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

PROGRESS REPORT IV

Period Covered

March 27, 1964 - June 25, 1964

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⑤ Food Machinery and Chemical
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CHEMICAL RESEARCH AND DEVELOPMENT CENTER

CENTRAL RESEARCH DEPARTMENT

Princeton, New Jersey

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I. SUMMARY

↓ Hydrogen-containing oxetanes have been successfully prepared for the first time by the photolysis of hexafluoroacetone with ethylene and vinylidene fluoride. In both cases polymeric products, in addition to oxetanes, were found. All of the polymeric products isolated to date are of low molecular weight. The reaction offers promise of affording a new route to linear polyethers.

A new elastomer system has been discovered involving the condensation of a fluorine-containing diol with a fluorocarbon diene. This product is presently being characterized but its low T_g (-57°C) is very encouraging.

Attempts to modify the $\text{C}_6\text{F}_6/\text{CF}_2=\text{CH}_2$ system by incorporation of termonomers have not proved successful.

Attempts to use the thermal cycloaddition of fluorocarbons as a polymer forming reaction have proved unsuccessful. () ↗

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 the development of block copolymers as well as several approaches to the synthesis of fluorocarbon polymers containing a heteroatom in the backbone.

Availability of sufficient quantities of starting materials has permitted an intensive investigation of: (a) block copolymers consisting of fluorocarbon units alternating with fluoroalkyl siloxane units, (b) polyethers derived by the condensation of diols with diolefins, and (c) polyethers derived from oxetanes. In the latter case, polymers of low molecular weight (ca. 600) have been formed in situ during the irradiation of a mixture of hexafluoroacetone and hydrogen-containing olefins, i. e. ethylene and vinylidene fluoride. Since these products were formed along with the expected oxetanes, there is considerable resemblance to the fluoronitroso-fluorolefin polymerization in which there is a competition between formation of the linear polymeric product and the cyclic adduct. It is believed that investigation of this system will afford a technique to enhance formation of linear product at the expense of the cyclic adduct, the oxetane.

C. Project Costs

The contract was extended for two months by Modification No. 3 to allow for additional time in which to complete polymerization studies currently in progress. The extension did not require additional funding. Progress in polymerization research had been delayed in the early stages of the program because of the difficulty in obtaining monomers in large enough quantities to permit meaningful experimentation. This resulted in sufficient funds remaining in the contract as of 30 June 1964 to cover the cost of approximately a two-man professional effort for an additional two months.

Approximately 80% of the work is completed to date. It is estimated that 82.7% of the estimated costs have been incurred to date. To the best of FMC's knowledge the funds remaining unexpended are sufficient to complete the work called for by the contract.



III. DISCUSSION OF RESULTS

A. Monomer Procurement

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

<u>Monomer Number</u>	<u>Monomer or Precursor</u>	<u>Amount</u>	<u>Supplier</u>
205	1, 1, 2, 5, 6, 6-Hexafluoro-hexadiene-1, 5	19.5 g.	Dr. P. Tarrant, Univ. of Florida
206	Perfluorostyrene	12.7 g.	Dr. P. Tarrant, Univ. of Florida
511	Perfluoroglutaryl dichloride	2 lbs.	Hooker Chemical Corp.
508	2, 2, 3, 3, 4, 4-Hexafluoro-pentane-1, 5	100 g.	Aldrich Chemical Co.
1	Chlorotrifluoroethylene (Genetron 1113)	24 lbs.	Allied Chemical Corp. General Chemical Div.
	Bromotrifluoromethane (Freon 13B1)	6 lbs.	E. I. duPont deNemours Co.
40	Vinyl fluoride	3 lbs.	E. I. duPont deNemours Co.
9	1, 1-Dichlorodifluoroethylene (Genetron 1112a)	1 lb.	Allied Chemical Corp. General Chemical Div.
	1, 2-Dichlorotetrafluorocyclobutene	100 g.	Columbia Organic Chemicals, Inc.
	Dimethylchlorosilane	4 lbs.	Dow Corning Corp.
2	Vinylidene fluoride (Freon 1132a)	12 lbs.	E. I. duPont deNemours Co.
14	Hexafluoropropylene	3 lbs.	Columbia Organic Chemicals, Inc.
512	Hexafluoroacetone (6FK)	2 lbs.	Allied Chemical Corp. General Chemical Div.
	Pentafluorobenzoic acid	200 g.	Imperial Smelting Corp.
	Bromopentafluorobenzene	50 g.	Imperial Smelting Corp.
	Hexafluorobenzene	50 g.	Imperial Smelting Corp.
	p-Aminotetrafluorobenzoic acid	100 g.	Imperial Smelting Corp.
	Dibromodifluoromethane	1 kg.	Columbia Organic Chemicals, Inc.

The following monomers were ordered but not received during the period of this report (except for the amounts so noted):

<u>Monomer Number</u>	<u>Monomer or Precursor</u>	<u>Amount</u>	<u>Supplier</u>
508	2, 2, 3, 3, 4, 4-Hexafluoro-pentane-1, 5 (225g. received)	1 kg.	Aldrich Chemical Co.
507	2-Azaperfluoropropene (60g. received)	554 g.	Peninsular ChemResearch



The following monomers have been prepared by FMC during the period covered by this report:

Monomer Number	Monomer	Amount
504	1, 1-Bis(trifluoromethyl)oxetane	25 g
505	1, 1-Bis(trifluoromethyl)-3, 3-difluoro δ xetane	50 g.
506	1, 1-Bis(trifluoromethyl)-2, 2-difluoro δ xetane	50 g.
509	cis-Perfluoroheptatriene-1, 3, 6	25 g.
510	trans-Perfluoroheptatriene-1, 3, 6	25 g.
302	4-Chloroperfluoroheptadiene-1, 6	250 g.

B. Polymerization Research

With the availability of various monomers for this program assured, polymerization studies have now been sustained. These studies have been developed over two broad areas: (1) vinyl polymer systems, and (2) condensation polymers of fluorocarbons.

At present, research in vinyl-type polymerization has the short range objective of the modification of the $C_3F_6/CF_2=CH_2$ system and the long range objective of polymeric polyethers.

Research on condensation-type polymerizations, all of a short range nature, may be briefly described as an extension of some of the more interesting and well-known reactions of fluorocarbon chemistry to polymer chemistry. Two such reactions studied during this quarter are: (1) the cyclocodimerization of fluoro δ lefins, and (2) the base catalyzed addition of alcohols to fluoro δ lefins.

1. Vinyl Polymerization

a. Modification of Vinylidene Fluoride/Hexafluoropropylene Emulsion Polymerization System

Improvement in the low temperature flexibility and solvent resistance of the vinylidene fluoride/hexafluoropropylene elastomer was sought by modification of the emulsion polymerized $CF_2=CH_2/CF_3CF=CF_2$ system with novel fluoro δ lefinic monomers.

The work reported herein was concerned with terpolymerization of the following fluoro δ lefins in the above system:





II

Initial studies were concerned with preparing 70/30 mole % $\text{CF}_2=\text{CH}_2/\text{CF}_3\text{CF}=\text{CF}_2$ emulsion polymers as controls for the latter runs involving termonomers.

Terpolymerization of the disiloxane I with $\text{CF}_2=\text{CH}_2/\text{C}_3\text{F}_6$ was attempted at 70°C charging the disiloxane to the aqueous phase and with high system pressures (ca. 630 psig). An elastomeric product was recovered which appeared to be identical by infrared analysis to the control $\text{CF}_2=\text{CH}_2/\text{C}_3\text{F}_6$ copolymer but with a slightly lower T_g (-26°C). After extraction with pentane to remove the unreacted disiloxane I, the product analyzed 1.2% silicon. Thus the specimen appeared to be a modified vinylidene fluoride/hexafluoropropylene polymer but further work is in progress to characterize the sample unequivocally.

An effort was made to co-cure the disiloxane (I) with Viton A elastomer by rubber milling the respective ingredients followed by vulcanization with benzoyl peroxide. The experiment was unsuccessful, however, as the disiloxane could be quantitatively extracted from the compounded stock after subjecting the latter to curing conditions. The glass transition temperature of the compounded stock was measured (prior to extraction) in the Gehman torsional stiffness tester. A value of $T_g = -20^\circ\text{C}$ was obtained which is almost identical to the value reported for unplasticized Viton A.

The incorporation of the vinyl cyclobutane (II) into the vinylidene fluoride/hexafluoropropylene emulsion polymerization system was examined at 35°C using low pressures (25 psig) and by charging the former into the reactor with the aqueous emulsion ingredients.

A low conversion to a white, brittle powder was achieved which analyzed 58% fluorine and 0.25% chlorine. The product appeared to be largely a polymer of vinylidene fluoride with incorporation of a minor proportion of the fluorine-containing vinyl cyclobutane monomer.

