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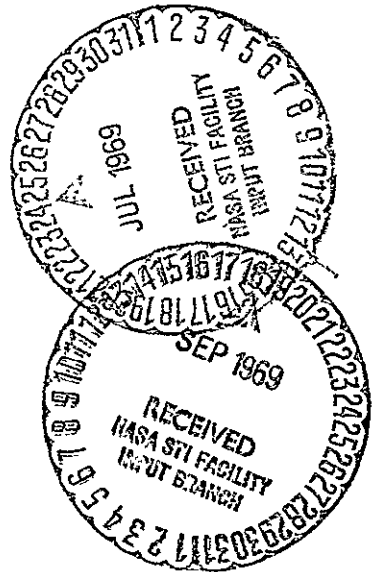
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GEORGE C. MARSHALL SPACE FLIGHT CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For the Period
June 1967 through May 1968

DEVELOPMENT OF VULCANIZABLE ELASTOMERS
SUITABLE FOR USE IN CONTACT WITH
LIQUID OXYGEN

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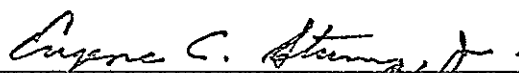
FIFTH ANNUAL SUMMARY REPORT
CONTRACT NO. NAS8-5352

For the Period
June 1967¹ through May 1968

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FOREWORD

This report was prepared by Peninsular ChemResearch, Inc., in partial fulfillment of the terms of Contract No. NAS8-5352, "Development of Vulcanizable Elastomers Suitable for Use in Contact With Liquid Oxygen," with the George C. Marshall Space Flight Center of the National Aeronautics and Space Agency. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratory, Material Division, of the George C. Marshall Space Flight Center. Dr. William Hill acted as the Contracting Officer's Technical Representative.

Other personnel who have contributed to this research were Dr. Paul D. Schuman, Senior Research Chemist; Pamela Overton, Research Chemist; and Marvin Hamlin, Technician. Drs. George B. Butler and Paul Tarrant served as consultants. In addition, Dr. Wallace S. Brey of the University of Florida obtained and interpreted NMR spectra, and Dr. Robert J. Hanrahan, also of the University of Florida, assisted in radiation induced polymerization studies.

ABSTRACT

The homopolymers of $\text{CH}_2=\text{CHCO}_2\text{CH}_2(\text{CF}_2\text{CF}_2)_n\text{H}$, ($n = 1, 2,$ and 3) have been prepared and their low temperature tensile properties studied. Increasing values of n were found to bring about increasing elongations and decreasing tensile strength and toughness. Attempts to prepare copolymers with vinylidene fluoride were unsuccessful. Attempts to prepare cyclopolymers of perfluoroglutaraldehyde, perfluoroglutaryl fluoride, and perfluoro-3-oxaheptadiene-1,6 were unsuccessful. Poly-anhydrides of fluorocarbon dicarboxylic acids were found to be hydrolytically unstable. Polycondensation of perfluoroaldehyde hydrates with fluorocarbon dicarboxylic acids did not produce the expected linear polyesters. Work was begun on the preparation of esters derived from oligomers of hexafluoropropylene oxide:

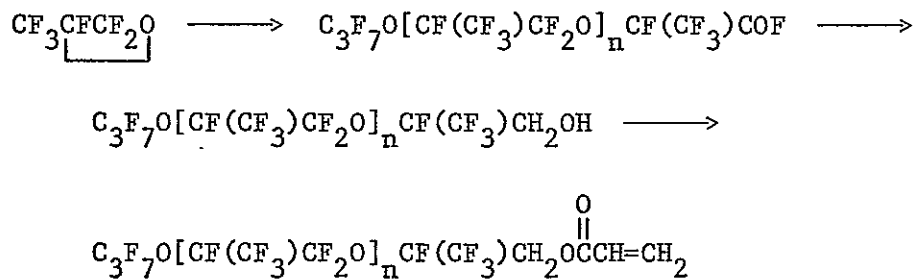


TABLE OF CONTENTS

<u>Chapter</u>	<u>Page</u>
INTRODUCTION.....	1
DISCUSSION.....	3
A. Fluorine-Containing Acrylates.....	3
1. Polymer Testing.....	3
2. Polymerization.....	5
3. Monomer Synthesis.....	6
B. Cyclic Polymers.....	9
1. Polyglutaraldehyde.....	9
2. Poly(perfluoroglutaryl fluoride).....	11
3. Poly(perfluoro-3-oxaheptadiene-1,6).....	12
C. Linear Polymers Having Oxygen in the Chain.....	13
1. Polyanhydrides.....	13
2. Polyesters from gem-Diols.....	14
3. Miscellaneous Polyethers.....	15
EXPERIMENTAL.....	17
A. Acrylates.....	17
1. Testing.....	17
2. Polymerization.....	17
a. Emulsion System.....	18
b. Bulk System.....	18

TABLE OF CONTENTS
(Continued)

