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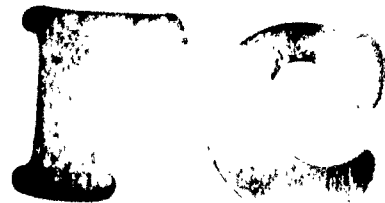
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WADC TECHNICAL REPORT 55-193

PART 2



FLUORINE-CONTAINING POLYETHERS

OGDEN R. PIERCE

DONALD D. SMITH

ROBERT M. MURCH

DOW CORNING CORPORATION

FEBRUARY 1956

WRIGHT AIR DEVELOPMENT CENTER

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MATERIALS LABORATORY
CONTRACT No. AF 33(616)-2417
SUPPLEMENTAL AGREEMENT No. S2(55-1563)
PROJECT No. 7340
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WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
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FOREWORD

This report was prepared by the Dow Corning Corporation under USAF Contract No. 33(616)-2417, Supplemental Agreement No. S2(55-1563). 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 work conducted from April 1955 to November 1955.

Abstract

This research was initiated to explore the preparation of fluorine-containing polyethers for possible use as thermally stable elastomers.

Investigations of several moners were conducted. Indications are that hypohalogenation of fluorine containing olefins generally is unsuccessful.

The preparation of epoxides by reaction of fluorine containing olefins with peracids has been briefly explored.

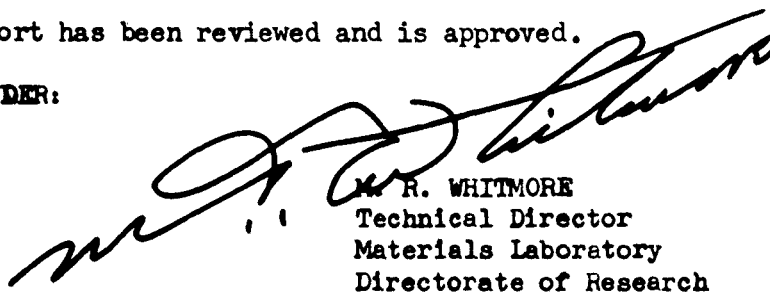
The synthesis of epoxides using fluorine containing ketones as precursors was studied and the results indicate the approach warrants exploitation.

In the area of polymerization the use of free radical initiators was studied. In no instance was a satisfactory rubber obtained. The polymers prepared were quite solvent resistant and could conceivably find applications where good rubbery character is not necessary.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

WADC TR 55-193, pt 2

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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, several investigations were conducted. A rather extensive study of the hypohalogenation of fluorine-containing olefins has indicated that the reaction generally fails. In only one instance was a reaction observed, that involving 3,3,3-trifluoro-2-methylpropene and hypochlorous acid. An impure product was obtained which yielded an epoxide on treatment with aqueous base. On the basis of the investigation, it is felt that this approach to epoxides is not feasible at this time.

The preparation of epoxides by reaction of fluorine-containing olefins with peracids has been studied. The use of perbenzoic acid with 3,3,3-trifluoro-2-methylpropene was attempted under various conditions but no reaction was obtained. Extension of this work to include trifluoroperacetic acid as the oxidizing agent failed to yield any epoxide. It is felt that the brief nature of the exploratory work precludes any comments on the feasibility of the approach.

As an additional approach to the synthesis of epoxides, the preparation of fluorine-containing ketones to be used as precursors to the epoxides was studied from the viewpoint of the reaction of an acid chloride with a fluorine-containing olefin to form the ketone. It was found that acetyl chloride reacted with vinylidene fluoride in the presence of aluminum

chloride to give both methyl chlorodifluoroethyl ketone and methyl trichloroethyl ketone in fair yield. While time did not permit further study of this reaction, it is felt that this approach warrants exploitation.

In the area of polymers, the use of free radical initiators was studied. The reaction of 3,3,3-trifluoro-1,2-epoxypropane with benzoyl peroxide and tertiary butyl hydroperoxide failed to yield any polymer. Exposure of the monomer to a relatively high dosage of gamma radiation from radioactive cobalt also failed to produce any polymer. The optimum polymerization system was found to comprise the use of ferric chloride (2-3% by wt.) at 90-100°C for a period of 64 hours. Polymers of 3,3,3-trifluoro-1,2-epoxypropane prepared in this manner were found to have a weight-average molecular weight of 230,000.

Vulcanization of the above polymer as well as a copolymer with 3,3,3-trifluoro-2-methyl-1,2-epoxypropane was studied using both peroxides and diisocyanates as vulcanizing agents. In no instance was a satisfactory rubber obtained. By incorporation of a considerable amount of silicone rubber (Dow Corning 200) gum into poly(trifluoropropylene oxide) it was possible to obtain a rubbery vulcanizate. However, the unsatisfactory nature of this product with regard to tensile strength discouraged further development of this approach. It is emphasized that the polymers prepared are quite solvent resistant in themselves and could conceivably find applications where good rubbery character is not necessary.

III. General Discussion

The previous summary report (1) pertaining to this program noted that the most feasible approach to the preparation of fluorine-containing polyethers appeared to be via the polymerization of fluorine-containing epoxides. The effect of various catalysts on the polymerization of the selected monomers -3,3,3-trifluoro-1,2-epoxypropane and 2-methyl-3,3,3-trifluoro-1,2-epoxypropane- as well as the syntheses of these and other monomers and monomer intermediates were also described in that report. The present report summarizes the work done on the polyether program during the past six month period.

A. Preparation of Monomers

3,3,3-Trifluoro-1,2-epoxypropane was prepared using the reaction sequence (1,2):

- a. $\text{CF}_3\text{COCH}_3 + \text{Br}_2 \xrightarrow{\text{H}_2\text{SO}_4} \text{CF}_3\text{COCH}_2\text{Br}$
- b. $\text{CF}_3\text{COCH}_2\text{Br} + \text{LiAlH}_4 \longrightarrow \text{CF}_3\text{CHOHCH}_2\text{Br}$
- c. $\text{CF}_3\text{CHOHCH}_2\text{Br} + \text{NaOH (50\% aq.)} \longrightarrow \text{CF}_3\overline{\text{CHCH}_2}\text{O}$

2-methyl-3,3,3-trifluoro-1,2-epoxypropane was synthesized as shown.

