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HYBRID FLUOROSILICONES FOR AIRCRAFT FUEL TANK SEALANTS
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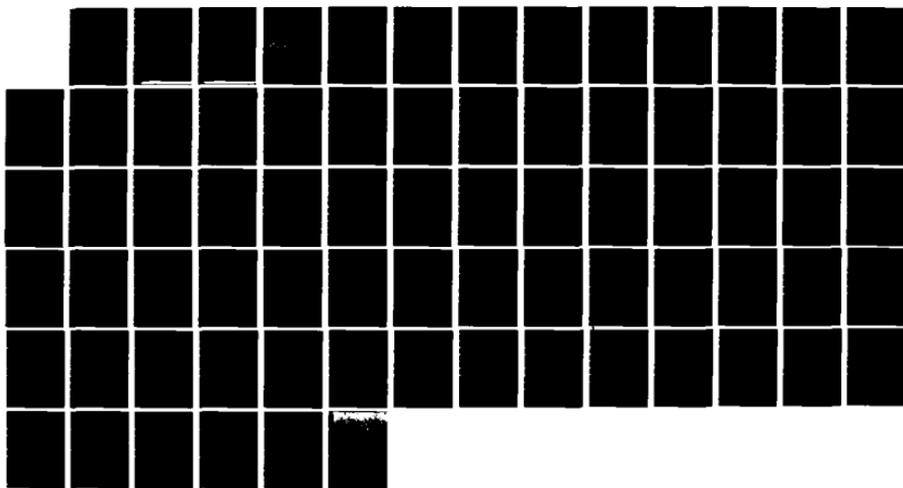
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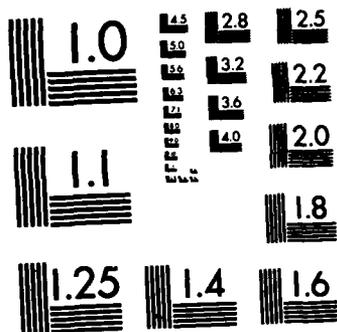
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Part IV

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AD - A134286

HYBRID FLUROSILICONES FOR AIRCRAFT FUEL TANK SEALANTS

Part IV. Synthesis of Fluorocarbon and Fluorocarbon Ether Hybrid Fluorosilicone Polymers

DOW CORNING CORPORATION
MIDLAND, MICHIGAN 48640

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Final Report covering period 25 January 1973 to 25 January 1974

MAY 1974

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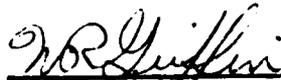
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This technical report has been reviewed and is approved for publication.



W. R. GRIFFIN
Project Monitor

FOR THE COMMANDER



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Elastomers and Coatings Branch
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Two fluoroether silicone (FES) elastomeric polymers were synthesized, and cured research samples were delivered to AFML for evaluation. These polymers were based on the $-(CF_2)_2O(CF_2)_nO(CF_2)_2-$ ($n = 2,5$) backbone unit. A one-step synthesis of $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$ from commercially available starting materials was demonstrated: about 110 g of this fluoroether was prepared, and over 500 g of $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$ was synthesized. (Continued on reverse side)		

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Coupling studies of the α,ω -diodoperfluoroethers have shown: (1) A good yield (71%) of dimer and trimer is produced by photolysis of $I(CF_2)_2O(CF_2)_2O(CF_2)_2I/Hg/C_2F_6$; (2) Fair yields (ca. 40%) of dimer and trimer are produced by heating copper-bronze powder with the ether, but some hydrogen endblocked materials are also produced; (3) Heating with Hg or Cu(Hg) produces mercury-inserted fluoroether oligomers.

The following samples of LS/FCS-210 copolymer sealants were prepared and submitted to AFML for evaluation:

- 1 pound LS/FCS-210 (0.9/1.0), unformulated
- 1 pound LS/FCS-210 (0.9/1.0), formulated
- Research sample LS/FCS-210 (1-1.2/1.0), unformulated
- Research sample LS/FCS-210 (1.5/1.0), unformulated

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A B S T R A C T

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A one-step synthesis of $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$ from commercially available starting materials was demonstrated; about 110 g of this fluoroether was prepared, and over 500 g of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$ was synthesized.

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In addition, we have attempted to prepare samples of alternating LS/FCS-210 copolymers having the following ratios: 1/1, 1.5/1, 2/1. Analyses are pending.

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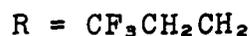
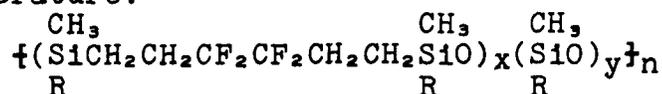
INTRODUCTION

The objective of this work is the synthesis and evaluation of hybrid fluorosilicone polymers which possess fuel and reversion resistance at elevated temperatures. These polymers are intended for use as seals and sealants in aircraft applications where exposure to extreme environmental conditions is encountered.

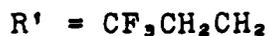
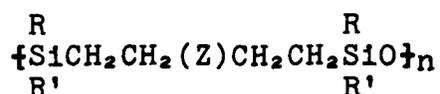
In order to accomplish this objective a simultaneous two-phase program was conducted to develop fluorosilicone hybrid polymers and to synthesize perfluoroalkylene ether segments for these hybrid polymers. An outline of the program follows.

A. Fluorosilicone Hybrid Copolymers

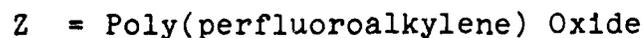
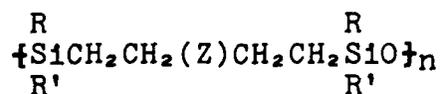
RTV curable copolymer systems possessing an improved glass transition temperature.



B. Fluorosilicone-Fluoroether Hybrid Polymers (FES)



C. Fluorosilicone-Poly(fluoroether) Hybrid Polymers (PFES)



Several synthetic routes were investigated in an effort to develop a feasible preparative method for the desired difunctional poly(fluoroether).

DISCUSSION

A. Fluorosilicone-Fluoroether Hybrid Polymers (FES)

1. Preparation of $X(CF_2)_2O(CF_2)_nO(CF_2)_2X$

Several methods of preparing functional perfluorocarbon ethers have appeared in the literature. Thus, perfluorooxydiacetic and perfluorooxydipropionic acid fluorides have been prepared by electro-chemical fluorination (1). The yields were low but the products could be further reacted to give longer chain polyethers. Perfluorooxydiacetic acid has been prepared (2) from dichloromaleic anhydride using SF_4 , a relatively expensive reagent, to prepare the intermediate 3,4-dichloroperfluoro-2,5-dihydrofuran (3) which was subsequently oxidized. The addition of perfluoropropylene oxide to a metal fluoride salt of a perfluorocarbon diacid fluoride yields perfluoroethers with acid fluoride functionality (4) but inseparable isomeric mixtures were obtained.

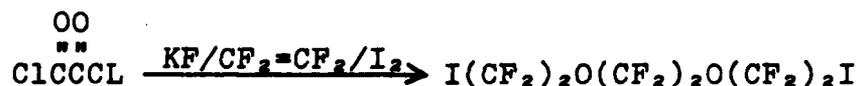
Although the literature is bereft of facile syntheses of α,ω -dihaloperfluoroethers, several years ago Evans and co-workers reported (5) a novel preparation in which a fluorinated carbonyl compound, a metal fluoride, an olefin, and a halogen were reacted to yield a primary α -halopolyfluoroether. This report prompted an investigation in this laboratory to determine if the reaction could be modified to give α,ω -dihaloperfluorocarbon ethers. The feasibility of the synthetic approach was verified by the preparation of α,ω -dibromoperfluorodiethyl ether and α,ω -dibromoperfluoroethylpropyl ether from bromodifluoroacetyl fluoride (6) and bromotetrafluoropropionyl fluoride (7), respectively.

The utility of this approach in the synthesis of α,ω -difunctional ethers was further enhanced by the fact that the technology to produce the required halo-functional perfluorocarbon acids in large quantities was developed at Dow Corning (8,9).

The scope of this reaction has since been enlarged (10) to include the preparation of α,ω -difunctional perfluorodiethers which lend additional flexibility to the molecule as a consequence of their increased oxygen content.

a. Preparation of $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$

Efforts to refine the synthesis of $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$ (10), which is a low cost alternative to $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$ and $Br(CF_2)_5O(CF_2)_2Br$, have shown that $ClCOCOC1$ can be converted directly to $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$, thereby bypassing the synthesis of $FCOCOF$ which is a fairly difficult material to handle.



It was demonstrated that NaF was totally ineffective in the conversion of $ClCOCOC1$ to the title compound either in diglyme, or in a diglyme/acetonitrile reaction medium. On the other hand, KF in diglyme did effect the desired reaction, although the yield was slightly lower than that achieved in a stepwise sequence, in which $FCOCOF$ was isolated (20% vs. 26% respectively). This may be due to the formation of a KCl coating on the surface of the KF in the direct synthesis.

In an effort to account for the relatively low yield (20-26%) in the conversion of $ClCOCOC1$ to $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$, volatile materials were collected before and after hydrolysis of the reaction mixture and subjected to glc/mass spec analysis. The former sample was shown to contain a $-CF_2CF_2I$ fragment-containing species ($m/e = 312$)

in addition to $\text{CF}_2=\text{CF}_2$, $\text{CF}_3\text{CF}_2\text{I}$, and $\text{ClCF}_2\text{CF}_2\text{I}$. A reasonable structure for the precursor to the $-\text{CF}_2\text{CF}_2\text{I}$ fragment based on a molecular weight of 312 is $\text{CF}_3\text{OCF}_2\text{CF}_2\text{I}$. The presence of this compound would indicate that fragmentation of oxalyl fluoride or an alkoxide or mono-ether derived from it is occurring, but further data are necessary to substantiate this possibility.

The volatile materials collected after a small amount of water was added to the reaction mixture include acetone, a fact for which no ready explanation is available.

About 110 g of the title ether have been prepared via in situ generation of FCOCOF during this contract period.

b. Preparation of $\text{FCO}(\text{CF}_2)_3\text{COF}$ and $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{I}$

About 675 g of perfluoroglutaryl fluoride was prepared in 97% yield from perfluoroglutaryl chloride. A portion of this was converted to 522 g of $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{I}$ (47% distilled yield), and a 50 g sample of this material was delivered to W. R. Griffin of AFML.

2. Addition of $\text{CH}_2=\text{CH}_2$ to $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_n\text{O}(\text{CF}_2)_2\text{I}$

a. $n = 2$

A total of 166 g of $\text{I}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{I}$ was obtained in 95% yield after rocking $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{I}$ with a slight excess of ethylene at 200°C in an autoclave.

b. $n = 5$

About 95% yield (106 g total) of $\text{I}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{I}$ was obtained after treating $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{I}$ with ethylene as described above.

3. Preparation of $\text{CH}_2=\text{CH}(\text{CF}_2)_2\text{O}(\text{CF}_2)_n\text{O}(\text{CF}_2)_2\text{CH}=\text{CH}_2$

a. $n = 2$

Dehydrohalogenation of $\text{I}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2(\text{CH}_2)\text{I}$ proceeded smoothly to give a total of 66 g of the title compound in 68% yield (ca. 91% including intercuts).

b. $n = 5$

Dehydrohalogenation of $\text{I}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{I}$ produced 53 g (88% yield) of pure title compound.

4. Preparation of $\begin{array}{c} \text{CH}_3 \\ | \\ \text{ClSi}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_n\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{SiCl} \\ | \\ \text{CH}_2 \\ | \\ \text{CH}_2 \\ | \\ \text{CF}_3 \end{array} \quad \begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2 \\ | \\ \text{CH}_2 \\ | \\ \text{CF}_3 \end{array} \quad (\text{I})$

a. $n = 2$

About 23 g of pure I was produced in the addition of $(\text{CF}_3\text{CH}_2\text{CH}_2)(\text{CH}_3)\text{Si}(\text{H})\text{Cl}$ to $\text{CH}_2=\text{CH}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{CH}=\text{CH}_2$. The reaction was performed in a manner similar to that employed previously (10)

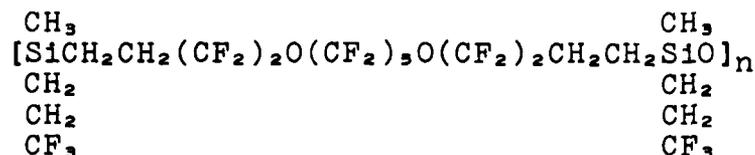
b. $n = 5$

Three distillations were necessary to achieve 96% purity for the 42 g of product from the reaction of $\text{CH}_2=\text{CH}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{CH}=\text{CH}_2$ and $(\text{CF}_3\text{CH}_2\text{CH}_2)(\text{CH}_3)\text{Si}(\text{H})\text{Cl}$. The final distillation was performed in a glass system, since it appeared that decomposition might be occurring on the metal surface of the spinning band column used in the initial distillations.

5. Preparation of FES-222-10 Sealant

An abbreviated nomenclature system for fluorosilicone-fluoroether hybrid polymers (FES) has been devised. The numbers employed refer only to fluorocarbon units - the first series to those contained within the polymer backbone, and the second to pendant

fluorocarbon chains attached to silicon. Each digit in the first series refers to a segment of fluorine-substituted carbon atoms, and it is assumed that an oxygen atom is interposed between each fluorocarbon segment. For example, FES-252-10 refers to:



Each digit in the second series of numbers refers to a pendant fluorocarbon group; notice that in the foregoing example there is only one such group per silicon atom, hence the '10' system. If each silicon atom contained two fluorocarbon pendant groups, the nomenclature employed would be '11'.

The chlorosilane I (n = 2) was hydrolyzed in an aqueous sodium bicarbonate-ether system in the usual manner (10), producing the corresponding silanediol which was endblocked by reaction with $\text{Vi}(\text{Me})_2\text{SiCl}$ and polymerized, yielding 16 g of a sealant consistency fluid polymer having a DP of ca. 10.

Thermal test results are presented in the appendix.

A research sample of the cured sealant was delivered to W. R. Griffin of the AFML for evaluation and testing.

