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

By

Jerome Hollander, Floyd D. Trischler, Edward S. Harrison
Richard T. Rafter, and Luis Acle

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FOREWORD

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Hollander served as program manager. This report covers the period 1 July
1964 to 30 June 1965.

Prepared by:

Jerome Hollander, PhD
Senior Research Chemist

Floyd D. Trischler
Senior Research Chemist

Approved by:

Rex B. Gosnell, PhD
Research Specialist

S. E. Susman, Manager
Chemical Research Department

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ABSTRACT ~~(Confidential)~~

Nine new highly halogenated polyurethanes and one new highly halogenated polycarbonate have been prepared. These polymers were tested for liquid oxygen (LOX) compatibility along with the seven highly halogenated polymers prepared last year. The results indicate that urethane linkages flanked on the alcohol side by a 1,1-dihydroperfluoroalkyl chain are stable to impact in LOX if the nitrogen is attached to a difluoromethylene, a tetrafluoro-p-phenylene, or a tetrachloro-p-phenylene group. The results also indicate that urethane, amide ,and ester groups do not, in themselves, impart LOX incompatibility. Polyurethanes prepared from hexafluoropentanediol were LOX compatible but those prepared from certain modified diols were LOX incompatible.

A number of other halogenated polymers such as polyamides, polyimides, polyureas, a polyester, a polycarbonate, and a polysulfite have been synthesized.

Preparations of synthetic studies have been carried out on additional monomers and prepolymers including halogenated diisocyanates and polyethers.

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I. SUMMARY

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

The LOX compatibility results obtained on those polymers sent to George C. Marshall Space Flight Center (MSFC) for testing show that the urethane linkage flanked on the alcohol side by a 1,1-dihydroperfluoroalkyl chain is stable to impact in LOX if the nitrogen is attached to a difluoromethylene, a tetrafluoro-p-phenylene, or a tetrachloro-p-phenylene group. Another conclusion which can be drawn from the results is that within a given series of polymers, urethane, amide, and ester groups do not impart LOX incompatibility. All the polyurethanes prepared from hexafluoropentanediol with various diisocyanates were LOX compatible. The polyurethanes containing modified diol portions — i.e., those prepared from hydroxyl-terminated poly(hexafluoropentamethylene carbonate), poly(hexafluoropentamethylene formal), and poly(trifluoropropylene oxide) — were LOX incompatible.

The polyurethane of tetrachloro-p-phenylene diisocyanate and hexafluoropentanediol was prepared, as was that of tetrafluoro-p-phenylene diisocyanate and pentanediol. The reaction of hexafluoropentamethylene-bischloroformate with hexafluoropentanediamine yielded a low molecular weight polyurethane. Polyurethanes were prepared by reaction of hydroxyl-terminated poly(hexafluoropentamethylene adipate) with tetrafluoro-p-phenylene diisocyanate, toluene-2,4-diisocyanate, and 4,4'-diisocyanato-octafluorobiphenyl. Also prepared were the polyurethanes of hydroxyl-terminated poly(hexafluoropentamethylene malonate) with tetrafluoro-p-phenylene diisocyanate and toluene 2,4-diisocyanate. The reaction of hydroxyl-terminated poly(hexafluoropentamethylene carbonate) with tetrafluoro-p-phenylene diisocyanate, toluene-2,4-diisocyanate, and tetrachloro-p-phenylene diisocyanate yielded the corresponding polyurethanes. Polyurethanes were also prepared by the reaction of tetrafluoro-p-phenylene diisocyanate with hydroxyl-terminated poly(hexafluoropentamethylene formal), poly(trifluoropropylene oxide), and the dihemiketal of hexafluoroacetone and hexafluoropentanediol.

The polyamides, polyimides, and polyureas prepared were poly(tetrafluoro-p-phenylene perfluoroglutaramide), poly(hexafluoropentamethylene adipamide), poly(hexafluoropentamethylene pyromellitimide), poly(tetrafluoro-p-phenylene urea), and poly(hexafluoropentamethylene tetrafluoro-p-phenylene urea).

Other polymers prepared were poly(hexafluoropentamethylene carbonate), poly(hexafluoropentamethylene tetrachlorophthalate), and poly(hexafluoropentamethylene sulfite). Attempts to prepare poly(hexafluoropentamethylene ether) and poly(tetrafluorotetramethylene ether) were unsuccessful.

A valuable new approach for the preparation of chloroformates and isocyanates has been discovered. Chlorocarbonyl pyridinium chloride, a crystalline

solid prepared by reaction of phosgene with pyridine, was used to prepare hexafluoropentamethylene-bischloroformate and various halogenated diisocyanates in excellent yields.

Monomers and intermediates which have been prepared for the first time include hexafluoropentamethylene diisocyanate, 4,4'-diisocyanato-octafluorobiphenyl, 2,3,5,6-tetrachloro-p-xylene-α,α'-diisocyanate, chloropentafluoroisopropyl alcohol, hexafluoropentamethylene-bischloroformate, p-aminotetrafluorobenzonitrile.

II. INTRODUCTION

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

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

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

The outstanding characteristics of polyurethanes in elastomers and adhesives for cryogenic application have been observed by several investigators.[1] Highly fluorinated polymers, including Teflon (TFE), FEP, Halon TFE, Kel-F, etc., have also demonstrated cryogenic capability. Although these available materials (such as Teflon) 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 mild curing conditions, or even of curing at ambient temperature. The coupling of this processing requirement with the need for cryogenic performance and LOX compatibility leads to the highly halogenated polyurethanes as the most logical polymer system.

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

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

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

(1) The type and level of halogen 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.

III. DISCUSSION

A. Liquid Oxygen Compatibility

In work performed prior to this report period, four fluorinated poly-
urethanes were prepared, one of which was tested for LOX compatibility. In
addition, two fluorinated polyamides and one fluorinated polyester were
prepared.

During this current report period, the six remaining polymers prepared
last year were tested for LOX compatibility along with eight new fluorinated
polyurethanes and one fluorinated polycarbonate which were synthesized. The
results are shown in tabular form in Section IV.

The four polyurethanes shown below passed the LOX impact test. The
thicknesses of the specimens tested are shown in parentheses.

1. $\left[\begin{matrix}O\\\parallel\\C\end{matrix}-NH(CF_2)_3-NH-\begin{matrix}O\\\parallel\\C\end{matrix}-O-CH_2(CF_2)_3CH_2-O\right]_x$ prepared from $OCN(CF_2)_3NCO$

   and $HOCH_2(CF_2)_3CH_2OH$ (20 mils)

2. $\left[\begin{matrix}O\\\parallel\\C\end{matrix}-NH-\underset{F\ F}{\overset{F\ F}{\bigcirc}}-NH-\begin{matrix}O\\\parallel\\C\end{matrix}-O-CH_2(CF_2)_3CH_2-O\right]_x$ from $OCN-\underset{F\ F}{\overset{F\ F}{\bigcirc}}-NCO$

   and $HOCH_2(CF_2)_3CH_2OH$ (26 mils)

3. $\left[\begin{matrix}O\\\parallel\\C\end{matrix}-NH-\underset{Cl\ Cl}{\overset{Cl\ Cl}{\bigcirc}}-NH-\begin{matrix}O\\\parallel\\C\end{matrix}-OCH_2(CF_2)_3CH_2-O\right]_x$ from $OCN-\underset{Cl\ Cl}{\overset{Cl\ Cl}{\bigcirc}}-NCO$

   and $HOCH_2(CF_2)_3CH_2OH$ (20 mils)

4. $\left[\begin{matrix}O\\\parallel\\C\end{matrix}-NH(CH_2)_6NH-\begin{matrix}O\\\parallel\\C\end{matrix}-O-CH_2(CF_2)_3CH_2-O\right]_x$ from $OCN(CH_2)_6NCO$

   and $HOCH_2(CF_2)_3CH_2OH$ (33 mils)

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Since these polyurethanes were LOX compatible (at least at the thickness tested), the assumption can be made that the urethane linkage flanked on the alcohol side by a 1,1-dihydroperfluoroalkyl chain such as hexafluoropentanediol,

$-NH-\overset{\overset{O}{\|}}{C}-O-CH_2-CF_2-$, is stable to impact in LOX if the nitrogen is flanked by difluoromethylene ($-CF_2-$) (as in polymer 1 above), tetrafluoro-p-phenylene
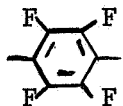
 (as in polymer 2 above), or by tetrachloro-p-phenylene
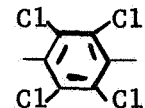
(as in polymer 3 above). The stability of the urethane attached to a methylene chain such as in polymer 4 is questionable, especially since the specimens tested were 33 mils thick.

In order to extend knowledge of the stability of various urethane link-ages, the following two polyurethanes should be prepared.

$$\left[NHCH_2(CF_2)_3CH_2NH-\overset{\overset{O}{\|}}{C}-O-CH_2(CF_2)_3CH_2-O-\overset{\overset{O}{\|}}{C}\right]_x$$
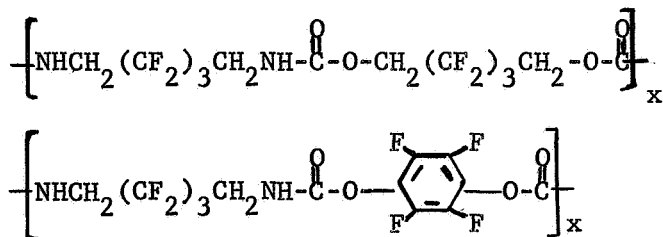
The first of these will provide information on the compatibility of the urethane linkage in which the nitrogen atom is linked to a 1,1-dihydroper-fluoroalkyl chain. Indications are that this type of urethane linkage would be LOX compatible since the two polyamides (5 and 6) shown below passed the LOX impact test.

5. $\left[NHCH_2(CF_2)_3CH_2NH-\overset{\overset{O}{\|}}{C}-(CF_2)_3-\overset{\overset{O}{\|}}{C}\right]_x$ (17 mils)

6. $\left[NHCH_2CH_2NH-\overset{\overset{O}{\|}}{C}-(CF_2)_3-\overset{\overset{O}{\|}}{C}\right]_x$ (20 mils)
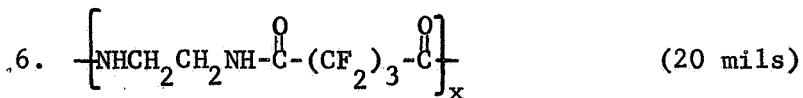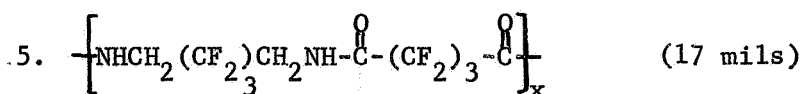
If this first polyurethane is incompatible, the incompatibility could be due to the combined $-CH_2-NH-\overset{\overset{O}{\|}}{C}-O-CH_2-$ grouping. Thus it is possible for this polyurethane to be incompatible and the second of the proposed poly-urethanes compatible.

The one polyester which was tested, poly(hexafluoropentamethylene perfluoro-glutarate) (7), was compatible at a thickness of 20 mils.

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

6
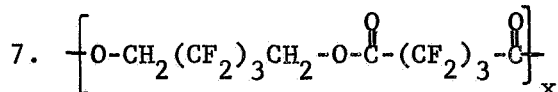
Polyesters of this type (i.e., those prepared from perfluorinated acids) are known to be hydrolytically unstable.[2-4] Hydroxyl-terminated polyesters were prepared from hexafluoropentanediol and the nonfluorinated acids, malonic and adipic. The polyurethanes prepared from these polyesters (polyurethanes 8-10) were all LOX incompatible.

$$8. \left\{ NH - \underset{F}{\overset{F}{\underset{F}{\overset{F}{\bigcirc}}}} - \underset{CH_3}{N} - \overset{O}{\overset{\|}{C}} - NH - \bigcirc - NH - \overset{O}{\overset{\|}{C}} - \left[OCH_2(CF_2)_3 CH_2 O - \overset{O}{\overset{\|}{C}} - CH_2 - \overset{O}{\overset{\|}{C}} \right]_x OCH_2(CF_2)_3 CH_2 - O - \overset{O}{\overset{\|}{C}} - NH - \bigcirc - \underset{CH_3}{NH} - \overset{O}{\overset{\|}{C}} \right\}_y$$

$$9. \left\{ \overset{O}{\overset{\|}{C}} - NH - \underset{CH_3}{\bigcirc} - NH - \overset{O}{\overset{\|}{C}} - \left[OCH_2(CF_2)_3 CH_2 O - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} \right]_x OCH_2(CF_2)_3 CH_2 - O \right\}_y$$

$$10. \left\{ \overset{O}{\overset{\|}{C}} - NH - \underset{F}{\overset{F}{\underset{F}{\overset{F}{\bigcirc}}}} - NH - \overset{O}{\overset{\|}{C}} - O - \left[CH_2(CF_2)_3 CH_2 - O - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} - O \right]_x CH_2(CF_2)_3 CH_2 - O - \overset{O}{\overset{\|}{C}} - NH \right.$$

$$\left. \underset{y}{\left\{ NH - \underset{F}{\overset{F}{\underset{F}{\overset{F}{\bigcirc}}}} - NH - \overset{O}{\overset{\|}{C}} - N - \underset{F}{\overset{F}{\underset{F}{\overset{F}{\bigcirc}}}} \right. \right.$$
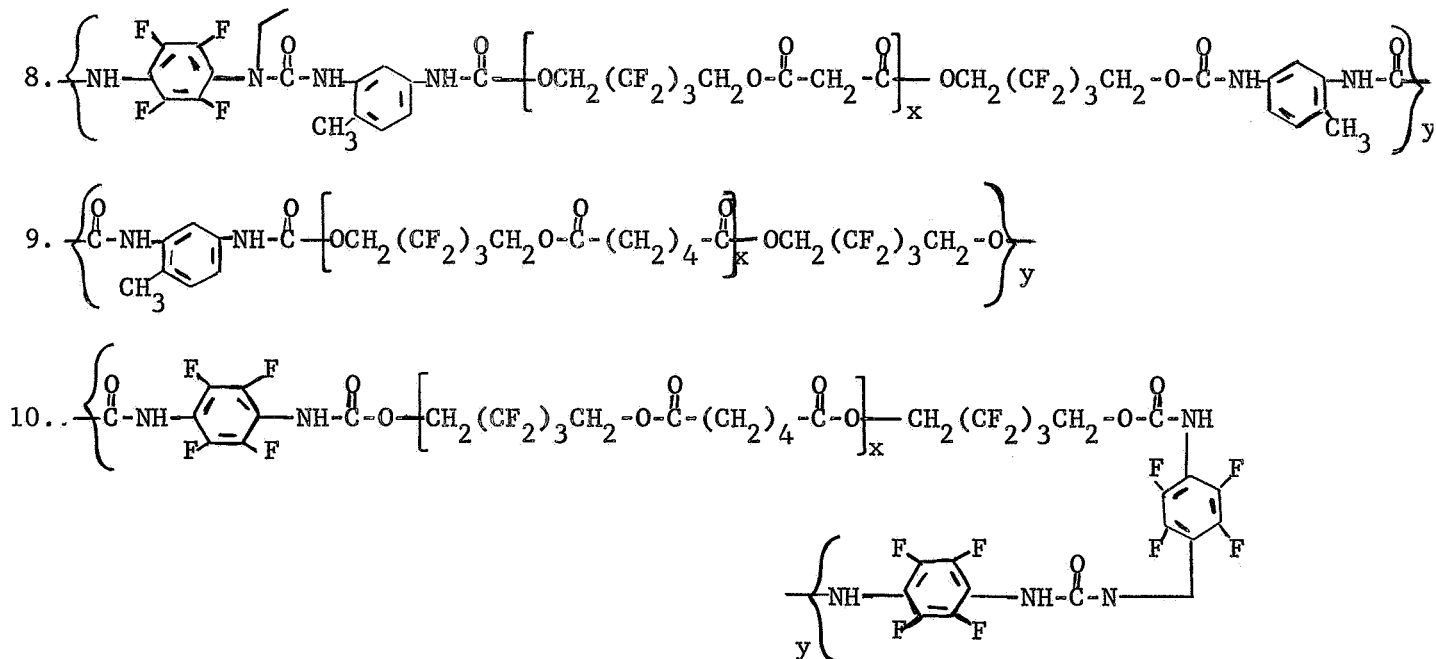
The incompatibility of polyurethanes 8 and 9 could be due to the toluene diisocyanate moiety or to the polyester portion of the polymer. Polyurethane 10, however, must be incompatible due to the polyester portion, since polyurethane 2 (from tetrafluoro-p-phenylene diisocyanate and hexafluoropentanediol) is LOX compatible.

The general structure of polymers 1, 5, and 7 is as follows:

$$\left[CH_2 - (CF_2)_3 - CH_2 - A - (CF_2)_3 - A \right]_x$$

$$A = -O - \overset{O}{\overset{\|}{C}} - NH - \quad \text{(Polyurethane)(Polymer 1)}$$

$$-NH - \overset{O}{\overset{\|}{C}} - \quad \text{(Polyamide)(Polymer 7)}$$

$$-O - \overset{O}{\overset{\|}{C}} - \quad \text{(Polyester)(Polymer 9)}$$
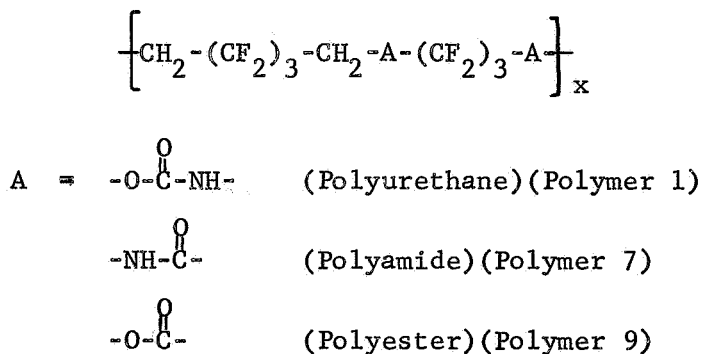
Because all three of these polymers passed the LOX test, it can be concluded that within a given series of polymers, urethane, amide, and ester groups do not impart LOX incompatibility.

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All the polyurethanes prepared from hexafluoropentanediol with various diisocyanates (polyurethanes 1, 2, 3, and 4) were LOX compatible. In order to prepare polyurethanes possessing usable properties, such as flexibility, the diol portion was modified by using a partially fluorinated polycarbonate, a polyformal, and a polyether. The resulting polyurethanes (11 through 16) were all LOX incompatible.

11. $\left\{ \begin{matrix} O \\ \| \\ C \end{matrix} - N - \begin{matrix} F \\ \bigcirc \\ F \end{matrix} \begin{matrix} F \\ \\ F \end{matrix} - NH - \begin{matrix} O \\ \| \\ C \end{matrix} - OCH_2(CF_2)_3CH_2 - O - \left[CH_2 - O - CH_2(CF_2)_3CH_2 - O \right]_x \right\}_y$

12. $\left\{ \begin{matrix} O \\ \| \\ C \end{matrix} - N - \begin{matrix} F \\ \bigcirc \\ F \end{matrix} \begin{matrix} F \\ \\ F \end{matrix} - NH - \begin{matrix} O \\ \| \\ C \end{matrix} - OCH_2(CF_2)_3CH_2 - O - \left[\begin{matrix} CF_3 \\ | \\ CH \end{matrix} - CH_2 - O \right]_x \right\}_y$

13. $CH_3 - \bigcirc \begin{matrix} OCN \\ \end{matrix} - NH - \begin{matrix} O \\ \| \\ C \end{matrix} - \left[O - CH_2(CF_2)_3CH_2 - O - \begin{matrix} O \\ \| \\ C \end{matrix} \right]_x - OCH_2(CF_2)_3CH_2 - O - \begin{matrix} O \\ \| \\ C \end{matrix} - NH - \bigcirc \begin{matrix} NCO \\ \end{matrix} - CH_3$
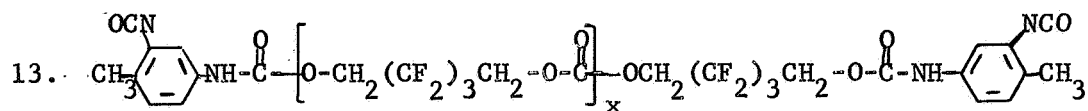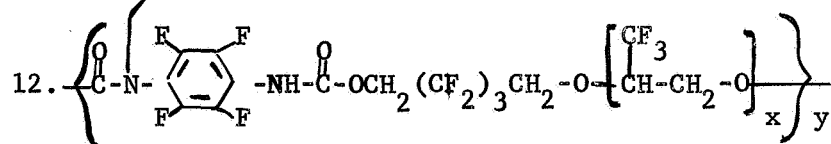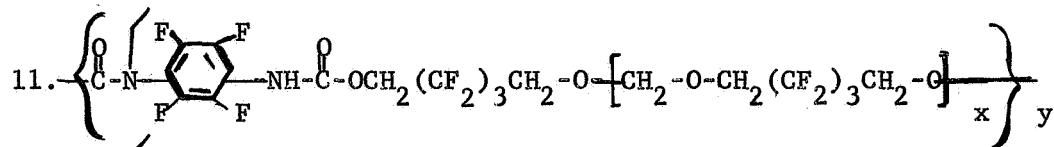
14. Previous prepolymer cured with tetrafluoro-p-phenylenediamine

15. $\left\{ \begin{matrix} O \\ \| \\ C \end{matrix} - N - \begin{matrix} F \\ \bigcirc \\ F \end{matrix} \begin{matrix} F \\ \\ F \end{matrix} - NH - \begin{matrix} O \\ \| \\ C \end{matrix} - \left[OCH_2(CF_2)_3CH_2 - O - \begin{matrix} O \\ \| \\ C \end{matrix} \right]_x - OCH_2(CF_2)_3CH_2 - O \right\}_y$
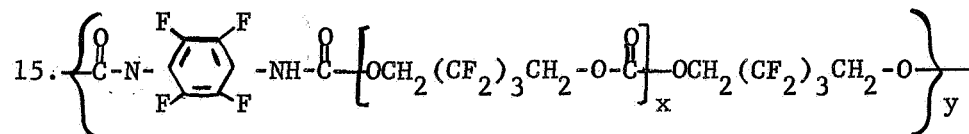
16. Previous polymer cured with tetrafluoro-p-phenylenediamine

Although the polyether-based polyurethanes (11 and 12) are LOX incompatible, they showed interesting low-temperature properties. It is likely that the incompatibility of 11 is due to the $-CH_2-O-CH_2-O-CH_2-$ structure. The incompatibility of 12 may be due to not enough fluorine in the polyether or to the lack of fluorine in the polyether backbone. Other polyethers containing more fluorine should be prepared.

Polyurethanes 13 through 16 were all prepared from hydroxyl-terminated poly(hexafluoropentamethylene carbonate). A moderately high molecular weight poly(hexafluoropentamethylene carbonate) (17) was also incompatible. The failure of this polycarbonate in the LOX compatibility test could be due to the carbonate linkage itself $\left(\begin{matrix} O \\ \| \\ -O-C-O- \end{matrix} \right)$, the methylene $\left(-CH_2- \right)$ grouping next to the carbonate link, or the combination of the two methylenes and the carbonate link $\left(\begin{matrix} O \\ \| \\ -CH_2-O-C-O-CH_2- \end{matrix} \right)$. Because this aliphatic polycarbonate and the polyurethanes prepared from it show interesting low-temperature properties, the reason for the incompatibility should be determined. LOX compatibility results of the following two polycarbonates (18 and 19) would pinpoint the cause of incompatibility in the aliphatic polycarbonate and in fluorinated polycarbonates in general.

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18. $\left[-O-\underset{\underset{F}{\overset{F}{|}}}{\underset{F}{\overset{F}{\bigcirc}}}-O-\overset{O}{\overset{\|}{C}}- \right]_x$

19. $\left[-O-\underset{\underset{F}{\overset{F}{|}}}{\underset{F}{\overset{F}{\bigcirc}}}-O-\overset{O}{\overset{\|}{C}}-O-CH_2(CF_2)_3CH_2-O-\overset{O}{\overset{\|}{C}}- \right]_x$
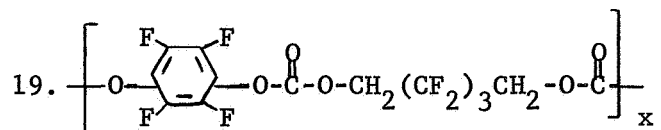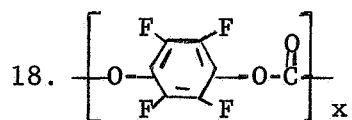
The polyurethanes that were LOX compatible were all 20 to 30 mils thick. The later specimens, all of which were 10 mils thick, failed to pass the compatibility test. In order to determine the reliability of the assumption that polyurethanes 1, 2, and 3 are compatible, polyurethane 2 will be tested at 10 mils and polyurethanes 12 and 15 at 30 mils. The LOX compatibility results of these three polyurethanes would then be available both at 10- and 30-mil thicknesses.

B. Polyurethanes

1. From Hexafluoropentanediol

A new highly fluorinated polyurethane, poly(hexafluoropentamethylene perfluorotrimethylene dicarbamate), was prepared on this program prior to this report period by reaction of perfluorotrimethylene diisocyanate and hexafluoropentanediol.

$$OCN(CF_2)_3NCO + HOCH_2(CF_2)_3CH_2OH \rightarrow \left[\overset{O}{\overset{\|}{C}}-NH(CF_2)_3NH-\overset{O}{\overset{\|}{C}}-O-CH_2(CF_2)_3CH_2-O- \right]_x$$
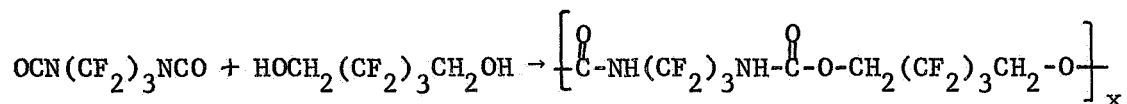
This polyurethane, although LOX compatible, was hydrolytically unstable. A polyurethane which was hydrolytically stable while still retaining LOX compatibility was prepared by using tetrafluoro-p-phenylene diisocyanate.

$$OCN-\underset{\underset{F}{\overset{F}{|}}}{\underset{F}{\overset{F}{\bigcirc}}}-NCO + HOCH_2(CF_2)_3CH_2OH \rightarrow \left[\overset{O}{\overset{\|}{C}}-NH-\underset{\underset{F}{\overset{F}{|}}}{\underset{F}{\overset{F}{\bigcirc}}}-NH-\overset{O}{\overset{\|}{C}}-OCH_2(CF_2)_3CH_2-O- \right]_x$$
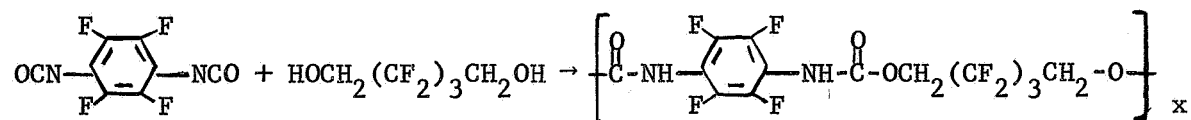
In a continuing program of preparation of polyurethanes containing various amounts and types of halogens, two new polyurethanes of this type, poly(hexafluoropentamethylene tetrachloro-p-phenylene dicarbamate) and poly(pentamethylene tetrafluoro-p-phenylenedicarbamate) were prepared this year. The former was prepared by reaction of tetrachloro-p-phenylene diisocyanate and hexafluoropentanediol.

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$$\text{OCN}\!-\!\underset{\underset{\text{Cl}\quad\text{Cl}}{}}{\overset{\overset{\text{Cl}\quad\text{Cl}}{}}{\bigcirc}}\!-\!\text{NCO} \quad + \quad \text{HOCH}_2(\text{CF}_2)_3\text{CH}_2\text{OH} \longrightarrow$$

$$\left[\underset{}{\overset{O}{\overset{\|}{\text{C}}}}\!-\!\overset{H}{\text{N}}\!-\!\underset{\underset{\text{Cl}\quad\text{Cl}}{}}{\overset{\overset{\text{Cl}\quad\text{Cl}}{}}{\bigcirc}}\!-\!\overset{H}{\text{N}}\!-\!\overset{O}{\overset{\|}{\text{C}}}\!-\!\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{O} \right]_x$$
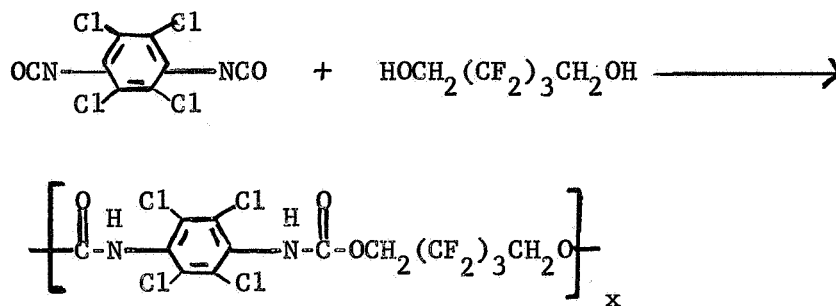
The polymer was a brown, brittle solid with a melting point of $190°\text{-}196°\text{C}$. Sample wafers were prepared and tested by MSFC for LOX compatibility. This polyurethane was LOX compatible. The tetrachloro-p-phenylene diisocyanate was prepared previously from tetrachloroterephthaloyl chloride by way of the Curtius reaction in 95% yield. This preparation was described in Annual Summary Report I (July 1964).

Poly(pentamethylene tetrafluoro-p-phenylenedicarbamate) was prepared by reaction of tetrafluoro-p-phenylene diisocyanate and 1,5-pentanediol in ethyl acetate solution.

$$\text{OCN}\!-\!\underset{\underset{\text{F}\quad\text{F}}{}}{\overset{\overset{\text{F}\quad\text{F}}{}}{\bigcirc}}\!-\!\text{NCO} \;+\; \text{HO(CH}_2)_5\text{OH} \qquad \left[\overset{O}{\overset{\|}{\text{C}}}\!-\!\text{NH}\!-\!\underset{\underset{\text{F}\quad\text{F}}{}}{\overset{\overset{\text{F}\quad\text{F}}{}}{\bigcirc}}\!-\!\text{NH}\!-\!\overset{O}{\overset{\|}{\text{C}}}\!-\!\text{O(CH}_2)_5\!-\!\text{O} \right]_x$$

The polymer was a white crystalline solid, having a melting point of $280°\text{-}281°\text{C}$.

Fluorinated polyurethanes having a methylene group between the urethane nitrogen and the difluoromethylene groups should possess good hydrolytic stability as well as LOX compatibility. The initial plan of preparation of polyurethanes of this type involved the reaction of hexafluoropentamethylene diisocyanate with various diols such as hexafluoropentanediol.
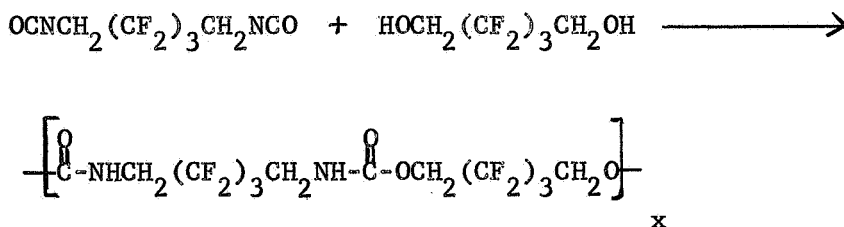
$$\text{OCNCH}_2(\text{CF}_2)_3\text{CH}_2\text{NCO} \;+\; \text{HOCH}_2(\text{CF}_2)_3\text{CH}_2\text{OH} \longrightarrow$$

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

The difficulties encountered in the preparation of hexafluoropentamethylene diisocyanate have hindered the preparation of this type of polyurethane.

An alternate approach involves the reaction of hexafluoropentanediamine with various bischloroformates such as hexafluoropentamethylene bischloroformate.

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Although the preparative method involving hexafluoropentamethylene diisocyanate is preferred (it can be used to prepare prepolymers for adhesive formulations), this alternate approach would yield the polyurethanes of desired structure which can be tested for LOX compatibility.

Poly(hexafluoropentamethylene hexafluoropentamethylenedicarbamate) was prepared by the interfacial polymerization of hexafluoropentamethylene bis-chloroformate and hexafluoropentanediamine.

$$Cl-\overset{O}{\overset{\|}{C}}-OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-Cl \;+\; H_2NCH_2(CF_2)_3CH_2NH_2 \longrightarrow$$

$$\left[NH-CH_2(CF_2)_3CH_2NH-\overset{O}{\overset{\|}{C}}-O-CH_2(CF_2)_3CH_2-O-\overset{O}{\overset{\|}{C}}\right]_x$$
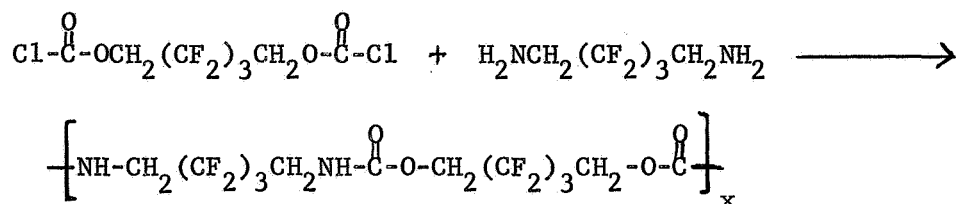
The polymer was an oil of low molecular weight. Apparently, the rate of hydrolysis of the chloroformate is much more rapid than the reaction of the bischloroformate with the diamine when a strong base such as sodium hydroxide is used as the acid acceptor. This polymerization will be attempted using a weaker base.

Another type of polyurethane which might be hydrolytically stable and LOX compatible is the poly-acylurethane. Two possible methods of preparation of a polyacylurethane, such as poly(hexafluoropentamethylene perfluoroglutaryl diisocyanate), are available.

The first method is the reaction of perfluoroglutaryl diisocyanate with hexafluoropentanediol. This method has been discontinued because of difficulties in the preparation of perfluoroglutaryl diisocyanate.

The second method involves the reaction of hexafluoropentamethylene bischloroformate with perfluoroglutaramide.

$$Cl-\overset{O}{\overset{\|}{C}}-OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-Cl \;+\; H_2N-\overset{O}{\overset{\|}{C}}-(CF_2)_3-\overset{O}{\overset{\|}{C}}-NH_2 \longrightarrow$$

$$\left[\overset{O}{\overset{\|}{C}}-OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-NH-\overset{O}{\overset{\|}{C}}-(CF_2)_3-\overset{O}{\overset{\|}{C}}-NH\right]_x$$
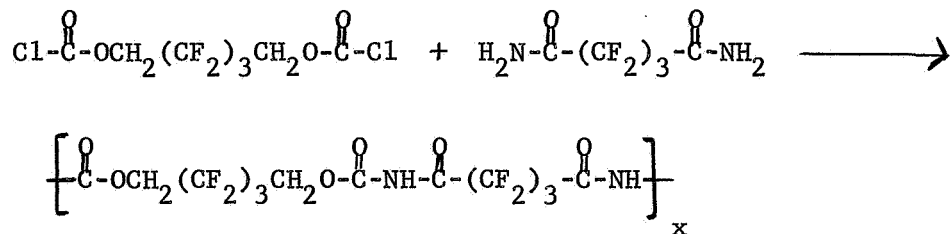
An attempt was made to prepare the polyacylurethane by this method. None of the desired polymer was isolated.

2. **From Hydroxyl-Terminated Polyesters**

a. **From Poly(hexafluoropentamethylene adipate).** — Hydroxyl-terminated polyesters have been commercially used in the preparation of nonfluorinated

polyurethanes.[5,6] Work on fluorine containing esters has shown that esters made from hydrocarbon acids and fluorinated diols possess the greatest hydrolytic stability.[2-4] Therefore, Narmco has limited its investigations to this type of hydroxyl-terminated fluorinated polyester.

In Annual Summary Report I (July 1964), the preparation of a highly elastomeric polyurethane was reported by reaction of toluene diisocyanate with the hydroxyl-terminated polyester of adipic acid and hexafluoropentadiol. This hydroxyl-terminated poly(hexafluoropentamethylene adipate) was reacted during this year with tetrafluoro-p-phenylene diisocyanate in ethyl acetate solution with stannous octoate as catalyst.

$$\text{OCN}-\underset{\underset{F}{F}}{\overset{\overset{F}{F}}{\bigcirc}}-\text{NCO} \;+\; \text{H}-\left[\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{O}-\overset{\text{O}}{\underset{}{\text{C}}}-(\text{CH}_2)_4\overset{\text{O}}{\underset{}{\text{C}}}\right]_x-\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{OH} \longrightarrow$$

$$\text{M.W.} = 1450$$

$$\left\{\overset{\text{O}}{\underset{}{\text{C}}}-\text{NH}-\underset{\underset{F}{F}}{\overset{\overset{F}{F}}{\bigcirc}}-\text{NH}-\text{C}-\left[\text{OCH}_2(\text{CF}_2)_3\text{O}-\overset{\text{O}}{\underset{}{\text{C}}}-(\text{CH}_2)_4-\overset{\text{O}}{\underset{}{\text{C}}}\right]_x-\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{O}\right\}_y$$
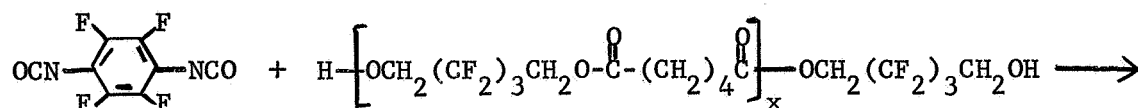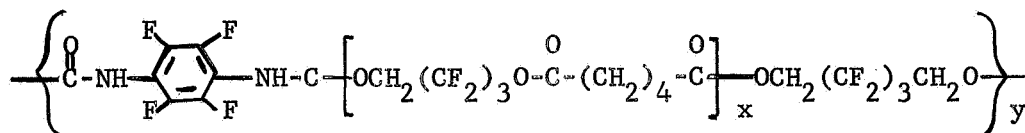
A 30% excess of diisocyanate was used and the resulting prepolymer was cured by formation of the allophanate at elevated temperatures. The cured polymer appeared to have good adhesion, but was not tough.

It was felt that a polyurethane of similar structure but of greatly improved toughness could be prepared by increasing the concentration of allophanate groups. Thus, a polyurethane was prepared using a diisocyanate-to-diol ratio of 2:1. The allophanate-cured polyurethane prepared by this method was an extremely tough, elastomeric material.

A similar polyurethane was prepared by the prepolymer route using triethylamine catalysis. The prepolymer, prepared by capping hydroxyl-terminated poly(hexafluoropentamethylene adipate) of molecular weight 1450 with tetrafluoro-p-phenylene diisocyanate, was then cured by reaction with tetrafluoro-p-phenylenediamine.

$$2\;\text{OCN}-\underset{\underset{F}{F}}{\overset{\overset{F}{F}}{\bigcirc}}-\text{NCO} \;+\; \text{HO}-\left[\text{CH}_2(\text{CF}_2)_3\text{CH}_2\text{O}-\overset{\text{O}}{\underset{}{\text{C}}}-(\text{CH}_2)_4-\overset{\text{O}}{\underset{}{\text{C}}}-\text{O}\right]_x-\text{CH}_2(\text{CF}_2)_3\text{CH}_2\text{OH} \longrightarrow$$

$$\text{M.W.} = 1450$$

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$$OCN-C_6F_4-NH-\overset{O}{\overset{\|}{C}}-O\left[CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O\right]_x CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-NH-C_6F_4-NCO$$

$$H_2N-C_6F_4-NH_2$$

$$\left\{\overset{O}{\overset{\|}{C}}-NH-C_6F_4-NH-\overset{O}{\overset{\|}{C}}-O\left[CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O\right]_x CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-NH-C_6F_4-N-\overset{O}{\overset{\|}{C}}-NH-C_6F_4-NH\right\}_y$$
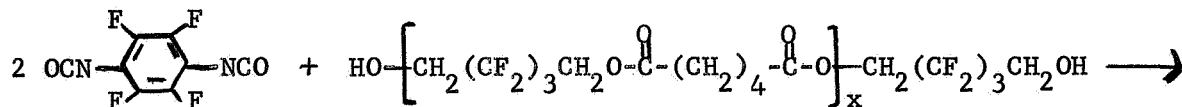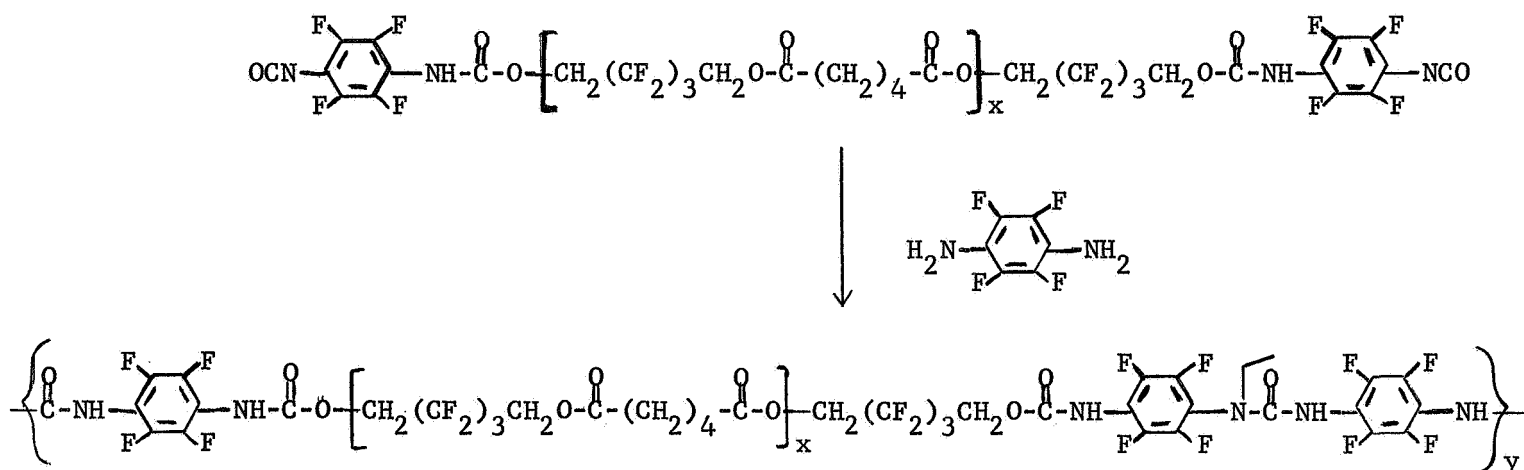
The diamine curing agent was added to a solution of the prepolymer to obtain good mixing; the solvent was then removed and the cure accomplished by heating at elevated temperature in a press. The polymer obtained was a tough elastomer. Samples were cut from the polymer film and submitted to MSFC for LOX compatibility testing. This polyurethane was sensitive to impact in LOX.

Difficulties have been experienced in the preparation of prepolymers from tetrafluoro-p-phenylene diisocyanate in the presence of catalysts. Premature gelation and rapid reaction of isocyanate functionality have been observed in the prepolymer. The preparation of polyurethane prepolymers have been shown to be a delicate matter due to complex side reaction which could occur.[7] The following reactions can result in undesired branching.

1. $\sim\sim N-\overset{O}{\overset{\|}{C}}-O\sim\sim$ + $\sim NCO$ $\longrightarrow$ $\sim\sim N-\overset{O}{\overset{\|}{C}}-O\sim$

    (with H on N)

    Isocyanate

    Allophanate

2. $2\ OCN-R-NCO + H_2O \longrightarrow OCN-R-NH-\overset{O}{\overset{\|}{C}}-NH-R-NCO + CO_2$

    Urea

    $\sim\sim\sim N-\overset{O}{\overset{\|}{C}}-N\sim\sim$ + $\sim\sim NCO$ $\longrightarrow$ $\sim\sim N-\overset{O}{\overset{\|}{C}}-N\sim\sim$

    Biuret

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3. 3 ∼NCO ⟶

Isocyanurate (trimer)

4. 2 ∼NCO ⟶

Dimer
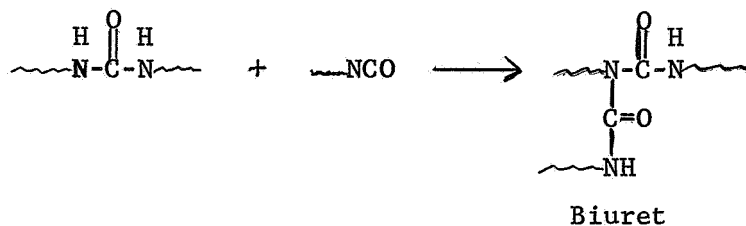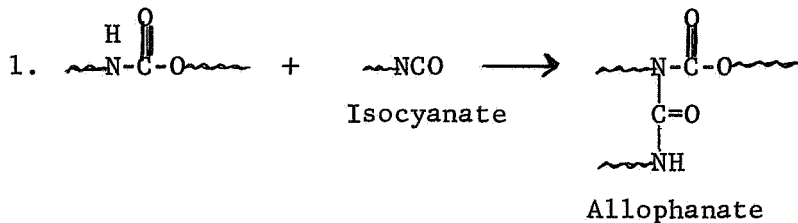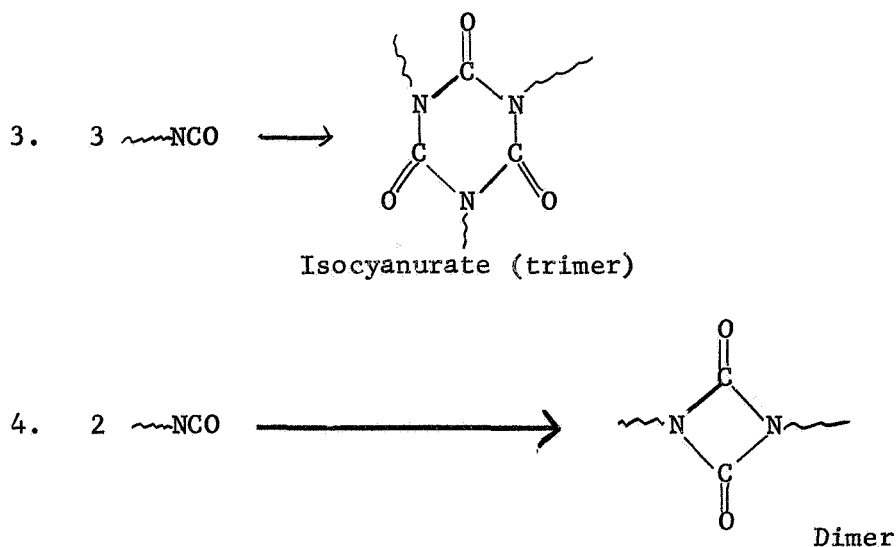
In general, acidic conditions do not favor these side reactions, while under basic conditions they occur much more readily.[8]

Adding to the difficulties is the exceptional reactivity of tetrafluoro-p-phenylene diisocyanate. Its ease of hydrolysis will be discussed later in this report. The ease with which side reactions 3 (trimerization) and 4 (dimerization) occur in the presence of basic catalysts is shown in an experiment conducted on tetrafluoro-p-phenylene diisocyanate. An infrared spectroscopic study* was carried out on three solutions of tetrafluoro-p-phenylene diisocyanate in trichloroethylene: one with no added catalyst, one with stannous octoate, and one with triethylamine. Immediately after preparation of the solutions, the infrared spectra are those of pure diisocyanate. After 100 hours at room temperature, the sample containing triethylamine showed an absorption band at 5.75 μ which is believed to be due to either a dimer or a trimer of the diisocyanate. The other two samples showed no change.

In an attempt to reduce the undesired branching, a prepolymer was prepared without catalyst and the reaction mixture was kept slightly acidic with benzoyl chloride. This prepolymer was cured with tetrafluoro-p-phenylenediamine which yielded a tough elastomeric polyurethane, but some localized amine-rich areas were apparent in the film which was prepared.

The effect of the length of the polyester chain on the properties of the final polyurethane was studied. A distinct improvement in the flexibility of the polyurethane was achieved by use of poly(hexafluoropentamethylene adipate) of 3200 molecular weight. The reaction was carried out as above without catalyst and with added benzoyl chloride. The cure polyurethane lacked toughness, however.

Two halogenated diols, tetrachloro-xylylenediol and hexafluoropentanediol, were evaluated as curing agents for the isocyanate-terminated prepolymer. It was felt that these diols, being less reactive than tetrafluoro-p-phenylene-diamine, might give a slower but more controllable cure.

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* Described in Section IV.E of this report.

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The prepolymer prepared from poly(hexafluoropentamethylene adipate) of molecular weight 1450 and tetrafluoro-p-phenylene diisocyanate in the presence of a small amount of benzoyl chloride was cured by reaction with tetrachloroxylylenediol. The polymer obtained was tough and flexible.

The same prepolymer was cured by reaction with hexafluoropentanediol. The reaction was so slow that stannous octoate catalyst had to be used. The polymer obtained was extremely flexible but had poor tear resistance.

Hydroxyl-terminated poly(hexafluoropentamethylene carbonate) and methylene-bis(orthochloroaniline) (MOCA) were also evaluated as curing agents. These materials were used because it was believed that they could be thoroughly mixed with the isocyanate-terminated prepolymer without solvent and with only a slight amount of heating.

Freshly prepared prepolymer was cured by heating it with hydroxyl-terminated poly(hexafluoropentamethylene carbonate) of molecular weight 1025 in a press at 160°C to 170°C for 20 minutes. A soft, highly elastic polymer was obtained.

The same prepolymer was cured by mixing with MOCA and heating in a press at 160°C to 170°C for ½ hour. The tough elastomer obtained was not uniform, having localized amine-rich areas. Apparently, the curing action of the amine was so fast that curing occurred before complete mixing of the prepolymer and amine was achieved.

The same isocyanate-terminated prepolymer prepared by reaction of tetra-fluoro-p-phenylene diisocyanate with hydroxyl-terminated poly(hexafluoropenta-methylene adipate) was cured with an amine-terminated curing agent prepared by capping an acid chloride-terminated poly(hexafluoropentamethylene adipate) with tetrafluoro-p-phenylenediamine. The cured polymer was crumbly and could not be pressed into a sheet.
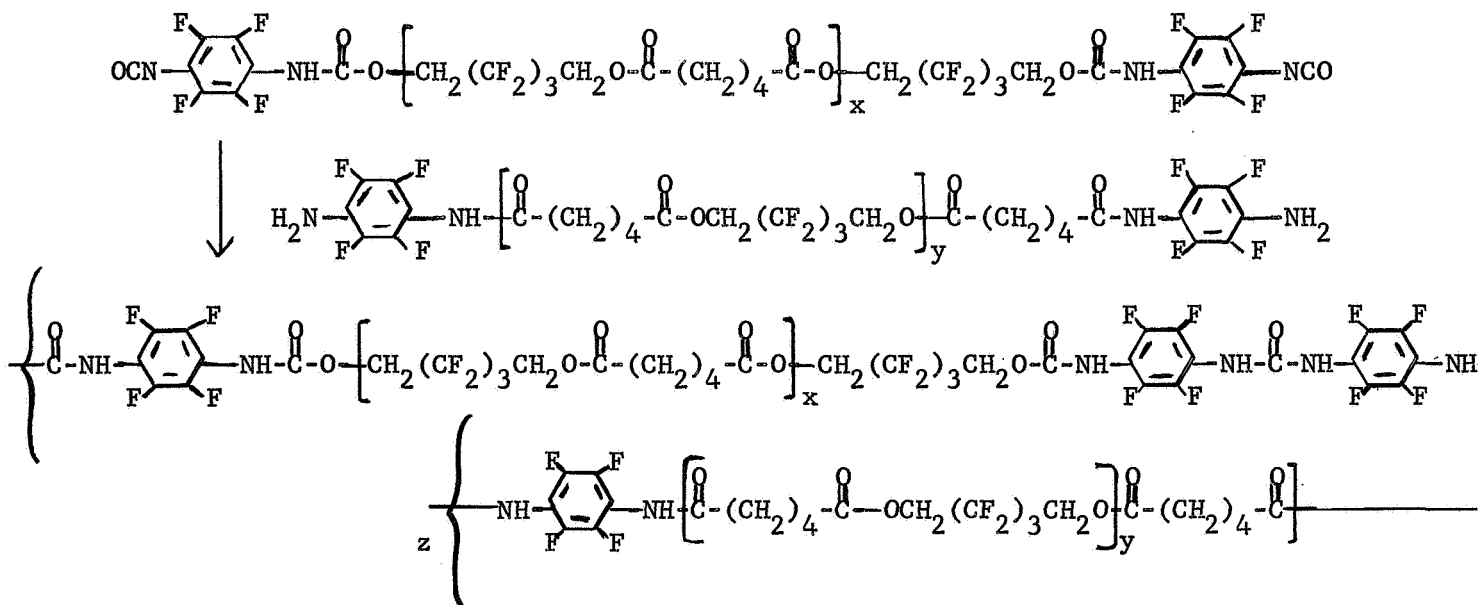
An isocyanate-terminated prepolymer was prepared in the melt from toluene-2,4-diisocyanate and the hydroxyl-terminated poly(hexafluoropentamethylene adipate) (M.W. 1900). This prepolymer was extremely tough and elastomeric, being a solid at room temperature, but thermoplastic. It was cured by heating in a press at $300°$-$350°F$ for $\frac{1}{2}$ hour, yielding an extremely flexible sheet. As the cured polymer contained no free isocyanate groups, it apparently reacted as expected on heating by means of allophanate formation.

$$H\text{-}\left[OCH_2(CF_2)_3CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\right]_x\text{-}OCH_2(CF_2)_3CH_2OH \quad + \quad CH_3\text{-}\underset{NCO}{\underset{\bigcirc}{}}\text{-}NCO \quad \longrightarrow$$

(M.W. = 1900)

$$CH_3\text{-}\underset{NCO}{\underset{\bigcirc}{}}\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\left[CH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\right]_x\text{-}O\text{-}CH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{N}\text{-}\underset{CH_3}{\underset{\bigcirc}{}}\text{-}NCO$$

Δ ↓

$$\left\{\begin{matrix}\overset{C=O}{\underset{NH}{|}}\\ CH_3\text{-}\underset{\bigcirc}{}\text{-}N\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\left[CH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\right]_x\text{-}O\text{-}CH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}N\text{-}\underset{CH_3}{\underset{\bigcirc}{}}\overset{NH\text{-}C}{\underset{}{}}\end{matrix}\right\}_y$$
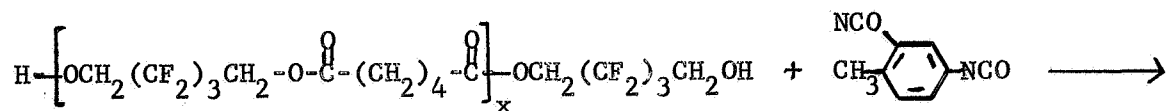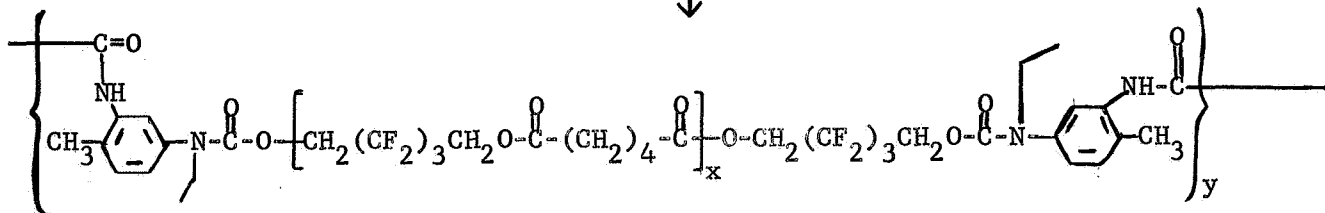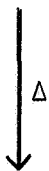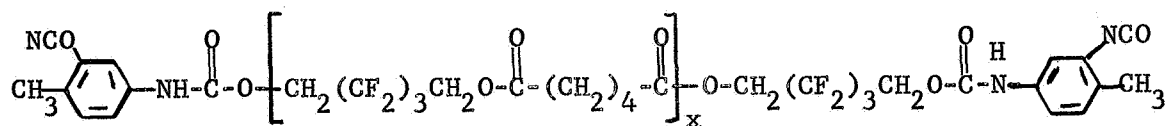
A polyurethane of similar structure was prepared using a hydroxyl-terminated poly(hexafluoropentamethylene adipate) of molecular weight 3200, using tetrafluoro-p-phenylenediamine as a curing agent.

$$2 \ CH_3\text{-}\underset{NCO}{\underset{\bigcirc}{}}\text{-}NCO \quad + \quad HO\text{-}\left[CH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\right]_x\text{-}CH_2(CF_2)_3CH_2OH \quad \longrightarrow$$

M.W. = 3200

$$CH_3\text{-}\underset{NCO}{\underset{\bigcirc}{}}\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\left[CH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\right]_x\text{-}CH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}\underset{CH_3}{\underset{\bigcirc}{}}\text{-}NCO$$

↓ $H_2N\text{-}\underset{F \ \ F}{\overset{F \ \ F}{\bigcirc}}\text{-}NH_2$

$$\left\{\left(\begin{array}{c}\overset{O}{\overset{\|}{C}}-NH-\underset{CH_3}{\bigcirc}-NH-\overset{O}{\overset{\|}{C}}-O-\left[CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O\right]_x CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-NH-\underset{CH_3}{\bigcirc}-NH-\overset{O}{\overset{\|}{C}}-NH-\underset{F\ F}{\overset{F\ F}{\bigcirc}}-NH\end{array}\right)_y\right.$$
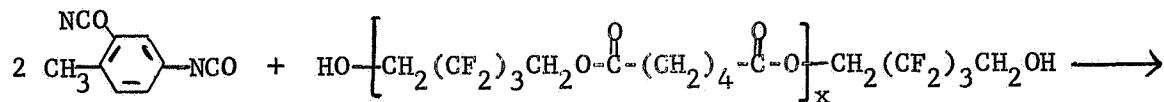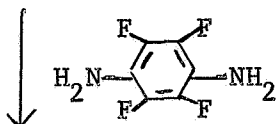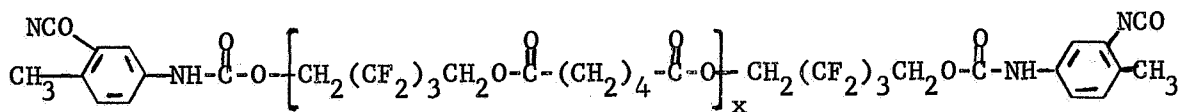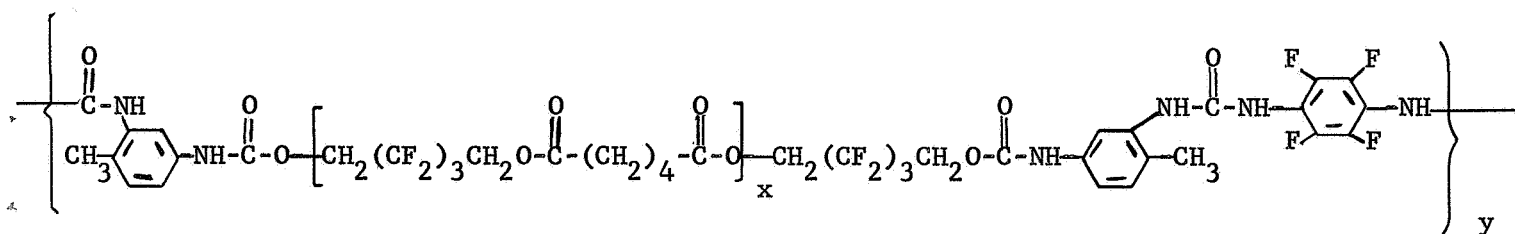
The polymer was an extremely flexible, colorless elastomer.

During previous preparations of isocyanate-terminated prepolymers, indications were that interesting foams could be produced by reaction with water. In a single experiment, a white, extremely flexible polyurethane foam was prepared by reaction of hydroxyl-terminated poly(hexafluoropentamethylene adipate) with excess toluene diisocyanate in the presence of stannous octoate and water. This simple experiment suggests that LOX-compatible polyurethane foams could be made from highly fluorinated monomers.

Another highly halogenated prepolymer was prepared from poly(hexafluoro-pentamethylene adipate) and tetrachloro-p-phenylene diisocyanate.

$$H-\left[OCH_2(CF_2)_3CH_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_x OCH_2(CF_2)_3CH_2OH \;+\; OCN-\underset{Cl\ Cl}{\overset{Cl\ Cl}{\bigcirc}}-NCO \longrightarrow$$

(M.W. = 1900)

$$OCN-\underset{Cl\ Cl}{\overset{Cl\ Cl}{\bigcirc}}-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\left[OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_x OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-\underset{Cl\ Cl}{\overset{Cl\ Cl}{\bigcirc}}-NCO$$
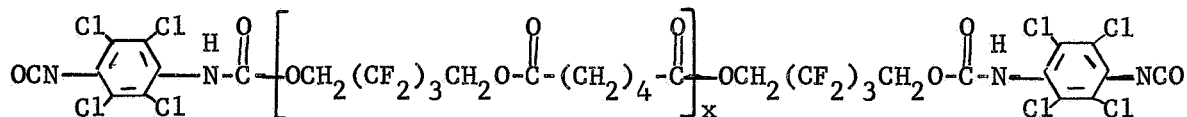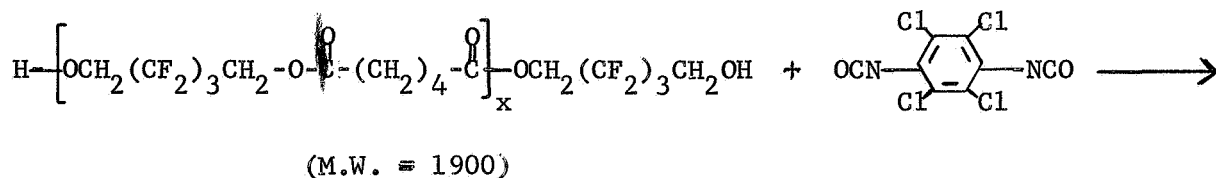
The prepolymer was an opaque, thermoplastic semisolid. An attempt to cure this prepolymer by heating with tetrafluoro-p-phenylenediamine in a press with stannous octoate as catalyst was unsuccessful.

$$OCN-\underset{Cl\ Cl}{\overset{Cl\ Cl}{\bigcirc}}-NH-\overset{O}{\overset{\|}{C}}-\left[O-CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_x O-CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-NH-\underset{Cl\ Cl}{\overset{Cl\ Cl}{\bigcirc}}-NCO$$

$$+\quad H_2N-\underset{F\ F}{\overset{F\ F}{\bigcirc}}-NH_2 \quad\xrightarrow{\quad\quad}\!\!\!\!/$$
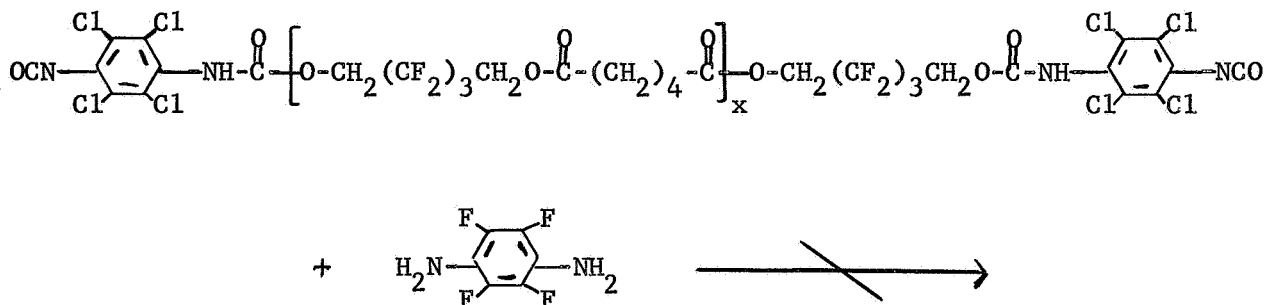
Earlier in this program,[9] the incorporation of the fluorinated bi-phenyl structure into a polyurethane to improve the tensile strength and other physical properties were discussed. This can be accomplished most

easily by use of 4,4'-diisocyanato-octafluorobiphenyl. The preparation of this new diisocyanate is described in Section III.E of this report.

A polyurethane was prepared by capping a hydroxyl-terminated poly(hexafluoropentamethylene adipate) of molecular weight 1680 with 4,4'-diisocyanato-octafluorobiphenyl and curing the resulting isocyanate-terminated prepolymer with tetrafluoro-p-phenylenediamine. The polymer obtained was an extremely tough elastomer.

$$\text{OCN-}\underset{F\quad F}{\overset{F\quad F}{\bigcirc}}\text{-}\underset{F\quad F}{\overset{F\quad F}{\bigcirc}}\text{-NCO} \;+\; \text{HO-}\!\left[\text{CH}_2(\text{CF}_2)_3\text{CH}_2 \text{-}\overset{O}{\overset{\|}{\text{C}}}\text{-}(\text{CH}_2)_4\text{-}\overset{O}{\overset{\|}{\text{C}}}\text{-O}\right]_x\!\!\text{CH}_2(\text{CF}_2)_3\text{CH}_2\text{OH} \longrightarrow$$

M.W. = 1680

$$\text{OCN-}\bigcirc\text{-}\bigcirc\text{-NH-}\overset{O}{\overset{\|}{\text{C}}}\text{-O-}\!\left[\text{CH}_2(\text{CF}_2)_3\text{CH}_2 \text{-}\overset{O}{\overset{\|}{\text{C}}}\text{-}(\text{CH}_2)_4\text{-}\overset{O}{\overset{\|}{\text{C}}}\text{-O}\right]_x\!\!\text{CH}_2(\text{CF}_2)_3\text{CH}_2\text{O-C-NH-}\bigcirc\text{-}\bigcirc\text{-NCO}$$

$$\downarrow \quad \text{H}_2\text{N-}\underset{F\quad F}{\overset{F\quad F}{\bigcirc}}\text{-NH}_2$$

$$\left\{\text{NH-}\bigcirc\text{-N-}\overset{O}{\overset{\|}{\text{C}}}\text{-NH-}\bigcirc\text{-}\bigcirc\text{-NH-}\overset{O}{\overset{\|}{\text{C}}}\text{-O-}\!\left[\text{CH}_2(\text{CF}_2)_3\text{CH}_2\text{O-}\overset{O}{\overset{\|}{\text{C}}}\text{-}(\text{CH}_2)_4\text{-}\overset{O}{\overset{\|}{\text{C}}}\text{-O}\right]_x\!\!\text{CH}_2(\text{CF}_2)_3\text{CH}_2\text{O-}\overset{O}{\overset{\|}{\text{C}}}\text{-NH}\right.$$

$$\left.\overset{O}{\overset{\|}{\text{C}}}\text{-NH-}\bigcirc\text{-}\bigcirc\right\}_y$$

b. **From Poly(hexafluoropentamethylene malonate).** — It was believed that polyesters of malonic acid and fluorinated diols would possess the smallest possible number of unfluorinated carbon atoms and still possibly be LOX compatible. Tetrafluoro-p-phenylene diisocyanate was reacted with the hydroxyl-terminated polyester, poly(hexafluoropentamethylene malonate) to yield a polyurethane. The preparation of the polyester is described in Section III.C.

$$\text{OCN-}\underset{F\quad F}{\overset{F\quad F}{\bigcirc}}\text{-NCO} \;+\; \text{H-}\!\left[\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{O-}\overset{O}{\overset{\|}{\text{C}}}\text{-CH}_2\text{-}\overset{O}{\overset{\|}{\text{C}}}\right]_x\!\!\text{OCH}_2(\text{CF}_2)\text{CH}_2\text{OH} \longrightarrow$$

$$\left\{\overset{O}{\overset{\|}{\text{C}}}\text{-NH-}\underset{F\quad F}{\overset{F\quad F}{\bigcirc}}\text{-NH-}\overset{O}{\overset{\|}{\text{C}}}\text{-}\!\left[\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{O-}\overset{O}{\overset{\|}{\text{C}}}\text{-CH}_2\text{-}\overset{O}{\overset{\|}{\text{C}}}\right]_x\!\!\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{O}\right\}_y$$

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An isocyanate-terminated prepolymer was prepared from the hydroxyl terminated poly(hexafluoropentamethylene malonate) and toluene-2,4'-diisocyanate.

$$H\text{-}\left[OCH_2(CF_2)_3CH_2\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\right]_x O\text{-}CH_2(CF_2)_3CH_2OH \quad + \quad CH_3\text{-}\overset{\overset{\displaystyle NCO}{}}{\underset{}{\bigcirc}}\text{-}NCO \quad \longrightarrow$$

(M.W. = 1779)

$$CH_3\text{-}\overset{\overset{\displaystyle NCO}{}}{\underset{}{\bigcirc}}\text{-}\underset{\displaystyle H}{N}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\left[OCH_2(CF_2)_3CH_2O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\right]_x OCH_2(CF_2)_3CH_2O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\underset{\displaystyle H}{N}\text{-}\overset{\overset{\displaystyle NCO}{}}{\underset{}{\bigcirc}}\text{-}CH_3$$
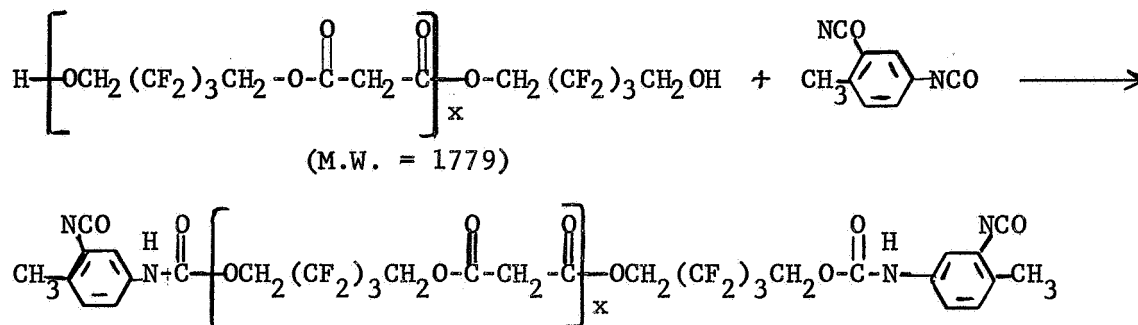
The prepolymer was a viscous liquid having an isocyanate equivalent weight of 838. It was chain-extended by reaction with 82% of the stoichiometric amount of tetrafluoro-p-phenylene diamine. The resultant isocyanate-terminated product was cured by reaction of the isocyanate end groups with the urea groups along an adjacent polymer chain. The tough elastomeric polymer which formed tended to embrittle on cooling. Twenty samples were cut from a sheet of the polymer and submitted to MSFC for LOX compatibility testing. This polyurethane was sensitive to impact in LOX.

Tetrachloro-p-phenylene diisocyanate was also used to prepare an isocyanate-terminated prepolymer from poly(hexafluoropentamethylene malonate).

$$H\text{-}\left[OCH_2(CF_2)_3CH_2O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\right]_x OCH_2(CF_2)_3CH_2OH \quad + \quad OCN\text{-}\overset{\overset{\displaystyle Cl \quad Cl}{}}{\underset{\displaystyle Cl \quad Cl}{\bigcirc}}\text{-}NCO \quad \longrightarrow$$

(M.W. = 1779)

$$OCN\text{-}\overset{\overset{\displaystyle Cl \quad Cl}{}}{\underset{\displaystyle Cl \quad Cl}{\bigcirc}}\text{-}\underset{\displaystyle H}{N}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\left[OCH_2(CF_2)_3CH_2O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\right]_x OCH_2(CF_2)_3CH_2O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\underset{\displaystyle H}{N}\text{-}\overset{\overset{\displaystyle Cl \quad Cl}{}}{\underset{\displaystyle Cl \quad Cl}{\bigcirc}}\text{-}NCO$$
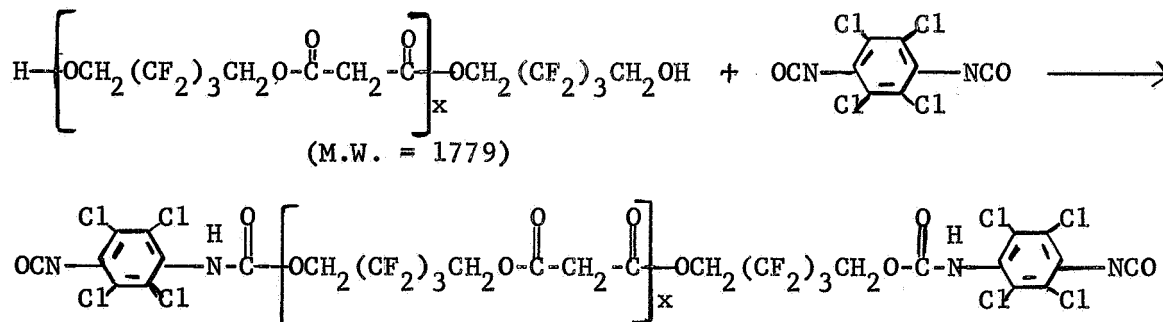
An unsuccessful attempt was made to cure this prepolymer with tetrafluoro-p-phenylene diamine and stannous octoate as catalyst.

In this attempted cure and in the one on the prepolymer from poly(hexafluoropentamethylene adipate), described above, the prepolymers were so unreactive that the tetrafluoro-p-phenylenediamine sublimed during the curing attempts.

