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FLUORINE-CONTAINING POLYETHERS

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FOREWORD

This report was prepared by the Dow Corning Corporation under USAF Contract No. 33(616)-2417. This contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials", Task No. 73404, "Synthesis and Evaluation of New Polymers", formerly RDO No. 617-11, "Synthesis and Evaluation of New Polymers", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt A. M. Lovelace acting as project engineer.

This report covers period of work from April 1954 to April 1955.

Abstract

1. Appreciable quantities of the two monomers, $CF_3\overline{CH-CH_2O}$ and $CF_3\overline{C(CH_3)CH_2O}$ have been prepared by reactions involving the dehydrohalogenation of the corresponding halohydrins.

2. Dehydrohalogenation studies were conducted using the following halohydrins: $CClF_2CH_2OH$, CCl_2FCH_2OH, $CClF_2CHOHCCl_2F$, $CClF_2CHOHCClF_2$, and $CCl_2FCHOHCCl_2F$. The corresponding epoxides were not obtained but rather extensive decomposition of the organic reactants was observed.

3. An investigation of the hypochlorination of the olefins, $CH_2=CF_2$, $CF_3C(CH_3) = CH_2$ and $C_3F_7CH=CH_2$, is in progress. The results are inconclusive at this time.

4. The preparation of a polyglycol formal was accomplished by reaction of a fluorine-containing glycol with dibutyl formal. The material was found to be thermally unstable.

5. The polymerization of both $CF_3\overline{CHCH_2O}$ and $CF_3\overline{C(CH_3)CH_2O}$ was accomplished using ferric chloride as a catalyst. In addition, copolymers of these two monomers were prepared in a similar manner.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
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Table of Contents

List of Tables

I. Introduction

The purpose of this research is to synthesize fluorine-containing polymers of the polyether type for evaluation as sealants, rubbers, coatings and adhesives. In particular, the desired properties are thermal stability (up to 500°F), fuel and oil resistance (up to 400°F), retention of properties at -65°F, and resistance to fuming nitric acid and ozone.

II. Summary and Conclusions

In the area of monomer preparation, the two epoxides, CF_2CHCH_2O and $CF_2C(CH_3)CH_2O$, have been prepared in appreciable quantities using a multistep synthesis starting from trifluoroacetic acid. While such a procedure is feasible from a laboratory standpoint, it will be necessary to devise alternate syntheses which are more direct in order to reach a practical commercial preparation of a fluorine-containing epoxide. In this connection, studies were begun on the hypochlorination of fluorine-containing olefins with hypochlorous acid. The olefins studied to date include $CH_2=CF_2$, $C_3F_7CH=CH_2$, and $CF_2C(CH_3)=CH_2$. While the results are inconclusive at present, recent patent literature has disclosed similar reactions which would indicate the feasibility of this approach.

Another approach to the preparation of a fluorine-containing epoxide has comprised the attempted dehydrochlorination of CCl_2FCH_2OH, $CClF_2CH_2OH$, $CClF_2CHOHCClF_2$, $CCl_2FCHOHCClF_2$, and $CCl_2FCHOHCCl_2F$. These materials are readily available from reduction of the corresponding acid chloride or ketone with lithium aluminum hydride. In all cases, dehydrochlorination was unsuccessful in producing an epoxide. Extensive decomposition of the alcohols occurred with formation of both inorganic chlorides and fluorides. The implication of these results may be that a

more reactive halogen, such as bromine, is required in the molecule for epoxide formation. Consequently, the preparation of $CHF_2CHOHCF_2Br$ is in progress for use in dehydrohalogenation experiments.

In the area of polymerization, the use of Lewis acid type catalysts has been investigated. Among the materials studied were $FeCl_3$, $AlCl_3$, SO_3 and BCl_3. The results indicate that ferric chloride is the best of the group insofar as conversion and molecular weight of polymer are concerned. In the consideration of reaction rate, aluminum chloride was found to promote the highest rate of polymerization. Using ferric chloride the homopolymers and copolymers of both $CF_3\overline{CHCH_2O}$ and $CF_3\overline{C(CH_3)CH_2O}$ have been prepared. The homopolymer of the former was found to be a solid while that of the latter was a liquid. Consequently, by varying the mole ratio of the two monomers, either liquid or solid copolymers may be prepared. Further study of these systems is in progress.

Another class of polyether polymer, the polyglycol formal, has been investigated. In general, polymers of this type have been prepared by reaction of an alpha-omega glycol with dibutylformal. Extension of this reaction to a fluorine-containing glycol gave a small yield of a polyformal which was found to be thermally unstable easily reverting to the original reactants. No further work along this line is contemplated.

III. General Discussion

A survey of the literature indicated the feasibility of synthesis of fluorine-containing monomers for the preparation of polyether type polymers (see Table 1), although little information was found regarding the fluorine-containing polymers themselves. Inasmuch as polymerization of monomer epoxides appeared to offer the most expedient route, that procedure was chosen as the first method of approach to the problem.

A. Preparation of Monomers

At the start of this program, the first fluorine-containing monomer selected for polymerization studies was 3,3,3-trifluoro-1,2-epoxypropane. This material was selected because its synthesis was reported (1) and the starting materials were readily available. The procedure employed was:

a. $CF_3COCH_3 + Br_2 \xrightarrow{H_2SO_4} CF_3COCH_2Br$ (70-80%)

b. $CF_3COCH_2Br + LiAlH_4 \longrightarrow CF_3CHOHCH_2Br$ (70-75%)

c. $CF_3CHOHCH_2Br + NaOH\ (50\%\ aq.) \longrightarrow CF_3\overline{CHCH_2O}$ (80-90%)

This epoxide has been successfully synthesized many times in the course of the present work. None of the indicated steps requires further comment.

During the synthesis of the analogous epoxide, 2-methyl-3,3,3-trifluoro-1,2-epoxypropane, several interesting facts were discovered. The syntheses involved in its preparation are:

Table 1

Literature Survey

Compound	Method of Prep.	Reference
CH_2FCHCH_2O	$CH_2ClCHCH_2O$ + HF or KF	21, 22
CF_3CHCH_2O	$CF_3CHOHCH_2Br$ + NaOH	1
$C_3F_7C(CH_3)CH_2O$	$C_3F_7C(OH)(CH_3)CH_2Cl$ + NaOH	16
$CF_3CHCHFO$	$CF_3CHOHCHFBr$ + NaOH	15
CF_2CH_2O	CCl_2CH_2O + SbF_3	23
$CF_2ClCClCCl_2O$	$CF_2ClCCl = CCl_2 + O_2$	24, 25, 26
$CF_2ClCFCCl_2O$	$CF_2ClCF = CCl_2 + O_2$	24, 25, 26
CF_3CFCF_2O	$CH_2ClCHCH_2O$ + HF/elect.	27

a. $CF_3CO_2H + ROH \longrightarrow CF_3CO_2R$

b. $CF_3CO_2R + CH_3MgBr \longrightarrow CF_3C(OH)(CH_3)_2 + ROH$

c. $CF_3C(OH)(CH_3)_2 + Cl_2 \longrightarrow CF_3C(OH)(CH_2Cl)CH_3$

d. $CF_3C(OH)(CH_2Cl)CH_3 + NaOH\ (50\%\ aq.) \longrightarrow CF_3\overline{C(CH_3)CH_2O}$

It has been reported (2) that the best yields in step ''b'' are obtained when the amyl ester is employed. While that particular ester has not been used in the present work, evidence has been obtained which indicates that the yield of trifluoro-t-butanol probably is not affected so much by the molecular weight of the alkyl group in the ester, but by one of two other factors. If ''R'' is ethyl, the ethanol formed in step ''b'' azeotropes with the trifluoro-t-butanol, thus lowering the yield (and purity) of the latter --- a fact noted by Henne et. al., (6). If ''R'' is methyl, it is difficult to obtain pure ester in step ''a''. When the usual esterification procedure (3) is employed, the methyl trifluoroacetate so obtained may be contaminated with unreacted trifluoroacetic acid which azeotropes with the ester. The use of this impure ester in step ''b'' produces deleterious effects, and the yield of the fluoro-t-butanol is lowered. If the methyl ester is properly purified, it is felt that the yield will be equivalent to that obtained from the amyl ester.

Step ''c'', the chlorination of 2-methyl-3,3,3,-trifluoro-2-buatnol, does not proceed in high yield to the monochlorinated product. An extensive study of several variables has resulted in a maximum yield of 56%.

Step ''d'', epoxidation of the alcohol to 2-methyl-3,3,3-trifluoro-1,2-epoxypropane, offers no difficulty, and 80% yields were regularly obtainable.

In an effort to circumvent the over-all low yield (20% avg.) of 2-methyl-3,3,3-trifluoro-1,2-epoxypropane from the starting trifluoroacetic acid, an alternative procedure was investigated.

a. $CF_3COCH_3 + Br_2 \longrightarrow CF_3COCH_2Br$

b. $CF_3COCH_2Br + CH_3MgBr \longrightarrow CF_3C(OH)(CH_2Br)CH_3$

c. $CF_3C(OH)(CH_2Br)CH_3 + NaOH$ (50% aq.) $\longrightarrow CF_3\overline{C(CH_3)CH_2O}$

The use of this procedure produced the epoxide in over-all yield of 20%, so that nothing was gained by its use. Here, as might be expected, the yield of bromohydrin was poor (33%), possibly because of the reactivity of the labile bromine in the ketone, or because of the decreased basicity of the carbonyl oxygen. Further, the bromohydrin was not very stable with respect to heat, making its purification difficult. This approach offered no advantage over that via the chlorohydrin, and it was not studied extensively.

