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

By

Jerome Hollander, Floyd D. Trischler, Edward S. Harrison,
Robert M. DeBorde, and Beatrix Y. Sanders

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FOREWORD

This report was prepared by Whittaker Corporation, Narmco Research & Development Division, under Contract No. NAS 8-11068, Control No. 1-6-54-01157(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 Trischler, Senior Research Chemists, Mr. Edward S. Harrison and Mrs. Beatrix Y. Sanders, Research Chemists, and Mr. Robert M. DeBorde, Associate Chemist. Dr. Jerome Hollander served as program manager. This report covers the period from 1 July 1966 to 30 November 1966.

Prepared by: Jerome Hollander

Jerome Hollander, PhD
Senior Research Chemist

Floyd D. Trischler

Floyd D. Trischler
Senior Research Chemist

Approved by: Rex B. Gosnell

Rex B. Gosnell, PhD
Assistant Manager
Chemistry Department

S. E. Susman

S. E. Susman, Manager
Chemistry Department

ABSTRACT

The purpose of this investigation is to develop structural adhesive systems suitable for use with liquid oxygen. Work was concentrated on the preparation of fluorinated polyurethanes.

Seven polyurethanes were prepared, five of which were tested for liquid oxygen compatibility.

Two polyurethanes were synthesized which show real promise as LOX-compatible adhesives. One polyurethane was prepared from tetrafluoro-m-phenylene diisocyanate and a polyether of perfluoropropylene oxide. The other polyurethane was prepared from tetrafluoro-p-phenylene diisocyanate and a polyether of hexafluorobenzene and hexafluoropentanediol. Initial lap shear specimens bonded with each of these polyurethanes gave extremely promising results.

Two other polyurethane systems were synthesized; one by reaction of the polyether from chloropentafluoroisopropyl alcohol with either of the tetrafluoro-phenylene diisocyanates, the other by reaction of tetrafluoro-m-phenylene diisocyanate with a hydroxyl-terminated polyurethane from hexafluoropentanediamine and hexafluoropentamethylene bischloroformate.

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

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I. INTRODUCTION

The present and future use of liquid oxygen (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 is not 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, such as Teflon and Kel-F, have also demonstrated cryogenic capability. Although these available materials form excellent bonds which offer LOX compatibility and cryogenic performance, the processing conditions required are prohibitive. Polyurethanes show greater utility in that they are capable of being cured under mild conditions, or even at ambient temperature. The coupling of this processing capability with good cryogenic performance and LOX compatibility intimates that the highly halogenated polyurethanes are the most logical polymer systems. Therefore, the 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 compatiblity of polymers. The information required includes:

1. The type and amount of halogen 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 so as 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.

II. SUMMARY

The work accomplished during the period covered by this report was concentrated on the preparation of fluorinated polyurethanes.

The LOX compatibility results obtained on polymers sent to George C. Marshall Space Flight Center (MSFC) for testing left the compatibility of some of these materials still in question. The polyurethane from hexafluoropentanediol and tetrafluoro-m-phenylene diisocyanate is almost certainly LOX compatible, but two flashes were obtained during 60 tests. The polyurethanes prepared from the polyether of chloropentafluoroisopropyl alcohol and from the polyether of hexafluorobenzene and hexafluoropentanediol were all LOX incompatible, but it is very possible that their incompatibility may be due to trapped solvent. The two polyurethanes prepared from the polyether of perfluoropropylene oxide were LOX compatible.

Two polyurethane systems were synthesized which show real promise of meeting the requirements for LOX-compatible adhesives. One system was prepared by reaction of tetrafluoro-m-phenylene diisocyanate with a hydroxyl-terminated polyether prepared from perfluoropropylene oxide. Initial lap shear specimens bonded with this polyurethane adhesive gave extremely promising results, especially at -320°F. Tests on additional lap shear specimens, subjected to 100% humidity for 4 weeks, indicated that the bond strength of this adhesive is only slightly affected by these drastic conditions. The hydroxyl-terminated polyether that is the base for this polyurethane was prepared by polymerization of perfluoropropylene oxide with perfluoroglutaryl fluoride and cesium fluoride, followed by reduction of the acid-fluoride end groups.

The other promising polyurethane system was synthesized by reaction of tetrafluoro-p-phenylene diisocyanate with a hydroxyl-terminated polyether of hexafluorobenzene and hexafluoropentanediol. Initial lap shear specimens bonded with this polyurethane adhesive also gave extremely promising results, especially at room temperature.

Two other polyurethanes were synthesized but showed little promise as candidates for the desired adhesive. One was prepared by reaction of the polyether from chloropentafluoroisopropyl alcohol with either of the tetrafluorophenylene diisocyanates. The other system was prepared by reacting tetrafluoro-m-phenylene diisocyanate with a low molecular weight, hydroxyl-terminated polyurethane from hexafluoropentanediamine and hexafluoropentamethylene bischloroformate.

In addition to the preparation of the polyurethane described above, polyethers from perfluoropropylene oxide were subjected to dehydration, reaction with hexafluorobenzene, and esterification in attempts to prepare other improved prepolymers.

Additional studies on the preparation of the hexafluorobenzene-hexafluoropentanediol polyether system were conducted using the dilithium salt of hexafluoropentanediol and using tetrahydrofuran (THF) as solvent with N,N-dimethylformamide (DMF) as a catalyst. The amine-terminated polyether of hexafluorobenzene and hexafluoropentanediol was prepared.

Another attempt to prepare a polyether by reaction of hexafluoropentanediol with perfluoropenta-1,4-diene was unsuccessful.

Attempts to prepare hydroxyl-terminated polyethers from hexafluoroisopropyl alcohol and trifluoroethanol were unsuccessful.

The reaction of poly(hexafluoropentamethylene carbonate) with sulfur tetrafluoride yielded a promising new polyether, but the similar reaction of poly(hexafluoropentamethylene perfluoroglutarate) failed.

Monomers prepared for the first time include the dilithium salt of hexafluoropentanediol and hexafluoropentamethylene bis(trifluoromethane sulfonate).

III. DISCUSSION

A. Liquid Oxygen Compatibility

During the current report period, six polyurethanes were prepared and tested for LOX compatibility. In addition, one fluorinated ether was prepared for use as a solvent and its LOX compatibility was tested. Results are shown in tabular form in Section IV.

Annual Summary Report III contained the results of the LOX-impact tests on 8-1/2 mil thick disks of poly(hexafluoropentamethylene tetrafluoro-m-phenylene dicarbamate). There were three reactions during 20 tests. Also described in that report was the preparation of a large amount of this polyurethane, of higher molecular weight, which was submitted as a powder for LOX testing. The results obtained during this report period showed that there were two reactions during 60 tests at the 10-kg meter energy level. These reactions could well have been due to cup flashes.

It was shown previously that the polyether prepared from chloropentafluoroisopropyl alcohol was LOX compatible when all traces of solvent were removed or when the polyether was prepared in a LOX-compatible solvent. The polyurethanes prepared from this polyether system by reaction with tetrafluoro-m-phenylene and -p-phenylene diisocyanates were LOX incompatible, probably because of trapped solvent. An attempt as made during this report period to again prepare the polyurethane from this polyether with tetrafluoro-m-phenylene diisocyanate, which would not contain any traces of LOX-incompatible solvents. In an attempt to find a solvent which could be used for the preparation of the hydroxy-terminated polyether, hexafluoropentamethylene oxide was prepared and tested for LOX compatibility. Although it was shown to be LOX compatible, it was not a good solvent for the preparation of the polyether. Inasmuch as a solvent could not be found which was both LOX compatible and suitable for the preparation of the polyether, the polymerization reaction was again run in THF. After preparing the polyurethane from this polyether and tetrafluoro-m-phenylene diisocyanate, an attempt was made to remove the THF by heating the polyurethane under vacuum at 60°C for a long period of time. Either the THF solvent could not be completely removed or the polyurethane system is truly LOX incompatible, as impact tests again showed five reactions out of 20 specimens tested.

The preparation of a high molecular weight polyether of hexafluorobenzene and hexafluoropentanediol was also described in the Annual Summary Report III. This polyether was LOX incompatible; because it was prepared in DMF, however, this incompatibility may be due to trapped solvent. During this report period, a hydroxy-terminated polyether of hexafluorobenzene and hexafluoropentanediol was prepared and polyurethanes prepared from it by reaction with tetrafluoro-m-phenylene diisocyanate and tetrafluoro-p-phenylene diisocyanate. Both of

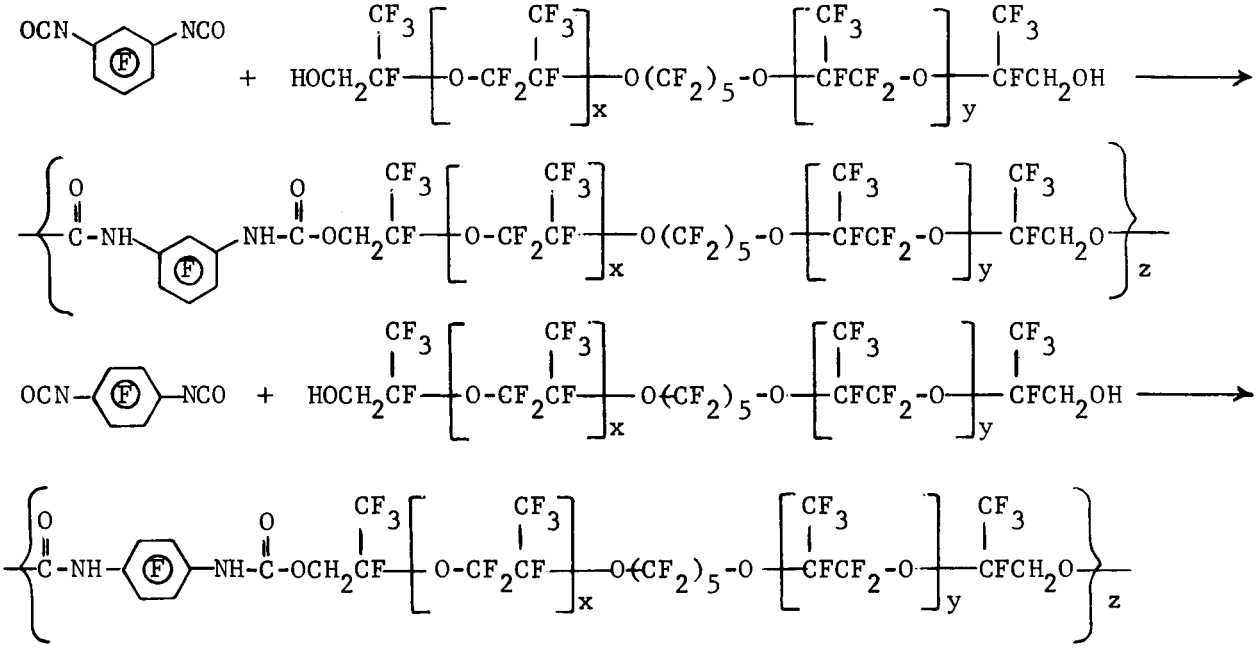
these polyurethanes were LOX incompatible. Since the hydroxy-terminated polyethers were prepared in DMF, this incompatibility most likely is due to trapped solvent.

Another new hydroxy-terminated polyether based on the polymerization of perfluoropropylene oxide was prepared during this report period. Polyurethanes were prepared by reaction of this polyether with both tetrafluoro-m-phenylene diisocyanate and tetrafluoro-p-phenylene diisocyanate and submitted for LOX-impact testing. Both polyurethanes were LOX-compatible.

B. Polyurethanes

1. From Poly(perfluoropropylene oxide)

One of the most significant developments achieved to date on this program, the preparation of almost completely fluorinated polyether-based polyurethanes, was accomplished during this report period. The preparation of the hydroxyl-terminated polyethers from perfluoropropylene oxide which were used to prepare these polyurethanes is described in the following section on polyethers. The polyethers were reacted with tetrafluoro-m-phenylene diisocyanate and with tetrafluoro-p-phenylene diisocyanate to yield polyurethanes. Polyethers of two molecular weights, 760 and 1510, were used.



Tetrafluoro-m-phenylene diisocyanate was reacted with 760 molecular weight polyether in the ratio of 1.5 to 1, and the resulting isocyanate-terminated material was cured with tetrafluoro-m-phenylenediamine. The product obtained was further cured in a heated press, yielding a clear brittle sheet.

When tetrafluoro-m-phenylene diisocyanate and 1510 molecular weight polyether were reacted in the ratio of 1.25 to 1 and the resulting polymer advanced in a heated press, a soft elastic sheet was obtained.

When these reactants were mixed in a ratio of 1.2 to 1 and then cured with tetrafluoro-m-phenylenediamine, a polymer was obtained which gave a fairly tough, but somewhat brittle sheet on further curing in a heated press. LOX-impact specimens were punched from this sheet.

Bonded lap shear test specimens were prepared by two methods, one involving a rapid high-temperature cure cycle and the other involving a slow low-temperature cure cycle.

For the first set of specimens, the 1510 molecular weight polyether and tetrafluoro-m-phenylene diisocyanate were mixed in a ratio of 1 to 1.5 at room temperature. A catalytic amount of stannous octoate was added. After being mixed for 5 minutes, glass beads were added and the viscous polyurethane was applied to 2014-T3 clad aluminum adherends. The bonded specimens were then heated in a press under 200-psi pressure at 160°F for 45 minutes, 220°F for 45 minutes, and finally at 325°F for 45 minutes. Two panels of bonded specimens were prepared by this method. The specimens (six bonds) from one panel were tested immediately after preparation. The bond specimens from the second panel were stored in a humidity chamber (100% humidity) for 4 weeks and then tested. Lap shear tests were run both at room temperature and at -320°F. The results ,particularly those at -320°F, for the specimens tested immediately after preparation, indicated that this polyurethane system was a most promising candidate for a LOX-compatible adhesive. The average lap shear strength was 1220 psi at room temperature and 3340 psi at -320°F. The test results on the bonded specimens subjected to extreme humidity conditions indicated that although some loss in strength occurred, the bond strength, especially at -320°F, is still more than sufficient to meet the requirements for the LOX-compatible adhesive.

A second set of lap shear test specimens were prepared as follows. A polyether of 1510 molecular weight and tetrafluoro-m-phenylene diisocyanate in a ratio of 1 to 2 were mixed at 65°C, cooled to room temperature, and a catalytic amount of stannous octoate added. After being stirred for 5 minutes, the viscous polyurethane was applied to the 2014-T3 clad aluminum adherends and glass beads sprinkled on the bond before joining. The adhesive was partially cured overnight at room temperature in a vacuum bag. The bonded specimens were then removed from the vacuum bag, and curing was completed by heating them at 160°F for 48 hours. The test results, in particular those at -320°F, verified that this polyurethane is indeed a most promising candidate for a LOX-compatible adhesive. The average lap shear strength was 1386 psi at room temperature and 3740 psi at -320°F.

Tetrafluoro-p-phenylene diisocyanate was reacted with 760 molecular weight polyether in the ratio of 1.1 to 1. The resulting polymer was cured in a heated press and yielded a clear brittle sheet.

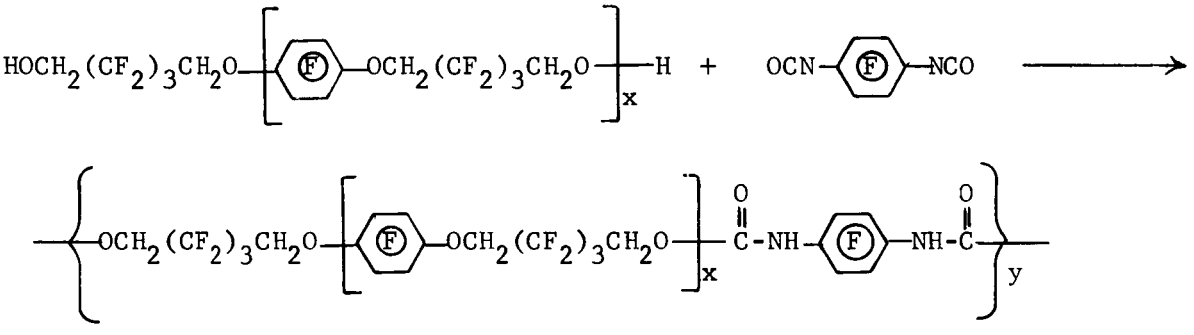
When the tetrafluoro-p-phenylene diisocyanate was reacted with 1510 molecular weight polyether in the ratio of 1.5 to 1 using a trace of stannous octoate as catalyst, a polymer was obtained which, when heat-cured in a press, yielded a tough elastic sheet. LOX-impact specimens were punched from this sheet.

The preparation of an amine-terminated polyether of hexafluorobenzene and hexafluoropentanediol is described in the following section of this report. This amine-terminated polyether was used as a curing agent with this polyurethane system. Tetrafluoro-p-phenylene diisocyanate and 1510 molecular weight perfluoropropylene ether based polyether were mixed in a ratio of 2 to 1 at 150°C. After cooling the mixture to 65°C, the amine-terminated polyether was stirred in. Curing was completed in a heated press, yielding an elastic sheet which had poor tear strength.

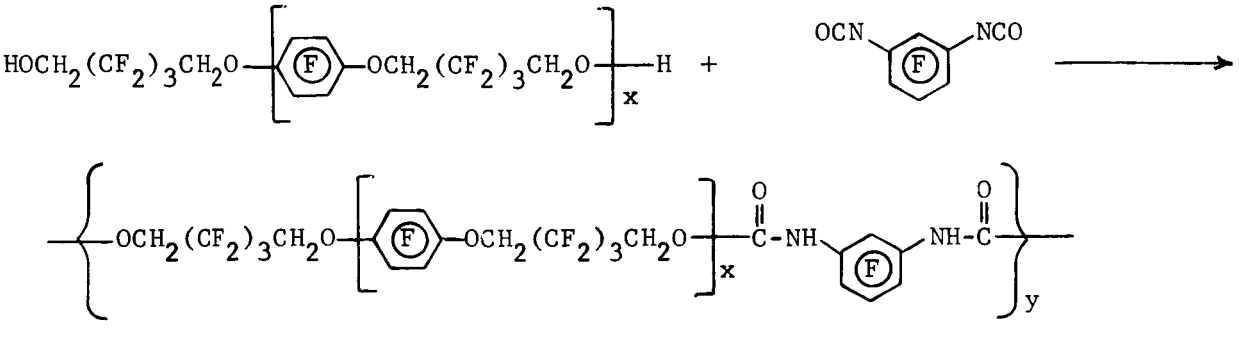
2. From the Hydroxyl-Terminated Polyether of Hexafluorobenzene and Hexafluoropentanediol

The preparation of a completely hydroxyl-terminated polyether of hexafluorobenzene and hexafluoropentanediol is described in the polyether section of this report.

A flexible polyurethane was prepared by reaction of a 2280 molecular weight polyether of hexafluorobenzene and hexafluoropentanediol with tetrafluoro-p-phenylene diisocyanate in the ratio of 1 to 1.05. This polyurethane was heat-cured in a press, yielding a 10-mil thick sheet from which LOX-impact test specimens were punched.



The reaction of the same 2280 molecular weight polyether with tetrafluoro-m-phenylene diisocyanate in the ratio of 1 to 1.05 also yielded a flexible polyurethane, from which a 14-mil thick sheet was prepared by a heated press cure. LOX-impact test specimens were also punched from this sheet.



The reaction of a 1500 molecular weight polyether with tetrafluoro-m-phenylene diisocyanate yielded a brittle polyurethane.

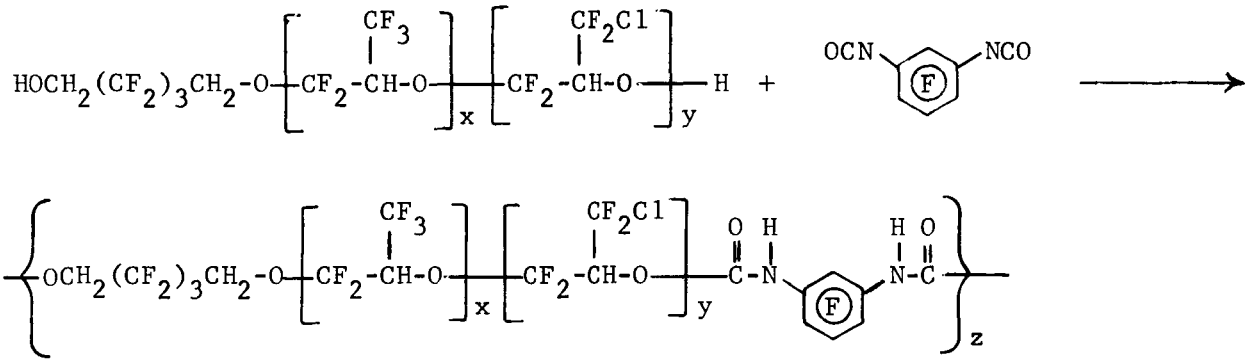
Bonded lap shear test specimens were prepared by mixing the 2280 molecular weight hexafluorobenzene-hexafluoropentanediol polyether and tetrafluoro-p-phenylene diisocyanate in a ratio of 1 to 1.05 at 70°C, then applying the viscous polyurethane to 2024-T3 clad aluminum adherends. The bonded specimens were heated at 275°F and 200 psi for 2 hours to complete the curing of the polyurethane. The results of the lap shear tests run both at room temperature and at -320°F indicate that this polyurethane system is indeed a promising adhesive candidate. The average lap shear strength was 2600 psi at room temperature and 800 psi at -320°F.

An attempt to prepare suitable bonds by reaction of the same 2280 molecular weight polyether with tetrafluoro-m-phenylene diisocyanate was unsuccessful. The reaction was so rapid that the polyurethane gelled before it could be properly applied to the aluminum test specimens.

3. From the Polyether of Chloropentafluoroisopropyl Alcohol

As was described in Annual Summary Report III, the polyether of chloropentafluoroisopropyl alcohol was found to be LOX compatible when all traces of solvent were removed. Therefore, additional effort was expended to prepare a usable LOX-compatible polyurethane adhesive from this polyether.

A 3860 molecular weight polyether prepared from chloropentafluoroisopropyl alcohol by initiation with the monosodium salt of hexafluoropentanediol reacted with tetrafluoro-m-phenylene diisocyanate in THF to form a polyurethane. This polymer was a soft, slightly elastic material.

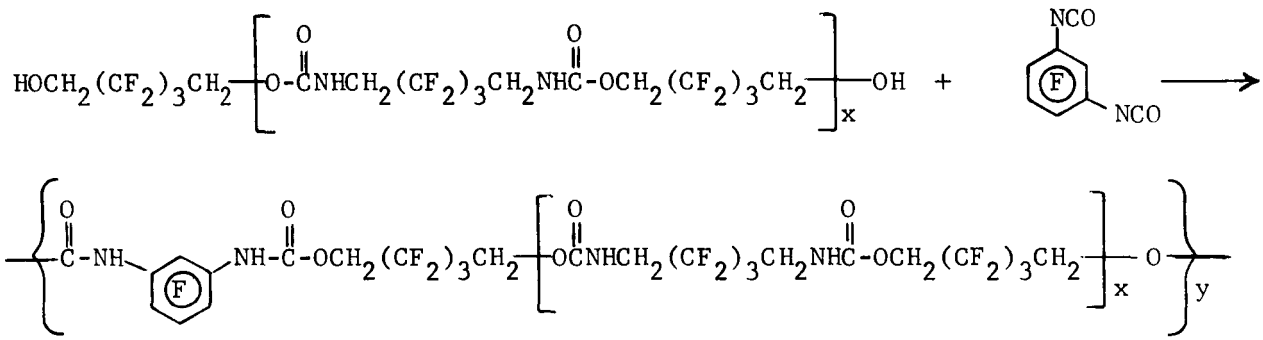


A fairly tough, slightly elastic polyurethane was prepared by reaction of tetrafluoro-m-phenylene diisocyanate with a 1325 molecular weight polyether of chloropentafluoroisopropyl alcohol. The polyurethane was cured in a heated press to a slightly elastic 21-mil thick sheet from which LOX-impact test specimens were punched.

