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

By

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SUMMARY REPORT V
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# FOREWORD

This report was prepared by Whittaker Corporation, Narmco Research & Development Division, under Contract No. NAS8-11068, Control No. 1-7-54-20106(1F), entitled "The Development of Structural Adhesive Systems Suitable for Use with Liquid Oxygen," for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the direction of the Propulsion and Vehicle Engineering Division, Engineering Materials Branch, with Dr. W. E. Hill acting as project officer. The research work was conducted in Narmco's laboratory by Dr. Jerome Hollander, Research Specialist, who served as program manager and principle investigator. Also contributing to the program were Mr. Floyd D. Trischler, Senior Chemist, and Messrs. Robert M. DeBorde, Edward Harrison and Peter Kovacs, Chemists. This report covers the period from 1 March 1967 to 30 November 1967.

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# ABSTRACT

Work during this program focused on the preparation of fluorinated polyurethanes and their use as LOX-compatible adhesives. Two polyurethanes synthesized from the polyether of perfluoropropylene oxide showed promise. The polyurethane prepared from tetrafluoro-m-phenylene diisocyanate and this polyether does not possess the required bond strengths unless prepared with catalyst; when catalyzed, however, its pot life is too short to be practical. The polyurethane prepared from 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene and the perfluoropropylene oxide polyether appears to meet the requirements of the desired LOX-compatible adhesive. Bonds made with this adhesive system meet strength requirements at both room temperature and -320°F if the system is prepared either by reacting the diisocyanate with the polyether or by using the isocyanate-terminated prepolymer. Two other polyurethanes were synthesized from the polyether of hexafluorobenzene and hexafluoropentanediol, and either tetrafluoro-m-phenylene diisocyanate or 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene. They had poor bond strengths when prepared without catalyst, however, and had such short pot lives when prepared with catalyst that they could not be used as adhesives. Synthetic studies were carried out on the polyether of perfluoropropylene oxide and the polyether of hexafluorobenzene and hexafluoropentanediol. A new diisocyanate, 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene, was synthesized.

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# I. SUMMARY

The polyurethane of the hexafluorobenzene-hexafluoropentanediol polyether and tetrafluoro-m-phenylene diisocyanate, prepared in the melt with stannous octoate catalyst, was LOX incompatible. It is possible that this incompatibility was due to the catalyst.

Two polyurethane systems based on the polyether of perfluoropropylene oxide were studied as adhesives. Lap shear test specimens were prepared with each of these polyurethanes, both by reaction of the diisocyanate with the hydroxyl-terminated polyether and by reaction of isocyanate-terminated prepolymer with additional polyether.

The polyurethanes prepared from 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene and the perfluoropropylene oxide polyether (Baglbond 420) gave excellent bonds by both methods when catalyst was used. The pot life of the Baglbond 420 adhesive prepared by the diisocyanate-diol method was very good, but the adhesive prepared from the isocyanate-terminated prepolymer had a relatively short pot life. Further studies on this system established that the optimum NCO:OH ratio with either method was 1.8:1, that the optimum molecular weight of polyether prepolymer was approximately 1150, and that catalyst was necessary to develop acceptable bond strengths.

The polyurethane prepared from tetrafluoro-m-phenylene diisocyanate and the perfluoropropylene oxide polyether (Baglbond 400) gave fair bonds by both methods of preparation when catalyst was used, but the pot life was too short to permit satisfactory use of these adhesives.

Two other promising polyurethane systems, based on the polyether of hexafluorobenzene and hexafluoropentanediol, were investigated as adhesives. Polyurethanes prepared by reaction of this polyether with either tetrafluoro-m-phenylene diisocyanate of 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene without using catalyst gave bonds which did not have the required strengths. Poor strengths were also exhibited by bonds prepared from the isocyanate-terminated prepolymers of these two polyurethane systems when no catalyst was used. Bonds could not be conveniently prepared from either of these isocyanate-terminated prepolymers when catalyst was used because of their very short pot lives.

Studies were continued on the preparation of hydroxyl-terminated polyethers of perfluoropropylene oxide. In the polymerization of perfluoropropylene oxide with perfluoroglutaryl fluoride and cesium fluoride, only the highest boiling distillation fraction obtained was completely acid-fluoride terminated.

Studies were also continued on the preparation of hydroxyl-terminated polyethers of hexafluorobenzene and hexafluoropentanediol. It was discovered that completely hydroxyl-terminated polyethers can be prepared in tetrahydrofuran solution when copper (I) iodide is used as catalyst.

A new diisocyanate, 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene, was prepared and characterized.

# II. 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 for many applications, including coatings, elastomers, and adhesives. The development of LOX-compatible adhesives which have structural utility at cryogenic temperatures is especially desired to achieve certain critical bonding operations in vehicles using LOX.

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

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

The outstanding characteristics of polyurethanes in elastomers and adhesives for cryogenic application have been observed by several investigators. Highly fluorinated polymers, such as Teflon and Kel-F, have also demonstrated cryogenic capability. Although these available materials form excellent bonds which offer LOX compatibility and cryogenic performance, the processing conditions required are prohibitive. Polyurethanes show greater utility in that they are capable of being cured under mild conditions, or even at ambient temperature. The coupling of this processing capability with good cryogenic performance and LOX compatibility intimates that the highly halogenated polyurethanes are the most logical polymer systems. Therefore, emphasis during this program was placed on the preparation of highly halogenated polyurethanes and the monomers required for their preparation.

A lesser amount of work was 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.

Fundamental research was carried out to obtain the following information regarding the LOX compatibility of polymers:

1. The type and amount of halogen necessary to impart LOX compatibility to candidate polymers.

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

The polymers prepared during this program were designed to provide 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.

Work carried out on this program prior to this report period indicated that polyurethanes prepared from hexafluoropentanediol and various halogenated diisocyanates are stable to impact in LOX. This year, modifying the diol portion of the polyurethane to impart useful low-temperature properties resulted in a highly fluorinated polyether, poly(perfluoropropylene oxide), which appears to be most promising as a urethane prepolymer. Initial lap shear specimens bonded with polyurethanes based on this polyether gave extremely promising results.

## III. DISCUSSION

### A. Liquid Oxygen Compatibility

Summary Report IV contained the LOX-impact test results in polyurethanes prepared from the hexafluorobenzene-hexafluoropentanediol polyethers and tetrafluoro-m-phenylene diisocyanate (Baglbond 300) and tetrafluoro-p-phenylene diisocyanate (Baglbond 310). Both of these polyurethanes were LOX incompatible. The incompatibility was ascribed to trapped N,N-dimethylformamide (DMF) solvent. This year, the Baglbond 300 polyurethane was again prepared, this time in the melt without solvent but with stannous octoate catalyst. Testing again showed it to be LOX incompatible. This polyurethane system may be LOX incompatible, but the incompatibility exhibited by these specimens may be due to the stannous octoate catalyst used in their preparation.

### B. Polyurethanes

#### 1. From Hydroxyl-Terminated Polyethers of Perfluoropropylene Oxide

Summary Report IV (January 1967) described the synthesis of polyurethanes by reaction of the polyether of perfluoropropylene oxide and tetrafluoro-m-phenylene diisocyanate. Lap shear test specimens bonded with this polyurethane adhesive system (Baglbond 400) exhibited strengths which were very promising.

This year, Baglbond 400 polyurethane was again used in the preparation of bonds. The perfluoropropylene oxide polyether used had a molecular weight of 1160. Considerable difficulty was encountered in making bonds with this adhesive system. When the reactants were mixed without catalyst, very little reaction occurred up to 90°C, but the mixture gelled rapidly if heated much above this temperature. If the reactants were mixed at as low a temperature as 65°C for any length of time, followed by cooling to room temperature and the addition of stannous octoate catalyst, gelation occurred almost immediately. By heating the reactants at 70°C for only 1 minute, cooling them to room temperature, then adding the catalyst, sufficient pot life was obtained to prepare bonds.

Using this method of synthesis for the polyurethanes, lap shear test specimens were prepared. Polyurethanes prepared from tetrafluoro-m-phenylene diisocyanate and 1160 molecular weight perfluoropropylene oxide in the ratios of 2:1 and 1.8:1 were used. All the specimens were cured by keeping them in a vacuum bag at 1/2-atm pressure (7.5 psi) overnight, then heating them for 48 hours at 160°F in air.

The average lap shear strengths of the Baglbond 400 bonds using and NCO:OH ratio of 2:1 were 1240 psi at room temperature and 3230 psi at -320°F. The average lap shear strengths of the Baglbond 400 bonds

with an NCO:OH ratio of 1.8:1 were 248 psi at room temperature and 253 psi at -320°F. The pot life of these adhesives was about 30 minutes.

If a polyurethane-based adhesive system is to be developed which is usable, however, an isocyanate-terminated prepolymer should be prepared. This would eliminate the use of the volatile diisocyanate. An isocyanate-terminated prepolymer was prepared by reaction of a polyether of perfluoropropylene oxide with tetrafluoro-m-phenylene diisocyanate. In the first attempt to prepare this prepolymer, too long a reaction time was used and gelation occurred, resulting in an infusible rubber. The isocyanate-terminated prepolymer was prepared successfully when the reaction was run at 80°C and the reaction time kept short.

Lap shear test specimens were prepared, using the polyurethane adhesive (Baglbond 400) made from this isocyanate-terminated prepolymer and a hydroxyl-terminated perfluoropropylene oxide polyether reacted in the ratio of 1.5:1. No catalyst was used. The pot life of this adhesive seemed to be about 30 minutes. The specimens were cured by keeping them overnight at room temperature in a vacuum bag at 1/2-atm pressure (7.5 lb/in.$^2$) then removing them from the bag and heating them for 24 hours at 160°F.

The average lap shear strengths of these bonds were 655 psi at room temperature and 451 psi at -320°F.

Because of the difficulty in using the Baglbond 400 adhesive system, even without catalyst, further investigations to improve the adhesive performance of this system were not considered worthwhile. Various approaches to extending the pot life were considered. The approach deemed most promising was through the use of diisocyanates that are less reactive than tetrafluoro-m-phenylene diisocyanate or tetrafluoro-p-phenylene diisocyanate. A diisocyanate which should be considerably less reactive is 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene. (The preparation of this new diisocyanate is described in the Monomer Section of this report.)

The polyurethane adhesive system prepared from 1160 molecular weight polyether of perfluoropropylene oxide and 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene (Baglbond 420) was used to bond lap shear test specimens. Specimens were bonded with polyurethanes prepared using NCO:OH ratios of 2:1 and 1.8:1 and stannous octoate catalyst. All the specimens were cured by keeping them in a vacuum bag at 1/2-atm pressure (7.5 psi) overnight, then heating them for 48 hours at 160°F in air. The pot life of these adhesives was about 3 hours.

The average lap shear strengths of the Baglbond 420 bonds with an NCO:OH ratio of 2:1 were 1940 psi at room temperature and 3650 psi at -320°F. The average lap shear strengths of the Baglbond 420 bonds with an NCO:OH ratio of 1.8:1 were 2025 psi at room temperature and 4730 psi at -320°F.

Significantly, this last set of bond strengths represented the achievement of the minimum tensile shear strength requirements (approximately 2000 psi at room temperature and 2300 psi at -320°F) by an adhesive system developed under this contract.

Additional specimens of these Baglbond 420 bonds prepared with NCO:OH ratios of 2:1 and 1.8:1 were tested at +250°F; the average lap shear strengths obtained were 93 psi and 107 psi respectively. The adhesive in these bonds became thermoplastic at this test temperature.

Since this Baglbond 420 adhesive appeared to be most promising, work was continued on this system. A study was carried out on the relationship between lap shear strength and the isocyanate:hydroxyl ratio. Lap shear test specimens were prepared in NCO:OH ratios of 1.2:1, 1.4:1, and 1.6:1 in addition to those above (1.8:1 and 2:1). The results, shown graphically in Figure 1, indicate that the room temperature lap shear strength of the bonds increases with increasing NCO:OH ratio to a maximum value at 1.9:1, then decreases. The crosslink density increases with increasing NCO:OH ratio; therefore, the bond strengths increase to a certain point. The crosslink density of the polyurethane probably reaches a point at the NCO:OH ratio of 1.9:1, after which any increase results in a progressively more brittle material.

The lap shear strengths of the bonds at -320°F show a similar trend but reach a maximum value at an NCO:OH ratio of 1.7:1. This is reasonable, because the polyurethane will not be brittle at room temperature until a much higher degree of crosslinking is reached.

Another study was conducted on the relationship between lap shear strength and molecular weight of the polyether prepolymer. The results, shown graphically in Figure 2, point out that the lap shear strength of the bonds, both at room temperature and at -320°F, decreases with increasing molecular weight in the range from 1160 to 2350.

Effort was then devoted to preparing bonds from the isocyanate-terminated Baglbond 420 prepolymer. An adhesive was synthesized by reaction of the isocyanate-terminated prepolymer with additional hydroxyl-terminated polyether in the molar ratio of 1.8:1 (the actual NCO:OH ratio in this adhesive was 1.28:1). The lap shear strengths of bonds made with this adhesive was quite poor, with values of 871 psi at room temperature and 125 psi at -320°F. The pot life of this adhesive was short, the material gelling within 15 minutes after mixing the reactants and stannous octoate catalyst. This short pot life is in sharp contrast to the long pot life (3 to 4 hours) exhibited by this adhesive system when it is prepared by reaction of the diisocyanate with the hydroxyl-terminated polyether in NCO:OH ratios ranging from 1.2 to 1.8.