Other chlorofluoroalcohols were prepared for investigation as possible epoxide intermediates. These include a) 2-chloro-2,2-difluoroethanol, b) 2,2-dichloro-2-fluoroethanol, c) 1,3-dichloro-1,1,3,3,-tetrafluoro-2-propanol, d) 1,3,3-trichloro-1,1,3-trifluoro-2-propanol, and e) 1,3-difluoro-1,1,3,3,-tetrachloro-2-propanol. The first two, ''a'' and ''b'' were prepared from the chlorofluoroacids via the acid chloride followed by

reduction with lithium aluminum hydride. The latter three, ''c'', ''d'' and ''e'', were prepared by reducing the corresponding chlorofluoroacetones with lithium aluminum hydride. Attempts to epoxidize these alcohols have resulted in failure. When heated with a strong, aqueous inorganic base, or with an organic base (quinoline) the alcohols were decomposed, losing HF about as readily as HCl. No epoxide was isolated and no alcohol was recovered.

An alternative route for the preparation of fluorine-containing halohydrins has been studied briefly, and this is being continued. This involves the addition of a hypohalous acid to a fluoroolefin, according to the equation:

$$C_nF_{2n+1}CY{=}CY_2 + HOX \longrightarrow C_nF_{2n+1}CY(OH)CXY_2$$

where Y is hydrogen, an alkyl group or halogen, and X is chloride or bromide. Shortly after this work was begun, a patent (4) was issued directly relating to this reaction. However, work was continued in order that new monomers for this experimental program could be obtained.

Among the olefins selected for study in the hypohalous acid addition program were a) vinylidene fluoride, b) 2-methyl-3,3,3-trifluoropropene and c) 3,3,4,4,5,5,5-heptafluoro-1-pentene. These were chosen because they were easily preparable or obtainable (vinylidene fluoride may be purchased), and because -- with ''a'' and ''c'' at least -- they would result in new halohydrins.

The attempted preparation of 2-methyl-3,3,3-trifluoropropene by dehydration of the corresponding tertiary butanol with sulfuric acid resulted in very low yield (25%), although this method is reported to give good yields (70%) where the alcohol contains a heptafluoropropyl group (5). Because the starting material was an azeotrope of ethanol and trifluoro-t-butanol, it is not possible to state with certainty whether this was due to the impurity or to the nature of the alcohol itself. It will not be investigated further, however, because pure trifluoro-t-butanol is known to dehydrate smoothly to the olefin with phosphorus pentoxide (6) and in the future that reagent will be employed.

3,3,4,4,5,5,5-Heptafluoro-1-pentene was synthesized as follows:

a. $C_3F_7CO_2H + LiAlH_4 \longrightarrow C_3F_7CHO$

b. $C_3F_7CHO + CH_3MgBr \longrightarrow C_3F_7CHOHCH_3$

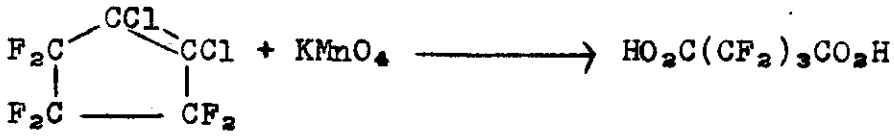
c. $C_3F_7CHOHCH_3 + P_2O_5 \longrightarrow C_3F_7CH{=}CH_2$

While steps ''a'' and ''c'' are reported (7,8,9) step ''b'' is not, although it has been used extensively in these and other laboratories. None of the steps indicated offers any untoward difficulties, and none needs any elaboration here.

Several procedures have been reported for the addition of hypohalous acids to olefins. The one chosen to start the studies in the present program was that reported by Kadesch (10), for the preparation of 1-chloro-3-butene-2-ol from butadiene.

In this procedure, a mixture of CO_2 and olefin is added to a solution of calcium hypochlorite, forming HOCl which adds to the olefin, and $CaCO_3$ which is removed by filtration. While trial runs using butadiene resulted in successful addition, no addition was achieved when the olefin used was vinylidene fluoride or heptafluoro-1-pentene. These experiments are being continued.

Two other monomers were prepared for the polyether program. These are dibutyl formal, prepared as described by Vogel (11); and 2,2,3,3,4,4-hexafluoro-1,5-pentanediol prepared by the following series of reactions (12, 13):

a. 

b. $HO_2C(CF_2)_3CO_2H + EtOH \longrightarrow EtO_2C(CF_2)_3CO_2Et$

c. $EtO_2C(CF_2)_3CO_2Et + LiAlH_4 \longrightarrow HOCH_2(CF_2)_3CH_2OH$

The diol and formal have been studied briefly in an attempt to form a polyglycol formal.

B. Preparation of Polymers

Thus far in this program, several fluorine-containing polyethers have been prepared. These are homopolymers of trifluoropropylene oxide ($CF_3\overline{CHCH_2O}$) and (trifluoromethyl)propylene oxide ($CF_3\overline{C(CH_3)CH_2O}$), and various copolymers of both oxides. Only acid catalyzed polymerization procedures have been investigated, using various Lewis acids, for the reason that basic catalysts might cause the loss of fluorine from the molecule. After

brief studies with propylene oxide (as a control) it was found that the same procedure could be extended with minor modifications to both fluorine-containing oxides, although the polymers obtained in each case were somewhat different in physical appearance.

The use of anhydrous ferric chloride in the polymerization of trifluoropropylene oxide results in the formation of a solid, amorphous polymer. The conversion of monomer to polymer with the use of that catalyst, ranges from 50-85% depending upon the concentration of catalyst. The use of aluminum chloride (in place of ferric chloride) results in almost quantitative conversions, but the polymer is a viscous liquid.

The polymerization of (trifluoromethyl)propylene oxide, on the other hand, yields only a viscous liquid polymer regardless of the catalyst. This is true, at least, with any of the catalysts thus far studied, all of which have been of the Lewis acid type. The following catalysts, listed in decreasing order of their activity toward converting monomer to polymer are: $AlCl_3 > FeCl_3 > SO_3 \gg BCl_3$. Little data are available regarding the comparative molecular weights of these polymers.

Copolymers of trifluoropropylene oxide and (trifluoromethyl)propylene oxide have been investigated briefly with promising results. Using ferric chloride catalyst and various ratios of oxides, gelatinous polymers are obtained. These polymers are of interest because they obviously have a higher

molecular weight than the polymer obtained from (trifluoromethyl)propylene oxide alone, and they contain methyl groups which enhances the probability of peroxide catalyzed cross-linking. At the present time there are not sufficient data to state whether these polymers are true copolymers, or whether they are a mixture of homopolymers, although the most likely supposition is that they are copolymers.

Several attempts have been made to increase the molecular weight of the liquid polymers obtained by the aluminum chloride catalyzed polymerization of both oxides and the ferric chloride catalyzed polymerization of (trifluoromethyl)propylene oxide. These polymers are, presumably, terminated by hydroxyl groups, and therefore, should react with acids, anhydrides, isocyanates, etc. The use of hexamethylene diisocyanate with these liquid polymers undoubtedly does increase their molecular weight (as evidenced by an apparent increase in viscosity) but the polymers remain liquids. Further work along these lines has been discontinued, pending studies now being made on the polymers to determine the structure more exactly, particularly with regard to the end groups.

Attempts to prepare a fluorine-containing polyglycol formal, after the manner described by Hill and Carrothers (14) did not appear promising. The reaction of dibutyl formal with 2,2,3,3,4,4-hexafluoro-1,5-pentanediol resulted in the formation of a high boiling liquid which decomposed on long standing, or heating at atmospheric pressure, liberating formaldehyde and the original glycol. Presumably the product was a monomeric or dimeric cyclic formal.

IV. Experimental

A. Preparation of Monomers

1-Bromo-3,3,3-trifluoroacetone (1)

1,1,1-Trifluoroacetone (846g., 7.5 moles) was dissolved in 2000 ml. of concentrated sulfuric acid and bromine (600g., 3.75 moles) was added over a 6 hour period. The product was separated by heating the acid mixture until no further distillation occurred. After refluxing the distillate for 2-3 hours to remove dissolved gases, it was rectified through a Todd column (12 mm. barrel packed with 1/8'' glass helices) to obtain 1054g. (5.5 moles, 73%) of 1-bromo-3,3,3-trifluoroacetone, b.p. 85-88°C, n_D^{25} 1.3765.

3,3,3-Trifluoro-1,2-epoxypropane (1)

1-Bromo-3,3,3-trifluoroacetone (274 g., 1.43 moles) was reduced with an ice cold, ethereal solution of lithium aluminum hydride (16.3 g., 0.43 mole) in the usual manner. After hydrolysis and separation, the ether was removed by distillation, and the remaining residue was dried over Drierite. The dried material was distilled in a Todd column (12 mm. barrel, filled with Heli-pak packing) to remove material boiling up to 90°C, then the residue in the pot--mostly 1-bromo-3,3,3-trifluoro-2-propanol--was added to 600 g. of hot (95-100°C) 50% aqueous sodium hydroxide solution (see the procedure (15) used for the preparation of 1,3,3,3-tetrafluoro-1,2-epoxypropane). The

volatile product was collected in an ice-cooled trap, dried by chilling to -70°C and decanting from the resulting ice, then distilled from 1-2 g. of calcium hydride through a Todd column (12 mm barrel filled with Heli-pak packing). There was obtained 88 g. (0.79 mole, 55% based on the bromoketone) of 3,3,3-trifluoro-1,2-epoxypropane, b.p. 39.5-40.5°C $n_D^{25} < 1.3$.