<u>Chapter</u>	<u>Page</u>
EXPERIMENTAL, continued	
3. Monomer Synthesis.....	18
a. Acrylate Esters.....	18
b. Hexafluoropropylene Oxide Oligomers.....	19
c. Reduction of Hexafluoropropylene Oxide Oligomers.....	21
B. Cyclic Polymers.....	22
1. Perfluoroglutaraldehyde.....	22
a. Polymerization.....	22
b. Acylation of Poly(perfluoro- glutaraldehyde).....	23
c. Monomer Preparation.....	24
2. Perfluoroglutaryl Fluoride.....	24
a. Attempted Polymerization.....	24
b. Monomer Preparation.....	25
3. Poly(perfluoro-3-oxaheptadiene-1,6).....	25
a. Attempted Polymerization.....	25
b. Monomer Preparation.....	26
C. Linear Polymers.....	28
1. Polyanhydrides.....	28
a. Polyadipic Anhydride.....	28
b. Tetrafluoroterephthalic Anhydride.....	28
c. Perfluoro-2-methyl-3-oxaoctanedioic Anhydride.....	29
2. Polyesters from gem-Diols.....	29
a. Polymerizations.....	29
b. Monomer Synthesis.....	30

TABLE OF CONTENTS
(Continued)

<u>Chapter</u>	<u>Page</u>
EXPERIMENTAL, continued	
3. Miscellaneous.....	30
a. Polyethers by a Williamson-type Synthesis.....	30
b. Reaction of C_3F_7I with O_2	30
c. $FOC(CF_2)_4OCF(CF_3)COF$ (A), $FOCCF(CF_3)O(CF_2)_5OCF(CF_3)COF$ (B) and $FOC(CF_2)_4OCF(CF_3)CF_2OCF(CF_3)COF$ (C)....	30
d. Preparation of Perfluoroadipoyl Fluoride.....	31
REFERENCES.....	44
DISTRIBUTION LIST.....	45
APPENDIX.....	1a

LIST OF ILLUSTRATIONS

<u>Figure</u>	<u>Page</u>
1. Stress <u>vs</u> Strain in Poly(trihydroperfluoroalkyl acrylates).....	33
2. Toughness <u>vs</u> Pendent Chain Length in Poly(trihydroperfluoroalkyl acrylates).....	34
3. Resiliency of Poly(trihydroperfluoroalkyl acrylates).....	35
4. Infrared Spectrum of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CH_2OH$	36
5. Infrared Spectrum of a Liquid Polymer of $(CF_2)_3(CHO)_2$	37
6. Infrared Spectrum of a Liquid Polymer of $(CF_2)_3(CHO)_2$ After Acylation.....	38
7. Infrared Spectrum of $(CF_2)_3(CHO)_2$	39
8. Infrared Spectrum of Perfluoroglutaryl Fluoride.....	40
9. Infrared Spectrum of Presumed $CF_2=CFO(CF_2)_2CF=CF_2$, Actual $CF_3CFHO(CF_2)_2CF=CF_2$	41
10. Infrared Spectrum of $\overset{O}{\parallel}FC(CF_2)_4OCF(CF_3)\overset{O}{\parallel}CF$	42
11. Infrared Spectrum of $\overset{O}{\parallel}FCCF(CF_3)O(CF_2)_5OCF(CF_3)\overset{O}{\parallel}CF$...	42
12. Infrared Spectrum of $FOC(CF_2)_4COF$	43

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Tensile Properties of Fluorine-Containing Acrylate Polymers.....	4
II	Relative Toughness of $H(CF_2CF_2)_nCH_2OCOCH=CH_2$ Polymers.....	4
III	Acrylate Esters $CH_2=CHCO_2CH_2R_f$	6
IV	Oligomerization of Hexafluoropropylene Oxide.....	21
V	Perfluoroglutaraldehyde (PFGA) Polymers.....	23
VI	Pyrolysis of $FCOCF(CF_3)O(CF_2)_4COF$	28

INTRODUCTION

This report describes work done during the fifth year of Contract No. NAS8-5352. The objective of the program is the development of elastomeric polymers which will retain useful mechanical properties at temperatures as low as -190°C , and which will be chemically compatible with liquid oxygen. Certain limitations are set on polymer structure by this double requirement for low temperature flexibility and LOX-compatibility,

To begin with, the preponderance of hydrogen in the molecule must be replaced by chlorine or, preferably, fluorine. The allowable limits of hydrogen content are rather sharply drawn, as may be seen from test data, reported in the previous Annual Summary Report, relating to copolymers of vinylidene fluoride ($\text{CH}_2=\text{CF}_2$) with perfluoro (methyl vinyl ether), $\text{CF}_3\text{OCF}=\text{CF}_2$. Thus, the copolymer containing 87.5 mole percent vinylidene fluoride detonated five times in 17 trials;¹ the copolymer containing 83.3 mole percent vinylidene fluoride detonated zero times in 20 trials. This difference in behavior may be attributed to a decrease in hydrogen content of 0.24 mole percent from 2.21 to 1.97%.

