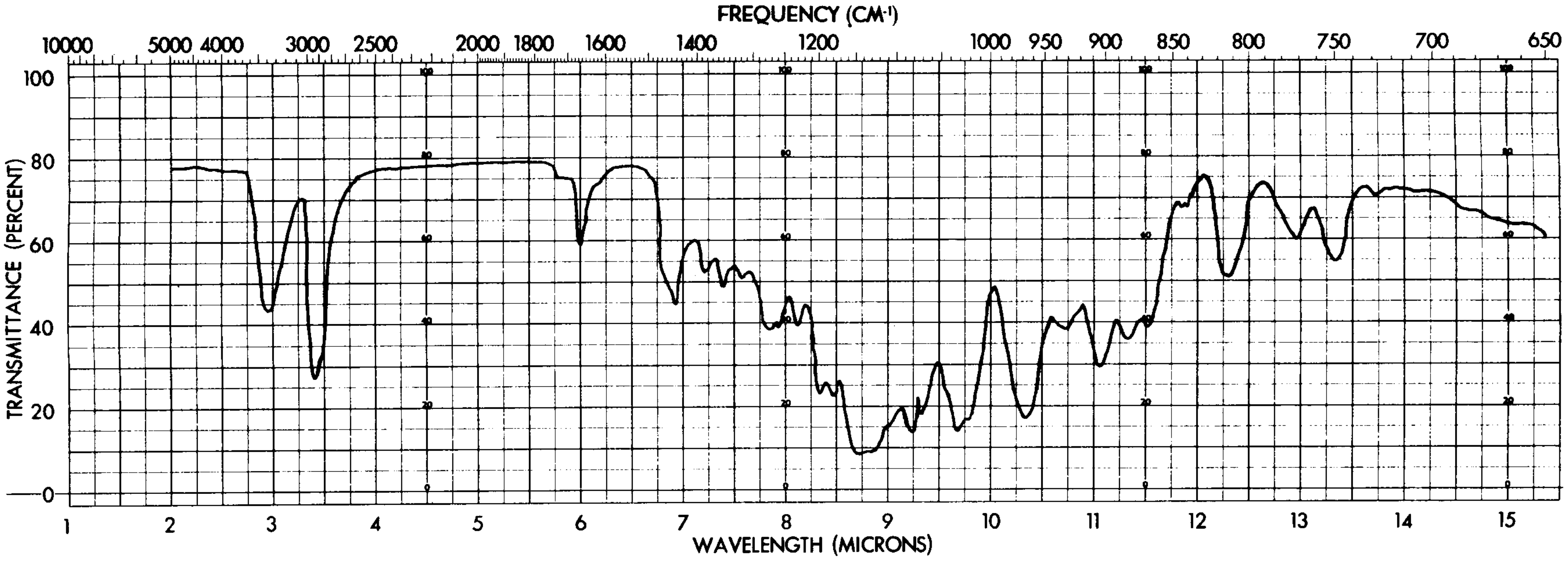


Figure 32. Monoacetal of Hexafluoropentanediol and Dihydropyran

After cooling, the unreacted gaseous products were allowed to evaporate and the bomb was opened; 3.1 g of waxy polymeric residue which was insoluble in common solvents was recovered. Fractionation under reduced pressure was unsuccessful. The infrared spectrum of the waxy product is consistent with a moderately high molecular weight telomer structure.

20. Preparation of Perfluoropenta-1,4-diene

a. Preparation of Sodium Salt of Kel-F Acid 683

Kel-F acid 683 (3,5,6-trichloroperfluorohexanoic acid) (100.0 g, 0.275 mole), sodium hydroxide (12.2 g, 0.306 mole) and 14 ml of water were vigorously stirred. Considerable heat was generated and steam was evolved from the reaction mass. The resulting chunky material was dried overnight in a vacuum oven at 40°C and 2 mm Hg, ground to a fine powder and dried 10 days in a vacuum desiccator over phosphorus pentoxide (3 changes). A fine, free-flowing powder was recovered(103.5 g, 100% yield).

b. Pyrolysis of Sodium Salt

$$CF_2Cl\text{-}CFCl\text{-}CF_2CFCl\text{-}CF_2COO^{\ominus} \xrightarrow[(-CO_2,\ Cl^{\ominus})]{\Delta} CF_2ClCFCl\text{-}CF_2CF{=}CF_2$$

The sodium salt from above was pyrolyzed in a 250-ml flask fitted with a Friederich condenser and vacuum fitting. The decarboxylation-dechlorination commenced at 150°C. Heating was continued, with intermittent shaking of the pyrolysis flask, to 270°C. There was a considerable amount of what appeared to be sublimation of the sodium salt. The crude product (68.7 g) was collected in the dry ice — acetone cooled traps, washed with 10% sodium carbonate, water, and dried over sodium sulfate. Distillation yielded 49.5 g (58.4% yield based on starting acid), bp 92°-93°C (literature value 92°-93°C/756 mm) (Reference 20).

c. Dechlorination

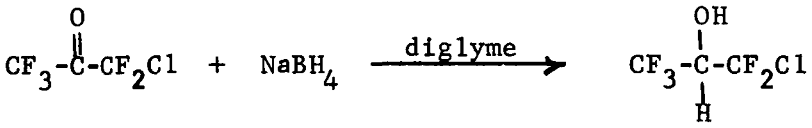
$$CF_2ClCFClCF_2CF{=}CF_2 \xrightarrow{Zn} CF_2{=}CFCF_2CF{=}CF_2$$

Zinc powder (23.8 g, 0.364 mole) was activated by suspending it in acetone (100 ml) and slowly adding concentrated hydrochloric acid (18.5 ml). Stirring was continued for 30 minutes after addition was completed. There was no more hydrogen gas generated at this time. After filtration, the activated zinc was dried in the vacuum oven at 70°C for 4 hours.