Ethyl and Methyl Trifluoroacetates(3)

These were prepared as described in the reference, except that distillation from phosphorous pentoxide was omitted.

2-Methyl-1,1,1-trifluoro-2-propanol (6)

A. Methyl magnesium bromide was prepared in a 5 l. 3-necked flask in the usual manner from methyl bromide and magnesium (134 g., 5.5 moles). Methyl trifluoroacetate (322 g., 2.5 moles) in ether was added to the ice cold Grignard solution over a 5 hour period. The excess reagent was destroyed by the addition of water, and ice-cold 30% sulfuric acid (1900 g.) was added to hydrolyze the complex. The organic portion was separated and dried over Drierite, then the ether was removed by distillation. Rectification of the residue through a Todd column (12 mm. barrel packed with 1/8'' glass helices) yielded 2-methyl-1,1,1-trifluoro-2-propanol (187 g., 1.46 moles, 59% yield), b.p. 80-82°C, n_D^{25} 1.3329.

B. The use of ethyl trifluoroacetate in the above procedure resulted in a product, b.p. 79.5-81.0°C, n_D^{25} 1.3401, apparently an azeotrope of the desired alcohol and ethanol.

3-Chloro-2-methyl-1,1,1-trifluoro-2-propanol

A. The procedure employed was similar to that reported by McBee, Pierce, and Marzluff (16).

The chlorination apparatus consisted of a vertical tube 51 mm. in diameter and 600 mm. in length sealed at the lower end. A heating element of nichrome ribbon was wrapped around the lower 150 mm. of the tube. The upper end was sealed with a neoprene stopper through which the following were fitted: a condenser connected to a Dry Ice-cooled trap, a thermometer well, a helical cooling coil, and a gas dispersion disc. The latter three extended to the bottom quarter of the tube. Chlorine was fed to the dispersion disc through a system comprised of a Dry Ice-cooled trap, safety bottle, bubbler containing concentrated sulfuric acid and another safety bottle. An eight watt germicidal ultraviolet bulb was used for catalytic illumination.

A solution was prepared containing 110 ml. of 2-methyl-1,1,1-trifluoro-2-propanol (128 g., 1.0 mole) and 220 ml. of carbon tetrachloride (395 g., 2.24 moles). This was placed in the reactor and heated to 65°C. The chlorine, (65 g., 0.915 mole) was weighed into a cold trap, then connected to the feed system. The rate of chlorine addition was controlled by partially withdrawing this trap from a Dewar flask. The chlorine addition was carried out during a seven hour period and the reaction temperature was maintained between 60-75°C.

Initially the reaction mixture remained colorless but it slowly developed a green color.

After completing the chlorine addition a stream of dry nitrogen was passed through the solution for six hours. This product was fractionated through a Todd column (12 mm barrel, packed with 1/8'' glass helices). There was obtained 46 g. (0.283 mole, 28.3%) of 2-methyl-3-chloro-1,1,1-trifluoro-2-propanol (b.p. 112-114°C, n_D^{25} 1.3740, specific gravity $\frac{25}{4}$ 1.387, M_R^D calc. 26.2, found 26.0)).

B. Using the same procedure, but with no solvent (which permits higher reaction temperature) and an improved ultraviolet light source (G.E. ''Black Light'', 8 watts) maximum chlorination yields of 56% have been obtained.

3-Bromo-2-methyl-1,1,1-trifluoro-2-propanol

Methyl magnesium bromide (2.0 moles in 1200 ml. of ether) was prepared in the usual way and added to 3-bromo-1,1,1-trifluoro-acetone (191 g., 1.0 mole) over a 3 hour period. After standing several hours, the excess Grignard reagent was destroyed with water and the complex was hydrolyzed by the addition of 500 ml. of ice cold 40% sulfuric acid solution. The organic layer was separated and dried over Drierite, then the ether was removed by distillation. Rectification of the residue through a Todd column (12 mm. barrel packed with 1/8'' glass helices) yielded 69 g. (0.33 mole, 33% yield) of 3-bromo-2-methyl-1,1,1-trifluoro-2-propanol, b.p. 122-5°C, n_D^{25} 1.3981. The product had a brown color, apparently caused by decomposition within the column.

2-Methyl-3,3,3-trifluoro-1,2-epoxypropane

A. This material was prepared in the same manner as 3,3,3-trifluoro-1,2-epoxypropane. 3-Chloro-2-methyl-1,1,1-trifluoro-2-propanol (164 g., 1.0 mole) was added to 200 g., of a 50% solution of NaOH. After drying and distilling, there was obtained 98 g. (0.78 mole, 78% yield) of 2-methyl-3,3,3-trifluoro-1,2-epoxypropane, b.p. 56.0°C, n_D^{25} 1.3125, M_R^D calc. 20.4, found 20.4.

B. The use of 3-bromo-2-methyl-1,1,1-trifluoro-2-propanol in the above procedure gave the same yield of epoxide.

2-Chloro-2,2-difluoroethanol

Chlorodifluoroacetic acid (130g., 1.0 mole, b.p. 121.5°C, obtained from the General Chemical Company) was converted to its acid chloride by reaction with benzoyl chloride (423 g.) after the manner described by Brown (17). The acid was added dropwise to the hot (150-60°C) benzoyl chloride during which time chlorodifluoroacetyl chloride distilled from the mixture. After addition was completed, the reaction mixture was heated to 180-90°C to force residual chloride from solution. The acid chloride was purified by distillation (b.r. 32-37°C, reported (18) b.p. 34°C) to obtain 107 g. (0.72 mole, 72%) of chlorodifluoroacetyl chloride.

Reduction of the acid chloride was achieved with lithium aluminum hydride (30 g., 0.8 mole) in the usual manner. The ethereal solution of the reaction product was dried over anhydrous sodium sulfate, then the ether was

removed by distillation. An attempt to dry the residue further with calcium hydride resulted in the formation of a salt, indicating the alcohol was acidic. Rectification of the dried material yielded 62 g. (0.54 mole, 75% on the basis of acid chloride, 54% on the basis of the original acid) of 2-chloro-2,2-difluoroethanol, b.p. 95-96°C, n_D^{25} 1.3585, M_R^D calc. 17.8, found 18.3.

2,2-Dichloro-2-fluoroethanol

Dichlorofluoroacetic acid (147 g., 1.0 mole, b.p. 162-3°C. obtained from the General Chemical Company) was converted to the acid chloride by reaction with benzoyl chloride using the same procedure described for the preparation of chlorodifluoroacetyl chloride. The yield of dichlorofluoroacetyl chloride (b.r. 70-90°C, reported (19) b.p. 75°C) was low (0.42 mole, 42%) and the material was quite impure.

Reduction of the acid chloride was accomplished with lithium aluminum hydride (10% excess). After hydrolysis and separation, the ethereal solution of product was dried over Drierite and then the ether was removed by distillation. Rectification of the residue yielded 30 g. (0.23 mole, 54% on the basis of acid chloride, 23% on the basis of the original acid) of 2,2-dichloro-2-fluoroethanol, b.p. 119-123°C, n_D^{25} 1.4155 M_R^D calc. 22.7, found 23.7.

1,3-Dichloro-1,1,3,3-tetrafluoro-2-propanol

1,3-Dichloro-1,1,3,3-tetrafluoroacetone (96 g., 0.48 mole b.p. 45-49°C, obtained from the General Chemical Company) was reduced with lithium aluminum hydride (5.0 g., 0.13 mole). After hydrolysis and separation, the ethereal solution of product was dried over anhydrous sodium sulfate. The ether was removed by distillation, and the residue was further dried over a large quantity of Drierite. Rectification of the dried material yielded 45 g. (0.22 mole, 47%) of 1,3-dichloro-1,1,3,3-tetrafluoro-2-propanol, b.p. 113.5-114.0°C, n_D^{25} 1.3721, M_R^D calc. 27.4, found 30.2.

1,3-Difluoro-1,1,3,3-tetrachloro-2-propanol

1,3-Difluoro-1,1,3,3-tetrachloroacetone (116 g., 0.5 mole, b.p. 105-8°C, obtained from the General Chemical Company) was reduced with lithium aluminum hydride (6 g., 0.13 mole) in the same manner as its dichlorotetrafluoro analog. There was obtained 91 g. (0.38 mole, 78%) of 1,3-difluoro-1,1,3,3-tetrachloro-2-propanol, b.p. 77.0-78.0°C /20 mm Hg, n_D^{25} 1.4578, M_R^D calc. 37.0, found 37.4.

Attempted Epoxidation of 1,3-Dichloro-1,1,3,3-tetrafluoro-2-propanol with Aqueous NaOH

A 1000 ml., 3-necked flask was equipped with a motor driven stirrer, addition funnel and thermometer well. The thermometer well was equipped with a side arm to allow gasses to escape, and this side arm was attached to a Dry-Ice-cooled trap.

