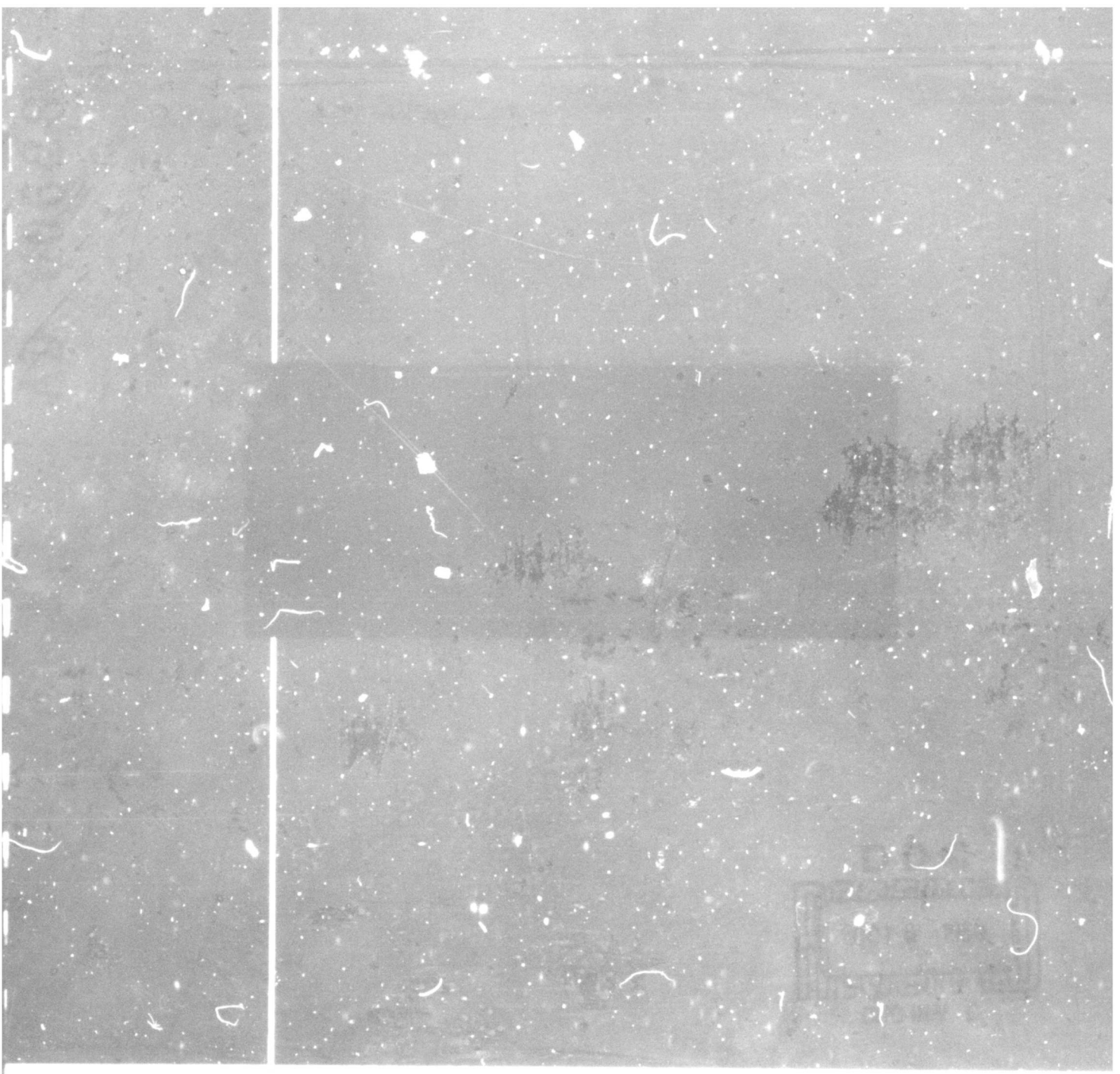


CHEMICAL RESEARCH & DEVELOPMENT CENTER

FMC CORPORATION

PRINCETON, NEW JERSEY

BLANK PAGE

SCIENTIFIC AND TECHNICAL INFORMATION FACILITY

operated for National Aeronautics and Space Administration by Documentation Incorporated

LOAN DOCUMENT TRANSMITTAL

Please attach a copy of this form to any loan documents sent to the Scientific and Technical Information Facility. A single copy of this form and the document should be sent to the following address:

Scientific and Technical Information Facility
Attention: NASA Representative
Box 5700
Bethesda 14, Maryland

Every effort will be made to return this document in the shortest possible time.

Please complete. Date sent: _____

Sent by: _____

SCIENTIFIC AND TECHNICAL
INFORMATION FACILITY
POST OFFICE BOX 5700
BETHESDA, MD. 20014

☐ checked for N numbers ☐ checked against N-62 numbers

See other side for NASA contractor report

For Facility Use Only

LOAN DOCUMENT PROCESSING RECORD

N62-_____ Date received: _____

X62-_____

THIS DOCUMENT IS ON LOAN

Please process as follows:	Date	Initials
☐ Film for Microform and make Xerox copy		
☐ Microform completed		
☐ Xerox copy made		
☐ Xerox copy sent to Input Station		
☐ Original sent to Mail Room		
☐ Document returned to sender		

THIS LOAN DOCUMENT FORM MUST BE SENT TO THE CASE FILE

Facility Test Form 443, Sept. 1962

COMPLETE FOR NASA CONTRACTOR DOCUMENTS ONLY

DOCUMENT TYPES

1. _____ Report is unclassified and is suitable for unlimited announcement and distribution to the aeronautics and space community, and for public sale.

2. _____ Report is unclassified, but contains information of limited usefulness and does not justify widespread automatic distribution to the aeronautical and space community. It can, however, be announced and made publicly available.

3. _____ Report is unclassified, but for official reasons, must be restricted as follows:

   a. _____ Government agencies and their contractors only.
   b. _____ Government agencies only.
   c. _____ NASA activities only.

4. _____ Report bears a security classification and is suitable for distribution within the limits of security considerations to:

   a. _____ Government agencies and their contractors only.
   b. _____ Government agencies only.
   c. _____ NASA activities only.

5. _____ Reprint of a journal article reporting NASA-supported work.

6. _____ Article prepared for journal publication (preprint or other copy) reporting NASA-supported work. (Normally handled as No. 2 above.)

   Estimated date of publication: _____

7. _____ Material for presentation at a meeting or conference
   Name of Meeting: _____ Date: _____
   Sponsor(s): _____

   a. _____ Scheduled for publication in proceedings. (Normally handled as No. 2 above.)

      Estimated date of publication: _____

   Not scheduled for publication in proceedings and subject to the following limitations or announcement and dissemination:

   b. _____ Government agencies and their contractors only.
   c. _____ Government agencies only.
   d. _____ NASA activities only.

U. S. ARMY CONTRACT DA19-129-AMC-147(N)

PROGRESS REPORT III

Period Covered

December 27, 1963 - March 26, 1964

DA 19-129-AMC-147(N)
Progress Report III

FMC CORPORATION

CHEMICAL RESEARCH AND DEVELOPMENT CENTER

CENTRAL RESEARCH DEPARTMENT

Princeton, New Jersey

April 15, 1964

Report No. PCR372
Project No. B-132

QM ELASTOMER CONTRACT

SUPERVISION: B. F. Landrum and W. L. Riedeman

PERSONNEL ASSIGNED: J. A. Gannon, C. A. Erickson, E. W. Cook and R. DeAngelo

AUTHORS: J. A. Gannon, C. A. Erickson and E. W. Cook

7068

TABLE OF CONTENTS

I. SUMMARY

Initial copolymerization studies of the thermal cycloaddition reaction of $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$ with $CF_2=CFCF_2CFClCF_2CF=CF_2$ resulted in the formation of mixtures of low molecular weight products. In another approach, work has been started on the inclusion of novel fluoroolefinic monomers in a vinylidene fluoride/hexafluoropropylene emulsion polymerization system.

The monomer synthesis portion of the program has been accelerated during the period covered by this report, and there is now in hand or in process, adequate supplies of the above disiloxane and heptadiene for a sustained polymerization study. In addition, syntheses of additional monomers; 3, 3, 4, 4-tetrafluorohexadiene-1, 5; 2, 2, 3, -tri(trifluoromethyl perfluorooxetane; 2, 2, 3, 4-tetra(trifluoromethyl) perfluorooxetane and bis(2-(2', 3', 3'-trifluorocyclo-1'-butenyl) ethyl dimethyl siloxane) have been completed or are in advanced stages of progress.

II. INTRODUCTION

A. Objectives

The objectives of this program are the development of high strength chemical resistant rubbers serviceable at low temperatures (down to -65° F.) and chemical resistant rubbers that have high strength and rubber-like properties at high temperatures (600° F. and above) through the investigation of fluorine-containing polymer systems.

B. Program

In order to achieve the above objectives,a broad program was planned embracing (a) the development of block copolymers composed of fluorocarbon units alternating with fluoroalkyl siloxane units and (b) the synthesis of fluorocarbon polymers containing a nitrogen, sulfur or oxygen heteroatom in the backbone of the macromolecule.