6. Preparation of FES-252-10 Sealant

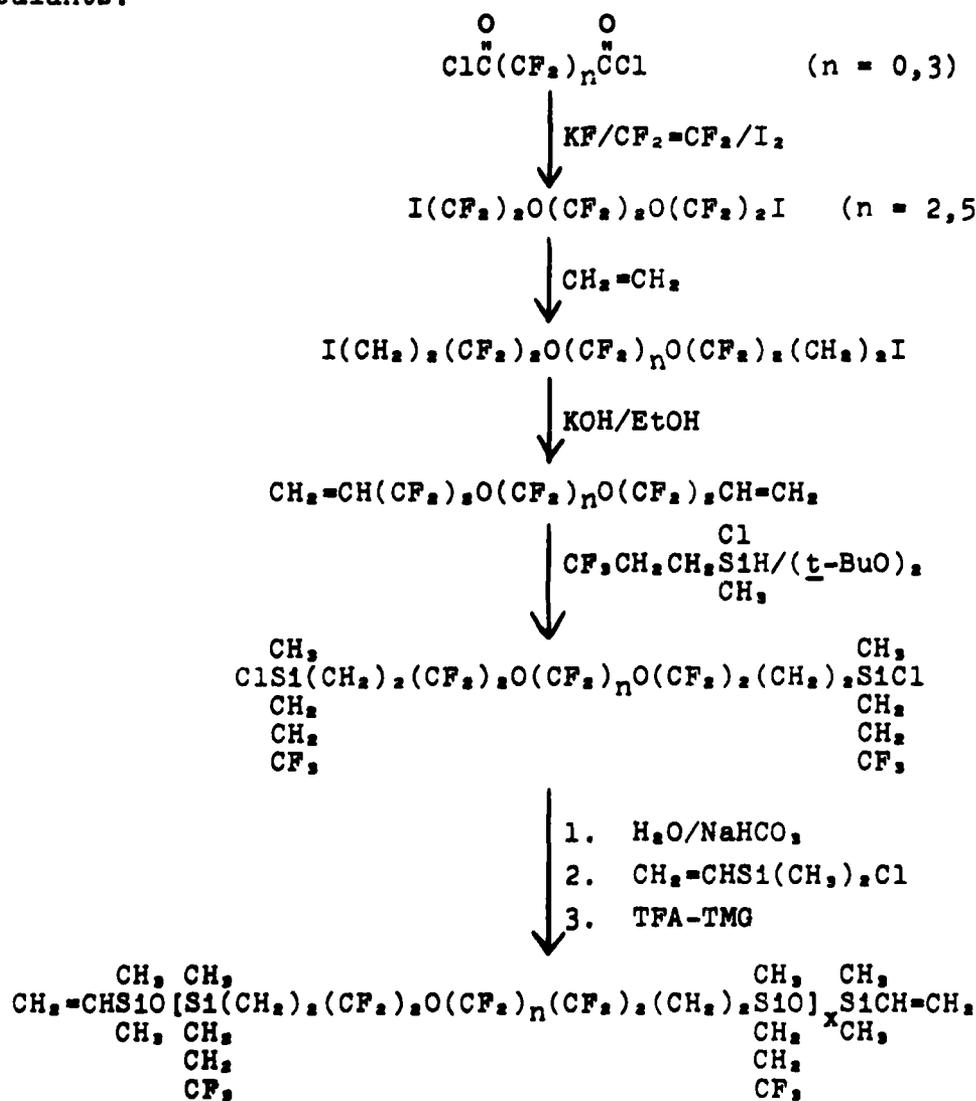
Hydrolysis of the chlorosilane I (n = 5) in an aqueous sodium bicarbonate-ether system (10) produced a silanediol which was endblocked with $\text{Vi}(\text{Me})_2\text{SiCl}$ and polymerized using TMG-TEA (10) to yield ca. 24 g of a sealant consistency fluid polymer having a DP of ca. 16.

The glass transition temperature of -52°C (-62°F) for this polymer is significantly lower than that observed for FES-222-10 ($T_g = -40^{\circ}\text{C}$, -40°F). This is thought to be a manifestation of the regularity present in the backbone of the FES-222-10.

Thermal test results are presented in the appendix.

A research sample of the cured sealant was delivered to W. R. Griffin of the AFML for evaluation and testing.

The following sequence summarizes the preparation of the FES sealants:



(n = 2, 5)

B. Poly(fluoroether)-Silicone Hybrid Polymers (PFES)

It has been established that linear poly(fluoroethers) possess excellent resistance to thermal and oxidative degradation at high temperatures, but there has been no report to our knowledge of a good elastomer based on such a system. We have approached this problem by attempting to couple α,ω -diiodopolyfluoroethers to obtain long chain poly(fluoroethers) possessing terminal functionality in the form of iodine. This functionality should be capable of modification which would allow the introduction of crosslinking sites, in analogy to previous work performed in our laboratories with α,ω -difunctional perfluoroethers (7).

We have conducted a number of studies aimed at evaluating the potential of various reagents and conditions for obtaining the desired coupled products (Table I). In addition to the standard thermal and ultraviolet irradiative methods carried out in the presence of mercury, we briefly looked at the coupling of organocopper and organosilver intermediates. Tamura and Kochi (11) reported that alkyl Grignard reagents have been coupled in good yields in the presence of stoichiometric amounts of silver salts. The mechanism is thought to involve a concerted bimolecular process. Although no reports have appeared in which this reaction was generalized to include fluorocarbons, the proposed mechanism certainly does not preclude that possibility. A fluoroether dimer was in fact detected when the reaction was attempted, but it unfortunately was hydrogen end-capped. We also attempted to convert what is believed to have

been an α,ω -diorganocopper reagent to the corresponding organosilver compound, but the only identifiable products indicated that reaction with solvent had occurred.

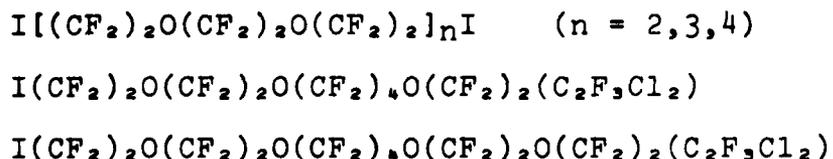
The most promising route appears at this time to be coupling with either Cu/heat or Hg/UV to produce oligomeric α,ω -diiodoperfluoroethers. All attempts to produce high molecular weight materials (> trimer) have been complicated by the introduction of hydrogen at the end positions.

1. Photolysis of $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{O}/\text{Hg}/\text{C}_7\text{H}_{16}$

Although only low molecular weight products (dimer and trimer, combined yield 71%) were formed in this particular reaction, no hydrogen end-capped materials were detected. This seems to indicate that the steps* taken to remove traces of hydrogen-containing impurities from the fluoroether starting material circumvented earlier difficulties (12), at least for this particular reaction.

2. Photolysis of $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{I}/\text{Hg}/\text{C}_2\text{F}_3\text{Cl}_3$

Photolysis of the title mixture produced dimeric, trimeric, and tetrameric products as well as products derived from fluoroether radical displacement of chlorine from solvent:



*Continuous water extraction followed by redistillation.

3. Photolysis of $I(CF_2)_2O(CF_2)_nO(CF_2)_2I/Hg/C_7F_{16}$ ($n = 2,5$)

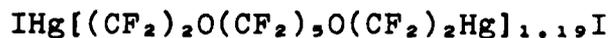
During the reaction, mercury salts were removed by filtration and replaced by fresh Hg in order to facilitate the coupling. The apparent high viscosity of the coupled product suggests much higher molecular weight than the product described in example B-1. It appears some hydrogen endblocking occurred; analysis is underway.

4. Photolysis of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I/Hg$

For this coupling reaction, the starting fluoroether was not extracted or redistilled to remove traces of hydrogen-containing impurities. Although it was apparent that coupling had occurred, a large degree of hydrogen end-capping was also present.

5. Reaction of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I/Hg/280^\circ C$

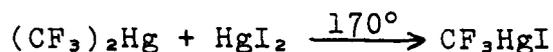
Treatment of the purified title ether with a 10-fold excess of mercury at 280° produced a viscous mercury-containing material. Reaction with powdered I_2 , which is a known (13) method of cleaving C-Hg bonds in fluorocarbons, led to the regeneration of pure starting fluoroether. Based on the quantity isolated, the average structure of the 'coupled' product is:



6. Reaction of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I/Hg/320^\circ C$

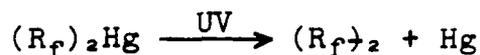
This reaction was conducted with a 10-fold excess of mercury at 200° for four days. A great deal of unreacted mercury was present at the end of this time, so the heat was increased to 380° . A large amount of red precipitate was formed (HgI_2) and

the viscosity of the organic material was great. After heating for an additional day at 320°, the viscosity of the organic material had decreased, and most of the red precipitate had either disappeared or been replaced by a yellow powder (Hg₂I₂ or HgI₂). These observations may indicate that at this temperature chain scission is occurring analogous to that reported by Emeléus (14):



7. Reaction of I(CF₂)₂O(CF₂)₅O(CF₂)₂I/Hg/360°C

X-ray fluorescence detected mercury in the product from this reaction, so the neat material was further irradiated to remove diorganomercury species. It was anticipated that this would induce homolytic scission of C-Hg bonds and coupling of the resulting radicals, in analogy to the work of Hazeline and co-workers (15) and Sharkey et al. (16):



Any organomercuriiodides remaining would then be converted to organoiodides by treatment with iodine (13). This sequence has been performed, but analysis is pending.

8. I(CF₂)₂O(CF₂)₅O(CF₂)₂I/Cu/170°C

Copper bronze powder was evaluated as an alternative coupling agent in the belief that its lower cost, lack of toxicity, and ease of handling offer significant advantages over mercury. The initial experiment, in which the surface of the metal was activated by iodine and hydrochloric acid, (17) proved to be the most successful. GLC analysis indicated a good (ca. 80%) conversion of starting material, and a reasonable yield of dimer and trimer (ca. 30% and 10% respectively). Small amounts of α-hydro-ω-iodoperfluoroethers were also identified.

9. $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_3\text{O}(\text{CF}_2)_2\text{I}/\text{Cu}/\text{DMF}/165^\circ\text{C}$

Although a trace of DMF has been shown to be a prerequisite for the copper coupling of 1-iodo-2-halotetrafluorocyclobutenes (18), no increase in yield of coupled products was observed in this reaction. Rather, the relative amount of α -hydro- ω -iodoperfluoroethers was increased.

10. $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_3\text{O}(\text{CF}_2)_2\text{I}/\text{Cu}/170^\circ\text{C}$

In this experiment the copper powder was activated with disodium EDTA as described by Lewin et al. (19). Only low molecular weight, hydrogen end-capped products were detected.

11. $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{I}/\text{Cu}/\text{Pyridine}/110^\circ\text{C}$

Pyridine is known (20) to be a good ligand for copper and a good solvent for aryl iodide-perfluoroalkyl iodide coupling and it was hoped that it would also facilitate coupling in this particular system. A golden color was observed when the reaction was initiated, but further heating produced an intractable black mixture.

12. $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{I}/\text{Cu}(\text{Hg})/165^\circ\text{C}$

Reaction with copper amalgam led to the formation of a number of organomercury species; the following were indicated by glc/mass spec: (1) $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{Hg}$; (2) $\text{Hg}[(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}-(\text{CF}_2)_2]_2\text{HgI}$; (3) higher molecular weight peaks.

13. $\text{X}(\text{CF}_2)_2\text{O}(\text{CF}_2)_3\text{O}(\text{CF}_2)_2\text{X}/\text{M}/\text{AgNO}_3$

We have found silver nitrate to be a poor reagent for effecting homo-coupling of the title ether under the following conditions: (1) $\text{X} = \text{I}$, $\text{M} = \text{Cu}$, 130° , DMSO; (2) $\text{X} = \text{I}$, $\text{M} = \text{Mg}$, 65° , THF; (3) $\text{X} = \text{Br}$, $\text{M} = \text{Mg}$, $0-35^\circ$, THF.

14. $I(CF_2)_2O(CF_2)_5O(CF_2)_2I/Zn/Ac_2O/CH_2Cl_2$

In contrast to a report by Henne (21) in which perfluoropropyl iodide was dimerized by a $Zn/Ac_2O/CH_2Cl_2$ mixture, only reduced products were obtained from this reaction.

C. FCS-210/Fluorosilicone 'Random' Copolymers

We have demonstrated previously (10) that copolymers in

which the FCS unit $(-Si(\overset{CH_3}{\underset{CH_2}{\underset{CH_2}{\underset{CF_3}}{\mid}}}{CH_2})_2(CF_2)_n(CH_2)_2SiO-)$ is linked to the

LS unit $(-SiO-)$ exhibit improved low temperature properties (as

manifested in Tg values) due to incorporation of the flexible siloxane linkage. It was of interest to prepare a number of samples in which the ratio of the monomeric units was varied, in order to determine the effect upon some of the other physical properties of the resulting polymers.

It was felt, a priori, that the ideal polymer backbone would be one which incorporates the LS unit in an alternating manner rather than one which might allow aggregation of a number (three or more) of LS units in succession. Such a random situation, it was believed, would be more favorable for reversion of the polymer, an important drawback in LS polymers. Since the method employed for the preparation of our initial copolymers (now termed 'random' copolymers) involved the condensation of $\equiv SiOH$ with $\equiv SiCl$ followed by condensation polymerization of the prepolymer it is possible that the HCl generated

in the first step causes prepolymer backbone rearrangement and/or silanol condensation (with attendant hydrolysis of $\equiv\text{SiCl}$ and eventual incorporation of LS* aggregates). The following research samples were prepared in this manner and delivered to W. R. Griffin of AFML: LS/FCS ratio (a) 0.9/1.0; (b) 1-1.2/1; (c) 1.5/1. In addition, one lb. of raw 0.9/1.0 LS/FCS copolymer and one lb. of formulated 0.9/1.0 LS/FCS copolymer was delivered to Mr. Griffin, AFML. It is interesting to note that, according to our analyses, in no case did a straightforward, stoichiometric reaction occur. Even a large excess (6.1/1) of $(\text{CF}_3\text{CH}_2\text{CH}_2)(\text{CH}_3)\text{SiCl}_2$ was insufficient to raise the LS/FCS ratio much above 1/1. The use of an excess of an 'LS' disiloxane $(\text{ClSiO}(\text{CH}_3\text{CH}_2\text{CH}_2)\text{SiCl})$ only raised the LS/FCS ratio to $(\text{CH}_2\text{CH}_2)_2\text{Si}_2\text{O}$ $(\text{CH}_2\text{CH}_2)_2\text{Si}_2\text{O}$ (CF_3CF_3)

1.5/1, and this required a sequential treatment in which the initial reaction mixture was hydrolyzed and neutralized before being once again subjected to treatment with the dichlorodisiloxane.

Our analytical data are presently incapable of allowing precise determination of the LS/FCS ratio in the copolymer. F^{19} NMR and H^1 NMR spectra give different results, and elemental analysis is relatively insensitive to variations of the LS/FCS ratio in the range with which we are concerned (e.g., for LS/FCS ratio of 1/1: %C = 34.54; %H = 4.74; %F = 39.74; %Si = 13.84; for 2/1 %C = 35.53; %H = 4.80; %F = 40.58; %Si = 14.69).