- d. $\text{CF}_3\text{CO}_2\text{H} + \text{ROH} \longrightarrow \text{CF}_3\text{CO}_2\text{R}$
- e. $\text{CF}_3\text{CO}_2\text{R} + \text{CH}_3\text{MgBr} \longrightarrow \text{CF}_3\text{C(OH)(CH}_3)_2$
- f. $\text{CF}_3\text{C(OH)(CH}_3)_2 + \text{Cl}_2 \longrightarrow \text{CF}_3\text{C(OH)(CH}_3)\text{CH}_2\text{Cl}$
- g. $\text{CF}_3\text{C(OH)(CH}_3)\text{CH}_2\text{Cl} + \text{NaOH (50\% aq.)} \longrightarrow \text{CF}_3\overline{\text{C(CH}_3)\text{CH}_2}\text{O}$

Swartz (3) has reported that the best yields in step 'e' were obtained with the use of the amyl ester. Henne (4) indirectly confirmed this by noting that the alcohol obtained from the ethyl ester was an azeotrope with ethanol. It was our supposition that good yields of pure alcohol could be obtained from the methyl ester, if that ester were of a high degree of purity. This supposition was confirmed, 69% yields being obtainable using pure methyl trifluoroacetate. The chlorination procedure used in step 'f' yielded a higher boiling material in addition to the monochloroalcohol. This higher boiling substance, presumably the dichloroalcohol, when treated with 50% aqueous base gave a product which did not freeze in a Dry Ice-trichloroethylene mixture and boiled in approximately the range expected of the compound $\text{CF}_3\overline{\text{C}(\text{CH}_2\text{Cl})\text{CH}_2\text{O}}$ or an isomer. Characterization by infrared and mass spectrographic analyses indicated that the material was impure $\text{CF}_3\overline{\text{C}(\text{CH}_3)\text{CHClO}}$.

Two other synthesis routes have been investigated as possible methods for the production of epoxides - the preparation of the intermediate halohydrin by the addition of a hypohalous acid to a fluorine-containing olefin, and the direct peracid oxidation of a fluorine-containing olefin to an epoxide. Two olefins have been employed in each of these procedures. 2-Methyl-3,3,3-trifluoropropene was prepared by the dehydration of 2-methyl-3,3,3-trifluoro-2-propanol; and 3,3,4,4,5,5,5-heptafluoro-1-pentene was prepared by the dehydration of

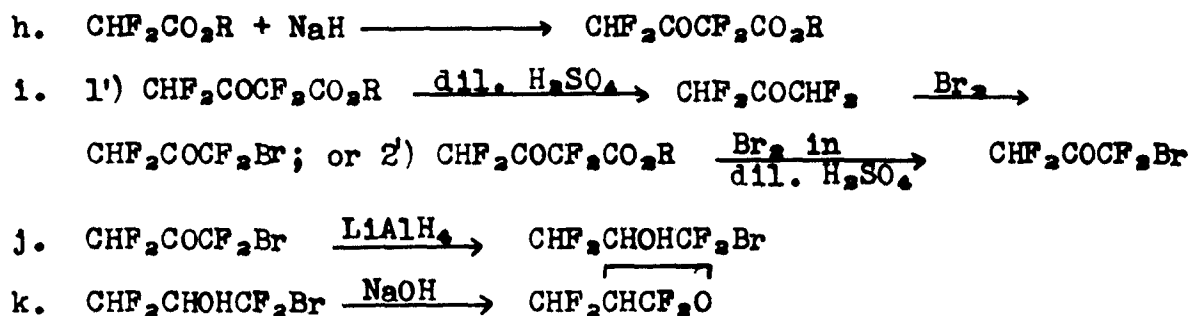
3,3,4,4,5,5,5-heptafluoro-2-pentanol which was obtained either by the addition of methyl magnesium halide to heptafluorobutyraldehyde (1) or by the reaction of methyl heptafluorobutyrate with mixed methyl and isopropyl magnesium halides (5).

A literature survey of the methods for adding hypohalous acids to olefins disclosed many references to this type of reaction, but only one (6) pertaining to fluorine-containing olefins. Application of the method of Kadesch (7), involving the in situ formation of hypochlorous acid in the presence of the olefin, failed with both of the fluorine-containing olefins. N-Bromosuccinimide, recently reported to be an excellent reagent for the addition of hypobromous acid to olefins (8), likewise failed to yield a bromohydrin. The addition of hypochlorous acid in the manner described by Coleman and Johnstone (9) was also unsuccessful when 3,3,4,4,5,5,5-heptafluoro-1-pentene was used; but with 2-methyl-3,3,3-trifluoropropene an addition product was obtained. This product was a mixture, part of which was a solid melting at 45°. The impure mixture, however, did yield some epoxide when treated with hot, 50% aqueous base.

The peracid oxidation of olefins to epoxides is well known (10). This method has the advantage of eliminating the preparation of an intermediate halohydrin, and for that reason a study of the method was incorporated into this program. No report could be found in the literature on the extension of peracid oxidation to fluorine-containing olefins; but it is known that negatively substituted olefins resist this type of

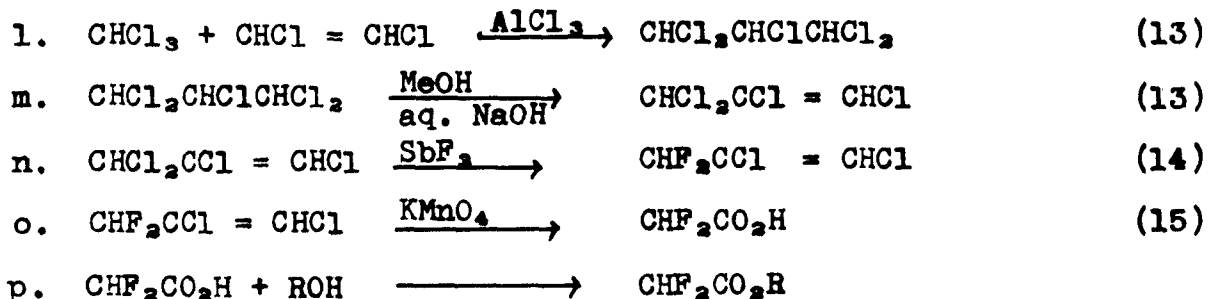
oxidation. The reaction of perbenzoic acid with 2-methyl-3,3,3-trifluoropropene did not yield an oxidation product. The reaction of peroxy trifluoroacetic acid with the same olefin, similarly failed to yield the desired epoxide.