Another adhesive was prepared by reaction of the isocyanate-terminated prepolymer with additional hydroxyl-terminated polyether in the molar ratio of 10:1 (the actual NCO:OH ratio in this adhesive was 1.8:1). The lap shear strengths of bonds made with this adhesive were excellent,
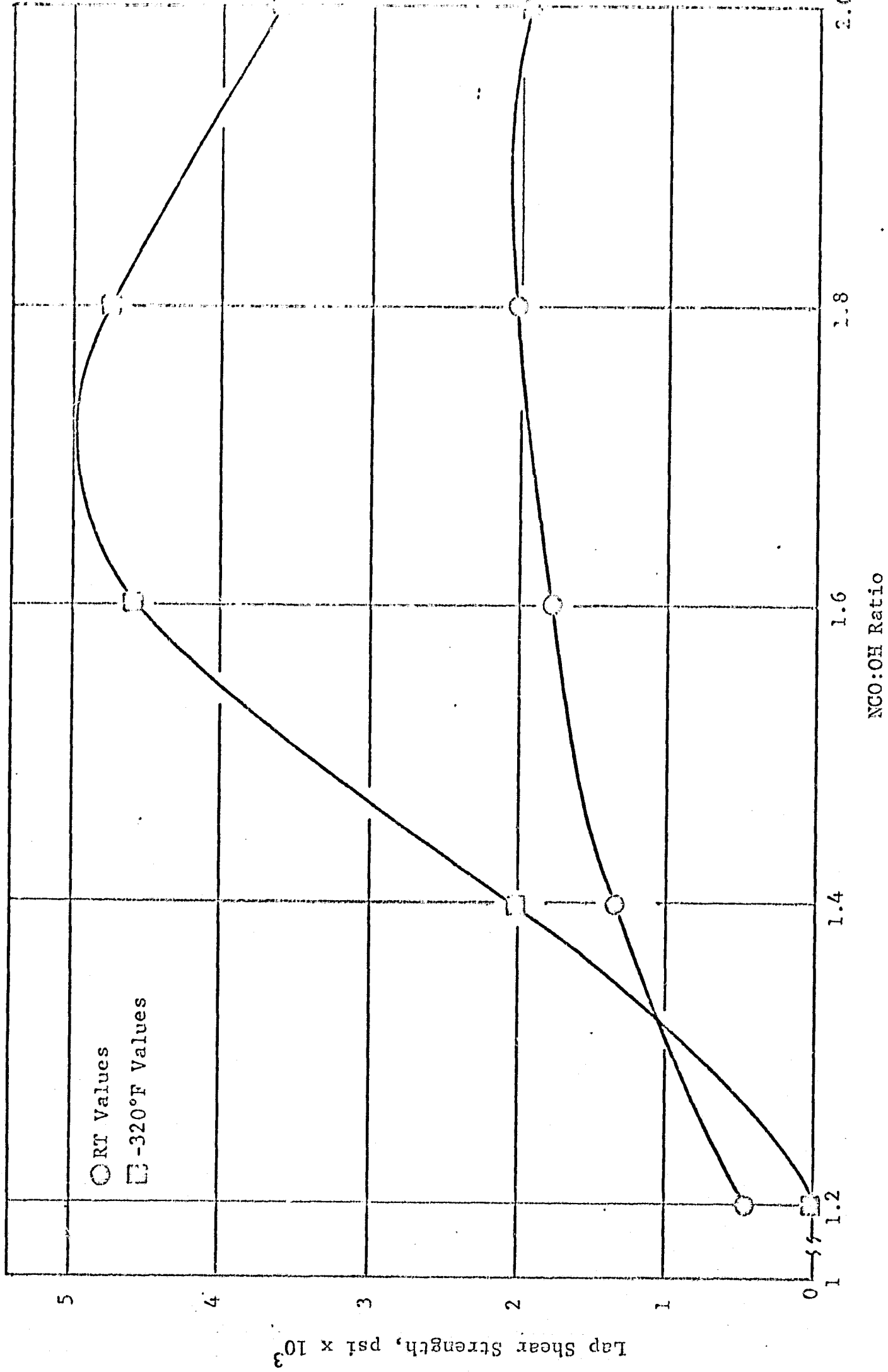
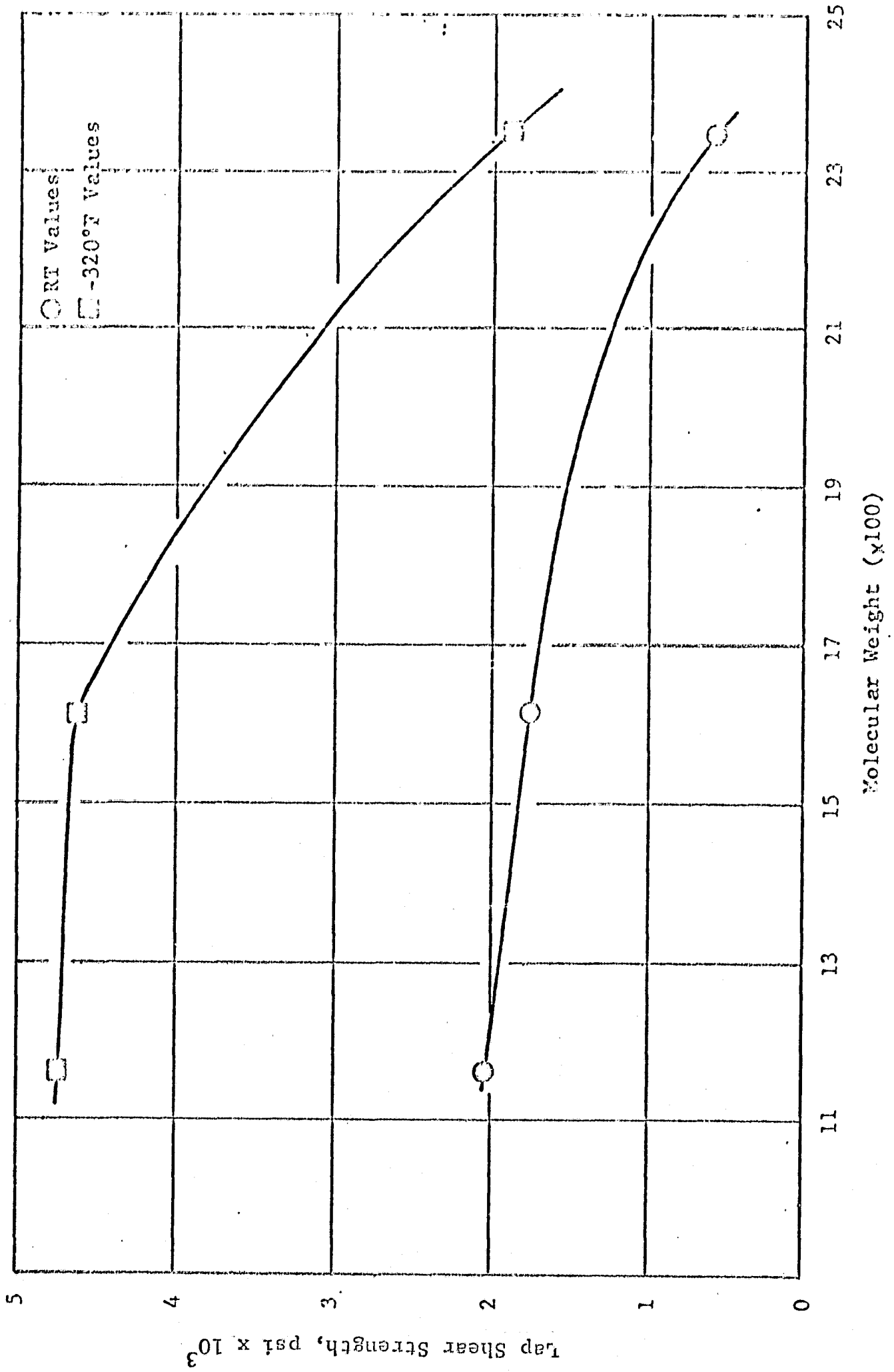Figure 1. Lap Shear Bond Strength versus NCO:OH Ratio
of Bagibond 420

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Figure 2. Lap Shear Bond Strength of Baglbond 420 versus Molecular Weight of Polyether Prepolymer

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having values of 2050 psi at room temperature and 3070 psi at -320°F. These values meet the minimum strength requirements, as stated in the contract, both at room temperature and at -320°F. The pot life of this adhesive was short, with the material gelling within 15 minutes after mixing the isocyanate-terminated prepolymer, the hydroxyl-terminated prepolymer, and stannous octoate catalyst. The gelled adhesive could still be spread easily on bonding panels if it was heated slightly with a heat gun.

All the Baglbond 420 polyurethanes used for the above-mentioned lap shear test specimens were prepared with stannous octoate catalyst. The effect of catalyst on the strength of the bonds was investigated by preparing lap shear test specimens using polyurethanes synthesized without catalyst. An adhesive was made by the uncatalyzed reaction of the di-isocyanate and polyether in an NCO:OH ratio of 1.8:1. The average lap shear strength of bonds prepared without catalyst was significantly less than the strength of the corresponding bonds prepared with catalyst:

|  | RT | -320°F |
|---|---|---|
| With Catalyst: | 2025 psi | 4730 psi |
| Without Catalyst: | 982 psi | 1166 psi |

An adhesive was also made by the uncatalyzed reaction of an isocyanate-terminated prepolymer with the polyether in an actual NCO:OH ratio of 1.8:1. The lap shear strengths of bonds made with this adhesive were also significantly lower than the bonds made from the same isocyanate-terminated prepolymer based adhesive in which catalyst was used.

|  | RT | -320°F |
|---|---|---|
| With Catalyst: | 2050 psi | 3070 psi |
| Without Catalyst: | 789 psi | 836 psi |

Because catalysis was required to obtain satisfactory bond strengths with this adhesive system, and because the pot life of this adhesive was fairly short when stannous octoate was used, a study of other catalysts was initiated. Bonds were made using adhesives catalyzed with tetrabutyl titanate, antimony trichloride, uranyl nitrate, and cobalt naphthenate. Bonds were also made, with stannous octoate again used as a control. New batches of both 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene and perfluoropropylene oxide polyether were prepared for this study. The lap shear strengths of all the bonds were extremely poor. The lap shear strengths of the control bonds made with stannous octoate were also very poor. This indicated that either one or both of the reactants were not of sufficient purity for the reaction to occur properly. This observation thus invalidated the results of this catalyst study.

A preliminary study of cure conditions was also carried out using these new reactants. The cure conditions used throughtout this current work were overnight at room temperature at 1/2-atm pressure (7.5 psi) in

a vacuum bag, followed by 48 hours at 160°F in air. Bonds were made using these conditions as a control. To determine if the initial overnight room temperature cure had to be carried out in vacuum, a set of bonds was cured overnight at room temperature at 1/2-atm pressure (7.5 psi) in air, followed by 48 hours at 160°F.

To determine if substantial strengths could be obtained without heat, a set of bonds was cured overnight at room temperature at 1/2-atm in a vacuum bag, followed by 12 days at room temperature in air. Because the control bonds exhibited very poor lap shear strength, the results of this cure study were considered to be invalid.

Two thin sheets of Baglbond 420 polyurethane were prepared by reacting the diisocyanate and polyether in the ratio of 1.8:1 and curing the resulting polymer in a heated press. One sheet was prepared with stannous octoate, and the other was prepared without catalyst. LOX-impact specimens were punched from each of these sheets. The specimens were submitted to Marshall Space Flight Center (MSFC) for testing but the tests have not been completed.

## 2. From Hydroxyl-Terminated Polyethers of Hexafluorobenzene and Hexafluoropentanediol

In Summary Report IV (January 1967), the preparation of polyurethanes by reaction of a polyether of hexafluorobenzene and hexafluoropentanediol with tetrafluoro-m-phenylene diisocyanate and tetrafluoro-p-phenylene diisocyanate were described. These reactions proceeded extremely fast, and the product polyurethanes were LOX incompatible. In that report, we speculated that the rapidity of the reactions and the apparent LOX incompatibility were both due to trapped DMF which had been used as the solvent in the preparation of the polyether prepolymers.

This year, we have prepared completely hydroxyl-terminated hexafluorobenzene-hexafluoropentanediol polyethers, using copper (I) iodide catalyst in tetrahydrofuran (THF) solvent. The reaction of these polyethers with tetrafluoro-m-phenylene diisocyanate was considerably slower than the same reaction described in Summary Report IV.

A limited evaluation was made of the adhesive performance of polyurethanes based on the polyethers of hexafluorobenzene and hexafluoropentanediol. Two attempts to prepare lap shear test specimens from tetrafluoro-m-phenylene diisocyanate and 3840 molecular weight polyether, reacted in a ratio of 1.2:1, were unsuccessful. The 3840 molecular weight polyether was so viscous that it had to be heated to 100°C before it could be stirred. At this temperature, reaction with the diisocyanate was so rapid that the mixture gelled to a rubber ball within 2 minutes. In a modified procedure, the temperature of the reaction mixture was quickly lowered to room temperature immediately after the addition of the diisocyanate to the heated polyether. The mixture gelled to a rubber ball within 7 minutes, barely allowing sufficient time to prepare bonds. The products obtained were tough elastomers

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which had apparently undergone some crosslinking through allophanate formation. Two possible approaches were tried to avoid this problem. One involved the use of a lower molecular weight polyether which would be stirrable at a temperature low enough to avoid allophanate formation. The other involved use of a less reactive diisocyanate.

Lap shear test specimens were successfully prepared, using a 2620 molecular weight hexafluorobenzene-hexafluoropentanediol polyether which needed heating only to 65°C in order to be stirrable. At this temperature, allophanate formation seems to be fairly slow, and gelation did not occur for 45 minutes to 1 hour. Lap shear test specimens were bonded with two polyurethanes; one (Baglbond 300) formed by reaction of the polyether with tetrafluoro-m-phenylene diisocyanate and the other (Baglbond 320) by reaction of the polyether with the less re-active 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene.

Two sets of lap shear test specimens were prepared from each of the polyurethanes. The ratio of diisocyanate to polyether in all the preparations was 1.2:1. Half of the specimens were cured by keeping them overnight at room temperature in vacuum bags at 1/2-atm pressure (7.5 lb/in.$^2$) then removing them from the bags and heating them for 24 hours at 160°F. The other half of the bonds were cured by applying 7.5 lb/in.$^2$ pressure to the bonds in the air overnight, then heating them for 24 hours at 160°F.

The average lap shear strengths of the bonds made with tetrafluoro-m-phenylene diisocyanate and cured initially in the vacuum bag were 478 psi at room temperature and 1897 psi at -320°F. The bonds made from the same polyurethane adhesive (Baglbond 300) but cured initially in air had strengths of 689 psi at room temperature and 2295 psi at -320°F.

The average lap shear strengths of the bonds made with 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene and cured initially in the vacuum bag were 374 psi at room temperature and 1338 psi at -320°F. The bonds made from the same polyurethane adhesive (Baglbond 320) but cured initially in air had strengths of 301 psi at room temperature and 1167 psi at -320°F.

The disappointingly low strengths of these bonds may be due to the low ratio of diisocyanate to polyether. Even a small amount of hydrolysis of diisocyanate groups would result in very few terminal isocyanate groups available for crosslinking.

All of the above adhesives, which gave low-strength bonds, were synthesized by reaction of the diisocyanate with the hydroxyl-terminated prepolymer in the ratio of 1.2:1 without catalyst. It was determined that, at least in the Baglbond 420 system, the optimum NCO:OH ratio is 1.8:1 and that catalyst is necessary to obtain satisfactory bond strengths. Therefore, an attempt was made to prepare bonds with Bagl-bond 320 adhesive synthesized from the reactants in an NCO:OH ratio of

1.8:1, using stannous octoate catalyst. After adding one drop of catalyst to the mixture of reactants, the material gelled within 1 minute to a rubber.

Initial attempts to prepare these polyurethanes from isocyanate-terminated prepolymers were unsuccessful. An attempt was made to prepare such a prepolymer by a reaction of a 4300 molecular weight polyether of hexafluorobenzene and hexafluoropentanediol with an excess of tetrafluoro-m-phenylene diisocyanate (Baglbond 300). The product obtained was a moderately tough elastomer which had apparently undergone some crosslinking through allophanate formation. It was necessary to heat the hydroxyl-terminated polyether to 65°C before it could be stirred. At that temperature, the diisocyanate was so reactive that allophanate formation apparently occurred.

Since bonding experiments indicated that 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene was considerably less reactive than tetrafluoro-m-phenylene diisocyanate, an attempt was made to prepare a similar isocyanate-terminated prepolymer with this chlorine-containing diisocyanate. The hydroxyl-terminated polyether used had to be heated to 100°C for stirring. At that temperature, even this diisocyanate was so reactive that allophanate formation occurred very quickly and resulted in a rubber. This rubber could be further cured by milling tetrafluoro-m-phenylenediamine into the material on a rubber mill and press curing at 300°F. A clear, amber sheet was obtained, but it was somewhat brittle.

By using lower molecular weight polyether, both of these isocyanate-terminated prepolymers were successfully synthesized and used to bond lap shear test specimens.

The isocyanate-terminated prepolymer from 1-chloro-2,4-diisocya-nato-3,5,6-trifluorobenzene was prepared without difficulty, and initial assessment of its storage life appeared very promising. It was stored in a refrigerator under a nitrogen atmosphere for 5 days with no apparent change in properties. Two sets of lap shear specimens were prepared, using the polyurethane adhesive (Baglbond 320) made from this isocyanate prepolymer and the hydroxyl-terminated hexafluorobenzene-hexafluoro-pentanediol polyether reacted in the ratio of 1.5:1. This adhesive had a pot life of about 2 hours. One set of specimens was cured by keeping the bonds overnight at room temperature in a vacuum bag at 1/2-atm pressure (7.5 lb/in.$^2$) then removing them from the bag and heating them for 48 hours at 160°F. The other set of specimens was cured by applying 7.5 lb/in.$^2$ pressure to the bonds in air overnight, then heating them for 48 hours at 160°F.