Generally, increasing the ratio of LS to FCS did lead to better low temperature properties (T_g). A tabular summary of these properties is presented in the appendix (Table II).

*LS = $\text{CF}_3\text{CH}_2\text{CH}_2\overset{\text{!}}{\text{SiO}}-\text{units.}$
 CH_3

1. Preparation of 0.9/1.0 LS/FCS Copolymer (Random)

About 2 lbs. of the title copolymer was prepared by

condensation of $(CF_3CH_2CH_2)(CH_3)SiCl_2$ (II) and $HO\overset{\overset{CH_3}{|}}{Si}(CH_2)_2(CF_2)_2(CH_2)_2-$
 $\overset{\overset{CH_2}{|}}{Si}(\overset{\overset{CH_2}{|}}{O})_2CF_3$ (III) followed by TMG-TFA catalyzed polymerization; $T_g = -39^\circ C$.

2. Reaction of III with Excess II

Treatment of III with 2.2 equivalents of II produced a copolymer with an LS/FCS ratio of 1-1.2/1 and $T_g = -41^\circ C$.

3. Sequential Reaction of Excess II with III

Reaction II with 37 equivalents of I followed by hydrolysis and drying and then further reaction of this mixture with 2.4 equivalents of II produced a copolymer with an LS/FCS ratio of about 1/1 and $T_g = -51^\circ C$.

4. Sequential Reaction of Excess $(ClSi)\overset{\overset{CH_3}{|}}{O}$ (IV) with III
 $\overset{\overset{CH_2}{|}}{Si}(\overset{\overset{CH_2}{|}}{O})_2CF_3$

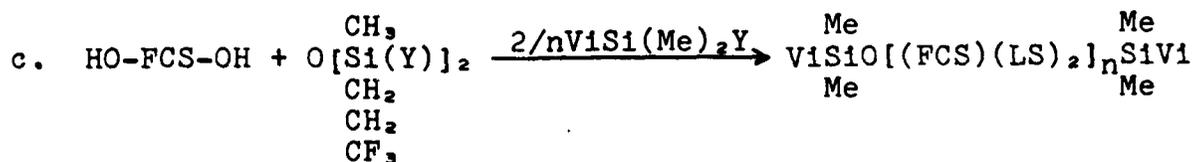
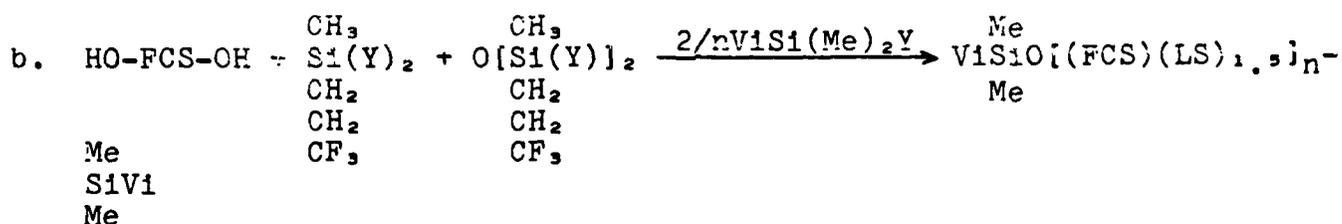
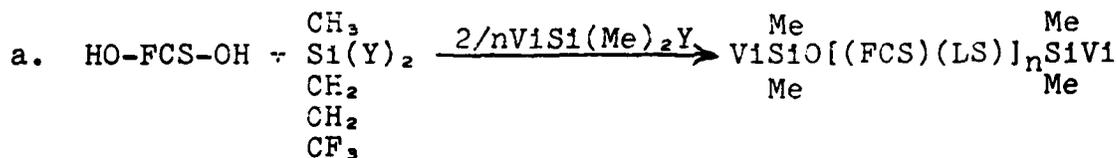
A sequential treatment of FCS-210 silanediol with 1.1 equivalents of IV in the above described manner, followed by reaction with an additional 0.85 equivalents of IV led to a copolymer possessing an LS/FCS ratio of about 1.5/1, $T_g = -41^\circ C$.

D. FCS-210/Fluorosilicone Alternating Copolymers

In order to prepare structurally discrete copolymer systems ('alternating copolymer') we have investigated a new synthetic route which should eliminate the possibility of polymer backbone

rearrangement. The following reactions have been attempted

(Y, a proprietary material, is a labile group reactive with $\equiv\text{SiOH}$):



The reactive monomers, $(\text{CF}_3\text{CH}_2\text{CH}_2)(\text{CH}_3)\text{Si(Y)}_2$, $[(\text{CF}_3\text{CH}_2\text{CH}_2)-(\text{CH}_3)\text{Si(Y)}]_2\text{O}$ and the endblocker $\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiY}$ were prepared according to a proprietary procedure available at Dow Corning. Since the reactive monomers and endblocker are proprietary materials, neither the preparation nor reactions will be discussed.

We are working with our Analytical Department to devise a method for determining whether or not an alternating structure has in fact been achieved; until such an analytical method is developed, it is anticipated that the results of TGA and confined heat tests will serve as an indication of the success of our method. Therefore, at this point our use of the term 'alternating copolymer' as opposed to 'random copolymer' refers primarily to the method of synthesis.

1. Attempted Preparation of Alternating 1/1 LS/FCS-210 Copolymer

The spectral analysis of this copolymer suggests that the ratio of the LS/FCS is 1.2/1. The molecular weight distribution was found to be fairly wide, 3.5. Therefore, it appears that the mechanical aspects of this procedure need some modification.

2. Attempted Preparation of Alternating 1.5/1 LS/FCS-210 Copolymer

Proton NMR analysis of the copolymer obtained by reaction of FCS-210 silanediol with an equimolar mixture of $(Pr_f^*)(Me)SiY_2$ and $[(Pr_f)(Me)(Y)Si]_2O$ indicates that the LS/FCS ratio is near 1.1/1. This suggests that a significant amount of either the difunctional LS material, or the difunctional disiloxane material did not take part in the reaction. If this synthetic method is to be used for future production of alternating copolymers it may be necessary to determine the relative reactivity of these two monomers in order to more closely control the LS/FCS ratio.

3. Attempted Preparation of Alternating 2/1 LS/FCS-210 Copolymer

FCS-210 silanediol was reacted with $[(Pr_f)(Me)(Y)Si]_2O$. Analysis of the product is underway.

E. Vulcanization of Copolymers

A small sample of the 1/1 alternating copolymer was formulated and cured using a standard technique available at Dow Corning. The physical and thermal properties will be determined and compared with samples of the random and other alternating copolymers.

* Pr_f = $CF_3CH_2CH_2-$

The copolymers resulting from the attempt to produce a 1.5/1 and 2/1 ratio alternating copolymers could not be cured successfully. A careful analysis of the copolymers indicates that a significant level (0.13 and 0.37%) of hydroxy groups is present in the copolymers, and therefore, the unsuccessful cure of the copolymers appears to be due to the destruction of the crosslinker by hydroxy groups. Further work in this area is in progress to eliminate the cure problem.

EXPERIMENTAL

Due to the sensitive nature of the reagents involved in the synthesis of the alternating LS/FCS-210 copolymer, all glassware was oven dried and reactions were conducted under an atmosphere of dry nitrogen. Similar precautions were observed for the fluoro-ether coupling reactions; in addition, the mercury was devolatilized for several hours before use and the fluoroethers were rigorously purified to exclude hydrocarbon contaminants.

Confined heat tests were run on several polymer samples (Table II). The LS/FCS-210 1/1 molar copolymer was superior to the others tested.

Programmed Thermal Gravimetric Analyses (TGA) were obtained for some of the polymers described within this report (Figures 1 through 5).

A. Fluorosilicone-Fluoroether Hybrid Polymers (FES)

1. Preparation of $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$

a. Reaction of $ClCOCOC1$ with $KF/CF_2=CF_2/I_2$

A heavy-wall glass ampoule containing a magnetic stirring bar was loaded with 138 g (2.37 mole) of finely powdered anhydrous KF, and heated in vacuo (250-300°C/0.15 mm) for 4 days. After it had cooled, 59.4 g (0.47 mole) of oxalyl chloride was distilled (in vacuo) into the ampoule. A mixture of anhydrous diglyme (810 ml), 307 g (1.21 mole) of finely powdered I_2 , and 15.8 g (0.1 mole) of ICl was introduced and the vessel was covered with aluminum foil and pressurized to 40 psi with $CF_2=CF_2$. After stirring for 126 hours the system was evacuated through a series of cold traps. GLC/mass spectral analysis of the products collected

indicated the presence of the following components: (a) $\text{CF}_3\text{CF}_2\text{I}$, (b) $\text{ICF}_2\text{CF}_2\text{Cl}$ and (c) a species of molecular weight 312 which contains a ICF_2CF_2 - fragment. After a few ml of water were injected, the traps were found to contain a small amount of acetone in addition to the fluorocarbons.

Hydrolysis of the reaction mixture with cold sodium thiosulfate solution was followed by a wash with dilute sodium bicarbonate solution. The thick, dark organic layer was distilled, giving 130 g of $\text{C}_2\text{F}_4\text{ICl}$ and $\text{C}_2\text{F}_4\text{I}_2$ and 54 g (20%) of $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{I}$.

b. Reaction of ClCOCOCl with $\text{NaF}/\text{CF}_2=\text{CF}_2/\text{I}_2$

A glass ampoule equipped with a magnetic stirring bar was loaded with 78 g of NaF (1.85 mole) and heated in vacuo ($270^\circ/0.4\text{mm}$) for 4 days. After it had cooled, 31.9 g (0.25 mole) of oxalyl chloride was distilled (in vacuo) into the ampoule. A mixture of dry diglyme (600 g) and powdered I_2 (150.2 g, 0.59 mole) was sucked into the reaction vessel, which was covered with aluminum foil and pressurized to 40 psi with $\text{CF}_2=\text{CF}_2$. After stirring for ca. 7 days, an aliquot was removed; glc analysis indicated that none of the desired product was present.

About 45 g (0.77 mole) of dry KF was added, and the reaction mixture was repressurized. Work up in the usual manner led to the isolation of only a small amount of $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{I}$, but relatively large quantities of $\text{ICF}_2\text{CF}_2\text{Cl}$ and $\text{ICF}_2\text{CF}_2\text{I}$.

A similar reaction employing a mixture of diglyme and acetonitrile as the reaction medium produced no $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{I}$.

2. Preparation of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$

About 675 g of perfluoroglutaryl fluoride was prepared (97% yield); 400 g of this was converted to 522 g of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$ (43% distilled yield) in the previously described manner (10).

3. Preparation of FES-222-10

a. Preparation of $I(CH_2)_2(CF_2)_2O(CF_2)_2O(CF_2)_2(CH_2)_2I$

A 300 ml autoclave was loaded with 117 g (0.20 mole) of $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$ and ca. 540 psi (ca. 0.45 mole) of $CH_2=CH_2$. After being placed in a rocker, the autoclave was slowly heated to $200^\circ C$, and maintained at that temperature for 21 hours. The product, a solid, was dissolved in diethyl ether, boiled with activated carbon, filtered, and recrystallized, giving rise to 122 g of $I(CH_2)_2(CF_2)_2O(CF_2)_2O(CF_2)_2(CH_2)_2I$ (95% yield).

An analytically pure sample was obtained by sublimation (m pt $46-47^\circ C$).

The IR spectrum is consistent with the suggested structure: $-CH_2-$ at $\sim 1442\text{ cm}^{-1}$ and $-CF_2-$ and $C-O-C$ at $1100-1350\text{ cm}^{-1}$. The mass spectrum shows a molecular ion at $m/e = 642$, $M^+ \cdot -I$ ($m/e = 515$), $M^+ \cdot -HFI$ ($m/e = 495$), and CH_2I ($m/e = 141$). The H^1 nmr spectrum contains a complex multiplet at $\tau = 7.2$; the F^{19} NMR spectrum shows $-CF_2O-$ ($A = 2.0, 2.0$), $\delta = 87.8, 89.3$; and $-CF_2CH_2-$ ($A = 2.0$), $\delta = 119$.

Anal. calc'd. for $C_{10}H_8F_8O_2I_2$: C, 18.71%; H, 1.25%; F, 35.51%.
Found: C, 19.0%; H, 1.68%; F, 35.1%.

b. Dehydrohalogenation of $I(CH_2)_2(CF_2)_2O(CF_2)_2O(CF_2)_2(CH_2)_2I$

A three neck 250 ml round bottom flask fitted with a condenser and magnetic stirrer was loaded with 10 g (0.178 mole)

of KOH and 60 ml of ethanol. After the KOH had dissolved, 42.8 g (0.067 mole) of the title ether was dissolved in 160 ml of an ethanol-diethyl ether mixture and added dropwise to the stirred reaction vessel. After about one day, the mixture was hydrolyzed, the resulting emulsion was extracted with diethyl ether, dried, and distilled, giving a total of 17.5 g of pure $\text{CH}_2=\text{CH}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}-(\text{CF}_2)_2\text{CH}=\text{CH}_2$ (68% yield, or 91% including intercuts).

The IR spectrum is consistent with the expected structure $\text{CH}_2=\text{CH}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{CH}=\text{CH}_2$, containing absorptions at 1652, 1420, 977, and 965 cm^{-1} ($-\text{CH}=\text{CH}_2$) and 1100-1350 cm^{-1} (CF_2 , $-\text{COC}-$). The mass spectrum exhibits a molecular ion at m/e 386, and fragment ions at m/e 243 (M^+ , $-\text{C}_4\text{H}_5\text{F}_4\text{O}$), 127 ($\text{C}_4\text{F}_4\text{H}_5$) and 77 ($\text{C}_3\text{F}_2\text{H}_3$).

The F^{19} and H^1 NMR spectra are also in agreement with the assigned structure: $\delta = 87.4, 88.3$ ($-\text{OCF}_2-$, m, $A = 8.0$); $\delta = 117$ ($-\text{CF}_2\text{CH}-$, m, $A = 4.0$); $\tau \sim 4.1$ ($\text{CH}_2=\text{CH}-$, m).

Anal. calc'd. for $\text{C}_{10}\text{H}_6\text{F}_{12}\text{O}_2$: C, 31.11; H, 1.57; F, 59.06.