A 50% aqueous solution of NaOH (500 g. of solution) was placed in the flask and heated to 95-100°C. 1,3-Dichloro-1,1,3,3-tetrafluoro-2-propanol (40.0 g.) was placed in the addition funnel and added slowly to the hot solution. After the addition of a few ml. of alcohol, the pot temperature rose spontaneously to 118°C, and subsequent addition was made without external heating. Nevertheless, the temperature of the reaction medium continued to rise, reaching a maximum of 135°C. After addition was complete, the contents of the flask were maintained at 120°C for several hours, then the reaction was discontinued. At this point the flask contained a white solid suspended in a liquid medium, and the cold trap contained a large amount of solid and 2-3 ml. of liquid.

The contents of the cold trap were separated by filtering quickly, and the solid was allowed to melt. The liquid thus formed was found to be water. The liquid filtrate was dried with calcium hydride, and distilled. While a distillate was obtained, the distillation apparatus was so large relative to the quantity of distillate that the thermometer was not wetted and the temperature of the distillate thus could not be obtained. This distillate was placed in a small vial, and sealed with paraffin. In spite of these precautions, the sample evaporated before any attempts to identify it could be made.

The strongly basic suspension in the original reaction flask was diluted with water to a volume of 2000 ml., whereupon most of the solid dissolved. This material was then placed in a continuous extraction apparatus, and extracted with ether for 40 hours, after which the aqueous portion was filtered from undissolved solids and discarded. The solid material was identified as sodium fluoride. (NaF is soluble only to the extent of 4-5 g. per 100 ml. of water -- it is much less soluble in water which contains large amounts of NaOH and NaCl. This explains its failure to dissolve in the first dilution).

The ethereal extract was distilled. After removal of all of the ether only 2-3 ml. of liquid remained. This residue was strongly basic, and further evaporation on a steam bath yielded a hygroscopic solid. Probably this was NaOH, extracted by the wet ether.

No epoxide was isolated, nor is it likely that any epoxide was formed as the result of the reaction. The low boiling liquid in the cold trap could hardly have been the desired epoxide, because of its volatility. The most logical conclusion is that the alcohol was completely decomposed by the strong, aqueous base.

Attempted Epoxidation of 1,3,3-Trichloro-1,1,3-trifluoro-2-propanol with Quinoline

The same apparatus was employed as described in the preceding experiment. Quinoline (140 g.) was placed in the flask, the apparatus was evacuated to a pressure of 100 mm Hg., and the quinoline was heated to 75°C. 1,3,3-Trichloro-1,1,3-tri-

fluoro-2-propanol (60g.) was added slowly from the addition funnel. No apparent reaction occurred, and no condensate was found in the cold trap. The temperature was raised slowly to 190°C, at which point a vigorous reaction occurred. The pot temperature rose spontaneously to 230°C, and white fumes were evolved. When reaction subsided, the cold trap was found to contain a mixture of quinoline and quinoline-HX salt. The material in the reaction flask was viscous and black, and on cooling it set to a solid, tarry mass. As in the case of the dichlorotetrafluoro analog with aqueous base it seems apparent that the alcohol was completely decomposed by the quinoline, the acids thus formed catalyzing the polymerization of the organic base.

Attempted Epoxidation of 1,3,-Difluoro-1,1,3,3-tetrachloro-2-propanol with Quinoline

Because in the previous experiment no reaction occurred below 190°C, at which time all of the reactants were in solution, it was felt that the slow addition of alcohol to hot quinoline might produce the epoxide (in this case 1,3-difluoro-1,3,3-trichloro-1,2-epoxypropane) which would distill from the mixture immediately. In this way, prolonged contact with the base would be avoided, and the opportunity for decomposition would be lessened. Accordingly, the thermometer well of the apparatus was replaced by a steam-heated reflux condenser, with the open end connected to the cold trap.

Quinoline (200 g.) was placed in the flask and heated until it refluxed slowly. The alcohol (91 g.) was added dropwise from the addition funnel. During addition the viscosity of the quinoline appeared to increase somewhat, and the reaction mixture occasionally gave off fumes indicating decomposition was occurring. When alcohol addition was complete, heating was continued for 1/2 hour. Upon cooling, the reaction mixture was a solid tarry mass.

A small amount of solid was found in the cold trap. At room temperature, this material was liquid (ca. 5 ml) which formed two layers. The lower layer, about half of the material, was identified as quinoline. The upper layer was lost during transfer, but it seems unlikely that this material could have been the desired epoxide because of its density, which was less than quinoline.

2-Methyl-3,3,3-trifluoropropene

The procedure used in this experiment was similar to that described by McBee, Pierce and Chen (5). The alcohol employed was an azeotrope of 2-methyl-3,3,3-trifluoro-2-propanol with ethanol. From 300 g. of this azeotrope and 1150 g. of concentrated sulfuric acid at 90-165°C there was obtained about 150 ml. of impure product. After thorough washing to remove SO_2 followed by distillation, 40 g. (0.36 mole, 24% based on the assumption that the starting material was two thirds trifluoro-t-butanol and one third ethanol as approximated from its refractive index) of 2-methyl-3,3,3-trifluoropropene was obtained, b.p. 6-7°C (6).

2,2,3,3,4,4,4-Heptafluorobutyraldehyde

The procedure used in this experiment was the same as that described in the literature (7,8) except that ethyl acetate was used to destroy excess lithium aluminum hydride. From 642 g. (3.0 moles) of heptafluorobutyric acid and 78 g. (2.0 moles) of lithium aluminum hydride there was obtained 271 g. (1.37 moles, 46%) of heptafluorobutyraldehyde, distilled from its aldehydrol and concentrated sulfuric acid.

3,3,4,4,5,5,5-Heptafluoro-2-pentanol

A three liter, three-necked flask was fitted with a cold-finger condenser, power-driven Hershberg-type stirrer, and a dropping funnel. Two moles of methyl magnesium bromide in 1200 ml. of ether was prepared in the flask in the conventional manner. 2,2,3,3,4,4,4-Heptafluorobutyraldehyde (271 g., 1.37 moles) dissolved in an equal volume of ether was added through the dropping funnel over a four hour period. (Because the Grignard reagent is a sufficiently strong base to polymerize the aldehyde, it was necessary to stir cautiously during the addition to prevent spattering with resultant plugging of the funnel). After completing the addition the reaction mixture was stirred for one hour, then poured onto a mixture of 200 g. of conc. H_2SO_4 and 1600 g. of crushed ice. The ether layer was separated and the aqueous layer extracted with three 400 ml. portions of ether. The ether solution was dried over Na_2SO_4, then the ether was removed by distillation through a one foot Vigreaux column. The remaining liquid was dried first over Drierite then over calcium hydride.

Fractionation through a Todd column, (12 mm. barrel packed with 1/8'' glass helices) yielded 153 g. (0.72 mole, 53%) of 3,3,4,4,5,5,5-heptafluoro-2-pentanol, b.p. 101-2°C (20).

3,3,4,4,5,5,5-Heptafluoro-1-pentene (9)

3,3,4,4,5,5,5-Heptafluoro-2-pentanol (153 g., 0.72 mole) was mixed with phosphorus pentoxide (150 g., 1.07 moles) and heated to 190-200°C. The olefin (117 g., 0.60 mole, 84%) was distilled from the mixture, b.p. 31°C.

Hypochlorination Studies

The procedure of Kadesch (10) was used throughout these experiments.

A. Hypochlorination of Butadiene

The reaction was carried out in a five-liter, three-necked flask, fitted with a Dry Ice-cooled cold-finger condenser, anchor-type stirrer, and gas inlet tube. The latter was connected by means of appropriate connections to a butadiene cylinder and a carbon dioxide cylinder. Two bubblers were interposed between the cylinders and inlet tube to indicate the rate of flow of each gas stream. The reaction flask was cooled with a salt-ice bath to maintain the reaction temperature near 0°C.

Calcium hypochlorite (140 g., 2.9 moles of Cl) was dissolved in 3850 g. of water and the solution was cooled to 0°C. Simultaneous streams of CO_2 and butadiene were passed into this solution with the carbon dioxide entering approximately six times as fast as the butadiene. After four hours, a test for free chlorine with a potassium iodide - starch solution indicated no free chlorine. Only 72 g. (1.33 moles) of butadiene had been added.

The reaction mixture was filtered from $CaCO_3$, and the clear filtrate was extracted with four 400 ml. portions of ether. The ethereal solution was dried over Na_2SO_4, then over $CaSO_4$. The ether was removed by distillation, leaving 28 g. of high boiling residue, presumably the mixed chlorohydroxybutenes. No further purification or characterization seemed appropriate.

B. Hypochlorination of Butadiene

A repeat of the above procedure using the same amount of calcium hypochlorite but a great excess of butadiene (360 g., 6.6 moles) yielded 43 g. of impure products.

C. Hypochlorination of Vinylidene Fluoride

A 3.5% solution of calcium hypochlorite in water was prepared (150 g. in 4130 g. of water) and a 200% excess of vinylidene fluoride (675 g., 10.5 moles) was added along with CO_2 in the manner previously described, over a seven hour period. The reaction mixture was filtered and extracted, then the ether was distilled from the extract. A residue was obtained which was too small (less than 10 g.) to warrant further purification.