Activated zinc (17. 6 g, 0.270 mole) was suspended in triglyme (100 ml) and the slurry heated to 70°C. 4,5-Dichloroperfluoropentene-1 (49.5 g, 0.17 mole) was added over a 3-hour period with no apparent reaction.

The temperature was increased slowly, and at 130°C the product began to distill (through a 6-in. helices-packed column). Heating was continued until the temperature of the reaction mixture was 192°C, at which temperature no more liquid was distilling. The crude product (36.6 g), upon redistillation through a 14-in., helices-packed, vacuum-jacketed column, yielded 23 g (62% yield) of perfluoropenta-1,4-diene (bp 33°-34°C, literature value 33°-34°C). The infrared spectrum is attached as Figure 33.

21. Preparation of Monochloropentafluoroisopropyl Alcohol



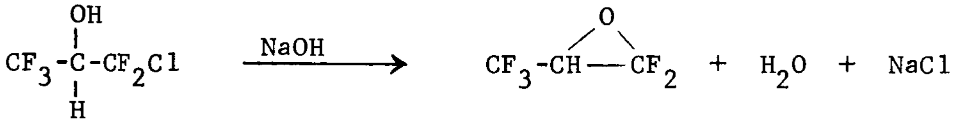
$$CF_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CF_2Cl + NaBH_4 \xrightarrow{\text{diglyme}} CF_3\text{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}\text{-}CF_2Cl$$

Chloropentafluoroacetone (210.0 g, 1.20 mole) was added to sodium borohydride (30.0 g, 0.794 mole) in 240 ml of dry diglyme over a 3-hour period at a temperature below 50°C. After standing overnight, the mixture was warmed to 40°C to remove any unreacted chloropentafluoroacetone. After cooling, the mixture was poured into 450 ml of concentrated hydrochloric acid. The organic layer was separated, washed with six 50-ml portions of acidified water, and dried over anhydrous magnesium sulfate. It was distilled from sulfuric acid, then redistilled, bp 80.5°-80.6°C.

Analysis:

	% C	% H	% Cl	% F
Calculated for $C_3H_2F_5ClO$:	19.50	1.08	19.2	51.4
Found:	20.31	1.54	19.69	53.55

22. Attempted Dehydrochlorination of Chloropentafluoroisopropyl Alcohol



Chloropentafluoroisopropanol (7.2 g, 0.0392 mole) was added dropwise to a stirred solution of sodium hydroxide (32.0 g, 0.784 mole) in 32 ml of water at 75°C. An exothermic reaction ensued, which caused a great deal of foaming, and the reaction flask was cooled in a dry ice — acetone bath. Only a small amount of water was recovered from the dry ice — acetone trap. A yellow, water-soluble solid, decomposing at 235°C, was left in the flask. The mixture in the reaction flask was made slightly acid with hydrochloric acid and evaporated to leave a white residue (NaCl) with a yellow discoloration. The above residue was extracted with ether in a Soxhlet extractor. Evaporation of the ether left a very small amount of residue which appeared to be polymeric in nature. None of the desired epoxide was isolated.