Found: C, 31.1; H, 1.60; F, 59.0.

c. Preparation of $(\text{CF}_3\text{CH}_2\text{CH}_2)(\text{CH}_3)(\text{Cl})\text{Si}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}-(\text{CF}_2)_2\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{Si}(\text{Cl})(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{CF}_3)$

A dry 250 ml round bottom flask equipped with a magnetic stirrer, condenser, and gas inlet was charged with 56.1 g (0.145 mole) of $\text{CH}_2=\text{CH}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{CH}=\text{CH}_2$, 173.1 g (0.980 mole) of (3,3,3-trifluoropropyl)methylchlorosilane, and 2.1 g (0.014 mole) of di-t-butylperoxide. The system was slowly purged with dry nitrogen while being heated to 60° overnight. An additional 3.5 g of di-t-butylperoxide was added and the reaction mixture was heated to

reflux (ca. 105°) for a day. GLC analysis indicated incomplete reaction.

About 5 g more of peroxide was added in two portions over a two day period, while maintaining a heavy reflux. Starting material was still present, so the low boiling materials (including $\text{CH}_2=\text{CH}(\text{CF}_2)_2-$

$\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{Si}^{\text{Prf}}\text{Cl}$) were stripped out of the reaction mixture

and retreated with (3,3,3-trifluoropropyl)methylchlorosilane and di-t-butylperoxide. The combined reaction mixtures were distilled

in vacuo to yield 22.6 g (25%) of pure $\text{ClSi}^{\text{Prf}}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}-$

$(\text{CF}_2)_2(\text{CH}_2)_2\text{Si}^{\text{Prf}}\text{Cl}$, (A) as well as ca. 20 g of somewhat impure (A).

The infrared spectrum of the product is virtually superimposable

upon that of $\text{ClSi}^{\text{Prf}}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{Si}^{\text{Prf}}\text{Cl}$; significant

IR absorptions appear at 3000 cm^{-1} , $1450-1100\text{ cm}^{-1}$, 990 cm^{-1} , 850 cm^{-1} , and 800 cm^{-1} . The F^{19} NMR spectrum contains absorptions at $\delta = 69.0$ (CF_2- , $A = 3.5$), $\delta = 88.0$ and 89.0 (OCF_2- , $A = 3.4, 4.1$) and $\delta = 118$ and 120 (CF_2-CH_2 , $A = 2.0, 2.0$). The H^1 NMR spectrum contains absorptions at $\tau = 7.8$ ($-\text{CF}_2\text{CH}_2-$) and $\tau = 8.93$ ($-\text{SiCH}_2^*\text{CH}_2\text{CF}_2$, $A = 8.4$) and $\tau = 9.51$ ($-\text{SiCH}_3$, $A = 3.0$) as well as peaks attributable to hydrolyzed products.

d. Hydrolysis and Polymerization of $(CF_3CH_2CH_2)-(CH_3)(Cl)Si(CH_2)_2(CF_2)_2O(CF_2)_2O(CF_2)_2(CH_2)_2Si(Cl)-(CH_3)(CH_2CH_2CF_3)$

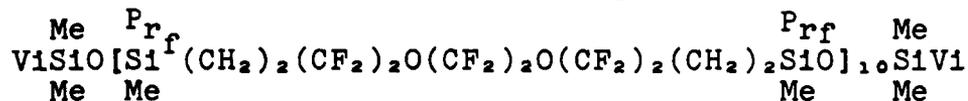
About 22.6 g (0.036 mole) of the title compound, dissolved in ether, was added to a vigorously stirred mixture of 100 ml ether, 200 ml water, and 30 g of $NaHCO_3$. After two hours the organic layer was separated, washed twice with saturated sodium chloride solution, and dried over Drierite.

The solution was filtered and stripped, yielding 20.4 g (91%) of silanediol which was added to a dry 50 ml round bottom flask fitted with a stirrer and gas inlet. Exactly 0.8 g (0.007 mole) of $ViSi(Me)_2Cl$ was added dropwise under a slow nitrogen sweep. After 15 minutes, the sweep rate was increased and the mixture was heated to 80° . After 2-1/2 days, the reaction mixture was heated to ca. 100° for 3 hours. After cooling, ether was added to the flask, and the resulting solution was hydrolyzed in aqueous $NaHCO_3$.

The organic layer was washed with saturated $NaCl$ solution, dried over $CaSO_4$, and stripped, yielding a cloudy liquid. This was placed in a polymerization flask under a nitrogen atmosphere and condensation was effected by adding 5 drops of tetramethylguanidine-trifluoroacetic acid and heating to $100^\circ C$ in vacuo overnight. The resulting polymer was dissolved in ether, washed with aqueous sodium bicarbonate, separated and dried over $CaSO_4$.

After removal of the ether in vacuo, the viscous polymer was stripped at 130°/0.30 mm, yielding 15.7 g.

The H¹NMR of the uncured polymer indicates a DP of 10, and a spectrum of consistent with the following structure:



FES-222-10

H¹NMR, $\tau = 8.0$ (-CH₂CF₂, s, m, A = 6.5); $\tau = 9.2$ (-SiCH₂-, m, A = 5.4); $\tau = 9.8$ (-SiCH₃-, m, A = 5.1).

F¹⁹NMR: $\delta = 69.6$ (CF₃, m, A = 3.2); $\delta = 88.4$ (CF₂O, m, A = 1.7); $\delta = 90.0$ (CF₂O, m, A = 2.1); $\delta = 119.8$ (CF₂CH₂, m, A = 2.0).

Anal. calc'd. for C₁₈H₂₂F₁₂Si₂O: C, 31.6; H, 3.22. Found: C, 31.9 ± 0.2; H, 3.51 ± 0.10.

The polymer was found to cure satisfactorily by an RTV method to yield a rubber. The Tg was shown by D.S.C. to be -40°C, and a programmed TGA in air showed a 50% weight loss at 375°C.

4. Preparation of FES-252-10

a. Preparation of I(CH₂)₂(CF₂)₂O(CF₂)₅O(CF₂)₂(CH₂)₂I

A 300 ml autoclave was loaded with 55 g (.075 mole) of I(CF₂)₂O(CF₂)₅O(CF₂)₂I which was then pressurized with CH₂=CH₂ (ca. .164 mole). The autoclave was placed in a rocker and slowly heated to 200°C. After 23 hours, it was cooled and opened, yielding 56.4 g (95%) of crude I(CH₂)₂(CF₂)₂O(CF₂)₅O(CF₂)₂(CH₂)₂I, a dark liquid.

The F¹⁹ and H¹NMR spectra are consistent with the assigned structure: $\delta = 83.6$ (-OCF₂-, m, A = 4.4); $\delta = 88.0$ (-OCF₂-, m, A = 3.9); $\delta = 119$ (-CH₂CF₂^{*}, m, A = 3.7); $\delta = 122$ (-CF₂CF₂^{*}CF₂-,

m, A = 2.0); δ = 125 (-OCF₂CF₂^{*}, m, A = 4.0); τ = 6.80, -CH₂I;
 τ = 7.27, -CH₂CF₂-.

The reaction was repeated, producing a total of 89 g of the product which was used without further purification.

b. Preparation of CH₂=CH(CF₂)₂O(CF₂)₅O(CF₂)₂CH=CH₂

About 89 g (0.11 mole) I(CH₂)₂(CF₂)₂O(CF₂)₅O-(CF₂)₂(CH₂)₂I was added dropwise to 25 g (0.45 mole) KOH in 110 ml of ethanol. After stirring overnight at room temperature, water was added, the organic layer was separated, washed with saturated NaCl, and distilled on a 36" spinning band distillation column. About 53 g (88% yield) of pure CH₂=CH(CF₂)₂O(CF₂)₅O(CF₂)₂CH=CH₂ were obtained (b.p. = 29°C/0.2 mm).

The F¹⁹ NMR spectrum is in agreement with the assigned structure:

δ = 83.5 (-OCF₂-, m, A = 3.9); δ = 87.8 (-OCF₂-, m, A = 4.0);
 δ = 122 (-CH₂CF₂-, m, A = 4.1); δ = 127 (-CF₂CF₂^{*}CF₂-, m, A = 2.1);
 δ = 130 (-OCF₂CF₂-, m, A = 4.0). The H¹ NMR spectrum exhibits an olefinic multiplet at τ = 4.1.

The infrared spectrum contains the following absorptions:

C=C, 1653 cm⁻¹; CH₂=C, 1420 cm⁻¹; -CF₂-, C-O-C, 1100-1250 cm⁻¹.
The mass spectrum shows a molecular ion at m/e 536 and fragment peaks corresponding to M⁺-F, M⁺-HF, and [(CF₂)₂O(CF₂)₂CH=CH₂]⁺.

Anal. calc'd. for C₁₃H₆F₁₈O₂: C, 29.00; H, 1.12; F, 63.79.

Found: C, 29.4; H, 1.12; F, 63.2.

c. Preparation of (CF₃CH₂CH₂)(CH₃)(Cl)Si(CH₂)₂(CF₂)₂-
O(CF₂)₅O(CF₂)₂(CH₂)₂Si(Cl)(CH₃)(CH₂CH₂CF₃)

A dry flask equipped with a mechanical stirrer and a reflux condenser was charged with 51.5 g (0.096 mole) of

$\text{CH}_2=\text{CH}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{CH}=\text{CH}_2$, 171 g (0.097 mole) of 3,3,3-trifluoropropylmethylchlorosilane, and 3.6 g (0.024 mole) of di-t-butylperoxide. The system was kept under a slight positive nitrogen pressure as it was heated to 105-110°C. After 24 hours, an additional 3.6 g of the peroxide was added and the heating was continued for an additional day. Three distillations of the reaction mixture produced 42 g (96% pure by glc) of the desired chlorosilane (49% yield).

The F^{19} and H^1 NMR spectra are consistent with the assigned structure: $\delta = 68.9$ (CF_3- , m, A = 5.7); $\delta = 83.0$ ($-\text{OCF}_2-$, m, A = 4.3); $\delta = 87.0$ ($-\text{OCF}_2-$, m, A = 3.9); $\delta = 120$ ($-\text{CH}_2\text{CF}_2-$, m, A = 4.0); $\delta = 123$ ($-\text{CF}_2\text{CF}_2^*\text{CF}_2-$, m, A = 2.1); $\delta = 126$ ($-\text{OCF}_2\text{CF}_2^*-$, m, A = 4.0); $\tau \sim 7.8$ ($-\text{CF}_X\text{CH}_2-$, m, A = 4.0); $\tau \sim 8.9$ ($-\text{SiCH}_2-$, m, A = 4.0); $\tau = 9.50$ ($-\text{SiCH}_3$, s, A = 3.0).

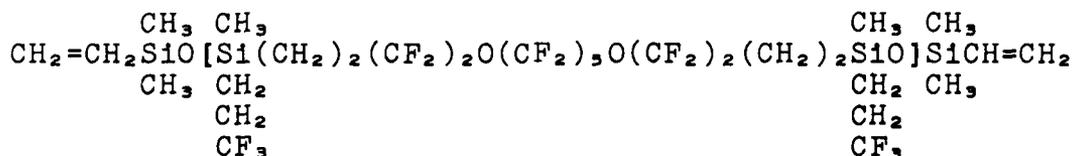
Anal. calc'd. for $\text{C}_{21}\text{H}_{22}\text{F}_{24}\text{Cl}_2\text{O}_2\text{Si}_2$: C, 28.3; H, 2.47; Cl, 7.97. Found: C, 28.7; H, 2.50; Cl, 8.25.

d. Hydrolysis and Polymerization of $(\text{CF}_3\text{CH}_2\text{CH}_2)(\text{CH}_3)-(\text{Cl})\text{Si}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{Si}(\text{Cl})(\text{CH}_3)-(\text{CH}_2\text{CH}_2\text{CF}_3)$

About 35.4 g (0.040 mole) of the chlorosilane were hydrolyzed in an aqueous sodium bicarbonate-ether system. The dried hydrolyzate was mixed with 0.55 g (0.0045 mole) of $\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiCl}$ under a stream of dry N_2 while it was heated to 100°C for ~ 4 hours. The reaction mixture was dissolved in ether, washed with aqueous sodium bicarbonate, separated, dried over Drierite, and stripped, yielding a viscous prepolymer.

The prepolymer was condensed in the presence of 5 drops of tetramethylguanidine-trifluoroacetic acid by heating to 110°C under vacuum overnight. The resulting polymer was dissolved in ether, washed with aqueous sodium bicarbonate, separated, and dried over Drierite.

After removal of the ether in vacuo, the viscous polymer was stripped at 150°C/.35 mm for several hours. Both H¹ and F¹⁹ NMR spectra are consistent with the structure:



and a DP of 16.4 is indicated.

Anal. calc'd for C₂₁H₂₂F₂₄O₃Si₂: C, 30.2; H, 2.63; Si, 6.71.

Found: C, 30.6; H, 2.91; Si, 6.86.

The polymer was found to cure by an RTV method to yield a rubber. The Tg was shown to be -52°C. Programmed TGA showed a 50% weight loss at 380°C.

B. Poly(fluoroether) Silicone Hybrid Polymers (PFES)

1. Reaction of I(CF₂)₂O(CF₂)₅O(CF₂)₂I/Hg/UV/Perfluoroheptane

About 19.1 g (0.026 mole) of I(CF₂)₂O(CF₂)₅O(CF₂)₂I (diglyme free), 64 g (0.320 mole) of Hg, and 33 cc of perfluoroheptane were placed in a 100 ml quartz ampoule. The ampoule was sealed, placed on a wrist-action shaker about 10 cm from a 350 watt UV light and irradiated for about 5 days. The product solution was filtered, stripped to remove solvent and distilled, yielding 6.1 g

of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$ (32% recovery), and 4.7 g of $I[(CF_2)_2O(CF_2)_5O(CF_2)_2]_2I$, b.p. 118-125°/0.30 mm.

A F^{19} NMR spectrum of the latter compound is consistent with the assigned structure: $\delta = 64.6$ (ICF_2- , m, A = 0.87); $\delta = 86.2$ ($ICF_2CF_2^*-$, m, A = 0.97); $\delta = 87.8$ ($-OCF_2-$, m, A = 3.10); $\delta = 125.8$ ($-OCF_2CF_2^*-$, m, A = 3.03); $\delta = 121.6$ ($-OCF_2CF_2CF_2^*-$, m, A = 1.03). The IR spectrum is very similar to that of the starting material. The mass spectrum contains a molecular ion at m/e 1218.

Anal. calc'd. for $C_{18}F_{36}O_4I_2$: C, 17.7; F, 56.15. Found: C, 17.8; F, 55.4.

The pot residue (3.0 g) consists of a number of components (as indicated by glc analysis), the most significant of which are the dimeric species (ca. 80%) and trimeric species (ca. 15%). The latter was identified by mass spectral analysis.

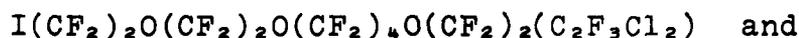
The yield (based on 68% conversion of starting material) is about 66% dimer and 5% trimer. Other, higher molecular weight species, are also present in small quantities.