D. Hypochlorination of 3,3,4,4,5,5,5-Heptafluoro-1-pentene

A 3% aqueous solution of calcium hypochlorite (38g. in 1210g. of H_2O) was prepared and cooled to 0°. 3,3,4,4,5,5,5-Heptafluoro-1-pentene (117g., 0.59 moles) was added and then a stream of CO_2 passed through the two-phased mixture. After four hours the solution was homogeneous. However, after extraction with carbon tetrachloride and subsequent distillation of this solvent, no product was obtained, and no olefin was recovered. The most likely assumption is that addition failed to occur, and the prolonged CO_2 sweep removed the olefin from the reaction mixture.

Dibutyl Formal

The procedure followed in this preparation was similar to that described by Vogel (11).

Paraformaldehyde (30g.), n-butanol (148g., 2.0 moles) and anhydrous $FeCl_3$ (4g.) were mixed and heated to reflux. After about 16 hours, the mixture was cooled and the water layer was removed. The organic layer was washed once with a 10% solution of Na_2CO_3, then several times with a solution made by mixing 40 ml. of 6% H_2O_2 with 5 ml. of 10% Na_2CO_3, and finally with water. After drying over anhydrous K_2CO_3, the material was distilled from CaH_2 through a Todd column (12 mm. barrel filled with Heli-Pak) to obtain 20g. of unreacted n-butanol and 93 g. (0.58 mole, 67% yield) of n-butyl formal, b.p. 182°C, n_D^{25} 1.4040.

2,2,3,3,4,4-Hexafluoro-1,5-pentanediol

1,2-Dichlorohexafluorocyclopentene (490 g., 2.0 moles) was suspended in 600 ml. of water by means of vigorous stirring, and oxidized by the portionwise addition of potassium permanganate (12). The resulting mixture was allowed to reflux for 24 hours, then it was cooled and filtered from the voluminous precipitate of manganese dioxide. The filter cake was washed several times with water, and the combined washing and filtrate were decolorized by the addition of a small amount of sodium bisulfite, then concentrated by evaporation to a volume of about 500 ml. The concentrated solution was acidified with 200 ml. of 96% sulfuric acid, and placed in a continuous extraction apparatus. After three days of extraction with ether, the aqueous portion was discarded. Ether was removed from the extract by distillation,

and the residue was dried by azeotropic distillation with benzene. The resulting crude hexafluoroglutaric acid was mixed with 95% ethanol (485 g.), benzene (500 ml.) and concentrated sulfuric acid (5 ml.), then refluxed with continuous removal of the benzene-alcohol-water azeotrope. When esterification was complete the excess alcohol and benzene were removed by distilling at atmospheric pressure, and the crude diethyl hexafluoroglutarate was distilled at reduced pressure through a short Vigreaux column. There was obtained 352 g. (1.19 moles, 59% based on the starting cyclopentene) of product; b.p. 64-72°C/1 mm., n_D^{25} 1.3575.

The diethyl hexafluoroglutarate was reduced by dissolving in an equal volume of anhydrous ether and adding the solution to lithium aluminum hydride (68.5 g., 1.8 moles) dissolved in 1500 ml. of ice-cold anhydrous ether. After working up the mixture in the usual manner there was obtained 249 g., (1.18 moles, 58% based on starting olefin, 99% based on diethyl hexafluoroglutarate) of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol; m.p. 76.5-78.0°C (13).

B. Preparation of Polymers

Apparatus

The apparatus in which all epoxide polymerizations were conducted is shown in Figure 1. The bottles containing the charge were placed in the safety tubes which were then fastened to the sample wheel. This wheel was rotated inside the box, which was heated by means of thermostatically controlled electrical heaters.

Procedure

All polymerizations were conducted in ordinary Coke bottles, carefully cleaned and dried before use. The bottle was flushed with dry nitrogen and weighed with its cap, the latter being fitted with a Teflon liner (0.003'' thickness) to prevent erosion of the cork. Solid catalyst was weighed into a dry test tube, then charged to the bottle. Liquid catalyst was pipetted directly into the bottle. After charging the catalyst, the oxide was pipetted into the bottle which was then capped, weighed, placed in the constant temperature air bath and tumbled for a desired length of time at 80°-90°C. The bottle was then removed from the apparatus and weighed to determine loss incurred through leakage. Unused monomer was removed by applying vacuum from a water aspirator, a cold trap being interposed between the flask and pump to collect the oxide for subsequent purification and re-use. The bottle with its contents and cap was weighed once again.

Conversions were calculated by dividing the weight of the polymer obtained, by the weight of monomer charged.

Polymerization of Propylene Oxide

A. Preparation of Catalyst ($FeCl_3$-Propylene Oxide Complex)

1. Anhydrous $FeCl_3$ (15g.) was dissolved in ca. 100 ml. of dry ether, and 25 ml. of propylene oxide was added over a 40 minute period with efficient stirring. During addition and subsequent distillation a dry, nitrogen atmosphere was maintained in the equipment (Nitrogen was used because it

was more convenient--the primary requirement is dryness). When refluxing had subsided, the ether was removed by distillation at atmospheric pressure, leaving a syrupy liquid which was dissolved in acetone and filtered through a plug of glass wool. Water was added to the filtrate until precipitation was complete, and the resulting solid was filtered with suction and air-dried at 50°C on a clay plate.

2. The same procedure was used as in Part 1 above, except that after filtering the acetone solution was removed from the filtrate by distillation at atmospheric pressure. Distillation was stopped when the pot temperature reached 80°C. The resulting syrupy liquid ($FeCl_3$-propylene oxide complex) was used without further treatment.

B. Polymer Purification

The polymer was removed from the bottle by repeated washings with hot n-hexane. Syrupy phosphoric acid was added to hydrolyze the polymer-$FeCl_3$ complex and precipitate iron salts, and the mixture was heated until all the polymer had dissolved, then anhydrous calcium sulfate, Nu-Char decolorizing charcoal, and Filter-Aid were added and the hot mixture was filtered. When the filtrate was chilled to 0°C, solid polymer precipitated, which was recovered by filtering. Evaporation of the hexane filtrate resulted in the recovery of additional polymer in the form of a heavy, dark-colored oil.

C. Experimental Data

These data are summarized in Table 2. It is evident that the $FeCl_3$-propylene oxide catalyst prepared according to the first procedure described above was not effective in the polymerization of propylene oxide. The use of the catalyst prepared according to the second procedure proved successful. It can be seen that the conversion of monomer to polymer is dependent upon the concentration of the catalyst. However, no attempt was made to determine the upper limit of catalyst concentration.

Table 2

Polymerization of Propylene Oxide (25 ml $CH_3\overline{CHCH_2O}$, 24 hours at 80-90°C)

Prepn. of Catalyst	Amount of Catalyst	Wt. Polymer(g)	% Conversion
Procedure 1	0.2g.	<1	<5
Procedure 1	0.2g.	<1	<5
Procedure 1	0.3g.	<1	<5
Procedure 1	0.3g.	<1	<5
Procedure 1	0.4g.	<1	<5
Procedure 1	0.4g.	<1	<5
Procedure 2	0.1 ml.	<1	<5
Procedure 2	0.2 ml.	2	9.6
Procedure 2	0.3 ml.	4	19.2
Procedure 2	0.4 ml.	10	48.2
Procedure 2	0.5 ml.	10	48.2
Procedure 2	0.6 ml.	15	72.3

Polymerization of 3,3,3-Trifluoro-1,2-Epoxypropane Using Ferric Chloride Catalyst

A. Catalyst

1. In the few instances where an $FeCl_3$-propylene oxide catalyst was used, it was prepared according to the second procedure described for the preparation of the propylene oxide catalyst.

2. Anhydrous ferric chloride (Fisher's C.P. grade) was used, for most of these polymerizations. It was used without further purification.

B. Polymer Purification

Polytrifluoropropylene oxide is not soluble in hexane. For this reason, alternative procedures were selected.

1. The polymer was dissolved in an excess of hot acetone acidified with 1 ml. of concentrated HCl per 100 ml. of acetone. The resulting solution was concentrated to a small volume by evaporation, then it was chilled and diluted to 8 or 10 times its volume with water. The solid polymer thus obtained was filtered and dried in a vacuum oven for several hours at 100°C. If the polymer was colored the above procedure was repeated, although the use of HCl in the acetone was unnecessary.

2. The polymer was dissolved in an excess of hot acetone acidified with 1 ml. of concentrated HCl per 100 ml. of acetone. The resulting solution was saturated with anhydrous ammonia to precipitate iron salts. The precipitate was filtered and washed with hot acetone several times. The filtrate and washings were concentrated to a small volume by evaporation, and treated as in procedure (1).

C. Experimental Data

Preliminary experiments showed that the $FeCl_3$-propylene oxide complex was not a suitable catalyst for the polymerization of 3,3,3-trifluoro-1,2-epoxypropane. Such a complex is required for propylene oxide polymerization, because that oxide reacts vigorously with anhydrous $FeCl_3$ at room temperature. Consequently, propylene oxide is complexed with $FeCl_3$ in ether solution before use. However, the reaction of 3,3,3-trifluoro-1,2-epoxypropane with anhydrous $FeCl_3$ is much less vigorous; probably because the fluorine-containing oxide is less basic than propylene oxide. The use of anhydrous $FeCl_3$ was found to be satisfactory in promoting the polymerization of the fluorine-containing oxide, as shown in Table 3 which lists the results of preliminary experiments.