Favorable low temperature mechanical properties appear to derive from combinations of structures giving non-crystallizing, heteroatomic chains, and long pendent groups. Precedent for the desirability of hetero-chains may be based on the low temperature properties of poly(thiocarbonyl fluoride), T_g -118° ;² nitroso rubber, T_g -50° ;³ and UV-, or isocyanate-coupled oligomers of hexafluoropropylene oxide.⁴ The interest in long pendent chains was fostered by reports of decreases in T_g of poly(alkyl methacrylates) amounting to 170°C , on increasing the length of the alkyl group from one to nine carbon atoms.⁵ Extrapolations of related data indicate that side chains of eighteen carbon atoms depress T_g in this series to -100°C .⁶ Effects of similar magnitude have

been observed in a series of polystyrenes with increasingly long para substituents. Poly(alkyl vinyl ethers) exhibited a minimum T_g at a pendent chain length of eight carbon atoms.⁷

On these bases, the synthetic effort on this contract has been directed towards polymers with heteroatoms in the chain; e.g., polyethers, polyanhydrides, and polyesters. In addition, it has been directed toward polymers with long pendent chains; e.g., poly(fluoroalkyl acrylates). The testing program has sought to correlate T_g and low-temperature tensile properties with these structural features.

DISCUSSION

A. Fluorine-Containing Acrylates

1. Polymer Testing

The testing program during the past year was restricted almost entirely to homopolymers of fluoroalkyl acrylate esters. The largest body of data has been accumulated for the homologous series $\text{CH}_2=\text{CHCO}_2\text{CH}_2(\text{CF}_2\text{CF}_2)_n\text{H}$, where $n = 1-3$. These monomers and their homopolymers are designated I, II, and III, respectively, throughout this report.

Low temperature mechanical properties were determined on these polymers, according to procedures developed at PCR and described in previous Annual Reports. Tensile and elongation data were obtained using uncured, unfilled specimens one inch in diameter, cut from 20-mil molded films. The test polymers were prepared by bulk polymerization with azobisisobutyronitrile as the initiator. The data obtained in this testing program are given in Table I.

The small amount of data presented limits the validity of any conclusions that may be drawn, but it would appear that pendent chain length has little effect on ultimate elongation below the glass temperature of these polymers. In contrast to this, a pronounced effect on low temperature tensile strength may be noted. A 75% loss in tensile strength occurs when the pendent chain length is increased from four to eight backbone atoms.

As a consequence of this, and contrary to what had been expected, the relative toughness of these polymers decreases with increased pendent chain length. (Toughness was measured as area under the stress-strain curve, Figure 1.) Table II summarizes the toughness of the three polymers

TABLE I
TENSILE PROPERTIES OF FLUORINE-CONTAINING
ACRYLATE POLYMERS

Polymer	t, °C	Tensile Strength		% Elongation
		Kg/cm ²		
I	19	18.16		525
		17.88		490
		<u>20.04</u>		<u>550</u>
Avg.			18.69	515
σ			0.82	22
I	-67	270.2		2.5
		259.3		10.5
		<u>326.0</u>		<u>34.5</u>
Avg.			285.2	15.8
σ			25.5	11.8
II	16	7.06		285
		<u>8.4</u>		<u>290</u>
Avg.			7.7	287
II	-53	90.9		20.0
	-75	118.1		20.5
		<u>102.8</u>		<u>25.0</u>
Avg.			110.4	22.5
III	16	9.36		205
III	-73	78.2		12
		42.9		8
		79.0		25
		<u>85.0</u>		<u>27</u>
Avg.			71.2	18
σ			10.9	5.4

TABLE II
RELATIVE TOUGHNESS OF H(CF₂CF₂)_nCH₂OCOCH=CH₂ POLYMERS

Polymer	n	Area Under Stress-Strain Curve		Relative Toughness
		(by Planimeter)		
I	1	135.5 cm ²		4.82
II	2	41.86 cm ²		1.49
III	3	28.12 cm ²		1.00

at about -73° . A plot of these values with respect to pendent chain length (Figure 2) shows a precipitous drop in toughness with increased chain length. Since little change in elongation is noted, a similar plot is obtained when tensile strength is plotted as a function of pendent chain length.

The results of these tests are surprising since it was anticipated that the side chain would, in effect, be an addition of a chemically bonded plasticizer. It was further anticipated that an increase in side chain length would improve low temperature properties.

Since the same values of toughness may be obtained for materials having greatly differing properties, i.e., high tensile-low elongation and low tensile-high elongation, it was considered advisable to carry out one further simple measure of low temperature properties of these polymers. This test was that of low temperature resiliency. The samples were subjected to a stretching force of 65% of their tensile strengths at -72°C , and permitted to equilibrate for 30 minutes. Upon removal of the weight, residual deformation was recorded as a function of time. The results are presented graphically in Figure 3.

It is interesting to note that recovery times increase in the order $\text{III} < \text{II} < \text{I}$. This coincides with the sequence of tensile strengths and toughness. On the basis of these data it would appear that internal plasticization by the pendent trihydroperfluoroalkyl groups increases in the expected way. The fact that the plasticizing effect of, for example, the trihydroperfluoroheptyl side chain is to produce a weak, soft material, was disappointing. The possibility still exists that copolymers might approach the low temperature elasticity of III, while retaining a useful portion of the strength of I. Extension of the data to the next higher homolog, $\text{CH}_2=\text{CHCO}_2\text{CH}_2(\text{CF}_2\text{CF}_2)_5\text{H}$, was not possible; the best polymer obtained from this monomer was a brittle wax having a $\overline{\text{DP}}$ of about five.