2. Reaction of $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$ with $Hg/UV/C_2F_3Cl_3$

An oven dried quartz tube was flushed with dry nitrogen and then loaded with 206 g (1.03 mole) of Hg which had been dried in vacuo (0.2 mm), and 26.7 g (0.046 mole) of doubly distilled $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$, and 70 g of dry $ClCF_2CFCl_2$ (F-113). The tube was sealed, mounted on a wrist-action shaker, and irradiated with a 140 W Hanovia quartz ultraviolet lamp at a distance of 2 inches while being cooled with air jets. A pea green precipitate

formed within a few minutes, and a red solid collected on the walls of the tube. A 350 W quartz UV lamp was substituted two days later, and the precipitate quickly became brown. After 8 days, it had become dark brown.

The ampoule was opened, and the reaction mixture was filtered. The filtrate was stripped, leaving a residue of 15.6 g. GLC analysis indicated that the viscous product contains 8 major components. After standing for one hour the product developed a pink color and emitted a very piercing odor. Mass spec/glc analysis demonstrated that in addition to the expected dimeric, trimeric, and tetrameric coupling products (i.e., $I[(CF_2)_2O(CF_2)_2O-(CF_2)_2]_nI$ ($n = 2,3,4$) which are the largest components of the mixture, the following products are indicated:



The latter apparently arise from fluoroether radical displacement of chlorine from the Freon 113.

F^{19} NMR indicated the possibility of a trace of H, i.e., $-CF_2I/-CF_2H \approx 20/1$. X-ray fluorescence indicates no detectable Hg (minimum detectable limit ≈ 50 ppm).

3. Reaction of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I/Hg/UV$

About 20.7 g (.028 mole) of the dried title ether were placed in a quartz polymerization flask with 66 g (.330 mole) of dry (1.0 mm/3 hours) Hg. The flask was irradiated with ultraviolet light (2537 Å) while stirring under a N_2 purge at 75°C.

After 66 hours, perfluoroheptane was added to the flask to dissolve the fluorocarbons. The mixture was filtered and stripped yielding ca. 7 g of a high boiling liquid which was washed successively with aqueous potassium iodide and sodium thiosulfate solutions in an attempt to remove any entrained mercury iodides. After several water washes the organic liquid was dried and then distilled. A fraction boiling at ca. 140°/0.05 mm was collected. Neither this fraction nor the residue contained mercury according to x-ray fluorescence. Mass spectral analysis indicated the presence of high molecular weight (i.e., > 1000) materials. Some iodine endblocking was present but it appeared that most of the material had been hydrogen endblocked.

4. Photolysis of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I/Hg/C_7F_{16}$

A quartz ampoule was loaded with 200 g (ca. 1 mole) of dry Hg, 15.3 g (0.02 mole) of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$, and 40 ml of C_7F_{16} , sealed, and irradiated with a 100 W mercury lamp at a distance of ca. 6 cm. while being agitated on a wrist-action shaker. The reaction was interrupted twice, filtered, and recharged with fresh Hg. Mass spec indicated that the product mixture contained peaks at ca. m/e 1000 and m/e 1100-1200 but there was no evidence for the presence of iodine.

5. Photolysis of $I(CF_2)_2O(CF_2)_nO(CF_2)_2I/Hg/C_7F_{16}$

A quartz tube of 100 ml capacity was loaded with 68 g (0.339 mole) of devolatilized mercury, 12.7 g (0.017 mole) of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$ (diglyme free), 9.75 g (0.017 mole) of $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$ (diglyme free), and 16.5 g of dry C_7F_{16} . The ampoule was sealed, placed on a wrist-action shaker, and irradiated

with a 350 watt ultraviolet light at a distance of 9 cm for one day. The tube was opened, and the reaction mixture was filtered. GLC analysis indicated the presence of a large amount of low molecular weight materials, so the ampoule was reloaded with the organic product and 71 g of fresh mercury and sealed once again. After 5 days of ultraviolet irradiation the tube was reopened. The black reaction mixture was filtered, and the solvent was removed, yielding 10.3 g of a viscous material.

Anal. calc'd. C, 22.5%; H, 0.08%; F, 69.8%; I, 0.13%.

No molecular ion at $m/e < 2500$ was observed in the mass spectrum. This indicates either that the molecular weight of the product(s) is greater than $m/e 2500$, or that the sample contains little or no iodine.* No F^{19} NMR could be obtained due to the insolubility of the sample.

6. Reaction of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$ with Hg

a. $280^\circ C$

About 47.6 g (0.065 mole) of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$, which had been extensively purified to remove diglyme, and 136 g (0.680 mole) of dry (1.0 mm/3 hours) Hg were placed in a 50 ml, heavy wall ampoule. The ampoule was sealed and heated to $280^\circ C$ with shaking for 66 hours. The ampoule was cooled, opened, and the contents were dissolved in Freon 113, filtered, and stripped to yield 26.7 g of a high boiling material which was noticeably cleaner than previously obtained products. F^{19} and H^1 NMR indicated coupling had occurred and little reduction had taken place. However, mercury was detected

*It has been demonstrated in our analytical laboratories that hydrofluorocarbons give poor difficult-to-interpret mass spectra.

by x-ray fluorescence in addition to iodine. In an attempt to remove this Hg, the material (26.3 g) was placed in a sealed tube with 24 g of iodine. The tube was heated to 120°C and agitated by a wrist-action shaker for 5 hours. The cooled ampoule was opened, the contents were dissolved in ether, washed with conc. $\text{Na}_2\text{S}_2\text{O}_3$ to remove I_2 , dried over Drierite, filtered and stripped, yielding 18 g of pure $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{I}$, identified by comparison of its glc retention time with that of an authentic sample.

b. 320°C

In a similar reaction, 26.7 g (0.036 mole) of dry $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{I}$ and 70 g (0.35 mole) of dry Hg were sealed together in a glass ampoule and heated with shaking at 200° for four days, one day at 280° and finally one day at 320°C. After the final heating period, much of the red solid (HgI_2) observed earlier had disappeared and the product appeared to be less viscous than it had been after heating to 200° and 280°.

A total of 11.1 g of a cloudy white product was isolated. In an attempt to remove mercury salts, this material was dissolved in F-113 and stirred with aqueous KI, 3.5 g of sticky solid precipitated which was both water and F-113 insoluble. The F-113 layer from above was stripped to yield 3.7 g of a cloudy white liquid. Analysis is pending.

c. 260°C

A pair of pyrex tubes (20 cc volume) were cleaned by soaking in chromic acid cleaning solution. After thorough rinsing with distilled water, the tubes were oven dried, cooled under a stream of dry nitrogen, and then loaded with 30 g (0.15 mole, A)

and 75 g (0.375 mole, B), respectively of devolatilized Hg, and 18.4 g (0.025 mole) of purified $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{I}$. The ampoules were cooled, evacuated, sealed and then heated with shaking to 260°C for 13 hours. At one point the temperature rose to ca. 300° for a brief period.

The reaction mixtures were extracted repeatedly with Freon 113. These extracts were filtered and stripped to give 14.7 g from reaction A and 12.7 g from B. Both products were beige, opaque, viscous liquids, although B was more viscous than A. Analyses are pending.

d. 360°C

Exactly 36.5 g (0.049 mole) of $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{I}$ (diglyme free) and 88 g (0.440 mole) of mercury were placed in a dry 50 ml ampoule and sealed under a N_2 atmosphere. The ampoule was heated with a heating tape to 360°C while shaking for one day. The cooled ampoule was opened and the contents were washed out with perfluoroheptane and Freon 113. Part of the ampoule contents was a very hard fused solid which was dissolved by shaking with concentrated $\text{Na}_2\text{S}_2\text{O}_3$. The aqueous layer was washed with Freon, which was combined with the product solution, and then filtered, dried over Drierite and stripped, yielding 11.9 g of a viscous, high boiling product. X-ray fluorescence indicates that Hg is present in the product.

In an attempt to remove the Hg, the material was placed in a quartz ampoule and irradiated with ultraviolet light for ca. 70 hours. The ampoule was opened, and the contents were dissolved in perfluoroheptane, filtered and stripped yielding 9.0 g of a viscous product.

About 4.2 g of the material was transferred to a thick walled glass ampoule along with 3.6 g of powdered I_2 . The ampoule was mounted on a wrist action shaker, sealed and heated to $130^\circ C$ for five hours. On opening the ampoule the contents were dissolved in Freon 113 which was washed with saturated $Na_2S_2O_3$ solution, saturated $NaCl$ solution and H_2O . The Freon layer was dried over $CaSO_4$ and the solvent removed on a rotary evaporator. The viscous product contained a finely divided yellow solid assumed to be sulfur arising from the $Na_2S_2O_3$ washing. This was filtered off by dissolving the material in a minimum amount of Freon 113. The Freon was then removed under vacuum. Only about 1 g of product was recovered, this is thought to be due to the formation of emulsions during the work-up procedure. GPC analysis is pending. F^{19} NMR cannot be obtained due to the insoluble nature of the sample.

7. Copper Coupling of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$

A sublimator was charged with 3.2 g (0.050 mole) of activated copper bronze and 16.0 g (0.022 mole) of $I(CF_2)_2O(CF_2)_5O(CF_2)_2O(CF_2)_2I$. The mixture was heated to $170^\circ C$ for ca. 24 hours. After cooling, 12 g (0.047 mole) of iodine and 5 ml of toluene were added, and the mixture heated to reflux overnight. The reaction mixture was hydrolyzed in a solution of sodium thiosulfate. GLC analysis of the separated organic layer indicated about 70% conversion of starting material. The principal product is $I[(CF_2)_2O(CF_2)_5O(CF_2)_2]_2I$ (ca. 60% of the product mixture).

Smaller amounts of the following products were also identified by mass spectrometry: $H(CF_2)_2O(CF_2)_5O(CF_2)_2I$, $H[(CF_2)_2O(CF_2)_5O(CF_2)_2]_2I$, $I[(CF_2)_2O(CF_2)_5O(CF_2)_2]_3I$.

8. DMF-Catalyzed Copper Coupling of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$

A sublimator was charged with 3.2 g (0.050 mole) of activated copper bronze and heated to 100°C overnight under a stream of dry nitrogen. Two drops of dry N,N-dimethylformamide and 16 g (0.022 mole) of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$ were added, and the mixture was heated to 165°C overnight. The cooled reaction mixture was extracted with diethyl ether and concentrated. GLC analysis indicates that the product mixture is quite similar to that of the previous reaction, except that the relative abundance of α -hydrogen containing materials has increased significantly.

9. Copper Coupling of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$

A three neck 25 ml flask was loaded with 3.7 g (0.058 mole) of copper bronze powder, activated with disodium EDTA according to Lewin et al. (14) and 14.3 g of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$, and heated to 140°C overnight. Little observable change had occurred so the mixture was heated to 170°C for 3 days. The cooled reaction mixture was alternately extracted with diethyl ether and perfluoroheptane. The combined extracts were filtered and stripped, giving 3.8 g of a viscous mixture, shown to be quite complex by glc analysis. GLC/mass spectral analysis was unable to provide identification of individual components, but all species appeared to be low molecular weight, hydrogen end-capped materials.

10. Attempted Copper Coupling of $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$
in Pyridine

A three neck flask fitted with a dropping funnel, reflux condenser and magnetic stirring bar was charged with 1.75 g (0.028 mole)

of freshly activated copper bronze, 8.0 g (0.014 mole) of $I(CF_2)_2O-(CF_2)_2O(CF_2)_2I$, and 25 ml of pyridine (distilled from KOH). The mixture was stirred overnight at $110^\circ C$, cooled, and filtered. The solvent was distilled, leaving a dark carbonaceous residue which was not further explored.

A sample extracted before the solvent was distilled was submitted for F^{19} NMR analysis in an attempt to detect an organo-copper species. No useful information was obtained.

11. Copper-Mercury Coupling of $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$

A sublimator was charged with 1.65 g (0.026 mole) of freshly activated copper bronze, 2.5 g (0.012 mole) of mercury, and 8.0 g (0.0136 mole) of $I(CF_2)_2O(CF_2)_2O(CF_2)_2I$, and heated to $160-170^\circ C$ for ca. 4 days. The mixture was extracted with diethyl ether and filtered. GLC analysis indicated the presence of few low molecular weight materials. Evaporation of the solvent deposited red crystals identified as HgI_2 by melting point, and a small amount of a viscous liquid which elutes to only a limited extent from the glc.

Mass spec/glc analysis identified the following species: (1) $I[(CF_2)_2O(CF_2)_2O(CF_2)_2]Hg$; (2) MWT = 462 (contains 1 Hg); (3) $Hg[(CF_2)_2O(CF_2)_2O(CF_2)_2]_2HgI$; (4) MWT = 1300 (contains two or more Hg atoms); (5) higher molecular weight peaks.

12. Reaction of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$ with $Cu/AgNO_3$

A 50 ml round bottom flask equipped with a condenser and magnetic stirrer was heated and flushed with dry nitrogen, and loaded with 0.7 g (0.011 mole) of activated copper bronze, 3.68 g (0.005 mole) of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$, and 10 ml of dimethylsulfoxide. The

mixture was stirred and heated for several hours at 130°C (mantle). The mixture became thick, and a yellow amorphous precipitate formed, 7.36 g (0.010 mole) of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$ was added, and the mixture heated (120° mantle) overnight. About 3.7 g (0.032 mole) of silver nitrate was added to the resulting dark green solution. The mixture was reheated and stirred for several days. Hydrolysis gave a small amount of an oily liquid containing several products according to GLC analysis. Mass spec/glc analysis indicated that some of the terminal iodine atoms had been replaced by thiomethyl radicals; higher molecular weight products were not identified.

13. Reaction of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$ with $Mg/AgNO_3$

A three neck, 50 ml round bottom flask fitted with a dropping funnel, condenser, and stirring bar was loaded with 0.28 g (0.0114 mole) of fine magnesium shavings and then heated under a dry nitrogen stream. After the flask had cooled, 20 ml of dry THF was introduced, along with a small crystal of iodine. About one-third of a solution of 3.68 g (0.005 mole) of $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$ in 5 ml of dry THF was added with no apparent result; as the reaction mixture was heated to reflux a precipitate formed, and the surface of the magnesium darkened. After ca. one hour, 1.7 g (0.010 mole) of $AgNO_3$ was added, and the reaction mixture was then heated and stirred for 3 days. Hydrolysis led to the isolation of an organic liquid which was shown to contain $H[(CF_2)_2O(CF_2)_5O(CF_2)_2]_2H$ by both H^1 NMR and mass spectral analysis.