Sufficient quantities of most of the starting materials necessary for scale-up of established synthetic procedures have been obtained from commercial suppliers. Moreover, adequate quantities of some monomers have been synthesized during the quarter, allowing polymerization research to be sustained.

It is fully anticipated that several polymer systems will be explored during the next quarter as preparative synthesis work will now provide a variety of monomers in ample quantities. Research on fluorinated aromatic compounds and nitrogen-containing monomers will be pursued in accordance with the modified scope of the project, as described in the 2nd Quarterly Progress Report.

Specifically, it is expected that the necessary "monomers" will become available to permit initiation of investigation of the following polymer systems during the next quarter:

1. $ClSi(CH_3)_2CH_2CH_2CF_2CF_2CH_2CH_2Si(CH_3)_2Cl$

$$\downarrow \text{HOH}$$

$$-O\left[-Si(CH_3)_2CH_2CH_2CF_2CF_2CH_2CH_2Si(CH_3)_2-O\right]_n$$

2. $C_4F_9N{=}CF_2 + CF_3CF{=}CF_2 \longrightarrow \left[CF(CF_3)-CF_2-N(C_4F_9)-CF_2\right]_n$

3. $(CF_3)_2\underline{CCF(CF_3)CF_2-O} \longrightarrow \left[C(CF_3)_2-CF(CF_3)-CF_2-O\right]_n$

In addition, substantial quantities of monomers are now on hand to allow further investigation of the following system:

$$CF_2{=}CFCF_2CFClCF_2CF{=}CF_2 + CF_2{=}CFCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2CF{=}CF_2$$

$$\downarrow$$

$$\left[CF_2 \quad CF_2CFCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2CF \right.$$
$$\left. CFCF_2CFClCF_2CF-CF_2 \quad CF_2\right]_n$$

The products achieved to date have been of too low molecular weight to warrant curing study, however, it is believed that proper choice of reaction conditions will allow higher molecular weights to be realized.

III. DISCUSSION OF RESULTS

A. Monomer Procurement

The following monomers and precursors were obtained during the period of this report:

Monomer Number	Monomer or Precursors	Amt.	Supplier
	*Bromopentafluorobenzene	500 g.	Imperial Smelting Corp.
	*Pentafluorobenzene	25 kg.	Imperial Smelting Corp.
	*Hexafluorobenzene	1 kg.	Imperial Smelting Corp.
	*Pentafluoroaniline	300 g.	Imperial Smelting Corp.
	*Pentafluorothiophenol	1 kg.	Imperial Smelting Corp.
	*Pentafluorophenyl hydrazine	250 g.	Imperial Smelting Corp.
	*4, 4' Diaminooctafluoro-biphenyl	100 g.	Imperial Smelting Corp.
	*Pentafluorophenol	1 kg.	Imperial Smelting Corp.
	C-7 fluoroalcohol	1 lb.	E. I. duPont deNemours Co.
	C-9 fluoroalcohol	1 lb.	E. I. duPont deNemours Co.
	C-11 fluoroalcohol	1 lb.	E. I. duPont deNemours Co.
	Difluorotetrachloroethane (Freon 112)	1 gal.	E. I. duPont deNemours Co.
2	Vinylidene fluoride (Freon 1132A)	6 lbs.	E. I. duPont deNemours Co.
	Methyldichlorosilane	2 lbs.	Dow Corning
	Dimethylchlorosilane	3 lbs.	Dow Corning
	Dimethyldichlorosilane	1 lb.	Dow Corning
	Diallyldimethylsilane	100 g.	Columbia Organic Chemicals, Inc.
	3, 4, 4-Trifluoro-4-bromo-3-chlorobutene-1	3 kg.	Columbia Organic Chemicals, Inc.
	Kel-F Acid No. 8114	1 lb.	Columbia Organic Chemicals, Inc.
	Kel-F Acid No. 8114	10 lbs.	3-M Company
14	Hexafluoropropylene	1 lb.	Columbia Organic Chemicals, Inc.
108	Perfluorobutene-2	2 lbs.	Halocarbon Products Corp.
	2, 2, 3, 3-Tetrachloro-hexafluorobutane	3 lbs.	Halocarbon Products Corp.
204	Trifluorovinyldimethyl-ethoxysilane	50 g.	Dr. P. Tarrant, Univ. of Florida
302	4-Chloroperfluoro-heptadiene-1, 6	32 g.	Dr. J. D. Park, Univ. of Colorado
301	Bis(2, 3, 3-trifluoro-bicyclobutenyl-1)	13 g.	Dr. J. D. Park, Univ. of Colorado

* See Appendix III for disposition of these materials.

Additional quantities of the following monomers and precursors were ordered but not received during the period of this report:

Monomer Number	Monomer or Precursors	Amt.	Supplier
1	Chlorotrifluoroethylene (Genetron 1113)	24 lbs.	Allied Chemical Corp. General Chemical Div.
	Hexafluoroacetone (6 FK)	1 lb.	Allied Chemical Corp. General Chemical Div.
	Dimethylchlorosilane	4 lbs.	Dow Corning

The following additional monomers and precursors were ordered but not received during the period of this report:

Monomer or Precursors	Amt.	Supplier
Kel-F Acid No. 683	10 lbs.	3-M Company
p-Aminotetrafluorobenzoic acid	100 g.	Imperial Smelting Corp.

The following monomers have been prepared by FMC:

Monomer Number	Monomer	Amt.
202	Bis(3, 4, 4-trifluoro-3-butenyl dimethyl) disiloxane	458 g.
302	4-Chloroperfluoroheptadiene-1, 6	95 g.
500	2, 2, 3-Trifluoro-3, 4, 4-trifluoromethyloxetane	100 g.

B. Monomer Master List

A complete list of monomers considered under previous Quartermater contracts with M. W. Kellogg and subsequently with 3-M is presented in Appendix I of this report. It has been decided to extend the system of assigning numbers to new monomers in a systematic fashion which would allow each of the present contractors to the Army Natick Laboratories to make number assignments to monomers which are prepared for the first time in their own laboratories. FMC will have the responsibility for keeping their master list up to date upon proper advice from the various contractors.

The system decided upon by the Army Natick Laboratories involved assigning a block of 100 numbers to the contractors as follows:

Originating Laboratory	Assigned Number Block
University of Florida	200 through 299
University of Colorado	300 through 399
Peninsular ChemResearch	400 through 499
FMC Corporation	500 through 599
Thiokol Chemical Corporation	600 through 699
U. S. Army Natick Laboratories	700 through 799

Those monomers and the appropriate number assignments of which FMC has been advised are presented in Appendix II.

In order to avoid confusion it has been agreed that only those monomers which do not appear elsewhere with a prior number assignment will be given an assignment under the block assignment system. For example, $C_4F_9N{=}CF_2$ is currently of interest to FMC and is being prepared in substantial quantities. Since this monomer was assigned number 81 on the Kellogg-3-M list, it will not be given another number, but will retain the number 81 for future identification.

C. Polymerization Research

Sufficient quantities of certain monomers were made available during the latter part of the report period to permit the commencement of polymerization studies. Initial emphasis was devoted to two areas of polymer research: (1) the thermal cycloaddition reaction of an alpha, omega divinyl fluoroolefin monomer with a difunctional fluoroolefinic siloxane prepolymer in the expectation of forming a block copolymer possessing alternate fluorocarbon and disiloxane moieties and (2) the incorporation of fluorine-containing olefins into a vinylidene fluoride/hexafluoropropylene elastomer system.

1. Copolymerization of $[CF_2{=}CF(CH_2)_2Si(CH_3)_2]_2O$ and $CF_2{=}CFCF_2CFClCF_2CF{=}CF_2$

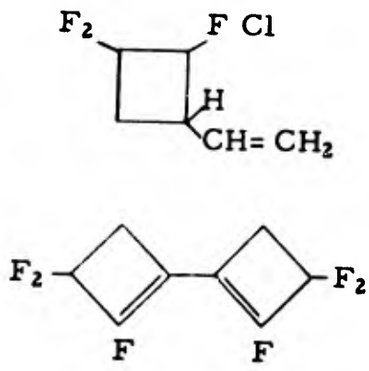
The thermal reaction of $[CF_2{=}CF(CH_2)_2Si(CH_3)_2]_2O$ with $CF_2{=}CFCF_2CFClCF_2CF{=}CF_2$ was attempted by heating equimolar quantities of the respective comonomers in a bomb at 200° C. but, in the initial experiment, some decomposition occurred and only a viscous tar was recovered after removal of unreacted monomers. Repetition of the experiment with identical comonomers but a reaction temperature of 150° C. resulted in the formation of a mixture of low molecular weight products.

Further experiments will attempt to provide optimum conditions for producing high molecular weight products from the cycloaddition reaction.

2. Modification of Vinylidene Fluoride/Hexafluoropropylene Emulsion Polymerization System

Experimentation commenced on the incorporation of various other fluorine-containing olefins into a vinylidene fluoride/hexafluoropropylene emulsion polymerization system. Results are incomplete but the interpolymerization of the following monomers will be attempted in the aforementioned system:

$$[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$$



Modification of an 80/20 mole % vinylidene fluoride/hexafluoropropylene elastomer will also be investigated by the direct incorporation of $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$ on a rubber mill and an attempt will be made to co-cure the fluoroolefin with the elastomer by means of a peroxide.