Table 3

Polymerization of 3,3,3-Trifluoro-1,2-epoxypropane
(10 ml. of the oxide, 24 hours at 80°-90°C).

Catalyst	Amount of Catalyst	Wt. Polymer (g.)	% Conversion
$FeCl_3$-P.O.[a]	0.3 ml.	<1[b]	<8
$FeCl_3$-P.O.[a]	0.5 ml.	2	16
$FeCl_3$-P.O.[a]	1.0 ml.	2	16
$FeCl_3$	0.05 g.	<1[c]	<8
$FeCl_3$	0.10 g.	6	50
$FeCl_3$	0.15 g.	8	67
$FeCl_3$	0.15 g.	<1	<8[d]
$FeCl_3$	0.30 g.	5	41[d]
$FeCl_3$	0.45 g.	8	67[d]

a. Activity of this catalyst checked against a control of propylene oxide.
b. No additional polymerization after 60 hours.
c. No additional polymerization after 48 hours.
d. Impure oxide used, which may account for low conversions at low concentrations of catalyst.

Following the results of the preliminary experiments, numerous tests were made to determine the effect of varying the concentration of catalysts. The results of all those tests are summarized in Table 4, and shown graphically in Figure 2.

Table 4

Composite Results for the Polymerization of 3,3,3-Trifluoro 1,2-epoxypropane with Anhydrous $FeCl_3$ (Ca. 12g. oxide, 80-90°C, 24 hours)

Wt. $FeCl_3$(g.)	% $FeCl_3$ (approx.)	% Conversion[a]	Remarks
0.10	1	54	These results were obtained with pure oxide and are reproducible. The polymer was pulpy and felt almost dry.
0.10	1	50	
0.15	1	69	
0.20	2	64	
0.30	2	73	
0.40	3	88	
1.0[b]	5	80	
0.15	1	8	These results were obtained with impure oxide. The polymer was waxier than those from pure monomer.
0.30	2	40	
0.45	4	65	

a. These figures are the average of several runs.
b. 20 g. of oxide.

Two facts are apparent:

1. The percent conversion increases with the amount of catalyst present (up to 5%) regardless of the purity of the monomer.

2. In those instances where conversions do not compare for similar amounts of catalyst, the purity of the monomer is not the same. However, the effect of the impurity may be overcome by increasing the amount of catalyst.

D. Physical Characteristics of the Polymer

1. The polymer after purification is a white, amorphous solid. Various batches thus far prepared have varied in consistency from a waxy substance to a dry, tough material.

2. Qualitative solubility tests on the polymer are as follows:

Soluble in: acetone, ethyl acetate

Slightly soluble in: Hexane, EtOH, MeOH, Et_2O

Insoluble in: $CHCl_3$, CCl_4, CH_2Cl_2, C_6H_6, MeC_6H_5, trichloroethylene, H_2O

3. The behavior of the polymer on heating has been found to vary from batch to batch, as might be expected. The data given below may be considered representative although in one preparation final liquefaction did not occur before 205°.

a. No visible change up to about 65°C

b. Material softens between 65°-80°C

c. No change in shape up to 90°C

d. Liquefaction occurs between 90°-120°C

E. Analytical Data

The polymer should analyze in a manner identical to the monomer, as indeed is the case.

For $(C_3H_3OF_3)_x$

Calc. % F = 50.8, found 50.5

No molecular weight data are as yet available.

Polymerization of 3,3,3-Trifluoro-1,2-epoxypropane Using Aluminum Chloride Catalyst

A. Catalyst

The catalyst used was Baker's C.P. aluminum chloride.

B. Polymer Purification

The polymer was purified using the second procedure described in the preceding section for the purification of polymer obtained with $FeCl_3$ catalyst.

Table 5

Polymerization of 3,3,3-Trifluoro-1,2-epoxypropane with Aluminum Chloride (80-90°C, 24 hours)

Wt. Oxide(g.)	Wt. $AlCl_3$(g.)	% Conversion	Intrinsic Viscosity(μ)
18.0	0.1	83[a]	0.040
17.0	0.2	91[a]	0.035
13.0	0.1	~100[b]	-----
13.0	0.2	~100[b]	-----

a. Purified polymer
b. Crude polymer

C. Experimental Data

These are given in Table 5. It can be seen that conversions are nearly 100% in all cases, showing that aluminum chloride is an effective catalyst.

D. Physical Properties of the Polymer

The polymer is a liquid. A comparison of intrinsic viscosities (acetone solution) shows it has a much lower molecular weight than the polymer obtained with ferric chloride catalysis.

Polymerization of 2-Methyl-3,3,3-trifluoro-1,2-epoxypropane Using Ferric Chloride Catalyst

A. Catalyst

The catalyst used was Fisher's C.P. anhydrous ferric chloride, except in the few cases where an $FeCl_3$-propylene oxide complex was employed. The latter was prepared according to the second procedure listed for the preparation of the propylene oxide catalyst.

B. Polymer Purification

The same methods used for the purification of $(CF_3CHCH_2O)_x$ were used in these studies.

C. Experimental Data

As in the case of the analogous oxide $CF_3\overline{CHCH_2O}$, preliminary tests showed that the use of $FeCl_3$-propylene oxide complex failed to cause polymerization; but that the direct use of anhydrous ferric chloride was successful.

The results of numerous experiments conducted are summarized in Table 6, and shown graphically in Figure 3.

Table 6

Composite Results for the Polymerization of 2-Methyl-3,3,3-trifluoro-1,2-epoxypropane with Anhydrous $FeCl_3$ (ca. 12 g. oxide, 80-90°C, 24 hours)

Wt. of $FeCl_3$ (g.)	% $FeCl_3$	% Conv.	Remarks
.05	.4	6	Impure oxide
.10	.9	26	Impure oxide
.12	1.0	9	Refractionated oxide
.12	1.1	4	Oxide fractionated once
.15	1.3	23	Impure oxide
.24	2.0	31	Oxide fractionated once
.24	2.0	45	Refractionated oxide
.24	2.1	27	Oxide fractionated once
.25	2.0	61[a]	
.50	4.0	66	
.50	4.0	69[a]	Refractionated oxide
.70	6.0	77[a]	
.70	6.0	75	
.72	6.0	62[b]	

a. Heating period 64 hours.
b. Average of three runs.

From Table 6 it can be seen that the rate of polymerization of this oxide is considerably slower than that of 3,3,3-trifluoro-1,2-epoxypropane. This is shown by the fact that comparable conversions are obtained only after 64 hours at 80-90°C, whereas 24 hours is sufficient for 3,3,3-trifluoro-1,2-epoxypropane. In either case, the purity of the monomer is important, impure oxides lower the conversion.

D. Physical Characteristics of the Polymer

The polymer after purification is a brownish oil, regardless of the amount of catalyst used. This oil has a viscosity-temperature slope similar to a mineral oil, and has a specific gravity of 1.3 (approx.).

E. Analytical Data

The polymer should analyze in a manner identical to the monomer. That it does not may be due to incomplete decomposition of the analytical sample or other factors not yet understood. Samples have been prepared for spectroscopic study, but no data are available on those samples at this writing.

For $(C_4H_5OF_3)_x$

Calc./% F = 45.2, found 42.7

Molecular weight data have been obtained by the method of boiling point elevation of an acetone solution on what were considered to be representative samples. From this method, average values of 980 were obtained. However, the method cannot be considered accurate.

A comparison of this polymer with that obtained by the ferric chloride or aluminum chloride catalyzed polymerizations of 3,3,3-trifluoro-1,2-epoxypropane, using intrinsic viscosity measurements, indicates that this polymer is lower in molecular weight.

Polymerization of 2-Methyl-3,3,3-trifluoro-1,2-epoxypropane Using Aluminum Chloride Catalyst

Owing to the vigorous reaction of the catalyst with the monomer, it was necessary to chill the oxide in Dry Ice before adding to aluminum chloride. No other change in the procedure was required.

A. Catalyst

Baker's C.P. grade aluminum chloride was employed.

B. Polymer Purification

The polymer was purified using the anhydrous ammonia procedure reported for the purification of $(CF_3CHCH_2O)_x$ using $FeCl_3$ catalyst.

C. Experimental Data

These are summarized in Table 7 and shown graphically in Figure 3. It is of interest to note that polymerization occurs about as well at room temperature as at 80-90°C.

Table 7

Polymerization of 2-Methyl-3,3,3-trifluoro-1,2-epoxypropane with $AlCl_3$ (Ca. 12 g. oxide, 24 hours).

Wt. % Catalyst	Temp. (°C)	Polymer Wt. (g.)	% Conversion
2.0	80-90	11.3	95
2.0	25	11.5	98
.5	80-90	.3	2
4.0	80-90	11.8	98

As in the case of 3,3,3-trifluoro-1,2-epoxypropane, conversions are nearly quantitative above 0.5 wt. % of catalyst.

D. Physical Properties of the Polymer

The polymers are liquid, regardless of catalyst concentration.

E. Analytical Data

Molecular weight data obtained by ebulliometric methods (acetone solution) indicate these polymers are greater in weight than those obtained by ferric chloride catalysis (2200 vs 980). As the method cannot be considered accurate, these figures must be interpreted with caution.

