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DATED 3 MAY, 1966

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

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JULY 1964

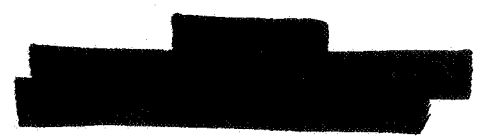
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George C. Marshall Space Flight Center
Huntsville, Alabama



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(Prepared under Contract No. NAS 8-11068 by Whittaker Corporation, Narmco
Research & Development Division, San Diego, California, Rex B. Gosnell,
Edward S. Harrison, Jerome Hollander, Beatrix Y. Sanders, and
Floyd D. Trischler)



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Annual Summary Report
1 July 1963 to 30 June 1964

Propulsion and Vehicle Engineering Division
National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama

Contract No. NAS 8-11068
Control No. TP 3-85355(IF)

by

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FOREWORD

This report was prepared by Whittaker Corporation, Narmco Research & Development Division, under Contract No. NAS 8-11068, Control No. TP 3-85355(IF), entitled "The Development of Structural Adhesive Systems Suitable for Use with Liquid Oxygen"(U), for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the direction of the Propulsion and Vehicle Engineering Division, Engineering Materials Branch, with Dr. J. M. Stuckey acting as project officer. The research work was conducted in Narmco's laboratory by Mr. Edward S. Harrison, Dr. Jerome Hollander, Mrs. Beatrix Y. Sanders, and Mr. Floyd D. Trischler, assisted by Mr. Luis Acle. Dr. Rex B. Gosnell served as program manager. This report covers the period 1 July 1963 to 30 June 1964.

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ABSTRACT

A highly fluorinated aliphatic polyurethane has been prepared which is LOX compatible. Three additional fluorinated polyurethanes have been prepared which are being tested for LOX compatibility.

Preparations or synthetic studies have been carried out on additional monomers including fluorinated and chlorinated diisocyanates, hydroxyl-terminated polyesters, and hydroxyl-terminated polyethers.

A number of other halogenated polymers such as polyamides, polyesters, and polyethers have been synthesized.

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I. INTRODUCTION

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

The development of such adhesives depends entirely upon 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:

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

II. DISCUSSION

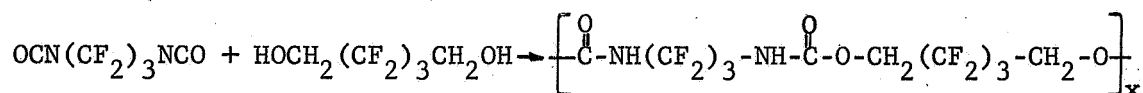
A. POLYURETHANES

The introduction of chlorine or fluorine into polyurethanes can be carried out in the polyol moiety, the isocyanate moiety, or both. Introduction of the halogen in the polyol is attractive because of the availability of some of these materials. (2-11) Introduction of the halogen into the isocyanate is more difficult and requires quite a synthetic effort. Halogen-containing polyols are promising, but higher levels of halogen content in a polymer can only be achieved if the isocyanate also contains considerable halogen.

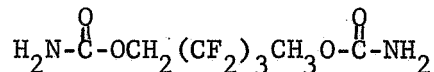
Hexafluoro-1,5-pentanediol is available (12) and has been used in Narmco's work as the halogenated diol in several polyurethane preparations.

1. Highly Fluorinated Aliphatic Polyurethane

Polyurethanes from perfluoroalkylene diisocyanates and fluorinated diols have been reported in a British Patent (13). This report is believed to be completely fictitious because it discusses the perfluorodiamine phosgenation route to perfluorotetramethylene diisocyanate. It is now well accepted that such perfluorinated amines do not exist. (14a) A polyurethane has been prepared by reaction of perfluorotrimethylene diisocyanate and hexafluoropentanediol in Narmco's work.

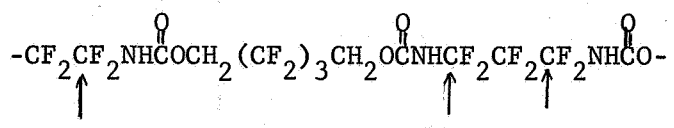


The material prepared was a rubbery solid which degraded to a liquid or sticky solid on standing overnight in air. When stored in dry nitrogen, the polymer did not undergo any change on standing. A study was conducted to establish the nature of the hydrolytic degradation of this polymer. The product obtained from the hydrolysis was shown to be the dicarbamate of hexafluoropentane-diol.



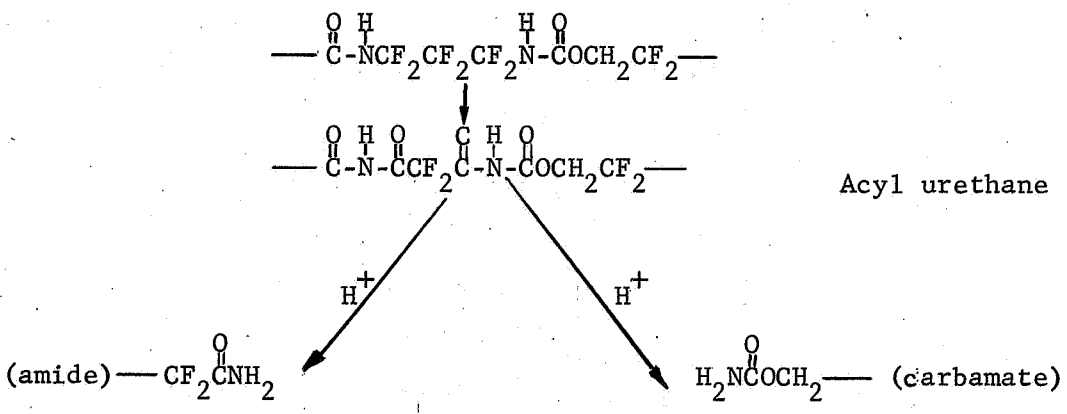
Apparently hydrolysis of the difluoromethylene groups adjacent to the carbamate nitrogen atoms is occurring by analogy to that reported, with several synthetic routes which would be expected to result in perfluorinated amines. (15-21)

Hydrolysis at these points along the chain, as shown by the arrows below, result in the dicarbamate fragment.



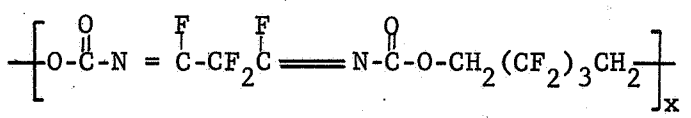
The balance of the polymer may appear in the hydrolysis products as very light materials or as difluoromalonic acid or a derivative thereof. Isolation or identification or any other fragments was not successful.

A logical intermediate in this degradation is the acyl urethane. The acyl urethane, however, would normally be stable, but certainly hydrogen fluoride would be present and could have considerable effect on its hydrolytic stability. Hydrolysis of the acyl urethane could result in at least two products, depending upon which bond to nitrogen proved to be more hydrolytically stable.



No evidence for difluoromalondiamide could be found. This compound has been reported and melts at 204°-205°C, which is considerably higher than the melting point of 135°-136.5°C which was observed for the carbamate.

It is interesting to note that this polymer exhibits good stability if protected from moisture. In fact, the fresh polymer was subjected to considerable thermal exposures in an attempt to cross link the system, with no serious degradation up to 280°C. However, it was observed that hydrogen fluoride is lost at 80°-90°C and it seems evident that the polymer is modified as shown:



This treatment gives some improvement, but the modified polymer also degrades to the dicarbamate, indicating that the remaining fluorine is still labile, much like an imino chloride.

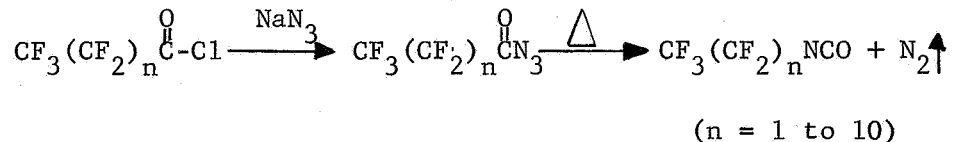
The postcure work was conducted to take advantage of the labile fluorine as a possibility in crosslinking the polyurethane and at the same time improving hydrolytic stability. The formation of the imino nitrogen appears to be preferred and therefore precludes that possibility.

The polymer resulting from the reaction of perfluoroglutaryl diisocyanate and hexafluoropentane diol contains 51.5% fluorine and offers other interesting properties. It is a tough material which was molded into twenty 0.020-in. x 11/16-in. wafers using high pressure at 150°-180°C.

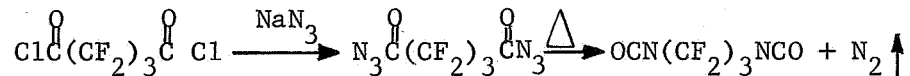
These wafers were submitted to George C. Marshall Space Flight Center (MSFC) for LOX tests which resulted in 0/20 reactions upon impact in LOX. This information is most significant because it indicates that the urethane linkage itself does not introduce LOX sensitivity, and, furthermore, that some hydrogen can be tolerated in the polymer in addition to urethane (>N-H) hydrogen.

a. Preparation of Perfluorotrimethylene Diisocyanate

Monofunctional perfluoroalkyl isocyanates have been prepared using the Curtius reaction. (22-26)



We have extended this reaction to the preparation of a perfluoroalkyl diisocyanate, perfluorotrimethylene diisocyanate.



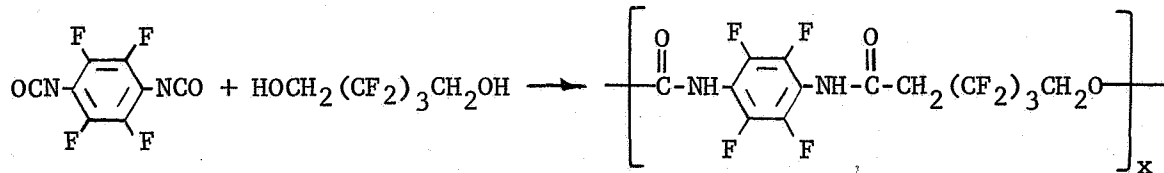
The yield of the diisocyanate is low at about 30%, but the efficiency could be considerably higher even at the 30% value if the monoisocyanate were recycled.

2. Highly Fluorinated Mixed Polyurethane

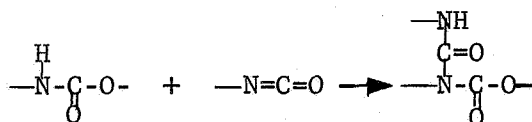
The hydrolytic degradation of the highly fluorinated aliphatic polyurethane just discussed indicates that perfluorinated aliphatic isocyanates may be impractical for polymer preparation and that systems must be selected which do not contain fluorine adjacent to nitrogen. Aromatic diisocyanates offer the greatest advantage because they can be perfluorinated and yet not have fluorine adjacent to the nitrogen atom.



A highly fluorinated mixed polyurethane prepared during this contract from tetrafluoro-p-phenylene diisocyanate and hexafluoropentanediol proved to be hydrolytically stable.



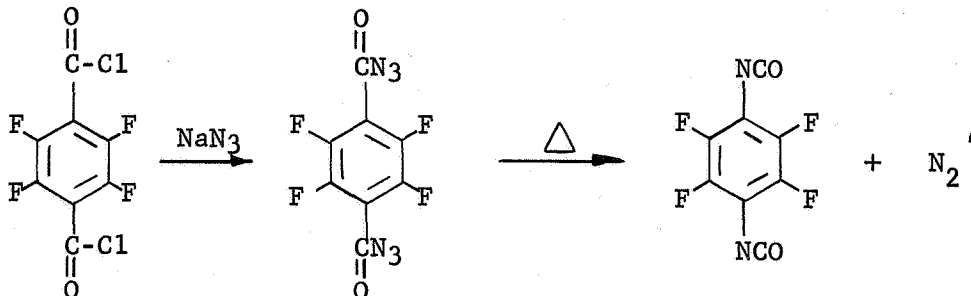
In the first method of preparation of this polymer, the diisocyanate solution was added to the diol solution containing triethylamine as a catalyst. A white, opaque, highly crystalline polyurethane was obtained. When the polymer was prepared by reverse addition (that is, by adding the diol solution containing catalyst to the diisocyanate solution), a gel formed early in the diol addition. The polymer obtained was considerably tougher than the polyurethane just described, but was still highly crystalline. This high degree of crystallinity is apparently due to branching from allophanate formation.



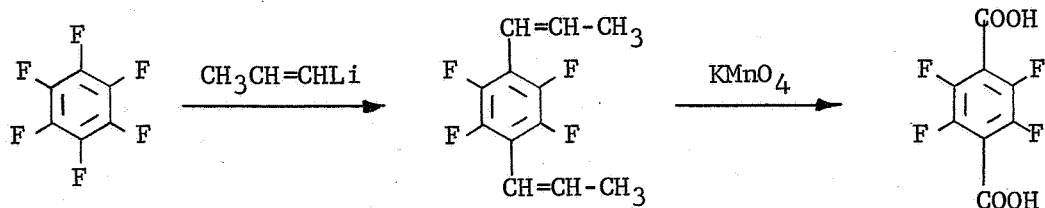
In the second method of preparation of this polyurethane, the triethylamine catalyst was added near the end of the polymerization. This was done in order to allow the maximum growth of linear polymer, then the triethylamine added to catalyze the complete reaction of remaining isocyanate groups. By this method, the branching due to allophanate formation was kept to a minimum. The polymer obtained was a light tan, waxy solid of fairly low crystallinity having a melting point in excess of 340°C. Sample wafers of this polymer were prepared and submitted to MSFC for LOX-impact testing.

a. Preparation of Tetrafluoro-p-Phenylene Diisocyanate

Two routes to this aromatic diisocyanate were investigated. The first involved the Curtius rearrangement of tetrafluoroterephthaloyl chloride.

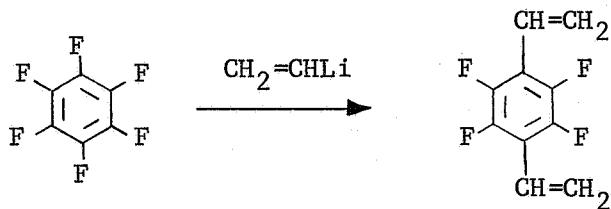


This route required the preparation of tetrafluoro-terephthalic acid. The preparation of this acid has been reported using the method shown below.⁽²⁷⁾ The yields were inadequate even for moderate laboratory scale-up.

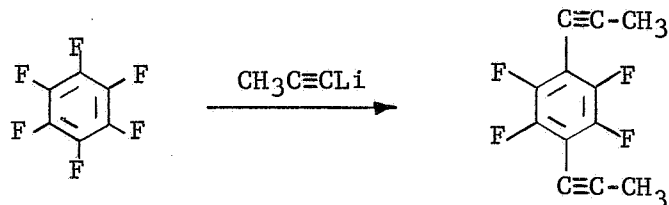


When this reaction sequence was attempted in this laboratory, considerable problems were encountered. The reaction sequence does produce the desired acid, but yields are intolerably low, with most of the difficulty being in the first step. The conversion of propenyl bromide to propenyl lithium is poor, with problems arising from low reactivity and coupling reactions. Cis- and trans-propenyl bromide cannot be separated by distillation and it is certain that both geometric isomers do not have the same reactivity; it is highly probable that one form prefers to couple rather than metalate. Consequently, considerable effort was expended in a search for an improved route to the acid.

Commercially available vinyl lithium was investigated in the same reaction. The isolation of divinyl tetrafluorobenzene is complicated by the ease with which it polymerizes. The nature of the polymer was not pursued because of a discrepancy in the experimental elemental analysis and the theoretical analysis.

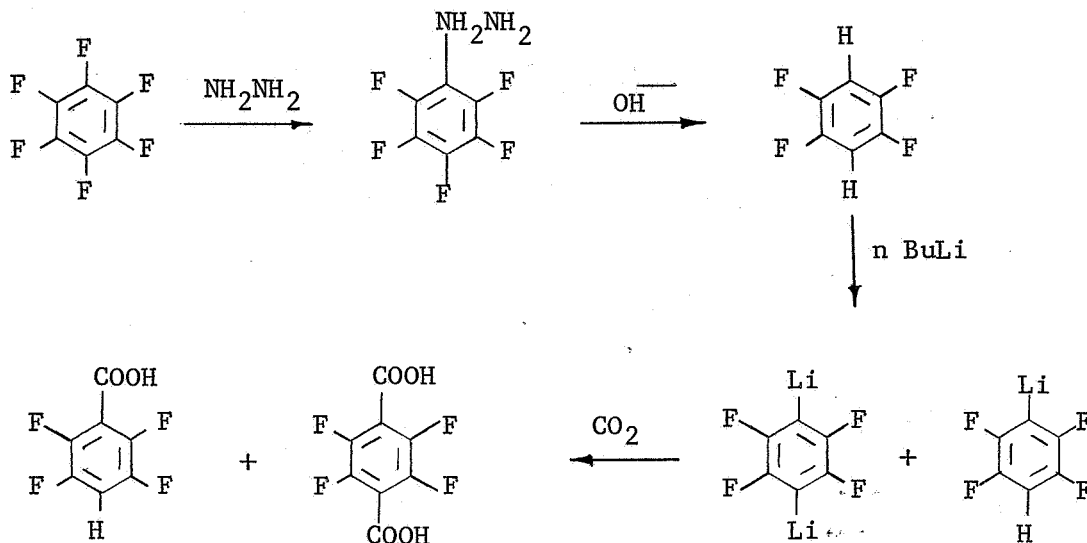


A modification of the above method has been studied involving the use of propynyl lithium rather than propenyl lithium as the nucleophilic agent. Propynyl lithium offers advantages in ease of preparation as well as increased strength as a nucleophile.



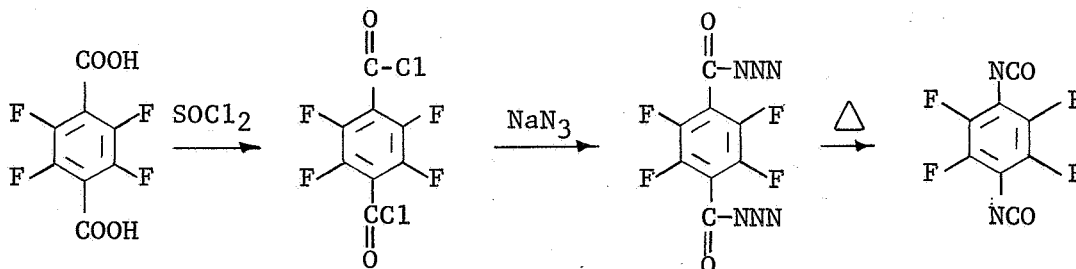
Similar reactions have been discussed and investigated by recent workers.⁽²⁸⁾⁽²⁹⁾

At least one other alternative route exists to tetrafluoroterephthalic acid.⁽³⁰⁾ This involves four steps and has the disadvantage of producing some of the mono acid.

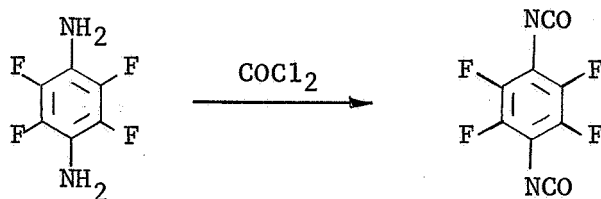


Because of the success that was achieved in the preparation of tetrafluoro-p-phenylenediamine, which will be discussed shortly, Narmco's work on this or any other route to tetrafluoroterephthalic acid was not pursued. The acid is now available in research quantities produced by recent improvements by Air Force and Peninsular Chemical workers using the hydrazine route.

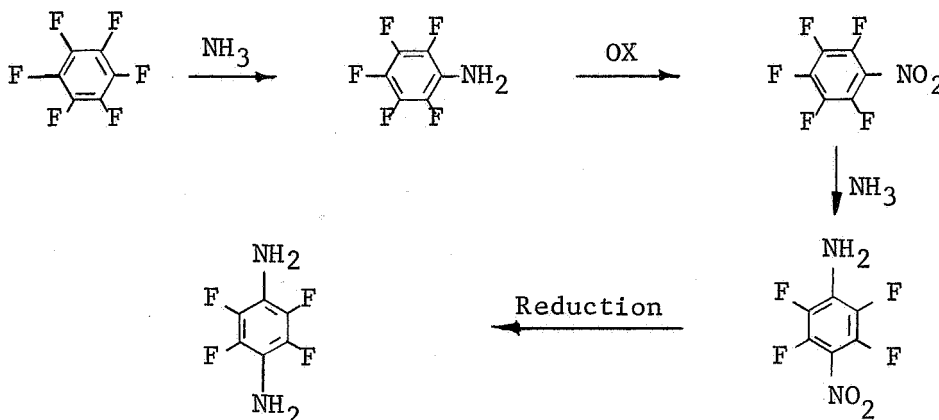
The remainder of this synthetic route to tetrafluoro-p-phenylene diisocyanate was carried out successfully and the diisocyanate used to prepare the mixed polyurethane.



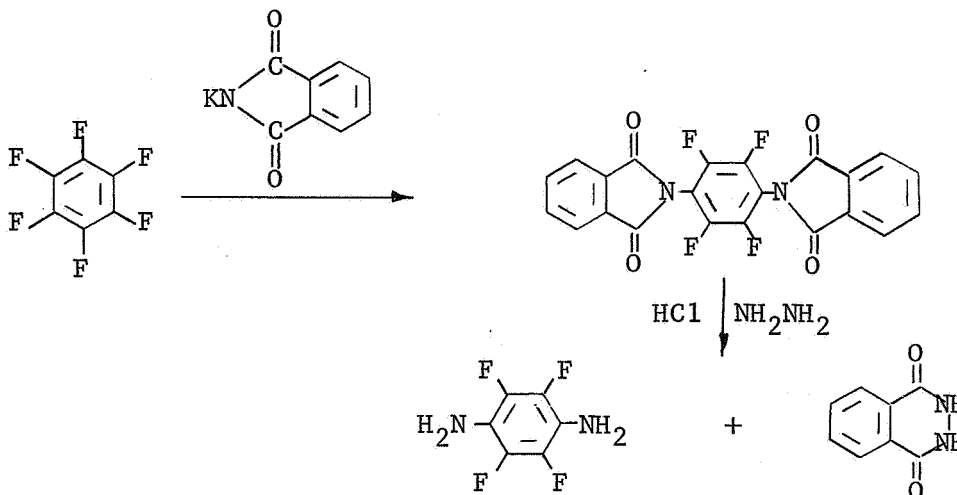
The second route to tetrafluoro-p-phenylene diisocyanate involved the preparation and phosgenation of tetrafluoro-p-phenylenediamine.



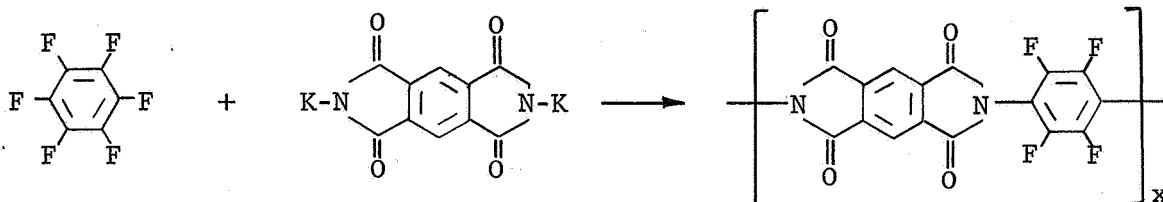
The literature reports that the tetrafluoro-p-phenylenediamine was prepared but the yield was reported to be very low. (31) The tetrafluoro-p-phenylenediamine melted at 144°-145°C and was reportedly obtained in an 8% yield from hexafluorobenzene following the sequence shown below:



The nucleophilic disubstitution of hexafluorobenzene had been receiving considerable attention as part of the investigations on this program, and attention was turned to this reaction as a means to prepare tetrafluoro-p-phenylenediamine. The reaction of hexafluorobenzene with potassium phthalimide was conceived and has been successful. The reactive fluorines behave as do aliphatic halides and undergo the Gabriel Synthesis to yield the diamine. Conversion of the diimide was achieved with hydrazine and hydrochloric acid.



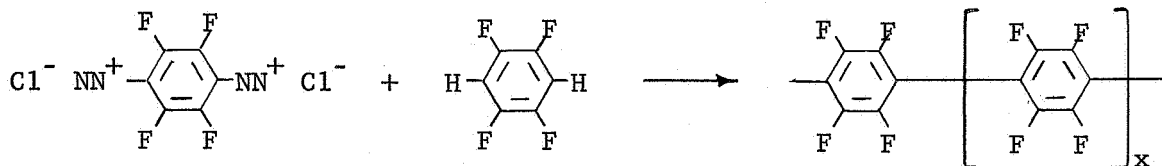
This reaction represents a convenient preparation which provides a route to a most interesting polymer intermediate. In addition, it could provide a means of preparing a polymeric imide directly from hexafluorobenzene.



This new reaction will be discussed later in this report. (Section D),

The preparation of the perfluoropolyimide could be pursued using the same approach.

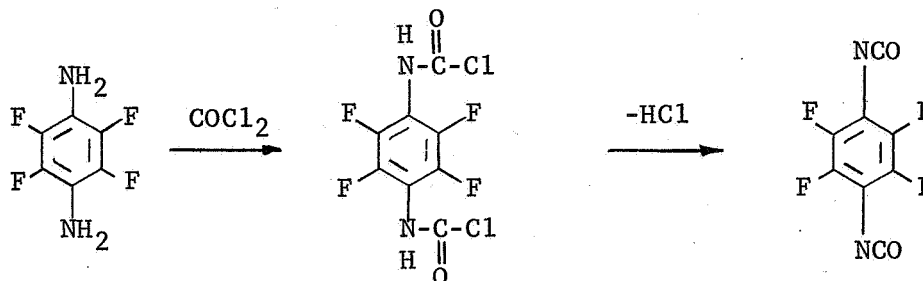
Tetrafluoro-p-phenylene diamine also offers considerable interest as a synthetic intermediate. In addition, other polymer systems of unusual nature can be visualized using the diamine; for example, a perfluoropolyphenyl may result by the following reaction:



The tetrazotized diamine may provide convenient routes to tetrafluoroterephthalonitrile, tetrafluorohydroquinone, tetra fluoroquinone, tetrafluoroterephthalic acid, and the other dihalo- compounds.

During the investigation of the reaction of hexafluorobenzene and potassium phthalimide, a number of variables were studied, including the type of solvent, the amount of solvent, reaction temperature, time, and concentration. The details are tabulated in the experimental section of this report; but the highest yield of tetrafluoro-p-phenylenediamine was obtained by using a 50% excess of potassium phthalimide in dimethylformamide at 135°C for 4 hours. The overall yield from hexafluorobenzene to tetrafluoro-p-phenylene diamine was 47%.

Tetrafluoro-p-phenylene diisocyanate was prepared from tetrafluoro-p-phenylenediamine by phosgenation in good yields.



The diisocyanate is extremely sensitive to moisture, and many problems were encountered in the workup of the reaction product. The apparatus used for the phosgenations is shown in the experimental section of this report.

In the earlier experiments, the phosgenation of tetrafluoro-p-phenylenediamine was carried out in toluene at -20°C . Different methods were studied to effect the dehydrochlorination of the dicarbamyl chloride. Distillation over calcium oxide, as in the method reported for monofunctional isocyanates in a 1953 patent,⁽³²⁾ caused excessive decomposition and none of the desired diisocyanate was obtained. It is very possible that the calcium oxide attacked the fluorine on the ring.

Dehydrohalogenation was also attempted by reaction of the dicarbamyl chloride with triethylamine. Only a polymeric material was obtained. The triethylamine may have catalyzed the homopolymerization of the diisocyanate. Attempted dehydrohalogenation by heating the dicarbamyl chloride at a higher temperature in o-dichlorobenzene as a solvent resulted in the elimination of hydrogen chloride; but no diisocyanate was isolated by distillation.

Early in the work, it was assumed that the low yield (compared to that of nonfluorinated diamines) was due to the stability of the carbamyl chloride formed as the intermediate product. A study of the progress of the reaction using infrared spectrophotometry and vapor phase chromatography (VPC) showed that this assumption was not valid. The low yields are due to several competitive reactions proceeding concurrently, the rates of which are influenced by the relative reactivities of the various constituents.

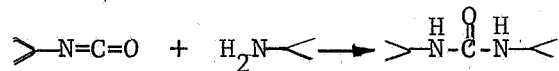
It appears that the initial step in the reaction (i.e., the reaction between phosgene and the diamine) is a relatively slow one. This is due to the decreased reactivity of the diamine. The fluorine atoms attached to the ring reduce the availability of the nitrogen electron

pair for attack on the carbonyl carbon of the phosgene molecule. However, once the reaction does occur and the resulting carbamyl chloride is formed, there appears to be an equilibrium established between the carbamyl chloride and the isocyanate formed as a result of the dehydrochlorination of the carbamyl chloride. This equilibrium is shifted toward the isocyanate with elevated temperature and the dehydrochlorination proceeds readily.

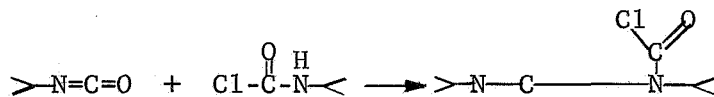
The possible competitive reactions mentioned previously enter into the picture in the following ways:

(a) The isocyanate (either mono or di) is a highly reactive material and possibly reacts as follows with

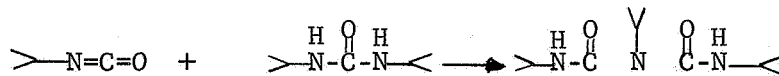
(1) Free amine (either mono or di) to form (poly)ureas



(2) Carbamyl chloride, to form an N-substituted chlorocarbonyl urea



(3) Urea, to form an N,N', N''-trisubstituted biuret



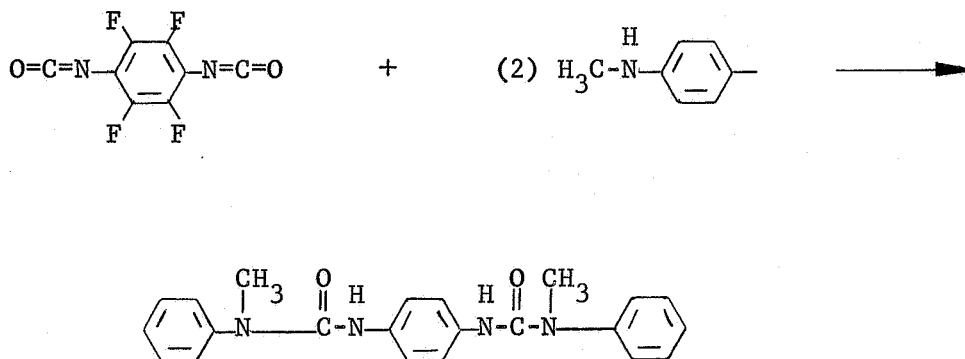
(b) The free amine is tied up as the amine hydrochloride. The hydrogen chloride is formed as a product in the initial reaction between phosgene and the diamine and in the dehydrochlorination of the carbamyl chloride. It appears that the amine hydrochloride is unstable at temperatures above approximately 80°C, and breaks down to give the free amine again.

From the foregoing, it appears that an atmospheric pressure reaction will invariably result in relatively low yield since the temperature necessary to decompose the amine hydrochloride results in a low concentration of dissolved phosgene and the competitive reactions of the isocyanate interfere to a greater extent.

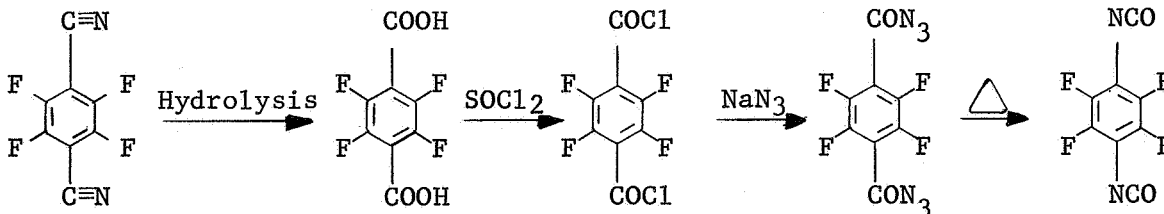
Using the information obtained in this study, various modifications were made in procedure. In later experiments, the phosgenation of tetrafluoro-p-phenylenediamine was run in toluene and the dehydrohalogenation carried out by refluxing the toluene solution. Anhydrous hydrogen chloride

was added following reflux of the reaction mixture. Prior evidence indicated that once the diisocyanate is formed, it cannot be converted to the carbamyl chloride by the simple addition of hydrogen chloride at any temperature above 0°C. The reason for the addition of the hydrogen chloride is to remove any unreacted amine from the solution by forming the insoluble amine hydrochloride. This reduces the amount of polyurea (which seems to be the major byproduct) formed during evaporation of the solvent. Tetrafluoro-p-phenylene diisocyanate was obtained in 46% yield by this procedure. The purity was established by VPC, elemental analysis, and the absence of amine or carbamyl chloride peaks in the infrared spectrum.

As further characterization of the tetrafluoro-p-phenylene diisocyanate, bis-(N-methyl-N-phenyl)-tetrafluoro-p-phenylene diurea, m.p. 233°-235°C, was prepared and its elemental analysis obtained.



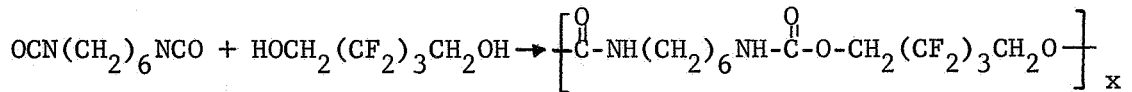
Another method that was considered for the preparation of tetrafluoro-p-phenylene diisocyanate involved the preparation and hydrolysis of 1,4-dicyano-tetrafluorobenzene. The resulting tetrafluoro-terephthalic acid would then be converted to the diisocyanate by way of the diazide.



No reaction was observed between hexafluorobenzene and copper (I) cyanide in N-methyl pyrrolidone.

3. Partially Fluorinated Aliphatic Polyurethane

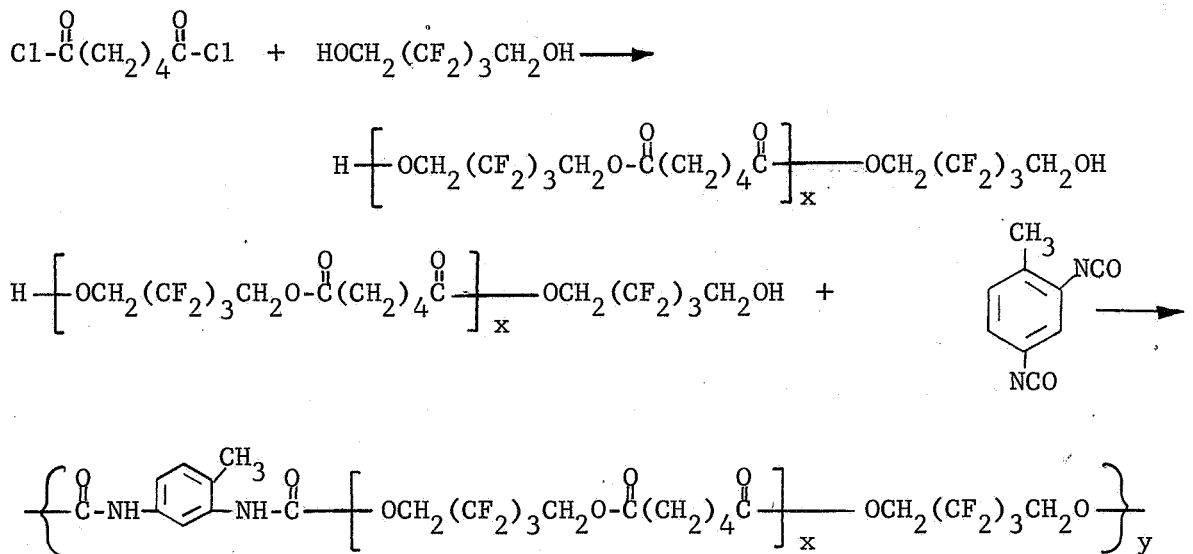
Since data regarding the effect of fluorine content on LOX compatibility is required, partially fluorinated polyurethanes must be evaluated. Polyurethanes of nonfluorinated diisocyanates and fluorinated diols have been prepared previously. (13) A polyurethane of hexafluoropentanediol and hexamethylene diisocyanate was prepared in Narmco's laboratory which was a colorless, brittle solid.



Sample wafers of this polyurethane were prepared and submitted to MSFC for LOX-impact tests.

4. Partially Fluorinated Mixed Polyurethane From a Partially Fluorinated Aliphatic Polyester Prepolymer

Hydroxyl-terminated polyesters have been used successfully in the preparation of nonfluorinated polyurethanes and should be exploited in this study. Work on fluorine containing esters have shown that esters made from hydrocarbon acids and fluorinated diols possess the greatest hydrolytic stability. (33) (34) Therefore, a hydroxyl-terminated polyester of moderate molecular weight (3300) was prepared by reaction of hexafluoropentanediol with adipoyl chloride in the ratio of 1.2 to 1. A polyurethane was made from this polyester and toluene diisocyanate.



The product obtained was a rubbery material. Sample wafers were prepared and submitted to MSFC for LOX-impact testing.

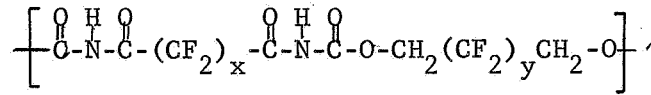


B. ADDITIONAL MONOMERS

Considerable work has been performed on the preparation of additional monomers and intermediates to be used in preparing other polyurethanes. This work will now be discussed.