Modification of $CF_2= CH_2/CF_3CF= CF_2$ systems with fluoroolefinic monomers may be expected to provide improved solvent resistance and/or improvement in low temperature properties. The use of multifunctional monomers e. g. , $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$, may possibly provide new sites for cross-linking in the elastomer compositions.

D. Monomer Synthesis

Preparation of $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$

Synthesis of the disiloxane, $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$, was continued during the quarter in order to provide large quantities of

the monomer for polymerization research studies. The synthetic procedure employed was provided by Prof. P. Tarrant[1] as described in the previous FMC quarterly report.[2]

Formation of the adduct, $CF_2BrCFClCH_2CH_2Si(CH_3)_2Cl$ by the platinum catalyzed addition reaction of $HSi(CH_3)_2Cl$ to $CH_2=CHCFClCF_2Br$ on a 5 mole scale provided a 38% yield of product (606 grams) in a bomb run conducted at 75° C. for 11 hours. Repetition of the reaction at atmosphere pressure under reflux conditions for 24 hours but with an excess of dimethylchlorosilane afforded a 57% yield of product (914 grams). A smaller scale run employing equimolar quantities of reactants at atmospheric pressure yielded only ca. 35% of product (100 grams).

It was originally presumed on the basis of a simple distillation that all of the unreacted starting materials in the reaction were recovered.[2] However, a careful fractionation of the low boiling portion of the reaction mixture revealed the presence of other by-products. V. P. C. analysis identified a major component (B. P. 70-73° C.) as dimethyldichlorosilane, $(CH_3)_2SiCl_2$, formed by a disproportionation occurring in the presence of the platinum catalyst. However, 52% of the butene, $CH_2=CHCFClCF_2Br$, was accounted for in the product and as unchanged starting material. The balance was presumed to have been consumed in the side-reaction mentioned above.

Hydrolysis of $CF_2BrCFClCH_2CH_2Si(CH_3)_2Cl$ to $[CF_2BrCFClCH_2CH_2Si(CH_3)_2]_2O$ proceeded readily, providing high yields of product (55-88%).

Dehalogenation of $[CF_2BrCFClCH_2CH_2Si(CH_3)_2]_2O$ to the desired monomer $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$ was conducted with zinc dust in tetrahydrofuran solvent and ca. 70% yields of product were realized. The use of isopropanol as solvent led to a lower yield of product. The following physical properties were obtained for the disiloxane monomer: b. p. 60-65° C. / 0. 5 mm, n_D^{25} 1. 3924. Tarrant[1] reported the following values for the compound b p. 95° C. / 6 mm, n_D^{20} 1. 3932. Vapor phase chromatographic analysis of a sample prepared at FMC and one submitted by P. Tarrant showed the presence of an identical major peak for the respective specimens; however, the former was shown to have a purity of 90% while the latter was 73% pure.

The total quantity of $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$ synthesized to date is 458 grams.

4-Chloroperfluoroheptadiene-1, 6

4-Chloroperfluoroheptadiene-1, 6 was prepared by the scheme given below:

a) $Cl(CF_2CFCl)_3CF_2COOH + NaOH \longrightarrow Cl(CF_2CFCl)_3CF_2COONa$

b) $Cl(CF_2CFCl)_3CF_2COONa \xrightarrow{\Delta} Cl(CF_2CFCl)_2CF_2CF=CF_2$

c) $Cl(CF_2CFCl)_2CF_2CF=CF_2 + Zn \longrightarrow CF_2=CFCF_2CFClCF_2CF=CF_2 + ZnCl_2$

The first two steps have been described several times in the literature,[3,4,5] and were repeated without difficulty. The sodium salt, however, must be thoroughly dried in order to obtain a maximum yield. The heptadiene is not well characterized. Boiling points of 103-103.5° C. (630 mm)[6] and 122° C. (760 mm)[4] have been reported.

Zinc dechlorinations of the heptene were conducted in a variety of solvents in order to find the best conditions for the preparation of the heptadiene. The following solvents were investigated: isopropanol, tetrahydrofuran, bis 2-(2-methoxyethoxy) ethyl ether, and diethylene glycol monoethyl ether. With all of the solvents except the latter, unreacted heptene was recovered, which could be recycled. Because of the discrepancy between boiling points reported by other investigators, wide distillation cuts were taken which were then analyzed by gas chromatography to determine the heptadiene content. The boiling points observed compare with the lower figure (103° C./630 mm) reported by the University of Colorado investigators.[6]

Tetrahydrofuran gave the highest yield of heptadiene (43.2%), at a heptene conversion of 56.2%. The unconverted heptene was recovered. The purity of the diene was 84.3%. A sample of recovered heptene was recycled with comparable yields and product purity. A summary of the yields and solvents used by various investigators is given in Table I.

At present, 39g. of the crude heptadiene is on hand and will be redistilled. The amount of heptene on hand is 300g. This should give about 100g. of the diene. A ten pound sample of the Kel-F Acid 8114 ($Cl(CF_2CFCl)_3CF_2COOH$) has just been received. About two pounds will be carried through the reaction sequence, which should provide an additional 200g. of the diene for polymerization work.

Polyfluorooxetanes

The synthesis of the polyfluorooxetanes by photo initiated additions of fluorocarbonyl compounds to fluoroolefins was first reported by

Harris and Coffman in 1962.[7] The procedure followed in these laboratories differed essentially from the Harris and Coffman procedure in that the charged gasses were photolyzed under isothermal conditions rather than isobaric conditions. Thus it was possible to follow the course of the reaction by noting the pressure drop whereas this was not possible in the previous procedure. The plot of pressure decrease as a function of time is presented in the experimental portion of this report. It is to be emphasized that this is raw data. Nevertheless several conclusions may be drawn from this data by cursory observation. First, the reaction between hexafluoroacetone and hexafluoropropylene to the oxetane is complete in approximately twelve hours using this procedure rather than the seven days previously reported. Second, the plot shows a straight line until the pressure has dropped to one-half the original pressure after which there is no further pressure drop. This indicates that the reaction is pressure independent over the range studied and no advantage is to be gained by operation under very low or very high pressures.

The second run, it will be noted, was conducted with benzophenone added to examine the possibility of photosensitization. The results, shown in Figure 1, indicate no significant difference in rate under the conditions employed. It should be realized, however, that observance of any rate dependence is contingent on having the photosensitizer in the gas phase. It may very well be the case that this did not occur here. Of the sundry photosensitizers available at present, only diacetyl would appear to have sufficient vapor pressure for further consideration. A photosensitized preparative method would be desirable here so that the reaction could be extended to other less reactive olefins for the synthesis of more interesting oxetanes. However, it is believed that the present experimental procedure is quite satisfactory for preparing sufficient quantities of 2, 2, 3-tri(trifluoromethyl) perfluorooxetane for polymerization investigation.

An interesting point is the claim by Harris and Coffman that the oxetane produced from hexafluoroacetone and hexafluoropropylene is exclusively the 2, 2, 3-tri(trifluoromethyl) isomer. Assuming that the structural identification is correct, preliminary evidence suggests that the 2, 2, 4 isomer is also produced, though in much lower amounts, with a ratio of isomers of approximately 18 : 1. Aside from the more extended boiling range of 48-55° C. (to insure all isomers would be collected), physical properties determined here agree with those of Harris and Coffman.[7]

The photolysis of hexafluoroacetone and perfluorobutene-2 appears from the experimental data to be somewhat more complicated

than originally envisioned. For example, there was no significant pressure drop during the course of the photolysis although some liquid product was obtained. This suggests, of course, that concurrent with the formation with some higher boiling product, a gaseous product (perhaps carbon monoxide) is also formed. Also, although it is hazardous to predict the boiling point of two cis-trans isomers because they sometimes vary as much as 20° C., the predicted boiling point for the 2, 2, 3, 4-tetra(trifluoromethyl)-perfluorooxetane is ca. 80° C. The observed boiling range of 60-63° C. does certainly appear to be low.

It is not possible to identify the compound by IR analysis other than to eliminate several possibilities. Because there is no absorption from the region 500 cm^{-1} to 2000 cm^{-1} it is possible to eliminate carbonyl and unsymmetrical double bond moieties. Further work toward elucidating the correct structure of this compound is now in progress.

Preparation of $[CH_2CF_2CF=CCH_2CH_2Si(CH_3)_2]_2O$

The preparation of $CH_2=CHCHCFClCF_2CH_2$, starting material for $[CH_2CF_2CF=CCH_2CH_2Si(CH_3)_2]_2O$, followed the procedure of Park and Lacher.[6] The cycloaddition of chlorotrifluoroethylene to butadiene proceeds readily, giving high yields of the vinyl cyclobutane with minimal amounts of side products. The addition of dimethylchlorosilane to the vinylcyclobutane also appears to be straightforward, although vigorous, and it shall be necessary in the future to add slowly one reactant to a heated solution to the other reactant. Structural identification and analysis is in progress and will be reported later. There still remain two steps, the hydrolysis of the intermediate chlorosilane and the final dehydrochlorination step.