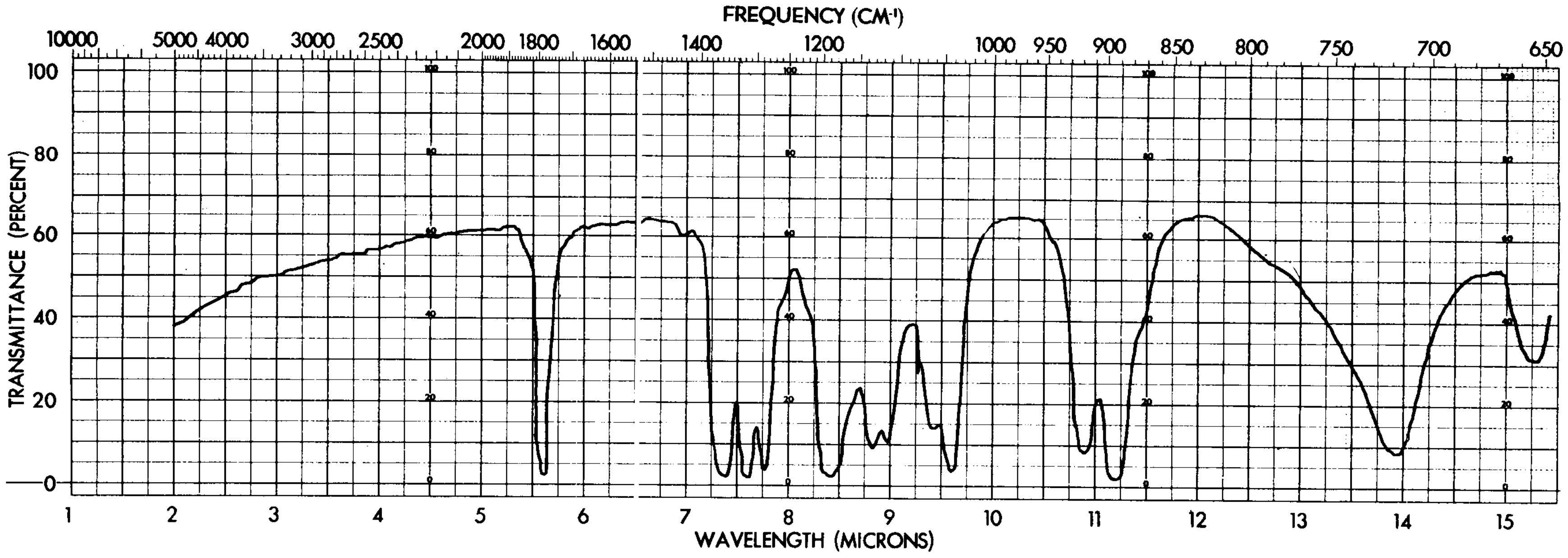


Figure 33. Perfluoropenta-1,4-diene

23. Preparation of the Monosodium Salt of Hexafluoropentanediol

a. Using Sodium Methoxide

$$HOCH_2(CF_2)_3CH_2OH + \overset{\oplus}{Na}\ \overset{\ominus}{OCH_3} \longrightarrow HOCH_2(CF_2)_3CH_2\overset{\ominus}{O}\ \overset{\oplus}{Na} + CH_3OH$$

Procedure 1. In Benzene. — Hexafluoropentanediol (120.0 g, 0.59 mole), sodium methoxide (27.0 g, 0.50 mole) and 1250 ml of benzene were mixed and the stirred slurry distilled. Approximately 500 ml of distillate (bp 78.4°-79.8°C) was collected. The amount of methanol in the distillate was only 0.103 mole (20.6% of theoretical). The slurry was cooled to 0°C with an ice bath and the solids filtered off and washed with three 250-ml portions of ether. The white crystalline material, insoluble in ether, was dried in a vacuum oven at 60°C overnight, yielding 122.0 g of salt. The equivalent weight was 264±2 (theoretical 234).

Analysis:

	% C	% H	% F	% Na
Calculated for $C_5H_5F_6O_2Na$:	25.6	2.14	48.8	9.8
Found:	25.1	2.64	45.7	8.9

A small portion of the solid material (3 g) was placed in a test tube and heated in an oil bath. When the temperature reached 190°C, a violent exotherm took place with consequent charring of the material and the evolution of gaseous decomposition products. The infrared spectrum of the vapors which had condensed on the test tube walls and which subsequently crystallized showed the material to be hexafluoropentanediol.

Procedure 2. In Xylene. — Hexafluoropentanediol (250.0 g, 1.18 mole), sodium methoxide (54.0 g, 1.0 mole) and 1.3 liters of xylene were mixed. The mixture was heated and a distillate began coming over at 70°C. The distillate was periodically examined by infrared spectroscopy for -OH absorption. A total of 500 ml was collected at which time the head temperature had reached 136.5°C and the distillate showed no more hydroxyl content. The residual mixture gradually darkened and thickened with increasing temperature and, at the termination of the distillation, was an almost black viscous sludge. The dark brown solids were filtered off with difficulty, washed with ether, and dried in a vacuum oven at 130°C. After ½ hour in the oven the material began decomposing in the same fashion as mentioned above (Procedure A). The remaining charred material was discarded.

Procedure 3. In Dioxane. — Sodium methoxide (27.0 g, 0.59 mole) was slowly added to methanol (250 ml) at 0°C. The resulting viscous sodium methoxide solution was added over a 1-hour period through an addition funnel, to a stirred solution of hexafluoropentanediol (126 g, 0.59 mole) dissolved in dried dioxane (1000 ml). The temperature was raised concurrently with the addition. The solution began darkening upon addition. Distillate began to appear at a head temperature of 64°C. Distillation was continued until the head temperature reached 101°C (50 ml of distillate had been collected up to this temperature). Upon cooling the dark reaction mixture to room temperature a semifluid gel was formed. Aliquots of the gel could not be dissolved in hexane or more dioxane. The remaining gel was poured into anhydrous ether (2 liters) and stirred vigorously. The solids were allowed to settle and the pale tan, supernatant liquid siphoned. The above ether extraction was repeated eight times with 1-liter portions of ether. The solids were then filtered and dried in a vacuum oven at room temperature overnight. The dried material was of a dough-like consistency. In an effort to produce a more crystalline product the solid material was again "scrubbed" with 1-liter portions of ether and stirred with a "Hirschberg" stirrer. This procedure was repeated four times and the suspension filtered. The solvent was removed on a rotary evaporator yielding the desired monosodium salt as an amorphous powder which had a neutralization equivalent of 234±0.5, (theoretical 234).

Analysis:

	% C	% H	% F	% Na
Calculated for $C_5H_5F_6O_2Na$:	25.6	2.14	48.8	9.8
Found:	25.32	2.12	46.2	10.55

Procedure 4. In Ether. — Sodium methoxide (59.2 g, 0.50 mole) was added to 200 ml of ether to form a finely divided suspension. A solution of hexafluoropentanediol (116.6 g, 0.055 mole) dissolved in 500 ml of ether was added to the sodium methoxide suspension over a 2-hour period. The resultant white solid was filtered, washed thoroughly with ether, and dried in a vacuum oven at 110°C for 24 hours. The weight of the sodium salt of hexafluoropentanediol was 98.3 g (85% yield). Its molecular weight was 232 (determined by potentiometric neutralization equivalent) (Calculated, 234).

In all of the above cases, the sodium salt of hexafluoropentanediol was contaminated with varying amounts of sodium methoxide which could not be removed.