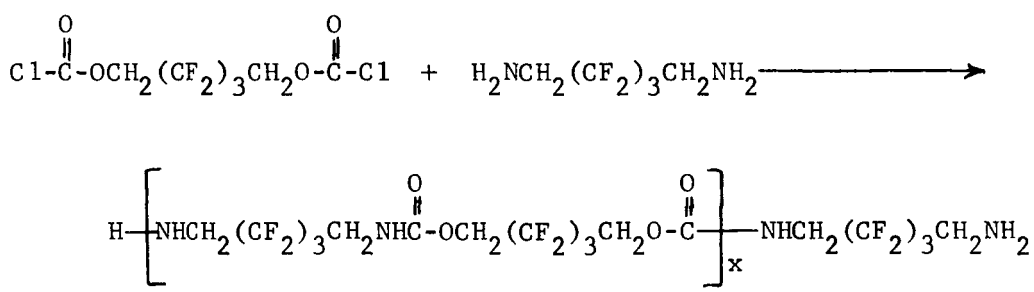
A similar polyurethane was prepared from tetrafluoro-p-phenylene diisocyanate and 1325 molecular weight polyether but it was a brittle material.

4. From Poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate)

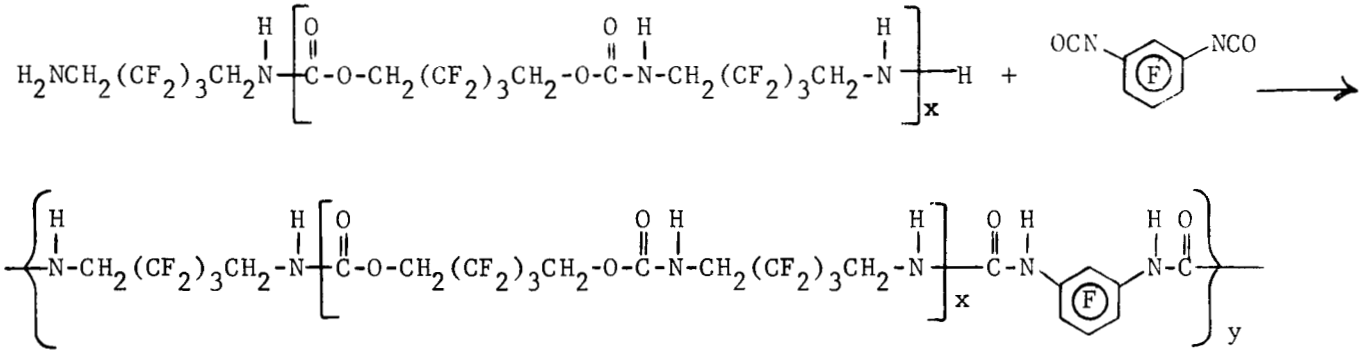
The preparation of a low molecular weight hydroxyl-terminated polyurethane from hexafluoropentanediamine and hexafluoropentamethylene bischloroformate was reported in Annual Summary Report III. This polyurethane system has been shown to be LOX compatible. The viscous, low molecular weight polyurethane was reacted during this report period with tetrafluoro-m-phenylene diisocyanate in an attempt to prepare a usable high molecular weight polyurethane. The polymer obtained was a brittle material.



A low molecular weight, amino-terminated polyurethane based on the same polymer system was prepared by reaction of hexafluoropentamethylene bischloroformate with excess hexafluoropentanediamine. This viscous polyurethane had a molecular weight of 750.



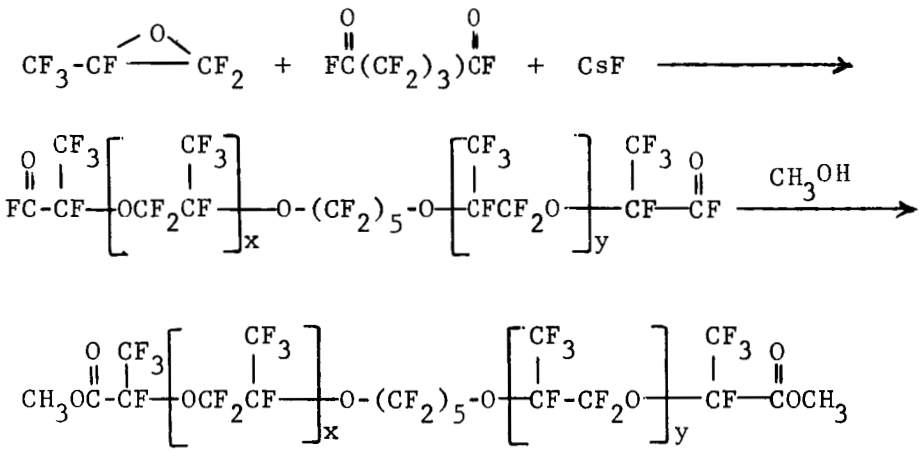
This polyurethane was reacted with tetrafluoro-m-phenylene diisocyanate to yield a cross-linked polyurethane-urea which became elastic at elevated temperatures but embrittled on cooling.



C. Polyethers

1. From Perfluoropropylene Oxide

The preparation of perfluoropropylene oxide was described in Annual Summary Report III. Also described in that report were several unsuccessful attempts at its polymerization. A recent patent (Reference 1) described the preparation of an acid fluoride terminated polyether by reaction of perfluoropropylene oxide with perfluoroglutaryl fluoride and cesium fluoride. The conversion of this acid fluoride terminated polyether to its diester was also described.



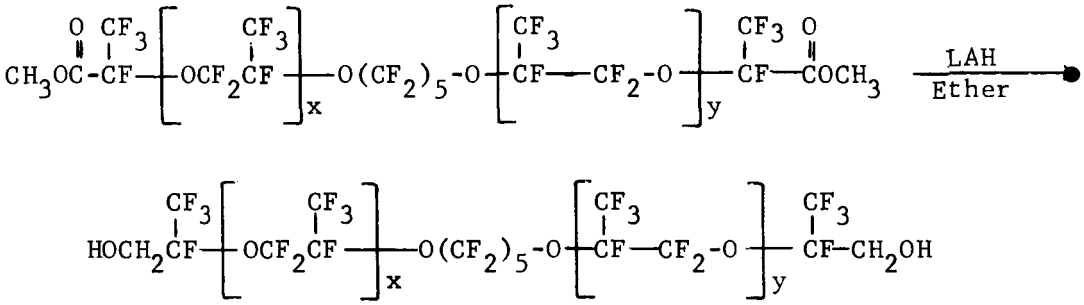
During this report period, we successfully carried out the polymerization of this polyether. Conversion of this polyether to a hydroxyl-terminated material was an exciting and important development.

The preparation of pure perfluoropropylene oxide is reported in the monomer section of this report. A preliminary study was made on the polymerization of perfluoropropylene oxide with perfluoroglutaryl fluoride and cesium fluoride. The yield and degree of polymerization of the acid fluoride

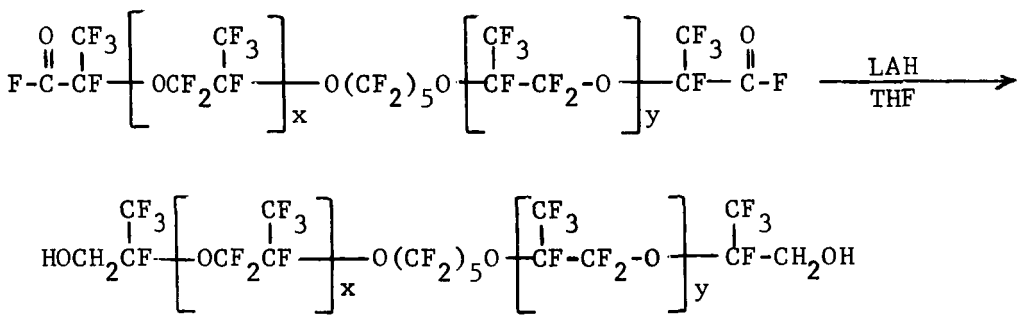
terminated polyether was shown to be drastically affected by the purity and dryness of the cesium fluoride. The molecular weights obtained varied from 445 to 1030. It is significant to note that the highest molecular weight material was obtained when the epoxide used was recovered from previous reactions.

The preparation of the polyether of perfluoropropylene oxide was then scaled up. Yields as high as 87% were obtained from these larger scale polymerizations. The best yields and highest molecular weight polyethers were obtained when perfluoro-2-methyl-3-oxaoctanedioyl fluoride (the monoether of perfluoroglutaryl fluoride and perfluoropropylene oxide) was used as the initiator along with recovered perfluoropropylene oxide.

The acid fluoride-terminated polyethers were initially converted to their methyl esters which were then reduced to the corresponding hydroxyl-terminated materials.

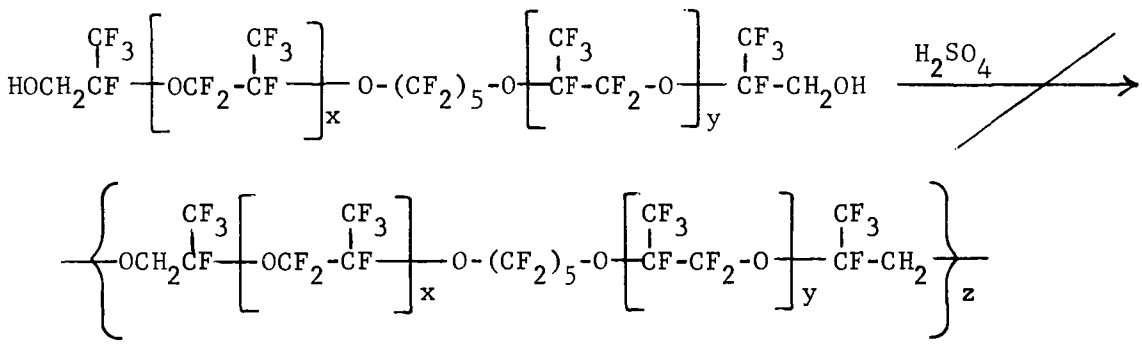


Although the yields were very good (consistently in the order of 80%), it was later found that the direct reduction of the acid fluoride-terminated polyethers by lithium aluminum hydride was a more rapid reaction and that the yields were virtually quantitative.

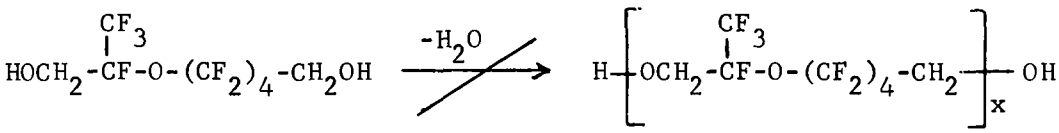


These hydroxyl-terminated polyethers were used to prepare the polyurethanes described in the first section of this report.

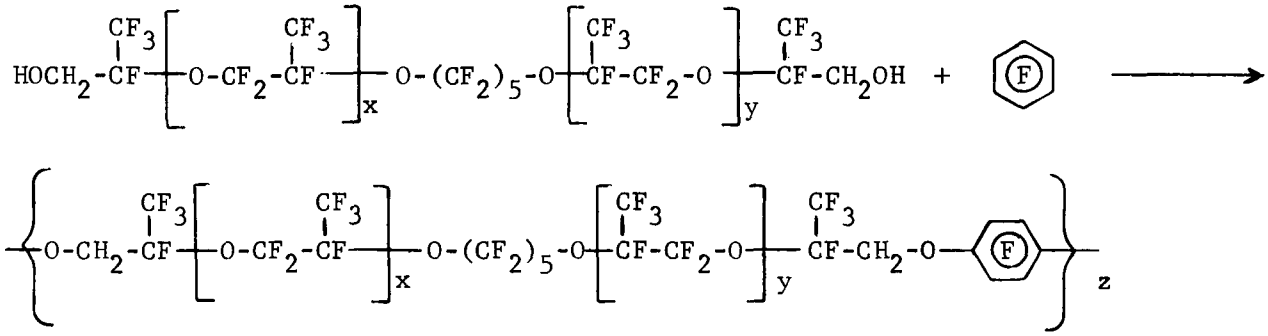
In an initial attempt to extend the molecular weight of polyethers prepared from perfluoropropylene oxide, a polyether of this type was heated with concentrated sulfuric acid at 180°-190°C for 18 hours. There was no indication of dehydration.



Unsuccessful attempts were also made to prepare polyethers from 2-trifluoromethyl-3-oxa-2,4,4,5,5,6,6,7,7-nonafluoro-1,8-octanediol (the monoether of perfluoropropylene oxide and perfluoroglutaryl fluoride) by dehydration with phosphorus pentoxide and with sulfuric acid.

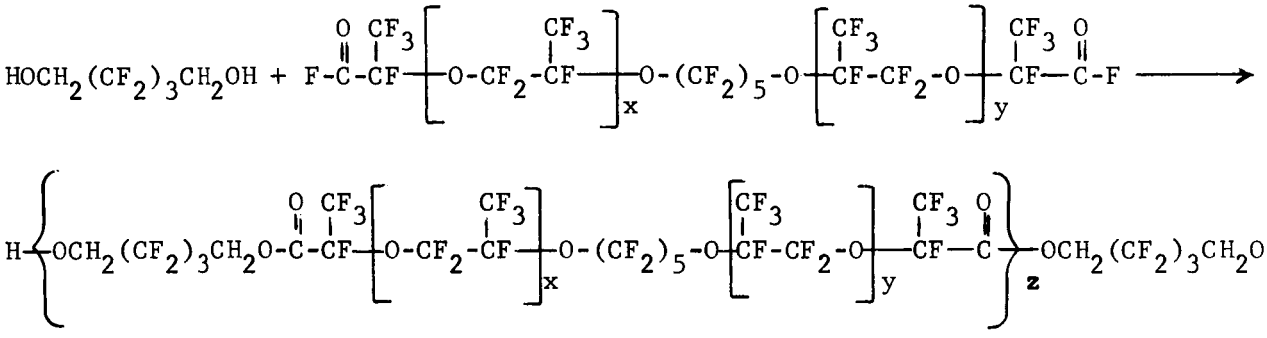


A preliminary study was carried out on the preparation of a polyether by reaction of hexafluorobenzene, potassium hydroxide, and a hydroxyl-terminated polyether from perfluoropropylene oxide.



The reaction was carried out both in DMF and in THF with a catalytic amount of DMF. In both reactions, material was obtained whose infrared spectra indicated the presence of both aliphatic and aromatic fluorines and the fluorinated aromatic ring. The molecular weight of these products, however, indicated that the only reaction that had occurred was the capping of a few of the ends with hexafluorobenzene.

Another preliminary study was begun on the preparation of polyesters based on the polyether from perfluoropropylene oxide. When an acid fluoride-terminated polyether prepared from perfluoropropylene oxide and perfluoroglutaryl fluoride was reacted with hexafluoropentanediol, a product was obtained in poor yield whose infrared spectrum indicated that it contained ester groups.



2. From Hexafluoropentanediol

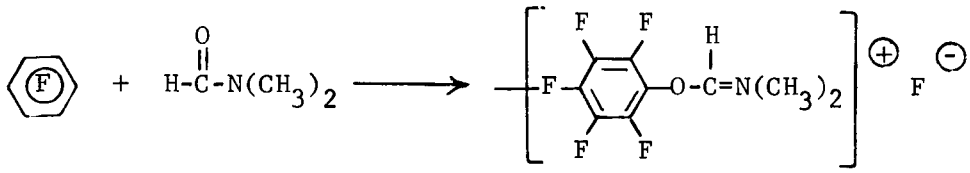
a. Polyethers of Hexafluorobenzene and Hexafluoropentanediol

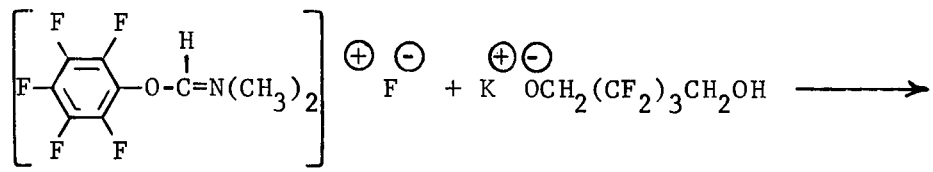
In an effort to more closely control the molecular weight of the polyether of hexafluorobenzene and hexafluoropentanediol and possibly obtain complete hydroxyl termination, a study was begun on the reaction of the dilithium salt of hexafluoropentanediol with hexafluorobenzene.

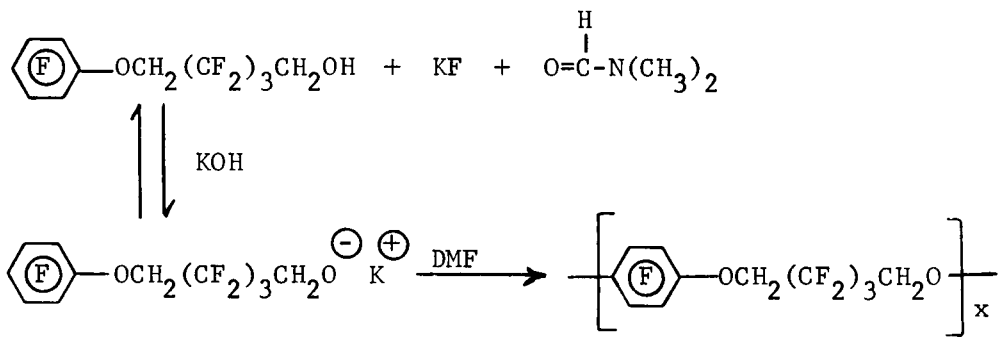
Pure dilithium salt of hexafluoropentanediol was prepared (described in the monomer section of this report) and reacted with hexafluorobenzene in the ratio of 1.02 to 1 in ethyl ether, THF, and DMF. No reaction took place in ethyl ether or in THF. A moderately low molecular weight (765) polyether was formed in refluxing DMF solution. This polyether was reacted further with dilithium salt in refluxing DMF in an attempt to increase the molecular weight and to obtain complete hydroxyl termination. A higher molecular weight material (1150) was obtained, but only about one-half of the ends were hydroxyl-terminated.

The reaction of the dilithium salt with hexafluorobenzene was repeated at room temperature in DMF. The ratio of dilithium salt to hexafluorobenzene was 1.02 to 1. The product from this reaction was of moderate molecular weight (1090) but it contained very few hydroxyl end groups.

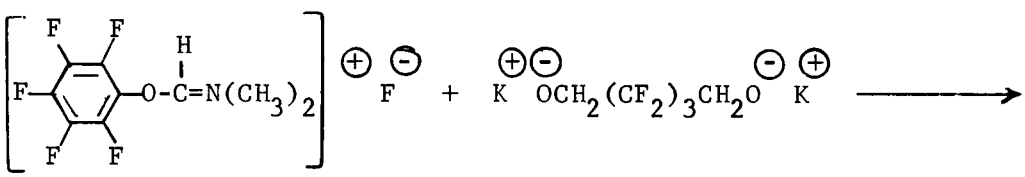
The use of DMF as the solvent for the preparation of polyethers of hexafluorobenzene and hexafluoropentanediol has probably been responsible for the LOX impact sensitivity of polyurethanes prepared from these polyethers. It is extremely difficult to completely remove all of the DMF from the polyethers and polyurethanes. The reactions of hexafluorobenzene with hexafluoropentanediol and potassium hydroxide and with the sodium salt of hexafluoropentanediol would not proceed, at least to any significant degree, in any other solvent tried. In Annual Summary Report III, it was suggested that this reaction occurred at an appreciable rate only in DMF because of salt formation followed by a nucleophillic displacement by the mono-anion or dianion of hexafluoropentanediol.

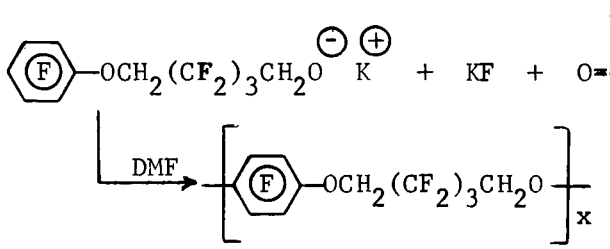
(1) 

(2) 



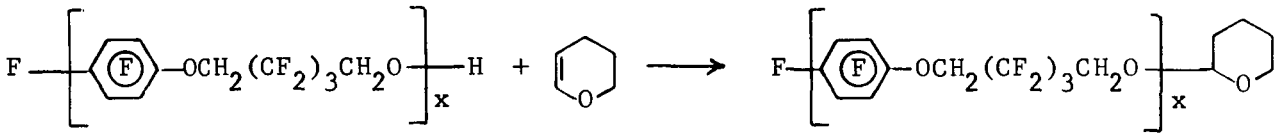
or

(2) 

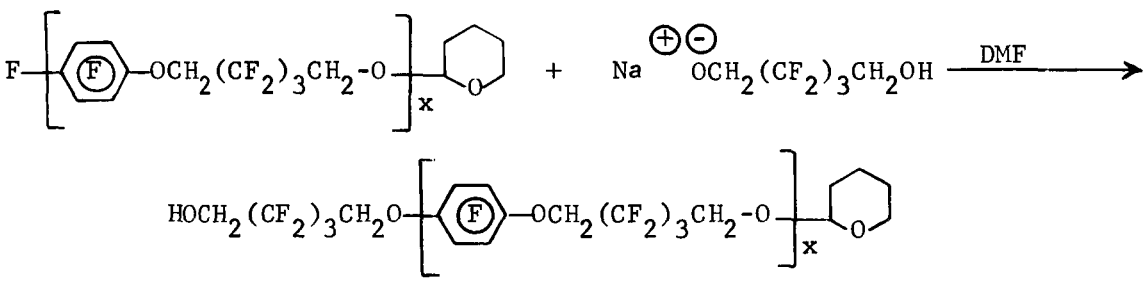


If this type of mechanism was indeed operating, only a catalytic amount of DMF would be required for the reaction to proceed. To test the validity of this assumption and to avoid the problem of use of the difficult-to-remove DMF as solvent, the reaction was run in THF with a catalytic amount of DMF. The reaction of hexafluorobenzene, hexafluoropentanediol and potassium hydroxide (1:1:2) in refluxing THF with a catalytic amount of DMF gave an 81% yield of the desired polyether (1850 molecular weight).

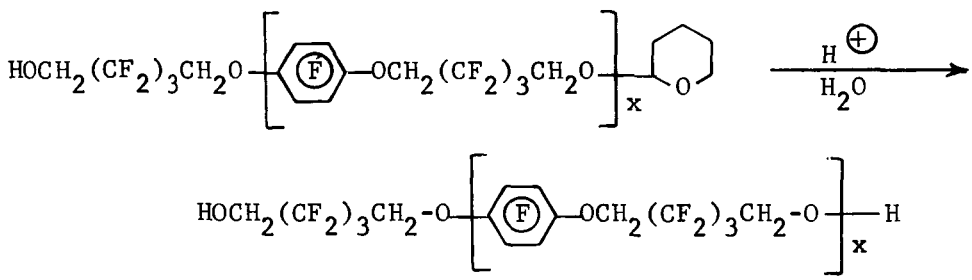
A new approach to the preparation of completely hydroxyl-terminated polyethers was initiated during this report period. Low molecular weight polyethers containing both hydroxyl and pentafluorobenzene end groups, were reacted with dihydropyran. This protected all of the hydroxyl groups, as indicated by the disappearance of hydroxyl absorptions in the infrared spectra of the products.



The capped polyethers were then reacted with the monosodium salt of hexafluoropentanediol in order to put ω-hydroxy-hexafluoropentoxy groups on all of the pentafluorophenyl ends of the polymers. The hydroxyl end group determinations and infrared spectra of the polyethers verified the presence of hydroxyl groups in the desired products.



Acid hydrolysis of the dihydropyran protecting groups yielded the desired hydroxyl-terminated polyethers.