In an attempt to prepare a monomer precursor from which a polyether could be prepared containing fluorine in the ether chain as well as in the side chain, the following procedure was devised:



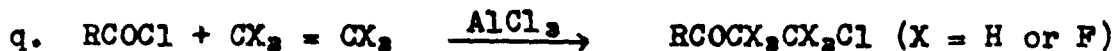
Steps "h" and "i(1)" (up to tetrafluoroacetone) have been reported (11), and the preparation of 1,3,3,3-tetrafluoro-1,2-epoxypropane has been reported (12) via a similar procedure.

A small quantity of methyl difluoroacetate was purchased from an outside source, but it proved to be unsuitable for the purpose (probably being of low purity), and no more was obtainable. Thus, it was necessary to synthesize the difluoroacetate starting material in the following manner:



Steps 'l' through 'p' were completed, but expiration of the contract prevented further investigation of steps 'h-k'.

Acylation of a fluorine-containing olefin also was briefly investigated. Had time permitted, the following sequence would have been studied:



A similar series of reactions for non-fluorine-containing reactants is reported (16).

The addition of acetyl chloride to vinylidene fluoride in the presence of aluminum chloride yielded two new ketones, methyl monochlorodifluoroethyl ketone and methyl trichloroethyl ketone. The structure of either one cannot be positively stated, but it is presumed that they are, respectively, $\text{CH}_3\text{COCH}_2\text{CF}_2\text{Cl}$ and $\text{CH}_3\text{COCH}_2\text{CCl}_3$.

B. Preparation of Polymers

Initially, polymerization studies were conducted mainly with the objective of determining what catalyst was most suitable for the polymerization of 3,3,3-trifluoro-1,2-epoxypropane and its analog 2-methyl-3,3,3-trifluoro-1,2-epoxypropane. The results of those studies were reported in detail (1), but - by way of introduction - they are summarized in the following paragraphs.

The polymerization of both epoxides was accomplished using a variety of materials of the Lewis acid type, the two most effective being aluminum chloride and ferric chloride.

The use of aluminum chloride with either epoxide results in rapid polymerization, and high conversion from monomer to polymer. This is true for concentrations of the catalyst from 0.5 - 4% by weight, in the temperature range 25° - 100°C. However, the degree of polymerization apparently is low, because only viscous liquids are obtained.

Ferric chloride catalysis produces different results. In the first place, the rate of polymerization of either monomer is considerably slower compared with aluminum chloride catalysis. Further, while with 2-methyl-3,3,3-trifluoro-1,2-epoxypropane only liquid polymers result, solid polymers are obtained from 3,3,3-trifluoro-1,2-epoxypropane. Thus it is apparent that the ferric chloride catalyzed polymerization of 3,3,3-trifluoro-1,2-epoxypropane is the better method to use for the production of rubber-like polymers. Conversion of monomer to polymer was increased by increasing the amount of catalyst to an upper limit of about 5% by weight of the monomer, using a temperature of 80-90°C for a period of 24 hours.

In the period covered by this report, it has been determined that similar conversions can be obtained, and that a superior polymer results, with lower concentrations of catalyst (2-3% by weight) but at a slightly higher temperature (90-100°C) over a longer period of time (64 hours). The molecular weight

of polymer prepared in this manner has been measured (by light scattering techniques) and found to have a weight-average molecular weight of 230,000.

Also studied briefly were those substances which promote free radical reactions. The use upon 3,3,3-trifluoro-1,2-epoxypropane of benzoyl peroxide, tertiary butyl hydroperoxide and Co^{60} irradiation was without effect.

C. Vulcanization Studies

Polymers of 3,3,3,-trifluoro-1,2-epoxypropane and copolymers of 3,3,3-trifluoro-1,2-epoxypropane with 2-methyl-3,3,3-trifluoro-1,2-epoxypropane were subjected to vulcanization studies, in order to determine their possible utility in rubber applications. Tests were conducted using peroxides and isocyanates on formulations of the polymers with fillers, and on blends of the polymers with polydimethyl siloxanes and fillers. The only instance in which a rubber-like material resulted was that in which a siloxane was incorporated. Even in this case, it is felt that the rubbery qualities were imparted by the siloxane, and that the polyether did not vulcanize. While vulcanizates of this type were found to possess increased solvent resistance, their tensile strength was considerably poorer than that exhibited by an undiluted polysiloxane.

IV. Experimental

A. Preparation of Monomers

2-Methyl-3,3,3-trifluoro-2-propanol

Methyl magnesium bromide was prepared by passing methyl bromide into a flask containing ether and magnesium (162 g., 6.5 moles). Methyl trifluoroacetate (320 g., 2.5 moles), freshly distilled from phosphorus pentoxide, was added and the mixture was stirred for 20 hours, the last four hours at reflux temperature. After hydrolysis, the dried organic layer was fractionally distilled to yield 221 g. (1.72 moles, 69% yield) of product, b.p. 80-82°C, n_D^{25} 1.3319.

Epoxidation of Dichlorotrifluoro t-Butyl Alcohol

The high boiling portions of several fractionations of 2-methyl-3-chloro-1,1,1-trifluoro-2-propanol were combined and refractionated. One cut from this fractionation (186 g., b.p. 139°C, n_D^{25} 1.4036) was presumed to be the dichloro alcohol.