2. Polymerization

Monomers I, II, and III were found to polymerize with equal facility in several systems. Bulk polymerization with VAZO (duPont's brand of azobisisobutyronitrile) at low pressure or at 1000 atmospheres,

and emulsion polymerization with potassium persulfate gave comparable results.

An attempt was made to effect a cure using γ -radiation. Samples of polymer I were exposed to a 200 curie ^{60}Co source for nine days at ambient temperature. Only insignificant improvements in tensile properties were observed. No work was done on chemical cures.

Several attempts were made to obtain copolymers of these acrylates with fluorine-containing vinyl monomers. In particular, the copolymerization of I was undertaken with vinylidene fluoride. The use of an emulsion recipe under autogenous pressure in a Fischer-Porter tube resulted in the production of two polymer phases. More than half of the combined monomer charge was recovered from an attempted bulk polymerization under autogenous pressure initiated by VAZO.

3. Monomer Synthesis

Following the work of Coddling,⁸ acrylate monomers were prepared by the reaction of the corresponding fluoroalcohol with either acrylyl chloride or a mixture of glacial acrylic acid and trifluoroacetic anhydride. The latter method enjoyed the advantages of speed, better yields, simplified work-up procedures, and gentler treatment of the product monomers. Table III summarizes the acrylate monomers, made by both general methods.

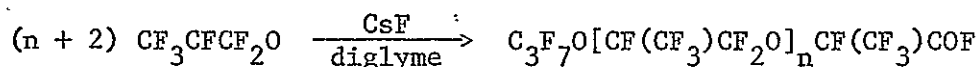
TABLE III

Acrylate Esters $\text{CH}_2=\text{CHCO}_2\text{CH}_2\text{R}_f$				
R_f	b. p.	n_D^{20}	Method	Yield
CF_3	87°	1.3567	1	67%
C_3F_7	117-119°	1.3371	1	79%
HCF_2CF_2	126-128°	1.3757	1	24%
			2	75%
$\text{H}(\text{CF}_2\text{CF}_2)_2$	57-59°/10mm	-	1	50%
$\text{H}(\text{CF}_2\text{CF}_2)_3$	71-75°/7mm	-	1	64%
$\text{H}(\text{CF}_2\text{CF}_2)_5$	110°/0.65mm		1	83%
			2	79%

As the characterization work on the α,α,ω -trihydroperfluoro-acrylates progressed, it became increasingly apparent that the $\text{H}(\text{CF}_2\text{CF}_2)_n\text{CH}_2$ - pendent group would probably not live up to expectation in its effect on low temperature mechanical properties. Earlier work in these laboratories has shown that duPont's Freon E fluids (which are essentially R_f -terminated fluorocarbon polyethers) were effective plasticizers for a number of experimental fluorine-containing polymers. By extension, the incorporation of a fluorocarbon polyether side-chain into the acrylate polymers suggested itself as a potentially most valuable approach to the goals of this project.

The oligomerization of hexafluoropropylene oxide gives rise to a series of acid fluorides having the generalized structure, $\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n\text{CF}(\text{CF}_3)\text{COF}$, where $n = 0-4$. Reduction of these acid fluorides would afford access to a homologous series of hydroxyl-terminated fluorocarbon polyethers - $\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n\text{CF}(\text{CF}_3)\text{CH}_2\text{OH}$ - having backbone chain lengths variable at will from 6 to 18 in steps of three. The acrylate esters of these alcohols would give homopolymers which could be considered as poly(acrylates) plasticized by chemically bound Freon E fluids. This reasoning justified an investigation of the synthesis of these polyfluoroalkoxyalkyl acrylates. Time did not permit the study of their polymerization.

An important synthetic problem had first to be solved. In the normal conduct of this reaction, the higher oligomers ($n > 2$) are the desired products and indeed constitute more than 80% of the product mixture. For practical reasons - boiling point of monomers and expected mechanical strength of the polymers - the lower oligomers are desired for this work. It was shown in some small scale pilot syntheses that variation of the ratio of catalyst to monomer had little effect upon the product distribution.



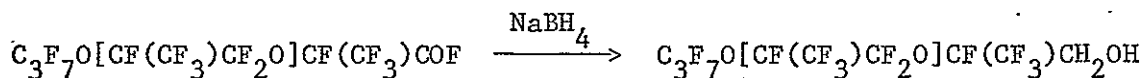
In addition, it was established that reaction temperature directly influenced rate, but not the magnitude of n .

Finally, an experiment was run wherein the product mixture was sampled at regular intervals, beginning at the earliest time when enough product (lower) phase was present to permit sample withdrawal. It was found that the relative amounts in the total product mixture of oligomers where $n = 0, 1, 2$, decreased sharply as the reaction proceeded. Therefore, the initial synthetic attempts were conducted using a relatively large amount of CsF catalyst, to increase production rate, and were interrupted after short contact times.