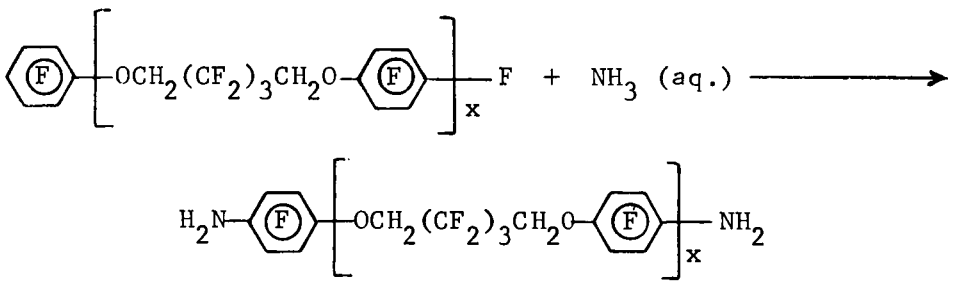


The polyurethanes which were subsequently prepared from these polyethers were described earlier in this report.

b. Amine-Terminated Polyether of Hexafluorobenzene and Hexafluoropentanediol

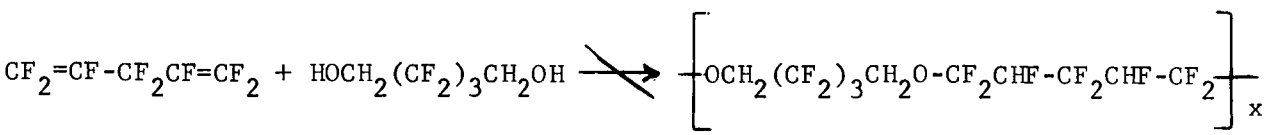
The synthesis of an amine-terminated polyether of hexafluorobenzene and hexafluoropentanediol was studied during this report period. This polyetherdiamine, when used as a curing agent, might produce more flexible polyurethanes.

The pentafluorophenyl-terminated polyether of hexafluorobenzene and hexafluoropentanediol was prepared by the method reported in Annual Summary Report III. As the first preparation attempted this quarter, the polyether was reacted with aqueous ammonia in a bomb for 26 hours at 116°C, but no reaction occurred. During the second attempt, the reactants were heated at 200°C for 16 hours. A 48% yield of a brown oil was obtained which was identified as the desired amine-terminated polyether by its infrared spectrum and the correlation between molecular weight (by VPO), and amine end-group analysis.

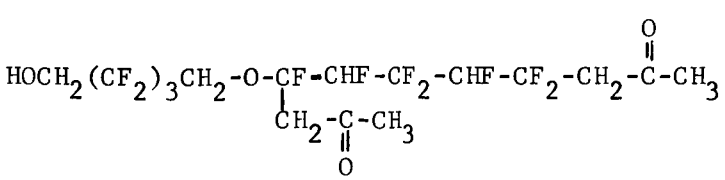


c. Polyether of Perfluoropenta-1,4-diene and Hexafluoropentanediol

An attempt was made previously to prepare this polyether by reaction of hexafluoropentanediol with perfluoropenta-1,4-diene using potassium hydroxide in acetone. This was described in Annual Summary Report III.



Instead of the desired polyether, the compound obtained was believed to consist of an addition product of 1 mole of hexafluoropentanediol, 1 mole of perfluoropenta-1,4-diene, and 2 moles of acetone. A suggested structure for this material is shown below.



This report period the reaction was repeated in THF. Only an extremely low yield of an oil was obtained which contained unsaturation as well as the expected hydroxyl groups.

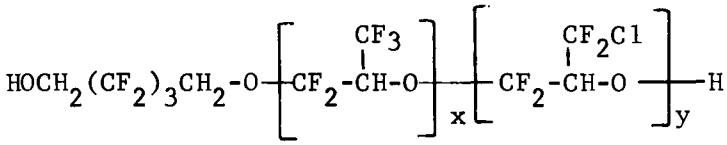
3. From Fluorinated Alcohols

a. Polyethers from Chloropentafluoroisopropyl Alcohol

The preparation of polyethers from chloropentafluoroisopropyl alcohol was described in Annual Summary Report III. These polyethers were shown to be LOX-compatible when devoid of incompatible solvents such as THF. During this report period, hexafluoropentamethylene oxide was shown to be LOX compatible. Therefore the polymerization of chloropentafluoroisopropyl alcohol in this solvent was attempted. The polymerization did proceed but the yield was disappointingly low. A large sample of hydroxyl-terminated polyether was prepared in THF solution, thoroughly dried, and stripped to remove solvent, and was then used to prepare polyurethanes for LOX compatibility testing.

As part of a continuing study of this system, a polyether from chloropentafluoroisopropyl alcohol, having a molecular weight of 3860, was cross-linked by heating the polymer to 140°C, the resultant polymer was insoluble in all solvents.

Previously, the polyether from chloropentafluoroisopropyl alcohol, initiated with the sodium salt of hexafluoropentanediol, was believed to have the following structure:



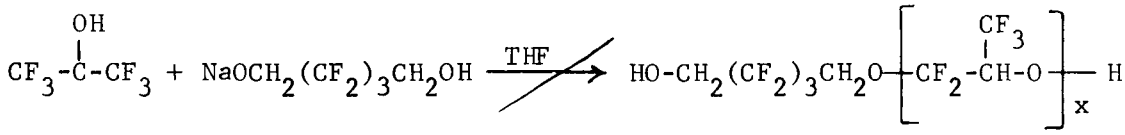
However, it seems unlikely that a cross-linked polymer could be prepared from a polymer having the above-mentioned structure by elimination of water.

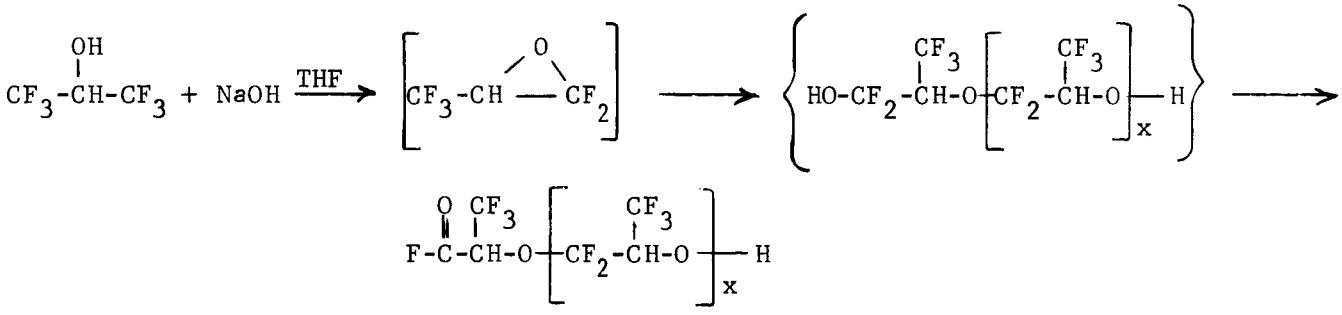
b. Polyethers from Hexafluoroisopropyl Alcohol and Trifluoroethanol

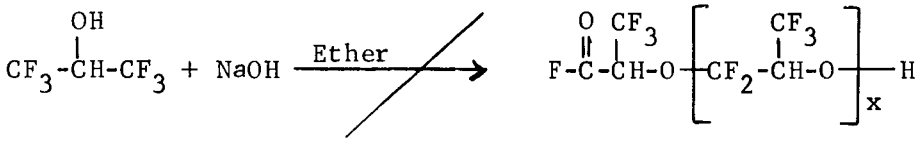
As discussed above, polymers believed to be polyethers were prepared by reaction of chloropentafluoroisopropyl alcohol with sodium hydroxide and with the sodium salt of hexafluoropentanediol.

Attempts were made to prepare similar polyethers from hexafluoroisopropyl alcohol and from trifluoroethanol. Hexafluoroisopropyl alcohol did not polymerize when the sodium salt of hexafluoropentanediol was used as the initiating base in THF solution. It did react with sodium hydroxide in THF solution to yield a yellow, rubbery polymer having a molecular weight of 1600 (by VPO). It is believed that this is a result of hydroxyl ion being more

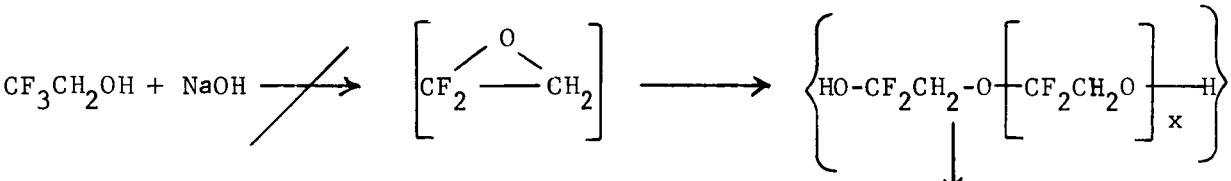
basic than the sodium salt of hexafluoropentanediol. In addition, it was found that this alcohol would not polymerize in ether using sodium hydroxide. Apparently solvation effects are important, and heterogeneous polymerization does not occur readily.

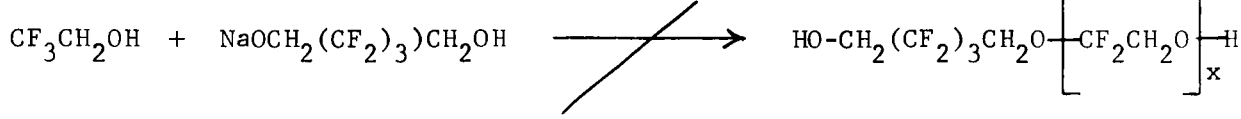






Trifluoroethanol failed to polymerize with either sodium hydroxide or the sodium salt of hexafluoropentanediol in THF solution.

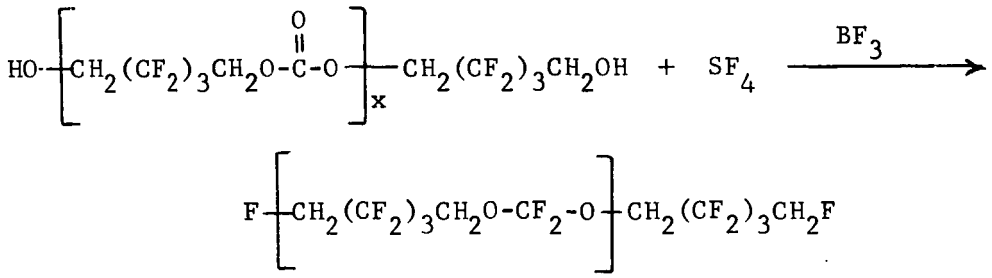




4. By Reaction of Poly(hexafluoropentamethylene carbonate) with Sulfur Tetrafluoride

Sulfur tetrafluoride has been used in the past to convert carbonyl groups to difluoromethylene groups. It was felt that desirable highly fluorinated polyethers might be preparable by reaction of poly(hexafluoropentamethylene carbonate) with sulfur tetrafluoride.

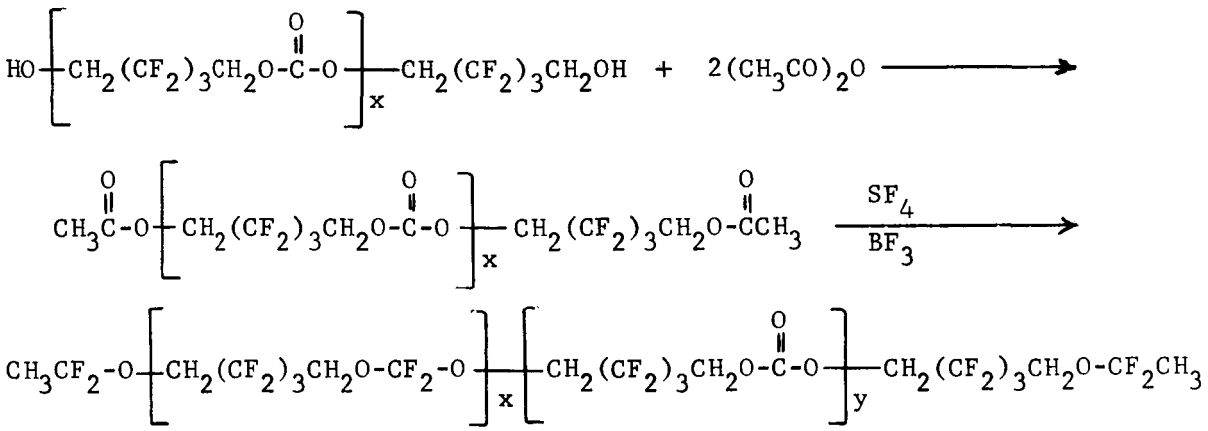
In order to demonstrate the feasibility of the reaction, hydroxyl-terminated poly(hexafluoropentamethylene carbonate) and sulfur tetrafluoride were reacted in a bomb. The product obtained appeared to be the desired polyether.



While the elemental analysis appeared to be consistent with the proposed structure, the infrared spectrum indicated the presence of some unreacted carbonate linkages.

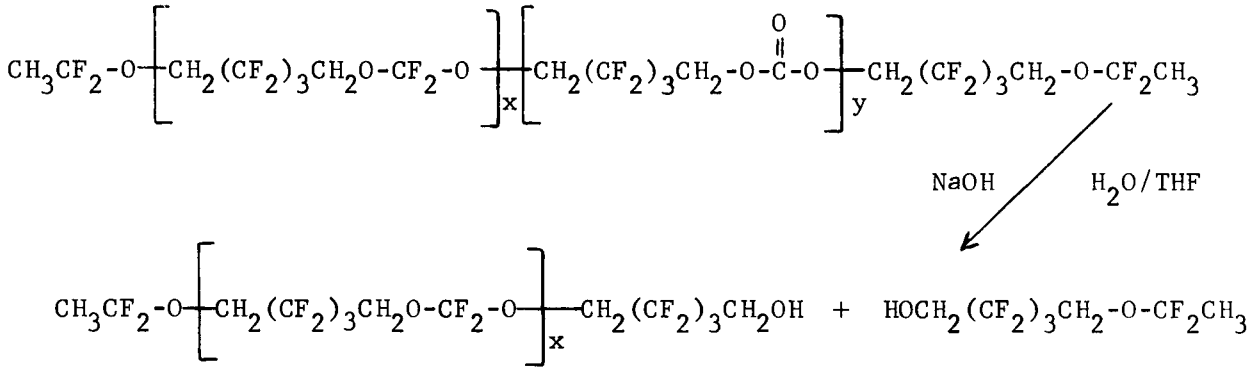
Although a hydroxyl-terminated polycarbonate can be used to demonstrate the feasibility of the reaction with sulfur tetrafluoride, the polymer obtained possesses unreactive fluoromethylene end groups, as shown above. To obtain a usable hydroxyl-terminated polyether, the hydroxyl end groups of the polycarbonate would have to be protected.

Accordingly, hydroxyl-terminated poly(hexafluoropentamethylene carbonate) was acetylated and the acetylated polycarbonate reacted with sulfur tetrafluoride in a bomb. The elemental analysis indicated that the product obtained was the desired polyether. The infrared spectrum of the product showed that some unreacted carbonate groups remained.



The molecular weights of this product, was considerably lower than the starting polycarbonate as was the product from the nonacetylated polycarbonate described above. Some cleavage must have occurred, either during the reaction with sulfur tetrafluoride or by hydrolysis during workup.

An attempt to hydrolyze the end groups by refluxing in hydrochloric acid failed to affect the polyether. Refluxing the polyether with 33% aqueous potassium hydroxide in THF, however, did bring about hydrolysis. The molecular weight (by VPO) and the hydroxyl equivalency of the hydrolysis product were approximately equal, indicating that only one end of the product was hydroxyl terminated. The infrared spectrum showed that all of the carbonate groups were gone. Based on this evidence, it appears that the α,α'-difluoroethoxy groups are not hydrolyzed under the conditions used, and that only the carbonate groups remaining after the sulfur tetrafluoride reaction, are hydrolyzed by base.



More vigorous hydrolysis conditions are apparently needed to hydrolyze the α,α'-difluoroethoxy end groups.

This series of reactions, by which a hydroxyl-terminated polycarbonate is converted to a polyether, results in considerable reduction in molecular weight. In the series of reactions discussed here, a hydroxyl-terminated polycarbonate of 1540 molecular weight was converted to a polyether of 625 molecular weight. This 625 molecular weight polyether is most likely an approximately 3 to 1 mixture of the tetraalkylene triether (where X in the formula = 1) and the hexaalkylene pentaether (where X = 2).

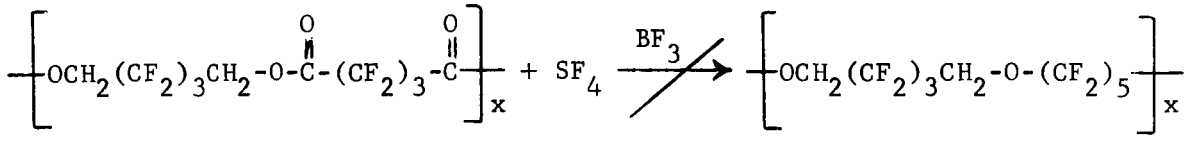
(X = 1) $CH_3CF_2O\text{-}CH_2(CF_2)_3CH_2\text{-}O\text{-}CF_2\text{-}O\text{-}CH_2(CF_2)_3CH_2OH$

(X = 2) $CH_3CF_2O\text{-}CH_2(CF_2)_3CH_2O\text{-}CF_2\text{-}O\text{-}CH_2(CF_2)_3CH_2O\text{-}CF_2\text{-}O\text{-}CH_2(CF_2)_3CH_2OH$

It is obvious that in order to obtain polyethers of reasonable molecular weight, higher molecular weight starting polycarbonates will have to be employed.

5. By Reaction of Poly(hexafluoropentamethylene perfluoroglutarate) with Sulfur Tetrafluoride

In addition to polycarbonates, polyesters might be converted by reaction with sulfur tetrafluoride to fluorinated polyethers. During the report period, poly(hexafluoropentamethylene perfluoroglutarate) was also reacted with sulfur tetrafluoride in an effort to prepare a fluorinated polyether.



The product obtained was essentially unreacted polyester, as indicated by its infrared spectrum and elemental analysis. The molecular weight of the product was considerably lower than that of the starting polyester.

The hydroxyl end groups must be protected in order to obtain polyethers with reactive end groups. Attempts to acetylate hydroxyl-terminated poly-(hexafluoropentamethylene perfluoroglutarate) with acetyl chloride, acetyl chloride in pyridine, and with acetic anhydride were unsuccessful. With the last two reagents, degradation of the polyester resulted.

D. Monomers

1. Dilithium Salt of Hexafluoropentanediol

As discussed in the polyether section of this report, it was desirable to prepare the dilithium salt of hexafluoropentanediol for use in the preparation of polyethers of hexafluorobenzene and hexafluoropentanediol. Initial attempts to prepare this dilithium salt by reaction of the diol with n-butyl lithium and methyl lithium (prepared from n-butyl bromide and methyl bromide respectively) yielded impure products. Inasmuch as lithium bromide, formed in the metalation reaction, forms ether soluble complexes with n-butyl lithium and methyl lithium, it was present during the formation of the lithium salts of hexafluoropentanediol. Therefore, lithium bromide was present in the products, probably complexed with salts of hexafluoropentanediol.

Unlike lithium bromide, lithium chloride does not form complexes with alkyl lithium compounds. Therefore, methyl chloride was used to prepare methyl lithium. This pure methyl lithium was reacted with hexafluoropentanediol to yield pure dilithium salt of hexafluoropentanediol.

2. Hexafluoroisopropyl Alcohol

Hexafluoroisopropyl alcohol was prepared by reduction of hexafluoroacetone with sodium borohydride following the procedure of Knunyants (Reference 2).

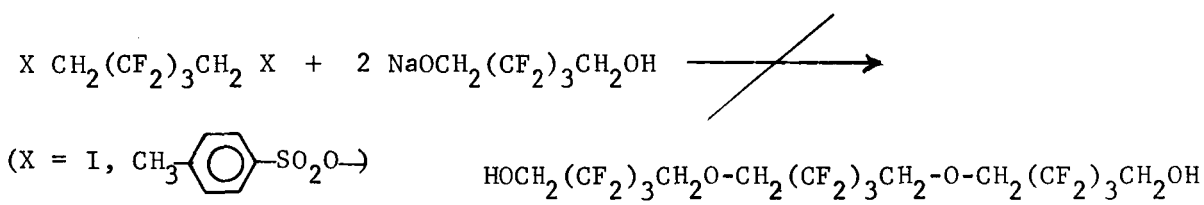
3. Hexafluoropentamethylene Oxide

As discussed in Annual Summary Report III, problems in the preparation of LOX-compatible polyethers from chloropentafluoroisopropyl alcohol were encountered because of the difficulty in removing the THF solvent from the product. Perfluorotributylamine, which is LOX compatible, was used as the solvent for the polymerization, but the yield was quite low.

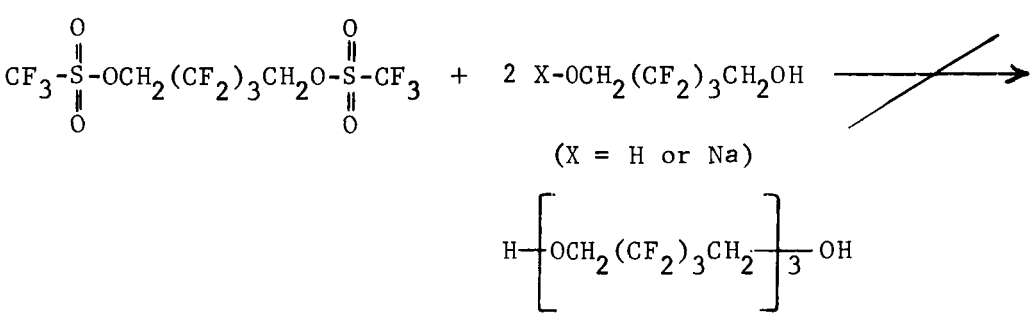
In an effort to find a better solvent for this polymerization, a large quantity of hexafluoropentamethylene ether was prepared. The preparation of this cyclic ether was described in Annual Summary Report I. A sample was submitted this quarter for LOX impact testing and the results (no reactions in 20 tests at 10 Kg-meter) indicated that this ether is LOX compatible. Polymerizations of chloropentafluoroisopropyl alcohol were run in this solvent.

4. Preparation and Reactions of Hexafluoropentamethylene Bis(trifluoromethane sulfonate)

Attempts were made during this program to prepare the diether, triether, and polyethers of hexafluoropentanediol by displacement of groups such as tosylate and iodide by the hexafluoropentanediol anion.



During this report period, the bis(trifluoromethane sulfonate) of hexafluoropentanediol was prepared and reacted with both the sodium salt of hexafluoropentanediol and hexafluoropentanediol in an attempt to prepare trihexafluoropentylene glycol.



The trifluoromethane sulfonate group is reported (Reference 2) to be such an excellent leaving group that its displacement by nucleophiles is extremely easy and rapid. Trifluoromethane sulfonate esters of fluorinated monoalcohols reportedly (Reference 3) undergo even alcoholysis quite readily. The bis(trifluoromethane sulfonate) of hexafluoropentanediol, however, appears to be extremely resistant to nucleophillic displacement. No reaction occurs with hexafluoropentanediol, as the starting materials recovered were unchanged. There was, however, considerable breakdown of the solvent (triglyme). When DMF was used as a solvent at 80°C, no reaction occurred. The only products obtained from the reaction of the disulfonate with the sodium salt of hexafluoropentanediol, after hydrolysis, were hexafluoropentanediol and, interestingly, hexafluoropentamethylene oxide.