Terpolymerization of 5 mole % of the vinyl cyclobutane (II) with 70/25 mole % $\text{CF}_2=\text{CH}_2/\text{C}_3\text{F}_6$ was attempted at 70°C using higher pressures (610 psig); a 10% conversion to a yellow, brittle powder was realized. The latter evidently resulted from homopolymerization of the fluorine-containing vinyl cyclobutane

monomer. Partial dehydrochlorination of the monomer appeared also to have occurred in the alkaline emulsion medium forming the polymerizable vinyl cyclobutene (III). The polymeric product

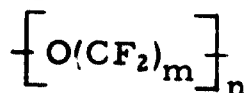


III

analyzed for 32% fluorine and 12.4% chlorine (theory, 33.4% fluorine and 20.8% chlorine).

b. Polyethers from Hexafluoroacetone and Olefins

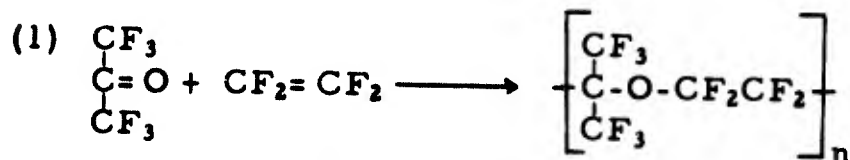
One of the most interesting and, at the same time, elusive class of fluorocarbon elastomers is the polyethers, the simplest example being the hypothetical polyether, IV. This class combines



IV

the advantage of the solvent resistant fluorocarbon backbone with the flexibilizing influence of the ether linkages. Further modification of this basic structure would be expected to enhance the desirable properties this class is believed to possess. For example, the inclusion of trifluoromethyl pendant groups would be expected to decrease the crystallinity of the polymer and thus enhance the low temperature properties desired. It should also be noted that the perfluorinated polyethers would be expected to show high thermal stability.

The recent availability of hexafluoroacetone makes attractive the possibility of its copolymerization with fluorinated ethylenes (Eq. 1).

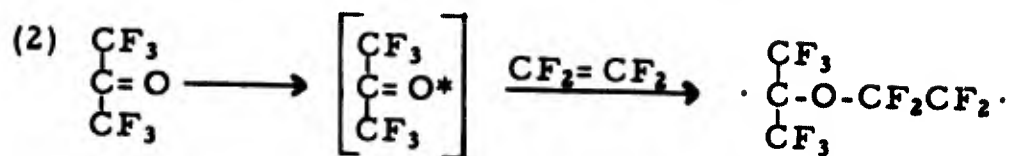


Examination of the literature concerned with fluorinated carbonyl compounds reveals several interesting parallels to the fluorinated nitroso compounds.

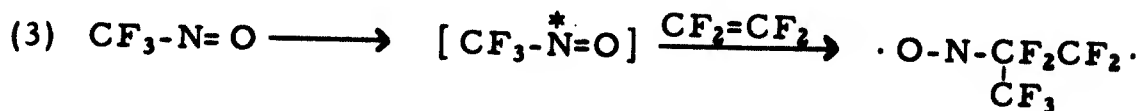
In as much as the nitroso compounds copolymerized via an $n_{\text{N}}-\pi^*$ transition, it was believed that a promising area in which to begin study would be the attainment of an $n_{\text{O}}-\pi^*$ transition of



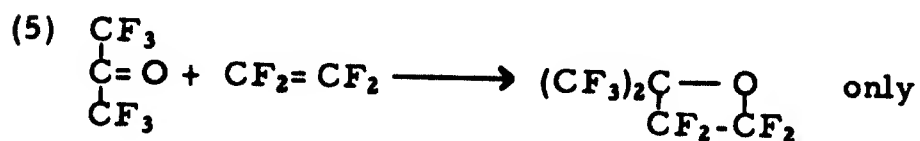
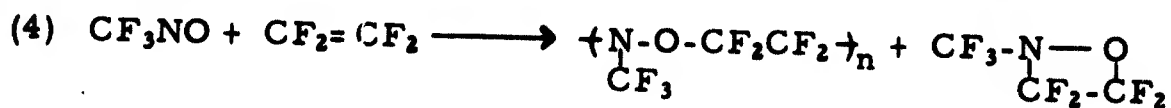
the carbonyl group (Eq. 2).



Such a scheme is closely akin to the nitroso copolymer formation (Eq. 3).



However, while the fluorinated nitrosoalkanes produce both oxazetidines and elastomer on reaction with olefins (Eq. 4), hexafluoroacetone has only been reported to produce oxetanes (Eq. 5).



Discussion with Dr. J. D. Park revealed that hydrogen-containing olefins such as 3, 3, 3-trifluoropropylene might provide a good point of departure for the synthesis of intermediate oxetanes that may be opened more readily.

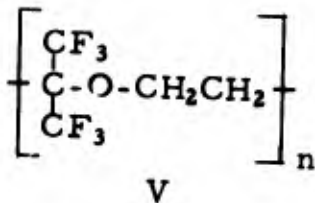
A review of the literature in this area has disclosed furthermore that no hydrogen-containing olefins had been utilized in this reaction.

Because of the work reported earlier and further characterized during this report period on the photolysis of hexafluoroacetone with perfluorobutene-2, it is clear that $n_{\text{O}}-\pi^*$ triplet state of the carbonyl must be energetically more stable than the olefin $\pi-\pi^*$ triplet state if inter-system crossing is to be prevented. Therefore, ethylene and vinylidene fluoride were chosen as model compounds for this study.

With both olefins, the photolysis with hexafluoroacetone yielded viscous oils along with oxetanes. Analysis of the oils revealed that, in both cases, the fluorine content was close to that calculated for a 1:1 CF_3COCF_3 /olefin polymer. The oil from photolysis of $\text{CF}_3\text{COCF}_3/\text{C}_2\text{H}_4$ has an average molecular weight of 570, while



the $\text{CF}_3\text{COCF}_3/\text{CH}_2=\text{CF}_2$ oil has an average molecular weight of 612. Both of these values agree approximately with a calculated molecular weight for three repeating carbonyl-olefin units. NMR analysis of the $\text{CF}_3\text{COCF}_3/\text{C}_2\text{H}_4$ oil suggests that methylene groups alpha and beta to an ether linkage are present, in accordance with the anticipated structure V. The ratio of the two

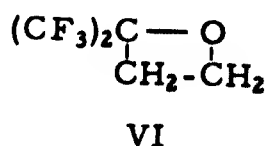


different methylenes does not appear to be quite the 1:1 expected for this structure however.

In order to investigate more fully this potentially interesting polymerization, a photolysis at 0°C in 3M's FC-43 perfluorinated solvent has been conducted. Results of this experiment are pending.

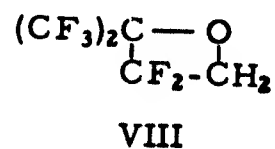
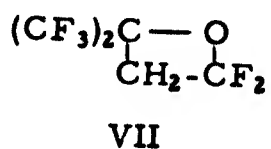
Although the oxetanes produced in this reaction are monomers, clarity is better preserved by discussing them at this point.

The oxetane (VI) produced by photolysis of hexafluoroacetone with ethylene was identified by its NMR spectrum. A triplet



centered at $\tau 7.06$ arises from the methylene beta to the oxygen while a triplet centered at $\tau 5.31$ ($J=8.0$ cps) arises from the methylene alpha to the ether linkage.

Two oxetanes (VII and VIII) can be isolated from the photolysis of hexafluoroacetone with vinylidene fluoride.



Oxetane VII was identified by its triplet centered at $\tau 6.59$ ($J=7.0$ cps) on its NMR spectrum, while oxetane VIII displayed a triplet centered at $\tau 5.00$ ($J=12.2$ cps). Interestingly, oxetane



VII was formed in larger amounts than the isomeric adduct VIII, the ratio being about 1.3:1.

In Quarterly Report III the photolysis of hexafluoroacetone with perfluorobutene-2 was stated to yield a compound whose identity was in question. Mass spectrographic analysis suggests that this compound is most likely perfluorodiisopropyl contaminated with a small amount of the desired oxetane. Evidently, the $\pi-\pi^*$ transition for the butene is energetically more favorable than the $n_O-\pi^*$ transition for the hexafluoroacetone and inter-system crossing occurred. This reaction will not be pursued further.