While this approach gave a product enriched in $n=0$ and $n=1$ oligomers, the quantities were limited. Thus, from 350 g. of hexafluoropropylene oxide in the presence of 34 g. of CsF, there were obtained 30 g. (8.6%) of dimer ($n=0$), and 68 g. (19%) of trimer ($n=1$), respectively. Another phenomenon causing lowered yields of the desired oligomers was noted during a second run under these same conditions. Gas chromatographic analysis of the crude product, which still contained suspended CsF, showed the presence of about 35% by weight of dimer and trimer. The mixture was stored overnight at room temperature in a sealed container. After 18 hours, the dimer and trimer were essentially absent from the mixture. It was tentatively concluded that the product mixture continues to equilibrate in the presence of cesium fluoride, and that at room temperature the higher oligomers are favored.

While more work remains to be done to substantiate this last hypothesis, practical steps were taken to avoid any continued consumption of dimer and trimer in storing the crude product. The reaction was carried out in a flask with a fritted disc sealed into the bottom, and lower (product) layer drawn off at hourly intervals. Thus, the product distribution was always that of the first hour of the reaction, when the rate of dimer and trimer production is believed to be highest. Further, it could be filtered away from cesium fluoride at the same time, to forestall loss of lower oligomers through redistribution reactions. The combined batches were distilled giving essentially the same product distribution observed in runs made over 24 hours in single batch operation. Thus, the problem of materially favoring the preparation of dimer and trimer remains unsolved.

Reduction of trimer acid fluoride to the corresponding alcohol -

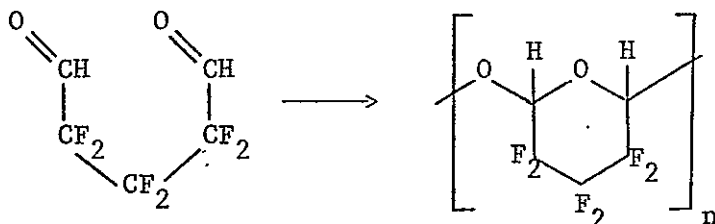


was carried out in the usual manner in monoglyme solution giving nearly quantitative yield of the desired perfluoroalkoxyalkanol. Its infrared spectrum is shown in Figure 4. Time did not permit an examination of the synthesis and polymerization of the acrylate esters of these alcohols.

B. Cyclic Polymers

1. Polyglutaraldehyde

The ether link is a most desirable feature of the main chain of a polymer for cryogenic application. In this position such a flexible unit should have even more favorable effects on low temperature flexibility and T_g than when it is in the pendent group. One of the more promising approaches to such polyethers appeared to be the cyclopolymerization of perfluoroglutaraldehyde.



A recent patent⁹ disclosing the first reported synthesis of perfluoroglutaraldehyde also points out that this aldehyde polymerizes spontaneously and exothermically to give a hard, solid polymer. It is possible that the mode of initiation may direct the polymerization either through a linear or cyclic mechanism. In these laboratories, it has been found that polymerization of perfluoroglutaraldehyde in Et_2O solution, using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as the initiator, gave a tacky liquid polymer which was soluble in polar organic solvents. The nature of this polymer indicated

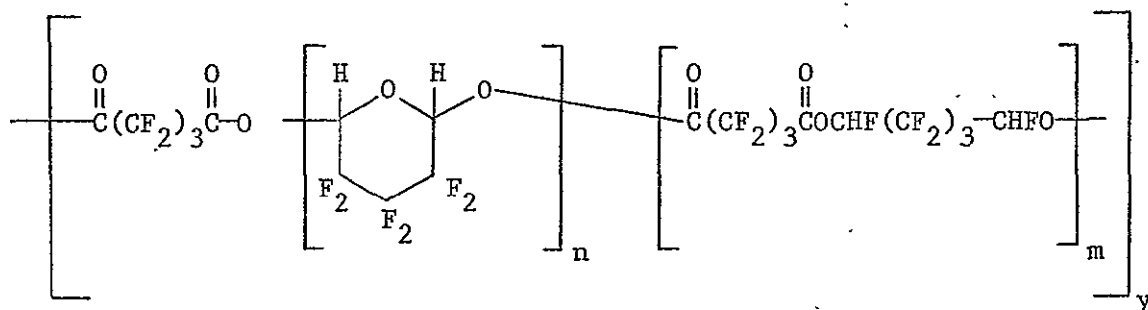
that cyclopolymerization was occurring rather than linear polymerization, since linear polymerization would result in an insoluble network polymer. By varying the initiator concentration from about 3 to 24 mole percent, molecular weights of 283 to 609 were obtained. This would correspond to values of n from about 1.4 to 2.9. When the polymerization was carried out in the absence of solvent, the resultant polymer was a brittle solid. In addition, attempts to copolymerize perfluoroglutaraldehyde with trifluoroacetaldehyde, in Et_2O solution, also gave liquid polymers.

The reason for the generally low molecular weight polymers obtained is not presently known. Although trace amounts of water may interrupt the cyclopolymerization, termination of the extent shown should not occur unless a relatively large amount of water were present.

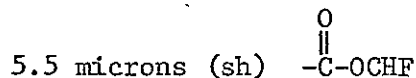
Infrared spectra of these liquid polymers suggest OH termination (broad maxima at about 3.0 microns), but surprisingly also show a maximum at 5.67 microns indicating the presence of a carbonyl group. Upon acylation of a liquid polymer the maximum at 3.0 microns disappeared and a shoulder appeared on the C=O group at about 6.8 microns. An infrared spectrum of this polymer before and after acylation is shown in Figures 5 and 6.