Previous efforts have also been made to prepare 3,3,4,4,5,5-hexafluoropimelonitrile by displacement of tosylate and iodide groups by cyanide ion.

$$XCH_2(CF_2)_3CH_2X + NaCN \longrightarrow NCCH_2(CF_2)_3CH_2CN$$

(X = I, CH_3-C$_6$H$_4$-SO_2O-)

An attempt was made to prepare this dinitrile by reaction of potassium cyanide and sodium cyanide with hexafluoropentamethylene bis(trifluoromethane sulfonate) in DMF solution. None of the desired dinitrile was obtained.

$$CF_3\text{-}S(=O)_2\text{-}OCH_2(CF_2)_3CH_2O\text{-}S(=O)_2\text{-}CF_3 + \underset{(2NaCN)}{2\ KCN} \xrightarrow{DMF} NCCH_2(CF_2)_3CH_2CN$$

5. Improved Preparation and Purification of Perfluoropropylene Oxide

A recent patent (Reference 1) describes the preparation of an acid fluoride terminated polyether prepared by reaction of perfluoropropylene oxide with perfluoroglutaryl fluoride and cesium fluoride.

$$CF_3\text{-}CF\text{-}CF_2 + FC(=O)(CF_2)_3C(=O)F + CsF \longrightarrow$$

$$FC(=O)\text{-}CF(CF_3)\text{-}\left[O\text{-}CF_2\text{-}CF(CF_3)\right]_m\text{-}O\text{-}(CF_2)_5\text{-}O\text{-}\left[CF(CF_3)\text{-}CF_2\text{-}O\right]_n\text{-}CF(CF_3)\text{-}C(=O)F$$

The preparation of perfluoropropylene oxide was described in Annual Summary Report III. The procedure used involved the addition of perfluoropropylene in the gas phase to an aqueous alcoholic solution of hydrogen peroxide and potassium hydroxide. During this report period, considerable work was carried out on the improvement of the yield of epoxide and its purification. The current preparative procedure involves adding the perfluoropropylene as a liquid and stirring the reaction mixture for a longer period of time. Considerable improvement in yield of epoxide has been achieved.

The crude product, which consisted of a mixture of perfluoropropylene oxide and unreacted perfluoropropylene, was originally purified by passing the gas mixture through a solution of iodine monobromide in acetic acid. This treatment, as described in Annual Summary Report III, only removed some of the olefin. During this report period, addition purification methods were investigated based on the addition of bromine to the olefin. After treatment of the mixture with bromine in a stainless steel gas cylinder at room temperature for an extended period of time, a considerable amount of olefin still remained. Bubbling the product mixture through a solution of bromine in carbon tetrachloride at room temperature resulted in removal of a large amount of olefin, but a considerable amount still remained. In a similar purification method, the product mixture was refluxed in a solution of bromine in carbon tetrachloride. This method was effective in removing all the olefin.

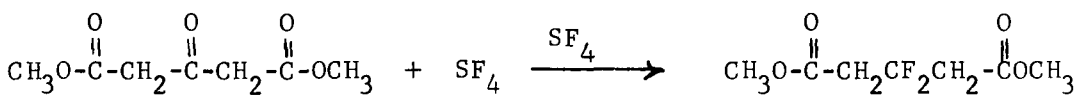
A considerable amount of perfluoropropylene oxide was prepared and purified during this report period.

6. Difluoroglutaric Acid

Because perfluorinated diacids result in fluorinated polyesters which are LOX compatible but hydrolytically unstable, it was believed that fluorinated diacids which have no fluorine atoms adjacent to the acid carbonyl might provide more stable fluorinated polyesters which are still LOX compatible.

During this report period, work was started on the synthesis of a diacid of this type, difluoroglutaric acid.

Dimethylacetone dicarboxylate was reacted with sulfur tetrafluoride in an attempt to prepare the dimethyl ester of difluoroglutaric acid. A liquid product was obtained which was shown to be a mixture of products by vapor phase chromatography (VPC) and elemental analysis. The starting diester was also shown by VPC to be a mixture.



7. 1,6-Diiodo-3,3,4,4-Tetrafluorohexane

Another diacid which might yield LOX compatible polyesters is tetrafluoroadipic acid. Work was started on the synthesis of this diacid.

The attempted reaction of 1,2-diiodotetrafluoroethane with ethylene in the presence of benzoyl peroxide, carried out four times in a stainless steel cylinder, was unsuccessful.

$$ICF_2CF_2I + 2CH_2{=}CH_2 \xrightarrow{BZP} ICH_2CH_2CF_2CF_2CH_2CH_2I$$

Hydrolysis and oxidation of the desired diiodohexane would yield tetrafluoroadipic acid.

$$ICH_2CH_2CF_2CF_2CH_2CH_2I \xrightarrow{hydrol.} \xrightarrow{oxid.} HOOCCH_2CF_2CF_2CH_2COOH$$

8. Reactions of Viton LM

Vinylidine fluoride-perfluoropropylene copolymers (Viton) can be cross-linked by aliphatic diamines. Because the Vitons are not sensitive to LOX, an effort was made this report period to react a low molecular weight Viton (LM) with the monosodium salt of hexafluoropentanediol in order to obtain reactive hydroxyl groups. However, there was no reaction.

$$\left[CF_2\text{-}CH_2\text{-}\underset{\displaystyle CF_3}{\underset{|}{C}}F\text{-}CF_2\right]_n + Na^{\oplus}\,{}^{\ominus}OCH_2(CF_2)_3CH_2OH \not\longrightarrow$$

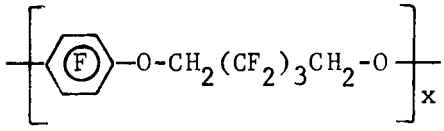
$$\left[CF_2\text{-}CH_2\text{-}\underset{\displaystyle CF_3}{\underset{|}{C}}F\text{-}CF_2\right]_x \left[CF_2\text{-}CH_2\text{-}\underset{\displaystyle O\\ |\\ CH_2(CF_2)_3CH_2OH}{\underset{|}{\overset{\displaystyle CF_3}{\overset{|}{C}}}}\text{-}CF_2\right]_y$$

Viton LM was also reacted with hexafluoropentanediamine to see if this extremely weak base would react. There was no apparent reaction.

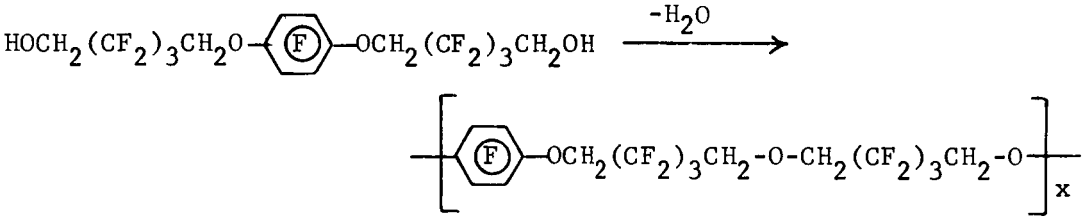
9. 1,4-Bis(5-hydroxyhexafluoropentoxy)-tetrafluorobenzene

Earlier in this report the preparation of a polyether prepared from hexafluorobenzene and hexafluoropentanediol was described. This structure of

this polyether consisted of alternating hexafluorobenzene and hexafluoropentanediol units.

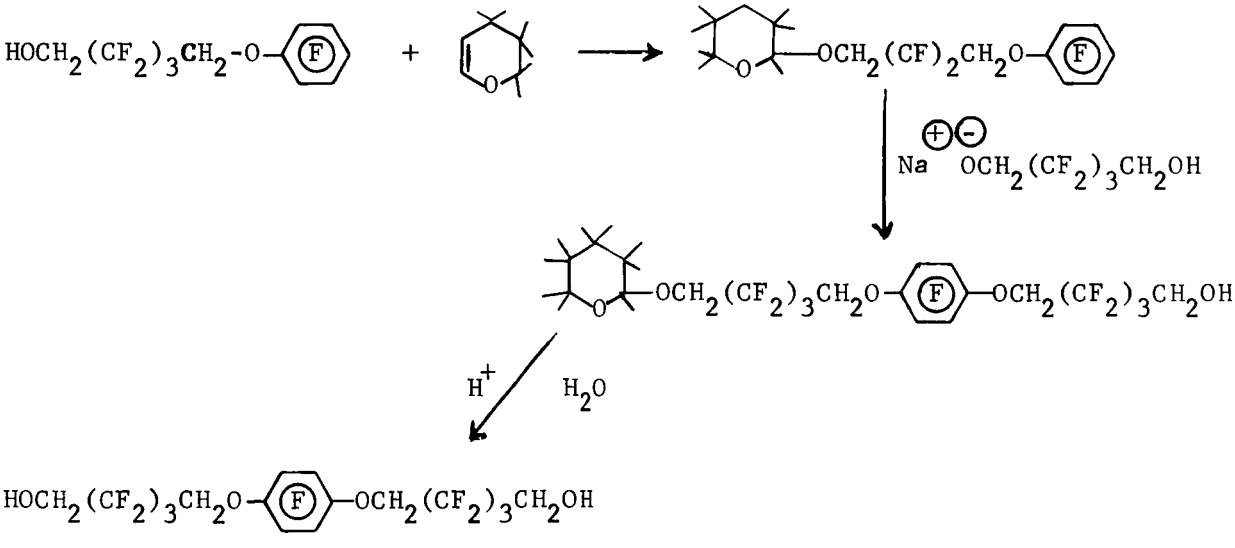


Another polyether based on these starting materials which should be more flexible than the above one would result from dehydration of 1,4-bis(5-hydroxy-hexafluoropentoxy)-tetrafluorobenzene.



An attempt was made to prepare this diether starting material by reacting hexafluorobenzene, hexafluoropentanediol and potassium hydroxide in the ratio of 1:2:2 at room temperature for 1 hour. A small amount of the desired diether was isolated, but the major product was polyether of 1040 molecular weight.

An alternate approach to the preparation of this diether involves a reaction sequence used successfully to prepare the completely hydroxyl-terminated polyether of hexafluorobenzene and hexafluoropentanediol. The monoether of hexafluorobenzene and hexafluoropentanediol could be capped with dihydropyran and reacted with the sodium salt of hexafluoropentanediol. Hydrolysis of the protecting tetrahydropyranyl groups should yield the desired product.



The monoether, 5-hydroxyhexafluoropentoxy-pentafluorobenzene, was prepared early in this program (reported in Annual Summary Report I) in very low yield by reaction of hexafluorobenzene, hexafluoropentanediol and potassium hydroxide without solvent, and by reaction of hexafluorobenzene with the monosodium salt of hexafluoropentanediol in di-n-butyl ether. During this report period, hexafluorobenzene, hexafluoropentanediol and potassium hydroxide in the ratio of 3:2:4 were reacted at 16°-18°C in DMF for 1-3/4 hours. The desired monoether was obtained in 38% yield along with higher molecular weight polyether.

The hydroxyl groups of this monoether were successfully capped by reaction with dihydropyran.

10. Monosodium Salt of 2-Trifluoromethyl-3-oxa-2,4,4,5,5,6,6,7,7-nonafluoro-1,8-octanediol

Two attempts were made to prepare the monosodium salt of 2-trifluoromethyl-3-oxa-2,4,4,5,5,6,6,7,7-nonafluoro-1,8-octanediol by reaction of this diol with sodium in p-dioxane and in ether. No reaction occurred in the p-dioxane, but a very small amount of the desired salt was isolated from the reaction in ether. This salt could be used to prepare polyethers by reaction with hexafluorobenzene.

IV. EXPERIMENTAL

A. LOX Compatibility Results

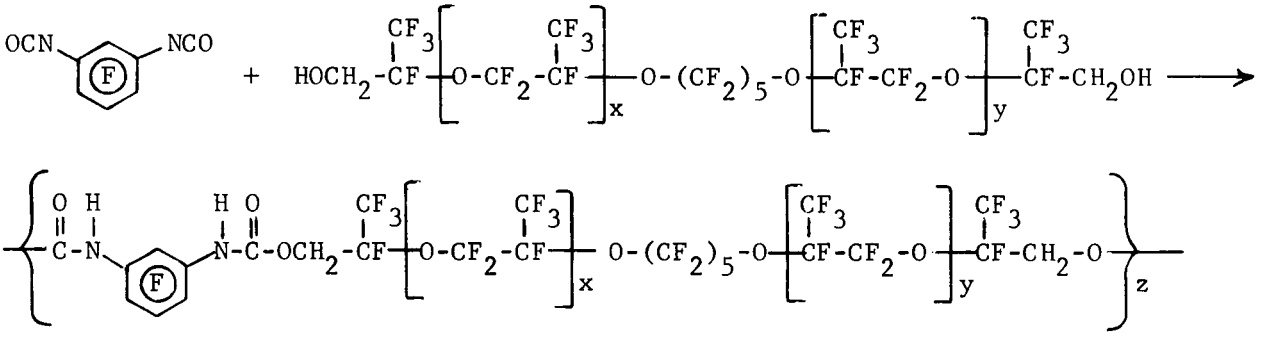
The results of all LOX-compatibility tests completed during this report period are presented in Table I.

B. Polyurethanes

1. From Perfluoropropylene Oxide

a. Polyurethane of Tetrafluoro-m-phenylene Diisocyanate and the Polyether from Perfluoropropylene Oxide

(1) Preparation



(a) With Low Molecular Weight Polyether

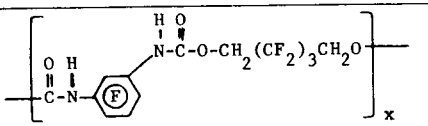
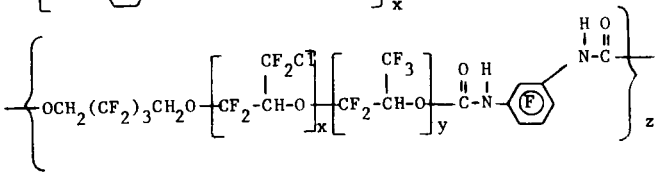
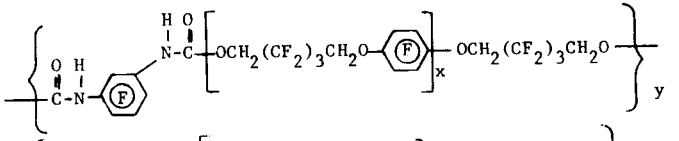
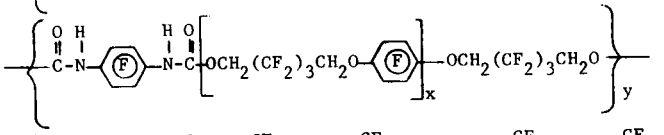
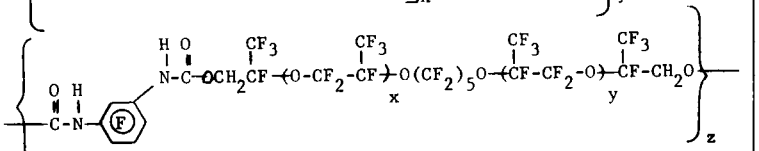
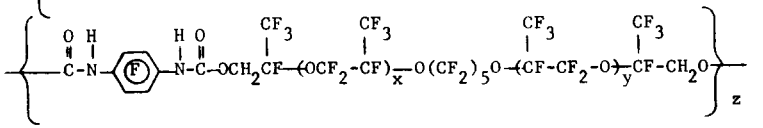
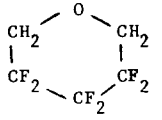
Tetrafluoro-m-phenylene diisocyanate (3.48 g, 0.015 mole) and the polyether from perfluoropropylene oxide of 760 molecular weight (7.06 g, 0.01 mole) were gradually heated to 60°C over a 20-minute period, followed by 15 minutes at 60°-65°C. The reaction mixture was heated to 145°C over a 10-minute period, then tetrafluoro-p-phenylenediamine (0.36 g, 0.002 mole) was added. The mass gelled in 1 minute. It was advanced in a press at 160°C for 1/2 hour to yield a clear yellow solid sheet that was brittle.

(b) With Higher Molecular Weight Polyether

Tetrafluoro-m-phenylene diisocyanate (1.72 g, 0.0074 mole) and the polyether from perfluoropropylene oxide of 1510 molecular weight (10.6 g, 0.007 mole) were stirred at 25°-30°C for 40 minutes, then gradually heated to 150°C over a 3-1/4 hour period. Additional tetrafluoro-m-phenylene diisocyanate (0.32 g, 0.0014 mole) was added at 150°C. The mixture gelled immediately. The product was advanced at 160°C in a press for 3/4 hour to yield a soft elastic sheet.

TABLE I

LOX COMPATIBILITY RESULTS

Name	Structure	Film Thickness, mils	LOX Results* No. Reactions
Poly(hexafluoropentamethylene tetrafluoro-m-phenylene dicarbamate)		Powder 8.5	2/60+ 3/20**
Polyurethane of tetrafluoro-m-phenylene Diisocyanate and Polyether of Chloropentafluoro-isopropyl alcohol		21 12	5/20++ 5/20++ **
Polyurethane of tetrafluoro-m-phenylene diisocyanate and polyether of hexafluorobenzene and hexafluoropentanediol		15	18/20+++
Polyurethane of tetrafluoro-p-phenylene diisocyanate and polyether of hexafluorobenzene and hexafluoropentanediol		10	14/20+++
Polyurethane of tetrafluoro-m-phenylene diisocyanate and poly(perfluoropropylene oxide)		14	0/20
Polyurethane of tetrafluoro-p-phenylene diisocyanate and poly(perfluoropropylene oxide)		5	0/20
Hexafluoropentamethylene oxide		Liquid	0/20

* Energy level = 10 Kg-M

** Reported in Annual Summary Report III, July 1966

\+ Reactions may well have been cup flashes

++ LOX sensitivity may be due to trapped THF solvent

+++ LOX sensitivity may be due to trapped DMF solvent

(c) With Higher Molecular Weight Polyether; Amine Cured

Tetrafluoro-m-phenylene diisocyanate (1.40 g, 0.006 mole) and 1510 molecular weight polyether from perfluoropropylene oxide (7.5 g, 0.005 mole) were stirred at 80°C for 1/2 hour. The mixture was then heated to 148°C and tetrafluoro-m-phenylenediamine (0.65 g, 0.00036 mole) added. After stirring for about 30 seconds, the mixture gelled. The product was advanced in a press under 20,000-lb pressure at 275°F for 2 hours to yield a fairly tough but somewhat brittle sheet. Disks (11/16 in.) were punched from this sheet and submitted to MSFC for LOX-compatibility testing.

(2) Lap Shear Test Specimens - High-Temperature Cure

The hydroxyl-terminated polyether from perfluoropropylene oxide of 1510 molecular weight (7.5 g, 0.005 mole) and tetrafluoro-m-phenylene diisocyanate (1.73 g, 0.0075 mole) were mixed. Stannous octoate (2 drops) was added; there was a slow exotherm to 35°C. A few glass beads (0.005 in. diameter) were stirred in and the polymer applied to etched (sulfuric acid/sodium dichromate solution) 2024-T3 clad aluminum adherends. The jigged specimens were put in a press at room temperature and 200 psi for 45 minutes, then heated for 45 minutes at 160°F, 45 minutes at 220°F, then 45 minutes at 325°F. Six of these bonded specimens were tested immediately after preparation (three bonds each at room temperature and at -320°F). The results are shown below.

	Room Temperature	-320°F (Liquid Nitrogen)
Lap Shear Strength, psi	1325	2450
	485	3550
	1115	4020*
Avg Lap Shear Strength, psi	975	3340

Another six of the bonded specimens were stored in a humidity chamber at 100% humidity for four weeks before testing. The results of these tests are shown below.

	Room Temperature	-320°F (Liquid Nitrogen)
Lap Shear Strength, psi	705	3750
	590	2690
	608	2330
Avg Lap Shear Strength, psi	634	2920

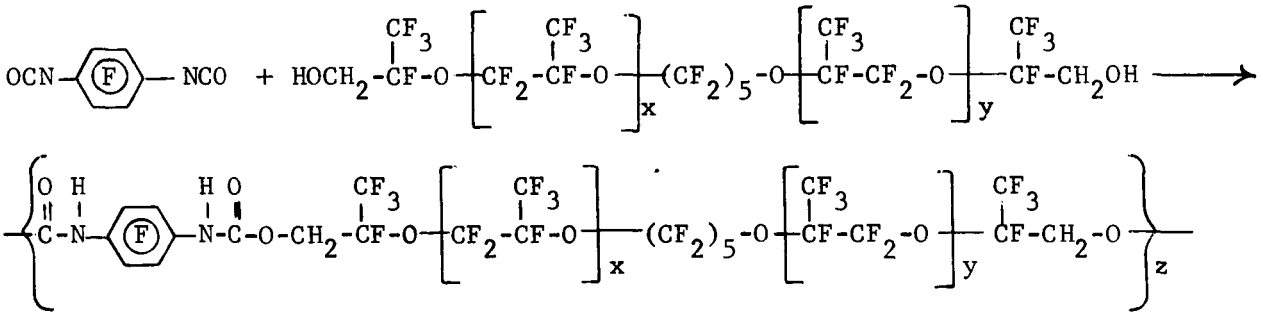
* Aluminum failed at the grip hole.

(3) Lap Shear Test Specimens - Low-Temperature Cure

The hydroxyl-terminated polyether from perfluoropropylene oxide of 1510 molecular weight (2.44 g, 0.0016 mole) and tetrafluoro-m-phenylene diisocyanate (0.75 g, 0.0032 mole) were heated to 65°C with mixing, then cooled to room temperature. Stannous octoate (2 drops) was added and the mixture stirred for 5 minutes at which time the viscosity of the polymer increased considerably. The material was applied to etched (sulfuric acid/sodium dichromate solution) 2024-T3 clad aluminum adherends, a few glass beads (0.005-in. diameter) sprinkled on the bonds, and allowed to gel overnight at room temperature in a vacuum bag. The specimens were removed from the bag and cured at 160°F for 48 hours. The test results (three tests each at room temperature and at -320°F) are shown below.

	Room Temperature	-320°F (Liquid Nitrogen)
Lap Shear Strength, psi	1060	3920
	1430	4120
	1670	3190
Avg Lap Shear Strength, psi	1386	3740

b. Polyurethane of Tetrafluoro-p-phenylene Diisocyanate and the Polyether from Perfluoropropylene Oxide



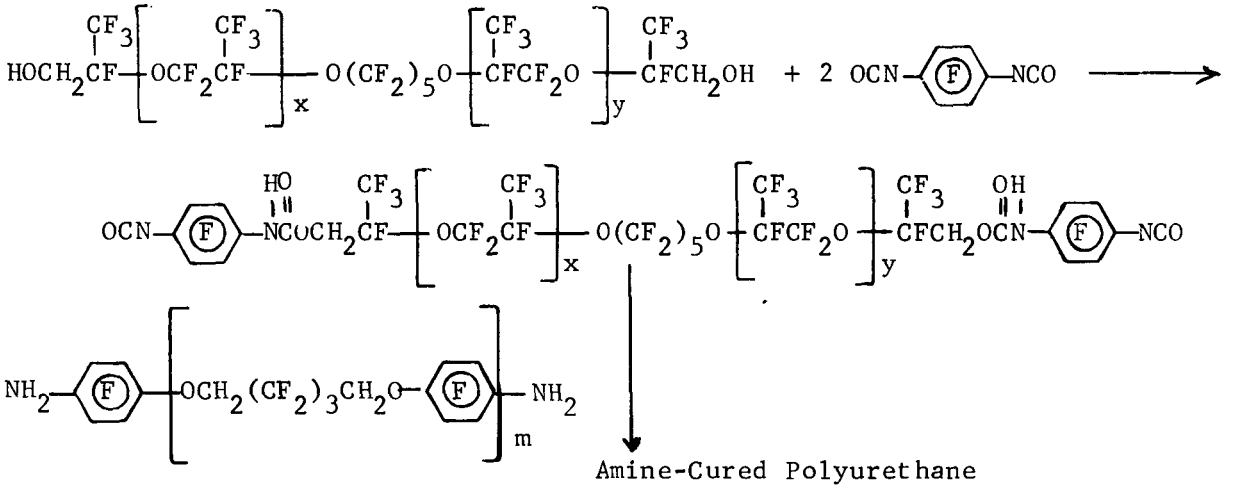
(1) With Low Molecular Weight Polyether

Tetrafluoro-p-phenylene diisocyanate (3.02 g, 0.013 mole) and the polyether from perfluoropropylene oxide of 760 molecular weight (9.88 g, 0.013 mole) were heated at 25°C to 80°C over a 15-minute period, followed by a gradual rise in temperature from 80°C to 120°C over a 20-minute period. It was then mixed at 115°-125°C for 2 hours. Additional tetrafluoro-p-phenylene diisocyanate (0.30 g, 0.0013 mole) was added. After the mixture had been stirred for 15 minutes at 125°-180°C, the polymer became a paste. The polymer was advanced in a press at 160°C for 1 hour to yield an extremely brittle polymer.