Preparation of $CH_2=CHCF_2CF_2CH=CH_2$ and $CF_3CH=CH_2$

$$CF_2Br_2 + CH_2=CH_2 \longrightarrow CF_2BrCH_2CH_2Br \longrightarrow CF_2BrCH=CH_2$$

$$CF_2BrCH=CH_2 \longrightarrow CF_3CH=CH_2 \quad CH_2=CHCF_2CF_2CH=CH_2$$

It has not been possible to improve upon the results of Tarrant and Lovelace[8] and Blomquist and Longone[9] in the benzoyl peroxide initiated addition of dibromodifluoromethane to ethylene. After a brief induction period a vigorous reaction occurs and it is easy to understand how Tarrant and Lovelace report a safety disc failure on their bomb. It was decided, therefore, to investigate a photolytic preparation, by

taking advantage of the photohomolysis of the carbon-bromine bond in dibromodifluoromethane.[10] Although it has not been possible to complete the work-up of this reaction during this report period, preliminary indications are that this is a more satisfactory procedure than the benzoyl peroxide initiated route.

To date, only a pilot dehydrobromination has been completed. The boiling range (49-51° C.) is not in good agreement with previous investigators (41-42° C.); this product is being examined further. Aside from this apparent discrepency it will be possible to conduct the dehydrobromination in excellent yields. The synthesis of $CF_3CH=CH_2$ and $CH_2=CHCF_2CF_2CH=CH_2$ await the production of sufficient quantities of $CF_2BrCH=CH_2$.

IV. EXPERIMENTAL

A. Polymerization Research

Reaction of $CF_2=CFCF_2CFClCF_2CF=CF_2$ with $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$

D-871-117 A 100cc. Aminco Bomb was charged in an air atmosphere, with 14.1g. (0.043 mole) of $CF_2=CFCF_2CFClCF_2CF=CF_2$ (99% purity) and 15.0g. (0.043 mole of $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$ (92.5% purity) and heated to 200° C. in a rocker assembly for 20 hours. After the heating period, the bomb was cooled and vented. The reaction mixture consisted of a tan colored, slightly viscous liquid which appeared to have undergone decomposition during the heating period. The latter was placed in a small distillation assembly employing a Widmer column and 7.35g. of unchanged $CF_2=CFCF_2CFClCF_2CF=CF_2$ was collected (b.p. 103-105° C./760 mm. Hg.) whereupon some further decomposition was noted. (Pot temperature ca. 150° C.). Distillation was continued under vacuum but extensive decomposition ensued and only 7.0g. of a black viscous residue remained which was not examined further.

D-871-120 The above experiment was repeated on a smaller scale (0.017 mole), using a 30 ml. capacity stainless steel Hoke cylinder, and under a helium atmosphere at 150° C. After vacuum stripping at 3 mm., to remove unreacted starting materials, a yellow liquid (~6g.) remained, which was shown to contain seven components by V.P.C. analysis. No further characterization was attempted as handling losses had greatly reduced the quantity of material.

B. Monomer Synthesis

1. Preparation of: $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$

$$CF_2BrCFClCH=CH_2 + HSi(CH_3)_2Cl \longrightarrow CF_2BrCFClCH_2CH_2Si(CH_3)_2Cl$$

I II

$$[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O \longleftarrow [CF_2BrCFClCH_2CH_2Si(CH_3)_2]_2O$$

IV III

Preparation of $CF_2BrCFClCH_2CH_2Si(CH_3)_2Cl$

D-871-108 A 2.7 liter Aminco Bomb was charged with 473g. (5 moles) of $H\text{-}Si(CH_3)_2Cl$, 1117.5g. (5 moles) of $CH_2=CHCFClCF_2Br$ and 10cc. of 0.1M H_2PtCl_6 in isopropanol in an air atmosphere. The bomb contents were then rocked at 75° C. for 11 hours. At the

conclusion of the heating period, the bomb was cooled, vented and the contents were decanted into a dry container for distillation. Distillation of the reaction mixture was performed at atmospheric pressure through a 14" insulated Vigreux column. Two fractions were collected, the first fraction (fraction I) distilling at 60-90° C. (uncorrected) and weighing 805g. and a second fraction (fraction II) distilling at 180-185° C. and weighing 606g. (38% yield of the desired product). Fraction I was redistilled in a Fenske helices-packed column and the following fractions were obtained:

BP° C.	Weight	Identity
23-70	56g.	-
70-73	279g.	$(CH_3)_2SiCl_2$
73-77	84g.	-
77-84	87g.	-
84-96	43g.	-
96-98.5	161g.	CH_2= $CHCFClCF_2Br$
Residue	94g.	-

The $(CH_3)_2SiCl_2$ was identified by vapor phase chromatography employing commercially available material as a reference compound.

The CH_2= $CHCFClCF_2Br$ recovered was identified by its boiling point and chemical properties; 52% of the butene was accounted for in the product and as unchanged starting material.

D798-145 A mixture of 1117g. (5.0 moles) of CH_2= $CHCFClCF_2Br$ 709g. (7.5 moles) of dimethylchlorosilane, and 10 ml. of an 0.1 molar solution in chloroplatinic acid in isopropanol was heated at reflux with stirring. After 3.5 hours, another 100g. (1.06 moles) of the silane added. After another 3.5 hours of refluxing, another 100g. (1.06 moles) of the silane was added. Stirring under reflux was continued for a total of twenty-four hours. The dark fuming liquid was distilled through a 15cm. Vigreux column to give 914g. (57.4%) of the desired product, b.p. 71-95° C. (16 mm.), n_D^{25} 1.4358, with a density of 1.42g./ml.@ 25° C.

Preparation of $[CF_2BrCFClCH_2CH_2Si(CH_3)_2]_2O$

This was carried out by heating at reflux temperature, a mixture of the silane with an excess of water, overnight. Then, the organic phase was water washed until acid-free, dried over magnesium sulfate and distilled. The results of several such preparative runs are summarized in Table IV.

Preparation of $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$

D798-144 To a stirred refluxing mixture of 58.6g. (0.9 mole) of zinc dust and 2g. of zinc chloride in 400 mls. of tetrahydrofuran was added 209g. (0.36 mole) of $[CF_2BrCFClCH_2CH_2Si(CH_3)_2]_2O$ (D798-142) over two hours. The reaction commenced almost immediately. After stirring an additional two hours at reflux, the mixture was filtered from the unreacted zinc. The filtrate was diluted with water and the organic phase taken up in methylene chloride. The organic layer was washed several times with water to remove zinc salts and dried over magnesium sulfate. Distillation gave an 85.9g. yield (68.2%) of the desired product, b.p. 60-65° C. (0.5 mm.), n_D^{25} 1.3924, density 1.05g./ml. @ 25° C. According to an analysis by gas chromatography, the product was 90.1% pure.

D798-149 A larger scale reaction was carried out, starting with 727g. (1.25 moles) of the halogenated disiloxane, giving 319g. of product (72.8% yield) on which analytical data has not yet been received.

C1129-4 The above reaction also was carried out on a 0.5 mole scale, using isopropanol as the solvent. In this case the yield of product (b.p. 204-210° C./760 mm.) was only 31.6%.

2. Preparation of: $CF_2=CFCF_2CFClCF_2CF=CF_2$

$$Cl(CF_2CFCl)_3CF_2CO_2H \longrightarrow Cl(CF_2CFCl)_3CF_2CO_2Na$$

I II

$$CF_2=CFCF_2CFClCF_2CF=CF_2 \longleftarrow CF_2ClCFClCF_2CFClCF_2CF=CF_2$$

IV III

Preparation of the Sodium Salt of $Cl(CF_2CFCl)_3CF_2COOH$ (II)

D798-134 To a solution of 37.5g. (0.937 mole) of sodium hydroxide in 100 ml. of water was added 449g. (0.937 mole) of $Cl(CF_2CFCl)_3CF_2COOH$ (I) over a one hour period with stirring. The mixture turned into a thick paste. Most of the water was removed by drying on a steam bath. Drying was completed by heating to 125° C. in an oven at a pressure of about 1 mm. The yield of slightly gray powder was 457g. (99.1% of theory).

The above preparation was repeated twice, on 250 and 500 gram scales (C1129-1, C1129-8, respectively). In these runs, the

final drying was carried out, in vacuo, over phosphorus pentoxide. The yields in both cases were virtually quantitative.

Preparation of 4, 6, 7-Trichloroperfluoro-1-heptene (III)

C1129-3 Exactly 267g. of $Cl(CF_2CFCl)_3CF_2COONa$ obtained in C1129-1 was transferred to a 1 liter round-bottom flask equipped with a distilling adaptor, Friedrich's condenser, vacuum adapter, and receiver. The system was evacuated through a dry ice-cooled trap to approximately 1 mm. pressure and then heated to approximately 150° C. Decarboxylation commenced within approximately 15 minutes and the pressure increased to ca. 10 mm. because of the carbon dioxide evolution. The heptene (III) came over quite smoothly to the ice-cooled receiver and was washed once with water, once with 10% aqueous sodium carbonate, once again with water, and dried over sodium sulfate. There was obtained 180.5g. of crude product. Infrared analysis of this crude product showed a strong adsorption band at $1770cm^{-1}$ indicating a terminal fluoroolefin and a weak adsorption band at $1720cm^{-1}$ indicating a small contaminant of internal olefin. There was no adsorption in the range $3500-2500cm^{-1}$ indicative of carbon hydrogen bonding which would be expected of a possible contaminant (due to incomplete drying of II). Distillation of this crude material gave 159g. of pure heptene (III) boiling at 161-162° C. This represents 75% of the theoretical possible yield from the starting $Cl(CF_2CFCl)_3CF_2COOH$.