The average lap shear strengths of the Baglbond 320 bonds cured initially in the vacuum bag were 450 psi at room temperature and 1290 psi at -320°F. The bonds cured initially in air had average strengths of 685 psi at room temperature and 1570 psi at -320°F.

Difficulties were encountered in the preparation of the isocyanate-terminated prepolymer from tetrafluoro-m-phenylene diisocyanate. In one attempt to prepare this prepolymer, the reaction temperature was allowed to increase slightly above that used in the preparation of the 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene based prepolymer. Gelation occurred, which resulted in a rubber that would not melt. The isocyanate-terminated prepolymer could be prepared successfully when the reaction temperature was kept below 90°C and the reaction time kept short. The storage life of this prepolymer appears to be fairly short. After being stored in a refrigerator under a nitrogen atmosphere for 4 days, this prepolymer had gelled and could not be melted.

Lap shear bonds were prepared by synthesizing the isocyanate-terminated prepolymer, storing it in the refrigerator overnight, and reacting it the next day with the hydroxyl-terminated polyether of hexafluorobenzene and hexafluoropentanediol in the ratio of 1.5:1. The pot life of this adhesive was only about 10 minutes. Two sets of lap shear specimens were prepared from this polyurethane adhesive (Baglbond 300). One set of specimens was cured by keeping the bonds overnight at room temperature in a vacuum bag at 1/2-atm pressure (7.5 lb/in.$^2$), then removing them from the bag and heating them for 48 hours at 160°F. The other set of specimens was cured by applying 7.5 lb/in.$^2$ pressure to the bonds in air overnight, then heating them for 48 hours at 160°F.

The average lap shear strengths of the Baglbond 300 bonds cured initially in the vacuum bag were 462 psi at room temperature and 1490 psi at -320°F. The bonds cured initially in air had average strengths of 188 psi at room temperature and 990 psi at -320°F.

The large differences in storage life of the isocyanate-terminated prepolymers and in pot life of the polyurethane adhesives just described point out the difference in reactivity of the two diisocyanates used. The 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene is fairly slow in its reaction, and the polyurethane system based on its reaction with the hydroxyl-terminated hexafluorobenzene-hexafluoropentanediol polyether is quite practical.

The preparation and LOX impact test results of polyurethanes prepared from the hexafluorobenzene-hexafluoropentanediol polyethers and tetrafluoro-m-phenylene diisocyanate (Baglbond 300) and tetrafluoro-p-phenylene diisocyanate (Baglbond 310) were described in Summary Report IV. These polyurethanes, prepared in DMF solvent were LOX incompatible.

This year, the Baglbond 300 polyurethane was again prepared, but in the melt with stannous octoate catalyst. It was again LOX incompatible. To determine if the incompatibility of these specimens was due to the stannous octoate, specimens were again prepared from a sheet of Baglbond 300 synthesized without solvent or catalyst. The LOX impact tests have not been completed at this writing.
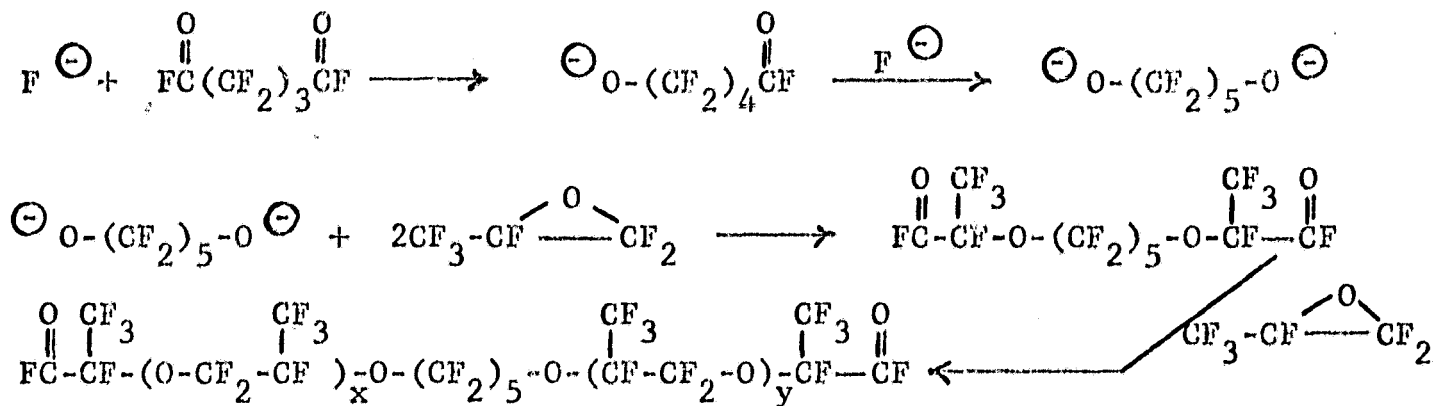
## C. Polyethers

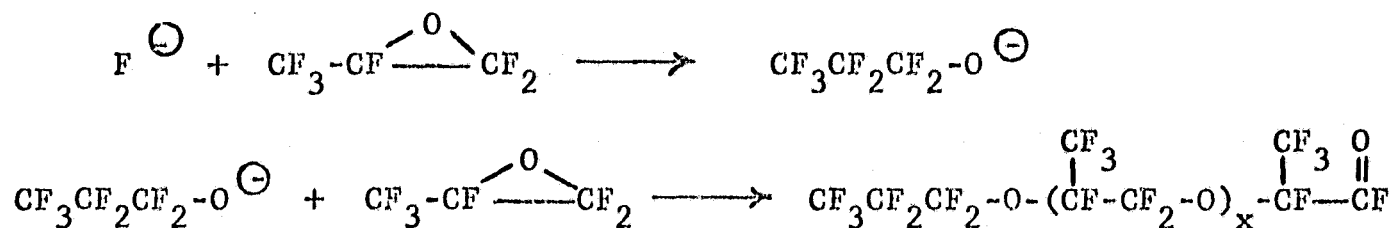### 1. From Perfluoropropylene Oxide

The synthesis of hydroxyl-terminated polyethers of perfluoro-propylene oxide was described in some detail in Summary Report IV. This year, additional polymerization reactions of perfluoropropylene oxide with perfluoroglutaryl fluoride and cesium fluoride were carried out. The polyether products were fractionally distilled at reduced pressures. In the first three polymerizations, four fractions were taken in each run. On the basis of our past work, we assumed that in each case, the lowest boiling fraction was the monoether of perfluoro-propylene oxide and perfluoroglutaryl fluoride. The second and third fractions from each run do not appear to be completely acid fluoride terminated. Fractions II and III from the first (medium size) run were combined and reduced with lithium aluminum hydride. The molecular weight of the hydroxyl-terminated product was 700 (by VPO) and its hydroxyl number was 542; it did not contain any acid groups or unreacted acid fluoride groups. The reduced Fractions II and III from the second run had molecular weights of 676 and 790 (by VPO) and hydroxyl numbers of 764 and 795, respectively.

It thus appears that the polyethers have some trifluoromethyl end groups which could result from competitive initiation by the fluoride ion.

Desired Reaction:

$$F^{\ominus} + FC(CF_2)_3CF \xrightarrow{\quad} {}^{\ominus}O\text{-}(CF_2)_4\overset{O}{C}F \xrightarrow{F^{\ominus}} {}^{\ominus}O\text{-}(CF_2)_5\text{-}O^{\ominus}$$

$$^{\ominus}O\text{-}(CF_2)_5\text{-}O^{\ominus} + 2CF_3\text{-}CF\overset{O}{\underset{}{\diagdown}}CF_2 \xrightarrow{\quad} FC\text{-}CF\text{-}O\text{-}(CF_2)_5\text{-}O\text{-}CF\text{-}CF$$

$$FC\text{-}CF\text{-}(O\text{-}CF_2\text{-}CF)_x\text{-}O\text{-}(CF_2)_5\text{-}O\text{-}(CF\text{-}CF_2\text{-}O)_y\text{-}CF\text{-}CF \xleftarrow{\quad} CF_3\text{-}CF\overset{O}{\underset{}{\diagdown}}CF_2$$

Competitive Reaction:

$$F^{\ominus} + CF_3\text{-}CF\overset{O}{\underset{}{\diagdown}}CF_2 \xrightarrow{\quad} CF_3CF_2CF_2\text{-}O^{\ominus}$$

$$CF_3CF_2CF_2\text{-}O^{\ominus} + CF_3\text{-}CF\overset{O}{\underset{}{\diagdown}}CF_2 \xrightarrow{\quad} CF_3CF_2CF_2\text{-}O\text{-}(CF\text{-}CF_2\text{-}O)_x\text{-}CF\text{-}CF$$

Fraction IV in each of these runs was completely acid fluoride terminated. Each was reduced with lithium aluminum hydride. The reduced fourth fraction from the first run had a molecular weight (by VPO)

of 945 and a hydroxyl number of 494; that from the second run a molecular weight of 1170 and a hydroxyl number of 560; and that from the third run a molecular weight of 1181.

In addition to the four distillable fractions in the third polymerization, a residue, representing 10% of the product, was obtained. This residue, when reduced with lithium aluminum hydride, yielded a hydroxyl-terminated polyether of molecular weight 2349 (determined by VPO).

From the analytical results of the reduced polyethers, it seems that only those growing polyether chains which have acid fluoride ends grow to any substantial molecular weight. Therefore, only the highest molecular weight fraction is completely acid fluoride-terminated when the polymerization is carried out by this one-step method.

A fourth, large-scale polymerization was conducted using the same procedure. Reduction of a selected fraction of this acid fluoride-terminated polyether yielded a large amount of hydroxyl-terminated polyether of 1100 molecular weight.

## 2. From Hexafluorobenzene and Hexafluoropentanediol

Until recently, we had been running the reaction of hexafluorobenzene with hexafluoropentanediol in DMF solution. Although the reaction proceeds readily in this solvent, difficulties were encountered in achieving moderately high molecular weights, predictable molecular weights, and complete hydroxyl termination. In addition to these problems, specimens of this polyurethane prepared in DMF solution were LOX incompatible. It was our belief that this incompatibility was due to trapped DMF. Because of these problems, it seemed advisable to reduce or eliminate the DMF, if possible.

The successful reaction of hexafluorobenzene, hexafluoropentanediol, and potassium hydroxide (in the ratio of 1:1:2) in THF solution with a catalytic amount of DMF was reported in Summary Report IV.

This year, investigations of this reaction continued.

Since water is formed in the reaction of hexafluorobenzene, hexafluoropentanediol and potassium hydroxide, a brief study was conducted to determine the effect of water on the polymerization. Two reactions were run under the same conditions, except that in one reaction, the water formed was removed by azeotropic distillation. The polymers obtained from the two reactions had essentially the same molecular weight distribution with the product from the reaction in which the water was removed having a slightly larger percentage of the higher molecular weight materials. The presence or absence of water, therefore, seems to have little effect on the course of the polymerization.

In order to prepare a moderate molecular weight polyether with some hydroxyl termination, the reaction was run in THF solution with a catalytic amount of DMF using a ratio of three parts of hexafluoropentanediol to two parts of hexafluorobenzene. The product obtained was a soft, rubbery material with a molecular weight of 3150 (determined by VPO). Since the same reaction, run under identical conditions but with a ratio of hexafluoropentanediol to hexafluorobenzene of 1:1 (reported in Summary Report IV) yielded 1850 molecular weight polymer, a brief study was conducted using other reactant ratios.

Since an increase in the relative amount of hexafluoropentanediol to hexafluorobenzene from 1:1 to 3:2 resulted in an increase in molecular weight rather than the expected decrease, the ratio of hexafluoropentanediol to hexafluorobenzene was increased further to see whether the molecular weight would continue to increase. Surprisingly, crosslinked polymers were obtained when the ratios of 2:1 and 3:1 were used. These polymers were gels which were insoluble in the THF reaction solvent. At this time, we can only speculate as to the mechanism or mechanisms by which crosslinking occurred in this polymer system.

Another study was conducted to see if DMF could be replaced by another catalyst. The reactions of hexafluoropentanediol, hexafluorobenzene, and potassium hydroxide were carried out under conditions identical to a previous reaction using DMF as catalyst, a ratio of three parts of diol to two parts of hexafluorobenzene in THF solution. Both new catalysts used, pyridine and copper (I) iodide, were effective in promoting the polymerization reaction. The product obtained using the pyridine catalyst was a white wax, while that obtained using copper (I) iodide catalyst was a soft pale yellow rubber similar in appearance to the product obtained when DMF was used. The molecular weights and hydroxyl numbers of the three polymers are shown in Table I.

TABLE I

MOLECULAR WEIGHTS AND HYDROXYL NUMBERS OF HEXAFLUOROBENZENE-
HEXAFLUOROPENTANEDIOL POLYETHERS PREPARED WITH VARIOUS CATALYSTS

| Catalyst | Mol Wt (VPO) | Hydroxyl No. |
|---|---|---|
| Pyridine | 2130 | 3018 |
| DMF | 3160 | 2430 |
| Copper (I) iodide | 4030 | 1972 |

Significantly, the polyether prepared using copper (I) iodide as catalyst is completely hydroxyl-terminated. All previous attempts to prepare completely hydroxyl-terminated polyethers directly have resulted in partially hydroxyl-terminated materials.

Repetition of this reaction, using the same ratio of reactants (1.5:1), resulted in a completely hydroxyl-terminated polyether of almost identical molecular weight (3840). In addition, completely hydroxyl-terminated polyethers were prepared using ratios of hexafluoropentanediol to hexafluorobenzene of 1.4:1 and 1.6:1.

When ratios of 1.2:1 and 1.3:1 were used, the products obtained did not appear to be completely hydroxyl terminated.

The molecular weights and hydroxyl numbers of the polyethers made with copper (I) iodide as catalyst are shown in Table II.

TABLE II

MOLECULAR WEIGHTS AND HYDROXYL NUMBERS OF HEXAFLUOROBENZENE-
HEXAFLUOROPENTANEDIOL POLYETHERS PREPARED USING COPPER (I)
IODIDE CATALYST

| Ratio of Hexafluoropentanediol to Hexafluorobenzene | Mol. Wt. (VPO) | Hydroxyl No. |
|---|---|---|
| 1.6 | 3160 | 1772 |
| 1.5 (Run 1) | 4030 | 1972 |
| (Run 2) | 3840 | 1528 |
| 1.4 (Run 1) | 2620 | 1480 |
| (Run 2) | 2900 | 1500 |
| 1.3 | 2035 | 1894 |
| 1.2 | 1530 | 1525 |

In all of the reactions of hexafluorobenzene with hexafluoropentanediol, the equivalent amount of potassium hydroxide used was assumed to be pure material. A reaction was run with a 15% excess of potassium hydroxide over the theoretical equivalent amount because commercially available potassium hydroxide has a minimum assay of 85% purity. The ratio of hexafluoropentanediol to hexafluorobenzene was 1.2:1. Instead of a low molecular weight polyether as obtained in the previously described 1.2:1 experiment using the theoretical amount of potassium hydroxide, the product obtained in this reaction was a high molecular weight rubber which was only slightly soluble in THF. The elemental analysis corresponds perfectly to the linear 1:1 hexafluorobenzene-hexafluoropentanediol polyether.

The base used in the preparation of the hexafluorobenzene-hexafluoropentanediol polyethers has always been potassium hydroxide. A reaction identical to that described above was run, but sodium hydroxide was used instead of potassium hydroxide. The polyether obtained

was not completely hydroxyl-terminated, as it had a molecular weight of 2100 (by VPO) and a hydroxyl number of 1945.