(2) With Higher Molecular Weight Polyether

Tetrafluoro-p-phenylene diisocyanate (2.09 g, 0.009 mole) and the polyether from perfluoropropylene oxide of 1510 molecular weight (9.1 g, 0.006 mole) was heated to 57°C over a 35-minute period. Two drops of stannous octoate were added, and the reaction temperature rose to 84°C and solidified. The mixture was then warmed to 110°C over a 10-minute period during which time the product liquified. After being heated to 120°C in 5 minutes, the material gelled. The polymer was advanced in a press at 160°C for 45 minutes to yield a fairly tough elastic sheet which was not brittle in liquid nitrogen. Samples were submitted to MSFC for LOX-compatibility testing.

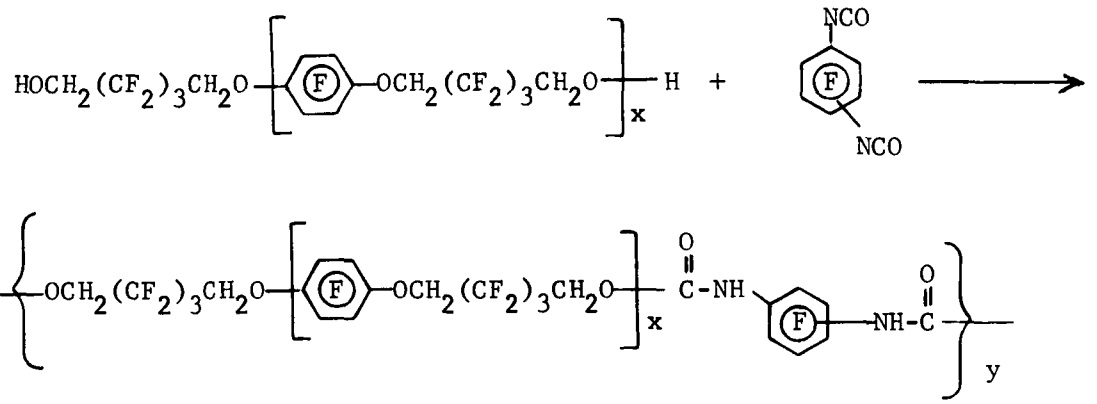
c. Preparation of a Liquid Fluorinated Diamine Cured Polyurethane of Tetrafluoro-p-phenylene Diisocyanate and the Polyether from Perfluoropropylene Oxide



The polyether from perfluoropropylene oxide of 1510 molecular weight (7.5 g, 0.005 mole) and tetrafluoro-p-phenylene diisocyanate (2.32 g, 0.01 mole) were mixed for 1 hour at room temperature. Infrared spectroscopy indicated that there had been very little reaction during this time. The mixture was slowly heated to 45°C, at which point sublimation of the diisocyanate slowly began. The mixture began clearing at 55°C, and at 65°C it became a clear homogeneous solution. The temperature was increased to 150°C over a 2-hour period. It was then cooled to 65°C. At this temperature the material was very viscous. The amine-terminated polyether of hexafluorobenzene and hexafluoropentanediol having a molecular weight of 665 (2.27 g, 0.0034 mole) was stirred in. The polymer gelled after 3 minutes. A sheet was formed by pressing the material between Teflon caul sheets under 2000-lb force at 150°C for 3 hours. The resulting material showed poor strength.

2. From Polyethers of Hexafluorobenzene and Hexafluoropentanediol

a. Preparation



The hydroxyl-terminated 2280 molecular weight polyether of hexafluorobenzene and hexafluoropentanediol (11.4 g, 0.005 mole) was heated in a 50-ml resin flask to 65°C; at this temperature, the material became fluid enough for easy stirring. Tetrafluoro-p-phenylene diisocyanate (1.22 g, 0.00525 mole) was added and the reaction mixture stirred. After 3 minutes, the mixture began to gel. The material was transferred to Teflon caul sheets and press-cured at 135°C under 200-psi pressure. The resulting 10-mil thick film was punched into 11/16-in. diameter disks which were submitted for LOX impact testing.

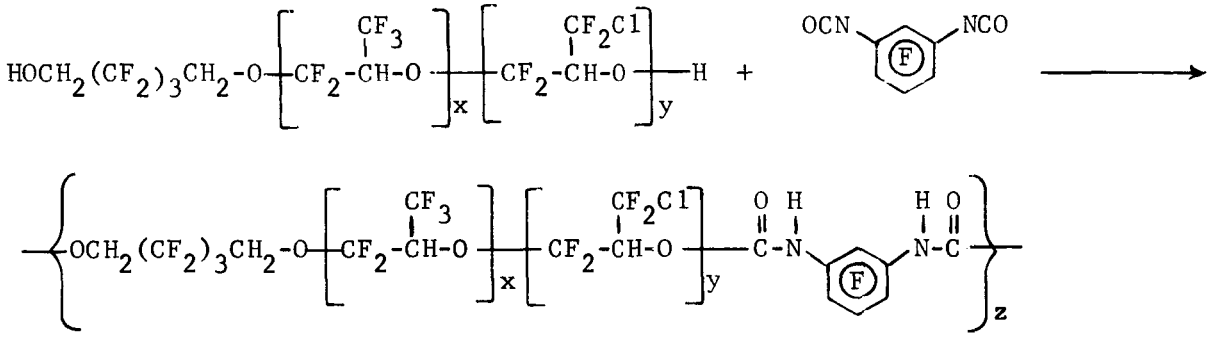
LOX impact test specimens (14 mil) were also prepared from the polyurethane of tetrafluoro-m-phenylene diisocyanate and the 2280 molecular weight polyether of hexafluorobenzene and hexafluoropentanediol. The ratios of reactants, reaction conditions, and press curing conditions were identical to those for the above preparation.

b. Lap Shear Test Specimens

The hydroxyl-terminated polyether of hexafluorobenzene and hexafluoropentanediol of 2280 molecular weight (5.7 g, 0.0025 mole) was warmed to 70°C and tetrafluoro-p-phenylene diisocyanate (0.61 g, 0.0025 mole) was quickly stirred in. Mixing was continued for 1-1/2 minutes at this temperature. The polymer was then rapidly applied to etched (sulfuric acid/sodium dichromate solution) 2024-T3 clad aluminum adherends. The specimens were cured in a press at 135°C under 200-psi pressure for 2 hours. The test results (three tests each at room temperature and at -320°F) are shown below.

	Room Temperature	-320°F (Liquid Nitrogen)
Lap Shear Strength, psi	1950	1170
	3020	810
	2900	420
Avg Lap Shear Strength, psi	2620	800

3. From the Polyether of Chloropentafluoroisopropyl Alcohol



a. In THF

The polyether from chloropentafluoroisopropyl alcohol, having a molecular weight of 3860 (4.03 g, 0.00104 mole), tetrafluoro-m-phenylene diisocyanate (0.24 g, 0.00104 mole) and 20 ml of THF were mixed for 2 hours at 70°C. Based on the infrared spectrum, all of the NCO groups were reacted. An additional 0.08 g (0.00035 mole) of diisocyanate was added and the solution stirred for an additional 2 hours at 70°C. The THF was then removed to yield a soft slightly elastic polymer.

b. In Hexafluoropentamethylene Oxide

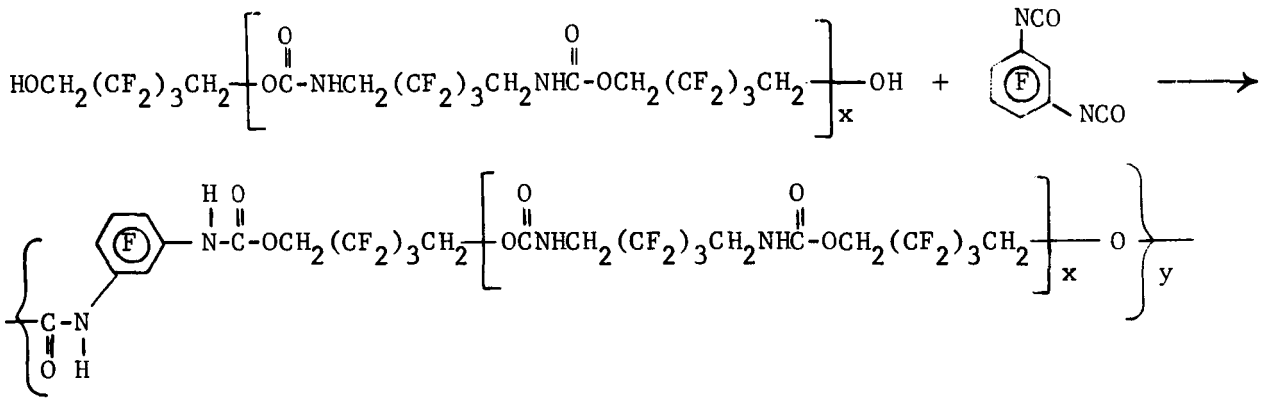
The polyether from chloropentafluoroisopropyl alcohol, having a molecular weight of 1325 (13.3 g, 0.01 mole), was dissolved in hexafluoropentamethylene oxide (10 ml) at 90°-95°C. Tetrafluoro-m-phenylene diisocyanate (2.32 g, 0.01 mole) was then added to the polyether at 90°C. The mixture was mixed for 5 minutes at 85°-90°C after which time the polymer gelled. The temperature was maintained at 90°-95°C for an additional 15 minutes, then the solvent was removed under reduced pressure. The polymer was advanced in a press at 150°-165°C for 1-1/2 hours to yield a slightly elastic sheet. Disks (21 mil thick; 11/16-in. diameter) were punched from the sheet and submitted to MSFC for LOX compatibility testing.

c. In Melt

The polyether from chloropentafluoroisopropyl alcohol (molecular weight 1325) (13.3 g, 0.01 mole) and tetrafluoro-p-phenylene diisocyanate (2.32 g, 0.01 mole) were mixed at 80°-90°C for 5 minutes. At the end of this time the mixture gelled. The product was then advanced in a press at 160°C for 1 hour. The product was brittle.

4. From Poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate)

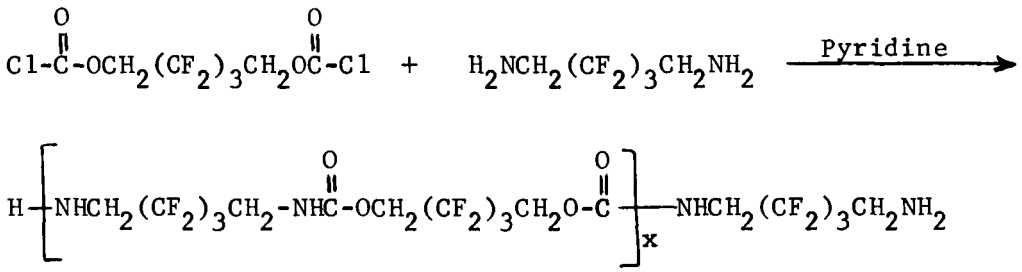
a. Polyurethane



Hydroxyl-terminated poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate) (MW 645) (10.3 g, 0.016 mole) was charged to a resin pot and heated to 120°C under a dry nitrogen flow. The prepolymer became molten and stirring was started. Tetrafluoro-m-phenylene diisocyanate (3.7 g, 0.016 mole) was added and heating continued to 180°C. Because some of the diisocyanate sublimed out of the reaction mass, 0.5 g more was added. Stirring was continued until the reaction mass gelled. The temperature was increased to 220°C and held at that temperature for 1 hour. Upon cooling, the polymer solidified to a dark brown brittle material.

b. Polyurethane-urea

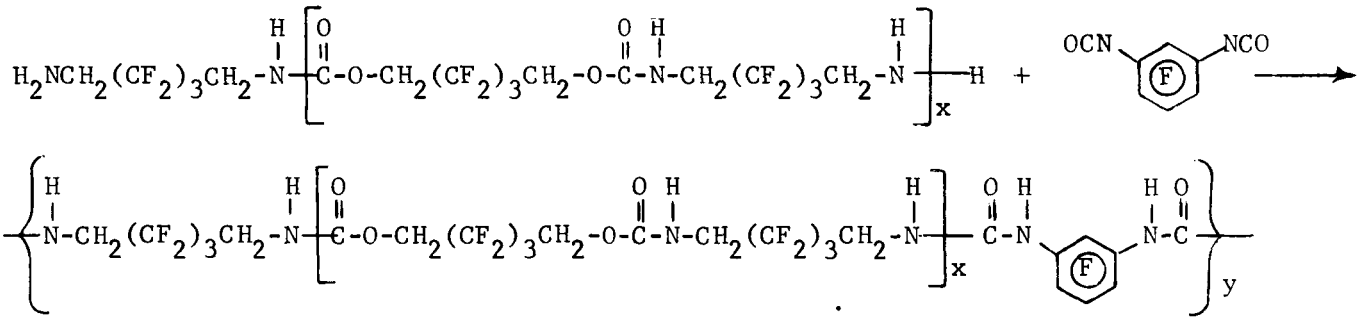
(1) Preparation of Amino-Terminated Poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate)



Hexafluoro-1,5-pentanediamine (22.3 g, 0.106 mole) was dissolved in THF (200 ml) and pyridine (14.0 g, 0.177 mole) was added. Hexafluoropentamethylene bischloroformate (29.7 g, 0.088 mole) was dissolved in THF (100 ml) and added to the diamine solution over a period of 2-1/2 hours. Additional THF was added to make a total of 450 ml of solvent, and stirring was continued for 2 hours. The pale orange precipitate of pyridine hydrochloride was filtered off (it was readily water soluble) and the dark filtrate poured into distilled

water with vigorous stirring. An emulsion formed which was broken by careful addition of sodium chloride. A mobile oil separated which was isolated, dissolved in ether, and dried over anhydrous magnesium sulfate. Removal of solvent under reduced pressure yielded 42.8 g (94%) of viscous polymer. The molecular weight, determined by VPO, was 750±30.

(2) Polyurethane-Urea from Poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate)

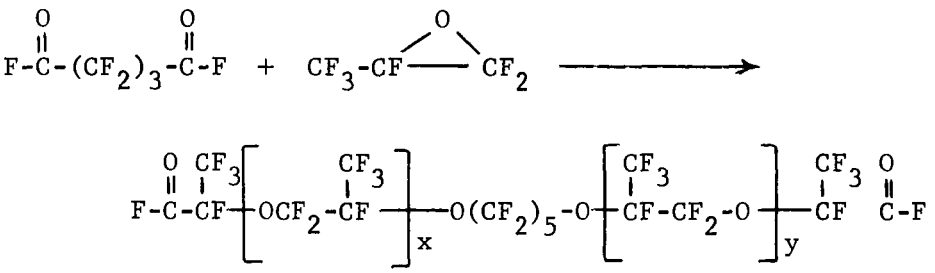


The amine-terminated poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate (MW 750) (20.0 g, 0.027 mole) was heated to 130°C, then tetrafluoro-m-phenylene diisocyanate (6.9 g, 0.03 mole) was added. The temperature was increased to 175°C; the mass gelled after 10 minutes. The mixture was held at 175°C for an additional 3 hours then cooled. At the end of this time the polymer became brittle.

C. Polyethers

1. From Perfluoropropylene Oxide

a. Preparation of Polyether from Perfluoroglutaryl Fluoride and Perfluoropropylene Oxide



(1) Preliminary Runs

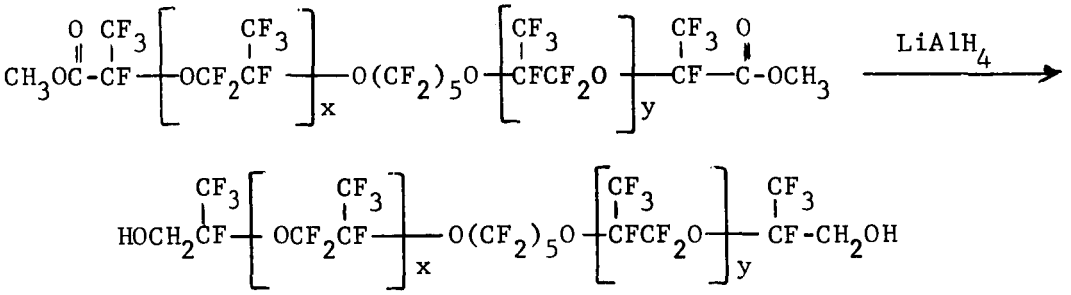
Cesium fluoride (2.0 g, 0.013 mole) was suspended in dry, redistilled diglyme (15 cc), and perfluoroglutaryl fluoride (12.2 g, 0.05 mole)

was added. The solution was cooled to -20°C to -30°C and perfluoropropylene oxide (45.0 g, 0.271 mole) was added slowly over a 3-1/2 hour period. The mixture was mixed for an additional period of time, then worked up. These preliminary runs are summarized in Table II.

(2) Larger Scale Runs

Perfluoroglutaryl fluoride, cesium fluoride (dried at 600°F) and dried, distilled diglyme were mixed, then cooled to -20°C to -30°C. Perfluoropropylene oxide was added over a 3-1/2 hour period at -25°C to -35°C. The mixture was stirred, then warmed to room temperature and the unreacted perfluoropropylene oxide collected. The product was then fractionally distilled. The results are summarized in Table III.

b. Reduction of the α,ω-Dimethyl Ester of Poly(perfluoropropylene oxide)



The 692 molecular weight polyether of perfluoropropylene oxide which had been initiated with perfluoroglutaryl fluoride and terminated as the α,ω-dimethyl ester (27.0 g, 0.039 mole) was dissolved in anhydrous ether (60 ml) and added slowly to a stirred suspension of lithium aluminum hydride (LAH) (1.9 g, 0.05 mole) in ether (250 ml). The addition was carried out over a 3-1/2 hour period. A thick pasty mass formed which precipitated from the clear ethereal solution. After standing overnight, additional ether (150 ml) was added and the mixture was vigorously stirred. Water (4.0 g, 0.022 mole) was carefully added to destroy the excess LAH. The reaction mixture was then poured into 5% sulfuric acid and the organic layer separated, washed twice with water, taken up in ether and dried over anhydrous magnesium sulfate. The aqueous layer was extracted with two 150-ml portions of ether and the ethereal extracts combined with the above ether solution. The solids were filtered and the solvent removed under reduced pressure, yielding 22.3 g (79.5%) of reduced product. Hydroxyl termination was determined to be virtually quantitative, as evidenced by infrared spectroscopy (no carbonyl absorption) and comparison of molecular weight by vapor pressure osmometry (720±20) and end group analysis. Hydroxyl equivalent weight was 379±5 g/equivalent.

TABLE II

PREPARATION OF POLYETHERS FROM PERFLUOROGLUTARYL FLUORIDE
AND PERFLUOROPROPYLENE OXIDE
PRELIMINARY RUNS

Reaction Conditions *		Fluorocarbon Product, g	** Yield-%	Product MW	Remarks
Time, hr	Temp, °C				
1	-25	2.4***	4.2	445	Cesium fluoride dried for 24 hr @ 120°C in a vacuum oven
3	-25	3.8 +	6.6	--	Cesium fluoride dried for 24 hr @ 120°C in a vacuum oven
2	-20 to -22	15.4***	26.9	482	Cesium fluoride dried for 2 days @ 315°C
4	-20 to -25	27.1***	47.5	643-1030	99.9% cesium fluoride dried for 2 days @ 315°C. Epoxide used was recovered from previous reactions

* After addition of all reactants.

** Based on starting materials.

*** Dimethyl ester of fluorocarbon ethers.

\+ Diacid fluoride of fluorocarbon ethers.

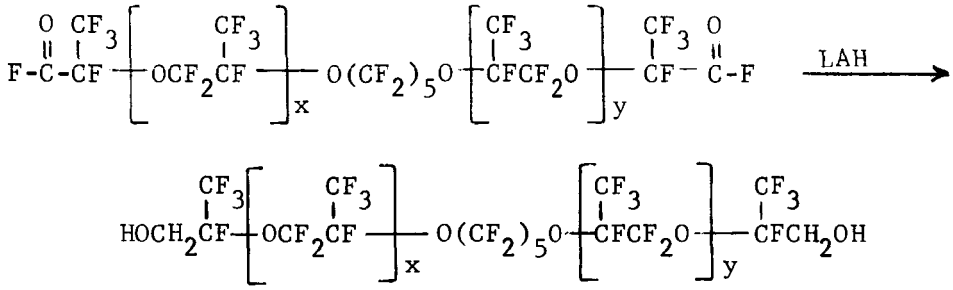
TABLE III

PREPARATION OF POLYETHERS FROM PERFLUOROPROPYLENE OXIDE
LARGE RUNS

Perfluoro-glutaryl Fluoride, moles	Cesium Fluoride, moles	Pefluoro-propylene Oxide, moles	Diglyme, cc	Reaction Conditions	Perfluoro-propylene Oxide Recovered, g	Fluorocarbon Products, g	Overall Yield, %	Product Molecular Wt
0.25	0.066	1.35	55	4 hr @ -20°C to -25°C	106[1]	61.7[2]	27	425 (VPO)
0.25					158	60.2[3]	21	--
0.147[4]		1.35[5]		4 hr @ -10°C to +20°C	None	Cut 1(64°-90°C @ 100 mm) 6.5 Cut 2(90°C @ 100 mm to 160°C @ 70 mm) 7.1 Cut 3(160°C @ 70 mm to 180°C @ 40 mm-6.9 Cut 4(180°C @ 40 mm to 175°C @ 18 mm)-7.3 Residue - 151.7	84	822 (end group analysis) -- -- -- 1510[6] (by VPO)
0.026	0.012	0.223[5]	9.6	4-1/2 hr @ -27°C to +20°C		Cut 1(57°C @ 100[2] mm to 100°C @ 90 mm)-14.1 Cut 2(100°C @ 90 mm to 180°C @ 40 mm)-12.0 Cut 3(180°C @ 40 mm to 180°C @ 2 mm)-3.0 Residue - 1.1	70	1134 (end group analysis) 1092 (end group analysis) 1384 (end group analysis) 3016 (end group analysis)
0.0437[4]	0.039	0.80[5]	33	4 hr @ -22°C to +20°C		Cut 1(61° to 90°C @ 100 mm)-28.1 Cut 2(90°C @ 100 mm to 120°C @ 8 mm)-25.2 Cut 3(120°C-160°C @ 8 mm)-12.9 Residue - 64.0	87	-- -- -- --

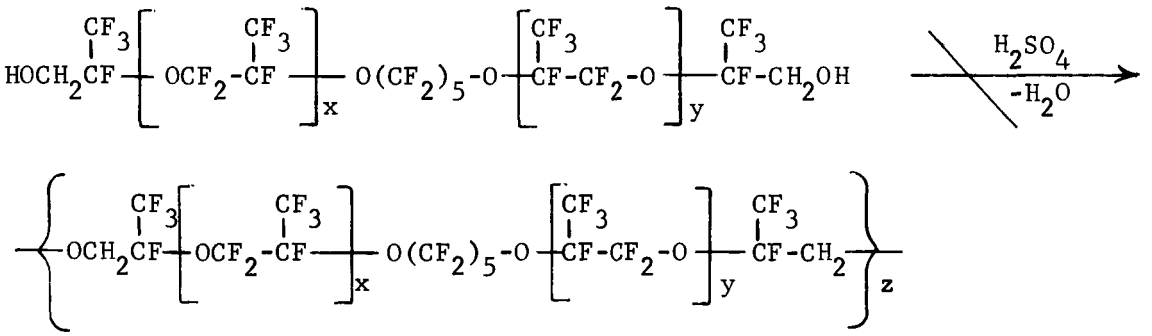
(1) Leak developed in perfluoropropylene oxide recovery system
(2) Recovered as dimethyl ester
(3) Recovered as diacid fluoride
(4) Perfluoro-2-methyl-3-oxaoctanedioyl fluoride
(5) Reused epoxide
(6) Molecular weight of hydroxyl-terminated material after reduction of diester

c. Reduction of the Acid Fluoride Terminated Polyether of Perfluoropropylene Oxide