14. Reaction of $\text{Br}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{Br}$ with Mg/AgNO_3

A three neck, 50 ml oven dried flask was assembled while hot and fitted with a dropping funnel and gas adapter. About 0.28 g (0.0114 mole) of finely divided magnesium was washed with diethyl ether, and then added to the flask, which was then heated with a hot gun. About 30 ml of dry THF was transferred into the flask along with 9.63 g (0.015 mole) of $\text{Br}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{Br}$ and 0.2 g of methyl iodide. The reaction mixture turned light yellow, and was cooled in ice; no further change was observed, so an additional 1.9 g (0.016 mole total) of methyl iodide was added, along with a small amount of methyl magnesium iodide. The mixture was stirred until the majority of the Mg was consumed, and then 1.7 g (0.010 mole) of AgNO_3 was added, and the solution was refluxed overnight. The mixture was hydrolyzed and extracted with diethyl ether. No products with a longer elution time than starting material were detected by glc analysis.

15. Reaction of $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{I}$ with $\text{Zn}/\text{Acetic Anhydride}$

A dry three neck 100 ml flask equipped with a mechanical stirrer, pressure-equalizing dropping funnel, and reflux condenser swept with dry nitrogen was loaded with 11.2 g (15 mmole) of the title ether, 2 g (31 mmole) of Zn dust, 11 ml acetic anhydride, and 30 ml of CH_2Cl_2 . The mixture was stirred for 30 minutes and then slowly heated to reflux. After 2 days the reaction mixture was allowed to cool. GLC analysis of the brown liquid indicated only products of lower retention time than starting materials, although

all of the α,ω -diiodoether had disappeared. The mixture was hydrolyzed, and extracted with Freon 113 which was stripped after drying. The result was a viscous brown liquid which contains $-\text{CF}_2\text{H}$, but no iodine according to mass spectral analysis.

C. FCS-210 Fluorosilicone 'Random' Copolymers

1. 0.9/1.0 LS/FCS-210 Copolymer

About 950 g (1.87 mole) of FCS-210 dichloride was hydrolyzed in an aqueous sodium bicarbonate-diethyl ether system. The dried, stripped hydrolyzate was mixed with 30.8 g (0.25 mole) of $\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiCl}$ and 393 g (1.87 mole) of $\text{CF}_3\text{CH}_2\text{CH}_2(\text{CH}_3)\text{SiCl}_2$ and then slowly heated to ca. 80°C and maintained at that temperature for a total of 8 hours under a stream of dry nitrogen. The reaction mixture was dissolved in 1 lb. of ether and treated with aqueous sodium bicarbonate. The organic layer was separated, dried, and stripped. The resulting prepolymer was condensed in the presence of ca. 20 drops of tetramethylguanidinetrifluoroacetic acid solution by heating to ca. 100°C in vacuo for 6 hours. The resulting polymer was dissolved in ether, washed with aqueous sodium bicarbonate, aqueous sodium chloride, and finally dried over Drierite. After removal of ether in vacuo, the viscous polymer was stripped at $150^\circ\text{C}/0.6$ mm for 5 hours, yielding 945 g of a viscous fluid polymer. The elemental analysis and spectral data suggest that the polymer is a vinyl endblocked 0.9/1.0 molar copolymer of (3,3,3-trifluoropropyl)methylsiloxane and FCS-210 with a DP of 18. The polymer was found to cure satisfactorily by an RTV method to yield a rubber. The T_g was shown by D.S.C. to be -39°C ; a programmed TGA in air showed a 50% weight loss at 410°C .

Anal. calc'd. for $C_{17.6}H_{28.3}F_{12.7}Si_{2.9}O_{1.9}$: C, 35.7; H, 4.78; Si, 13.7; F, 40.8. Found: C, 35.9; H, 4.91; Si, 13.2; F, 40.6.

2. Reaction of FCS-210 Silanediol with Excess $MeSi(Pr_f)(Cl)_2$

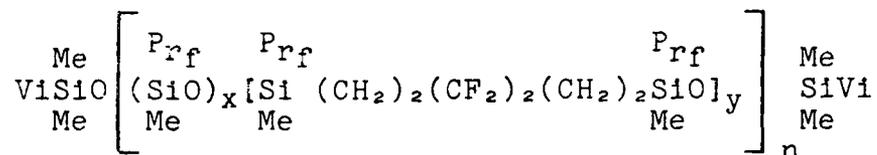
A dry 250 ml round bottom flask fitted with a dropping funnel, stirrer, thermowell, and gas inlet was loaded with 2.29 g (0.019 mole) $ViSi(Me)_2Cl$ and ca. 30 g of $MeSi(Pr_f)(Cl)_2$. Exactly

63.9 g (0.136 mole) of $HOSi^{Pr_f}(CH_2)_2(CF_2)_2(CH_2)_2Si^{Pr_f}OH$ (FCS-210 silane-

diol) was added dropwise under a slow nitrogen sweep, with rapid stirring. After ca. one-half of the FCS-210 silanediol had been added, the remainder of the $MeSi(Pr_f)(Cl)_2$, (total = 63.2 g = 0.299 mole) was added directly to the reaction flask, and then the addition of the FCS-210 silanediol was continued. After this had been completed, the rate of nitrogen flow was increased and the mixture was heated to about 100°C for 4.5 hours, and to 60°C overnight.

The reaction mixture was cooled, dissolved in ether and hydrolyzed with aqueous sodium bicarbonate. The organic layer was separated, dried over $CaSO_4$, filtered, and stripped. This prepolymer was condensed by treatment with 10 drops of tetramethylguanidine-trifluoroacetic acid at 100° in vacuo. The resulting polymer was dissolved in ether, washed successively with aqueous sodium bicarbonate and aqueous sodium chloride, and dried over Drierite. After removal of ether in vacuo a portion of the viscous polymer was stripped at 140°C/0.07 mm. About 17% of total weight of the polymer was stripped out as a low boiling mixture consisting of $(SiO)_n$ cyclic materials.

^1H and ^{19}F NMR analysis of the residue indicated that it is a vinyl endblocked copolymer of the following composition:



$$x = 1-1.2, y = 1, n = 32$$

Anal. calc'd. for $\text{C}_{18.8}\text{H}_{30.4}\text{F}_{13.6}\text{Si}_{3.2}\text{O}_{2.2}$ ($x = 1.2, y = 1$);
C, 32.54; H, 4.41; Si, 12.95. Found: C, 34.6; H, 4.92; Si, 14.6.

The polymer was found to cure by an RTV method to yield a high consistency rubber. The T_g was shown (by D.S.C.) to be -41°C ; a programmed TGA in air showed a 50% weight loss at 408°C .

3. Sequential Reaction of Excess $\text{MeSi}(\text{Prf})(\text{Cl})_2$ with FCS-210 Silanediol

A dry 250 ml round bottom flask fitted with a dropping funnel, stirrer, thermowell, and gas inlet was loaded with 64.2 g (0.136 mole) of FCS-210 silanediol, about 2.6 g (0.021 mole) of $\text{ViSi}(\text{Me})_2\text{Cl}$ was injected, and the mixture was stirred under a slow sweep of dry nitrogen for ca. 1-1/2 hours, and then 106 g (0.502 mole) of $\text{MeSi}(\text{Prf})\text{Cl}_2$ was added under a vigorous nitrogen sweep. After ca. one hour the reaction mixture was heated to 100° for 2 hours, and then overnight at 60° .

After cooling, the reaction mixture was dissolved in ether and hydrolyzed with aqueous sodium bicarbonate. The ethereal layer was separated, washed with aqueous sodium chloride, dried over Drierite, filtered, and then stripped on a rotary evaporator.

The resulting material was added to a dry reaction vessel, equipped as before, and treated with 72 g (0.33 mole) of $\text{MeSi}(\text{Pr}_f)(\text{Cl})_2$ under a dry nitrogen sweep. After heating at ca. 100°C for 20 hours, the product was hydrolyzed with aqueous NaHCO_3 , washed, dried, and stripped. The monomer was condensed by heating it to 100° in vacuo in the presence of 10 drops of tetramethylguanidine-trifluoroacetic acid. The product was dissolved in ether, neutralized with aqueous sodium bicarbonate, dried, and stripped at $140^\circ/0.02$ mm.

The spectral data suggest that the polymer is a vinyl endblocked 1.0/1.0 molar copolymer of FCS-210 and (3,3,3-trifluoropropyl)methylsiloxane, with a $\text{DP} = 36$.

F^{19} NMR: $\delta = 68.0$ (CF_3 -, $A = 9.5$); $\delta = 116.8$ ($-\text{CF}_2$ -, $A = 4.3$).

H^1 NMR: $\tau = 8.0$ ($-\text{CH}_2\text{CF}_2$ -, $A = 5.0$); $\tau = 9.2$ ($-\text{SiCH}_2$ -, $A = 4.9$); $\tau = 9.8$ ($-\text{SiCH}_3$, $A = 4.6$).

The polymer was found to cure by an RTV method to yield a high consistency rubber. The T_g was shown by D.S.C. to be -51°C and a programmed TGA in air showed a 50% weight loss at 390°C .

4. Preparation of $\begin{matrix} \text{Me Me} \\ \text{ClSiOSiCl} \\ \text{Pr}_f\text{Pr}_f \end{matrix}$

About 15 g of A29 (Rohm and Haas Amerblyst® Resin Catalyst) was rinsed repeatedly with anhydrous methanol, refluxed for 24 hours with the same reagent, and finally dried in a vacuum oven. This material, along with 250 g (1.2 mole) of $(\text{Pr}_f)(\text{Me})\text{Si}(\text{Cl})_2$ and 81 g (0.5 mole) of $\text{Me}_3\text{SiOSiMe}_3$, was loaded into a 500 ml round bottom flask and stirred for 65 hours. The catalyst was removed by filtration

and the filtrate was fractionated through a 12 inch glass helix-
packed column. About 75 g (48% yield) of pure ClSiOSiCl (b.p. 210-
 PrfPrf
Me Me

212°C) was collected.

5. Sequential Reaction of Excess ClSiOSiCl with FCS-210
 PrfPrf
Me Me
Silanediol

A 250 ml round bottom flask equipped as previously
described was loaded with 50 g (0.106 mole) of FCS-210 silanediol;
1.87 g (0.015 mole) of $\text{VSi}(\text{Me})_2\text{Cl}$ was added dropwise concurrently
with a portion of the 37.0 g (0.101 mole) of ClSiOSiCl . The mixture
 PrfPrf
Me Me

was stirred under a slow nitrogen sweep for a few minutes before the
remainder of the disiloxane was added. After two hours the flask
was heated to ca. 100°C. After three hours, an additional 3.5 g
 PrfPrf
(0.009 mole) of ClSiOSiCl was added. The mixture was heated to
Me Me
ca. 60°C for approximately 40 hours.

After cooling, ether was added and the resulting solution was
hydrolyzed with aqueous sodium bicarbonate, washed, separated, and
dried over CaSO_4 . The product was stripped at 150°/0.05 mm; a sizable
quantity of Prf
 $(\text{SiO})_n$ cyclics was isolated. H^1 and F^{19} NMR analysis
Me

of the residue indicated an LS/FCS ratio of only 1.06/1. Therefore,
 PrfPrf
it was further treated with 34.3 g (0.093 mole) of ClSiOSiCl and
Me Me

0.36 g VSiCl (0.003 mole) in a manner similar to that already
Me
described.

NMR analysis of the hydrolyzed product indicated an LS/FCS ratio of 1.5/1. F^{19} NMR: $\delta = 69.0$ (CF_3- , $A = 8.5$); $\delta = 116.4$ ($-CF_2-$, $A = 3.3$).

The monomer was condensed by heating to $100^\circ C$ in vacuo in the presence of 5 drops of tetramethylguanidine-trifluoroacetic acid. The product was dissolved in ether, neutralized with aqueous $NaHCO_3$, dried and stripped at $110^\circ C/.1$ mm.

The spectral data indicate the polymer is a vinyl endblocked 1.0/1.5 molar copolymer of FCS-210 and (3,3,3-trifluoropropyl)methylsiloxane, with a d.p. = 9.

H^1 NMR: $\tau = 4.0$ ($CH=CH_2$, $A = 1.0$); $\tau = 8.0$ (CH_2CF_2 , $A = 5.4$); $\tau = 9.1$ ($SiCH_2$, $A = 4.9$); $\tau = 9.77$ ($SiCH_3$, $A = 5.1$).

The polymer was found to cure by an RTV method to yield a high consistency rubber. The T_g was shown by D.S.C. to be $-41^\circ C$, a programmed TGA in air showed a 50% weight loss at $335^\circ C$.

Anal. calc'd. for $C_{20}H_{32.5}F_{14.5}Si_{3.5}O_{2.5}$: C, 35.0; H, 4.73; Si, 14.3; F, 40.2. Found: C, 35.6; H, 4.89; Si, 13.8; F, 42.0.

$Pr_f Pr_f$
6. Reaction of Excess $ClSiOSiCl$ with FCS-210 Silanediol
Me Me

In an attempt to prepare a 2/1 LS/FCS-210 copolymer, freshly prepared FCS-210 silanediol (54 g, 0.115 mole) was reacted with 50.4 g (0.138 mole) $ClSiOSiCl$ and 1.83 g (0.015 mole) $ViMe_2SiCl$.
 $Pr_f Pr_f$
Me Me

After addition was complete, the mixture was heated to $100^\circ C$ for 4 hours and then $75^\circ C$ overnight. The prepolymer was dissolved in ether, hydrolyzed with aq. $NaHCO_3$, washed with sat'd. $NaCl$, dried over $CaSO_4$, and stripped at $130-150^\circ C/.1$ mm for 48 hours to remove

Pr_f
(SiO)_n cyclics. An F^{19} NMR spectrum of the prepolymer indicated an Me

LS/FCS-210 ratio of 0.9/1.0. The prepolymer was not polymerized.

D. FCS-210/Fluorosilicone Alternating Copolymers

1. Preparation of an Alternating 1/1 LS/FCS-210 Copolymer

A 250 ml flask equipped with stirrer, addition funnel, gas inlet, and drying tube was assembled after oven drying all glassware at 200°C. The flask was charged with 39.6 g (0.084 mole) of FCS-210 silanediol and 50 ml of dry benzene. The endblocker, $\text{Vi}(\text{CH}_3)_2\text{SiY}$, was placed in 10 ml of dry benzene and added dropwise for the addition funnel. After stirring the reaction mixture for 10 minutes, the difunctional LS material, $\text{CH}_3\text{Pr}_f\text{SiY}_2$ mixed with 15 ml of dry benzene was added dropwise. The reaction became warm. After total addition the reaction was heated to reflux for 1.5 hours. The heat was then removed and the reaction stirred at room temperature for 65 hours. The reaction mixture was dissolved in 100 ml of diethyl ether and washed with 5% HCl, saturated NaHCO_3 solution, and saturated NaCl solution. The ether layer was dried over CaSO_4 and the ether removed on a rotary evaporator. A small amount of low boiling material was removed by heating the polymer at 80°C and 0.5 Torr for 18 hours.