This unexpected nonreactivity of prepolymers terminated by tetrachloro-p-phenylene diisocyanate prompted a brief study* on the relative rates of hydrolysis of (1) tetrafluoro-p-phenylene diisocyanate, (2) toluene 2,4-diisocyanate, and (3) tetrachloro-p-phenylene diisocyanate. A large variation was found among the three diisocyanates, with tetrafluoro-p-phenylene diisocyanate hydrolyzing almost instantly, toluene 2,4-diisocyanate fairly

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* Described in Section IV.E

rapidly, and tetrachloro-p-phenylene diisocyanate very slowly. The increased reactivity of tetrafluoro-p-phenylene diisocyanate can be explained by the strong electron withdrawing influence of the fluorinated aromatic ring. Narmco believes that the extraordinarily low reactivity of tetrachloro-p-phenylene diisocyanate is due to steric hindrance by the large chlorine atoms to attack on the isocyanate groups by water. This steric hindrance is also the reason that the two above-mentioned prepolymers failed to react with the curing agent, tetrafluoro-p-phenylenediamine, even with stannous octoate catalysis.

3. From Hydroxyl-Terminated Poly(hexafluoropentamethylene carbonate)

A new approach has been used at Narmco for the preparation of fluorinated bischloroformates. This is discussed later in Section III.E.

The formation of fluorinated bischloroformates opens a wide, new field in the preparation of fluorinated polyurethanes. Various hydroxyl-terminated polycarbonates could be prepared from hexafluoropentamethylene bischloroformate by reaction with an excess of various diols. These hydroxyl-terminated poly-carbonates can then be reacted with halogenated diisocyanates to form halogenated polyurethanes.

The molecular weight of the hydroxyl-terminated polycarbonate could be controlled by the proper stoichiometry of the bischloroformate and diol. The hydroxyl end groups are assured since any chloroformate end groups are hydrolyzed to hydroxyl with water.

The reaction of hexafluoropentamethylene bischloroformate with hexa-fluoropentanediol yielded the new hydroxyl-terminated poly(hexafluoropenta-methylene carbonate) as a white, opaque semisolid.

$$HOCH_2(CF_2)_3CH_2OH \quad + \quad Cl\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2(CF_2)_3CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl \quad \xrightarrow{} \quad \xrightarrow{H_2O}$$

$$H\text{--}\left[OCH_2(CF_2)_3CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\right]_x\text{--}OCH_2(CF_2)_3CH_2OH$$
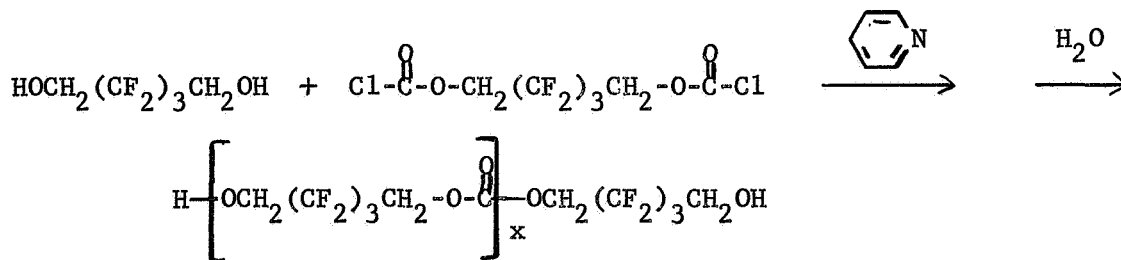
An isocyanate-terminated polyurethane was prepared by reaction of hydroxyl-terminated poly(hexafluoropentamethylene carbonate) with excess tetrafluoro-p-phenylene diisocyanate.

$$OCN\text{--}\underset{\underset{F}{}}{\overset{\overset{F}{}}{\underset{F}{\overset{F}{\bigcirc}}}}\text{--}NCO \quad + \quad HO\text{--}\left[CH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\right]_x\text{--}CH_2(CF_2)_3CH_2OH \quad \xrightarrow{}$$

$$\text{M.W.} = 1025$$

$$\text{OCN} - \left\{ \begin{array}{c} F \quad F \\ \text{\textbf{⬡}} \\ F \quad F \end{array} - NH-\overset{O}{\overset{\|}{C}}-O - \left[CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-O \right]_x - CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-NH \right\}_y \begin{array}{c} F \quad F \\ \text{\textbf{⬡}} \\ F \quad F \end{array} - NCO$$
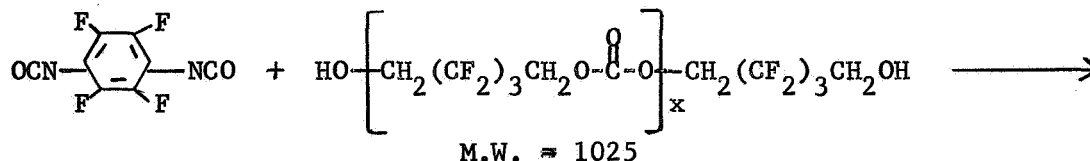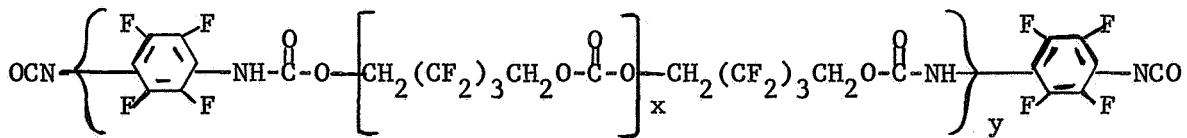
The polymer was molded in a press at 160°C to 170°C for ½ hour; this yielded a highly elastic thermoplastic polymer. These mold conditions may have caused some curing by formation of allophanate linkages, but the polymer still contained isocyanate groups.

An isocyanate-terminated polyurethane similar in structure was cured by reaction with tetrafluoro-p-phenylenediamine followed by heating in a press at 160°C to 170°C for ½ hour. The resulting elastomer had a tensile strength in excess of 2200 psi at room temperature. Samples of this elastomer were submitted to MSFC for LOX-compatibility testing. This polyurethane was found to be sensitive to impact in LOX.

A 50-g sample of an allophanate-cured polyurethane from tetrafluoro-p-phenylene diisocyanate and hydroxyl-terminated poly(hexafluoropentamethylene carbonate) was prepared. It was heat-cured in a press at 160°-175°C for ½ hour, yielding a tough, elastomeric film. One-hundred test specimens were punched from the film and submitted to MSFC for LOX compatibility testing. It was also sensitive to impact in LOX.

Because of the high degree of thermal stability exhibited by the poly-(hexafluoropentamethylene carbonate) described in Section III of this report (Other Polymers), this polyurethane was subjected to thermogravimetric analysis. The results showed that the polymer decomposition temperature was 320°±10°C in air and 300° ±10°C in helium. The thermograms indicate a subsequent decomposition temperature in both atmospheres at approximately 450°C. Since the decomposition temperature of the polycarbonate has been found to be approximately 450°C, the first decomposition temperature (320°C and 300°C) of the polyurethane is probably due to the breakdown of the urethane linkage. The thermograms are shown as Figures 1 and 2.

An elastomeric isocyanate-terminated prepolymer was prepared by reaction of toluene 2,4-diisocyanate with hydroxyl-terminated poly(hexafluoropenta-methylene carbonate). A thin film was prepared from this prepolymer, and samples were submitted to MSFC for LOX-impact testing. This prepolymer was sensitive to impact in LOX.

$$H - \left[OCH_2(CF_2)_3-CH_2-O-\overset{O}{\overset{\|}{C}} \right]_x OCH_2(CF_2)_3CH_2OH \; + \; CH_3 - \text{\textbf{⬡}} - NCO \longrightarrow$$

(M.W. = 1450)

$$\begin{array}{c} NCO \\ CH_3 - \text{\textbf{⬡}} \end{array} - \overset{H}{N}-\overset{O}{\overset{\|}{C}} - \left[OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}} \right]_x OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-N - \begin{array}{c} NCO \\ \text{\textbf{⬡}} - CH_3 \end{array}$$

21
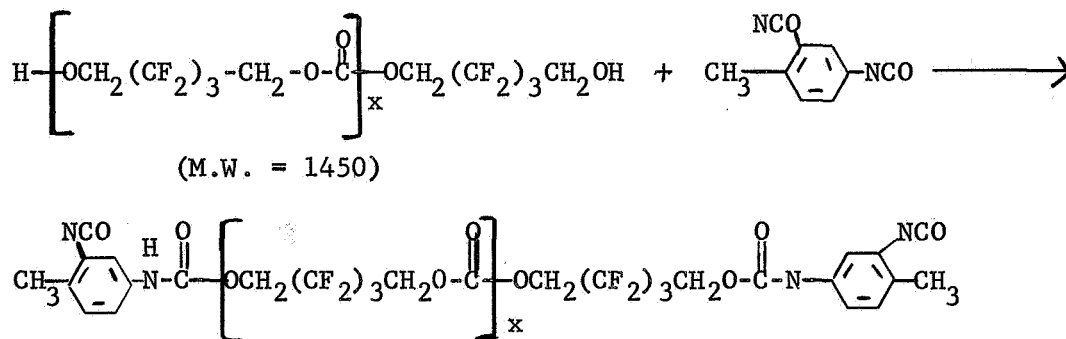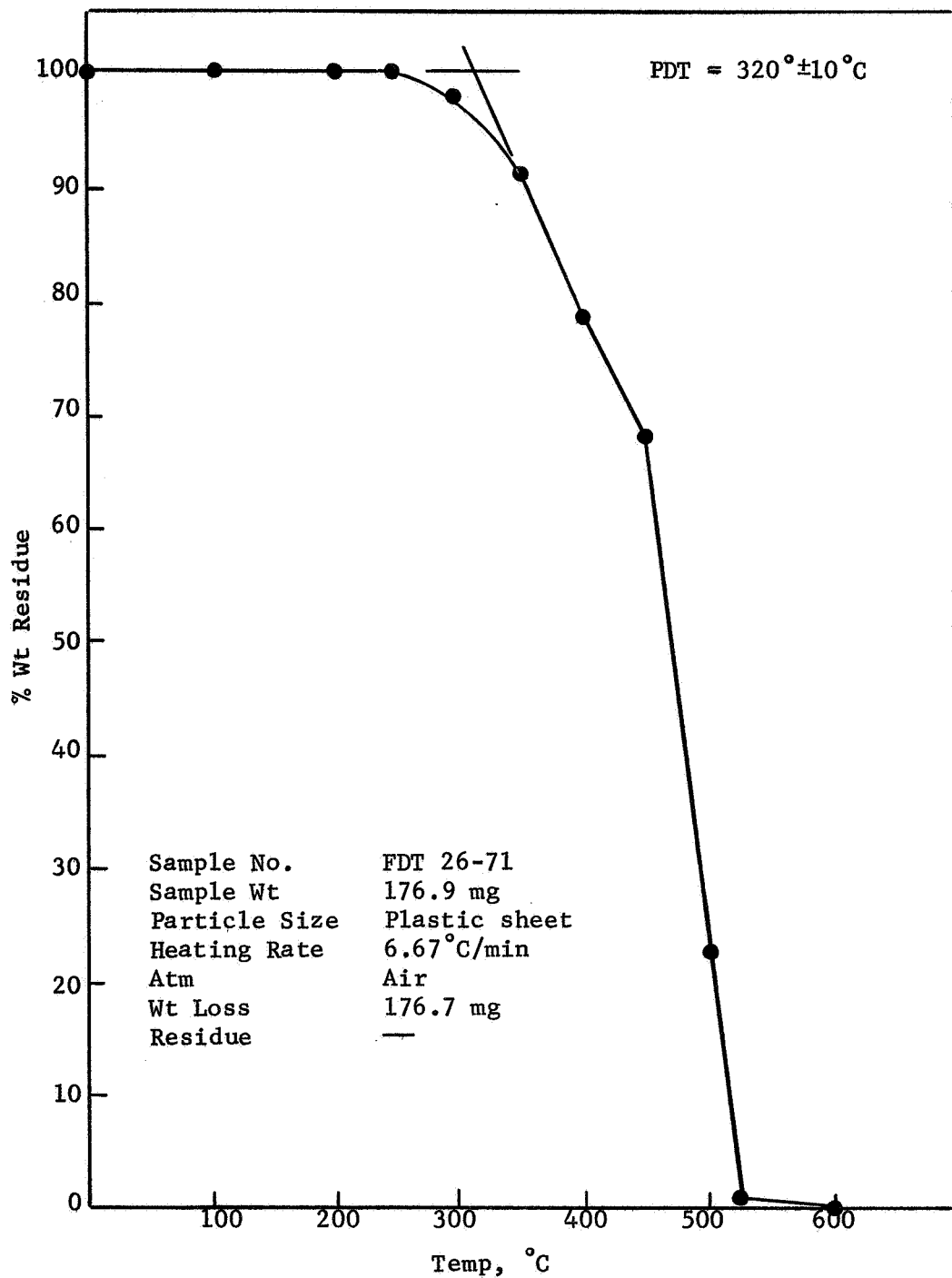
Figure 1. Thermogram of Polyurethane of Tetrafluoro-p-
phenylene Diisocyanate and Poly(hexafluoro-
pentamethylene carbonate) in Air

22
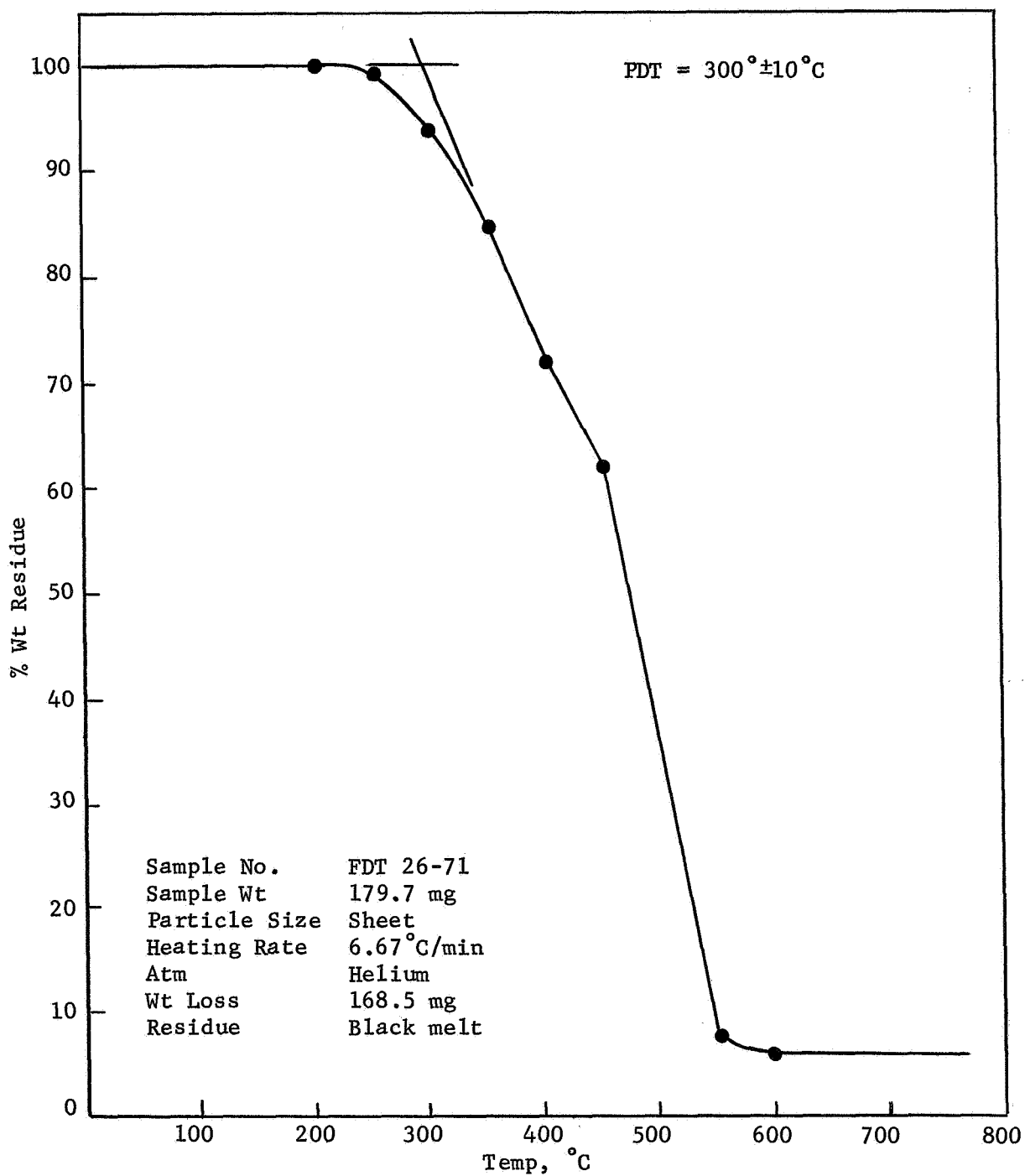
Figure 2. Thermogram of Polyurethane of Tetrafluoro-
p-phenylene Diisocyanate and Poly(hexa-
fluoropentamethylene carbonate) in Helium

Attempts to cure this elastomeric prepolymer by mixing the curing agent into the film were unsuccessful. Curing was achieved by mixing the tetrafluoro-p-phenylenediamine curing agent into a slurry of the freshly prepared prepolymer. After evaporation of the solvent, a thin sheet was formed in a press. Samples for LOX-impact testing were cut from the sheet. This polyurethane was found to be LOX sensitive.

$$CH_3\!\!\underset{NCO}{\diamond}\!\!-NCO \;+\; HO\!-\!\Big[CH_2(CF_2)_3CH_2O-\overset{O}{\underset{}{C}}-O\Big]_x\!-CH_2(CF_2)_3CH_2OH$$

$$\downarrow$$

$$CH_3\!\!\underset{NCO}{\diamond}\!\!-NH-\overset{O}{\underset{}{C}}-O\!-\!\Big[CH_2(CF_2)_3CH_2O-\overset{O}{\underset{}{C}}-O\Big]_x\!-CH_2(CF_2)_3CH_2O-\overset{O}{\underset{}{C}}-NH\!\!\underset{CH_3}{\overset{NCO}{\diamond}}$$

$$\downarrow \quad H_2N\!\!\underset{F\;\;F}{\overset{F\;\;F}{\diamond}}\!\!-NH_2$$

$$\Big\{\!\!-NH\!\!\underset{F\;\;F}{\overset{F\;\;F}{\diamond}}\!\!-NH-\overset{O}{\underset{}{C}}-NH\!\!\underset{CH_3}{\diamond}\!\!NH-\overset{O}{\underset{}{C}}\!-\!\Big[OCH_2(CF_2)_3CH_2O-\overset{O}{\underset{}{C}}\Big]_x\!-OCH_2(CF_2)_3CH_2O-\overset{O}{\underset{}{C}}-NH\!\!\underset{CH_3}{\diamond}\!\!N-\overset{O}{\underset{}{C}}\!\!\Big\}_y$$
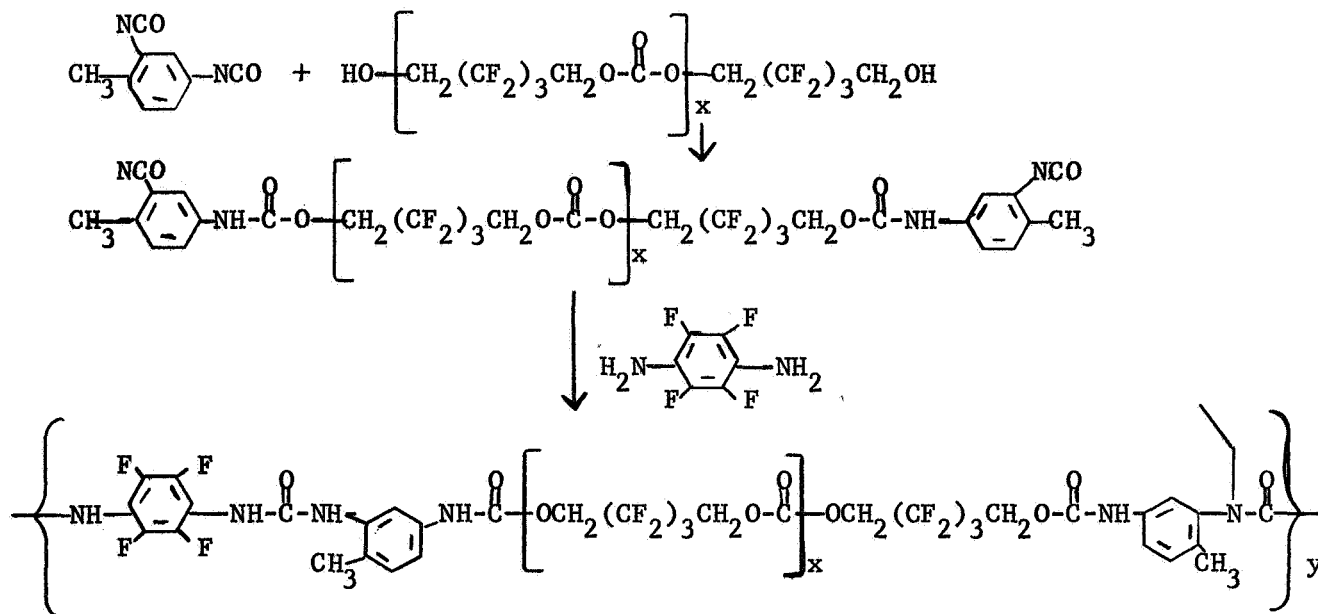
The preparation of another halogenated polycarbonate-base polyurethane was accomplished by reaction of hydroxyl-terminated poly(hexafluoropenta-methylene carbonate) with tetrachloro-p-phenylene diisocyanate in ethyl acetate solution. The polyurethane obtained was a light tan elastic polymer melting at 125°-135°C.

$$OCN\!\!\underset{Cl\;\;Cl}{\overset{Cl\;\;Cl}{\diamond}}\!\!-NCO \;+\; H\!-\!\Big[O\text{-}CH_2(CF_2)_3CH_2\text{-}O-\overset{O}{\underset{}{C}}\Big]_x\!-OCH_2(CF_2)_3CH_2OH \longrightarrow$$

(M.W. = 2450)

$$\Big\{\!\!-\overset{O}{\underset{}{C}}-NH\!\!\underset{Cl\;\;Cl}{\overset{Cl\;\;Cl}{\diamond}}\!\!-NH-\overset{O}{\underset{}{C}}\!-\!\Big[OCH_2(CF_2)_3CH_2O-\overset{O}{\underset{}{C}}\Big]_x\!-OCH_2(CF_2)_3CH_2O\!-\!\Big\}_y$$
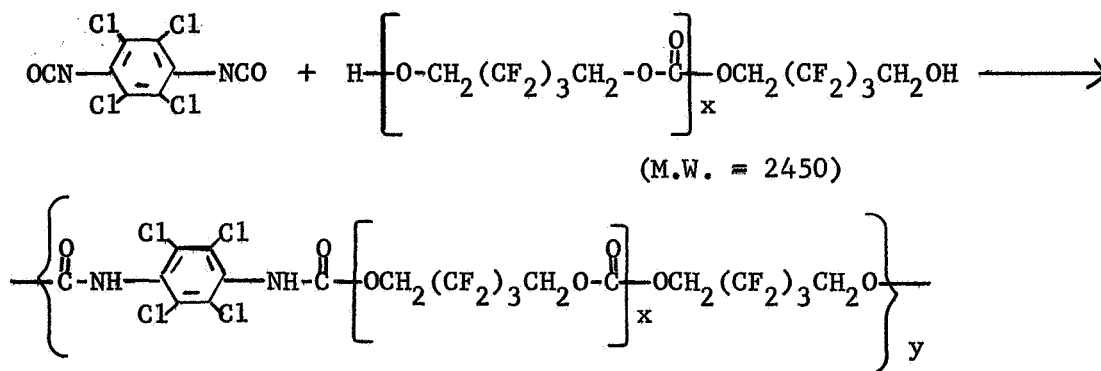
4. From Hydroxyl-Terminated Polyethers

Hydroxyl-terminated polyethers have found considerable use in the preparations of nonfluorinated polyurethanes.[10] One of the most important properties of polyether based polyurethanes is their improved flexibility. Narmco is thus interested in the fluorine-containing polyethers because of the probable

improvement in low-temperature properties of polyurethanes and since they would supply more basic information on the relation of LOX compatibility to structure.

Poly(hexafluoropentamethylene formal) was prepared by reaction of trioxane with hexafluoropentanediol. A polyurethane was prepared from this polyformal and tetrafluoro-p-phenylene diisocyanate. The polymer was molded in a press yielding a tough, flexible film from which samples were punched and submitted to MSFC for LOX compatibility testing. This polyurethane was sensitive to impact in LOX.

$$OCN-\underset{\substack{F\\F}}{\overset{\substack{F\\F}}{\bigcirc}}-NCO \;+\; H-\left[OCH_2\left(CF_2\right)_3 CH_2O-CH_2\right]_x OCH_2\left(CF_2\right)_3 CH_2OH \longrightarrow$$

M.W. ≈ 600

$$\left\{\overset{O}{\underset{\|}{C}}-NH-\underset{\substack{F\\F}}{\overset{\substack{F\\F}}{\bigcirc}}-NH-\overset{O}{\underset{\|}{C}}\left[OCH_2\left(CF_2\right)_3 CH_2O-CH_2\right]_x OCH_2\left(CF_2\right)_3 CH_2-O\right\}_y$$
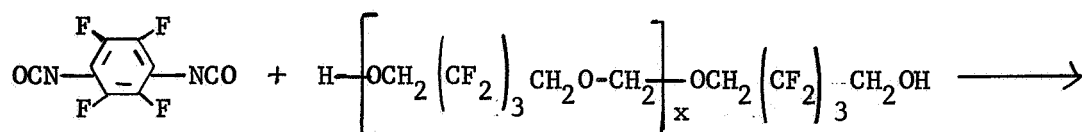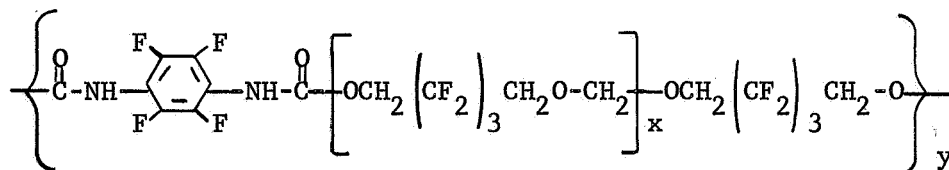
Notably, the reactivity of the hydroxyl-terminated polyformal toward tetrafluoro-p-phenylene diisocyanate was considerably greater than that of the hydroxyl-terminated polycarbonate. Whereas the polycarbonate and diisocyanate could be heated at $80°-90°C$ for 1-3/4 hours then at $130°-140°C$ for 1 hour before gelling, mixing the polyformal and the diisocyanate at $80°C$ resulted in immediate gelation. This increased reactivity indicates that the polyformal might be methylol-terminated rather than hexafluoropentanediol-terminated as in the polycarbonate. Unstabilized, nonfluorinated polyformals are always terminated with an alcohol group other than a methylol[11] probably because a terminal methylol group would be unstable, breaking down, possibly by a four-center reaction.

$$CH_2-CH_2 - \overset{..}{O} - CH_2 \longrightarrow CH_2-CH_2 - \underset{H}{\overset{|}{O}} \;+\; CH_2 = O$$
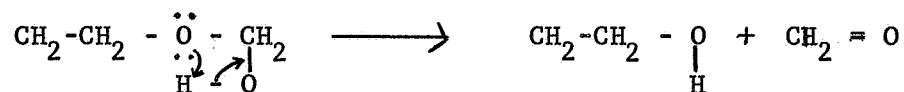
A fluorinated polyformal, such as poly(hexafluoropentamethylene formal), might be capable of having a stable terminal methylol group, because the electron-withdrawing ability of the β-difluoromethylene group could reduce the electron density around the ether oxygen sufficiently to hinder the four-center type elimination of formaldehyde.

$$\sim\sim CF_2-CH_2-\overset{..}{O}-CH_2 \;\;\not\longrightarrow\;\; \sim\sim CF_2-CH_2-\underset{H}{\overset{|}{O}} \;+\; CH_2 = O$$
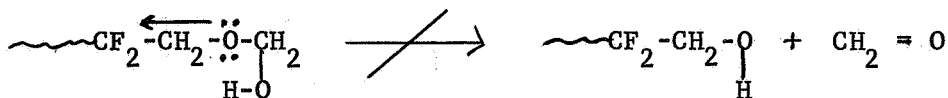
The preparation of polyethers from 3,3,3-trifluoro-1,2-epoxypropane is described in the Prepolymer Section of this report. A polyether of 970 molecular weight was prepared using the sodium salt of hexafluoropentanediol as initiator. A polyurethane was prepared by reaction of this polyether with tetrafluoro-p-phenylene diisocyanate. A film obtained from heat curing the polymer in a press at 175°C for ½ hour was elastic but soft. On exposure to atmospheric moisture and remolding, the film became tough and elastic. Samples of this film were punched and submitted to MSFC for LOX compatibility testing. This polyurethane was sensitive to impact in LOX.

$$\text{OCN-}\underset{F}{\overset{F}{\bigcirc}}\text{-NCO} + \text{HOCH}_2(\text{CF}_2)_3\text{CH}_2\text{O-}\left[\overset{\text{CF}_3}{\underset{}{\text{CH-CH}_2\text{-O}}}\right]_x\text{H}$$

M.W. = 970

$$\left\{\overset{O}{\underset{}{\text{C}}}\text{-NH-}\underset{F}{\overset{F}{\bigcirc}}\text{-NH-}\overset{O}{\underset{}{\text{C}}}\text{-O-CH}_2(\text{CF}_2)_3\text{CH}_2\text{-O-}\left[\overset{\text{CF}_3}{\underset{}{\text{CH-CH}_2\text{-O}}}\right]_x\right\}_y$$
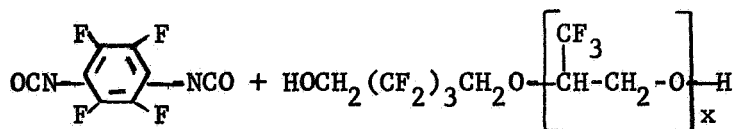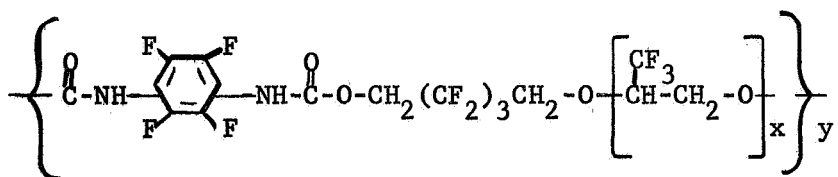
A similar polyether of molecular weight 2700, prepared using aluminum chloride as initiator, was reacted with tetrafluoro-p-phenylene diisocyanate to yield a polyurethane. The polymer yielded only a soft semisolid on curing with tetrafluoro-p-phenylenediamine and heating in a press. Either the molecular weight of the polyether was too high to yield a tough polymer or there was a substantial amount of terminal unsaturation in the polyether, hindering the formation of a high molecular weight polymer.

$$\text{OCN-}\underset{F}{\overset{F}{\bigcirc}}\text{-NCO} + \text{HO-}\left[\overset{\text{CF}_3}{\underset{}{\text{CH-CH}_2\text{-O}}}\right]_x\text{H} \longrightarrow \text{OCN-}\underset{F}{\overset{F}{\bigcirc}}\text{-NH-}\overset{O}{\underset{}{\text{C}}}\text{-O-}\left[\overset{\text{CF}_3}{\underset{}{\text{CH-CH}_2\text{-O}}}\right]_x\overset{O}{\underset{}{\text{C}}}\text{-NH-}\underset{F}{\overset{F}{\bigcirc}}\text{-NCO}$$

M.W. = 2700

$$\downarrow \text{H}_2\text{N-}\underset{F}{\overset{F}{\bigcirc}}\text{-NH}_2$$

$$\left\{\text{NH-}\underset{F}{\overset{F}{\bigcirc}}\text{-N-}\overset{O}{\underset{}{\text{C}}}\text{-NH-}\underset{F}{\overset{F}{\bigcirc}}\text{-NH-}\overset{O}{\underset{}{\text{C}}}\text{-O-}\left[\overset{\text{CF}_3}{\underset{}{\text{CH-CH}_2\text{-O}}}\right]_x\overset{O}{\underset{}{\text{C}}}\text{-NH-}\underset{F}{\overset{F}{\bigcirc}}\text{-N-}\overset{O}{\underset{}{\text{C}}}\right\}_y$$
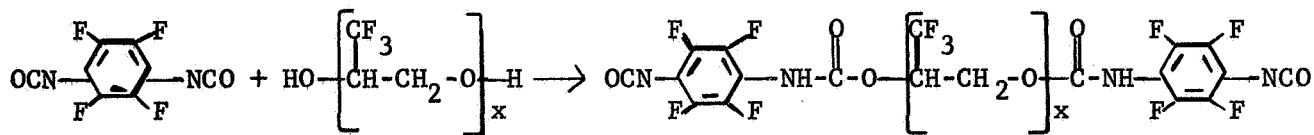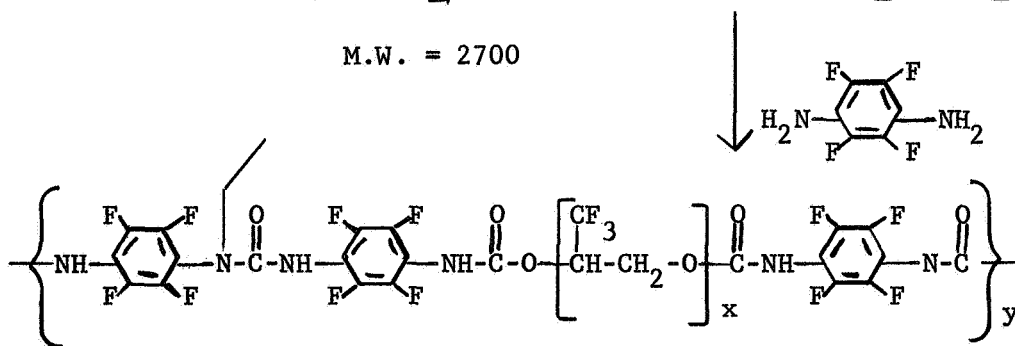
5. From the Dihemiketal of Hexafluoroacetone and Hexafluoropentanediol

The preparation of the dihemiketal of hexafluoroacetone and hexafluoropentanediol is described in Section III.E. In an effort to introduce ketal linkages into a polyurethane, this dihemiketal was reacted with tetrafluoro-p-phenylene diisocyanate. It was hoped that ketal groups might impart flexibility to the polyurethane. The reaction was slow, but on long reaction time yielded an isocyanate-terminated prepolymer.

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

$$\downarrow + 2 \ OCN\text{-}\langle C_6F_4 \rangle\text{-}NCO$$

$$OCN\text{-}\langle C_6F_4\rangle\text{-}NH\text{-}\overset{O}{C}\text{-}O\text{-}\underset{CF_3}{\overset{CF_3}{C}}\text{-}OCH_2(CF_2)_3CH_2O\text{-}\underset{CF_3}{\overset{CF_3}{C}}\text{-}O\text{-}\overset{O}{C}\text{-}NH\text{-}\langle C_6F_4\rangle\text{-}NCO$$
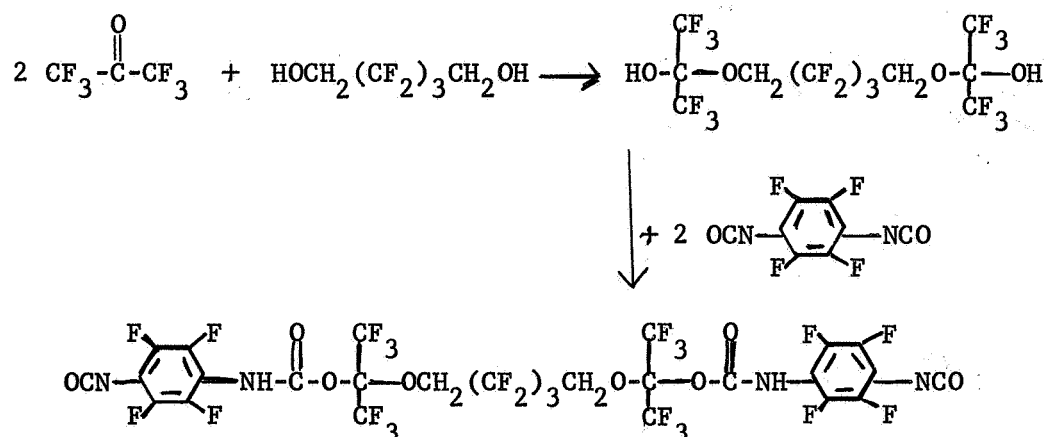
The reaction of N-methylaniline with the prepolymer failed to yield a solid derivative, possibly because of the reaction of N-methylaniline with some reactive site in addition to the terminal isocyanate groups.

A polymer was obtained by reaction of the prepolymer with tetrafluoro-p-phenylenediamine. Heating this polymer in a press resulted in a flaky thin film.

$$OCN\text{-}\langle C_6F_4\rangle\text{-}NH\text{-}\overset{O}{C}\text{-}O\text{-}\underset{CF_3}{\overset{CF_3}{C}}\text{-}OCH_2(CF_2)_3CH_2O\text{-}\underset{CF_3}{\overset{CF_3}{C}}\text{-}O\text{-}\overset{O}{C}\text{-}NH\text{-}\langle C_6F_4\rangle\text{-}NCO \ + \ H_2N\text{-}\langle C_6F_4\rangle\text{-}NH_2$$

$$\left[NH\text{-}\langle C_6F_4\rangle\text{-}N\text{-}\overset{O}{C}\text{-}NH\text{-}\langle C_6F_4\rangle\text{-}NH\text{-}\overset{O}{C}\text{-}O\text{-}\underset{CF_3}{\overset{CF_3}{C}}\text{-}OCH_2(CF_2)_3CH_2O\text{-}\underset{CF_3}{\overset{CF_3}{C}}\text{-}O\text{-}\overset{O}{C}\text{-}NH\text{-}\langle C_6F_4\rangle\text{-}N\text{-}\overset{O}{C} \right]_x$$
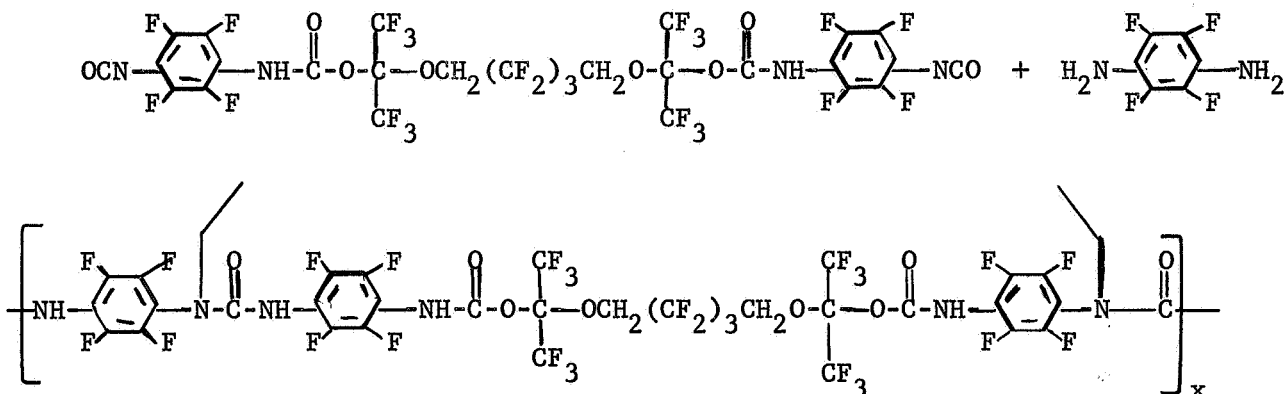
C. Prepolymers

1. Hydroxyl-Terminated Poly(hexafluoropentamethylene adipate)

The preparation of hydroxyl-terminated poly(hexafluoropentamethylene adipate) was reported in Annual Summary Report I (July 1964), by reaction of adipyl chloride with hexafluoropentanediol. This prepolymer was prepared again during this report period using essentially the same procedure.

$$Cl\text{-}\overset{O}{C}\text{-}(CH_2)_4\text{-}\overset{O}{C}\text{-}Cl \ + \ HOCH_2(CF_2)_3CH_2OH \longrightarrow$$

$$H\text{-}\left[OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{C}\text{-}(CH_2)_4\text{-}\overset{O}{C} \right]_x OCH_2(CF_2)_3CH_2OH$$

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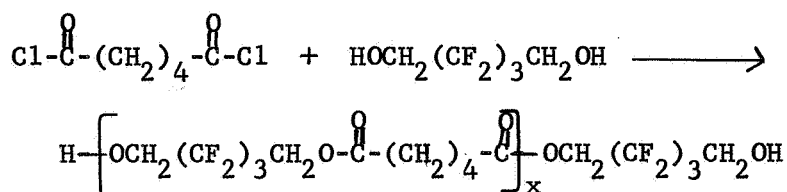
2. Hydroxyl-Terminated Poly(hexafluoropentamethylene malonate)

The reaction of diethyl malonate and excess hexafluoropentanediol at 170°C with lead (II) oxide as catalyst yielded a viscous liquid, identified by its elemental analysis and infrared spectrum as hydroxyl-terminated poly (hexafluoropentamethylene malonate).

$$C_2H_5\text{-O-}\overset{O}{\overset{\|}{C}}\text{-CH}_2\text{-}\overset{O}{\overset{\|}{C}}\text{-O-C}_2H_5 \quad + \quad HOCH_2(CF_2)_3CH_2OH \quad \xrightarrow{\;PbO\;}$$

$$H\left[O\text{-CH}_2(CF_2)_3CH_2\text{-O-}\overset{O}{\overset{\|}{C}}\text{-CH}_2\text{-}\overset{O}{\overset{\|}{C}}\right]_x O\text{-CH}_2(CF_2)_3CH_2OH$$
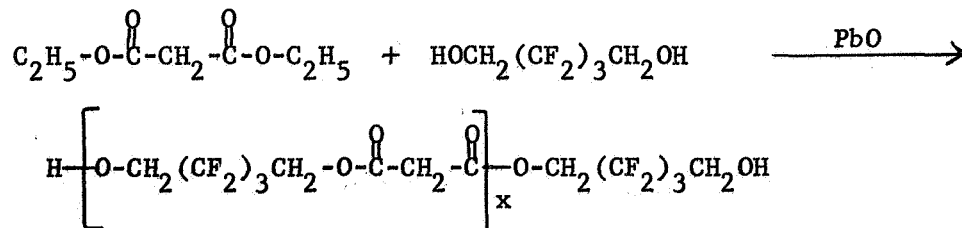
Attempts to prepare this polymer at 80°C with catalyst and at 170°C without catalyst were unsuccessful.

3. Hydroxyl-Terminated Poly(hexafluoropentamethylene carbonate)

The new compound, hexafluoropentamethylene-bischloroformate, has been prepared by Narmco. The preparation is described in Section III.E.. This bischloroformate was reacted with hexafluoropentanediol in dioxane yielding hydroxyl-terminated poly(hexafluoropentamethylene carbonate). The reaction was carried out using a stoichiometric amount of pyridine. Thus, the reacting species is most probably the dipyridinium complex of the bis-chloroformate.

$$HOCH_2(CF_2)_3CH_2OH \; + \; \text{[dipyridinium bischloroformate complex]} \longrightarrow \; \xrightarrow{\;H_2O\;}$$

$$H\left[OCH_2(CF_2)_3CH_2\text{O-}\overset{O}{\overset{\|}{C}}\right]_x OCH_2(CF_2)_3CH_2OH$$
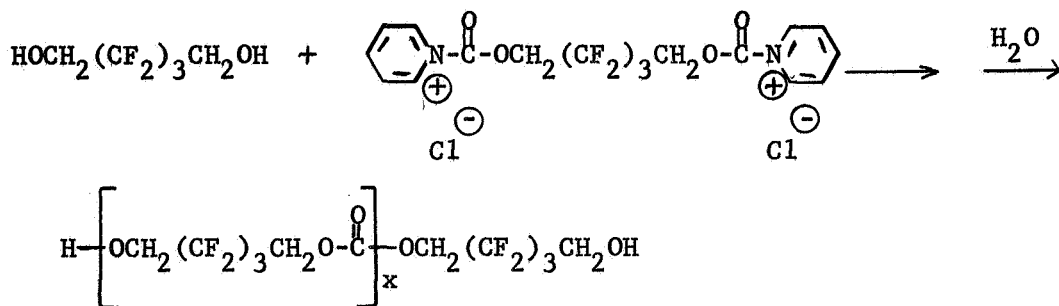
A brief study of different solvents and of the order of addition was conducted on this reaction. The reaction was run in two solvents, ethyl ether and N,N-dimethylformamide (DMF), by adding the bischloroformate to a solution of the diol containing a stoichiometric amount of pyridine. The reaction was also run in DMF using reverse addition; i.e., by adding a solution of the diol to a solution of the bischloroformate containing pyridine. In the reverse addition method, an activated complex of the bischloroformate and pyridine was formed before addition of the diol. Although the products obtained from the three runs had almost identical molecular weights (as determined by hydroxyl end groups), the physical properties varied considerably. The products from the two normal addition runs were semisolids while the product from the reverse addition run in DMF was a viscous yellow oil.

On standing, the product from the ether solution run crystallized while the products from the two DMF solution runs became less viscous oils. The infrared spectra of the oils exhibit a strong absorption band at 6.05 μ and vapor phase chromatography shows the absence of any DMF. This indicates that the DMF may have entered into the reaction in some manner.

4. Hydroxyl-Terminated Esters from Hexafluoroacetone

The incorporation of ketal groupings into the polyester portion of a polyester-based polyurethane might increase the flexibility of the polymer. Therefore, an attempt was made to prepare a mixed hydroxyl-terminated polyester. The reaction of hexafluoroacetone monohydrate with adipyl chloride yielded a liquid believed to be the acid chloride-terminated diester. The preparation of this diester is described in Section III.E.. This diester was reacted with hexafluoropentanediol, which yielded a viscous liquid, tentatively identified as the desired hydroxyl-terminated polyester.

5. Amine-Terminated Prepolymer Curing Agents

The use of tetrafluoro-p-phenylenediamine as a curing agent for isocyanate-terminated prepolymers has been complicated by the fact that it is a fairly high-melting solid. This amine has been used with some success by dissolving it in solvent, then combining it with the prepolymer in solution, then removing the solvent prior to heat curing. This method, however, is not practical for adhesive applications.

Thus, attempts were made to prepare liquid or low-melting amine-terminated prepolymers which could be used as curing agents for isocyanate-terminated prepolymers.

In one attempt, the isocyanate-terminated prepolymer, prepared from tetrafluoro-p-phenylene diisocyanate and hydroxyl-terminated poly(hexafluoropentamethylene adipate) of molecular weight 3200, was reacted with a 100% molar excess of tetrafluoro-p-phenylenediamine. The prepolymer obtained was amine-terminated, but was an infusible solid.

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$$H\text{---}[OCH_2(CF_2)_3\text{-}CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}]_x\text{---}OCH_2(CF_2)_3CH_2OH \ + \ 2 \ OCN\text{---}\underset{F \ \ F}{\overset{F \ \ F}{\bigcirc}}\text{---}NCO \ \longrightarrow$$

M.W. = 3200

$$OCN\text{---}\underset{F \ \ F}{\overset{F \ \ F}{\bigcirc}}\text{---}NH\text{-}\overset{O}{\overset{\|}{C}}[OCH_2(CF_2)_3\text{-}CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}]_x\text{---}OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{---}\underset{F \ \ F}{\overset{F \ \ F}{\bigcirc}}\text{---}NCO$$

$$\downarrow \ 2 \ H_2N\text{---}\underset{F \ \ F}{\overset{F \ \ F}{\bigcirc}}\text{---}NH_2$$

$$H_2N\text{---}\underset{F \ \ F}{\overset{F \ \ F}{\bigcirc}}\text{---}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{---}\underset{F \ \ F}{\overset{F \ \ F}{\bigcirc}}\text{---}NH\text{-}\overset{O}{\overset{\|}{C}}[OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}]_x\text{---}OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{---}\underset{F \ \ F}{\overset{F \ \ F}{\bigcirc}}\text{---}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{---}\underset{F \ \ F}{\overset{F \ \ F}{\bigcirc}}\text{---}NH_2$$

In another series of reactions, an acid chloride-terminated polyester was prepared by reaction of hexafluoropentanediol with excess adipyl chloride. This polyester was capped by reaction with tetrafluoro-p-phenylenediamine to yield a liquid, amine-terminated prepolymer.

$$4 \ Cl\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl \ + \ 3 \ HO\text{-}CH_2(CF_2)_3CH_2\text{-}OH \ \longrightarrow$$

$$Cl\text{---}[\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_2(CF_2)_3CH_2O]_3\text{---}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl \ + \ 6 \ HCl$$

$$\downarrow \ 2 \ H_2N\text{---}\underset{F \ \ F}{\overset{F \ \ F}{\bigcirc}}\text{---}NH_2$$

$$H_2N\text{---}\underset{F \ \ F}{\overset{F \ \ F}{\bigcirc}}\text{---}NH\text{---}[\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_2(CF_2)_3CH_2O]_3\text{---}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{---}\underset{F \ \ F}{\overset{F \ \ F}{\bigcirc}}\text{---}NH_2$$

6. Hydroxyl-Terminated Polyacetals

a. Poly(hexafluoropentamethylene formal). — Smith[12] attempted to prepare a fluorine-containing polyglycol formal by reaction of dibutyl formal with hexafluoropentanediol. The product obtained was a high-boiling liquid which decomposed on long standing, or on heating at atmospheric pressure, liberating formaldehyde and the original glycol. The desired polyglycol,

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identified by its infrared spectrum, was obtained when this reaction was repeated in Narmco's laboratory. The yield, however, was extremely low.

$$HOCH_2(CF_2)_3CH_2OH \quad + \quad C_4H_9O-CH_2O-C_4H_9$$

$$HOCH_2(CF_2)_3CH_2O\left[CH_2O-CH_2(CF_2)_3CH_2O\right]_x H$$
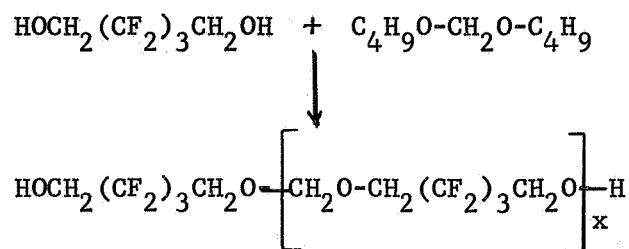
The same hydroxyl-terminated polyformal was prepared in 57% yield by the reaction of 2,2,3,3,4,4-hexafluoropentanediol with trioxane in the presence of p-toluenesulfonic acid. Its molecular weight was 835.

$$HOCH_2(CF_2)_3CH_2OH \quad + \quad$$

p-Toluenesulfonic
Acid

$$HOCH_2(CF_2)_3CH_2O\left[CH_2-OCH_2(CF_2)_3CH_2O\right]_x H$$

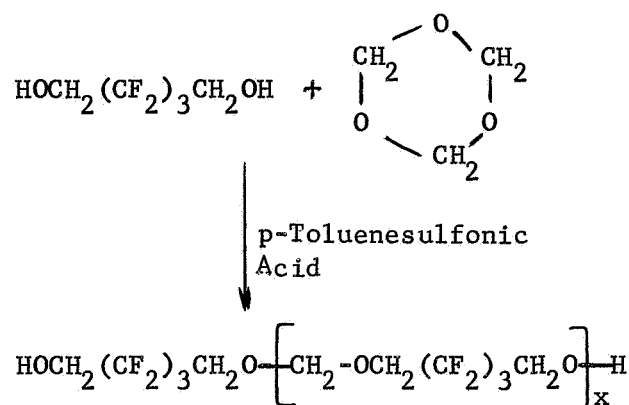b. **From Perfluoroaldehydes.** — The preparation of solid and liquid polyacetals from fluorinated aldehydes has been reported.[13] Attempts were made to prepare a low molecular weight, hydroxyl-terminated polyacetal. Since prior work has indicated that aldehydes having relatively long alkyl groups have less tendency to form crystalline polymers, most of the work was carried out using perfluorobutyraldehyde.

Perfluorobutyraldehyde, prepared by dehydration of its hydrate, was polymerized to a white, brittle solid by sulfuric acid and by acetic anhydride catalysts.

$$CF_3CF_2CF_2-\overset{O}{\overset{\|}{C}}-H \longrightarrow \left[\begin{matrix} C_3F_7 \\ | \\ C-O \\ | \\ H \end{matrix}\right]_x$$
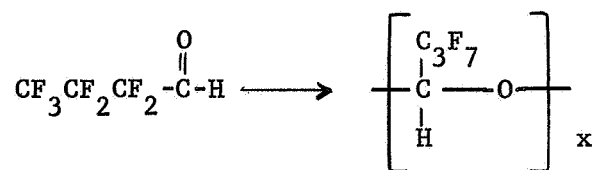
The polymer was insoluble in all solvents tried, and on heating to its melting point (280°-300°C), it vaporized, possibly depolymerizing back to perfluorobutyraldehyde. An attempt to polymerize perfluorobutyraldehyde using cumene hydroperoxide was unsuccessful.

An attempt was made to prepare low molecular weight polymers by stopping sulfuric acid catalyzed polymerizations of perfluorobutyraldehyde after various short periods of time. The polymerizations were stopped by addition of sodium bicarbonate. The only product obtained in each of the runs was a water-soluble perfluorobutyraldehyde hydrate.

All examples of polymerization of fluorinated aldehydes in the literature involve the use of anhydrous aldehydes. It was considered possible, however, that an aldehyde hydrate could be dehydrated directly to a polyacetal. An attempt to polymerize trifluoroacetaldehyde to a polymer by dehydration with sulfuric acid yielded only water-soluble materials. Either no polymer was formed, or the polymer decomposed on addition of water.

$$\underset{\underset{\underset{H}{|}}{\underset{|}{C}}{\overset{\overset{CF_3}{|}}{HO-C-OH}} \xrightarrow{\;\;H_2SO_4\;\;} \Big/ \qquad H-\Big[O-\underset{\underset{H}{|}}{\overset{\overset{CF_3}{|}}{C}}\Big]_x OH$$
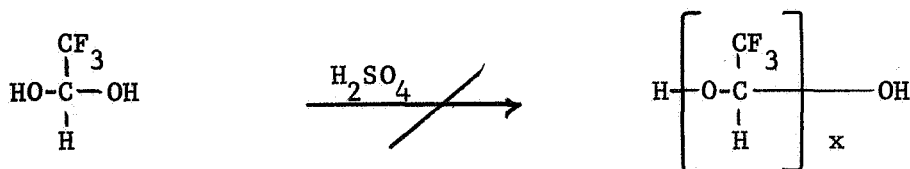
Dehydration of perfluorobutyraldehyde hydrate with sulfuric acid, on the other hand, yielded a solid polymer that melted at 80°-90°C and was insoluble in water. Its infrared spectrum indicates that this polymer is hydroxyl 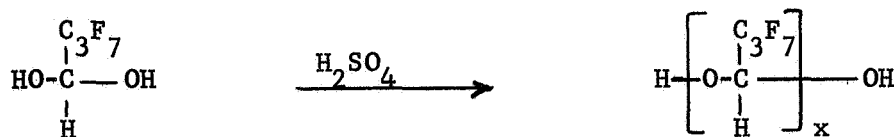terminated. The polymer, like the high-melting polymer prepared from anhydrous perfluorobutyraldehyde, vaporizes at its melting point.

$$\underset{\underset{\underset{H}{|}}{\underset{|}{C}}{\overset{\overset{C_3F_7}{|}}{HO-C-OH}} \xrightarrow{\;\;H_2SO_4\;\;} \qquad H-\Big[O-\underset{\underset{H}{|}}{\overset{\overset{C_3F_7}{|}}{C}}\Big]_x OH$$

The work just described seems to indicate that fluorinated polyacetals derived from perfluorinated aldehydes show little promise as prepolymers due to their crystalline nature and their lack of stability to heat.

c. Other Polyketals and Polyacetals. — Because of the success in preparing poly(hexafluoropentamethylene formal) from hexafluoropentanediol and trioxane, an attempt was made to prepare a similar polyketal from hexafluoroacetone. However, the reaction of hexafluoropentanediol with hexafluoroacetone in the presence of p-toluenesulfonic acid failed to yield the desired polyketal.

$$HOCH_2(CF_2)_3CH_2OH \;+\; CF_3-\overset{\overset{O}{\|}}{C}-CF_3 \xrightarrow[\text{No reaction}]{\text{p-Toluenesulfonic Acid}}$$

$$HOCH_2(CF_2)_3CH_2-O\Big[\underset{\underset{CF_3}{|}}{\overset{\overset{CF_3}{|}}{C}}-O-CH_2(CF_2)_3CH_2-O\Big]_x H$$
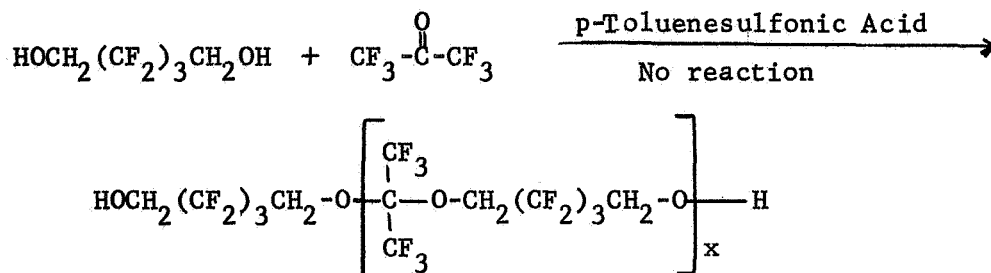
An attempt was also made to prepare a similar polyacetal from perfluoro-butyraldehyde. The reaction of hexafluoropentanediol with perfluorobutyr-aldehyde in the presence of p-toluenesulfonic acid failed to yield the desired polyacetal.

$$HOCH_2(CF_2)_3CH_2OH + C_3F_7CHO \xrightarrow{\text{p-Toluenesulfonic}} HO\left[CH_2(CF_2)_3CH_2-O-\overset{\overset{\displaystyle C_3F_7}{|}}{CH}-O\right]_x CH_2(CF_2)_3CH_2OH$$
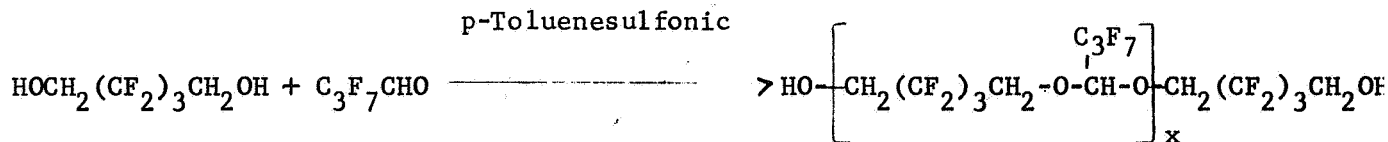
7. Hydroxyl-Terminated Polyethers

a. **From Poly(hexafluoropentamethylene carbonate).** — The improvement of low-temperature properties of polyurethanes by incorporation of ether linkages into the polymers has been discussed previously. Mention[14] of the conversion of aliphatic polycarbonates to polyethers led to an attempt to convert poly-(hexafluoropentamethylene carbonate) to poly(hexafluoropentamethylene oxide) by heating.

$$HO\left[CH_2(CF_2)_3CH_2O-\overset{\overset{\displaystyle O}{\|}}{C}-O\right]_x CH_2(CF_2)_3CH_2OH \xrightarrow{\quad\Delta\quad} \not\longrightarrow$$

$$HO-CH_2(CF_2)_3CH_2O\left[-CH_2(CF_2)_3CH_2OH\right]_x + CO_2\uparrow$$
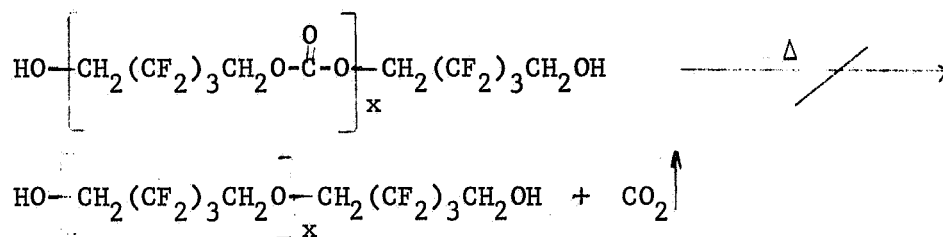
No loss of carbon dioxide occurred on heating the polycarbonate at $280°$-$300°C$ for $\frac{1}{2}$ hour, and the infrared spectrum was unchanged. The unexpected thermal stability is discussed in more detail in the following section on other polymers.

b. **From 3,3,3-Trifluoro-1,2-epoxypropane.** — Smith and coworkers have described the polymerization of 3,3,3-trifluoro-1,2-epoxypropane using Friedel-Crafts catalysts such as aluminum chloride and ferric chloride.[12] The polymer obtained using ferric chloride was a solid of 230,000 molecular weight, while that from aluminum chloride was a viscous liquid. No attempt was made to determine the type of end group present and no anionic polymerization was attempted. Jones and coworkers investigated the polymerization of 1,1,1-trifluoro-2,3-butylene oxide with various types of catalysts such as Friedel-Crafts and potassium hydroxide.[15] In all cases, viscous liquid polymers resulted. With potassium hydroxide as catalyst, a yield of only 10% was obtained. Again, no attempt was made to determine the type of end groups present in these polyethers.

Liquid hydroxy-terminated polyethers of 3,3,3-trifluoro-1,2-epoxypropane which contain over 50% fluorine were prepared in this laboratory. The molecular weights of these polyethers, as determined by vapor pressure osmometry (VPO) were in the range of 1150 to 4300.
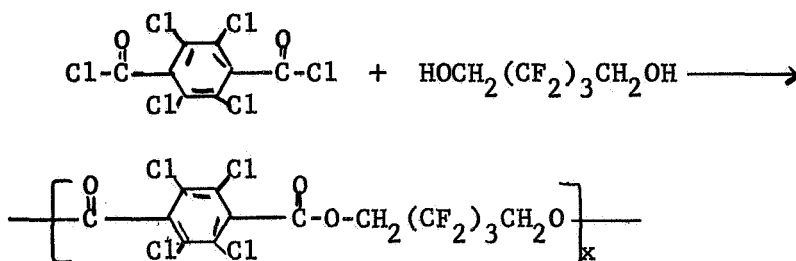
33

$$CF_3\text{-}CH\underset{\diagdown O\diagup}{}CH_2 \longrightarrow RO\text{-}\left[\begin{array}{c} CF_3 \\ | \\ CH\text{-}CH_2\text{-}O \end{array}\right]_x\text{-}H$$

$$R = H\text{- or } HO\text{-}CH_2(CF_2)_3CH_2\text{-}$$

Cationic polymerization of this monomer was carried out using two Friedel-Crafts catalysts, boron trifluoride (gas) and aluminum chloride. Based on its infrared spectrum, the polymer obtained using aluminum chloride catalysis showed no functional groups other than hydroxyl. A 35-g sample of the polyether of 3,3,3-trifluoro-1,2-epoxypropane was then prepared using aluminum chloride as initiator. The boron trifluoride initiated polyether was identical to the aforementioned polyether with a trace of impurity containing unsaturation. Narmco believes that this polymeric impurity is a result of a competing reaction involving fluoride ion abstraction as proposed below:

1. Initiation: $BF_3 + F\text{-}CF_2\text{-}CH\underset{\diagdown O\diagup}{}CH_2 \longrightarrow BF_4^- + CF_2\text{=}CH\text{-}O\text{-}CH_2^+$

2. Propagation: $CF_2\text{=}CH\text{-}O\text{-}CH_2^+ + CF_3\text{-}CH\underset{\diagdown O\diagup}{}CH_2 \longrightarrow CF_2\text{=}CH\text{-}O\text{-}CH_2\text{-}O^+$ (CH-CF$_3$, CH$_2$)

$$\downarrow$$

$$CF_2\text{=}CH\text{-}O\text{-}CH_2\text{-}\left[\begin{array}{c}CF_3\\|\\O\text{-}CH\text{-}CH_2\end{array}\right]_x\text{-}O\text{-}\overset{CF_3}{\underset{}{CH}}\text{-}CH_2^+ \longleftarrow CF_2\text{=}CH\text{-}O\text{-}CH_2\text{-}O\text{-}\overset{CF_3}{\underset{}{CH}}\text{-}CH_2^+$$

3. Termination: $CF_2\text{=}CH\text{-}O\text{-}CH_2\text{-}\left[\begin{array}{c}CF_3\\|\\O\text{-}CH\text{-}CH_2\end{array}\right]_x\text{-}O\text{-}\overset{CF_3}{\underset{}{CH}}\text{-}CH_2^+ + BF_4^- \longrightarrow$

$$CF_2\text{=}CH\text{-}O\text{-}CH_2\text{-}\left[\begin{array}{c}CF_3\\|\\O\text{-}CH\text{-}CH_2\end{array}\right]_x\text{-}O\text{-}\overset{CF_3}{\underset{}{CH}}\text{-}CH_2F + BF_3$$

Polyethers have been successfully prepared also by anionic polymerization using potassium hydroxide and the monosodium salt of hexafluoropentanediol.

In contrast to the low yield (10%) of polyether reported by Jones with potassium hydroxide catalysis, Narmco has been able to prepare a colorless polyether of 3,3,3-trifluoro-1,2-epoxypropane in 61% yield with an unexpectedly high molecular weight of 4300. Based on the infrared spectrum, the polymer

contains hydroxyl termination with some unsaturation. Narmco believes that this unsaturation arises from the abstraction of a proton from the epoxide by hydroxyl ion as illustrated below:

1. Initiation:

$$CF_3-CH-C\overset{H}{\underset{H}{<}} + OH^- \longrightarrow CF_3-CH=CH-O^- + H_2O$$

2. Propagation:

$$CF_3-CH=CH-O^- + CF_3-CH-CH_2$$

$$CF_3-CH=CH-O\left[\overset{CF_3}{\underset{}{CH}}-CH_2-O\right]_x\overset{CF_3}{\underset{}{CH}}-CH_2O^- \longleftarrow CF_3-CH=CH-O-\overset{CF_3}{\underset{}{CH}}-CH_2O^-$$

3. Termination:

$$CF_3-CH=CH-O\left[\overset{CF_3}{\underset{}{CH}}-CH_2-O\right]_x\overset{CF_3}{\underset{}{CH}}-CH_2-O^- + H_2O \longrightarrow$$

$$CF_3-CH=CH-O\left[\overset{CF_3}{\underset{}{CH}}-CH_2-O\right]_x\overset{CF_3}{\underset{}{CH}}-CH_2-OH + OH^-$$

The monosodium salt of hexafluoropentanediol was used as an anionic initiator for the polymerization of this epoxide in order to obtain primary hydroxyl termination on both ends of the polymer.

A 40-g sample of the polyether of 3,3,3-trifluoro-1,2-epoxypropane was then prepared using the sodium salt of hexafluoropentanediol (prepared by reaction of hexafluoropentanediol with sodium hydride) as initiator.

$$CF_3-CH-CH_2 \xrightarrow{NaOCH_2(CF_2)_3CH_2OH} HO-CH_2(CF_2)_3CH_2-O\left[\overset{CF_3}{\underset{}{CH}}-CH_2-O\right]_x H$$

The polyether obtained in 72.3% yield was a clear, viscous liquid whose molecular weight was 970 as determined by vapor pressure osmometry (VPO), and 1000 by end-group analysis.

D. Other Polymers

Although the major emphasis in this program has been on the preparation of highly halogenated polyurethanes, a small amount of work has been directed

toward the preparation of highly halogenated analogs of other common polymers which have demonstrated some particular characteristics in adhesive formulations. These polymers have also been prepared in order to obtain additional basic information in regard to the effect of molecular structure and fluorine content on LOX compatibility.

1. Polyesters — Poly(hexafluoropentamethylene tetrachloroterephthalate)

Poly(hexafluoropentamethylene tetrachloroterephthalate) was prepared by the melt polymerization of hexafluoropentanediol and tetrachloroterephthaloyl chloride at $210°$-$220°C$ for 17 hours.

$$Cl-\overset{O}{\underset{}{C}}\overset{Cl\quad Cl}{\underset{Cl\quad Cl}{\bigcirc}}\overset{O}{\underset{}{C}}-Cl \;+\; HOCH_2(CF_2)_3CH_2OH \longrightarrow$$

$$-\left[\overset{O}{\underset{}{C}}\overset{Cl\quad Cl}{\underset{Cl\quad Cl}{\bigcirc}}\overset{O}{\underset{}{C}}-O-CH_2(CF_2)_3CH_2O\right]_x-$$

The polymer was a black, brittle solid melting above $380°C$.

2. Polycarbonates

a. Poly(hexafluoropentamethylene carbonate). — The preparation of the new hydroxyl-terminated poly(hexafluoropentamethylene carbonate) has been described in Section III.C of this report.

The need to prepare larger samples of hydroxyl-terminated poly(hexa-fluoropentamethylene carbonate) prompted further study of the preparation of the polycarbonate directly from hexafluoropentanediol by reaction with pyridine and phosgene without isolation of the extremely toxic bischloro-formate.

$$HOCH_2(CF_2)_3CH_2OH \;+\; COCl_2 \;+\; \bigcirc^{N}$$

$$\downarrow$$

$$H-\left[O-CH_2(CF_2)_3CH_2-O-\overset{O}{\underset{}{C}}\right]_x-O-CH_2(CF_2)_3CH_2OH$$
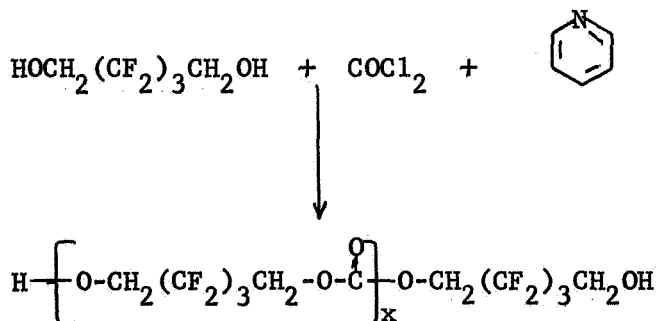
The reaction was carried out using two methods. In the first (Method A) the monopyridinium complex is formed in situ by addition of pyridine to phosgene in solvent. The complex immediately reacts with the hexafluoro-pentanediol which is being added along with the pyridine.

$$\text{pyridine} + COCl_2 \longrightarrow \text{pyridinium-}\overset{O}{\overset{\|}{C}}\text{-Cl} \quad Cl^{\ominus}$$

$$\text{pyridinium-}\overset{O}{\overset{\|}{C}}\text{-Cl} \quad Cl^{\ominus} + HOCH_2(CF_2)_3CH_2OH \longrightarrow Cl\text{-}\overset{O}{\overset{\|}{C}}\text{-OCH}_2(CF_2)_3CH_2OH + \text{pyridinium-H} \; Cl^{\ominus}$$

$$\downarrow \text{pyridine}$$

$$H\text{---}\Big[OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\Big]_k OCH_2(CF_2)_3CH_2OH \xleftarrow{HOCH_2(CF_2)_3CH_2OH} \text{pyridinium-}\overset{O}{\overset{\|}{C}}\text{-OCH}_2(CF_2)_3CH_2OH \quad Cl^{\ominus}$$
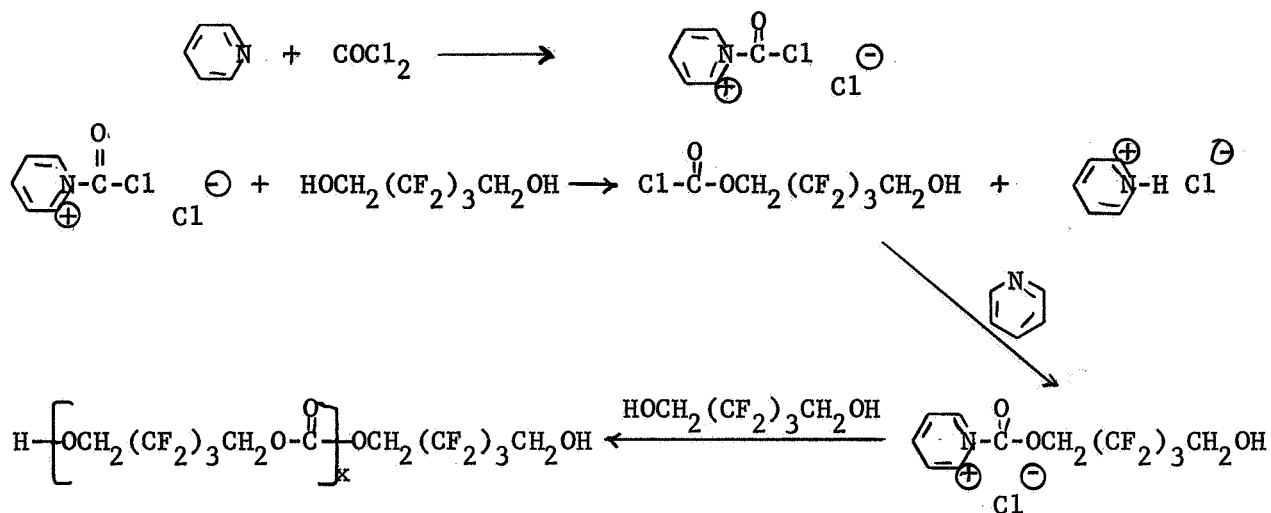
In the second (Method B) the dipyridinium carbonyl chloride complex was preformed in solution and added to hexafluoropentanediol in solution.

$$\text{pyridinium-}\overset{O}{\overset{\|}{C}}\text{-N-pyridinium} \quad 2 \; Cl^{\ominus} + HOCH_2(CF_2)_3CH_2OH$$

$$\downarrow$$

$$\text{pyridinium-}\overset{O}{\overset{\|}{C}}\text{-OCH}_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-N-pyridinium} \quad Cl^{\ominus} \quad Cl^{\ominus}$$

$$\downarrow HOCH_2(CF_2)_3CH_2OH$$

$$H\text{---}\Big[OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\Big]_x OCH_2(CF_2)_3CH_2OH$$
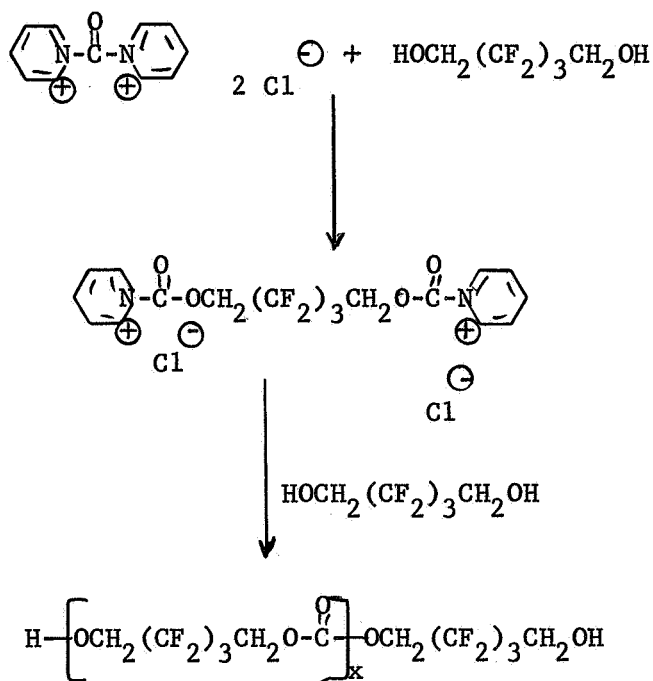
The results of the various runs are shown in Table 1.