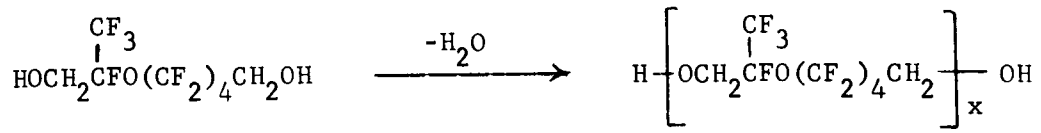
The 1183 molecular weight acid fluoride terminated polyether of perfluoropropylene oxide (7.1 g, 0.006 mole) was added over a 2-hour period to a solution of LAH (1.3 g, 0.032 mole) in THF (150 ml). The polyether was only slightly soluble in the solvent; the reaction was rapid, however, as indicated by the rapid temperature increase of the solution. Stirring was continued for 1 hour after addition was completed, then the excess LAH was destroyed by the cautious addition of water. The resulting gray slurry was poured into iced 5% sulfuric acid (500 ml). The organic layer was separated and the acid extracted with two 100-ml portions of ether. The ether extracts were added to the separated product and washed with two 100-ml portions of ether. The ethereal solution was dried over anhydrous magnesium sulfate for 16 hours. After filtration, the solvent was stripped yielding 6.9 g (100%) of a mobile slightly milky liquid. The molecular weight by VPO was 930±25 and the hydroxyl number was 473 g/equivalent.

d. Attempted Dehydration of Hydroxyl-Terminated Fluorinated Polyether



A polyether from perfluoropropylene oxide (4.4 g) having an approximate molecular weight of 900 and concentrated sulfuric acid (100 ml) were heated at 180°-190°C for 18 hours. There was no apparent reaction.

e. Attempted Dehydration of 2-Trifluoromethyl-3-oxa-2,4,4,5,5,6,6,7,7-nonafluoro-1,8-octanediol



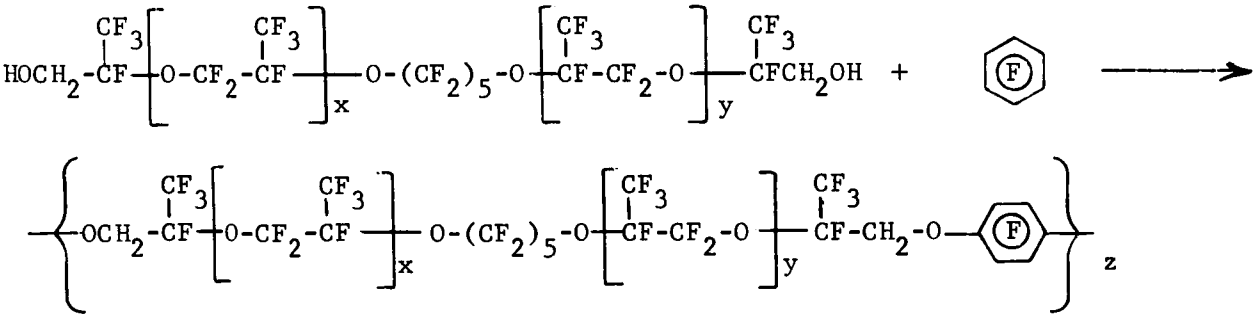
(1) Using Phosphorus Pentoxide

Phosphorus pentoxide (5.0 g, 0.036 mole)-2-trifluoromethyl-3-oxa-2,4,4,5,5,6,6,7,7-nonafluoro-1,8-octanediol (3.8 g, 0.01 mole) and diglyme (100 ml) were refluxed for 4 hours. The solution darkened as the temperature increased. After 1/2 hour at reflux, the solution was dark brown. After being allowed to cool overnight, the solution was concentrated under reduced pressure and poured into water. A small amount of a mobile liquid was obtained. The water was decanted and the dense organic material was dissolved in THF. After drying the THF solution over anhydrous magnesium sulfate, and filtering and stripping the solvent under reduced pressure, 2.6 g (68%) of starting material was recovered in the form of a brown oil. The molecular weight by VPO was 493±15 and the hydroxyl number was 907 g/equivalent.

(2) Using Sulfuric Acid

The ether used as starting material in (1) above (3.8 g, 0.01 mole) was dissolved in concentrated sulfuric acid (100 ml) and heated at 120°C for 4 hours. There was no apparent reaction.

f. Reaction of Hydroxyl-Terminated Fluorinated Polyether with Hexafluorobenzene



(1) In DMF

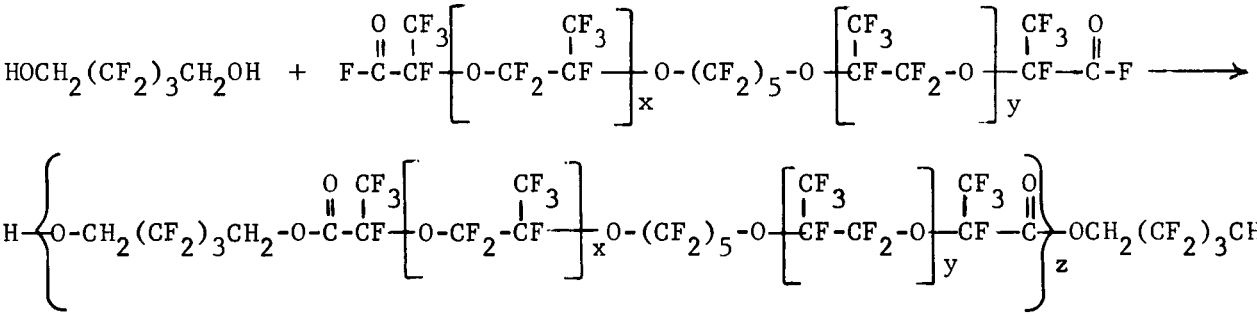
The fluorinated hydroxyl terminated polyether of 868 molecular weight (8.68 g, 0.01 mole), hexafluorobenzene (1.86 g, 0.01 mole), and potassium hydroxide (1.1 g, 0.02 mole) were refluxed overnight in DMF. The solution was cooled and poured into water with stirring. Hydrochloric acid was added until the solution had a pH of about 4, at which point the product settled out

as a yellow oil. This oil was washed four times with distilled water, then dissolved in ether and dried over anhydrous magnesium sulfate. Evaporation of the ether under reduced pressure yielded 4.3 g of product. The infrared spectrum indicated both aliphatic and aromatic fluorines and the fluorinated aromatic ring were present. The molecular weight by VPO was 840±25 indicating that only a few hydroxyl ends had reacted.

(2) In THF and DMF as Catalyst

The fluorinated hydroxyl terminated polyether of 868 molecular weight (8.68 g, 0.01 mole), hexafluorobenzene (1.86 g, 0.01 mole), and potassium hydroxide (1.1 g, 0.02 mole) were refluxed overnight in 50 ml of THF with 0.5 g of DMF added as a catalyst. The solution was cooled and poured into water with stirring. Hydrochloric acid was added until the pH of the solution reached about 4, at which point the product settled out as a white oil. This oil was washed four times with distilled water and was then dissolved in ether and dried over anhydrous magnesium sulfate. Evaporation of the ether under reduced pressure yielded 6.0 g of product. The infrared spectrum indicated the fluorinated aromatic ring and both aromatic and aliphatic fluorines were present. The molecular weight by VPO was 870± 25 indicating that only a few hydroxyl ends had reacted.

g. Preparation of a Fluorinated Polyether-Polyester

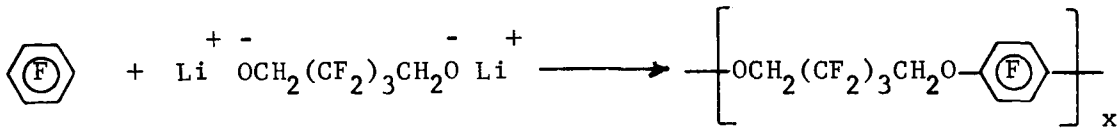


The acid fluoride terminated polyether from perfluoropropylene oxide of 820 molecular weight (26.3 g, 0.032 mole) and hexafluoropentanediol (9.5 g, 0.045 mole) were heated to 75°C over a 1/2-hour period and from 75°C to 115°C over a 1/2-hour period. The reaction mixture was then heated at 110°-120°C for 16 hours. The product was vacuum-distilled to 200°C at 2 mm to yield 7.6 of polyester which was insoluble in methyl ethyl ketone, pyridine, dioxane, and chloroform. The polymer had the typical ester absorption in the infrared spectrum.

2. From Hexafluoropentanediol

a. Polyethers of Hexafluorobenzene and Hexafluoropentanediol

(1) Preparation of Polyethers of Hexafluorobenzene and Hexafluoropentanediol Using the Dilithium Salt of Hexafluoropentanediol



(a) In Refluxing DMF

Hexafluorobenzene (2.33 g, 0.0125 mole) was dissolved in DMF (25 ml), the dilithium salt of hexafluoropentanediol (3.00 g , 0.0134 mole) was added, and the solution refluxed overnight (138°C). The resulting brown solution was poured into water (500 ml). The oil was separated, taken up in THF, and the water treatment repeated twice. After separation, the oil was dissolve in THF and dried over anhydrous magnesium sulfate. Removal of the solvent left 4.7 g of polyether. The molecular weight (by VPO) was 765.

(b) In THF and in Ether

The reaction was similarly run in refluxing THF and also in ether at room temperature. No polymer was formed in either case.

(c) Advancement of Polyether in Refluxing DMF

In an attempt to increase the molecular weight and obtain complete hydroxyl termination, the polyether from (a) above (3.0 g, 0.0039 mole) was reacted with the dilithium salt of hexafluoropentanediol (3.0 g, 0.013 mole) in refluxing DMF overnight. Workup yielded 3.9 g of dark brown solid polyether. The molecular weight (by VPO) was 1150 and its hydroxyl equivalent was 1089 g/hydroxyl.

(d) In DMF at Room Temperature

Hexafluorobenzene (4.65 g, 0.025 mole) was dissolved in DMF (25 ml), and the dilithium salt of hexafluoropentanediol (5.95 g, 0.0255 mole) in DMF (25 ml) was added immediately. The temperature of the reaction rose to 60°C then slowly fell to room temperature. The solution was stirred at room temperature, under nitrogen, for 10 days. The resultant pale tan solution was poured into distilled water (500 ml) and stirred vigorously. The aqueous layer was decanted (pH 8) and the polymeric precipitate taken up in THF (50 ml) and again poured into water. The pale yellow precipitate was once again separated and dissolved in THF. The polymer solution was dried

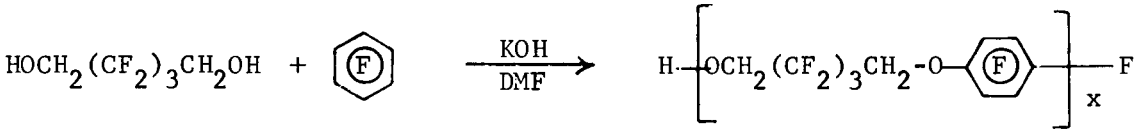
over anhydrous magnesium sulfate. After filtering, the solvent was stripped under reduced pressure, yielding a slightly yellow polymer (5.6 g). Extraction of the original aqueous layer yielded a small amount (1.3 g) of deeper yellow polymer. A total of 6.9 g (77%) of product was obtained. The molecular weight of the precipitated polymer by VPO was 1090±20, and the hydroxyl equivalent was 5550 g/equivalent.

(2) Preparation of Polyether of Hexafluorobenzene and Hexafluoropentanediol Using Hexafluoropentanediol and Potassium Hydroxide in THF with DMF as Catalyst

Hexafluorobenzene (3.7 g, 0.02 mole), hexafluoropentanediol (4.24 g, 0.02 mole), potassium hydroxide (2.2 g, 0.04 mole) and DMF (1.0 g) were refluxed overnight in 50 ml of THF. The solution was poured into water with stirring. A white semisolid was recovered from the water, and was again washed several times with water. With each successive washing the product became more viscous. The solid was then taken up in THF and dried over anhydrous magnesium sulfate. The THF was evaporated under reduced pressure, yielding 6.0 g (81%) of a white solid with a molecular weight of 1850±50.

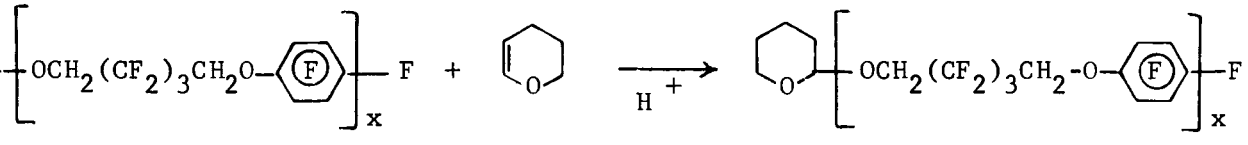
(3) Preparation of Completely Hydroxyl-Terminated Polyethers of Hexafluorobenzene and Hexafluoropentanediol

(a) Polyethers with Mixed End-Groups



These polyethers were prepared in DMF solution by the procedure described in Annual Summary Report III. The ratio of reactants, yields, molecular weights (by VPO), and hydroxyl equivalent weights are shown in Table IV.

(b) Capping of the Polyethers of Hexafluorobenzene and Hexafluoropentanediol with Dihydropyran



The hexafluorobenzene-hexafluoropentanediol polyether, dihydropyran, and concentrated hydrochloric acid were reacted at reflux temperature for 16 hours. Infrared spectroscopy and end group analysis indicated that the polyethers obtained contained no free hydroxyl groups. The molecular weights (by VPO) of the capped polyethers are listed in Table IV. A typical reaction is described below.

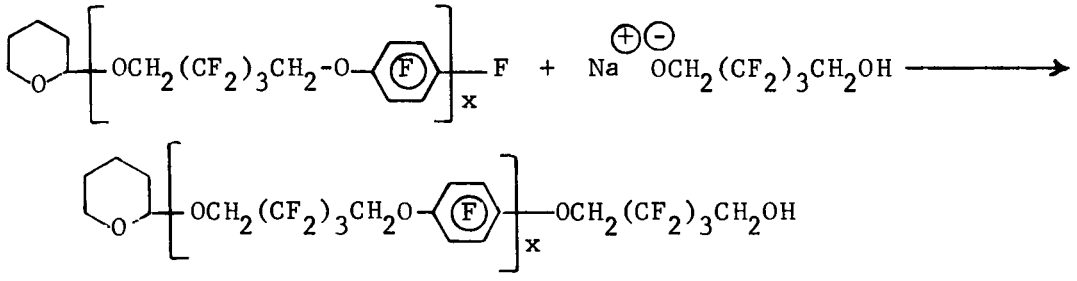
TABLE IV

PREPARATIONS OF COMPLETELY HYDROXYL-TERMINATED POLYETHERS
OF HEXAFLUOROBENZENE (HFB) AND HEXAFLUOROPENTANEDIOL (HFPD)

Reaction of HFB & HFPD in DMF				Capping with Dihydropyran	Reaction of Capped Polyether with $NaOCH_2(CF_2)_3CH_2OH$		Hydrolysis of Capped Ends	
Ratio HFPD:HFB	Yield	Hydroxyl Equivalent	MW (VPO)	MW (VPO)	Hydroxyl Equivalent	MW (VPO)	Hydroxyl Equivalent	MW (VPO)
3:2	--	990	1260	955	--	1206	1150	2340
3:2	73%	2800	1342	16 hr 795 72 hr 850	1330	1820	805	1500
3:2	71%	1640	1400	795	1109	1750	1145	2120
1.2:1	77%	2750	1480	800	1160	1770	1395	1630

Into a 1000-ml, three-necked flask equipped with stirrer, condenser, and drying tube were introduced the hexafluorobenzene-hexafluoropentanediol polyether (168 g) (MW 1400 by VPO; OH eq wt. 1640), dihydropyran (400 ml), and 20 drops of concentrated hydrochloric acid. The mixture was stirred at reflux for 16 hours, cooled, and the excess dihydropyran stripped, yielding 180 g of light brown viscous liquid.

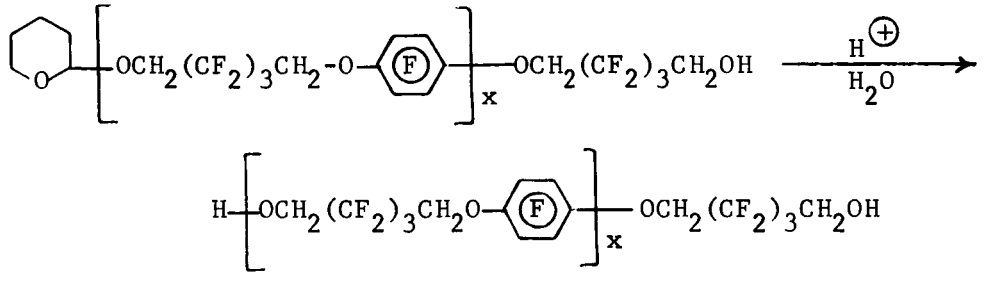
(c) Reaction of the Capped Hexafluorobenzene-Hexafluoropentanediol Polyethers with the Sodium Salt of Hexafluoropentanediol



A typical run is described as follows.

The capped polyether described above (114 g) (MW 795 by VPO), the monosodium salt of hexafluoropentanediol (89 g), and DMF (400 ml) were stirred at 130°C for 16 hours. The polymer was isolated by pouring into hot water. The aqueous layer was decanted and the organic portion subsequently washed three times for 1-1/2 hours with boiling water. The gum was then dissolved in ether, dried with anhydrous sodium sulfate, and stripped. A dark brown viscous liquid, 128 g, was obtained. The infrared spectrum of this liquid product indicated the presence of hydroxyl groups. The molecular weights (by VPO) and the hydroxyl equivalent weights of the various runs are shown in Table IV.

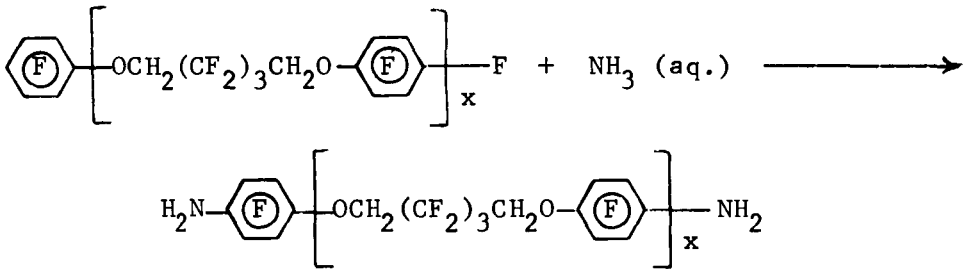
(d) Acid Hydrolysis of Capped Polyethers



A typical hydrolysis is illustrated below. The product from the above reaction of the capped polyether with monosodium salt of hexafluoropentanediol was dissolved in 300 ml of THF and refluxed with 200 ml of 2N hydrochloric acid for 2 hours. The product was extracted with ether,

treated with charcoal, and dried over anhydrous magnesium sulfate. The ether was evaporated yielding a light brown, viscous liquid. The molecular weights (by VPO) and the hydroxyl equivalent weights of the various hydrolyses are listed in Table IV.

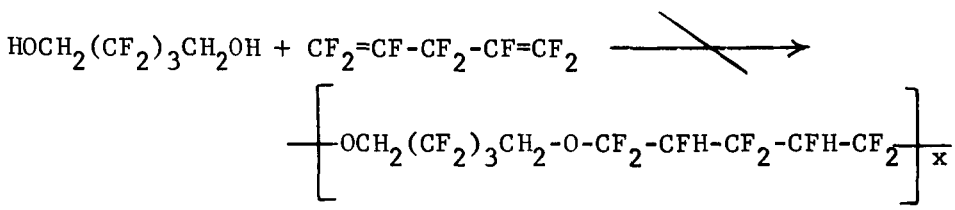
b. Preparation of Amine-Terminated Polyether of Hexafluorobenzene and Hexafluoropentanediol



Run 1: The pentafluorophenyl-terminated polyether of hexafluoropentanediol and hexafluorobenzene having a molecular weight of 635 (9.0 g, 0.014 mole) and ammonium hydroxide (15 ml, 0.23 mole) were reacted in a bomb at 116°C for 26 hours. There was no apparent reaction.

Run 2: The above reaction was repeated at a temperature of 200°C for 16 hours. The reaction mixture was then extracted with ether and the ether solution dried over anhydrous magnesium sulfate. After filtering and evaporating the ether, 5 g of a red brown oil remained. This oil was dissolved in THF and decolorized with charcoal. After drying the THF solution over anhydrous magnesium sulfate and a small amount of sodium metabisulfite, the solution was filtered and the solvent evaporated, leaving 4.3 g of a red-brown oil. This oil was identified by its infrared spectrum, as the desired amine-terminated polyether. Its molecular weight was 686 and its amine equivalent weight was 392.

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

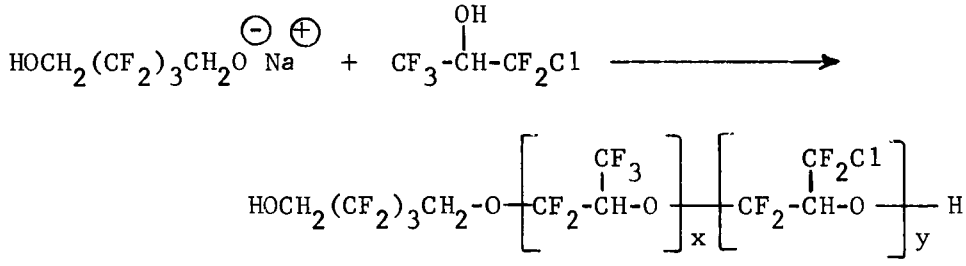


Hexafluoropentanediol (4.90 g, 0.023 mole) and potassium hydroxide (0.20 g, 0.0036 mole) were dissolved in 15 ml of THF, then cooled to -78°C. Perfluoropenta-1,4-diene (4.20 g, 0.20 mole) was then added, mixed for 15 minutes at -78-C, and slowly warmed to room temperature with stirring. The solution was agitated for 4 days at room temperature, filtered and the THF removed. The

residue was then washed thrice with water, dissolved in ether and dried. After removal of the ether, 0.7 g of an oily product was obtained. Based on the infrared spectrum, the product contained unsaturation as well as the expected hydroxyl groups.

3. From Fluorinated Alcohols

a. Preparation of Polyether from Chloropentafluoroisopropyl Alcohol



(1) In Hexafluoropentamethylene Oxide

The monosodium salt of hexafluoropentanediol (17.5 g, 0.075 mole) was suspended in hexafluoropentamethylene oxide (50 ml), then chloropentafluoroisopropyl alcohol (13.9 g, 0.075 mole) was added over a 5-minute period. The slurry was slowly heated to 80°C, at which temperature the sodium salt appeared to dissolve. The mixture was stirred at 90°-100°C for 18 hours. The slurry was cooled, filtered and the solvent removed from the filtrate. The residue was washed repeatedly with water, dissolved in ether, then dried with anhydrous magnesium sulfate. The ether was removed, yielding 2.6 g (23.7%) of polymer.