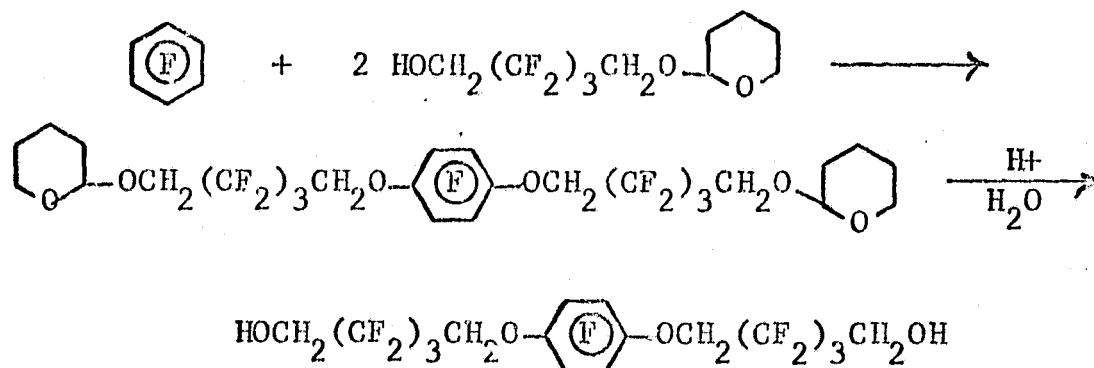Since several copper salt catalyzed reactions involving displacement of aromatic halides proceed best in nitrobenzene solvent, this reaction of hexafluorobenzene with hexafluoropentanediol and potassium hydroxide was run in nitrobenzene. None of the desired polyether was obtained.

In order to fully understand the reactions leading to the poly-ethers of hexafluorobenzene and hexafluoropentanediol, the monoether, 5-hydroxy-hexafluoropentoxy-pentafluorobenzene, was prepared and polymerized. A small amount of this monoether had been isolated earlier in this program. It was not possible to obtain this monoether in any amounts directly by reaction of hexafluorobenzene and hexafluoropentanediol, probably because of its extreme reactivity as an AB monomer. Quantities of this monoether were prepared by the following series of reactions using dihydropyran as a protecting group to prevent further reaction of the intermediates.

$$HOCH_2(CF_2)_3CH_2OH \ + \ \text{[pyran]} \ \xrightarrow{H^+} \ HOCH_2(CF_2)_3CH_2O\text{[pyranyl]}$$

$$HOCH_2(CF_2)_3CH_2O\text{[pyranyl]} \ + \ \text{[F-benzene]} \ \xrightarrow[\text{THF}]{\substack{KOH \\ Catalyst}} \ \text{[F-benzene]}-OCH_2(CF_2)_3CH_2O\text{[pyranyl]}$$

$$\text{[F-benzene]}-OCH_2(CF_2)_3CH_2O\text{[pyranyl]} \ \xrightarrow[H_2O]{H+} \ \text{[F-benzene]}-OCH_2(CF_2)_3CH_2OH$$
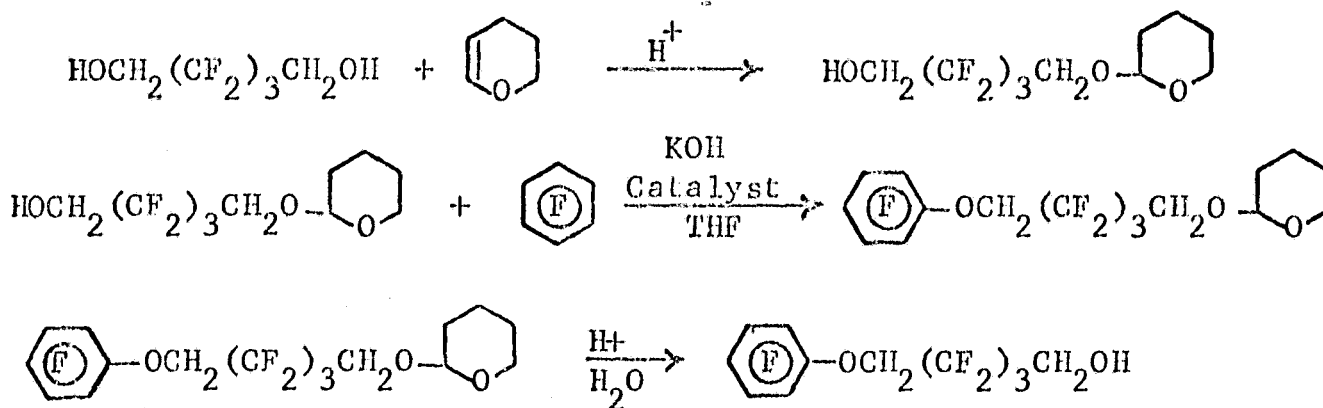
In the first reaction, the diacetal was also obtained, but separation could be accomplished by fractional distillation. The product of the second reaction, the monoether-monoacetal, was not isolated, but was hydrolyzed as shown in the third reaction to the desired monoether. Two catalysts were used successfully in the second reaction, DMF and copper (I) iodide. A small amount of diether was obtained, along with the desired monoether. This diether could be prepared in fair yield by reaction of hexafluorobenzene with an excess of the monoacetal.

$$\text{[F-benzene]} \ + \ 2 \ HOCH_2(CF_2)_3CH_2O\text{[pyranyl]} \ \longrightarrow$$

$$\text{[pyranyl]}O-OCH_2(CF_2)_3CH_2O-\text{[F-benzene]}-OCH_2(CF_2)_3CH_2O\text{[pyranyl]} \ \xrightarrow[H_2O]{H+}$$

$$HOCH_2(CF_2)_3CH_2O-\text{[F-benzene]}-OCH_2(CF_2)_3CH_2OH$$

The monoether, 5-hydroxyl-hexafluoropentoxy-pentafluorobenzene, was reacted with potassium hydroxide in THF, using copper (I) iodide catalyst. High molecular weight polyether could not be prepared from this monomer. The product obtained when commercial potassium hydroxide was used had a molecular weight of 1300. The product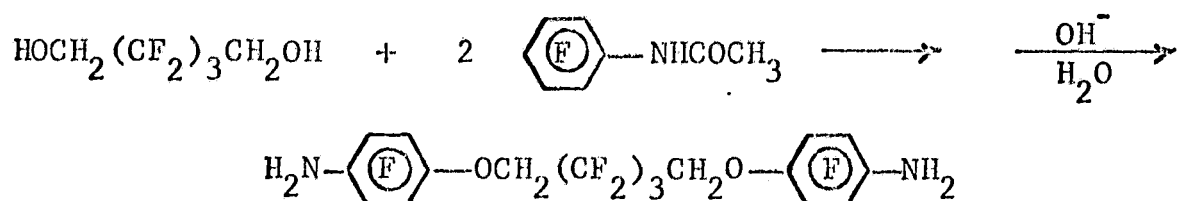 obtained when fused potassium hydroxide was used had a molecular weight of 860. When commercial potassium hydroxide was used in 15% excess, the product had a molecular weight of 1730.

As mentioned several times during this program, a liquid or low-melting solid LOX-compatible curing agent is desirable. One such curing agent might be 1,5-bis(4-amino-tetrafluorophenoxy)hexafluoropentane. In view of the ease with which hexafluoropentanediol reacts with hexafluorobenzene in the presence of potassium hydroxide and copper (I) iodide in THF solution, the reaction of hexafluoropentanediol with pentafluoroaniline was attempted under similar reaction conditions.

$$HOCH_2(CF_2)_3CH_2OH + 2 \langle F \rangle -NH_2 \xrightarrow[THF]{KOH, CuI}$$

$$H_2N \langle F \rangle -OCH_2(CF_2)_3CH_2O \langle F \rangle -NH_2$$
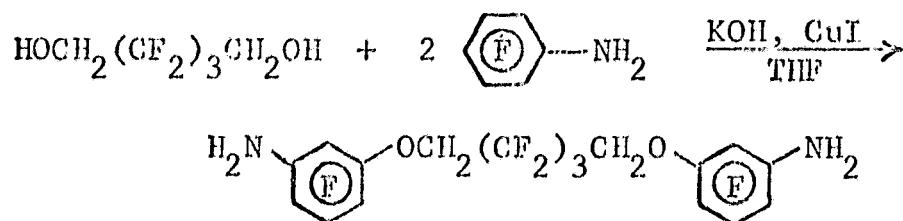
A small amount of product was obtained which was tentatively identified as the desired amino-terminated diether by its infrared spectrum.

Since the above reaction does not seem to proceed readily, N-acetylpentafluoroaniline was prepared for use in the same reaction. We felt that acetylation of the amine would reduce its mesomeric electron donation and allow more facile nucleophillic attack on the para position.

$$HOCH_2(CF_2)_3CH_2OH + 2 \langle F \rangle -NHCOCH_3 \longrightarrow \xrightarrow[H_2O]{OH^-}$$

$$H_2N-\langle F \rangle -OCH_2(CF_2)_3CH_2O-\langle F \rangle -NH_2$$

The reaction of N-acetyl-pentafluoroaniline with hexafluoropentanediol, potassium hydroxide and copper (I) iodide as catlyst in THE solution did not yield any product. The reaction run in DMF solution yielded a product which was tentatively identified as the desired diamine.

## D. Monomers

Additional amounts of tetrafluoro-m-phenylene diisocyanate, perfluoropropylene oxide, and perfluoroglutaryl fluoride, the syntheses

of which have been described previously, were prepared during this report period.

One approach to extend the cure time of the polyurethane system based on the polyether of hexafluorobenzene and hexafluoropentanediol involves the use of diisocyanates that are less reactive than tetrafluoro-m-phenylene diisocyanate or tetrafluoro-p-phenylene diisocyanate. A diisocyanate which should be considerably less reactive is 1-chloro-2,4-diisocyanato-trifluorobenzene. The synthesis of this diisocyanate was investigated. Reaction of chloropentafluorobenzene with aqueous ammonia yielded the diamine precursor. Phosgenation of the diamine yielded the desired diisocyanate.
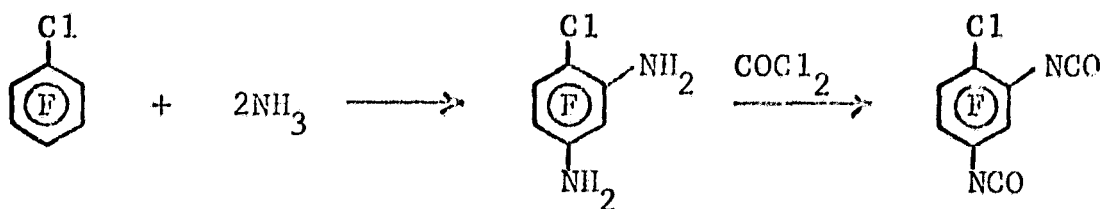


Brooke and coworkers reported[*] that chloropentafluorobenzene reacted with ammonia to yield a mixture of the three chloro-tetrafluoroanilines. The ratio of isomers was determined by vapor phase chromatography (VPC) to be 25 ortho:5 meta:70 para. No diamine derivatives were isolated or identified by these workers.

During this report period, the reaction of chloropentafluorobenzene with aqueous ammonia was carried out in an autoclave at two temperatures, 200°C and 235°C. Details of the amounts of reactants and reaction conditions are described in the experimental section of this report.

The products of these reactions were shown to consist of four distinct compounds by VPC. Two of these compounds, represented by the first two peaks on the chromatograms, were separated by distillation from the remaining materials. Elemental analysis of the mixture of these two compounds established that they are two isomeric chloro-tetrafluoroanilines. Recrystallization of a crude reaction mixture which contained 90% of the compound represented by peak 4 on the chromatogram yielded one pure solid compound. The elemental analysis of this compound checks closely with that of one of the chloro-trifluorophenylene diamines.

According to the information available from our experiments and from Brooke's work, it appears likely that the reaction of chloropentafluorobenzene with aqueous ammonia results first in the formation of

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[*] G. M. Brooke et al., Proc. Chem. Soc., 213 (1963).

4-chloro-tetrafluoroaniline and 2-chloro-tetrafluoroaniline. These two monoamines then react further with excess ammonia to yield 1-chloro-2,4-diaminotrifluorobenzene and 2-chloro-1,3-diaminotrifluorobenzene.
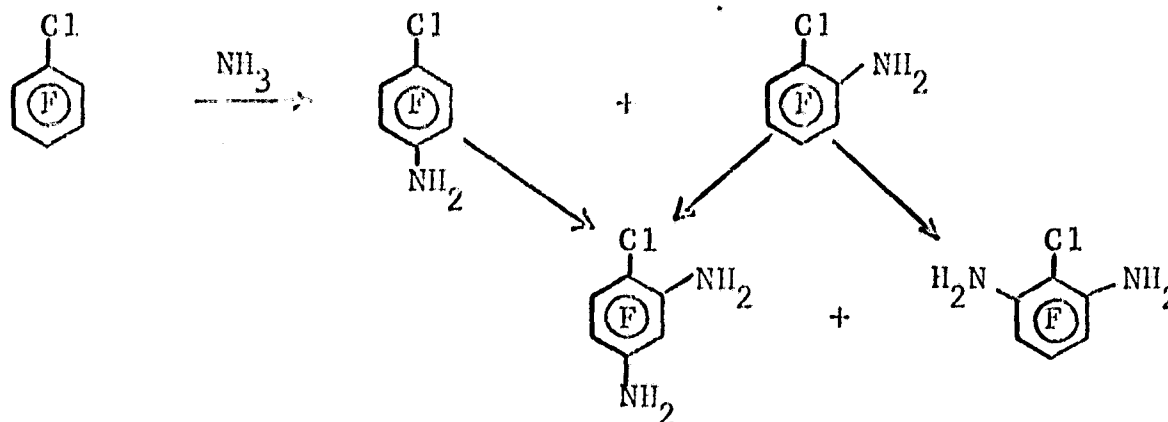


Large amounts of 1-chloro-2,4-diamino-trifluorobenzene were prepared by reaction at 235°C and subsequent purification.

Reaction of this diamine with chlorocarbonyl pyridinium chloride, using the procedure described several times during the course of this program for the preparation of the tetrafluoro phenylene diisocyanates, yielded 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene in 44% yield. The product was identified by its infrared spectrum and elemental analysis.
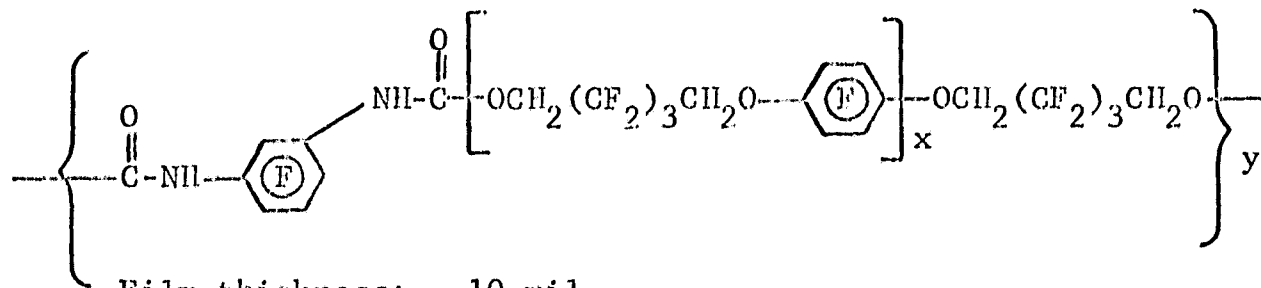
N-acetyl-pentafluoroaniline, which was used in an attempt to prepare a liquid curing agent, was prepared following the method of Brooke.*

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* G. M. Brooke et al., J. Chem. Soc., 2088-2094 (1965).