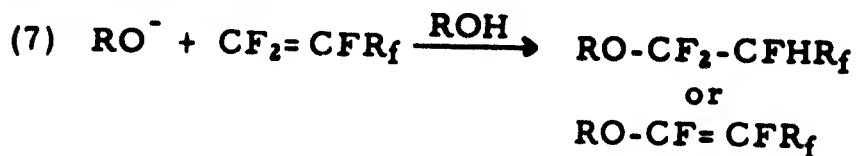
2. Condensation Polymerization

The ever advancing art of monomer synthesis in the fluorocarbon area now makes the field of condensation polymerization an attractive area for research on the synthesis of fluorinated elastomers. Also, the extension of the well-known condensation reactions of fluorine chemistry to the difunctional moieties for polymerization research may be aptly described as a short range program.

a. Addition of Highly Fluorinated Diols to Highly Fluorinated Dienes

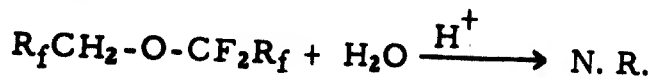
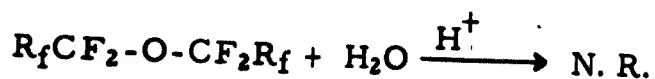
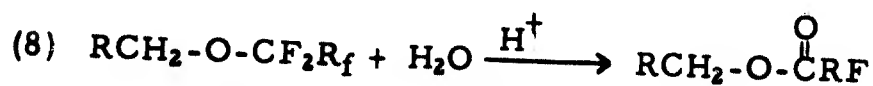
As has been described elsewhere in this report, a basic tenet of the polymer research effort is the desirability of incorporating heteroatoms in the polymer backbone, such as nitrogen or oxygen. One example of a desirable polymer type, then, would be the class of perfluorinated polyethers (IV) mentioned previously. Long range research towards the preparation of these polyethers is described elsewhere in this report, but the additional possibility of synthesizing a highly fluorinated polyether elastomer by condensation techniques in order to help evaluate the potential of this class of polymer is highly desirable. Of course, these condensation polymers should a priori be useful polymers in their own right, but the economics of large scale production would normally be expected to favor the vinyl-type elastomers, and hence the long range project described elsewhere.

One of the oldest known and best studied reactions of fluorine chemistry is the nucleophilic attack of alkoxides, amines, halides, etc. on unsaturated fluorocarbons. The nucleophiles most thoroughly studied, particularly by Park and his students, are the potassium alkoxides (Eq. 7).



The product, either the β -hydroether or the vinyl ether, is determined by the availability of a proton in the reaction medium, and by the basicity of the intermediate carbanion relative to the nucleophile employed. For terminal fluorolefins, generally, the saturated ether is the expected product (except under aprotic conditions).

The hydrolytic stability of these saturated ethers varies over a tremendous range. On one end of the spectrum are those ethers of the type $R-CH_2-O-CF_2R_f$ which are hydrolytically very unstable (Eq. 8). On the other hand 3M's "FC-75", a perfluorinated cyclic ether, and the recently discovered perfluorinated oxetanes, examples of the type $R_fCF_2-O-CF_2R_f$, are quite stable to hydrolysis.



R= hydrocarbon radical

R_f = fluorocarbon radical

It is obvious that, whatever the reason, the location of perfluorinated segments on both sides of the ether oxygen greatly enhances the resistance of these compounds to hydrolysis.

It would be expected then, that the preparation of a polyether from a highly fluorinated diol and a perfluorinated diene should produce an interesting elastomer. The recent availability of several fluorinated dienes from Professor Park at the University of Colorado, in particular 4-chloroperfluoroheptadiene-1, 6 (monomer No. 302), and the availability of 2, 2, 3, 3, 4, 4-hexafluoropentane-1, 5 from Aldrich Chemical Company has now allowed examination of this system.

It must be strongly emphasized that the conditions for this polymerization were selected only to demonstrate feasibility; no attempt was made to determine the best conditions for this polymerization with respect to maximum yield and conversion, and improved polymer characteristics. Such a study depended on the demonstrated feasibility of the polymerization, and is currently in progress.

Like many condensation-type polymerizations, the base catalyzed addition of 2, 2, 3, 3, 4, 4-hexafluoropentane-1, 5 to the



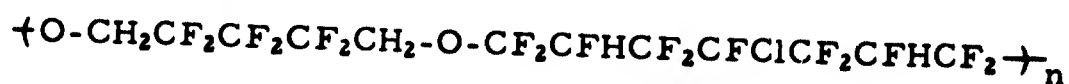
4-chloroperfluoroheptadiene is initially a rapid reaction; and as the chain length continues to increase the reaction slows down. Thus, rubber-like material is produced only after a period of 24 to 72 hours. Prior to this time only oils are obtained.

These oils, lower molecular weight products of the polymerization, were isolated from every reaction and had increasingly high viscosities with longer reaction times.

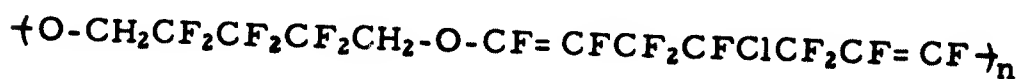
It is to be expected then, that the characterization of this oil would help indicate the structure of the rubbery polymer.

Perhaps the most straightforward analytical technique for this particular structure is proton NMR as the structures IX-XIII considered possible may be readily identified by this technique.

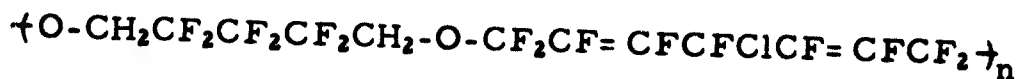
Polymer chain:



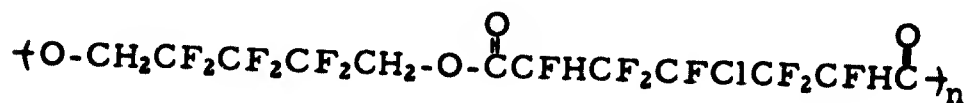
IX



Xa

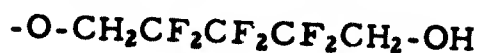


Xb

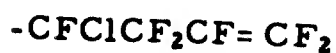


XI

Terminal groups:



XII



XIII

The NMR spectra of several samples of this oil display a triplet centered at τ 5.58 (relative to tetramethylsilane) attributable to the protons alpha to an ether oxygen, and a triplet centered at τ 5.97, attributable to the protons alpha to a hydroxyl oxygen.



Additionally, the tertiary proton of the polyether (IX) would be expected to show a doublet from the alpha fluorine further split into two pentuplets by the beta fluorines. An incompletely resolved peak appears to be one-half of this requirement; the other half being obscured by the methylene resonance lines. Should this be the case, the tertiary proton resonance absorption is centered at about τ 5.0, a shift that is anticipated for such a system. Also, one sample displays what appears to be a triplet centered at about τ 5.25, attributable to the methylene group as in polyether Xa, although the methylene group of polyether IX is 10 times more abundant.

There is no evidence observed in these samples of any proton resonance affected by an ester group such as polyester XI.

Succinctly then, it appears likely that the rubbery polymer is mainly polyether IX with a minor amount (probably less than 10% of polyvinyl ether Xa (or Xb). Pendant terminal groups may be either unreacted olefin (XIII) or alcohol (XII). As the ratio of the ether-methylene groups to the hydroxyl-methylene groups of the oils varies from 1:1 to 2:1, it would appear that the unreacted hydroxyl groups predominate.

Attempts to characterize the elastomer have been frustrated in some cases because of its insolubility. Although this elastomer swells in acetone, it has not been possible to dissolve it in toluene, carbon tetrachloride, hexane, ethyl ether, Freon 113, 3M's FC-43, 3M's FC-75, ethanol, or Fluorolube FS-5.

However it is possible to measure several physical properties of the polymer with the Perkin-Elmer Differential Scanning Calorimeter. With this recently developed instrument it is possible to determine properties such as T_g , T_m , and decomposition temperatures. Although these determinations are still in progress, the T_g of all the samples submitted appear to have values between -44°C and -57°C . The differential calorimeter spectra indicate a strong endotherm at about -22°C along with a smaller endotherm at about -30°C . These are ascribed to a loss of crystallinity and possibly a loss of hydrogen bonding.

The samples studied thus far appear to begin decomposing at about 180°C .



b. Copolymerization of [CF₂=CFCH₂CH₂Si(CH₃)₂]₂O with CF₂=CF-CF₂CFC1CF₂CF=CF₂

The copolymerization of [CF₂=CFCH₂CH₂Si(CH₃)₂]₂O with CF₂=CF-CF₂CFC1CF₂CF=CF₂ by thermal cycloaddition was examined in detail by studying the behavior of the respective monomers alone in thermal reactions which would be expected to compete with the desired copolymerization reaction. Thermal reactions of the di-functional monomers when heated singly can result in cycloadditions leading to dimers, trimers, etc. and, possibly, formation of homopolymers. Accordingly, a sample of [CF₂=CFCH₂CH₂Si(CH₃)₂]₂O was subjected to a temperature of 150° C for 20 hrs. in a stainless steel reactor but a violent decomposition ensued leaving a dense carbonaceous residue. Attempts to repeat the experiment in a glass tube on a small scale in the presence of stainless steel filings from the steel reactor were unsuccessful as the disiloxane was recovered unchanged. A subsequent experiment conducted in a sealed glass tube at 150° C for an extended time period (ca. 40 days) failed to reveal any instability.