Polymerization of 2-Methyl-3,3,3-trifluoro-1,2-epoxypropane Using SO_3 and BCl_3 Catalysts

A. Catalysts

The catalysts used in these experiments were SO_3 in liquid form (Sulfan B, from the General Chemical Company), and anhydrous BCl_3 (obtained from Matheson).

B. Polymer Purification

Not enough polymer was obtained with these catalysts to warrant purification.

C. Experimental Data

These are summarized in Table 8 and shown graphically in Figure 3.

Table 8

Polymerizations of 2-Methyl-3,3,3-trifluoro-1,2-epoxypropane with BCl_3 and SO_3 (ca. 12 g. oxide, 80-90°C, 24 hours)

Catalyst	Wt. % Catalysts	Polymer Wt. (g.)	% Conversion
SO_3	1.2	0.3	3
SO_3	2.0	1.9	16
SO_3	2.0	3.0	25
SO_3	1.0	0.8	7
SO_3	2.0	1.3	11
SO_3	4.0	2.4	19
BCl_3	2.0	1.1	9
BCl_3	4.0	1.7	14

Copolymerization of 3,3,3-Trifluoro-1,2-epoxypropane with 2-Methyl-3,3,3-trifluoro-1,2-epoxypropane

A. Catalyst

Only anhydrous $FeCl_3$ (Fisher's C.P.) was studied as a catalyst.

B. Polymer Purification

The polymeric material was purified using the anhydrous ammonia procedure reported for the purification of $(CF_3CHCH_2O)_x$.

C. Experimental Data

These are summarized in Table 9. It is evident that excellent conversions are obtainable, although whether or not the polymer is a true copolymer or a mixture of homopolymers is not certain.

Table 9

Copolymerization of $CF_3\overline{CHCH_2O}$ with $CF_3\overline{C(CH_3)CH_2O}$ Using $FeCl_3$ Catalyst (80-90°C, 24 hours)

Vol. % CF_3CHCH_2O	Vol. % $CF_3C(CH_3)CH_2O$	Wt. Combined Oxides(g.)	Wt. % $FeCl_3$	Wt. Polymer(g.)	% Conversion
95	5	12.5	5	8.5	68
95	5	12.5	5	9.5	76
90	10	12.5	5	8.5	68
90	10	12.5	5	8.5	68
80	20	13.0	5	9.0	69
80	20	13.0	5	9.5	73
50	50	----	5	---	90[a]
50	50	----	6	---	95[a]

a. The recovered monomer mixture had n_D^{25} 1.3052. In all other cases $n_D^{25} < 1.3$.

D. Physical Properties of the Polymer

The polymers become increasingly dark-colored and tacky as the percent of $CF_3\overline{C(CH_3)CH_2O}$ is increased.

E. Analytical Data

Because these polymers were prepared for vulcanization studies, no analytical data were obtained.

Attempts to Increase the Molecular Weight of Liquid Polytrifluoropropylene Oxide

The procedure employed in these experiments was to mix the polymer and reagent together with catalyst (if used), seal them in a glass ampoule and heat in an oven at 110°C for varying lengths of time. Whether or not reaction had occurred was determined visually by comparing the viscosities of the treated polymers with an untreated sample.

A. When maleic anhydride was employed (2g. of polymer, 0.2 g. of anhydride) using p-toluene sulfonic acid (0.02 g.) as catalyst, no change in viscosity of the fluid was observed after heating overnight. The maleic anhydride remained undissolved in the liquid.

B. Using hexamethylene diisocyanate (2g. of polymer, 0.2 g. of diisocyanate) with pyridine (0.02 g.), the viscosity of the polymer had increased noticeably after heating overnight, and some solid material had formed. There was not sufficient solid material present to permit its characterization.

In all probability, the chain length of the polymer--and consequently, its molecular weight -- is increased by diisocyanate. Lack of a suitable method for determining molecular weights prevents a more conclusive statement.

Attempts to Increase the Molecular Weight of Poly(trifluoromethyl) propylene Oxide

The study of methods of increasing the molecular weight of poly(trifluoromethyl)propylene oxide was conducted using hexamethylene diisocyanate. Three lg. samples of the polymer were mixed respectively with 0.05 g., 0.1 g. and 0.2 g. portions of

the diisocyanate in small glass ampoules. A fourth ampoule was loaded with the oxide and no diisocyanate. The ampoules were sealed and placed in a 150°C oven for twenty-four hours.

After this reaction period the samples were cooled and a definite change could be noted in every sample containing the diisocyanate. The polymer sample containing no reagent did not appear to be changed but the sample containing 5% diisocyanate was a brown, highly-viscous liquid. The samples containing 10% and 20% reagent were darker brown and more viscous than initially, although not as viscous as the sample containing 5% reagent. Possibly all polymers are of equally high molecular weight, but dilution with the diisocyanate lowers the apparent viscosity. Here again, lack of a suitable method for determining molecular weights has hampered this part of the program.

Polyglycol Formals

A. An attempt was made to react 2,2,3,3,4,4-hexafluoro-1,5-pentanediol with butyl formal exactly as described by Hill and Carrothers (14) who employed the non-fluorine-containing analogs. Butyl formal and 5% excess glycol, together with a catalytic amount of anhydrous $FeCl_3$, were heated together at atmospheric pressure, then under reduced pressure. While some reaction occurred, as evidenced by the production of impure butanol, the results were inconclusive. A large amount of charring occurred, and most of the glycol was recovered unchanged.

B. A 300 ml. flask was fitted with a 6 inch, glass helices packed column topped with a variable take-off head. The flask was charged with 22 g. of glycol, 16 g. of butyl formal and 0.1 g. of p-toluene sulfonic acid. A vacuum was applied (25 mm. Hg) and the flask was heated until the skin temperature rose to 130°C. The contents of the flask never exceeded 100°C. A small amount of reflux was observed, but no non-condensible product was evolved as evidenced by the absence of any liquid in the cold trap interposed between the apparatus and the pump. After 24 hours of heating, the material in the pot had darkened slightly, and upon cooling, part of the mixture crystallized.

The reaction mixture was diluted with benzene and heated until all the solid dissolved. Upon cooling there was precipitated 11 g. of solid identified as unreacted glycol (50% recovery).

The benzene was evaporated in a stream of air, after which the residue weighed 25 g. This residue was a brown colored liquid, and it had an odor characteristic of butyl formal. When it was heated on a steam bath in a stream of air, the odor of formaldehyde became apparent when the weight had been reduced to 15 g. The odor of butyl formal no longer was present. Upon prolonged standing, additional glycol was precipitated.

It is apparent that a glycol formal was formed as a product of the reaction between the fluorine-containing glycol and butyl formal. However, the material is unstable, decomposing with heat or on long standing. This would indicate that the formal (either linear, or a cyclic monomer or dimer) undergoes spontaneous reaction to reform the monomers.