D798-137 A 605g. (1.23 mole) quantity of $Cl(CF_2CFCl)_3CF_2COONa$ (D798-134) was divided in two equal portions. Each was pyrolyzed by slowly heating to 370° C. at a pressure of 4 mm. The distillate was collected in an ice-cooled receiver followed by a dry ice-acetone cooled trap. The total yield was 461g. The distillate was washed first with 5% aqueous sodium bicarbonate solution and then with water and dried over magnesium sulfate. The product was distilled through a 15cm. Vigreux column, giving a 427g. yield (87.0%) of the desired product, b.p. 65-70° C. (20 mm.), n_D^{25} 1.3639, and with a density of 1.78g./ml. @ 25° C. Analysis by gas chromatography indicated that the product was 92.3% pure.

One additional run (C1129-9) was carried out, using the material obtained in C1129-8, to yield an additional 315g. of heptene, b.p. 160-163° C./760 mm. (Yield: 74.5%, based on starting $Cl(CF_2CFCl)_3CF_2COOH$).

Note: Barnhart et al.,[3] give the following data for 4, 6, 7-trichloroperfluoro-1-heptene: b.p. 156-157° C./760 mm., n_D^{20} 1.3639, and d_4^{20} 1.800.

Preparation of 4-Chloroperfluoroheptadiene-1, 6 (IV)

D798-141 To a stirred refluxing mixture of 16g. (0. 25 mole) of zinc dust, 1g. of zinc chloride, and 25 ml. of isopropanol was added 39. 9g. (0. 1 mole) of 4, 6, 7-trichloroperfluoro-1-heptene (D798-137) over a six hour period. After refluxing an additional 0. 5 hour, the mixture was filtered from unreacted zinc and the filtrate diluted with several volumes of water. The organic layer was taken up in methylene chloride, water washed several times, and dried over magnesium sulfate. Distillation gave a 11. 3g. of product, b. p. 97-112° C. /761 mm.), n_D^{25} 1. 3311. The purity by gas chromatography was 67. 5%. The yield of crude product based on heptene actually consumed was 40. 9%. Unreacted material recovered was 6. 5g. (16. 3% of the amount charged).

This zinc dechlorination reaction was repeated several times, using other solvents, i. e., tetrahydrofuran, bis-2-(2-methoxyethoxy) ethyl ether and diethylene glycol monoethyl ether. One run (D798-148), carried out in isopropanol solvent utilized recovered heptene. In run D798-146, the procedure described above was modified to the extent that the reaction was carried out at 100° C. /85 mm. with a short Vigreux column and a still head added to the apparatus, and heptadiene removed as it formed. The crude product so obtained was redistilled.

Some details of this series of reactions are summarized in Table II.

Note: The physical contents reported by Park and Lacher[6] for 4-chloroheptadiene-1, 6 are: b. p. 103-103. 5° C. /630 mm. and n_D^{23} 1. 3326. Fearn and Wall,[4] however, report a boiling point of 122° C. / 760 mm. In their report, Park and Lacher claim to have confirmed the structure of their compound by means of NMR spectroscopy.

3. Preparation of: $CH_2=CHCF_2CF_2CH=CH_2$ and $CF_3CH=CH_2$

$$CF_2Br_2 + CH_2=CH_2 \longrightarrow \underset{\text{I}}{CF_2BrCH_2CH_2Br} \longrightarrow \underset{\text{II}}{CF_2BrCH=CH_2}$$

$$\underset{\text{III}}{CF_3CH=CH_2} \qquad \underset{\text{IV}}{CH_2=CHCF_2CF_2CH=CH_2}$$

Preparation of $CF_2BrCH_2CH_2Br$

C1129-32 A 2 liter Aminco Bomb was charged with 15g. benzoyl peroxide, evacuated, purged with bone-dry nitrogen, further evacuated,

and finally charged with 550g. (2.62 moles) CF_2Br_2. The bomb was placed in a barricaded rocker and charged with 350 psig CP ethylene while rocking and was then rapidly heated to 90° C. Very shortly thereafter an exotherm occurred raising the bomb temperature to 120° C. momentarily with a pressure rise to 900 psig. Immediately thereafter the pressure fell to 200 psig and there remained. Heating was continued at 90° C. for 2 hours or 4 half-lives of the initiator, benzoyl peroxide. The bomb was cooled to room temperature and the volatiles collected in a dry-ice cooled trap. The liquid product was steam distilled, the lower organic layer separated, and dried over sodium sulfate. Distillation gave 203g. (0.966 mole) of unreacted CF_2Br_2 and 135g. (0.567 mole) of the dibromodifluoropropane (I) boiling at 125-126° C./760 mm. (Lit. 81.5-82° C./173 mm.). Thus, 63% of the CF_2Br_2 charged into the bomb is consumed with 35% of the consumed CF_2Br_2 producing the desired product (the over-all yield of product is 23% of total reactant charged into the bomb). The bomb runs made according to the above procedure are summarized in Table III.

Preparation of $CF_2BrCH=CH_2$

C1129-38 In a 500 ml. Morton flask equipped with a stirrer, addition funnel, and distillation take-off adaptor containing 30g. KOH in 200 ml. H_2O, and heated to ca. 80° C., were added 100g. $CF_2BrCH_2CH_2Br$. During the course of the addition, product distilled from the reaction mixture at 40-60° C. When the addition was complete, a lower organic layer was observed in the bottom of the flask, so distillation was continued. The distillate was separated from the lighter aqueous layer, dried over sodium sulfate and rectified. Three fractions were collected, (1) 19g. of 3-bromo-3, 3-difluoropropylene, b.p. 49-51° C., (2) 24.5g. of unreacted starting material, b.p. 125-129° C., and (3) 18g. of higher boiling materials. The boiling point for the bromodifluoropropylene reported in the literature[9] is 41-42° C. The yield of bromodifluoropropylene, based on $CF_2BrCH_2CH_2Br$ converted, was 35%.

4. Preparation of: $(CF_3)_2\underline{CCF(CF_3)CF_2O}$

$$CF_3COCF_3 + CF_3CF=CF_2 \longrightarrow (CF_3)_2\underline{CCF(CF_3)CF_2O}$$

I

+

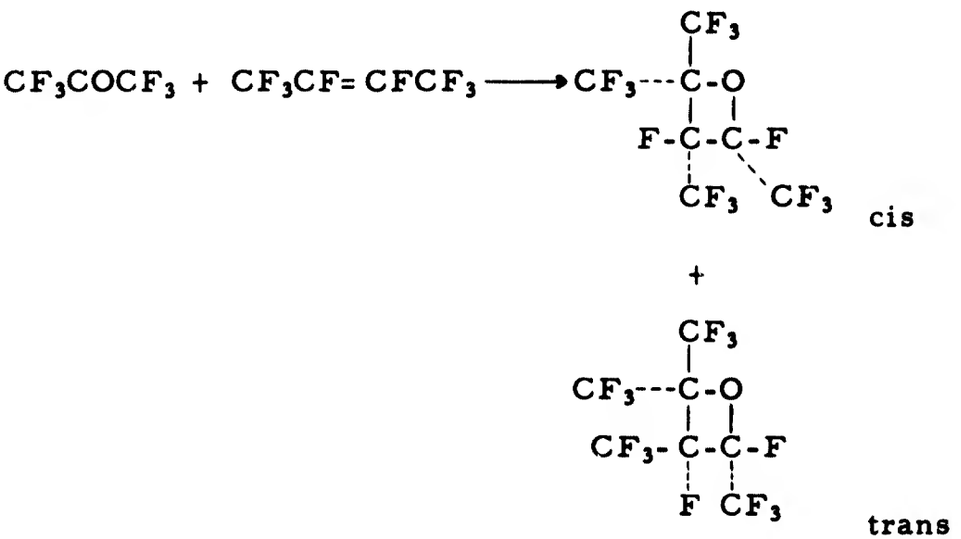
$(CF_3)_2\underline{CCF_2CF(CF_3)O}$

II

C1129-30 The apparatus employed in this preparation was a 12 liter round-bottom flask equipped with an outlet connected to a Hg. manometer, an inlet for charging and evacuating, and a Hanovia water-jacketed quartz immersion well with a 450 watt high pressure Hg. ultraviolet lamp. The flask was evacuated and then charged with 300 mm. $CF_3CF=CF_2$ and 300 mm. CF_3COCF_3. During the irradiation the pressure drop was followed as a function of time and is recorded in Figure 1. When the pressure dropped to a value of 1/2 of the total original charge the lamp was extinguished and the flask evacuated through a dry-ice cooled trap. The contents of the trap were rectified to give 44.5g. of product boiling at 48-55° C. A wide boiling range was collected to insure that both possible isomers would be collected. VPC analysis indicated that the product consisted of 90% of one isomer, presumably the 2, 2, 3 isomer (I), and 5% of the other isomer, presumably the 2, 2, 4 isomer (II).