Thermal reactions of CF₂=CF-CF₂CFC1CF₂CF=CF₂ alone were also investigated at elevated temperatures. The heptadiene was recovered unchanged after heating at 150° C for 20 hrs. but a brittle amber solid was recovered in low conversion (ca. 2%) after 20 hrs. at 200° C. The latter exhibited terminal CF₂=CF- groups in the infrared spectra (1790cm⁻¹).

Copolymerization of [CF₂=CFCH₂CH₂Si(CH₃)₂]₂O with CF₂=CF-CF₂CFC1CF₂CF=CF₂ was examined by heating equimolar quantities of the monomers at 150° C for ca. 42 days; no marked change in viscosity was observed but the results of the experiment are incomplete. Similar runs employing the respective monomers alone were conducted and work-up is also incomplete.

C. Monomer Synthesis

1. Preparation of 4-Chloroperfluoroheptadiene-1, 6 and Perfluoroheptatriene-1, 3, 6

An additional sample of 5, 6, 7-trichloroperfluoroheptene-1 was prepared in 86.6% yield and with a purity of 90.7% by the pyrolysis of sodium 3, 5, 7, 8-tetrachloroperfluoroctanoate as described in the previous report. All of the heptene on hand was dechlorinated with zinc in two experiments. Three distillations were required to obtain product of 90% purity. In the first experiment, a one mole run, the total yield of heptadiene was 122.6g. or 34.8% after correcting for impurities.

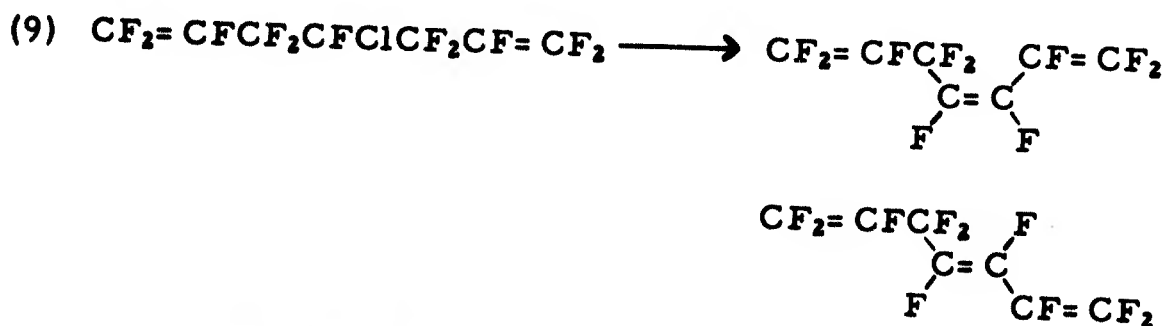


In the second, a 1.5 mole run, the yield was 154.9g. or 28.5%. The dechlorination of recovered heptene in the latter run was carried out in isopropanol (all other reactions were carried out in tetrahydrofuran) with a somewhat longer reaction time. A considerable quantity of low boilers were recovered.

It was previously noted that the yield of 4-chloroperfluoroheptadiene obtained by various investigators was abnormally low for a simple dechlorination. A considerable quantity of lower boiling material was always obtained concurrently with the desired heptadiene, and in fact in one instance the amount of low boiling material actually exceeded the desired product. Accordingly, this product was investigated further.

VPC analysis indicated that this material mainly consisted of two compounds in essentially equimolar quantities. Accordingly, these two compounds were separated and isolated with a Wilkins Instrument Co. "Autoprep".

Examination of the IR spectra, boiling points, and elemental analysis indicate that these two compounds are the cis and trans isomers of perfluoroheptatriene-1, 3, 6, which undoubtedly arises by dechloro-fluorination of 4-chloroperfluoroheptadiene (Eq. 9).

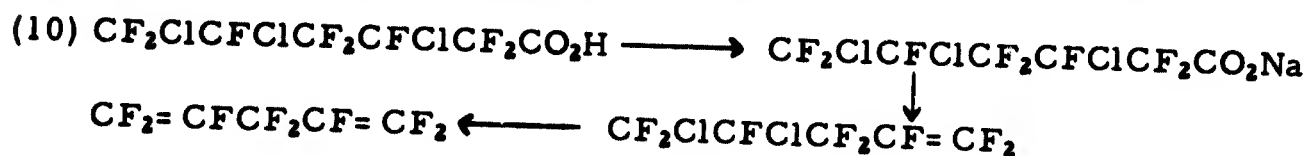


In one instance, the dehalogenation of 4, 5, 7-trichloroperfluoroheptene-1 yielded 27% heptatriene and only 16% heptadiene. This method can therefore be considered to be a satisfactory synthetic procedure for the preparation of perfluoroheptatriene.

It is anticipated that these potentially interesting monomers can now be incorporated into future polymer systems.

2. Preparation of Perfluoropentadiene-1, 4

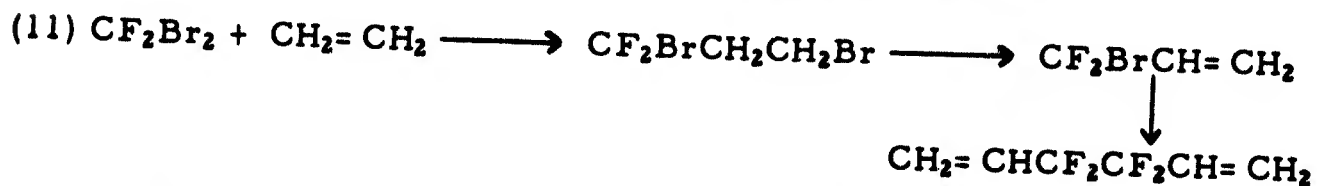
The route selected for the preparation of perfluoropentadiene-1, 4 follows the procedure of Park and Lacher:¹



About 1 kg. of the anhydrous sodium salt has been prepared, of this, approximately 400g. has been decarboxylated to the pentene in 70% yield. The final dechlorination has not been completed.

3. Attempted Preparation of 3, 3, 4, 4-Tetrafluorohexadiene-1, 5

The following route to the desired hexadiene was attempted:



Studies on the photolytic preparation of the intermediate propane, reported in preliminary form in Quarterly Report III, have now been completed. It has been possible to achieve yields of the order of 50% by this method vs. yields of the order of 25% via the benzoyl peroxide-initiated method.

Several methods were tried to dehydrobrominate the dibromodifluoropropane. The method of Tarrant et al.² (use of hot aqueous potassium hydroxide) gave poor yields, apparently because the starting propane steam-distilled without reacting. Use of cold ethanolic potassium hydroxide gave the best yields (43%).

In the Quarterly Report III, the question of structure of the propylene was raised. Proton NMR spectral analysis confirmed the structure as being 3-bromo-3, 3-difluoropropylene-1 and not the isomeric 3-bromo-1, 1-difluoropropylene-1.

For the coupling step, magnesium in ethyl ether, butyl ether, and tetrahydrofuran, and zinc in dioxane were tried. Only in the case of magnesium in tetrahydrofuran did any reaction occur. The product could not be separated, however, apparently because its boiling point was too close to that of the solvent.

An alternate route to the hexadiene from tetrafluoroethylene diiodide and ethylene^{3, 4} has been initiated. Preparation of the tetrafluoroethylene diiodide has been hampered by corrosive side reactions with the bomb lining. This reaction must now await equipment modification.



IV. EXPERIMENTALA. Polymerization Research1. Vinyl Polymerizationsa. Modification of Vinylidene Fluoride/Hexafluoropropylene Emulsion Polymerization SystemEmulsion Polymerization of $CF_2=CH_2/CF_3CF=CF_2$

The following procedure is typical for the emulsion polymerization runs tabulated in Table I.

D-871-143 A 110 ml. Aminco bomb was charged with 42g. of a 3.8% aqueous solution of potassium persulfate, 17.6g. of a 9.1% solution of disodium hydrogen phosphate and 20g. of a 10% solution of the sodium salt of perfluorooctanoic acid. The bomb was then closed, cooled in dry ice and evacuated. Then, 20g. of $CF_2=CH_2$ (70 mole %) and 20g. of $CF_3CF=CF_2$ (30 mole %) were charged to a 75 ml. stainless steel cylinder by gaseous transfer in vacuo. The 75 ml. cylinder was then attached to the Aminco bomb via an oxygen regulator. The former was opened at a temperature of 50° C (500 psig) and the reducing value was set to deliver 450 psig to the Aminco bomb which was also heated to 50° C. The assembly was rocked for 17 hrs. at which time the pressure had dropped to 300 psig. The bomb was cooled, the unreacted monomers vented and the product (a bluish latex) was decanted. The latter was coagulated with a 10% aqueous solution of aluminum sulfate and a white elastomeric product was recovered by filtration. After thorough washing with water and drying in an oven at 60° C overnight a weight of 6.7g. of product was obtained, representing a 17% conversion based on the total monomer charge of 40g.