TABLE 1

PREPARATIONS OF POLY(HEXAFLUOROPENTAMETHYLENE CARBONATE)

Ratio of Reactants HFPD[a]/COCl$_2$/Pyridine	Solvent	Expected M.W.	Experimentally Determined M.W.	Method of Addition
1/1/2	ClCH$_2$-CH$_2$Cl	∞	840[b]	A
1/1/2	ClCH$_2$-CH$_2$Cl	∞	1040[b]	B
1/1/2	CH$_2$Cl$_2$/ether	∞	700[b]	B
10/7/14	Cl$_2$C=CCl$_2$	1150	4850[c]	B
9/8/16	CCL$_3$F	1850	5900[c]	B
8/9/18	CCL$_3$F	1850	1800[c]	A

(a) Hexafluoropentanediol
(b) By hydroxyl end group analysis
(c) By vapor phase osmometry

The reactions in which equivalent amounts of hexafluoropentanediol and pyridine were used (i.e., a 1:2 ratio) resulted in polycarbonates of lower molecular weight than expected. When an excess of hexafluoropentanediol over pyridine was used, polycarbonates of higher molecular weight than expected were obtained.

The polycarbonate of 5900 molecular weight was pressed into a film and samples submitted to MSFC for LOX-compatibility testing. This polycarbonate was sensitive to impact in LOX.

As mentioned in the discussion on the attempted preparation of a poly-ether from this polycarbonate, it seems to possess an unexpectedly high degree of thermal stability. The polycarbonate of 5900 molecular weight was subjected to thermogravimetric analysis. The results show a polymer decomposition temperature of 450° ±10°C in both air and helium atmospheres with a maximum rate of weight loss of 10.90% per minute and 10.22% per minute respectively at a heating rate of 6.67°C per minute. The thermograms are shown in Figures 3 and 4.

b. Attempted Preparation of Poly(hexafluoropentamethylene tetrachloro-p-xylylene carbonate). — As was discussed earlier in this report, hydroxyl-terminated polycarbonates can be prepared by reaction of hexafluoropenta-methylene bischloroformate with various diols. In an attempt to prepare a
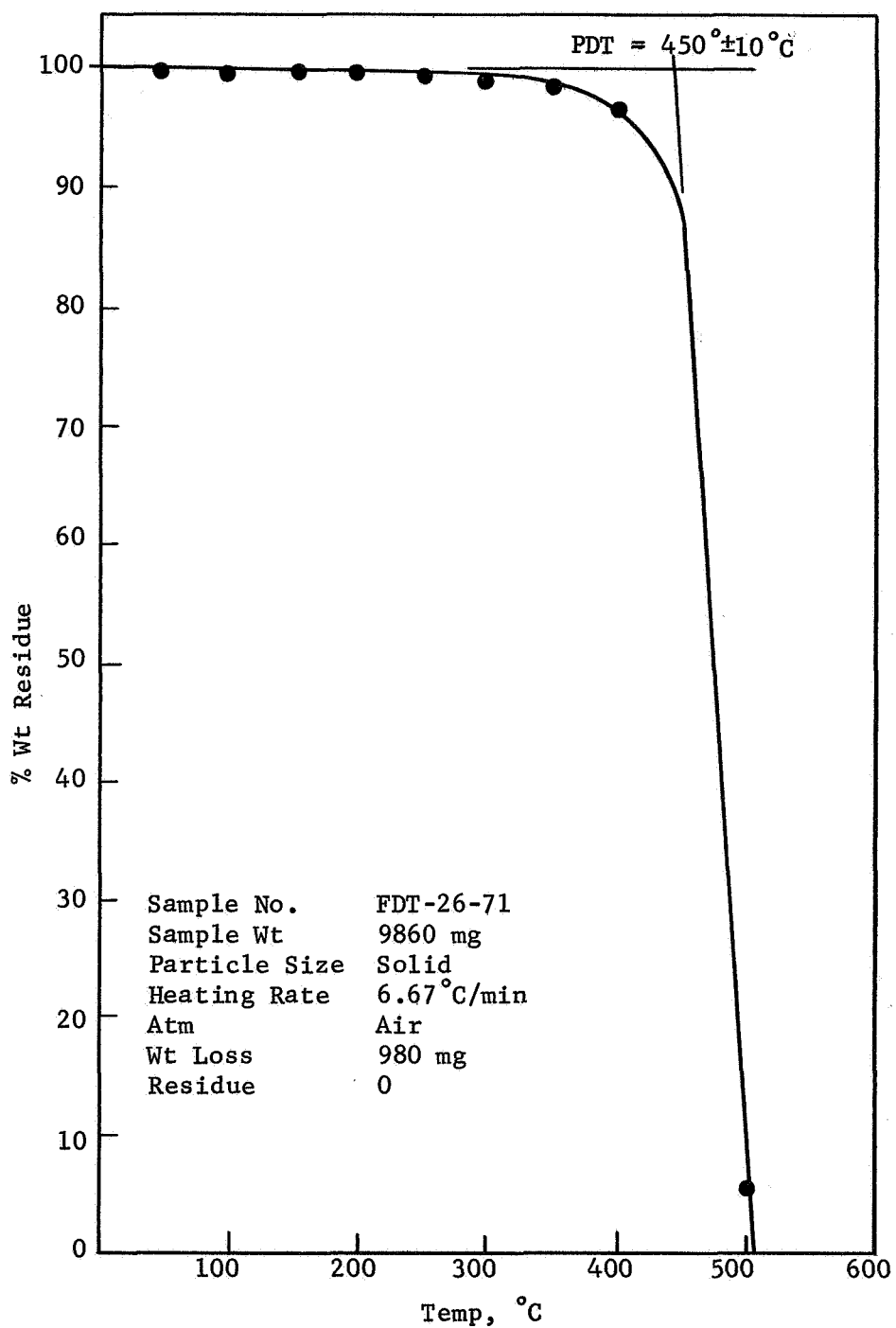
Figure 3. Thermogram of Poly(hexafluoropentamethylene
carbonate) in Air
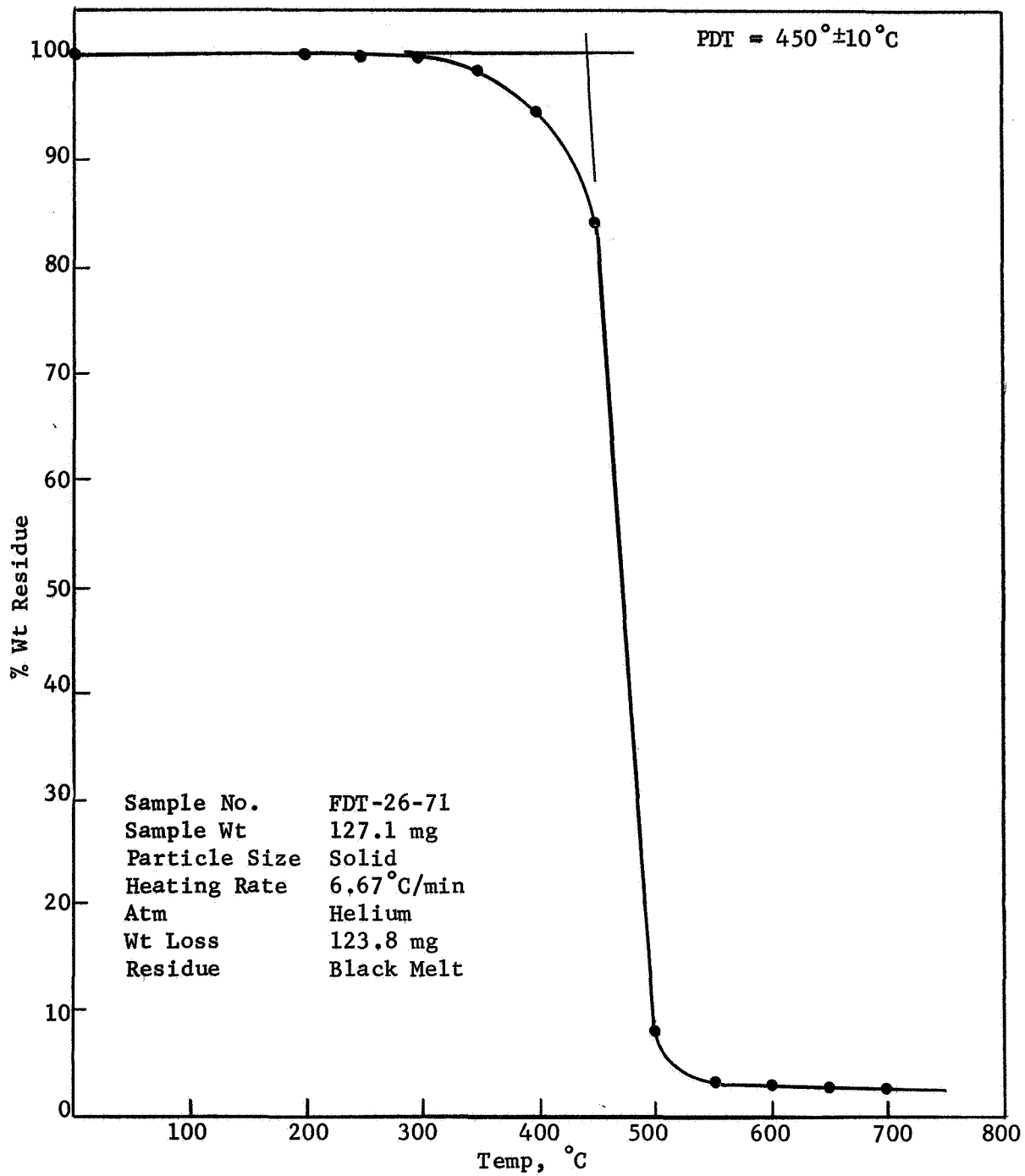
Figure 4. Thermogram of Poly(hexafluoropentamethylene carbonate) in Helium

The figure contains the following labels and data:

PDT = 450°±10°C

Y-axis: % Wt Residue (marked 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100)

X-axis: Temp, °C (marked 100, 200, 300, 400, 500, 600, 700, 800)

Sample No.   FDT-26-71
Sample Wt   127.1 mg
Particle Size   Solid
Heating Rate   6.67°C/min
Atm   Helium
Wt Loss   123.8 mg
Residue   Black Melt

polycarbonate of tetrachloroxylylene diol and hexafluoropentamethylene bis-chloroformate, no polymer was obtained.

$$\text{HOCH}_2 \underset{Cl}{\overset{Cl}{\underset{Cl}{\bigcirc}}} \text{CH}_2\text{OH} \ + \ \text{Cl-} \overset{O}{\overset{\|}{C}}\text{-OCH}_2(\text{CF}_2)_3\text{CH}_2\text{O-}\overset{O}{\overset{\|}{C}}\text{-Cl} \longrightarrow\!\!\!\!\!/\!\!\!\!\!\longrightarrow$$

$$\left[\text{OCH}_2 \underset{Cl}{\overset{Cl}{\underset{Cl}{\bigcirc}}} \text{CH}_2\text{O-}\overset{O}{\overset{\|}{C}}\text{-OCH}_2(\text{CF}_2)_3\text{CH}_2\text{O-}\overset{O}{\overset{\|}{C}} \right]_x$$
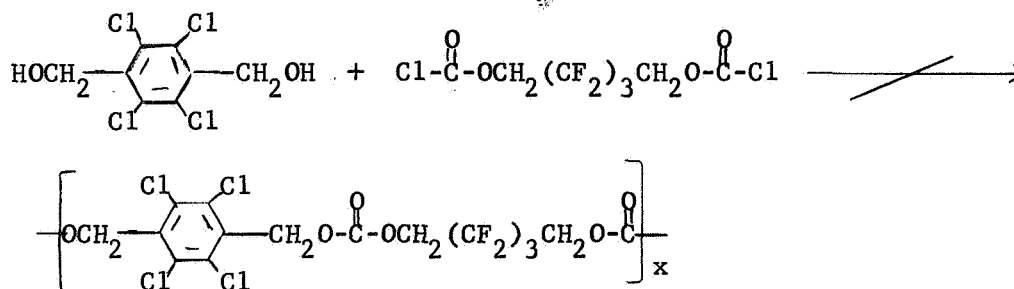
In a subsequent experiment, run in DMF solvent, a monocarbonate was isolated in 94% yield.

3. Polyethers

a. Poly(hexafluoropentamethylene ether). — The preparation of the cyclic ether, hexafluoropentamethylene oxide, was described in Annual Summary Report I (July 1964). An unsuccessful attempt to polymerize this cyclic ether with boron trifluoride — etherate was also described in that report.

During this report period, additional attempts were made to initiate ring opening of hexafluoropentamethylene oxide with both bases and acids.

$$\underset{CF_2}{\overset{CH_2}{\underset{|}{|}}} \overset{O}{\underset{CF_2}{\diagup\diagdown}} \underset{CF_2}{\overset{CH_2}{\underset{|}{|}}} \quad + \quad \begin{array}{c} \text{Base} \\ \text{or} \\ \text{Acid} \end{array} \quad \longrightarrow\!\!\!\!\!/\!\!\!\!\!\longrightarrow \quad \left[\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{-O} \right]_x$$
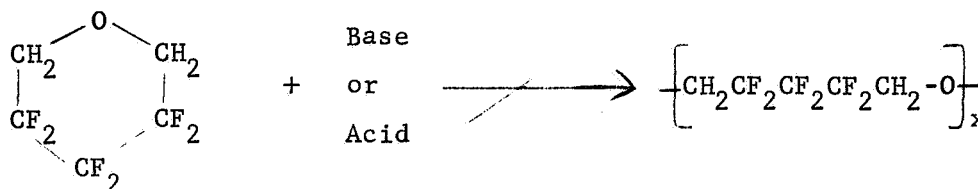
In separate experiments, the cyclic ether was treated with triethylamine, solid potassium hydroxide, aqueous potassium hydroxide, phosphorus pentafluoride, phosphorus pentafluoride-tetrahydrofuran complex, and rubidium fluoride. None of these catalysts caused polymerization after standing for 30 days.

An attempt to polymerize this cyclic oxide by long refluxing in the presence of aluminum chloride was unsuccessful.

An attempt was also made to cause polymerization using boron trifluoride as catalyst. A solid which formed on reaction of hexafluoropentamethylene oxide at $0°C$ may have been a complex of the oxide and boron trifluoride similar to that formed between tetrahydrofuran and phosphorus pentafluoride. It did not, however, cause polymerization of a fresh sample of hexafluoropentamethylene oxide over a 2-week period at a temperature of $-10°C$. Passing boron trifluoride

into a sample of the cyclic oxide at room temperature for 1 hour, then allowing the solution to stand for 2 days, resulted in the formation of a small amount of a dense, dark oil. Workup of this oil indicated that it is probably also a complex of the oxide and boron trifluoride.

Early in this program, it was thought that the cyclic sulfite, hexa- fluoropentamethylene sulfite, underwent polymerization to a polyether with boron trifluoride or hydrogen chloride. It was felt that a small amount of this cyclic sulfite might initiate the polymerization of the hexafluoropenta- methylene oxide. The polymerization of hexafluoropentamethylene oxide with a trace of hexafluoropentamethylene sulfite was attempted with both boron trifluoride-etherate and hydrogen chloride as catalysts. No polymerization took place in either reaction.

    b. <u>Poly(tetrafluorotetramethylene ether)</u>. — The preparation of 3,3,4,4- tetrafluorotetramethylene oxide was achieved this year and will be described in the monomer section. Since tetrahydrofuran can be polymerized, attempts were made to polymerize this cyclic ether using (1) aluminum chloride, (2) phosphorus pentafluoride—tetrahydrofuran complex, (3) phosphorus penta- fluoride, and (4) boron trifluoride as catalysts. No noticeable reaction took place with the first three catalysts. With phosphorus pentafluoride catalyst, a small amount of liquid formed which is probably a complex of the cyclic ether and phosphorus pentafluoride. A crystalline solid was formed with boron trifluoride catalysis, which is also probably a complex of the cyclic ether and boron trifluoride.

$$\underset{\substack{| \\ CF_2}}{CH_2}\overset{O}{\diagup\diagdown}\underset{\substack{| \\ CF_2}}{CH_2} \;\;\xrightarrow{\;\;\not\;\;}\;\; -\left[CH_2CF_2CF_2CH_2-O\right]_x-$$
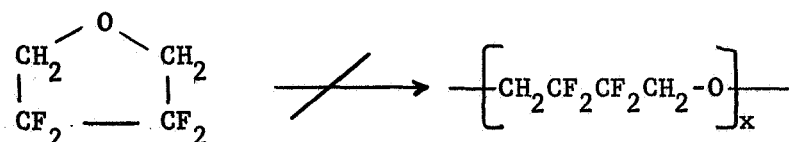
4. <u>Poly(hexafluoropentamethylene sulfite)</u>

The polymer described in Annual Summary Report I (July 1964), prepared by the reaction of hexafluoropentamethylene sulfite with either boron tri- fluoride-etherate or hydrogen chloride, was tentatively assigned the structure of poly(hexafluoropentamethylene oxide). This same polymer was prepared by reaction of hexafluoropentamethylene sulfite with phosphorus pentafluoride during this year. The polymer was stripped of unreacted cyclic sulfite and phosphorus pentafluoride, and the elemental analysis was obtained. The polymer was heated for 1-½ hours in a solution of sodium bicarbonate, during which time sulfur dioxide evolution was detected. The material had become considerably less viscous during the heating. A sample of the material was isolated and the elemental analysis and molecular weight determined by vapor phase osmometry. The remaining material was heated in the sodium bicarbonate solution for an additional 4 hours. At the end of this time, all the material had dissolved in the solution from which only hexafluoropentanediol was isolated.

The experimental molecular weight (472) and the elemental analysis of the material after hydrolysis for 1-½ hours correspond closely to two logical structures, A and B.

$$HOCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{S}}-OCH_2(CF_2)_3CH_2OH$$

A

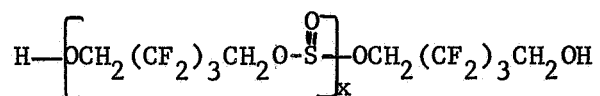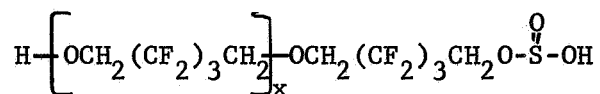$$HOCH_2(CF_2)_3CH_2O-CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{S}}-OH$$
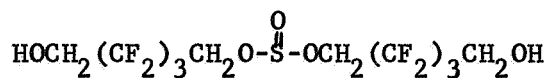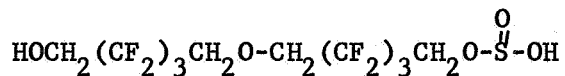
B

The first of these structures, A, would have resulted from hydrolysis of a polysulfite C, while the second would come from hydrolysis of a sulfite-terminated polyether, D.

$$H-\left[OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{S}}\right]_x OCH_2(CF_2)_3CH_2OH$$

C

$$H-\left[OCH_2(CF_2)_3CH_2\right]_x OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{S}}-OH$$

D

The elemental analysis of the polymer before hydrolysis showed that the polymer contained 8.95% sulfur. The polyether D, where x was any number larger than 1, would contain a considerably smaller percentage of sulfur. From this evidence, then, it appears that the polymer obtained by acid-catalyzed polymerization of hexafluoropentamethylene sulfite is a polysulfite of structure C. This polysulfite, on extensive hydrolysis, will yield hexafluoropentanediol.

5. Polyamides

a. **From Perfluoroglutaryl Chloride.** — Poly(hexafluoropentamethylene perfluoroglutaramide) was prepared and samples submitted to MSFC for LOX testing last year. The LOX testing conducted during this report period showed that this polyamide was LOX compatible.

The preparation of poly(ethylene perfluoroglutaramide) was also described in Annual Summary Report I (July 1964). Samples of this prepolymer were prepared and forwarded to MSFC for LOX-impact testing. This polymer was LOX compatible.

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The preparation of poly(tetrafluoro-p-phenylene perfluoroglutaramide) via the interfacial polymerization technique was reported in Annual Summary Report I (July 1964). The polymer formed has always been of low molecular weight, apparently as a result of premature precipitation of the polymer before high molecular weight has been achieved.

In an effort to increase the molecular weight of the polymer, o-dichlorobenzene was used as the organic solvent. The concentration of the monomers were also decreased in their respective solvents. Nevertheless, the resultant polymer failed to proceed to a high molecular weight.

b. **From Hexafluoropentanediamine.** — Poly(hexafluoropentamethylene adipamide) was prepared by the interfacial polymerization of hexafluoropentamethylenediamine and adipyl chloride.

$$H_2NCH_2(CF_2)_3CH_2NH_2 \ + \ Cl-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow$$

$$-\!\!\left[\!\!-\overset{H}{\overset{|}{N}}-CH_2-(CF_2)_3-CH_2-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\!\!-\right]_{\!x}\!\!-$$
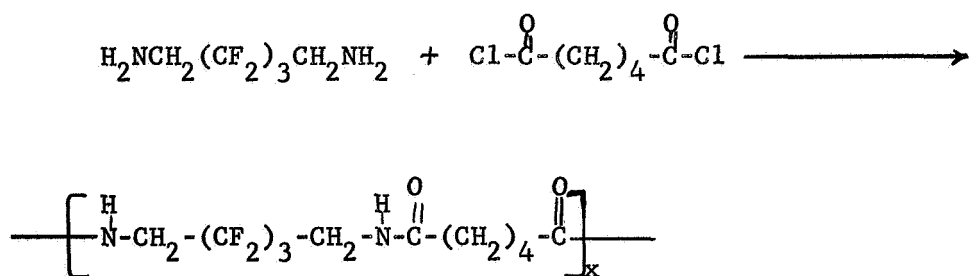
The polymer was light tan and had a melting point of $130°-140°C$.

Poly(hexafluoropentamethylene tetrachloroterephthalamide) could not be prepared by the interfacial polymerization of hexafluoropentanediamine and tetrachloroterephthaloyl chloride.

6. **Polyureas**

Chlorocarbonyl pyridinium chloride was prepared by reaction of pyridine and phosgene. The preparation and reactions of this material will be discussed in detail in Section III.E of this report.

Tetrafluoro-p-phenylene diamine was reacted with chlorocarbonyl pyridinium chloride and excess phosgene. Although 2 moles of chlorocarbonyl pyridinium chloride were present for each mole of diamine, only 1 mole reacted to yield diisocyanate as shown in the equations below. The other mole was consumed by the hydrogen chloride formed by dehydrohalogenation of the intermediate dicarbamyl chloride. Since the rate of reaction of phosgene with the diamine is slow, the reaction of diisocyanate formed with unreacted diamine is rapid enough to be competitive. This reaction leads to the formation of polyurea.

$$4 \ COCl_2 \ + \ 1 \ \langle\ \rangle N \longrightarrow 1 \ \langle\ \rangle\overset{\oplus}{N}-\overset{O}{\overset{\|}{C}}-Cl \ \underset{Cl}{\ominus} \ + \ 3 \ COCl_2$$

1/4 H$_2$N—C$_6$F$_4$—NH$_2$ + 1/2 [C$_5$H$_5$N$^+$-C(=O)-Cl] Cl$^-$ ⟶

1/4 Cl-C(=O)-NH—C$_6$F$_4$—NH-C(=O)-Cl + 1/2 [C$_5$H$_5$N$^+$-H] Cl$^-$

1/4 OCN—C$_6$F$_4$—NCO + 1/2 HCl

1/2 [C$_5$H$_5$N$^+$-C(=O)-Cl] Cl$^-$

H$_2$N—C$_6$F$_4$—NH$_2$
Unreacted

1/2 [C$_5$H$_5$N$^+$-H] Cl$^-$ + 1/2 COCl$_2$

H—[NH—C$_6$F$_4$—NH-C(=O)]$_x$—NH—C$_6$F$_4$—NH$_2$
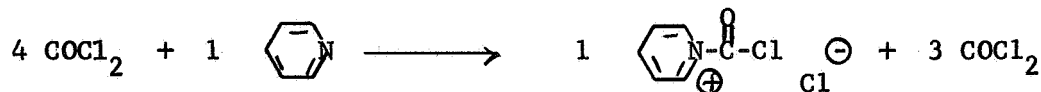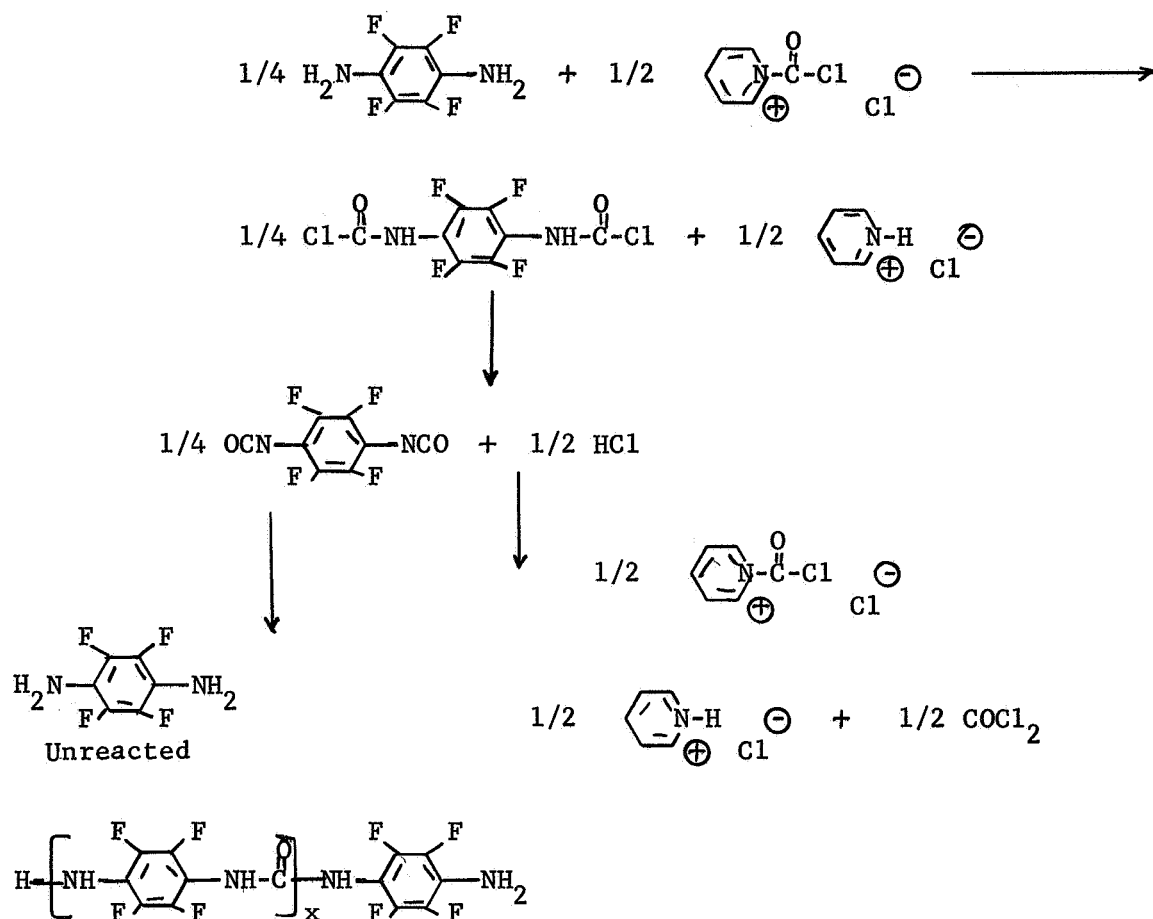
The major product obtained was a white solid whose infrared spectrum and elemental analysis indicate its structure to be poly(tetrafluoro-p-phenylene urea).

The mixed polyurea, poly(hexafluoropentamethylene tetrafluoro-p-phenylene urea), was prepared by reaction of tetrafluoro-p-phenylene diisocyanate with hexafluoropentanediamine in DMF solvent.

OCN—C$_6$F$_4$—NCO + H$_2$N-CH$_2$(CF$_2$)$_3$CH$_2$-NH$_2$ ⟶

—[C(=O)-NH—C$_6$F$_4$—NH-C(=O)-NH-CH$_2$(CF$_2$)$_3$CH$_2$-NH]$_x$—
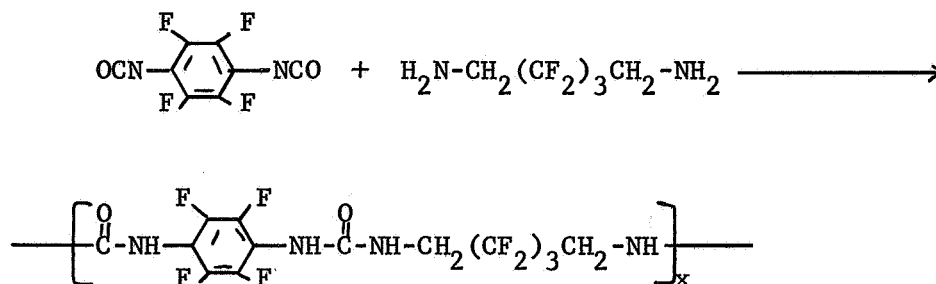
The product was isolated by precipitating it from DMF solution with water. The polymer obtained was a light tan solid melting at 280°-290°C with decomposition.

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7. Polyimides — Poly(hexafluoropentamethylene pyromellitimide)

A partially fluorinated polyimide was prepared from hexafluoropentane-diamine and pyromellitic dianhydride. In the polymerization, the diamine solution was added to a solution of the pyromellitic dianhydride.

$$H_2NCH_2(CF_2)_3CH_2NH_2 + \text{(pyromellitic dianhydride)} \longrightarrow$$

$$\left[\text{-(imide ring)-}N-CH_2-(CF_2)_3-CH_2- \right]_x$$
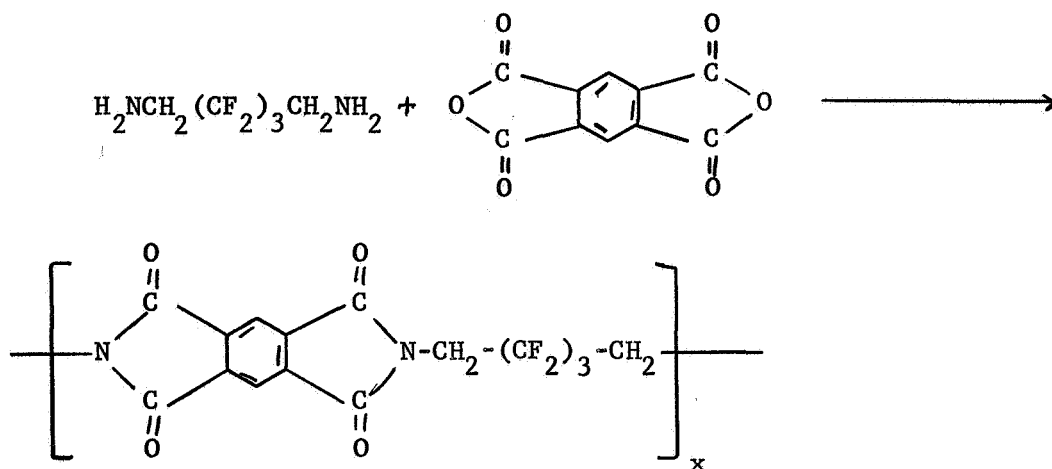
The polymer formed was of low molecular weight with a melting point of $330°C$ to $340°C$.

It was reported[16] that polyamides became degraded in excess dianhydride. The molecular weight was also found to vary considerably with the choice of solvents. It was believed that a higher molecular weight polymer could be formed by a better choice of solvents, and by adding the dianhydride solution to the diamine. Thus, the reaction was repeated in dimethyl acetamide. The mode of addition was reversed and the concentration of the reactants was reduced by dilution. No significant increase in molecular weight was obtained.

E. Monomers

1. Hexafluoropentamethylene Bischloroformate

No highly fluorinated chloroformates have been reported, although chloroformates containing a small number of fluorine atoms have been prepared and converted to carbamates.[17]

Serious problems were encountered in the initial attempts to prepare bischloroformates. This was due to the unusually low reactivity of fluorinated alcohols with phosgene, coupled with the high reactivity of fluorinated chloroformates with alcohols. Initially, elevated temperatures were used to promote the reaction of phosgene with hexafluoropentanediol. The high temperature, however, also increased the rate of polycarbonate formation occurring by reaction of the bischloroformate formed with the unreacted diol. This is the same problem encountered in the preparation of the fluorinated diisocyanates.

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Tertiary amines have been used as catalysts in the preparation of iso-cyanates[18] and similar catalysis was considered for chloroformate prepara-tion. However, in the case of highly fluorinated compounds, it is felt that simple catalysis would only promote additional polymer formation due to the high reactivity of the fluorinated bischloroformates as observed in the case of fluorinated diisocyanates.

A new approach has been used at Narmco for the preparation of chloro-formates and isocyanates. This approach has resulted in higher yields and less byproducts than were heretofore possible, due to the milder reaction conditions. In an effort to avoid the problem of polymer formation, pyridine was reacted with phosgene in diethyl ether, forming a solid crystalline com-pound, chlorocarbonyl pyridinium chloride.
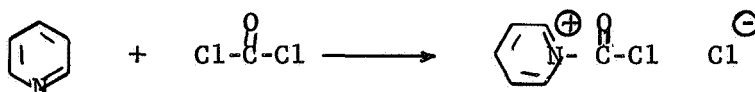
Compounds similar in type have been prepared and some have been charac-terized. Adkins prepared and characterized solid ionic compounds of aliphatic acid chlorides and tertiary amines such as acetyl pyridinium chloride and propionyl triethylammonium chloride.[19] Similar type compounds have also been prepared[20] from aromatic acid chlorides and tertiary amines. While the aliphatic compounds are stable only at relatively low temperatures, the aromatic compounds are stable to moderately high temperatures. For example, α-furoyl pyridinium chloride[19] decomposes at $60°C$, while p-nitrobenzoyl pyridinium chloride[20] decomposes at $115°-120°C$. While the products of decomposition were not identified in the former case, the products obtained in the latter case were p-nitrobenzoyl chloride and pyridine. Compounds of phosgene with tertiary amines have been isolated and a similar structure proposed. Goubeau and Winkelman[21] and Rudenko et al.[22] isolated a solid compound by reaction of phosgene and trimethylamine at low temperatures. The latter authors proposed that the structure was chlorocarbonyl trimethyl-ammonium chloride,
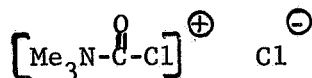

Lastovskii[23] proposed that this type of compound is formed as the reactive intermediate in the preparation of tetra-substituted ureas from tertiary amines and phosgene at high temperatures. Dominikiewicz[24] and Puschin[25] isolated a solid compound by reaction of phosgene with hexamethylenetetramine. It seems now that this compound possesses an ionic structure similar to those discussed above.

Chlorocarbonyl pyridinium chloride reacts much more rapidly with alcohols than does phosgene itself. For example, in the preparation of hexafluoro-pentamethylene bischloroformate using chlorocarbonyl pyridinium chloride, the reaction temperature exceeded room temperature. The yield of bischloro-formate was 83.2% and the product was of very high purity.

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When hexafluoropentanediol was reacted with phosgene at room tempera-
ture in either di-n-butyl ether or diethyl carbitol, the reaction was very
slow. On heating the reaction to reflux, polycarbonate was formed slowly,
and unreacted hexafluoropentanediol was recovered from the solution.

The reaction of an alcohol with chlorocarbonyl pyridinium chloride
proceeds in the following manner to form a chloroformate.
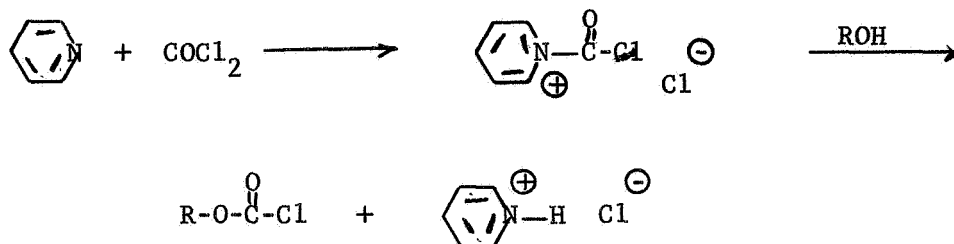
Pyridine is always tied up either as the chlorocarbonyl pyridinium
chloride or as pyridine hydrochloride; hence, there is no possibility of
catalysis of the reaction between chloroformate and alcohol to produce a
carbonate ester.

## 2. Hexafluoropentamethylene Diisocyanate

The reaction between hexafluoropentamethylene diamine and chlorocarbonyl
pyridinium chloride proceeded in a smooth fashion, resulting in a pure com-
pound in good yield.

The infrared spectrum of this material suggests that it is either a
carbamyl chloride-isocyanate (I, below) or the diisocyanate existing, at
least partially, as the dimer (II, below) at room temperature. There is a
strong doublet at 5.54 μ and 5.75 μ. This proposed cyclic uretidione (II)
would bear a strong resemblance to a cyclic imide structure, and certain
analogies may possibly be drawn between the two. In a normal five-membered
cyclic imide, these absorptions would be at 5.65 μ and 5.88 μ.[26] In this
case, however, the absorptions would be expected to appear at a higher
frequency due to the greater amount of ring strain as well as the inductive
effect of fluorine.
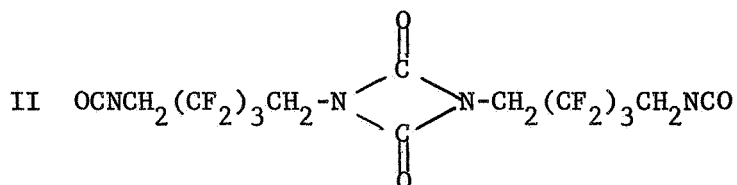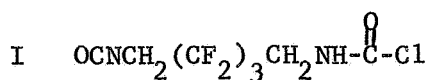
The spectra of the N-methyl aniline derivative exhibit none of the above absorption bands. This is taken as evidence that if the uretidione grouping is present, it is extremely reactive, and is readily opened by nucleophilic attack and behaves in a manner identical to the isocyanate group itself. The carbamyl chloride-isocyanate (I) would give the same derivative as the diisocyanate.

An attempt was made to prepare hexafluoropentamethylene diisocyanate by reaction of the di-p-toluenesulfonate of hexafluoropentanediol with potassium cyanate. None of the desired product was obtained.
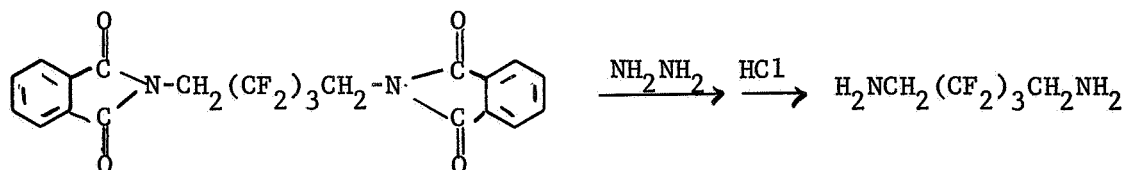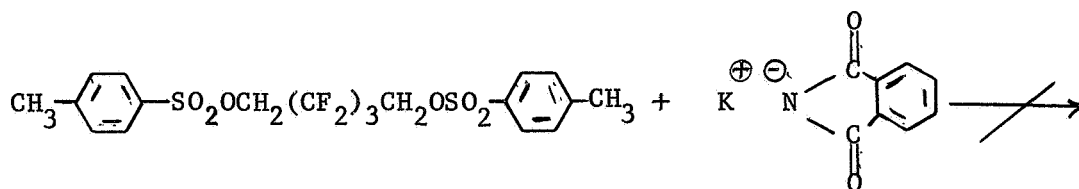
$$CH_3-\langle\ \rangle-SO_2OCH_2(CF_2)_3CH_2OSO_2-\langle\ \rangle-CH_3 \xrightarrow{KNCO} OCN-CH_2(CF_2)_3CH_2-NCO$$
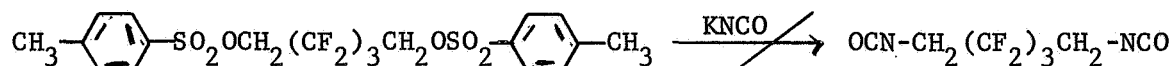
3. Di-p-Toluenesulfonate of Hexafluoropentanediol

The preparation of the di-p-toluenesulfonate of hexafluoropentanediol was successfully carried out in 77% yield by reaction of the diol with p-toluene-sulfonyl chloride in pyridine solvent at low temperature, a method used previously for the preparation of fluorinated monotosylates. This new method is an improvement over the method reported for the preparation of the same ditosylate earlier in this program (Annual Summary Report I, July 1964).

4. Hexafluoropentanediamine

The preparation of hexafluoropentanediamine by the lithium aluminum hydride reduction of perfluoroglutaramide was reported in Annual Summary Report I (July 1964). During this report period, the preparation of this diamine was attempted by reaction of the di-p-toluenesulfonate of hexafluoro-pentanediol with potassium phthalimide. No reaction took place.

$$CH_3-\langle\ \rangle-SO_2OCH_2(CF_2)_3CH_2OSO_2-\langle\ \rangle-CH_3 + K^{\oplus}\ {}^{\ominus}N \xrightarrow{\ \ \ }$$

$$\xrightarrow{NH_2NH_2} \xrightarrow{HCl} H_2NCH_2(CF_2)_3CH_2NH_2$$

5. Attempted Preparation of Hexafluoropentamethylene Sulfate

Another method for the preparation of isocyanates is by the reaction of alkyl sulfates with potassium cyanate.

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$$R_2SO_4 \quad + \quad 2\ KCNO \quad \longrightarrow \quad 2\ RNCO \quad + \quad K_2SO_4$$

A possible route to hexafluoropentamethylene diisocyanate would be by way of the cyclic alkyl sulfate and potassium cyanate.

cyclic sulfate structure $+ KCNO \longrightarrow OCNCH_2(CF_2)_3CH_2NCO$
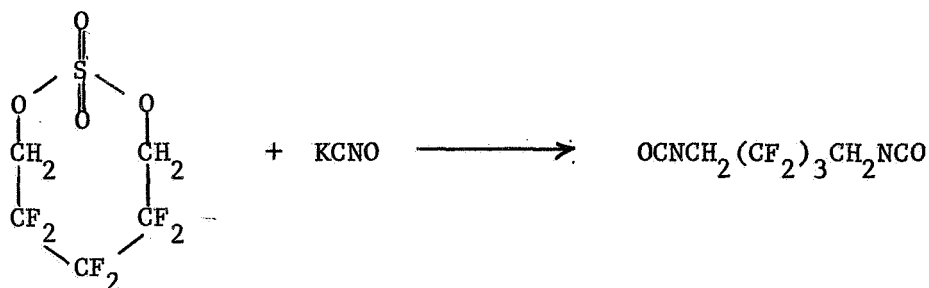
The cyclic sulfate might be formed in a reaction analogous to that in which the cyclic sulfite of hexafluoropentanediol is formed.

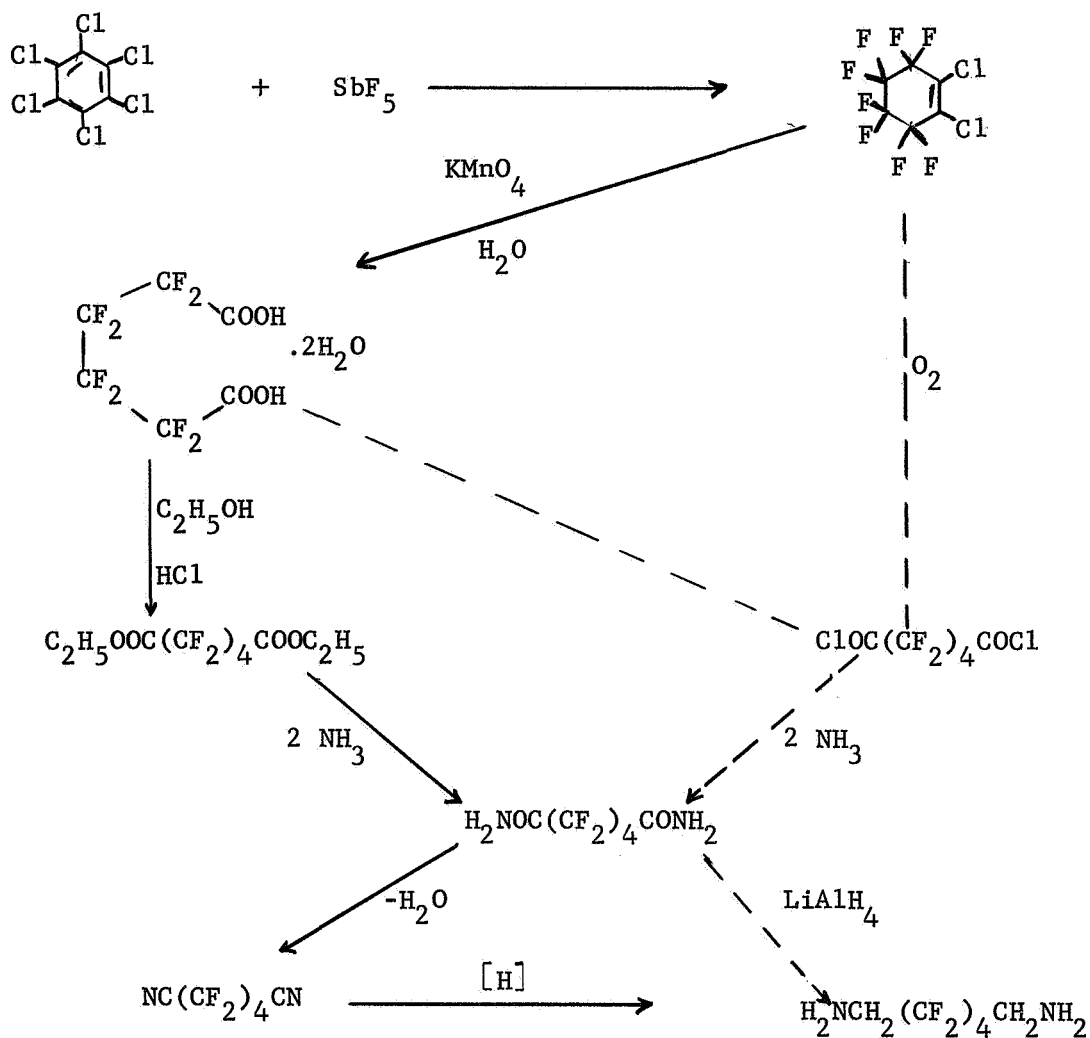diol structure $+ SO_2Cl_2 \longrightarrow$ cyclic sulfate structure
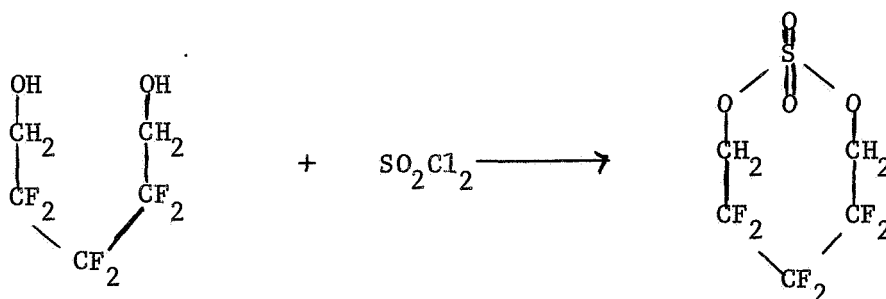
In an attempt to prepare the cyclic sulfate, hexafluoropentanediol was reacted with sulfuryl chloride in pyridine. No cyclic sulfate was isolated, possibly due to difficulty in the workup. Consequently, further changes are necessary in order to simplify the isolation of any products formed.

6. Perfluoroadipamide

Due to the difficulties being encountered in the preparation of hexa-fluoropentamethylene diisocyanate, work was begun on the preparation of octafluorohexanediamine, to be used for conversion to octafluorohexamethylene diisocyanate. In the corresponding series of nonfluorinated diamines, 1,6-hexanediamine can be readily converted to its corresponding diisocyanate while no mention can be found in the literature of the similar conversion of 1,5-pentanediamine. The reaction scheme to be used for the preparation of octafluorohexanediamine is essentially that described by McBee.[27] It is shown below with alternative steps shown with dotted lines.

$$+ \quad SbF_5 \quad \longrightarrow$$

$$\xrightarrow{KMnO_4} \quad \xleftarrow{H_2O}$$

Perfluoroadipic acid · $2H_2O$:

$$
\begin{array}{c}
CF_2\!-\!CF_2\!-\!COOH \\
CF_2\!-\!CF_2\!-\!CF_2\!-\!COOH
\end{array} \cdot 2H_2O
$$

$$\Big\downarrow C_2H_5OH \quad HCl$$

$$C_2H_5OOC(CF_2)_4COOC_2H_5$$

$$O_2$$

$$ClOC(CF_2)_4COCl$$

$$\xrightarrow{2\ NH_3}$$

$$\xrightarrow{2\ NH_3}$$

$$H_2NOC(CF_2)_4CONH_2$$

$$\xrightarrow{-H_2O}$$

$$\xrightarrow{LiAlH_4}$$

$$NC(CF_2)_4CN \xrightarrow{\ [H]\ } H_2NCH_2(CF_2)_4CH_2NH_2$$
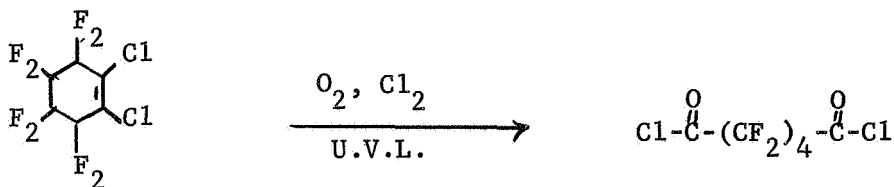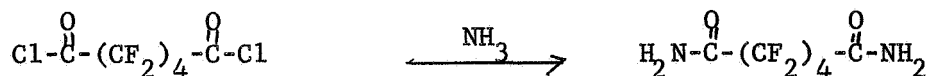
The conversion of hexachlorobenzene to 1,2-dichlorooctafluorocyclo-hexene was accomplished in 46.1% yield using the procedure described by McBee.

McBee has reported a poor yield in the oxidation of octafluoro-1,2-dichlorocyclohexene to perfluoroadipic acid in basic solution; however, good yields of similar fluorinated acids have been reported for permanganate oxidations carried out in acetone. Consequently, the oxidation was attempted in acetone solution. The white crystalline product obtained did not give the correct value for the desired diacid by neutralization equivalent. Its structure is still in doubt.

Perfluoroadipyl chloride was successfully prepared from 1,2-dichloro-octafluorocyclohexene by direct oxidation using a modification of the vapor-phase oxidation method of Baranackas and Gelfand.[28] The conditions and apparatus designed in this laboratory for the photo-oxidative cleavage are described in the experimental section of this report.

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$$F_2 \text{ ring with } Cl, Cl, F_2 \xrightarrow[\text{U.V.L.}]{O_2, \ Cl_2} \quad Cl\text{-}\overset{O}{\underset{\|}{C}}\text{-}(CF_2)_4\text{-}\overset{O}{\underset{\|}{C}}\text{-}Cl$$

The reaction of perfluoroadipyl chloride with ammonia yielded perfluoro-adipamide in an 84% yield.

$$Cl\text{-}\overset{O}{\underset{\|}{C}}\text{-}(CF_2)_4\text{-}\overset{O}{\underset{\|}{C}}\text{-}Cl \xrightarrow{NH_3} H_2N\text{-}\overset{O}{\underset{\|}{C}}\text{-}(CF_2)_4\text{-}\overset{O}{\underset{\|}{C}}\text{-}NH_2$$
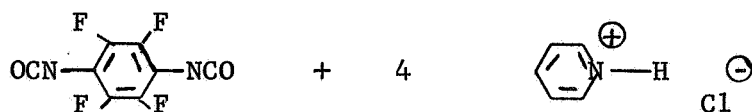
7. Improvement in the Preparation of Tetrafluoro-p-phenylenediamine

The unique method developed in this laboratory for the preparation of tetrafluoro-p-phenylenediamine by reaction of hexafluorobenzene with potassium phthalimide (Gabriel reaction) was reported in Annual Summary Report I (July 1964). The highest yield obtained by this method has been 47%, which is considerably higher than those obtained by any other known method. During the early work on this method, it was assumed that the mechanism of cleavage of phthalimido intermediates in the Gabriel reaction has not been fully and satisfactorily studied. Thus, in the early work, three moles of hydrazine per mole of diphthalimido-tetrafluorobenzene were used, the intended ratio being 2:1 with a 50% excess. On further consideration of the cleavage mechanism, it was felt that an alternative mechanism might be operating which would require 4 moles of hydrazine. This year, the preparation of tetrafluoro-p-phenylenediamine has been carried out using the same method as before except that 6 moles (50% excess) of hydrazine per mole of diphthalimido-tetrafluoro-benzene was used in the cleavage. The yield of tetrafluoro-p-phenylene-diamine obtained was 68%.
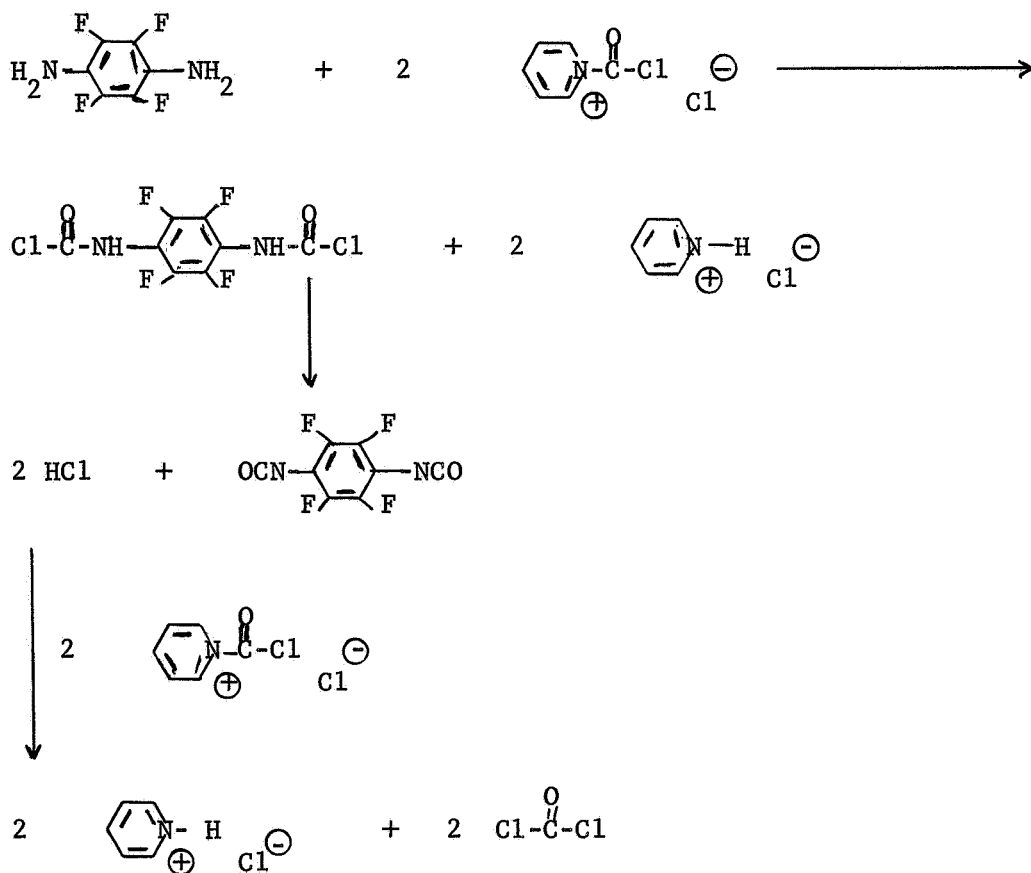
8. Improvement in Preparation of Tetrafluoro-p-phenylene Diisocyanate

The use of chlorocarbonyl pyridinium chloride was successfully extended to the preparation of tetrafluoro-p-phenylene diisocyanate. The reaction of an amine with chlorocarbonyl pyridinium chloride to form an isocyanate proceeds in a manner similar to an alcohol with one exception. This exception is that the carbamyl chloride, formed in the initial reaction of the amine with the complex, will dehydrochlorinate spontaneously and the resultant hydrogen chloride will react with the chlorocarbonyl pyridinium chloride. Thus, 4 moles of chlorocarbonyl pyridinium chloride were required to react fully with 1 mole of tetrafluoro-p-phenylenediamine.

$$H_2N\text{-}\underset{F \quad F}{\overset{F \quad F}{\text{(ring)}}}\text{-}NH_2 \quad + \quad 4 \ \underset{\oplus}{\text{(pyridinium)}}\overset{O}{\underset{\|}{N}}\text{-}C\text{-}Cl \quad \overset{\ominus}{Cl} \longrightarrow$$

The 2 extra moles of chlorocarbonyl pyridinium chloride react with the hydrogen chloride liberated from the intermediate dicarbamyl chloride without catalyzing polymerization of the diisocyanate formed with unreacted diamine.
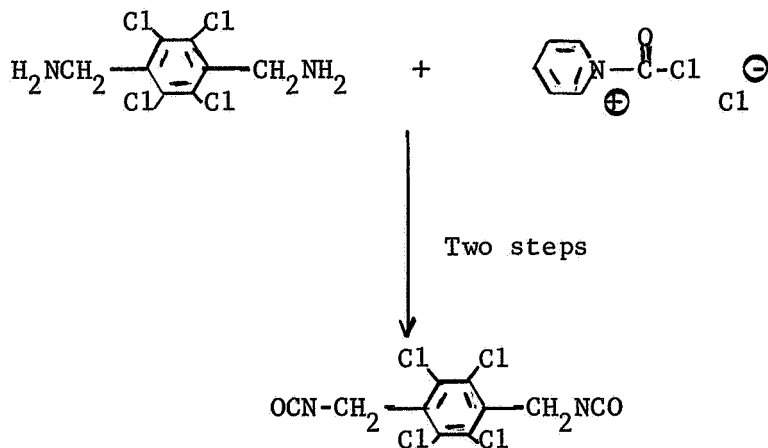

Using this ratio of reactants, tetrafluoro-p-phenylene diisocyanate was prepared in a crude yield of 78%. Purification reduced the yield to 53% of very pure diisocyanate. By improved reaction and workup procedure, the yield of pure diisocyanate was increased to 81%.

In a separate experiment, chlorocarbonyl pyridinium chloride was shown to react rapidly and completely with hydrogen chloride yielding pyridinium chloride and phosgene as proposed in the above mechanism.

9.   Attempted Preparation of Perfluoroglutaryl Diisocyanate

An urethane polymer which has a fluorinated methylene group adjacent to the -N- group in the carbamate linkage exhibits hydrolytic instability with

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loss of HF and subsequent chain scission. One possible means of avoiding this situation is the replacement of the difluoro methylene group, α to the nitrogen, with a carbonyl group. This might cancel any hydrolytic instability with the possible added benefit of not increasing liquid oxygen incompatibility. To obtain such a situation, the acyl isocyanate could be prepared and reacted with hydroxyl containing materials in the usual fashion.

$$R_F CF_2 NCO \quad + \quad R'_F CH_2 OH \longrightarrow R_F-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{C}}-\overset{\displaystyle H}{\underset{}{N}}-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2 R'_F$$

Hydrolytically unstable

$$R_F-\overset{\overset{\displaystyle O}{\|}}{C}-NCO \quad + \quad R'_F CH_2 OH \longrightarrow R_F-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\displaystyle H}{\underset{}{N}}-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2 R'_F$$

Possibly hydrolytically stable

One method of preparation of the diacylisocyanate is by reaction of a diamide with phosgene. For Narmco's work, hexafluoroglutaramide was used as the starting material. This material is almost completely insoluble in the usual solvents which lend themselves to phosgenation reactions. A 50/50 mixture of 3-methyl sulfolane and dimethyl sulfoxide was found to be a good solvent and also had a freezing point low enough to allow condensation of phosgene.

In the reaction of chlorocarbonyl pyridinium chloride with perfluoro-glutaramide, none of the desired product was obtained although a considerable amount of pyridine hydrochloride was isolated. The chlorocarbonyl pyridinium chloride apparently reacts with the solvent since unidentified sulfur con-taining materials were observed.

10. 2,3,5,6-Tetrachloro-p-xylylene-α,α'-diisocyanate

The low degree of reactivity of the isocyanate groups in tetrachloro-p-phenylene diisocyanate and the resulting difficulty in curing urethane prepolymers terminated with it have been described previously in this report. A new chlorinated diisocyanate, 2,3,5,6-tetrachloro-p-xylylene-α,α-diisocyanate, which should be more reactive, has been prepared by Narmco's usual phosgenation method. 2,3,5,6-Tetrachloro-p-xylylenediamine was reacted with chlorocarbonyl pyridinium chloride in tetrahydrofuran to give the desired diisocyanate in 68.5% yield. It was characterized by conversion to the di-N-methyl-anilino derivative.

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Various prepolymers and polyurethanes will be prepared from this diisocyanate.

11. 4,4'-Diisocyanato-octafluorobiphenyl

4,4'-Diisocyanato-octafluorobiphenyl was prepared in 62.8% yield by reaction of 4,4'-diamino-octafluorobiphenyl with chlorocarbonyl pyridinium chloride in diethyl ether using Narmco's usual procedure. Its identity was established by elemental analysis, infrared spectrum, and isocyanate equivalency. The di-N-methylanilino derivative was prepared for characterization purposes.
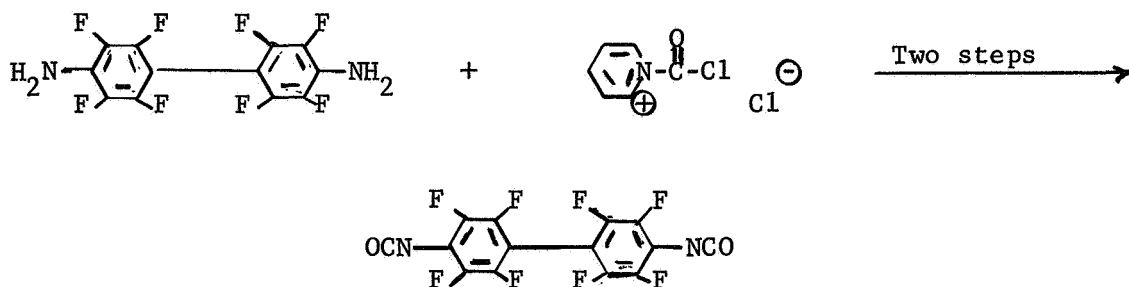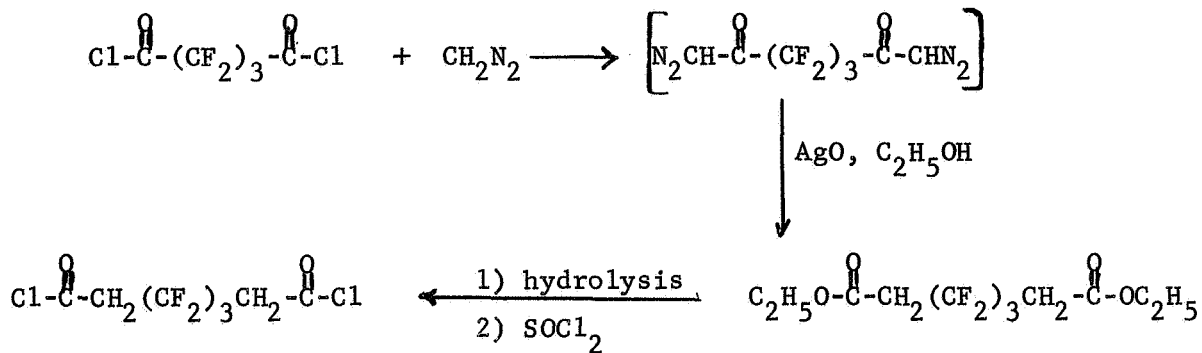

12. Attempted Preparation of Diethyl 3,3,4,4,5,5-Hexafluoropimelate

Polyesters prepared from perfluorinated dibasic acids are quite hydrolytically unstable and therefore are unsatisfactory as prepolymers for polyurethanes. Polyesters prepared from nonfluorinated dibasic acids and fluorinated diols have been investigated during this program as polyurethane prepolymers. Difficulties encountered in the preparation of polyesters from diethyl malonate and hexafluoropentanediol have made them unattractive. Poly (hexafluoropentamethylene adipate) has been shown to be LOX incompatible. Polyesters prepared from 3,3,4,4,5,5-hexafluoropimelic acid and hexafluoropentanediol should be much more stable to hydrolysis than polyesters of perfluorinated dibasic acids, and might well be LOX compatible.

Work has begun on two separate reaction paths leading to the preparation of 3,3,4,4,5,5-hexafluoropimelyl chloride.
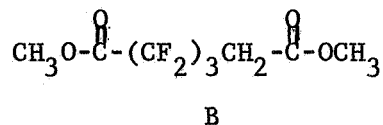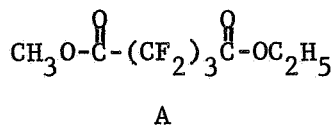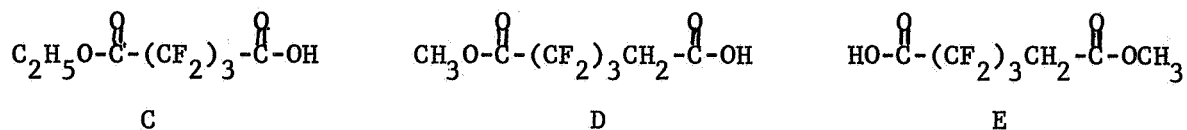
Path A

$$Cl-\overset{O}{\underset{}{C}}-(CF_2)_3-\overset{O}{\underset{}{C}}-Cl \quad + \quad CH_2N_2 \longrightarrow \left[N_2CH-\overset{O}{\underset{}{C}}-(CF_2)_3-\overset{O}{\underset{}{C}}-CHN_2\right]$$

AgO, C_2H_5OH

$$Cl-\overset{O}{\underset{}{C}}-CH_2(CF_2)_3CH_2-\overset{O}{\underset{}{C}}-Cl \quad \underset{\text{2) } SOCl_2}{\overset{\text{1) hydrolysis}}{\longleftarrow}} \quad C_2H_5O-\overset{O}{\underset{}{C}}-CH_2(CF_2)_3CH_2-\overset{O}{\underset{}{C}}-OC_2H_5$$

Path B

$$CH_3\text{-}\langle\!\!\langle\,\rangle\!\!\rangle\text{-}SO_2-O-CH_2(CF_2)_3CH_2-O-SO_2\text{-}\langle\!\!\langle\,\rangle\!\!\rangle\text{-}CH_3$$

KCN   KI

$$NC-CH_2(CF_2)_3CH_2CN \quad \underset{}{\overset{KCN}{\longleftarrow}} \quad I-CH_2(CF_2)_3CH_2-I$$

1) hydrolysis

2) $SOCl_2$

$$Cl-\overset{O}{\underset{}{C}}-CH_2(CF_2)_3CH_2-\overset{O}{\underset{}{C}}-Cl$$
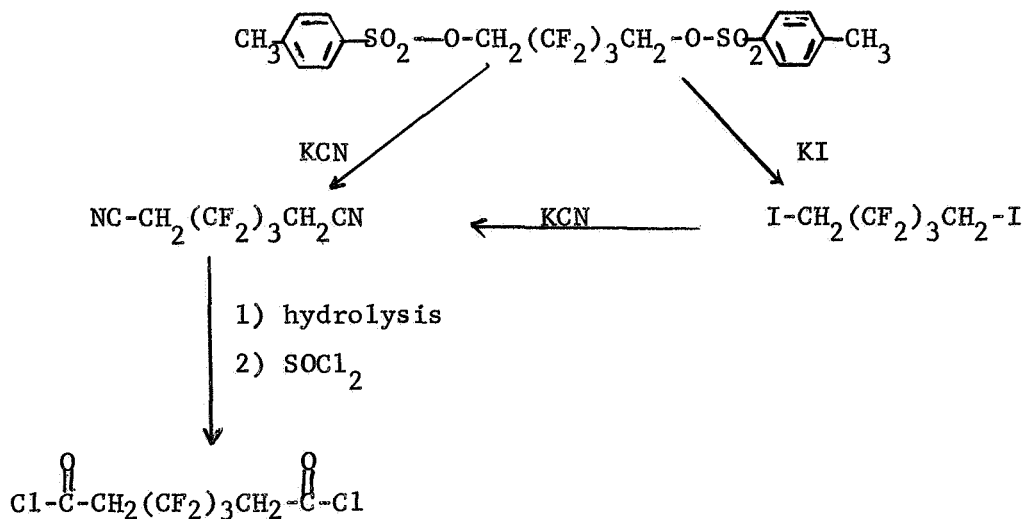
Following path A, the Arndt-Eistert reaction was carried out on per-fluoroglutaryl chloride in order to prepare diethyl perfluoropimelate following the procedure of Schweiker and coworkers.[29]

Two fractions were obtained by fractional distillation of the reaction product. The elemental analysis indicates that the lower boiling fraction (bp 51°-52°C) is either methylethyl perfluoroglutarate (A) or dimethyl-2,2,3,3,4,4-hexafluoroadipate (B),

$$CH_3O-\overset{O}{\underset{}{C}}-(CF_2)_3\overset{O}{\underset{}{C}}-OC_2H_5$$

A

$$CH_3O-\overset{O}{\underset{}{C}}-(CF_2)_3CH_2-\overset{O}{\underset{}{C}}-OCH_3$$
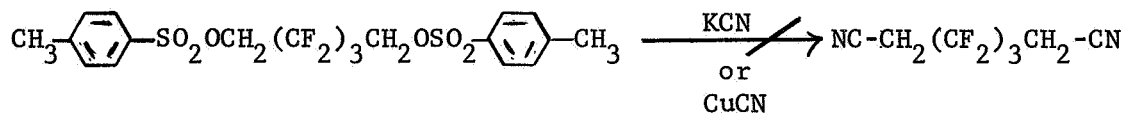
B

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and that the higher boiling fraction (bp 89°-91°C) (the infrared spectrum shows the presence of an acid group) is either monoethyl perfluoroglutarate (C), or one of the monomethyl-2,2,3,3,4-hexafluoroadipates (D and E).
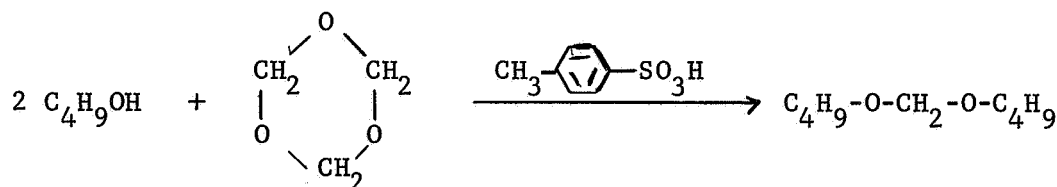
$$C_2H_5O-\overset{O}{\overset{\|}{C}}-(CF_2)_3-\overset{O}{\overset{\|}{C}}-OH \qquad CH_3O-\overset{O}{\overset{\|}{C}}-(CF_2)_3CH_2-\overset{O}{\overset{\|}{C}}-OH \qquad HO-\overset{O}{\overset{\|}{C}}-(CF_2)_3CH_2-\overset{O}{\overset{\|}{C}}-OCH_3$$

$$\qquad\qquad C \qquad\qquad\qquad\qquad\qquad D \qquad\qquad\qquad\qquad\qquad E$$

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

Attempts were made to prepare 3,3,4,4,5,5-hexafluoropimelonitrile by reaction of the ditosylate with both potassium cyanide and cuprous cyanide in a variety of solvents. No reaction occurred in any of the cases studied.

$$CH_3-\langle\bigcirc\rangle-SO_2OCH_2(CF_2)_3CH_2OSO_2-\langle\bigcirc\rangle-CH_3 \xrightarrow[\text{or}\\ \text{CuCN}]{KCN} \not\rightarrow NC-CH_2(CF_2)_3CH_2-CN$$

14. Dibutoxymethane

Dibutoxymethane was prepared by reaction of n-butanol with symmetrical trioxane in the presence of p-toluenesulfonic acid.

$$2\ C_4H_9OH \quad + \quad \begin{matrix} & O & \\ CH_2 & & CH_2 \\ | & & | \\ O & & O \\ & CH_2 & \end{matrix} \quad \xrightarrow{CH_3-\langle\bigcirc\rangle-SO_3H} \quad C_4H_9-O-CH_2-O-C_4H_9$$

15. 3,3,3-Trifluoro-1,2-epoxypropane

3,3,3-Trifluoro-1,2-epoxypropane was prepared in 47.5% yield starting from 1,1,1-trifluoroacetone by the following series of reactions described by McBee and Burton.[30, 31]

$$CF_3-\overset{O}{\overset{\|}{C}}-CH_3 \quad \xrightarrow[H_2SO_4]{Br_2} \quad CF_3-\overset{O}{\overset{\|}{C}}-CH_2Br$$

$$CF_3-\overset{O}{\overset{\|}{C}}-CH_2Br \quad \xrightarrow{LiAlH_4} \quad CF_3-\overset{OH}{\overset{|}{C}H}-CH_2Br$$

$$CF_3-\overset{OH}{\overset{|}{C}H}-CH_2Br \quad \xrightarrow{NaOH} \quad CF_3-CH\overset{O}{\overbrace{\qquad}}CH_2$$
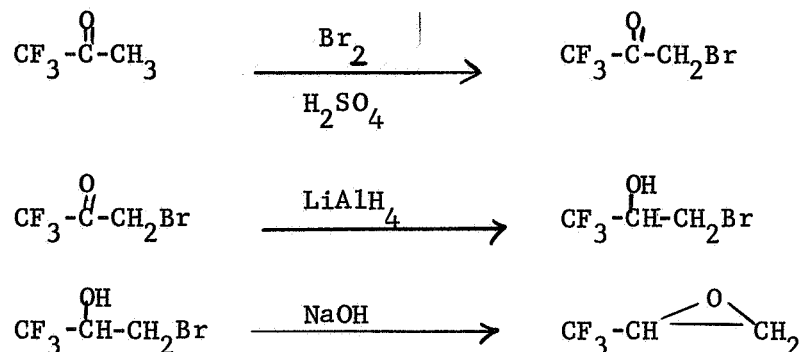
16. Attempted Preparation of Perfluoro-1,2-epoxypropane

The polyurethane prepared from the polyether of 3,3,3-trifluoro-1,2-epoxypropane and tetrafluoro-p-phenylene diisocyanate possessed very interesting low—temperature properties but was LOX incompatible. In order to impart LOX compatibility to this type of polyurethane, more highly fluorinated polyethers are required.
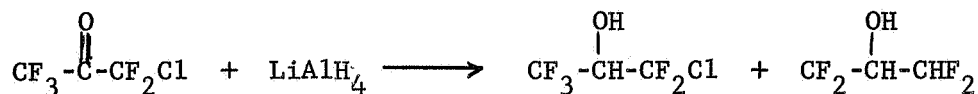
Perfluorinated epoxides have recently been prepared and are reported to undergo Lewis acid catalyzed polymerization.[32] An attempt was made to prepare perfluoro-1,2-epoxypropane using the published procedure and to convert it without isolation to the polyether using an anionic initiator, the monosodium salt of hexafluoropentanediol. No polyether was obtained. Further studies will be conducted on the preparation and polymerization of perfluoro-1,2-epoxypropane.