C1129-33 The flask employed in the above preparation was utilized for this preparation. One gram benzophenone was added to the flask which was then evacuated and charged with 300 mm. of CF_3COCF_3 and 300 mm. $CF_3CF=CF_2$, as before. The pressure drop during irradiation was followed as a function of time and is presented in Figure 1. After irradiation the flask was evacuated and the material collected in the trap distilled to give 45.0g. of product boiling at 48-55° C. (Lit.[7] b.p. 51-52° C.).

5. Preparation of: $(CF_3)_2CCF(CF_3)CF(CF_3)O$



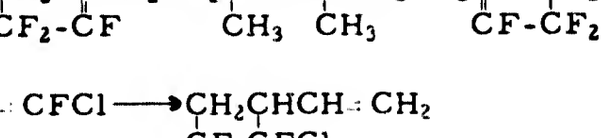
C1129-34 Into the 12 liter round-bottom flask used before was charged 300 mm. hexafluoroacetone and 300 mm. $CF_3CF=CFCF_3$. After irradiating 16 hours no pressure drop was recorded. The flask

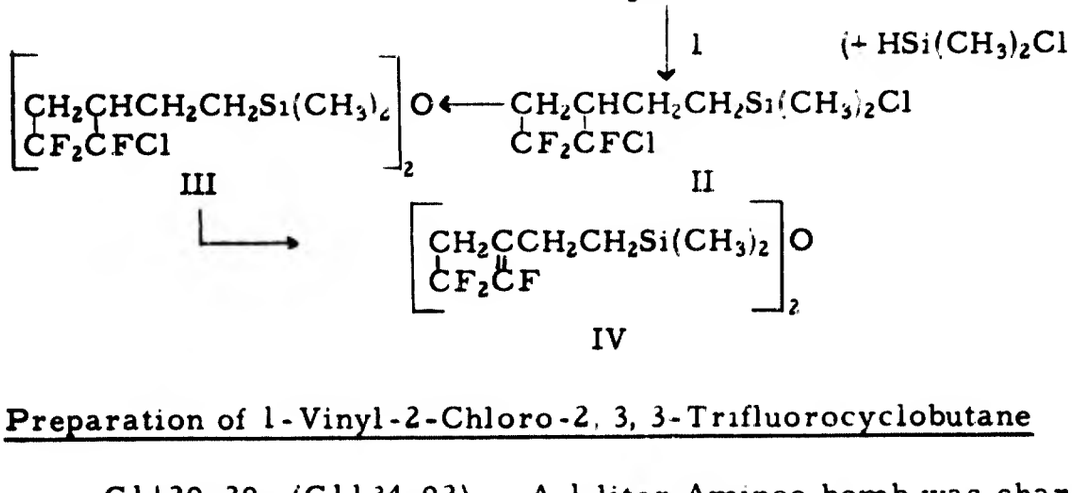
was evacuated through a dry-ice cooled trap and the material collected in the trap distilled to give 7.5g. of material boiling 60-63° C.

C1481-2 Into the evacuated flask mentioned above was charged 302 mm. CF_3COCF_3 and 302 mm. $CF_3CF=CFCF_3$. After irradiating for 18 hours a pressure drop of 4 mm. was observed. A small amount of liquid had collected and the flask was pumped down through a dry-ice cooled trap. The material collected in the trap was distilled and 8g. of material boiling at 58-64° C. collected.

IR analysis of these two products indicated no carbonyl or double bond adsorption. Further identification is in progress.

6. Preparation of:





Preparation of 1-Vinyl-2-Chloro-2, 3, 3-Trifluorocyclobutane

C1129-29, (C1134-92) A 1 liter Aminco bomb was charged with 10 ml. dipentene (Hercules No. 122) sealed, and evacuated. The bomb was cooled in dry-ice and 0.3 lb. (ca. 150g.) butadiene and 0.6 lb. (ca. 250g.) chlorotrifluoroethylene were charged. The bomb was then placed in a barricaded rocker and slowly heated to 150° C. The maximum pressure of 350 psig was noted and by the time the bomb had reached 150° C., one hour later, the pressure was only 50 psig. The bomb was cooled to room temperature and the volatile products vented through a dry-ice cooled trap (2-5 ml. collected). The liquid material from the bomb was steam distilled, the organic layer separated, and dried over sodium sulfate. Distillation afforded 200.0g. of product boiling at 113-116° C.; which was identical to that of the material supplied by Park.[6] It is not possible to calculate meaningful yield data on this run as the scale used for weighing the charging cylinders was not accurate for the small differences.

A second run (C1129-35) employing an identical charge of reactants under the same conditions gave 163g. of the vinylcyclobutane, b.p. 113-116° C.

Preparation of
2-(2'-Chloro-2', 3', 3'-trifluorocyclobutyl)ethyldimethylchlorosilane

C1129-36 In a 500 ml. round-bottom flask fitted with a magnetic stirrer, heating mantle and reflux condenser was added 100g. (0.59 mole) of the vinyl cyclobutane (I) 29g. (0.31 mole) chlorodimethylsilane, and 1 ml. of 0.1M H_2PtCl_6. After the solution was stirred at room temperature for 30 minutes, the flask was slowly heated. Shortly after heating was begun a vigorous reaction occured, causing the condenser to be forcibly ejected with loss of some material. Much of the material was recovered by rinsing the inside and outside of the flask with methylene chloride. Distillation of the methylene chloride solution afforded a fraction boiling at 110-120° C. at atmospheric pressure. This was subsequently redistilled under vacuum to produce 50.0g. of product boiling at 51° C./5 mm. Structural characterization of this product is now in progress. The yield is 61% from chlorodimethylsilane. The vinyl cyclobutane was used in excess as a planned later addition of more chlorodimethylsilane was not possible.

REFERENCES

[1] Semi-Annual Report I - Contract DA-19-129-AMC-79(N). "Research on Synthesis of Unsaturated Fluorocarbon Compounds". P. Tarrant, April 1 - September 20, 1963.

[2] FMC Progress Report II - U. S. Army Contract DA-19-129-AMC-147(N), September 27 - December 26, 1963.

[3] Barnhart, W. S., et al., J. Chem. Eng. Data, 2, 80 (1957).

[4] Fearn, J. E., and Wall, L. A., SPE Trans., 3, 231 (1963).

[5] Park, J. D., and Lacher, J. R., W. A. D. C. Technical Report 56 - 590, Part 1, pp. 21 - 22 (1957).

[6] Park, J. D., and Lacher, J. R., Ninth Quarterly Report, Contract DA-19-129-QM-1926 (1964).

[7] Harris and Coffman, J. Am. Chem. Soc. 84, 1553 (1962).

[8] Tarrant and Lovelace, J. Am. Chem. Soc. 76, 3466 (1954).

[9] Bloomquist and Longone, J. Am. Chem. Soc. 79, 4981 (1957).

[10] Walling and Huyser, Org. Reactions 13, 91 (1963).

TABLE I

SOLVENTS EMPLOYED IN THE DECHLORINATION OF HEPTENE TO HEPTADIENE

Worker	Method	Yield
Park and Lacher[1]	Zn in dibutoxytetraethylene glycol	43%
Fearn and Wall[2]	Zn in bis 2(2-methoxyethoxy) ethyl ether	24%
Straus and Wall[3]	Zn in bis 2(2-methoxyethoxy) ethyl ether/acetone	n/a
Park and Lacher[4]	Zn in dibutoxytetraethylene glycol	20%
FMC	Zn in tetrahydrofuran	36.5%[5]
FMC	Zn in isopropanol	40.0%[5]
FMC	Zn in bis 2(2-methoxyethoxy) ethyl ether	56.2%[6]
FMC	Zn in diethylene glycol mono-ethyl ether	9%
FMC	Zn in diethylene glycol mono-ethyl ether	16%

[1]Park and Lacher — WADC Tech. Report 56-590 Part 1 (1957)

[2] Fearn and Wall — SPE Transactions 331 (1963)

[3]Straus and Wall — SPE Transactions 56 (1964)

[4]Park and Lacher — 9th Quarterly Report DA-19-129-QM-1926 (1964)

[5]In hand yields were converted to 100% purity basis from v. p. c. analytical data.

[6]Yield of crude product.

ew
4/13/64

TABLE II

PREPARATION OF 4-CHLOROPERFLUOROHEPTADIENE-1, 6
BY DECHLORINATING 4, 6, 7-TRICHLOROPERFLUOROHEPTENE-1

Ref. No.	Solvent	Reaction Time (hrs.)	Heptene Charge (g.)	Product Wt. (g.)	b. p. 's of Products	Heptene Recov. %	Purity of Product[1]	n_D^{25}	Product Yield[2] %
D798-141	Isopropanol	6.5	25.0	11.3	97-112° /761mm.	43.8	67.5%	1.3311	27.6
D798-148[3]	Isopropanol	4.0	36.6	12.7	102-125°/ 745mm.	13.6	82.0%	1.3316	40.0
D798-140	Tetrahydro-furan	4.0	25.0	8.0	109-122° /761mm.	43.8	84.3%	1.3361	36.4
D798-146	Bis-2-(2-methoxy-ethoxy)ethyl ether	4.0	25.0	7.9	101-115° /767mm.	57.3	64.3%	1.3314	36.1
C1129-5	Diethylene glycol monoethyl ether	~ 2.0	159	13.2	105-111° /764mm.	-	-	-	9.0[4]
C1129-10	Diethylene glycol monoethyl ether	~ 2.8	315	40.6	108-110° /760mm.	-	-	-	16.0[4]

[1] By vapor phase chromatography.