Attempted Curing of Viton A with $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$

D-871-152 The following ingredients were blended on a cold rubber mill with Viton A elastomer (vinylidene fluoride/hexafluoropropylene 80/20 mole %):

<u>Ingredient</u>	<u>Parts by weight</u>
Viton A	100
Magnesium oxide	15
$[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$	10
Benzoyl peroxide	2



The stock was molded 30 min. at 300° F into four 6 in. by 6 in. plaques. All four plaques contained bubbles upon opening the molds. Two of the plaques were passed again through the rubber mill. One of the plaques was then molded for 15 min. at 230° F and the other was molded by gradually increasing the mold temperature from 80° F to 230° F and applying 40 tons pressure for 5 min. before cooling. The molded specimens were then oven cured by gradually increasing the temperature from 200° to 350° F over a 6 hr. period. Finally, the upper temperature (350° F) was maintained for 18 hrs.

One specimen was then cut into small pieces and subjected to a pentane extraction overnight in a Soxhlet apparatus. After drying in an oven at 50° C overnight the specimen was analyzed for silicon but the results were negative. A glass transition temperature (T_g) measurement performed on the unextracted specimen in the Gehman apparatus showed the sample to have a $T_g = -20^\circ \text{C}$. A similar measurement performed on a differential scanning calorimeter resulted in a $T_g = -23^\circ \text{C}$. A sample of gum Viton A was found to have a $T_g = -22^\circ \text{C}$.

b. Co-polymerization of Hexafluoroacetone with Olefins

1, 1-bis(trifluoromethyl)oxetane and polymer

C-1129-43 Into an evacuated 12 l. 3-neck flask containing a Hanovia 450 watt high pressure Hg lamp in a quartz insert was charged 300 mm. hexafluoroacetone and 300 mm. ethylene. After 8 hrs. irradiation the pressure decreased 280 mm. and the lamp was extinguished. The flask was pumped down and the liquid products thus stripped off were separated directly by means of preparative VPC. The oxetane accounted for about 80% of the product; another product, accounting for the remainder of the volatile product has not yet been identified.

The IR spectrum of the oxetane, b. p. 85. 5° C, 761 mm. (micro), is reproduced in Figure 5.

The oil remaining in the flask analyzed for 55 5%F, and had an average molecular weight of 570 (vapor pressure Osmometer, benzene solution).

1, 1-bis(trifluoromethyl) -2, 2-difluoroðxetane, 1, 1-bis(trifluoromethyl) -3, 3-difluoroðxetane, and polymer.

C-1129-52 The 12 l. flask containing the 450 watt Hg lamp was evacuated and charged with 300 mm. hexafluoroacetone and



300 mm. vinylidene fluoride. After 4.5 hrs. irradiation there was a pressure decrease of 294 mm. and the lamp was extinguished. The volatile liquid product was washed with water, dried over sodium sulfate, and distilled, b. p. 58-62° C. The two isomers were separated and isolated by preparative VPC. 1,1-bis(trifluoromethyl)-2,2-difluoroöxetane, b. p. 65.2° C, 761 mm. (micro), IR spectrum, Figure 3. 1,1-bis(trifluoromethyl)-3,3-difluoroöxetane, b. p. 58.0° C, 761 mm. (micro), IR spectrum, Figure 4. The proton NMR is discussed elsewhere.

The white opaque nonvolatile oil remaining in the flask analyzed for 62% F and had an average molecular weight of 612 (vapor pressure Osmometer, methanol solution).

2. Condensation Polymerizations

a. Copolymerization of $[\text{CF}_2=\text{CF}-\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2]_2\text{O}$ with $\text{CF}_2=\text{CFCF}_2\text{CFClCF}_2\text{CF}=\text{CF}_2$

The following procedure is typical for the thermal reactions of $[\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2]_2\text{O}$ and $\text{CF}_2=\text{CFCF}_2\text{CFClCF}_2\text{CF}=\text{CF}_2$ tabulated in Table II.

C-1529-3 A 30 ml. Pyrex tube equipped with a Teflon needle valve on one end was charged with a mixture of 5.00g. of $[\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2]_2\text{O}$ (0.014 mole) and 5.68g. (0.014 mole) of $\text{CF}_2=\text{CFCF}_2\text{CFClCF}_2\text{CF}=\text{CF}_2$. The tube was then cooled in liquid nitrogen, evacuated and closed. The tube was then placed in a thermostated oil bath at 150° C and allowed to remain in the bath for ca. 42 days as little change in viscosity was noted. Characterization of the tube contents is incomplete.

b. Copolymerization of 4-Chloroperfluoroheptadiene with 2,2,3,3,4,4-Hexafluoropentane diol-1,5

The following experiment is typical of those carried out. All are tabulated in Table III.

C-1129-71 To 11g. (50 mmole) of the pentane diol in 20 ml. acetone was added 3.0g. potassium hydroxide. This mixture was then rapidly poured into 16g. of the heptadiene contained in a 250 ml. Erlenmeyer flask and the resultant mixture stirred magnetically. The light yellow color which formed immediately slowly darkened and, after 72 hrs., tan to brown polymer was found in the flask along with a viscous oil. The oil was dissolved in acetone, the solution decanted, and the polymer washed with acetone. The



polymer was leached in a Soxhlet extractor overnight and then dried in a vacuum oven.

Using this procedure the yield of elastomer is generally about 20%, while the lower molecular weight oils are obtained in about 50% yield. The value of T_g appears to be in the neighborhood of -50°C . Proton NMR spectra of the oils have been discussed elsewhere.

B. Monomer Synthesis

1. Preparation of 4-Chloroperfluoroheptadiene-1, 6

The experimental details of this synthesis, via dechlorination of 4, 6, 7-trichloroperfluoroheptene-1, have been reported earlier. Runs conducted during this report period are summarized in Table IV.

About 12g. of the heptadiene was isolated in 98 mole percent purity by gas chromatography.

2. Preparation of cis- and trans-Perfluoroheptatriene-1, 3, 6

These two isomeric trienes were isolated from the $82-98^\circ\text{C}$ fraction obtained in experiment C-1129-10 (Quarterly Report III⁵). A total of 58.2g. of the two heptatrienes were present in equimolar amounts, the yield being 27% from the heptenes charged. Cis-Perfluoroheptatriene: b. p. 81.5°C , 761 mm. (micro) IR spectrum: Figure 1; trans-perfluoroheptatriene: b. p. 86°C , 761 mm. (micro); IR spectrum: Figure 2.

3. Preparation of Perfluoropentadiene-1, 4

C-1129-42 To two 505g. (2.78 mole total) portions of $\text{CF}_2\text{ClCFClCF}_2\text{CFClCF}_2\text{CO}_2\text{H}$ in a 2 l. beaker was rapidly added with stirring 60g. sodium hydroxide in 60 ml. water to each. There was considerable heat generated, evolving most of the water as steam. The two pasty fractions were combined and further dehydrated in a vacuum oven. The solid was then pulverized and dried over phosphorous pentoxide until there was no further moisture pick-up. About 1 week and 5 changes were required. There was obtained 1048g. (2.72 mole) of finely powdered, free flowing, white sodium salt in 98% yield.

C-1129-51 In a 1 l. round-bottomed flask, 433g. (1.13 mole) $\text{CF}_2\text{ClCFClCF}_2\text{CFClCF}_2\text{CO}_2\text{Na}$ was pyrolyzed at about 150°C . The pentene was pumped off as it formed into a cooled receiver. Distillation afforded 223.4g. (0.789 mole) of the pentene, b. p. $92-3^\circ\text{C}$, 756 mm. (lit. ¹, 86°C , 630 mm.) in 70% yield. There were mechanical losses from the powdered sodium salt being carried away by the rapid carbon dioxide evolution.



The dechlorination of the 4, 5-dichloroperfluoropentene-1 is in progress.

4. Preparation of 1, 3-Dibromo-3, 3-difluoropropane

A number of runs were conducted towards the preparation of this compound. The following is typical.

C-1129-39 A 12 l. flask equipped with a quartz immersion well containing a 450 watt high pressure Hg lamp was intermittently charged with equibaric amounts of dibromodifluoromethane and ethylene. After a total of 179g. (0.895 mole) dibromodifluoromethane had been charged, the liquid product was isolated, washed twice with water, and dried over sodium sulfate. The fraction b. p. 110-133° C was collected, 54.6g. (0.417 mole), 47% yield.