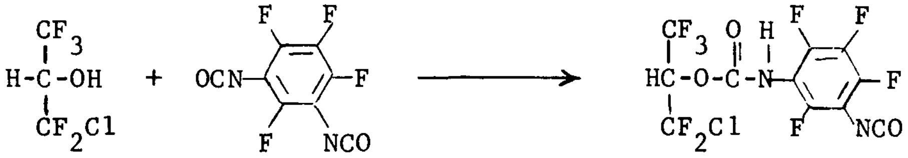
b. Using Sodium

Portions of hexafluoropentanediol were added to sodium metal in refluxing di-n-butyl ether. It was necessary to maintain reflux for a 2-hour period to achieve complete disappearance of all the sodium metal. The sodium salt was filtered and bottled under nitrogen.

Analysis:

	% C	% H	% F	% Na
Calculated for $C_5H_5F_6O_2Na$:	25.6	2.14	48.8	9.8
Found:	25.26	2.67	48.32	9.57

24. Preparation of Chloropentafluoroisopropyl-3-isocyanato-tetrafluorophenyl Carbamate



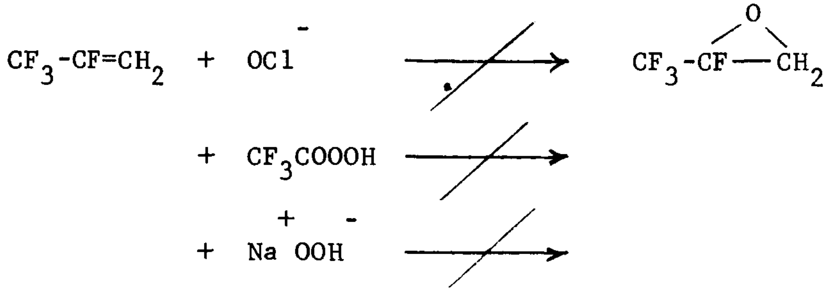
Chloropentafluoroisopropanol (2.8 g, 0.015 mole) and tetrafluoro-m-phenylene diisocyanate (7.0 g, 0.030 mole) were mixed and heated to 60°C. After 3½ hours at 60°-80°C, the OH peak had disappeared and a strong urethane peak had developed in the infrared spectrum.

25. Preparation of 2,3,3,3-Tetrafluoropropene

$$CF_3\text{-}CF_2\text{-}CH_2I \xrightarrow{Zn} CF_3\text{-}CF{=}CH_2 + ZnIF$$

A Vigreaux column was fixed atop a condenser, resulting in a total vertical column height of 150 cm. The output of the Vigreaux was fed into two traps, in series, cooled with dry ice — acetone. A slurry of zinc dust (21.2 g, 0.325 mole) in 300 ml of glacial acetic acid was heated to reflux temperatures and redistilled 2,2,3,3,3-pentafluoropropyl iodide (62.0 g, 0.238 mole) was added over a 2-hour period. Refluxing was continued for 2 hours after the addition. The trapped olefin product was transferred to a stainless steel cylinder (under vacuum). The yield of 2,3,3,3-tetrafluoropropene was 24.9 g (92%). Vapor pressure chromatography showed the product to be > 99% pure. The infrared spectrum is attached as Figure 34.

26. Attempted Preparation of 2,3,3,3-Tetrafluoro-1,2-epoxypropane



a. Using Sodium Hypochlorite

Chlorine gas (0.5 mole) was bubbled into 175 ml of distilled water. The resulting solution was partially neutralized (pH 6.8) with dilute sodium hydroxide. Analysis for OCl^- ion showed a concentration of 0.48 mole/182 ml solution.