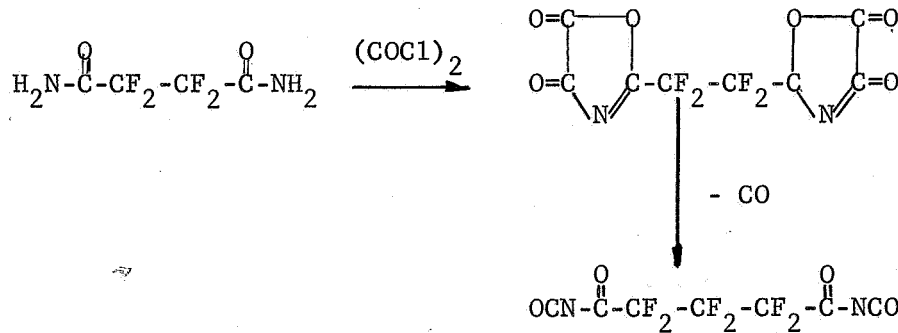
1. Perfluoroglutaryl Diisocyanate

As was reported earlier in this report, perfluorinated polyurethanes containing fluorine atoms adjacent to nitrogen are hydrolytically unstable. These polymers degrade to form dicarbamates on hydrolysis. Diacylisocyanates are of considerable interest since polyacylurethanes prepared from these compounds would not contain any fluorine atoms adjacent to nitrogen and would probably be resistant to hydrolysis.



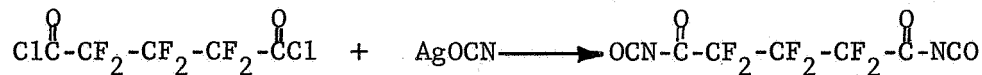
Acylisocyanates have been prepared from amides and oxalyl chloride,^{(35) (36)} by pyrolysis of the ureide from acid chlorides and urea,⁽³⁷⁾ and by the reaction of acid chlorides with silver⁽³⁸⁾ or sodium⁽³⁹⁾ cyanates.

An attempted preparation of perfluoroglutaryl diisocyanate by reaction of perfluoroglutaramide with oxalyl chloride at atmospheric pressure was unsuccessful.



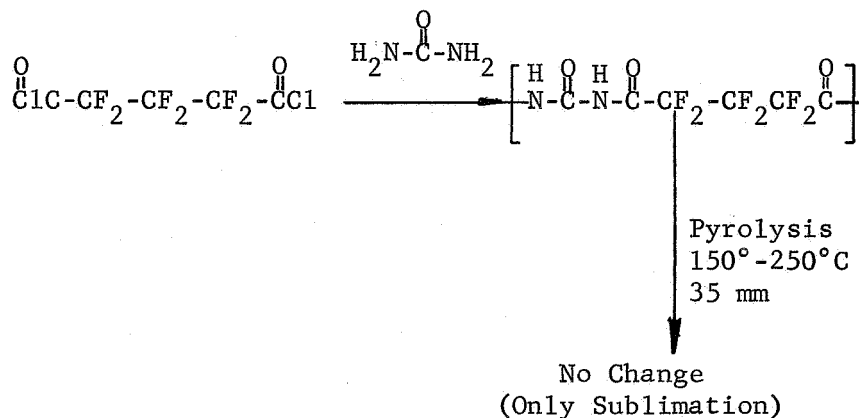
At elevated pressures, however, encouraging results were obtained. A product, tentatively identified as the desired perfluoroglutaryl diisocyanate, was obtained in an autoclave at 170°C. Its boiling point was 55°C and its infrared spectrum (see Experimental Section) shows a carbonyl absorption band at 1785 cm⁻¹ (similar to an acid chloride) and the characteristic NCO absorption band at 2220 cm⁻¹.

Apparently, perfluoroglutaryl diisocyanate was also formed by the silver cyanate method.



The product had the same chromatographic retention time as the material from the oxalyl chloride-amide reaction and appeared to be identical, although isolation is difficult.

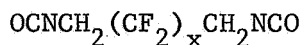
Pyrolysis of the ureide obtained by the reaction of urea and perfluoroglutaryl chloride following the general method in the literature was not successful. An infusible but volatile crystalline material was obtained whose identity is unknown.



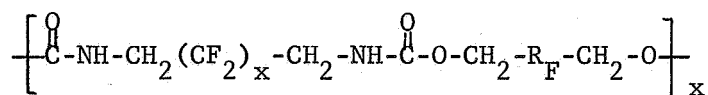
A larger amount of the perfluoroglutaryl diisocyanate will be prepared by the diamide-oxalyl chloride method and used to prepare a polyurethane.

2. Hexafluoropentamethylene Diisocyanate

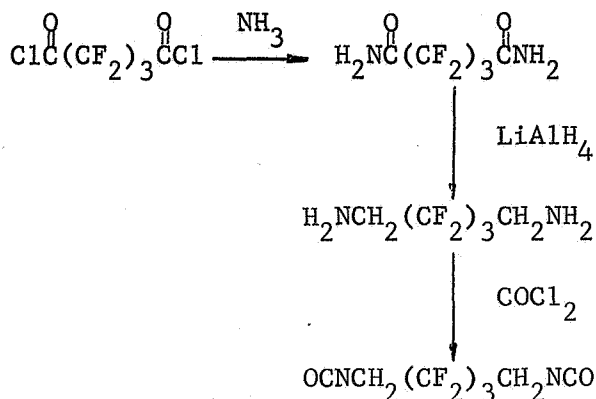
Another method of avoiding the hydrolytic instability of the perfluorinated polyurethanes would be by use of isocyanates of the following structure to prepare polyurethanes.



Polyurethanes prepared from this type of diisocyanate would have a high fluorine content but would not have the hydrolytic instability problem associated with the configuration $-\text{CF}_2-\overset{\text{H}}{\text{N}}-$ since their structure would be



The first route to hexafluoropentamethylene diisocyanate attempted was via the phosgenation of hexafluoropentanediamine.



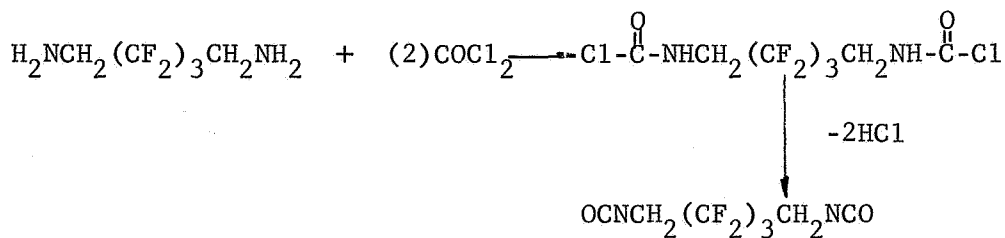
The first step, the ammoniation of perfluoroglutaryl chloride, afforded no difficulty. Several fluorinated monoamides have been prepared by this method. (24) (39) (40)

Monofunctional fluoroalkylamines have been prepared by reduction of the corresponding amides. (25) The reduction of perfluoroglutaronitrile is reported in the literature (41) where the hexafluoropentanediamine formed is described as a red oil. Narmco has prepared the true hexafluoropentanediamine, which is a white solid, m.p. 52°-53°C, by the lithium aluminum hydride reduction of perfluoroglutaramide. Its identity was established by elemental analysis and the preparation of the dibenzamide derivative.

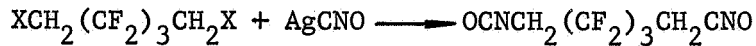
Fluorinated monoisocyanates have been prepared by phosgenation of 1,1-dihydroperfluoroalkylamines. (32) (42) Narmco has attempted to prepare hexafluoropentamethylene diisocyanate by the phosgenation of hexafluoropentanediamine, but has not been successful so far.

As in the preparation of tetrafluoro-p-phenylene diisocyanate, there are several competitive reactions that could be occurring concurrently with the desired reaction. A few of these are outlined below.

Desired reaction:

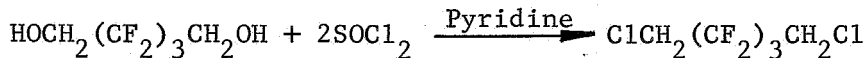


An alternate approach to the preparation of hexafluoropentamethylene diisocyanate is the reaction of a 1,5-dihalo-2,2,3,3,4,4-hexafluoropentane with silver cyanate.

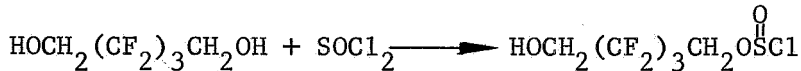


A likely method of preparation of 1,5-dichloro-2,2,3,3,4,4-hexafluoropentane would be from the readily available hexafluoropentane diol. Fluorinated alcohols containing the grouping $-\text{CF}_2-\text{CH}_2\text{OH}$, however, are much more acidic than ordinary alkyl alcohols, being almost as acidic as phenol. (43) (44) Like the phenols, the fluoro-alcohols are cleaved only with difficulty at the carbon-oxygen bond, so that direct exchange of the hydroxyl function for halide groups has been reported only in isolated cases. (14b) Halide substitution has been accomplished by reaction of methane-, ethane-, benzene-, and p-toluene-sulfonate esters of fluorinated alcohols with sodium iodide, lithium chloride, and lithium bromide in diethylene glycol at elevated temperatures, usually in excess of 200°C. (45-48) The use of chlorosulfate and sulfate esters has lowered the temperature required for this conversion somewhat. (49)

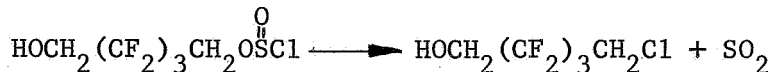
Surprisingly, Narmco has been able to prepare 1,5-dichlorohexafluoropentane directly from hexafluoropentane diol in excellent yield by reaction with thionyl chloride in pyridine at low temperature (80°-90°C).



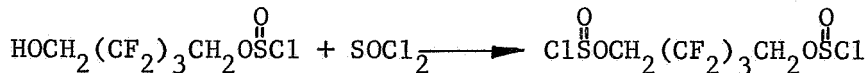
Narmco believes that the ease with which this diol is converted to the dichloro compound is due to the ready formation of a cyclic sulfite. The initial reaction between hexafluoropentane diol and thionyl chloride is most likely the formation of the monochlorosulfite ester.



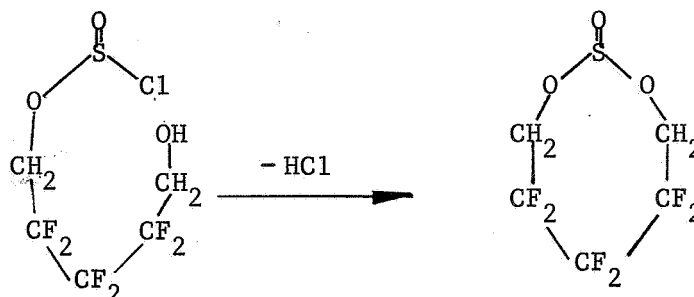
This intermediate product could give 1-chloro-5-hydroxyhexafluoropentane with loss of sulfur dioxide,



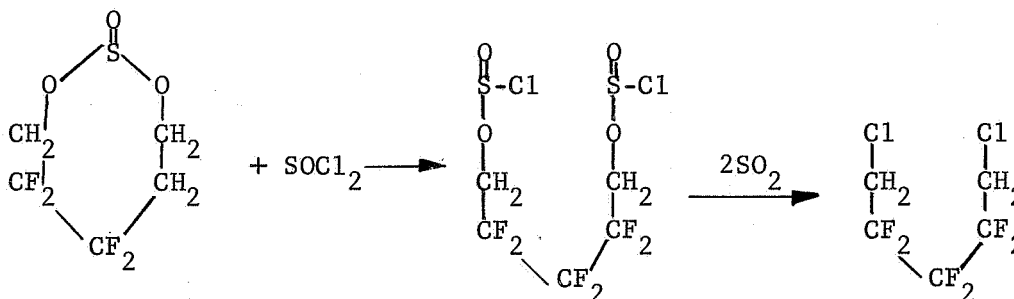
or it could react with another mole of thionyl chloride to give the dichlorosulfite ester.



Apparently, instead of either of these reactions occurring, there is a great tendency for this intermediate to lose hydrogen chloride intramolecularly and cyclize to the cyclic sulfite.



The cyclic sulfite then reacts with another mole of thionyl chloride to form the dichlorosulfite which decomposes with loss of sulfur dioxide yielding 1,5-dichloro-hexafluoropentane.



Only one intermediate, which was identified as hexafluoropentamethylene sulfite, was observed when this reaction was followed using the VPC. This cyclic sulfite was prepared independently by reaction of hexafluoropentanediol with thionyl chloride at room temperature. Its structure was established by elemental analysis and its infrared spectrum, which shows a strong absorption band at 1220 cm^{-1} characteristic of cyclic sulfites. (50) The reaction of the cyclic sulfite with thionyl chloride in pyridine yielded 1,5-dichlorohexafluoropentane. This strongly indicates that the cyclic sulfite is the intermediate through which the 1,5-dichloro-hexafluoropentane is formed.

Attempts to prepare hexafluoropentamethylene diisocyanate by reaction of 1,5-dichlorohexafluoropentane with silver cyanate both at atmospheric and elevated pressures were unsuccessful.

Since the dichloro compound is completely unreactive to silver cyanate, it was believed that use of the di-iodo derivative might possibly result in the desired diisocyanate.

In the reaction of hexafluoropentandiol with iodine, no 1,5-di-iodo-hexafluoropentane was formed. In the halogen exchange reaction between 1,5-dichloro-hexafluoropentane and sodium iodide in acetone solution, none of the desired diiodide formed.

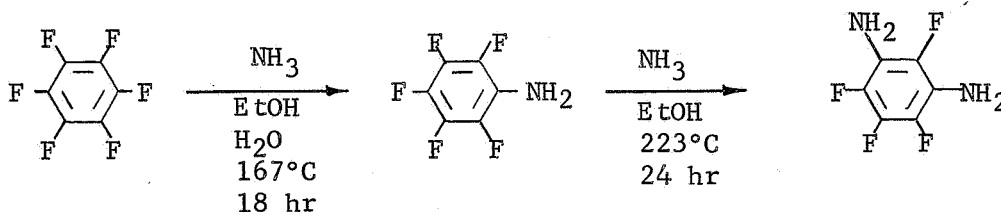
3. Tetrachloro-p-Phenylene Diisocyanate

Since information is required on the type as well as amount of halogen necessary to impart LOX compatibility to polymers, tetrachloro-p-phenylene diisocyanate was prepared for use in making polyurethanes and polyureas. It was prepared by the Curtius reaction. In contrast to the decomposition of the tetrafluoro-p-phenylene diacyl azide, which proceeded rapidly and in only fair yield, the decomposition of the tetrachloro-p-phenylene diacyl azide proceeded slowly even at elevated temperature giving an unexpectedly high yield of diisocyanate. The tetrachloroterephthaloyl chloride used for the preparation of the diacyl azide was obtained from Hooker Chemical Corporation. Although the nitrogen analysis for the diisocyanate is low, the infrared spectrum indicates that it is quite pure, with only a trace of acid chloride present.

4. Tetrafluoro-m-Phenylenediamine

Tetrafluoro-m-phenylenediamine is of considerable interest along with tetrafluoro-p-phenylenediamine for the preparation of highly fluorinated polymers including polyureas, polyamides, and polyimides. Its conversion to tetrafluoro-m-phenylene diisocyanate is important since it is known that polyurethanes prepared from meta-diisocyanates impart a lower degree of crystallinity and greater solubility than the corresponding polyurethanes from para-diisocyanates.

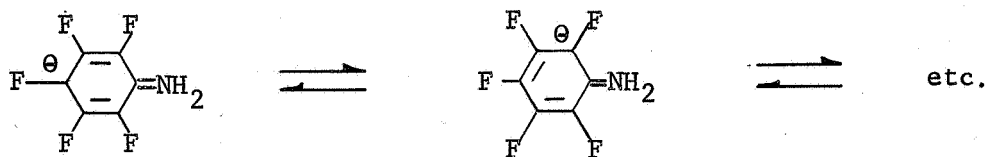
Tetrafluoro-m-phenylenediamine has been reported in the literature⁽³¹⁾ and the reaction sequence is shown below:



2.5% yield

It is interesting to note that the above reaction is in contrast to most nucleophilic disubstitutions of hexafluorobenzene, which proceed to give the para isomer. Further consideration, however, reveals that the meta isomer might be expected because of the electromeric effect of the first amino group attached to the ring.



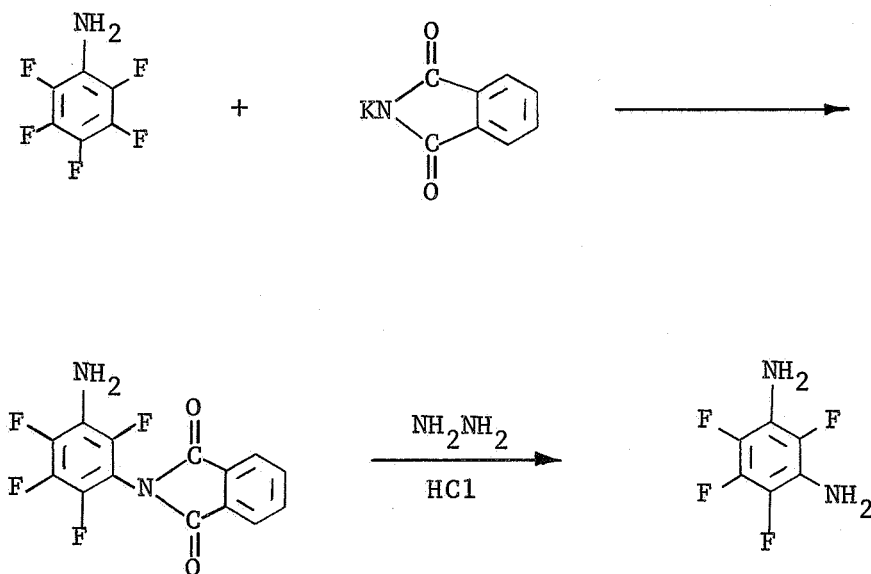


The resulting effect upon orientation of an additional nucleophilic attack is contrary to an electrophilic attack. The reaction at the meta position is favored.

The yield of tetrafluoro-m-phenylene diamine reported is low (2.5%) but the compound was characterized by a melting point of 129.5°-131°C.

In Narmco's work, the first method attempted to prepare this diamine in respectable yield involved a modification of the above method, which consisted of operating at ambient pressure with low concentrations of ammonia in high-boiling solvents. Characterization of the reaction mixtures were carried out by means of VPC and infrared spectrophotometry. None of the desired diamine was detected in any of the runs using this procedure.

The success achieved in preparing tetrafluoro-p-phenylenediamine by use of the Gabriel reaction using potassium phthalimide with hexafluoro-benzene led to the second method. Since the amine group in pentafluoroaniline is meta directing as indicated by the formation of tetrafluoro-m-phenylenediamine, it was felt that the reaction of pentafluoroaniline with potassium phthalimide might yield the desired meta diamine.



A 13.4% yield of tetrafluoro-m-phenylene diamine was obtained on the first attempt. Although the aromatic ring of pentafluoroaniline is deactivated by the amino group toward nucleophilic attack, its electron density is still low enough to react with the phthalimido anion.

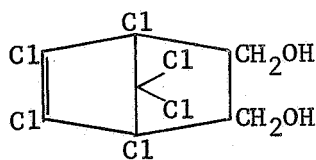
5. Tetrachloro-p-Phenylenediamine

Due to the success of the Gabriel reaction in the preparation of tetrafluoro-p-phenylenediamine, the reaction of potassium phthalimide with hexachlorobenzene was attempted. The anticipated product, tetrachloro-p-phenylenediamine could be used in the preparation of chlorine-containing polyurethanes and polyamides which would yield valuable information on the relation of type of halogen to LOX compatibility. None of the desired diamine was isolated from the reaction, however.

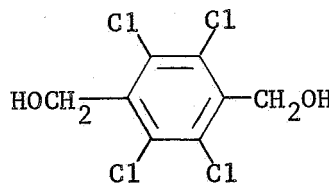
6. Hydroxyl-Terminated Polyesters and Diesters

Hydroxyl-terminated polyesters have been used successfully to a great extent in the preparation of nonfluorinated polyurethanes. (51) An excellent review on the preparation and use of polyesters for urethanes is given by Muller. (52)

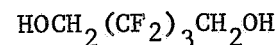
The initial experiments performed were aimed at the preparation of hydroxyl-terminated diesters of perfluoroglutaric acid. Perfluoroglutaryl chloride was reacted with three diols, HET diol (I) tetrachloro-p-xylene α, α' -diol, (II) and hexafluoropentanediol (III) in a molar ratio of 1:2.



I



II



III

Reaction in pyridine failed to yield any diesters. Only unreacted diols were recovered. When these reactions were carried out in refluxing toluene, hydrogen chloride was eliminated and di- or polyesters formed slowly. The HET diol reacted with the perfluoroglutaryl chloride most rapidly, the tetrachloro-p-xylene α, α' -diol more slowly, and as expected, the hexafluoropentanediol very slowly. The products of these reactions appear to be mixtures of diesters and low molecular weight polyesters containing acid chloride end groups. Apparently, polyesters form even when the ratio of diol to diacid chloride is 2:1. Emphasis was then shifted to the preparation of hydroxyl-terminated polyesters rather than diesters of perfluoroglutaric acid.

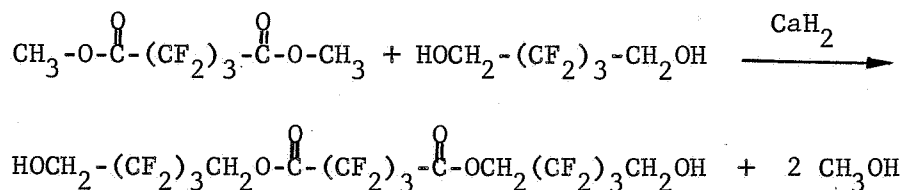
Perfluoroglutaryl chloride was reacted with HET diol and hexafluoropentanediol in a molar ratio of 1:1.05. These reactions were carried out in refluxing toluene, and by refluxing the reactions without solvent. Indications are that there are some acid chloride end groups in the polyesters obtained.

Further studies of these reactions were carried out with 20% molar excess of the diols and by refluxing the reactants without solvent. The products obtained were viscous liquid polyesters. These polyesters contain some acid chloride end groups which must be removed to give the desired completely hydroxyl-terminated polyesters.

Difficulties were encountered in trying to determine the molecular weights of the polyesters prepared using a vapor pressure osmometer, due to the presence of reactive chloride (acid chloride end groups).

Moderate molecular weight polyesters were obtained from the reaction of perfluoroglutaryl chloride with hexafluoropentanediol and ethylene glycol, and from the reaction of adipoyl chloride with hexafluoropentanediol and HET diol. The diols were used in 20% excess. These reactions were run without solvent at high temperature for a long period of time, trapping the hydrogen chloride evolved, and stripping off at high vacuum any traces of hydrogen chloride remaining in the polymer. Samples of the polyester prepared from perfluoroglutaryl chloride and hexafluoropentanediol were sent to MSFC for LOX-impact testing. The polyester prepared from adipoyl chloride and hexafluoropentanediol was converted into a polyurethane with toluene diisocyanate as described previously.

The preparation of the diester of perfluoroglutaryl chloride and hexafluoropentanediol was attempted by means of a transesterification of dimethyl perfluoroglutarate with hexafluoropentanediol using calcium hydride as a catalyst. The desired reaction was not successful.



An interesting reaction was observed during an attempt to react methanol with the remaining acid chloride end groups of the moderate molecular weight polyester of perfluoroglutaryl chloride and hexafluoropentanediol.

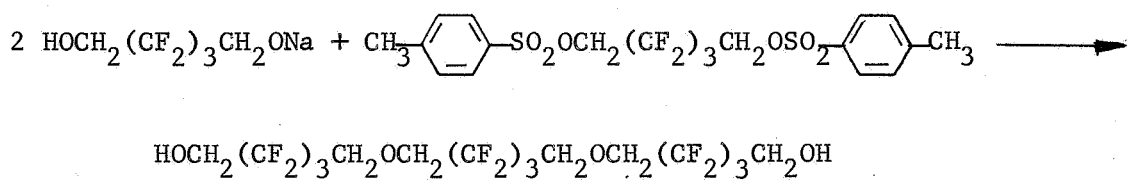
Refluxing the polyester with excess methanol yielded diethyl perfluoroglutarate and hexafluoropentane diol.

This is the reverse type of reaction to that above for the attempted transesterification of dimethyl perfluoroglutarate. This is indicative of the hydrolytic instability of the esters and polyesters of fluorinated acids. The polyesters prepared from perfluoroglutaric chloride were so unstable that molecular weight determination by hydroxyl number was not possible. Titration of the polyesters with 0.1N NaOH could not give a stable end point. Hydroxyl determination by the phthalic anhydride - pyridine method and phenyl isocyanate - dibutylamine method hydrolyzed the polyesters completely to the fluorinated acids. This hydrolytic instability also accounts for the inability to isolate diesters from the reactions run in pyridine. The diesters were obviously hydrolyzed back to the starting diols during the isolation in which aqueous acid was used. Similar evidence as to the instability of polyesters made from fluorinated acids and fluorinated diols and hydrocarbon diols has been presented in NRL Report 4493 (33) and WADC Technical Report 56-11. (34) On the other hand, polyesters made from adipoyl chloride and hexafluoropentane-1,3-diol were stable to 0.1N NaOH.

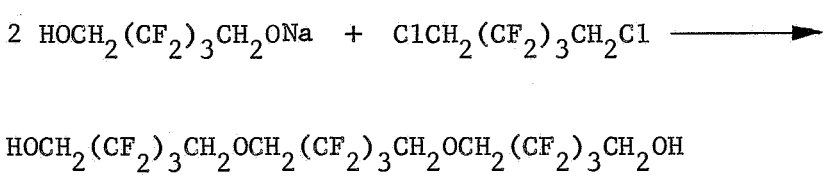
7. Hydroxyl-Terminated Ethers and Polyethers

Hydroxyl-terminated polyethers have found considerable use in the preparations of nonfluorinated polyurethanes. Thus, Narmco is interested in the fluorine-containing polyethers for this purpose, and since they would supply more needed basic information on the relation of LOX compatibility to structure.

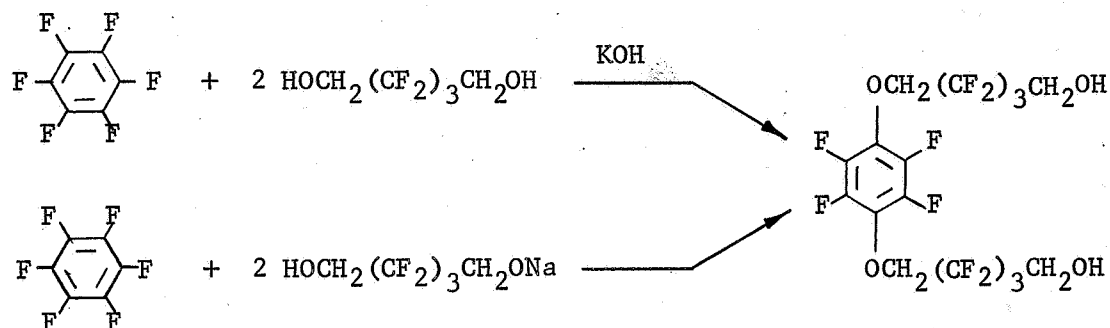
The preparation of tri-hexafluoropentamethylene glycol was investigated in Narmco's laboratory by two routes. The reaction of the di-p-toluene-sulfonate ester of hexafluoropentane-1,3-diol with the monosodium salt of hexafluoropentane-1,3-diol failed to yield any of the desired diether.



The reaction of 1,5-dichloro-hexafluoropentane with the monosodium salt of hexafluoropentane-1,3-diol was carried out in an attempt to prepare the same diether by another route. None of the diether was obtained by this method.

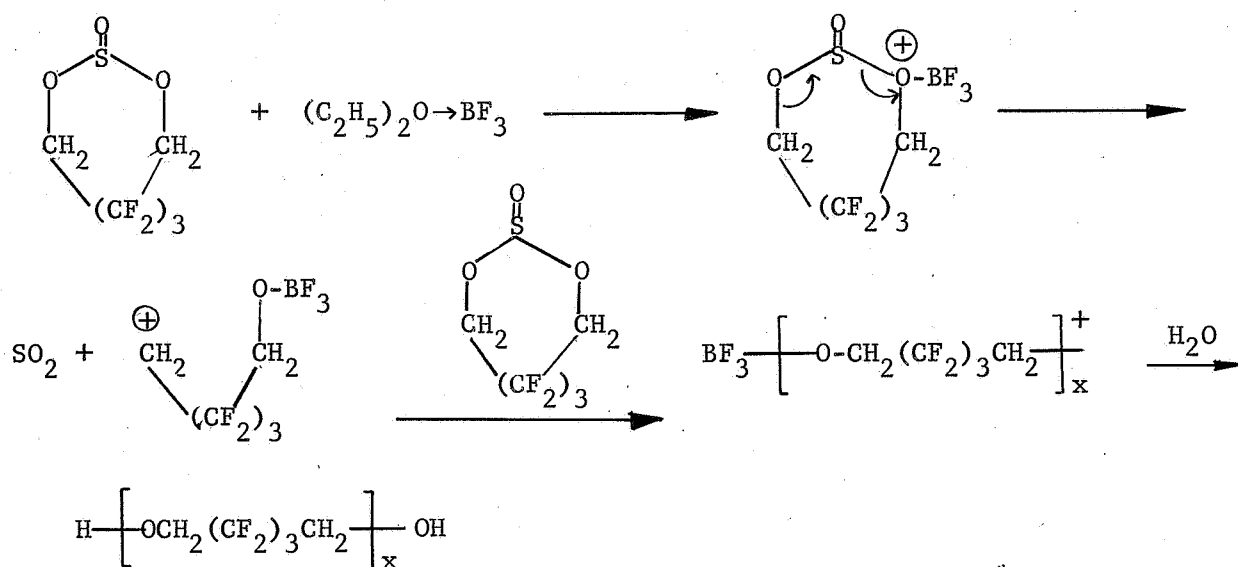


Denivelle and Chesneau⁽⁵³⁾ reported the preparation of the diglycyl ether of hexafluorobenzene by reaction of hexafluorobenzene with ethylene glycol. In Narmco's work, reaction of hexafluorobenzene with both hexafluoropentenediol in the presence of potassium hydroxide with the monosodium salt of hexafluoropentenediol yielded the same yellow oil.



The infrared spectrum indicates that this oil is the desired diether, 1,4-bis-(5-hydroxy-hexafluoropentoxy)-tetrafluorobenzene.

The reaction of hexafluoropentamethylene sulfite with thionyl chloride in pyridine to yield 1,5-dichloro-hexafluoropentane was discussed earlier. In view of the ease with which the thionyl chloride-pyridine complex, apparently acting as a Lewis acid, opened the cyclic sulfite ring, it seemed feasible that hexafluoropentamethylene sulfite could be polymerized by a complex such as boron trifluoride-etherate. The hexafluoropentamethylene sulfite, prepared by reaction of hexafluoropentenediol with thionyl chloride, gave a pale yellow, viscous polyether when allowed to stand at room temperature for three days with a catalytic amount of boron trifluoride-etherate. It seems feasible that the polymerization proceeds by way of the following mechanism.



The cyclic ether, hexafluoropentamethylene oxide, was prepared by dehydration of hexafluoropentanediol according to the procedure of Henne and Richter.⁽⁹⁾ The attempted polymerization of this cyclic ether with boron trifluoride-etherate failed to give any polyether. Apparently, the carbon-oxygen bond in this cyclic ether is considerably stronger than the carbon-oxygen bond in the cyclic sulfite.

C. POLYAMIDES

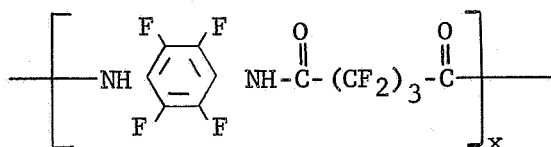
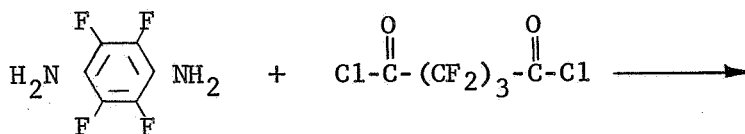
The preparation of highly fluorinated polyamides is also of considerable interest for adhesive applications. In addition to high molecular weight materials, amine-terminated lower molecular weight polymers are of interest because of their potential utility in the reaction with fluorinated diisocyanate to form polyamide-polyureas. The fluorinated amines have been found to be very weakly basic and consequently have reduced reactivities. This provides the possibility of using them in a two-part system with an isocyanate-terminated prepolymer. Such a system would have similar curing characteristics as many existing conventional "Moca" cured systems.

Fluorinated and partially fluorinated aliphatic polyamides have been prepared previously by melt polymerization.⁽⁵⁴⁾ These polymers were reported to be of low molecular weight and could not be transformed into high polyamides or super-polyamides by continued heating. The presence of fluorine in one or both of the monomeric substances apparently profoundly influences the capacity of the monomers to yield polyamides. High molecular weight polyamides, however, are not necessary for subsequent reaction with isocyanate-terminated prepolymers.

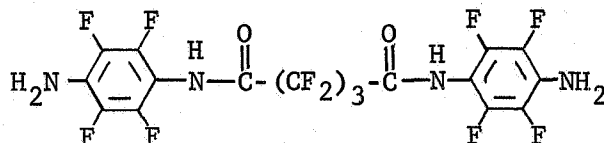
The most successful route to fluorinated and partially fluorinated polyamides was found in Narmco's work to be by interfacial polymerization. In all cases, it was found that the polymer produced by the interfacial method was light colored and of higher molecular weight than those produced by either melt or solution polymerization, which were always black.

1. Poly(tetrafluoro-p-phenylene perfluoroglutaramide)

This polymer was prepared via interfacial polymerization from tetrafluoro-p-phenylenediamine and perfluoroglutaryl chloride in 33% yield.



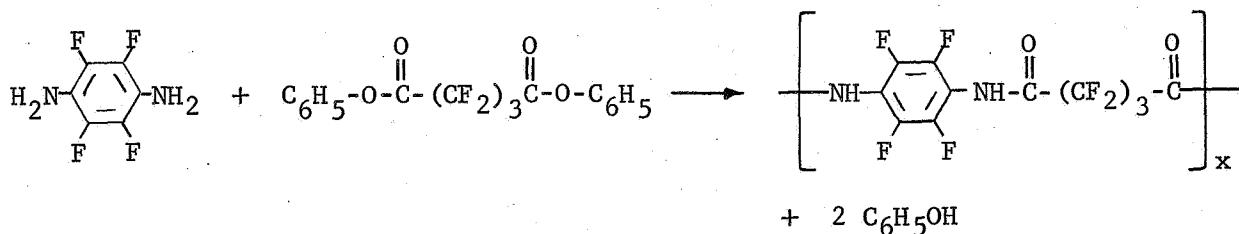
The product formed is highly crystalline and of low molecular weight as indicated by the low inherent viscosity, 0.013 in dimethylformamide (DMF) at 30°C, and the low melting point (157°C to 159°C). It is more likely that the product formed is of the following structure as indicated by the infrared spectrum and the elemental analysis:



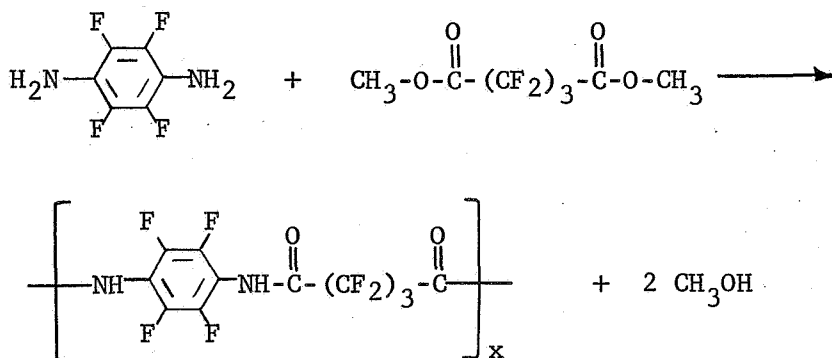
Elemental Analysis:	<u>% C</u>	<u>% F</u>	<u>% N</u>	<u>% H</u>
Calculated:	36.2	47.2	9.9	1.1
Found:	36.52	47.1	9.70	1.43

Solution polymerizations in N-methyl pyrrolidone, pyridine and dimethylacetamide were successful, but low molecular weight black polymers were obtained.

The melt polymerization of tetrafluoro-p-phenylenediamine and diphenyl perfluoroglutarate at temperatures in excess of 200°C produced only black, brittle, low molecular weight polymers. The diphenyl ester of perfluoroglutaric acid was prepared in pyridine in 63% yield.

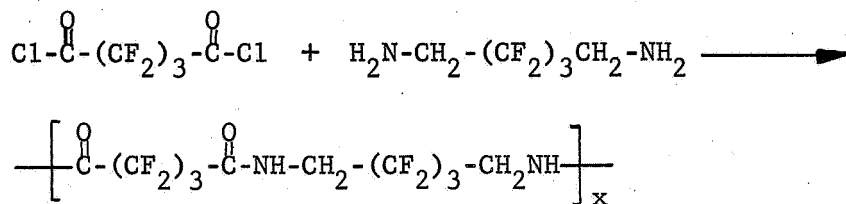


The solution polymerization of tetrafluoro-p-phenylenediamine and dimethyl perfluoroglutarate in polyphosphoric acid was unsuccessful. Dimethyl perfluoroglutarate was prepared in a 67.5% overall yield from perfluoroglutaric acid.