F^{19} NMR indicated an LS/FCS-210 ratio in the polymer of 1/1.1. H^1 NMR showed no vinyl protons present in the polymers. Apparently no endblocking had occurred. Analysis determined that the polymer contained $0.12 \pm 0.01\%$ free OH groups by weight.

Anal. calc'd. for $\text{C}_{16}\text{H}_2\text{Si}_3\text{O}_2\text{F}_{13}$: C, 35.5; H, 4.80; Si, 13.84.
Found: C, 36.2; H, 5.08; Si, 13.9.

A 100 ml flask was equipped with stirrer, gas inlet, dropping funnel, and drying tube. Under a dry nitrogen sweep the glassware was thoroughly dried by heating with a hot air gun. A slow nitrogen sweep was continued throughout the reaction. About 56 g (0.119 mole) of FCS-210 silanediol was placed in the flask. The vinyl endblocking material, $\text{Vi}(\text{CH}_3)_2\text{SiY}$, was added dropwise while the reaction was stirred and a slight but noticeable exotherm occurred. The reaction was stirred at room temperature for 45 hours. The difunctional monomer, $\text{CH}_3\text{Pr}_f\text{SiY}_2$, was added dropwise and the reaction became warm. It was stirred at room temperature for 48 hours. The reaction was dissolved in diethyl ether and washed with saturated sodium chloride and distilled water. After drying the ether layer over CaSO_4 , the ether was removed on a rotary evaporator. Any low boiling material was removed by heating the polymer at 140°C and .02 Torr for 4 days.

^1H NMR indicates that this polymer is vinyl endblocked and that the average degree of polymerization is 17. Also the LS/FCS-210/Vi ratio is 1.2/1/0.12. The molecular weight distribution was determined by gpc and was calibrated against an LS polymer standard. $\bar{M}_w = 18,500$, $\bar{M}_n = 5,310$. The amount of free OH in the polymer is $0.070 \pm .005\%$ by weight.

Anal. calc'd. for $\text{C}_{18}\text{H}_2\text{Si}_3\text{O}_2\text{F}_{13}$: C, 35.52; H, 4.80; Si, 13.84; F, 40.58. Found: C, 34.9; H, 4.9; Si, 14.8; F, 37.6.

2. Preparation of an Alternating 1.5/1 LS/FCS-210 Copolymer

The equipment used and the procedures for the reaction to form the polymer and for isolating the polymer are the same as described for the preparation of the 1/1 copolymer. In order to achieve the 1.5/1 LS/FCS ratio an equal molar mixture of the difunctional LS material, $\text{MePr}_f\text{SiY}_2$, and the difunctional disiloxane

material, $O(\text{MePr}_f\text{SiY})_2$, was added to the endblocked FCS-210 silanediol.

^1H NMR indicates that the product is vinyl endblocked and has an average degree of polymerization of 17. Also the ratio of LS/FCS-210/V1 determined by ^1H NMR is 1.1/1.0/0.12; ^{19}F NMR indicates an LS/FCS ratio of 1.7/1.0. The molecular weight was determined by gpc using a column calibrated against an LS polymer standard showed two major peaks, one at mass 19,900 and one at mass 667. The peak at the larger mass was quite broad. The lower molecular weight peak is comprised of LS cyclic trimer and tetramer. Molecular weight determined by ebulliometry in THF solvent was $M_n = 2,500$. The amount of free OH in the polymer is $0.37 \pm 0.03\%$ by weight.

Anal. calc'd. for $\text{C}_{40}\text{H}_{65}\text{Si}_7\text{O}_5\text{F}_{29}$: C, 34.98; H, 4.78; Si, 14.31; F, 40.11. Found: C, 35.0; H, 4.78; Si, 15.5; F, 36.0.

3. Preparation of a 2/1 Ratio LS/FCS-210 Alternating Copolymer

The equipment used and the procedures for the reaction to form the polymer and for isolating the polymer are the same as described for the preparation of the 1/1 copolymer. The 2/1 ratio was achieved by adding an equimolar amount of the difunctional disiloxane monomer, $O(\text{CH}_3\text{Pr}_f\text{SiY})_2$, to the FCS-210 silanediol.

The amount of free OH in the polymer is $0.13 \pm .01\%$ by weight. ^{19}F NMR indicates an LS/FCS ratio of 1.4/1.0.

Anal. calc'd. for $\text{C}_{22}\text{H}_{36}\text{Si}_4\text{O}_3\text{F}_{16}$: C, 35.38; H, 4.86; Si, 15.04; F, 40.70. Found: C, 35.4; H, 4.9; Si, 14.1; F, 37.2.

4. Attempted Reduction of the Amount of Free OH in the 2/1
Ratio Alternating Copolymer

A 50 ml flask equipped with a stirrer, gas inlet, and drying tube was dried with the heat from a hot air gun. The flask was charged with 24 g of the 2/1 ratio LS/FCS-210 alternating copolymer. While the reaction was stirred and excess of vinyl endblocking material, $\text{Vi}(\text{CH}_3)_2\text{Si}$, was added. The reaction was stirred for 24 hours.

Analyses are pending-

SUMMARY

The objective of this exploratory development is the synthesis and evaluation of hybrid fluorosilicone sealants for possible use as integral fuel tank sealants and other applications in high performance aircraft.

Two fluoroether silicone (FES) sealants have been prepared. As expected, their low temperature properties were improved with respect to FCS sealants, at little sacrifice in high temperature performance.

During this report period emphasis has been placed on developing a route to α,ω -diiodopoly(fluoroethers) for incorporation into hybrid poly(fluoroether)fluorosilicone polymers (PFES) to achieve better low temperature flexibility while retaining a high degree of reversion and fuel resistance at elevated temperatures. While encouraging yields of dimers and trimers have been obtained, it has not yet been possible to achieve exclusively iodine endblocked oligomers or polymers. Development work was continued to improve the low temperature flexibility as well as the reversion resistance of the hybrid fluorocarbon-fluorosilicone polymer system (FCS) through copolymerization with Dow Corning LS fluorosilicone. It is expected that the thermal stability of the copolymer would be maximized in an alternating AB structure. The reagents which should be capable of effecting this arrangement have been synthesized and were used in attempts to prepare LS/FCS-210 copolymers having molar ratios of 1/1, 1.5/1 and 2/1. Analysis of the samples is underway.

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APPENDIX

Table I

Coupling Reactions of α,ω -Diodoperfluoroethers

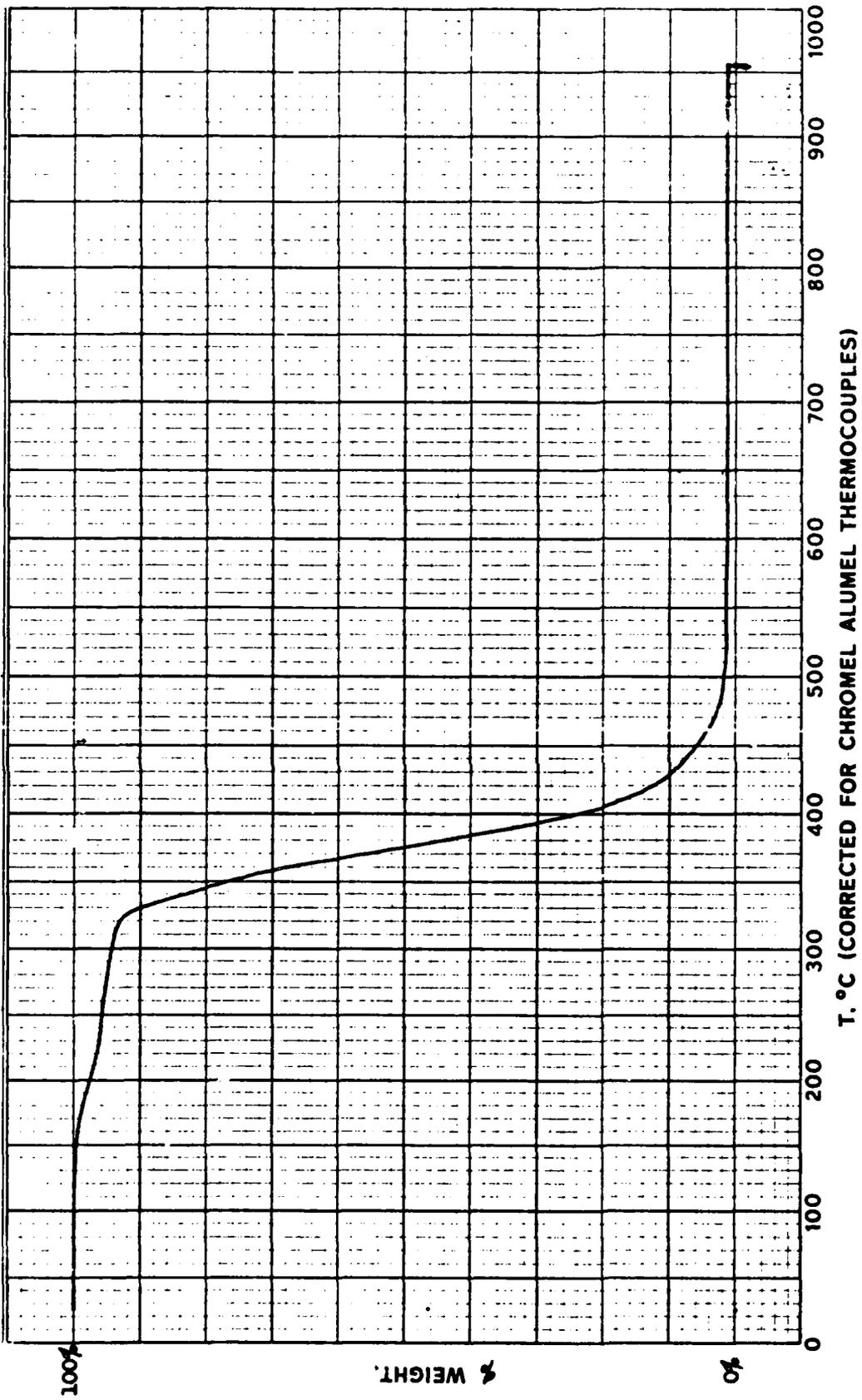
Diodoether	Reaction Conditions	Product Data								Comments
		Mol. Wt. > 1000		I-Present		H-Present		Yes	No	
		Yes	No	Yes	No	Yes	No			
$I(CF_2)_2O(CF_2)_5O(CF_2)_2I$	Hg/UV/ C_7F_{16}	x		x				x		Dimer, Trimer (71% yield)
$I(CF_2)_2O(CF_2)_2O(CF_2)_2I$	Hg/UV/ $C_2F_5Cl_3$	x		x				x		Oligomers, Displacement of Cl from solvent
$I(CF_2)_2O(CF_2)_5O(CF_2)_2I$	Hg/UV/Freon 113	x			x				x	
$I(CF_2)_2O(CF_2)_5O(CF_2)_2I$	Hg/UV/75°C	x		x					x	
$I(CF_2)_2O(CF_2)_nO(CF_2)_2I$	Hg/UV/Freon 113	x		x				x		n = 2,5
$I(CF_2)_2O(CF_2)_5O(CF_2)_2I$	Hg/270°C	x		x				x		dp = 3
$I(CF_2)_2O(CF_2)_5O(CF_2)_2I$	Hg/280°C	x		x				x		Very little coupling; preliminary Hg insertion
$I(CF_2)_2O(CF_2)_5O(CF_2)_2I$	Zn/ $Ac_2O/CH_2Cl_2/40^\circ C$		x		x				x	
$I(CF_2)_2O(CF_2)_5O(CF_2)_2I$	Cu/DMSO/ $AgNO_3/130^\circ C$		x		x					Reaction with solvent
$I(CF_2)_2O(CF_2)_5O(CF_2)_2I$	Mg/ $AgNO_3/THF$	x			x				x	Dimer
$I(CF_2)_2O(CF_2)_5O(CF_2)_2I$	$Cu^+/170^\circ C$	x		x					x	Dimer, Trimer (40% yield)
$I(CF_2)_2O(CF_2)_5O(CF_2)_2I$	$Cu^*/DMF/165^\circ C$	x		x					x	Dimer, Trimer
$I(CF_2)_2O(CF_2)_5O(CF_2)_2I$	$Cu^+/170^\circ C$		x		x				x	
$I(CF_2)_2O(CF_2)_5O(CF_2)_2I$	Cu/Pyr-idine/110°C									Intractable
$I(CF_2)_2O(CF_2)_5O(CF_2)_2I$	Cu(Hg)/165°C	x		x					x	Hg insertion