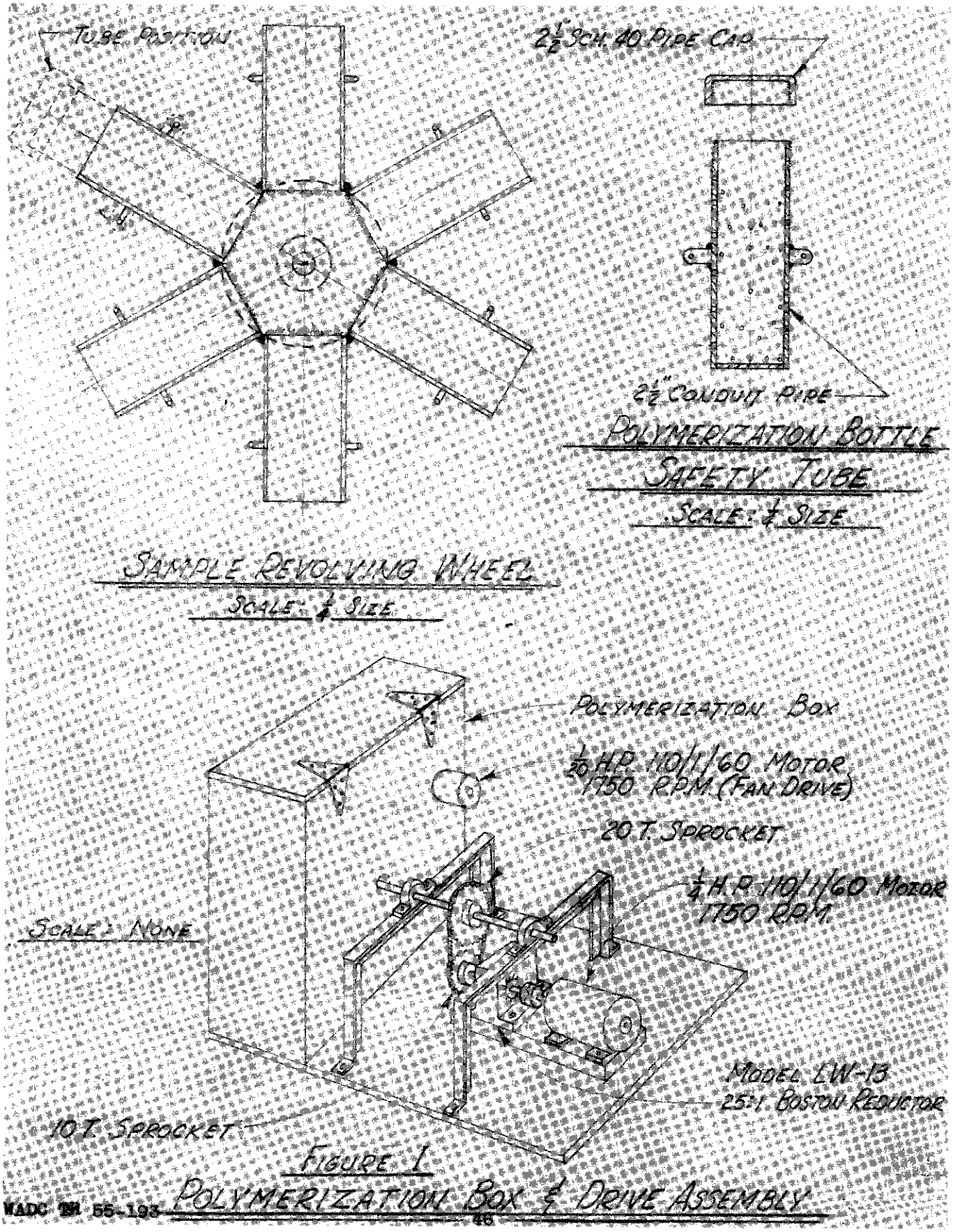
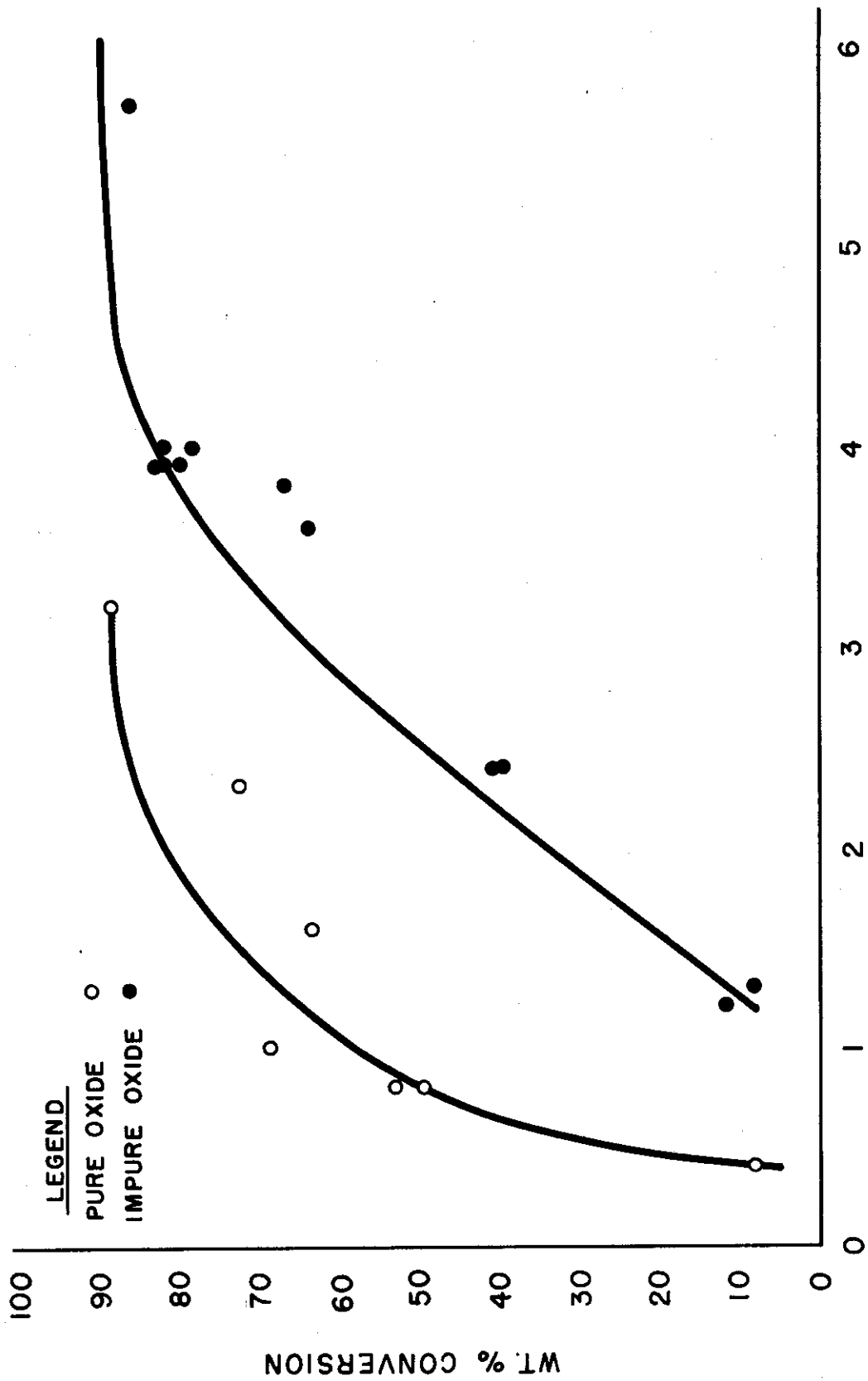


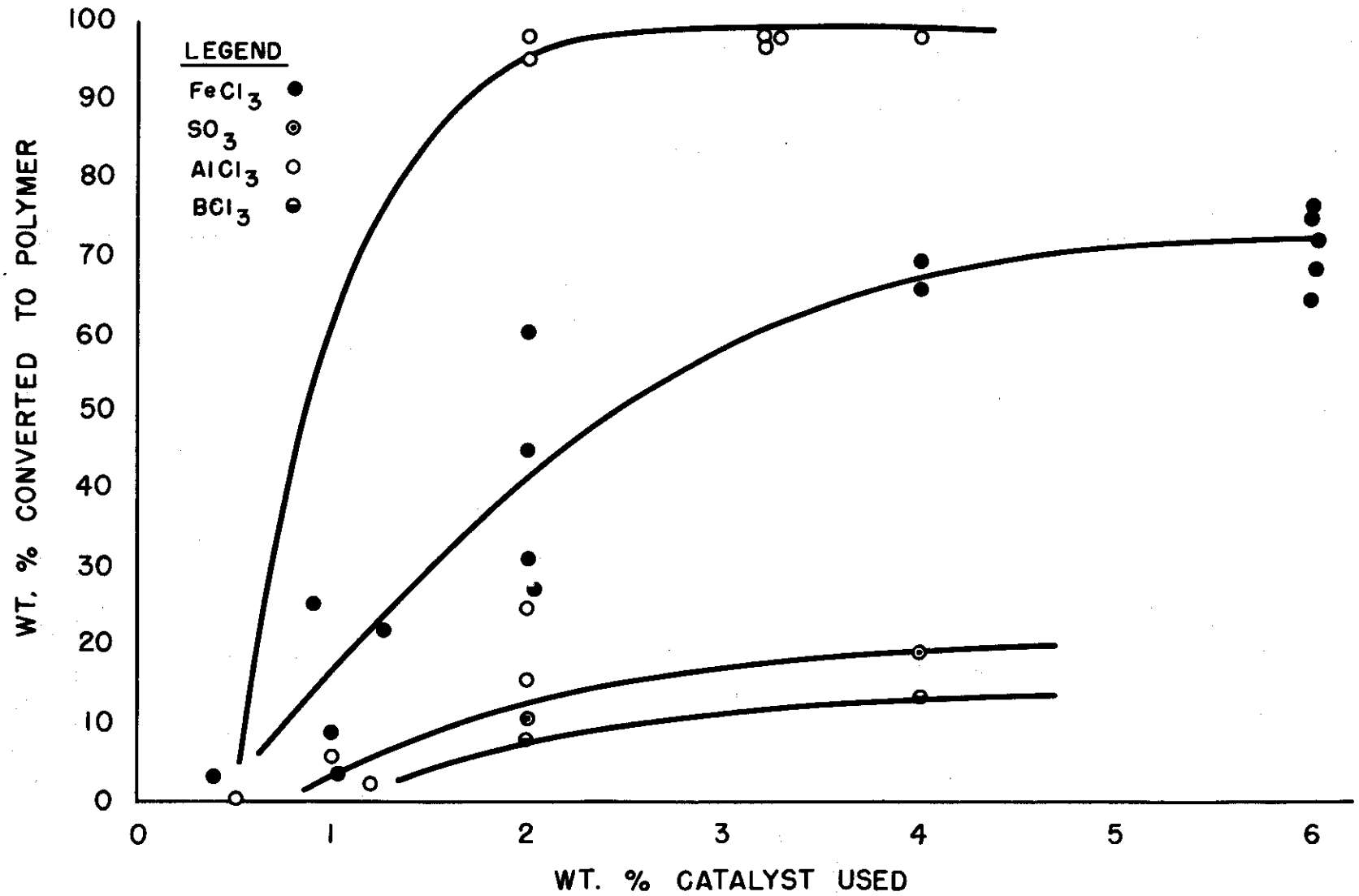
FIGURE 1

POLYMERIZATION BOX & DRIVE ASSEMBLY



POLYMERIZATION OF 3,3,3-TRIFLUORO-1,2-EPOXYPROPANE

FIGURE 2



POLYMERIZATION OF 2-METHYL-3,3,3-TRIFLUORO-1,2-EPOXYPROPANE

FIGURE 3

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