17. Chloropentafluoroisopropyl Alcohol

Polyurethanes prepared from the polyether of 2-hydro-pentafluoro-1,2-epoxypropane might well be LOX compatible. A study on the preparation of this epoxide by dehydrochlorination of chloropentafluoroisopropyl alcohol has begun.

$$
\underset{\displaystyle CF_3}{\overset{\displaystyle OH}{\underset{|}{CF_3\text{-}CH\text{-}CF_2Cl}}} \longrightarrow CF_3\text{-}CH\overset{O}{\underset{}{\diagup\diagdown}}CF_2
$$

Chloropentafluoroisopropyl alcohol was prepared by lithium aluminum hydride reduction of chloropentafluoroacetone. In addition to the desired product, hydropentafluoroisopropyl alcohol was also isolated from the reduction.

$$
\underset{\displaystyle CF_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CF_2Cl}{} + LiAlH_4 \longrightarrow \underset{\displaystyle CF_3\text{-}\overset{OH}{\underset{|}{CH}}\text{-}CF_2Cl}{} + \underset{\displaystyle CF_2\text{-}\overset{OH}{\underset{|}{CH}}\text{-}CHF_2}{}
$$

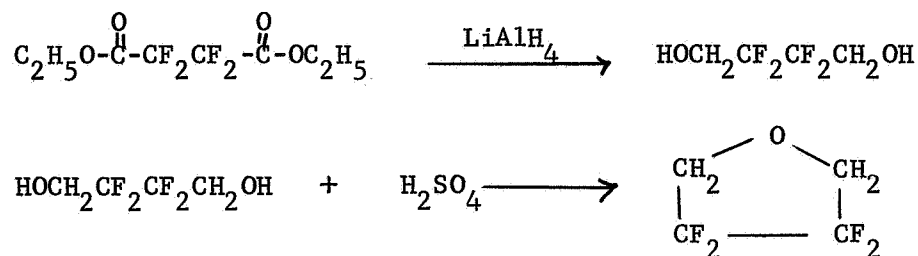## 18. Attempted Preparation of Trihexafluoropentamethylene Glycol

An attempt to prepare trihexafluoropentamethylene glycol by reaction of the di-p-toluenesulfonate ester of hexafluoropentanediol with the monosodium salt of hexafluoropentanediol in di-n-butyl ether solvent was described in Annual Summary Report I (July 1964). Polyurethanes could be prepared from this diether or from the polyether which might be formed by dehydration of this diether. This reaction was again repeated unsuccessfully using diethylene glycol as solvent.

$$
CH_3\!\!-\!\!\langle\ \rangle\!\!-\!\!SO_2O\text{-}CH_2(CF_2)_3CH_2OSO_2\!\!-\!\!\langle\ \rangle\!\!-\!\!CH_3 + NaOCH_2(CF_2)_3CH_2OH \xrightarrow{HOCH_2CH_2OH} \not\longrightarrow
$$

$$
HOCH_2(CF_2)_3CH_2OCH_2(CF_2)_3CH_2OCH_2(CF_2)_3CH_2OH
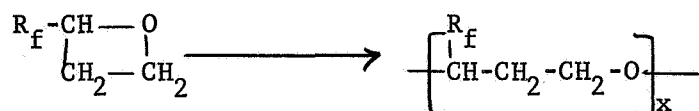$$
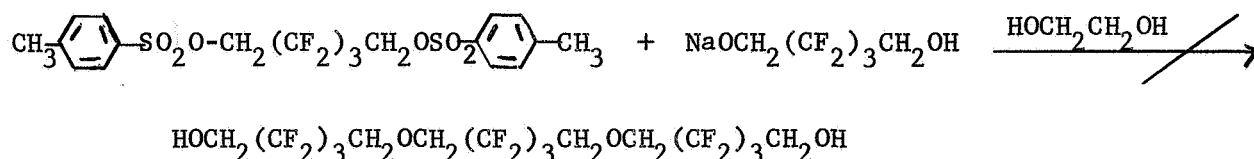
19. 3,3,4,4-Tetrafluoro-tetramethylene Oxide

2,2,3,3-Tetrafluorobutanediol was prepared by reduction of diethyl perfluorosuccinate with lithium aluminum hydride. Dehydration of this diol resulted in a 67% yield of 3,3,4,4-tetrafluorotetramethylene oxide.
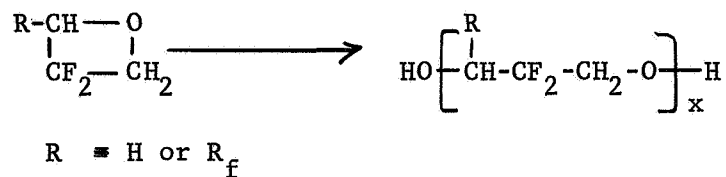
$$C_2H_5O-\overset{O}{\overset{\|}{C}}-CF_2CF_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \quad \xrightarrow{\text{LiAlH}_4} \quad HOCH_2CF_2CF_2CH_2OH$$

$$HOCH_2CF_2CF_2CH_2OH \quad + \quad H_2SO_4 \longrightarrow \quad \begin{array}{c} CH_2 \overset{O}{\diagup \diagdown} CH_2 \\ | \qquad\qquad | \\ CF_2 \underline{\qquad} CF_2 \end{array}$$

20. Attempted Preparation of 3,3-Difluorooxetane

Polyethers have been prepared by polymerization of 2-perfluoroalkyl oxetanes.[33] These polyethers contain only hydrocarbon backbones.

$$\begin{array}{c} R_f\text{-}CH \text{---} O \\ | \qquad | \\ CH_2 \text{---} CH_2 \end{array} \longrightarrow \quad \left[\begin{array}{c} R_f \\ | \\ CH\text{-}CH_2\text{-}CH_2\text{-}O \end{array}\right]_x$$

Polymerization of 3,3-difluorooxetanes would yield hydroxyl-terminated polyethers containing fluorine atoms in the polymer backbone.

$$\begin{array}{c} R\text{-}CH \text{---} O \\ | \qquad | \\ CF_2 \text{---} CH_2 \end{array} \longrightarrow \quad HO\left[\begin{array}{c} R \\ | \\ CH\text{-}CF_2\text{-}CH_2\text{-}O \end{array}\right]_x H$$

$$R = H \text{ or } R_f$$

A study of the preparation of 3,3-difluorooxetane was begun. 2,2-Difluoropropane-1,3-diol was prepared by reduction of diethyl-2,2-difluoromalonate using lithium aluminum hydride according to the procedure of McBee.[34]

$$C_2H_5O-\overset{O}{\overset{\|}{C}}-CF_2-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \quad \xrightarrow{\text{LiAlH}_4} \quad HOCH_2CF_2CH_2OH$$
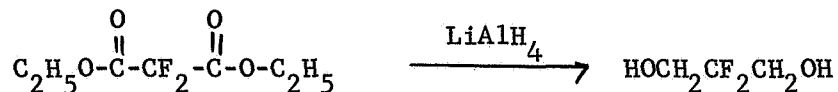
An attempt was made to dehydrate this diol to prepare 3,3-difluorooxetane. A low-boiling liquid was obtained whose identity is under investigation.

$$\text{HOCH}_2\text{CF}_2\text{CH}_2\text{OH} \quad + \quad \text{H}_2\text{SO}_4 \longrightarrow$$
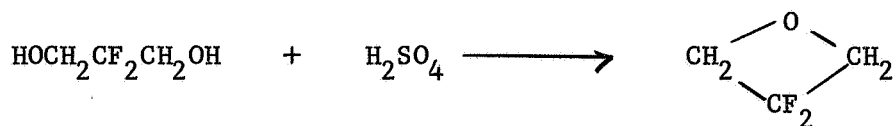
21. Diether of Hexafluorobenzene and Hexafluoropentanediol

The preparation of the diether of hexafluorobenzene and hexafluoropentanediol was described in Annual Summary Report I (July 1964). The yield described was quite low and an attempt was made to improve the yield by carrying out the reaction of hexafluorobenzene with hexafluoropentanediol and potassium hydroxide in N-methylpyrrolidone.
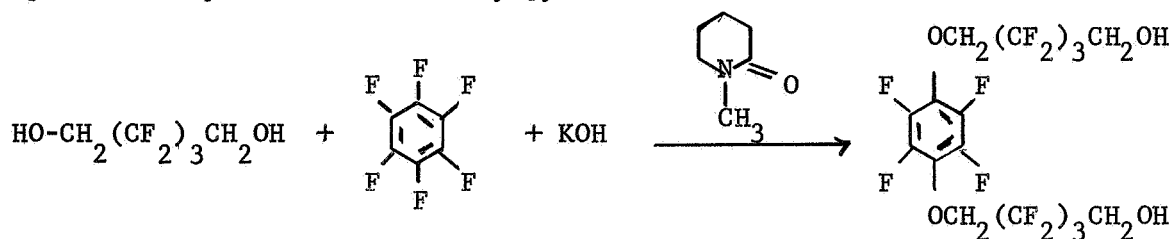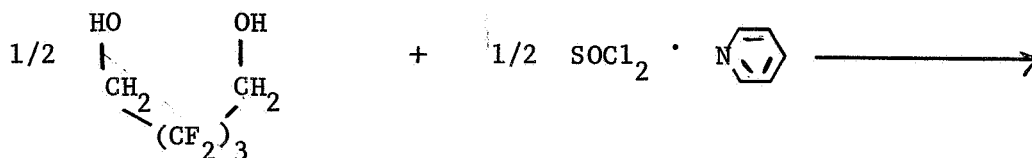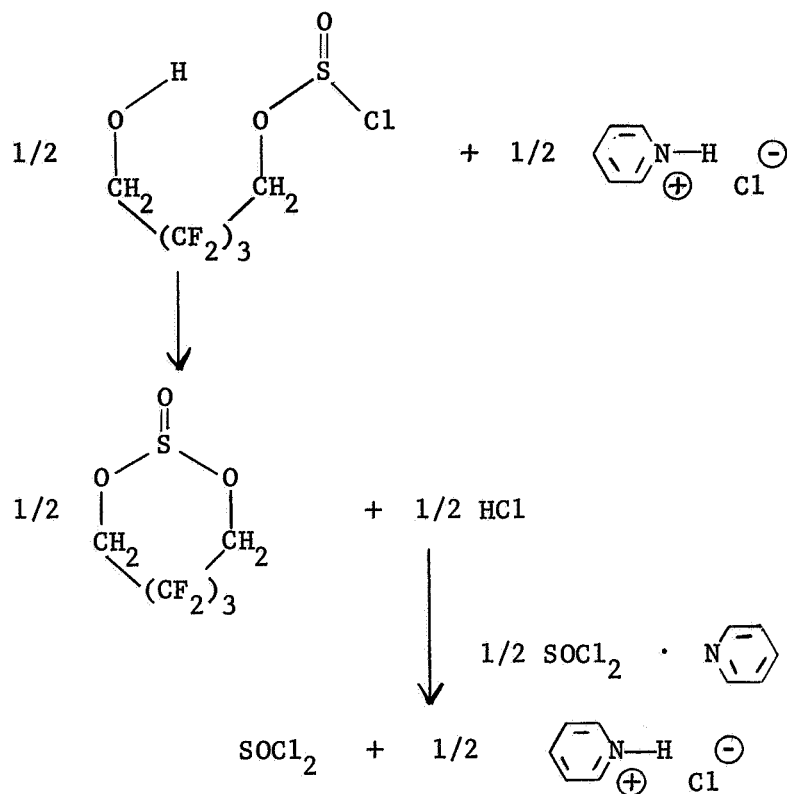

Only a small amount of diether product was obtained. Apparently, a great deal of decomposition occurred in N-methylpyrrolidone.

22. Study of the Reaction Mechanism in the Formation of Cyclic Sulfite from Hexafluoropentanediol with Thionyl Chloride in the Presence of Pyridine

The preparation of hexafluoropentamethylene sulfite was described in Annual Summary Report I (July 1964). The reaction was carried out in pyridine as a solvent which caused difficulties in the isolation of the pure product. Due to the ease of hydrolysis of the cyclic sulfite, the pyridine hydrochloride formed in the reaction of hexafluoropentanediol with thionyl chloride and the excess pyridine could not be removed by use of acid.

This year, a brief study on the mechanism of the formation of the cyclic sulfite led to an improved method of preparation. In an attempt to determine if the intermediate chlorosulfite would lose hydrogen chloride without the presence of an acceptor, such as pyridine, hexafluoropentanediol was added to an equimolar amount of preformed pyridine thionyl chloride complex in ether solution. A mixture of approximately equal amounts of cyclic sulfite and starting diol was obtained.

1/2 (structure: chlorosulfite ester of fluorinated diol)

+ 1/2 (pyridinium N—H, $Cl^{\ominus}$)

$\downarrow$

1/2 (cyclic sulfite structure) + 1/2 HCl

$\downarrow$

1/2 $SOCl_2$ · (pyridine)

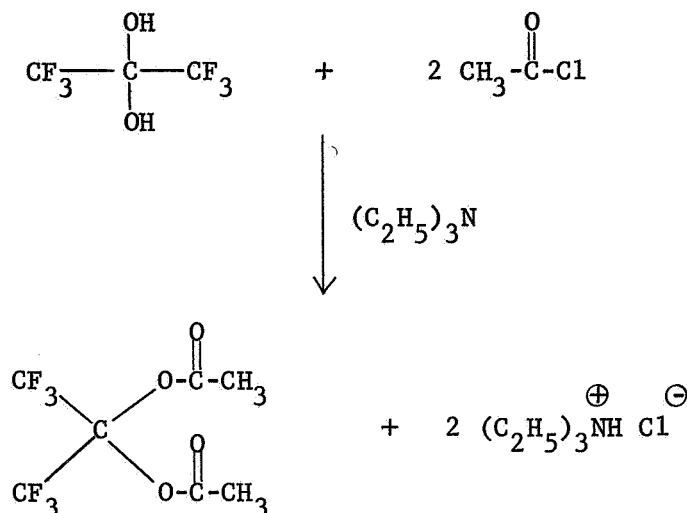$SOCl_2$ + 1/2 (pyridinium N—H, $Cl^{\ominus}$)

The intermediate chlorosulfite apparently loses hydrogen chloride so readily that, as the cyclic sulfite forms, the hydrogen chloride eliminated consumes part of the pyridine thionyl chloride complex. Therefore, only one-half of the complex is available to form cyclic sulfite and one-half of the diol remains unreacted.

By using 1 extra mole of pyridine along with the pyridine thionyl chloride complex, the eliminated hydrogen chloride is taken up, allowing the reaction to go to completion.

1 (diol structure: HO—CH_2...$(CF_2)_3$...CH_2—OH) + 1 $SOCl_2$ · (pyridine) + 1 (pyridine) $\longrightarrow$

1 (chlorosulfite structure) + 1 (pyridinium N—H, $Cl^{\ominus}$)

$\downarrow$

61

O
‖
S
O   O
1 | | +   1 HCl
CH₂   CH₂
\(CF₂)₃/

1 [pyridine] N

↓ 1

1 [pyridinium]N—H ⊖
                ⊕ Cl

Using this method, a 68% yield of hexafluoropentamethylene sulfite was obtained in pure form. No problems were encountered in the isolation and purification of the product since no pyridine was present and the pyridinium chloride could be filtered from the ether solution of the product.

23. Diester from Adipyl Chloride and Hexafluoroacetone Monohydrate

A diester was prepared by reaction of hexafluoroacetone monohydrate with adipyl chloride which was tentatively identified as the desired product.

$$
\underset{CF_3}{\overset{CF_3}{HO-\!\!\overset{|}{\underset{|}{C}}\!\!-OH}} + 2\ Cl-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow
$$

Cl-C(=O)-(CH₂)₄-C(=O)-O
Cl-C(=O)-(CH₂)₄-C(=O)-O
                              C(CF₃)(CF₃)

The existence of two different carbonyl absorptions at 5.6 μ and 5.8 μ in the infrared spectrum of the diester is consistent with the expected structure of the product. One of the peaks can be assigned to the carbonyl of the ester, and the other absorption peak to the acid chloride carbonyl. Analysis for chloride ion by both the silver nitrate gravimetric method and elemental analysis exhibited good correlation with the calculated value. However, elemental analysis for the other elements reveals that the product may not be the desired diacid chloride.

24. 2,2-Diacetoxy-hexafluoropropane

The reaction of hexafluoroacetone hydrate with adipyl chloride is described above. The subsequent reaction of the product with hexafluoro-pentanediol was described in Section III.C of this report. The identities of the products were questionable. In order to use any hydroxyl-terminated polyester of this nature, however, the hydroxyl-equivalency must be determined. Thus, any polyester must be stable under the conditions used for the

hydroxyl determination. It was decided to test the stability of a simple diester of hexafluoroacetone hydrate. An attempt was made to prepare 2,2-diacetoxy-hexafluoropropane by reaction of hexafluoroacetone hydrate with acetyl chloride using triethylamine as acid acceptor.

$$
\underset{\overset{|}{OH}}{\overset{\overset{OH}{|}}{CF_3-C-CF_3}} \quad + \quad 2 \ CH_3-\overset{\overset{O}{\|}}{C}-Cl
$$

$$\downarrow \ (C_2H_5)_3N$$

$$
\underset{CF_3}{\overset{CF_3}{\diagdown}} \hspace{-0.3em} C \hspace{-0.3em} \underset{O-\overset{\overset{O}{\|}}{C}-CH_3}{\overset{O-\overset{\overset{O}{\|}}{C}-CH_3}{\diagup}} \quad + \quad 2 \ (C_2H_5)_3\overset{\oplus}{NH} \ \overset{\ominus}{Cl}
$$

Although a nearly quantitative yield of triethylamine hydrochloride was obtained, none of the desired diester was isolated on distillation of the crude product. It appears that either the acetyl chloride and triethylamine reacted with the water from hexafluoroacetone hydrate, or that the desired diacetate product, if formed, was unstable to heat. Therefore, esters of hexafluoroacetone hydrate apparently are not suitable for use in polymer preparation.

25. Dihemiketal of Hexafluoroacetone and Hexafluoropentanediol

The preparation of a dihemiketal of hexafluoroacetone and hexafluoropentanediol was investigated.

$$
CF_3-\overset{\overset{O}{\|}}{C}-CF_3 \quad + \quad HOCH_2(CF_2)_3CH_2OH \longrightarrow \underset{\overset{|}{CF_3}}{\overset{\overset{CF_3}{|}}{HO-C-OCH_2}}(CF_2)_3CH_2\underset{\overset{|}{CF_3}}{\overset{\overset{CF_3}{|}}{O-C-OH}}
$$
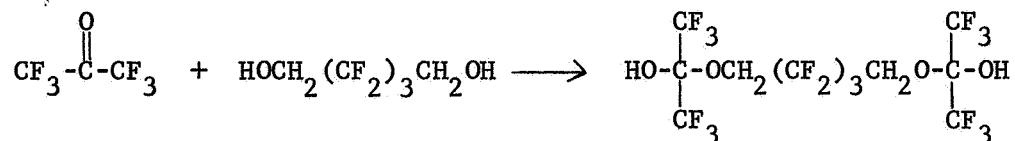
The infrared spectrum of the product obtained indicated that the desired reaction had proceeded. Isolation of the product was a problem caused by its apparent instability. An attempt was made to trap the dihemiketal by reaction of an ether solution of the product with p-toluenesulfonyl chloride. No reaction took place, indicating that the hydroxyl groups of the dihemiketal are quite unreactive. The dihemiketal was, however, reacted with the extremely reactive tetrafluoro-p-phenylene diisocyanate to yield a polyurethane as described in Section III.B.

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26. Attempted Preparation of p-Amino-tetrafluorobenzylamine (p-Amino-tetrafluorobenzonitrile)

As discussed in Section II.B, isocyanate-terminated prepolymers prepared from tetrafluoro-p-phenylene diisocyanate are difficult to cure because of the exceptional reactivity of the terminal isocyanate groups. It was felt that prepolymers prepared from p-isocyanato-tetrafluorobenzyl isocyanate would be less reactive and could be cured with less difficulty.

An attempted preparation of the precursor, p-amino-tetrafluorobenzylamine by reduction of p-amino-tetrafluorobenzamide with lithium aluminum hydride resulted in a 21% yield of p-amino-tetrafluorobenzonitrile.

$$H_2N-C_6F_4-\overset{\overset{\text{O}}{\|}}{C}-NH_2 + LiAlH_4 \longrightarrow$$

$$\nrightarrow H_2N-C_6F_4-CH_2NH_2$$

$$\longrightarrow H_2N-C_6F_4-C\equiv N$$
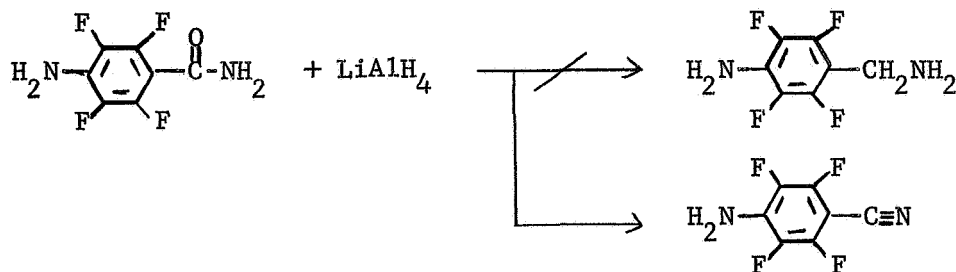
This unprecedented dehydration of an amide by lithium aluminum hydride is quite interesting, but no mechanism for this dehydration can be proposed at this time.

27. 2-Imino-hexafluoropropane

The need for a liquid or low-melting solid curing agent has prompted a study on the preparation of the amino-terminated diurethane from hexafluoropentanediol and 2-amino-2-isocyanato-hexafluoropropane.

$$OCN-\overset{\overset{\text{CF}_3}{|}}{\underset{\underset{\text{CF}_3}{|}}{C}}-NH_2 \; + \; HO-CH_2(CF_2)_3CH_2-OH \longrightarrow$$

$$H_2N-\overset{\overset{\text{CF}_3}{|}}{\underset{\underset{\text{CF}_3}{|}}{C}}-NH-\overset{\overset{\text{O}}{\|}}{C}-OCH_2(CF_2)_3CH_2O-\overset{\overset{\text{O}}{\|}}{C}-NH-\overset{\overset{\text{CF}_3}{|}}{\underset{\underset{\text{CF}_3}{|}}{C}}-NH_2$$
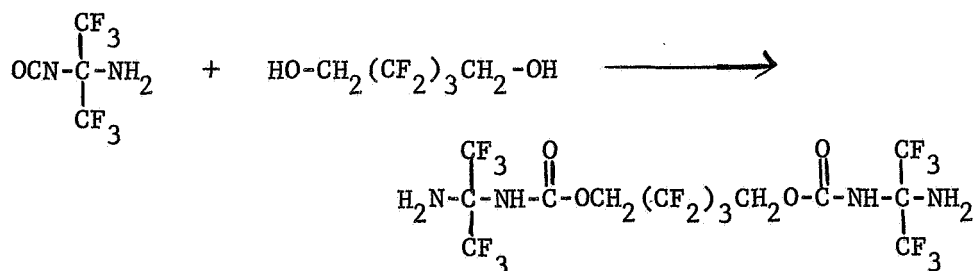
The preparation of the amino-isocyanate was recently reported by Middleton and Krespan[35] by the following series of reactions.

$$CF_3-\overset{\overset{\text{O}}{\|}}{C}-CF_3 \xrightarrow{NH_3} CF_3-\overset{\overset{\text{OH}}{|}}{\underset{\underset{\text{NH}_2}{|}}{C}}-CF_3 \xrightarrow{POCl_3} CF_3-\overset{\overset{\text{NH}}{\|}}{C}-CF_3 \xrightarrow{HNCO} CF_3-\overset{\overset{\text{NH}_2}{|}}{\underset{\underset{\text{NCO}}{|}}{C}}-CF_3$$
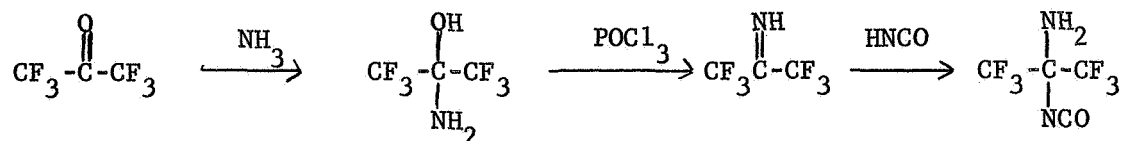
2-Imino-hexafluoropropane was prepared but attempts to convert it to the amino-isocyanate have been delayed due to the difficulties encountered in preparing isocyanic acid.

28. Eutectic Curing Agents

An attempt was made to prepare a liquid curing agent by forming a eutectic mixture of tetrafluoro-p-phenylenediamine with other fluorinated materials. Neither pentafluoroaniline nor hydroxyl-terminated poly(hexafluoropentamethylene adipate) gave a liquid or low-melting solid when mixed with tetrafluoro-p-phenylenediamine.

29. Monosodium Salt of Hexafluoropentanediol

The preparation of the monosodium salt of hexafluoropentanediol by reaction of hexafluoropentanediol with sodium metal in di-n-butyl ether was described in Annual Summary Report I (July 1964). This monosodium salt was prepared this year in 79% yield by reaction of hexafluoropentanediol with sodium hydride in ethyl ether.

IV. EXPERIMENTAL

A. LOX Compatibility Results

The results of all LOX compatibility tests are presented in Table 2.

B. Polyurethanes

1. From Hexafluoropentanediol

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

$$
\underset{\substack{Cl \quad Cl \\ \\ Cl \quad Cl}}{OCN-\!\!\bigcirc\!\!-NCO} \;+\; HOCH_2(CF_2)_3\!\!-\!\!CH_2OH \longrightarrow
$$

$$
\left[\!\!\begin{array}{c} \overset{O}{\underset{\|}{C}}-\overset{H}{\underset{|}{N}}\!\!\underset{\substack{Cl \\ \\ Cl}}{\bigcirc}\!\!\overset{Cl}{\underset{\substack{\\ Cl}}{}}\overset{H}{\underset{|}{N}}-\overset{O}{\underset{\|}{C}}-OCH_2-(CF_2)_3-CH_2O \end{array}\!\!\right]_x
$$
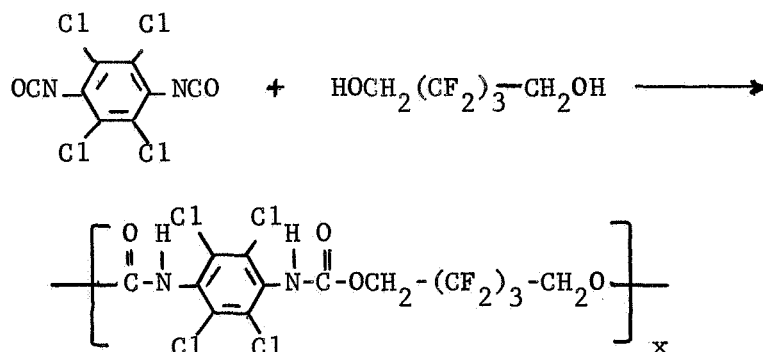
Hexafluoropentanediol (10.6 g, 0.05 mole) in 25 ml of ethyl acetate was charged to a 100-ml, three-necked flask equipped with a stirrer, condenser, dropping funnel, thermometer, and dry nitrogen inlet. Tetrachloro-p-phenylene diisocyanate (14.9 g, 0.05 mole) in 35 ml of ethyl acetate was added to the diol solution in 5 minutes with mixing under nitrogen.

The slurry was stirred for ½ hour at 30°-35°C, then refluxed at 82°C for 1½ hours. The ethyl acetate was removed and 40 ml of o-dichlorobenzene was added. The slurry was mixed at 130°-140°C under nitrogen. Triethylamine (5 drops) was added and the slurry heated for 3 hours at 100°C. The slurry was then filtered and the polymer residue dried in a vacuum oven at 130°-140°C for 4 hours to yield 16.0 g of brown polymer, mp 190°-196°C. Samples of the polymer were prepared for LOX-compatibility testing by using a 11/16-in. diameter pellet mold at 200°F and 40,000-lb pressure.

b. Preparation of Poly(pentamethylene tetrafluoro-p-phenylenedicarbamate)

$$
\underset{\substack{F \quad F \\ \\ F \quad F}}{OCN-\!\!\bigcirc\!\!-NCO} \;+\; HO(CH_2)_5OH \longrightarrow
$$

$$
\left[\!\!\begin{array}{c} \overset{O}{\underset{\|}{C}}-NH\!\!\underset{\substack{F \\ \\ F}}{\bigcirc}\!\!\overset{F}{\underset{\substack{\\ F}}{}}NH-\overset{O}{\underset{\|}{C}}-O-(CH_2)_5-O \end{array}\!\!\right]_x
$$

66
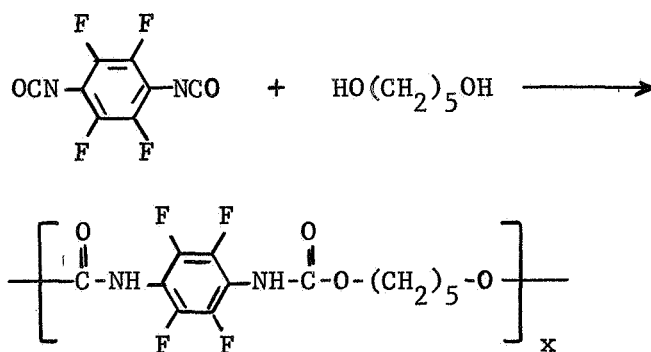
TABLE 2

LOX COMPATIBILITY RESULTS

Name of Polymer	Polymer Structure	Fluorine, %	Film Thickness, mils	LOX Results*, No. of Reactions	Remarks
Poly(hexafluoropenta-methylene hexafluoro-trimethylene di-carbamate)	$\left[O\text{-}CH_2(CF_2)_3CH_2\text{-}O\text{-}C\text{-}N(CF_2)_3\text{-}N\text{-}C \right]_n$	51.0	20	0/20	Hydro-lytically unstable
Poly(hexafluoropenta-methylene tetrafluoro-p-phenylene dicarbamate)	$\left[O\text{-}CH_2(CF_2)_3CH_2\text{-}O\text{-}C\text{-}N\text{-}\langle\text{C}_6F_4\rangle\text{-}N\text{-}C \right]_n$	42.8	26	0/20	--
Poly(hexafluoropenta-methylene tetrachloro-p-phenylene di-carbamate)	$\left[OCH_2(CF_2)_3CH_2\text{-}O\text{-}C\text{-}N\text{-}\langle\text{C}_6Cl_4\rangle\text{-}N\text{-}C \right]_n$	**50.2	20	0/20	--
Poly(hexafluoropenta-methylene hexa-methylene di-carbamate)	$\left[O\text{-}CH_2(CF_2)_3CH_2O\text{-}C\text{-}N(CH_2)_6\text{-}N\text{-}C \right]_n$	32.4	33	0/20	--
Poly(hexafluoropenta-methylene perfluoro-glutaramide)	$\left[N\text{-}CH_2(CF_2)_3CH_2\text{-}N\text{-}C\text{-}(CF_2)_3\text{-}C \right]_n$	55.0	17	0/20	--
Poly(ethylene per-fluoroglutaramide)	$\left[N\text{-}CH_2CH_2\text{-}N\text{-}C\text{-}(CF_2)_3\text{-}C \right]_n$	43.2	20	0/20	--
Poly(hexafluoropenta-methylene perfluoro-glutarate)	$\left[O\text{-}CH_2(CF_2)_3CH_2\text{-}O\text{-}C\text{-}(CF_2)_3\text{-}C \right]_n$	54.8	20	0/20	Hydro-lytically unstable

(continued on next page)
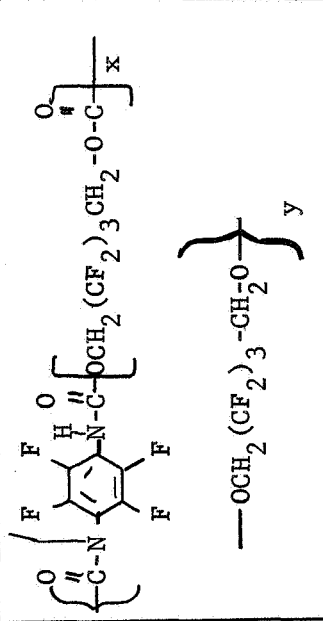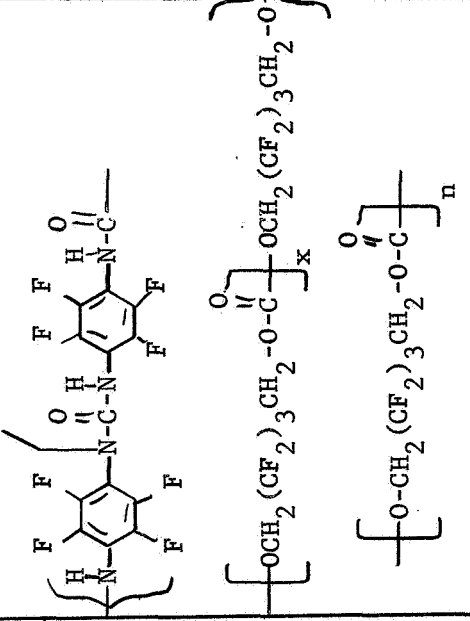
67

TABLE 2 (Continued)

Name of Polymer	Polymer Structure	Fluorine, %	Film Thickness, mils	LOX Results*, No. of Reactions	Remarks
Tetrafluoro-p-phenylenediamine cured Polyurethane of Toluene-2,4-diisocyanate and Poly(hexafluoropentamethylene malonate)		30.5	10	4/20	--
Polyurethane of Poly(hexafluoropentamethylene adipate) and Toluene-2,4-diisocyanate		33.4	21	20/20	--
Tetrafluoro-p-phenylenediamine cured Polyurethane of Poly(hexafluoropentamethylene adipate) and tetrafluoro-p-phenylenediisocyanate		35.0	10	3/20	--

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TABLE 2 (Continued)

Name of Polymer	Polymer Structure	Fluorine, %	Film Thick-ness, mils	LOX Results*, No. of Reactions	Remarks
Polyurethane of Tetra-fluoro-p-phenylene di-isocyanate and Poly-(hexafluoropenta-methylene formal)		45.7	18	19/20	--
Polyurethane of Tetra-fluoro-p-phenylene diisocyanate and Poly-(3,3,3-Trifluoro-1-propylene oxide)		46.2	10	9/20	--
Polyurethane Prepolymer of Toluene-2,4-di-isocyanate and Poly-(hexafluoropenta-methylene carbonate)		38.4	10	2/20	--
Tetrafluoro-p-phenylene diamine cured Poly-urethane of Toluene-2,4-diisocyanate and Poly-(hexafluoropenta-methylene carbonate)		38.7	10	5/20	--

(continued on next page)

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TABLE 2 (Continued)

Name of Polymer	Polymer Structure	Fluorine, %	Film Thickness, mils	LOX Results* No. of Reactions	Remarks
Polyurethane of Tetrafluoro-p-phenylene Diisocyanate and Poly(hexafluoropentamethylene carbonate)	$\left[\overset{O}{\overset{\|}{C}}-N\overset{H}{\underset{\|}{}}\text{(tetrafluorophenylene)}N\overset{H}{\underset{\|}{}}-\overset{O}{\overset{\|}{C}}-OCH_2(CF_2)_3CH_2-O-\overset{O}{\overset{\|}{C}}\right]_x \quad \left[OCH_2(CF_2)_3-CH_2O\right]_y$	45.6	10	19/20 20/20 (7.6 KG) 14/20 (5.3 KG)	--
Tetrafluoro-p-phenylene diamine cured polyurethane of tetrafluoro-p-phenylene diisocyanate and Poly(hexafluoropentamethylene carbonate)	$N\overset{H}{\underset{\|}{}}\text{(tetrafluorophenylene)}N\overset{H}{\underset{\|}{}}-\overset{O}{\overset{\|}{C}}\text{(tetrafluorophenylene)}\overset{H}{\underset{\|}{N}}-\overset{O}{\overset{\|}{C}}\left[OCH_2(CF_2)_3CH_2-O-\overset{O}{\overset{\|}{C}}\right]_x\left[OCH_2(CF_2)_3CH_2-O\right]_y$	43.7	10	18/20	--
Poly(hexafluoropentamethylene carbonate)	$\left[O-CH_2(CF_2)_3CH_2-O-\overset{O}{\overset{\|}{C}}\right]_n$	47.8	10	19/20	--

* Energy level = 10 KG.-M.

** Total % halogen

70

Into a 100-ml, three-necked flask equipped with a stirrer, reflux condenser, and addition funnel with a nitrogen inlet was placed 1,5-pentanediol (2.1 g, 0.02 mole) dissolved in 10 ml of ethyl acetate. The system was flushed with nitrogen and the polymerization run under a nitrogen atmosphere. Tetrafluoro-p-phenylene diisocyanate (4.6 g, 0.02 mole) dissolved in 15 ml of ethyl acetate was added slowly with stirring over a period of 25 minutes. Almost immediately, a white precipitate came out of solution. The mixture was stirred at room temperature for 1½ hours, then at reflux (77°C) for 2½ hours. The white solid was filtered and dried in a vacuum oven at 70°C yielding 6.1 g (91%) of polyurethane melting at 280°-281°C. The infrared spectrum of the polymer is attached as Figure 5.

c. Preparation of Poly(hexafluoropentamethylene hexafluoropentamethylene-dicarbamate)

$$Cl-\overset{\overset{O}{\|}}{C}-O-CH_2-(CF_2)_3-CH_2-O-\overset{\overset{O}{\|}}{C}-Cl \quad + \quad H_2N-CH_2-(CF_2)_3CH_2-NH_2 \longrightarrow$$

$$-\left[O-CH_2(CF_2)_3-CH_2-O-\overset{\overset{O}{\|}}{\underset{}{C}}\overset{\overset{H}{|}}{\underset{}{N}}-CH_2-(CF_2)_3-CH_2-\overset{\overset{H}{|}}{\underset{}{N}}\overset{\overset{O}{\|}}{\underset{}{C}}\right]_x$$
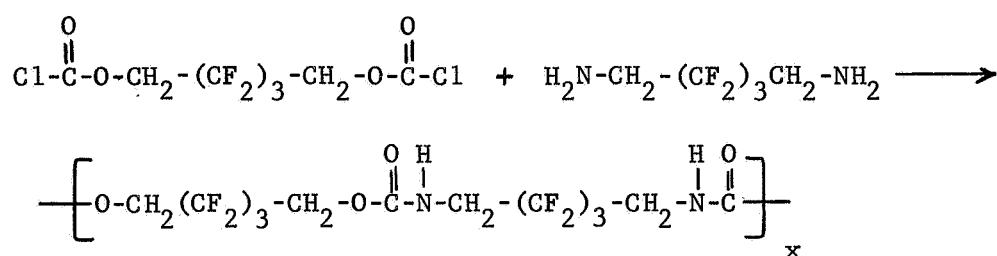
Into a 250-ml, three-necked flask equipped with a stirrer, condenser, dropping funnel, thermometer, and nitrogen inlet, was added hexafluoropentane-diamine (4.20 g, 0.02 mole), sodium hydroxide (1.76 g, 0.044 mole) and 100 ml of water. Hexafluoropentamethylene bischloroformate* (6.74 g, 0.02 mole) in 50 ml of methylene chloride was rapidly added to the diamine solution at 0°-25°C. The methylene chloride solution was decanted, and the polymer dried in a vacuum oven at 40°-50°C for 4 hours to yield a viscous oil. Apparently, the rate of hydrolysis of the chloroformate is faster than the reaction with hexafluoro-pentanediamine.

d. Attempted Preparation of Poly(hexafluoropentamethylene perfluoro-glutaryl dicarbamate)

$$H_2N-\overset{\overset{O}{\|}}{C}-(CF_2)_3-\overset{\overset{O}{\|}}{C}-NH_2 \quad + \quad Cl-\overset{\overset{O}{\|}}{C}-OCH_2(CF_2)_3CH_2O-\overset{\overset{O}{\|}}{C}-Cl \quad \overset{Pyridine}{\longrightarrow}$$

$$-\left[\overset{\overset{H}{|}}{\underset{}{N}}\overset{\overset{O}{\|}}{\underset{}{C}}-(CF_2)_3-\overset{\overset{O}{\|}}{\underset{}{C}}\overset{\overset{H}{|}}{\underset{}{N}}\overset{\overset{O}{\|}}{\underset{}{C}}-OCH_2(CF_2)_3CH_2O-\overset{\overset{O}{\|}}{\underset{}{C}}\right]_x$$
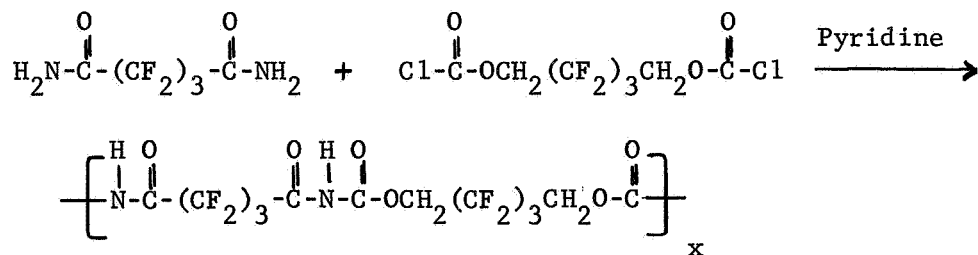
Hexafluoropentamethylene bischloroformate (10.8 g, 0.032 mole) was added to a 100-ml, three-necked, round-bottomed flask equipped with a stirrer, condenser, addition funnel, thermometer, and dry nitrogen purge. Perfluoro-glutaramide [7.55 g, 0.032 mole as a 10.0% solution in pyridine (75.5 ml)] was

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* Preparation described in Section IV.E.
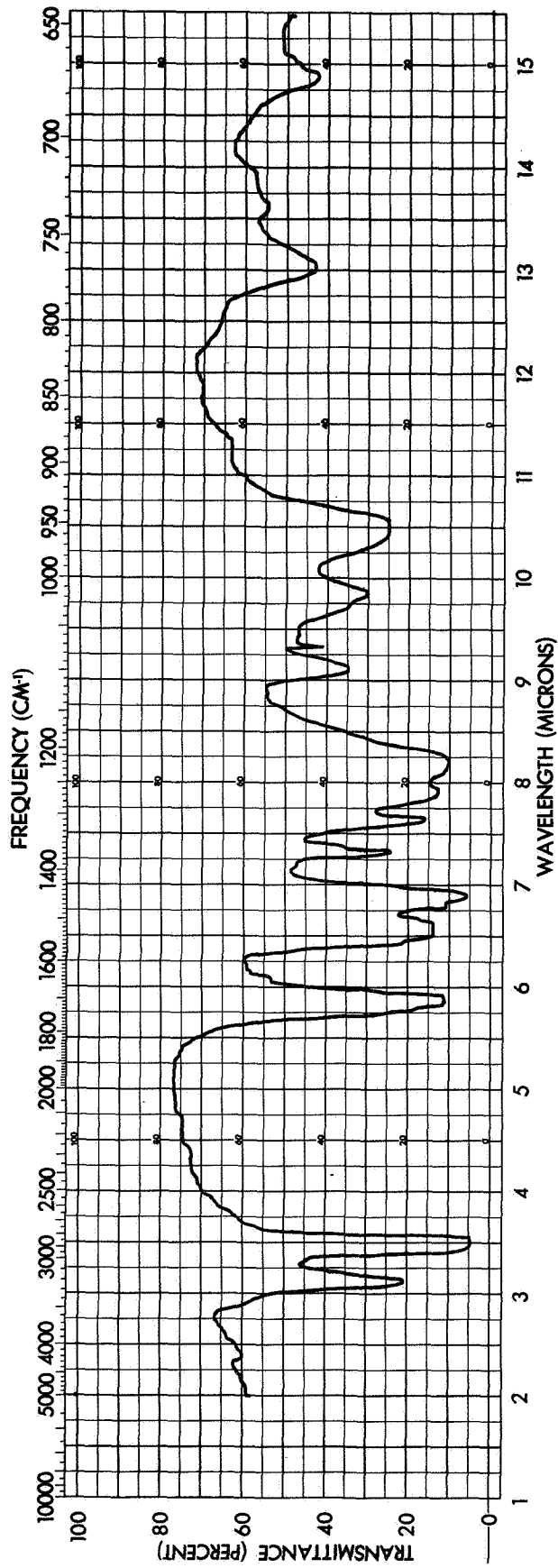
Figure 5. Poly(hexamethylene tetrafluoro-p-phenylenecarbamate)

·added slowly to the stirred bischloroformate. After approximately 20 ml of the diamide had been added, the reaction began to exotherm and a large mass of what appeared to be a polymeric material formed. Continuous mixing subsequently broke up the mass. The remainder of the diamide solution was added and the temperature raised to reflux (115°C). All the solids went into solution. The temperature was held at reflux for 4 hours followed by cooling to room temperature. The excess pyridine was stripped off, yielding a crystalline material of undetermined structure. None of the desired material was isolated.

2. From Hydroxyl-Terminated Polyesters

a. From Poly(hexafluoropentamethylene adipate)*

(1) And Tetrafluoro-p-phenylene Diisocyanate

(a) Preparation of Polyurethane from Tetrafluoro-p-Phenylene Diisocyanate and Poly(hexafluoropentamethylene adipate)

$$OCN-\underset{\underset{F\quad F}{}}{\overset{\overset{F\quad F}{}}{\bigcirc}}-NCO \;+\; H-\left[OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}\right]-OCH_2(CF_2)_3CH_2OH \longrightarrow$$

M.W. = 1450

$$\left\{\overset{O}{\overset{\|}{C}}-NH-\underset{\underset{F\quad F}{}}{\overset{\overset{F\quad F}{}}{\bigcirc}}-NH-\overset{O}{\overset{\|}{C}}\left[OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_x OCH_2(CF_2)_3CH_2O\right\}_y$$
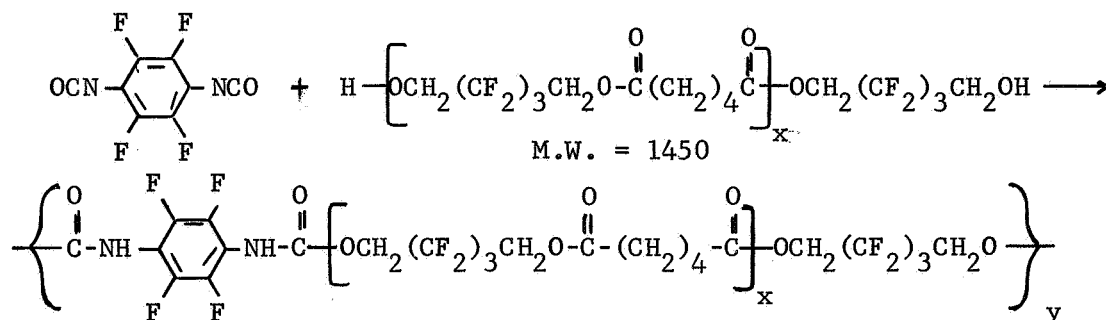
Poly(hexafluoropentamethylene adipate) (7.3 g, 0.005 mole) of 1450 molecular weight and tetrafluoro-p-phenylene diisocyanate (1.4 g, 0.0065 mole) were mixed at 300°F under nitrogen. Stannous octoate (2 drops) was added and the polymer mixed for 15 minutes at 300°F under nitrogen. The product was then cured in a press at 250°F for 20 minutes, then ½ hour at 325°F. The polymer appeared to have bood adhesion, but was not tough.

(b) Preparation of an Allophanate-Cured Fluorinated Polyurethane
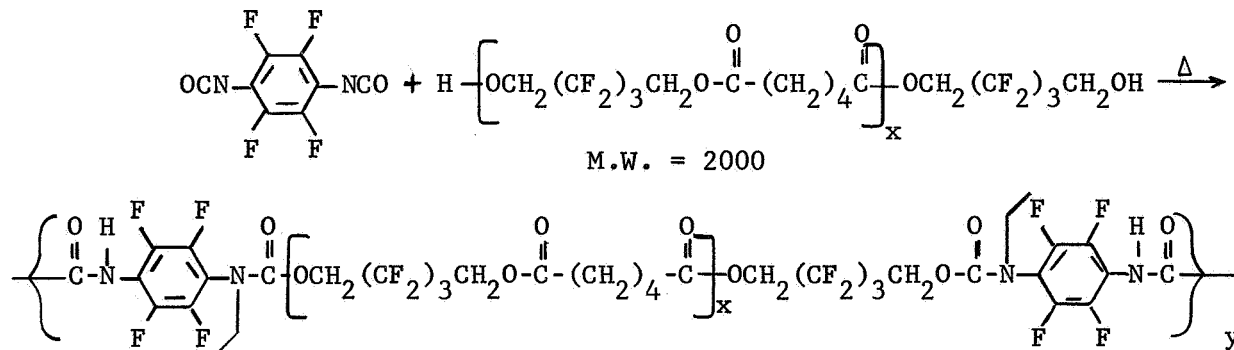
$$OCN-\underset{\underset{F\quad F}{}}{\overset{\overset{F\quad F}{}}{\bigcirc}}-NCO \;+\; H-\left[OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-(CH_2)_4\overset{O}{\overset{\|}{C}}\right]-OCH_2(CF_2)_3CH_2OH \overset{\Delta}{\longrightarrow}$$

M.W. = 2000

$$\left\{\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\underset{\underset{F\quad F}{}}{\overset{\overset{F\quad F}{}}{\bigcirc}}-N-\overset{O}{\overset{\|}{C}}\left[OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_x OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-N-\underset{\underset{F\quad F}{}}{\overset{\overset{F\quad F}{}}{\bigcirc}}-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}\right\}_y$$

---

* Preparation described in Section IV.C.

Poly(hexafluoropentamethylene adipate) of 2000 molecular weight (10.0 g, 0.01 mole) and tetrafluoro-p-phenylene diisocyanate (4.6 g, 0.02 mole) were placed in a 50-ml, three-necked flask equipped with a stirrer, condenser, thermometer, and nitrogen inlet. The mixture was stirred for 2½ hours at 80°-90°C, then ½ hour at 140°-150°C under nitrogen. The polymer was cooled to 80°C, then two drops of stannous octoate were added. The polymer was then mixed for 15 minutes at 80°-90°C, followed by 30 minutes at 140°-150°C under nitrogen. The polymer was cooled overnight to yield a tough, flexible polymer.

(c) Preparation of Amine-Cured Polyurethane of Tetrafluoro-p-Phenylene Diisocyanate and Poly(hexafluoropentamethylene adipate)

M.W. = 1450
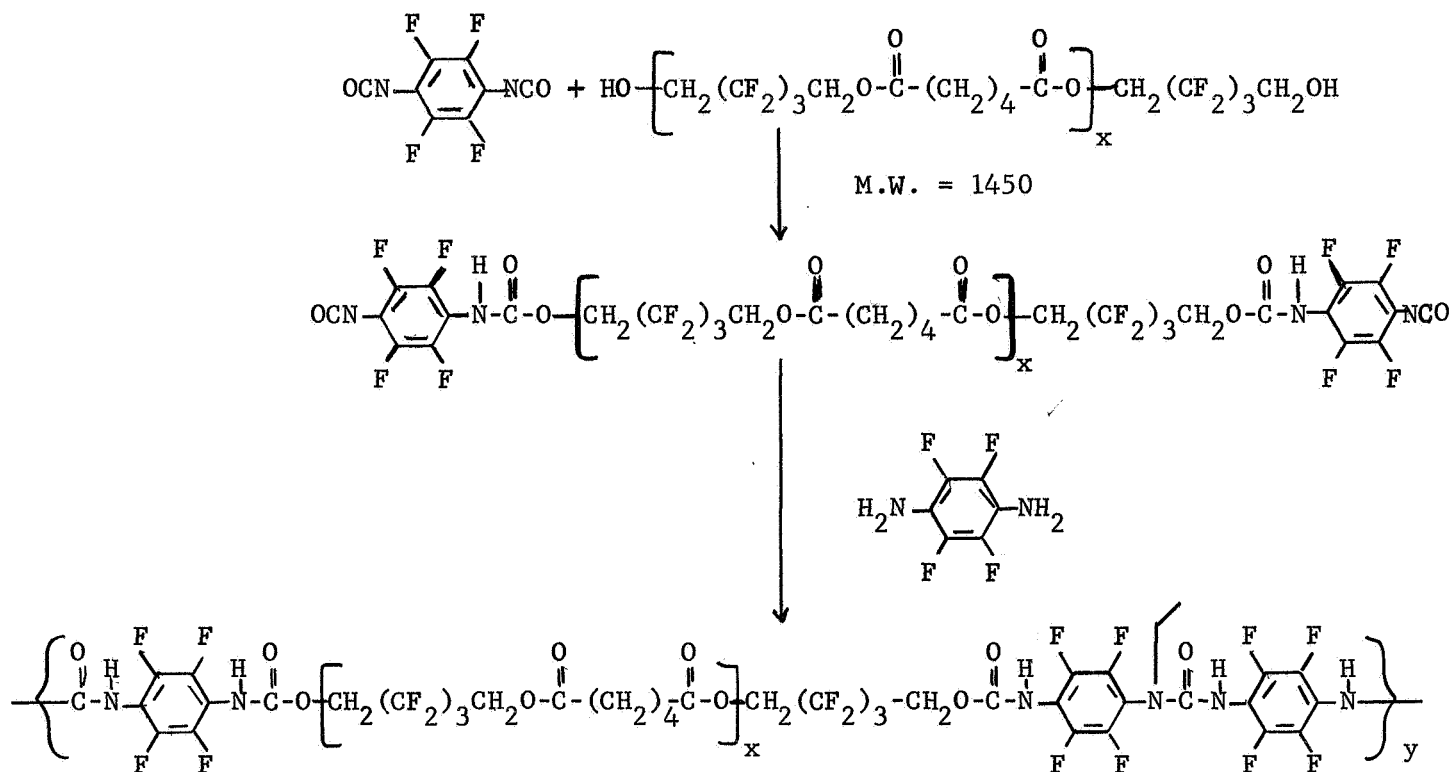
Tetrafluoro-p-phenylene diisocyanate (4.6 g, 0.02 mole) in 10 ml of dry ethyl acetate was added to a 100-ml, three-necked flask equipped with a condenser, stirrer, thermometer, and nitrogen inlet. Poly(hexafluoropentamethylene adipate) of 1450 molecular weight (14.5 g, 0.01 mole) in 10 ml of dry ethyl acetate containing triethylamine (1 drop) was slowly added to the diisocyanate solution. The solution was mixed for 4 hours at 80°C under nitrogen. Triethylamine (2 drops) in dry ethyl acetate (5 ml) was added. After an additional ½ hour at 80°C, the infrared spectrum indicated only traces of hydroxyl groups. The prepolymer was cooled to about 40°C, then tetrafluoro-p-phenylene-diamine (0.7 g, 0.0039 mole) in dry ethyl acetate (5 ml) was added. The solvent was removed in a vacuum oven at 70°-80°C. A sheet of the polymer was cured in a press at 325°F for ½ hour to yield a tough elastomer. Samples were punched from the polymer film and submitted to MSFC for LOX-compatibility testing.

(d)　Preparation of an Amine-Cured Fluorinated Polyurethane of
　　　Tetrafluoro-p-phenylene Diisocyanate and Poly(hexafluoro-
　　　pentamethylene adipate) without Catalysis

　　　　　Poly(hexafluoropentamethylene adipate) of 1450 molecular weight
(10.2 g, 0.007 mole), benzoyl chloride (1 drop), and tetrafluoro-p-phenylene
diisocyanate (3.2 g, 0.014 mole) were charged to a 25-ml, three-necked flask
equipped with a stirrer, condenser, thermometer and nitrogen inlet. The mixture
was stirred for 1½ hours at 80°-100°C under nitrogen. Based on the infrared
spectrum, most of the hydroxyl groups were consumed. The prepolymer was heated
to 150°C, then tetrafluoro-p-phenylenediamine (0.5 g, 0.0027 mole) was added.
The mass gelled immediately. The polymer was cured in a press at 325°F for
½ hour. The cured polymer was tough and elastomeric, but localized amine-rich
areas were apparent in the film.

(e)　Preparation of a Highly Flexible Amine-Cured Polyurethane of
　　　Tetrafluoro-p-Phenylene Diisocyanate and Poly(hexafluoro-
　　　pentamethylene adipate)

　　　　　Poly(hexafluoropentamethylene adipate) of 3200 molecular weight
(10.3 g, 0.0032 mole), tetrafluoro-p-phenylene diisocyanate (1.5 g, 0.0065 mole)
and benzoyl chloride (1 drop) were charged to a 25-ml, three-necked flask equipped
with a stirrer, condenser, thermometer, and nitrogen inlet. The mixture was
stirred for ½ hour at 80°C under nitrogen. Based on the infrared spectrum, the
hydroxyl groups were consumed. The prepolymer was heated to 150°C, and tetrafluoro-
p-phenylenediamine (0.3 g, 0.00167 mole) was added. The mass gelled immediately.
The polymer was cured in a press at 325°F for ½ hour, which yielded an elastomer
which was extremely flexible, but lacked toughness.

(f)　Preparation of a Tetrachloro-xylylenediol-Cured Polyurethane
　　　of Tetrafluoro-p-phenylene Diisocyanate and Poly(hexafluoro-
　　　pentamethylene adipate)

　　　　　Tetrafluoro-p-phenylene diisocyanate (5.3 g, 0.026 mole) in
dry ethyl acetate (15 ml) containing 1 drop of benzoyl chloride was added to a
50-ml, three-necked flask equipped with a stirrer, condenser, thermometer, and
nitrogen inlet. Poly(hexafluoropentamethylene adipate) of 1450 molecular weight
(11.1 g, 0.0076 mole) dissolved in 6 ml of dry ethyl acetate was then added.
The solution was mixed for 4 hours at 80°C under nitrogen, then cooled to room
temperature. Tetrachloro-xylylenediol (3.8 g, 0.0137 mole) was added as a slurry
in dry ethyl acetate (10 ml) to the prepolymer solution. The diol did not appear
to dissolve. The ethyl acetate was removed in a vacuum oven at 80°C for ½ hour.
The polymer was then molded in a press at 325°F for ½ hour. There was only a
slight flow of the product. The polymer was tough and flexible.

(g)　Preparation of a Hexafluoropentanediol-Cured Polyurethane
　　　of Tetrafluoro-p-phenylene Diisocyanate and Poly(hexafluoro-
　　　pentamethylene adipate)

　　　　　Poly(hexafluoropentamethylene adipate) of 1450 molecular weight
(14.0 g, 0.005 mole), tetrafluoro-p-phenylene diisocyanate (3.5 g, 0.015 mole)
and benzoyl chloride (1 drop) were placed in a 35-ml, three-necked flask equipped
with a stirrer, condenser, thermometer, and nitrogen inlet. The ingredients were

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mixed for 4 hours at 75°-85°C, then for 2 hours at 110°-115°C under nitrogen.
Based on the infrared spectrum, most of the hydroxyl groups were consumed.
Hexafluoropentanediol (1.9 g, 0.009 mole) was then added to the prepolymer at
100°-110°C. The product was a liquid. Stannous octoate (2 drops) was then
added. Within ½ minute, the mass gelled. The polymer was cured in a press at
325°F for ½ hour and yielded an extremely flexible polymer having poor tear
resistance.

(h) Preparation of a Polycarbonate-Cured Polyurethane

Poly(hexafluoropentamethylene adipate) of 2000 molecular
weight (10.0 g, 0.005 mole) and three drops of benzoyl chloride were charged to
a 25-ml, three-necked flask equipped with a stirrer, condenser, thermometer, and
nitrogen inlet. Tetrafluoro-p-phenylene diisocyanate (3.5 g, 0.015 mole) was
then added and the ingredients agitated for 1½ hours at 90°-100°C under nitrogen.
Based on the infrared spectrum, all of the hydroxyl groups had been consumed.
Poly(hexafluoropentamethylene carbonate)* of 1025 molecular weight (9.2 g,
0.009 mole) was then added and the polymer mixed at 50°C under nitrogen. The
polymer was then cured in a press at 160°-170°C for 20 minutes; a soft, highly
elastic polymer was obtained.

(i) Methylene-bis(o-chloroaniline) Cured Fluorinated Polyurethane

Poly(hexafluoropentamethylene adipate) of 2800 molecular weight
(14.0 g, 0.005 mole), tetrafluoro-p-phenylene diisocyanate (2.3 g, 0.01 mole)
and benzoyl chloride (two drops) were charged to a 25-ml, three-necked flask
equipped with a stirrer, condenser, thermometer, and nitrogen inlet. The ingre-
dients were mixed at 90°-110°C for 4 hours under nitrogen. Based on the infrared
spectrum, all of the hydroxyl groups had been consumed. The polymer was cooled
to 100°C, then molten methylene bis(o-chloroaniline) (MOCA) (1.1 g, 0.004 mole)
was added. The mass gelled immediately. The polymer was then cured in a press
at 160°-170°C for ½ hour to yield a tough elastomer. The product was not uni-
form, as there were localized amine-rich areas. Apparently, the amine was too
rapid a curing agent for the fluorinated polyurethane.

(j) Preparation of a Cured Polyurethane from the Isocyanate-
Terminated Poly(hexafluoropentamethylene adipate) of
Tetrafluoro-p-phenylene Diisocyanate and the Amine-Terminated
Poly(hexafluoropentamethylene adipate) of Tetrafluoro-p-
phenylenediamine

Tetrafluoro-p-phenylene diisocyanate (1.39 g, 0.0060 mole)
dissolved in 3 ml of dry ethyl acetate was placed in a 25-ml, round-bottomed
flask equipped with a stirrer, addition funnel, thermometer, condenser, and
nitrogen inlet. Through the delivery funnel was added poly(hexafluoropenta-
methylene adipate) of 1680 molecular weight (5.04 g, 0.0030 mole) in 5 ml of
dry ethyl acetate. The mixture was heated to reflux until the hydroxyl absorp-
tion in the infrared spectrum disappeared (16 hours). A solution of bis(p-
amino-tetrafluorophenyl amide) of poly(hexafluoropentamethylene adipate) of
1640 molecular weight (3.93 g, 0.0024 mole) in 5 ml of dry ethyl acetate was

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* Preparation described in IV.C.

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then added to the polyurethane solution. The mixture was stirred vigorously for 10 minutes, then transferred to an evaporating dish. The solvent was removed under vacuum at 60°C. The polymer was cured in a press at 20,000 psi and 325°F for ½ hour. The cured polymer was crumbly and had failed to fuse in the press.

(2) And Toluene-2,4-diisocyanate

(a) Allophanate-Cured Polyurethane

$$H\text{---}[OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}]_x\text{---}OCH_2(CF_2)_3CH_2OH \; + \; CH_3\text{---}\underset{}{\bigcirc}\text{---}NCO \;\longrightarrow$$

M.W. = 1900

$$CH_3\text{---}\bigcirc\text{---}\overset{H}{N}\text{-}\overset{O}{\overset{\|}{C}}\text{---}[OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}]_x\text{---}OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{N}\text{---}\bigcirc\text{---}CH_3$$

Δ

$$\left\{ \begin{array}{c} \text{---}C=O \\ | \\ N\text{-}H \end{array} \right. CH_3\text{---}\bigcirc\text{---}N\text{-}\overset{O}{\overset{\|}{C}}\text{---}[O\text{-}CH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}]_x\text{---}O\text{-}CH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}N\text{---}\bigcirc\text{---}CH_3 \right\}_y$$
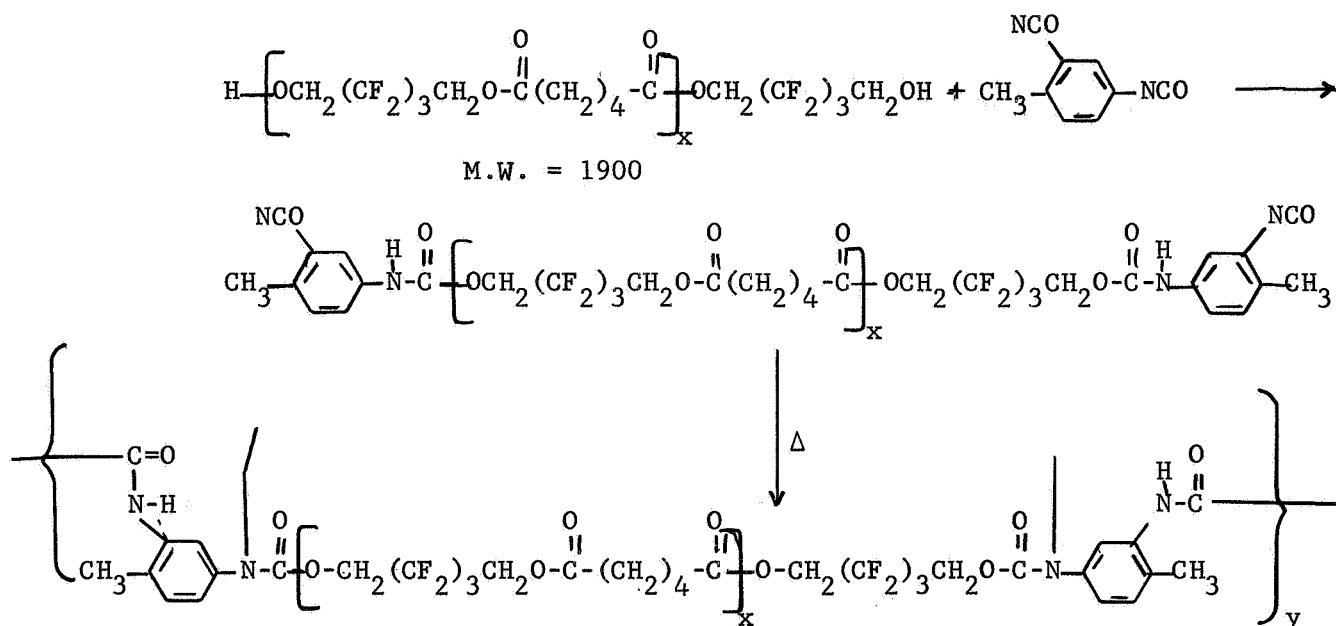
Toluene-2,4-diisocyanate (TDI) (10.4 g, 0.06 mole) was added to a 100-ml, three-necked flask equipped with a stirrer, condenser, dropping funnel, thermometer, and nitrogen inlet. Stannous octoate (2 drops) in poly(hexafluoropentamethylene adipate) of 1900 molecular weight (27.0 g, 0.015 mole) was added to the TDI at 80°C over a 45-minute period with mixing under nitrogen. The reaction was stirred for 2 hours at 80°-100°C under nitrogen. The excess TDI was removed via vacuum distillation at 160°-180°C, at which time the polymer gelled. The infrared spectrum revealed the polymer was NCO terminated, and contained little or no OH groups. The polymer was thermoplastic, extremely tough and elastic; it was insoluble in DMF and pyridine, but swelled considerably. The NCO equivalent weight was found to be 710.

This isocyanate-terminated prepolymer was pressed in the form of a sheet in a press at 300°F to 350°F for ½ hour. The resultant sheet was extremely flexible and contained no free isocyanate groups. The polymer had apparently cured by means of allophanate formation.