2. Poly(hexafluoropentamethylene perfluoroglutaramide)

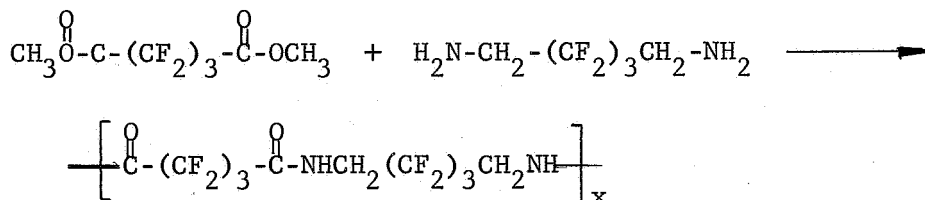
A fluorinated aliphatic polyamide of moderate molecular weight was prepared by the interfacial polymerization of perfluoroglutaryl chloride and hexafluoropentanediamine.



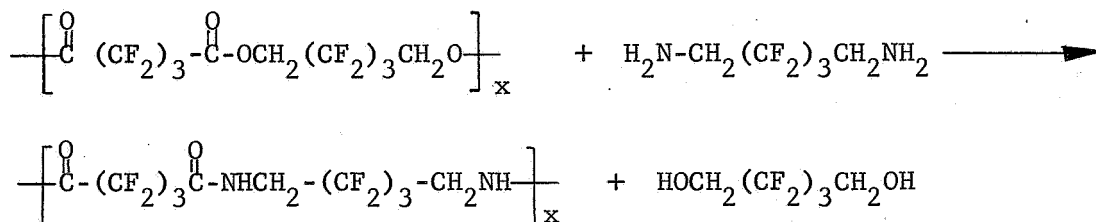
The light tan polymer had an inherent viscosity in DMF of 0.16 at 30°C, and a melting point of 185°C to 190°C. Samples were sent to MSFC for LOX-impact testing.

The solution polymerization of perfluoroglutaryl chloride and hexafluoropentanediamine in butyl ether yield a low molecular weight black, sticky polymer, while the use of pyridine as the solvent yielded a black polymer having a melting point of 105°C to 110°C.

The use of polyphosphoric acid has been reported to be especially suited to condensations reactions wherein the amine is weakly basic.⁽⁵⁵⁾ The solution polymerization of dimethyl perfluoroglutarate and hexafluoropentanediamine in polyphosphoric acid yielded only a trace of black brittle polymer.



Although fluorinated amides have been prepared from simple esters and nonfluorinated amines, the use of fluorine containing amines have not been reported.⁽⁵⁶⁾ Since polyesters of perfluoroglutaryl chloride and hexafluoropentanediol have been found to be unusually reactive in our work with fluorinated polyesters, a fluorinated polyamide has been prepared from this polyester and hexafluoropentanediamine both via solution and melt polymerization techniques. In both cases, however, the polymer was black and of relatively low molecular weight.



3. Poly(ethylene perfluoroglutaramide)

In order to determine the level of fluorine content necessary to impart LOX compatibility, a polyamide of perfluoroglutaroyl chloride and ethylenediamine was prepared via interfacial polymerization. The white polymer had a melting point in excess of 300°C and an inherent viscosity of 0.059 in DMF at 30°C.

4. Attempted Preparation of Poly(tetrafluoro-p-phenylene tetrachloroterephthalamide)

The preparation of poly(tetrafluoro-p-phenylene tetrachloroterephthalamide) from tetrafluoro-p-phenylene diamine and tetrachloroterephthaloyl chloride by the interfacial method was unsuccessful.

5. Attempted Preparation of Poly(methylene hexafluoroglutaramide)

The preparation of 1-n-polyamides by the reaction of formaldehyde with dinitriles was been reported.⁽⁵⁷⁾ An unsuccessful attempt was made to prepare a 1-n-polyamide of hexafluoroglutaronitrile and formaldehyde.

D. POLYESTERS

Polyesters prepared from fluorinated diols with fluorinated and nonfluorinated acids have been reported.⁽⁵⁸⁻⁶²⁾ In all cases, the molecular weight of the polyester is decreased when fluorine is contained in either the acid or diol moiety. Furthermore, the addition of fluorine in the polymer raises its brittle temperature.

Polyesters prepared from fluorinated acids are known to be unstable hydrolytically.⁽³³⁾⁽³⁴⁾ Nevertheless, additional basic information was required regarding the effect of ester linkages on LOX compatibility.

Fluorinated polyesters were prepared by melt polymerization from HET diol, ethylene glycol, hexafluoropentanediol and tetrachloroxylylene diol as the hydroxy moiety, and adipoyl chloride and perfluoroglutaroyl chloride as the acid moiety.

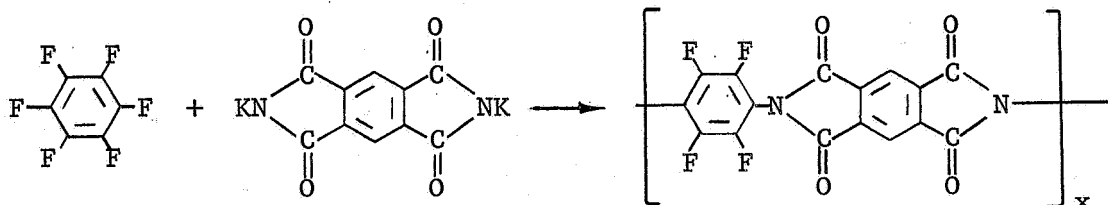
The polyesters of HET diol and tetrachloroxylylene diol with either acid chloride were brittle, black glassy polymers having a high melting point. The polyesters of hexafluoropentanediol and ethylene glycol with perfluoroglutaroyl chloride were liquids which crystallized on standing.

An attempt was made to prepare a high molecular weight fluorinated aliphatic polyester by the interfacial technique. A polyester of hexafluoropentanediol and perfluoroglutaroyl chloride was prepared which was a colorless, viscous oil in 32.2% yield. On standing, the polymer crystallized. This polymer was so sensitive to hydrolysis that serious degradation was apparent in less than 3 hours at room temperature.

E. OTHER POLYMERS

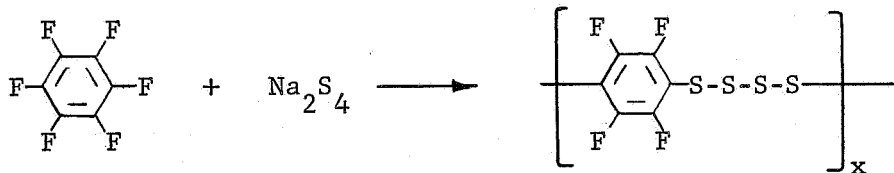
Attempts were made to prepare various other types of fluorinated and partially fluorinated polymers in order to obtain additional basic information in regard to the effect of molecular structure and fluorine content on LOX compatibility.

Since hexafluorobenzene reacts smoothly with potassium phthalimide to obtain 1,4-diphthalimido-tetrafluorobenzene (Gabriel reaction), an attempt was made to prepare poly(tetrafluoro-p-phenylene pyromellitimide).

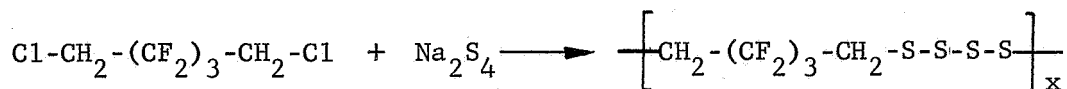


In practice, however, no reaction occurred.

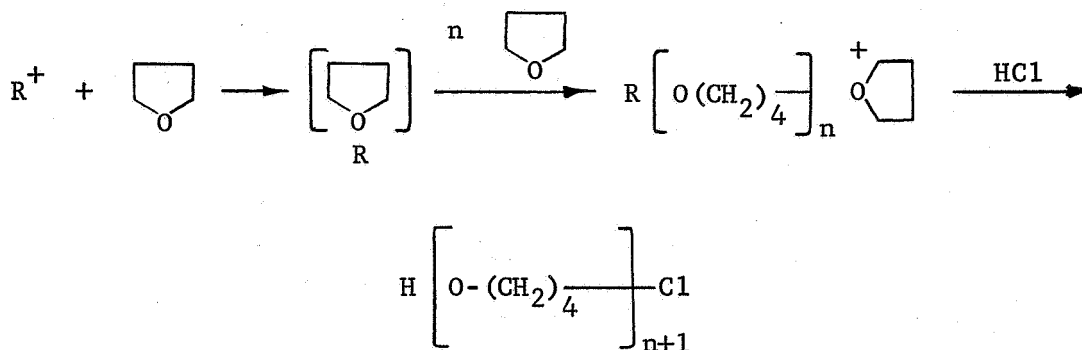
Several attempts were made to prepare polysulfides in order to determine the effect of C-S and S-S linkages on LOX compatibility. In an effort to polymerize hexafluorobenzene with sodium tetrasulfide, no reaction occurred.



Sodium tetrasulfide and 1,5-dichloro-2,2,3,3,4,4-hexafluoropentane also failed to polymerize.



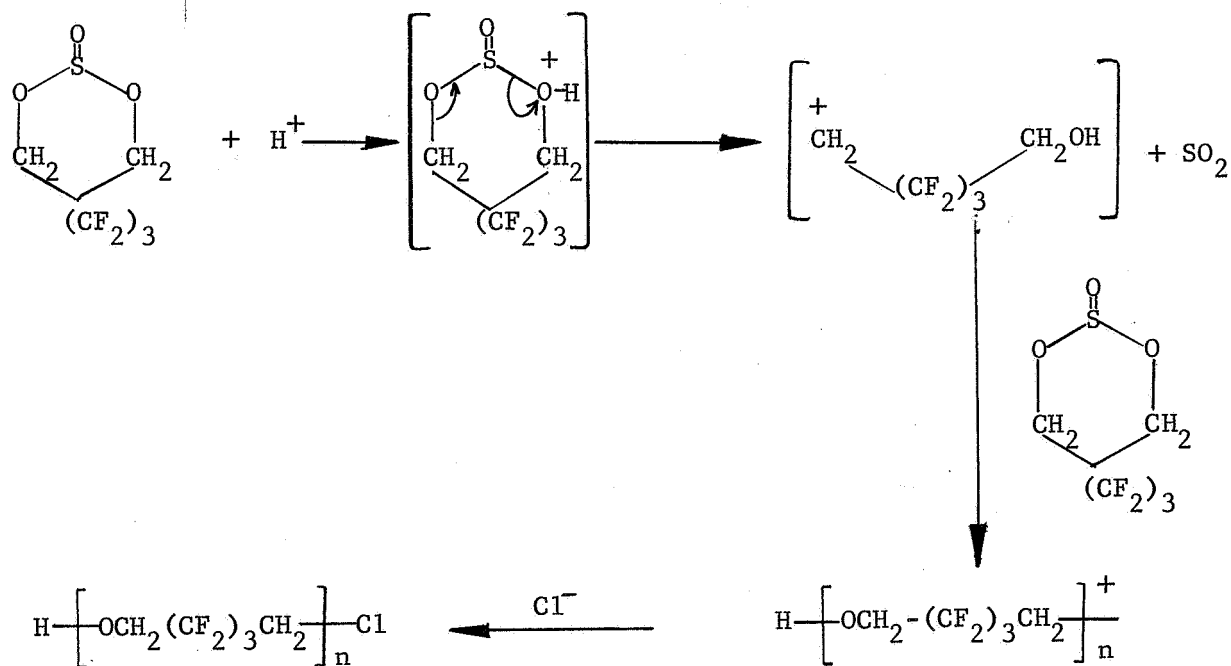
Cyclic ethers such as tetrahydrofuran have been polymerized with the use of Lewis acid catalysts such as BF_3 , SnCl_4 , SbCl_5 , SbCl_3 , PF_5 , and SO_2Cl_2 . Oxonium salt such as $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{BF}_3$ have also been used as catalysts for this polymerization.⁽⁶³⁾ The polymerization has been pictured as proceeding as the consequence of the formation of an oxonium ion, followed by rupture of the tetrahydrofuran ring to generate a carbonium ion. This ion reacts with the second tetrahydrofuran ring, which in turn is opened, and thus polymerization is propagated. The chain reaction is terminated when reaction with an anion occurs.



There is no reference in the literature regarding polymerization of cyclic sulfites to polyethers.

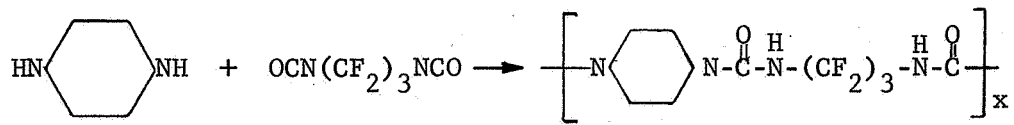
Since the hexafluoropentamethylenesulfite can be readily cleaved, it was believed that a fluorinated polyether could be prepared by the Lewis acid catalysis of the cyclic sulfite.

A fluorinated polyether was prepared by bubbling anhydrous HCl through hexafluoropentamethylenesulfite. The polymer produced was a dark brown semisolid. It is believed that the polymerization proceeds through a mechanism similar to that proposed for the polymerization with boron trifluoride-etherate discussed earlier.



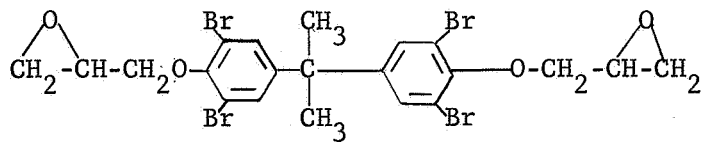
A fluorinated polyether could not be prepared from hexafluoropentamethylene oxide and anhydrous HCl, presumably due to the carbon-oxygen bond in the cyclic ether being stronger than the carbon-oxygen bond in the cyclic sulfite.

Fluorinated polyureas are of interest both as polymers per se and as amine-terminated polyureas for use in cross-linking isocyanate terminated prepolymers. Poly (N,N'-Piperazinohexafluorotrimethyleneurea) was prepared from piperazine and perfluorotrimethylene diisocyanate.



The polymer formed was an amber, brittle solid which hydrolyzed on exposure to air overnight.

Both tetrafluoro-p-phenylenediamine and hexafluoropentanediamine have been briefly investigated as curing agents for Dow's brominated epoxy resin (DER 542).



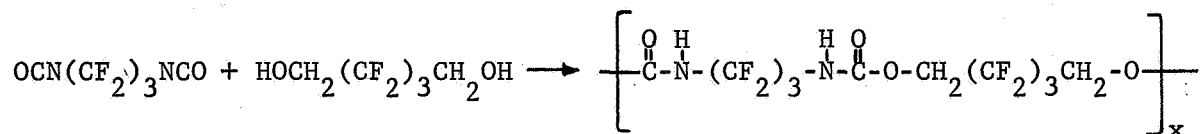
Surprisingly, tetrafluoro-p-phenylenediamine gave the best results, although the cure was very slow. The resulting polymer was hard, with only moderate strength. The aliphatic diamine reacted considerably faster but resulted in a very brittle polymer with poor strength.

III. EXPERIMENTAL

A. POLYURETHANES

1. Poly(hexafluoropentamethylené perfluorotrimethylenedicarbamate)

a. Polymer Synthesis



The polymer was prepared in a 25-ml flask equipped with a stirrer, thermometer, dry nitrogen inlet, condenser, and dropping funnel. The complete system was thoroughly purged with nitrogen, and perfluorotrimethylene diisocyanate (3.2 g, 0.0137 mole, 90% pure), plus 2.9 g of ethyl acetate (dry) was charged to the flask. Hexafluoropentane-diol (2.9 g, 0.0137 mole) was dissolved in 2.9 g of dry ethyl acetate. The solution was filtered and added to the dropping funnel along with 1 drop of triethyl amine.

The diol solution was slowly added to the diisocyanate solution with mixing over a 20-minute period under nitrogen. The temperature rose from 26°C to 37°C. The polymer solution was mixed for an additional 20 minutes under nitrogen, then the temperature was slowly raised to reflux (87°C). The solution was refluxed and stirred for 1 hour under nitrogen, then cooled under nitrogen.

The polymer solution was stripped at 125°C under vacuum for 1-1/2 hours, resulting a very rubbery opaque polymer. The polymer degraded to an oil on exposure to air overnight, while a sample stored under dry nitrogen remained unchanged.

After the determination of the melting point, which was in excess of 300°C, the sample was observed to have improved hydrolytic stability, and did not become liquid after 24 hours in moist air. This improvement in hydrolytic stability was pursued as described in the following section.

b. Crosslinking of Polymer by Postcure

The polymer prepared above was subjected to various degrees of post-cure, and the effect on hydrolytic stability is shown in Table 1.

c. Polymer Degradation Products

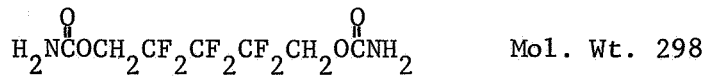
The polymer prepared above was exposed to the atmosphere for 1 month in a glass crystallizing dish. During this period, the glass was

TABLE 1
THE EFFECT OF POSTCURE ON
POLY (HEXAFLUOROPENTAMETHYLENE PERFLUOROTRIMETHYLENEDICARBAMATE)

Postcure Temp, °C	Time, hr	Melting Point of Postcured Polymer, °C	Softening Temp After 24 Hr in Water, °C	Remarks
150-180	1	> 300	70	All specimens lost HF at about 80-90°C
200-230	1	> 300	80	
250-280	1	> 300	90	Polymer becomes brittle after postcure
280-330	1	> 300	> 300	Very brittle after postcure; 7 days in water gave a softening point of 165°C

All polymers evidenced degradation after 10 days atmospheric exposure.

attacked by HF being formed in the hydrolysis. The polymer first became oily, then later became a white solid mass which could be recrystallized from water to yield a product melting at 135°-136.5°C. Vapor phase osmometry indicated a molecular weight of 315 ±15. Using infrared data and results of elemental analysis, the identity of the compound has been established as the dicarbamate of hexafluoropentane diol.



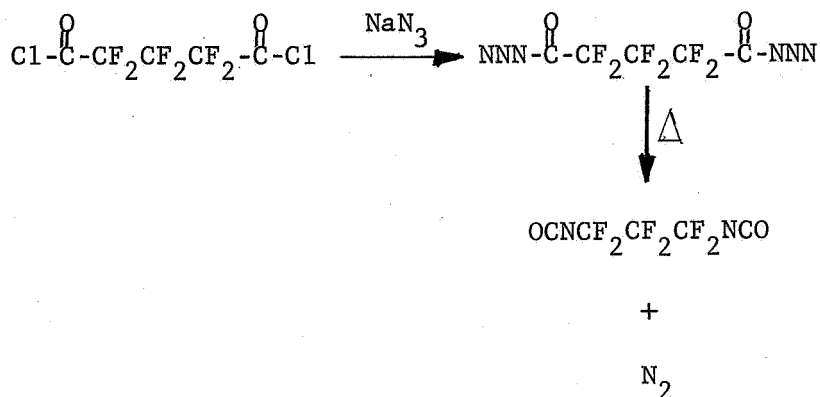
Elemental Analysis:	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% F</u>
Found:	29.22	2.71	9.45	37.75
Calculated:	28.2	2.68	9.40	38.3

d. Specimens for LOX-Impact Testing

Fresh polymer prepared above was used in the preparation of samples for LOX tests. The polymer was molded in the form of a wafer, 1 1/16-in. in diameter and 0.020-in. thick. Twenty discs were molded using 150°-180°C at 3000 psi for 15 minutes. No heat postcure was used on these samples. The molded specimens were sealed in a vial under nitrogen and shipped to MSFC for LOX-impact tests.

Attempts to prepare films by casting the polymer solution were not successful.

e. Preparation of Perfluorotrimethylene Diisocyanate



(1) Purification of Perfluoroglutaryl Chloride

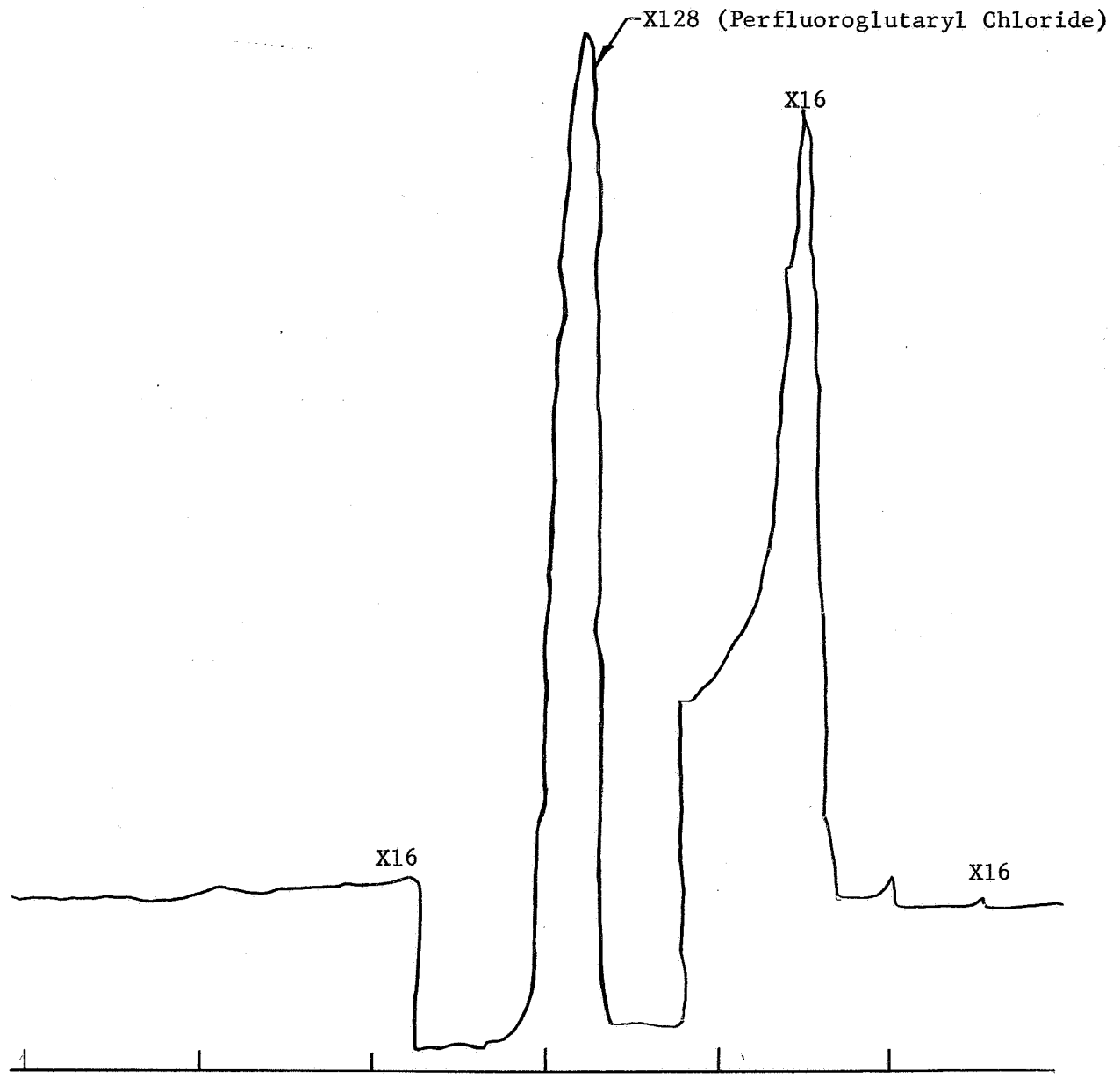
A 0.02-μl sample of the crude dichloride, as received from Hooker Chemical Corporation, was evaluated by VPC using a C-column at 125°C and 15-psi helium pressure. The crude dichloride contained considerable impurities, which were not identified.

The crude perfluoroglutaryl chloride was purified by careful fractionation, using a vacuum-jacketed column 43-in. long. The fractionated product was found to have an approximate purity of 91% as determined by VPC (see Figure 1). A longer packed column gave a product with a higher purity of 95.2% by VPC. The infrared spectrum is shown in Figure 2.

Elemental Analysis:	<u>% C</u>	<u>% F</u>	<u>% H</u>	<u>% Cl</u>
Found:	21.41	41.12	0.22	25.46
Calculated:	21.6	41.2	0.0	25.6

(2) Activation of Sodium Azide

Sodium azide (40 g) was moistened with 2.0 ml of 95% hydrazine and ground in a mortar until homogeneous. The material was left



Fractionated Perfluoroglutaryl Chloride (Cut #3)
C-Column 125°C 15 psi 0.02μ l 91% Acid Chloride

Figure 1. Vapor Phase Chromatography of Fractionated Perfluoroglutaryl Chloride



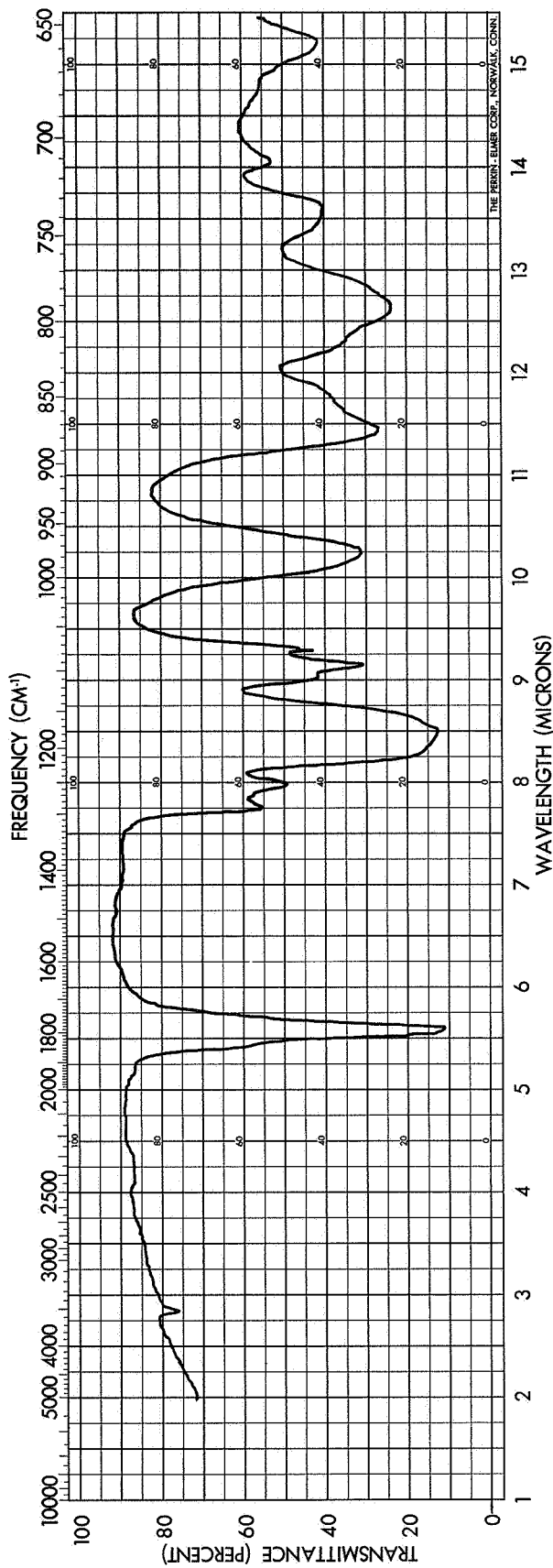


Figure 2. Infrared Spectrum of Perfluoroglutaryl Chloride

standing overnight, then dissolved in 100 ml of hot water in a 2-liter beaker. To the solution was added 1600 ml of cold acetone, and the mixture was allowed to stand for 1 hour. The precipitated sodium azide was collected, washed with acetone, and dried in air. The resulting cake was crushed in a mortar and dried in vacuum at room temperature for 20 minutes. This activated azide was used within 24 hours to avoid any appreciable loss in reactivity. The activity can be regenerated by dissolving the sodium azide in water, and reprecipitating with acetone.

(3) Preparation of Perfluoroglutaryldiazide

The diazide was prepared in a 250-ml flask equipped with a stirrer, thermometer, dry nitrogen inlet, dropping funnel, and condenser. The complete system was thoroughly purged with nitrogen, and a slurry of activated sodium azide (26 g, 0.4 mole) in 65 g of dry xylene was added to the flask. Fractionated hexafluoroglutaryl chloride (27.6 g, 0.1 mole, 91% pure) was then added slowly by means of a dropping funnel over a 43-minute period at 23.5°-38.5°C. After the addition of the acid chloride was complete, the mass was stirred for 20 hours at 23°-28°C. A dry nitrogen purge was maintained throughout the reaction.

(4) Curtius Rearrangement of Perfluoroglutaryl Diazide

The slurry from the azide preparation was slowly heated to reflux over a 1-1/2 hour period. At 28°C, slow decomposition of the azide started with evolution of nitrogen, and the slurry turned from white to a very pale pink. At 92°C, the decomposition became rapid with a deepening of the pink color. As the decomposition subsided at 115°-120°C, the color turned from a pink to a light tan. The slurry was then refluxed (115°-120°C) for 1 hour after the cessation of nitrogen evolution. The organic material was distilled out of the reaction flask, then fractionated.

The fraction boiling at 81°-84°C weighed 4.4 g and was found to be approximately 93% perfluorotrimethylene diisocyanate as determined by VPC (see Figure 3). The overall yield was 27%.

Distillation was repeated with a modified packed column to yield a product of about 99% purity by VPC; b.p. 75°-76°C; $d_{27} 1.795$, g/ml; n_D^{25} , 1.3310.

Elemental Analysis:	<u>% C</u>	<u>% F</u>	<u>% N</u>
Found:	25.80	49.08	11.81
Calculated:	25.6	48.7	12.0

An infrared spectrum of this compound is shown in Figure 4. Note the typical isocyanate absorption at 4.5 μ .

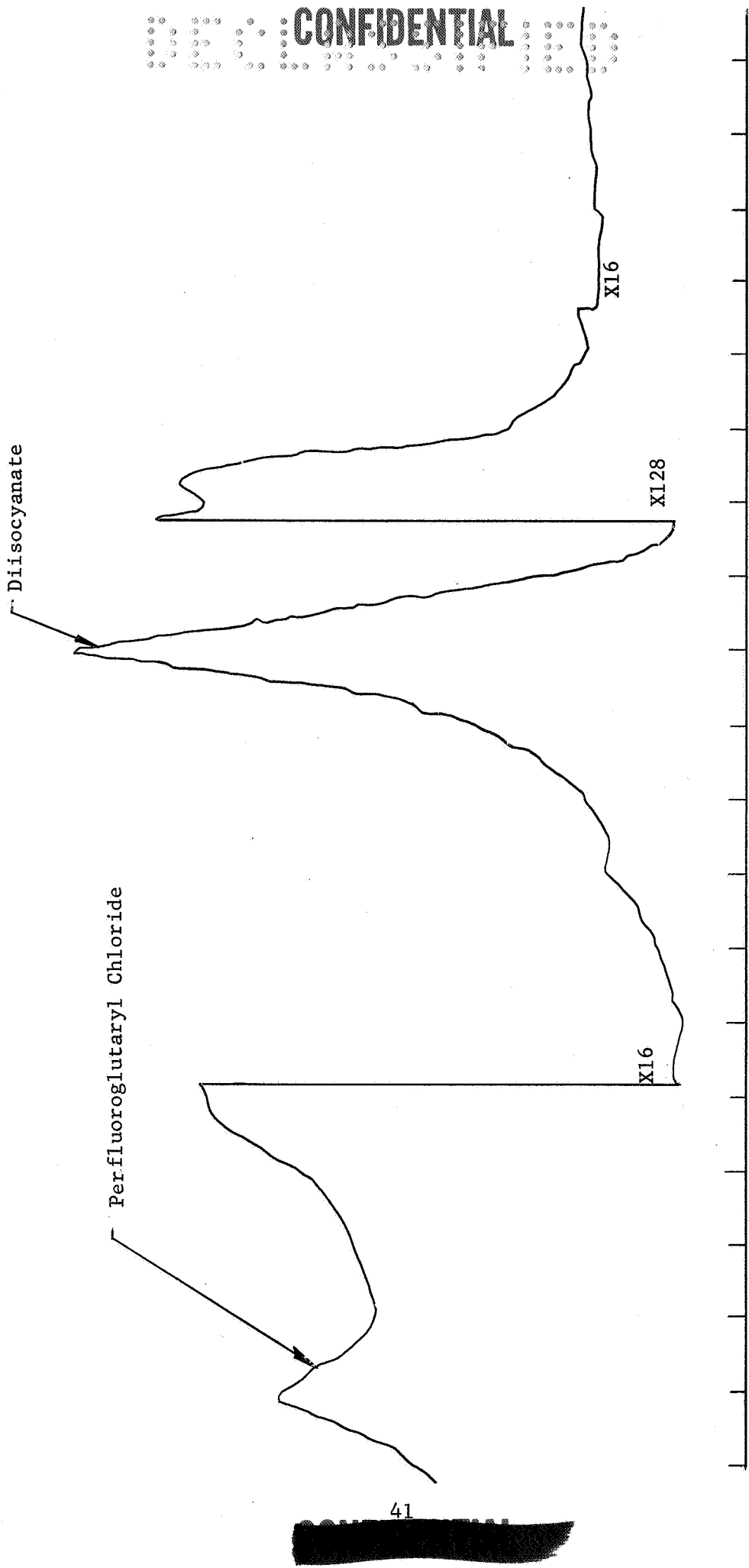


Figure 3. Vapor Phase Chromatograph of Perfluorotrimethylene Diisocyanate

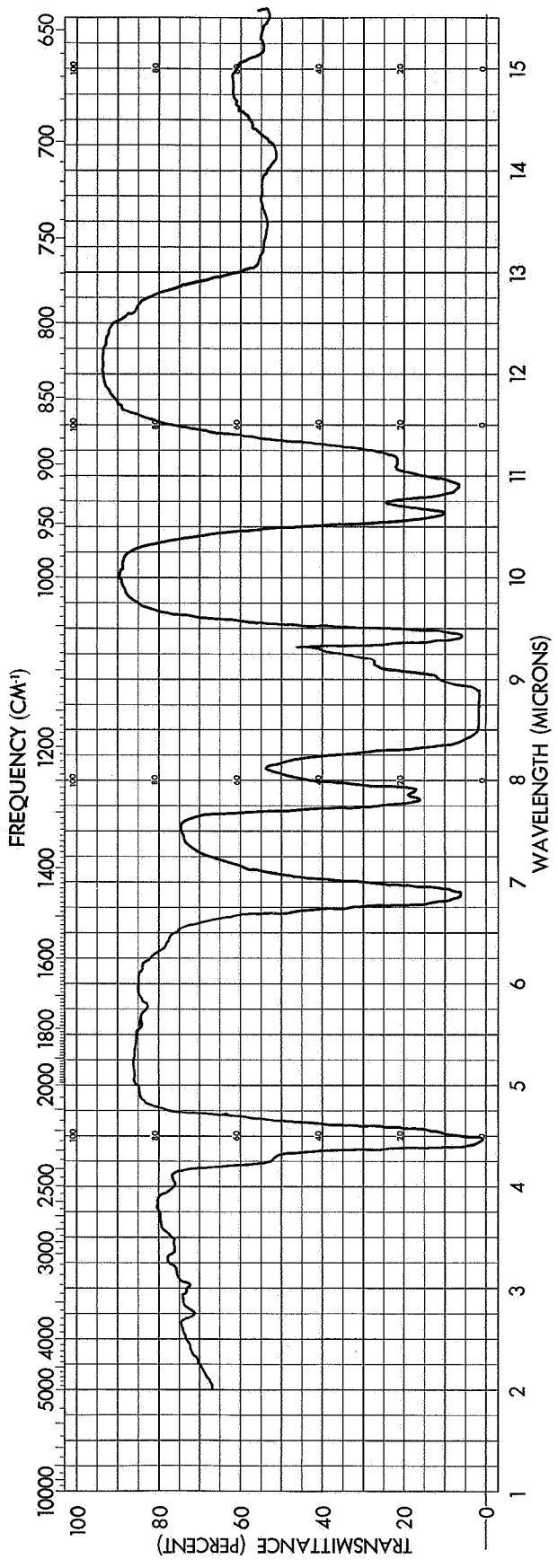
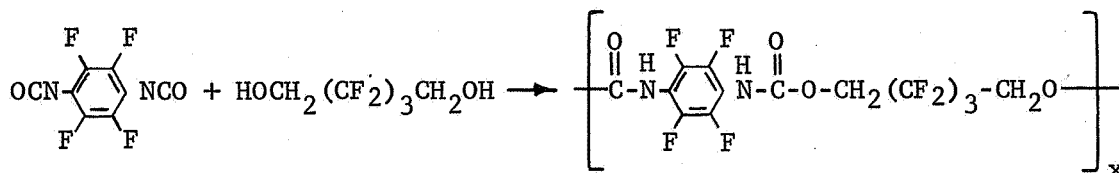


Figure 4. Infrared Spectrum of Perfluorotrimethylene Diisocyanate (Purity 99+% by VPC)

2. Poly(hexafluoropentamethylene tetrafluoro-p-phenylenedicarbamate)

a. Polymer Synthesis



Method 1

Hexafluoropentane diol (2.26 g, 0.0107 mole) was dissolved in 10 ml of dry ethyl acetate containing 1 drop of triethylamine. The diol solution was added to a 25-ml three-necked flask fitted with a stirrer, dropping funnel, thermometer, condenser, and dry nitrogen inlet. Tetrafluoro-p-phenylene diisocyanate (2.47 g, 0.0107 mole) was dissolved in 5 ml of dry ethyl acetate and added to the diol solution over a 25-minute period with stirring under nitrogen. The temperature rose from 24°C to 36°C. Some of the polymer began to precipitate after approximately one-half of the diisocyanate was added.

The polymer system was stirred for 1/2 hour at 25°-30°C, then at 75°-78°C for 2-1/2 hours under nitrogen. An additional 15 ml of dry ethyl acetate was required to facilitate stirring. The solvent was removed and the residue was dried in a vacuum oven at 90°-100°C for 2 hours to yield 4.32 g of a white, opaque crystalline polymer, m.p. 262°-265°C.

The polymer is extremely brittle and crystalline due to branching from allophanate formation. Attempts to mold 11/16-in. discs for LOX compatibility have been unsuccessful. Films cast from solutions of the polymer have also been unsatisfactory. The polymer was stable to hydrolysis on exposure to moist air.