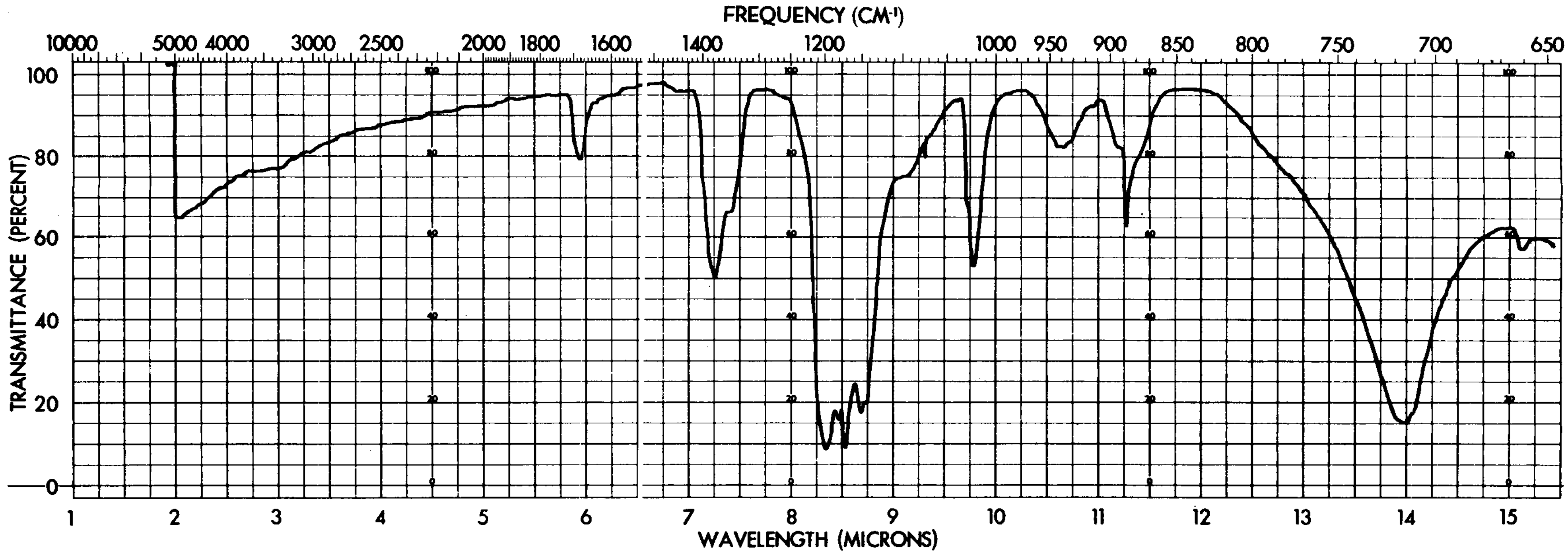


Figure 34. 2,3,3,3-Tetrafluoropropene

Acetonitrile (150 ml) was cooled to -40°C and the 2,3,3,3-tetrafluoropropene (19.0 g, 0.17 mole) was bubbled in. The solution was allowed to warm to 10°C. No refluxing was observed under the dry ice — acetone filled Dewar condenser. The hypochlorite solution was introduced dropwise over a 15-minute period. Immediately upon addition, the olefin began refluxing. The pH of the solution was continually monitored during addition and adjusted to a pH of 7 by the addition of dilute sodium hydroxide solution. The stirred reaction mixture was allowed to stand under reflux for 3 hours. The gaseous materials were distilled off, trapped, and condensed into a stainless steel bomb. None of the desired material was obtained.

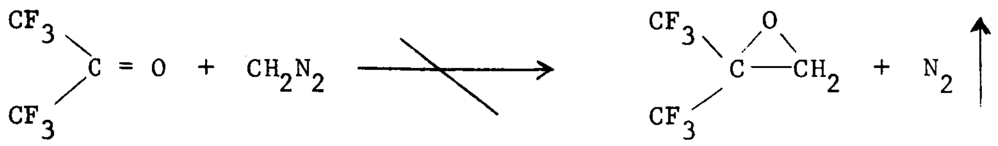
b. Using Peroxytrifluoroacetic Acid

Trifluoroacetic anhydride (49.9 g, 0.246 mole) was added to a suspension of 90% hydrogen peroxide (5.52 ml, 0.393 mole) in 50 ml of methylene chloride at 0°C over a 20-minute period. Stirring was continued in the cold for ½ hour, during which time the mixture became homogeneous. 2,3,3,3-Tetrafluoropropene (18.1 g, 0.316 mole) was condensed into a mixture of disodium hydrogen phosphate (117.0 g, 0.43 mole) in methylene chloride (300 ml) at -50°C. The peroxytrifluoroacetic acid solution was added over a 2-hour period. The temperature was maintained between -35°C and -45°C during the addition. This temperature was maintained for an additional 3-hour period. The mixture was allowed to come to room temperature and the volatile materials allowed to distill out of the reaction mixture and condense in dry ice — acetone cooled traps. After the products were transferred to a stainless steel bomb, the volatile constituents were examined by infrared spectroscopy and found to be unreacted starting material with a small percentage of methylene chloride contamination.

c. Using Basic Hydrogen Peroxide

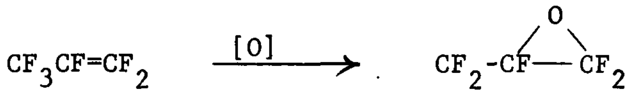
Potassium hydroxide (28.0 g, 0.50 mole) was dissolved in water (50 ml) and mixed with methanol (250 ml). Hydrogen peroxide solution (30%, 175 ml) was added and the solution cooled to -36°C with stirring. A soft slush was formed at this temperature. 2,3,3,3-Tetrafluoropropene (22.3 g, 0.196 mole) was condensed into the caustic solution over a 1½-hour period. Stirring was continued for an additional 2 hours at -36°C to -40°C. The reaction mixture was allowed to warm to room temperature and the volatile components (21.9 g) trapped and transferred to a stainless steel bomb. The material was identified as starting material by infrared spectrophotometry and vapor phase chromatography (98% recovery).

27. Attempted Preparation of 3,3,3-Trifluoro-2-(trifluoromethyl)-1,2-epoxypropane



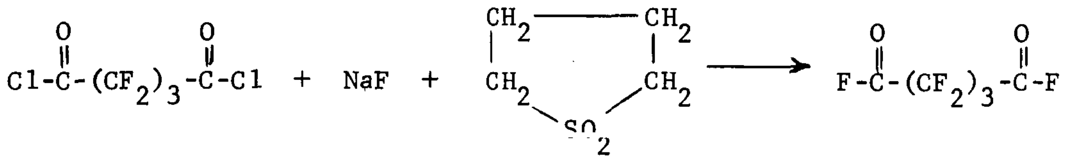
A dry solution of diazomethane (0.10 mole) in 1320 ml of diethyl ether was prepared from "Diazald." A considerable excess of hexafluoroacetone (> 0.4 mole) was bubbled into the ethereal diazomethane solution at 10°C. The solution was then held at approximately 15°C for 24 hours. The ether was carefully distilled off through a 120-cm, helices-packed column. After repeated separations by means of preparative gas chromatography the residual material was determined to be composed of the various hydrated species of hexafluoroacetone. None of the desired epoxide was obtained.