Several later modifications were attempted in order to obtain a flow system. A 5 l. flask was employed with a stopcock on the bottom for liquid removal. This system was not as satisfactory, however, because of the necessity of a finely controlled, stable rate of introduction of the reactants. This could not be achieved without continuous monitoring. Also, it appeared that an optimum rate of introduction and temperature would have to be determined for highest yields.

5. Preparation of 3-Bromo-3, 3-difluoropropene

C-1491-13 The following methods of dehydrobromination of 1, 3-dibromo-1, 1-difluoropropane were examined:

a. Use of hot aqueous potassium hydroxide

Following the method of Tarrant², 47.6g. (0.2 mole) of 1, 3-dibromo-1, 1-difluoropropane was added over 0.5 hr. to a hot (80° C) stirred solution of 56g. of 85% potassium hydroxide in 100 ml. of water. A heavy organic liquid distilled with a little water. This distillate was recycled in an attempt to insure maximum conversion. The organic layer in the second distillation was separated, dried, and distilled. Only 3.1g. of liquid distilled at 40-42° C, the expected boiling point of the product. Most came over at a much higher temperature and is, presumably, unreacted starting material.

b. Use of Tributylamine

To 93g. (0.5 mole) of tributylamine at 125° C was added 47.6g. (0.2 mole) of 1, 3-dibromo-1, 1-difluoropropane over 1.0 hr. At



the end of the addition, a vigorous exothermic reaction occurred and 3.0g. of colorless liquid distilled, which, although quite impure, contained none of the desired product, according to its infrared spectrum. No more product could be removed from the black liquid in the pot, even after dissolving in dilute hydrochloric acid.

c. Use of hot aqueous sodium hydroxide

Experiment (a) was repeated using 50% sodium hydroxide solution at 130° C. No reaction occurred.

d. Use of cold ethanolic potassium hydroxide

A solution of 18g. (0.27 mole) of potassium hydroxide in 125 ml. of ethanol was added to 59.5g. (0.25 mole) of 1,3-dibromo-1,1-difluoropropane in 25 ml. of ethanol over 2.0 hr. while keeping the temperature at 15° C. A heavy white precipitate formed. After stirring an additional 0.5 hr., the mixture was diluted with 200 ml. of water, the organic layer separated, and the aqueous layer (still alkaline) extracted with tetrachloroethane. After drying, the product was distilled over potassium hydroxide to give 16.8g. (53.5%) of colorless liquid, b.p. 40-41° C (762 mm.), n_D^{25} 1.3751. (lit.²: b.p. 42° C, n_D^{25} 1.3773).

6. Preparation of Tetrafluoroethylene

The following was a typical preparation of tetrafluoroethylene from tetrafluoroethylene dibromide:

C-1129-56 To a stirred, heated mixture of 140g. zinc in 400 ml. tetrahydrofuran in a 3 necked Morton flask equipped with a pressure-addition funnel and condenser with gas outlet, was added approximately 1 ml. tetrafluoroethylene dibromide. After about 45 min. addition was resumed and 520g (2.00 moles) tetrafluoroethylene dibromide was added over a period of 3 hrs. The tetrafluoroethylene generated was collected in a liquid nitrogen cooled trap to which approximately 1 ml. d-limonene was added. The tetrafluoroethylene was then transferred in a vacuum system to a 500 ml. Hoke stainless steel cylinder containing approximately 2 ml. d-limonene. The yield was virtually quantitative.

A total ca. 1 kg. tetrafluoroethylene was prepared by this procedure.



7. Purification of $[\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2]_2\text{O}$

C-1481-3 About 25g. of the disiloxane of 99.7% purity has been isolated by preparative gas chromatographic techniques for polymerization studies.

Molecular weight (Osmometer), calc. for $\text{C}_{12}\text{H}_{20}\text{F}_6\text{Si}_2\text{O}$: 350.45; found 352.



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- ⁴ Knunyants, Khrlakyan, Zeifman, and Shokina, Izvestiya Akad. Nauk SSSR, 384 (1964).
- ⁵ FMC Progress Report III - U. S. Army Contract DA-19-129-AMC-147(N), December 27, 1963 - March 26, 1964.



TABLE I

MODIFICATION OF VINYLIDENE FLUORIDE/HEXAFLUOROPROPYLENE EMULSION
POLYMERIZATION SYSTEM

Exp. No.	Mole % Charge		Na ₂ HPO ₄ (phr)	P. (psig)	Temp. (°C)	Conv. (%)	Product		
	CF ₂ =CH ₂	CF ₃ CF=CF ₂					%F	%Cl	Description
D-871-136 ¹	70	30	4	315	35	0	-	-	-
D-871-143	70	30	4	450	50	17	63.6	-	Rubber
D-871-145	70	30	4	600	70	45	64.7	-	Rubber
C-1529-19	70	30	8	560	50	22.5	-	-	Rubber
C-1529-22	70	30	8	700	70	42.5	-	-	Rubber
D-871-123 ²	70	27	3 [CF ₂ =CFCH ₂ CH ₂ Si(CH ₃) ₂] ₂ O	20	35	1.2	61	-	Yellow Powder
D-871-148 ²	70	25	5 [CF ₂ =CFCH ₂ CH ₂ Si(CH ₃) ₂] ₂ O	630	70	11	66.7	1.2	Rubber
C-1529-23 ³	70	25	5 [CF ₂ =CFCH ₂ CH ₂ Si(CH ₃) ₂] ₂ O	500	50	3.7	-	-	Leathery Solid
D-871-128 ²	70	27	3 CF ₂ CFC1 CH ₂ CHCH=CH ₂	25	35	4	58	- 0.25	White Powder
D-871-149 ²	70	25	5 CF ₂ CFC1 CH ₂ CHCH=CH ₂	610	70	10	32	- 12.4	Yellow Powder

Polymerization Recipe

Ingredient	Parts by Weight
Monomers	100
Water	200-400
Sodium Perfluorooctanoate	5
Disodium Hydrogen Phosphate	Variable
Potassium Persulfate	4

Polymerization Time: 17 hrs.

Notes: ¹ Polymerization Time = 7 hrs.² Termonomer charged to Aminco bomb with aqueous ingredients.³ Termonomer charged to 75ml. cylinder with CF₂=CH₂ and CF₃CF=CF₂.

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TABLE II

COPOLYMERIZATION OF $[\text{CF}_2 = \text{CFCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2]_2\text{O}$ WITH $(\text{CF}_2 = \text{CFCF}_2)_2\text{CFCI}$

Exp. No.	Charge		Temp. °C	Time	Comments
	$[\text{CF}_2 = \text{CFCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2]_2\text{O}$	$(\text{CF}_2 = \text{CFCF}_2)_2\text{CFCI}$			
C-1529-3	5.00g. (0.014 mole)	4.68g. (0.014 mole)	150	~ 42 days	Work-up incomplete
D-871-140	-	20g. (0.06 mole)	150	20 hrs.	No reaction
D-871-144	-	18g. (0.054 mole)	200	20 hrs.	~ 2% conversion of a brittle, amber solid
C-1529-5	-	6.09g. (0.018 mole)	150	~ 42 days	Work-up incomplete
D-871-141 ¹	14.0g. (0.04 mole)	-	150	20 hrs.	Violent decomposi- tion
C-1529-11	4.97g. (0.014 mole)	-	150	~ 42 days	Work-up incomplete

Note:

¹ Stainless steel reactor employedJAG:ls
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TABLE III

COPOLYMERIZATION OF 4-CHLOROPERFLUOROHEPTADIENE WITH
2,2,3,3,4,4-HEXAFLUOROPENTANEDIOL-1,5

Exp. No.	Amt. Diol (g.)	Amt. Diene (g.)	KOH (g.)	Solvent Amt. (g.)	Oil Amt. ² (g.)	Polymer ¹	
						Amt. (g.)	T m
C-1129-64	5.5 (25mmole)	8.0 (25mmole)	1.5	10 acetone	-	~3	+19° (+15) ⁴
C-1129-65	11	16	3.0	50 acetone	11.0	none	-
C-1129-66	5.5	8.0	1.5	10 acetone	5.7	8.1 ⁵	-
C-1129-67	5.5	8.2	1.5	10 acetone	5.5	2.1	-48° ⁶
C-1129-68	5.5	8.0	1.7	10 acetone	8	3.5	-47°
C-1129-69	5.5	8.0	1.5	10 DMF	black tar	-	-
C-1129-70	5.5	8.0	1.5	25 H ₂ O	no reaction	observed	-
C-1129-71	11	16	3.0	20 acetone	13.4	5.7 ⁷	-57°
							-22° (-30°)

Notes:

- ¹ Constants determined with Differential Scanning Calorimeter.
- ² There are mechanical losses.
- ³ Initial run indicated -44°, repeated determinations agree with -59° value.
- ⁴ Figure in parenthesis is smaller endotherm. See discussion.
- ⁵ Lower molecular weight products not extracted from polymer.
- ⁶ Not well defined.
- ⁷ Sample forwarded to Army Natick Laboratories.