Method 2

Hexafluoropentanediol (0.0142 mole, 3.02 g) was dissolved in 10 ml of dry ethyl acetate and added to a 50-ml, three-necked flask equipped with a stirrer, condenser, dropping funnel, thermometer, and nitrogen inlet. Tetrafluoro-p-phenylene diisocyanate (0.0142 mole, 3.30 g) in 12 ml of dry ethyl acetate was added to the diol solution in 5 minutes with mixing under nitrogen. The solution was mixed for 24 hours at 80°-82°C under nitrogen, after which practically all of the diisocyanate had reacted. One drop of triethylamine was added and the solution stirred for one additional hour. The ethyl acetate was removed in a vacuum oven to yield 4.0 g of a light tan, waxy polymer, m.p. >340°C (see Figure 5).

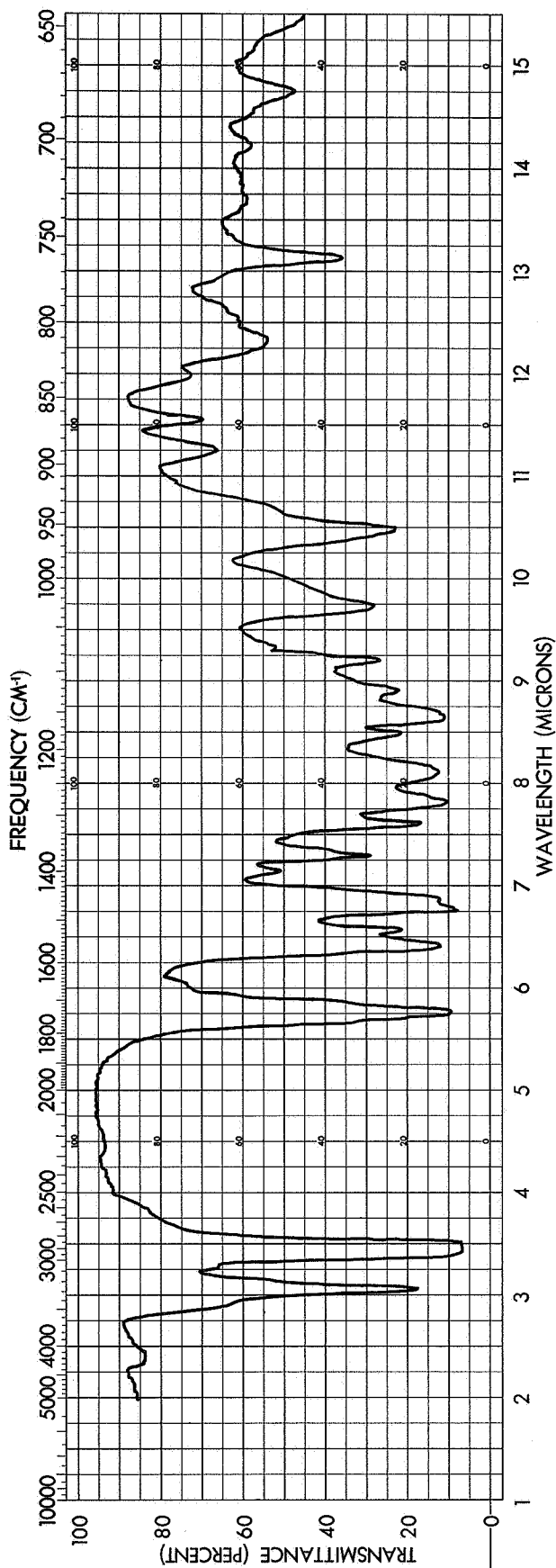
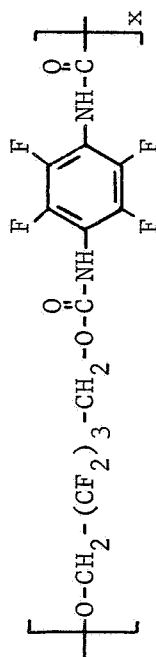


Figure 5. Infrared Spectrum of Poly(hexafluoropentamethylene Tetrafluoro-p-phenylenedicarbamate)



The polymer was of low molecular weight as shown by its inherent viscosity in DMF of 0.032 at 30°C.

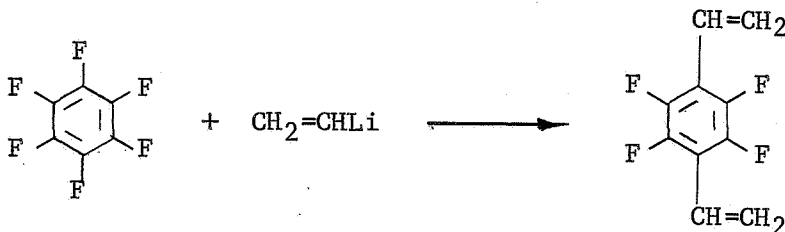
b. Specimens for LoX Impact Testing

The polymer prepared above was molded in the form of a wafer, 11/16 in. in diameter and 0.020-in. thick, using a pellet mold. Twenty discs were molded using 5000 pounds pressure at ambient temperature for 1 minute. The molded specimens were placed in a vial and shipped to MSFC for LOX-impact tests.

c. Preparation of Tetrafluoro-p-phenylene Diisocyanate

(1) Via the Curtius Reaction

(a) Attempted Preparation of 1,4-Divinyl Tetrafluorobenzene



Into a three-necked, 2000-ml flask equipped with a thermometer, a condenser with drying tube, stirrer, and an addition funnel, were introduced 200 ml of 2M vinyl lithium in tetrahydrofuran and 200 ml of anhydrous ether. Hexafluorobenzene (37.2 g, 0.2 mole) was slowly added keeping the temperature below 44°C. As soon as the hexafluorobenzene was introduced the mixture became bright red and became a darker red during the continued addition of hexafluorobenzene. The mixture was refluxed for 16 hours after the addition of hexafluorobenzene was complete. The reaction mixture remained highly colored. Iced, saturated aqueous ammonium chloride (500 ml) was slowly added, resulting in an appreciable exotherm. The water and ether layers were separated and the insoluble salts filtered off. The ether layer was dried with anhydrous sodium sulfate and the ether was subsequently removed by stripping under vacuum. A very small amount of white oily material (less than 10%) was produced. The last traces of ether removed were analyzed by VPC and contained considerable amounts of what appears to be monovinylpentafluorobenzene and divinyltetrafluorobenzene. Heating the product to 85°C caused it to polymerize.

The presence of product in the stripped solvent indicated that the divinyl compound is fairly volatile, and fractionation of the ether is required. The fact that the red

color persisted throughout the reaction time seems to indicate a reverse addition might be helpful.

In a subsequent experiment in which the reaction was performed using reverse addition, hexafluorobenzene (37.2 g, 0.2 mole) and 200 ml of anhydrous ether were added to a 1000-ml three-necked flask equipped with a stirrer, condenser, thermometer, and an addition funnel which contained vinyl lithium in tetrahydrofuran (200 ml, approximately 2M). The mixture turned from white to lilac to purple, and after refluxing overnight, it turned greyish white. The workup described above was followed, except that the ether layer was fractionated at atmospheric pressure. A very slight exotherm was observed during hydrolysis.

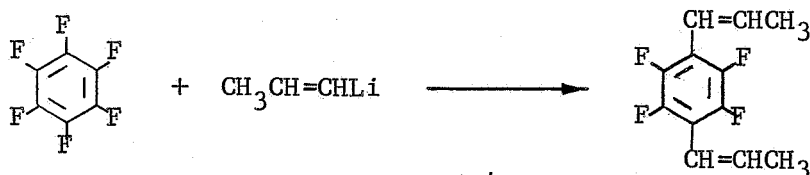
During the fractionation of the last traces of tetrahydrofuran (pot temperature 80°C), the product spontaneously polymerized with an exotherm, resulting in an increase of the pot temperature to 350°C. During this rapid polymerization, considerable amounts of volatile material were lost and this was presumed to be vinylpentafluorobenzene. The yield of polymer was 35%.

The same procedure was repeated with a 3:1 ratio of vinyl lithium to hexafluorobenzene with similar results. The yield of polymer was 95% of the theoretical.

Further studies and characterization of this infusible polymer have not been attempted because of the discrepancy in the elemental analysis, which casts some doubt as to the actual composition of the polymer.

Elemental Analysis:	<u>% C</u>	<u>% H</u>	<u>% F</u>	<u>Total %</u>
Found:	54.57	5.05	28.18	87.0
Calculated:	59.4	2.97	37.6	100.0

(b) Preparation of 1,4 Dipropenyl Tetrafluorobenzene



i. Preparation of Propenyl Lithium⁽⁶⁴⁾

In a three-necked flask (equipped with stirrer, condenser, drying tube, addition funnel, and nitrogen inlet), were placed 1 liter of anhydrous ether and 12 g (0.1 mole) of propenyl bromide. Lithium, 6.9 g (1 mole) was cut into small pieces under nitrogen and introduced into the flask.

The mixture was stirred under a gentle flow of nitrogen until reaction started (about 20 minutes) which was indicated by the appearance of white turbidity and an exotherm. The remainder of the propenyl bromide, 49 g (0.4 mole), was then added dropwise at such a rate that the solution refluxed gently. The mixture changed from white to light pink. After all the bromide was added, the mixture was stirred for 3 more hours and refluxed to ensure complete reaction.

At the end of this period, all the lithium had not reacted. Additional propenyl bromide was added until all the lithium had reacted. This indicated a problem of reactivity with the propenyl bromide. Careful fractionation of 1-bromo-1-propene through a 6-ft, 20-plate column indicated considerable impurity and also revealed that the purchased 1-bromo-1-propene is a mixture of the cis (b.p. 59°-50°C) and the trans (b.p. 63.3°C). It was also revealed that a considerable quantity of light fractions were present, which were later identified as 2-bromo-propene (b.p. 48.5°C). All subsequent preparations were carried out with the fraction boiling from 58°-64°C.

ii. Preparation of 1,4-Dipropenyltetrafluorobenzene

To the ether solution, containing 0.5 M dipropenyl lithium were gradually added 37.2 g (0.2 mole) of hexafluorobenzene in 50-ml anhydrous ether. After all the hexafluorobenzene had been added, the mixture was stirred for 3 hours more at reflux. As the hexafluorobenzene was added, the color of the solution changed from pink to dark orange-brown. After the mixture was cooled, 500 ml of iced saturated aqueous ammonium chloride solution were slowly added. A very thick, gelatinous emulsion was formed. The layers were separated and the emulsion was broken by the addition of 200 ml of aqueous NH_4Cl . The ether layer was dried with Na_2SO_4 - K_2CO_3 (120 g - 60 g).

The solution was then filtered, and the ether distilled off. The residue was recrystallized from a methanol-ether mixture. Only 10.6 g of 1,4-dipropenyltetrafluorobenzene were obtained. The product had a broad melting range just above room temperature and probably consisted of a mixture of products arising from the cis isomer, the trans isomer, and the 2-bromo isomer in the original "1-bromo-1-propene."

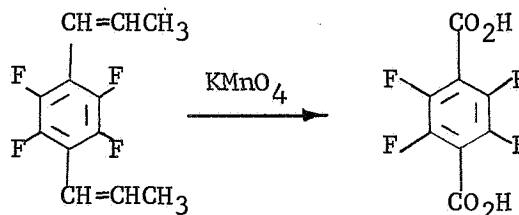
iii. Preparation of 1,4-Dipropenyltetrafluorobenzene
(3:1 Molar Ratio)

Using the same procedure described above, but with 3 moles of propenyl lithium to 1 mole of hexafluorobenzene, a yield of 60% of dipropenyltetrafluorobenzene (based on hexafluorobenzene) was obtained (m.p. 82°-85°C).

iv. Preparation of 1,4-Dipropenyltetrafluorobenzene Using Lithium Dispersion

The lithium dispersion in mineral oil (25 g of approximately 30% lithium suspensoid) was washed with dry hexane and then with dry ether. The lithium and 500 ml of anhydrous ether were placed in a 2-liter, three-necked flask equipped with a condenser, drying tube, stirrer, and an addition funnel. Propenyl bromide (b.p. 58°-63°C), (12 g, 0.1 mole) was added until reaction started and then the balance of the propenyl bromide (49 g, 0.4 mole) was added dropwise, maintaining gentle reflux. The mixture was refluxed for 3 hours after the addition of the bromide. Unreacted lithium remained in suspension. Hexafluorobenzene (37.2 g, 0.2 mole) was added dropwise, maintaining a gentle reflux, and then the mixture was held at reflux for 18 hours. Iced, saturated aqueous ammonium chloride (500 ml) was added dropwise. The ether and water layers were separated and the ether layer dried with magnesium sulfate overnight. The ether was then removed under vacuum. The crude product weighed 42 g, and was a brown oil in which crystals formed upon standing. The yield was 90%, assuming the composition to be dipropenyltetrafluorobenzene.

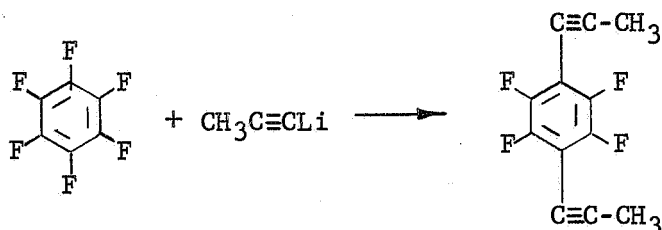
(c) Oxidation of 1,4-Dipropenyltetrafluorobenzene to Tetrafluoroterephthalic Acid



A solution of 4.6 g (0.02 mole) of 1,4-dipropenyltetrafluorobenzene in 150 ml of dry acetone was cooled to 0°C. Potassium permanganate (1.89 g, 0.12 mole) was added and

the mixture stirred for 3 hours at 0°C. The mixture was then placed in a refrigerator for 18 hours at 0°C. Water (250 ml) was then added and the acetone removed under vacuum. Sulfuric acid (45 ml) was added to the solution and SO₂ gas bubbled through until the solution became colorless. The water layer was then extracted with ether for 18 hours, and the ethereal solution was then dried with MgSO₄ and evaporated to dryness. The crude mass was recrystallized from water forming white crystals of tetrafluoroterephthalic acid (m.p. 278°-281°C; literature reports 283°-284°C.⁽⁶⁵⁾ The yield was 3.2 g (67.2%).

(d) Preparation of 1,4-Dipropynyltetrafluorobenzene

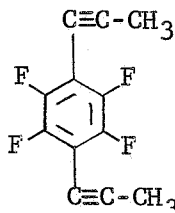


Into a three-necked, 2000-ml flask equipped with a Dewar condenser, mechanical stirrer, and a gas inlet were introduced 1000 ml of liquid ammonia. Lithium wire (3.5 g, 0.5 mole) was added and stirred for 1 hour. Propyne was then rapidly introduced until the reaction mixture turned white. The propyne addition was continued until a 50% excess had been added and the reaction mixture became transparent (1.5 hours). The ammonia and excess propyne were removed under vacuum. To the remaining solid mass was added 500 ml of freshly distilled tetrahydrofuran, and the mixture was stirred until a uniform slurry of propynyl lithium was obtained. To the slurry was added hexafluorobenzene (40 g, 0.22 mole) and the reaction mixture maintained at reflux with a dry nitrogen purge for 24 hours. During the reaction some solvent and hexafluorobenzene were swept out of the system but were returned to the reaction by means of a dry-ice trap. Upon completion of the reaction time, 500 ml of cold saturated ammonium chloride was added and the layers separated. The ether layer was dried with magnesium sulfate for 24 hours. The tetrahydrofuran was then stripped under vacuum until a dry red-brown powder was obtained (m.p. 75°-85°C). The crude product weighed 40.5 g, and analysis by vapor phase chromatography (VPC) indicated it contained a 5:1 ratio of the dipropynyl to the mono-propynyl derivative. It also contained considerable amounts of unidentified material. Identification of dipropynyltetrafluorobenzene was based on the similarity of VPC retention time observed with the previously prepared dipropenyltetrafluorobenzene.

The above reaction was repeated with the modifications as indicated below:

Propynyl lithium (0.5 mole) was prepared as described above, but vacuum and heat were applied to the solid propynyl lithium before it was dispersed in tetrahydrofuran. This was an effort to remove all traces of ammonia, which was believed to be causing some byproduct with hexafluorobenzene. After the removal of ammonia, the reaction with hexafluorobenzene was conducted in the same manner. Because purification by crystallization and extraction had both failed, sublimation was attempted.

Into a vacuum sublimation apparatus was placed 20 g of the solid product from the above reaction. Sublimation was successfully carried out at 100°-150°C at 1 mm, with pure white needles of 1,4-dipropynyltetrafluorobenzene being obtained. The recovery was very low, being less than 10%. The white needles of 1,4-dipropynyltetrafluorobenzene melted at 173°-175°C. The infrared spectrum supports this compound and is shown in Figure 6.



Elemental Analysis:	<u>% C</u>	<u>% H</u>	<u>% F</u>
Found:	63.21	3.21	33.57
Calculated:	63.65	2.66	33.65

The hydrolysis step in the reaction sequence described earlier was eliminated because it was believed that losses were being introduced by this step, and since it is not necessary to the reaction sequence. The resulting dry product was sublimed but the yield was again less than 10% of 1,4-dipropynyltetrafluorobenzene.

The sublimation step was also eliminated and the permanganate (see below) oxidation carried out on the crude reaction product. It seemed apparent that the heat required for sublimation (100°-150°C) was sufficient to cause polymerization.

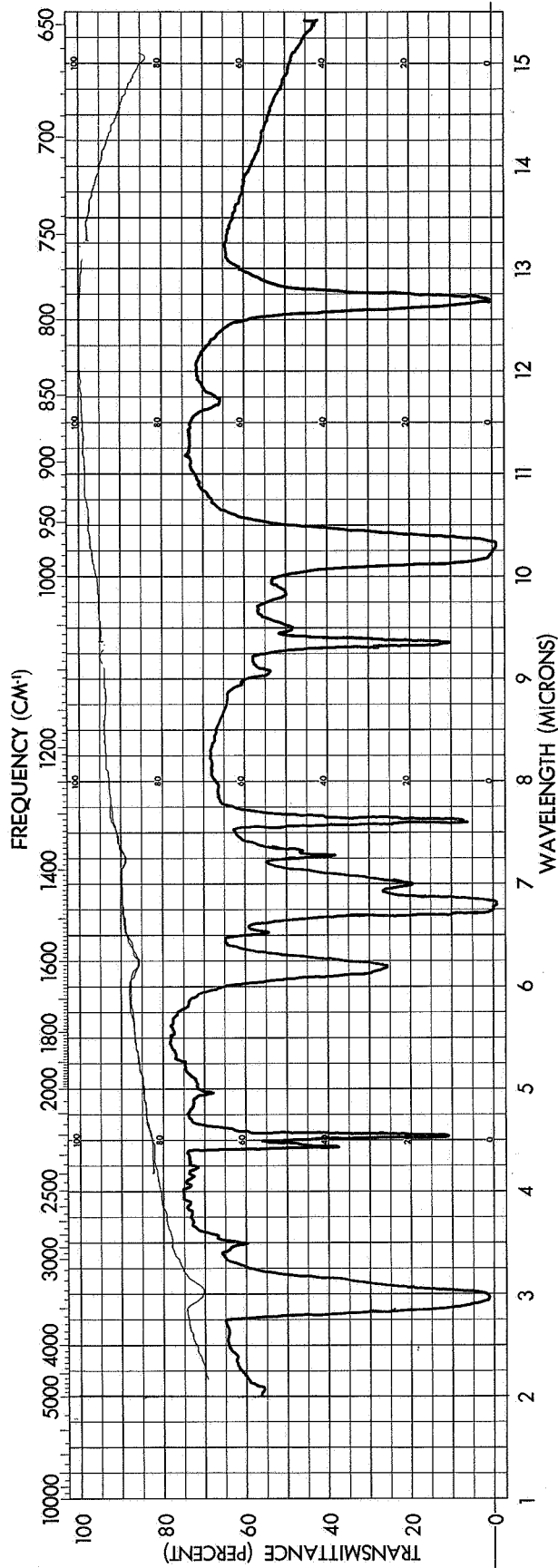


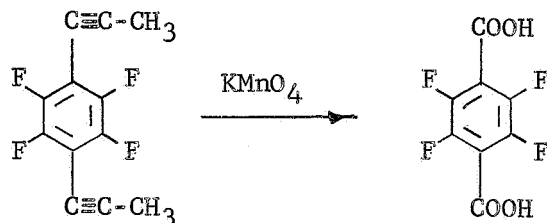
Figure 6. Infrared Spectrum of 1,4-Dipropynyltetrafluorobenzene (KBr Pellet)

The oxidation of the product prepared from 0.5 mole of propynyl lithium resulted in tetrafluoroterephthalic acid, but the yield was only 10%.

Analysis by VPC indicates that the crude reaction product from the dipropynylation contains considerably more dipropynyltetrafluorobenzene than is actually isolated or accounted for in oxidation to the acid.

Other reaction variables were studied by appropriate modifications of the reaction sequence described above. These results are tabulated in Table 2.

(e) Oxidation of 1,4-Dipropynyltetrafluorobenzene to Tetrafluoroterephthalic Acid



A solution of 1,4-dipropynyltetrafluorobenzene (15.0 g, 0.01 mole) in 450 ml of dry acetone was cooled to 0°C. Potassium permanganate (56 g) was added and the mixture stirred for 3 hours at 0°C. The mixture was then placed in a refrigerator for 18 hours at 0°C. Water (750 ml) was then added and the acetone removed under vacuum. Sulfuric acid (90 ml) was added to the solution and SO₂ gas bubbled through until the solution became colorless. The water layer was then extracted with ether for 18 hours, and the ethereal solution was then dried with MgSO₄ and evaporated to dryness. The crude mass was recrystallized from water forming white crystals of tetrafluoroterephthalic acid (m.p. 276°-280°C; literature reports 283°-284°C).⁽⁶⁵⁾ Yield was 10 g (63.8%)

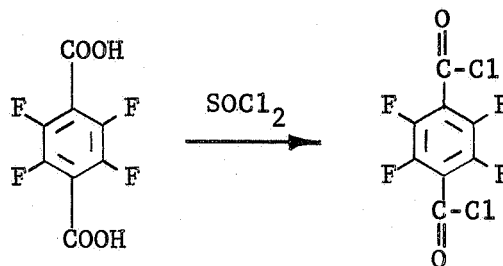
TABLE 2

PREPARATION OF 1,4-DIPROPYNYLTETRAFLUOROBENZENE

Propynyl Reagent	Solvent	Temp, °C	Time, hr	% Conversion	% Efficiency* (Actually Isolated)	Remarks
Lithium	Et ₂ O	35	24	0	0	No reaction
	THF	65	24	100	10	Sublimation attempted and found unsatisfactory; material polymerizes; GLC indicates 30%-35% efficiency but not isolatable
Sodium	THF	-80	8	25	0	25% yield of monopropynyl compound by GLC; not isolated
	THF	0	12 days	100	0	35%-40% yield and efficiencies by GLC; workup is incomplete
	THF	25	48	100	10	25%-30% yield and efficiency by GLC; high losses in workup
Sodium	N-methyl-pyrrolidone	66	24	100	0	Unidentified black polymer was only product
	THF	65	24	100	0	Tarry material; could not isolate dipropynyl compound
Sodium	THF	25	48	75	33	Isolated efficiency much improved. Less byproducts

* $\frac{\text{Yield}}{\text{Conversion}} = \text{Efficiency}$

(f) Preparation of Tetrafluoroterephthaloyl Chloride



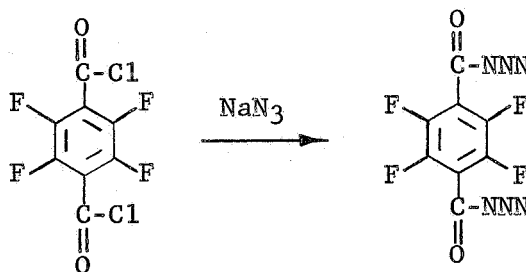
Tetrafluoroterephthalic acid (14 g, 0.056 mole) was reacted with thionyl chloride (60 ml) and dimethylformamide (5 drops) at reflux for 3 hours. The thionyl chloride was then stripped and the product distilled. The resulting acid chloride, tetrafluoroterephthaloyl chloride, boiled at 220°C and was recrystallized from dry hexane, m.p. 36°-38°C. Yield was 70%.

Analysis by VPC indicates a purity in excess of 99%.

Elemental Analysis:	<u>% C</u>	<u>% H</u>	<u>% F</u>	<u>% Cl</u>
Found:	35.11	0.23	27.70	25.86
Calculated:	34.91	0.00	27.63	25.82

The compound was further characterized by an infrared absorption spectrum showing expected characteristics (see Figure 7).

(g) Preparation of Tetrafluoro-p-phenylene Diacylazide



A 250-ml flask, fitted with a stirrer, thermometer, dry nitrogen inlet, dropping funnel and condenser, was purged

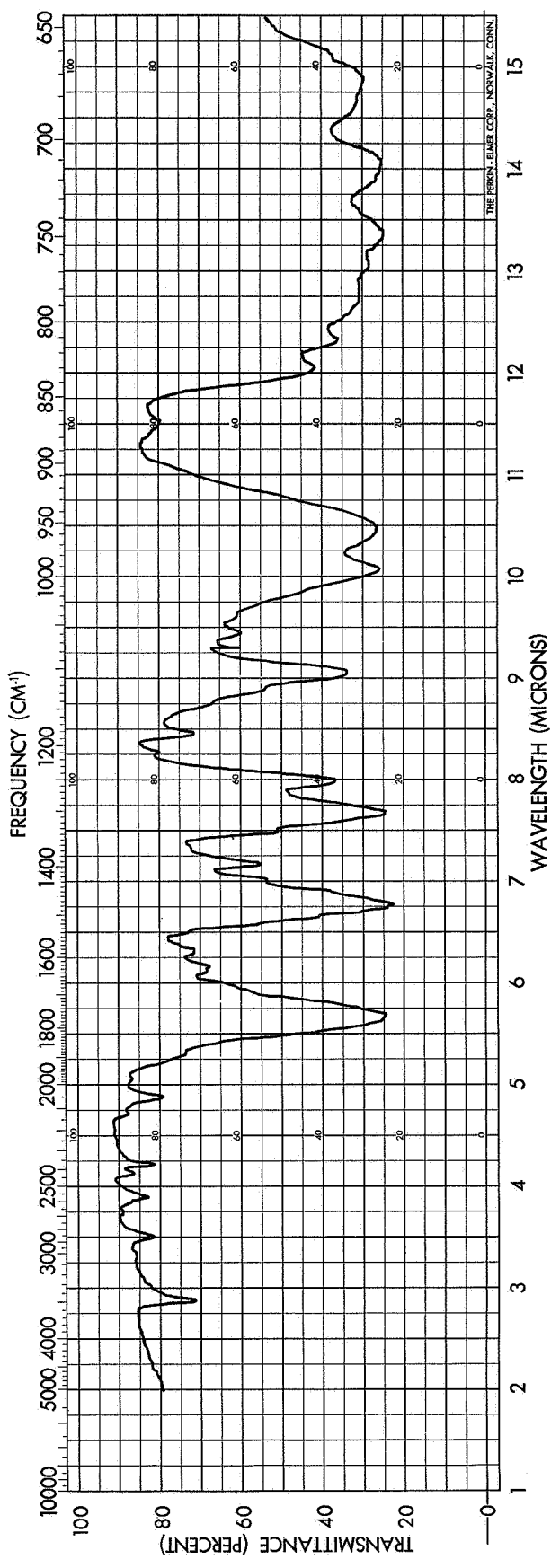
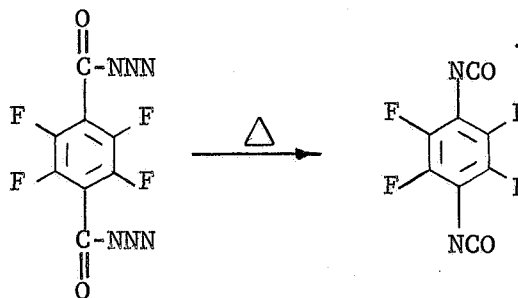


Figure 7. Infrared Spectrum of Tetrafluoroterephthaloyl Chloride (Purity 99+% by Vapor Phase Chromatography)

with dry nitrogen. A slurry of activated sodium azide (13.0 g, 0.2 mole) in dry xylene (56.4 g) was added to the flask. Distilled tetrafluoroterephthaloyl chloride (13.7 g, 0.05 mole; about 87% pure) was dissolved in dry xylene (8.6 g) and added to the dropping funnel. The dichloride solution was slowly added over a 40-minute period at 24°-35°C with mixing while maintaining a dry nitrogen atmosphere. Slow decomposition of the azide was apparent for the first 5 hours of the diazide preparation. The mass was stirred for a total of 20 hours at 25°C to 27°C under dry nitrogen after all the dichloride had been added.

(h) Curtius Rearrangement of Tetrafluoro-p-phenylene Diacylazide
Tetrafluoro-p-phenylene Diisocyanate

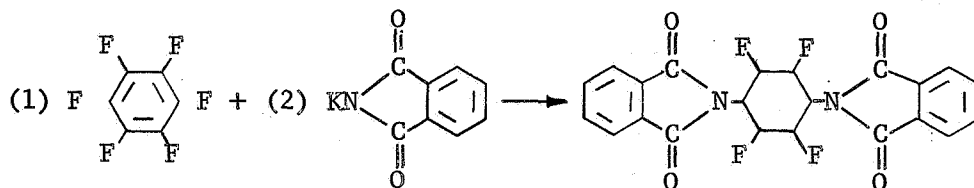


The slurry from the above diazide preparation was slowly heated to reflux over a 1-hour period with stirring. Slow decomposition of the azide started at 40°C. The slurry was refluxed and stirred for 1 hour after the cessation of the nitrogen evolution. The slurry was then cooled to ambient temperature under dry nitrogen, then filtered. The filter cake was washed twice with dry xylene. Xylene was removed from the solution by fractionation at 75-mm pressure. The diisocyanate was then fractionated at 5-mm pressure. Two heart fractions were taken. The fraction boiling at 76°C to 80°C (at 5 mm) weighed 0.34 g and was found to be approximately 96.4% tetrafluoro-p-phenylene diisocyanate as determined by VPC. The fraction boiling at 81°C to 84°C (at 5 mm) weighed 2.53 g and was found to be approximately 85.2% diisocyanate. The overall yield was approximately 31%. The infrared spectrum of this material has a very strong absorption peak at 4.5 μ . The impurities which were indicated in the gas chromatograph are compounds which contain carbonyl as indicated by infrared. There is strong absorption at 5.7 μ and contamination of the diisocyanate with unreacted acid chloride and monoisocyanate seems probable.

Distillation as a means of purification of tetrafluoro-p-phenylene diisocyanate is not desirable because of its reactivity. Alternately, it has been found that the diisocyanate can be recrystallized from hexane to give much improved purity (93.3%). The melting point determination also indicated impurity (30°-35°C).

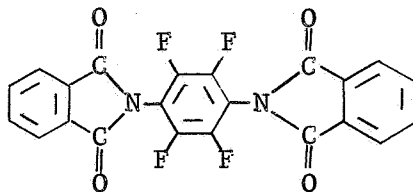
(2) Via the Gabriel Reaction

(a) Preparation of 1,4-Diphthalimidotetrafluorobenzene



Into a 500-ml flask equipped with a stirrer and a reflux condenser were placed hexafluorobenzene (18.6 g, 0.1 mole), potassium phthalimide (55.2 g, 0.3 mole), and n-methyl pyrrolidone (300 ml). The reaction was heated to 135°C and stirred for 8 hours, then poured into 1200 ml of water. The tan solid was filtered, washed with water, and dried in an air oven at 100°C. The dry solid weighed 44 g. Recrystallization from pyridine gave 20 g of a tan-colored material melting at 365°-375°C with sublimation beginning at 315°C. Recrystallizing of a portion of this material again from pyridine gave a white powder with only a slight improvement in melting point (370°-375°C).

The diphthalimide structure was indicated by the determination of ϵ_{\max} at 315 m μ which was observed to be twice that found for N-phenylphthalimide. The infrared spectrum supported the identity (see Figure 8). Elemental analysis was consistent with the diimide structure.



m.p. 370°-375°C

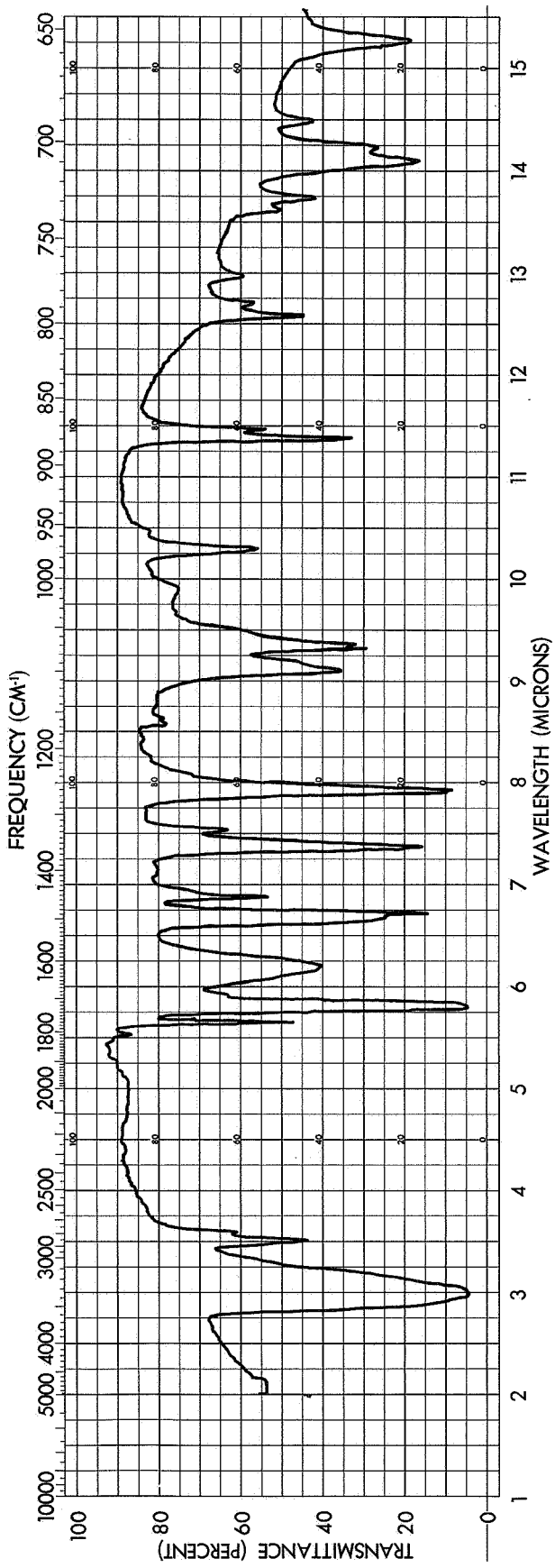


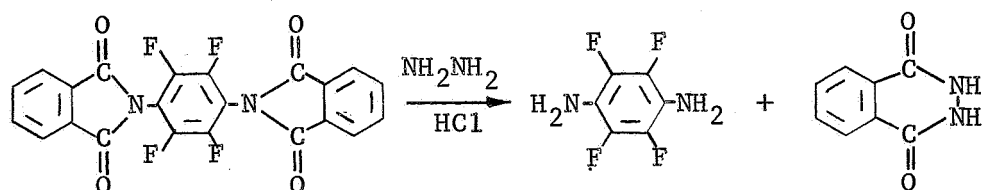
Figure 8. Infrared Spectrum of 1,4-Diphthalimidotetrafluorobenzene (KBr Pellet)

Elemental Analysis:	<u>% C</u>	<u>% H</u>	<u>% F</u>	<u>% N</u>
Found:	60.64	1.79	16.27	6.37
Calculated:	60.0	1.8	17.2	6.4

The above reaction was repeated under various reaction conditions in order to determine their effect on the yield of the tetrafluoro-p-phenylenediamine (see Table 3). (The other products in this reaction were not isolated or identified.) The slurry was then cooled to room temperature and then added to 1 liter of water with mixing. The crude diimide precipitate was filtered and washed with water.

The reaction variables conducted during the preparation of the 1,4-diphthalimidotetrafluorobenzene affected the yield of the diamine, as described in Table 3.

(b) Preparation of Tetrafluoro-p-phenylenediamine



The crude, 1,4-diphthalimidotetrafluorobenzene, hydrazine (9.6 g, 0.3 moles) and ethanol were charged to a 1-liter, three-necked flask equipped with a stirrer, thermometer, and condenser. The slurry was mixed for 1-1/4 hours at 80°-82°C, then 100 ml of concentrated hydrochloric acid was added. The mixture was heated at 82°-85°C for 30 minutes with stirring, 100 ml of water was added, and the slurry cooled. The phthalhydrazide was removed by filtration.

The alcohol in the amine hydrochloride solution was removed by evaporation, the solution charcoal-treated, then filtered to remove the last traces of phthalhydrazide. The solution was cooled to 10°-15°C and made alkaline with sodium hydroxide while maintaining the temperature at 10°-15°C. The crude diamine was removed by filtration, recrystallized from water and dried in a vacuum oven at 55°-60°C for 2 hours.

Although the use of dimethylformamide as the solvent did not substantially increase the yield of the diamine, the reaction and workup was simplified, possibly due to a decrease in the amount of higher substituted materials.