The probable presence of terminal hydroxyl groups suggested chain extension through reaction with a diisocyanate or by acylation with a diacid halide.

To investigate this possibility, a solid polymer, initiated with triethylamine and presumed to have the desired cyclic structure, was treated with excess perfluoroglutaryl fluoride, in an attempt to obtain the proposed structure shown below.



The infrared spectrum of the resulting viscous liquid product showed infrared absorptions in the carbonyl region as follows:



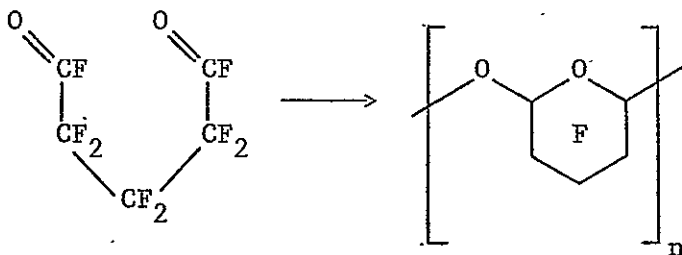
5.6 microns (strong) aldehyde C=O

Thus, reaction appears to have been incomplete, and the products complex.

In an attempt to complete the hydration of the aldehyde carbonyl functions in the polymer, a sample was shaken in wet acetone for several hours. The intensity ratio of the OH and C=O peaks in the infrared spectrum was not materially changed. This was unexpected, since the carbonyl group in the monomer hydrates rapidly and quantitatively. No further work was undertaken on this system.

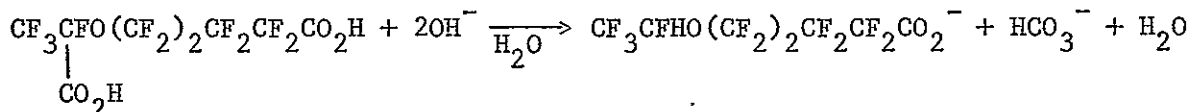
2. Poly(perfluoroglutaryl fluoride)

Perfluoroglutaryl fluoride should also be capable of cyclo-polymerization to a polyether, in a manner analogous to that proposed for perfluoroglutaraldehyde.



Attempts were made to demonstrate this reaction by anionic (triethylamine) initiation, and by gamma radiation. No evidence for polymerization could be found.

group which was attached to carbon. Attempts to obtain a neutralization equivalent of the acid precursor by back-titrating a solution of the acid in excess base gave three end-points, two of which correspond to sodium carbonate. From these data it was deduced that the 1:1 adduct acid gave an unstable anion, and that attempts to prepare the salt for pyrolysis proceeded as shown below:



Bicarbonate was a sufficiently strong base to bring about the decarboxylation.

A possible alternate synthesis of the desired diene was suggested by the work of Fritz and Selman,¹⁰ who obtained olefins upon passing fluorocarbon acid fluoride vapors over salts such as sodium sulfate at 400-600°C. Several runs were made under various conditions using the 1:1 hexafluoropropylene oxide:perfluoroglutaryl fluoride adduct. Only traces of diene could be detected in the infrared spectra of the products. The project was abandoned.

C. Linear Polymers Having Oxygen in the Chain

1. Polyanhydrides

The search for polymers having oxygen atoms in the chain was extended to polyanhydrides. Many years ago Carothers¹¹ demonstrated that polymeric anhydrides could be synthesized providing only that the difunctional acid would not dehydrate intramolecularly to form a stable ring structure. Sebacic acid, which would form an eight membered intramolecular ring or a 22-membered intermolecular ring, could be polymerized to a high molecular weight, fiber-forming polymer. However, polyanhydrides of aliphatic dicarboxylic acids are quite hydrolytically unstable.

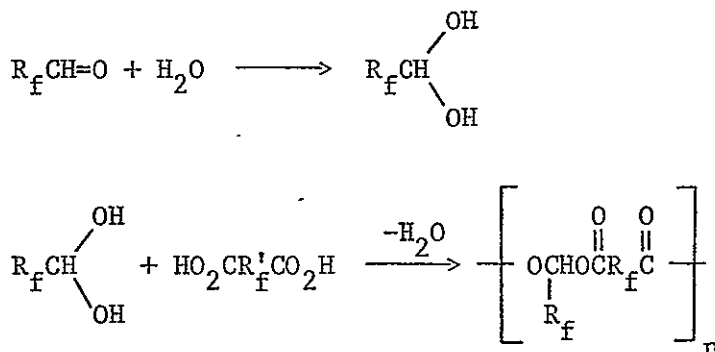
On the other hand, polyanhydrides of aromatic dicarboxylic acids exhibit hydrolytic stabilities similar to that of poly(ethylene terephthalate). By virtue of the hydrophobic nature of fluorocarbons, it was considered possible that the polyanhydrides of perfluoroaliphatic dicarboxylic acids might show enhanced hydrolytic stability.