[2] Based on heptene actually converted. In hand yields corrected to 100% purity basis, from v. p. c. data.

[3] Recovered heptene used in this run.

[4] In hand yield, based on heptene charged.

ls
1/13/61

TABLE III

BENZOYL PEROXIDE INITIATED PREPARATION OF $CF_2BrCH_2CH_2Br$

Reference:	CF_2Br_2 Charged	CF_2Br_2 Recovered[a]	$CF_2BrCH_2CH_2Br$ Produced	Comments
C1129-24 (C1134-70)	910g.	113g. (12%)[b]	- (-%)[c]	5g. Bz_2O_2 used. Bomb heated to 50°. No reaction, Considerable loss is mechanical (spillages)
C1129-26 (C1134-79)	460g.	118g. (26%)	96.6g. (25%)	10g. Bz_2O_2 used
C1129-27 (C1134-84)	577g.	14.8g. (2.6%)	138g. (22%)	15g. Bz_2O_2 used
C1129-28 (C1134-88)	459g.	- (-%)	9.3g. (0.6%)	15g. Bz_2O_2 used Bomb assumed to have leaked.
C1129-31 (C1134-94)	773g.	188g. (24%)	125g. (19%)	15g. Bz_2O_2 used. Some telomers also formed
C1129-32 (C1134-101)	550g.	203g. (37%)	135g. (35%)	15g. Bz_2O_2 used. Some telomers also formed.

a. Recovery of CF_2Br_2 was often accompanied by large handling losses; these amounts could be increased with rigorous conditions.

b. Amount of CF_2Br_2 recovered, expressed as per cent.

c. Yield of $CF_2BrCH_2CH_2Br$ from CF_2Br_2 consumed, expressed as per cent.

ls
4/13/64

TABLE IV

PREPARATION OF $[CF_2BrCFClCH_2CH_2Si(CH_3)_2]_2O$ FROM $CF_2BrCFClCH_2CH_2Si(CH_3)_2Cl$

(All overnight at reflux temperature)

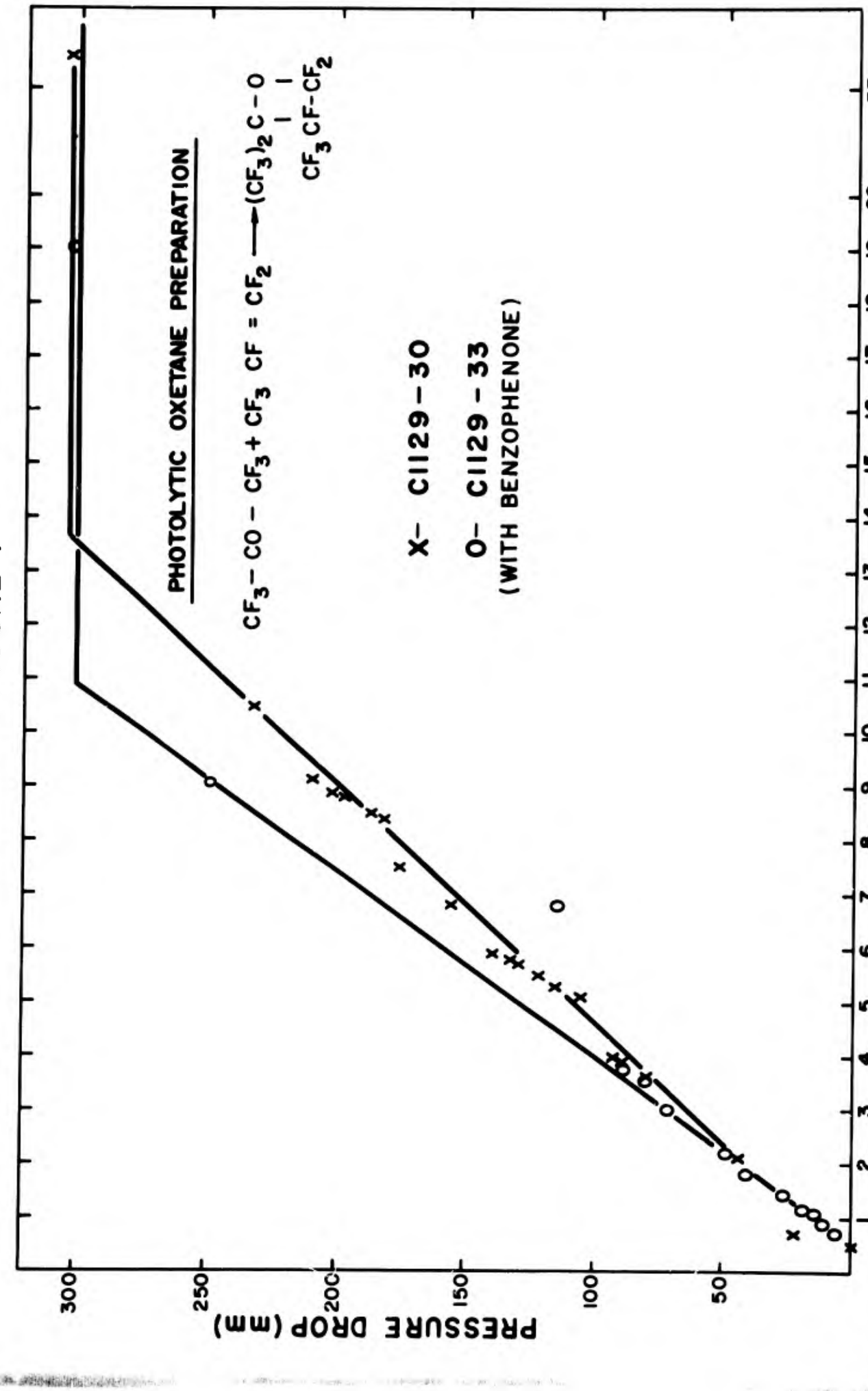
Reference No.	Charge gms. (moles) Chlorosilane	Water	Boiling Range of Product Collected	Wt. of Product (g.)	Yield of Product
D798-147	914 (2.87)	700 (39)	105-42° C. /0.7 mm.	735	88.0%
D798-142	307 (0.97)	250 (14)	113-20° C. /0.5 mm.	240	85.5%
D871-111	363 (1.14)	250 (14)	126-27° C. /1.2 mm.	213	63.8%
C1129-2	351 (1.11)	250 (14)	85-110° C. /20 mm.	277[1]	80.0%[2]
C1129-15	100 (0.32)	200 (11)	104-11° C. /1 mm.	40	43.5%

[1] 93% pure by V.P.C. analysis.

[2] In hand yield corrected to 100% purity, from V.P.C. data.

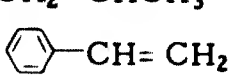
ew
4/16/64

FIGURE 1


PHOTOLYTIC OXETANE PREPARATION
$CF_3-CO-CF_3+CF_3\ CF=CF_2 \longrightarrow (CF_3)_2C-O$
CF_3CF-CF_2
X- C1129-30
O- C1129-33
(WITH BENZOPHENONE)
PRESSURE DROP (mm)
300
250
200
150
100
50
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 37
ELAPSED TIME (HRS)

APPENDIX I

The following is the Monomer List developed during the period 1950-1962 under U. S. Army Quartermaster Corps' sponsorship of contracts with the M. W. Kellogg Company and 3-M.

Monomer No.	Formula
1	$CF_2=CFCl$
2	$CF_2=CH_2$
3	$CH_2=CHCH=CH_2$
4	$CF_2=CFCF=CF_2$
5	$CH_2=CH(CH_3)CH=CH_2$
6	$CH_2=C(CH_3)_2$
7	$\underline{CF_2CF=CFCF_2}$
8	$CH_2=CHCl$
9	$CF_2=CCl_2$
10	$CH_2=CHCH_3$
11	
12	$CH_2=CCl_2$
13	$CH_2=CClCH=CH_2$
14	$CF_2=CFCF_3$
15	$CF_2=CFCN$
16	$CH_2=CHCN$
17	$CH_2=CHCO_2C_4H_9$ (n)
17A	$CH_2=CHCO_2CH_3$
18	$CF_2=CHCl$
19	$CF_3CCl=CClCF_3$
20	$CF_3C\equiv CCF_3$
21	$CF_2=CFH$
22	$CH_2=CFCl$
23	$CF_3CH=CHCF_3$ (cis)

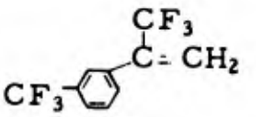
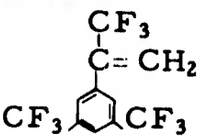
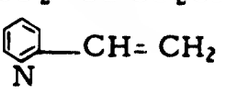
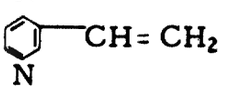
APPENDIX I - Continued