28. Preparation of Perfluoro-1,2-epoxypropane



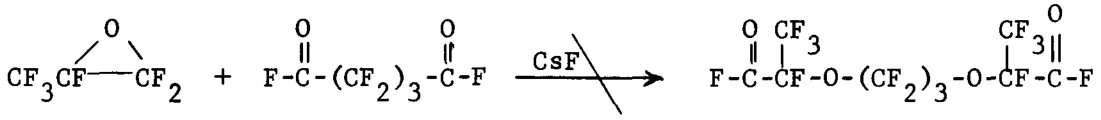
Water (90 ml) and potassium hydroxide (50.4 g, 0.9 mole) were mixed. Methanol (450 ml) was then added and the solution cooled to -40°C. Hydrogen peroxide (295 ml of 30%) was added, then perfluoropropylene (72.0 g,0.48 mole) was condensed into the solution. The mixture was stirred for 1½ hours at -40°C, then it was warmed to -25°C and the off-gases collected. Based on the infrared spectrum, the product (10.0 g) was an approximately equimolar mixture of the olefin and the epoxide.

29. Preparation of Perfluoroglutaryl Fluoride



Perfluoroglutaryl chloride (166.0 g, 0.6 mole) was added to a slurry of sodium fluoride (101.0 g, 2.4 mole) in sulfolane (270 ml) at 40°C over an 18-minute period. The slurry was mixed at 40°-60°C for 1½ hours, followed by 2½ hours at 60°-90°C. The products were then distilled from the slurry and fractionated. Analysis showing the absence of chloride and the infrared spectrum indicated that the main product, bp 45.5°-47°C, was the desired diacid fluoride. The infrared spectrum is shown as Figure 35.

30. Attempted Preparation of Perfluoro-2,10-dimethyl-3,9-dioxaundecenedioyl Fluoride



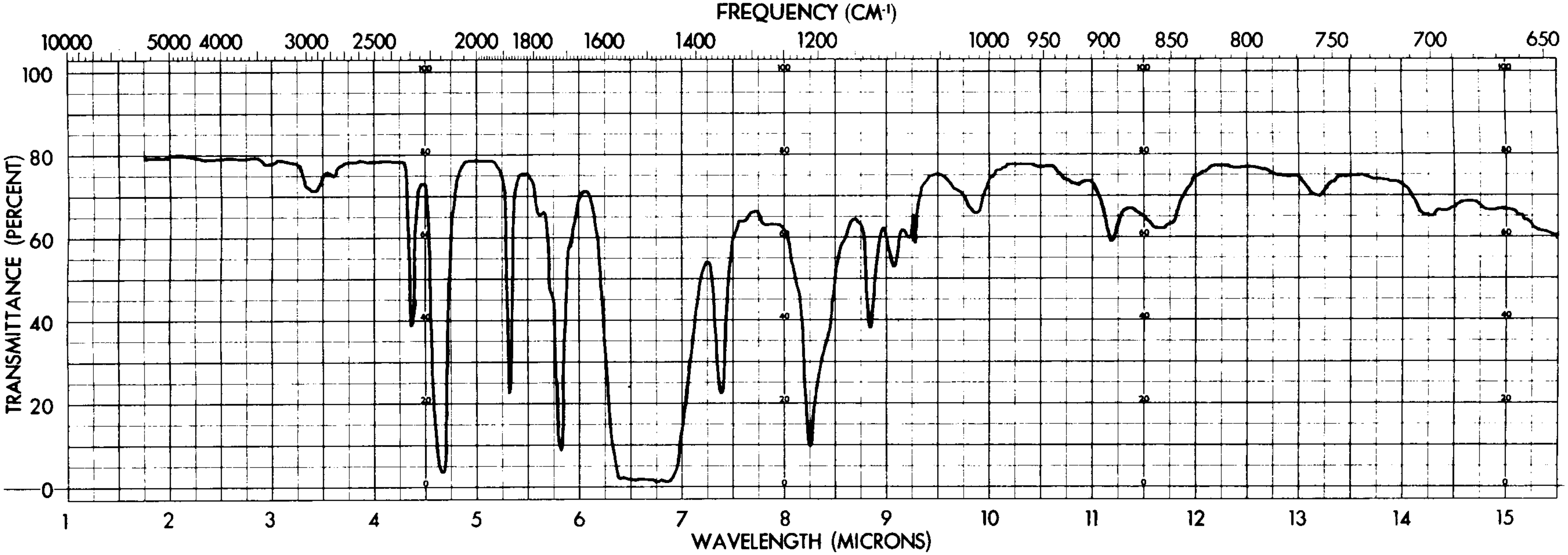
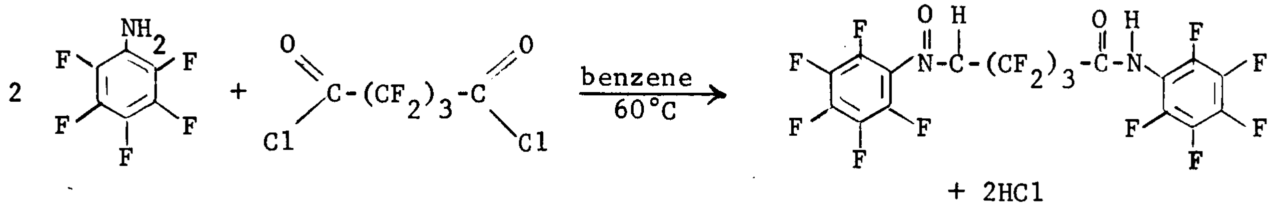


Figure 35. Perfluoroglutaryl Fluoride in Carbon Disulfide

Crude perfluoropropylene oxide (12.3 g, 0.074 mole), cesium fluoride (1.1 g), perfluoroglutaryl fluoride (9.1 g, 0.0373 mole) and tetraglyme (11 ml) were charged to a steel bomb at liquid nitrogen temperature. The bomb was permitted to warm up to room temperature and left at room temperature overnight. The residue was then fractionated. None of the desired product was isolated.