This product was added to a hot (100°C) solution of 200 g. of NaOH in 200 g. of water. The reaction mixture was held at about 100°C for four hours. The product obtained from this reaction was dried by freezing out the water in a Dry Ice-acetone mixture. Fractionation through a Podbielniak Mini-Cal column gave 77 g. of a material, b.p. 69°C, n_D^{25} 1.3430, sp. gr. 1.332. The theoretical molar refraction for $\text{CF}_3\text{C}(\text{CH}_2\text{Cl})\text{CH}_2\text{O}$ or one of its isomers is 25.2, found (for this material) 25.4.

Elemental analysis indicated that this material was impure.

For $C_4H_4F_3ClO$

Calc. % Cl 22.0, % F 35.3

Found % Cl 24.0, % F 37.6

However, both infrared and mass spectrographic analyses indicated that the material contained an epoxide ring, and that the chlorine was attached to the ring carbon atom. Thus the material isolated contains -- in part at least -- some of the compound $CF_3C(CH_3)CHClO$.

2-Methyl-3,3,3-trifluoropropene

2-Methyl-1,1,1-trifluoro-2-propanol (160 g., 1.25 moles) and phosphorus pentoxide (190g., 1.34 moles) were mixed with cooling in a 5000 ml. flask. The large flask was required to contain the material, which swells considerably upon heating. A Dry Ice-cooled trap was connected to the flask, and the flask was gradually heated to 240°C over a 16 hour period. The crude olefin was redistilled to yield 89 g. (0.21 mole, 65% yield) of pure product, b.p. 6-7°C.

3,3,4,4,5,5,5-Heptafluoro-2-pentanol (Mixed Grignard Procedure) (5)

Because a large quantity of the alcohol was desired for subsequent dehydration, this experiment was conducted in a 20 gal. Pfaudler kettle.

An ethereal solution of methyl magnesium chloride (45 lbs. of solution, containing 30 g. moles of CH_3MgCl obtained from the Dow Corning Grignard department) was placed in the kettle. Magnesium chips (2.7 lbs., 50 g. atoms) were suspended

in this solution, and isopropyl bromide (15 lbs., 55 g. moles) was added. When all of the magnesium was dissolved, methyl heptafluorobutyrate (7435 g., 35 g. moles) was added slowly, and the mixture was allowed to stir overnight.

After destroying excess Grignard with water, the solution was hydrolyzed with cold hydrochloric acid solution. The organic layer was separated and dried over sodium sulfate. The ether was removed by distillation through a short Vigreux column. The residue was distilled through the Vigreux column, and the resulting distillate was thoroughly dried by refluxing with calcium hydride. The dried material was distilled through a 100 plate Podbielniak Hyper-Cal column, to obtain 2164 g. (33% yield) of $C_5F_7CHOHCH_3$, b.p. 101-2°C, n_D^{25} 1.3102.

3,3,4,4,5,5,5-Heptafluoro-1-pentene (17)

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% yield) was distilled from the mixture, b.p. 31°C.

Hypochlorination of 2-Methyl-3,3,3-trifluoropropene

A variation of the procedure of Kadesch (7) was employed in this experiment.

Calcium hypochlorite (100 g., 2.0 moles) was dissolved in 3000 ml. of water, the solution was cooled to 0-3°C and saturated with carbon dioxide. The olefin (130g., 1.2 moles) was added to this cold solution slowly, using a Dry Ice-cooled condenser

on the reaction flask. Reflux occurred during addition of the olefin, but ceased when addition was completed. A Dry Ice-cooled trap was attached to the flask, and the reaction mixture was allowed to stir for 24 hours, after which time 60 g. (0.55 mole) of unreacted olefin was recovered.

The reaction mixture was filtered, saturated with salt, and extracted with ether. The ether was removed by distillation, and the last traces of ether were removed through a Podbielniak Mini-Cal column. A higher boiling residue (12 g.) remained, which may have contained some chlorohydrin. An attempt to fractionally distill this residue was unsuccessful. Failure to account for more of the olefin may have been due to its high vapor pressure, which would interfere with its separation from ether.

Attempted Hypobromination Using N-Bromosuccinimide (8)

N-Bromosuccinimide (89 g., 0.5 mole) was placed in a 1000 ml. flask and 200 g. of water was added rapidly. Then during a half-hour-period, 98 g. (0.5mole) of 3,3,4,4,5,5,5-heptafluoro-1-pentene was added, the mixture was stirred for seventy-two hours without apparent reaction. The reaction mixture was filtered and the filtrate was extracted with ether. Concentration of this ether solution gave too little residue to make further purification practical.

A second, similar attempt, and one employing 2-methyl-3,3,3-trifluoropropene, likewise were unsuccessful.

Preparation of Hypochlorous Acid Solution (9):

A 5000 ml., 3-necked flask was fitted with a Dry-Ice-cooled reflux condenser, Hirshberg stirrer and an addition funnel. A solution of mercuric chloride (25 g.) in 500 ml. of water was placed in the flask, which was then immersed in a salt-ice-water bath. An ice cold solution of sodium hydroxide (190 g. of NaOH in 500 ml. of water plus 800 g. of crushed ice) was poured into the flask, and gaseous chlorine was bubbled into the cold (0-5°C) mixture until it was no longer cloudy, then nitric acid (1600 ml., 1.5N) was added. The concentration of HOCl in the solution was found to be 2%.

The analytical procedure followed was the addition of an aliquot portion to excess potassium iodide dissolved in hydrochloric acid, then titrating the liberated iodine with sodium thiosulfate.

Attempted Hypochlorination of 3,3,4,4,5,5,5-Heptafluoro-1-pentene

3,3,4,4,5,5,5-Heptafluoro-1-pentene, (196 g., 0.53 mole) was placed in a 1000 ml. flask fitted with a Dry Ice-cooled reflux condenser, stirrer and dropping funnel. The reaction flask was cooled with an ice-water bath. A 250 ml portion of 2% HOCl solution was added and stirred for three hours. A test with acidified KI solution showed the presence of unreacted HOCl. Agitation of the mixture was continued for sixteen hours but the presence of HOCl could still be detected. The reaction mixture was extracted with ether. Distillation of the ethereal solution yielded 89 g. of unreacted olefin and no higher boiling product. It was assumed no reaction occurred.