(b) Preparation of a Highly Flexible Amine-Cured Polyurethane

$$CH_3 \overset{NCO}{\underset{}{\bigcirc}} NCO \ + \ HO \left[CH_2(CF_2)_3 CH_2 O \overset{O}{\underset{\|}{C}} (CH_2)_4 \overset{O}{\underset{\|}{C}} O \right]_x CH_2(CF_2)_3 CH_2 OH$$

$$M.W. = 3200$$

$$CH_3 \overset{NCO}{\underset{}{\bigcirc}} \overset{H}{\underset{}{N}} \overset{O}{\underset{\|}{C}} O \left[CH_2(CF_2)_3 CH_2 O \overset{O}{\underset{\|}{C}} (CH_2)_4 \overset{O}{\underset{\|}{C}} O \right]_x CH_2(CF_2)_3 CH_2 O \overset{O}{\underset{\|}{C}} \overset{H}{\underset{}{N}} \overset{NCO}{\underset{}{\bigcirc}} CH_3$$

$$H_2N \overset{F \quad F}{\underset{F \quad F}{\bigcirc}} NH_2$$

$$\left\{ \overset{O}{\underset{\|}{C}} \overset{H}{\underset{}{N}} \overset{}{\underset{}{\bigcirc}} \overset{H}{\underset{}{N}} \overset{O}{\underset{\|}{C}} O \left[CH_2(CF_2)_3 CH_2 O \overset{O}{\underset{\|}{C}} (CH_2)_4 \overset{O}{\underset{\|}{C}} O \right]_x CH_2(CF_2)_3 CH_2 O \overset{O}{\underset{\|}{C}} \overset{H}{\underset{}{N}} \overset{}{\underset{}{\bigcirc}} \overset{H}{\underset{}{N}} \overset{O}{\underset{\|}{C}} \overset{H}{\underset{}{N}} \overset{F \quad F}{\underset{F \quad F}{\bigcirc}} NH \right\}_y$$
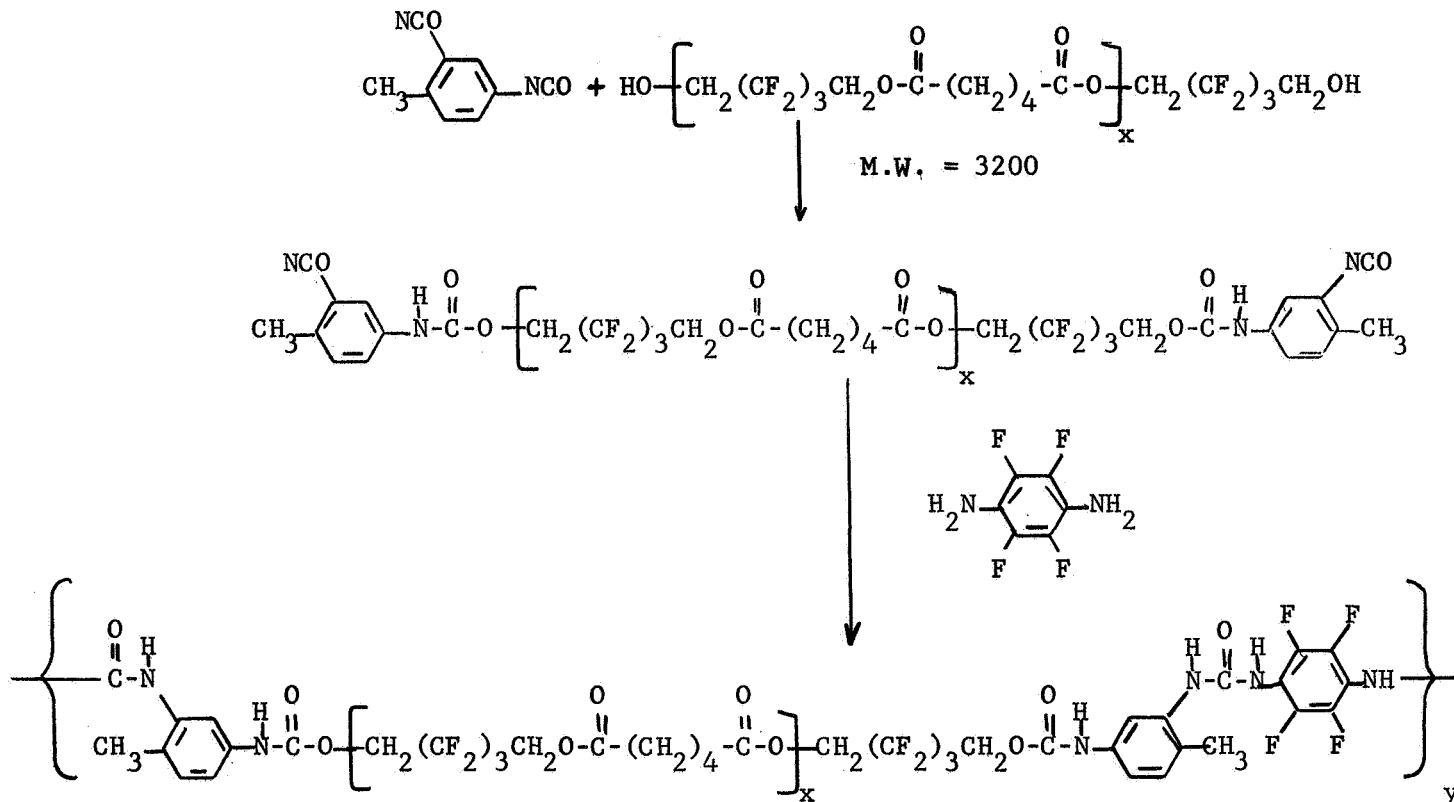
Poly(hexafluoropentamethylene adipate) of 3200 molecular weight (10.3 g, 0.0032 mole) and toluené diisocyanate (1.1 g, 0.0065 mole) were added to a 25-ml, three-necked flask equipped with a stirrer, condenser, thermometer, and nitrogen inlet. These ingredients were mixed and stannous octoate (2 drops) was added. The mixture was stirred for 15 minutes at 80°-90°C under nitrogen. Based on the infrared spectrum, all of the hydroxyl groups had been consumed. The prepolymer was heated to 150°C and tetrafluoro-p-phenylenediamine (0.4 g, 0.0026 mole) was added and mixed. The polymer was cured in a press at 325°F for ½ hour. The resultant polymer was colorless and extremely flexible.

(c) Preparation of a Fluorinated Polyurethane Foam

Poly(hexafluoropentamethylene adipate) of 1450 molecular weight (4.4 g, 0.003 mole), stannous octoate (2 drops), and water (3 drops) were thoroughly mixed. Toluene diisocyanate (1.6 g, 0.009 mole) was added and the mass thoroughly mixed. The foam was permitted to rise for 15 minutes at room temperature, then cured at 66°C for 2 hours. The foam was white and extremely flexible.

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ORIGINAL DOCUMENT

b. **From Poly(hexafluoropentamethylene malonate)***

    (1) Preparation of Polyurethane from Tetrafluoro-p-phenylene Diisocyanate

$$\text{H}-\left[\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{CH}_2-\overset{\overset{\text{O}}{\|}}{\text{C}}\right]_x\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{OH} + \text{OCN}-\underset{\underset{\text{F}\quad\text{F}}{}}{\overset{\overset{\text{F}\quad\text{F}}{}}{\bigcirc}}-\text{NCO} \longrightarrow$$

M.W. = 1779

$$\left\{-\overset{\overset{\text{O}}{\|}}{\text{C}}-\overset{\text{H}}{\text{N}}-\underset{\underset{\text{F}\quad\text{F}}{}}{\overset{\overset{\text{F}\quad\text{F}}{}}{\bigcirc}}-\overset{\text{H}}{\text{N}}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\left[\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{CH}_2-\overset{\overset{\text{O}}{\|}}{\text{C}}\right]_x\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{O}-\right\}_y$$
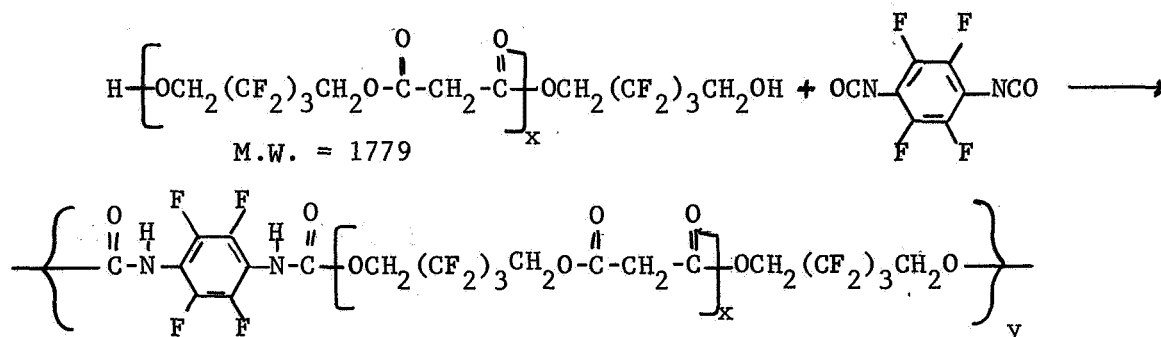
    Poly(hexafluoropentamethylene malonate) of 1779 molecular weight (40.9 g, 0.023 mole) was dissolved in 20 ml of anhydrous ethyl acetate and charged to a three-necked, round-bottomed flask fitted with a condenser, stirrer, addition funnel, and thermometer. Tetrafluoro-p-phenylene diisocyanate (5.4 g, 0.023 mole), dissolved in 10 ml of anhydrous ethyl acetate, was added to the reaction flask and the mixture stirred at room temperature under a nitrogen atmosphere overnight. The progress of the reaction was followed by infrared spectroscopy during subsequent steps. The reaction was stirred at reflux (80°C) for 3 hours. The infrared spectrum indicated that only a slight reaction had taken place. Stannous octoate (2 drops) was added and reflux continued for 2 hours. Filtration at this point proved to be very difficult, so the reaction mixture was transferred to an evaporating dish and the solvent evaporated under reduced pressure. A tacky grease containing free OH was isolated. A portion of this residue (9.0 g) in 50 ml of dry ethyl acetate was reacted with additional tetrafluoro-p-phenylene diisocyanate (2.7 g) in 20 ml of dry ethyl acetate at reflux temperature in the presence of stannous octoate (2 drops) for 16 hours. The mixture was transferred to 200 ml of dry hexane, stirred vigorously, and filtered. The residue was dried 2 hours in a vacuum oven at 80°C and < 1-mm Hg. A white, amorphous, solid polymer (9.7 g, 82.9%) was obtained, melting at 190°-200°C.

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* Preparation described in Section IV.C.

(2) Preparation and Curing of the Toluene-2,4-diisocyanate-Terminated Prepolymer

$$H\text{-}[OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}]_x OCH_2(CF_2)_3CH_2OH + \text{(toluene-2,4-diisocyanate)} \longrightarrow$$

M.W. = 1779

$$\text{CH}_3\text{-...-}\overset{H}{N}\text{-}\overset{O}{\overset{\|}{C}}[OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}]_x OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{N}\text{-...-CH}_3$$

$$+ \quad H_2N\text{-}(C_6F_4)\text{-}NH_2$$

$$\downarrow$$

$$[\ldots]_y$$
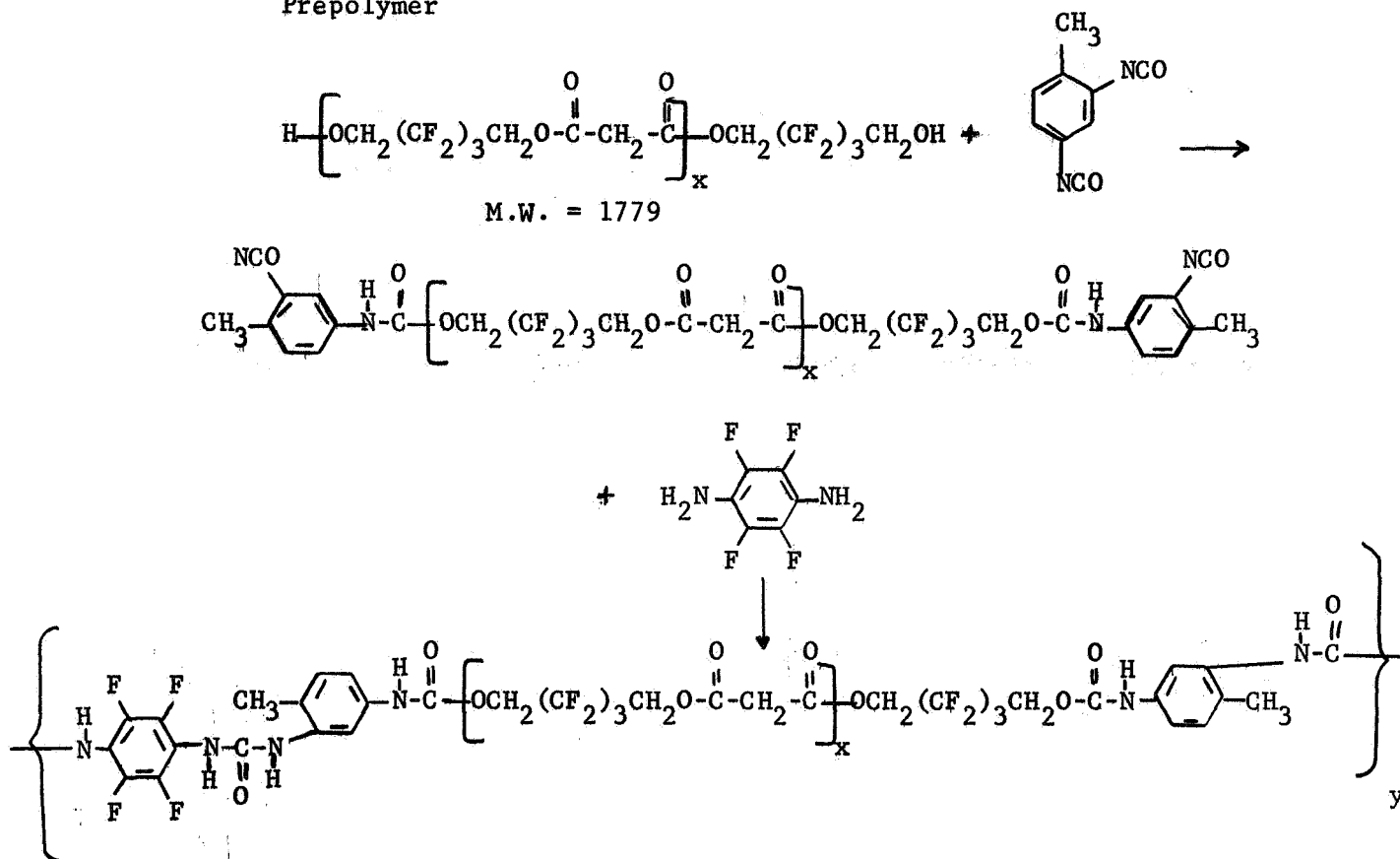
Toluene-2,4-diisocyanate (13.9 g, 0.08 mole) was added to a 100-ml, three-necked flask equipped with a stirrer, condenser, thermometer, dropping funnel and nitrogen inlet. Stannous octoate (2 drops) in the hydroxyl-terminated poly(hexafluoropentamethylene malonate) of 1779 molecular weight (36.9 g, 0.02 mole) were added to the TDI at 50°-80°C in 40 minutes with mixing under nitrogen. The solution was then stirred for 1½ hours at 80°-100°C under nitrogen. The unreacted TDI was removed by vacuum distillation to 160°C to yield a viscous liquid. The prepolymer contained little or no OH groups and was NCO terminated, as indicated by the infrared spectrum which is attached as Figure 6. The NCO equivalent weight was found to be 838.

Tetrafluoro-p-phenylene diamine (2.2 g, 0.0123 mole) and this NCO-terminated prepolymer (24.0 g, 0.015 mole) were mixed at 150°C for 5 minutes, then placed in a cavity mold. The polymer was cured for 15 minutes at 120°C, followed by ½ hour at 150°C. The cured polymer was flexible when warm, but tended to embrittle on cooling. Twenty specimens were punched from a sheet of the polymer and submitted for LOX-compatibility testing.

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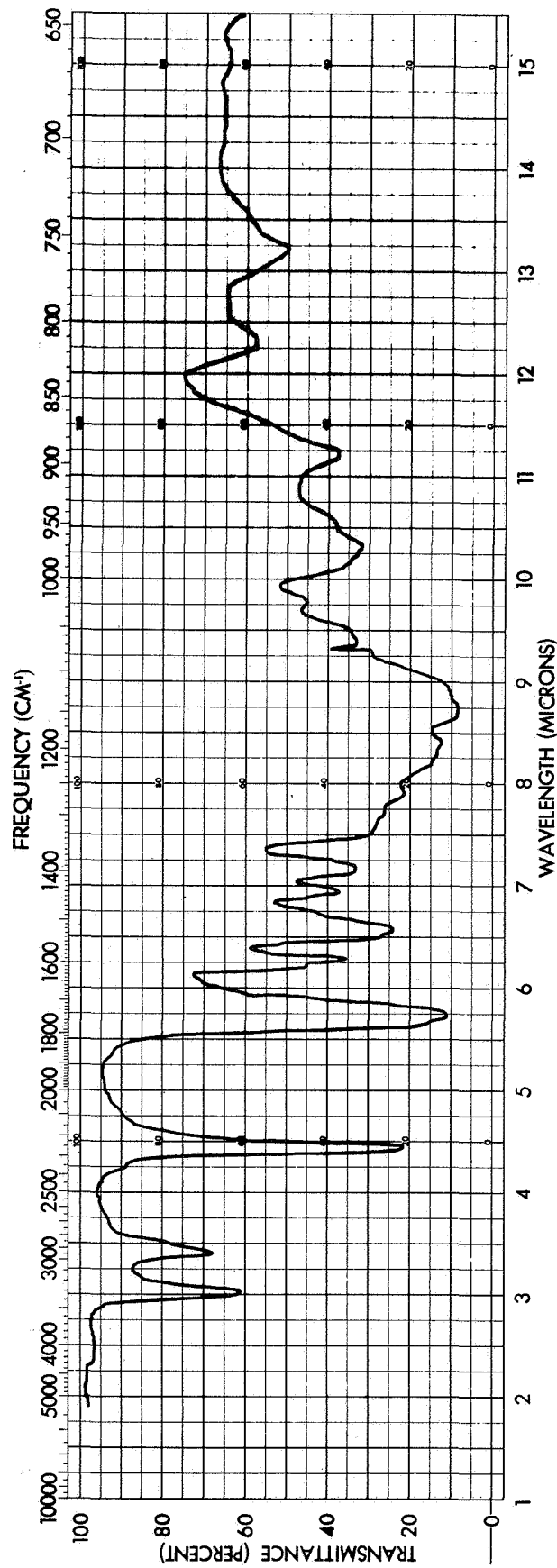
Figure 6. NCO-Terminated Prepolymer of Toluene-2,4-Diisocyanate and Poly(hexafluoropentamethylene malonate)

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(3) Preparation and Attempted Cure of the Tetrachloro-p-phenylene Diisocyanate-Terminated Prepolymer

$$H\text{-}\left[OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\right]_x OCH_2(CF_2)_3CH_2OH + OCN\text{-}\underset{Cl\quad Cl}{\overset{Cl\quad Cl}{\bigcirc}}\text{-}NCO \longrightarrow$$

M.W. = 1779

$$OCN\text{-}\underset{Cl\quad Cl}{\overset{Cl\quad Cl}{\bigcirc}}\text{-}\overset{H}{N}\text{-}\overset{O}{\overset{\|}{C}}\left[OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\right]_x OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{N}\text{-}\underset{Cl\quad Cl}{\overset{Cl\quad Cl}{\bigcirc}}\text{-}NCO$$

$$+ \quad H_2N\text{-}\underset{F\quad F}{\overset{F\quad F}{\bigcirc}}\text{-}NH_2 \quad \diagdown\!\!\!\longrightarrow$$

$$\left\{\overset{H}{N}\text{-}\underset{F\quad F}{\overset{F\quad F}{\bigcirc}}\text{-}\overset{H}{N}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{N}\text{-}\underset{Cl\quad Cl}{\overset{Cl\quad Cl}{\bigcirc}}\text{-}\overset{H}{N}\text{-}\overset{O}{\overset{\|}{C}}\left[OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\right]_x OCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{N}\text{-}\underset{Cl\quad Cl}{\overset{Cl\quad Cl}{\bigcirc}}\text{-}\overset{H}{N}\text{-}\overset{O}{\overset{\|}{C}}\right\}_y$$
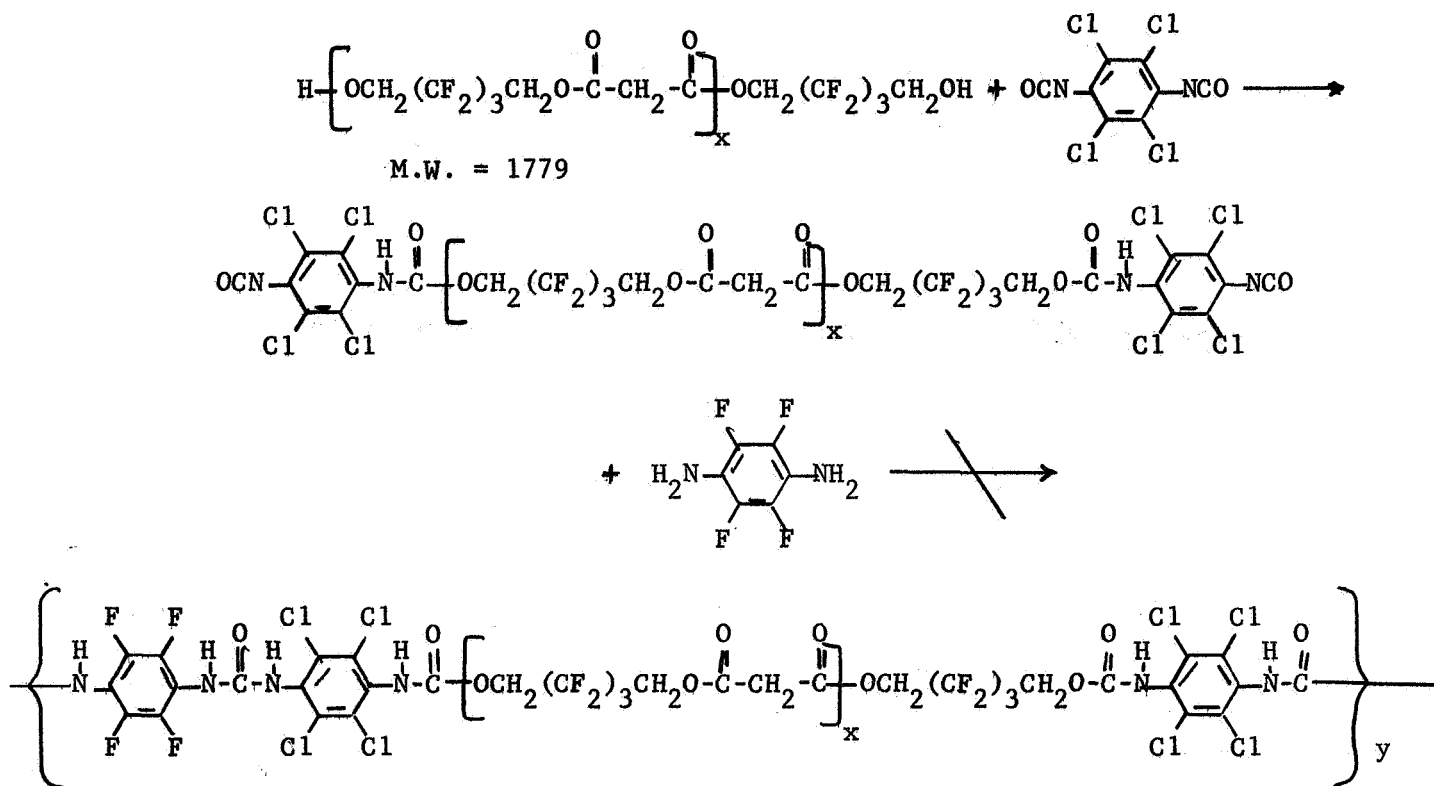
Tetrachloro-p-phenylene diisocyanate (11.9 g, 0.04 mole) in dry xylene (20 ml) was placed in a 100-ml, three-necked flask equipped with a stirrer, condenser, dropping funnel, thermometer, and nitrogen inlet. The hydroxyl-terminated poly(hexafluoropentamethylene malonate) of 1779 molecular weight (25.2 g, 0.02 mole) was added to the diisocyanate at 80°-100°C under nitrogen over a period of ½ hour. The slurry was mixed for 1 hour at 80°-100°C under nitrogen; there was no apparent reaction. The slurry was then stirred for 1 hour at 135°-140°C under nitrogen. There was only a slight reaction. Stannous octoate (2 drops) was added and the reaction mixed for 1½ hours at 135°-140°C under nitrogen. The xylene was removed via vacuum distillation to yield a viscous hazy liquid. The NCO equivalent was found to be 553. The infrared spectrum indicated that the prepolymer contained no OH groups and was NCO terminated.

This prepolymer (6.6 g, 0.006 mole) was melted at 150°C and tetrafluoro-p-phenylene diamine (0.88 g, 0.0049 mole, 82% of theoretical) was stirred into the melted prepolymer. The mixed material was cured in a heated platen press for 15 minutes at 250°F followed by 15 additional minutes at 300°F. The resulting polymer was soft and gumlike. As an alternate cure cycle, the prepolymer and the diamine curing agent were mixed as above and cured for 30 minutes at 300°F followed by 90 minutes at 350°F. The resulting material was a dark brown, tarlike gum. There was no apparent reaction in either case. There was, however, evidence of sublimed diamine.

3. **From Hydroxyl-Terminated Poly(hexafluoropentamethylene carbonate)***

 a. **And Tetrafluoro-p-phenylene Diisocyanate**

  (1) Preparation of an Isocyanate-Terminated Polyurethane

$$OCN-\underset{F\ F}{\overset{F\ F}{\boxed{}}}-NCO \;+\; HO-\left[CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-O\right]-CH_2(CF_2)_3CH_2OH \longrightarrow$$

$$M.W. = 1025$$

$$OCN-\left\{\underset{F\ F}{\overset{F\ F}{\boxed{}}}-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-O-\left[CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-O\right]_x-CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-\underset{H}{N}\right\}_y-\underset{F\ F}{\overset{F\ F}{\boxed{}}}-NCO$$
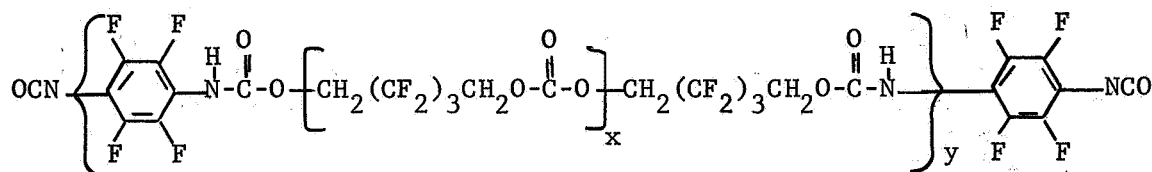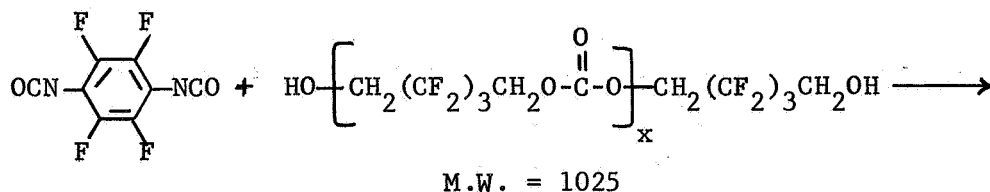
Poly(hexafluoropentamethylene carbonate) of 1025 molecular weight (10.3 g, 0.01 mole) was added to a 25-ml, three-necked flask equipped with a stirrer, condenser, nitrogen inlet, and thermometer. Tetrafluoro-p-phenylene diisocyanate (3.5 g, 0.015 mole) was then added to the polycarbonate at room temperature under nitrogen with mixing. The temperature of the mass rose from 30°C to 85°C within 3 minutes, with gelation occurring. The prepolymer was molded in a press at 160°-170°C for ½ hour; this yielded a highly elastic thermoplastic prepolymer containing free isocyanate groups.

  (2) Preparation of an Amine-Cure Polyurethane
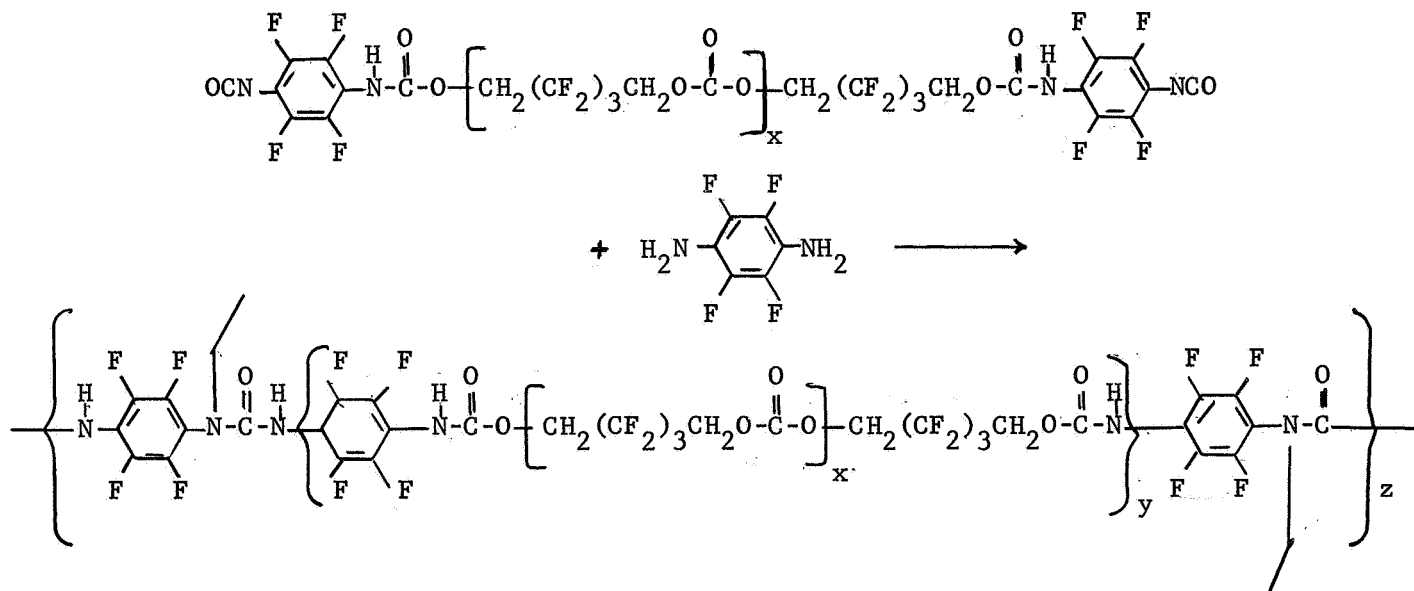
$$OCN-\underset{F\ F}{\overset{F\ F}{\boxed{}}}-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-O-\left[CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-O\right]_x-CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\underset{F\ F}{\overset{F\ F}{\boxed{}}}-NCO$$

$$+\; H_2N-\underset{F\ F}{\overset{F\ F}{\boxed{}}}-NH_2 \longrightarrow$$

$$\left[\underset{H}{N}-\underset{F\ F}{\overset{F\ F}{\boxed{}}}-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\underset{F\ F}{\overset{F\ F}{\boxed{}}}-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-O-\left[CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-O\right]_{x'}-CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-\underset{H}{N}\right]_y-\underset{F\ F}{\overset{F\ F}{\boxed{}}}-\underset{H}{N}-\overset{O}{\overset{\|}{C}}\Bigg]_z$$

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* Preparation described in Section IV.C.

Poly(hexafluoropentamethylene carbonate) of 1075 molecular weight (21.5 g, 0.02 mole) was dissolved in dry ethyl acetate (25 ml), then charged to a 250-ml, three-necked flask equipped with a stirrer, condenser, thermometer, and nitrogen inlet. Tetrafluoro-p-phenylene diisocyanate (6.2 g, 0.027 mole) in dry ethyl acetate (25 ml) was added to the polycarbonate solution with mixing under nitrogen. The temperature rose from 25°C to 37°C. The solution was then mixed for 1½ hours at 80°C under nitrogen. The infrared spectrum indicated a trace of hydroxyl groups and the absence of isocyanate groups. Tetrafluoro-p-phenylene diisocyanate (1.1 g, 0.0047 mole) in dry ethyl acetate (20 ml) was then added and the solution stirred for 1 hour at 80°C under nitrogen. The infrared spectrum showed the presence of a trace of hydroxyl and isocyanate groups. An additional 25 ml of ethyl acetate was added to facilitate mixing. Tetrafluoro-p-phenylene diisocyanate (1.1 g, 0.0047 mole) in dry ethyl acetate was then added to the polymer solution. The solution was agitated for an additional 2 hours at 80°C under nitrogen, after which 40 ml of ethyl acetate was added to prevent gelation. The solution was then cooled to room temperature and tetrafluoro-p-phenylenediamine (0.4 g, 0.0022 mole) in dry ethyl acetate (25 ml) added. The solvent was removed in a vacuum oven at 100°C for 1 hour. The polymer was then cured in a press at 160°-170°C for ½ hour, which yielded a tough elastomer. The tensile strength of this polymer was in excess of 2200 psi at room temperature. Samples were submitted to MSFC for LOX-compatibility testing.

(3) Preparation of an Allophanate-Cured Polycarbonate-Polyurethane

$$OCN-\underset{F\ F}{\overset{F\ F}{\bigcirc}}-NCO + H\left[O-CH_2(CF_2)_3CH_2-O-\overset{O}{\overset{\|}{C}}\right]OCH_2(CF_2)_3CH_2OH \longrightarrow$$

M.W. = 1750

$$\left\{\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\underset{F\ F}{\overset{F\ F}{\bigcirc}}-\overset{O}{\overset{\|}{N}-C}\left[O-CH_2(CF_2)_3CH_2-O-\overset{O}{\overset{\|}{C}}\right]OCH_2(CF_2)_3-CH_2-O\right\}_y$$
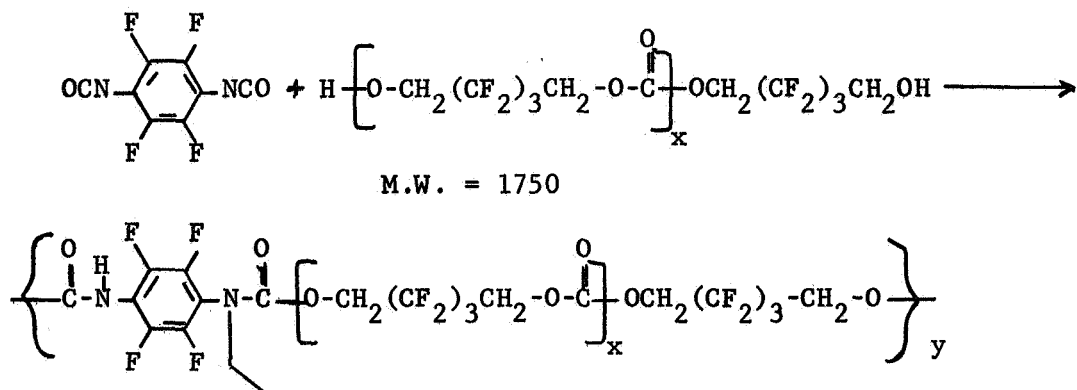
Poly(hexafluoropentamethylene carbonate) of 1750 molecular weight (31.0 g, 0.018 mole) was added to a 100-ml resin flask equipped with a stirrer, nitrogen inlet, thermometer, and nitrogen outlet. The polycarbonate was then melted at 70°-80°C with mixing under nitrogen. Tetrafluoro-p-phenylene diisocyanate (5.1 g, 0.022 mole) was then added with mixing under nitrogen. The solution was stirred for 1-3/4 hours at 80°-90°C followed by 1 hour at 130°-140°C. Because the polymer began to gel, it was removed from the flask and molded in a press at 160°-175°C for ½ hour. The resultant polymer was a tough, elastomeric film. One-hundred samples were punched and submitted to MSFC for LOX compatibility testing.

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b. And Toluene-2,4-diisocyanate

(1) Preparation of a NCO-Terminated Polyurethane Prepolymer

$$H\left[OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}\right]_x OCH_2(CF_2)_3CH_2OH \quad + \quad \text{(TDI)} \quad \longrightarrow$$

M.W. = 1450
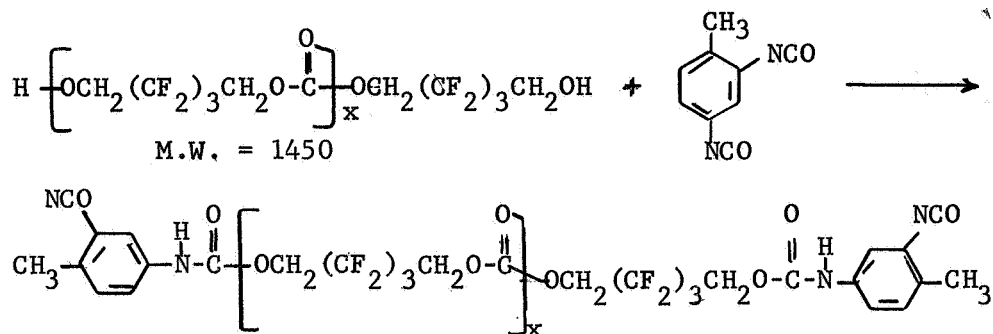
Toluene-2,4-diisocyanate (5.3 g, 0.03 mole) and dry ethyl acetate (5 ml) were charged to a 100-ml, three-necked flask equipped with a stirrer, condenser, dropping funnel, thermometer and nitrogen inlet. Stannous octoate (2 drops), the OH-terminated poly(hexafluoropentamethylene carbonate) of 1450 molecular weight (21.7 g, 0.015 mole) and dry ethyl acetate (20 ml) was added to the TDI solution at 70°C to 80°C over a 30-minute period with mixing under nitrogen. The solution was mixed for 1 hour at 80°C under nitrogen, then the ethyl acetate was removed via vacuum distillation to 140°C. The prepolymer was a white, tough, elastomeric solid. The infrared spectrum revealed that there was little or no OH groups, and that there was NCO termination. Figure 7 is the infrared spectrum of a film of the polymer.

This prepolymer was molded in a press at 300°F to 350°F to form an 11-mil sheet. Twenty specimens of 11/16-in. diameter were punched from the film and submitted to MSFC for LOX-compatibility testing.

(2) Amine-Cured Isocyanate-Terminated Prepolymer

87
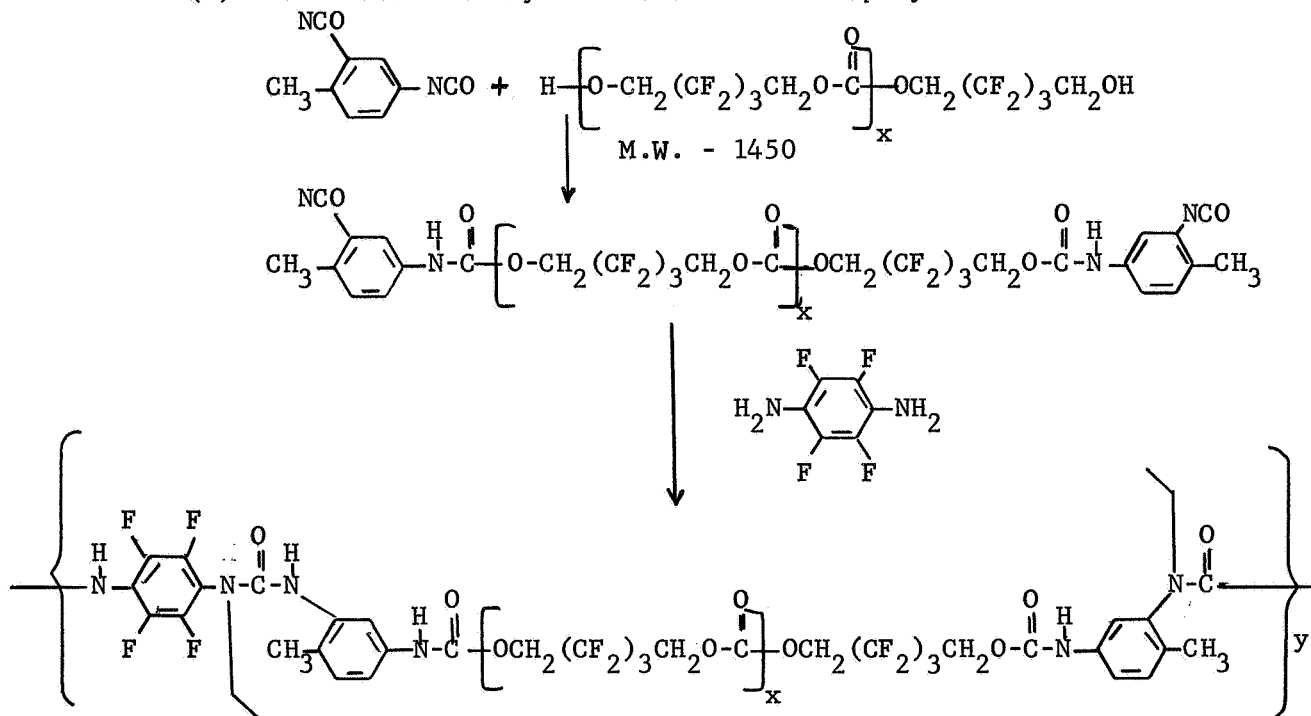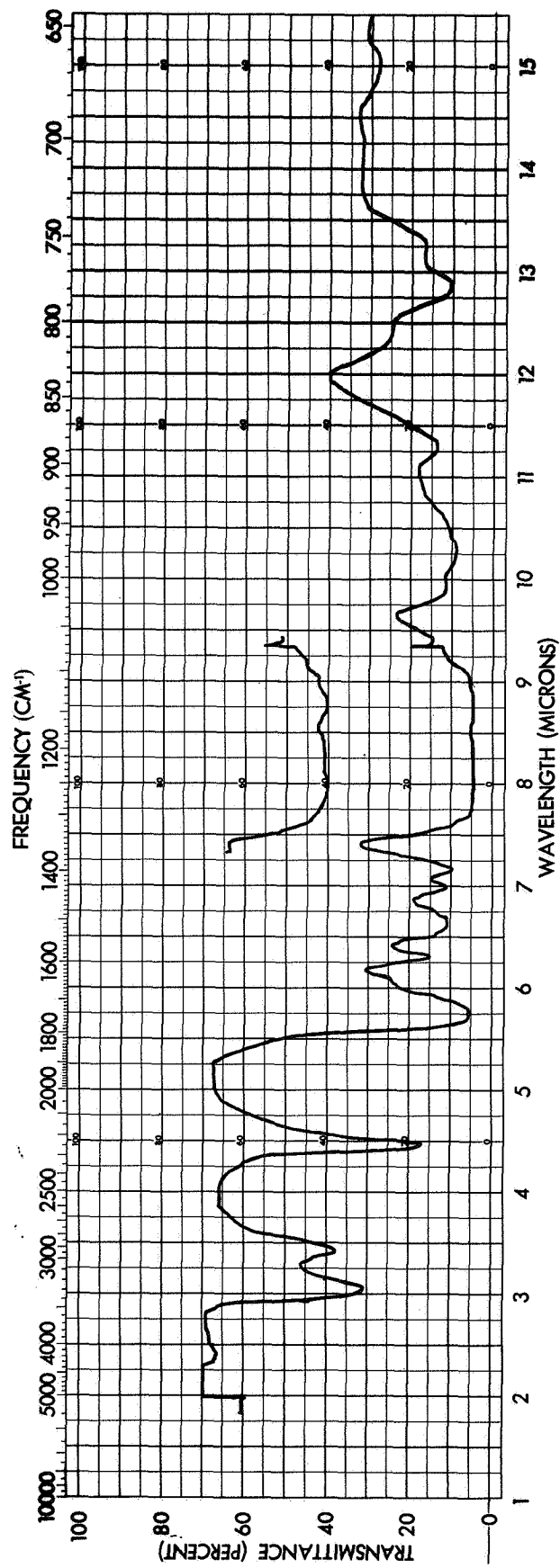
Figure 7. NCO-Terminated Prepolymer of Toluene-2,4-Diisocyanate and Poly(hexafluoropentamethylene carbonate)

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Hydroxyl-terminated poly(hexafluoropentamethylene carbonate) (10.8 g, 0.00745 mole), toluene-2,4-diisocyanate (2.6 g, 0.0194 mole) and dry ethyl acetate (22 ml) were placed in a 50-ml, three-necked flask equipped with a stirrer, condenser, thermometer, and nitrogen inlet. The solution was mixed and stannous octoate (2 drops) was added. The solution was mixed at 80°C for ½ hour under nitrogen during which time the solution became turbid. The infrared spectrum revealed that all hydroxyl groups had been consumed. The slurry was cooled to room temperature, and tetrafluoro-p-phenylene diamine (1.1 g, 0.006 mole) dissolved in dry ethyl acetate (5 ml) was added. The ethyl acetate was removed in a vacuum oven at 80°C for 1 hour and the polymer formed into a sheet in a press at 300°-350°F. The film tended to become brittle and contained free isocyanate groups. Samples were punched from the film and submitted to MSFC for LOX-compatibility testing.

c. **Preparation of a Polyurethane from Tetrachloro-p-phenylene Diisocyanate**

M.W. = 2450
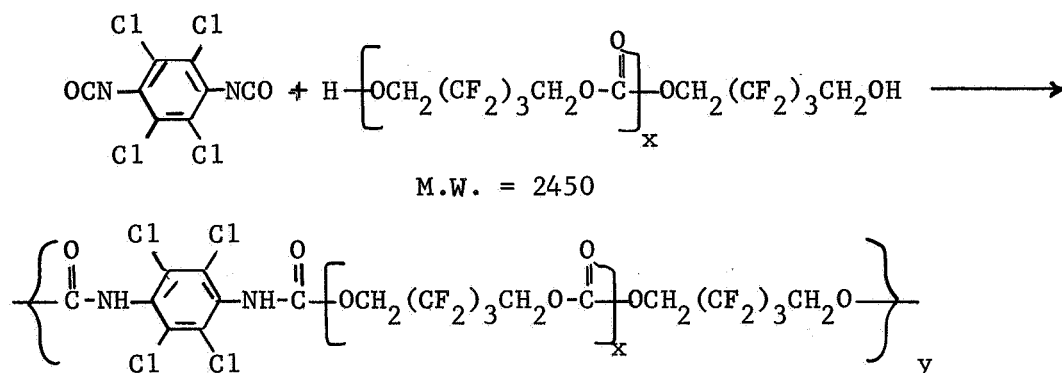
Poly(hexafluoropentamethylene carbonate) of 2450 molecular weight(4.1 g, 0.0017 mole), dissolved in 10 ml of dry ethyl acetate, was charged to a three-necked, round-bottomed flask equipped with stirrer, condenser, thermometer, dropping funnel, and nitrogen inlet. Tetrachloro-p-phenylene diisocyanate (1.9 g, 0.0063 mole),dissolved in 20 ml of dry ethyl acetate, and 3 drops of triethylamine, were added to the refluxing solution over a 3-hour period. Refluxing was continued for 1 hour after the final addition. The resulting polymer was filtered and dried in a vacuum oven for 3 hours to yield a light tan elastic polymer melting at 125°-135°C.

4. **From Hydroxyl-Terminated Polyethers**

a. **Preparation of a Polyformal-Polyurethane**

M.W. = 600
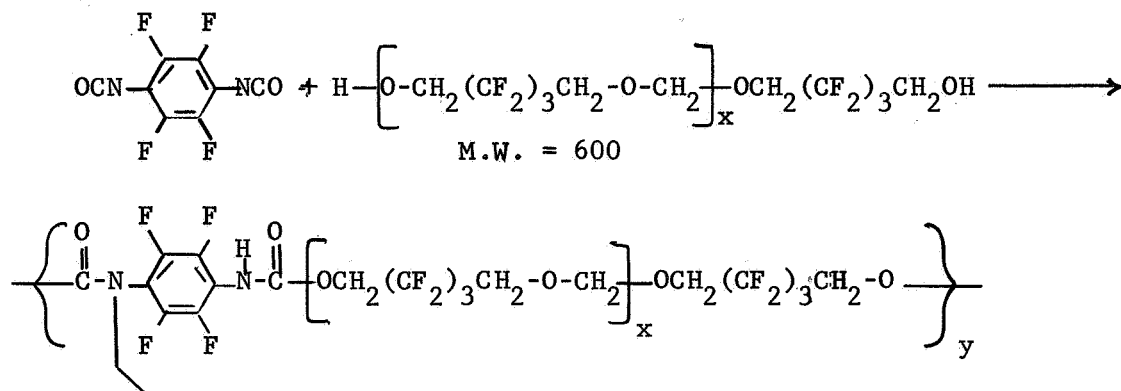
Poly(hexafluoropentamethylene formal)* of 600 molecular weight (7.0 g, 0.0117 mole) was charged to a 40-ml glass beaker and heated to 80°C. Tetrafluoro-p-phenylene diisocyanate (3.0 g, 0.013 mole) was then melted in a Teflon beaker under nitrogen. The polyformal at 80°C was added to the molten diisocyanate at 80°C with mixing under nitrogen. The polymer, which gelled immediately, was quickly molded in a press at 160°-175°C for ½ hour. The polymer showed only slight flow and was flexible and extremely tough. Samples were punched and submitted to MSFC for LOX compatibility testing.

b. **Preparation of a Polyurethane from the Polyether of 3,3,3-Trifluoro-1,2-epoxypropane**

(1) Using Polyether Initiated with the Monosodium Salt of Hexafluoropentanediol
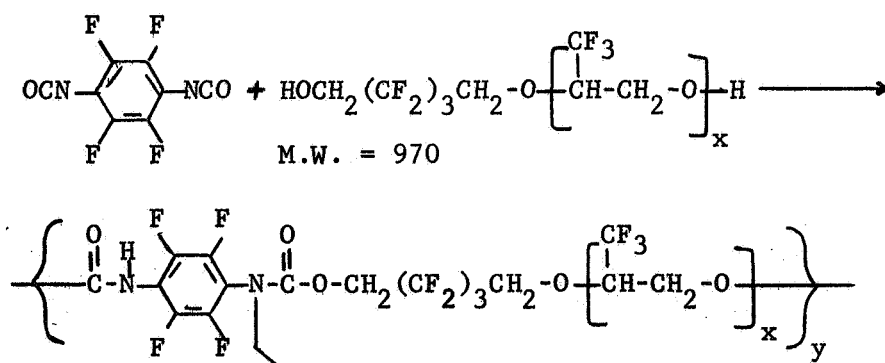
Tetrafluoro-p-phenylene diisocyanate (2.9 g, 0.0124 mole) was placed in a 100-ml resin pot equipped with a stirrer, nitrogen inlet, thermometer, and nitrogen outlet. The diisocyanate was then melted at 90°-100°C. Poly(3,3,3-trifluoro-1-propylene oxide)* of 970 molecular weight (8.0 g, 0.00825 mole) was heated to 60°-70°C and then added to the warm diisocyanate with mixing under nitrogen. The solution was mixed for 40 minutes at 80°-90°C under nitrogen. The infrared spectrum indicated that there was still a considerable amount of hydroxyl groups present. The solution was mixed for an additional 125 minutes at 80°-90°C during which time the polymer gelled. It was then heated in a press at 160°-175°C for ½ hour to yield a soft, elastic film. The polymer was left exposed to atmospheric moisture for 20 minutes, then remolded in a press at 160°-175°C for ½ hour. The product flowed excessively. The polymer was left exposed to atmospheric moisture for an additional 20 minutes, then remolded in a press to yield a clear, tough elastic film. Samples of the film were submitted to MSFC for LOX compatibility testing.

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* Preparation described in Section IV.C.

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(2) Using Polyether Prepared by Initiation with Aluminum Chloride

$$\text{OCN-}\!\!\bigcirc\!\!\text{-NCO} \;+\; \text{HO-}\!\!\left[\text{CH(CF}_3)\text{-CH}_2\text{-O}\right]_x\!\!\text{-H} \longrightarrow$$

M.W. = 2700

$$\text{OCN-}\!\!\bigcirc\!\!\text{-N(H)-C(O)-O-}\!\!\left[\text{CH(CF}_3)\text{-CH}_2\text{-O}\right]_x\!\!\text{-C(O)-N(H)-}\!\!\bigcirc\!\!\text{-NCO}$$

$$\downarrow \quad \text{H}_2\text{N-}\!\!\bigcirc\!\!\text{-NH}_2$$

$$\left\{ \text{-N(H)-}\!\!\bigcirc\!\!\text{-N(H)-C(O)-N(H)-}\!\!\bigcirc\!\!\text{-N(H)-C(O)-O-}\!\!\left[\text{CH(CF}_3)\text{-CH}_2\text{-O}\right]_x\!\!\text{-C(O)-N(H)-}\!\!\bigcirc\!\!\text{-N-C(O)-} \right\}_y$$
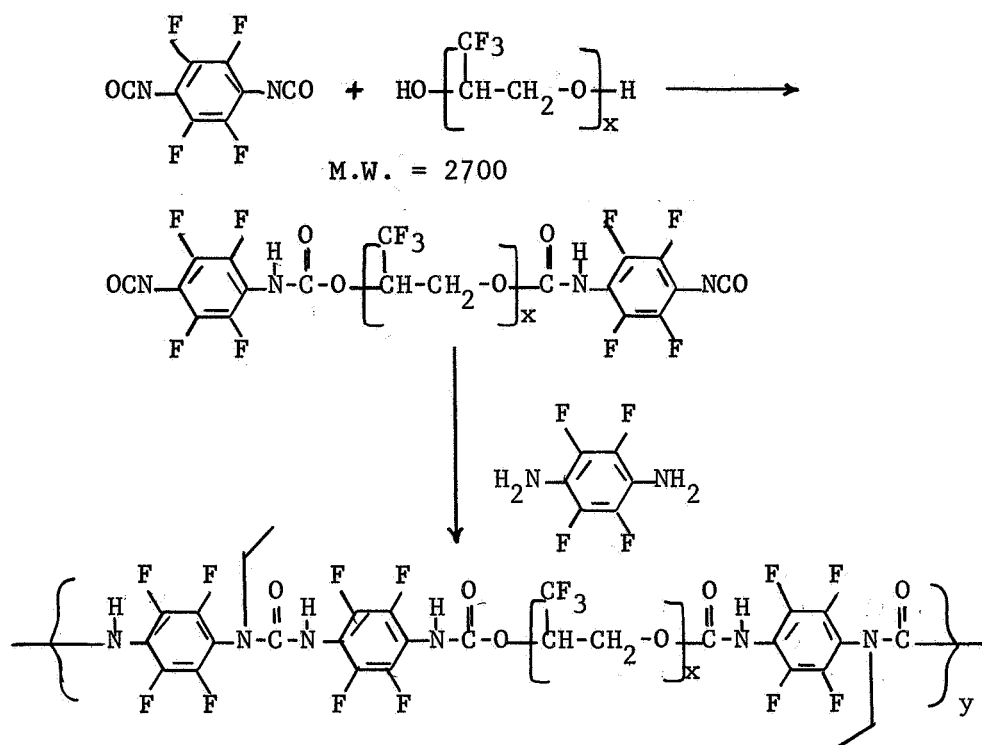
Tetrafluoro-p-phenylene diisocyanate (1.6 g, 0.007 mole) was added to a 100-ml resin flask equipped with a nitrogen inlet, thermometer, nitrogen outlet, and stirrer. The diisocyanate was melted at 80°-90°C under nitrogen. Poly(3,3,3-trifluoro-1-propylene oxide) of 2700 molecular weight (9.5 g, 0.0035 mole) at 80°-90°C was added to the molten diisocyanate with mixing under nitrogen. The solution was mixed for 1 hour at 80°-90°C under nitrogen. Based on the infrared spectrum, only a slight reaction had occurred.

The mixture was then stirred at 130°-140°C for 3 hours under nitrogen. A large portion of the polyether remained unreacted. Stannous octoate (1 drop) was then added and the mixture stirred for 3/4 hours at 130°-140°C under nitrogen. The infrared spectrum indicated that only a negligible amount of hydroxyl groups remained. Tetrafluoro-p-phenylene diamine (0.3 g, 0.0017 mole) was added to the prepolymer, after which time the mass became a soft semisolid. The polymer was cured in a press at 160°-175°C for ½ hour to yield a soft semisolid.

5. Preparation of a Polyurethane of Tetrafluoro-p-phenylene Diisocyanate and the Dihemiketal of Hexafluoroacetone and Hexafluoropentanediol

a. Preparation of an Isocyanate-Terminated Prepolymer
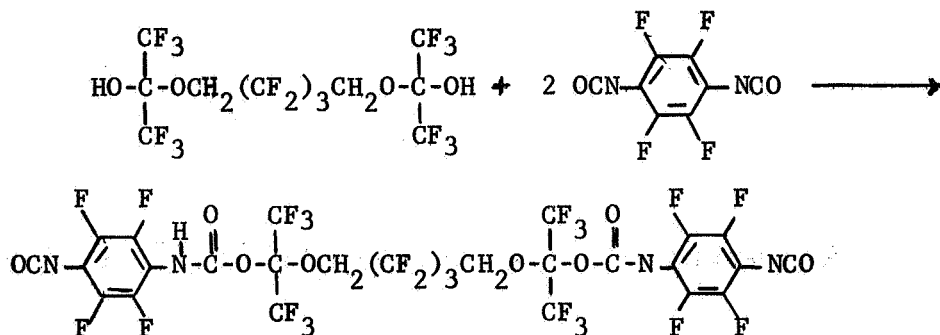
To an aliquot of the dihemiketal of hexafluoroacetone and hexafluoropentanediol was added enough tetrafluoro-p-phenylene diisocyanate to cap the ends. This ethereal solution became cloudy after 1 hour. Stannous octoate was added as catalyst and the reaction mixture was stirred at room temperature for 1 week. At the end of this time, the infrared spectrum of the ether solution showed that the hydroxyl groups had disappeared. The suspension of this prepolymer in ether was used without further isolation.

b. Preparation of the Tetrafluoro-p-phenylenediamine Cured Polymer
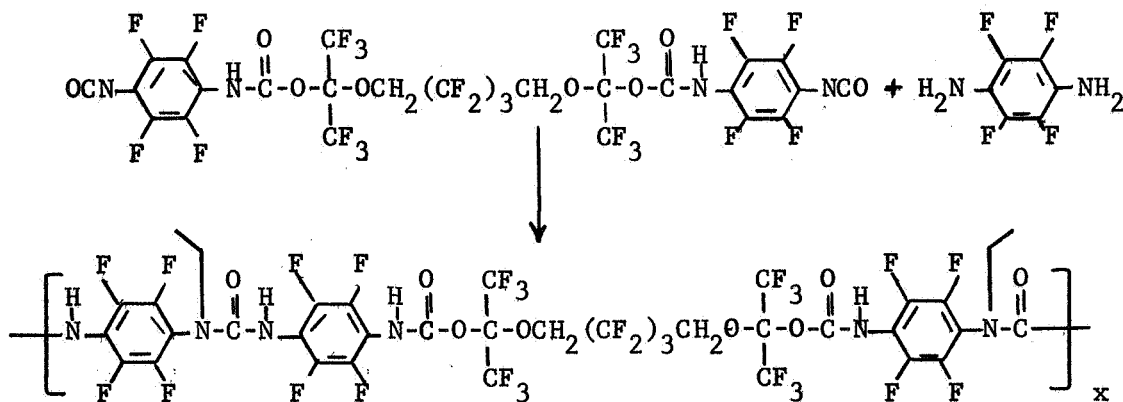
One-half of the ethereal suspension of the isocyanate-terminated prepolymer was transferred to a 25-ml flask, and tetrafluoro-p-phenylenediamine (80% of theoretical) was added with stirring. The solution became a cloudy pink after a few minutes, and was warmed to reflux. The ether solvent was replaced with ethyl acetate and the solution was maintained near 75°C for 16 hours. The solvent was then removed, leaving a light brown, solid polymer. An attempt was made to form a sheet of the polymer in a press, but only a flaky, thin film resulted.

C. Prepolymers

1. Preparation of Poly(hexafluoropentamethylene adipate)

$$\underset{\underset{O}{\parallel}}{Cl-C}-(CH_2)_4-\underset{\underset{O}{\parallel}}{C}-Cl \ + \ HO-CH_2-(CF_2)_3CH_2OH \longrightarrow$$

$$H\left[OCH_2(CF_2)_3CH_2O-\underset{\underset{O}{\parallel}}{C}-(CH_2)_4-\underset{\underset{O}{\parallel}}{C}\right]_x OCH_2(CF_2)_3CH_2OH$$
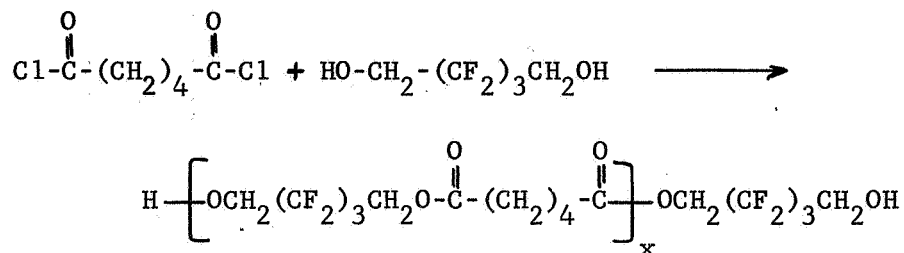
Into a 500-ml, three-necked flask equipped with a thermometer, nitrogen inlet, stirrer, and reflux condenser attached to a water trap were introduced hexafluoropentanediol (95.4 g, 0.45 mole) and freshly distilled adipoyl chloride (54.9 g, 0.32 mole). The mixture was heated at 55°C for 1 hour, 115°C for 44 hours, and finally, under full vacuum, at 210°C for 1 hour. The clear, viscous yellow liquid was heated in a rotary evaporator at 80°-90°C for 3 hours. The yield was 108.3 g (84.4%). The molecular weight, based on hydroxy end group determination, was 1900.

2. Preparation of Poly(hexafluoropentamethylene malonate)

$$HOCH_2(CF_2)_3CH_2OH \ + \ C_2H_5O-\underset{\underset{O}{\parallel}}{C}-CH_2-\underset{\underset{O}{\parallel}}{C}-OC_2H_5 \ \xrightarrow{PbO}$$

$$H\left[OCH_2(CF_2)_3CH_2O-\underset{\underset{O}{\parallel}}{C}-CH_2-\underset{\underset{O}{\parallel}}{C}\right]_x OCH_2(CF_2)_3CH_2OH$$
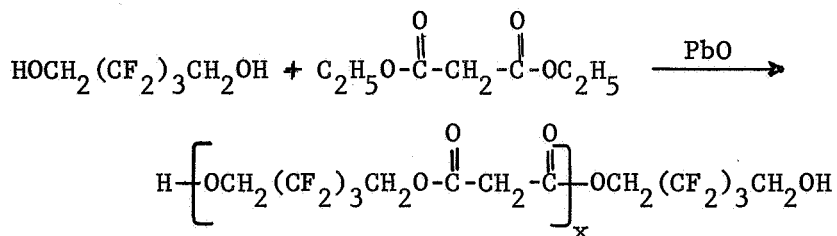
The general method for preparing polyesters of hexafluoropentanediol and diethyl malonate was as follows: Into a three-necked flask were placed the diethyl malonate, hexafluoropentanediol, and a small amount of lead (II) oxide. The flask was equipped with a stirrer, nitrogen inlet, a distilling column, and a thermometer. Vapors passing out of the top of the column were condensed and collected in a dry ice-acetone trap. The flask was heated to 170°C with stirring under nitrogen, where a clear colorless liquid collected in the trap. The flask was maintained near 170°C for several hours when no more low-boiling liquid was collected. The viscous liquid and solid hexafluoro-pentanediol in the reaction flask were taken up in ether and filtered to remove lead (II) oxide. The filtrate was stripped of ether and heated near 160°C under vacuum to remove remaining hexafluoropentanediol. The polyester isolated was clear, golden-yellow, and viscous.

The results of two typical runs are summarized in Table 3.

TABLE 3

PREPARATION OF POLY(HEXAFLUOROPENTAMETHYLENE MALONATE)

Moles Diol Used	Moles Diester Used	Ratio of Hexafluoropentanediol to Diethyl Malonate	% Yield	* M.W.
1.6	1.4	1.14	48.6	1779
0.75	0.70	1.07	47.1	1509

* Calculated by end-group determination for -OH

The elemental analysis of the polyester of 1779 molecular weight was as follows:

	% C	% H	% F
Calculated:	33.56	2.23	42.27
Found:	33.90	2.33	42.12

The infrared spectrum is attached as Figure 8.

3. **Preparation of Poly(hexafluoropentamethylene carbonate)**

$$HOCH_2(CF_2)_3CH_2OH + Cl-\overset{O}{\overset{\|}{C}}-OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{\text{pyridine}} \xrightarrow{H_2O}$$

$$H \left[OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}} \right]_x OCH_2(CF_2)_3CH_2OH$$

M.W. = 1450
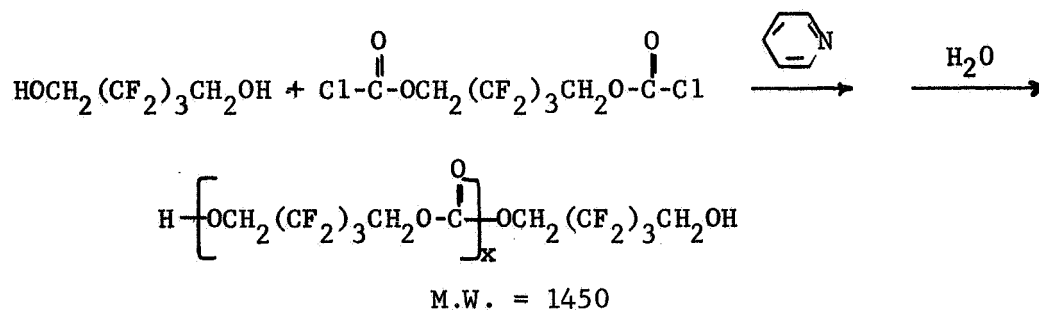
Hexafluoropentanediol (42.4 g, 0.2 mole) was dissolved in 100 ml of dioxane and charged to a 250-ml, three-necked, round-bottomed flask equipped with an argon purge inlet, addition funnel, stirrer, reflux condenser, and stirrer. Pyridine (32 ml, 0.41 mole) was then added to the diol solution. Hexafluoro-pentamethylene bischloroformate* (56.1 g, 0.166 mole) was dissolved in 30 ml of dioxane and added to the reaction mixture of the rate of 0.75 ml/minute under nitrogen with mixing, during which the reaction temperature increased to 40°C. The last 15 ml of bischloroformate solution was added at 45°C at the rate of 5 drops per minute. At the conclusion of the bischloroformate addition, the temperature was increased to reflux (101°C) and held 3 hours under nitrogen with mixing. After cooling to room temperature, the mixture was poured into 300 ml

* The preparation is described in Section IV.E.

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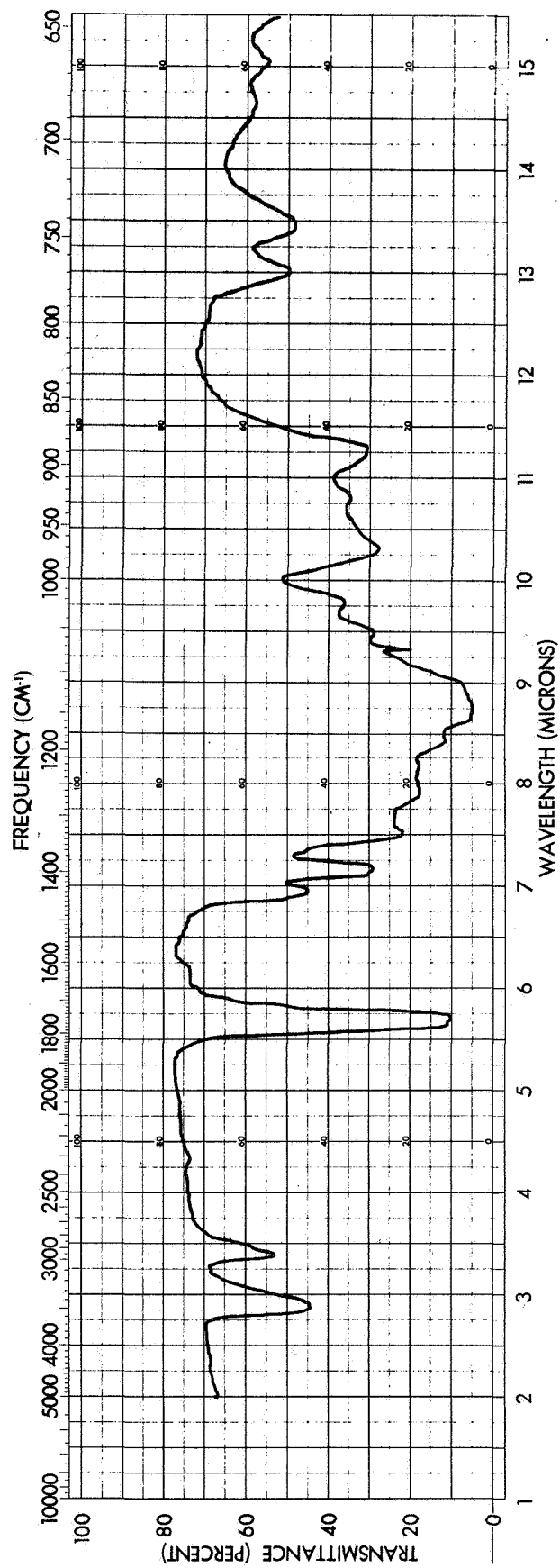
Figure 8. Poly(hexafluoropentamethylene malonate)

of distilled water and boiled 10 minutes. The mixture was cooled and the aqueous layer decanted, An additional 300 ml of distilled water was added to the polymeric residue and boiled again for 15 minutes. After cooling to room temperature, the water was decanted, and the polymer dried in a vacuum oven for 1 hour. The partially dry polymer was taken up in 400 ml of diethyl ether and the solution dried overnight over magnesium sulfate. The magnesium sulfate was filtered and the ether stripped under reduced pressure yielding 61.5 g (66.7%) of a white, opaque semisolid. The infrared spectrum of the polycarbonate is attached as Figure 9.

4. Preparation of Polyester from the Diester of Adipyl Chloride and Hexafluoroacetone Monohydrate and Hexafluoropentanediol

$$Cl-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-\overset{CF_3}{\underset{CF_3}{\overset{\|}{C}}}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-Cl \quad + \quad HOCH_2(CF_2)_3CH_2OH \longrightarrow$$

$$HO-CH_2-(CF_2)_3-CH_2O\left[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-\overset{CF_3}{\underset{CF_3}{\overset{\|}{C}}}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OCH_2-(CF_2)_3-CH_2-O\right]_x H$$
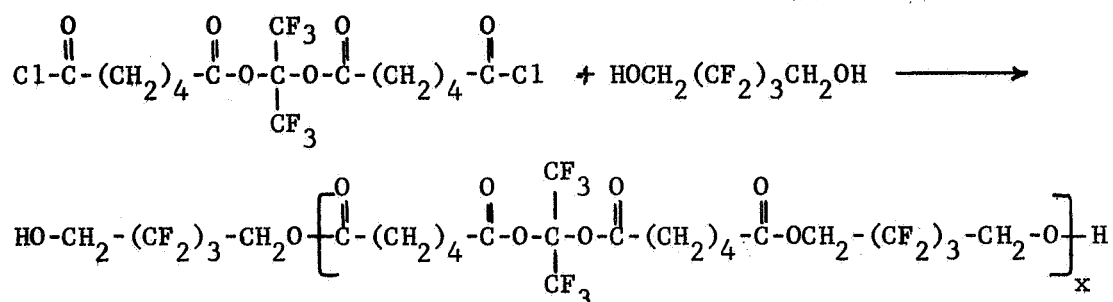
Into a 250-ml, three-necked flask fitted with thermometer, nitrogen gas inlet, stirrer, and condenser attached to a water trap were placed the diester of adipyl chloride and hexafluoroacetone monohydrate (43.3 g, 0.0907 mole), and hexafluoropentanediol (25.0 g, 0.118 mole). The flask was heated slowly to 50°C and held at that temperature for 2 hours. No hydrogen chloride was evolved. The flask was heated to 90°C and maintained at that temperature for about 64 additional hours, during which time hydrogen chloride was evolved. The liquid had become quite viscous, brown in color, and contained a small amount of solid. Titration of the water trap revealed that 74% of the theoretical amount of hydrogen chloride had been collected. The reaction mixture was dissolved in ether and filtered through a sintered glass funnel. The ether and unreacted starting materials were stripped off, leaving 45.9 g (74.4% yield) of a hazy brown viscous liquid tentatively identified by its infrared spectrum (Figure 10) as the desired polyester.