31. Preparation of N,N'-Di-pentafluorophenyl-perfluoroglutaramide



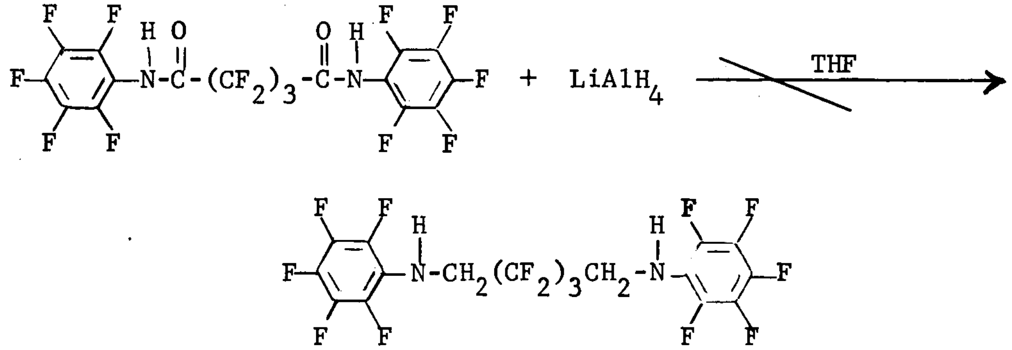
Perfluoroglutaryl chloride (22.8 g, 0.0822 mole) was added to a solution of pentafluoroaniline (30.0 g, 0.164 mole) in 350 ml of benzene at 60°C over a 45-minute period with mixing. The reaction was followed to completion by titrating the hydrochloric acid in the trap. Filtration yielded 41.5 g (89% yield) of the desired product, mp 197°-198°C.

Analysis:

	% C	% H	% F	% N
Calculated for $C_{17}H_2F_{16}N_2O_2$:	35.8	0.33	53.4	4.9
Found:	34.4	0.50	52.4	4.9

32. Attempted Preparation of N,N'-Di-pentafluorophenyl-hexafluoropentane-diamine

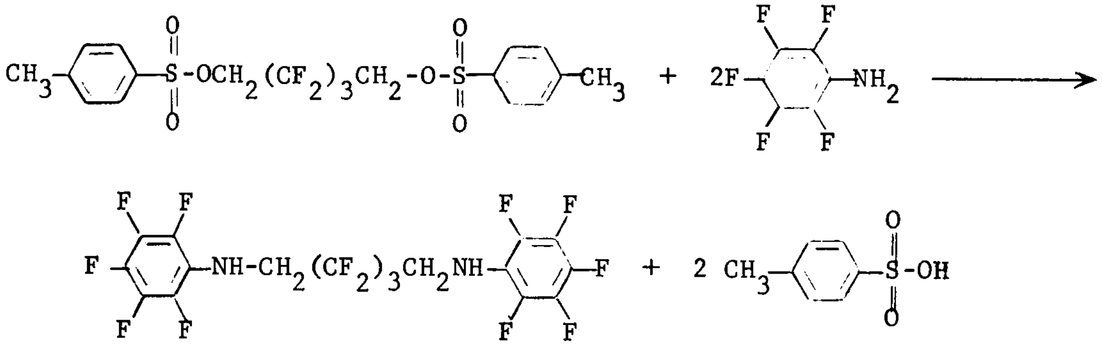
a. Method 1. Reduction of N,N'-Di-pentafluorophenyl-perfluoroglutaramide



Tetrahydrofuran (THF) was dried with freshly cut sodium and 150 ml of this THF was added to a 500 ml flask previously purged with dry nitrogen. Powdered LAH (1.9 g, 0.05 mole) was added to the THF with stirring. N,N'-Di-pentafluorophenyl-perfluoroglutaramide (11.4 g, 0.02 mole) in 100 ml of dry THF was added dropwise to the stirred suspension over a period of 2 hours. After addition was complete, heat was applied and THF allowed to reflux for 3 hours. After cooling, 10 ml of water was added to decompose the excess LAH. The gray inorganic solids were filtered off; the clear yellow filtrate was first dried over anhydrous magnesium sulfate and then evaporated to dryness leaving an orange solid. This material was identified by its infrared spectrum and melting point as unreacted N,N'-di-pentafluorophenyl-perfluoroglutaramide. Recovery of this starting diamine was 94%.