Hypochlorination of 2-Methyl-3,3,3-trifluoropropene

2-Methyl-3,3,3-trifluoropropene (89 g., 0.81 mole) was placed in the reaction flask and cooled. Six 250 g. portions of 2% HOCl solution were added during a thirty-hour period, each portion being added after obtaining a negative test for HOCl from the preceding portion. Sixteen hours after addition of the sixth portion a positive test for HOCl was obtained, indicating reaction was complete. The reaction mixture was extracted with ether, and the ethereal solution dried over Drierite. After removal of the ether by distillation, the residue was distilled through a Podbielniak Mini-Cal column (concentric tube barrel). There was obtained 50 g. of material, (b.p. 112°C, m.p. ca 20°C) which solidified on the condenser.

A similar reaction was conducted and the product obtained was combined with the solid product from the first run. This material was fractionated through a Podbielniak Min-Cal column and the product cut (38 g., b.p. 116°C) had a melting point of 41-48°C. This 116°C cut was refractionated through the same column to obtain a smaller portion (center cut, m.p. 45°C) of material for analysis. Analytical data on this material indicated it might be the impure addition product of HOCl and the olefin. Infrared analysis shows the absence of any 2-methyl-3-chloro-1,1,1-trifluoro-2-propanol.

For $C_4H_6F_3ClO$

Calc. % Cl 21.9, % F 35.0

Found % Cl 25.0, % F 37.5

A further attempt to characterize this product was made by treating a 16 g. portion of the combined 116°C cuts with 50% aqueous NaOH at 100°C in the manner described previously for the epoxidation of the chlorinated alcohol. The four grams of material thus obtained was shown to contain (by infrared analysis), 70% of the compound 2-methyl-3,3,3-trifluoro-1,2-epoxypropane. Thus it is shown that some oxidation of the olefin has been effected.

Preparation of Perbenzoic Acid (18)

In a one-liter Erlenmeyer flask 11 g. (0.48 g. atom) of sodium was dissolved in 200 ml. of methyl alcohol and the solution was cooled to 0°C. A solution of 100 g. (0.42 mole) of benzoyl peroxide in 400 ml of chloroform was added to the sodium methoxide solution. The temperature of the reaction mixture was held between -5° and 0°C during this addition. The mixture was immediately transferred to a two-liter flask and extracted with 500 ml of cold water. The organic layer was discarded and the aqueous layer was washed with carbon tetrachloride, discarding the washings. The sodium perbenzoate in the aqueous solution was converted to perbenzoic acid by the addition of 500 ml, 1N sulfuric acid solution. The product was extracted with benzene and dried over sodium sulfate. The yield was calculated by adding an aliquot portion of the benzene solution to an excess of KI then titrating with standard sodium thiosulfate. There was obtained 36.7 g. of perbenzoic acid, a yield of 65%.

Attempted Epoxidation of 2-Methyl-3,3,3-trifluoropropene with Perbenzoic Acid.

A one-liter, three-necked flask was fitted with a thermometer well, stirrer, and Dry Ice-cooled reflux condenser. 2-Methyl-3,3,3-trifluoropropene (27.5g., 0.25 mole) was placed in the flask and cooled to 0°C. A solution of perbenzoic acid (36.5 g., 0.27 mole) in 400 ml of benzene was added to the cold olefin. The reaction mixture was held below 0°C for twenty-four hours. Tests for the peracid were made periodically. No decrease in the peracid concentration was noted until the reaction temperature was raised to 10°C. During the following six days as the temperature was gradually increased to 70°C, the peracid concentration steadily decreased. After this reaction period the small amount of remaining perbenzoic acid (approx. 10% of the original amount) was destroyed with KI. Iodine was destroyed with $\text{Na}_2\text{S}_2\text{O}_3$, and benzoic acid was removed by extraction with dilute sodium hydroxide. Distillation of the benzene solution resulted in the recovery of one-third of the starting olefin. Presumably additional olefin was lost through handling and no epoxide was isolated.

Attempted Epoxidation of 2-Methyl-3,3,3-Trifluoropropene with Peroxytrifluoroacetic Acid

The method used for this attempt was that outlined by Emmons and Pogano (19). The choice of the buffer in this experiment was governed by their experience with negatively substituted olefins.

A solution of peroxytrifluoroacetic acid was prepared from 7.0 ml (0.25 mole) of 90% hydrogen peroxide, 63 g. (0.30 mole) of trifluoroacetic anhydride and 50 ml of methylene chloride. This reagent was added during a one-hour period to a stirred mixture of 22 g (0.2 mole) of 2-methyl-1,1,1-trifluoropropene, 200 ml of methylene chloride, and as a buffer 113 g (0.8 mole) of disodium hydrogen phosphate. The solution was held at the reflux temperature of the olefin (6°C) for four hours. The resulting mixture was stirred with 500 ml. of water until the inorganic salts dissolved. The two layers were separated and the aqueous layer was extracted with three 50 ml portions of methylene chloride. The combined methylene chloride solutions were dried over sodium sulfate, then calcium sulfate. The solvent was removed through a Todd column (12 mm barrel, packed with 1/8 in. glass helices). The residue (8 g.) was found by infrared analysis to contain none of the desired 2-methyl-3,3,3-trifluoro-1,2-epoxypropane.

Reaction of Methyl Difluoroacetate with Sodium Hydride (11)

A 1000 ml 3-necked flask was equipped with a stirrer and a reflux condenser fitted with a gas inlet tube to permit the maintenance of a nitrogen atmosphere. The third neck was used to charge the flask, and was stoppered during reaction.

Methyl difluoroacetate (103 g., 0.94 mole, obtained from the Caribou Chemical Company and distilled from phosphorus pentoxide before use) was placed in the flask, and sodium hydride (8g., 0.3 mole) was added in one portion. When the initial

vigorous reaction had subsided, the flask was heated to 90°C and kept at that temperature until the evolution of hydrogen had ceased. A solution of ice cold 20% sulfuric acid was added to the flask, then the organic layer was separated. The acid layer was extracted several times with ether, and the combined ether washings and organic material were dried over Drierite.