## A.   LOX Compatibility Results

The result of the one LOX-compatibility test completed this year
is shown below for the polyurethane of tetrafluoro-m-phenylene diiso-
cyanate and the polyether of hexafluorobenzene and hexafluoropentane-
diol.

$$-\left\{ \begin{array}{c} O \\ \| \\ C-NH- \end{array} \langle F \rangle \begin{array}{c} O \\ \| \\ NH-C- \end{array} \left[ -OCH_2(CF_2)_3CH_2O---\langle F \rangle- \right]_x -OCH_2(CF_2)_3CH_2O- \right\}_y$$

Film thickness:   10 mil

LOX Results (Energy level = 10 Kg-M):   19 reactions/20 tests
(LOX sensitivity may be due to stannous octoate used
as catalyst)


## B.   Polyurethanes


1.   From Hydroxyl-Terminated Polyethers of Perfluoropropylene Oxide

a.   And Tetrafluoro-m-phenylene Diisocyanate (Baglbond 400)

(1)   Lap Shear Test Specimens from Diisocyanate and Diol

(a)   NCO:OH ratio of 2:1

Unsuccessful Attempt 1 — The perfluoropropylene oxide
polyether (MW 1160; 8.1 g, 0.007 mole), tetrafluoro-m-phenylene di-
isocyanate (3.25 g, 0.014 mole) and some 4-mil diameter glass beads
were mixed at 68°C for 2 minutes, then allowed to cool to room tempera-
ture.  One drop of stannous octoate was added and the mixture stirred.
Within 1 minute, the mixture had gelled and could not be applied to
the bonds.

Unsuccessful Attempt 2 — The reaction was repeated
using the same amounts of materials.  They were mixed and heated from
room temperature to 54°C over a 5-minute period, then stirred at 65°C
for 5 minutes and stirred with a vacuum pump pulling on it (to degas
it) at 65°C for an additional 5 minutes.  The mixture was still very
fluid.  It was cooled to 0°C, then warmed to room temperature and
2 drops of stannous octoate added and stirred at room temperature.
Within 2 minutes, the mixture had again gelled.

Unsuccessful Attempt (Without Catalyst) — The reaction
was again repeated, using the same amounts of materials.  They were
mixed and heated at 65°-70°C for 10 minutes, and at 70°-80°C for

5 minutes. The mixture was then stirred and heated at 80°C with the vacuum pump on it, then cooled to room temperature. It was still fluid. The mixture was heated again at 65°-82°C for 10 minutes, then at 82°-90°C for 10 minutes with the vacuum pump on it. It was still liquid. Some diisocyanate had condensed on the upper walls of the resin flask so the walls were heated with a heat gun. The mixture gelled almost immediately.

Successful Preparation — The perfluoropropylene oxide polyether (MW 1160; 8.1 g, 0.007 mole), tetrafluoro-m-phenylene diisocyanate (3.25 g, 0.014 mole), and some 4-mil diameter glass beads were mixed at 70°C for 1 minute, then cooled quickly to room temperature with ice water. One drop of stannous octoate was added and the mixture stirred at room temperature for 1 minute, then for 4 more minutes at room temperature with the vacuum pump on it to degas the material. The mixture was still fluid, so one more drop of stannous octoate was added, the mixture stirred for one minute, then stirred with the vacuum pump on it for 2 minutes more. The adhesive was then applied to bonding panels (2024-T3 clad aluminum etched with sulfuric acid — sodium dichromate) which were heated.

The bonded panels were cured by keeping them at room temperature overnight in a vacuum bag at 1/2-atm pressure (7.5 psi), then heating them at 160°F (71°C) in an oven in air for 48 hours. The pot life of this adhesive was about 30 minutes. The average lap shear strengths were 1240 psi at room temperature (three tests; high value 1340, low value 1110) and 3230 psi at -320°F (three tests, high value 3630, low value 3000).

(b)   NCO:OH Ratio of 1.8:1

The perfluoropropylene oxide polyether (MW 1160; 8.1 g, 0.007 mole), tetrafluoro-m-phenylene diisocyanate (2.92 g, 0.0126 mole), and some 4-mil diameter glass beads were mixed and heated at 70°C for 1 minute, then cooled quickly to room temperature with ice water. One drop of stannous octoate was added and the mixture stirred at room temperature for 1 minute, then for 3 minutes at room temperature with the vacuum pump on it. The mixture was still fluid, so 1 more drop of stannous octoate was added and the mixture stirred at room temperature for 30 seconds, then for 2 minutes at room temperature with the vacuum pump on it. The adhesive was then applied to the 2024-T3 clad aluminum bonding panels (etched with sulfuric acid — sodium dichromate).

The bonds were cured by keeping them at room temperature in a vacuum bag at 1/2-atm pressure (7.5 psi) overnight, then heating them in air at 160°F (71°C) in an oven for 48 hours. The pot life of this adhesive was about 30 minutes. The average lap shear strengths were 258 psi at room temperature (three tests; high value 296, low value 202) and 253 psi at -320°F (three tests; high value 346, low value 173).

(2)  Preparation of Isocyanate-Terminated Prepolymer

(a)  Unsuccessful Attempt

A sample of 945 molecular weight hydroxyl-terminated polyether of perfluoropropylene oxide (10 g, 0.01 mole) and tetrafluoro-m-phenylene diisocyanate (4.64 g, 0.2 mole) was mixed at room temperature for 40 minutes. At the end of this time, the infrared spectrum of the mixture indicated there were still unreacted hydroxyl groups. The mixture was then warmed to 80°C over a period of 20 minutes and stirred at 80°C for 3-1/4 hours. At the end of this time, the material had gelled.

The gelled polyurethane was pressed at 290°F and under 1200-psi pressure. The clear, colorless 17-mil thick sheet which resulted was very tough.

(b)  Successful Preparation

The hydroxyl-terminated perfluoropropylene oxide polyether of 945 molecular weight (7.4 g, 0.008 mole) and tetrafluoro-m-phenylene diisocyanate (3.71 g, 0.016 mole) were stirred at room temperature for 8 minutes, at 50°C for 15 minutes, at 50°-80°C for 22 minutes, and at 80°C for 10 minutes. The prepolymer had no hydroxyl groups (indicated by its infrared spectrum).

(3)  Lap Shear Test Specimens from Isocyanate-Terminated Prepolymer

The isocyanate-terminated prepolymer (11.1 g, 0.008 mole) described above, which had been stored overnight in the refrigerator, was warmed to 67°C and 1160 molecular weight hydroxyl-terminated polyether of perfluoropropylene oxide (6.15 g, 0.053 mole) was added. The mixture was stirred for 5 minutes at 67°C, then for an additional 10 minutes at 67°C with a vacuum (3 mm Hg) applied. The resulting adhesive was applied to etched (sulfuric acid — sodium dichromate solution) 2024-T3 clad aluminum adherends which were warmed with a heat gun. Glass beads (4 mils average diameter) were sprinkled on the test panels. The specimens were cured overnight at room temperature in a vacuum bag at a pressure of 1/2 atm, then for 24 hours at 160°F in air. The pot life of the adhesive was approximately 30 minutes. The average lap shear strengths were 655 psi at room temperature (six tests; high value 752, low value 554) and 451 psi at -320°F (six tests, high value 505, low value 420).

b.  And 1-Chloro-2,4-diisocyanato-3,5,6-trifluorobenzene (Baglbond 420)

(1)  Lap Shear Test Specimens from Diisocyanate and Diol

### (a)   NCO:OH Ratio of 2:1

A sample of 1160 MW perfluoropropylene oxide poly-
ether (8.1 g, 0.007 mole), and 1-chloro-2,4-diisocyanato-3,5,6-tri-
fluorobenzene (3.48 g, 0.014 mole) and some 4-mil diameter glass beads
were mixed and heated at 70°C for 3 minutes then cooled quickly to room
temperature with ice water.  One drop of stannous octoate was added
and the mixture stirred for 2 minutes at room temperature then for an
additional 5 minutes at room temperature with the vacuum pump pulling
on it.  The adhesive was then applied to heated aluminum bonds.

The bonds were cured by keeping them at room tempera-
ture overnight in a vacuum bag at 1/2-atm pressure (7.5 psi), then
heating them at 160°F (71°C) for 48 hours in air in an oven.  The pot
life of this adhesive was better than 4 hours.  (It could be spread even
after 4 hours when the adhesive had been heated with a heat gun.)  The
average lap shear strengths were 1940 psi at room temperature (six tests;
high value 2630, low value 1460), 3650 psi at -320°F (six tests; high
value 4270, low value 3250), and 93 psi at +250°F (three tests; high
value 119, low value 78).

### (b)   NCO:OH Ratio of 1.8:1

The perfluoropropylene oxide polyether (1160 MW;
8.1 g, 0.007 mole), 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene
(3.13 g, 0.0126 mole), and some 4-mil diameter glass beads were mixed
at 60°-70°C for 3 minutes, then cooled quickly to room temperature with
ice water.  One drop of stannous octoate was added and the mixture
stirred at room temperature for 2 minutes, then stirred with the vacuum
pump on it at room temperature for an additional 5 minutes.  The adhe-
sive was then applied to heated bonding panels.

The bonds were cured by keeping them at 1/2-atm
pressure (7.5 psi) overnight in a vacuum bag, then in an oven in air at
160°F (71°C) for 48 hours.  The pot life of this adhesive was better
than 3 hours.  (It could be spread even after 3 hours when the adhesive
had been heated with a heat gun.)  The average lap shear strengths were
2025 psi at room temperature (six tests, high value 2440, low value
1720), 4730 psi at -320°F (six tests, high value 5340, low value 3790),
and 107 psi at +250°F (three tests, high value 116, low value 101).

### (c)   NCO:OH Ratio of 1.6:1

A sample of 1200 molecular weight perfluoropropylene
oxide polyether (8.4 g, 0.007 mole), 1-chloro-2,4-diisocyanato-3,5,6-
trifluorobenzene (2.78 g, 0.0112 mole), and some 4-mil diameter glass
beads were mixed and heated to 70°C for 3 minutes, then cooled quickly
to room temperature with ice water.  One drop of stannous octoate was
added and the mixture stirred at room temperature for 2 minutes, then
for an additional 5 minutes at room temperature in vacuo.  The adhesive
was then applied to heated 2024-T3 clad aluminum bonding panels and cured

as in examples (a) and (b) above. The average lap shear strengths were 1770 psi at room temperature (six tests, high value 2330, low value 706) and 4595 psi at -320°F (six tests, high value 5740, low value 2040).

(d) NCO:OH Ratio of 1.4:1

This synthesis was conducted exactly as in the preceding example, but 2.44 g (0.0098 mole) of 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene was used. The average lap shear strengths were 1365 psi at room temperature (six tests; high value 1540, low value 1100) and 2000 psi at -320°F (six tests; high value 3300, low value 600).

(e) NCO:OH Ratio of 1.2:1

This synthesis was also conducted exactly as in the one using NCO:OH of 1.6:1 except that 2.09 g (0.0084 mole) of 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene was used. The average lap shear strengths were 456 psi at room temperature (six tests, high value 584, low value 280) and 0 psi at -320°F.

(f) Using 1614 Molecular Weight Poly(perfluoropropylene oxide) with NCO:OH Ratio of 1.8:1

This synthesis was identical to that in experiment (b), except that 7.3 g (0.0045 mole) of 1614 molecular weight poly-(perfluoropropylene oxide) and 2.01 g (0.0081 mole) of 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene (NCO:OH ratio = 1.8:1) were used. The average lap shear strengths were 1760 psi at room temperature (six tests; high value 2040, low value 1480) and 4630 psi at -320°F (six tests; high value 5200, low value 3640).

(g) Using 2349 Molecular Weight Poly(perfluoropropylene oxide) with NCO:OH Ratio of 1.8:1

This synthesis was also identical to that in experiment (b), except that 6.0 g (0.0026 mole) of 2349 molecular weight poly(perfluoropropylene oxide) and 1.17 g (0.0047 mole) of 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene (NCO:OH ratio = 1.8:1) were employed. The average lap shear strengths were 573 psi at room temperature (six tests; high value 879, low value 368) and 1865 psi at -320°F (six tests; high value 2900, low value 800).

(2) Lap Shear Test Specimens from Isocyanate-Terminated Prepolymer

(a) Ratio = 1.8:1 (Actual NCO:OH ratio = 1.28:1)

The isocyanate-terminated prepolymer was prepared by mixing 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene (1.87 g, 0.0075 mole) and 1200 molecular weight perfluoropropylene oxide polyether

(4.5 g, 0.00375 mole) at 70°C for 15 minutes, at 70°-80°C for 5 minutes, and at 80°-100°C for 10 minutes. The prepolymer was stored overnight in the refrigerator.

The above isocyanate-terminated prepolymer, additional 1200 molecular weight hydroxyl-terminated perfluoropropylene oxide polyether (2.52 g, 0.0021 mole), and some 4-mil diameter glass beads were heated to 70°C, stirred at that temperature for 3 minutes, then cooled quickly with an ice water bath. One drop of stannous octoate catalyst was added and the mixture stirred at room temperature for 7 minutes. During the last 5 minutes, the system was degassed with a vacuum pump. The adhesive was then applied to heated 2024-T3 clad aluminum bonding panels. The bonds were cured at room temperature overnight at a pressure of 1/2-atm in a vacuum bag, then at 163°F for 48 hours in air. The average lap shear strengths were 871 psi at room temperature (six tests; high value 971, low value 737) and 125 psi at -320°F (six tests; high value 291, low value 0).

(b) Ratio = 10:1 (Actual NCO:OH ratio = 1.8:1)

With catalyst — The isocyanate-terminated prepolymer was prepared by mixing 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene (1.99 g, 0.008 mole) and 1200 molecular weight perfluoropropylene oxide polyether (4.8 g, 0.004 mole) at 60°-80°C for 20 minutes and at 80°-100°C for 10 minutes.

After keeping the prepolymer at room temperature for 1/2 hour, additional 1200 molecular weight hydroxyl-terminated perfluoropropylene oxide polyether (0.52 g, 0.0004 mole) and some glass beads were added and the mixture stirred for 1 minute. One drop of stannous octoate was added and the mixture stirred at room temperature for 2 minutes. The system was degassed during the second minute with a vacuum pump. The adhesive, which had gelled, was then applied to heated bonding panels. By heating the adhesive, it could readily be spread on the panels. The bonds were cured as described in example (a) above. The average lap shear strengths were 2050 psi at room temperature (six tests; high value 2310, low value 1360) and 3070 psi at -320°F (six tests; high value 3680, low value 2060).

(3) Lap Shear Test Specimens Prepared without Catalyst

(a) From Diisocyanate and Diol in NCO:OH Ratio of 1.8:1

A sample of 1200 molecular weight perfluoropropylene oxide polyether (7.2 g, 0.0006 mole), 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene (2.68 g, 0.0108 mole), and some 4-mil diameter glass beads were stirred at room temperature for 5 minutes. The mixture was then stirred at 60°-70°C for 15 minutes, 70°-80°C for 10 minutes, and 80°-85°C for 10 minutes and 100°-110°C for 10 minutes in vacuo. The adhesive was then applied to heated bonding panels and cured at room

temperature overnight at a pressure of 1/2-atm in a vacuum bag, then at 163°F for 48 hours in air. The average lap shear strengths were 982 psi at room temperature (six tests; high value 1200, low value 588) and 1166 psi at -320°F (six tests; high value 1584, low value 600).

(b) From Isocyanate-Terminated Prepolymer in Actual NCO:OH Ratio of 1.8:1

The isocyanate-terminated prepolymer was prepared as described in (2) (b) above and allowed to stand at room temperature for 3/4 hour.

This prepolymer, additional perfluoropropylene oxide polyether (0.52 g, 0.0004 mole), and some glass beads were mixed at room temperature for 35 minutes. The system was degassed with a vacuum pump during the last 30 minutes of stirring. The adhesive was then applied to bonding panels and cured as in item (a) above. The average lap shear strengths were 789 psi at room temperature (six tests; high value 1000, low value 540) and 836 psi at -320°F (six tests; high value 990, low value 634).