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TABLE IV

PREPARATION OF 4-CHLOROPERFLUROHEPTADIENE-1,6 BY DECHLORINATION OF
4,6,7-TRICHLOROPERFLUROHEPTENE-1

Exp. No.	Source of Heptene	Solvent	Reaction Time ¹ (hrs.)	Heptene Charged (g.)	b. p. of Product °C	n _D ²⁰ of Product	Purity of Product ²	Product Yield (g.)	Product Yield ³ (%)	Heptene Recovered (%)
C-1491-3	D798-137B 92.3% pure	THF	5.33	399.5	(1)110-111 (2)111-112	1.3311	93.8% 92.5%	78.8	34.1	33.8
C-1491-4	Recovered from above	THF	5.0	135	109-111	1.3305	95.8	16.9	21.2	31.1
C-1491-6	D798-152B 98.7% pure	THF	4.5	599.2	108-111	1.3305	92.5	112.6	38.7	45.4
C-1491-7	Recovered from above	Isopro- panol	5.5	276	108-111	1.3328	85.6	42.4 ⁴	13.8	5.3

Notes: In the first experiment, a second cut was obtained by redistilling the fore and tail cut. Usually, three distillations were required to obtain products of the purity shown.

¹ Includes addition time

² Determined by VPC

³ Based on heptene actually converted, heptadiene yield corrected for impurities.

⁴ An additional quantity of low boilers containing perfluoroheptatriene was obtained.

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FIGURE 1
Infrared Spectrum of cis-Perfluoroheptatriene-1, 3, 6
(neat, 0.015 mm.)

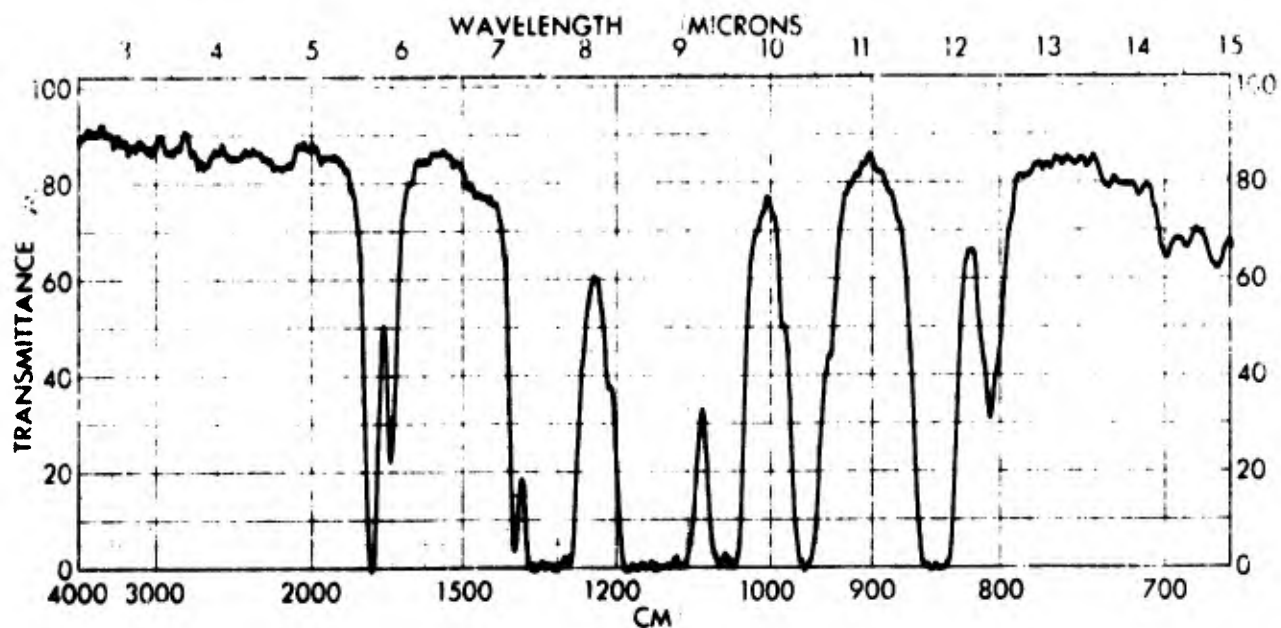


FIGURE 2
Infrared Spectrum of trans-Perfluoroheptatriene-1, 3, 6
(neat, 0.015 mm.)