The ether was removed by distillation. An attempt to distill the residue resulted in decomposition of the liquid with the evolution of HF at a pot temperature of 180°C. The expected boiling point of methyl difluoroacetodifluoroacetate is well below that temperature ($\text{CHF}_2\text{COCF}_2\text{CO}_2\text{C}_2\text{H}_5$ b.p. 143°), so it can be concluded that none was present.

1,1,2,3,3-Pentachloropropane (13)

A 5000 ml. 3-necked flask was equipped with a Hirshberg stirrer, an addition funnel and a reflux condenser. Powdered aluminum chloride (250 g.) was dissolved in chloroform (300 g.) contained in the flask, then a solution of 1,2-dichloroethylene (1000 g., 10.3 moles) in chloroform (2500 g.) was added slowly from the addition funnel. Initially, the reaction was slow, the color of the solution gradually darkening until one-third of the solution was added. Then it became quite vigorous, requiring external cooling; and finally moderated during addition of the final third of the dichloroethylene-chloroform solution.

Water was added to destroy AlCl_3 , and the mixture was steam distilled. The organic layer of the distillate was separated and dried over calcium chloride. After removal of the chloroform by distillation at atmospheric pressure, the pentachloropropane was distilled through a Todd column (12 mm. barrel packed with 1/8 inch glass helices) to obtain 1685 g. (7.7 moles, 75% yield) of product, b.p. $93^\circ/20$ mm, n_D^{25} 1.5110.

1,2,3,3-Tetrachloropropene (13)

1,1,2,3,3-Pentachloropropane (2550 g., 11.7 moles) was dissolved in methanol (1000 ml.) and a solution of sodium hydroxide (580 g. in 1000 ml of water) was added slowly to the mixture. The resulting homogeneous solution was diluted with a large volume of water to remove the methanol. The organic layer was separated and steam distilled. The organic layer of the steam distillate was separated, dried over calcium chloride and distilled under reduced pressure through a Todd column (12 mm. barrel packed with 1/8 inch glass helices). There was obtained 1555 g. (8.6 moles, 74% yield) of product, b.p. $72-76^\circ/25$ mm., n_D^{25} 1.5165, reported (13) n_D^{20} 1.5275.

A repeat of the above experiment was conducted without the use of methanol. The only difference noted was that the dehydrohalogenation was much slower -- due to the heterogeneity of the reaction mixture -- and external heating was required to complete the reaction. The yield and the refractive index of the product were the same as in the previous experiment.

1,2-Dichloro-3,3-difluoropropene (14)

A 2000 ml., 3-necked flask was equipped with a Hirshberg stirrer, addition funnel and a condenser set for distillation. Powdered antimony trifluoride (225 g., 1.25 moles) was placed in the flask, and 1,2,3,3-tetrachloropropene was added to make a paste. Heat was applied and when distillation began, the remainder of the tetrachloropropene (225 g., 1.25 moles in all) was added at the same rate as the distillate was removed. The distillate was caught in a receiver containing 200 ml. of concentrated hydrochloric acid.

The organic layer in the receiver was separated, washed three times with water and dried over Drierite. Distillation of the dried organic material through a Todd column (12 mm. barrel packed with 1/8 inch glass helices) yielded 73 g. (0.5 mole, 40.0% yield) of product, b.p. 90.0-90.5°C, n_D^{25} 1.4129.

The use of antimony pentachloride in the above procedure had a deleterious effect. About 1 ml. of $SbCl_5$ dissolved in the tetrachloropropene reduced the yield to 20%.

1,1-Difluoroacetic Acid (15)

A solution of sodium carbonate (600 g., 6 moles) and potassium permanganate (2030 g., 12.9 moles) in 3500 ml. of water was cooled in an ice water-bath, and 1,2-dichloro-3,3-difluoropropene (1059 g., 7.20 moles) was added slowly with rapid stirring. The reaction mixture was allowed to stir overnight, then it was filtered. The massive cake of manganese dioxide was washed several times with water, and the washings were combined with the filtrate.

The filtrate was acidified with concentrated sulfuric acid and placed in an extraction apparatus arranged for continuous extraction with ether. After three days, the aqueous portion was discarded, and the ether extract was dried over Drierite. The ether was then removed by distillation, and the crude acid was distilled through a short Vigreux column. There was obtained 279 g. (2.9 moles, 40% yield) of impure difluoroacetic acid, b.p. 118-131°C.

Ethyl 1,1-Difluoroacetate

An ice-cold solution of ethanol (276 g., 6 moles) in concentrated sulfuric acid (350 g., 3.3 moles) was added to 1,1-difluoroacetic acid (279 g., 2.9 moles, crude acid). The mixture was refluxed for one hour, then allowed to stand overnight. The organic ester was separated by distillation, then it was fractionally distilled from phosphorus pentoxide (Todd column, 12 mm. barrel packed with 1/8 in. Pyrex glass helices) to obtain 250 g. (2 moles, 70% yield) of ethyl difluoroacetate, b.p. 98.7°C.

Reaction of Acetyl Chloride with Vinylidene Fluoride

The procedure reported by Sondheimer and Woodward (16) was followed in this experiment.

Acetyl chloride (255 g., 3.25 moles) was added to a suspension of powdered aluminum chloride (455 g., 3.41 moles) in 1000 ml. of chloroform. The mixture was chilled in a salt-ice-water bath, and vinylidene fluoride (obtained from the General Chemical Company as 'Genetron 150') was bubbled into

the flask at such a rate that the reaction temperature was maintained between 0-5°C. When it appeared that the olefin was no longer being absorbed (3 hours after addition was started) the solution was poured onto a mixture of 500 ml. of concentrated hydrochloric acid and 2500 g. of crushed ice. The organic layer was separated and washed successively with dilute hydrochloric acid, 10% sodium bicarbonate solution, and water, then it was dried over Drierite.

The chloroform was removed by distillation at atmospheric pressure, and the dark colored residue was distilled under reduced pressure to obtain a colorless liquid, b.p. 50-75°C/20 mm. Fractional distillation of this distillate through a Todd column (12 mm. barrel, packed with 1/8 inch Pyrex glass helices) yielded two products. Fraction 'A', b.p. 43.0-45.0°C/29 mm., n_D^{25} 1.3822, d_4^{25} 1.280; and Fraction 'B', b.p. 72.0°C/28 mm., n_D^{25} 1.4690, d_4^{25} 1.366. Both fractions contained a carbonyl group (infrared analysis), and Fraction 'A' gave a positive test with 2,4-dinitrophenylhydrazine reagent. Anal. Fraction 'A' % F = 27.4, % Cl = 28.0. Fraction 'B' % F = nil, % Cl = 59.9.