* I_2/HCl activated
 +Disodium EDTA activated

Table II

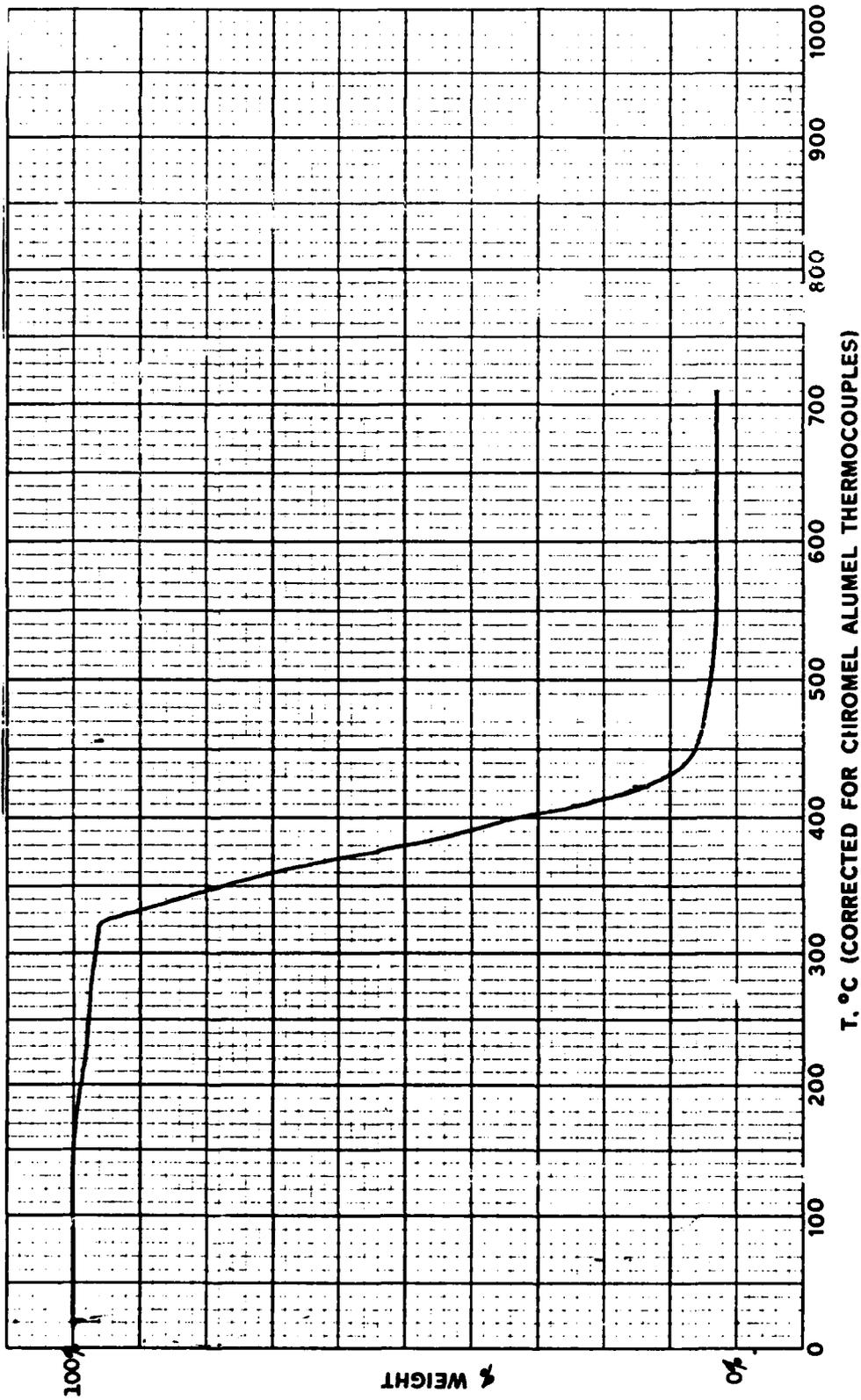
Confined Heat Tests

<u>Polymer</u>	<u>250°C/24 Hours</u>	<u>275°C/24 Hours</u>
LS Rubber	Softer, Less Elastic	Sticky Fluid
FES-222	No Apparent Change	Soft, Inelastic
FES-252	Slightly Softer	Soft, Slightly Elastic
1.0/1.0 LS/FCS-210 (Random)	No Apparent Change	No Apparent Change



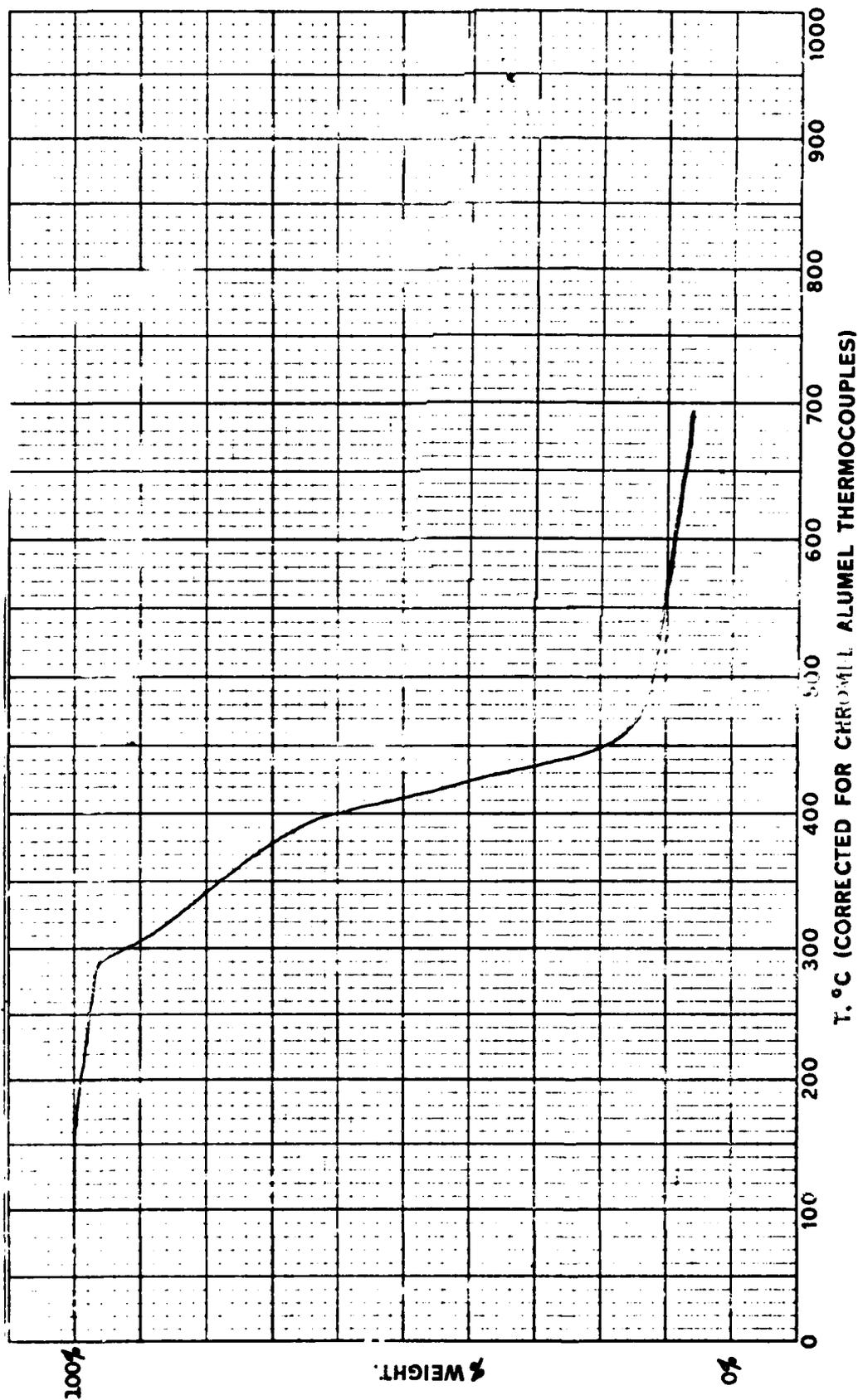
Thermal Gravimetric Analysis of FES-222-10 Polymer
(Unformulated) Air, 200 cc/min. Heating Rate 5°C/min.

Figure I



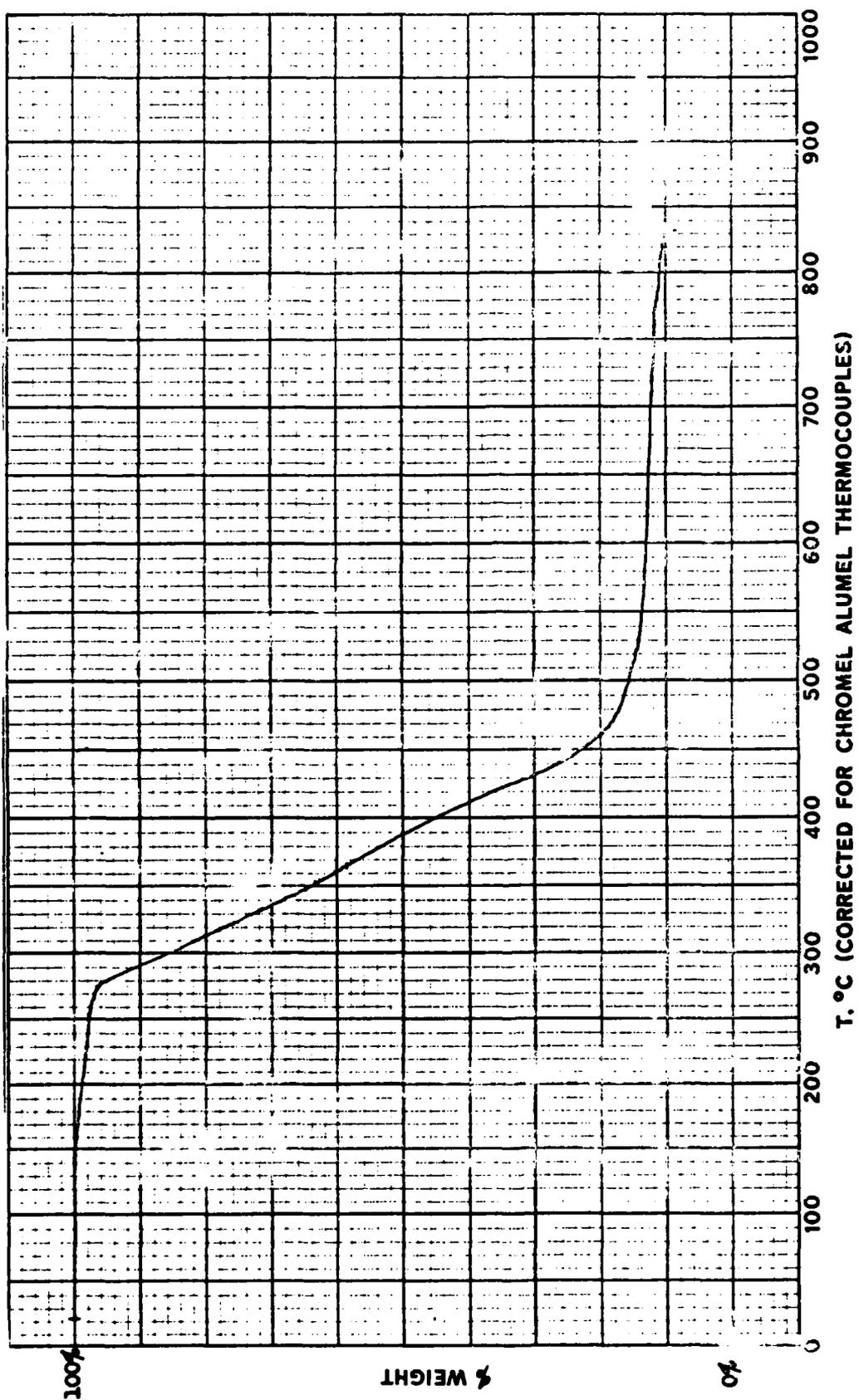
Thermal Gravimetric Analysis of FES-252-10 Polymer
(Unformulated) Air, 200 cc/min. Heating Rate 10°C/min.

Figure II



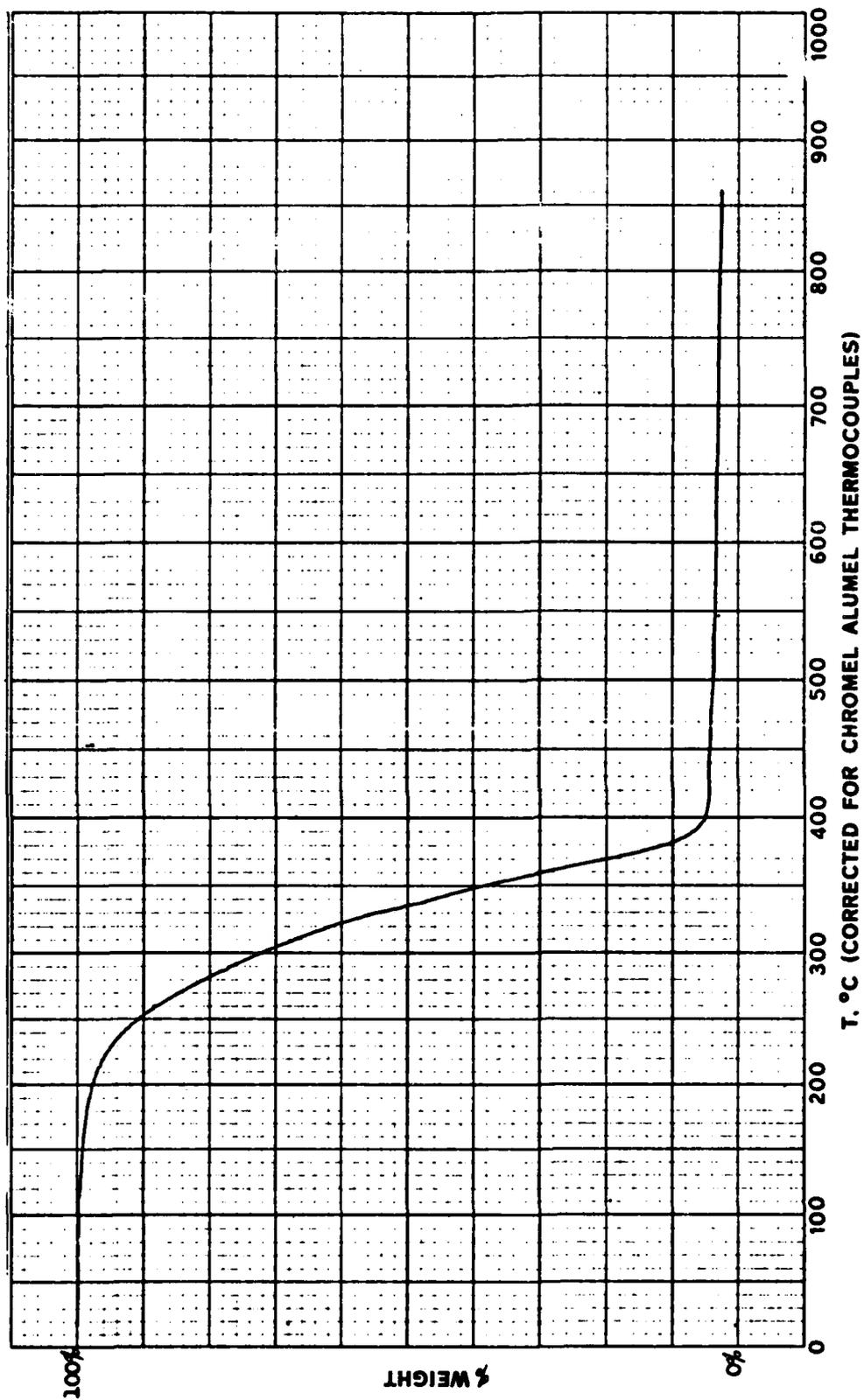
Thermal Gravimetric Analysis of 0.9/1.0 LS/FCS-210 Random Copolymer (Unformulated) Air, 200 cc/min. Heating Rate 5°C/min.

Figure III



Thermal Gravimetric Analysis of 1.0/1.0 LS/FCS-210 Random Copolymer (Unformulated) Air, 200 cc/min. Heating Rate 5°C/min.

Figure IV



Thermal Gravimetric Analysis of 1.5/1.0 LS/FCS-210 Random Copolymer (Unformulated) Air, 200 cc/min. Heating Rate 5°C/min.

Figure V

END

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