(4) LOX-Impact Test Specimens

(a) With Catalyst

Hydroxyl-terminated perfluoropropylene oxide polyether of 1100 molecular weight (11 g, 0.01 mole) and 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene were mixed at room temperature for 5 minutes. One drop of stannous octoate catalyst was added and the mixture stirred for 17 minutes at room temperature. During the last 15 minutes the system was degassed with a vacuum pump. The product was then poured onto Teflon caul sheets, allowed to stand at room temperature for 1/2 hour, then warmed on a hot plate until it gelled. It was then cured in a press at 275°F without pressure for 1/2 hour, then at 275°F and 15,000-lb pressure for 2-1/2 hours. 104 disks (11/16-in. diameter) were punched from the resulting 5.5 mil thick clear, colorless, flexible film.

(b) Without Catalyst

Hydroxyl-terminated perfluoropropylene oxide polyether of 1100 molecular weight (8.8 g, 0.008 mole) and 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene (3.58 g, 0.0144 mole) were heated at 70°C for 1/2 hour, 90°-100°C for 1 hour, and 100°-130°C for 1-1/4 hours. The gelled product was then transferred to Teflon caul sheets and heated in a press at 275°C with no pressure for 1-1/2 hours then at 275°F and 15,000-lb pressure for 2 hours. 104 disks (11/16-in. diameter) were punched from the resulting 4.3 mil thick clear, coloress, flexible film.

2. From Hydroxyl-Terminated Polyethers of Hexafluorobenzene and Hexafluoropentanediol

  a. And Tetrafluoro-m-phenylene Diisocyanate (Baglbond 300)

  (1) Preparation of Lap Shear Test Specimens from Diisocyanate and Diol

  (a) Unsuccessful Attempts using 3840 Molecular Weight Polyether

A 3840 molecular weight polyether of hexafluorobenzene and hexafluoropentanediol (10 g, 0.0026 mole) was heated in a resin flask under nitrogen to 110°C. The polyether was stirred and tetrafluoro-m-phenylene diisocyanate (0.72 g, 0.0031 mole) was added. In about 2 minutes, the mixture gelled to a rubber ball and could not be spread on the bonding pads.

The same amounts of reactants as above were combined at 110°C and the temperature lowered to room temperature and stirring continued. The mixture gelled in about 7 minutes to a rubber ball, precluding its application to the bonding pads.

  (b) Preparation of bonds using 2620 Molecular Weight Polyether

The hydroxyl-terminated polyether of hexafluorobenzene and hexafluoropentanediol of 2620 molecular weight (10 g, 0.0038 mole) was warmed to 65°C, a few glass beads (0.005-in. diameter) added, and tetrafluoro-m-phenylene diisocyanate (1.07 g, 0.0046 mole) quickly stirred in. The mixture was stirred briefly, then applied to etched (sulfuric acid — sodium dichromate solution) 2024-T3 clad aluminum adherends which were warmed with a heat gun. Four sets of specimens were made. Two sets were cured as follows. The specimens were kept overnight at room temperature in a vacuum bag at a pressure of 1.2-atm (7.5 psi) then removed from the bags and heated at 160°F for 24 hours. The average lap shear strengths were 478 psi at room temperature (six tests; high value 716, low value 313) and 1897 psi at -320°F (six tests; high value 2200, low value 1160).

The other two sets were cured as follows. The specimens were kept overnight in air with weights on them which applied 1/2-atm pressure (7.5 psi) to each bond, then heated at 160°F for 24 hours. The average lap shear strengths were 689 psi at room temperature (six tests; high value 864, low value 574) and 2295 psi at -320°F (six tests; high value 2530, low value 2000).

(2)  Preparation of Isocyanate-terminated Prepolymer

(a)  Unsuccessful Attempts

The 4030 molecular weight hydroxyl terminated hexa-
fluorobenzene-hexafluoropentanediol polyether (10.0 g, 0.0025 mole) was
warmed in a resin flask to 65°C and tetrafluoro-m-phenylene diisocyanate
(1.64 g, 0.0075 mole) was added and the reaction mixture stirred. After
45 minutes the mixture gelled. A vacuum was applied and excess diiso-
cyanate was stripped from the system at 65°C. Upon cooling, the material
was found to be a moderately tough elastomer. Infrared spectroscopy
demonstrated that the polymer contained excess isocyanate groups. An
attempt was made at curing this polymer by adding tetrafluoro-m-
phenylenediamine. The diamine proved to be insoluble in the resin.
Press curing at 275°F resulted in a homogeneous, partially cured sheet
which was not tough.

A sample of 2900 molecular weight hydroxyl-termi-
nated hexafluorobenzene-hexafluoropentanediol polyether (12.3 g,
0.0042 mole) was warmed to 80°C in a resin flask under nitrogen,
cooled to 60°C, and tetrafluoro-m-phenylene diisocyanate (1.95 g,
0.084 mole) added. The mixture was heated at 60°C for 5 minutes, then
at 60°-120°C over a period of 30 minutes. The temperature of the mix-
ture was lowered to 80°C and vacuum (3 mm Hg) applied to the mixture
and held at 80°C for 15 minutes. At the end of this time, the material
had gelled.

(b)  Successful Preparations

The same amounts of reactants as in item (a) above
were stirred at 50°C for 1/2 hour, at 50°-80°C over a period of 7 min-
utes, then at 80°C for 20 minutes. Vacuum (3 mm Hg) was then applied
for 10 minutes to the mixture held at 80°C. The first prepolymer pre-
pared this way gelled on standing under nitrogen in a refrigerator
for 4 days. The prepolymer had no hydroxyls (indicated by its infra-
red spectrum).

The second prepolymer prepared this way was stored
under nitrogen in a refrigerator overnight and used to make bonds the
next day.

(3)  Lap Shear Test Specimens from Isocyanate-terminated
Prepolymer

The above isocyanate-terminated prepolymer (14 g,
0.0042 mole), which had been stored overnight in the refrigerator,
was warmed to 80°C and 2900 molecular weight hydroxyl-terminated
hexafluorobenzene-hexafluoropentanediol polyether (8.1 g, 0.0028 mole)
was melted and added along with some 4-mil diameter glass beads. The
mixture was stirred for 5 minutes at 90°C, then vacuum (3 mm Hg) was
applied to the mixture kept at 80°-90°C for 10 minutes. The resulting

adhesive was applied to etched (sulfuric acid — sodium dichromate solution) 2024-T3 clad aluminum adherends which were warmed with a heat gun. After two test panels were bonded (about 10 minutes), the adhesive gelled. Half of the specimens were cured overnight at room temperature in a vacuum bag at a pressure of 1/2 atm, then for 48 hours in air at 160°F. The average lap shear strengths were 462 psi at room temperature (three tests; high value 540, low value 400) and 1490 psi at -320°F (three tests; high value 1720, low value 1110).

The other half of the specimens were cured by weighting them in air overnight with 1/2-atm pressure (7.5 psi) to each bond, then heating them in air at 160°F for 48 hours. The average lap shear strengths were 188 psi at room temperature (three tests; high value 225, low value 162) and 990 psi at -320°F (three tests; high value 1010, low value 960).

(4)  LOX-Impact Test Specimens

The hydroxyl-terminated polyether of hexafluorobenzene and hexafluoropentanediol (MW 4030) (10.0 g, 0.0025 mole) was warmed to 65°C in a resin pot. The material was easily stirrable at this temperature. Tetrafluoro-m-phenylene diisocyanate (0.70 g, 0.0030 mole) (NCO:OH = 1.2:1) was then added and the reaction mixture stirred under nitrogen. The diisocyanate was readily soluble in the polyether. After 30 minutes at 65°C there had been only a slight increase in viscosity. Nuocure 28 (stannous octoate, 1 drop) was added and stirring continued. The mixture gelled within one minute. The partially gelled resinous material was transferred to clean Teflon sheets and pressed at 275°F for 1-1/2 hours. Specimens for LOX compatibility were punched from the resulting 10.2 mil thick clear flexible film. These specimens gave 19 reactions in 20 tests.

A second set of LOX-impact test specimens was prepared without catalyst. A 2900 molecular weight polyether of hexafluoro-benzene and hexafluoropentanediol (10 g, 0.0034 mole) was heated to 100°C. After lowering the temperature to 70°C, tetrafluoro-m-phenylene diisocyanate (1.42 g, 0.0061 mole) was added and the mixture stirred at 70°-75°C for 10 minutes then at 75°-98°C for 10 minutes. The gelled product was transferred to Teflon caul sheets and heated in a press at 275°F without pressure for 1/2 hour then at 275°F with 20,000-lb pressure for 2 hours. Specimens for LOX compatibility testing (11/16-in. diameter disks) were punched from the resulting 12-mil thick film.

b.  And 1-Chloro-2,4-diisocyanato-3,5-6-trifluorobenzene (Baglbond 320)

(1)  Preparation of Lap Shear Test Specimens from Diiso-cyanate and Diol with NCO:OH Ratio of 1.2:1

The hydroxyl-terminated polyether of hexafluorobenzene and hexafluoropentanediol of 2620 molecular weight (10 g, 0.0038 mole) was

warmed to 65°C, a few glass beads (0.005-in. diameter) added, and 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene (1.24 g, 0.0046 mole) quickly stirred in. The mixture was stirred briefly, then applied to etched (sulfuric acid — sodium dichromate solution) 2024-T3 clad aluminum adherends which were heated with a heat gun. Four sets of specimens was made. Two sets were cured overnight at room temperature in a vacuum bag at 1/2-atm pressure, then at 160°F for 24 hours. The average lap shear strengths were 374 psi at room temperature (six tests; high value 438, low value 295) and 1340 psi at -320°F (six tests; high value 1660, low value 990).

The other two sets were cured in air overnight with weights on then applying 1/2-atm pressure (7.5 psi), then at 160°F for 24 hours. The average lap shear strengths were 301 psi at room temperature (six tests; high value 328, low value 280) and 1167 psi at -320°F (six tests; high value 1520, low value 960).

· (2) Attempted Preparation of Lap Shear Test Specimens from Diisocyanate and Diol with NCO:OH Ratio of 1.8:1

Hydroxyl-terminated polyether of hexafluorobenzene and hexafluoropentanediol (molecular weight 2900 ) (8.7 g, 0.003 mole) was warmed to 70°C and 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene (1.34 g, 0.0054 mole) and some 4-mil diameter glass beads were added. The mixture was stirred at 70°C for 3 minutes, then cooled quickly with an ice water bath. One drop of stannous octoate was added and the mixture stirred. Within 1 minute, the mixture had gelled and the resulting rubber could not be spread on bonds even with heating.

, (3) Preparation of Isocyanate-terminated Prepolymer

(a) Unsuccessful Attempt

A 3160 molecular weight hydroxyl-terminated hexafluorobenzene-hexafluoropentanediol polyether (10 g, 0.0032 mole) was warmed in a resin flask to 100°C and 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene (2.4 g, 0.0096 mole) was quickly stirred in. Almost immediately, the very viscous mixture gelled and became a rubber ball.

The amber rubber ball and tetrafluoro-m-phenylene diamine (0.9 g, 0.005 mole) were kneaded together and mixed in a rubber mill for about 5 minutes. The milled rubber was then heated in a press at 300°F and 9000-lb ram pressure for 1 hour. The product was a clear amber sheet that was somewhat brittle.

(b) Successful Preparation

A sample of 2900 molecular weight hydroxyl-terminated hexafluorobenzene-hexafluoropentanediol polyether (13.5 g, 0.0047 mole) was warmed in a resin flask under nitrogen to 80°C and 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene (2.34 g, 0.0094 mole) was added.

The reaction mixture was stirred at 45°C for 5 minutes then at 80°C for 20 minutes. A vacuum (6 mm Hg) was applied to the mixture held at 80°C for 10 minutes. The product had no unreacted hydroxyls, as indicated by its infrared spectrum.

### (4) Lap Shear Test Specimens from Isocyanate-terminated Prepolymer

The above-described isocynate-terminated prepolymer(15 g, 0.0044 mole), which had been stored under nitrogen in a refrigerator for 5 days, was warmed to 60°C and 2900 molecular weight hydroxyl-terminated hexafluorobenzene-hexafluoropentanediol polyether (8.4 g, 0.0029 mole; ratio = 1.5:1) was melted and added along with some 4-mil diameter glass beads. The mixture was stirred for 5 minutes at 65°-80°C, then vacuum (3 mm Hg) was applied for 12 minutes to the stirred mixture held at 80°C. The resulting adhesive was then applied to ethed (sulfuric acid — sodium dichromate solution) 2024-T3 clad aluminum adherends which were warmed with a heat gun. Half of the specimens were cured overnight at room temperature in a vacuum bag at a pressure of 1/2 atm, then for 48 hours in air at 160°F. The average lap shear strengths were 450 psi at room temperature (six tests; high value 529, low value 373) and 1290 psi at -320°F (six tests; high value 1504, low value 1080).

The other half of the specimens were cured by keeping weights on them in air overnight which applied 1/2-atm pressure (7.5 psi) to each bond, then heating them in air at 160°F for 48 hours. The average lap shear strengths were 685 psi at room temperature (six tests; high value 922, low value 525) and 1570 psi at -320°F (six tests; high value 1720, low value 1310).

## C. Polyethers

### 1. From Perfluoropropylene Oxide

#### a. Polymerization of Perfluoropropylene Oxide with Perfluoroglutaryl Fluoride

Three polymerizations were carried out, using the procedure described previously in Summary Report IV for the reaction of perfluoropropylene oxide, perfluoroglutaryl fluoride and cesium fluoride.

In the first polymerization, perfluoropropylene oxide (98 g, 0.6 mole), perfluoroglutaryl fluoride (14.6 g, 0.06 mole) cesium fluoride (4.6 g, 0.03 mole), and diglyme (25 ml) were used. The reaction product was fractionally distilled, with the following fractions being isolated.

| Fraction | Boiling Point | Weight |
|---|---|---|
| I | 45°-66°C/120 mm | 24.0 g |
| II* | 70°C/92 mm to 90°C/60 mm | 36.4 g |
| III* | 90°C/50 mm to 80°C/20 mm | 23.0 g |
| IV | 130°-136°C/5 mm | 39.3 g |

These fractions were reduced, using the procedure described in Summary Report IV for the reduction of acid fluoride terminated polyethers of perfluoropropylene oxide. Fractions II and III were combined before reduction. The reduced products had the following molecular weights and hydroxyl numbers.

| Reduced Fraction | Mol Wt (VPO) | Hydroxyl No. |
|---|---|---|
| II & III Combined | 700 | 542 |
| IV | 945 | 494 |

In the second and third polymerization, which were of a much larger scale, perfluoropropylene oxide (500 g, 3.0 mole), perfluoroglutaryl fluoride (73 g, 0.3 mole), cesium fluoride (22.3 g, 0.15 mole) and diglyme (125 ml) were used. The reaction products were fractionally distilled, with the following fractions being collected.

| Run 2: | Fraction | Boiling Point | Weight |
|---|---|---|---|
| | I** | 35°-75°C/92 mm | 80.0 g |
| | II** | 80°C/92 mm to 92°C/60 mm | 223.0 g |
| | III** | 92°C/60 mm to 90°C/4 mm | 80.5 g |
| | IV | 120°C/4 mm to 135°C/2 mm | 208.1 g |

| Run 3: | Fraction | Boiling Point | Weight |
|---|---|---|---|
| | I | 40°-75°C/92 mm | 57.6 g |
| | II | 80°C/92 mm to 92°C/60 mm | 119.3 g |
| | III | 110°C/60 mm to 140°C/18 mm | 98.5 g |
| | IV | 140°C/18 mm to 184°C/18 mm | 75.0 g |
| | Residue | -- | 38.3 g |

Fractions II, III, and IV of run 2 and Fraction IV and the residue of run 3 were reduced using the procedure described in Summary Report IV. The reduced products had the following molecular weights and hydroxyl numbers.

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* In cuts II and III, 23 g were fluorocarbon products.