These results are best explained by denoting Fraction 'A' as $\text{CH}_3\text{COCH}_2\text{CF}_2\text{Cl}$ (or $\text{CH}_3\text{COCF}_2\text{CH}_2\text{Cl}$) contaminated with a small amount of dichloroketone, and Fraction 'B' as $\text{CH}_3\text{COCH}_2\text{CCl}_3$ (or $\text{CH}_3\text{COCCl}_2\text{CH}_2\text{Cl}$).

For $\text{CH}_3\text{COCH}_2\text{CF}_2\text{Cl}$ (calc.) % F = 26.7, % Cl = 24.9, M_R^D 26.0, found 25.5.

For $\text{CH}_3\text{COCH}_2\text{CCl}_3$ (calc.) % F = nil, % Cl = 60.6, M_R^D 35.7, found 35.2.

B. Preparation of Polymers

The polymerization apparatus, procedure and methods of purification are described elsewhere (1). With regard to polymer purification, it should be noted that the ammonia precipitation of ferric ion (described in the preceding reference) cannot be employed where more than 10 g. of polymer is obtained, because solutions of such an amount of polymer in a reasonable concentration in acetone are too viscous to filter.

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

The experimental data are summarized in Table I. From this table, it can be concluded that the optimum conditions for polymerization are 2-3% of ferric chloride at 90-100°C for 64 hours. Equally high conversions can be obtained from higher catalyst concentrations (5-6%) over a 24 hour period (1), but the polymers obtained under those conditions do not have the toughness, and they are waxier than those produced under the above mentioned conditions.

A sample of polymer prepared according to the above optimum conditions was found to have a weight-average molecular weight of 230,000.*

* Molecular weight data were obtained by Drs. O. K. Johansson and G. Pollnow of the Dow Corning Physical Chem Laboratories. Light-scattering procedures were used.

Table I

Polymerization of 3,3,3-Trifluoro-1,2-epoxypropane Using Ferric Chloride Catalyst at 90-100°C														
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>15</u>
Wt. of oxide (g.)	12.0	12.0	18.5	19.0	18.5	12.0	12.0	19.0	19.0	18.5	18.0	19.0	19.0	12.0
Wt. of FeCl ₃ (g.)	0.1	0.2	0.45	0.45	0.45	0.1	0.2	0.45	0.45	0.45	0.60	0.60	0.60	0.2
% FeCl ₃	0.8	1.6	2.4	2.4	2.4	0.8	1.6	2.4	2.4	2.5	3.3	3.2	3.2	1.6
Time (hrs.)	41	41	48	48	48	64	64	64	64	64	64	64	64	72
Wt. of polymer (g.)	1.0	2.5	14.0	13.0	13.0	5.0	4.5	15.5	15.5	14.5	15.5	15.0	15.5	5.0
% Conversion	8.3	20.9	76.7	68.4	70.3	41.6	37.5	81.6	81.6	78.3	86.2	78.9	81.6	41.6

Reaction of 3,3,3-Trifluoro-1,2-epoxypropane with Free Radical Catalysts

1. A 5 ml. sample of the epoxide was submitted to Co^{60} radiation.** No polymerization had occurred after 16.2 Mrev. exposure.

2. Small samples (12.5 g.) of the epoxide were treated with 0.1 g. of tert. butyl hydroperoxide and benzoyl peroxide, respectively. No polymerization had occurred after 72 hours at 90-100°C.

C. Vulcanization Studies***

1. Initial work involved compounding $\{\text{CF}_3\text{CHCH}_2\text{O}\}_x$ with a silica filler followed by attempts to vulcanize with peroxide catalyst.

100 parts $\{\text{CF}_3\text{CHCH}_2\text{O}\}_x$

30 parts H1-S11 (303)

5 parts Bz_2O_2

With and without 10 parts ZnO

A press cure⁺ at 125°C for 45 minutes failed to produce a rubber with either sample; both stocks remained soft and exhibited no traceable cross-linking.

** Radiation studies were conducted by Dr. B. Wilkinson of The Dow Chemical Company, Nuclear Research Laboratory.

*** Vulcanization studies were conducted by R. J. Koch of the Dow Corning Silastic Research Laboratory.

+ Press cure means a strip measuring 1/16 in. x 1 in. x 3 in. was heated in a hydraulic ram press at a pressure of 600 lbs./sq.in.

The compounded stock was extremely dry and would only band to the mill roll when the rolls were close; when sheeted off the roll it readily fell apart. In later work it was found that 20-25 parts of Hi-Sil would produce a better milling and handling stock which would remain intact on sheeting from the mill.

2. Copolymers were studied next. It was hoped that the methyl group attached to the polyether chain would result in a more readily vulcanizable structure.

Four stocks were prepared (including a control) having the following formulations:

100 parts $\{CF_3CHCH_2O\}_x$ or the copolymer containing $\{CF_3CHCH_2O\}_x$ and 10, 20 or 50% (by vol.) of $\{CF_3C(CH_3)CH_2O\}_x$
20 parts Hi-Sil (303)
5 parts Bz_2O_2

The control stock containing $\{CF_3CHCH_2O\}_x$ was still soft after press curing at 125°C for 10 and 30 minutes; press curing the stocks containing the copolymers for 10 minutes at 125°C resulted in soft, unvulcanized samples which were disagreeably odorous.

The copolymer containing 10% $\{CF_3C(CH_3)CH_2O\}_x$ was heated, stripped under a high vacuum, and then compounded into a similar stock with an additional 5 parts of ZnO. This stock also failed to vulcanize after a press cure at 125°C for 10 minutes.