TABLE 3

PREPARATION OF TETRAFLUORO-P-PHENYLENEDIAMINE

Hexafluorobenzene, moles	Potassium Phthalimide, moles	Solvent (ml) N-methyl pyrrolidone	Reaction Time, hr	Reaction Temp, °C	Yield of Purified Amine, %
0.1	0.3	600	4	135	24.5
0.1	0.3	300	4	135	30.0
0.1	0.3	150	4	135	42.0
0.1	0.3	100	4	135	42.0
0.1	0.2	150	4	135	21.4
0.1	0.4	300	4	135	0.6
0.1	0.3	300	72	80	24.0
0.1	0.3	300	14	150	7.0
0.1	0.3	150	72	RT	0
0.1	0.3	300	16	190	4.2
0.1	0.2	150	4	190	17.8
0.1	0.3	300*	28	80	0
0.1	0.3	150**	4	135	44.5

* Solvent was methyl ethyl ketone (MEK)

** Solvent was dimethylformamide

The diamine preparation was scaled-up by reacting 2.0 moles of hexafluorobenzene with 6 moles of potassium phthalimide in 3 liters of dimethylformamide at 135°C for 4 hours. The recrystallized tetrafluoro-p-phenylenediamine obtained from this reaction weighed 120 g; m.p. 143.5°-145°C. Sublimation occurs readily at 120°C to form colorless needles with no improvement in melting point. The infrared spectrum supports the identity as the diamine (see Figure 9).

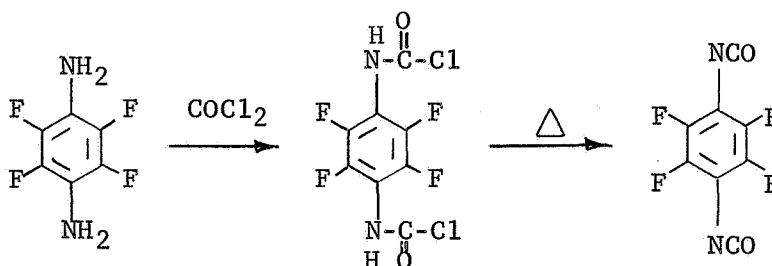
Elemental Analysis:	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% F</u>
Found:	40.30	2.44	15.23	42.40
Calculated:	39.9	2.2	15.5	42.1

A previous report on this compound gives a value of 144°-145°C for the melting point. (31)

An improved purification procedure was subsequently used in which the crude diamine was removed from the reaction pot in the pure form via steam distillation. The pure diamine was therefore recovered directly in 47% yield using the optimum preparative procedure.

At attempt to further improve the procedure by cleaving the diphthalimidohexafluorobenzene in DMF was unsuccessful. It was necessary to precipitate the diimide first by pouring the DMF solution in water, filtering and redissolving in ethanol.

(c) Preparation of Tetrafluoro-p-phenylene Diisocyanate



A permanent reaction apparatus for phosgenation was constructed which ensures safe handling and also removes chlorine from the phosgene. This apparatus provides close control of the reaction (see Figure 10).

To a three-necked, 2-liter, round-bottom flask fitted with a gas inlet, addition funnel (wrapped with a heating tape) fitted with an argon-fed gas inlet, Dewar condenser, and

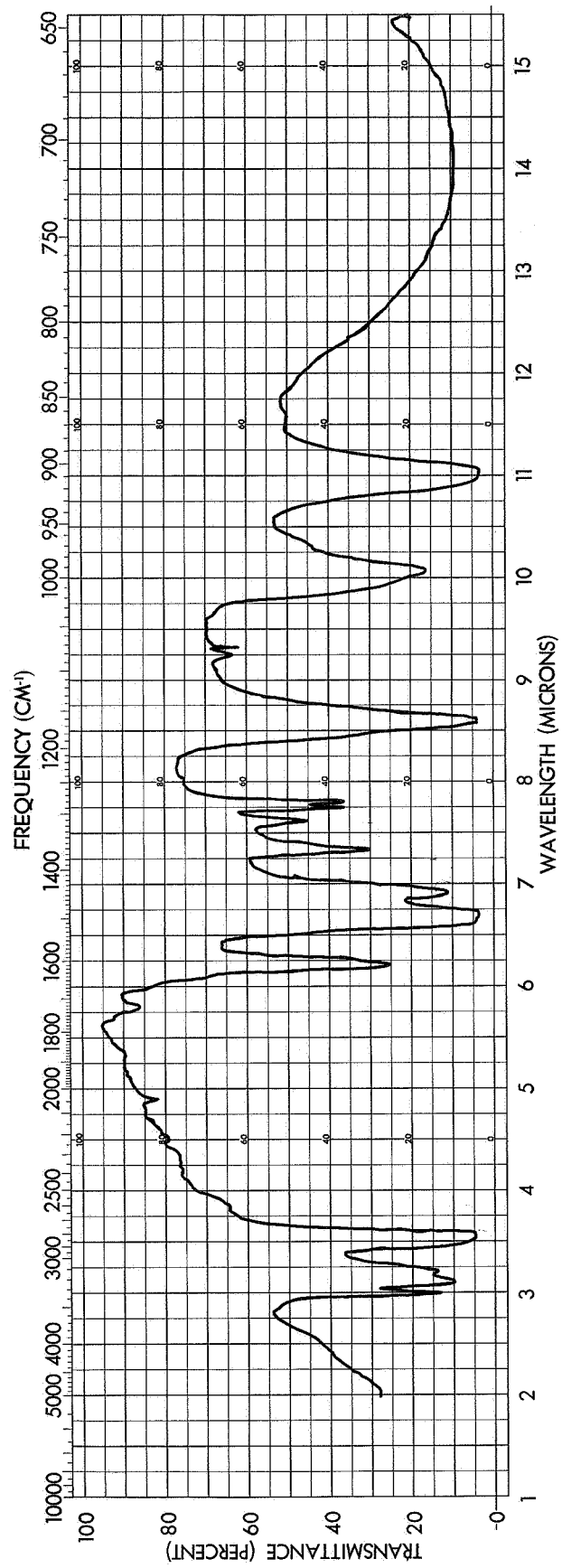


Figure 9. Infrared Spectrum of Tetrafluoro-p-phenylenediamine (Nujol Mull)

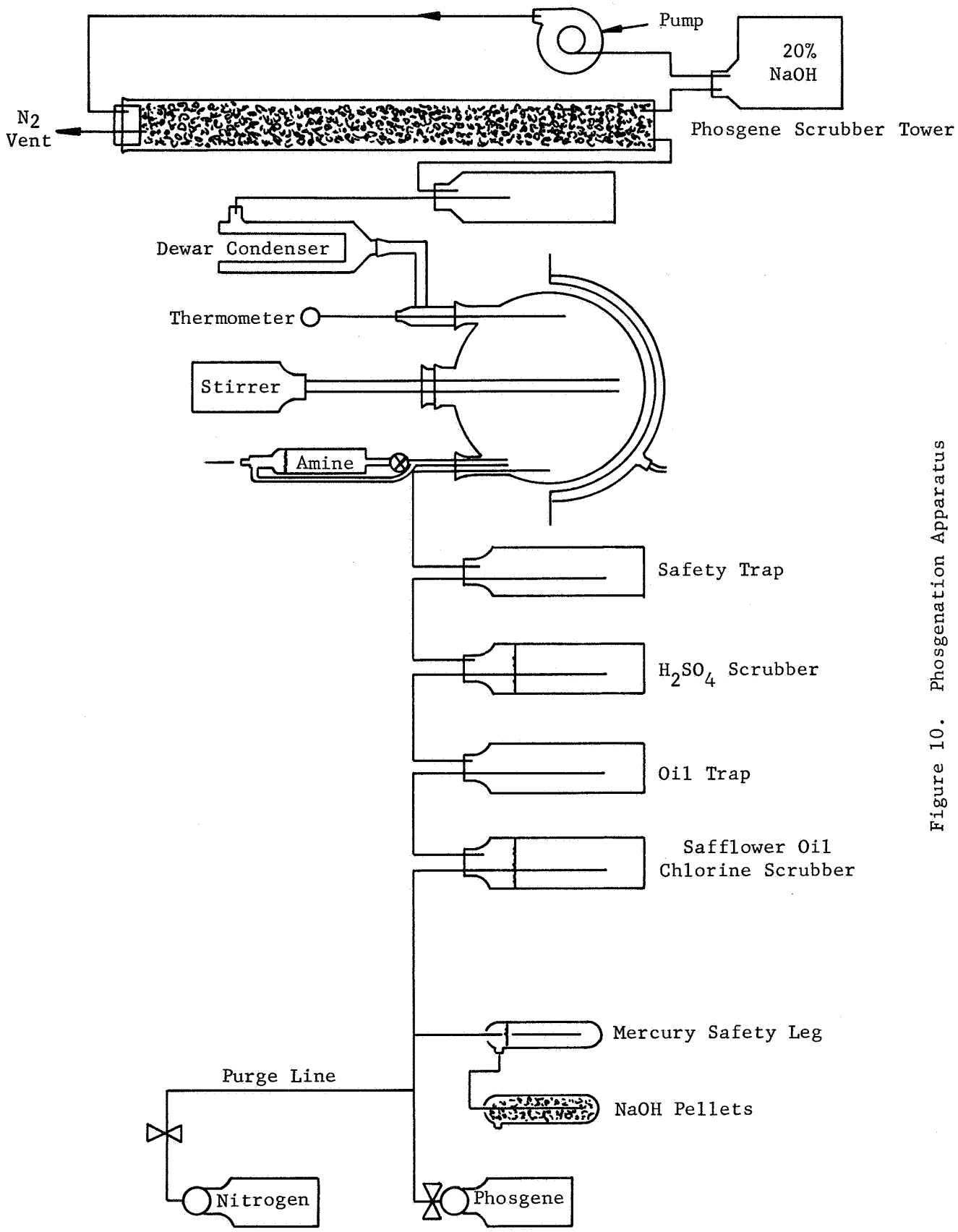
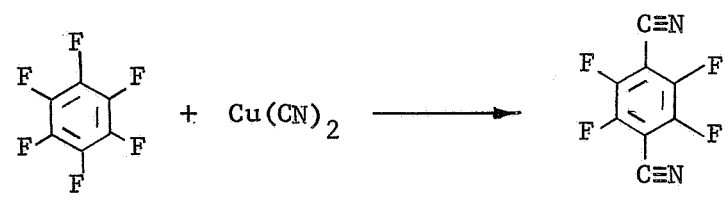


Figure 10. Phosgenation Apparatus

magnetic stirrer, was charged 100 ml of liquid phosgene at -20°C . Tetrafluoro-p-phenylenediamine (25.8 g, 0.14 mole) was dissolved in 350 ml of hot toluene (dried over magnesium sulfate) and added to the addition funnel which was kept at 80°C . The hot diamine solution was added to the cold liquid phosgene over a 2-hour period with continual input of gaseous phosgene which had been passed through a safflower oil gas scrubber followed by passage through a sulfuric acid gas scrubber. After addition of the diamine was complete, the dry ice acetone bath was removed from the reaction flask and the solution allowed to come to room temperature, where it was held for $\frac{1}{2}$ hour. An oil bath was placed under the reaction flask, and the temperature slowly increased. The dry ice - acetone mixture was removed from the Dewar condenser and the escaping phosgene allowed to pass through the caustic-solution-fed rock column scrubber. The temperature was raised to 103°C over a 2-hour period with continual input of gaseous phosgene. The solution was allowed to reflux for a 2-hour period. Following the refluxing period, the phosgene input was interrupted and anhydrous hydrogen chloride was bubbled into the solution. The oil bath was replaced with an ice-water bath and the solution rapidly cooled to 0°C with continual input of hydrogen chloride. Hexane (200 ml), dried over magnesium sulfate, was added to the resulting slurry. The precipitated amine hydrochloride (and any other precipitated material, such as urea, biuret, etc.) was filtered through a fritted glass funnel. The filtrate was evaporated to dryness at reduced pressure and ambient temperature. The residue was extracted with five successive 250-ml portions of dry hexane and the combined extracts evaporated to dryness. The total yield of tetrafluoro-p-phenylene diisocyanate was 15.4 g (46%), which was obtained as colorless crystals, m.p. $65^{\circ}\text{--}68^{\circ}\text{C}$, b.p. $65^{\circ}\text{C}/5\text{ mm}$. Purity was over 99% as determined by VPC. An infrared spectrum is shown in Figure 11.

Elemental Analysis:	<u>% C</u>	<u>% H</u>	<u>% F</u>	<u>% N</u>
Found:	41.3	0	12.1	32.8
Calculated:	41.26	0.06	11.94	32.80

(3) Attempted Preparation of 1,5-Dicyanotetrafluorobenzene



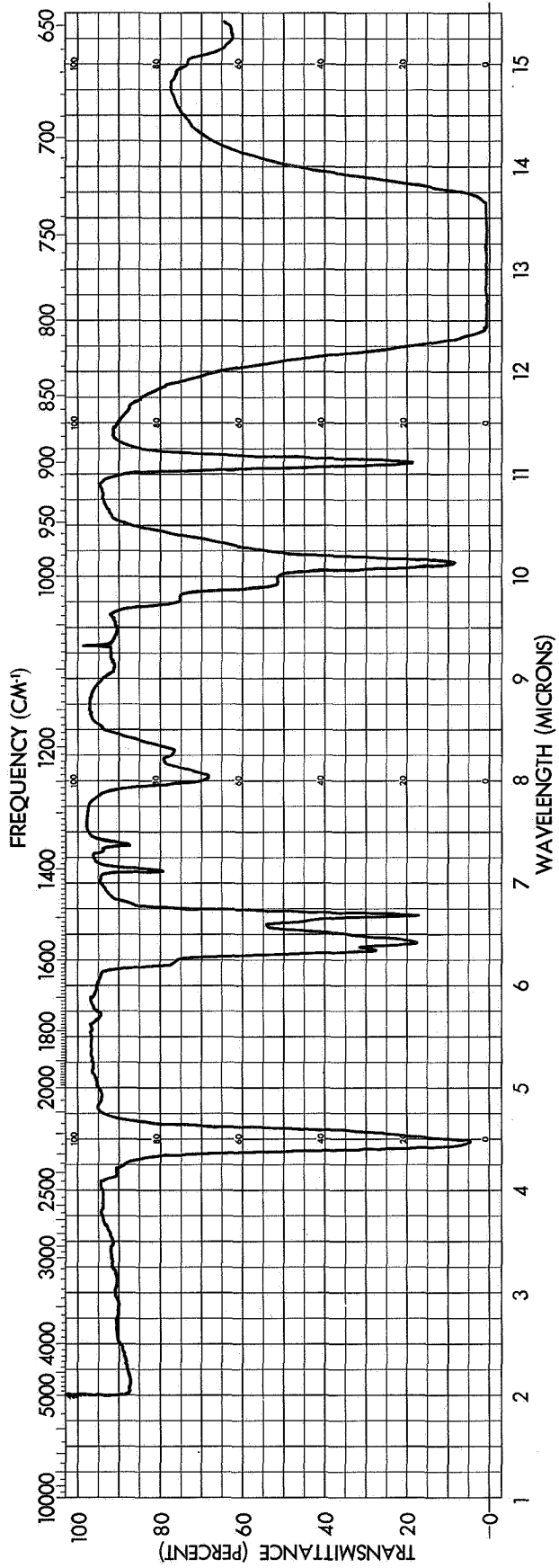
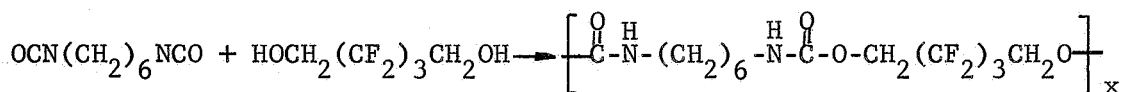


Figure 11. Infrared Spectrum of Tetrafluoro-p-phenylene Diisocyanate (CCl₄ solution)

Into a 500-ml 3-necked flast equipped with stirrer, thermometer, condenser and addition funnel, were introduced cuprous cyanide (26.83 g, 0.3 mole) and N-methylpyrrolidone (300 ml). Heat was applied until all the cuprous cyanide was dissolved (90°C), and hexafluorobenzene (18.6 g, 0.1 mole) was slowly added maintaining a gentle reflux. After refluxing for 8 hours, the solution was cooled and 150 ml of water were added. Copper (I) cyanide and hexafluorobenzene were recovered. There was no apparent reaction.

3. Poly(hexafluoropentamethylene hexamethylenedicarbamate)

a. Polymer Synthesis



Into a 100-ml, three-necked flask equipped with a stirrer, condenser, dropping funnel, thermometer, and dry nitrogen inlet was introduced hexafluoropentanediol (21.2 g, 0.1 mole) plus 1 drop of triethylamine dissolved in 25 ml of dry ethyl acetate. Hexamethylene diisocyanate (16.8 g 0.1 mole) dissolved in 15 ml of dry ethyl acetate was added to the diol solution over a ½-hr period, with stirring, under nitrogen.

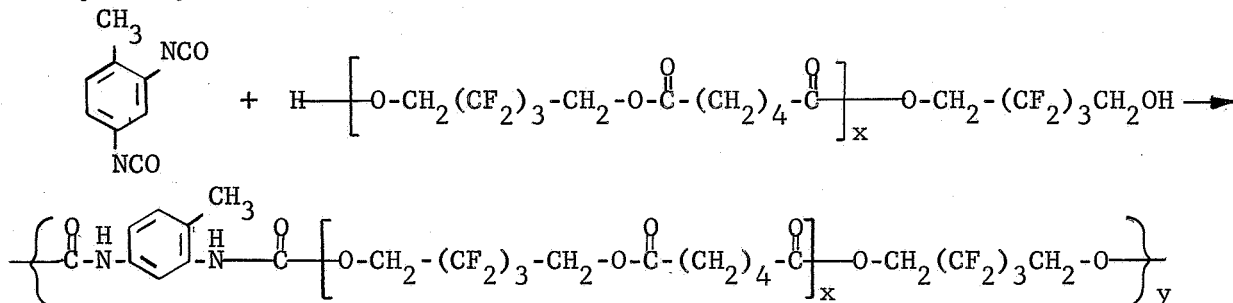
The temperature rose from 24°C to 42°C. The solution was then stirred at 80°C for 16 hours under nitrogen. The polymer was then dried to yield 37.2 g of white, opaque polymer melting at 90°-95°C. The inherent viscosity in DMF was 0.21 at 30°C. Figure 12 is the infrared spectrum of the polymer.

b. Specimens for LOX-Impact Testing

The polymer prepared above was molded in the form of a wafer, 11/16 in. in diameter and 0.020-in. thick, using a pellet mold. Twenty discs were molded using contact pressure for 5 minutes at 175°F to 200°F, 5 minutes at 2000-lb pressure at 175°F to 200°F, then cooled to 125°F at 2000-lb pressure. Two samples were made simultaneously. The molded specimens were placed in a vial and shipped to MSFC for LOX-impact tests.

4. Poly[poly(hexafluoropentamethylene adipate) 2,4-tolylenedicarbamate]

a. Polymer Synthesis



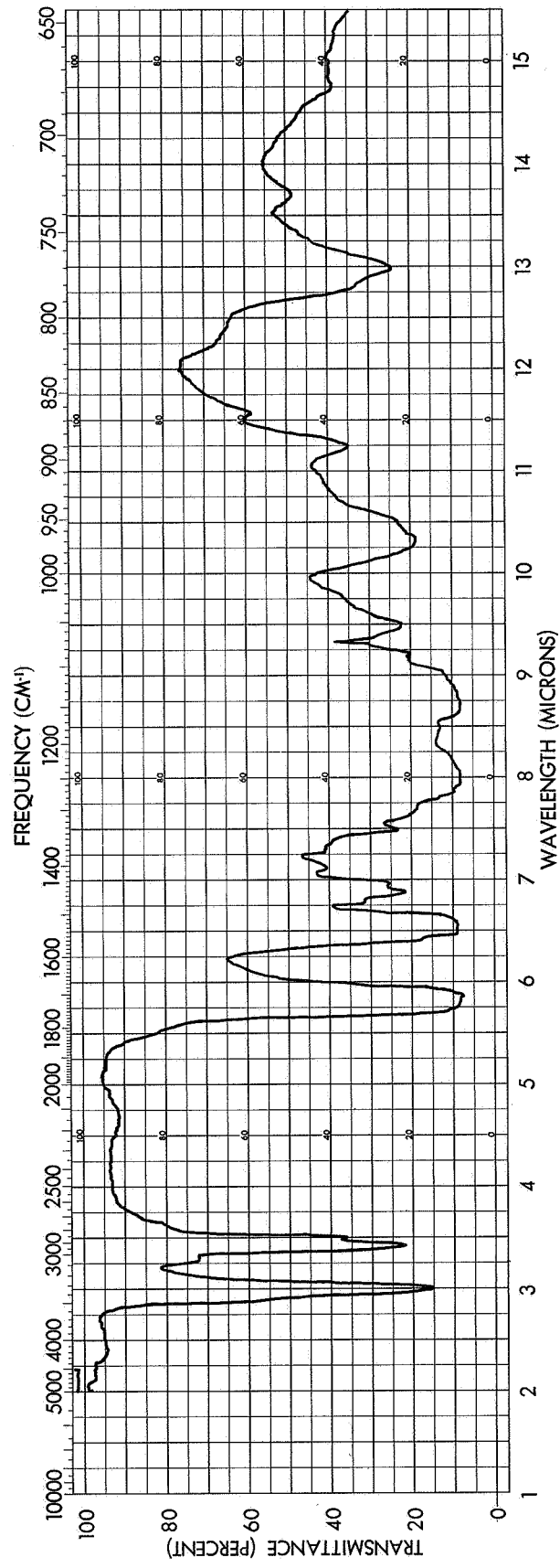
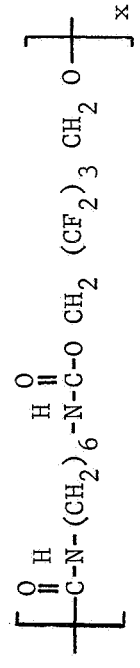


Figure 12. Infrared Spectrum of Poly (hexafluoropentamethylene Hexamethylenedicarbamate)



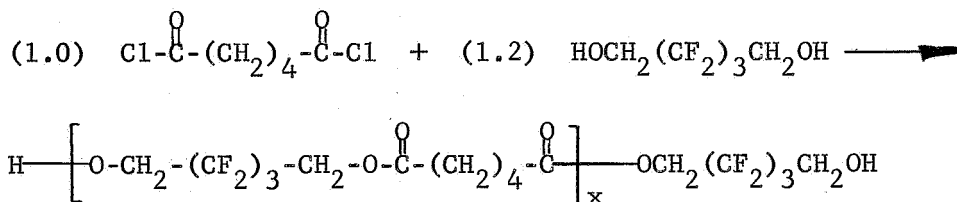
Into a 100-ml, 3-neck flask was placed toluene-2-4-diisocyanate (0.86 g, 0.005 mole) and 15.3 g of poly(hexafluoropentamethylene adipate) which contained terminal OH groups. The flask was fitted with a stirrer and heated in a silicone oil bath to 80°C. The brown mixture, heated under nitrogen at 80°C for 21½ hours, became viscous. Triethylamine (5 ml) was added and after ½ hour the mixture had solidified into a rubbery substance. The solid was washed with ethyl acetate, dried, and stored under nitrogen. Yield was 16.0 g. The inherent viscosity in DMF was 0.10 at 30°C. The infrared spectrum of the polymer is attached as Figure 13.

b. Specimens for LOX-Impact Testing

A sample of the polyurethane described above was prepared for LOX-impact tests. A spacer was made from a sheet of aluminum 0.020-in. thick containing 23 holes of 13/16-in. diameter.

Weighed samples of approximately 0.5-0.6 g of polymer were sandwiched between two Teflon sheets and in the holes of the aluminum spacer. All materials were previously cleaned with acetone and rinsed with trichloroethylene. This was then pressed out at 8000 lb at 149°C. After 10 minutes, the press was cooled and the samples were removed at 38°C. The sample discs were stamped out from the aluminum sheet with an 11/16-in. punch, packaged, and sent to MSFC for LOX-impact tests.

c. Preparation of Poly(hexafluoropentamethylene adipate)



Hexafluoropentanediol (76.3 g, 0.36 mole) and distilled adipoyl chloride (54.9 g, 0.3 mole) were charged to a 500-ml, three necked flask equipped with a stirrer, thermometer, and condenser attached to a water trap. The solution was heated while mixing. At 45°C, HCl was evolved. The temperature was maintained at 45°C to 60°C for 3 hours, during which most of the HCl was evolved. The temperature was raised to 120°C and the reaction continued for an additional 20 hours. The unreacted monomers and HCl was removed under vacuum at 210°C for 2 hours. Yield of the polymer which was a viscous liquid was 102.0 g. The molecular weight of the polymer as determined by end group analysis (hydroxyl number) was 3300. The inherent viscosity of the polymer in DMF was 0.055 at 30°C. The infrared spectrum of the polymer is attached as Figure 14.



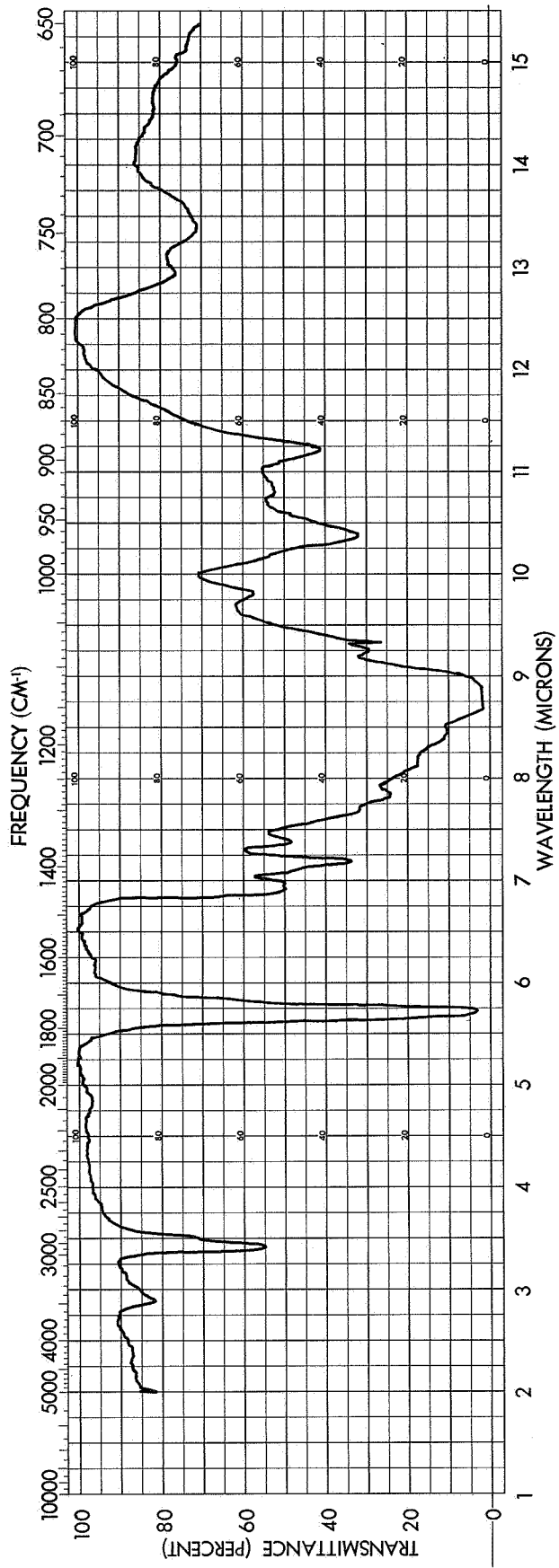
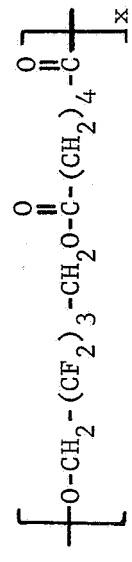


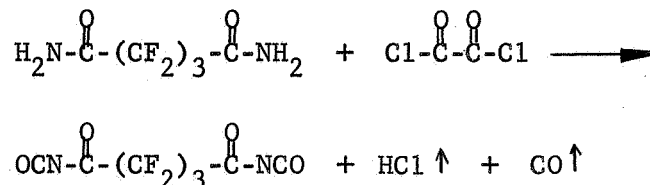
Figure 14. Infrared Spectrum of Poly(hexafluoropentamethylene Adipate)



B. ADDITIONAL MONOMERS

1. Preparation of Perfluoroglutaryl Diisocyanate

a. Synthesis from Hexafluoroglutaramide



(1) At Atmospheric Pressure

Into a 250-ml, three-necked flask equipped with a thermometer, addition funnel, condenser, and nitrogen inlet were introduced dry hexafluoroglutaramide (11.9 g, 0.05 mole) and dry ethylene dichloride (100 ml). The solution was stirred while oxalyl chloride (15.9 g, 0.125 mole) was added dropwise during the course of 30 minutes. The mixture was stirred and refluxed for an additional 16 hours. Infrared analysis of the mixture gave no indication of isocyanate formation. Toluene as a solvent gave similarly negative results.

(2) At Elevated Temperature and Pressure

Into a 100-ml glass-lined autoclave were introduced hexafluoroglutaramide (11.9 g, 0.05 mole), oxalyl chloride (15.9 g, 0.125 mole) and dichloroethylene (170 ml). The vessel was flushed with nitrogen and closed. The reaction was carried out at 150°C for 16 hours. An infrared spectrum of the product showed a considerable concentration of isocyanate, but separation was not successful because of the high volatility of the product and close boiling points between product and solvent. A white crystalline, unidentified solid (m.p. 30°-36°C, b.p. 164°C) weighing 5.85 g (mol. wt. 380 ±20) was isolated.

Elemental Analysis:	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% F</u>	<u>% O</u>
Found:	26.24	0.63	5.25	49.80	18.02

Separation of the reaction mixture in the preparative chromatograph was attempted but was not effective because of a difficult combination of (1) low product concentration; (2) high volatility; and (3) high reactivity (helium carrier was probably contaminated with a small amount of water).

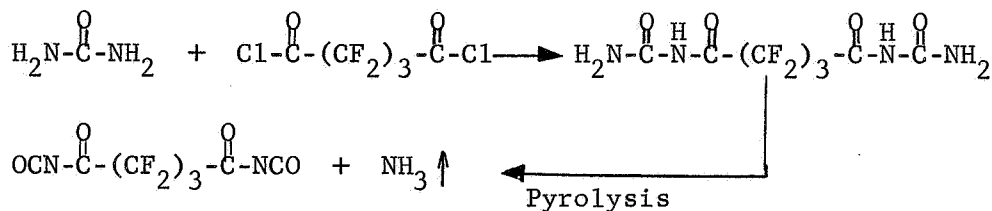
(3) Repeat in Tetrachloroethylene

The same procedure as above was followed using tetrachloroethylene (b.p. 121°C). The reaction time was extended to 50 hours at 180°C. Infrared analysis of the product gave no indication of isocyanate.

(4) Repeat in Sym-tetrachloroethane

The same procedure described in (2) above was followed but with sym-tetrachloroethane (b.p. 144°-146°C). The reaction was carried out for 16 hours at 168°C. Infrared and VPC showed that the liquid obtained had a purity of 95%. It was very reactive to moisture in air and extremely volatile, with a boiling point of about 55°C. It has a very irritating odor. An infrared spectrum of the perfluoroglutaryl diisocyanate is shown in Figure 15.

b. Attempted Synthesis from Ureide Pyrolysis



Into a 250-ml, three-necked flask equipped with stirrer, thermometer, condenser, and addition funnel were introduced urea (6.0 g, 0.1 mole) and ethylene dichloride (150 ml). To the stirring solution was slowly added hexafluoroglutaryl chloride (27.7 g, 0.1 mole), and the mixture was refluxed for 24 hours. A white solid formed during the course of the reaction. The solvent was removed by vacuum-stripping and the pyrolysis of the ureide attempted at 150°-250°C at 35-mm pressure. No isocyanate was obtained. The solid material (14.3 g) was recrystallized from methanol to yield a white solid which sublimed easily at 300°C but would not melt at 500°C.

c. Attempted Synthesis from Silver Cyanate



Into a 100-ml, three-necked flask equipped with stirrer, condenser, addition funnel, and nitrogen inlet was introduced silver cyanate (6.3 g, 0.042 mole) and dry ether (20 ml). A slurry formed upon stirring. The dropwise addition of perfluoroglutaryl chloride

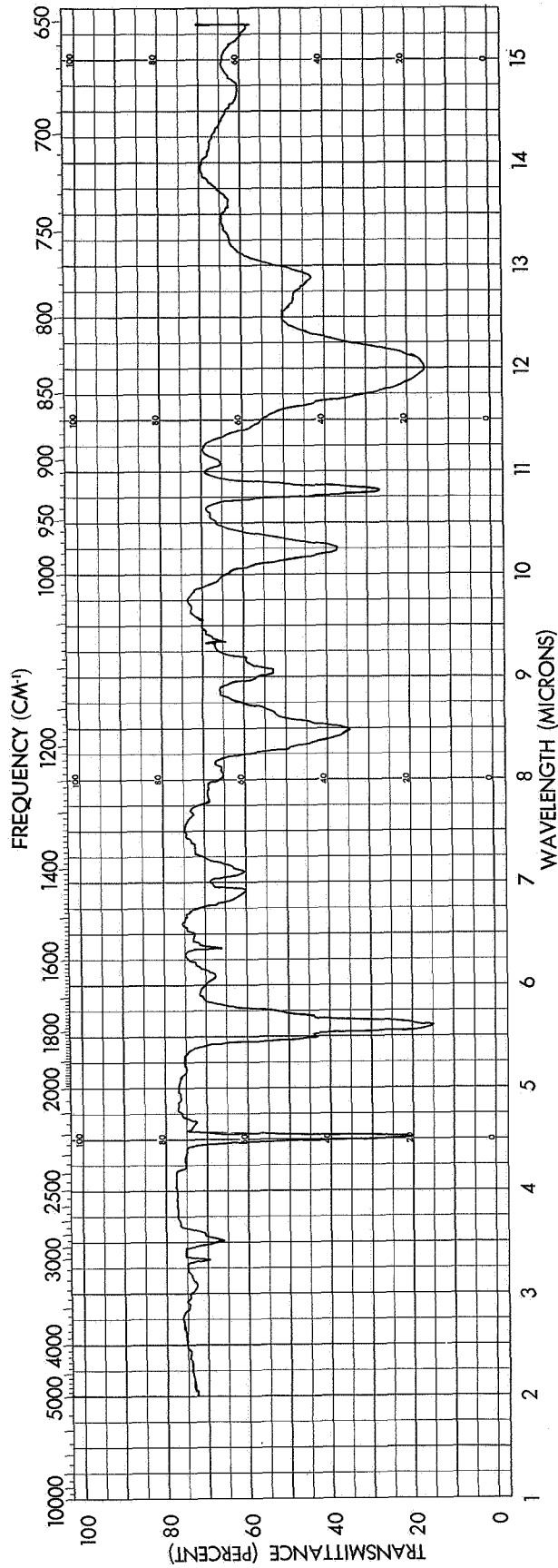


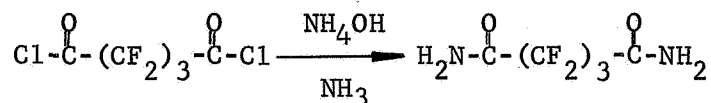
Figure 15. Infrared Spectrum of Perfluoroglutaryl Diisocyanate

(5.53 g, 0.02 mole) in dry ether (30 ml) was followed by refluxing for 5 hours. An infrared spectrum of the ether layer had a strong peak at 4.5 μ . Analysis by VPC indicated a product with the same retention time as the product from the perfluoroglutaramide-oxalyl chloride reaction. Isolation of the acyl isocyanate was not successful.

2. Hexafluoropentamethylene Diisocyanate

a. Via Phosgenation of the Diamine

(1) Preparation of Perfluoroglutaramide



A 4-liter resin flask equipped with stirrer, thermometer, Dewar condenser, addition funnel, and nitrogen inlet was charged with concentrated ammonium hydroxide (900 ml) and cooled to -30°C. Ammonia gas was bubbled through slowly while perfluoroglutaroyl chloride (508 g, 320 ml, 1.835 mole) was added simultaneously. The reaction was completed in 2 hours. A nitrogen purge at the top of a bypass addition funnel throughout the addition prevented the perfluoroglutaramide from plugging the funnel outlet. The excess ammonia was removed and the solid amide was filtered, dried, and recrystallized from water. Yield 370.0 g, 82.6%; m.p. 212°-215°C.

(2) Preparation of Hexafluoropentanediamine

Perfluoroglutaramide (47.6 g, 0.2 moles) dissolved in 900 ml of dry tetrahydrofuran (THF) was added to lithium aluminum hydride (19.0 g, 0.5 mole) (LiAlH₄) in 300 ml of dry THF. The reaction was refluxed for 22 hours. The mixture was cooled to 30°C and 36 g of distilled water was added very slowly to destroy excess LiAlH₄. The THF was stripped and the product fractionally distilled at reduced pressure. A 43% yield of white solid, m.p. 52°-53°C, b.p. 40°-45°C/1 mm, was obtained. An infrared spectrum is shown in Figure 16.