** Fractions I, II, and III all contained fluorocarbon product and diglyme.

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| Run 2: | Reduced Fraction | Mol Wt (VPO) | Hydroxyl No. |
|--------|------------------|--------------|--------------|
|        | II               | 676 ±30      | 764 ±25      |
|        | III              | 790 ±10      | 795 ±1       |
|        | IV               | 1170 ±10     | 580 ±2       |
| Run 3: | IV               | 1181         | --           |
|        | Residue          | 2349         | --           |

A fourth polymerization was carried out using the procedure described previously in Summary Report IV and 945.4 g of polyether boiling between 26°C at 7 mm and 85°C at 4 mm were removed by distillation. The higher molecular weight residue weighed 483.8 g.

The 483.8 g of residue was reduced using the procedure described in Summary Report IV. The hydroxyl-terminated perfluoropropylene oxide polyether obtained weighed 419.4 g and had a molecular weight of 1100 (determined by VPO).

b. Polymerization of Perfluoropropylene Oxide with the Monoether of Perfluoropropylene Oxide and Perfluoroglutaryl Fluoride

The polymerization was carried out, using the procedure described in Summary Report IV for the reaction of perfluoropropylene oxide, monoether of perfluoropropylene oxide and perfluoroglutaryl fluoride, and cesium fluoride.

Perfluoropropylene oxide (100 g, 0.6 mole), Fraction I (bp 45°-66°C/120 mm) (12.3 g, 0.03 mole) from the first polymerization described above, cesium fluoride (2.3 g, 0.015 mole), and diglyme (25 ml) were used. The reaction product was fractionally distilled.

| Fraction | Boiling Point | Weight |
|----------|---------------|--------|
| I*       | 62°-90°C/90 mm | 63.5 g |
| II*      | 90°C/90 mm to 90°C/4 mm | 34.9 g |
| III      | 90°C/4 mm | 11.0 g |

These fractions were reduced using the procedure described in Summary Report IV for the reduction of acid fluoride terminated polyethers of perfluoropropylene oxide. Fractions I and II were combined before reduction. The reduced Fractions I and II had a molecular weight (by VPO) of 770 and a hydroxyl number of 690.

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* Fractions I and II both contained some diglyme.

## 2. From Hexafluorobenzene and Hexafluoropentanediol

### a. Study of the Effect of Water on the Polymerization

#### (1) Water Present

Hexafluorobenzene (18.6 g, 0.1 mole), hexafluoropentane-diol (21.2 g, 0.1 mole) and potassium hydroxide (11.2 g, 0.2 mole) were added to dioxane (150 ml) and benzene (30 ml). Dimethylformamide (1 ml) was added and the mixture stirred at reflux overnight. Workup of the resulting brown mixture followed by partial separation of various molecular weight fractions resulted in recovery of 16.2 g of polymer, ranging from viscous oils to rubbery elastomers. The bulk of the isolate polymer (9.3 g, 58%) had a molecular weight of 1010±50 (as determined by VPO).

#### (2) Water Removed by Azeotropic Distillation

The same quantities and reaction conditions were repeated with the exception that the water formed in the reaction plus any present initially was removed by azeotropic distillation (7.8 ml water recovered) into a Dean-Stark trap. The workup and separation procedure described in item (1) above was repeated. The recovered polymer (21.8 g) had essentially the same molecular weight distribution as that described in item (1). The bulk of the material (17.8 g, 81%) had a molecular weight of 1325 ±60 (determined by VPO).

### b. Polymerizations in Tetrahydrofuran

#### (1) With N,N-Dimethylformamide

##### (a) Hexafluoropentanediol:Hexafluorobenzene (3:2)

Hexafluoropentanediol (63.6 g, 0.3 mole) and hexa-fluorobenzene (37.2 g, 0.2 mole) were dissolved in THF (500 ml). Potassium hydroxide (33.7 g, 0.6 mole) and DMF (3 ml) were added and the mixture stirred. There was a slow rise in temperature to 29°C. Heat was applied and the solution was refluxed overnight (68°C). After cooling, the pale yellow solution was poured into 2% hydrochloric acid (1:1) with rapid stirring. A white, sticky solid came out of the solution. Thorough washing with distilled water resulted in coagulation to a solid mass. The polymer was taken up in THF and dried over magnesium sulfate. The solvent was stripped under reduced pressure (at 150°C, yielding a very pale yellow, transparent material (84.0 g). The rubbery semisolid had a molecular weight of 3160 ±300 (by VPO) and a hydroxyl number of 2430 g/equivalent.

(b)    Hexafluoropentanediol:Hexafluorobenzene (2:1)

Hexafluoropentanediol (42.4 g, 0.2 mole), hexafluoro-
benzene (18.6 g, 0.1 mole), potassium hydroxide (22.4 g, 0.4 mole) and
DMF (1.2 ml) were refluxed overnight in THF (250 ml).  An insoluble
(crosslinked) gel had formed which was partially discolored.  The polymer
was so swollen with solvent that characterization could not be
accomplished.

(c)    Hexafluoropentanediol:Hexafluorobenzene (3:1)

Hexafluoropentanediol (31.8 g, 0.15 mole), hexa-
fluorobenzene (9.3 g, 0.05 mole), potassium hydroxide (16.8 g, 0.3 mole)
and DMF (1.2 ml) were refluxed overnight in THF (250 ml).  A crosslinked
swollen gel very similar to that described in item (b) above had formed.

c.   Variation of Catalyst

(1)   Pyridine

Hexafluoropentanediol (31.8 g, 0.15 mole), hexafluoro-
benzene (18.6, 0.1 mole), potassium hydroxide (16.0 g, 0.3 mole), and
pyridine (1.2 g) were stirred in THF (250 ml) at room temperature over-
night.  The slightly yellow solution was poured into 2% hydrochloric acid
with rapid stirring.  The precipitated polymer was thoroughly washed
with distilled water, dissolved in THF, dried over anhydrous magnesium
sulfate, and the solvent stripped under reduced pressure at 150°C.  The
resulting white, partially crystalline, waxy polymer (33.0 g) had a
molecular weight of 2130 ±100 (determined by VPO) and a hydroxyl number
of 3018 ±40 g/equivalent.

(2)   Copper (I) Iodide

Hexafluoropentanediol (31.8 g, 0.15 mole) hexafluoro-
benzene (18.6 g, 0.1 mole), copper (I) iodide (2.1 g, 0.011 mole) and
potassium hydroxide (16.8 g, 0.3 mole) were refluxed in THF (250 ml)
overnight.  After cooling, the reaction mixture was poured into 1%
ammonium hydroxide.  The blue aqueous layer was decanted and the wet
polymer dissolved in THF.  The solution was then poured into distilled
water and the polymer again dissolved in ether and dried over anhydrous
magnesium sulfate. After stripping the solvent under reduced pressure
at 150°C, a very pale yellow rubbery polymer was obtained.  The molecu-
lar weight was 4030 ±50 (determined by VPO) and the hydroxyl number
was 1972 ±30, indicating complete hydroxyl termination.

d.   Preparation of Polyethers from Hexafluorobenzene and Hexa-
fluoropentanediol Using Copper (I) Iodide

(1)   Hexafluoropentanediol:Hexafluorobenzene (1.5:1)

Hexafluoropentanediol (31.8 g, 0.15 mole), hexafluoro-
benzene (18.6 g, 0.10 mole), potassium hydroxide (16.8 g, 0.30 mole),

and copper (I) iodide (2.1 g) were stirred overnight in 250 ml of re-
fluxing THF. After it had been cooled to room temperature, the solution
was poured into 2000 ml of a 1% solution of ammonium hydroxide. A
white solid settled out and was separated and redissolved in THF. The
product was washed again with ammonium hydroxide solution, then with
dilute hydrochloric acid solution, and finally with pure water. The
product was dissolved in ether and dried over anhydrous magnesium sul-
fate. The magnesium sulfate was filtered off and the ether evaporated
under reduced pressure on the rotary evaporator, yielding 29.1 g of a
yellow semisolid. The molecular weight was 3840 ±30 (determined by
VPO) and the equivalent weight was 1528 (determined by hydroxyl end
group analysis).

(2) Hexafluoropentanediol:Hexafluorobenzene (1.4:1)

(a) Run 1

Another run was made, using hexafluoropentanediol
(29.7 g, 0.14 mole), hexafluorobenzene (18.6 g, 0.1 mole), copper (I)
iodide (2.1 g), and potassium hydroxide (15.7 g, 0.28 mole). The
procedure and workup was exactly as that above. The polyether obtained
weighed 29.0 g, and had a molecular weight of 2620 ±100 (determined by
VPO) and an equivalent weight of 1480 ±50 (determined by hydroxyl end
group analysis).

(b) Run 2

The amounts used were hexafluorobenzene (74.4 g,
0.4 mole), hexafluoropentanediol (118.8 g, 0.56 mole), potassium
hydroxide (62.8 g, 1.12 mole), copper (I) iodide (5 g), and THF
(700 ml). We obtained 131 g of polyether; molecular weight (by VPO)
2900, hydroxyl number 1500.

(3) Hexafluoropentanediol:Hexafluorobenzene (1.6:1)

Another run was made with hexafluoropentanediol (33.9 g,
0.16 mole), hexafluorobenzene (18.6 g, 0.1 mole), copper (I) iodide
(2.1 g), and potassium hydroxide (17.9 g, 0.32 mole). The procedure
and workup was exactly as those above. The polyether obtained weighed
37.2 g and had a molecular weight of 3160 ±50 (determined by VPO) and
an equivalent weight of 1772 ±30 (determined by hydroxyl end group
analysis).

(4) Hexafluoropentanediol:Hexafluorobenzene (1.3:1)

The amounts used were hexafluorobenzene (74.4 g, 0.4 mole),
hexafluoropentanediol (110.2 g, 0.52 mole), potassium hydroxide (58.2 g,
1.04 mole), copper (I) iodide (5 g), and THF (700 ml). We obtained
133.2 g of polyether. It had a molecular weight of 2035 (determined
by VPO) and an equivalent weight of 1894 ±100 (determined by hydroxyl
end group analysis).

(5)  Hexafluoropentanediol:Hexafluorobenzene (1.2:1)

Another run was made using hexafluoropentanediol (25.4 g, 0.12 mole), hexafluorobenzene (18.6 g, 0.1 mole), copper (I) iodide (2.1 g), and potassium hydroxide (13.4 g, 0.24 mole). The polyether obtained weighed 20 g and had a molecular weight of 1530 ±50 (determined by VPO) with an equivalent weight of 1525 ±75 (determined by hydroxyl end group analysis).

(6)  High Molecular Weight Rubber from Hexafluoropentane-
     diol:Hexafluorobenzene of 1.2:1

Another run was made using hexafluoropentanediol (25.4 g, 0.12 mole), hexafluorobenzene (18.6 g, 0.1 mole), copper (I) iodide (2.1 g), and potassium hydroxide (15.8 g, 0.24 mole considering KOH 85% pure). A yellow rubber had come out of solution after overnight reflux. The rubber was dried in a vacuum oven at 60°C for 1-1/2 weeks. The dried product weighed 22.4 g.

| Analysis: | % C | % H | % F · |
|---|---|---|---|
| Calculated for $C_{11}H_4F_{10}O_2$: | 36.9 | 1.12 | 53.2 |
| Found: | 36.98 | 1.12 | 54.2 |

(7)  Hexafluoropentanediol:Hexafluorobenzene of 1.4:1
     with Sodium Hydroxide

The amounts used were the same as in experiment (2)(b) above except that sodium hydroxide (44.8 g, 1.12 mole) was used instead of the potassium hydroxide. We obtained 132.8 g of polyether; molecular weight (by VPO) 2100, hydroxyl number 1945.

e.  Attempted Preparation of Polyether from Hexafluorobenzene
    and Hexafluoropentanediol with Copper (I) Iodide in
    Nitrobenzene

Hexafluoropentanediol (31.8 g, 0.15 mole), hexafluorobenzene (18.6 g, 0.10 mole), copper (I) iodide (2.1 g), and potassium hydroxide (16.8 g, 0.3 mole) were stirred overnight in 250 ml of nitrobenzene at 35°C. The solution was then stirred at 60°C for 1-1/2 hours. The nitrobenzene was then evaporated on the rotary evaporator and the products dissolved in THF. The THF solution was poured into a dilute ammonium hydroxide solution and a yellow oil settled out. This oil was dissolved in ether and dried over anhydrous magnesium sulfate. After the magnesium sulfate had been filtered off, the ether was evaporated on the rotary evaporator; 6.5 g of a yellow oil was recovered. The infrared spectrum showed no hydroxy, and little or no fluorine was present. Nitrobenzene contamination was evident.

f. Preparation of a Polyether from 5-Hydroxyhexafluoropentoxy-pentafluorobenzene

(1) Preparation of the Monoacetal of Hexafluoropentanediol and Dihydropyran

(a) Preparation of a Small Amount of Monoacetal

Hexafluoropentanediol (106 g, 0.5 mole) was mixed with dihydropyran (500 ml) and a catalytic amount of concentrated hydrochloric acid (2 drops) was added. There was still some undissolved diol at this time. After shaking overnight, a clear solution was obtained. Fractionation under reduced pressure yielded 57.4 g (39% yield) of the monoacetal, bp 120°-125°C at 5 mm Hg and 88.5 g (46% yield) of the di-acetal, bp 152°-156°C at 5 mm Hg.

(b) Preparation of a Large Amount of Monoacetal

Hexafluoropentanediol (212 6, 1.0 mole) was dissolved with heating in 700 ml of dihydropyran. After the solution had cooled to room temperature, three drops of concentrated hydrochloric acid was added to the stirred solution. The temperature of the solution rose to 60°C in 5 minutes. The solution was quickly brought to room temperature with an ice bath and was stirred for 2 days at that temperature. A drying tube was used to keep the reaction free from moisture. Several pellets of potassium hydroxide were added and the solution was stirred for 1 hour. The solution was decanted off the pellets and distilled under a vacuum. The first fraction, boiling at 53°-90°C, weighed 25 g and was a mixture of the monoacetal and unreacted hexafluoropentane-diol. The second fraction, boiling at 110°-112°C, weighed 265 g and was the diacetal.

(c) Preparation of a Large Amount of Monoacetal in Tetrahydrofuran

Hexafluoropentanediol (212 g, 1.0 mole), dihydro-pyran (84 g, 1.0 mole) and 4 drops of concentrated hydrochloric acid were dissolved in 600 ml of THF. The solution was stirred at room temperature for 3 days in a 2-liter Erlenmeyer flask equipped with a thermometer and drying tube. Several pellets of potassium hydroxide were added and the solution was stirred for 1/2 hour. The solution was poured into water and a white oil settled to the bottom. This oil was separated, dissolved in ether, and dried over anhydrous sodium sulfate. After the drying agent had been filtered off, the ether was stripped on the rotary evaporator and the product distilled under vacuum at 2 mm Hg. The following fractions were obtained:

|  | bp, °C | Weight |
|---|---|---|
| Fraction 1 | 86-95 | 3.0 g |
| Fraction 2 | 95-99 | 99.5 g |
| Fraction 3 | 99-100 | 7.5 g |
| Fraction 4 | 100-102 | 11.0 g |
| Residue |  | 85 g |

Fractions 2, 3, and 4 were all the desired monoacetal. The yield of monoacetal was therefore 118 g (39%). The residue was mainly diacetal.