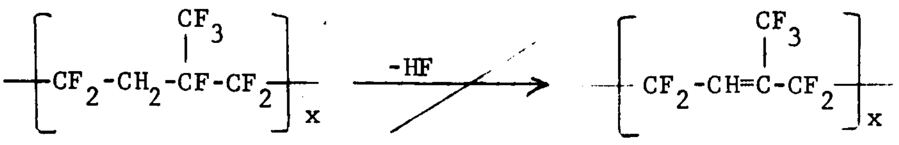
The above reaction was repeated identically as above, except that the reflux period was increased to 44 hours. Unreacted N,N'-di-pentafluorophenyl-perfluoroglutaramide was recovered in 87% yield.

b. Method 2. Attempted Reaction of Hexafluoropentamethylene Ditosylate with Pentafluoroaniline



Hexafluoropentamethylene-1,5-ditosylate (16.7 g, 0.0323 mole) and pentafluoroaniline (11.8 g, 0.0645 mole) were refluxed for 65 hours. After cooling, the mixture was poured into 600 ml of distilled water. A slightly discolored fluffy precipitate formed. The solids were filtered off and dried (16.8 g). Recrystallization from ethanol gave a white powder whose spectrum and melting point (95.5°-96.5°C) were identical with the starting ditosylate. None of the desired diamine was obtained.

33. Attempted Dehydrofluorination of Viton LM



Viton LM (20.0 g), sodium hydroxide (4.0 g, 0.1 mole) and 30 ml of DMF were mixed at 100°C during which operation the solution turned black. There was no dehydrofluorination.

Viton LM (10.0 g) and 30 ml of tributylamine were mixed for 1 hour at 160°-170°C, followed by 18 hours at 120°-140°C. The infrared spectrum indicated that there was no reaction.

V. CONCLUSIONS

LOX Compatibility

Specimen thickness seems to be without effect on the LOX sensitivity of those fluorinated polyurethanes that are truly LOX compatible.

Urethane linkages flanked on the alcohol side by a 1,1-dihydroperfluoroalkyl chain are LOX compatible if the nitrogen is also attached to a 1,1-dihydroperfluoroalkyl chain, but LOX incompatible if attached to a nonfluorinated alkyl chain or a benzyl methylene group.

Polymers containing carbonate linkages are LOX incompatible.

Polyesters in which the acid portion is a nonfluorinated aromatic acid are LOX incompatible.

A partially fluorinated polyether, prepared from chloropentafluoroisopropyl alcohol, is LOX compatible.

Properties of Materials Investigated

The polyurethane prepared by reaction of the polyether of chlorpentafluoroisopropyl alcohol with tetrafluoro-m-phenylene diisocyanate shows promise of being developed into a usable adhesive system.

Reactions of hexafluoropentamethylene bischloroformate or tetrafluoro-p-phenylene bischloroformate with a short chain fluorinated diamine, such as hexafluoro-1,5-pentanediamine, failed to provide adhesive systems because the resulting polyurethanes are brittle.

The polyurethane from tetrachloro-p-xylylene diisocyanate and hexafluoropentanediol is also too brittle to be usable as an adhesive.

Prepolymers containing p-hydroxy-tetrafluorophenoxy end groups are unsuitable for preparation of polyurethanes because of inertness with fluorinated diisocyanates.

The mixed aliphatic-aromatic polycarbonate, poly(hexafluoropentamethylene tetrafluoro-p-phenylene carbonate) was a tougher, more usable polymer than its all-aliphatic analogue, poly(hexafluoropentamethylene carbonate), but it was less thermally stable.

Polyethers of hexafluorobenzene and hexafluoropentanediol show promise of being converted to useable hydroxyl-terminated prepolymers.

The reaction of polycarbonates with sulfur tetrafluoride seems to be a promising new method of preparing highly fluorinated polyethers.

Tetrafluoro-m-phenylene diisocyanate is a more useful diisocyanate than its para isomer because it is a liquid and provides easier processability.

1,5-Diiodohexafluoropentane, like the di-p-toluenesulfonate of hexafluoropentanediol, is very unreactive toward nucleophiles.

The pure monosodium salt of hexafluoropentanediol cannot be prepared using sodium methoxide.

VI. RECOMMENDATIONS FOR FUTURE WORK

Work should continue on the preparation of polyurethanes from three types of diols. Considered to be the most promising diols are highly fluorinated polyethers, fluorinated diols with considerably longer chains, and the hydroxyl-terminated polyesters of $\alpha,\alpha,\alpha,\alpha'$-tetrahydro-perfluoro-dicarboxylic acids.

Because the LOX sensitivity of poly(hexafluoropentamethylene tetrafluoro-p-phenylene ether) samples is believed to be due to trapped solvent, this polyether should be prepared and tested again with special care being taken to eliminate all traces of solvent.

Work should continue on the preparation of completely hydroxyl-terminated prepolymers of this type and the preparation of flexible polyurethanes from these prepolymers.

Because the high molecular weight polyether of chloropentafluoroisopropyl alcohol is LOX compatible, efforts should continue to prepare a fairly long chain prepolymer and flexible polyurethanes based on this prepolymer.

Initial indications are that fluoroalkyl polycarbonates react with sulfur tetrafluoride to yield polyethers; the study of this reaction should be continued. In addition, this sulfur tetrafluoride reaction should be extended to other polymers, such as poly(hexafluoropentamethylene perfluoroglutarate, which would yield highly fluorinated polyethers.

The polyurethanes prepared from hexafluoropentanediol are LOX compatible, but are brittle solids. Therefore, fluorinated diols, with considerably longer chains should be prepared for use in the preparations of flexible polyurethanes.

Polyesters of fluorinated diols and perfluorinated acids, although hydrolytically unstable, are LOX compatible. Therefore, hydroxyl-terminated polyesters of $\alpha,\alpha,\alpha,\alpha'$-tetrahydroperfluoro-dicarboxylic acids should be prepared for synthesis of polyurethanes.

Efforts should be directed toward the development of the most promising polymer into a LOX-compatible adhesive system.

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