5. Amine-Terminated Prepolymer Curing Agents

a. Preparation of an Amine-Terminated Prepolymer

$$H\left[OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_x OCH_2(CF_2)_3CH_2OH \quad + \quad 2 \; OCN-\underset{F \quad F}{\overset{F \quad F}{\underset{\bigcirc}{}}}-NCO$$

M.W. = 3200

96
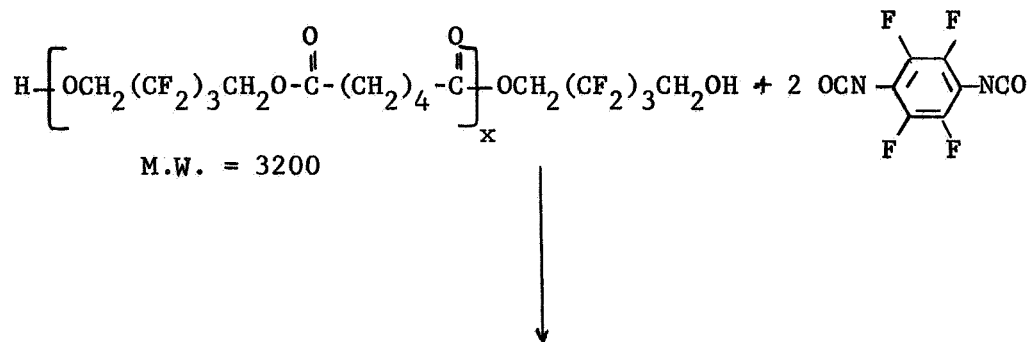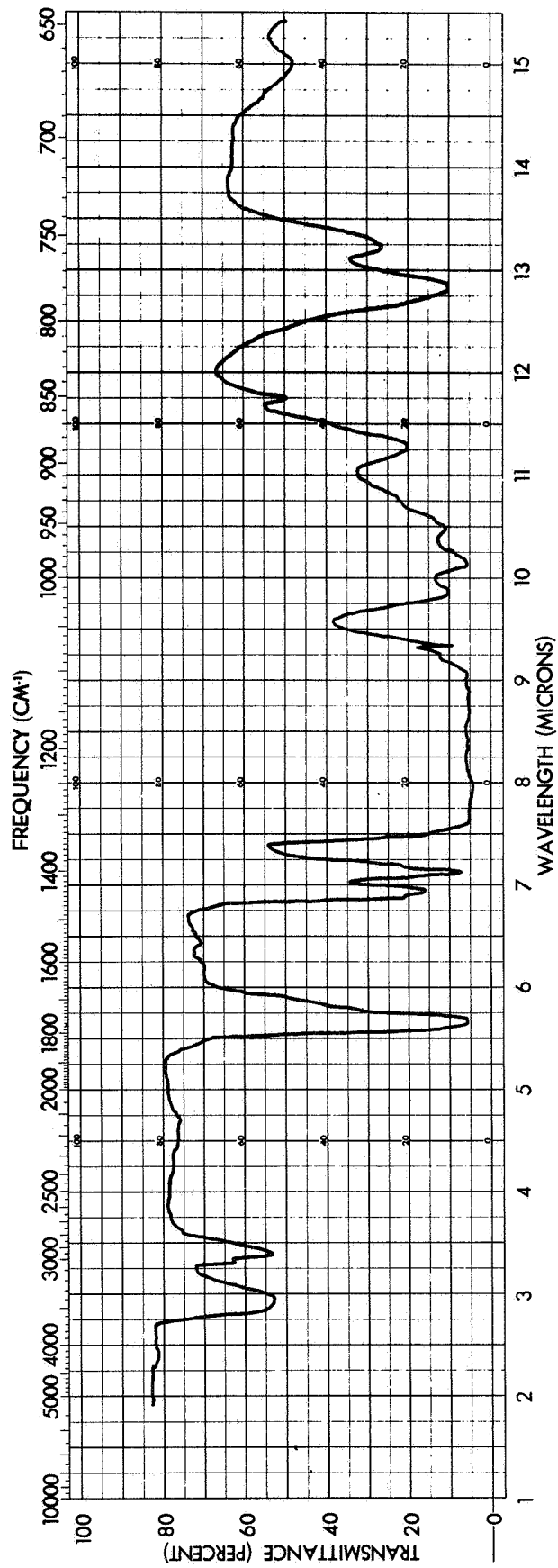
Figure 9. Poly(hexafluoropentamethylene carbonate)

97
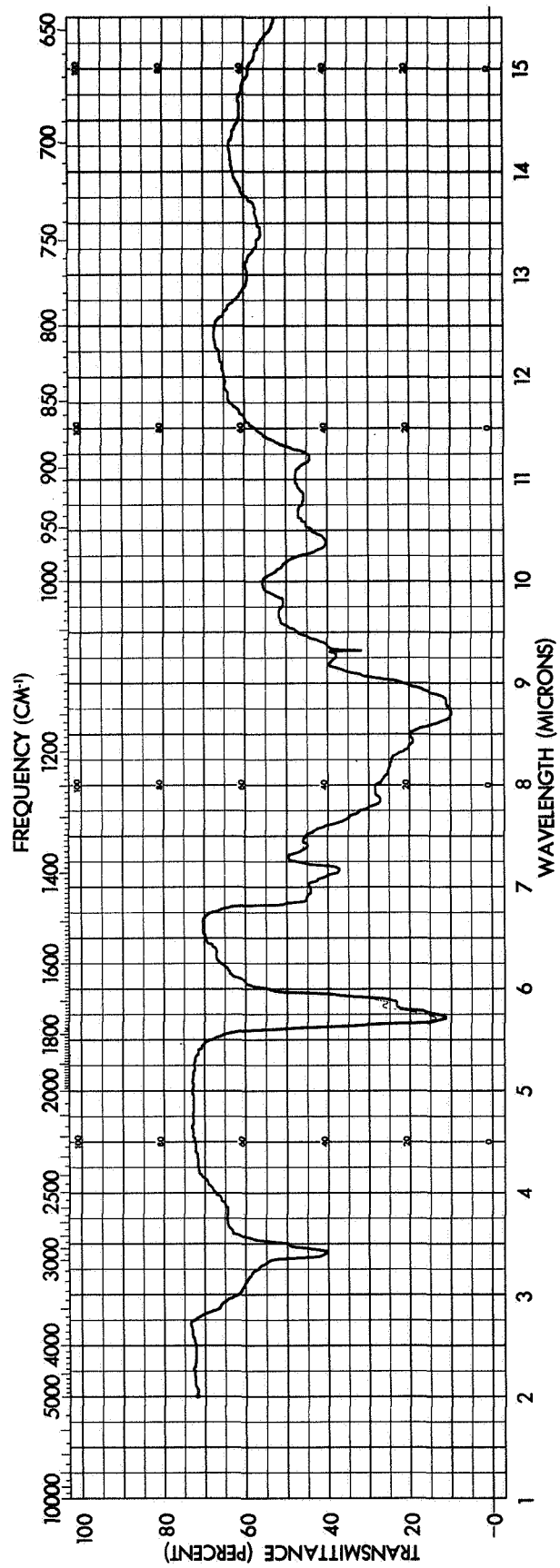
Figure 10. Infrared Spectrum of Polyester from the Diester of Adipyl Chloride and Hexafluoroacetone Monohydrate and Hexafluoropentanediol

$$\text{OCN}-\underset{F}{\overset{F}{\bigcirc}}\!\!-\underset{H}{\overset{O}{N\!-\!C}}\!\!\left[OCH_2(CF_2)_3CH_2O\!-\!\overset{O}{\underset{}{C}}\!-\!(CH_2)_4\!-\!\overset{O}{\underset{}{C}}\right]_x\!\!OCH_2(CF_2)_3CH_2O\!-\!\overset{O}{\underset{}{C}}\!-\!\underset{H}{N}\!\!-\underset{F}{\overset{F}{\bigcirc}}\!\!-\text{NCO}$$

$$2\ H_2N-\underset{F}{\overset{F}{\bigcirc}}-NH_2$$

$$H_2N-\bigcirc-\underset{H}{\overset{O\ H}{N\!-\!C\!-\!N}}-\bigcirc-\underset{H}{\overset{O}{N\!-\!C}}\left[OCH_2(CF_2)_3CH_2O\!-\!\overset{O}{C}\!-\!(CH_2)_4\!-\!\overset{O}{C}\right]_x OCH_2(CF_2)_3CH_2O\!-\!\overset{O}{C}\!-\!N-\bigcirc-\underset{H}{\overset{O\ H}{N\!-\!C\!-\!N}}-\bigcirc-NH_2$$
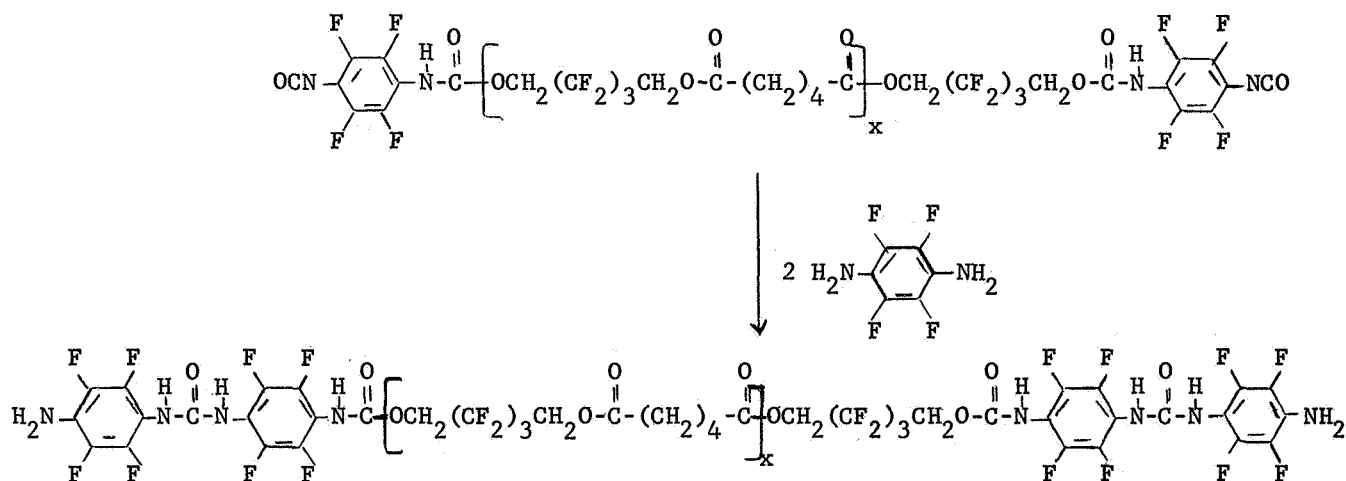
In a three-necked microflask equipped with a stirrer, condenser, thermometer, addition funnel and nitrogen inlet were placed tetrafluoro-p-phenylene diisocyanate (0.928 g, 0.004 mole) and 1 ml of ethyl acetate. A solution of hydroxyl-terminated poly(hexafluoropentamethylene adipate) of 3200 molecular weight (6.4 g, 0.002 mole) dissolved in 7 ml of ethyl acetate was added slowly, with constant stirring, at room temperature. When the addition was completed, the mixture was heated to reflux (80°C) for approximately 3 hours. At this time, an infrared spectrum indicated that most of the hydroxyl groups had reacted. The mixture was cooled to room temperature and a solution of tetra-fluoro-p-phenylene diamine (0.720 g, 0.004 mole) in approximately 1 ml of ethyl acetate was then introduced into the reaction flask. The material immediately turned to a semisolid, sticky mass. An infrared spectrum showed no free amino groups. Removal of solvent yielded a solid which did not melt up to 300°C.

b. <u>Preparation of the Amine-Terminated Diamide of Tetrafluoro-p-phenylenediamine and Poly(hexafluoropentamethylene adipate)</u>

$$4\ Cl\!-\!\overset{O}{\underset{}{C}}\!-\!(CH_2)_4\!-\!\overset{O}{\underset{}{C}}\!-\!Cl\ +\ 3\ HOCH_2(CF_2)_3CH_2OH\ \longrightarrow$$

$$Cl\!\left[\overset{O}{\underset{}{C}}(CH_2)_4\!-\!\overset{O}{\underset{}{C}}\!-\!OCH_2(CF_2)_3CH_2O\right]_3\!\!\overset{O}{\underset{}{C}}\!-\!(CH_2)_4\!-\!\overset{O}{\underset{}{C}}\!-\!Cl\ +\ 6\ HCl$$

$$2\ H_2N-\bigcirc-NH_2$$

$$H_2N-\bigcirc-\underset{H}{\overset{O}{N}}\!\left[\overset{O}{\underset{}{C}}\!-\!(CH_2)_4\!-\!\overset{O}{\underset{}{C}}\!-\!OCH_2(CF_2)_3CH_2O\right]_3\!\!\overset{O}{\underset{}{C}}\!-\!(CH_2)_4\!-\!\overset{O}{\underset{}{C}}\!-\!N-\bigcirc-NH_2$$

99
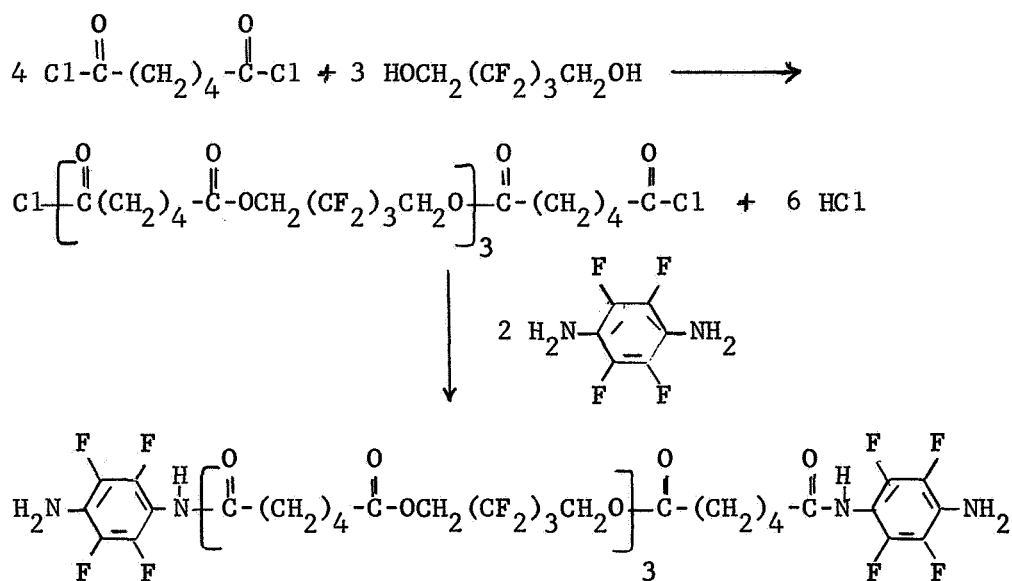
Hexafluoropentanediol (50.9 g, 0.24 mole) was charged to a reaction flask fitted with a reflux condenser, nitrogen inlet, effluent vapor water trap, thermometer, and stirring motor. Freshly distilled adipyl chloride (58.6 g, 0.32 mole) was added, forming a white slurry, the temperature being increased to 45 °C when hydrogen chloride gas (which was trapped out and subsequently titrated) began coming off. After 30 minutes at 50 °C, the slurry became a clear, viscous liquid. The temperature was held at 50 °C for 4 hours, then raised to 100 °C. After 3½ hours at 100 °C, the material darkened considerably, so further heating was discontinued. The dark brown viscous liquid was taken up in tetrahydrofuran (THF) (100 ml). Decolorizing charcoal failed to dispel the color. Tetrafluoro-p-phenylenediamine (28.8 g, 0.16 mole) and triethylamine (16.2 g, 0.16 mole) dissolved in 100 ml of THF were charged to a reaction flask fitted with a reflux condenser, addition funnel, stirring motor, and nitrogen inlet. The acid chloride terminated polyester solution in THF was added over a 2-hour period. The temperature of the reaction mixture rose to 33 °C. The temperature was raised to reflux (66 °C) and held overnight. The solid triethylamine hydrochloride was filtered off and the filtrate stripped free of solvent, yielding 115.7 g of dark brown viscous polymer contaminated with undissolved free tetrafluoro-p-phenylenediamine. The contaminated polymer was extracted (3 times) by boiling in 200 ml of hexane. The hexane layer was decanted while hot. The pure product was a brown viscous liquid.

6. Hydroxyl-Terminated Polyacetals

    a. Preparation of Poly(hexafluoropentamethylene formal)

        (1) From Dibutoxy Methane

$$HOCH_2(CF_2)_3CH_2OH + C_4H_9-O-CH_2-O-C_4H_9$$

$$\downarrow$$

$$HOCH_2(CF_2)_3CH_2O\left[CH_2O-CH_2(CF_2)_3CH_2O\right]_x H$$
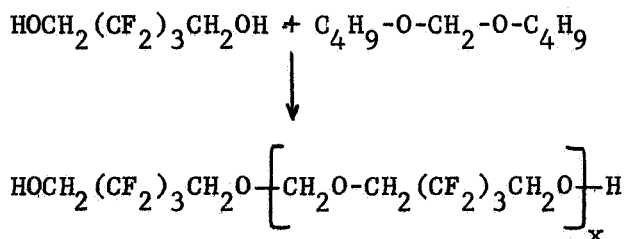
    Dibutoxymethane (11.2 g, 0.07 mole), hexafluoropentanediol (16.3 g, 0.077 mole), and ferric chloride were charged to a 50-ml, three-necked flask equipped with a stirrer, condenser, dean-stark trap, thermometer, and nitrogen inlet. The mixture was stirred at 160 °C to 170 °C for 3 hours under nitrogen, during which time 2.0 ml of butanol (15.8% of theory) was removed. The black solution was heated for 12 additional hours at 160°-170 °C, followed by 24 hours at 230°-240 °C under nitrogen with mixing. The product was vacuum distilled to 230 °C. The black residue was then dissolved in ether, washed with dilute ammonium hydroxide, then with water. The ether layer was dried with magnesium sulfate and the ether removed to yield a 1.2 g (5.4%) of black polyformal. Figure 11 is the infrared spectrum of the polymer.
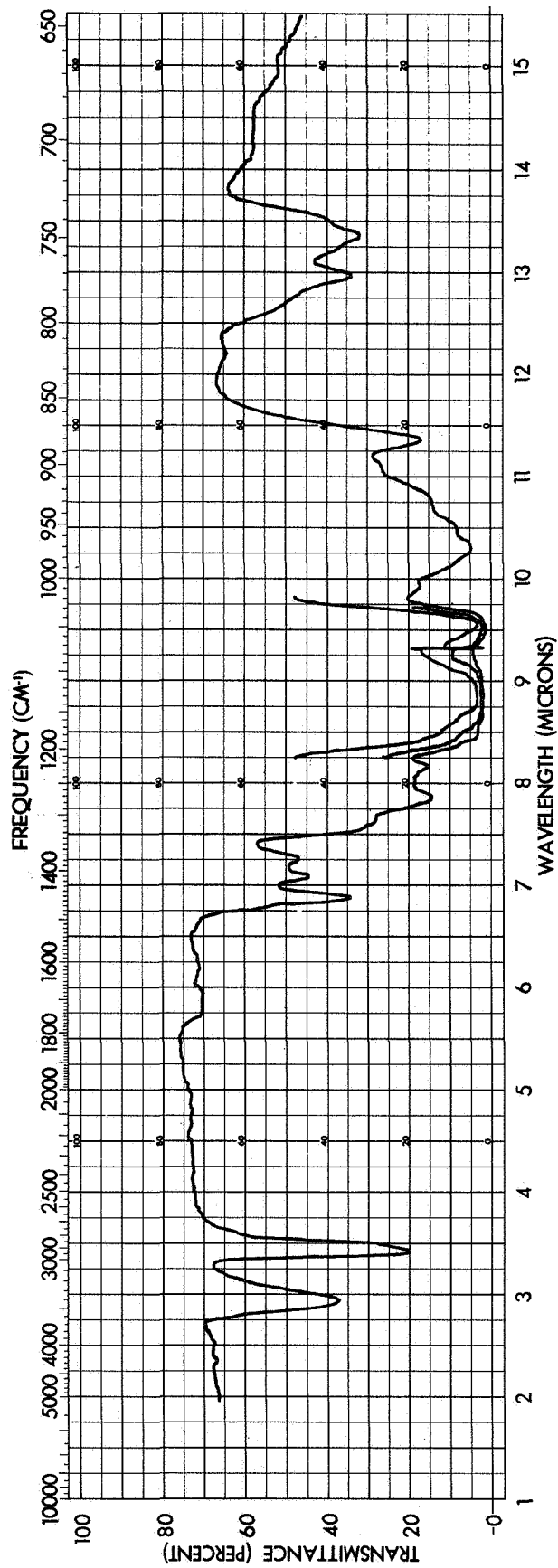
Figure 11. Poly(hexafluoropentamethyleneformal)

(2) From Trioxane and Hexafluoropentanediol

$$HOCH_2(CF_2)_3CH_2OH \quad + \quad \begin{array}{c} O \\ CH_2 \qquad CH_2 \\ | \qquad\qquad | \\ O \qquad\qquad O \\ CH_2 \end{array}$$

p-Toluenesulfonic Acid

$$HOCH_2(CF_2)_3CH_2O-\left[CH_2-O-CH_2(CF_2)_3CH_2O\right]_x H$$
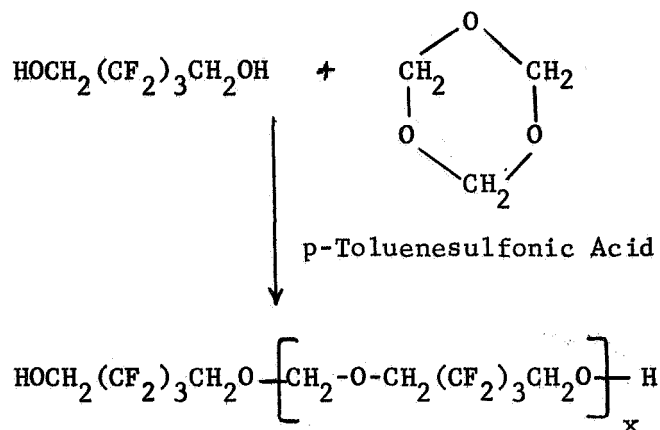
Hexafluoropentanediol (53.0 g, 0.25 mole), sym. trioxane (7.5 g, 0.083 mole) and p-toluenesulfonic acid (1.5 g) were mixed at 110°-120°C for 17 hours under nitrogen in a 100-ml, three-necked flask equipped with a stirrer, condenser, thermometer, and nitrogen inlet. Benzene was then added and the water removed by azeotropic distillation to yield 3.8 ml (84.5%) of water. The crude product was dissolved in ether, washed with 5% hydrogen peroxide solution containing 10 ml of 10% sodium carbonate, then washed with water. The ether extracts were dried with potassium carbonate and the ether removed to yield a clear, nearly colorless oil. The 15 g of oil was distilled to yield 12.6 g (56.7%) of poly(hexafluoropentamethylene formal). The molecular weight as determined by vapor phase osmometry was 835 ±20, while by end group determination (hydroxyl equivalents) the value was 950. The elemental analysis for the polymer of X=3 was as follows:

	% C	% H	% F
Calculated:	31.3	2.7	51.6
Found:	31.30	2.76	51.34

b. From Perfluoroaldehydes

(1) From Perfluorobutyraldehyde

(a) Preparation of Perfluorobutyraldehyde[36][37]

$$CF_3CF_2CF_2-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-H \quad \xrightarrow{P_2O_5} \quad CF_3CF_2CF_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$$
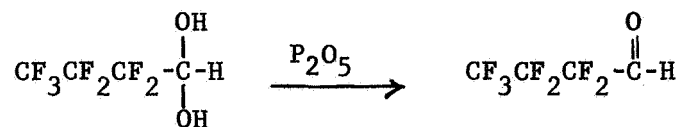
Perfluorobutyraldehyde hydrate was slowly added to a flask containing phosphorus pentoxide. The vaporized perfluorobutyraldehyde was passed through a reflux condenser and collected in a flask cooled with dry ice — acetone and equipped with a Dewar condenser. The collected perfluorobutyraldehyde was chromatographically pure.

(b) Polymerization of Perfluorobutyraldehyde

$$CF_3CF_2CF_2-\overset{\overset{\displaystyle O}{\|}}{C}-H \longrightarrow \left[\begin{array}{c} C_3H_7 \\ | \\ C-O \\ | \\ H \end{array} \right]_x$$

First Method — Perfluorobutyraldehyde (2.1 g, 0.0105 mole) plus concentrated sulfuric acid (1 drop) were placed in a stoppered vial. After ½ hour, the polymer had become a semisolid. After 3/4 hour, the product had solidified. After 3 days, the polymer was a brittle solid having a mp of 280°-300°C with vaporization. The polymer was insoluble in water, chloroform, DMF, acetone and ether. The infrared spectrum is attached as Figure 12.

Second Method — Perfluorobutyraldehyde (1.5 g, 0.0075 mole) and acetic anhydride (1 drop) were placed in a stoppered vial. There was no apparent reaction after 2 hours. After 3 days, the polymer had solidified.

Third Method — Perfluorobutyraldehyde (2.3 g, 0.0116 mole) containing cumene hydroperoxide (1 drop) was charged to a stoppered vial. After 3 days, there was no apparent reaction.

(c) Attempted Preparation of Low Molecular Weight
     Perfluorobutyraldehyde Polymer

The polymerization of perfluorobutyraldehyde was conducted for 10, 20, 30, and 35 minutes. Perfluorobutyraldehyde (2.1 g, 0.0105 mole) containing concentrated sulfuric acid (1 drop) was placed in each of five vials. The polymerization was terminated by dissolving the polymer in ether and washing the ether solution with dilute sodium bicarbonate solution. The ether solution was dried with anhydrous magnesium sulfate, then the ether was evaporated. In all cases, no low molecular weight polymer was formed; only the hydrate of perfluorobutyraldehyde resulted.

(2) Attempted Polymerization of Trifluoroacetaldehyde Hydrate
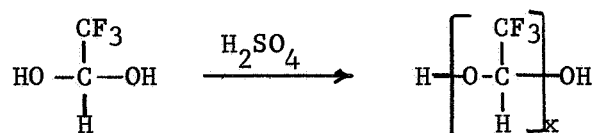
$$HO-\overset{\overset{\displaystyle CF_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH \xrightarrow{\ H_2SO_4\ } H-\left[O-\overset{\overset{\displaystyle CF_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} \right]_x OH$$

Trifluoroacetaldehyde hydrate (2½ ml) was added to concentrated sulfuric acid (5 ml) in a stoppered vial. After 3 days, the solid which had formed was washed with water. All of the product dissolved. Either no polymer was formed or the polymer decomposed immediately on addition of water.

(3) Polymerization of Perfluorobutyraldehyde Hydrate

$$HO-\overset{\overset{\displaystyle C_3F_7}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH \xrightarrow{\ H_2SO_4\ } H-\left[O-\overset{\overset{\displaystyle C_3F_7}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} \right]_x OH$$

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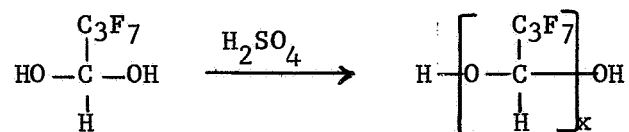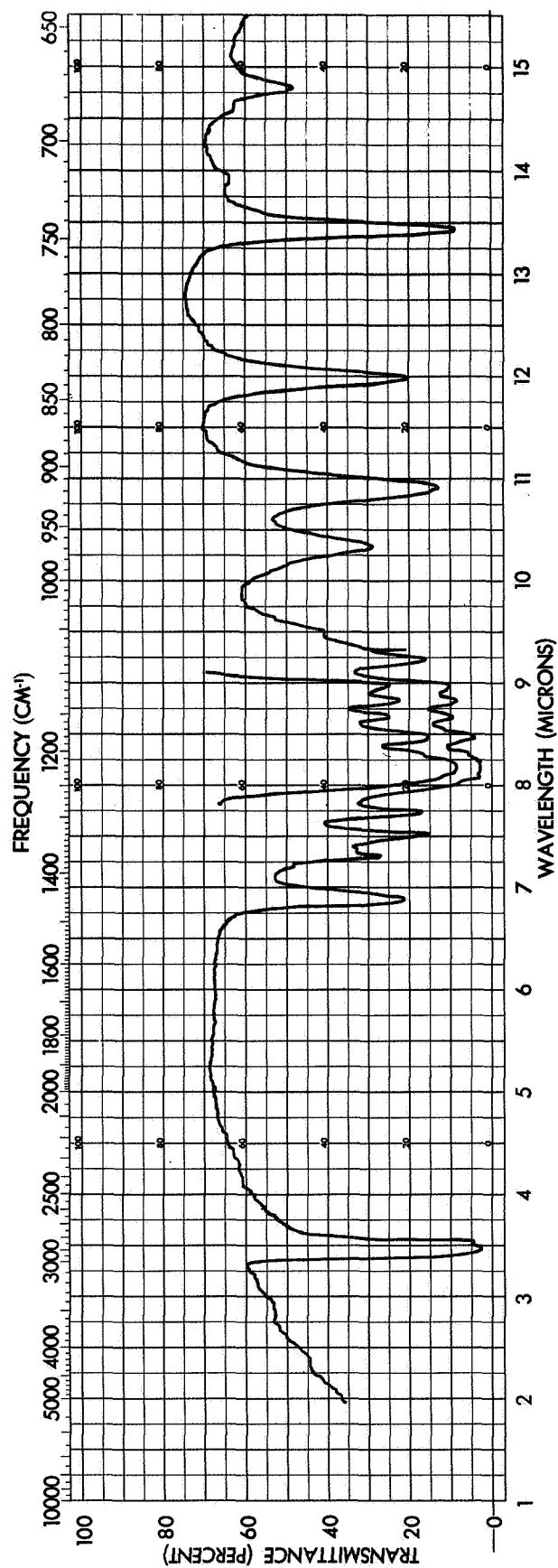
Figure 12.   Perfluorobutyraldehyde Polymer

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Perfluorobutyraldehyde hydrate (2½ ml) was added to concentrated sulfuric acid (5 ml) in a stoppered vial. The solution became turbid immediately. After 3 days, the solid polymer was washed twice with water, once with dilute sodium bicarbonate solution, then twice with ethanol. The polymer was dried at room temperature under vacuum. The melting point of the polymer was 80°-90°C with vaporization. The infrared spectrum is attached as Figure 13 and indicates the polymer is OH terminated.

c. Attempted Preparation of the Polyketal from Hexafluoroacetone and Hexafluoropentanediol
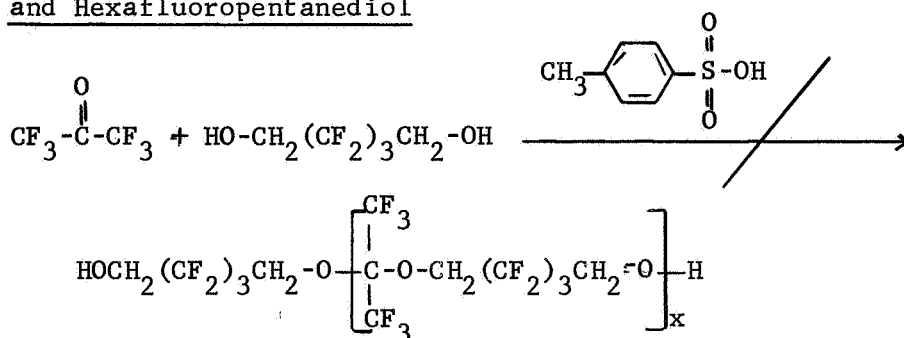
Into a Carius tube was placed hexafluoropentanediol (10.6 g, 0.05 mole) and p-toluenesulfonic acid (8.6 g, 0.05 mole). The tube was cooled in a liquid nitrogen bath and hexafluoroacetone (8.3 g, 0.05 mole, 6 ml) was condensed in. The tube was evacuated, sealed, and left in a 100°C oven for 24 hours. It was then removed, cooled in dry ice — acetone, and opened. The light-brown solid recovered was a mixture of unreacted starting materials.

d. Attempted Preparation of the Polyformal of Perfluorobutyraldehyde and Hexafluoropentanediol
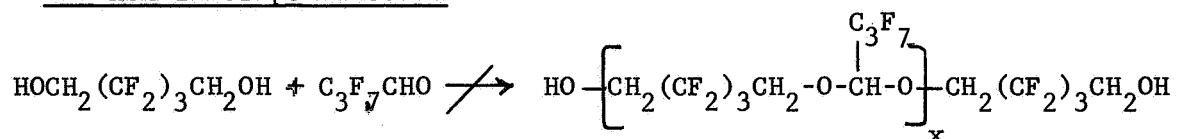
Perfluorobutyraldehyde (2.0 g, 0.01 mole, prepared by distillation of the hydrate from phosphorus pentoxide),was condensed at -50°C into a 100-ml, three-necked flask equipped with a stirrer, nitrogen inlet, thermometer, and dry ice — acetone condenser. Hexafluoropentanediol (2.1 g, 0.01 mole), di- butyl ether (35 ml), and p-toluenesulfonic acid (0.1 g) were then added to the flask with mixing under nitrogen. The solution was mixed at -50°C for ½ hour, then the temperature raised to room temperature over a 2-hour period under nitrogen. The dry ice — acetone condenser was then replaced with a water con- denser and the solution mixed for 18 hours at 120°-130°C, then cooled. The mixture was washed with dilute sodium carbonate, then with water. The solution was then dried with potassium carbonate and the butyl ether removed. Only hexafluoropentanediol was recovered.
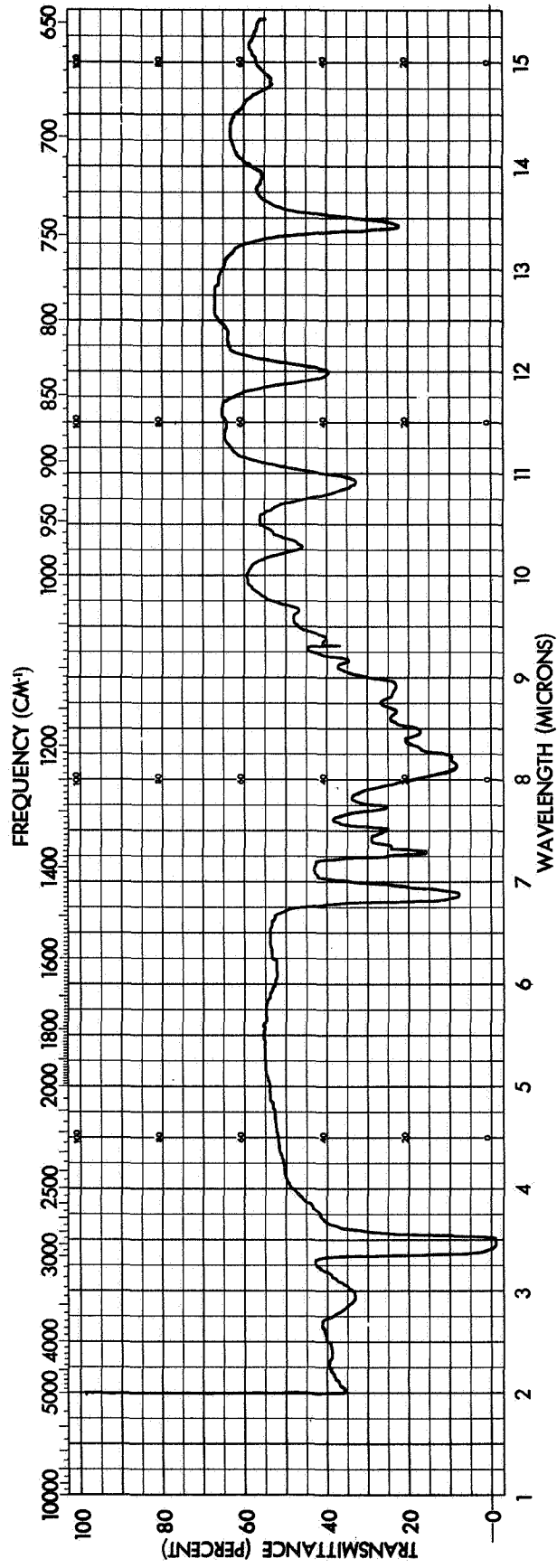
Figure 13. Perfluorobutyraldehyde Hydrate Polymer

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7. Hydroxyl-Terminated Polyethers

a. Attempted Preparation of Poly(hexafluoropentamethylene oxide) from Poly(hexafluoropentamethylene carbonate)

$$\text{HO} \underbrace{\left[\text{CH}_2(\text{CF}_2)_3\text{CH}_2\text{O}-\overset{\overset{\displaystyle O}{\|}}{\text{C}}-\text{O} \right]}_{x} \text{CH}_2(\text{CF}_2)_3\text{CH}_2\text{OH} \quad \xrightarrow{\;\Delta\;}\;\not\to$$

$$\text{HO} \underbrace{\left[\text{CH}_2(\text{CF}_2)_3\text{CH}_2-\text{O} \right]}_{x} \text{CH}_2(\text{CF}_2)_3\text{CH}_2\text{OH} \; + \; \text{CO}_2 \uparrow$$
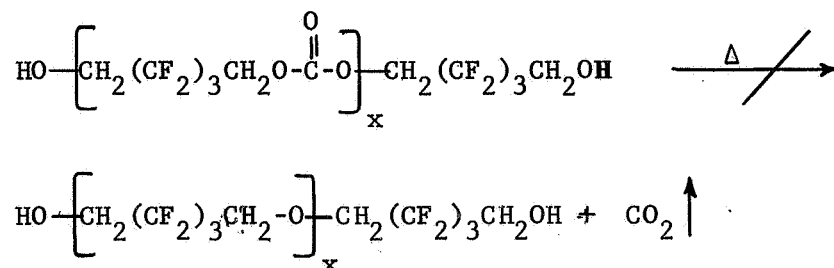
Poly(hexafluoropentamethylene carbonate) of 1075 molecular weight was heated at 280°-300°C for $\frac{1}{2}$ hour. There was no decarboxylation and only a slight darkening of the color of the polymer. The infrared spectrum of the material after heating was identical to that before heating.

b. Polymerization of 3,3,3-Trifluoro-1,2-epoxypropane

(1) Using Boron Trifluoride Catalysis

$$\text{CF}_3\text{-CH}\overset{\displaystyle O}{\underset{\textstyle }{\diagup\diagdown}}\text{CH}_2 \quad \xrightarrow{\;\text{BF}_3\;}\quad \text{HO} \underbrace{\left[\overset{\displaystyle \text{CF}_3}{\underset{\textstyle }{\overset{|}{\text{CH}}}}-\text{CH}_2\text{O} \right]}_{x}\text{H}$$
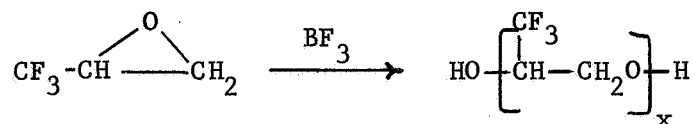
3,3,3-Trifluoro-1,2-epoxypropane (3.0 g, 0.0267 mole) and hexane (3 ml) were charged to a vial which had been cooled in dry ice — acetone. The ether was not soluble in the hexane. Boron trifluoride gas was then passed slowly into the ether for $\frac{1}{2}$ minute while being cooled in a dry ice — acetone bath. The mixture was left standing for $\frac{1}{2}$ hour, during which time the product froze. The slurry was warmed to just above its freezing point and boron trifluoride was passed through the epoxide for an additional $\frac{1}{2}$ minute. After standing for $\frac{1}{2}$ hour, the product was warmed to approximately 0°C, and boron trifluoride passed through the viscous material for 1 minute, then left standing for 1 hour. The polymer was dissolved in ether, then washed with dilute sodium bicarbonate solution. The ether layer was removed and dried with magnesium sulfate. The ether was evaporated and the product stripped on a rotary evaporator at 115°C to yield 1.7 g of a viscous, light tan polymer. Two drops of an impurity, immiscible with the principal product, was also observed. An infrared spectrum of the polymer (see Figure 14) appeared to be a hydroxyl-terminated polyether. The molecular weight by vapor phase osmometry was 1150 ±70. The hydroxyl value, using 3,5-dinitrobenzoyl chloride, was 1013 g per hydroxyl group. It was found by infrared spectrometry that 3,5-dinitrobenzoyl chloride did not react with all the hydroxyl group. The secondary hydroxyl groups probably remained unreacted. An infrared spectrum of the impurity (see Figure 15) indicated the compound probably contains terminal unsaturation.
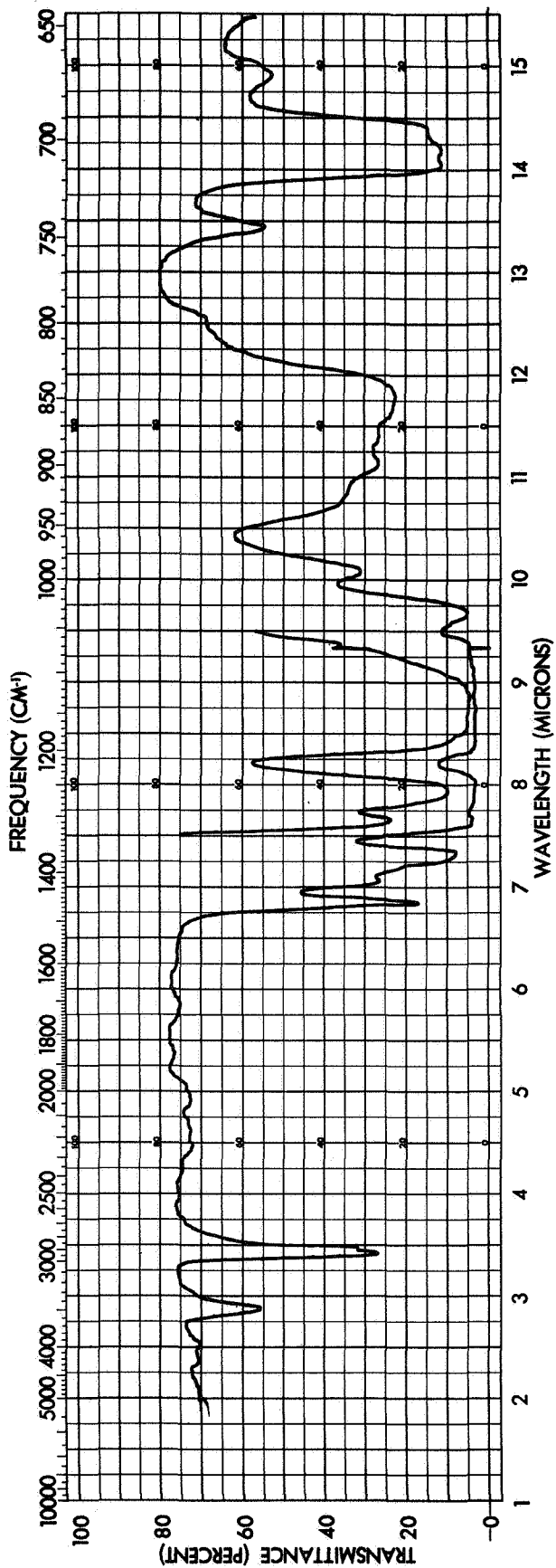
Figure 14. Poly(trifluoro-oxypropylene) glycol (BF$_3$ catalysis)
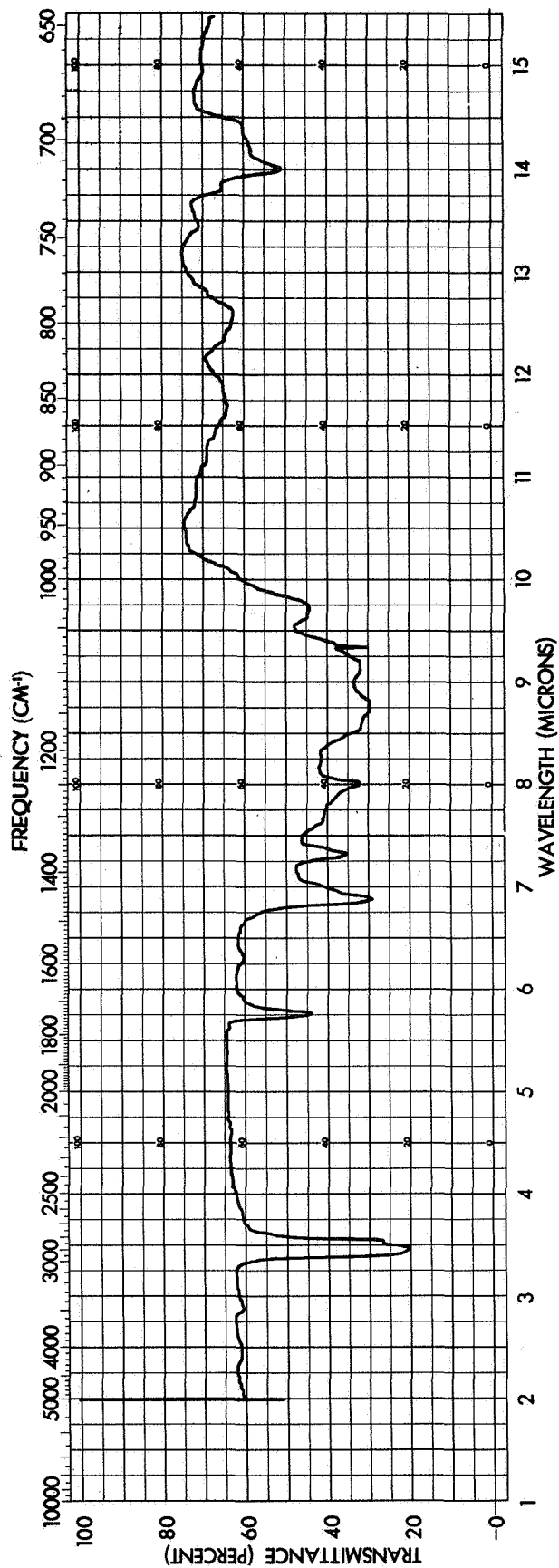
Figure 15. Impurity from Boron Trifluoride Polymerization of 3,3,3-Trifluoro-1,2-Epoxypropane

(2) Using Aluminum Chloride Catalysis.

Preparation No. 1 — 3,3,3-Trifluoro-1,2-epoxypropane (3.0 g, 0.027 mole) and aluminum chloride (0.1 g, 0.0008 mole) were reacted for 114 hours at room temperature in a glass bottle. The black viscous oil was dissolved in ether, washed with dilute ammonium hydroxide, the the ether dried with magnesium sulfate. The ether was removed to yield 1.4 g (46.7%) of viscous tan polymer. The infrared spectrum was identical to that obtained by the poly- merization using boron trifluoride catalysis; there was no unsaturation. The molecular weight by vapor phase osmometry (VPO) was 1240 ±50.

Preparation No. 2 — 3,3,3-Trifluoro-1,2-epoxypropane (45 g, 0.4 mole) was placed in a test tube and cooled to -78°C. Aluminum chloride (1.3 g, 0.1 mole) was then added in small amounts with additional cooling. The mixture was kept at -78°C for 1 hour, an additional 22.5 g (0.2 mole) of the epoxide added, and the mixture allowed to come to room temperature over a period of 24 hours. The tube was then shaken for 120 hours at room temperature. The contents were washed out with isopropyl ether and the ether solution washed with water. The water was acidified, the layers separated, and the ether layer dried over anhydrous magnesium sulfate. The solution was treated with charcoal and the solvent removed under reduced pressure, leaving 35 g of a clear, viscous oil. The polymer had a molecular weight of 2800 ±70, as determined by VPO.

(3) Using Potassium Hydroxide Catalysis

3,3,3-Trifluoro-1,2-epoxypropane (3.4 g, 0.03 mole) and potassium hydroxide (0.15 g, 0.0027 mole) were charged to a Carius combustion tube and sealed. The tube was then wrapped in glass cloth and placed in a sealed metal pipe. The polymerization was conducted at 90°-95°C for 84 hours, then the tube was cooled. The polymer was dissolved in ether, washed with dilute hydrochloride acid then with water, and the ether dried with magnesium sulfate. The ether was removed and the polymer purified by heating under vacuum at 90°-100°C. The polymer remaining was a colorless viscous oil weighing 2.1 g (61.7%). The infrared spectrum (see Figure 16) indicates hydroxyl termination, with some unsaturation having a different structure from the unsaturation in the impurity obtained along with the boron trifluoride prepared polymer. The molecular weight by VPO was 4300 ±300.

(4) Using the Monosodium Salt of Hexafluoropentanediol* as the Initiator

$$HOCH_2(CF_2)_3CH_2O^-Na^+ + \overset{CF_3}{\underset{CH}{\overset{|}{\underset{\diagdown}{}}}} \overset{O}{\overset{\diagup\diagdown}{}} CH_2 \longrightarrow$$

$$HOCH_2(CF_2)_3CH_2-O\left[\overset{CF_3}{\underset{CH-CH_2}{\overset{|}{}}}-O\right]_x H$$
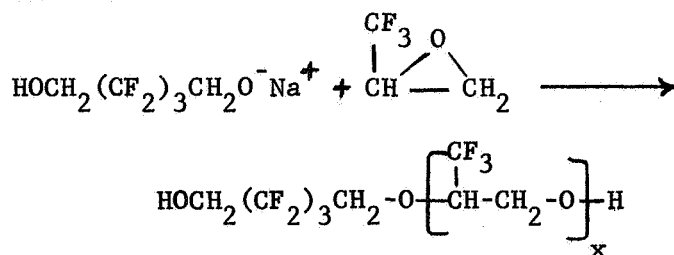
Preparation No. 1 — 3,3,3-Trifluoro-1,2-epoxypropane (6.5 g, 0.058 mole) and the monosodium salt of hexafluoropentanediol (0.48 g, 0.0021 mole) were charged to a Carius combustion tube and sealed. The polymerization condi- tions and workup was identical to that using potassium hydroxide catalysis. The

* Preparation described in Section IV.E.

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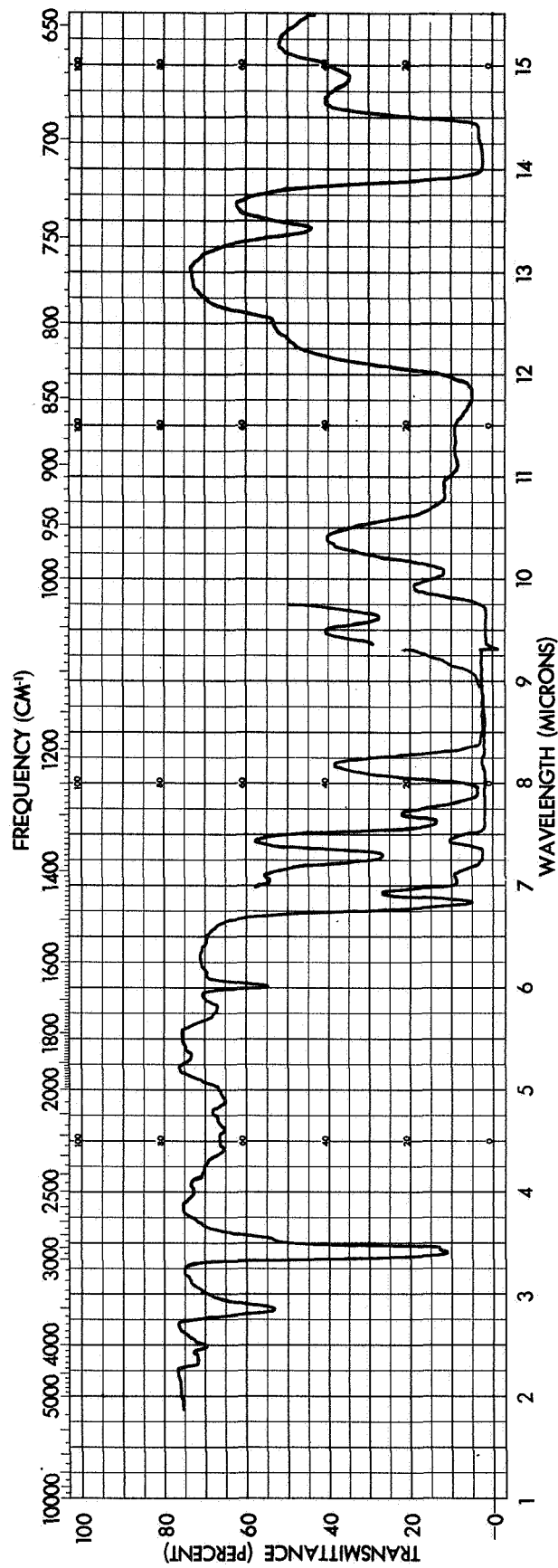
Figure 16.   Poly(trifluoro-oxypropylene) glycol (KOH catalysis)

polymer obtained was a yellow viscous oil weighing 2.5 g (38.5%). The infrared spectrum indicated hydroxyl termination with no unsaturation. The molecular weight by VPO was 2570 ±50.

Preparation No. 2 — The monosodium salt of hexafluoropentanediol (11.7 g, 0.05 mole) was placed in a pressure tube followed by 3,3,3-trifluoro-1,2-epoxypropane (45 g, 0.4 mole) at -78°C. The tube was sealed, placed in a closed iron pipe and left in an oven at 88°-89°C for 88 hours. The tube was then opened at room temperature and the contents rinsed out with ether. The ether solution was washed with water and dried over anhydrous magnesium sulfate. The ether was removed by distillation leaving a yellow viscous liquid. This was dissolved in diisopropyl ether and treated with charcoal. Again the solvent was removed under reduced pressure, leaving 41 g (72.3% yield) of clear, yellowish polyether. The molecular weight of the polyether determined by VPO was 970 ±25 and by end group analysis, 1000.

D. Other Polymers

1. <u>Preparation of Poly(hexafluoropentamethylene tetrachloroterephthalate)</u>
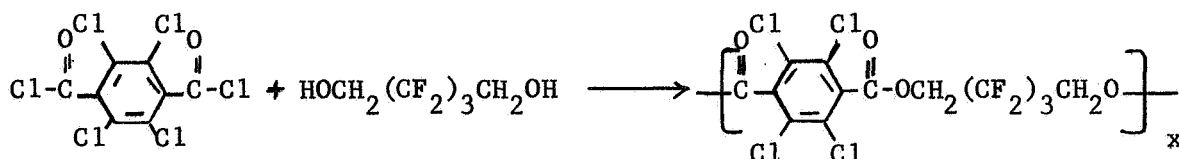
Tetrachloroterephthaloyl chloride (17.1 g, 0.05 mole) was dissolved in 50 ml of N-methyl pyrollidone and added to a 250-ml, three-necked, round-bottomed flask fitted with stirrer, dropping funnel, nitrogen inlet, condenser, and thermometer. Hexafluoropentanediol (10.6 g, 0.05 mole) dissolved in 50 ml of N-methyl pyrrolidone was added over a 10-minute period under a nitrogen purge. There was no exotherm. The temperature was increased to 190°C and held for 10 minutes with no apparent reaction. Pyridine (10 ml) was added and the reaction mixture stirred at 180°-190°C for 18 hours. Again, there was no apparent reaction. The pyridine and N-methyl pyrrolidone was stripped off under reduced pressure, leaving a black residue. None of the desired material was isolated.

In a repeat experiment, hexafluoropentanediol (10.6 g, 0.05 mole), tetrachloroterephthaloyl chloride (17.6 g, 0.05 mole) and o-dichlorobenzene (25 ml) was added to a 250-ml, three-necked flask equipped with a stirrer, condenser, nitrogen inlet and thermometer. The mixture was stirred for 1 hour at 30°-40°C, 1 hour at 100°C, 1 hour at 130°-140°C, and 4 days at 170°-180°C, all under nitrogen. The o-dichlorobenzene was removed via vacuum distillation and the residue stirred at 210°C to 220°C for 17 hours under nitrogen, during which the polymer gelled. The residue was dried in a vacuum oven for 4 hours at 140°-150°C to yield 14.1 g (59%) of black polymer, mp >380°C. The infrared spectrum is attached as Figure 17.
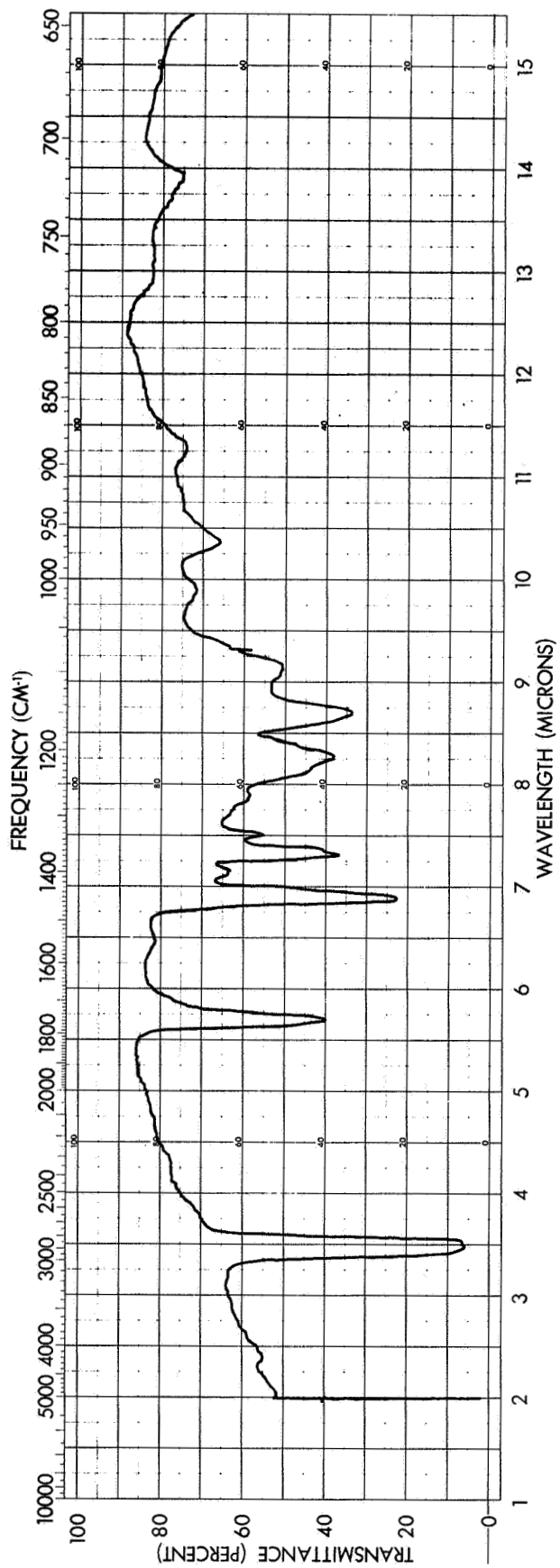
Figure 17. Poly(hexafluoropentamethylene tetrachloroterephthalate)

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2. Polycarbonates

a. Preparation of Poly(hexafluoropentamethylene carbonate)

$$HO-CH_2(CF_2)_3CH_2-OH \ + \ COCl_2 \ + \ 2 \ \langle pyridine \rangle$$

$$\downarrow$$

$$HO\left[CH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-O\right]_x CH_2(CF_2)_3CH_2OH$$
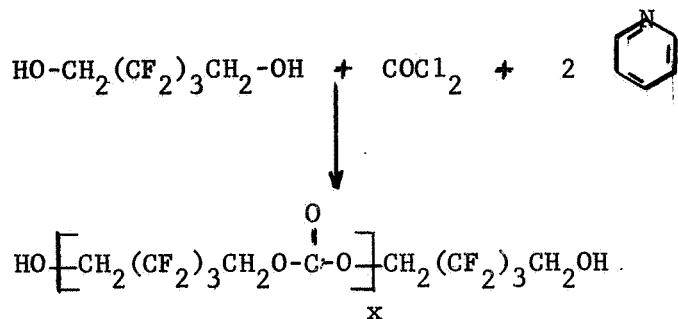
Procedure A — Phosgene was condensed into the particular solvent under study at 0°C in a three-necked, round-bottomed flask fitted with a Dewar reflux condenser, addition funnel, stirrer, nitrogen inlet, and phosgene inlet. A solution of hexafluoropentanediol and pyridine in the same solvent was added to the phosgene solution over a 30-60 minute period. The resultant solution was stirred 4 hours at room temperature and then poured into a dilute solution of hydrochloric acid (pH 3). The mixture was then boiled for 30 minutes, cooled, and the water decanted. The boiling procedure was repeated. After separation from the water layer, the residual solvent (if any) was stripped off under reduced pressure. The polymer was then taken up in ether, dried over anhydrous magnesium sulfate, filtered, and the ether stripped off under reduced pressure.

Procedure B — Hexafluoropentanediol was dissolved in the particular solvent under study (or ether/solvent mixture where the insolubility of hexafluoropentanediol was a problem) and charged to a three-necked, round-bottomed flask fitted with a stirrer, nitrogen inlet, Dewar reflux condenser, and an addition funnel fitted with a phosgene bubbler inlet. Pyridine was dissolved in the solvent and charged to the addition funnel. Phosgene was then bubbled into the pyridine solution at room temperature. Following a 15-minute dry nitrogen purge of the phosgene line, the resultant slurry was added to the hexafluoropentanediol solution over 30-60 minute period. After addition, the solution was stirred for 4 hours. The workup of the resultant polymer was accomplished in the same manner as in Procedure A.

b. Attempted Preparation of Poly(hexafluoropentamethylene tetrachloro-p-xylylene carbonate)

$$HOCH_2-\langle C_6(Cl)_4 \rangle-CH_2OH \ + \ Cl-\overset{O}{\overset{\|}{C}}-OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-Cl \ \longrightarrow$$

$$\left[-OCH_2-\langle C_6(Cl)_4 \rangle-CH_2O-\overset{O}{\overset{\|}{C}}-OCH_2(CF_2)_3CH_2O-\overset{O}{\overset{\|}{C}}-\right]_x$$
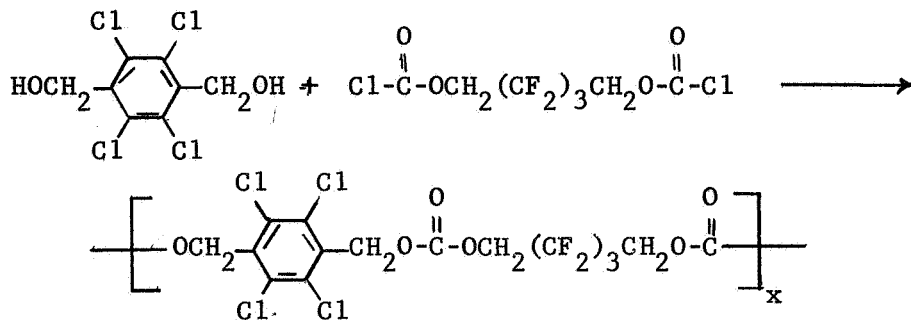
Pyridine (200 ml) and 2,3,5,6-tetrachloro-p-xylylene-α,α' diol (13.8 g, 0.05 moles) were charged to a three-necked, round-bottomed flask fitted with a stirrer, reflux condenser, thermometer, addition funnel, and dry nitrogen purge. Hexafluoropentamethylene bischloroformate (16.9 g, 0.05 moles) was added over a period of 1 hour at a continually diminishing rate with mixing under nitrogen. The temperature was increased to reflux (106°C) and stirred for 16 hours under nitrogen. After cooling to room temperature, the reaction mixture was poured into 400 ml of distilled water. When the residue was worked up, only starting materials were recovered.

3. Polyethers

    a. Attempted Preparation of Poly(hexafluoropentamethylene oxide)
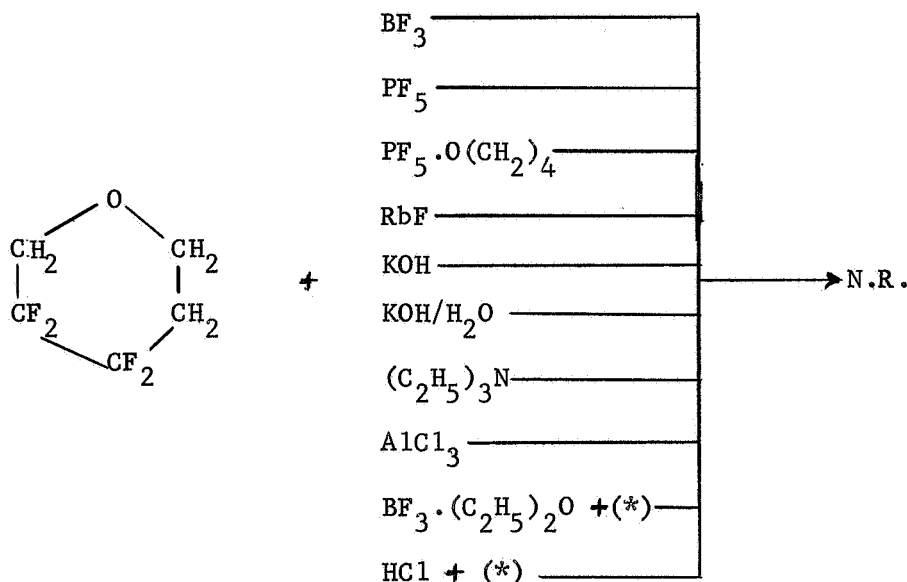
An attempt was made to initiate the ring opening of hexafluoropenta-methylene oxide with various reagents. Small samples of hexafluoropenta-methylene oxide were allowed to stand at room temperature in the dark with (1) triethylamine, (2) solid potassium hydroxide, (3) aqueous potassium hydroxide, (4) phosphorus pentafluoride — tetrahydrofuran complex, (5) phosphorus penta-fluoride (bubbled in), (6) hydrogen chloride plus hexafluoropentamethylene sulfite, (7) boron trifluoride, (8) aluminum chloride, (9) boron trifluoride — etherate plus hexafluoropentamethylene sulfite, and (10) rubidium fluoride. After a total of 30 days, none of the samples showed any visible sign of reaction. The infrared spectrum of each was identical to that of unreacted hexafluoropentamethylene oxide.

(*) Hexafluoropentamethylene sulfite

b. **Attempted Polymerization of Tetrafluorotetramethylene Oxide**

(1) Aluminum Chloride Catalysis

$$\text{(cyclic ether)} \xrightarrow{\text{AlCl}_3} \big[\!-\!OCH_2CF_2CF_2CH_2\!-\!\big]_x$$
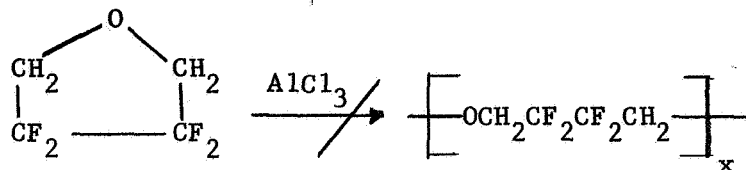
Tetrafluorotetramethylene oxide (5.8 g, 0.04 mole) and aluminum chloride (0.3 g, 5 mole percent) were charged to a 20-ml flask equipped with a reflux condenser. The mixture was then refluxed for 64 hours at 70°C. There was no reaction.

(2) Boron Trifluoride Catalysis

A two-necked flask equipped with reflux condenser and gas inlet was charged with a small sample of 3,3,4,4-tetrafluorotetramethylene oxide. It was cooled to 0°C and boron trifluoride was bubbled in for 1 hour. At the end of this period, some solid had formed and the liquid had darkened. At the end of one week at room temperature, more solid had deposited and the clear liquid was golden in color. The solid was in the form of separate, clear, color-less diamond-shaped crystals. This is probably the cyclic ether — boron trifluoride complex.

(3) Phosphorus Pentafluoride, Sodium Methoxide, and Phosphorus Penta-fluoride — Tetrahydrofuran Complex Catalysis

A small sample of 3,3,4,4-tetrafluoro-tetramethylene oxide was placed into a two-necked flask equipped with a reflux condenser and a gas inlet. Phosphorus pentafluoride gas was bubbled into the liquid for 90 minutes. After 1 day, the solution had deposited both an oil and a solid on the bottom of the flask. The white solid did not melt, but decomposition began at 250°C. The brown oil was tentatively identified as the complex of the cyclic ether with phosphorus pentafluoride. Clear liquid remaining in the flask was unreacted 3,3,4,4-tetrafluorotetramethylene oxide. Separate solutions of the cyclic ether were allowed to stand with (1) sodium methoxide and (2) the complex formed by reaction of THF with phosphorus pentafluoride. After 20 days, there was no change from unreacted 3,3,4,4-tetrafluorotetramethylene oxide.

4. **Poly(hexafluoropentamethylene sulfite)**

$$\text{(cyclic sulfite)} + PF_5 \longrightarrow H\big[\!-\!OCH_2(CF_2)_3\!-\!CH_2\!-\!O\!-\!\overset{O}{\overset{\|}{S}}\!-\!\big]_x OCH_2(CF_2)_3CH_2OH$$
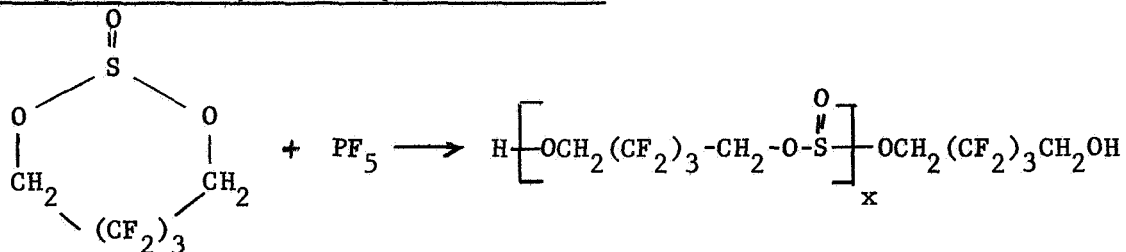
A 50-ml, two-necked flask was fitted with a reflux condenser and a gas bubbler. The flask was tared, charged with hexafluoropentamethylene sulfite (19.1 g, 0.074 mole), and cooled to 1°C with an ice bath. Addition of phosphorus pentafluoride gas was followed by weight increase. Over a 2-hour period, 15% phosphorus pentafluoride was added and the liquid had become a deep red-brown gel. This was stripped of unreacted hexafluoropentamethylene sulfite by vacuum distillation and a sample of the polymer subjected to elemental analysis. Its infrared spectrum is shown in Figure 18.

Analysis:	% C	% H	% F	% S	% P
Found:	24.30	2.57	45.46	8.95	1.09

The remainder of the material was warmed for 1½ hours in a solution of sodium bicarbonate. The color lightened considerably, and the viscosity appeared to decrease. Evidence for evolution of sulfur dioxide was noted by manganese dioxide precipitation in a solution of potassium permanganate. A sample of the material was dissolved in ether, dried, stripped of solvent, and analyzed.

Analysis:	% C	% H	% F	% S	% P
Calculated for $C_{10}H_{10}F_{12}SO_5$:*	25.5	2.1	48.5	6.8	0
Found:	28.25	3.00	48.19	6.96	0

Molecular weight determination by VPO was 472 g/mole. The remaining material was hydrolyzed further in the sodium bicarbonate solution for 4 hours. Further evolution of sulfur dioxide was noted, and the polymer had become soluble. Evaporation of the acidic aqueous solution yielded only hexafluoropentanediol.

5. Polyamides

a. From Perfluoroglutaryl Chloride

(1) Poly(ethylene perfluoroglutaramide)

LOX-Impact Testing Specimens — Twenty LOX-compatibility test specimens (11/16-in. diameter, 20 mils thick) were prepared from poly(ethylene perfluoroglutaramide). These samples were prepared in a pellet mold at 15,000-lb pressure at room temperature.

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* Possible structure: $HOCH_2(CF_2)_3CH_2O\text{-}\overset{O}{\underset{\parallel}{S}}\text{-}OCH_2(CF_2)_3CH_2OH$
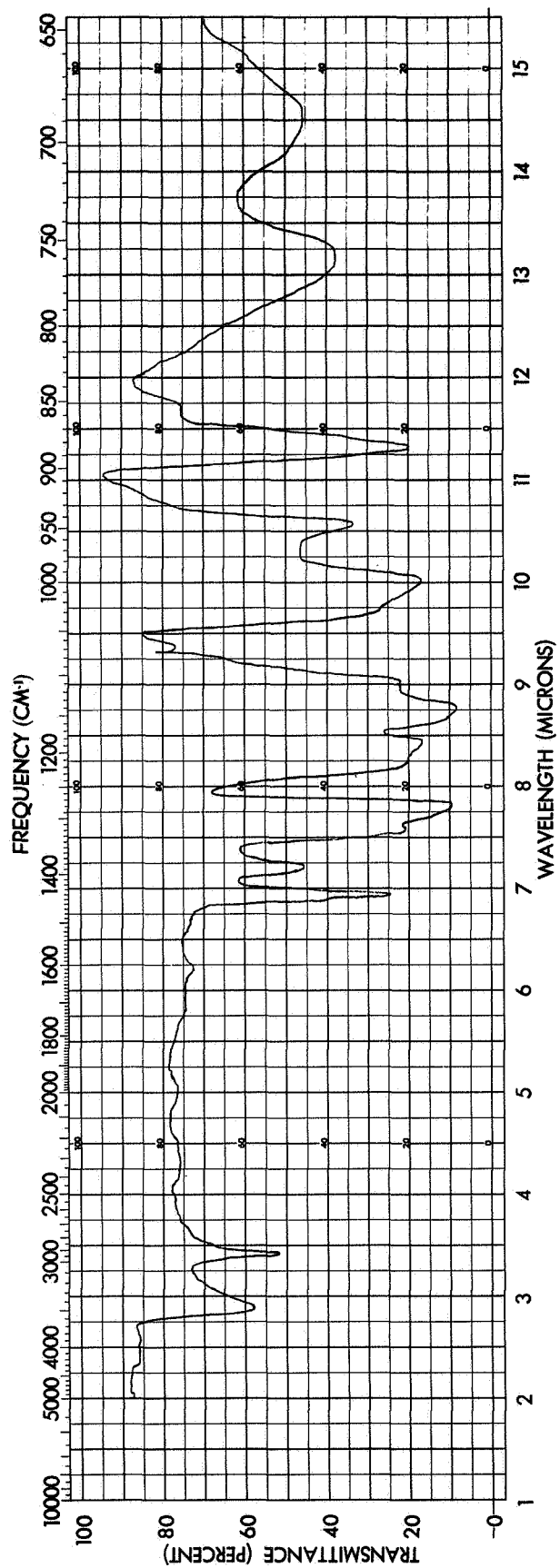
Figure 18. Poly(hexafluoropentamethylene sulfite)

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(2) Poly(tetrafluoro-p-phenylene perfluoroglutaramide)

$$H_2N-\underset{F\ F}{\underset{F\ F}{\bigcirc}}-NH_2 \ + \ Cl-\overset{O}{\overset{\|}{C}}-(CF_2)_3-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow$$

$$\left[-N-\underset{F\ F}{\underset{F\ F}{\bigcirc}}-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-(CF_2)_3-\overset{O}{\overset{\|}{C}} \right]_x$$
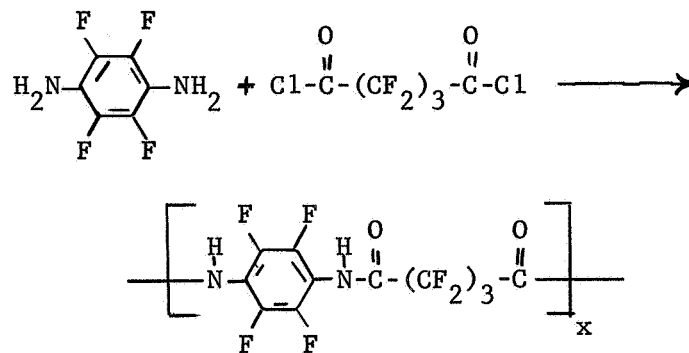
Tetrafluoro-p-phenylenediamine (11.3 g, 0.063 mole), potassium hydroxide (7.1 g, 0.126 mole) and water (4.5 liter) were added to a 12-liter, three-necked flask equipped with a stirrer, thermometer, and dropping funnel. Perfluoroglutaryl chloride (10.0 g, 0.036 mole) in o-dichlorobenzene (1 liter) was rapidly added to the vigorously stirred diamine solution at 60°C. The slurry was mixed for an additional ½ hour, then filtered. The residue was dried in a vacuum oven at 60°-70°C for 3 hours to yield 0.9 g of polyamide. The polymer formed was of apparent low molecular weight, mp 135°-140°C.

b. **From Hexafluoropentanediamine**

(1) Poly(hexafluoropentamethylene adipamide)

$$H_2NCH_2(CF_2)_3CH_2NH_2 \ + \ Cl-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow$$

$$\left[-\overset{H}{N}-CH_2-(CF_2)_3-CH_2-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}} \right]_x$$
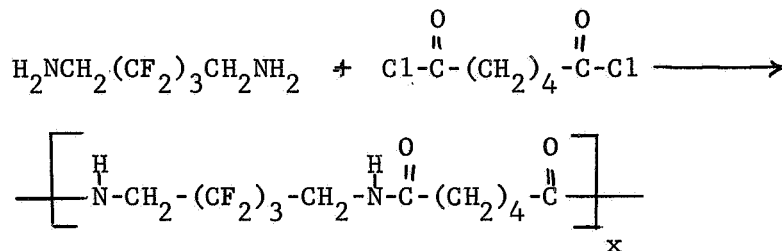
Hexafluoropentanediamine (10.6 g, 0.05 mole), potassium hydroxide (6.2 g, 0.11 mole) and water (500 ml) were charged to a 1-liter, three-necked flask equipped with a stirrer, thermometer, and dropping funnel. Distilled adipoyl.chloride (9.2 g, 0.05 mole) in benzene (300 ml) was rapidly added to the diamine solution at 20°C with vigorous mixing. The slurry was rapidly stirred for an additional 15 minutes, then filtered. The residue was dried in a vacuum oven at 60°-80°C for 2 hours to yield 6.3 g (37.6% of light tan polymer, mp 130°-140°C. The infrared spectrum is attached as Figure 19.