Perfluoroadipic acid was recovered unchanged after heating alone in a nitrogen sweep. Dehydration in refluxing acetic anhydride gave a black, liquid product which regenerated the free acid on contact with atmospheric moisture.

Acting on the assumption that perfluoroadipic acid was forming cyclic anhydrides, longer chain dicarboxylic acids were next studied. Heating perfluoro-2-methyl-3-oxaocanedioic acid, which would form nine-membered rings on intramolecular cyclodehydration, with acetic anhydride gave only a low melting solid. Similarly, tetrafluoroterephthalic acid, which should be totally incapable of forming rings, gave only black, viscous liquid products on refluxing with acetic anhydride.

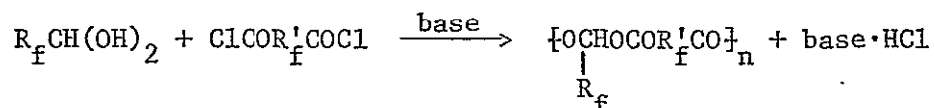
2. Polyesters from gem-Diols

In a further effort to increase the number of heteroatoms per repeating unit in the polymer backbone, the synthesis of polyesters derived from gem-diols was undertaken. These materials would have the backbone sequence C-O-C-O-C, in addition to pendent fluorocarbon groups and fluorocarbon backbone units. The synthetic sequence envisioned is shown below:



By proper selection of the acid moiety, additional flexible links could be included in the chain; for example ether links, by the use of $HO_2CCF(CF_3)O(CF_2)_4CO_2H$.

Hydrates of perfluoroaldehydes are known to be quite stable, forming readily when pure aldehydes are brought in contact with atmospheric moisture. However, they equilibrate with free aldehyde and water in contact with acids, a fact which prevented the use of a simple acid-catalyzed polyesterification procedure for this investigation. Therefore, it was necessary to react the aldehyde hydrate with a diacid chloride in the presence of excess base.

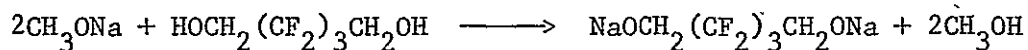


The first experiments used perfluorobutyraldehyde hydrate and tetrafluoroterephthaloyl chloride in pyridine. The latter served as base, solvent, and catalyst. The products were black solids which were soluble to varying degrees in all common solvents including water. Separation from pyridine hydrochloride was effected by extracting the product into acetone. No characterizable material could be recovered from the acetone solution.

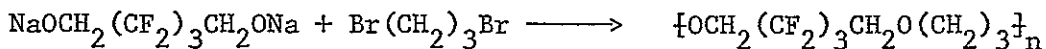
Interfacial polymerization was attempted. The aqueous layer contained trifluoroacetaldehyde hydrate and sodium hydroxide; the non-aqueous (benzene) layer, tetrafluoroterephthaloyl chloride.¹² No polymer phase separated either at rest at room temperature or in a blender (ca 1000 rpm). The starting acid chloride was recovered unchanged from the benzene layer.

3. Miscellaneous Polyethers

A Williamson-type synthesis was envisioned as a direct route to highly fluorinated polyethers.

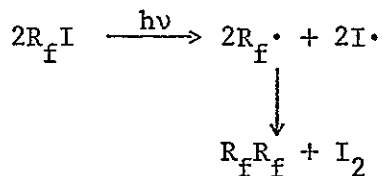


The novel disodium salt of hexafluoropentanediol was prepared by the methathetical reaction of hexafluoropentanediol with sodium methylate in vacuo without solvent. The salt was treated with 1,3-dibromopropane in a model polymerization reaction:



Explosions were experienced in the Williamson reaction and subsequently in a repeat preparation of the disodium salt. Apparently the salt itself is unstable at 80°C.

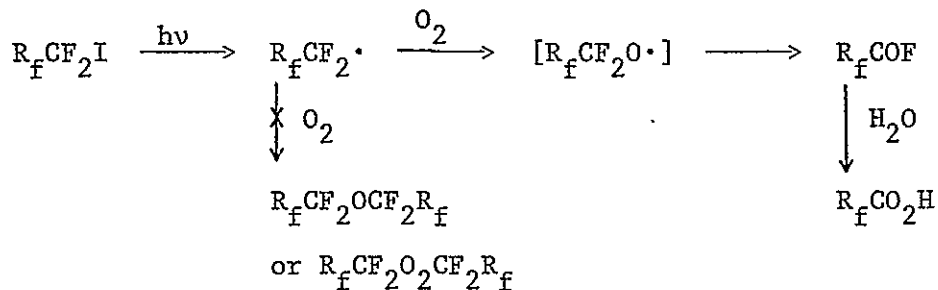
Attempts to prepare poly(fluorocarbon peroxides) through reaction of fluorocarbon hypofluorites with fluorocarbon alkoxides were described in the Fourth Annual Report. During this period a different approach to the synthesis of peroxides was attempted. Since fluorocarbon iodides cleave easily to give a fluorocarbon radical,



it was reasoned that if the iodide were irradiated in the presence of O₂, the usual coupling reaction might be averted by oxygen insertion either as a peroxide or an oxide.