Elemental Analysis:	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% F</u>
Found:	28.81	3.62	13.54	54.11
Calculated:	28.5	3.8	13.3	54.2

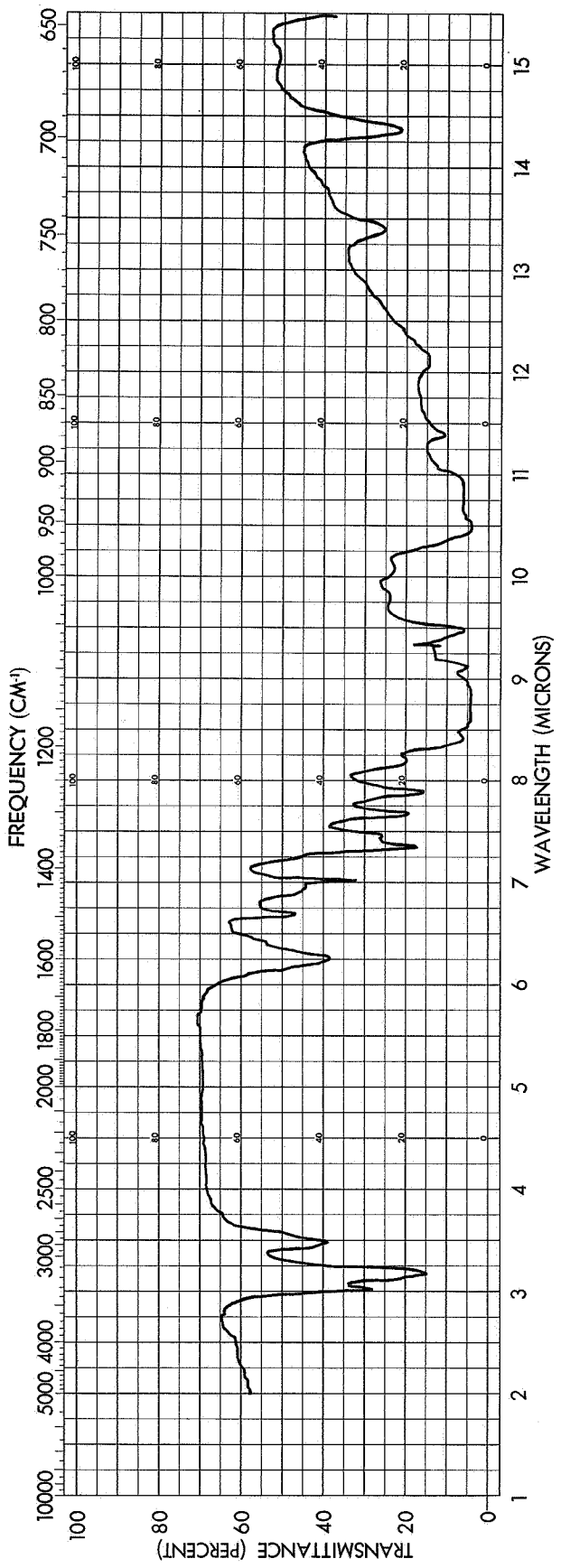
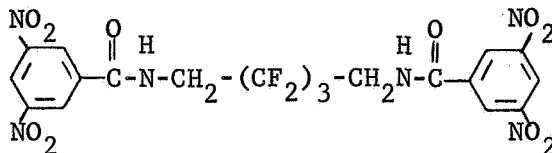
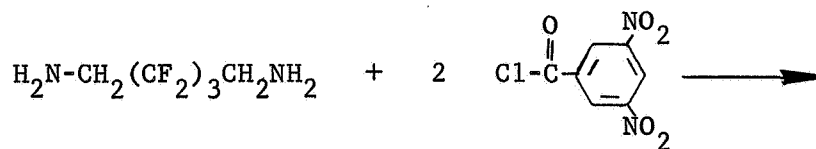


Figure 16. Infrared Spectrum of Hexafluoro-1,5-pentanediamine

(3) Hexafluoropentamethylene-bis-(3,5-dinitrobenzamide) Derivative of Hexafluorotentanediamine



Hexafluoropentane diamine (2.10 g, 0.01 mole), 3,5-dinitrobenzoyl chloride (4.61 g, 0.02 mole), pyridine (10 ml), and benzene (150 ml) were added to a 500-ml, three-necked flask equipped with a stirrer, condenser, thermometer, and nitrogen inlet. The slurry was mixed for 2 hours at 60°-70°C under nitrogen. The slurry was added to 100 ml of water and the benzene layer separated. The benzene was dried with MgSO_4 and the product crystallized from benzene and dried, m.p. = 204°-208°C. The infrared spectrum is shown in Figure 17.

Elemental Analysis:	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% F</u>
Found:	38.11	2.19	13.82	19.17
Calculated:	38.1	2.01	14.1	19.1

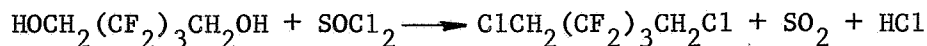
(4) Attempted Preparation of Hexafluoropentamethylene Diisocyanate

Hexafluoropentamethylene diisocyanate (28.8 g, 0.3 mole) in 350 ml of carbon tetrachloride was added to phosgene (60 ml) at -30°C over a period of 1-1/2 hours. The reaction mixture was then allowed to warm to room temperature. After standing overnight under Argon, the carbon tetrachloride and unreacted phosgene were distilled off, and the dry residue heated with an oil bath. At approximately 120°C, the solid began melting and hydrogen chloride was given off. However, no product was collected, indicating polymerization had occurred.

b. From 1,5-Dichloro-2,2,3,3,4,4-Hexafluoropentane

(1) Preparation of 1,5-Dichloro-2,2,3,3,4,4-Hexafluoropentane

(a) From Hexafluoropentane diol

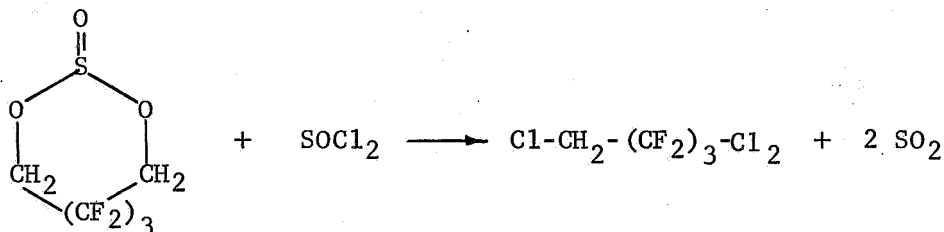


Hexafluoropentane diol (6 g, 0.05 mole) was dissolved in pyridine (20 ml) and added to a 100-ml, three-necked flask equipped with a stirrer, thermometer, condenser, dropping funnel, and drying tube. Thionyl chloride (23.8 g, 0.2 mole) was added slowly over a 1-hour period with stirring at 23°-42°C. A precipitate formed during the initial addition, but redissolved later. The slurry was heated at 80°-90°C for 25 hours.

The solution was then distilled. The dichloride which boiled at 140°-142°C weighed 9.2 g and represented a yield of 73.5%. An infrared spectrum of the 1,5-dichloro-2,2,3,3,4,4-hexafluoropentane is shown in Figure 18.

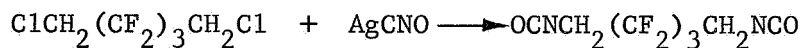
Elemental Analysis:	<u>% C</u>	<u>% Cl</u>	<u>% H</u>	<u>% F</u>
Found:	24.19	28.67	1.84	45.58
Calculated:	24.1	28.6	1.61	45.8

(b) From Hexafluoropentamethylene Sulfite



Into a 50-ml, three-necked flask equipped with a condenser, stirrer, and thermometer were introduced hexafluoropentamethylene sulfite (15.48 g, 0.060 mole). The mixture was stirred for 3 hours and then heated to 80°C. No apparent formation of dichloride had taken place after 17 hours as shown by VPC analysis. Pyridine (15 drops) was added and the reaction was run at 90°C for an additional 24 hours. The VPC analysis then showed that the cyclic sulfite had been converted to the dichloride.

(2) Attempted Preparation of Hexafluoropentamethylene Diisocyanate



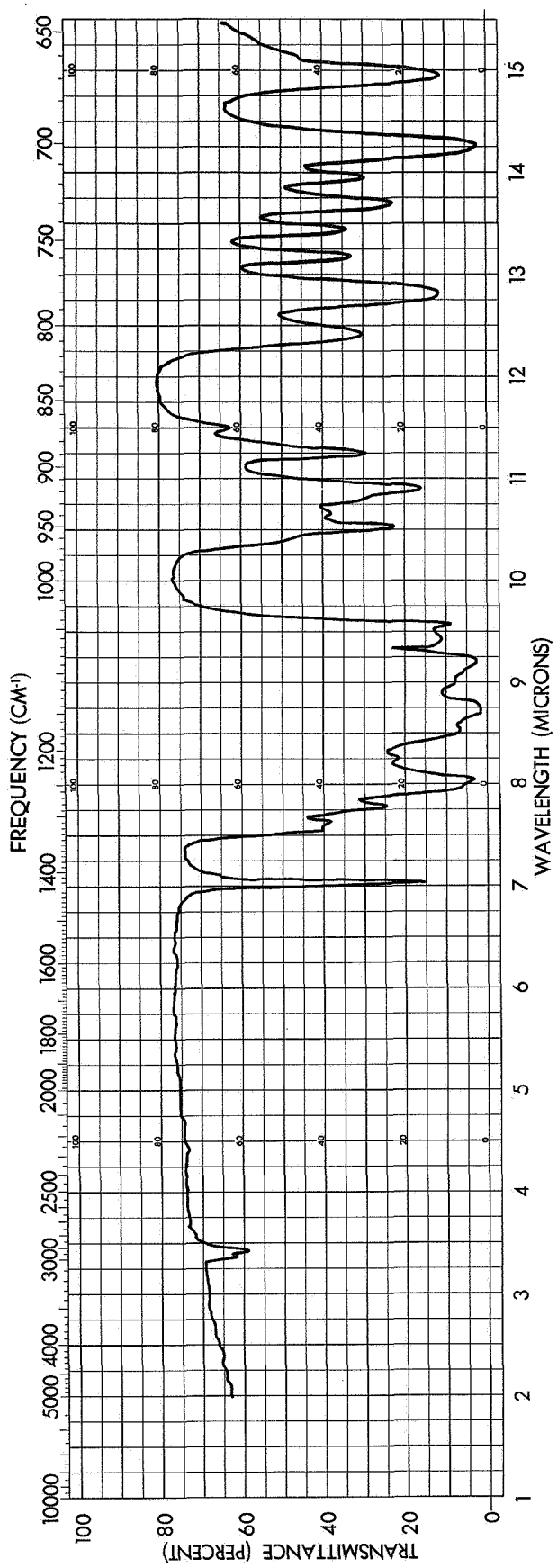


Figure 18. Infrared Spectrum of 1,5-dichloro-2,2,3,3,4,4-hexafluoropentane

(a) At Atmospheric Pressure

Silver cyanate (9.00 g, 0.06 mole) suspended in 50 ml of dry tetrahydrofuran (THF) was charged to a 100-ml, three-necked flask equipped with a dropping funnel, stirrer, thermometer, condenser and dry nitrogen inlet. The 1,5-dichloro-2,2,3,3,4,4-hexafluoropentane (7.50 g, 0.03 mole) was added rapidly to the silver cyanate slurry with stirring under nitrogen.

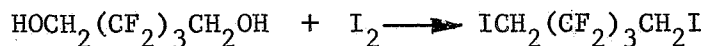
The slurry was stirred at 60°-65°C for 3 days under nitrogen. During this time, no material was produced which gave infrared absorption at 4.5 μ.

(b) At Elevated Pressure

Into a pressure bomb were introduced 1,4-dichloro-2,2,3,3,4,4-hexafluoropentane (15 g, 0.06 mole) and silver cyanate (18.0 g, 0.12 mole). These were allowed to react under pressure at 250°C for 48 hours. The contents of the bomb were then removed at room temperature and found to contain no isocyanate.

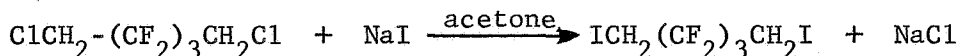
c. Attempted Preparation of 1,5-Diiodo-2,2,3,3,4,4-Hexafluoropentane

(1) From Hexafluoropentane Diol



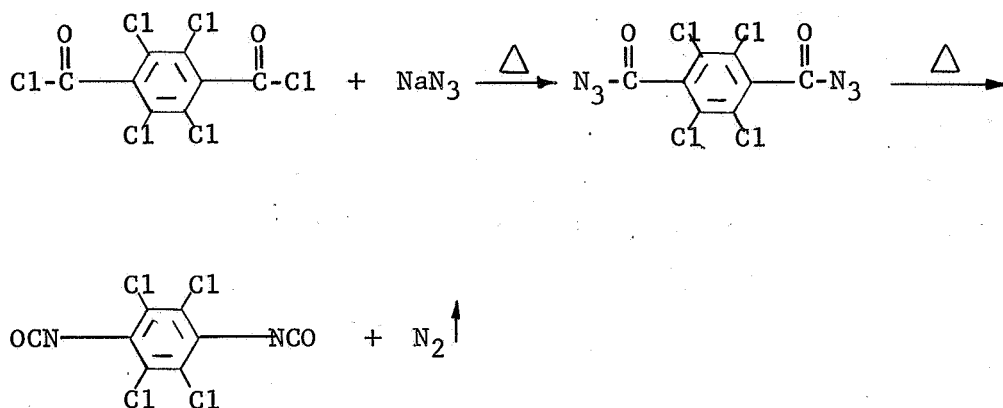
Into a 500-ml flask equipped with a stirrer, condenser, and thermometer was added 85% phosphoric acid (67.5 ml) and P₂O₅ (32.5 g). The solution was cooled to room temperature with mixing. Hexafluoropentane diol (0.25 mole, 53.0 g) plus potassium iodide (166.0 g, 1 mole) was then added. The slurry was mixed at 110°-120°C for 18 hours, then cooled and 130 ml of water added. Ether (175 ml) was added and the ether layer separated, washed three times with 10% sodium thiosulfate, then twice with saturated sodium chloride. The ether was dried over magnesium sulfate and evaporated. Either there was no reaction or any iodo product formed was hydrolyzed in the workup.

(2) From 1,5-Dichloro-2,2,3,3,4,4-Hexafluoropentane



Sodium iodide (30.0 g, 0.2 mole) was dissolved in 215 ml of acetone in a 250-ml, three-necked flask equipped with a stirrer condenser, and thermometer. 1,5-Dichloro-2,2,3,3,4,4-hexafluoropentane (12.45 g, 0.05 mole) was added and the solution refluxed and stirred for 24 hours. There was no reaction.

3. Preparation of Tetrachloro-p-phenylene Diisocyanate



Into a 500-ml, three-necked flask equipped with a stirrer, condenser, thermometer, dropping funnel, and nitrogen inlet were added activated NaN_3 (26.0 g, 0.4 mole) and 100 ml of dry xylene. Tetrachloro-terephthaloyl chloride (34.1 g, 0.1 mole) in 200 ml of dry xylene was added to the NaN_3 slurry over a 45-minute period with mixing at 24°C to 26°C under nitrogen. The slurry was mixed for 20 hours at 24°C to 26°C under nitrogen. The slurry was then heated to 135°C over a 2-hour period, very slow decomposition starting at 110°C . The slurry was mixed at 135°C to 140°C for 24 hours. The slurry was cooled to room temperature then filtered. The xylene was removed from the filtrate and the resultant residue dried to yield 28.2 g of tetrachloro-p-phenylene diisocyanate. Yield = 94.5%. m.p. = $91.5^\circ\text{--}93.5^\circ\text{C}$. The infrared spectrum is shown in Figure 19.

Elemental Analysis:	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% Cl</u>
Found:	32.59	0.30	7.70	48.50
Calculated:	32.2	0	9.4	47.7

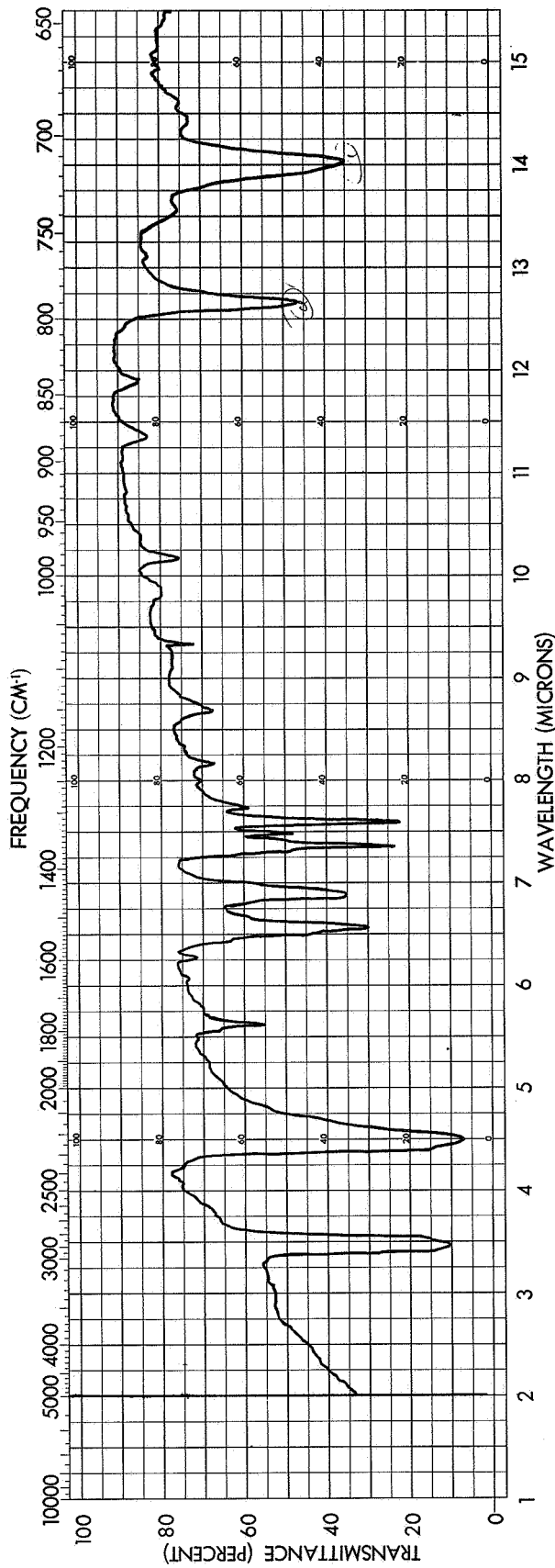
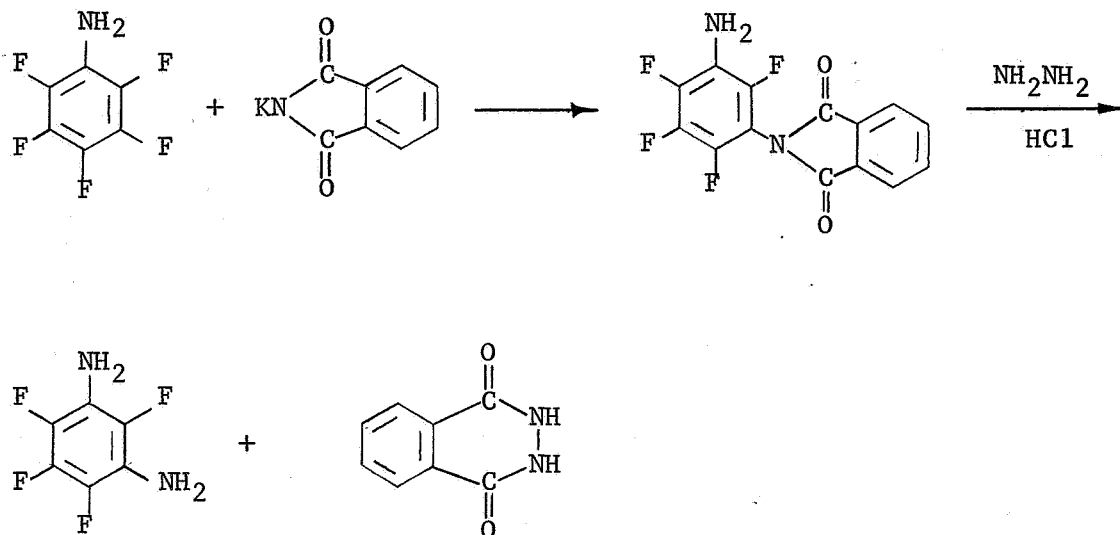


Figure 19. Infrared Spectrum of Tetrachloro-p-phenylene Diisocyanate

4. Preparation of Tetrafluoro-m-Phenylenediamine

a. From Pentafluoroaniline

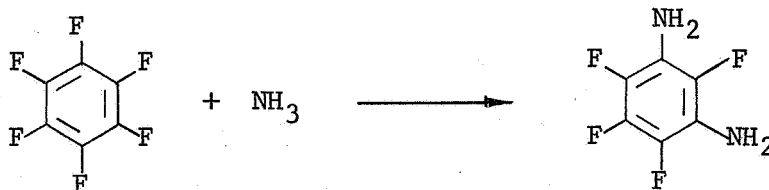


A 500-ml, three-necked, round-bottom flask fitted with a reflux condenser, thermometer and mag-bar stirrer was charged with pentafluoroaniline (9.15 g, 0.05 mole), potassium phthalimide (9.25 g, 0.05 mole) and redistilled dimethylformamide (100 ml). The reaction mixture was heated in an oil bath, over a hot plate, to 135°C and held at temperature for 1½ hours. The temperature was reduced to 60°C and the solvent stripped off under reduced pressure. Ethyl alcohol (5 ml) plus anhydrous hydrazine (4 ml) were added to the almost dry residue. The mixture was refluxed (78°-80°C) for 1½ hours. Concentrated HCl (20 ml) was added to the warm solution and reflux continued an additional ½ hour. The precipitate of phthalhydrazide was filtered off, washed with 80 ml ethyl alcohol, and the combined filtrates concentrated to ≈ 40 ml under reduced pressure.

The solution was made slightly basic (pH 8-9) with NaOH solution, and steam distilled. Aqueous distillate (200 ml) was collected and extracted three times with 200-ml portions of ether. The ether extracts were combined and the ether stripped off. The white

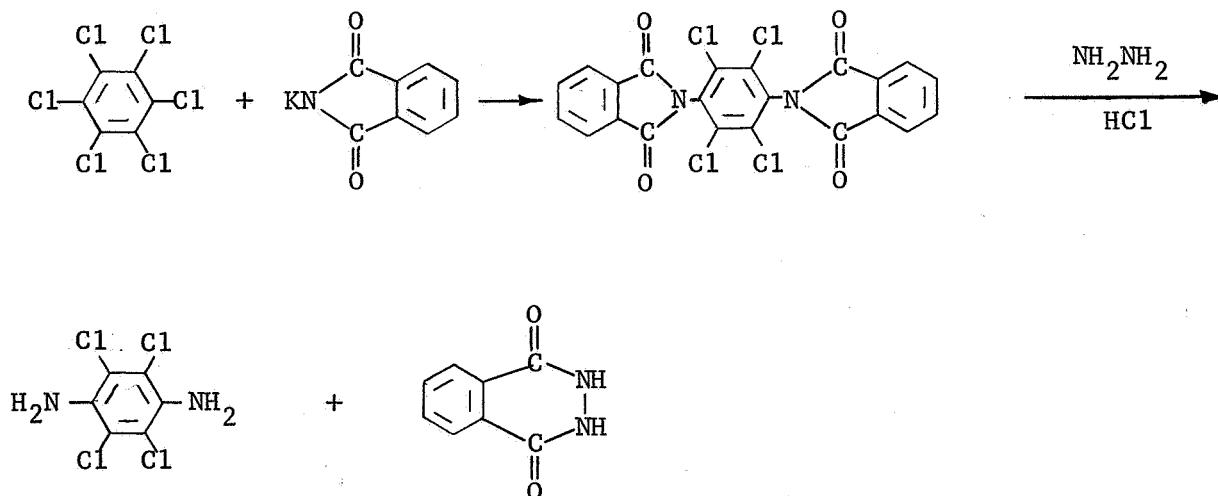
crystalline residue was recrystallized from 60°-90°C ligroin.
 Yield = 1.2 g (13.4%) tetrafluoro-m-phenylenediamine. m.p. = 129°-130°C
 (with sublimation); literature value 129.5°-131°C. (66) The infrared
 spectrum was identical to that of the p-isomer.

b. Attempted Preparation from Hexafluorobenzene



Hexafluorobenzene (9.3 g, 0.05 mole) and 60 ml of glycerine were placed in a 100-ml, three-necked flask with a thermometer, gas sparger, and a condenser. Ammonia gas was introduced through the gas sparger and the temperature was raised to 82°C. Samples were taken at various time intervals and at various temperatures, and analyzed by infrared and gas chromatography. There was no indication of diamine being formed by either analytical method. Similar results were obtained using dioxane, dibutyl ether, ethylene glycol, phenyl ether and methyl carbitol (diethylene glycol monomethyl ether).

5. Attempted Preparation of Tetrachloro-p-phenylenediamine



Hexachlorobenzene (85.5g, 0.3 mole) potassium phthalimide (148 g, 0.8 mole) and N-methyl pyrrolidone (400 ml) were charged to a 1-liter three-necked flask equipped with a stirrer, condenser, and thermometer. The mixture was heated to 202°C in 2 hours with mixing, then mixed at 202°C for an additional 50 hours. The mixture was cooled and added to 1 liter of water with mixing. The slurry was filtered and the residue dried. The residue was then slurried in ethanol, and hydrazine (25.6 g, 0.8 mole) was added. The mixture was refluxed and stirred for 3 hours. Concentrated HCl was added and the ethanol was removed. After filtration, the filtrate was neutralized. There was no apparent reaction.

6. Preparation of Hydroxyl-Terminated Polyesters and Diesters

a. General Method for Reactions Using Pyridine as Solvent

Into a three-necked flask equipped with stirrer, condenser, thermometer, and addition funnel were introduced the solvent and the diol. Perfluoroglutaryl chloride was then added dropwise, keeping the temperature below 70°C. After all the acid chloride was added, the mixture was refluxed for 16-20 hours. It was cooled and poured into a 10% aqueous HCl. The precipitated material was filtered off and recrystallized. It was analyzed by infrared and melting point determinations. The experimental conditions and results of the esterifications run in pyridine are shown in Table 4.

b. General Method for the Preparation of Polyesters in Toluene

Into a three-necked flask equipped with stirrer, thermometer, addition funnel, and condenser attached to a distilled water trap were introduced the diol and toluene. Hexafluoroglutaryl chloride was then added dropwise keeping the temperature below 70°C. After all the acid chloride was added, the reaction mixture was refluxed overnight. Hydrogen chloride was collected in the water trap during the reaction. Upon completion of the reaction time, the solution was titrated with 0.1 N NaOH. The toluene solution of the polyester was then treated with charcoal and the toluene stripped off. Molecular weight determination by vapor pressure osmometer was not successful due to volatile contamination (probably HCl and acid chloride). The experimental conditions and results of the experiments run in toluene are listed in Table 5.

c. General Method for Preparation of Polyesters in the Melt

Into a three-necked flask equipped with a stirrer, thermometer, and condenser attached to a water trap were introduced the diol and the diacid chloride. The mixture was heated at 70°C for 3 hours and then the temperature was slowly increased to 160°C and held for 12 hours, then held at 200°C for 3 hours. Vacuum (1-mm Hg) was applied to the mixture during the last hour at 200°C. Excess diol was removed under vacuum. Molecular weight determinations were unsuccessfully attempted by vapor pressure osmometry.

TABLE 4
ESTERIFICATIONS IN PYRIDINE

Solvent, pyridine, ml	Diols, moles	Hexafluoroglutaric chloride moles	Temp, °C	Time, hr	% Yield Polyester	Analysis*
150	I 0.105	0.05	110	16	0	0.09 mole diol, m.p. 203°-213°C, recovered
150	II 0.105	0.05	110	16	0	0.08 mole diol, m.p. 231°-233°C, recovered
100	III 0.105	0.05	110	16	0	Crude diol recovered

* There was no carbonyl absorption in the infrared spectra.

I HET diol

II 2,3,5,6-tetrachloro-p-xylene- α, α' -diol

III 2,2,3,3,4,4-hexafluoropentanediol

TABLE 5
ESTERIFICATIONS IN TOLUENE

Solvent, toluene, ml	Diol, moles	Hexafluoroglutaric chloride, moles	Temp, °C	Time, hr	% Yield Polyester	Analysis*
250	I 0.1	0.05	110	18	98.6 Glassy semisolid	Nearly quantitative HCl given off; chloride still present
250	II 0.1	0.05	110	18	60 White solid, m.p. 140°-170°C	85% HCl given off; 10 g diol recovered
150	III 0.1	0.05	110	18	--	10% HCl given off; diol recovered
250	I 0.105	0.1	110	18	83 Black, glassy solid	70% HCl given off; chloride still present
250	III 0.21	0.2	110	--	87 Tan, viscous liquid	83% HCl given off; chloride still present

* All materials had strong infrared absorption at 5.6 μ.

I HET diol

II 2,3,5,6-tetrachloro-p-xylene- α, α' -diol

III 2,2,3,3,4,4'-hexafluoropentanediol

The chloride in the polyester, either as acid chloride or trapped hydrochloric acid, was determined by reaction with an excess of ammonium hydroxide (approximately 1N) and back titrated with 0.5 N HCl using methyl orange indicator. A blank was run simultaneously. All the polyesters attempted still contain reactive chloride.

The last reaction, shown in Table 6, was carried out for a longer time at 220°C to allow all the acid chloride to react.

The experimental conditions and results of the esterifications conducted without solvent are shown in Tables 6 and 7.

The infrared spectrum of poly(hexafluoropentamethylene hexafluoroglutarate) is attached as Figure 20.

d. Transesterification of Dimethyl hexafluoroglutarate with 2,2,3,3,4,4-hexafluoropentane diol

Into a 100-ml, three-necked flask equipped with stirrer, thermometer, Dean-Stark trap, and condenser were introduced dimethylhexafluoroglutarate (21.0 g, 0.078 mole), hexafluoropentane diol (17.4 g, 0.082 mole) and CaH₂ (0.01 g). The reaction was run for 18 hours at 170°-180°C. There was no evidence of the formation of methanol. The temperature was reduced to 100°C and the system was placed under reduced pressure (70 mm) for 18 hours. No methanol was produced.

e. Attempted Conversion of Acid Chloride End Groups to Methyl Esters

Into a 250-ml, three-necked flask equipped with stirrer, thermometer, and condenser were introduced 30 g of polyester made from hexafluoroglutarylchloride and hexafluoropentane diol (1:1.2 mole). Methanol (100 ml) was added and the mixture refluxed for 12 hours. The methanol was stripped off and distillation produced a clear liquid (b.p. 100°-103°C at 30 mm) and white crystals, m.p. 71°-74°C. These materials were identified as dimethyl hexafluoroglutarate and hexafluoropentane diol, respectively.

7. Hydroxyl Terminated Ethers and Polyethers

a. Trihexafluoropentamethylene Glycol

(1) From Hexafluoropentamethylene-bis-(p-toluenesulfonate)

(a) Preparation of Hexafluoropentamethylene-bis-(p-toluenesulfonate)

TABLE 6
ESTERIFICATIONS IN THE MELT

Diol, moles	Perfluoroglutaric chloride, moles	Temp, °C	Time, hr	% Yield Polyester	Analysis
I 0.105	0.1	75 160 220	3	83.5 Dark brown, glassy solid	86.3% HCl given off; chloride still present in polymer
II 0.21	0.2	75 160 220	3	93.8 Brown, viscous liquid	99.7% HCl given off; chloride still present in polymer
I 0.24	0.2	75 160 220	3 12 2	88.4 Brown, viscous liquid	Chloride still present in polymer
II 0.36	0.3	75 160 220	3 12 60	67 Brown gum	99.5% HCl given off

I HET diol

II 2,2,3,3,4,4-hexafluoropentane diol

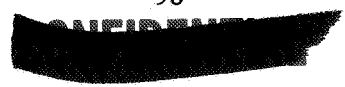


TABLE 7
ESTERIFICATIONS IN THE MELT

Diol, moles	Acid Chloride, moles	Temp, °C	Time, hr	% Yield Polyester	Analysis
I 0.24	A, 0.2	65 160-180	3 24	98	$\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-} \end{array}$ @ 5.75 μ , 98% yield HCl
II 0.36	B, 0.3	90 160-180	3 24	92	$\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-} \end{array}$ @ 5.65 μ , 99% yield HCl
III 0.24	B, 0.2	90 200-220	3 24	94	$\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-} \end{array}$ @ 5.6 μ , 95% yield HCl
III 0.24	A, 0.2	70 200-220	3 24	90	$\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-} \end{array}$ @ 5.75 μ ,* 98% yield HCl

* See Figure 20

- | | |
|---------------------------|------------------------------|
| I HET diol | A. Adipoyl chloride |
| II Ethylene glycol | B. Perfluoroglutarylchloride |
| III Hexafluoropentanediol | |



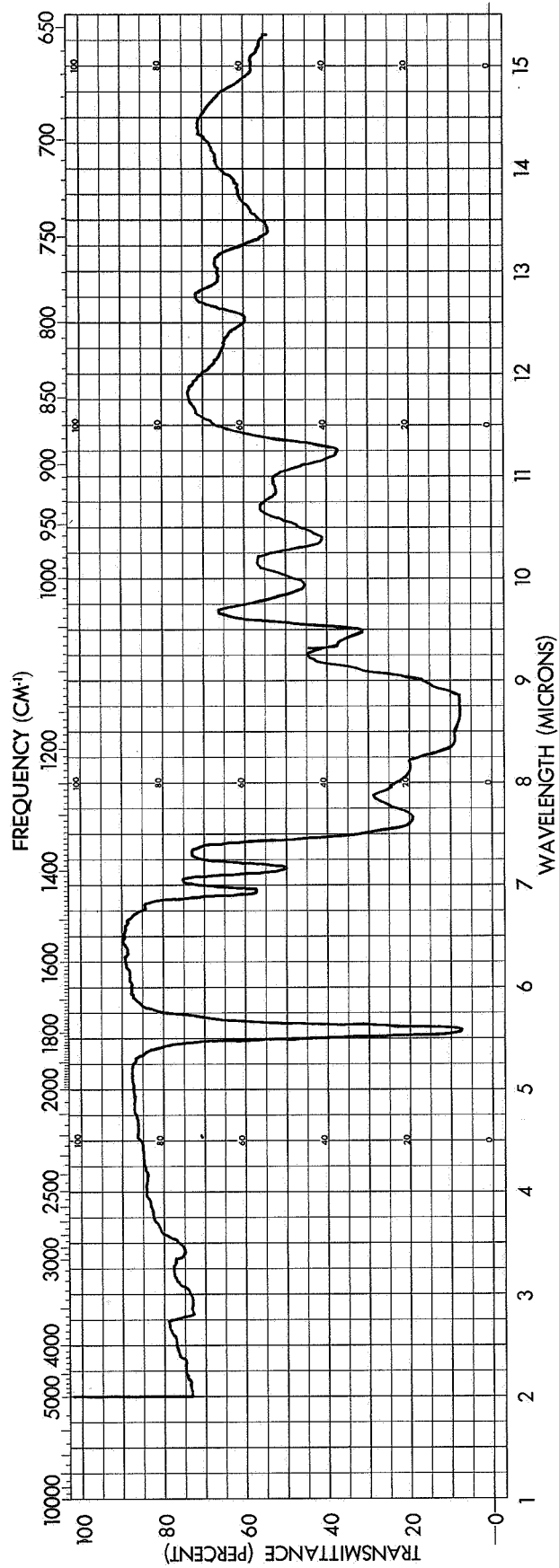
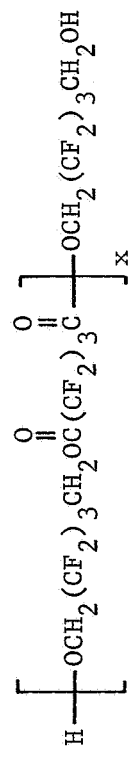
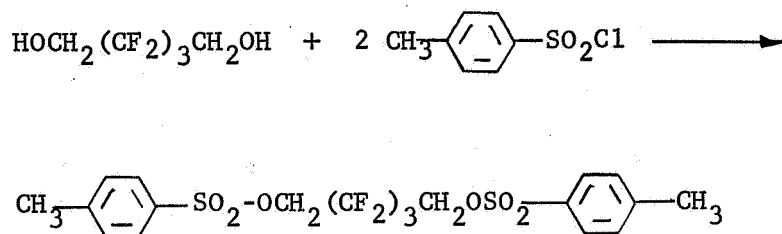


Figure 20. Infrared Spectrum of Poly(hexafluoropentamethylene Hexafluoroglutarate)





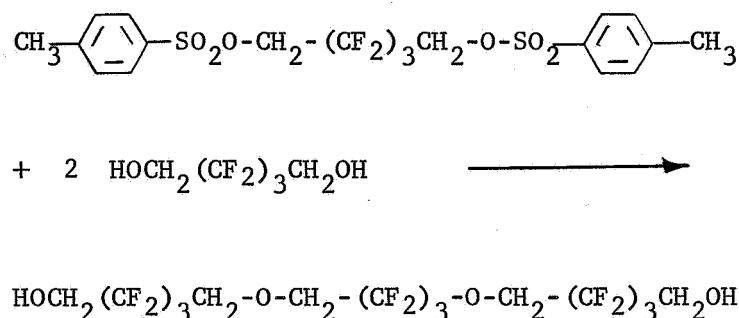
To hexafluoropentanediol (10.6 g, 0.05 mole) dissolved in ether (25 ml), toluene (25 ml), and pyridine (50 ml), in a 1-liter flask equipped with a stirrer, addition funnel, thermometer, and reflux condenser was added slowly p-toluene sulfonyl chloride (19.1 g, 0.1 mole) dissolved in toluene (100 ml). The reaction mixture was stirred and heated at reflux for 44 hours. Pyridine hydrochloride (6.5 g) was filtered from the hot solution; p-toluene sulfonic acid (m.p. 90°-94°C) (2.75 g) and unreacted p-toluene sulfonyl chloride (0.5 g) precipitated out of the solution on cooling. The toluene solution was washed with dilute hydrochloric acid, water, 5% sodium hydroxide solution and again with water. The toluene solution was dried over anhydrous sodium sulfate.

The product was isolated by evaporation of the toluene solution. Recrystallization from di-n-butyl ether gave 14.9 g (57% yield) of the product obtained as white crystals, m.p. 96°-97°C. The infrared spectrum is shown in Figure 21.