(2) Attempted Preparation of Poly(hexafluoropentamethylene tetrachloroterephthalamide)

$$H_2N-CH_2(CF_2)_3CH_2-NH_2 \ + \ Cl-\overset{O}{\overset{\|}{C}}-\underset{Cl\ Cl}{\overset{Cl\ Cl}{\bigcirc}}-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow$$

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

119
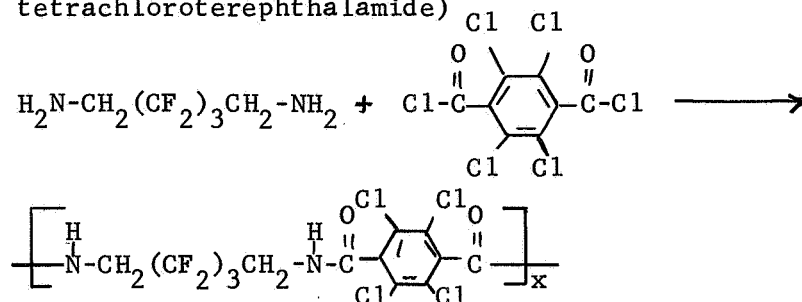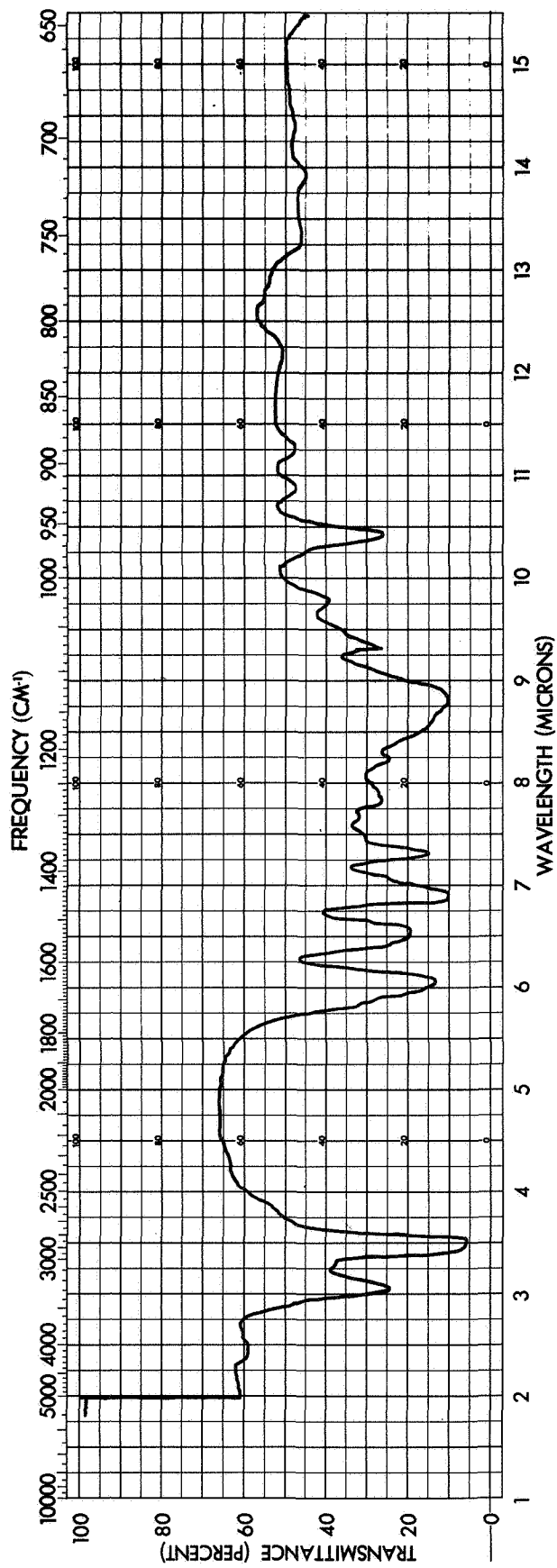
Figure 19. Poly(hexafluoropentamethylene adipamide)

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Into a 12-liter, three-necked flask equipped with a stirrer, thermo-meter, and dropping funnel were charged hexafluoropentanediamine (13.2 g, 0.063 mole), potassium hydroxide (7.10 g, 0.126 mole) and 4.5 liter of water. Tetrachloroterephthaloyl chloride (12.3 g, 0.036 mole) in methylene chloride (1 liter) was rapidly added with vigorous mixing to the diamine solution. The mixture was agitated vigorously for ½ hour at 30°C. There was no reaction.

6. Polyureas

a. Poly(tetrafluoro-p-phenylene urea)

Phosgene (~ 100 ml, 1 mole) was condensed at 0°C in the reaction flask of the usual phosgenation apparatus. Pyridine (15.8 g, 0.2 mole) was dissolved in 84 ml of dry ether and added to the phosgene, followed by an additional 100 ml of ether. Tetrafluoro-p-phenylenediamine (18.0 g, 0.1 mole) was dissolved in 200 ml of dry ether and added over a period of 1 hour. The reaction mixture was held at 0°C for 1½ hours, followed by 1 hour at room temperature. The slurry was filtered and the residue washed twice with ether and twice with water. The insoluble polyurea was dried overnight in a vacuum oven, yielding a brittle material melting at 305°-315°C with decomposition.

Elemental Analysis:	%C	% H	% N	% F
Calculated for $C_7H_2N_2O$:	40.7	1.0	13.6	36.8
Found:	39.2	1.7	13.1	33.6

b. Poly(hexafluoropentamethylene tetrafluoro-p-phenylene urea)
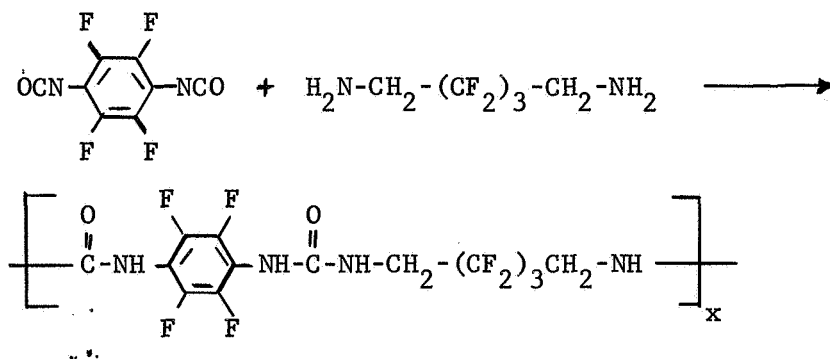
In a 100-ml, three-necked flask equipped with a stirrer, reflux conden-ser, and addition funnel with a nitrogen inlet, was placed hexafluoropentanedi-amine (2.1 g, 0.01 mole) dissolved in 30 ml of N,N-dimethylformamide. The system was under an atmosphere of nitrogen throughout the reaction. To this solution was added tetrafluoro-p-phenylene diisocyanate (2.3 g, 0.01 mole) dissolved in 10 ml of DMF over a 5-minute period. The reaction mixture was stirred at room temperature for 2 hours, then at 100°C for 24 hours. Ten drops of tin octoate were added and the mixture stirred at 150°C for 3 hours. The clear solution was poured into water with vigorous stirring. The fluffy, white precipitate was filtered and dried in a vacuum oven at 80°C. The polyurea obtained was a tan solid weighing 2.0 g (45%) mp 280°-290°C (with decomposition). Figure 20 is the infrared spectrum of the polymer.
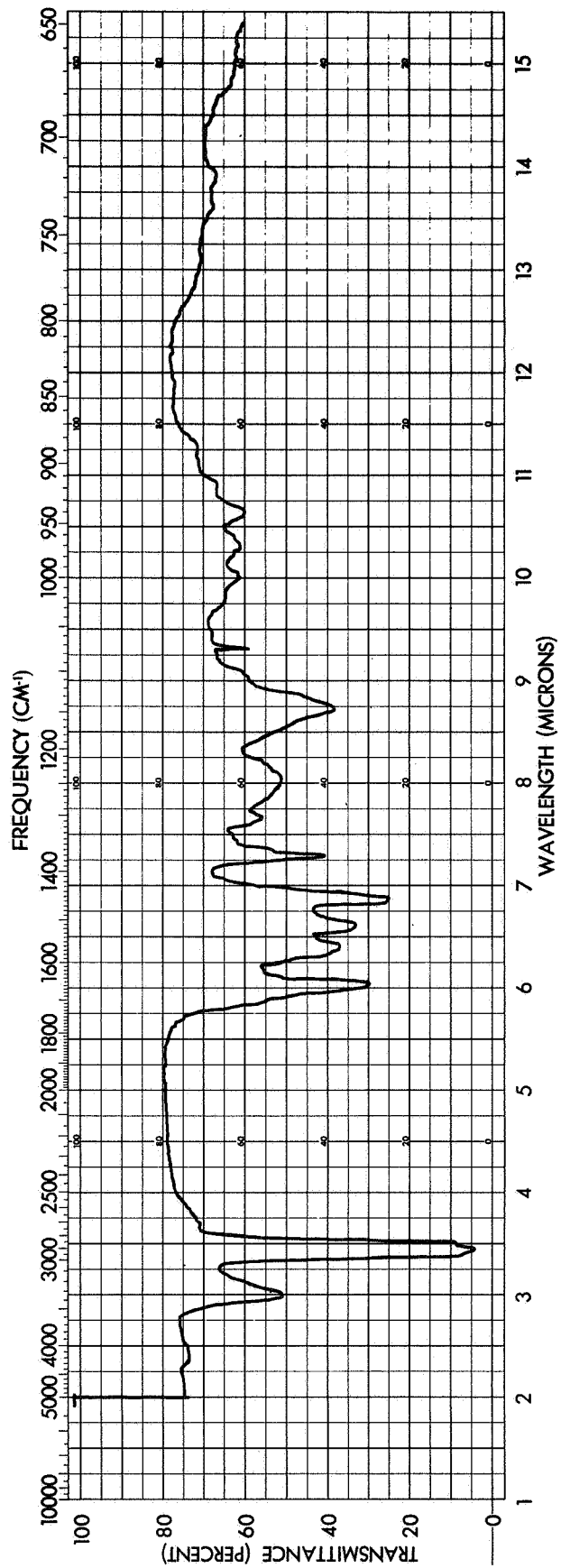
Figure 20. Poly(hexafluoropentamethylene tetrafluoro-p-phenylene urea)

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7. Polyimides

a. Preparation of Poly(hexafluoropentamethylene pyromellitimide)

$$H_2N-CH_2(CF_2)_3CH_2-NH_2 \quad + \quad$$

$$\longrightarrow$$
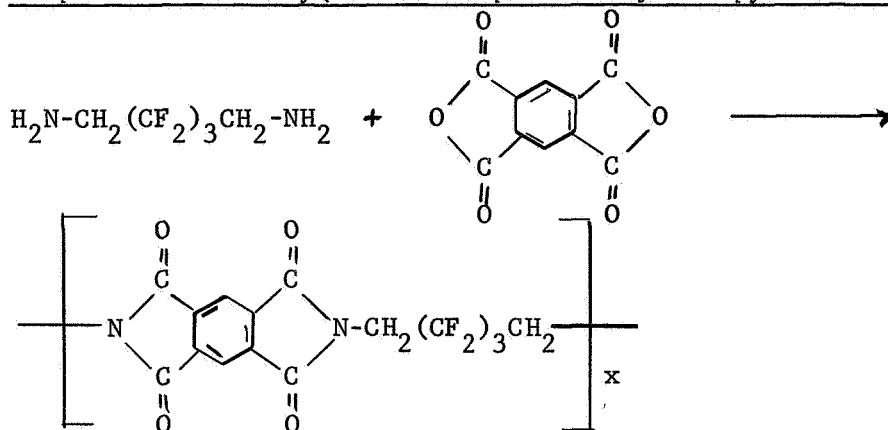
Hexafluoropentanediamine (4.20 g, 0.02 mole) in DMAC (30 ml) was added to a 100-ml, three-necked flask equipped with a stirrer, condenser, thermometer, dropping funnel, and nitrogen inelt. Recrystallized pyromellitic dianhydride (4.40 g, 0.02 mole) in DMAC (30 ml) was slowly added to the stirred diamine solution over a 1½ hour period at 0°C to 10°C under nitrogen. The solution was mixed for 2 hours at 70°-80°C under nitrogen, then poured into water. The slurry was filtered and the polymeric residue dried in a vacuum oven at 80°-90°C for 24 hours to yield 4.0 g of product (mp 347°-355°C) with darkening. The inherent viscosity in concentrated sulfuric acid was 0.049 at 25°C, indicating the product was of apparent low molecular weight. The infrared spectrum is attached as Figure 21.

E. Monomers

1. Preparation of Hexafluoropentamethylene Bischloroformate

$$HOCH_2(CF_2)_3CH_2OH \quad +$$

$$\longrightarrow \quad Cl-\overset{O}{\overset{\|}{C}}-O-CH_2(CF_2)_3CH_2-O-\overset{O}{\overset{\|}{C}}-Cl$$
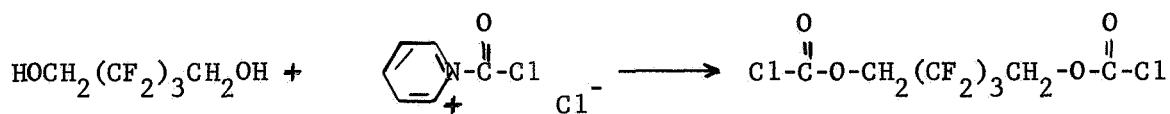
Phosgene (56.0 g, 0.55 mole) was condensed at -20°C in dry ether (500 ml) in the reaction flask of the phosgenation apparatus. Pyridine (39.0 g, 0.5 mole), dissolved in dry ether (80 ml) was added to the mixed phosgene solution over a 10-minute period. The yellow precipitate of chloro-carbonyl pyridinium chloride was stirred for an additional 15 minutes at -20°C. Hexafluoropentane diol (42.4 g, 0.2 mole) in dry ether (250 ml) was added to the stirred slurry over a 30-minute period. The mixture was allowed to warm to room temperature and held for 3 hours with constant agitation. The solids were filtered under argon and the ether stripped from the clear filtrated under reduced pressure to yield 56.1 g (83.2%) of product. The crude product was fractionally distilled under reduced pressure through an 8-in. glass helix packed column. The purified bischloroformate distilled at 74°-76°C at 2-3 mm. The overall yield of purified material was 71.5%. The infrared spectrum is attached as Figure 22.
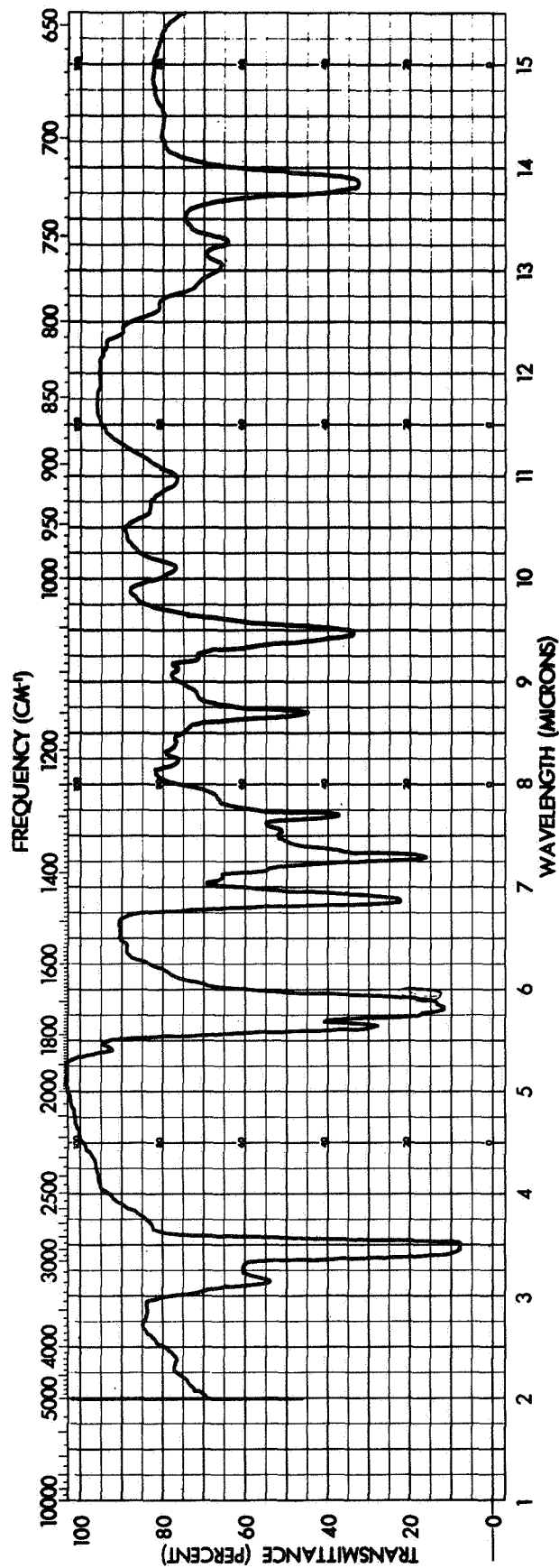
Figure 21. Poly(hexafluoropentamethylene Pyromellitimide)

124
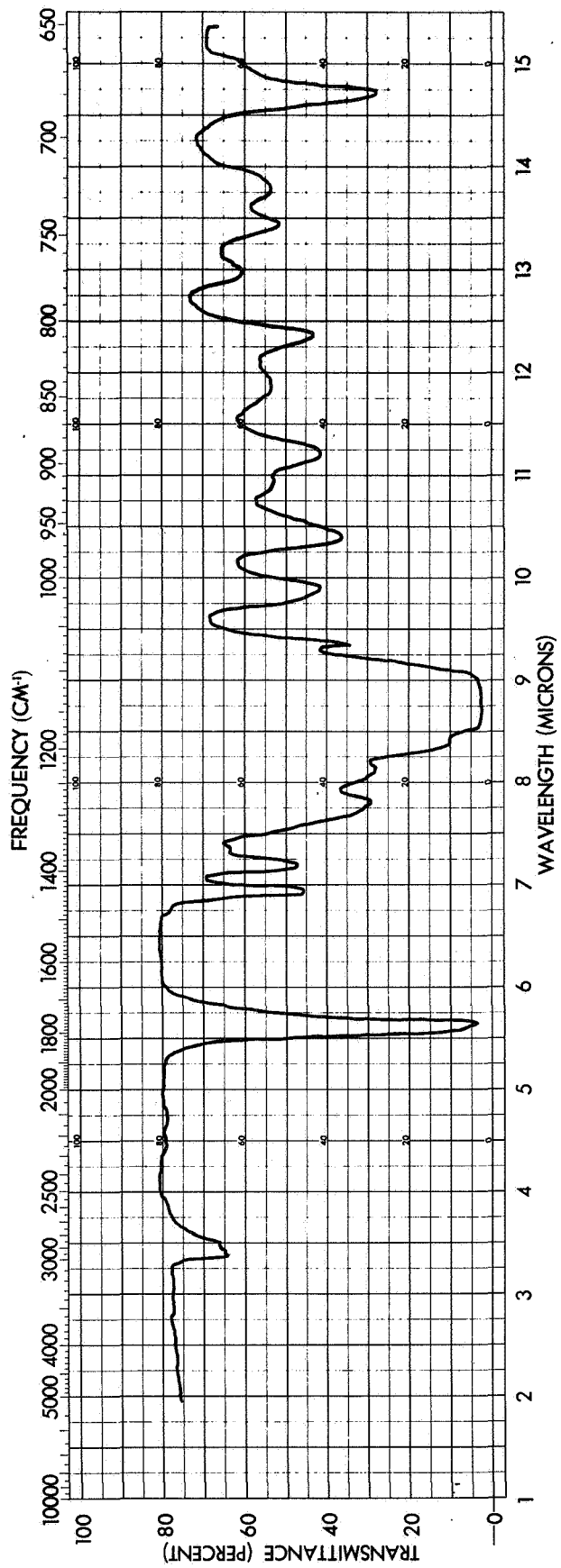
Figure 22. Hexafluoropentamethylene Bischloroformate

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|	Analysis:	% C	% H	% Cl	% F
Calculated for $C_7H_4O_4Cl_2F_6$:		24.92	1.19	21.03	33.83
	Found:	24.59	1.21	21.00	34.05

No tests have been run on the degree of toxicity of the bischloroformate, but it is believed that this material may be at least as toxic as phosgene.

The hexafluoropentamethylene biscarbamate derivative was prepared by passing ammonia into a hexane solution of hexafluoropentamethylene bischloroformate, then recrystallizing the product from water. The melting point of the biscarbamate was 135.5°-137°C.

	Elemental Analysis:	% C	% H	% N	% F
Calculated for $C_7H_8F_6N_2O_4$:		28.1	2.7	9.4	38.3
	Found:	27.94	2.61	9.1	37.6

2. **Preparation of Hexafluoropentamethylene Diisocyanate**

   a. **From Phosgenation of Hexafluoropentamethylenediamine**

$$H_2NCH_2(CF_2)_3CH_2NH_2 + \underset{+}{\bigcirc}\overset{O}{\underset{}{N-\overset{\|}{C}-Cl}}\ Cl^- \longrightarrow OCN-CH_2(CF_2)_3CH_2-NCO$$
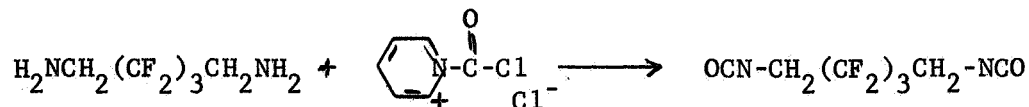
   Phosgene (0.5 mole) was condensed in the reaction flask of the phosgenation apparatus containing dry ether (300 ml) at -30°C. Pyridine (35.5 g, 0.45 mole) in dry ether (50 ml) was added to the stirred phosgene solution over a 10-minute period. The mixing was continued for an additional 15 minutes. Hexafluoropentanediamine (21.0 g, 0.1 mole) in dry ether (150 ml) was added to the stirred chlorocarbonyl pyridinium chloride slurry over a 30-minute period. The reaction mixture was warmed to room temperature and held for 3 hours with mixing. The solids were filtered and the ether stripped off from the filtrate. The residue was fractionally distilled under reduced pressure to yield 16.0 g (61%) of crude diisocyanate, bp 62°C/1 mm. Figure 23 is an infrared spectrum of the crude hexafluoropentamethylene diisocyanate.

   b. **Attempted Preparation from Ditosyl Ester of Hexafluoropentanediol**

$$CH_3-\bigcirc-\overset{O}{\underset{O}{\overset{\|}{S}}}-O-CH_2(CF_2)_3CH_2-O-\overset{O}{\underset{O}{\overset{\|}{S}}}-\bigcirc-CH_3 \xrightarrow{KNCO} OCN-CH_2(CF_2)_3CH_2-NCO$$
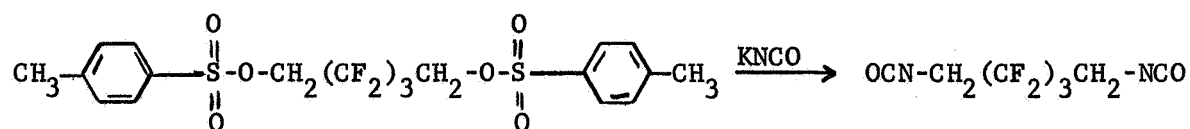
   The ditosyl ester of hexafluoropentanediol (26.6 g, 0.05 mole) was added to triglime (150 ml) in a three-necked, round-bottomed flask fitted with a stirrer, reflux condenser, and dry nitrogen gas inlet. Potassium cyanate
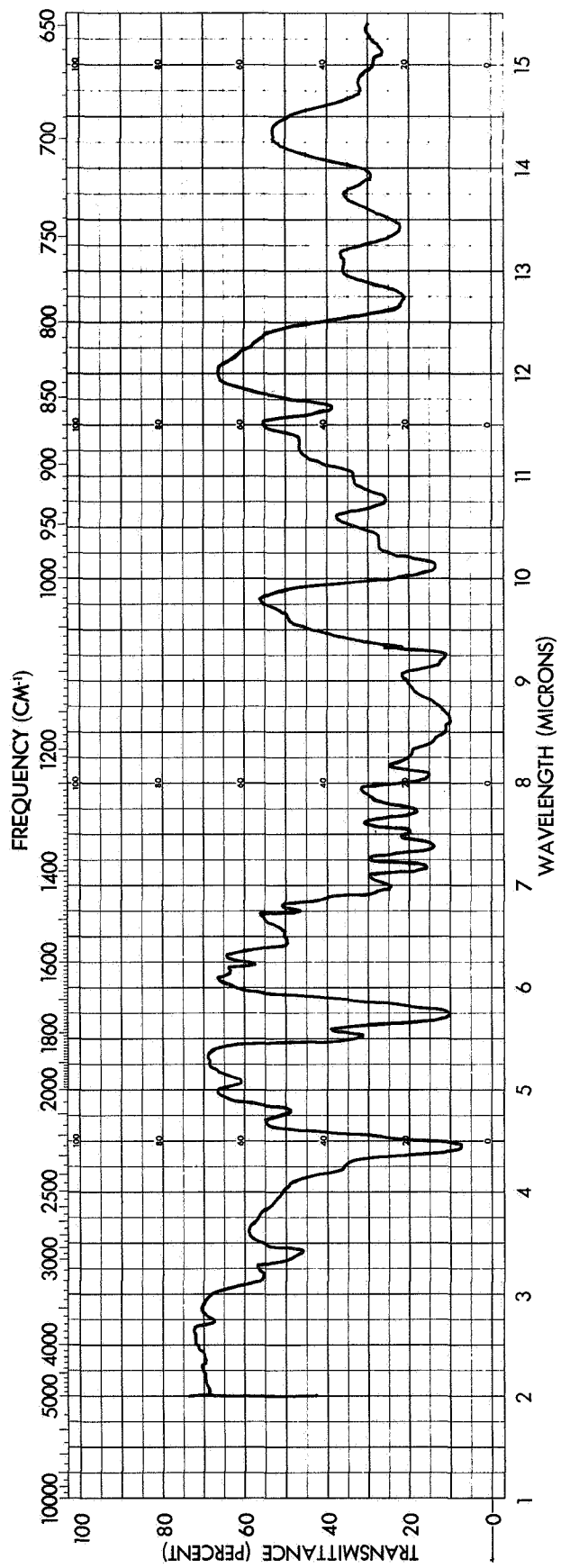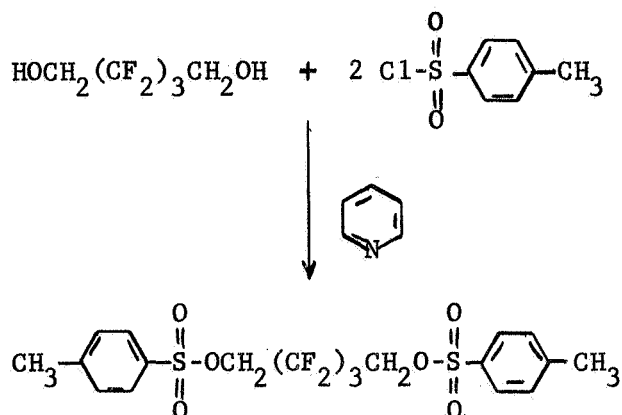
Figure 23. Crude Hexafluoropentamethylene Diisocyanate
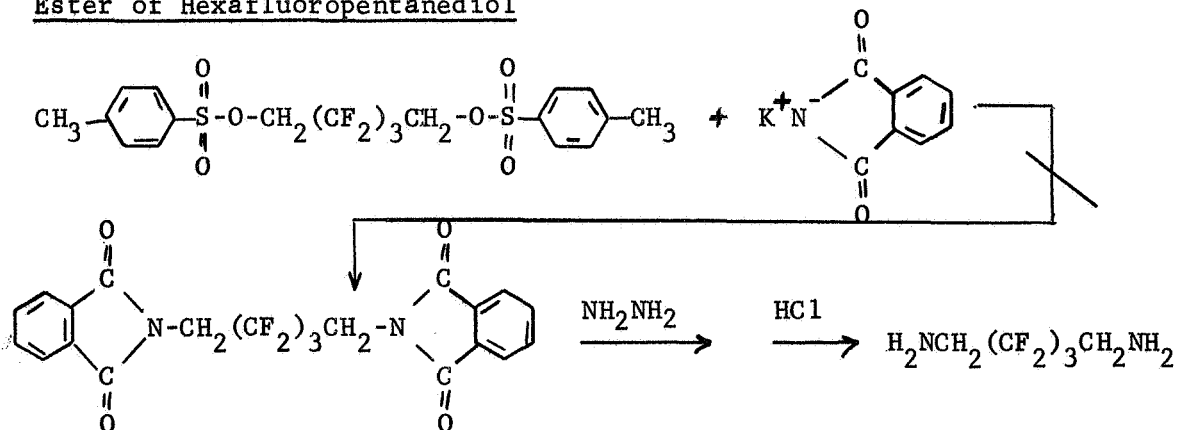
127

(8.1 g, 0.10 moles) was added and the temperature raised to reflux and maintained at reflux (196°C) for 24 hours. The solution was cooled, the solids filtered off, and the liquid distilled under reduced pressure. None of the desired material was obtained.

### 3. Preparation of the Ditosylate of Hexafluoropentanediol

$$HOCH_2(CF_2)_3CH_2OH \quad + \quad 2 \; Cl\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}\langle\bigcirc\rangle\text{-}CH_3$$

$$\downarrow \quad \langle\bigcirc\rangle_N$$

$$CH_3\text{-}\langle\bigcirc\rangle\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}OCH_2(CF_2)_3CH_2O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}\langle\bigcirc\rangle\text{-}CH_3$$

To a 12-liter, three-necked flask equipped with a thermometer, reflux condenser, stirrer, and addition funnel, were added hexafluoropentanediol (914.4 g, 4.31 mole) and freshly distilled pyridine (1274 g, 16.2 mole, 1300 ml). To this was added the complex formed from mixing p-toluenesulfonyl chloride (1809.2 g, 9.49 mole) and pyridine (2940 g, 37.2 mole, 3000 ml). Addition was carried out over a 2-hour period, with stirring, and the reaction temperature was maintained between 10°C and 15°C. The orange reaction solution became turbid midway through the addition. When the addition was complete, the solution was stirred for an additional hour at 15°C. The reaction mass was then poured into 4 liters of stirred ice-water. An orange precipitate immediately fell out of solution. The solid was filtered, washed with water (which removed the orange color), and dried. The yield of crude white ditosylate was 1731.6 (77.3%). The melting point was 82°-91.5°C; literature[38] value 92°-94°C. The crude product was recrystallized from ethanol. The melting point was 96.5°-97.5°C (uncorrected).

4. Attempted Preparation of Hexafluoropentanediamine from the Ditosyl Ester of Hexafluoropentanediol

$$CH_3\text{-}\langle\bigcirc\rangle\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}O\text{-}CH_2(CF_2)_3CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}\langle\bigcirc\rangle\text{-}CH_3 \quad + \quad K^{+}\overset{-}{N}\langle\cdots\rangle \nrightarrow$$

$$\langle\cdots\rangle N\text{-}CH_2(CF_2)_3CH_2\text{-}N\langle\cdots\rangle \xrightarrow{NH_2NH_2} \xrightarrow{HCl} H_2NCH_2(CF_2)_3CH_2NH_2$$

The ditosyl ester of hexafluoropentanediol (10.4 g, 0.02 mole) and potassium phthalimide (11.1 g, 0.06 mole) in N-methyl pyrrolidone were mixed at 202°C for 16 hours. The reaction mixture was poured into water, filtered and dried. There was no reaction.

5. **Attempted Preparation of Hexafluoropentamethylene Sulfate**
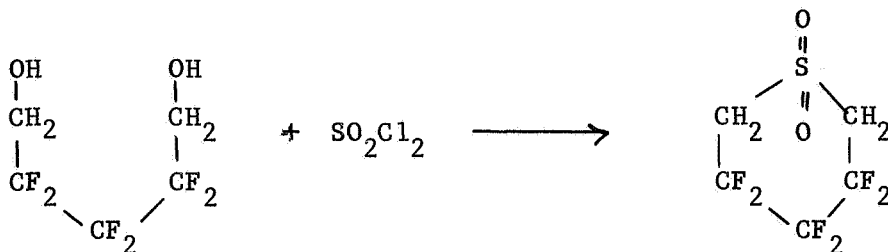
Into a 250-ml, three-necked flask equipped with a stirrer, condenser, thermometer, and dropping funnel was added hexafluoropentanediol (42.4 g, 0.2 mole) in 50 ml of pyridine. Sulfuryl chloride (40.5 g, 0.3 mole) was added to the pyridine solution at 8°-16°C over a 25-minute period with mixing. An additional 50 ml of pyridine was required to facilitate mixing. The slurry was then stirred for ½ hour at 7°-15°C, then 3 hours at room temperature, then filtered. After distilling the filtrate to 270°C, a black semisolid remained which could not be purified.

6. **Preparation of Perfluoroadipamide**

    a. **Preparation of 1,2-Dichloro-octafluorocyclohexene**
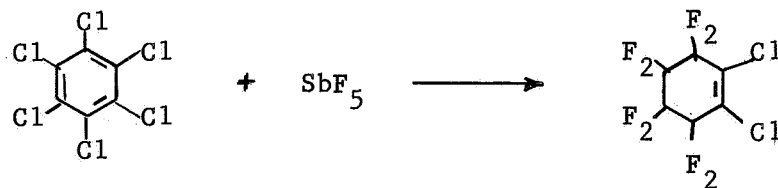
Hexachlorobenzene (681 g, 2.39 mole) was charged to a 3-liter, three-necked, round-bottomed flask fitted with a stirring motor, addition funnel, dry nitrogen purge, thermometer, and reflux condenser in series with a Vigreaux column and a dry ice — acetone packed Dewar condenser. Antimony pentafluoride (2270 g, 10.04 moles) was added, forming a slurry which gradually turned a sky-blue color. The heavy slurry was stirred overnight (by this time the color had deepened to a dark blue). The temperature was increased to 100°C (by means of an oil bath) and held for 2 hours. The color turned a dark royal purple. The condenser was changed to a distilling arrangement and the receiver fitted with a dry ice — acetone filled Dewar flask. The temperature of the slurry was increased to 130°C at which point the slurry solidified. The temperature was increased to 155°-160°C when material slowly began distilling. The distillation was continued until no more distillate was collected (4 hours). The distillate was then steam-distilled, the pink organic layer separated and washed twice with

250-ml portions of 17% hydrochloride acid. (The pink color was discharged upon addition of the acid.) The organic layer was again separated and dried over anhydrous magnesium sulfate. After filtration, the crude 1,2-dichlorooctafluoro-cyclohexene was distilled through a 12-in. helix packed column, the fraction boiling at 110°-113°C being collected. (Lit. value 111°-113°C[27]). The yield was 325.2 g (46.1%). The infrared spectrum is given in Figure 24.

	% C	% F	% Cl
Calculated for $C_6Cl_2F_8$:	24.4	51.5	24.1
Found:	23.9	51.4	24.5

b, Attempted Preparation of Perfluoroadipic Acid Dihydrate
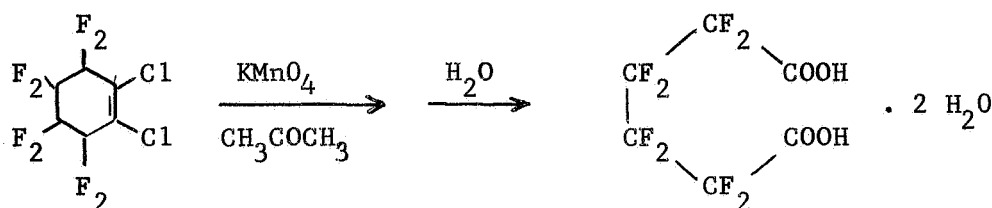
Acetone was purified by refluxing in the presence of potassium permanganate until a pink color remained, followed by distillation over anhydrous magnesium sulfate. Potassium permanganate (3.65 g, 0.023 mole) was added to 100 ml of purified acetone in a 250-ml, three-necked, round-bottomed flask fitted with a dry ice — acetone filled Dewar condenser, stirrer, thermometer, dry nitrogen purge, and addition funnel. 1,2-Dichlorooctafluorocyclohexene (6.5 g, 0.022 mole) was slowly added to the stirrer permanganate solution. After 2 ml of the olefin had been added, the temperature of the reaction mixture had risen to 40°C along with the formation of a brown precipitate. An ice-water cooling bath was placed under the reaction flask and the slow addition continued. The mixture was held at 0°C for ½ hour following addition of the olefin. The temperature was raised to 25°C and the solution allowed to stand for 45 minutes at room temperature. Upon addition of water (25 ml), a flocculent brown precipitate of manganese dioxide formed. The solids were filtered off and the acetone removed from the strongly acidic filtrate by distillation. The excess water was azeotroped with benzene and the resulting clear solution stripped of solvent under reduced pressure. A white crystalline material (6.0 g) was recovered. This material melted with decomposition at 226°-242°C. Extraction in a Soxhlet-Allihn apparatus with di-isopropyl ether for 16 hours was unsuccessful (no transfer of material to the solvent). Titration of the residue with aqueous potassium hydroxide resulted in an acid equivalent of 554 g/mole-COOH (theoretical for perfluoroadipic acid dihydrate = 163 g/mole-COOH).
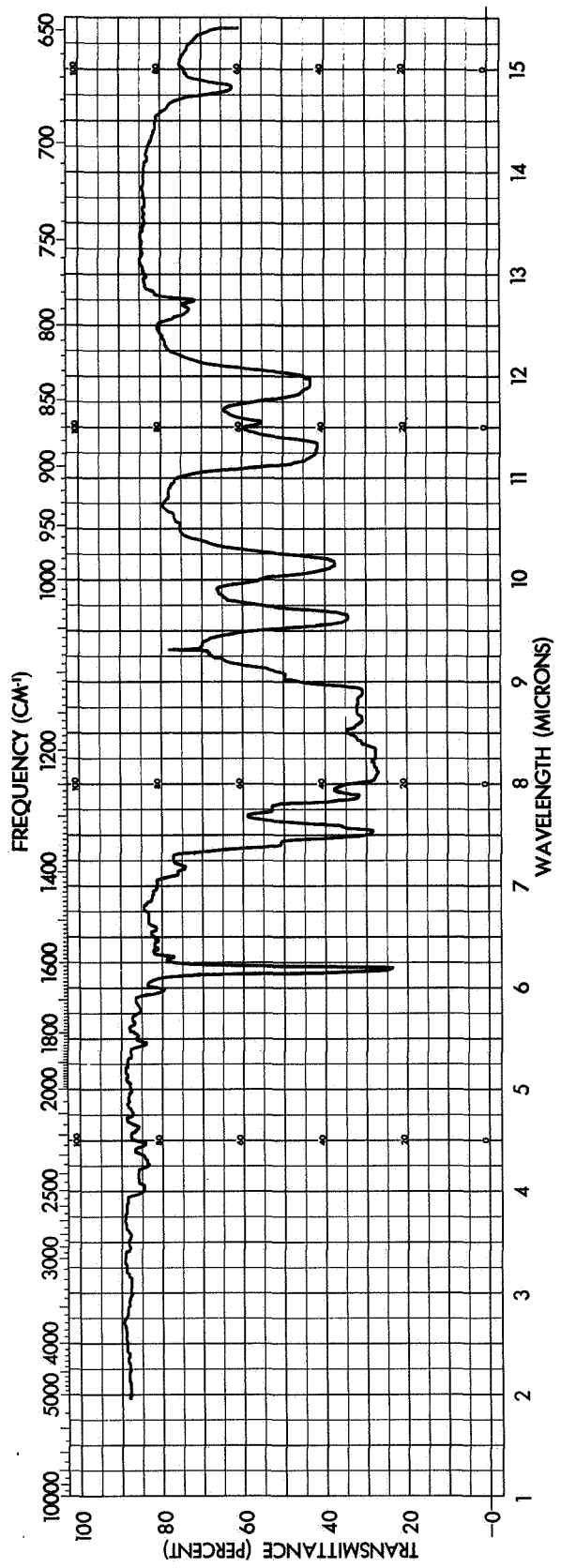
c. Preparation of Perfluoroadipyl Chloride

130
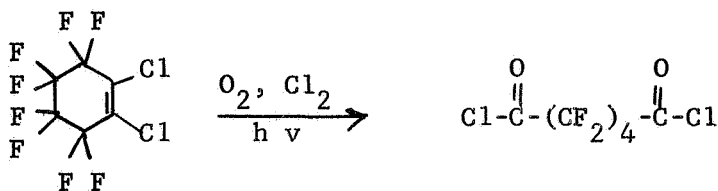
Figure 24. 1,2-Dichlorooctafluorocyclohexene

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1,2-Dichloro-octafluoro cyclohexene (475.5 g, 1.61 mole) was charged to the 1-liter, three-necked, round-bottomed flask fitted as illustrated in Figure 25. The olefin was circulated through the illuminated Vycor column at approximately 10 ml/minute against a counter-current flow of oxygen gas ($\sim$ 10 ml/minute) and chlorine gas (10 ml/minute) at a temperature of 25°-30°C. The reaction was continued for a total of 20 hours. The reaction mixture was distilled through a vacuum-jacketed, helix-packed, 1-cm x 30-in. column, the fraction boiling at 130°-132°C being collected [literature value 131°C [28]]. The yield of perfluoroadipyl chloride was 56.7 g (10.6%). Analysis by vapor phase chromatography indicates a 99+% purity. Its infrared spectrum is shown in Figure 26.

d. Preparation of Perfluoroadipamide

$$\underset{\substack{\text{O}\\||}}{\text{Cl-C}}-(CF_2)_4-\underset{\substack{\text{O}\\||}}{\text{C-Cl}} + NH_3 \longrightarrow \underset{\substack{\text{O}\\||}}{H_2N-C}-(CF_2)_4-\underset{\substack{\text{O}\\||}}{\text{C-NH}_2}$$

A 250-ml, round-bottomed flask equipped with a stirrer, thermometer, addition funnel, and Dewar condenser was cooled to -30°C. Ammonium hydroxide (50 ml of 15 N NH_4OH, 0.75 mole of NH_3) and approximately 20 ml of liquid ammonia (1 mole) were introduced to the cooled flask. Perfluoroadipyl chloride (32.7 g, 0.1 mole) was added dropwise with continuous stirring. After all the acid chloride had been added, the Dewar condenser was removed and the excess ammonia allowed to evaporate. The slurry was filtered and the crude diamide dried in a vacuum oven at 90°C. The weight of crude diamide was 24.1 g (84% yield). A small amount of crude diamide was recrystallized from water. The pure diamide had a melting point of 243°-244°C (lit. value 237°C uncorrected) [27] The infrared spectrum is attached as Figure 27.

7. Improvement in the Process for the Preparation of Tetrafluoro-p-phenylenediamine

Tetrafluoro-p-phenylenediamine was prepared as described on Page 59 of Annual Summary Report I (July 1964) with the following change: The crude 1,4-diphthalimidotetrafluorobenzene was reacted with 6 moles of hydrazine per mole of diphthalimide. The previous ratio had been 3:1. This increased the yield from 47% to 64%. Ether extractions of the filtrate raised the yield to 68%.

8. Tetrafluoro-p-phenylene Diisocyanate

a. Improvement in Preparation

To Dry Ice — Acetone Trap

Dry Ice — Acetone Condenser

24-in. x 1-in. Vycor Column

Flow Regulator Valve

Reflector Shield

Flowmeter

Cl_2 (gas)

Ultraviolet Lamp

O_2 (gas)
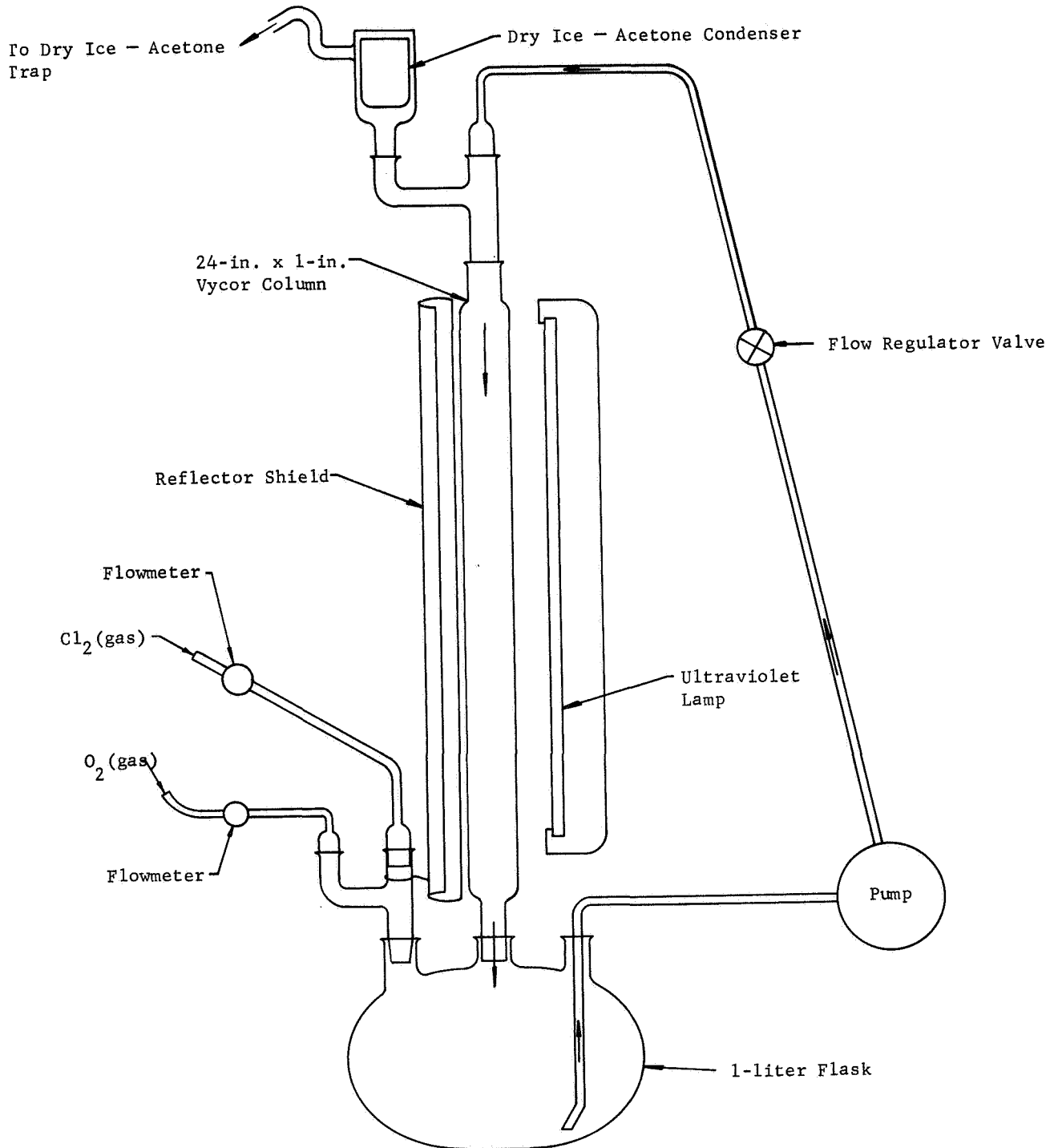
Flowmeter

Pump
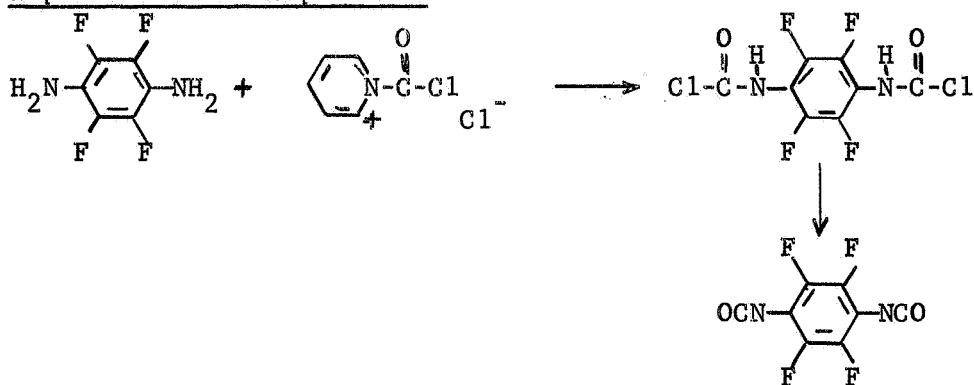
1-liter Flask
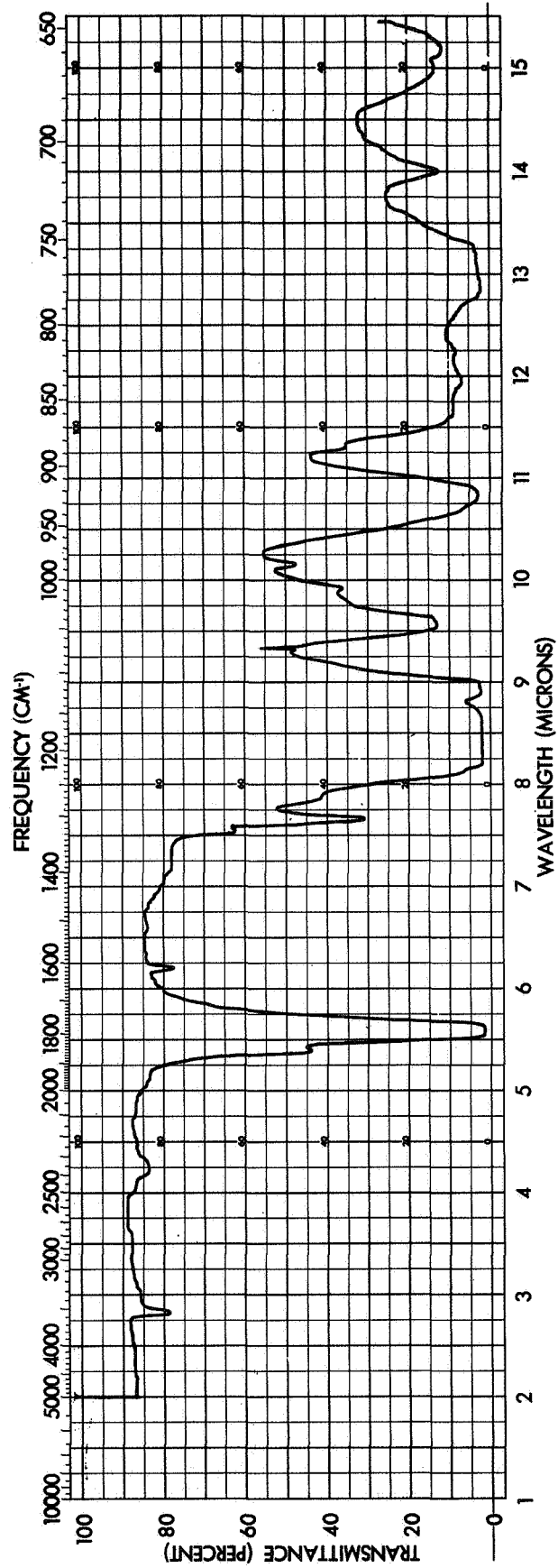
Figure 25. Photo-oxidative Cleavage Apparatus
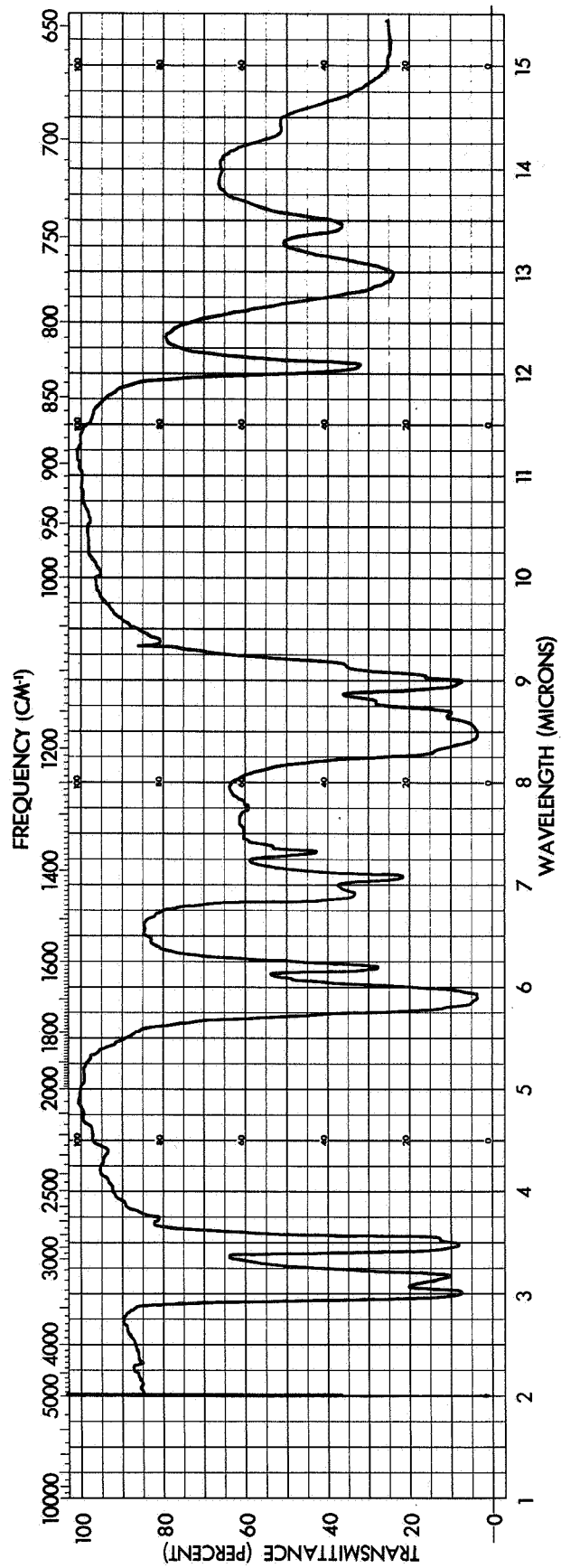
Figure 26. Perfluoroadipyl Chloride

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Figure 27. Perfluoroadipamide

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Phosgene (65 g, 0.64 mole) was condensed into 200 ml of dry ether at $0°C$ in a 2-liter, three-necked, round-bottomed flask fitted with a dry ice — acetone filled Dewar condenser, two addition funnels fitted with pressure equalizing arms under argon purge, stirring motor, and gas ($COCl_2$) inlet tube. Pyridine (49 g, 0.62 mole) was added to the phosgene solution, and a yellow precipitate of chlorocarbonyl pyridinium chloride formed. Tetrafluoro-p-phenylenediamine (19.4 g, 0.11 mole) dissolved in 250 ml of dry ether was added over a 15-minute period to the reaction mixture which was cooled in an ice bath. The cooling bath was removed and the solution stirred at room temperature for 3 hours. The white precipitate was filtered from the ether solution and the ether evaporated from the filtrate to yield 18.1 g (78%) of crude diisocyanate. The crude diisocyanate was extracted for 3 hours with dry hexane in a Soxhlet extracter under argon. The hexane was evaporated under reduced pressure yielding 13.0 g (53%) of tetrafluoro-p-phenylene diisocyanate.

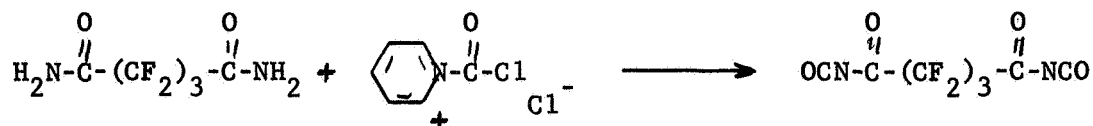b. Study of Dimerization and Trimerization

Three solutions of tetrafluoro-p-phenylene diisocyanate (0.5 g) in trichloroethylene (10 ml) were prepared. Three drops of stannous octoate was added to Solution No. 2 and three drops of triethylamine to Solution No. 3. Nothing was added to Solution No. 1. Immediately after preparation, the infrared spectra of the solutions were identical and showed no absorption bands between 4.5 μ and 6.35 μ. After 100 hours at room temperature, the spectra of Solutions Nos. 1 and 2 were unchanged, but the spectrum of Solution No. 3, containing triethylamine, showed new absorption bands at 5.75 μ and 7.15 μ. These bands are indicative of dimerization or trimerization of the isocyanate group. The infrared spectra of these solutions are shown in Figure 28 (immediately after preparation) and Figure 29 (after 100 hours).

c. Hydrolysis of Tetrachloro-p-phenylene Diisocyanate, Toluene-2,4-Diisocyanate and Tetrafluoro-p-phenylene Diisocyanate

Tetrachloro-p-phenylene diisocyanate was finely pulverized and suspended in boiling water for 2½ hours. Based on the infrared spectra, there was only slight hydrolysis. Under the same conditions, toluene-2,4-diisocyanate hydrolyzed within 10 minutes to the diamine, and tetrafluoro-p-phenylene diisocyanate hydrolyzed with extreme rapidity.

Tetrachloro-p-phenylene diisocyanate was dissolved in tetrahydrofuran. When water was added, there was slow evolution of carbon dioxide. Under the same conditions, toluene-2,4-diisocyanate hydrolyzed quickly with rapid evolution of carbon dioxide, and tetrafluoro-p-phenylene diisocyanate hydrolyzed almost instantly.

9. Attempted Preparation of Perfluoroglutaryl Diisocyanate

$$H_2N-\overset{\overset{O}{\|}}{C}-(CF_2)_3-\overset{\overset{O}{\|}}{C}-NH_2 \; + \; \left[\begin{array}{c}\text{pyridinium}\end{array}\right]\!N-\overset{\overset{O}{\|}}{C}-Cl \;\; Cl^- \longrightarrow OCN-\overset{\overset{O}{\|}}{C}-(CF_2)_3-\overset{\overset{O}{\|}}{C}-NCO$$

Phosgene (0.3 mole) was condensed into 200 ml of a 50/50 mixture of dimethylsulfoxide and 3-methyl sulfolane at $0°C$ in the reaction flask of the phosgenation apparatus. Pyridine (19.7 g, 0.25 mole) in 50 ml of the same
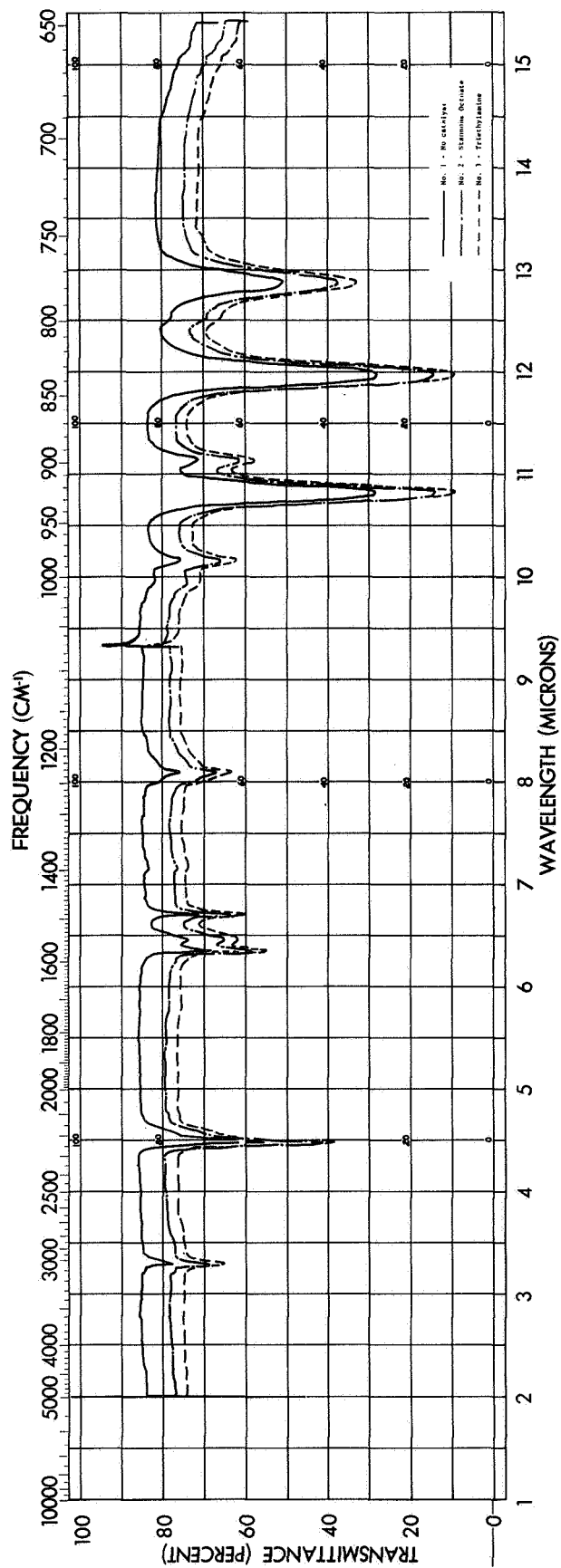
Figure 28. Solutions of Tetrafluoro-p-phenylene Diisocyanate in Trichloroethylene
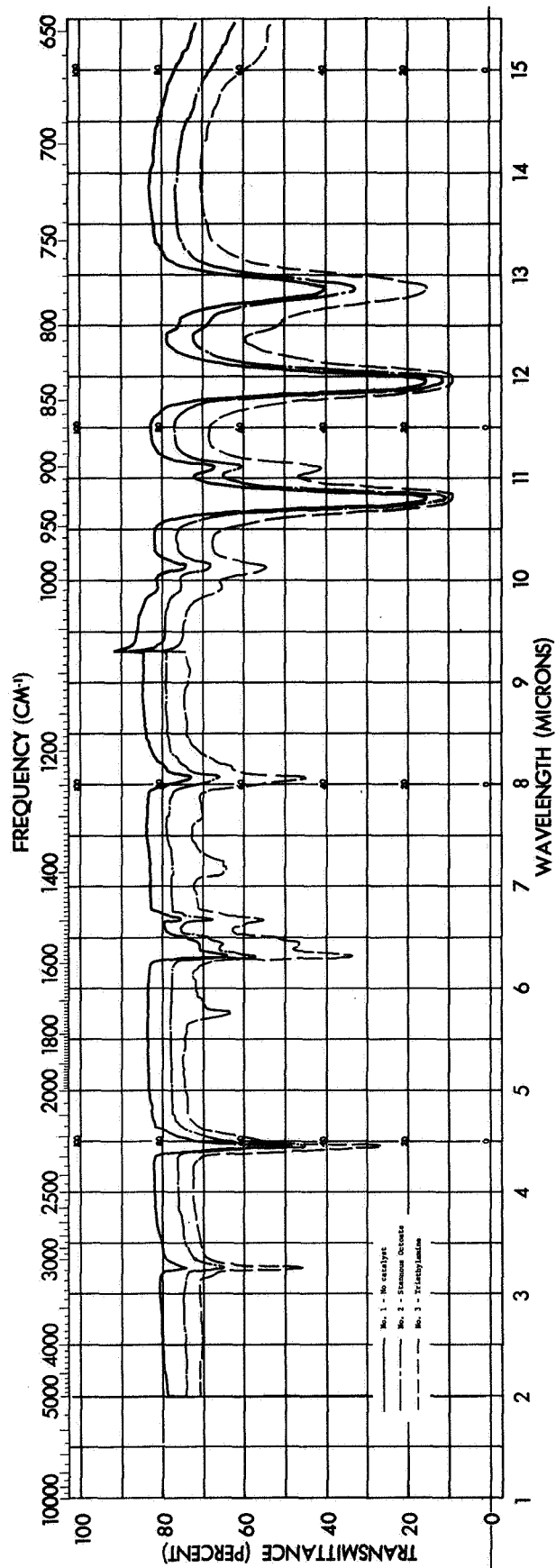Immediately after Preparation

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Figure 29. Solution of Tetrafluoro-p-phenylene Diisocyanate in Trichloroethylene after 100 Hours

solvent was added over a 10-minute interval with mixing. No precipitate formed. Perfluoroglutaramide (14.5 g, 0.061 mole) was dissolved in 100 ml of the above solvent mixture and added over a 15-minute period with stirring. The mixture was allowed to come to room temperature and held for 3 hours with constant agitation. The clear yellow-brown solution was distilled with an argon purge; the first fraction boiled at 70°C. Sublimation of a white crystalline material (pyridine hydrochloride) occurred at 80°C. The head temperature continued to rise to 140°C. The distillation was discontinued overnight and continued the following day. The distillate was collected in a receiver chilled with a dry ice — acetone mixture. Upon warming the distillate, a very low boiling material (less than -10°C) began coming off which had a sulfurlike odor. None of the desired product was obtained.

10. Preparation of 2,3,5,6-Tetrachloro-p-xylylene-α,α'-diisocyanate
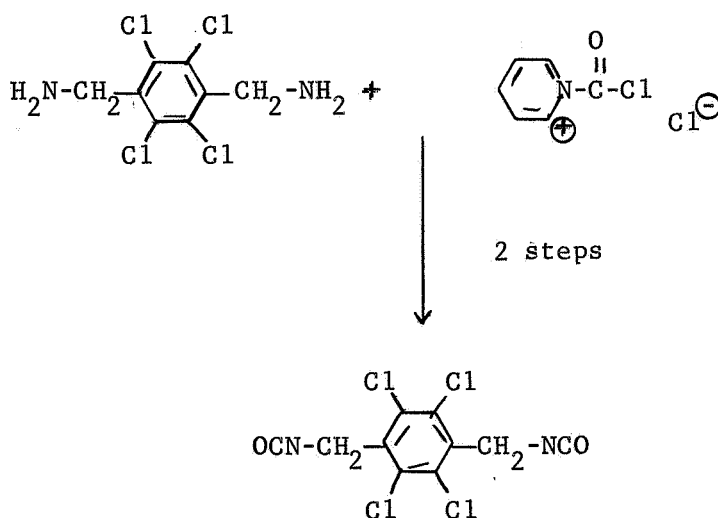
Phosgene (45 g, 0.45 mole) was condensed (at -30°C) into THF (which had been dried over sodium) in the reaction flask of the phosgenation apparatus. Pyridine (31.69 g, 0.40 mole) in THF (50 ml) was added to the phosgene solution. The yellow slurry of chlorocarbonyl pyridinium chloride formed. The temperature was allowed to rise to 25°C and 2,3,5,6-tetrachloro-p-xylylene-α,α'-diamine (27.4 g, 0.1 mole) dissolved in THF (500 ml) was slowly added to the reaction mixture. The slurry was stirred at room temperature for 40 hours. The yellow precipitate slowly faded to a yellowish gray. The solids were filtered off. The residue was soluble in water only with difficulty. The filtrate was stripped of solvent yielding 36.1 g of parchmentlike material. Xylene (200 ml) was added and the mixture refluxed (139°C) for 2 hours, with evolution of hydrogen chloride. The insoluble residue (0.5 g) was filtered from the hot solution and the clear filtrate allowed to stand overnight at room temperature, during which a semisolid gel formed. The gel was broken with hexane (200 ml). An insoluble residue (5.7 g), very similar in appearance to the parchmentlike material described above, was filtered off. The filtrate stood for 40 hours at room temperature during which time 0.2 g of additional polymeric material formed and precipitated. The precipitate was removed by filtration, followed by stripping of the filtrate at reduced pressure to yield 22.3 g (68.5%) of tan crystalline material, mp 101°-105°C. Extraction of the crude material with ligroine in the Soxhlet extraction apparatus, followed by stripping off the solvent under reduced pressure yielded 13.8 g (42.3% overall yield) of purified 2,3,5,6-tetrachloro-p-xylylene-α,α'-diisocyanate, mp 106°-108°C. The infrared spectrum is presented as Figure 30.
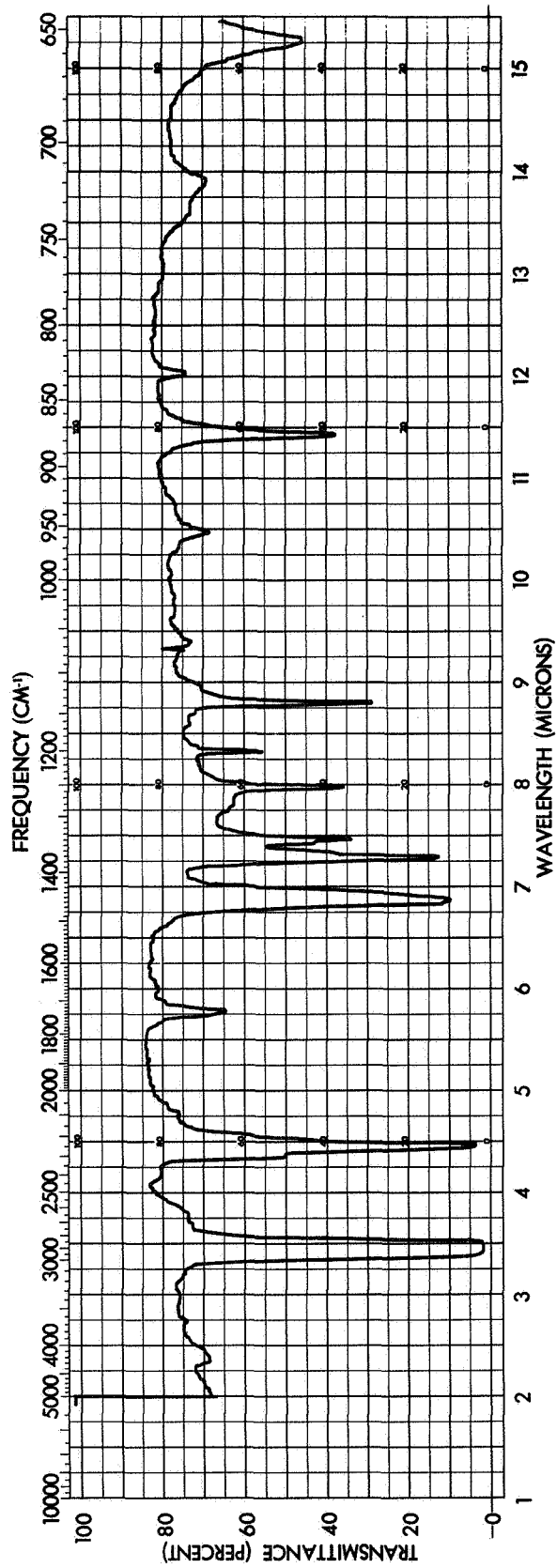
Figure 30. 2,3,5,6-Tetrachloro-p-Xylylene-α,α'-Diisocyanate

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a. Preparation of Di-N-methylanilino Derivative of 2,3,5-6-
    Tetrachloro-p-xylylene-α,α'-diisocyanate

2,3,5,6-Tetrachloro-p-xylylene-α,α'-diisocyanate (0.69 g, 0.0018 mole) was dissolved in dry benzene (10 ml). Excess N-methylaniline (1.0 g, 0.01 mole) was added and the solution refluxed for 15 minutes. The white crystalline solid was filtered off and washed twice with hexane. The melting point of the di-anilino derivative was 236°-238°C. The infrared spectrum is shown as Figure 31.

11. Preparation of 4,4'-Diisocyanato-octafluorobiphenyl
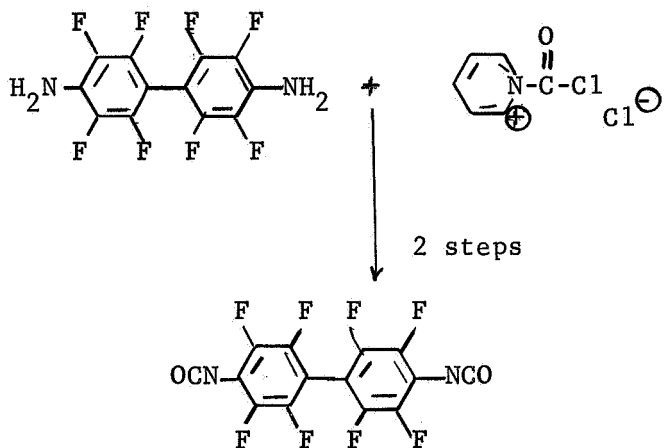
Phosgene (50 g, 0.5 mole) was condensed in 500 ml of anhydrous ether at -40°C in the flask of the phosgenation apparatus. Pyridine (31.6 g, 0.40 mole) in 100 ml of ether was added and the resulting yellow slurry was allowed to slowly warm to room temperature as 4,4'-diamino-octafluorobiphenyl (32.8 g, 0.1 mole) in 400 ml of ether was added over a 45-minute period. The yellow color of the chlorocarbonyl pyridinium chloride slurry slowly faded, being re-placed by the white precipitate of pyridinium chloride. After 2 hours of stirring at room temperature, the solids were filtered off and the ether stripped from the filtrate yielding 32.7 g of crude 4,4'-diisocyanato-octa-fluorobiphenyl. The crude product was extracted with dry ligroine in the Soxhlett apparatus. The solvent was stripped under reduced pressure yielding 23.3 g (62.8% yield) of 4,4'-diisocyanato-octafluorobiphenyl as a white crystalline solid, mp 68.5°-69.5°C. The molecular weight (based on isocyanate equivalency) was determined to be 374 (theoretical M.W. = 380). The infrared spectrum is shown as Figure 32.