(2) In THF

The sodium salt of hexafluoropentanediol (155.4 g, 0.663 mole) was dissolved in THF (450 ml). Chloropentafluoroisopropyl alcohol (122.7 g, 0.663 mole) was added over a 5-minute period, at the end of which time the temperature of the mixture had risen to 42°C. It was stirred for 10 minutes at 42°C, then the reaction temperature rose to 67°C over a 10 minute period. The mixture was stirred at 65°-70°C for 18 hours, cooled, and filtered. The THF was removed and the residue washed repeatedly with hot water. The residue was then dried for 15 hours at 62°C in a vacuum oven to yield 75.8 g (76.5%) of polymer, having a molecular weight of 1325 by VPO.

(3) Advancement of the Polyether from Chloropentafluoroisopropyl Alcohol

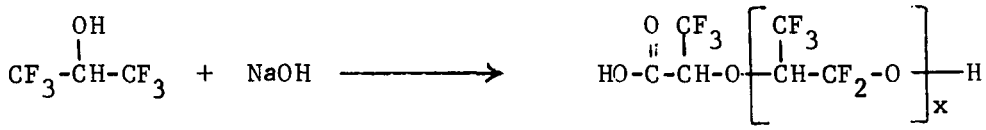
The polyether from chloropentafluoroisopropyl alcohol having a molecular weight of 3860 was slowly heated to 100°C over a 1/2-hour period,

at which point water began to evolve. As the polymer was gradually heated from 100°C to 140°C over a 1/2-hour period with evolution of water, the polymer gelled. The final polymer was insoluble in all common solvents. The elemental analysis of the polymer before and after advancement was as follows:

	% C	% H	% Cl	% F
Before Advancement:	25.0	2.28	0.79	51.61
After Advancement:	26.98	1.18	0.80	56.83

b. Preparation of the Polyether from Hexafluoroisopropyl Alcohol

(1) Sodium Hydroxide Initiation



(a) At Room Temperature

A slurry was made by vigorously stirring sodium hydroxide pellets (2.0 g, 0.05 mole) and sodium dried THF (20 ml). Hexafluoroisopropyl alcohol (8.3 g, 0.05 mole) dissolved in THF (15 ml) was added over a period of 10 minutes. The reaction was run at room temperature for 16 hours during which a white precipitate formed. The solution was dried over magnesium sulfate. After filtration, the THF was stripped from the solution and 6.5 g of light yellow polymer isolated which was washed twice with hot water and dried. The molecular weight was determined to be 1600 (by VPO).

Analysis:

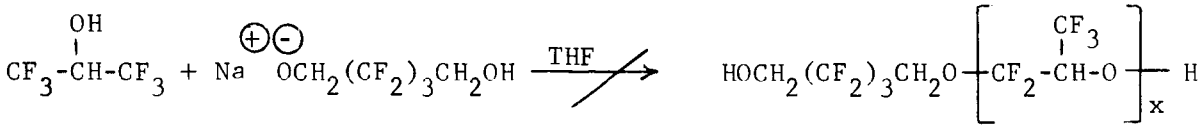
	% C	% H	% F
Calculated for C_3HF_5O:	24.30	0.68	64.1
Found:	19.73	0.69	53.79

(b) At Elevated Temperature

Hexafluoroisopropyl alcohol (33.6 g, 0.2 mole), pulverized sodium hydroxide (8.0 g, 0.2 mole) and 130 ml of THF were mixed overnight at 60°-65°C. The THF was then removed and the residue washed with water, and dried in a vacuum oven at 60°C for 6 hours. The resultant polymer was a light tan semisolid having a melting point of 73°-78°C, with apparent water evolution at 115°-120°C. The yield of the polymer was 14.0 g (47.3%).

When the above reaction was repeated using ether as a replacement for the THF, no reaction occurred.

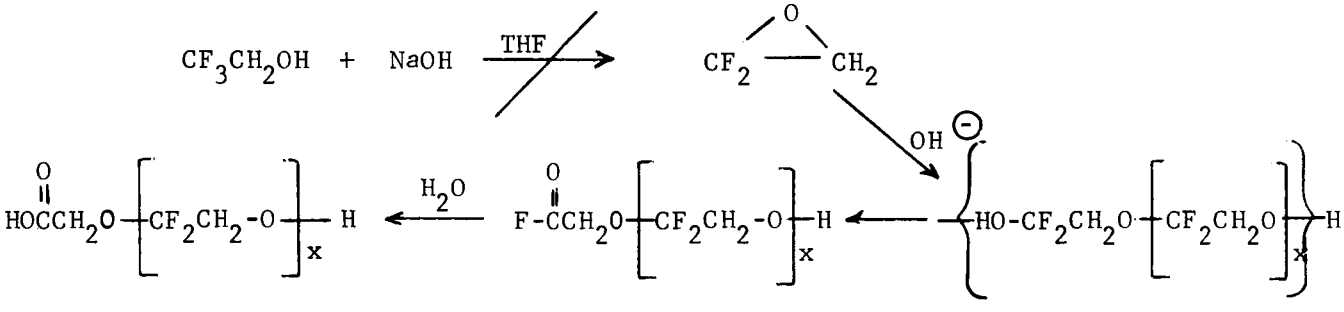
(2) Unsuccessful Attempt Using the Sodium Salt of Hexafluoropentanediol as the Initiator



Hexafluoroisopropyl alcohol (11.6 g, 0.07 mole), the monosodium salt of hexafluoropentanediol (16.4 g, 0.07 mole), and dry THF (50 ml) were mixed for 16 hours at reflux. There was no apparent reaction.

c. Attempted Preparation of Poly(1,1-difluoroethylene oxide)

(1) With Sodium Hydroxide



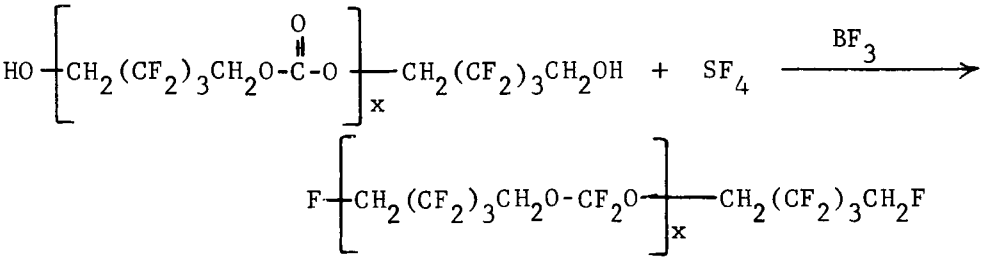
Trifluoroethanol (20.0 g, 0.02 mole) was dissolved in THF (400 ml). Sodium hydroxide (8.0 g, 0.20 mole) was added and the mixture refluxed for 70 hours. After cooling, the pale brown liquid was decanted off the precipitated salts. The solvent was stripped under reduced pressure, yielding a tan semicrystalline material (9.3 g). This was dissolved in water (readily soluble), extracted with ether, and dried over anhydrous magnesium sulfate. None of the desired material was obtained.

(2) With Sodium Salt of Hexafluoropentanediol

The above experiment was repeated with the monosodium salt of hexafluoropentanediol; the same negative results were obtained.

4. By Reaction of Poly(hexafluoropentamethylene carbonate) with Sulfur Tetrafluoride

a. Preparation of the Polyether from Hydroxyl-Terminated Poly(hexafluoropentamethylene carbonate) and Sulfur Tetrafluoride



Poly(hexafluoropentamethylene carbonate) (30.0 g), having a molecular weight of 1845 by VPO, sulfur tetrafluoride (27.0 g), and boron trifluoride (1.0 g) were reacted in a bomb at 200°C for 16 hours. After cooling, the bomb was opened and the ether soluble product washed three times with water. The ether layer was separated, treated with charcoal, and dried over magnesium sulfate. Removal of the solvent under reduced pressure yielded 28 g of light yellow viscous liquid. The infrared spectrum was consistent with the proposed structure except for the presence of some residual carbonate linkages. The molecular weight by VPO was 1015.

Starting Polycarbonate Analysis:

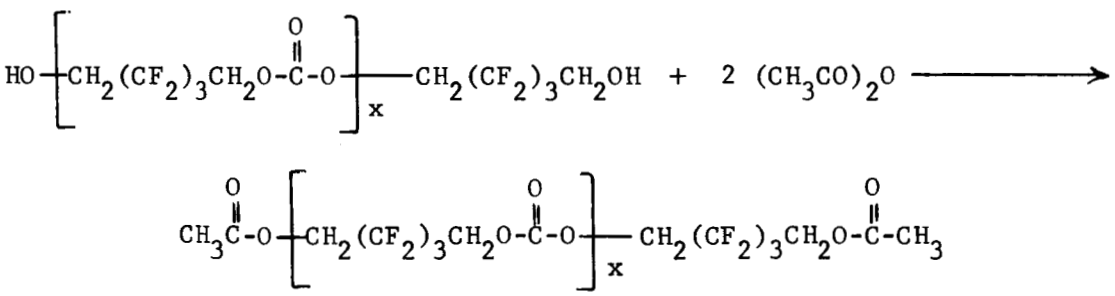
	% C	% H	% F
Calculated for $C_6H_4F_6O_3$:	30.2	1.68	47.9
Found:	30.43	2.08	45.14

Product Analysis:

Calculated for $C_6H_4F_8O_2$:	27.7	1.54	58.5
Found:	27.94	1.49	55.43

b. Preparation of a Hydroxyl-Terminated Polyether from Poly(hexafluoropentamethylene carbonate)

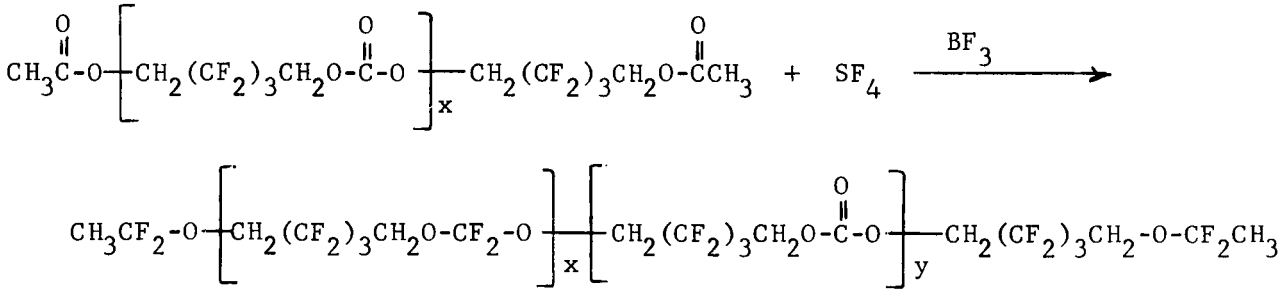
(1) Acetylation of Poly(hexafluoropentamethylene carbonate)



Poly(hexafluoropentamethylene carbonate) (15 g, 0.01 mole, MW 1540 by VPO; OH wt. 940), acetic anhydride (6 g), sodium acetate (1 g), and acetic acid (50 ml) were refluxed for 4 hours. The mixture was cooled and poured into ice water. The organic layer was extracted with ether and washed with 5% sodium carbonate solution. The solution was dried and the ether evaporated leaving a light yellow liquid (13.5 g) which crystallized on standing. The infrared spectrum indicated that no hydroxyl groups were present in the product. The molecular weight (by VPO) was 1880.

Analysis:	% C	% H	% F
Calculated:	31.3	2.0	46.3
Found:	32.11	1.75	45.37

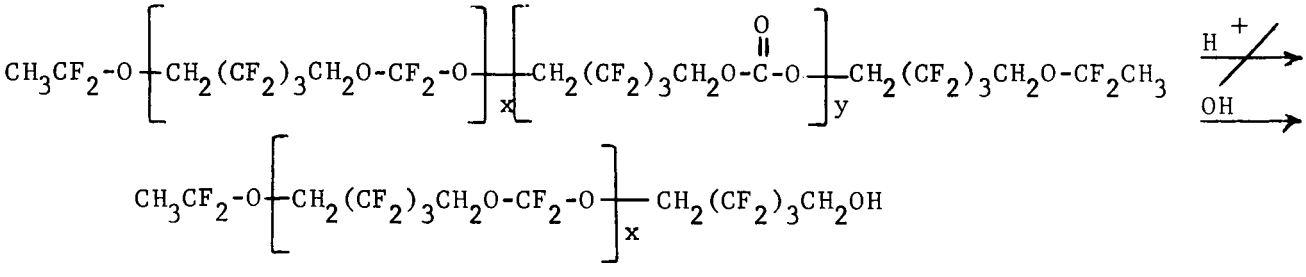
(2) Reaction of Acetylated Polycarbonate with Sulfur Tetrafluoride



A 75-ml stainless steel bomb, charged with the acetylated polyester (12.5 g), (MW 1880 by VPO) (described in (1) above), sulfur tetrafluoride (12 g), and a trace of boron trifluoride, was heated at 200°C for 16 hours. After cooling, the bomb was opened and the brown liquid recovered was washed with 2% sodium carbonate solution and extracted with ether. The ether extract was treated with charcoal and dried over anhydrous sodium sulfate. The ether was evaporated, yielding 10 g of product. The infrared spectrum still indicated the presence of carbonate groups. The molecular weight (by VPO) was 700, approximately one-half of the molecular weight of the starting polycarbonate.

Analysis:	% C	% H	% F
Calculated for Acetylated Polycarbonate:	31.3	2.0	46.3
Calculated for Polyether, $C_6H_4F_7O_2$:	27.7	1.54	58.5
Found:	26.63	1.51	61.07

(3) Hydrolysis of the Polyether



(a) With Acid

An attempt was made to hydrolyze the acetyl end groups of the polyether by refluxing in hydrochloric acid for 4 hours. There was no apparent reaction.

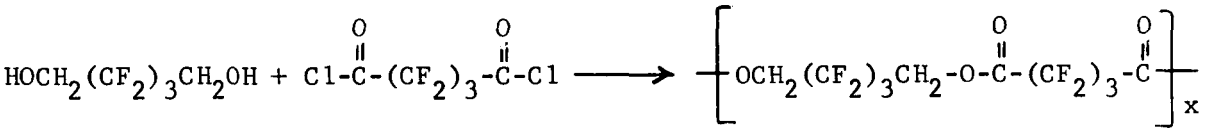
(b) With Base

The polyether of 700 molecular weight (20 g) and 33% aqueous potassium hydroxide (75 g) were refluxed in THF (50 ml) for 1 hour. The polymer was extracted with ether, washed twice with water and treated with charcoal. The ether was dried over anhydrous magnesium sulfate and stripped to yield a light brown liquid (16.0 g). The infrared spectrum contained the expected hydroxyl absorption with an absence of any carbonyl absorption. The molecular weight by VPO was 625, and the hydroxyl equivalency was 665.

Analysis:	% C	% H	% F
Calculated for $C_{14.5}H_{13}F_{18}O_{4.5}$:	29.0	2.18	57.0
Found:	28.08	1.96	59.91

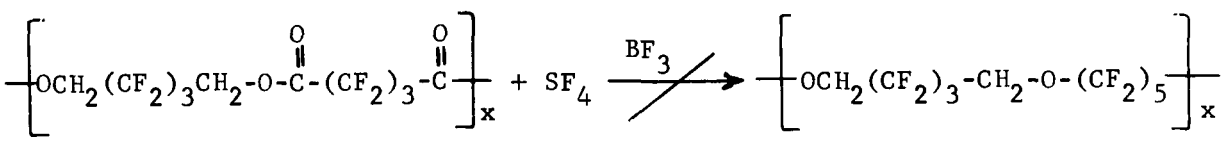
5. By Reaction of Poly(hexafluoropentamethylene perfluoroglutarate) with Sulfur Tetrafluoride

a. Preparation of Poly(hexafluoropentamethylene perfluoroglutarate)



Hexafluoropentanediol (101.6 g, 0.48 mole) and perfluoroglutaryl chloride (110.8 g, 0.4 mole) were stirred at 78°C for 2 hours, followed by 16 hours at 110°-120°C. Hydrogen chloride evolution was observed as soon as the diol went into solution at 78°C. The temperature was then increased to 200°C for 2 hours and the excess diol stripped under reduced pressure at 200°-210°C during 6 hours. A 76% yield (150 g) of a pale yellow viscous liquid was obtained which crystallized on standing. The molecular weight by VPO was 3244.

b. Reaction of Poly(hexafluoropentamethylene perfluoroglutarate) with Sulfur Tetrafluoride

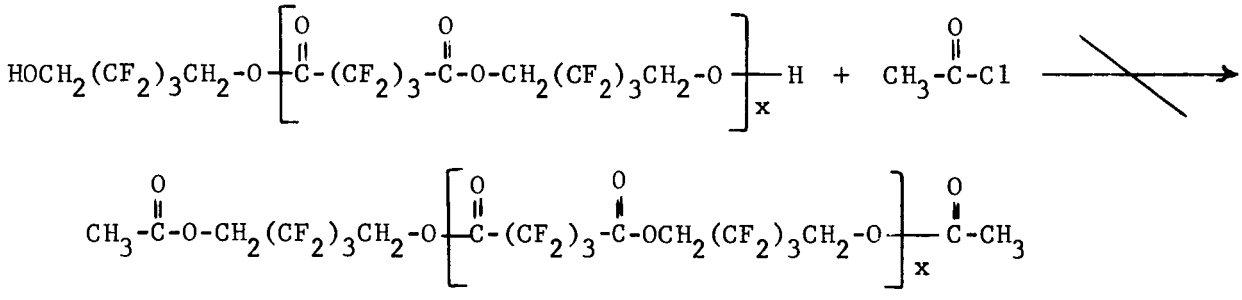


Poly(hexafluoropentamethylene perfluoroglutarate) of 4020 molecular weight (20 g), sulfur tetrafluoride (20 g), and boron trifluoride (0.5 g) were reacted in a bomb for 16 hours at 200°C. The bomb was cooled and the white product dissolved in ether, then washed three times with water. The ether solution was dried with magnesium sulfate and 19 g of product was obtained after removal of the solvent. The infrared spectrum indicated a decrease in the hydroxyl and carbonyl peaks. The molecular weight, as determined by VPO, was 1760.

Analysis:

	% C	% H	% F
Calculated for Polyester:	29.4	0.98	56.0
Calculated for Polyether:	26.1	0.87	66.0
Found:	28.08	1.38	56.73

c. Attempted Acetylation of the Hydroxyl-Terminated Poly(hexafluoropentamethylene perfluoroglutarate)



(1) With Acetyl Chloride

Hydroxyl-terminated poly(hexafluoropentamethylene perfluoroglutarate) of 3244 molecular weight (15 g) and acetyl chloride (15 g) were refluxed for 4 hours. The excess acetyl chloride was then removed. The infrared spectrum of the viscous liquid remaining was identical to that of starting material, except for a slight decrease in the hydroxyl peak. The molecular weight by VPO was 4195.

(2) With Acetyl Chloride in Pyridine

The above reaction was repeated using pyridine as an acid acceptor as follows: The polyester (20 g) was dissolved in 50 ml of pyridine. Acetyl chloride (15 g) was slowly added and the mixture reacted at 80°C for 4 hours, cooled and poured into 500 ml of 10% hydrochloric acid. The product was extracted with ether, washed twice with water, and dried over magnesium sulfate. A black viscous liquid was obtained after removal of the ether. The polyester apparently depolymerized under the basic conditions.

(3) With Acetic Anhydride

The procedure described above for the acetylation of hydroxyl-terminated poly(hexafluoropentamethylene carbonate) was followed with poly-(hexafluoropentamethylene perfluoroglutarate). Degradation of the polyester occurred.

D. Monomers

1. Preparation of the Dilithium Salt of Hexafluoropentanediol

a. From n-Butyl Lithium (Prepared from n-butyl bromide)

$$2\ Li + CH_3CH_2CH_2CH_2Br \longrightarrow CH_3CH_2CH_2CH_2Li + LiBr$$

$$2\ CH_3CH_2CH_2CH_2Li + HOCH_2(CF_2)_3CH_2OH \not\longrightarrow$$

$$Li^{\oplus\ominus}\ OCH_2(CF_2)_3CH_2O^{\ominus\oplus}\ Li + 2\ CH_3CH_2CH_2CH_3\uparrow$$

Dry ether (500 ml) containing lithium metal (8.6 g, 1.25 mole) was cooled to -10°C, then n-butyl bromide (69.0 g, 0.5 mole) was added over a 1-1/2-hour period with stirring under nitrogen. The solution was warmed to +10°C and stirred for 1 additional hour, then placed in a refrigerator overnight. It was then filtered through glass wool.

Hexafluoropentanediol (42.4 g, 0.2 mole) in ether (200 ml) was added to this n-butyl lithium solution at 5°C over a 4-hour period. A small amount of fine white solid formed and was filtered off. Hexane was added to the ether solution causing precipitation of 62.3 g of a white solid. Analysis showed that 65% of this solid was lithium bromide and the remainder was probably the monolithium salt of hexafluoropentanediol. The equivalent weight of the solid was 720. This amounts to an equivalent weight of 250 when corrected for lithium bromide content (theoretical equivalent weight for the dilithium salt = 112; for the monolithium salt = 224).

b. From Methyl Lithium (Prepared from methyl bromide)

Hexafluoropentanediol (84.8 g, 0.4 mole) was dissolved in 1 ℓ of ether. Methyl lithium (2.15 M solution, 466 ml, 1.0 mole) in ether was slowly added over a 2-hour period. There was a very vigorous evolution of gas, and a dense white precipitate formed. Stirring was continued for an additional 2 hours. The product was filtered off and dried under vacuum in a dessicator for 16 hours. The solid product obtained weighed 121 g (theoretical yield = 89.6 g) and had an equivalent weight of 172.7 (theoretical equivalent weight = 112). The excess material was lithium bromide which was in the original methyl

lithium solution as the soluble complex salt. Elemental analysis indicated a complex product with the possibility of an ether of crystallization being present.

c. Preparation of Methyl Lithium Solution

Lithium metal ribbon (13.96 g, 2.00 mole) was cut into approximately 1/16-in. x 1/2-in. pieces and dropped into dry ether under an argon flush. The clean lithium chunks were filtered off and transferred to a 2-ℓ flask fitted with an argon inlet, condenser, low temperature thermometer, and stirrer and containing anhydrous ether (1000 ml). The contents of the flask were cooled to -25°C, and methyl chloride (50.5 g, 1.0 mole) was added over a 3-hour period. A white precipitate gradually formed during the addition. Stirring was continued at -25°C, and the slurry was allowed to stand overnight at room temperature. All subsequent operations were carried out in a polyethylene "dry bag" under an argon atmosphere. The precipitate of lithium chloride was filtered off and the resulting ethereal solution analyzed for methyl lithium and chloride ion concentration.

$$\underline{M}_{CH_3Li} = 0.89 \text{ mole/liter} \qquad \underline{M}_{Cl^-} = 0.078 \text{ mole/liter}$$

d. Preparation of the Di-Lithium Salt of Hexafluoropentanediol

Hexafluoropentanediol (74.2 g, 0.35 mole) was dissolved in ether (300 ml) and added to the stirred methyl lithium solution from above (850 ml, 0.89 $\underline{M}$ = 0.756 mole). The addition was carried out in the "dry bag," under argon, at room temperature. There was a vigorous evolution of gas upon addition and a precipitate began to form after approximately 50 ml of the diol solution had been added. The addition was carried out over a 4-hour period. Another 1000 ml of ether were added to facilitate stirring, and the stirring was continued for 3 additional hours. The semigelatinous solid was filtered off and transferred (wet) to a vacuum desiccator and dried (at 1 mm Hg) overnight. The resulting solid material was broken up and again stripped of solvent, yielding 82 g of product. The equivalent weight was 118.2 g/equivalent (theory = 112 g/equivalent).