Monomer No.	Formula
24	$CF_2=CF_2$
25	$CF_3CH=CHCF_3$ (trans)
26	$CH_2=CHC_6H_4CH=CH_2$
27	$CF_3C(CH_3)=CH_2$
28	$CH_2=CFCH=CH_2$
29	$(CF_3)_2C=CF_2$
30	$CF_2=CFBr$
31	$CH_2=CH_2$
32	$CF_2=CCl-CF_3$
33	$CF_3C(CH_3)=CHCOOH$
34	$CH_2=CHC(=O)-NH_2$
35	$CF_3CH=CH_2$
36	$CH_2=CHBr$
37	$CF_2=CHCH=CH_2$
38	$CCl_2=CClCF_3$
39	$CH_2=CClCF_3$
40	$CH_2=CFH$
41	$CF_2=CHC(CH_3)=CH_2$
42	$CF_2=CHCF_3$
43	$CH_2=CHCH=CHCF_3$
44	$CF_2=C(CH_3)CH=CH_2$
45	$CH_2=CH-OC(=O)-CH_3$
45A	$CH_2=CHOC(=O)CH_2CH_2CH_3$

APPENDIX I - Continued

Monomer No.	Formula
45B	$CH_2=CHOCCH_2Cl$ (O above C)
46	$C_6H_5CH=CHCOOCH_3$
47	$CH_2=CHOC_2H_5$
48	$CH_2=CHOCH_2CH_2Cl$
49	$CH_2=CHOCH_2CH(CH_3)_2$
50	$CF_2=C(CH_3)CF=CH_2$
51	$CF_2=CHCF=CH_2$
52	$C_2H_5O_2CCH=CHCO_2C_2H_5$ (trans)
53	$C_2H_5O_2CCH=CHCO_2C_2H_5$ (cis)
54	$CH_2=CH\text{-}Si(OC_2H_5)_3$
55	$CF_2=CFC_6H_5$
56	$CF_2=CF\text{-}CH=CH_2$
57	$CH_2=C(CN)(CF_3)$
58	$CF_2=CFCH=CF_2$
59	$CH_3(CH_2)_{16}COOCH=CH_2$
60	$CF_2Cl(CFClCF_2)_2CF=CF_2$
61	$CF_2ClCF=CFCF_2Cl$
62	$CF_2CFC(CH_3)=CF_2$
63	$CH_2=CH\text{-}C_6H_3(CF_3)_2$ 3, 4, & 3, 5 isomers
64	$CH_2=C(CF_3)CO_2CH_3$
65	$CF_2=CFCH_2CH=CH_2$
66	$(CN)_2$
67	$CF_3CF=CH_2$

APPENDIX I - Continued

Monomer No.	Formula
68	$CF_2=CFCH=CFH$
69	$C_6H_5C(CF_3)=CH_2$
70	
71	
72	$CH_2=CHOCF_2CF_2H$
73	$Cl(CF_2CFCl)_2CF_2CO_2CH_2CH=CH_2$
73A	$Cl(CF_2CFCl)_3CF_2CO_2CH_2CH=CH_2$
74	$CH_2=C(CF_3)CH=CH_2$
75	$CH_2=CHCH_2CO_2CF_2(CF_2CFCl)_2CF_2O_2CCH_2CH=CH_2$
76	$CF_2=CFCF_2CFCl_2$
77	$CF_2=CH-C(CF_3)=CH_2$
77A	$CF_3CH=C(CF_3)CH_3$
78	$CH_2=CHOCF_2CHClF$
78A	$CHCl=CHOCF_2CHClF$
79	$CF_3CH=CClCF_3$
80	$CF_3CF_2CF_2CHO$
81	$C_4F_9N=CF_2$
82	$CF_2=CFCF_2Cl$
83	
84	
85	$CF_2=CFCF_2OCH_2CF_3$

APPENDIX I - Continued

Monomer No.	Formula
86	$CF_2=CClCF=CF_2$
87	$CF_2=CFCCl=CH_2$
88	$CF_2=CClCH=CF_2$
89	$ClCF_2CFClCF_2CO_2CH=CH_2$
90	$CF_2=CFCF_2CFClCF_2Cl$
91	$CF_2=CFCF_2CF_3$
92	$CF_3CH=CHCH=CHCF_3$
93	$CFCl_2CF=CH_2$
94	CF_3CHO
95	$CF_2=CFC(CF_3)-CF_2$
96	$CF_2=C(CF_3)CH=CH_2$
97	$CF_2=CFCF_2CF_2H$
98	$CF_2=CF(CF_2)_4H$
99	$CF_2=CFCF_2CO_2C_2H_5$
100	$CF_2=CFCF_2CF=CF_2$
101	$C_2F_5CH=CH_2$
102	$C_3F_7CH=CH_2$
103	$CF_3CH_2CH_2CH=CH_2$
104	$CF_3(CH_2CH_2)_2CH=CH_2$
105	$CH_2-CH-CF(CFCl-CF_2)-CF_2$
106	CF_3CH-CH_2 (epoxide)
107	$C_3F_7CH_2OCH=CH_2$
108	$CF_3CF=CFCF_3$
109	CF_2-CF CH_2-CH

APPENDIX I - Continued

Monomer No.	Formula
110	$CF_3CH_2OCH=CH_2$
111	CF_2O
112	$CF_3CH_2CH=CH_2$
113	$C_3F_7CH_2CH=CH_2$
114	$(CF_3)_2C=CH_2$
115*	$CH_2=CHCF_2OCF_3$
116*	$CH_2=CHCF_2OC_3F_7$
117*	$CF_2=CHCF_2OCF_3$
118*	$CF_2=CHCF_2OC_3F_7$
119*	$CF_2=CFCF_2OCF_3$
120*	$CF_2=CFCF_2OC_3F_7$
121*	$CH_2=CHOCF_2CF_3$
122*	$CF_2=CFOCF_3$
123*	$CF_2=CFOC_3F_7$
124*	$CF_2=CHOCH_2CF_3$
125	$CF_3CF_2CF=CH_2$
126	$C_5F_{11}CF\text{-}CF_2$ (O)
127	$CF_3N=O$
128	$CF_2=CFC_6H_4CO_2H$
129	$CFCl=CFOCH_3$
130	C_3F_7NO

* Monomers 115-124 were requested, however, samples were never received. It is assumed that attempts to prepare these structures were unsuccessful.

APPENDIX I - Continued

Monomer No.	Formula
131	C_2F_5NO
132	$C_3F_7N{=}CF_2$
133	$C_8F_{17}NO$
134	$CF_2CFCl(NO)(NO_2)$
135	$CF_2CCl_2(NO)(NO_2)$
136	$ONCF_2CF_2NO_2$
137	$CF_2ClCFClNO$
138	CF_2ClCF_2NO
139	$CF_3CCl{=}C(OCH_3)CF_3$
140	$CH_2{=}C(OCH_2CF_3)CH{=}CH_2$
141	$C_3F_6(NO)(NO_2)$
142	$CF_2{=}CFCF_2CO_2H$
143	$CF_3CF_2CF_2COF$
144	Cl_2CS
145	$HCF_2CF_2CF_2CF_2NO$
146	HCF_2CF_2NO
147	CH_3CF_2NO
148P	$(CF_3CFCF_2)_2Hg$
149	CCl_3CCl_2NO

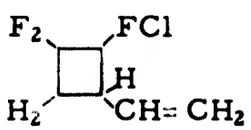
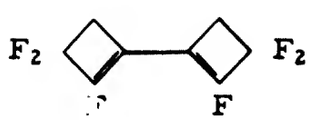
APPENDIX II

The following is the list of monomer assignments received to date under the system decided upon by The Army Natick Laboratories and described in the letter to B. F. Landrum from C. B. Griffis, reference AMXRE-CRP, dated 31 January 1964:

University of Florida

Monomer No.	Formula
200	$CF_2=CFCH_2CH_2Si(CH_3)_3$
201	$CF_2=CFSi(CH_3)_3$
202	$CF_2=CFCH_2CH_2\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{Si}}-O-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{Si}}CH_2CH_2CF=CF_2$
203	$C_6F_5\overset{\overset{O}{\Vert}}{C}-CF_3$
204	$EtOSi(CH_3)_2CF=CF_2$

University of Colorado

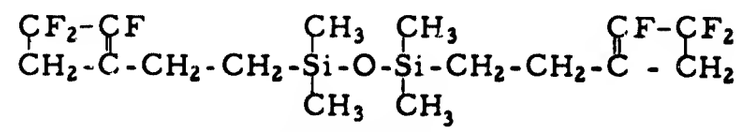
Monomer No.	Formula
300	
301	
302	$CF_2=CFCF_2CFClCF_2CF=CF_2$

APPENDIX II - Continued

Peninsular ChemResearch

Monomer No.	Formula
400	$F_2C=S$
401	C_6F_5NO
402	$SF_5CH=CH_2$
403	$CF_3SCF=CF_2$
404	$(CF_3)_2C=S$
405	$CF_3N=SF_2$
406	C_6H_5NO
407	$[CF_3CF_2CH_2CH_2Si(CH_3)O]_3$
408	$[CF_3CF_2CH_2CH_2Si(CH_3)O]_4$

FMC Corporation

Monomer No.	Formula
500	$CF_3\text{-}\underline{CFCF_2C(CF_3)_2O}$
501	$CH_2=CHCF_2CF_2CH=CH_2$
502	
503	$(CF_3)_2\underline{CCF(CF_3)CF(CF_3)O}$