Elemental analysis of 4,4'-Diisocyanato-Octafluorobiphenyl

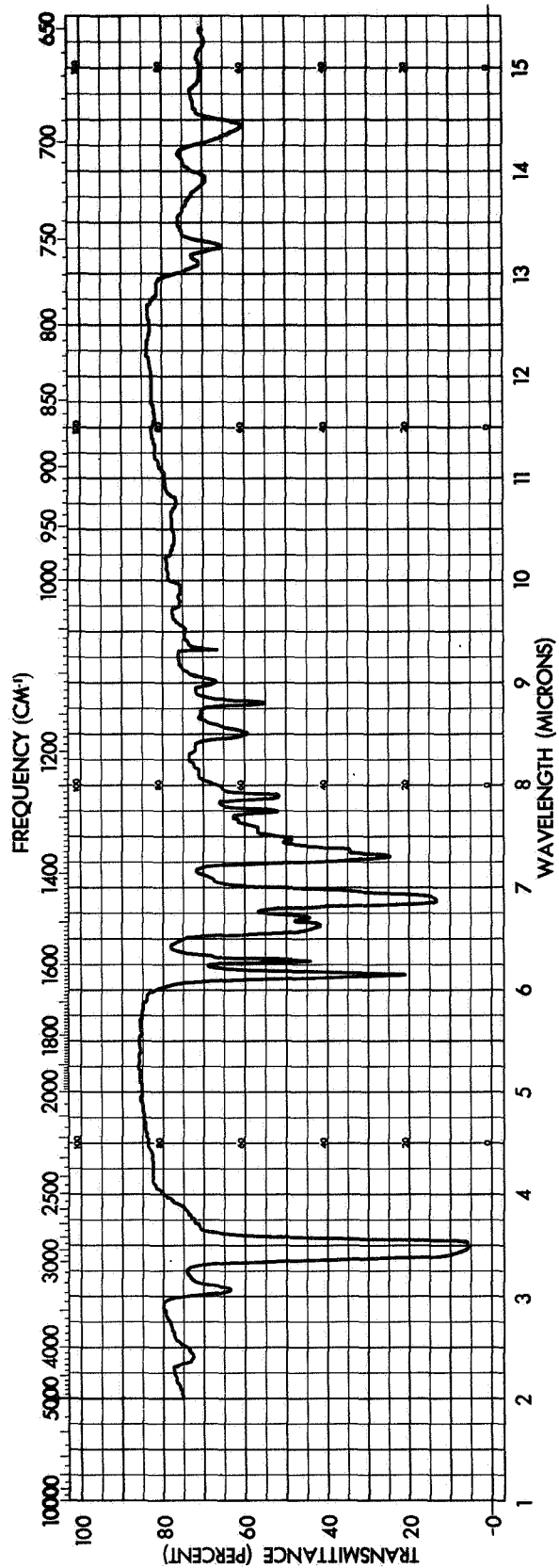|	% C	% F	% N
Calculated for $C_{14}N_2O_2F_8$:	44.23	39.98	7.12
Found:	44.73	39.85	7.22

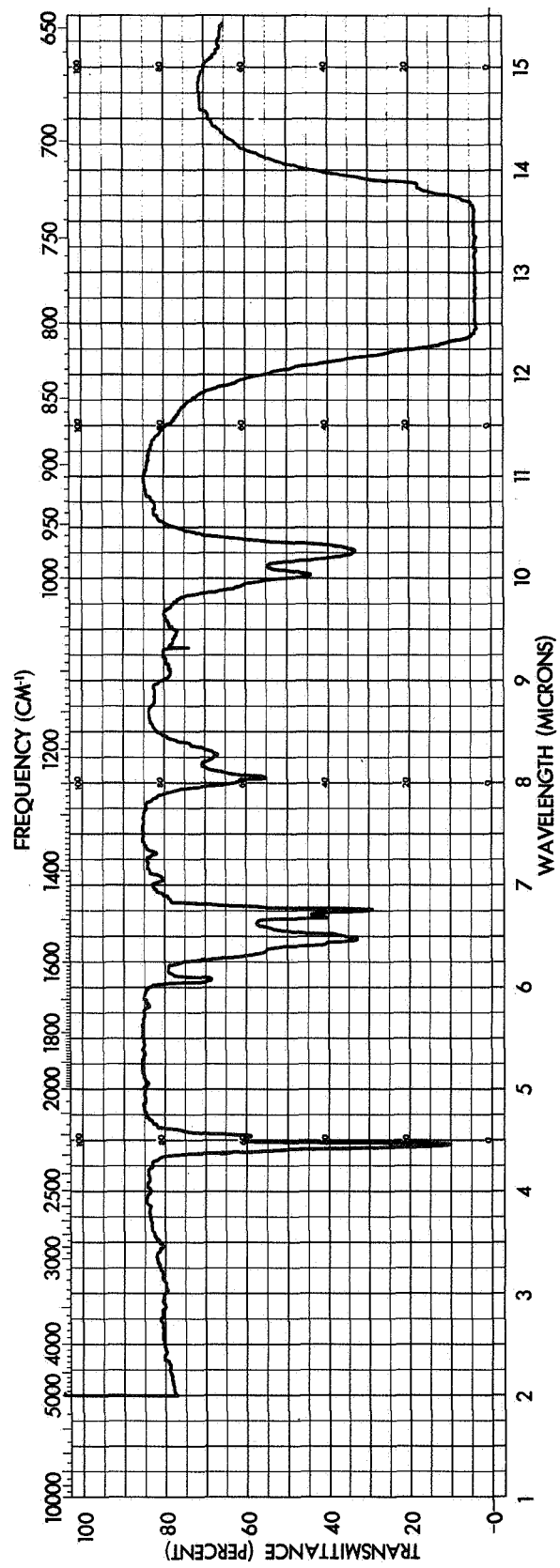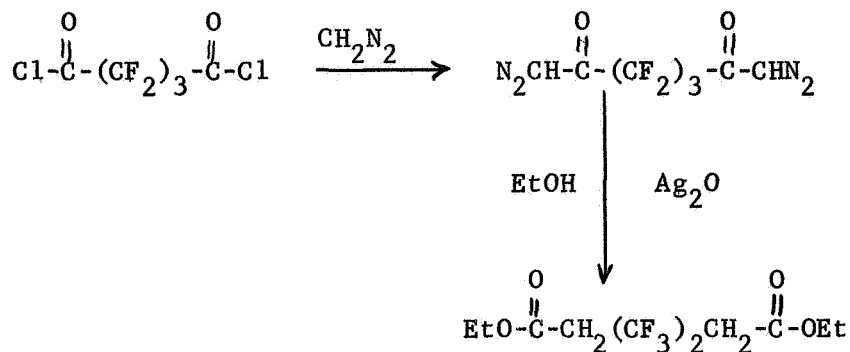Figure 31. Di-N-Methylanilino Derivative of 2,3,5,6-Tetrachloro-p-Xylylene-α,α'-Diisocyanate

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Figure 32. 4,4'-Diisocyanato-Octafluorobiphenyl (In carbon tetrachloride)

12. Attempted Preparation of Diethyl 3,3,4,4,5,5-Hexafluoropimelate

$$Cl-\overset{\overset{O}{\|}}{C}-(CF_2)_3-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{CH_2N_2} N_2CH-\overset{\overset{O}{\|}}{C}-(CF_2)_3-\overset{\overset{O}{\|}}{C}-CHN_2$$

$$EtOH \quad \Big\downarrow \quad Ag_2O$$

$$EtO-\overset{\overset{O}{\|}}{C}-CH_2(CF_3)_2CH_2-\overset{\overset{O}{\|}}{C}-OEt$$

a. Preparation of Diazomethane [39]

Redistilled carbitol (2-ethoxy-ethoxy ethanol, 1 liter), diethyl ether (300 ml), water (300 ml), and potassium hydroxide (168 g) were charged to a 12-liter, three-necked, round-bottomed flask fitted with an air-driven stirring motor, addition funnel, and distillation head fitted with a water-cooled condenser. The outlet of the condenser was fed into two series connected collection flasks at 0°C (ice-bath cooled). The inlet tube of the second receiver dipped below the surface of 200 ml of anhydrous ether. The alkaline solution was heated to 70°-80°C on a steam bath and N-methyl-N-nitroso-p-toluenesulfonamide (Diazald) (602 g, 2.80 mole) in 4 liters of ether was added over a 16-hour period. The ether distillates were combined, dried over potassium hydroxide, and the diazomethane content determined by reaction of an aliquot with benzoic acid and back titration of the excess with potassium hydroxide, yield: 4500 ml of 0.46 M diazomethane solution (74%).

b. Preparation of Bis-diazo(3,3,4,4,5,5-hexafluoroheptane-2,6-dione)

The ethereal solution of diazomethane was charged to a 12-liter, three-necked, round-bottomed flask fitted with a reflux condenser, air—driven stirrer motor, dry nitrogen inlet, and addition funnel. The solution was cooled to 5°C (ice bath). Perfluoroglutaryl chloride (121 g, 0.68 mole) in 400 ml of anhydrous ether was added to the cooled solution, with stirring, over a 3-hour period. Following addition, the ice bath was removed and the solution stirred for 3 hours at room temperature. The ether was stripped off under reduced pressure yielding a dark red oil.

c. Preparation of Diethyl-3,3,4,4,5,5-hexafluoropimelate

Without further purification, the crude diazoketone was dissolved in 300 ml of anhydrous ethanol and charged to a 1-liter, three-necked flask fitted with a stirring motor, reflux condenser, and addition funnel. The solution was heated to 65°C and a slurry of silver oxide (7.0 g) in 250 ml of ethanol was added over a 1-hour period. The solution was refluxed for 24 hours, decolorizing charcoal added, and the mixture filtered hot. The filtrate was fractionally distilled under reduced pressure, yielding two fractions boiling at 51°-52°C/ 2 mm and 89°-91°C/3 mm. None of the desired product was obtained.

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

$$CH_3-\left\langle \bigcirc \right\rangle-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-CH_2(CF_2)_3CH_2-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\left\langle \bigcirc \right\rangle-CH_3 \xrightarrow[CuCN]{KCN} NC-CH_2(CF_2)_3CH_2-CN$$
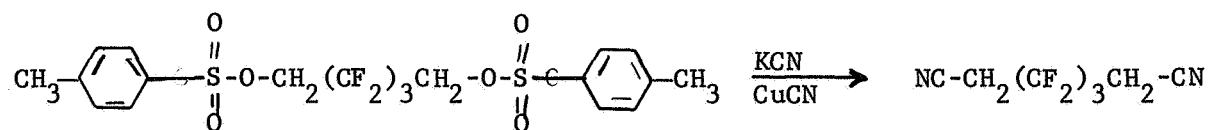
The ditosyl ester of hexafluoropentanediol was charged to a 500-ml, three-necked, round-bottomed flask fitted with a stirrer, reflux condenser, and dry nitrogen gas inlet. Following addition of the appropriate solvent, the other reagent(s) was(were) added. The mixture was refluxed for 24 hours. The solutions were cooled and the solids filtered off. The solid material was examined for reaction products by infrared spectroscopy. The liquid portion was fractionally distilled under reduced pressure. In no case was any of the desired product obtained.

Table 4 lists the quantities, reactants, and solvents utilized.

TABLE 4

REACTIONS OF DITOSYL ESTER OF HEXAFLUOROPENTANEDIOL WITH METAL CYANIDES

Ditosyl Ester of Hexafluoropentanediol, moles	Potassium Cyanide, moles	Cuprous Cyanide, moles	Solvent System, ml	Reflux Temp, °C
0.05	0.25	--	Acetonitrile (250)	88
		--	Acetonitrile (125) + methyl cellosolve (125)	96
		--	Methyl cellosolve (250)	190
	0.10	--	Diethylacetamide (150)	170
	0.10	0.02	Diethylacetamide (150)	170
	--	0.10	Diethylacetamide (150)	170
0.02	0.10*	--	N-methyl pyrrolidone	202

* Sodium cyanide

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14. Preparation of Dibutoxymethane

$$2 \ C_4H_9OH \ + \ \underset{\substack{\text{trioxane}}}{} \ \xrightarrow{\text{CH}_3\langle\!\!\!\!\!\bigcirc\!\!\!\!\!\rangle\text{SO}_3\text{H}} \ C_4H_9\text{-}O\text{-}CH_2\text{-}O\text{-}C_4H_9$$
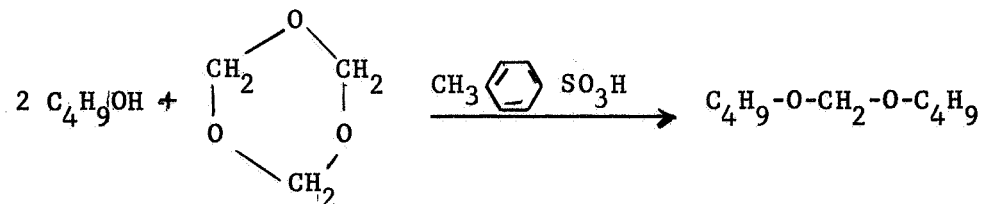
Symmetrical trioxane (30.0 g, 0.33 mole), n-butanol (87.5 g, 2.53 mole) and p-toluenesulfonic acid (5.0 g) were charged to a 500-ml, three-necked flask equipped with a stirrer, thermometer, and condenser fitted with a drying tube. The solution was refluxed and stirred at 100°-110°C for 17 hours. The solution was then cooled to room temperature and washed with a 2½% solution of sodium carbonate to remove the acid. The impure product was then washed with a solution of 5% hydrogen peroxide containing 10 ml of 10% sodium carbonate to remove the unreacted aldehyde. It was then washed with water and dried with anhydrous potassium carbonate. The crude formal was then fractionated to remove the pure dibutoxymethane, bp 180.5°C (lit. value 181°C).[40] The infrared spectrum is attached as Figure 33.
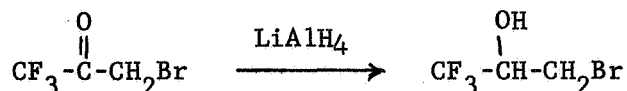
15. Preparation of 3,3,3-Trifluoro-1,2-epoxypropane

a. Bromination of 1,1,1-Trifluoroacetone[30]

A 500-ml, round-bottomed flask was equipped with a stirrer, thermometer, addition funnel, and Dewar condenser and cooled using a dry ice — acetone bath. Into this flask were introduced 1,1,1-trifluoroacetone (141.5 g, 1.26 mole) and 230 ml of concentrated sulfuric acid. The mixture was allowed to reach room temperature, then bromine (100 g, 0.625 mole) was added dropwise with constant stirring over a period of 4½ hours. When all the bromine had been added, the mixture was transferred to a separatory funnel. The top portion containing principally the 3-bromo-1,1,1-trifluoroacetone was removed. The bottom layer was distilled and the fraction boiling to 90°C was combined with the top portion. The crude product was then fractionally distilled using a 6-ft column. The product, 3-bromo-1,1,1-trifluoroacetone, was collected at 85°-86.5°C (literature value 85°-86.8°C). The yield was 74%; a vapor phase chromatograph showed the product to be 99+% pure. An infrared spectrum is shown as Figure 34.

b. Preparation of 3-Bromo-1,1,1-trifluoro-2-propanol

$$\underset{\text{CF}_3\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-CH}_2\text{Br}}{} \ \xrightarrow{\text{LiAlH}_4} \ \underset{\text{CF}_3\text{-}\overset{\text{OH}}{\overset{\text{\textbar}}{\text{CH}}}\text{-CH}_2\text{Br}}{}$$

A 1-liter, three-necked, round-bottomed flask was equipped with a stirrer, thermometer, condenser, and addition funnel. The apparatus was flushed with nitrogen for 15 minutes, then cooled using a dry ice — ethyl acetate bath. Lithium aluminum hydride (10.6 g, 0.78 mole) and 400 ml of anhydrous diethyl ether were introduced. The dry ice — ethyl acetate bath was removed and 3-bromo-1,1,1-trifluoro-2-propanone (169 g, 0.89 mole) dissolved in 150 ml of ether was added dropwise at such a rate as to produce a gentle reflux.
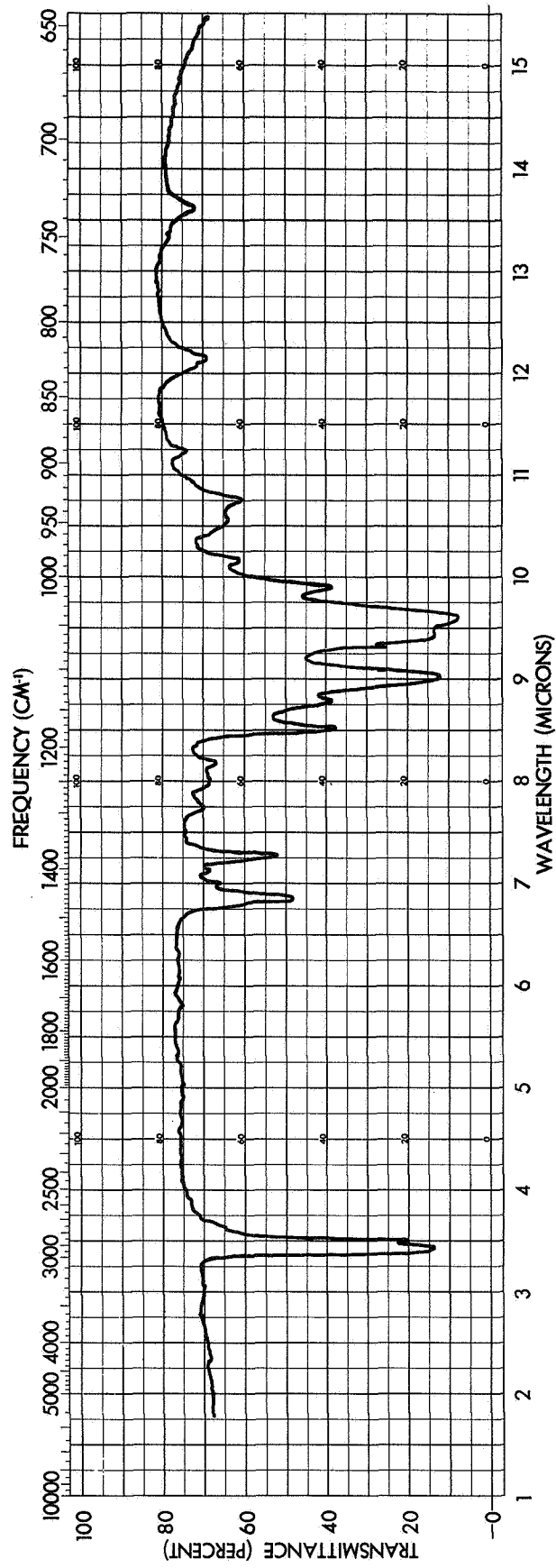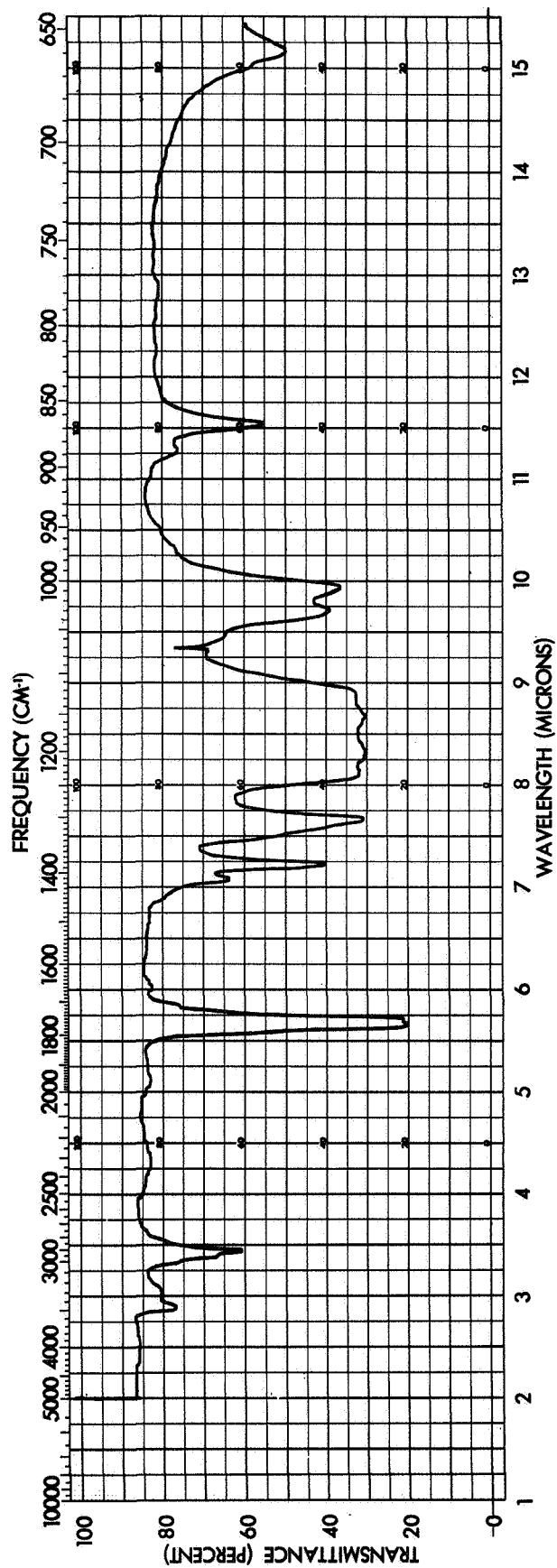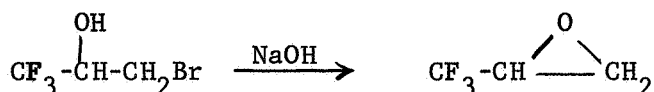
146

Figure 33.   Dibutoxymethane

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Figure 34. 3-Bromo-1,1,1-Trifluoroacetone

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Approximately 15 minutes after the addition of the ketone, sufficient water was added to destroy the excess lithium aluminum hydride (external cooling was necessary) followed immediately by 400 ml of 20% sulfuric acid. The mixture was then transferred to a separatory funnel and the sulfuric acid layer separated and washed with ether. The ether washings were combined with the ether layer. The ether solution was then dried over anhydrous magnesium sulfate and fractionally distilled using a 2-ft column. The 3-bromo-1,1,1-trifluoro-2-propanol distilled at 124°-126°C. (Lit. value 124.2°-124.5°C)[31] The total yield was 84.5%. The infrared spectrum is attached as Figure 35.

    c. Preparation of 3,3,3-Trifluoro-1,2-epoxypropane

$$\underset{\displaystyle CF_3-\overset{\displaystyle OH}{\overset{|}{C}}H-CH_2Br}{} \xrightarrow{\text{NaOH}} \underset{\displaystyle CF_3-CH\overset{O}{\diagup\diagdown}CH_2}{}$$

    A solution of sodium hydroxide (230 g) in 215 g of water was placed in a 500-ml, three-necked, round-bottomed flask equipped with a stirrer, addition funnel, thermometer, and Claisen head. The receiving flask equipped with a Dewar condenser, was cooled in a dry ice — acetone bath. The solution was heated to 98°C and 3-bromo-1,1,1-trifluoro-2-propanol (55.0 g, 0.284 mole) was added dropwise. The product distilled at 35°-38°C (lit. value 39.1°-39.3°C).[31] The distillation was continued for 15 minutes after the addition of the alcohol. The receiving flask was then cooled to -60°C and the ice removed by filtration to obtain pure product. The yield was 76%. The infrared spectrum is shown in Figure 36. The overall yield of 3,3,3-trifluoro-1,2-epoxypropane from 1,1,1-trifluoroacetone was 47.5%.

16. Attempted Preparation of Perfluoro-1,2-epoxypropane

$$CF_3-CF{=}CF_2 \xrightarrow{(O)} CF_3-CF\overset{O}{\diagup\diagdown}CF_2$$
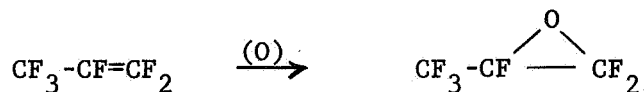
    Methanol (375 ml), potassium hydroxide (42.0 g, 0.75 mole) and water (75 ml) were charged to a 1-liter, three-necked flask equipped with a stirrer, gas inlet, thermometer and dry ice — acetone condenser. The condenser outlet led to two consecutive dry ice — acetone traps. The mixture was cooled to -40°C, then hydrogen peroxide (262.5 ml of 30%) was added. Perfluoropropene (60.0 g, 0.4 mole) was added to the stirred mixture below the liquid level over a 15-minute period. The solution was stirred for 1½ hours at -40°C. The solution was heated to -25°C, and the off-gases were collected in the traps. The product was then transferred directly to a metal cylinder containing 1.0 g of the monosodium salt of hexafluoropentanediol. The bomb was held at room temperature for 24 hours. On purification, no polymeric material was isolated.

17. Preparation of Chloropentafluoroisopropyl Alcohol

$$\underset{\displaystyle CF_3-\overset{O}{\overset{\|}{C}}-CF_2Cl}{} + LiAlH_4 \longrightarrow \underset{\displaystyle CF_3-\overset{OH}{\overset{|}{C}}H-CF_2Cl}{}$$
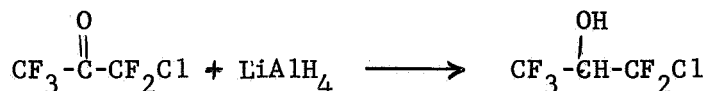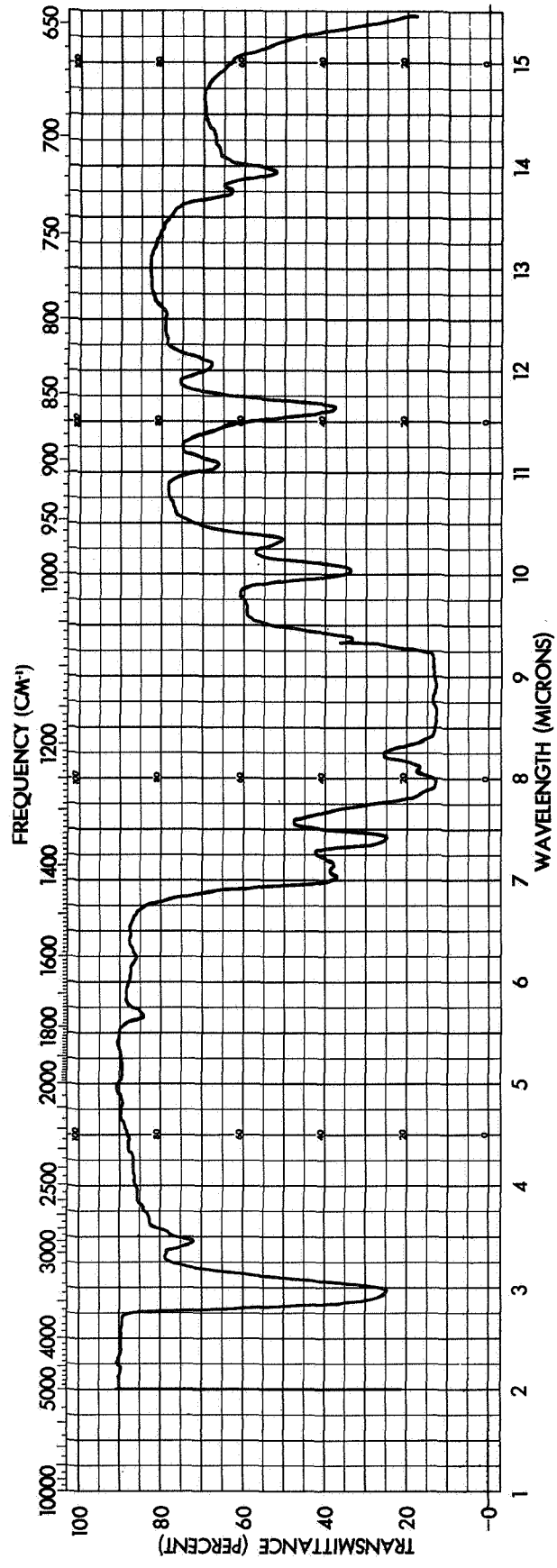
Figure 35. 3-Bromo-1,1,1-Trifluoro-2-Propanol
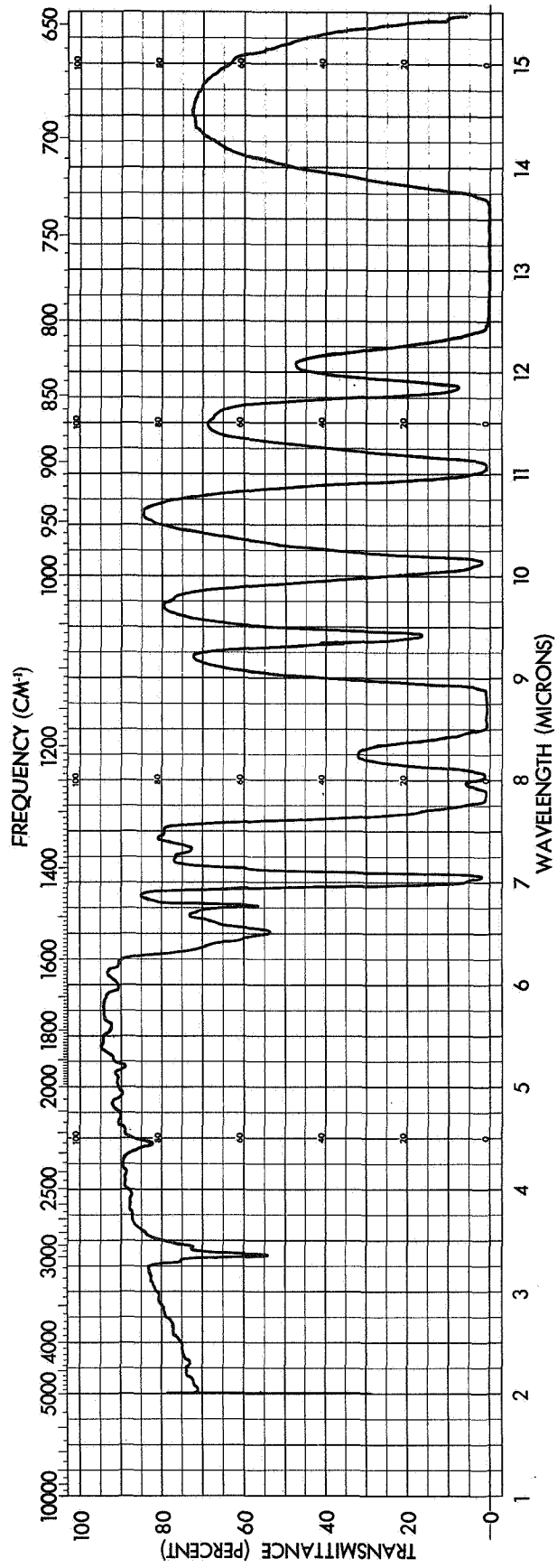
Figure 36. 3,3,3-Trifluoro-1,2-Epoxypropane (In Carbon Tetrachloride)

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Ether (300 ml) and lithium aluminum hydride (19.0 g, 0.5 mole) were charged to a 1-liter, three-necked flask equipped with a stirrer, Dewar condenser, thermometer and gas inlet. Chloropentafluoroacetone (148 g, 1.0 mole) was then introduced into the flask at -78°C. The slurry was mixed for ½ hour after the final addition of the ketone. Water was added cautiously until the evolution of hydrogen ceased, then 200 ml of 15% sulfuric acid was added. The layers were separated, the water layer washed with ether, and the ether layers combined and dried with magnesium sulfate. The ether was then removed and the crude reaction product fractionated, then separated in a preparative gas chromatograph. The reaction products consisted of the desired chloropentafluoroisopropyl alcohol, hydropentafluoroisopropyl alcohol, and an unidentified material.

18. Attempted Preparation of Trihexafluoropentamethylene Glycol

$$CH_3\text{-}\langle\rangle\text{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}\text{-O-CH}_2(CF_2)_3CH_2\text{-O-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}\text{-}\langle\rangle\text{-}CH_3 + Na^+{}^-OCH_2(CF_2)_3CH_2OH \longrightarrow$$

$$HO\text{-}[CH_2(CF_2)_3CH_2\text{-O}]_3\text{-}H$$
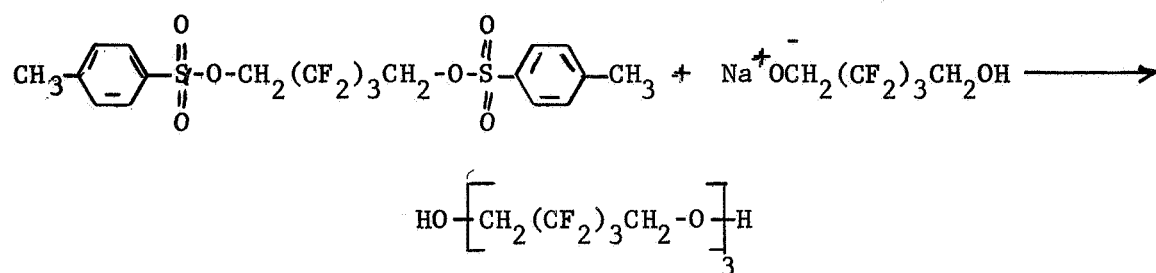
The ditosyl ester of hexafluoropentanediol (10.4 g, 0.02 mole), the monosodium salt of hexafluoropentanediol (9.4 g, 0.04 mole) and diethylene glycol (125 g) were added to a 250-ml, three-necked flask equipped with a stirrer, thermometer and condenser. The mixture was heated with stirring at 195°-200°C for 16 hours. The mixture was cooled, poured into water, filtered and dried. There was no reaction.

19. Preparation of 3,3,4,4-Tetrafluoro-tetramethylene Oxide

a. Preparation of 2,2,3,3-Tetrafluorobutanediol

$$\begin{array}{c} {}^{COOC_2H_5} \\ CF_2 \\ | \\ CF_2 \\ {}_{COOC_2H_5} \end{array} \xrightarrow{\text{LiAlH}_4} \begin{array}{c} {}^{CH_2OH} \\ CF_2 \\ | \\ CF_2 \\ {}_{CH_2OH} \end{array}$$
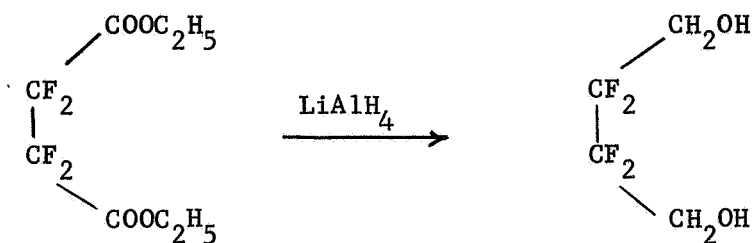
Tetrafluorobutanediol was prepared according to the procedure of McBee.[34] Its melting point was 83.0°-84.0°C (uncorrected) as compared to literature values of 85°C[34] and 80°-80.6°C.[41]

b. Preparation of 3,3,4,4-Tetrafluorotetramethylene Oxide[41]

$$HOCH_2CF_2CF_2CH_2OH + H_2SO_4 \longrightarrow \begin{array}{c} \overset{O}{\diagup\diagdown} \\ CH_2 \quad CH_2 \\ | \qquad | \\ CF_2 \text{---} CF_2 \end{array}$$
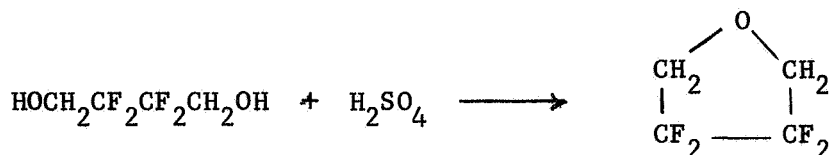
A 100-ml, three-necked flask equipped with stirrer and distilling head was placed into an oil bath. The flask was charged with tetrafluorobutanediol (9.8 g, 0.0605 mole) and concentrated sulfuric acid (15 g, 0.15 mole). Stirring was begun and the oil bath heated to 185°C. At a head temperature of about 40°C, a clear liquid distilled. The distillate was dried with Drierite, filtered, and redistilled. Clear, colorless 3,3,4,4-tetrafluoro-tetramethylene oxide was collected from 45°-47°C. The yield was 5.9 g (67%). The infrared spectrum is shown as Figure 37.

20. Attempted Preparation of 3,3-Difluorooxetane

a. Preparation of 2,2-Difluoropropane-1,3-diol

$$
\begin{array}{c}
COOC_2H_5 \\
| \\
CF_2 \\
| \\
COOC_2H_5
\end{array}
\quad + \quad LiAlH_4 \quad \longrightarrow \quad
\begin{array}{c}
CH_2OH \\
| \\
CF_2 \\
| \\
CH_2OH
\end{array}
$$
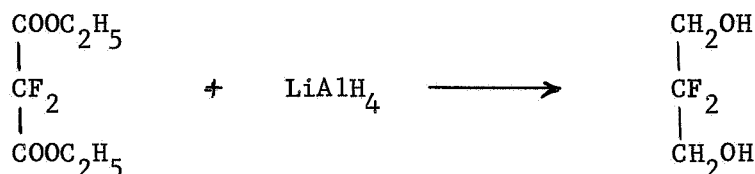
A 2-liter, three-necked flask fitted with a nitrogen gas inlet, addition funnel, stirrer, and reflux condenser was purged with nitrogen. To the flask was added lithium aluminum hydride (32.0 g, 0.843 mole) in 250 ml of anhydrous diethyl ether. On adding diethyl 2,2-difluoromalonate (103 g, 0.525 mole) to ether (200 ml), a white precipitate formed, which was possibly a complex of the fluorinated ester with ether. This slurry was added from an addition funnel over a 6-hour period to the ether solution of lithium aluminum hydride with continuous mixing under nitrogen. During the 6-hour addition, 250 ml of ether were added. When the addition was complete, the reaction mass was stirred for 16 hours at room temperature. Water (36 g, 0.2 mole) was then added dropwise over a period of 1½ hours, and the slurry was stirred for 1 additional hour. The reaction mixture was poured into 1 liter of 10% sulfuric acid solution, the ether layer separated, and the aqueous layer extracted thrice with ether. The ether extracts were combined and the ether removed by distillation. Benzene was then added and distillation continued to remove water. When no more water was evident in the distillate, the hot benzene solution was poured into a beaker. No diol crystallized. Upon removal of the solvent, the crude 2,2-difluoropropane-1,3-diol was recovered as an orange oil. Attempts to sublime solid product from the oil failed. Other attempts to purify this compound have been unsuccessful to date.

b. Attempted Preparation of 3,3-Difluorooxetane

$$
\begin{array}{c}
CH_2OH \\
| \\
CF_2 \\
| \\
CH_2OH
\end{array}
\quad \xrightarrow{H_2SO_4} \quad
\begin{array}{c}
CH_2 \\
/ \quad \backslash \\
CF_2 \quad \quad O \\
\backslash \quad / \\
CH_2
\end{array}
$$
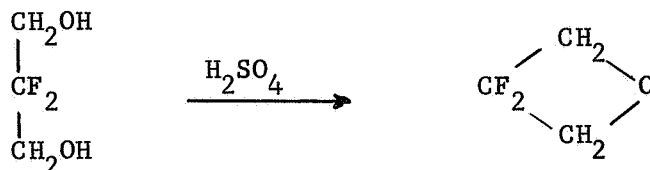
A 100-ml, three-necked flask was fitted with a nitrogen gas inlet, stirrer, and distilling head attached to a receiver immersed in a dry ice — acetone bath. Into the reaction flask was placed crude 2,2-difluoropropane-1,3-diol (10.9 g, 0.097 mole).
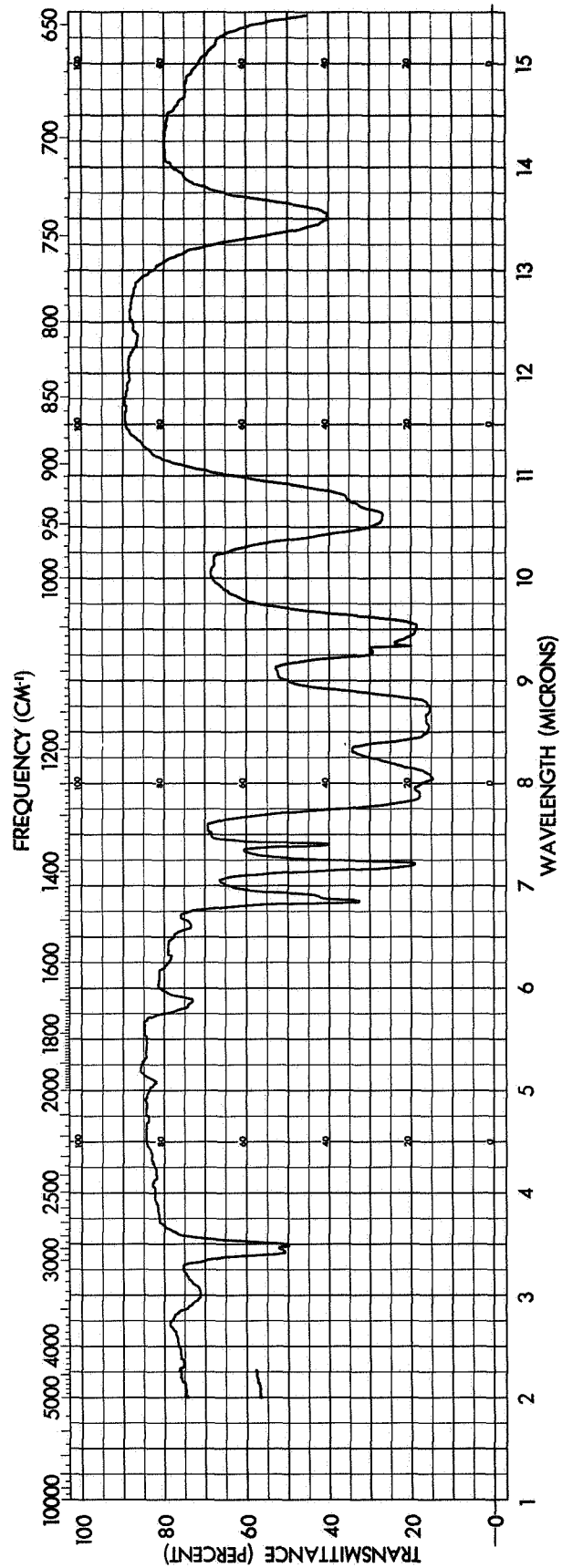
Figure 37. 3,3,4,4-Tetrafluorotetramethylene Oxide

Concentrated sulfuric acid (40 g, 0.41 mole) was added with stirring and the mixture was heated in an oil bath to 185°C. A clear, colorless liquid which boiled below room temperature was collected in the receiver. Vapor phase chromatography showed two major peaks. The crude product was purified by distillation yielding 7.8 g of liquid. None of the desired product was obtained.

21. Preparation of the Diether of Hexafluorobenzene and Hexafluoropentanediol
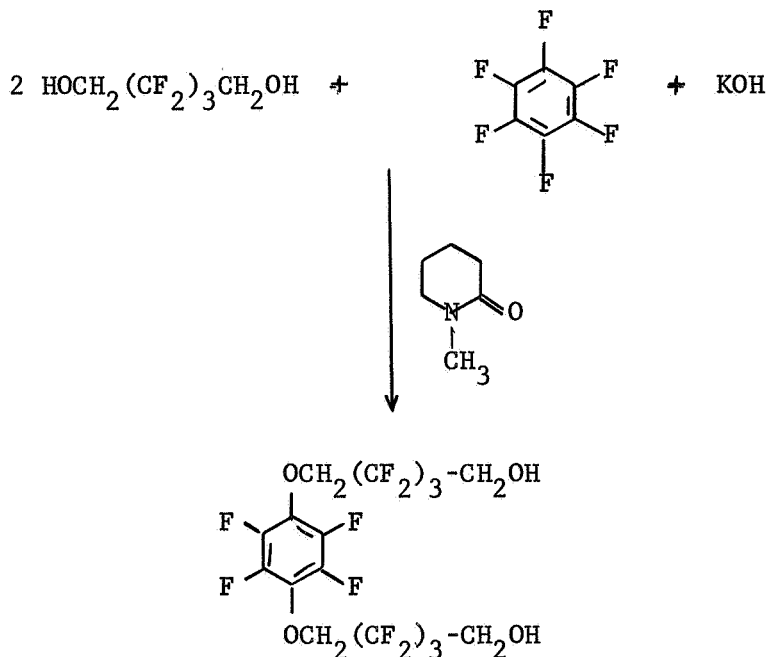
Into a 1-liter, three-necked flask fitted with a nitrogen gas inlet, thermometer, stirrer, and reflux condenser were placed hexafluoropentanediol (46.6 g, 0.22 mole), hexafluorobenzene (18.6 g, 0.1 mole), and potassium hydroxide (11.2 g, 0.2 mole). The reactants were dissolved in 250 ml of N-methylpyrrolidone. The reaction mixture darkened considerably during the first few minutes of heating. The pot temperature was maintained at 100°C for 8 hours; then increased to 180°C for 30 hours, during which time a clear, colorless liquid refluxed from 125°-150°C. The flask was cooled and the black reaction mixture was poured into water. A black semisolid was filtered off and washed with ether. Ether and sodium chloride were added to the liquid, and the aqueous phase (pH 5) separated. The black ethereal solution was washed twice with water, sodium chloride being used in each wash to break up the almost total emulsion in the funnel. The dark ethereal solution was dried over magnesium sulfate for 3 days and filtered. The bulk of the solvent was stripped off and the residue was distilled under vacuum. Two fractions were collected. One fraction, 4.1 g, was collected from 98°-134°C at < 2 mm, solidifying in the receiving flask. Less than 1 g of a green liquid was collected from 134°-170°C at < 2 mm. The solid was identified by its infrared spectrum as hexafluoropentanediol. An infrared spectrum of the liquid compared favorably with the spectrum of the desired product obtained by another route (reported in Annual Summary Report I, July 1964).

22. Study of the Reaction Mechanism in the Formation of Cyclic Sulfite from Hexafluoropentanediol with Thionyl Chloride in the Presence of Pyridine

$$
\begin{array}{c}
\text{OH} \quad\quad \text{OH} \\
| \quad\quad\quad | \\
CH_2 \quad\quad CH_2 \quad + \quad SOCl_2 \quad\xrightarrow{\text{Pyridine}}\quad
\begin{array}{c}
\nearrow S\nwarrow \\
OO \\
| \quad\quad\quad | \\
CH_2 \quad\quad CH_2 \\
| \quad\quad\quad | \\
CF_2 \quad\quad CF_2 \\
\nwarrow CF_2 \nearrow
\end{array} \\
| \quad\quad\quad | \\
CH_2 \quad\quad CF_2 \\
\nwarrow CF_2 \nearrow
\end{array}
$$
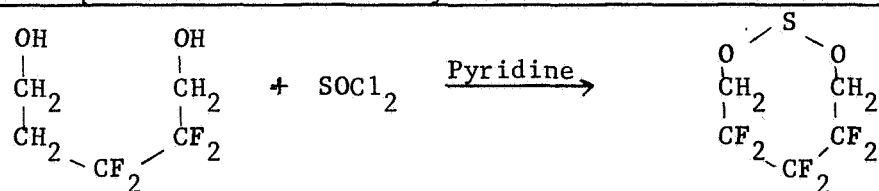
a. First Method of Preparation

Pyridine (7.9 g, 0.1 mole) was dissolved in 25 ml of dry ether and charged to a three-necked, round-bottomed flask fitted with a condenser, stirrer, addition funnel, and thermometer. Thionyl chloride (11.9 g, 0.1 mole) was dissolved in 25 ml of ether and combined with the pyridine solution. The mixture was stirred and chilled to 0°C with an ice water bath. Hexafluoropentanediol (21.2 g, 0.1 mole) was dissolved in 200 ml of dry ether and charged to the addition funnel. The diol solution was introduced dropwise into the pyridine-thionyl chloride solution. The addition rate was slow due to the exothermic nature of the reaction. A white precipitate formed. Upon addition of approximately one-half the diol solution, the exotherm ceased and no additional precipitate was formed with subsequent addition of the remaining diol solution. However, the precipitate became a greaselike, gelatinous mass and the reaction solution was allowed to stand overnight at room temperature. The greasy precipitate was broken up by the addition of 200 ml of ether. The precipitate was filtered and the filtrate evaporated under reduced pressure. A viscous oil remained. The infrared spectrum and vapor phase chromatograph indicate the residue to be a mixture of approximately equal amounts of unreacted hexafluoropentanediol and hexafluoropentamethylene sulfite.

b. Improved Method of Preparation

The reaction was carried out in a similar fashion as in item a. above with the same order of addition, temperatures, times, etc. The only exception was that the amount of pyridine was increased to 15.8 g (0.2 mole). This time, no greaselike material was formed and the reaction proceeded smoothly. After standing overnight at room temperature, the precipitate was filtered, the filtrate washed twice with water, the ether layer separated, and dried over anhydrous magnesium sulfate. The magnesium sulfate was filtered and the filtrate distilled under reduced pressure. Hexafluoropentamethylene sulfite (17.4 g, 68% yield) distilled at 60°-64°C at 3-5 mm Hg.

23. Diester from Adipyl Chloride and Hexafluoroacetone Monohydrate

a. Preparation of Hexafluoroacetone Monohydrate

$$
\begin{array}{ccc}
O & & OH \\
\| & & | \\
CF_3-C-CF_3 \; + \; H_2O \; \longrightarrow & & CF_3-C-CF_3 \\
& & | \\
& & OH
\end{array}
$$
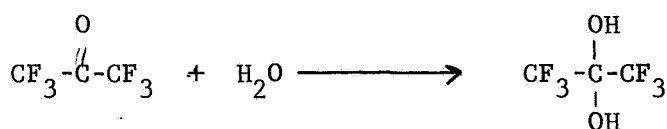
Into a calibrated 250-ml, three-necked flask fitted with dry ice — acetone condenser, nitrogen gas inlet, thermometer, stirrer, and addition funnel was condensed an excess (greater than 0.5 mole) of hexafluoroacetone. A dry ice bath was used to contain the hexafluoroacetone in the flask. To this was added, with stirring, water (9 g, 0.5 mole) in 50 ml of THF. During

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the addition, the solution became dark orange in color. After the water had been added, the dry ice bath was removed and and unreacted hexafluoroacetone was allowed to reflux. After 1 hour of stirring at room temperature, the dry ice in the condenser was not replenished, allowing evaporation of the excess hexafluoroacetone. The solution was stirred for an additional 16 hours, when an infrared spectrum showed no carbonyl absorption. The hexafluoroacetone hydrate was used without isolation.

b. Diester

(1) First Attempt

Into a 500-ml, three-necked flask equipped with a nitrogen gas inlet, thermometer, addition funnel, stirrer, and reflux condenser attached to a water trap was placed adipyl chloride (91.5 g, 0.5 mole). Hexafluoroacetone monohydrate (46 g, 0.25 mole) in 50 ml of THF was added slowly; no noticeable exothermic reaction occurring. After the addition was complete, the water trap was checked for evolved hydrogen chloride, but no significant amount was detected. Twelve drops of triethylamine was added to the reaction flask to catalyze the reaction. An exothermic reaction ensued, generating a fuming cloud, and hydrogen chloride gas began to pass into the water trap which contained sodium hydroxide. As the temperature of the reaction mixture rose to 45°C, a dry ice — acetone cooling bath was applied to cool the reaction. Due to the absence of an underpressure device, this cooling caused suck-back of the contents of the water trap into the reaction flask. Less than a second later, the contents of the reaction flask detonated. The cause of this detonation has not been explained.

(2) Second Attempt

This reaction was repeated using an equivalent amount of triethylamine to react with the hydrogen chloride generated in the reaction. The following procedure was used. Into a 500-ml, three-necked flask equipped with a nitrogen gas inlet, thermometer, stirrer, condenser, and two addition funnels was placed adipyl chloride (91.5 g, 0.5 mole) in 50 ml of THF. Into one of the delivery funnels was placed hexafluoroacetone monohydrate (46 g, 0.25 mole) in 50 ml of THF. Into the other delivery funnel was placed triethyl-amine (50.5 g, 0.5 mole, 69.9 ml) in 50 ml of THF. The triethylamine solution was added dropwise with stirring to the adipyl chloride. The hexafluoroacetone monohydrate solution was added simultaneously, care being exercised so that the volume of monohydrate added never exceeded the volume of triethylamine in the reaction flask. The exothermic reaction was maintained between -10°C and -20°C by means of a dry ice — acetone bath. The triethylamine formed a yellow solid immediately upon addition, followed slowly by replacement with a white solid when the hexafluoroacetone monohydrate was added. After the additions were complete, the contents were stirred at room temperature for almost 72 hours. Then the white solid was filtered off through a sintered glass funnel under nitrogen. It weighed 66.4 g (95.5% of theoretical triethylamine hydrochloride).
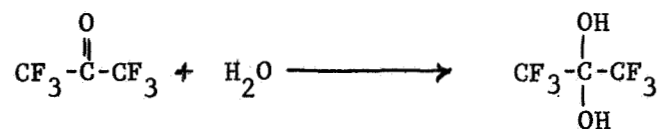
The filtrate was stripped of solvent and unreacted starting materials yielding 81.2 g (68% yield) of liquid tentatively identified by its infrared spectrum as the di-acid chloride-terminated diester of adipyl chloride and hexafluoroacetone monohydrate (Figure 38.).

	% C	% H	% Cl	% F
Analysis:				
Calculated for $C_{15}H_{16}O_6Cl_2F_6$:	37.7	3.4	14.9	23.9
Found:	49.6	5.5	15.3	6.0

Chloride analysis: An excess of silver nitrate solution was added to 5.6862 g of the diacid dichloride. White silver chloride immediately precipitated and, after drying, weighed 3.2808 g (96.6% yield based on structure).
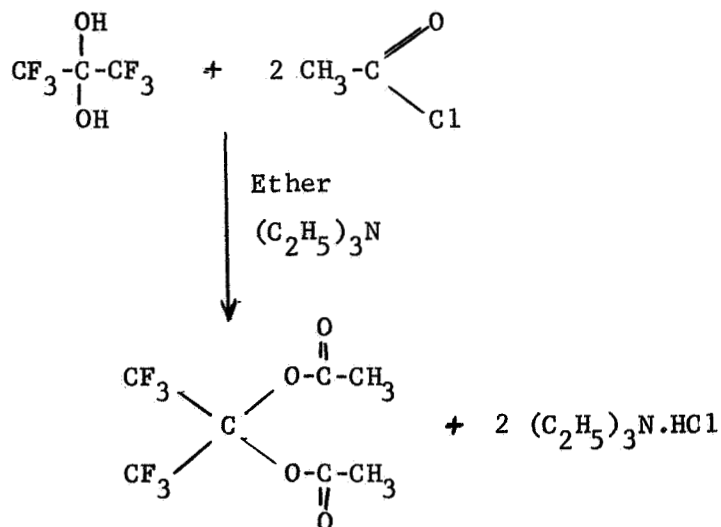
24. Preparation of 2,2'-Diacetoxy-hexafluoropropane

a. Preparation of Hexafluoroacetone Monohydrate

$$CF_3-\overset{\overset{\displaystyle O}{\|}}{C}-CF_3 \; + \; H_2O \longrightarrow CF_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CF_3$$

Into a calibrated 100-ml, three-necked flask equipped with dry ice condenser, nitrogen gas inlet, stirrer, and addition funnel was condensed hexafluoroacetone (42 g, 0.25 mole, 29.0 cc). Hexafluoroacetone was contained by means of a dry ice — acetone bath. To the flask was added with stirring, water (4.5 g, 0.25 mole). A solid immediately formed in the flask. Fifty milliliters of ether were added to maintain a fluid solution. The ethereal solution was used below without further isolation.

b. Preparation of 2,2-Diacetoxy-hexafluoropropane

$$CF_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CF_3 \; + \; 2\; CH_3-C\overset{\diagup O}{\diagdown Cl}$$

$$\Big\downarrow \quad \begin{array}{l} \text{Ether} \\ (C_2H_5)_3N \end{array}$$

$$\begin{array}{c} CF_3 \diagdown \qquad \diagup O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \\ C \\ CF_3 \diagup \qquad \diagdown O-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3 \end{array} \qquad + \; 2\; (C_2H_5)_3N \cdot HCl$$
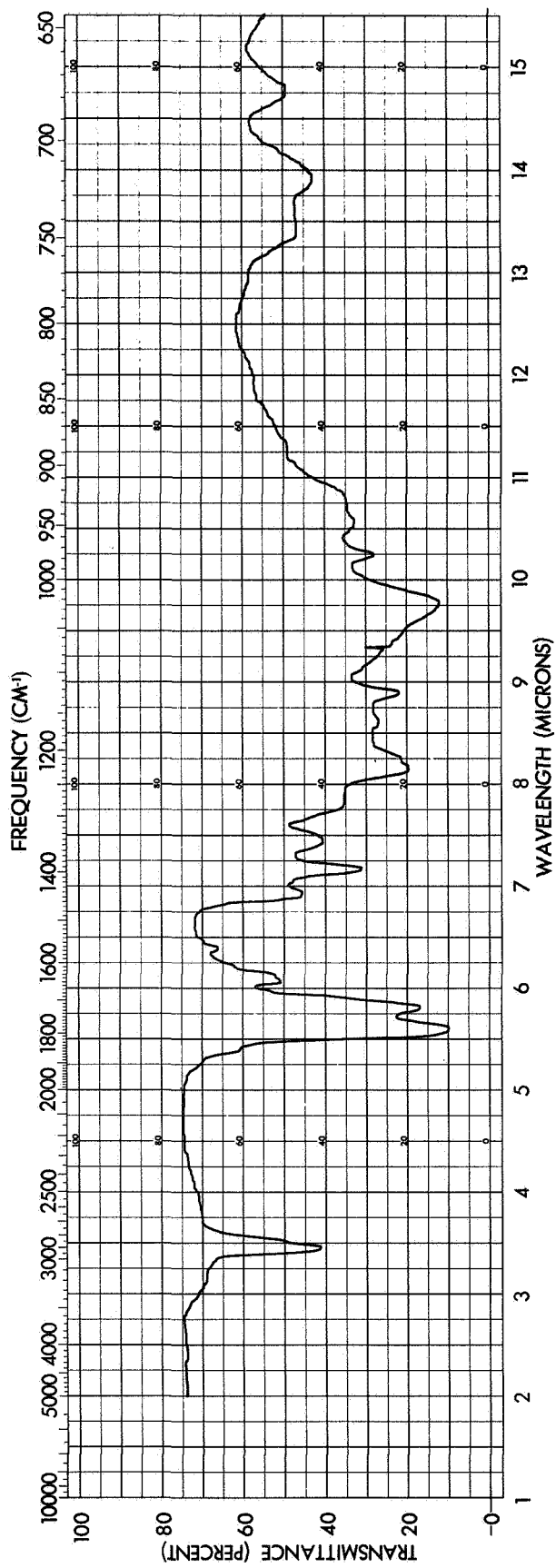
Figure 38. Di-Acid Chloride Terminated Diester of Adipyl Chloride and
Hexafluoroacetone Monohydrate

The ethereal solution of hexafluoroacetone monohydrate from the previous reaction was transferred to a 500-ml, three-necked flask equipped with nitrogen gas inlet, thermometer, stirrer, and two delivery funnels. Into one of the delivery funnels was placed acetyl chloride (39.3 g, 0.5 mole, 35.5 ml). The other addition funnel was charged with triethylamine (50.5 g, 0.5 mole, 69.9 ml). The flask was maintained near 0°C. Triethylamine was added slowly, with stirring, followed by simultaneous addition of acetyl chloride. White fumes evolved, and a solid formed in the flask. Another 150 ml of ether were added to maintain solution. The reaction mixture was stirred for 3 days at room temperature. The white triethylamine hydrochloride was filtered off, washed with ether, and dried. The yield was 64.2 g (93.4%). The bulk of ether solvent was stripped off from the bright, deep pink solution and the remaining liquid distilled. One fraction, collected from 35°-70°C was a clear, colorless liquid, the identity of which has not yet been established. The second fraction, a clear yellow liquid boiling at 87°-110°C was identified as being mostly a hydrate of hexafluoroacetone. The residue yielded no further distillate upon further heating.

25. Preparation of Dihemiketal from Hexafluoroacetone and Hexafluoropentanediol

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

A 500-ml, three-necked flask fitted with stirrer, dry ice — acetone condenser, and an addition funnel was placed into a dry ice bath. Hexafluoroacetone (66.4 g, 0.4 mole) was passed in and condensed. Hexafluoropentanediol (42.4 g, 0.2 mole) in 250 ml of diethyl ether was slowly added with stirring. The reaction mixture was stirred for 17 hours at room temperature. Evaporation of the ethyl ether at reduced pressure yielded a viscous liquid. The infrared spectrum of this liquid showed no carbonyl absorption and a definite shifting of the hydroxyl absorption typical of hemiketal formation. On heating the liquid or exposing it to moisture, only hexafluoropentanediol was isolated.

a. Attempted Preparation of the p-Toluenesulfonate from the Dihemiketal from Hexafluoroacetone and Hexafluoropentanediol

HCl

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The ether solution of the hemiketal was transferred to a 1-liter, three-necked flask equipped with addition funnel, thermometer, stirrer, and reflux condenser. Pyridine (31.6, 0.4 mole) was added with stirring. p-Toluenesulfonyl chloride (76.2 g, 0.4 mole) dissolved in 30 ml of ether was added and the reaction mixture heated at reflux for 20 hours. Unreacted p-toluenesulfonyl chloride and hexafluoropentanediol (from decomposition of the dihemiketal) were recovered.

26. Attempted Preparation of p-Amino-tetrafluorobenzylamine
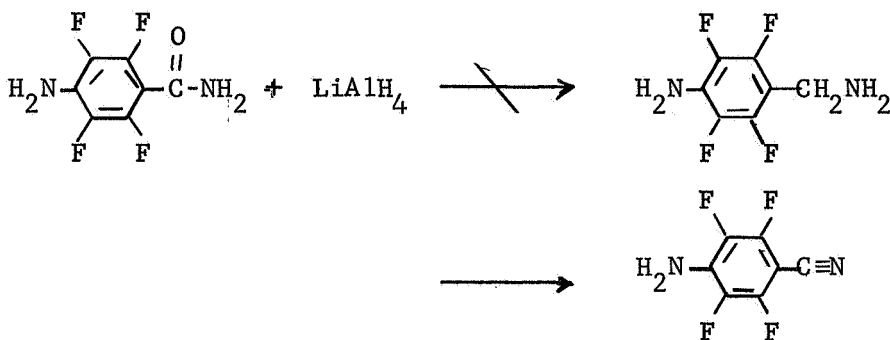
Tetrahydrofuran (THF) (300 ml) was added to a 1-liter, three-necked flask equipped with an air stirrer, condenser, nitrogen inlet, and thermometer. Lithium aluminum hydride (LAH) (8.5 g, 0.225 mole) was added to the ether with mixing under nitrogen. Tetrafluoro-p-aminobenzamide (20.8 g, 0.1 mole) in 200 ml of THF was added to the LAH slurry over a 1-hour period at $15°-25°C$ under nitrogen. The slurry was mixed for an additional 4 hours at $20°-25°C$. It was then cooled to $10°C$, 10 ml of water was slowly added with mixing under a rapid stream of nitrogen over a 45-minute period, then left standing overnight. The mixture was then filtered and the filtrate dried with magnesium sulfate. The THF slurry was filtered, then the THF removed on a rotary evaporator to yield 11.8 g of crude product. The crude product was sublimed to yield 21% of tetrafluoro-p-aminobenzonitrile, mp $77°-80°C$. Its infrared spectrum is shown as Figure 39.

Elemental analysis:

	% C	% H	% F	% N
Calculated for $C_7H_2F_4N_2$:	44.2	1.1	40.0	14.7
Found:	44.49	1.30	39.67	14.51

27. Preparation of 2-Imino-hexafluoropropane
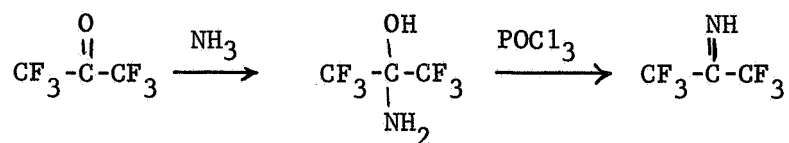
Hexafluoroacetone (1.0 mole) was condensed into a three-necked flask at $-20°C$. The flask was fitted with a dry ice — acetone filled Dewar condenser, addition funnel, gas inlet, and Magbar stirrer. Ammonia gas (1.1 mole) was slowly fed into the cold liquid, forming a white powder. Any unreacted material was allowed to escape at room temperature. The fluffy white powder (60 g) was then dissolved in 1 liter of distilled pyridine. The pyridine solution of
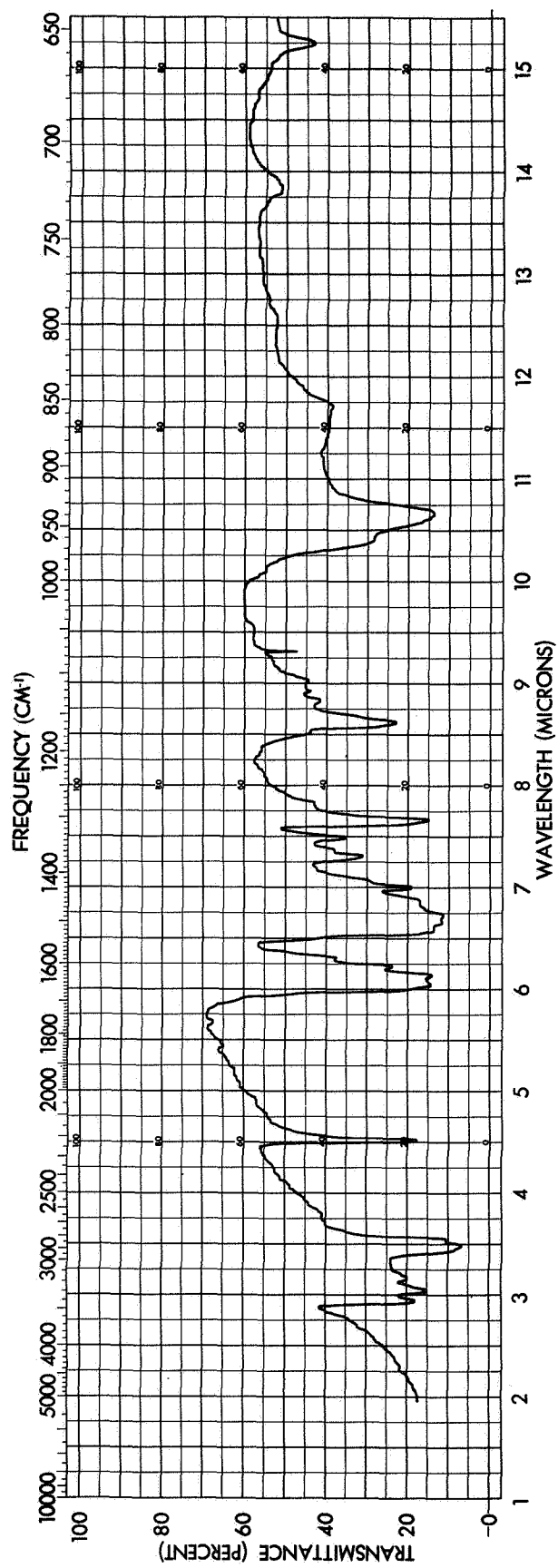
161.

Figure 39. p-Amino-tetrafluorobenzonitrile

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2-amino-2-hydroxyhexafluoropropane was chilled to -70°C and phosphorus oxy-chloride (140 ml, 1.4 mole) was slowly added. The solution was slowly allowed to come to room temperature. After 1 hour at room temperature, the solution was distilled through an 18-in., helix-packed, vacuum-jacketed column. The fraction boiling at 19°-20°C was collected. The yield was 40.0 g (25%).

## 28. Attempted Preparation of a Curing Agent for Fluorinated Polyurethanes

a. Attempted Preparation of a Low-Melting Amine Curing Agent

A mixture of tetrafluoro-p-phenylenediamine (1.15 g, 0.0064 mole) and pentafluoroaniline (0.60 g, 0.0032 mole) was prepared. The mixture crystallized at 125°C.

b. Attempted Preparation of an Amine-Diol Mixed Eutectic Curing Agent

Tetrafluoro-p-phenylenediamine (2.0 g, 0.011 mole) and hydroxyl-terminated poly(hexafluoropentamethylene adipate) of 1450 molecular weight (2.0 g, 0.014 mole) were mixed. The diamine was insoluble in the polyester.

29. Preparation of Monosodium Salt of Hexafluoropentanediol

$$HOCH_2(CF_2)_3CH_2OH + NaH \xrightarrow{Et_2O} HOCH_2(CF_2)_3CH_2 ONa + H_2 \uparrow$$
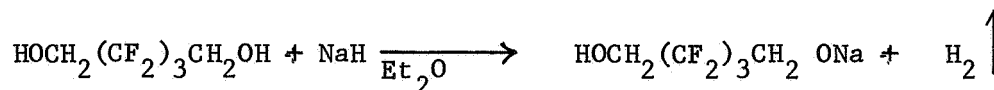
Hexafluoropentanediol (85 g, 0.4 mole) was dissolved in diethyl ether. A dispersion of sodium hydride in mineral oil (20 g of mixture containing 9.6 g, 0.4 mole of NaH) was dissolved in ether and added to the diol solution. When the addition was completed, the solution was stirred for 45 minutes and the solids filtered. The precipitate was washed with ether and boiling hexane, filtered again, and dried under vacuum. The salt isolated weighed 74.2 g (79%) yield and its neutralization equivalent was 250 (theoretical 234).

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V. CONCLUSIONS

LOX Compatibility

Certain conclusions can be drawn from the LOX compatibility tests obtained on those polymers sent to MSFC for testing. Urethane linkages flanked on the alcohol side by a 1,1-dihydroperfluoroalkyl chain are LOX compatible if the nitrogen is attached to a difluoromethylene, tetrafluoro-p-phenylene, or tetrachloro-p-phenylene group. Urethane, amide, and ester groups do not, in themselves, impart LOX incompatibility. Polyurethanes in which the diol portion is a partially fluorinated, hydroxyl-terminated polycarbonate, containing the $-CH_2-O-\overset{\overset{O}{\parallel}}{C}-O-CH_2-$ structure, a polyformate containing the CH_2-O-CH_2- $O-CH_2-$ structure, or a polyether containing the $-\overset{\overset{R_f}{|}}{CH}-CH_2-O-\overset{\overset{R_f}{|}}{CH}-CH_2-$ structure are LOX incompatible.

Properties of Materials Investigated

Certain conclusions can be drawn from the properties of the materials prepared during this investigation.

An adhesive system cannot be prepared from hexafluoropentanediol and an aromatic or short chain aliphatic diisocyanate because the resulting polyurethanes are brittle.

Although they are not LOX compatible, polyurethanes prepared from partially fluorinated hydroxyl-terminated polyesters, polyethers, and polycarbonates could be developed into adhesive systems because these polymers are extremely flexible.

Dihemiketals prepared from hexafluoroacetone, such as the dihemiketal of hexafluoroacetone and hexafluoropentanediol, are not usable as prepolymers since the polyurethanes formed from them are brittle.

Tetrafluoro-p-phenylene diisocyanate and the isocyanate-terminated prepolymers prepared from it are much more reactive than their nonfluorinated analogs.

Tetrachloro-p-phenylene diisocyanate and its prepolymers are much less reactive than their nonhalogenated analogs.

Hydroxyl-terminated polyesters of hexafluoroacetone are not suitable for the preparation of polyurethanes because they are unstable even to gentle heating.

Polyacetals prepared from perfluoroaldehydes show little promise as prepolymers due to their crystalline nature and lack of stability to heat.

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Poly(hexafluoropentamethylene carbonate) exhibits an unexpectedly high degree of thermal stability.

Hexafluoropentamethylene oxide and tetrafluoro-tetramethylene oxide are extremely stable to ring scission and cannot be polymerized to polyethers.

Chlorocarbonyl pyridinium chloride is a very useful reagent for the phosgenation of amines and alcohols. This type of salt is necessary for the preparation of highly halogenated isocyanates and chloroformates.

VI. RECOMMENDATIONS FOR FUTURE WORK

The scope of the program should be narrowed to the preparation of poly-urethanes from three types of diols: more highly fluorinated polyethers, considerably longer chain fluorinated diols, and hydroxyl-terminated poly-esters of $\alpha,\alpha,\alpha',\alpha'$-tetrahydro-perfluoro-dicarboxylic acids. These three types of diols are considered, on the basis of the conclusions presented in this report, to be the most promising systems.

Although LOX incompatible, the polyurethane prepared from poly(trifluoro-propylene oxide) showed interesting low-temperature properties; because of this, polyethers containing more fluorine, especially in the polymer back-bone, should be prepared.

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

Poly(hexafluoropentamethylene perfluoroglutarate), although hydrolytically unstable, was LOX compatible. Hydroxyl-terminated polyesters of $\alpha,\alpha,\alpha',\alpha'$-tetrahydroperfluoro-dicarboxylic acids should be prepared and polyurethanes made from them.

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

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