Elemental Analysis for $\text{C}_{19}\text{H}_{18}\text{F}_6\text{S}_2\text{O}_6$:

	<u>% C</u>	<u>% H</u>	<u>% F</u>	<u>% S</u>
Found:	43.82	3.64	22.01	12.16
Calculated:	43.85	3.46	21.92	12.31

(b) Attempted Preparation of Tri(hexafluoropentamethylene) Glycol



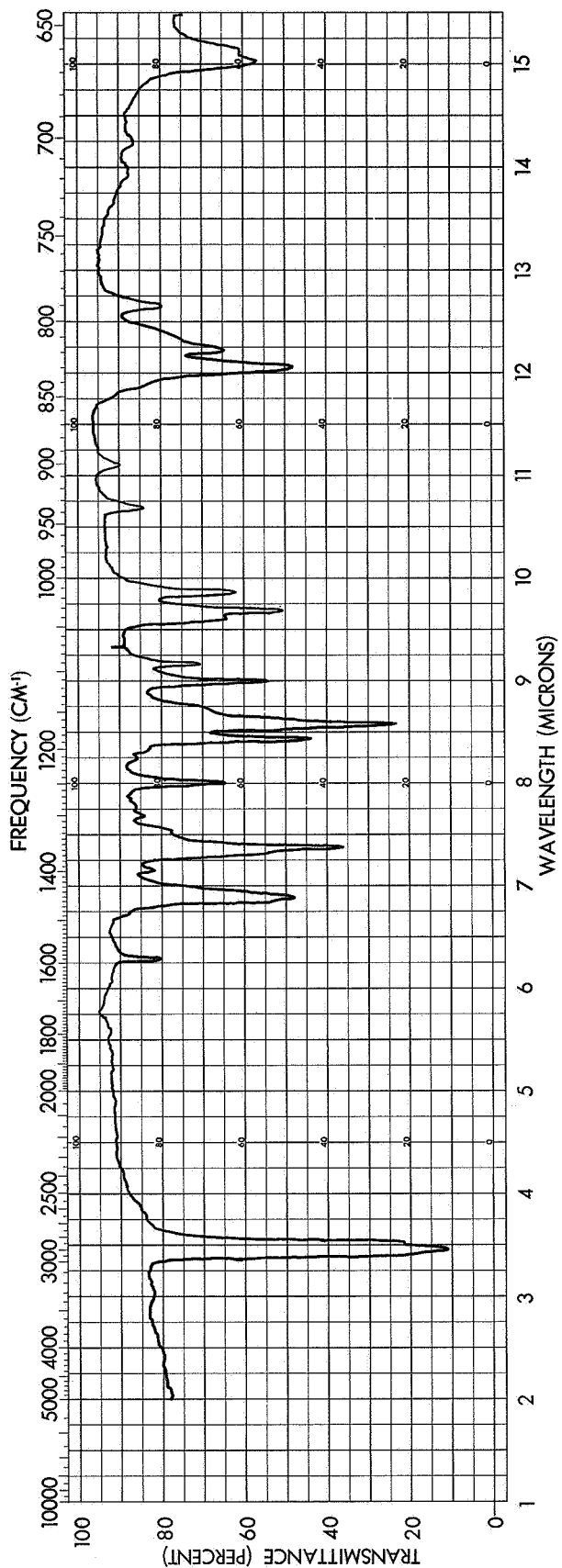
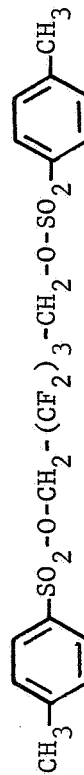
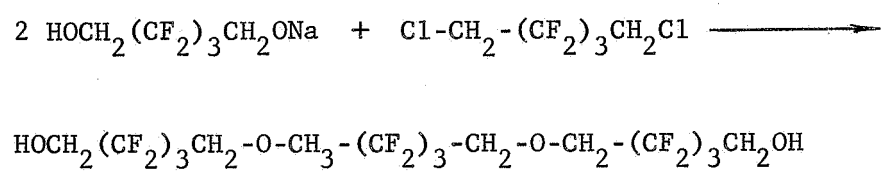


Figure 21. Infrared Spectrum of Hexafluoropentamethylene-bis-(p-toluenesulfonate)



In a 100-ml, three-necked flask equipped with a stirrer, reflux condenser and addition funnel, was placed hexafluoropentanediol (3.6 g, 0.017 mole) dissolved in di-n-butyl ether (20 ml). To this was added sodium metal (0.39 g, 0.017 mole), and the mixture stirred and heated at reflux for 3 hours, during which time all of the sodium disappeared. To this solution was added a hot solution of di-p-toluene-sulfonate of hexafluoropentanediol (6.0 g, 0.017 mole) and the reaction mixture stirred and heated at reflux for 43 hours. After filtering off 2.4 g of water-soluble grey solid from the hot solution, 1.8 g of unreacted di-p-toluene-sulfonate of hexafluoropentanediol (m.p. 96°-97°C) settled out of the cooled solution. Evaporation of the di-n-butyl ether yielded 1.62 g of hexafluoropentanediol. None of the desired diether was obtained.

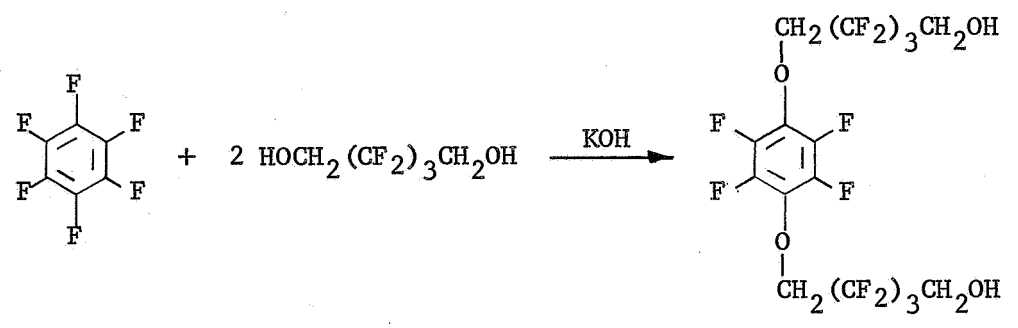
(2) From 1,5-Dichloro-2,2,3,3,4,4-Hexafluoropentane



In a 500-ml, three-necked flask equipped with a stirrer, reflux condenser, and addition funnel purged with nitrogen were placed hexafluoropentanediol (15.3 g, 0.072 mole) dissolved in 100 ml of di-n-butyl ether. Sodium metal (0.072 mole, 1.66 g) was added in small pieces and the mixture stirred and refluxed for 2 hours, during which time all of the sodium disappeared. A solution of 1,5-dichloro-2,2,3,3,4,4-hexafluoropentane (10.0 g, 0.036 mole) in 50 ml of di-n-butyl ether was added slowly with stirring. The reaction mixture was stirred and heated at reflux for 19 hours. There was no apparent reaction.

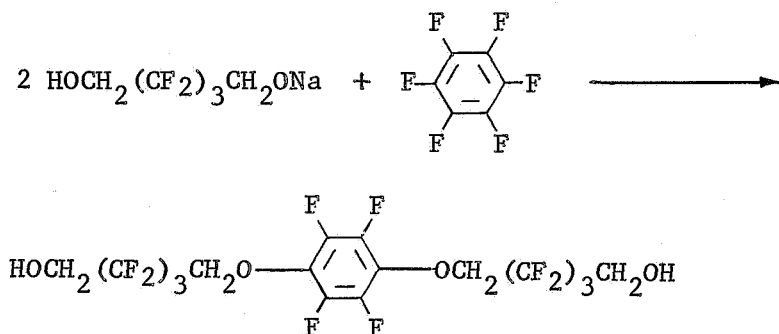
b. 1,4-bis-(5-Hydroxy-hexafluoropentoxy)-Tetrafluorobenzene

(1) From Potassium Hydroxide and Hexafluorobenzene



In a 50-ml, three-necked flask were placed hexafluorobenzene (9.3 g, 0.05 mole), hexafluoropentanediol (21.2 g, 0.1 mole) and potassium hydroxide (5.6 g, 0.1 mole). The mixture was stirred and heated under reflux for 41 hours. The viscous oil resulting was poured into water and extracted with ether. After drying, the ether was evaporated off at reduced pressure leaving a dark oil. Distillation at reduced pressure yielded 6.9 g of unreacted hexafluoropentane diol (m.p. 76°-78°C, b.p. 102°-103°C/1 mm) and 2.5 g of a yellow viscous oil (b.p. 140°-160°C/1.5 mm). The infrared spectrum of this oil indicates that it is the desired diether, 1,4-bis-(5-hydroxy-hexafluoropentoxy)-tetrafluorobenzene. The infrared spectrum is attached as Figure 22.

(2) From Mono-Sodium Salt of Hexafluoropentanediol



Hexafluoropentanediol (21.2 g, 0.1 mole), dissolved in 100 ml of di-n-butyl ether, was placed in a 500-ml, three-necked flask equipped with a stirrer, addition funnel, and reflux condenser. Sodium metal (2.3 g, 0.1 mole) was added and the mixture stirred and heated at reflux for 2 hours, during which time all of the sodium disappeared. A solution of hexafluorobenzene (9.6 g, 0.05 mole) in 50 ml of di-n-butyl ether was added and the mixture stirred and heated at reflux for 2 hours. On cooling, unreacted monosodium salt of hexafluoropentanediol precipitated out. Water was added to dissolve this solid and the mixture extracted with ethyl ether. The ethyl ether - di-n-butyl ether extracts yielded 2.6 g of 1,4-bis-(5-hydroxy-hexafluoropentoxy)-tetrafluorobenzene as a yellow oil. The infrared spectrum was identical to that of the product obtained from hexafluoropentane-diol (Figure 22).

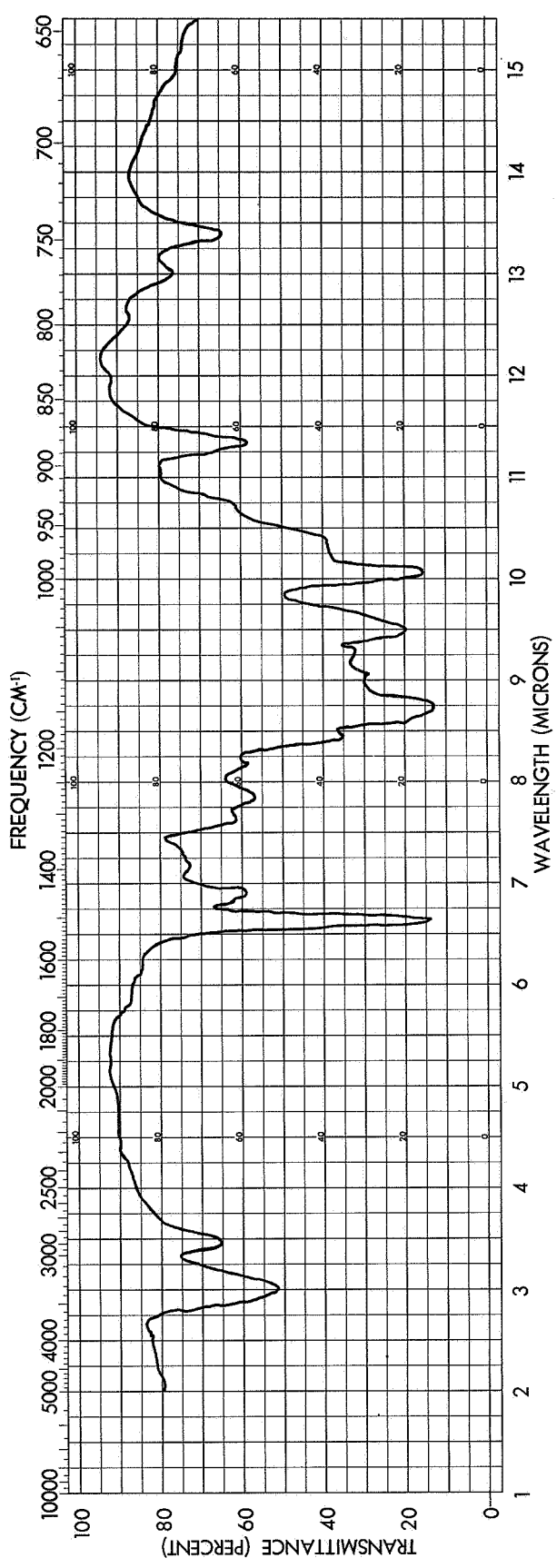
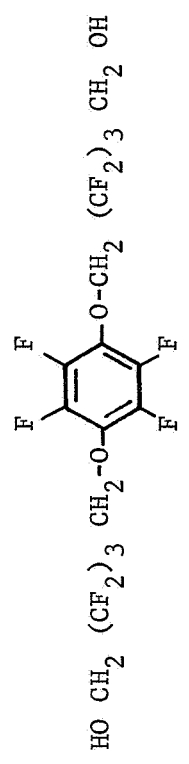


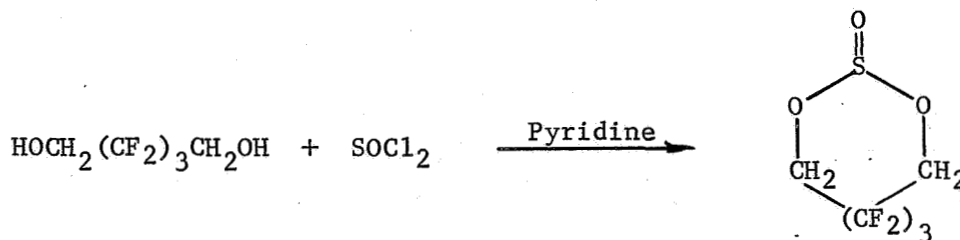
Figure 22. Infrared Spectrum of 1,4-bis-(5-hydroxy-hexafluoropentoxy)-tetrafluorobenzene



c. Poly(hexafluoropentamethylene ether)

(1) From Hexafluoropentamethylene Sulfite

(a) Preparation of Hexafluoropentamethylene Sulfite

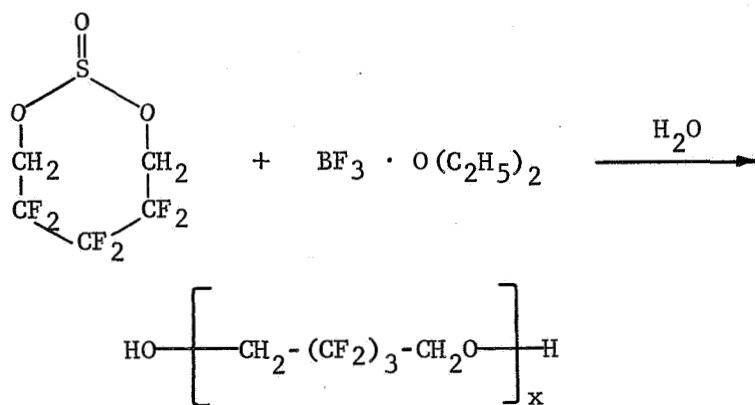


Into a 1-liter, three-necked flask equipped with a thermometer, addition funnel, stirrer, and condenser with drying tube were introduced 127.2 g (0.6 mole) of hexafluoropentanediol and 200 ml of freshly distilled pyridine. Thionyl chloride (1.2 mole, 87 ml) was slowly added, keeping the temperature between 24°-30°C using an ice bath. The reaction was run for 2 hours at 25°C. Vapor phase chromatographic analysis showed no unreacted hexafluoropentanediol.

The mixture was extracted with ether without hydrolyzing. The pyridine hydrochloride was filtered off and the ether layer was distilled. The product was obtained with some pyridine hydrochloride impurity. It was redissolved in ether and 150 ml of water was added to dissolve the pyridine hydrochloride. The ether layer was redistilled. The product was obtained in 62% yield as a colorless liquid, b.p. 178°C (see Figure 23).

Elemental Analysis:	<u>% C</u>	<u>% H</u>	<u>% F</u>
Found:	23.94	1.65	44.90
Calculated:	23.3	1.55	44.2

(b) Polymerization of Hexafluoropentamethylene Sulfite



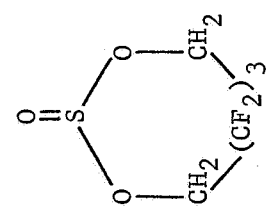
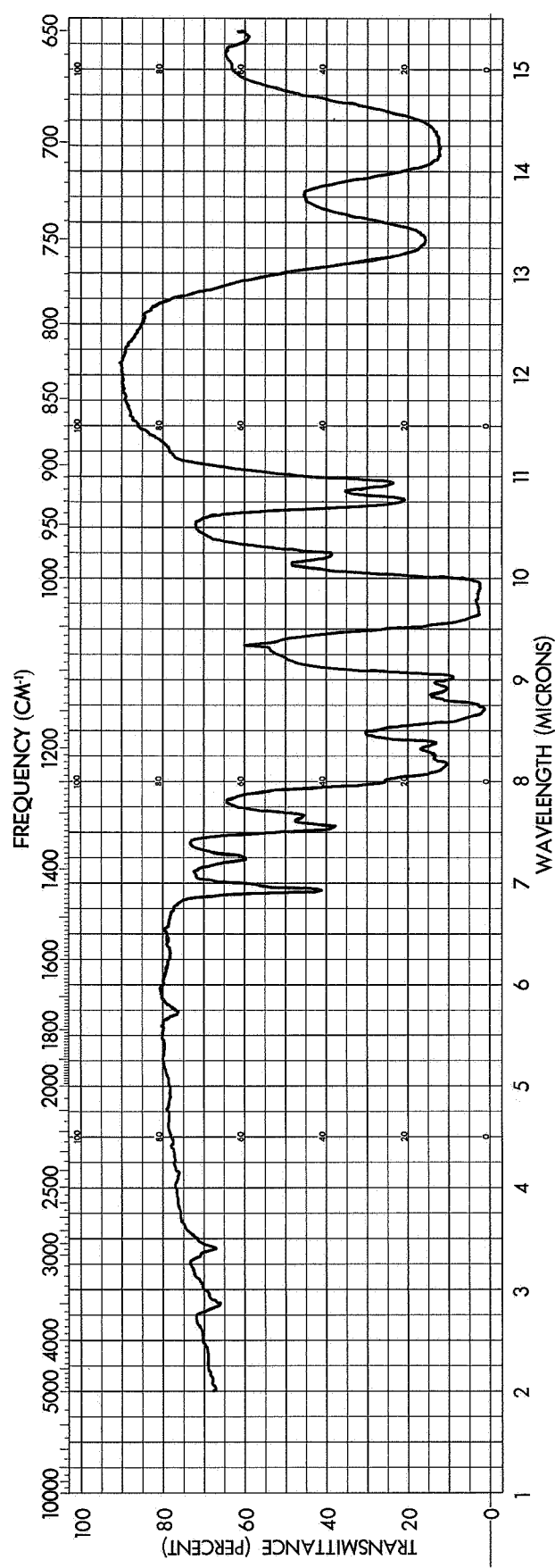


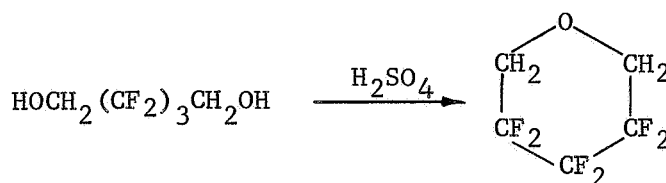
Figure 23. Infrared Spectrum of Hexafluoropentamethylene Sulfite

Into a 10-ml, two-necked flask were placed hexafluoropentamethylene sulfite (10 ml). This was then cooled to dry ice temperature under an atmosphere of nitrogen. Approximately 1 ml of BF_3 -etherate was added and the mixture was allowed to warm to room temperature. After standing at room temperature for 3 days, the solution became a viscous oil.

The liquid obtained was washed with water and extracted with ether. The ethereal solution was dried with MgSO_4 , filtered, and evaporated. A pale yellow, viscous oil was isolated. Yield was 9.3 g.

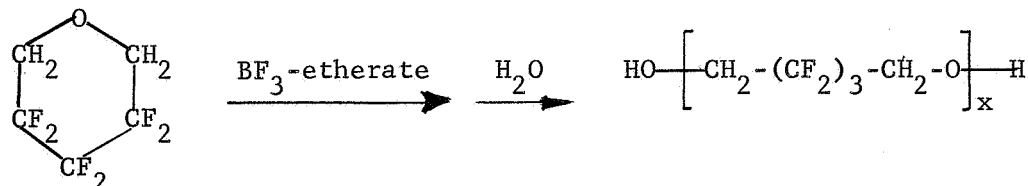
(2) Attempted Preparation from Hexafluoropentamethylene Oxide

(a) Preparation of Hexafluoropentamethylene Oxide



Into a 500-ml, three-necked flask equipped with stirrer, thermometer, and distilling head were introduced hexafluoropentanediol (126.5 g, 0.59 mole) and concentrated sulfuric acid (215.6 g, 2.7 mole). The mixture was stirred and heated. When the temperature reached 170°C , a cloudy liquid distilled over, head temperature 75°C . The temperature was increased to 250°C until no more ether distilled. The distillate was dried over Drierite and redistilled from phosphorous pentoxide. An 80% yield of cyclic ether (b.p. $99^\circ\text{-}100^\circ\text{C}$, m.p. 25°C) was obtained. See Figure 24 for the infrared spectrum.

(b) Attempted Polymerization of Hexafluoropentamethylene Oxide



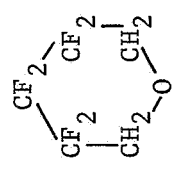
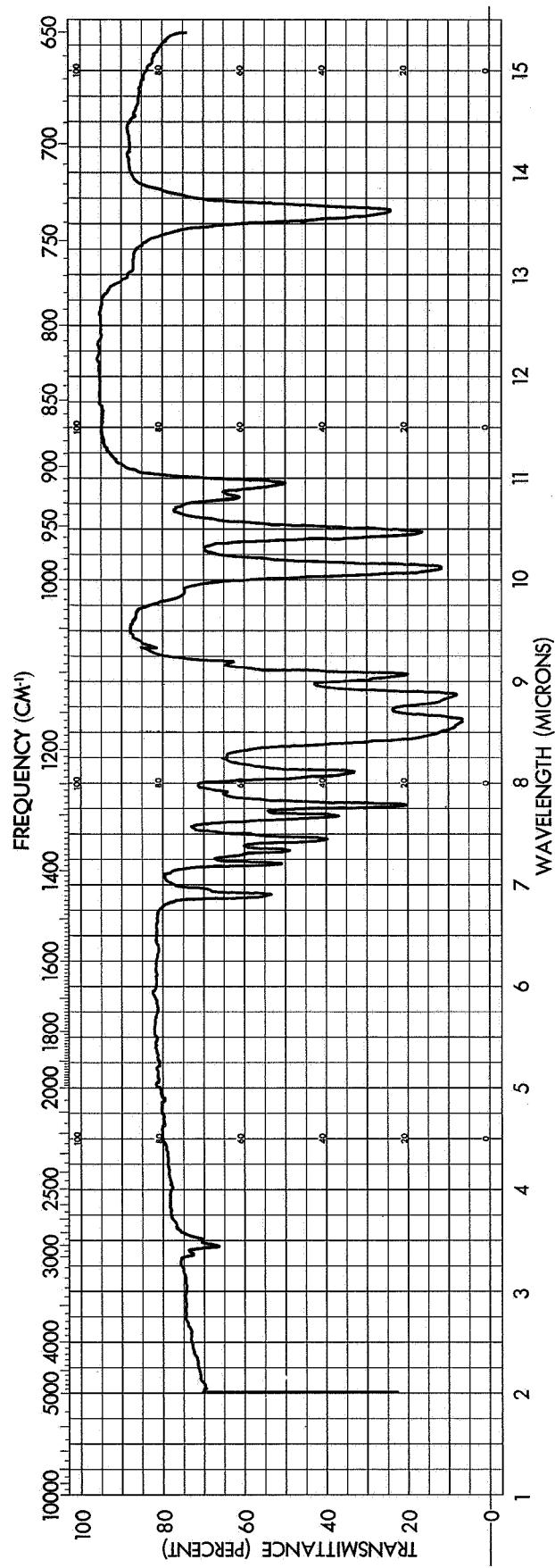


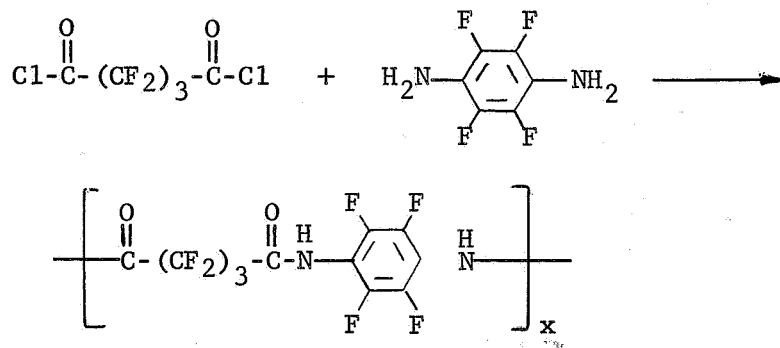
Figure 24. Infrared Spectrum of Hexafluoropentamethylene Oxide

A 20-ml, two-necked flask fitted with a calcium chloride drying tube was swept with nitrogen. Into the flask were added 3,3,4,4,5,5-hexafluoropentamethylene oxide (19.5 g, 0.1 mole) and the flask was cooled to dry-ice temperature. BF_3 -etherate (1.35 g) was then added. The solution was mixed and allowed to warm up to room temperature within 25 minutes. After standing for 3 days, there was no reaction. Further study is warranted.

B. POLYAMIDES

1. Poly(tetrafluoro-p-phenylene perfluoroglutaramide)

a. From perfluoroglutaryl chloride



(1) Interfacial Polymerization

Tetrafluoro-p-phenylenediamine (0.05 mole, 9.00 g) was dissolved in 725 ml of hot water, then added to a 1-liter, three-necked flask equipped with a stirrer, condenser, dropping funnel, and nitrogen inlet. Sodium hydroxide (0.125 mole, 5.00 g) was added to the amine slurry at 50°C. Perfluoroglutaryl chloride (0.05 mole, 13.85 g) dissolved in 135 ml of benzene was added in 10 minutes to the amine slurry with vigorous mixing under nitrogen. The slurry was then agitated overnight. The polymer was removed by filtration and dried to a vacuum oven. The infrared spectrum confirmed the presence of the amide (see Figure 25). The results of three typical runs are summarized in Table 8. The inherent viscosity of the polymer made at 50°C was 0.013 in DMF at 30°C. The melting point was 157°-159°C.

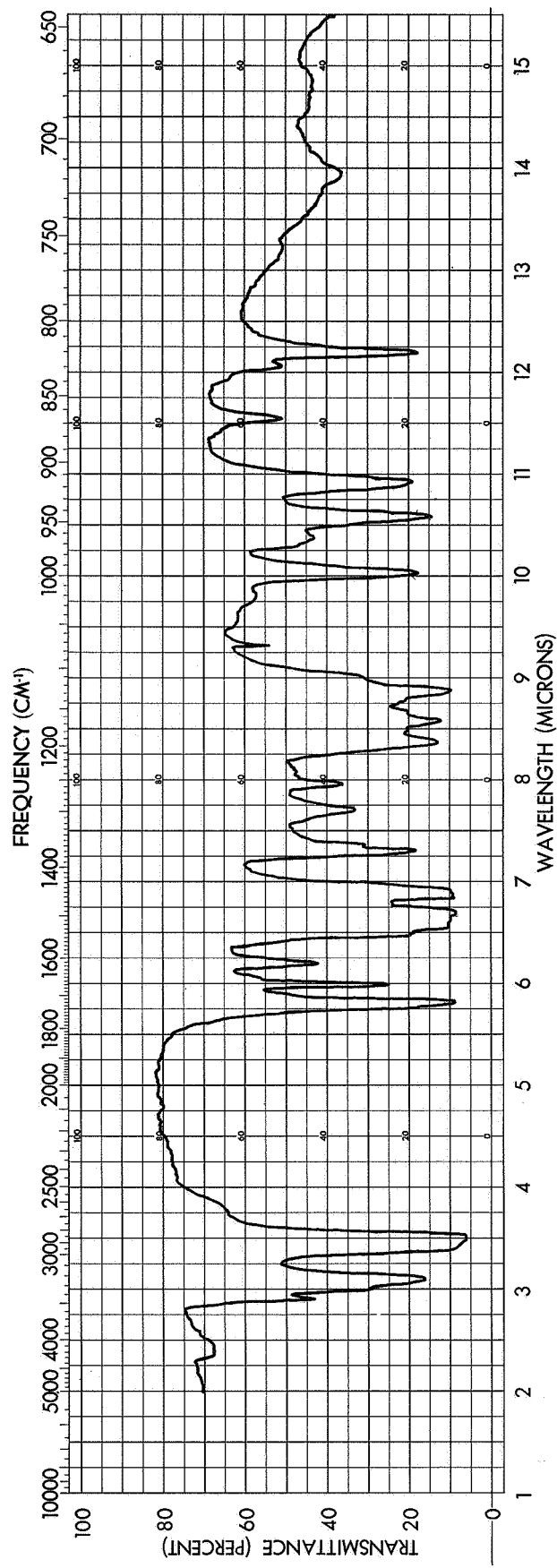


Figure 25. Infrared Spectrum of Poly(tetrafluoro-p-phenylene Perfluoroglutaramide)

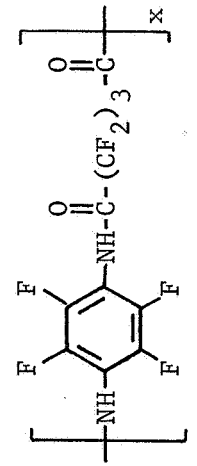


TABLE 8

INTERFACIAL PREPARATION OF
POLY(TETRAFLUORO-P-PHENYLENE PERFLUOROGLUTARAMIDE)

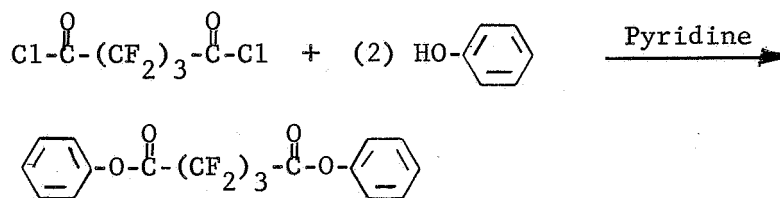
Reaction Temp, °C	% Yield	m.p., °C
30	33.0	150-153
50	33.1	157-159
80	19.2	147-152

(2) Solution Polymerization

Tetrafluoro-p-phenylenediamine (3.60 g, 0.02 mole) was dissolved in 35 ml of N-methyl pyrrolidone and charged to a 100-ml, three-necked flask equipped with a stirrer, condenser, dropping funnel, thermometer, and nitrogen inlet. Perfluoroglutaryl chloride (5.54 g, 0.02 mole) was added dropwise to the amine solution over a 20-minute period at 26°-49°C with vigorous stirring under nitrogen, then cooled and poured into water. The precipitated polymer was removed by filtration and dried in a vacuum oven at 45°C for 4 hours to yield a dark, brittle polymer which was soluble in acetone. The melting point was in excess of 300°C. Pyridine and dimethylacetamide as solvents gave similar results.

b. From Diphenyl Perfluoroglutarate

(1) Preparation of Diphenyl Perfluoroglutarate

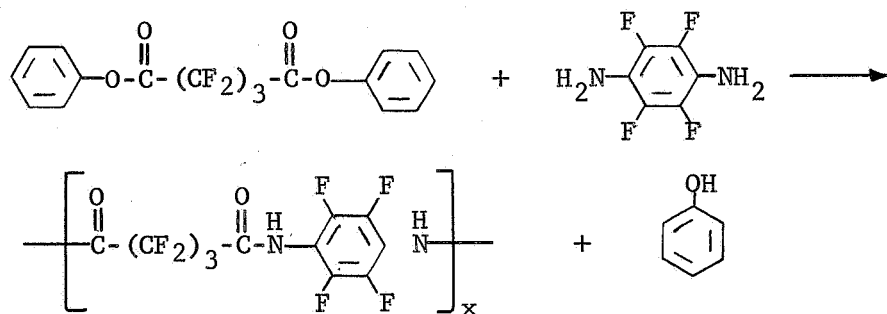


Phenol (14.1 g, 0.15 mole) was dissolved in pyridine (70.0 g) in a three-necked flask equipped with a stirrer, condenser, thermometer and addition funnel. Perfluoroglutaryl chloride (13.8 g, 0.05 mole) was added to the phenol solution over a 20-minute period during which the temperature increased from 25°C to 59°C and pyridine hydrochloride precipitated. The slurry was stirred for 10 minutes at 45°-49°C, then overnight at 80°-90°C.

The solution was cooled to 0°C, then filtered. The residue (pyridine hydrochloride) was washed with pyridine. The filtrate was added to 300 ml of ether with mixing. The slurry was filtered and the residue washed with ether. The ether and pyridine were removed and the residue vacuum-fractionated. The diphenyl ester boiled at 189°-190°C at 7 mm. The yield was 63%. An infrared spectrum is shown in Figure 26.

Elemental Analysis:	<u>% C</u>	<u>% H</u>	<u>% F</u>
Found:	50.71	2.67	29.03
Calculated:	52.2	2.6	29.2

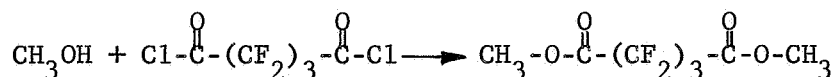
(2) Melt Polymerization



Tetrafluoro-p-phenylenediamine (2.70 g, 0.015 mole) plus diphenyl perfluoroglutarate (5.88 g, 0.015 mole) was charged to a side arm test tube which was purged with nitrogen. The mixture was gradually heated in an oil bath to 240°C under nitrogen at 187°C; the solution became purple, and at 195°C phenol began to evolve. The solution was held at 230°C to 240°C under nitrogen for 1½ hours, then evacuated for ½ hour. The black, brittle polymer was then cooled under vacuum, m.p. = 273°C.

c. From Dimethyl Perfluoroglutarate

(1) Preparation of Dimethyl Perfluoroglutarate



Methanol (25.6 g, 0.8 mole) was charged to a 100-ml, three-necked flask equipped with a stirrer, condenser, dropping funnel and thermometer. Perfluoroglutaroyl chloride (55.2 g, 0.2 mole) was added to the methanol over a 1-hour period with mixing. The

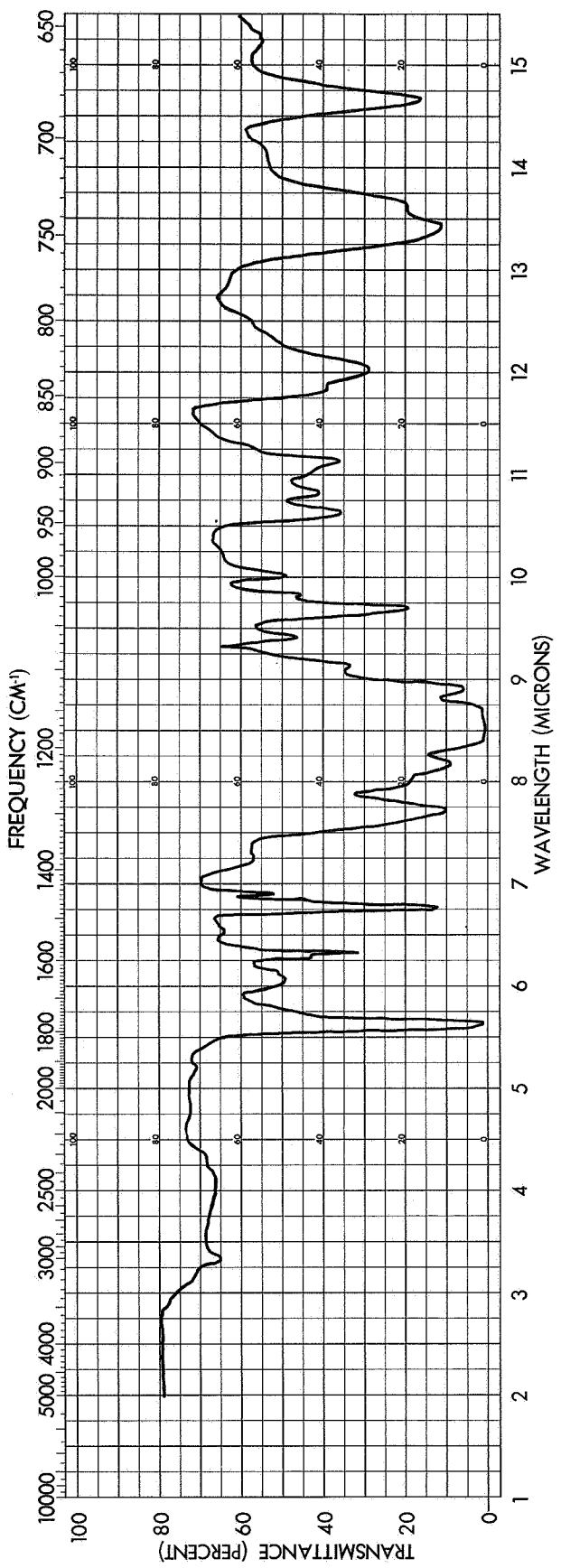
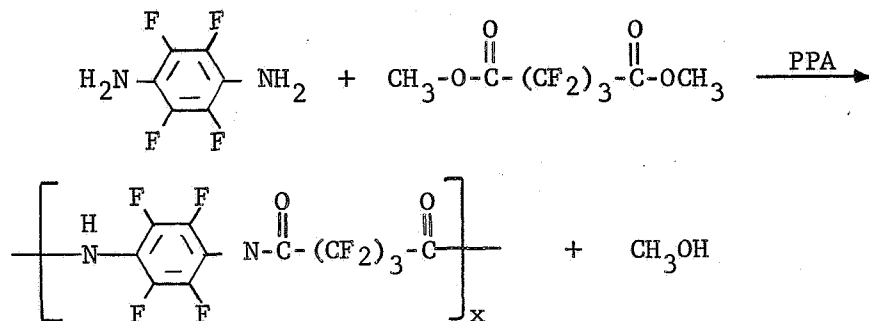


Figure 26. Infrared Spectrum of Diphenyl Perfluoroglutarate

temperature rose from 25°C to 42°C. An additional 15 ml of methanol was added and the solution was refluxed and stirred for 4½ hours. The dimethyl ester, which was recovered in a yield of 67.5%, boiled at 101°-103°C at 31 mm. An infrared spectrum is shown in Figure 27.