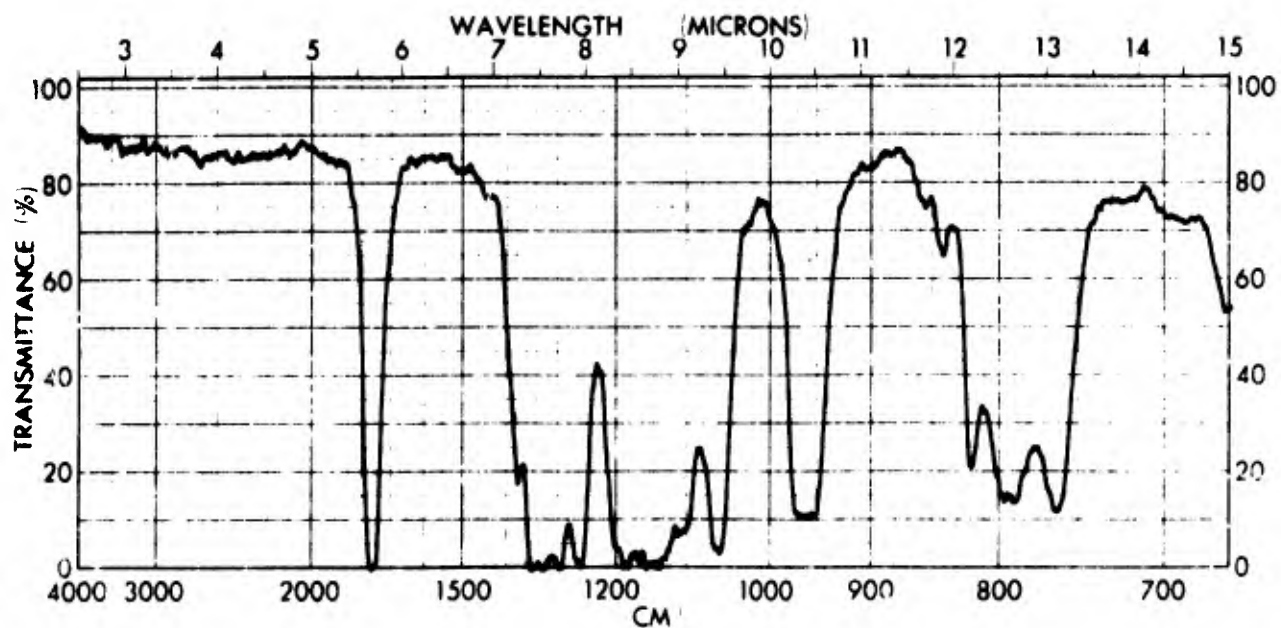


FIGURE 3

Infrared Spectrum of 1, 1-bis(Trifluoromethyl)-2, 2-difluoroethane

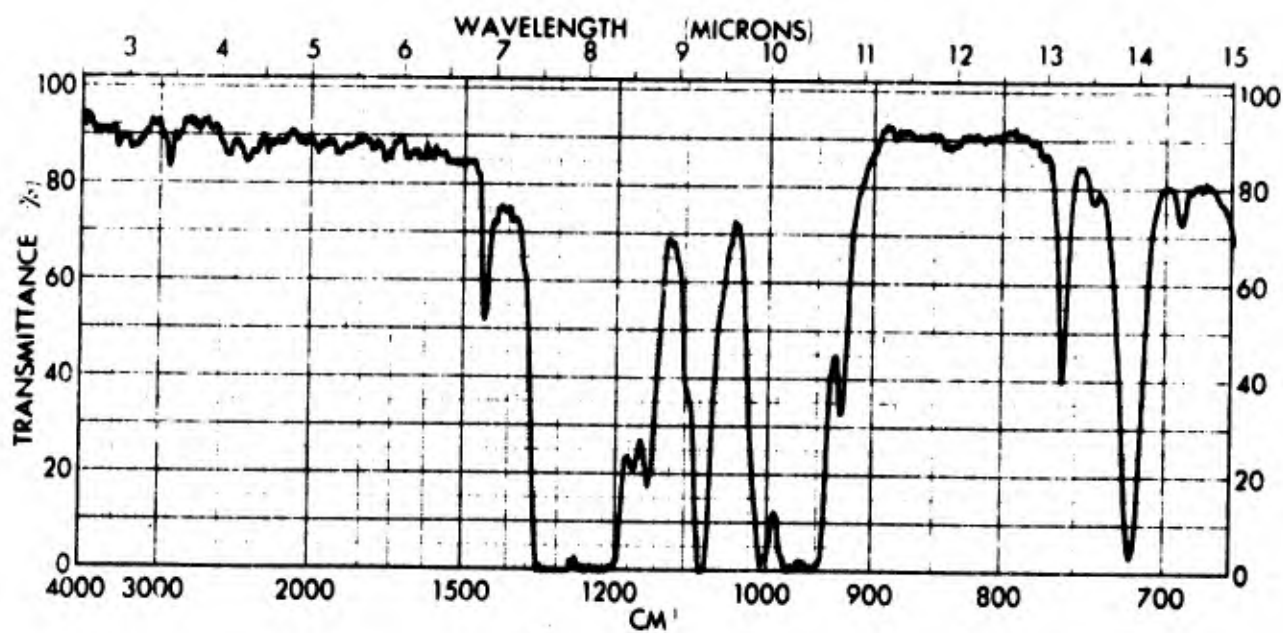


FIGURE 4

Infrared Spectrum of 1, 1-bis(Trifluoromethyl)-3, 3-difluoroethane

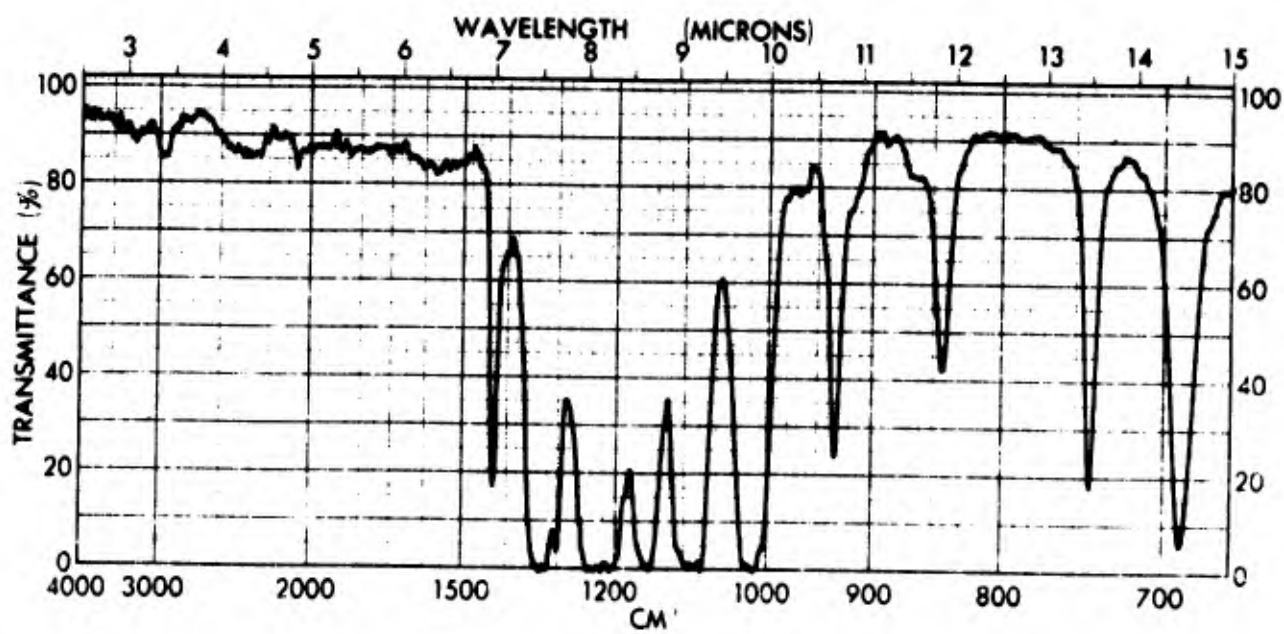
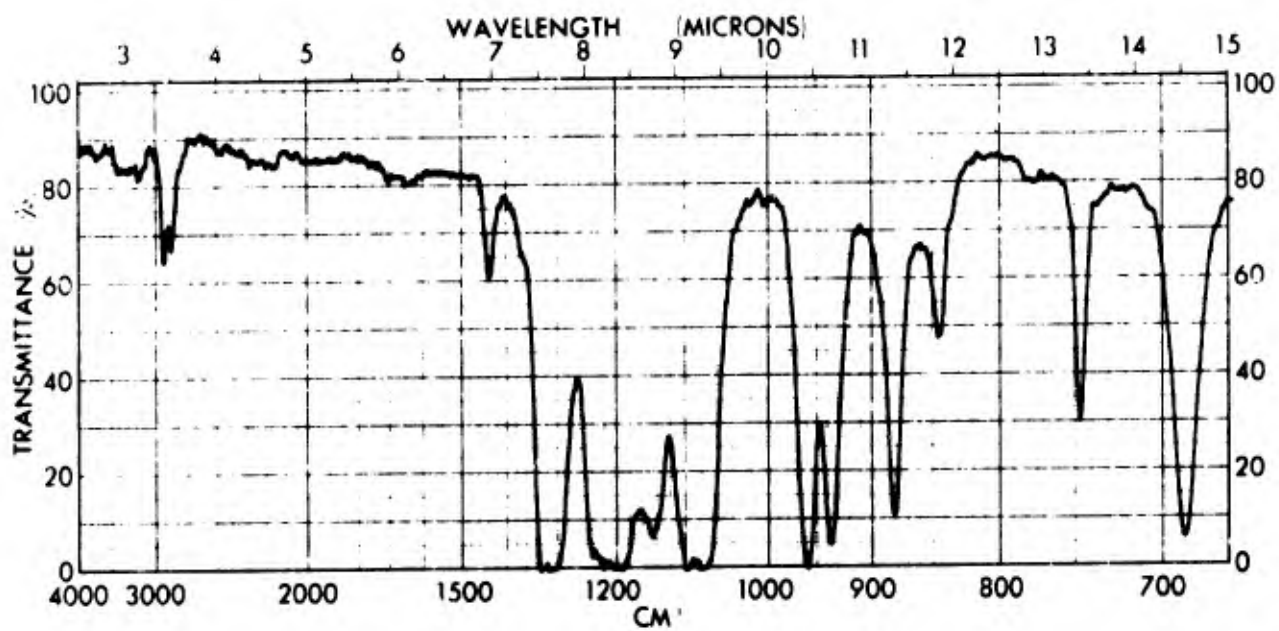


FIGURE 5
Infrared Spectrum of 1, 1-bis(Trifluoromethyl)oxetane



APPENDIX I

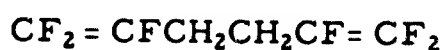
The following is the list of monomer assignments compiled during the period covered by this report. For previous assignments, Quarterly Report III⁵ should be consulted.

Monomer No.

Formula

University of Florida

205

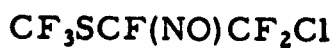


206

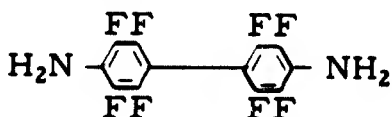


Peninsular ChemResearch

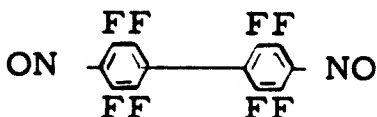
409



410



411



412



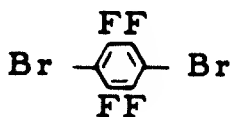
413



414

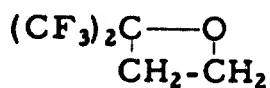


415

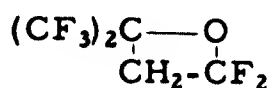


FMC Corporation

504



505



APPENDIX I - Continued

<u>Monomer No.</u>	<u>Formula</u>
506	$(\text{CF}_3)\text{C} \begin{array}{l} \text{--- O} \\ \\ \text{CF}_2\text{---CH}_2 \end{array}$
507	$\text{CF}_3\text{-N=CF}_2$
508	$\text{HO-CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{-OH}$
509	$\text{cis-CF}_2=\text{CFCF}=\text{CFCF}_2\text{CF}=\text{CF}_2$
510	$\text{trans-CF}_2=\text{CFCF}=\text{CFCF}_2\text{CF}=\text{CF}_2$
511	$\text{ClOC}(\text{CF}_2)_3\text{COCl}$
512	CF_3COCF_3