(2) Preparation of 5-Hydroxyhexafluoropentoxy-penta-fluorobenzene

(a) Using Dimethylformamide Catalyst

Hexafluorobenzene (26.0 g, 0.14 mole), the mono-pyranyl acetal of hexafluoropentanediol (20.0 g, 0.07 mole) and potassium hydroxide (4.7 g, 0.14 mole) were dissolved in THF (250 ml). Dimethyl-formamide (10 drops) was added with stirring. There was a slow rise in temperature to 33°C. Heat was applied and the reaction mixture was refluxed (68°C) for 3-1/2 hours. After cooling, the slightly yellow solution (along with the precipitated salts) was poured into 2 liters of distilled water. The resulting partial emulsion was salted out and allowed to stand overnight. The monoacetal product, which was a yellow oil, was hydrolyzed by stirring with dilute hydrochloric acid. The monoether product was extracted with ether and the ether solution dried over anhydrous magnesium sulfate. After filtering the drying agent and evaporating the solvent, the monoether was distilled under reduced pressure, 13.9 g (52.5% yield) of product boiling at 100°-102°C at 2 mm Hg being obtained.

| Analysis: | % C | % H | % F |
|---|---|---|---|
| Calculated for $C_{11}H_5F_{11}O_2$: | 35.0 | 1.3 | 55.1 |
| Found: | 35.15 | 1.48 | 54.84 |

(b) Using Copper (I) Iodide Catalyst

A 2000-ml three-necked flask, equipped with a con-denser, stirrer and thermometer was charged with the monoacetal of hexafluoropentanediol (120.7 g, 0.425 mole), hexafluorobenzene (156 g, 0.84 mole), potassium hydroxide (32.4 g, 0.56 mole) and THF (1200 ml) (dried over CaH). After adding a catalytic amount of pulverized copper (I) iodide, a spontaneous reaction started with the temperature rising to 45°C. After 3-1/2 hours of refluxing, the solution was poured into 5 liters of water and extracted with 1200 ml of diethyl ether. Upon evaporation of diethyl ether, the dark yellow oil was stirred with 600 ml of water and 2 ml of concentrated hydrochloric acid for 24 hours. After completing the hydrolysis, the product was extracted with 500 ml of diethyl ether and dried over anhydrous magnesium sulfate. After re-moval of the diethyl ether by evaporation at reduced pressure, the product was vacuum distilled. Two fractions were obtained. The first reaction, which was slightly impure monoether, bp 96°-106°C/2.3-2.5 mm Hg, weighed 19.6 g. The second fraction, bp 105°-107°C/2.3-2.4 mm Hg, weigh 83.6 g and was pure monoether. The total yield of the monoether, 5-hydroxyhexafluoropentoxy pentafluorobenzene, was 64%.

(3) Preparation of the Diether of Hexafluoropentanediol and Hexafluorobenzene

The monopyranyl acetal of hexafluoropentanediol (20.0 g, 0.07 mole), potassium hydroxide (4.7 g, 0.14 mole), and DMF (10 drops) were added to THF (100 ml), and heated to reflux. Hexafluorobenzene (6.5 g, 0.035 mole) was dissolved in THF (150 ml) and added to the refluxing acetal solution over a 2-hour period. Reflux was continued for 1-1/2 hours after addition. After cooling, the reaction mixture was poured into 2 liters of distilled water. The partial emulsion was broken with salt and allowed to stand overnight. The aqueous layer was decanted and the product dissolved in THF. The THF was evaporated at reduced pressure and the product hydrolyzed by stirring with hot dilute hydrochloric acid. After decanting the hydrochloric acid, the brown oil was dissolved in THF, decolorized with charcoal, and dried over anhydrous magnesium sulfate. The drying agent was filtered off and the THF solvent evaporated at reduced pressure yielding the diether as a light brown oil.

| Analysis: | % C | % H | % F |
|---|---|---|---|
| Calculated for $C_{16}H_{10}F_{16}O_4$: | 33.7 | 1.8 | 53.53 |
| Found: | 33.69 | 1.91 | 53.53 |

(4) Preparation of a Polyether from 5-Hydroxyhexafluoropentoxypentafluorobenzene

(a) With Equimolar Potassium Hydroxide

Potassium hydroxide (1.7 g, 0.03 mole), and copper (I) iodide (0.42 g) were placed in 50 ml of THF in a 100 ml, three-necked flask equipped with addition funnel, thermometer, condenser, and stirrer. This was followed by dropwise addition of 5-hydroxyhexafluoropentoxy-pentafluorobenzene (11.2 g, 0.03 mole) over a 2-hour period to the stirred solution. An exotherm to 29°C was observed. The solution was then refluxed overnight. The cooled solution was poured into 500 ml of a 1% solution of ammonium hydroxide. The polyether settled out and was separated and dissolved in THF. The polyether was then washed in turn with dilute ammonium hydroxide solution, dilute hydrochloric acid solution, and distilled water. Finally, the product was dissolved in ether and dried over anhydrous magnesium sulfate. The magnesium sulfate was filtered off and the ether removed on the rotary evaporator, then 6.5 g of polyether was collected which had a molecular weight of 1300 ±100 (determined by VPO) and an equivalent weight of 1965 (determined by hydroxyl end group analysis).

(b) With 15% Excess Potassium Hydroxide

The reaction was repeated using a 15% excess of potassium hydroxide. Potassium hydroxide (2.2 g, 0.36 mole), 5-hydroxyhexafluoropentoxy-pentafluorobenzene (11.2 g, 0.03 mole), copper (I)

iodide (0.42 g), and THF (50 ml) were used. The procedure and workup were the same as the run above, using an equimolar amount of potassium hydroxide. The product weighed 6.8 g and had a molecular weight of 1730 ±100 (determined by VPO). No hydroxyl end groups were present (determined by hydroxyl end group analysis).

### (c) With Fused Potassium Hydroxide

The reaction was repeated, using an equimolar amount of fused potassium hydroxide. Fused potassium hydroxide (1.7 g, 0.03 mole), 5-hydroxyhexafluoropentoxy-pentafluorobenzene (11.2 g, 0.03 mole), copper (I) iodide (0.42 g), and THF (50 ml) were used. The procedure and workup were the same as above. The product weighed 7.7 g, had a molecular weight of 860 ±80 (determined by VPO), and an equivalent weight of 1594 (determined by hydroxyl end group analysis).

### g. Attempted Preparation of the Amino-terminated Diether of Hexafluorobenzene and Hexafluoropentanediol

#### (1) Reaction of Hexafluoropentanediol with Pentafluoroaniline

Pentafluoroaniline (40.9 g, 0.45 mole), hexafluoropentanediol (21.2 g, 0.1 mole), potassium hydroxide (14.0 g, 0.25 mole) and copper (I) iodide (2.1 g) were added to THF (250 ml). The reaction mixture was heated to reflux and stirred for 16 hours. After cooling, the mixture (now brown) was poured into 1 liter of distilled water. The organic layer was separated and the aqueous solution extracted with three 100-ml portions of ether. The organic phases were combined and dried over anhydrous magnesium sulfate. After filtering off the drying agent and evaporating the solvent, the reaction product was distilled under reduced pressure. After distillation of the unreacted starting material, 7 g of a residue remained. The infrared spectrum of this residue indicated that it might be the desired 1,5-bis(4-amino-tetrafluorophenoxy)hexafluoropentane.

#### (2) Reaction of Hexafluoropentanediol with N-acetylpentafluoroaniline

##### (a) With Copper (I) Iodide in Tetrahydrofuran

N-acetyl-pentafluoroaniline (9.0 g, 0.04 mole), hexafluoropentanediol (4.24 g, 0.02 mole), potassium hydroxide (2.6 g, 0.04 mole), and a catalytic amount of copper (I) iodide were added to THF (250 ml). The reaction mixture was refluxed for 24 hours. After cooling, no product had come out of solution and the solution was poured into water. Extraction of the THF-water solution yielded none of the desired product.

(b)  With Dimethylformamide

N-acetyl-pentafluoroaniline (9.0 g, 0.04 mole), hexa-
fluoropentanediol (4.24 g, 0.02 mole), potassium hydrodie (2.6 g,
0.04 mole), and DMF (250 ml) were refluxed for 24 hours. After cooling,
the solution was poured into water and an oil settled out. The oil was
dissolved in ether and dried over anhydrous magnesium sulfate. Evapora-
tion of the ether yielded a brown, viscous oil. The infrared spectrum
of this oil indicated that it might be the desired 1,5-bis(4-amino-
tetrafluorophenoxy)hexafluoropentane.

### D.  Monomers

### 1.  1-Chloro-2,4-diamino-3,5,6-trifluorobenzene

**a.** Reaction of Chloropentafluorobenzene with Aqueous Ammonia

Chloropentafluorobenzene and excess concentrated ammonium
hydroxide were reacted in a shaking autoclave at elevated temperature.
The reaction conditions are described in Table III, along with the
product yield and distribution as determined by VPC. The reaction mix-
ture was filtered, the solid products washed with water, and dried.
The products were purified by distillation followed by recrystalliza-
tion.

TABLE III

REACTIONS OF CHLOROPENTAFLUOROBENZENE
AND CONCENTRATED AMMONIUM HYDROXIDE

| Run No. | CPFB, moles | NH$_3$, moles | Reaction Conditions | | Distribution of Products by VPC Analysis, % | | | | Approximate Yield of Fluorinated Products |
|---|---|---|---|---|---|---|---|---|---|
| | | | Time, hr | Temp, °C | Peak 1 | Peak 2 | Peak 3 | Peak 4 | |
| 1 | 0.1 | 1.5 | 41 | 200 | 35* (1) | | 35 | 30 | 80 |
| 1A | --** | 1.0 | 16 | 200 | 5* | | 35 | 60 | 63 |
| 2 | 0.1 | 0.38 | 2.5 | 235 | 40 | 45 | 5 | 10 | 85 |
| 3 | 0.15 | 2.25 | 3.5 | 235 | 3 | 3 | 4 | 90 (2) | 78 |

\* Peaks not separated.

\*\* 16 g of product from Reaction 1 (approximately 0.08 mole) was used
   as starting material.

Note: All reactions run in a 200-ml autoclave.

Vapor phase chromotography indicated there were four products. The products, represented by the first two peaks on the chromatogram, [shown as (1) in Table III], were separated and purified by distillation. The mixture of these products was a solid melting at approximately 55°C. The elemental analysis of this mixture is shown below:

| Analysis of (1): | % C | % H | % Cl | % F |
|---|---|---|---|---|
| Calculated for $C_6H_2ClF_4N$: | 36.1 | 1.0 | 17.8 | 36.1 |
| Found: | 35.91 | 1.07 | 17.24 | 35.62 |

Another of the products, represented by peak 4 on the chromatogram, shown as (2) in Table III, was the principle product in one of the runs. This product was separated and purified by repeated recrystallizations from hexane. It was a solid, melting at 135°-136°C. Its elemental analysis is shown below:

| Analysis of (2): | % C | % H | % Cl | % F | % N |
|---|---|---|---|---|---|
| Calculated for $C_6H_4ClF_3N_2$: | 36.6 | 2.04 | 18.1 | 29.0 | ·14.25 |
| Found: | 37.65 | 2.41 | 17.08 | 27.52 | 15.30 |

The high carbon and hydrogen analysis is probably due to hexane contamination.

b. Preparation of a Large Amount of 1-Chloro-2,4-diamino-3,5,6-trifluorobenzene

Chloropentafluorobenzene (70 g, 0.35 mole) and 700 ml of concentrated ammonium hydroxide was heated in an autoclave at 235°C for 4 hours. After cooling, the solid product was filtered off and the aqueous mother liquor extracted with 1500 ml of diethyl ether. Upon removal of the diethyl ether, the solid residue was combined with 6 liters of hexane, which was used to extract the black tarry residue. After two separate treatments with activated charcoal, 22.3 g (33.5% yield) of product crystallized out of the benzene-ether solution as white needles, mp 134°-135°C.

2. 1-Chloro-2,4-diisocyanato-3,5,6-trifluorobenzene

a. Run 1

Ether (2000 ml) was cooled under nitrogen with a dry ice — acetone bath. Phosgene (145 g, 1.45 mole) was added in the liquid phase to the cold ether over a 10-minute period. Pyridine (100 g, 1.26 mole) dissolved in ether was added to the solution over a 1/2-hour period. 1-Chloro-2,4-diamino-3,5,6-trifluorobenzene (57.5 g, 0.29 mole) dissolved in ether was then added over a period of 45 minutes. The

solution was then stirred for 3 hours cold and 1 hour while warming to room temperature. The pyridinium chloride was filtered off and the ether evaporated on the rotary evaporator. Vacuum distillation of the product yielded 31.4 g (44%) of the diisocyanate, bp 74°-77°C/1.6 mm Hg.

| Analysis: | % C | % Cl | % F | % N |
|---|---|---|---|---|
| Calculated for $C_8ClF_3N_2O_2$: | 38.6 | 14.27 | 23.0 | 11.25 |
| Found: | 38.8 | 14.19 | 23.1 | 11.28 |

**b. Run 2**

35.7 g (36% yield)of 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene, bp 118°-120°C/7 mm, were prepared using the procedure described in run 1 above.

**3. N-Acetyl-pentafluoroaniline**

N-acetyl-pentafluoroaniline was prepared according to the method described by Brooke.*

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* Ibid.

# V. CONCLUSIONS

Excellent bonds can be made with the polyurethane adhesive system prepared by reaction of the polyether of perfluoropropylene oxide with 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene (Baglbond 420).

In the Baglbond 420 adhesive system, the optimum lap shear strengths of bonds made via the diisocyanate-polyether reaction are obtained with an isocyanate to hydroxyl ratio of 1.8:1.

In the Baglbond 420 adhesive system, the lap shear strength of bonds made from the isocyanate-terminated prepolymer were comparable to those made via the diisocyanate-polyether reaction when the NCO:OH ratio of each was 1.8:1.

The lap shear strength of bonds prepared with the Baglbond 420 adhesive system decreases with increasing molecular weight of the polyether prepolymer over the molecular weight range from 1160 to 2350.

In the Baglbond 420 adhesive system, bonds prepared with stannous octoate catalyst possess considerably greater lap shear strength than bonds prepared without catalyst.

Although fairly good bonds can be made from the polyurethane adhesive prepared by reaction of the polyether of perfluoropropylene oxide with tetrafluoro-m-phenylene diisocyanate (Baglbond 400) if catalyst is used, this adhesive system is difficult to work with due to its short pot life.

Bonds can be made using polyurethanes prepared by reaction of the polyether of hexafluorobenzene and hexafluoropentanediol with either tetrafluoro-m-phenylene diisocyanate or 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene in a ratio of 1:1.2 without catalyst, but these bonds do not possess the required strength.

The pot life of the polyurethane adhesives (Baglbond 320) prepared from 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene and the polyether of hexafluorobenzene and hexafluoropentanediol in the ratio of 1.8:1 with stannous octoate catalyst is so short that bonds cannot be prepared from it.

Isocyanate-terminated polyurethane prepolymers can be prepared conveniently by reaction of hexafluorobenzene-hexafluoropentanediol polyethers with 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene, but diol cured polyurethane adhesives prepared from them without catalyst gave low strength bonds.

Isocyanate-terminated polyurethane prepolymers can be prepared by the reaction of the hexafluorobenzene-hexafluoropentanediol polyether with tetrafluoro-m-phenylene diisocyanate, but the preparation of diol cured polyurethane adhesives (Baglbond 300) from them is difficult because of the short pot life even without a catalyst.

The one-step polymerization of perfluoropropylene oxide with perfluoroglutaryl fluoride and cesium fluoride in diglyme yields a series of fractions on distillation, only the highest boiling of which is completely diacid fluoride terminated.

The formation of polyether by reaction of hexafluorobenzene with hexafluoropentanediol and potassium hydroxide is not significantly affected by the presence or absence of water.

The reaction of hexafluorobenzene with hexafluoropentanediol and potassium hydroxide in tetrahydrofuran solution can be catalyzed by pyridine or copper (I) iodide in addition to N,N-dimethylformamide.

The reaction of hexafluorobenzene with hexafluoropentanediol and potassium hydroxide in tetrahydrofuran solution catalyzed by copper (I) iodide can yield completely hydroxyl-terminated polyethers.