3. The next series involved higher peroxide additions with the $\{CF_3CHCH_2O\}_x$ polymer.

The following stocks were prepared:

100 parts $\{CF_3CHCH_2O\}_x$

20 parts Hi-Sil (303)

8 parts Bz_2O_2

With and without 5 parts ZnO

After press curing 15 minutes at 125°C, the sample without ZnO was still soft; the sample containing ZnO held together somewhat and the strip appeared to be slightly rubbery.

A similar stock was then prepared as above but with increased peroxide and metal oxide content (i.e., 12 and 10 parts respectively). After press curing for 10 minutes at 125°C the sample appeared to be slightly rubbery and spongy. After remilling with an additional 10 parts of "Cadet 35" and pressing at 125°C, the sample appeared to be more spongy but possessed little strength and fell apart readily.

To another sample containing 100 parts $\{CF_3CHCH_2O\}_x$ and 30 parts Hi-Sil, was added 5 parts of tertiary butyl perbenzoate; press curing at 150°C for 20 minutes resulted in a soupy, viscous mixture.

The effect of peroxides on the polyethers was then studied. Both the $\{CF_3CHCH_2O\}_x$ polymer and the copolymer containing 10% $\{CF_3C(CH_3)CH_2O\}_x$ were milled with 5 parts Bz_2O_2 per hundred parts of polyether and heated between magnesium plates for 20 minutes at 125°C. The polyethers appeared to depolymerize to a fluid consistency under these conditions.

This behavior was then checked on a new batch of $\{CF_3CHCH_2O\}_x$ with both benzoyl peroxide and dicumyl peroxide. Three parts of peroxide were milled into 100 parts of the polyether; after press curing at 125°C for 30 minutes between stainless steel plates these samples were compared with a control which originally contained no peroxide. Although the peroxide-containing polyethers did not break down to a fluid as previously noted they were definitely of lower consistency than the control sample.

4. Stocks were prepared having the following formulation:

100 parts $\{CF_3CHCH_2O\}_x$	}
10 parts Me_2SiO polymer	
30 parts H1-Sil	
4.3 or 8.5 parts "'Cadet 35'"	

The above stocks still handled poorly; they were dry and crumbled readily on sheeting from the mill. A press cure for 10 minutes at 125°C resulted in no vulcanization; the samples crumbled and fell apart.

A blend was then prepared containing equal amounts of both the polyether and the polysiloxane and then vulcanized with conventional amounts of Bz_2O_2 . The following formulations were used and physical properties obtained.

a. (Control) 100 parts Me_2SiO polymer

30 parts H1-Sil

1.5 parts Bz_2O_2

b. 100 parts $\left\{ \begin{array}{l} 50 \text{ parts } (CF_3CHCH_2O)_x \\ 50 \text{ parts } Me_2SiO \text{ polymer} \\ 30 \text{ parts H1-Sil} \end{array} \right\}$

1.5, 2.0 parts Bz_2O_2

<u>Description</u>	<u>Cure</u> ^a	<u>Durometer</u>	<u>T.S.</u>	<u>E</u>
Control (Me_2SiO) _x	AM-10'/125°C	44	535	495
	24 hrs./250°C(oven)	51	509	400
(50/50) with 1.5 parts Bz_2O_2	AM-10'/125°C	53	299	530 flow; stock dead
	24 hrs./150°C(oven)	63	283	160 good recovery
(50/50) with 2.0 parts Bz_2O_2	AM-10'/125°C	53	299	495 dead stock; flow
	24 hrs./150°C(oven)	69	394	125 good recovery
	24 hrs./200°C(oven)	95 +	Samples were rigid and slightly brittle.	
	24 hrs./250°C(oven)	95 +		

a. AM = as molded by press cure.

The press cured samples were immersed in ASTM No. 3 oil for 24 hours at 150°C; the samples were found to swell 21.6 and 54.7% respectively. Although attractive decreases in oil swell were obtained with the blends, the poor heat stability and initial vulcanizate properties offset the advantages gained. Also it is felt that the polyether acts as little more than a diluent in the rubber.

5. A final attempt was made to vulcanize a later batch of the 50% $\{CF_3C(CH_3)CH_2O\}_x$ copolymer. In this work 'X' filler was employed along with moderate to high peroxide additions. The following stocks were prepared:

100 parts	$\{CF_3CHCH_2O\}_x$	}
	50% $\{CF_3C(CH_3)CH_2O\}_x$	
20 parts	'X' filler	
3 parts	Bz_2O_2	}

With and without 5 parts ZnO

After press curing at 125°C for 15 minutes the sample stocks were still soft with no trace of vulcanization. The sample not containing ZnO was remilled with 10 parts Bz_2O_2 and 5 parts ZnO and press cured for 20 minutes at 125°C, after which the stock still appeared to be soft. Similar formulations were then prepared with 6 parts Bz_2O_2 and 5 parts ZnO and with both 'X' and H1-Sil filler. These were press cured for 90 minutes at 125°C with little change in results.

6. This phase of the work involved the use of isocyanates. Stocks were prepared containing 100 parts $\{CF_3CHCH_2O\}_x$, 20 parts 'X' filler and either 4 parts of triphenylmethane triisocyanate or 4 parts of m-tolylene diisocyanate. Press cures at 140°C for 30 to 90 minutes only resulted in stiffening the stock slightly. A sample similar to the one containing 4 parts of the triisocyanate but with an additional part of triethylamine was prepared; under the same curing conditions little change in result was noted.

Two more stocks were prepared with an excess of both the di- and the triisocyanate.

- a. 100 parts $\{CF_3CHCH_2O\}_x$
20 parts 'X' filler
21.6 parts Triphenylmethane triisocyanates
- b. 120 parts (as above)
15.4 parts m-Tolylene diisocyanate

The samples were placed in a mold and press cured at 140°C for 90 minutes, which greatly increased the stiffness of the stocks but did not result in a rubber. The samples possessed little strength--even after heating an additional 24 hours at 150°C.

The above sample cured with diisocyanate was remilled and another 5 parts of m-tolylene diisocyanate was added. Press curing at 140°C for 90 minutes gave a slightly stiffer stock, but again without strength. It may possibly be that moisture and surface hydroxyl groups on the silica filler interfere with this chain lengthening and cross-linking step.

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