2. Preparation of Hexafluoroisopropyl Alcohol

$$CF_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CF_3 + NaBH_4 \longrightarrow CF_3\text{-}\overset{\overset{OH}{|}}{CH}\text{-}CF_3$$

Into a 1000-ml, three-necked flask equipped with stirrer, thermometer, and addition funnel were introduced freshly distilled diglyme (250 ml) and sodium borohydride (20 g). The mixture was heated to 100°C to allow solution of the hydride. The solution was cooled and hexafluoroacetone (approximately 75 g) was added during 2 hours. After the addition was finished it was stirred for 2 hours at room temperature and heated to 50°-70°C for 1 hour to

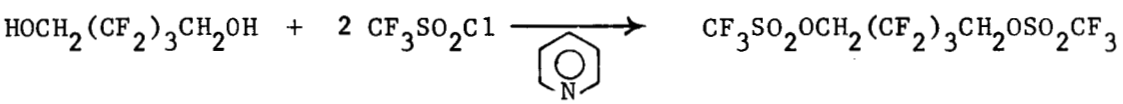
remove unreacted hexafluoroacetone. The cooled solution was poured into 350 ml of 12% hydrochloric acid. The oil that separated was washed with water, dried over magnesium sulfate, and distilled. Fifty grams of material boiling between 58°C and 85°C were collected, which was redistilled yielding 38 g of > 97% pure hexafluoroisopropanol, bp 58°C.

3. Preparation of Hexafluoropentamethylene Oxide

Hexafluoropentamethylene oxide was prepared following the procedure described in Annual Summary Report I.

4. Preparation and Reactions of Hexafluoropentamethylene Bis(trifluoromethane Sulfonate)

a. Preparation of Hexafluoropentamethylene Bis(trifluoromethane sulfonate)

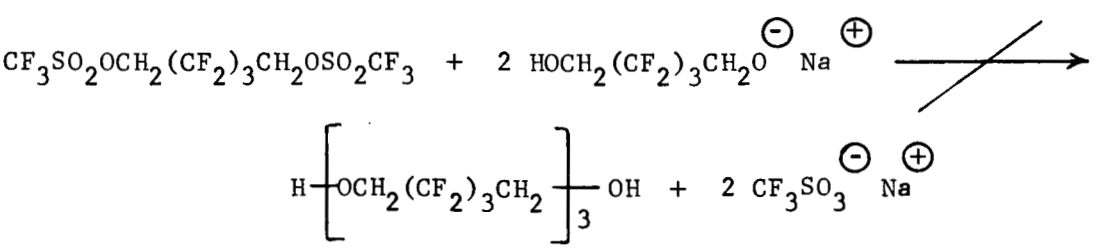


Hexafluoropentanediol (10.6 g, 0.05 mole) and pyridine (8.7 g, 0.11 mole) were dissolved in methylene chloride (50 ml) and charged to the reaction flask. The flask was cooled with an ice-water bath to 10°C. Trifluoromethanesulfonyl chloride (16.8 g, 0.1 mole) in methylene chloride (25 ml) was added at such a rate that the stirred reaction temperature was held between 15°C and 20°C (45 minutes). Pyridine hydrochloride precipitated during the addition. Heat was applied and stirring was continued for 3 hours at reflux (40°C). The reaction mixture was filtered and the solvent stripped under reduced pressure. The crude disulfonate was distilled, the fraction boiling between 90°C and 92°C at 1 mm Hg was collected; 16.4 g (68.5% yield) of product was obtained.

Analysis:	% C	% H	% F	% S
Calculated for $C_7H_4O_6S_2F_{12}$:	17.64	0.84	47.89	13.44
Found:	17.55	0.79	47.76	13.57

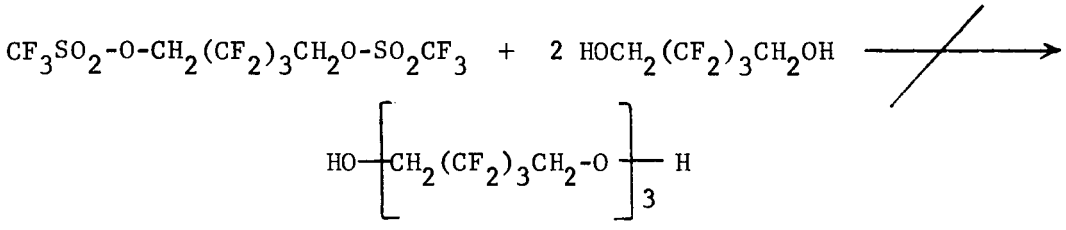
b. Attempted Preparation of Tri(hexafluoropentylene) Glycol

(1) With the Monosodium Salt of Hexafluoropentanediol



The monosodium salt of hexafluoropentanediol (5.85 g, 0.025 mole) was partially dissolved in THF (50 ml). Hexafluoropentamethylene bis(trifluoromethane sulfonate) (4.6 g, 0.01 mole) in THF (25 ml) was added with stirring. There was a slow exotherm to 31°C. When the temperature began to decrease, it was raised to reflux. After 4 hours of reflux, the mixture was cooled, poured into water (200 ml), and acidified. The denser organic layer was separated, dried over anhydrous magnesium sulfate, and distilled. The fraction boiling between 90°C and 103°C (approximately 2 g) was shown to be hexafluoropentamethylene oxide and some hexafluoropentanediol. Subsequent distillation, under reduced pressure, of the remaining material, resulted in recovery of more diol. None of the desired material was recovered.

(2) With Hexafluoropentanediol



(a) In Diglyme

Hexafluoropentanediol (5.1 g, 0.024 mole) and hexafluoropentamethylene-bis(trifluoromethane sulfonate) (5.5 g, 0.0115 mole) were dissolved in triglyme (50 ml) (bp 192°-193°C). The solution was refluxed overnight. At the end of this time, the temperature (at reflux) was only 130°C. The solution was then distilled under atmospheric pressure until the pot temperature was 195°C. Several cuts were obtained but none of these were fluorine-containing materials. Distillation was continued under reduced pressure. The fraction boiling between 85°C and 95°C at 1 mm Hg was collected (9.7 g). Upon standing, a white solid precipitated. This was filtered off (4.3 g) and identified as hexafluoropentanediol by infrared spectroscopy. The filtrate was washed quickly with dilute sodium hydroxide, then with water and dried over anhydrous magnesium sulfate. The infrared spectrum of this liquid was identical to that of the starting disulfonate ester.

(b) In DMF

Hexafluoropentamethylene bis(trifluoromethane sulfonate) (3.3 g, 0.007 mole) and hexafluoropentanediol (4.24 g, 0.02 mole) were refluxed for 18 hours in 25 ml of DMF. Most of the DMF was then stripped off on the rotary evaporator. The remaining solution was distilled under vacuum, yielding 2.4 g of a liquid, boiling at 92°-94°C at 1.5 mm Hg, and 4.0 g of a brown solid as residue. None of the desired product was isolated.

c. Attempted Preparation of 3,3,4,4,5,5-Hexafluoropimelonitrile

$$CF_3CO_2OCH_2(CF_2)_3CH_2OSO_2CF_3 + \underset{(2NaCN)}{2\ KCN} \xrightarrow{DMF} \not\rightarrow$$

$$NCCH_2(CF_2)_3CH_2CN + 2\ CF_3SO_3^{\ominus}\ K^{\oplus}$$

(1) With Potassium Cyanide

Potassium cyanide (1.6 g, 0.028 mole) was dissolved in DMF (50 ml) and charged to a reaction flask. Hexafluoropentamethylene-bis(trifluoromethane sulfonate) (4.7 g, 0.01 mole) in DMF (25 ml) was added. The solution became dark red upon addition. The stirred solution was heated to 80°C and held at that temperature for 6 hours, then was allowed to cool and stand overnight. The dark brown mixture was poured into water (200 ml). There were no insolubles. The aqueous mixture was extracted with three 50-ml portions of ether, the ether extracts dried over anhydrous magnesium sulfate and the solvent stripped under reduced pressure. A small amount (< 1 g) of dark brown liquid which was shown to be DMF and < 1 g of fluorine containing material were isolated which showed no nitrile peak by infrared spectroscopy.

(2) With Sodium Cyanide

Hexafluoropentamethylene bis(trifluoromethane sulfonate)(3.3 g, 0.007 mole) and sodium cyanide (2.0 g, 0.04 mole) were refluxed in 25 ml of DMF for 18 hours. There was no apparent reaction.

5. Perfluoropropylene Oxide

a. Improved Preparation of Perfluoropropylene Oxide

$$CF_3\text{-}CF{=}CF_2 + H_2O \xrightarrow{OH^-} CF_3\text{-}\underset{\diagdown\ O\ \diagup}{CF}\text{-}CF_2$$

1. Potassium hydroxide (100.8 g, 1.8 mole), methanol (900 ml), and water (180 ml) were charged to a three-necked flask equipped with a dry ice-acetone condenser, thermometer and stirrer. The solution was cooled to -35°C, and 590 ml of 30% hydrogen peroxide was added. At a solution temperature of -40°C, perfluoropropylene (144.0 g, 0.95 mole) was added as a liquid. The solution was stirred for 2-1/2 hours at a temperature of between -35°C and -40°C. The product was distilled and collected in dry ice — acetone traps as the solution temperature was allowed to rise to +10°C over a 1-hour period. The mixture of epoxide and unreacted olefin was then distilled from the traps to a stainless steel bomb. The yield of crude product was 72.4 g.

2. This reaction was run exactly as above, except that the time allowed for stirring the solution at temperatures between -35°C and -40°C was 2-3/4 hours, and time for collection of product was 1-1/2 hours. The weight of crude product obtained was 73.0 g. However, the infrared spectrum showed a marked improvement in the ratio of epoxide to olefin over the previous run.

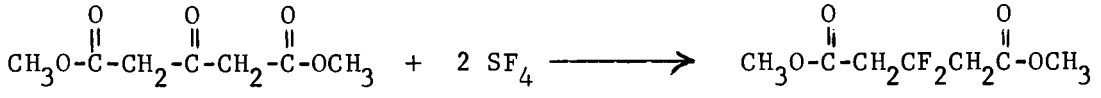
b. Attempted Purification of Crude Perfluoropropylene Oxide

A mixture of perfluoropropylene oxide and perfluoropropylene (72.4 g total) was bubbled through 200 ml of carbon tetrachloride containing 30 g of bromine at room temperature, the product being collected in a dry ice — acetone trap. The mixture was passed through the bromine solution at a rate of about 1/2 g per minute. Upon completion of the reaction, mercury was added to the collected product to remove any bromine that had been swept over. The product was then distilled into a stainless steel bomb. An infrared spectrum of the product (51.0 g) showed some improvement in the ratio of epoxide to olefin, but the olefin remaining was still a large portion of the total.

c. Purification of Crude Perfluoropropylene Oxide

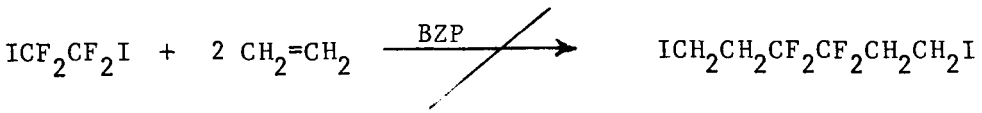
Bromine (30 g) and carbon tetrachloride (1000 ml) were charged to a 2-ℓ flask fitted with a stirrer, thermometer, gas bubble tube, and a dry ice — acetone condenser. A mixture of perfluoropropylene oxide and perfluoropropylene (73.0 g total) was bubbled into the bromine solution at -20°C over a 1/2 hour period. The solution was then held at a gentle reflux for an additional 1-1/2 hours. The product was allowed to distill into a dry ice — acetone trap. Mercury was added to remove any bromine that had been swept over, and the product was redistilled into a stainless steel bomb. An infrared spectrum of the product (24.0 g) showed no olefin remaining.

6. Preparation of Dimethyl Ester of Difluoroglutaric Acid



Sulfur tetrafluoride (21.6 g, 0.2 mole) was condensed into a bomb containing dimethylacetone dicarboxylate (17.4 g, 0.1 mole), and heated in the shaker overnight at 172°C. The excess sulfur tetrafluoride was then allowed to escape. The liquid was removed, the bomb washed with ether, and the ether extract combined with the liquid. Sodium fluoride was added to remove any hydrogen fluoride and filtered. The filtrate was distilled under vacuum to yield 4.5 g of a yellow liquid boiling at 60°-64°C at 2 mm Hg. The elemental analysis and VPC indicated that this liquid was a mixture of products.

7. Attempted Preparation of 1,6-Diiodo-3,3,4,4-Tetrafluorohexane

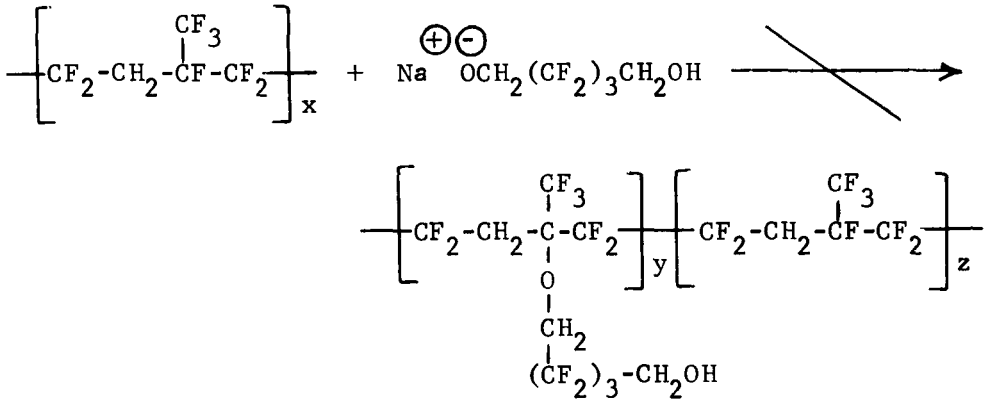


1,2-Diiodotetrafluoroethane (35.4 g, 0.1 mole) was charged to a 300-ml stainless steel bomb. Benzoyl peroxide (BZP)(0.1 g) was added and the bomb was cooled in liquid nitrogen. The bomb was then repeatedly purged with dry nitrogen and evacuated. Ethylene (8.1 g, 0.29 mole) was condensed in and the sealed bomb transferred to a heated shaker mechanism. The bomb was heated to 127°C and held at this temperature for 10 hours. After cooling, the volatile materials were vented (8.0 g of unreacted ethylene) and the contents of the bomb transferred to a distillation flask. Distillation of this material yielded only unreacted 1,2-diiodotetrafluoroethane and some iodine.

The reaction was repeated three times with the same results.

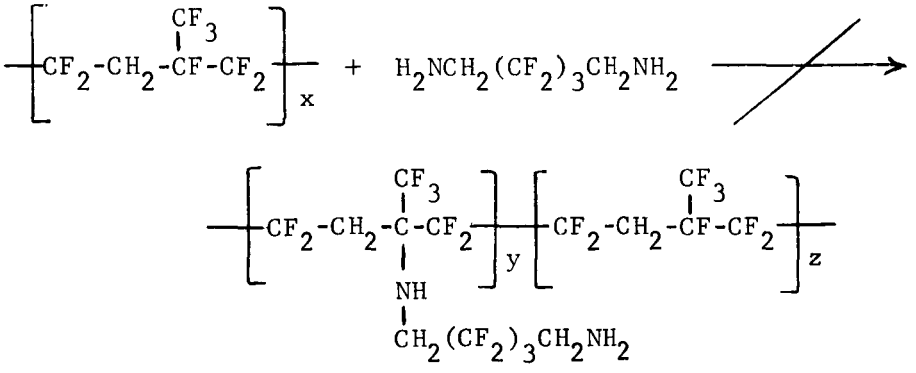
8. Reactions of Viton LM

a. Attempted Reaction of Viton LM with the Monosodium Salt of Hexafluoropentanediol



Viton LM, having a molecular weight of 2520 (25.2 g, 0.01 mole), the monosodium salt of hexafluoroepntanediol (7.0 g, 0.03 mole) and dimethyl-acetamide (DMAC) (30 ml) were mixed at 150°C overnight. Based on the infrared spectrum, there was no reaction.

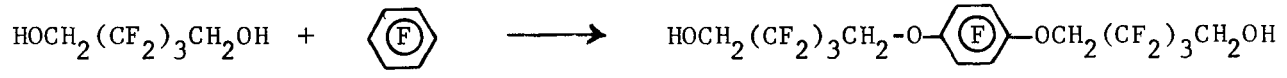
b. Attempted Reaction of Viton LM with Hexafluoropentanediamine



Viton LM (25.2 g, 0.01 mole) and hexafluoropentanediamine (6.3 g, 0.03 mole) were mixed at 190°-210°C for 24 hours under nitrogen. There was no apparent reaction.

9. Attempted Preparation of 1,4-Bis(5-hydroxyhexafluoropentoxy)tetrafluorobenzene

a. By Reaction of Hexafluorobenzene and Hexafluoropentanediol



Hexafluorobenzene (18.6 g, 0.1 mole), hexafluoropentanediol (42.4 g, 0.2 mole), potassium hydroxide (11.2 g, 0.2 mole), and DMF (150 ml) were stirred for 1 hour. The solution temperature rose to 68°C in the first 1/2 hour, then returned to room temperature. The solution was poured into water with stirring, and a white semisolid was recovered from the water. It was dissolved in THF and again poured into water. The product was then dissolved in THF and dried over anhydrous magnesium sulfate. After the THF was removed, the product was frationally distilled (0.5-1.0 mm Hg).

Cut 1 - bp 78°-124°C @ 0.5-1.0 mm - 3.5 g (liquid) - VPO = 370±10 - Hydroxyl equivalent wt = 757

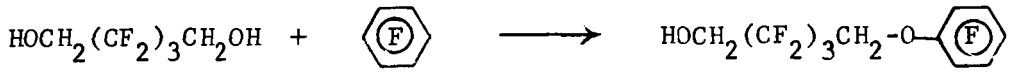
Cut 2 - bp 172°-188°C @ 0.5-1.0 mm - 3.7 g (white solid) - VPO = 525±15 - Hydroxyl equivalent wt = 421

Residue- 20.0 g (brown solid) - VPO = 1040±20- Hydroxyl equivalent wt = 797

A portion of Cut 2, which remained in the distilling head after the distillation, was sent for elemental analysis.

Analysis:	% C	% H	% F
Calculated for $C_{16}H_{10}F_{16}O_4$:	33.6	1.75	53.3
Found:	33.42	1.66	52.32

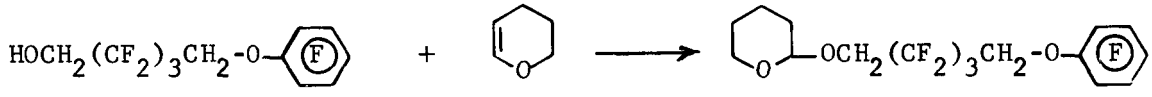
b. Preparation of 5-Hydroxyhexafluoropentoxy-pentafluorobenzene



Hexafluorobenzene (55.8 g, 0.3 mole) and potassium hydroxide (22.4 g, 0.42 mole) were mixed in 250 ml of DMF. Hexafluoropentanediol (42.4 g, 0.2 mole) in 200 ml of DMF was added slowly with stirring over a 1-1/4 hour period. During the addition, the temperature of the solution was held at 16°-18°C by using an ice water bath. The solution was stirred for an additional 30 minutes at 18°C after the addition was completed. The solution was then poured into water, the product extracted with ether and dried over anhydrous magnesium sulfate. The ether was removed and the product vacuum-distilled.

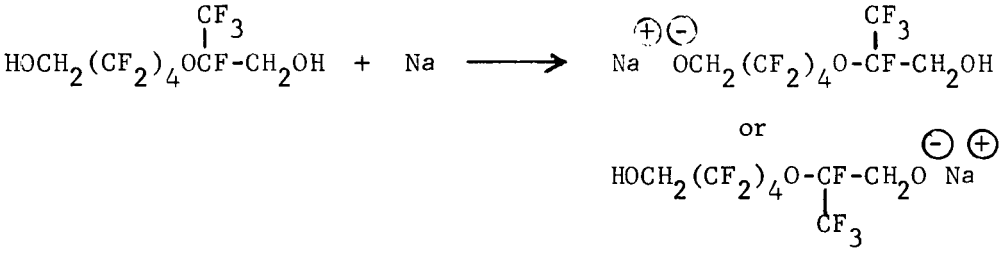
Cut 1 - bp 55°-110°C/8 mm	4.0 g	(primarily DMF)
Cut 2 - bp 115°-170°C/8 mm	14.4 g	(Liquid mono-ether)
Cut 3 - bp 183°-184°C/8 mm	29.5 g	(Crystalline solid)
Residue	25.0 g	

c. Capping of 5-Hydroxyhexafluoropentoxy-pentafluorobenzene with Dihydropyran



The monoether (5.0 g, 0.0132 mole) was refluxed overnight in 13 ml of dihydropyran with 1 drop of concentrated hydrochloric acid as a catalyst. After the solution had cooled, two pellets of potassium hydroxide were added and the solution stirred for 1/2 hour. The solution was poured into water, and the dihydropyran solution separated and dissolved in ether. The ether solution was then dried over magnesium sulfate. Evaporation of the ether under reduced pressure gave 4.5 g of product. The infrared spectrum showed very little remaining hydroxyl, indicating that the reaction proceeded as desired.

10. Attempted Preparation of the Monosodium Salt of 2-Trifluoromethyl-3-oxa-2,4,4,5,5,6,6,7,7-nonafluoro-1,8-octanediol



a. In p-Dioxane

Sodium metal (0.27 g, 0.012 mole) and 2-trifluoromethyl-3-oxa-2,4,4,5,5,6,6,7,7-nonafluoro-1,8-octanediol (5.0 g, 0.012 mole) were refluxed overnight in p-dioxane (50 ml). There was no apparent reaction.

b. In Ether

Sodium metal (0.27 g, 0.012 mole) and 2-trifluoromethyl-3-oxa-2,4,4,5,5,6,6,7,7-nonafluoro-1,8-octanediol (5.0 g, 0.012 mole) were refluxed in 50 ml of ether under nitrogen. After several days, a fine white precipitate had settled out. The solid (0.5 g) was filtered and bottled under nitrogen. The equivalent weight was 335 (calculated equivalent weight, 400).

V. CONCLUSIONS

The polyurethane synthesized by reaction of tetrafluoro-m-phenylene diisocyanate with a hydroxyl-terminated polyether prepared from perfluoropropylene oxide shows real promise as a LOX-compatible adhesive.

The polyurethane synthesized by reaction of tetrafluoro-p-phenylene diisocyanate with a hydroxyl-terminated polyether of hexafluorobenzene and hexafluoropentanediol also shows good potential as a LOX-compatible adhesive.

A usable polyurethane cannot be prepared from the polyether of chloropentafluoroisopropyl alcohol.

The polyurethane prepared by reaction of tetrafluoro-m-phenylene diisocyanate with a hydroxyl-terminated polyurethane from hexafluoropentanediamine and hexafluoropentamethylene bischloroformate was too brittle to be usable as an adhesive.

Considerably cleaner polyethers can be prepared by reaction of hexafluorobenzene with the dilithium salt of hexafluoropentanediol than with hexafluoropentanediol and potassium hydroxide or with the monosodium salt of hexafluoropentanediol.

Contrary to earlier beliefs, DMF is not the only solvent in which hexafluorobenzene reacts with hexafluoropentanediol and potassium hydroxide to give a polyether in good yield; the reaction proceeds well in THF with DMF present only as a catalyst.

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

The reaction of fluorinated polyesters with sulfur tetrafluoride is not a promising method of preparing highly fluorinated polyethers.

VI. RECOMMENDATIONS FOR FUTURE WORK

Work should continue on the optimization of the polyurethane adhesive system based on the polyether from perfluoropropylene oxide.

Work should also continue on the optimization of the polyurethane adhesive system based on the polyether of hexafluorobenzene and hexafluoropentanediol.

Initial experiments indicate that fluoroalkyl polycarbonates react with sulfur tetrafluoride to yield polyethers; the study of this reaction should be continued.

REFERENCES

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2. I. L. Knunyants and M. P. Krasuskaya, Russian Patent 138,604, 1 July 1960, No. 674012/23

3. R. L. Hansen, J. Am. Chem. Soc., 30, 4322 (1965)