(2) Attempted Polymerization in Polyphosphoric Acid

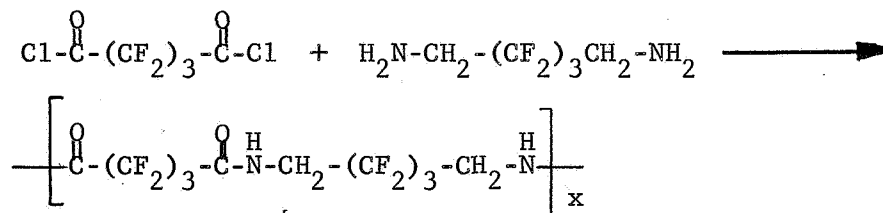


Polyphosphoric acid (60 ml) was charged to a 100-ml, three-necked flask equipped with a stirrer, condenser, thermometer, and dry nitrogen inlet. The air was removed by heating to 100°C under vacuum, then venting with dry nitrogen.

Tetrafluoro-p-phenylenediamine (2.70 g, 0.015 mole) and dimethyl perfluoroglutarate (4.00 g, 0.015 mole) was then added to the polyphosphoric acid under nitrogen. The solution was heated and stirred to 120°C over a 4-hour period, followed by 4½ hours at 150°C under nitrogen. The mixture was then poured into 300 ml of hot water with mixing, neutralized with KOH, cooled and filtered. No polymer was obtained.

2. Poly(hexafluoropentamethylene perfluoroglutaramide)

a. From Perfluoroglutaryl Chloride



(1) Interfacial Polymerization

Hexafluoropentanediamine (15.28 g, 0.0727 mole) was dissolved in 430 ml of water containing NaOH (7.20 g, 0.18 mole) in a 1-liter,

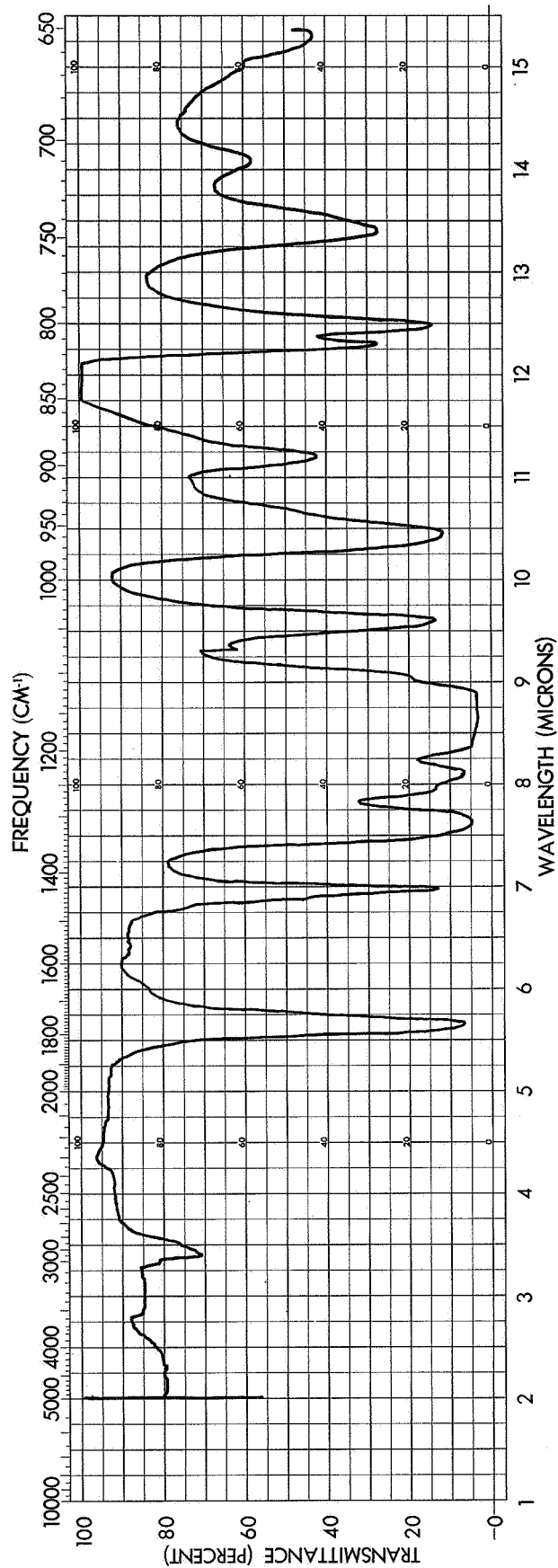


Figure 27. Infrared Spectrum of Dimethyl Perfluoroglutarate

three-necked flask equipped with a stirrer, condenser, dropping funnel, thermometer, and nitrogen inlet. Perfluoroglutaryl chloride (20.05 g, 0.0727 mole) in 165 ml of benzene was added to the diamine solution over a 10-minute period with vigorous mixing under nitrogen. The temperature rose from 31°-42°C. The slurry was mixed for 1 hour at 30°-40°C under nitrogen, then filtered. The residue was dried in a vacuum oven for 80°C for 3 hours to yield 17.5 g of light tan polymer. Yield = 58.3%, m.p. = 185°C to 190°C. The infrared spectrum of the polymer is attached as Figure 28. The inherent viscosity in DMF was 0.16 at 30°C.

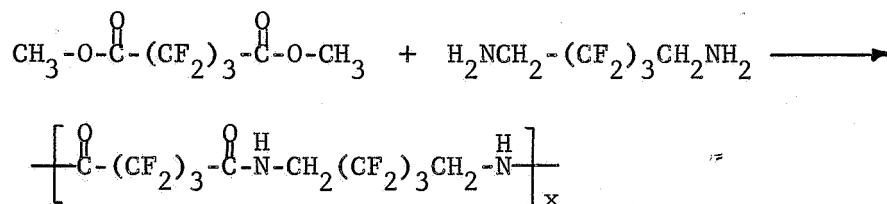
Samples were prepared for LOX-impact testing by using a 11/16-in. pellet mold. The polymer was compacted at 200°F to 225°F at 5000-lb pressure, then cooled to 150°F. These samples were submitted to MSFC for LOX-impact testing.

(2) Solution Polymerization

Perfluoroglutaryl chloride (5.52 g, 0.02 mole) was dissolved in 15 ml of butyl ether and charged to a 100-ml, three-necked flask equipped with a stirrer, condenser, dropping funnel, thermometer, and dry nitrogen inlet. Hexafluoropentanediamine (4.20 g, 0.02 mole) was dissolved in 20 ml of butyl ether and added to the dichloride solution over a 10-minute period with stirring under nitrogen. The temperature rose from 28°C to 46°C with the formation of a precipitate, probably amine hydrochloride. The slurry was then mixed for ½ hour at 30°C to 40°C under nitrogen.

Triethyl amine (2.02 g, 0.02 mole) was added slowly to the reaction with stirring under nitrogen, during which time the temperature rose from 35°C to 50°C. The slurry was mixed 15 minutes, then heated to 80°-90°C over a 20-minute period. White crystals of sublimed triethyl amine hydrochloride formed on the upper portion of the flask. Additional triethyl amine (2.02 g, 0.02 mole) was then added, and the mixture stirred for 4 hours at 100°-110°C under nitrogen. The sticky tar residue which remained was dried in a vacuum oven at 100°C for 3 hours to yield 7.96 g of a tan semi-solid polymer. When the polymerization was conducted in pyridine, a black, brittle polymer having a melting point of 105°-110°C was obtained.

b. From Dimethyl Perfluoroglutarate



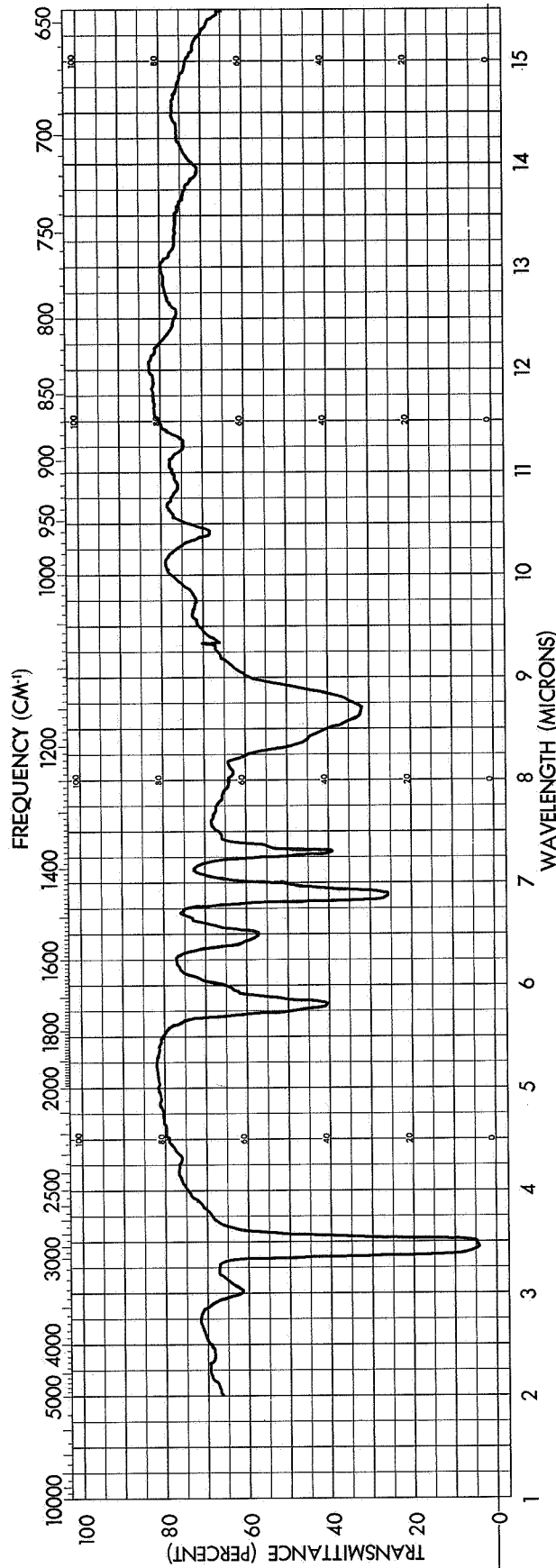
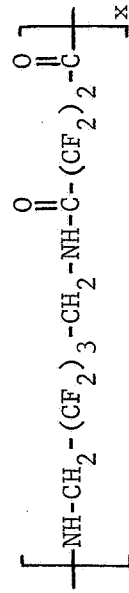


Figure 28. Infrared Spectrum of Poly(hexafluoropentamethylamethylene Perfluoroglutaramide)

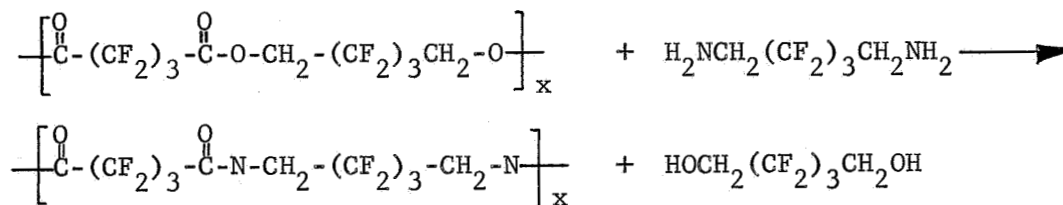


(1) Attempted Polymerization in Polyphosphoric Acid

Polyphosphoric acid (100 ml) was charged to a 250-ml, three-necked flask equipped with a stirrer, condenser, thermometer, and dry nitrogen inlet. The polyphosphoric was purged of air by heating to 100°C under vacuum, then venting with dry nitrogen.

Hexafluoropentanediamine (4.20 g, 0.02 mole) plus dimethyl perfluoroglutarate (5.34 g, 0.02 mole) was then added to the polyphosphoric acid. The solution was stirred at 150°-160°C for 24 hours under nitrogen. The light tan reaction mixture was then poured into 300 ml of hot water, neutralized with KOH, cooled to 20°-25°C, then filtered. The residue was dried in a vacuum oven at 60°-70°C for 3 hours to yield a trace of black polymer.

c. From Poly(hexafluoropentamethylene perfluoroglutarate)



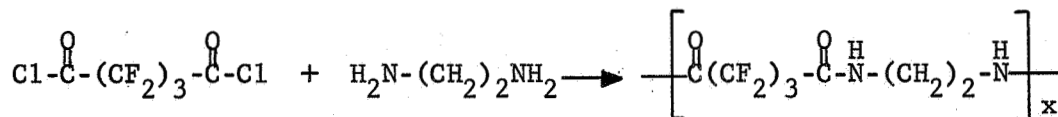
(1) Attempted Solution Polymerization

Poly(hexafluoropentamethylene hexafluoroglutarate) (21.90 g) was slurried in 10 ml of butyl ether in a 100-ml, three-necked flask equipped with a stirrer, condenser, thermometer, addition funnel, and nitrogen inlet. Hexafluoropentanediamine (0.05 mole, 10.50 g) dissolved in 10 ml of butyl ether was added to the polyester slurry over a 5-minute period with mixing under nitrogen. The slurry was mixed for 24 hours at 140°-145°C under nitrogen. The tan polymer was dried in a vacuum oven at 140°-145°C, during which time the material turned black (m.p. 135°-160°C). No reaction occurred when the polymerization was attempted in tetrahydrofuran.

(2) Melt Polymerization

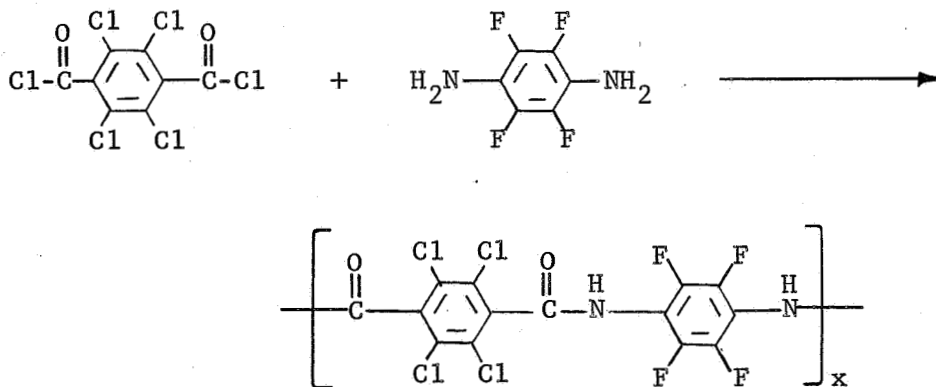
The polyester (21.90 g) was added to a 100-ml, three-necked flask equipped with a stirrer, condenser, dropping funnel, thermometer, and nitrogen inlet. The molten hexafluoropentanediamine (0.05 mole, 10.50 g) was added to the molten polyester at 130°C over a 25-minute period with mixing under nitrogen. The solution was mixed for 18 hours at 140°-150°C under nitrogen. The polymer which resulted was a black semisolid.

3. Poly(Ethylene Perfluoroglutaramide)



Ethylene diamine (9.0 g, 0.15 mole), NaOH (16 g, 0.4 mole) and 260 ml of water was added to a 1-liter, three-necked flask equipped with a stirrer, condenser, dropping funnel, thermometer, and nitrogen inlet. Perfluoroglutaryl chloride (41.4 g, 0.15 mole) in 330 ml of benzene was added to the diamine solution over a 25-minute period with mixing under nitrogen. The slurry was mixed for 1 hour at 30°C to 33°C under nitrogen. The slurry was then filtered and the residue dried in a vacuum oven at 55°C for 3 hours to yield 22.0 g of white polymer. m.p. = 300°C. Yield = 55.7%. The infrared spectrum is attached as Figure 29. The inherent viscosity in DMF was 0.059 at 30°C.

4. Attempted Preparation of Poly(tetrafluoro-p-phenylene tetrachloroterephthalamide)



Into a 1-liter, three-necked flask, equipped with a stirrer, condenser, dropping funnel, and nitrogen inlet was charged 435 ml of water, NaOH (3.00 g, 0.075 mole), and tetrafluoro-p-phenylene diamine (5.40 g, 0.03 mole). Tetrachloroterephthaloyl chloride (10.23 g, 0.03 mole) in 80 ml of benzene was added to the amine solution at 48°C over a 5-minute period with vigorous mixing under nitrogen. The slurry was mixed for 4 hours at 30°C to 45°C under nitrogen, then filtered. There was little (if any) reaction.

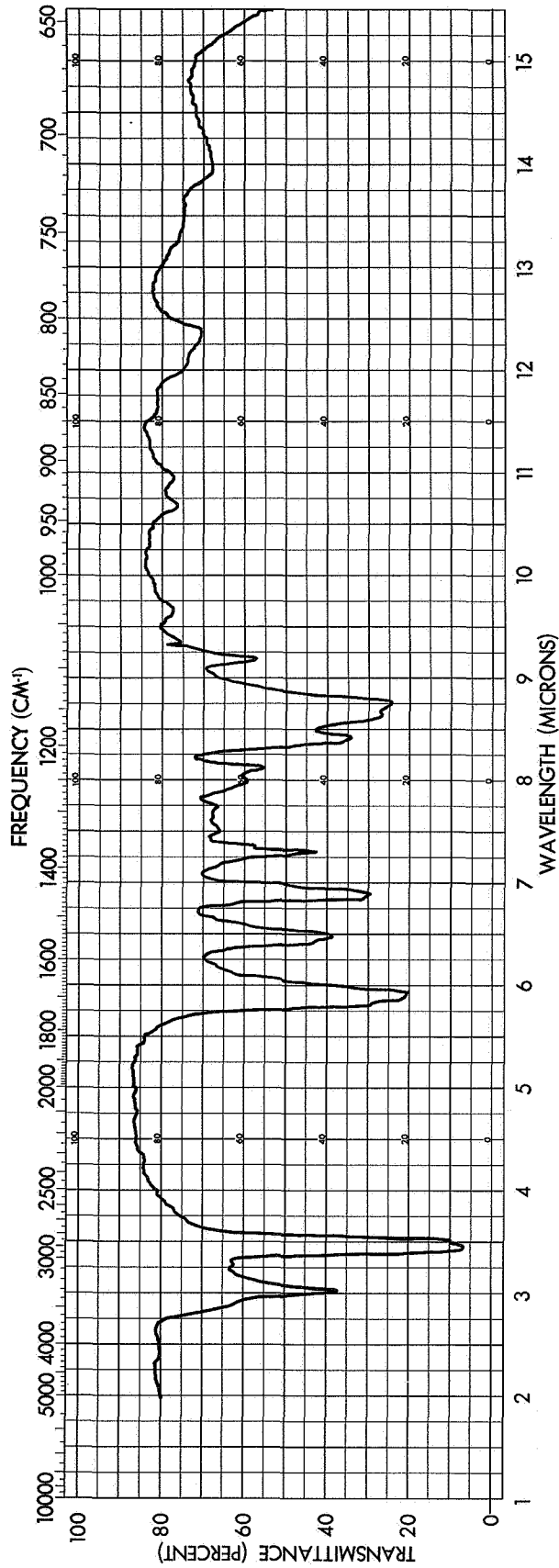
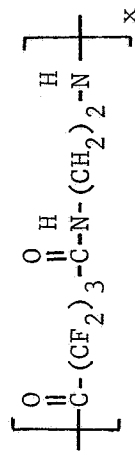
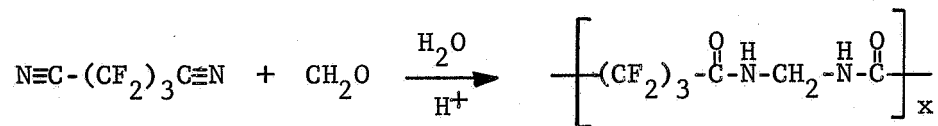


Figure 29. Infrared Spectrum of Poly(ethylene Perfluoroglutaramide)



5. Attempted Preparation of Poly(methylene perfluoroglutaramide)



Perfluoroglutaronitrile (10.1 g, 0.05 mole), paraformaldehyde (1.54 g, 0.0171 mole) and 60 ml of formic acid was charged to a 500-ml, three-necked flask equipped with a stirrer, condenser, thermometer, and addition funnel. The slurry was cooled to 6°C with mixing, then H₂SO₄ (20 g) was added over a 7-minute period with mixing at 6°C to 13°C. The slurry was mixed for 1½ hours at 25°C to 26°C, then added to 250 ml of water with mixing. There was no reaction.

C. POLYESTERS

1. Melt Polymerization

Into a three-necked flask equipped with a stirrer, thermometer and condenser attached to a water trap were introduced the diol and the diacid chloride. The mixture was heated at 70°C for 3 hours, and then the temperature was slowly increased to 160°C and held for 12 hours, then held at 200°C for 3 hours. Vacuum (1-mm Hg) was applied to the mixture during the last hour at 200°C. Excess diol was removed under vacuum. Molecular weight determinations were unsuccessfully attempted by vapor phase osmometry.

The chloride in the polyester, either as acid chloride or trapped hydrochloric acid, was determined by reaction with an excess of ammonium hydroxide, (approximately 1N), and back titrated with 0.5N HCl using methyl orange indicator. A blank was run simultaneously. All the polyesters prepared still contain reactive chloride.

The experimental conditions and results of the esterifications conducted without solvent are shown in Table 9.

2. Interfacial Polymerization

a. Poly(hexafluoropentamethylene perfluoroglutarate)

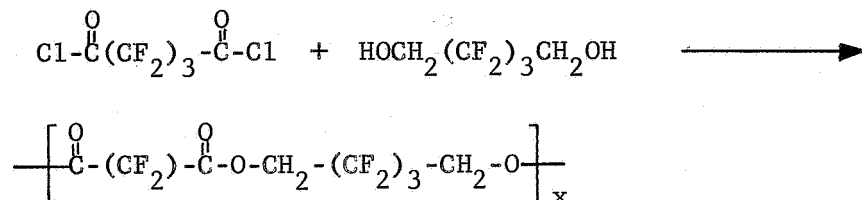


TABLE 9
ESTERIFICATIONS IN THE MELT

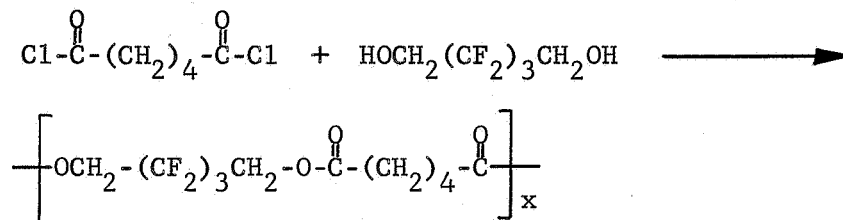
Diol, Moles	Acid Chloride, Moles	Temp, °C	Time, hr	% Yield Polyester	Analysis
I, 0.2	A, 0.2	65 200-220	4 52	80	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$ @ 5.75 μ , 90% yield HCl
II, 0.3	B, 0.3	90 200-220	3 70	90	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$ @ 5.65 μ , 90% yield HCl
III, 0.2	B, 0.2	75 200-220	3 96	95	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$ @ 5.6 μ , 94% yield HCl
IV, 0.2	B, 0.2	70 200	3 50	> 90	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$ @ 5.6 μ , 85% yield HCl
III, 0.2	A, 0.2	70 200-220	3 68	> 95	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$ @ 5.75 μ , 90% yield HCl
I, 0.15	B, 0.15	75 200	2 48	> 90	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$ @ 5.6 μ , 95% yield HCl

- I. HET diol
- II. Ethylene glycol
- III. Hexafluoropentanediol
- IV. Tetrachloroxylylene diol

- A. Adipoyl Chloride
- B. Perfluoroglutarylchloride

Hexafluoropentanediol (0.06 mole, 12.72 g) was dissolved in 240 ml of water containing sodium hydroxide (0.14 mole, 5.60 g), then added to a 500-ml, three-necked flask equipped with a stirrer, condenser, thermometer, dropping funnel, and nitrogen inlet. Perfluoroglutaryl chloride (0.06 mole, 16.56 g) in 120 ml of benzene was added to the diol solution in 2-10 minutes with vigorous mixing under nitrogen. The slurry was mixed further, the water and benzene decanted, and the polyester dried in a vacuum oven to yield a colorless, viscous oil which crystallized on standing (see Table 10).

b. Preparation of Poly(hexafluoropentamethylene adipate)



Hexafluoropentanediol (21.2 g, 0.1 mole) was dissolved in 400 ml of water containing NaOH (8.8 g, 0.22 mole), then added to a 1-liter, three-necked flask equipped with a stirrer, condenser, dropping funnel and nitrogen inlet. Adipoyl chloride (18.3 g, 0.1 mole) in 130 ml of benzene was added to the diol solution in 17 minutes with vigorous mixing at 25°C to 30°C under nitrogen. The slurry was mixed for 2 hours at 25°C to 30°C under nitrogen. The water and benzene was decanted and the polymer remained as an oil.

D. OTHER POLYMERS

1. Attempted Preparation of Poly(tetrafluoro-p-phenylene pyromellitimide)

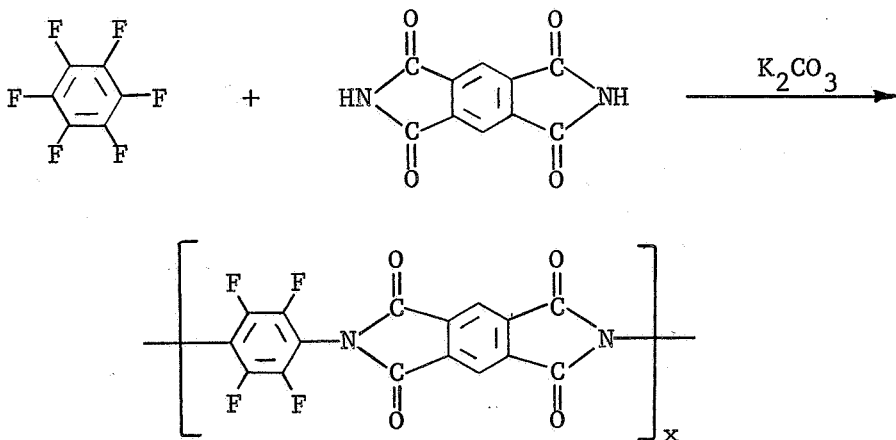


TABLE 10

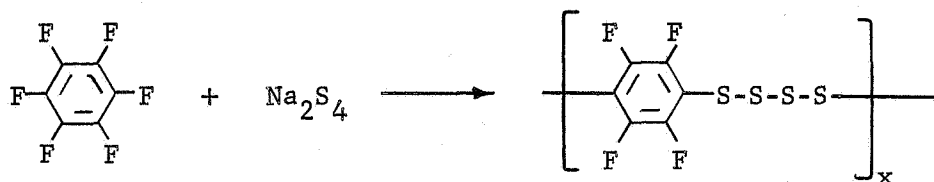
POLY(HEXAFLUOROPENTAMETHYLENE PERAFLUROGLUTARATE)
INTERFACIAL POLYMERIZATION

Temp of Dichloride Addition, °C	Reaction Temp, °C	Reaction Time	% Yield	Remarks
5-10	11-18	5 min	32.3	Clear, colorless, viscous oil, which crystallized on standing
29-42	30-42	3 hr	8.0	Clear, colorless, viscous oil
30-44	30	42 hr	0	Polyester apparently had hydrolyzed

Hexafluorobenzene (9.3 g, 0.05 mole), pyromellitic diimide (10.8 g, 0.05 mole), potassium carbonate (6.9 g, 0.05 mole) and 100 ml of distilled N-methyl pyrrolidone were charged to a 250-ml, three-necked flask equipped with a stirrer, condenser and thermometer. The slurry was heated to 170°C over a 2-hour period with mixing, then mixed at 170°C to 180°C for 4 hours. There was no apparent reaction.

2. Polysulfides

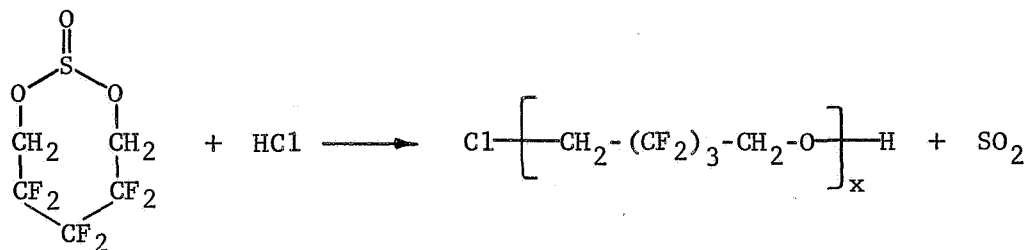
a. Attempted Preparation of Poly(tetrafluoro-p-phenylene tetrasulfide)



Sulfur (18.8 g, 0.59 mole), Na₂S · 9 H₂O (48.0 g, 0.2 mole), and 75 ml of water was added to a 250-ml, three-necked flask equipped with a stirrer, condenser, thermometer, and dropping funnel. The solution was refluxed and stirred for 1 hour, then cooled to 70°C. Hexafluorobenzene (37.2 g, 0.2 mole) was added to the solution at 70°C with mixing over a 3/4-hour period. The solution was mixed for an additional 1 hour at 70°C, then cooled. There was no apparent reaction.

3. Poly(hexafluoropentamethylene ether)

a. From Hexafluoropentamethylene sulfite

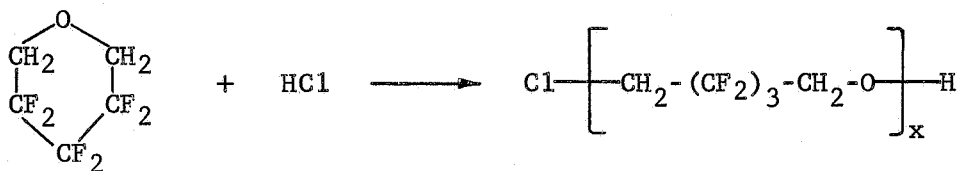


Into a 50-ml Erlenmeyer flask was placed hexafluoropentamethylene sulfite (10.1 g, 0.039 mole), HCl gas was bubbled into the liquid at room temperature. The sulfite changed little as indicated by infrared spectra.

Next, the solution was heated under reflux in a 100-ml, three-necked flask fitted with a condenser, thermometer, and a HCl gas inlet tube. After bubbling HCl gas into the solution for 3 hours at 140°C, the liquid had become quite viscous, and a white solid appeared on the

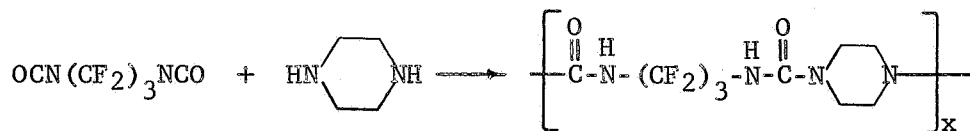
inside walls of the reaction vessel and in the coils of the condenser. The white solid had a melting point of 73°-77°C (unpurified). The melting point of pure hexafluoropentane diol is 78°-80°C. An infrared spectrum of the solid was similar to the spectrum for hexafluoropentane diol. The liquid from the reaction flask was washed with water and extracted with ether. The ethereal solution was then dried over MgSO₄, filtered and evaporated. The dark brown semisolid polymer remained.

b. Attempted Preparation from Hexafluoropentamethylene Oxide



Into a 50-ml Erlenmeyer flask, fitted with a reflux condenser, was placed a sample of 3,3,4,4,5,5-hexafluoropentamethylene oxide. Hydrogen chloride was bubbled through the liquid at room temperature for 45 minutes. There was no reaction. When this reaction was run at 80°C for 45 minutes; no polyether was formed.

4. Poly(N,N'Piperazine perfluototrimethyleneurea)



A 25-ml flask equipped with a stirrer, condenser, thermometer, dropping funnel, and dry nitrogen inlet was completely purged with dry nitrogen. Into the flask was charged perfluorotrimethylene diisocyanate (2.15 g, 0.009 mole, 95% pure) plus 2.95 g of dry ethyl acetate. Piperazine (0.79 g, 0.0092 mole) was dissolved in 6.93 g of pyridine and added to the dropping funnel.

The piperazine solution was slowly added to the diisocyanate solution over a 13-minute period with mixing under nitrogen. The reaction temperature rose from 30°C to 55°C. The polyurea which formed precipitated immediately. The slurry was then heated and stirred for 20 minutes at 70°C to 94°C under nitrogen.



The polymer slurry was stripped at 125°C for 3 hours under vacuum to yield an amber, brittle polymer. On exposure to air overnight, the polymer degraded to a soft semisolid. A sample stored under dry nitrogen remained unchanged.

5. Halogenated Epoxy Resins

- a. A mixture of 8.3 g of DER 542 and 1.0 g of tetrafluoro-p-phenylenediamine (12 phr) was heated at 300°F for 24 hours. Upon examination, the polymer was still tacky at 300°F; consequently, it was cured 24 additional hours at 300°F. This cure resulted in a hard amber polymer with moderate strength.
- b. A mixture of 7.2 g of DER 542 and 1.0 g of hexafluoropentanediamine were reacted according to the following schedule:

- 1 hr @ 150°F
- 1 hr @ 200°F
- 2 hr @ 250°F
- 2 hr @ 300°F
- 1 hr @ 325°F

The slow heatup was required due to the low reactivity and the high volatility of the diamine. After completion of the cure, the polymer was very dark amber and was very brittle.

IV. SUMMARY

Perfluorotrimethylene diisocyanate was prepared by the Curtius degradation of perfluoroglutaryl diazide. The polyurethane prepared from this diisocyanate and hexafluoropentane diol is LOX-compatible in the thickness tested, showing that the urethane linkage itself does not cause LOX incompatibility. This polyurethane, however, is hydrolytically unstable. One solution to this instability problem was achieved by preparation of the polyurethane from tetrafluoro-p-phenylene diisocyanate and hexafluoropentane diol which is hydrolytically stable. The tetrafluoro-p-phenylene diisocyanate has been prepared here for the first time by two methods: the Curtius degradation of tetrafluoroterephthaloyl azide, and the phosgenation of tetrafluoro-p-phenylenediamine. The first practical method of synthesis of tetrafluoro-p-phenylenediamine has been achieved by the reaction of potassium phthalimide with hexafluorobenzene (Gabriel reaction).

The polyurethane of hexamethylene diisocyanate and hexafluoropentane diol was successfully prepared.

An elastomeric polyurethane was prepared by reaction of toluene diisocyanate with a hydroxyl-terminated polyester prepared from adipoyl chloride and hexafluoropentane diol.

Additional monomers and intermediates which have been prepared include perfluoroglutaryl diisocyanate, hexafluoropentanediamine, tetrachloro-p-phenylene diisocyanate, and tetrafluoro-m-phenylenediamine. The first three compounds were prepared here for the first time and the last was prepared in greatly improved yield by a new method.

A number of hydroxyl-terminated polyesters prepared from perfluoroglutaryl chloride and adipoyl chloride with various halogenated diols were prepared. Valuable information on the hydrolytic stability of fluorinated esters was obtained from this work.

An interesting diether was obtained by reaction of the monosodium salt of hexafluoropentane diol with hexafluorobenzene. A hydroxyl-terminated polyether was obtained by a novel preparation, the polymerization of a cyclic sulfite. The polymerization of hexafluoropentamethylene sulfite appears to be the first report of the polymerization of a cyclic sulfite.

During this work, a unique and surprisingly facile conversion of hexafluoropentane diol to 1,5-dichloro-hexafluoropentane was discovered.

Three polyamides, poly(tetrafluoro-p-phenylene perfluoroglutaramide), poly(hexafluoropentamethylene perfluoroglutaramide), and poly(ethylene perfluoroglutaramide) were synthesized. The attempted preparation of poly(tetrafluoro-p-phenylene tetrachloroterephthalamide) and poly(methylene perfluoroglutaramide) was unsuccessful.

A number of moderate molecular weight polyester were prepared from perfluoroglutaryl chloride and adipoyl chloride with various halogenated diols.

The attempted preparation of a fluorinated polyimide by a unique method was unsuccessful.

Attempted preparations of fluorinated polysulfides were unsuccessful.

V. FUTURE WORK

1. Continuation of Fundamental Study of Halogenated Polyurethanes

The preparation of polyurethanes which are hydrolytically stable as well as LOX-compatible will be continued. Additional diisocyanates that will be made include hexafluoroglutaryl diisocyanate, hexafluoropentamethylene diisocyanate, tetrafluoro-m-phenylene diisocyanate, and hexafluorotolylene diisocyanate. The investigation of the polyol moiety will be continued in the area of hydroxyl-terminated polyesters and polyethers. The preparation of diisocyanates and diols containing long chain fluoroalkyl groups will be investigated. These monomers are of interest for the preparation of non-crystalline polyurethanes. Studies on the effect of structure of the polyurethane on LOX compatibility, adhesive properties, and hydrolytic stability in order to obtain additional basic knowledge of these systems will be continued.

2. Synthesis of Other New Fluorine-Containing Adhesive Polymers

Although the major direction will be toward development and evaluation of the highly fluorinated polyurethane-type adhesives, some effort will be put into the synthesis of other highly halogenated polymers. Using the monomers previously prepared or commercially available, a number of highly fluorinated analogues of several common polymers will be prepared. These polymers include polyesters, polycarbonates, polyethers, polyamides, polyimides, and possibly some heterocyclic polymers, such as polybenzimidazoles.

3. Synthesis of Quantities of Highly Fluorinated Polyurethane Type Polymers

All highly halogenated polyurethane polymers exhibiting promising properties will be prepared in sufficient quantities to permit full evaluation. Small-scale polymerization studies will be continued as required to establish monomer reactivity, polymer production, and product properties. Based on data obtained on LOX compatibility, hydrolytic stability, and adhesive characteristics, the more promising polymers will be selected for future optimization studies.

4. Adhesive Development and Optimization Program

Halogenated polyurethanes showing the greatest promise will be exhaustively studied in order to optimize the properties of the adhesive or adhesive system. This will include the investigation of isocyanate terminated prepolymers, effects of catalysts, and structural modifications needed to impart special properties and processing characteristics to the polymer. Process studies will be conducted on promising adhesives for possible commercial application and manufacturing, keeping in mind all factors affecting cost reduction.

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