In a simple attempt to determine the feasibility of this reaction, C₃F₇I was irradiated with a 450-watt Havyonia u.v. lamp while passing O₂ through the system. Chromatographic analysis of the reaction product indicated only starting iodide present. However, an infrared spectrum of the crude product showed a major maximum at 5.6 microns and a broad maximum at 3.5 microns, suggesting the presence of COOH. A water wash of the reaction product was highly acidic.

It would appear that little or no ether or peroxide was formed, but that the reaction proceeded as outlined below:



EXPERIMENTAL

A. Acrylates

1. Testing

Tensile strength, elongation, resilience, and toughness data were obtained by suspending a suitably shaped specimen of 20 mil film between two arbors 5/32" in diameter. The specimens were ring shaped, and for the weaker films had to be doubled to perform adequately. A stress of about 1.8×10^{-3} kg/cm² was placed on the sample at room temperature in order to collapse the ring on the arbors; the sample was cooled to test temperature (-65 to -75°C) with Dry Ice, and a tared pan was suspended from the lower arbor. The pan was then hand-loaded with lead shot at regular intervals (to give some degree of control over strain rate). Loading was continued to the break-point of the sample. Where sufficient polymer was available, at least three replicates were run.

2. Polymerization

The acrylate esters $\text{CH}_2=\text{CHCO}_2\text{CH}_2(\text{CF}_2\text{CF}_2)_n\text{H}$, $n=1, 2, 3$, were polymerized in bulk using azobisisobutyronitrile as already described,¹³ The homologue $n = 5$ was polymerized in solution.

A mixture of 5 g. of $\text{CH}_2=\text{CHCO}_2\text{CH}_2(\text{CF}_2\text{CF}_2)_5\text{H}$, 5 g. of benzene, and 0.01 g. of azobisisobutyronitrile was degassed and sealed in an evacuated Fischer-Porter tube. Polymerization occurred on shaking overnight at 48°C. The crude polymer was freed of benzene, and its molecular weight determined by vapor pressure osmometry. $\bar{M}_n = 2900$, from which $\bar{DP} = \text{ca } 5$.

Attempted copolymerizations were carried out in emulsion and in bulk.

a. Emulsion system

Recipe:

Monomer (2 g. $\text{CH}_2=\text{CHCO}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{H}$, 3.8 g. $\text{CH}_2=\text{CF}_2$)	5.8 g.
Distilled, degassed water	10.4 g.
$\text{K}_2\text{S}_2\text{O}_8$	0.32 g.
Detergent	0.17 g.

The reactants were combined, deaired, and sealed in a Fischer-Porter tube under vacuum. After shaking at 48° for 22 hours, the tube was opened, and 1.3 g. of polymer recovered by coagulation of the latex. The crude polymer was dried in vacuo over the weekend, and submitted to the Analytical Department for characterization. Attempts to determine its \overline{M}_n were thwarted by its incomplete solubility in all common solvents. In methyl ethyl ketone, the most nearly suitable solvent, a portion of the solid polymer dissolved readily, leaving behind a granular residue which was not swollen by MEK. No effort has been made to determine low temperature mechanical properties of this material, since it appears to consist of two polymer phases.

b. Bulk system

Recipe:

$\text{CH}_2=\text{CHCO}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{H}$	2.0 g.
$\text{CH}_2=\text{CF}_2$	3.8 g.
VAZO	0.01 g.

The deaired reactants were warmed to 40-45° in an evacuated Fischer-Porter tube for 5 hours. Upon opening the tube, it was found to contain 1.9 g. of unreacted vinylidene fluoride and a small amount of friable polymer, of which there was insufficient for characterization.

3. Monomer Synthesis

a. Acrylate esters

For larger scale synthesis of the acrylate esters, the method described by Bittles¹⁴ was used. Typically, to a 1-liter flask fitted with

a Dean-Stark trap was added 332 g. (1 mole) of $\text{H}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{OH}$, 300 ml. of benzene, 84 g. (1.16 moles) of $\text{CH}_2=\text{CHCOOH}$, 5 g. of 2,5-di-tert-butylhydroquinone and 5 ml. of H_2SO_4 . The reaction mixture was maintained at reflux and the progress of the reaction was monitored by noting the amount of water collected.

After approximately 15 hours at reflux, benzene was removed by distillation and the reaction product was washed several times with water and dried over MgSO_4 . Distillation under vacuum, through a 300-mm. vacuum jacketed column packed with 3/16" glass helices, yielded 254 g. (0.66 mole) of $\text{H}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{OOCCH}=\text{CH}_2$, b.p. $43^\circ/0.5\text{mm}$.

Alternately the procedure of Coddling¹ could be used. For example, $\text{H}(\text{CF}_2\text{CF}_2)_5\text{CH}_2\text{OH}$ was added to an ice-cold mixture of one equivalent of glacial acrylic acid and excess trifluoroacetic anhydride. After 2 1/2 hours at room temperature the solid product was dissolved in CCl_4 and washed well with water. The organic layer was dried over anhydrous MgSO_4 and distilled without a column. There was obtained a 75% yield of the ester, $\text{CH}_2=\text{CHCO}_2\text{CH}_2(\text{CF}_2\text{CF}_2)_5\text{H}$, b.p. $99-110^\circ/1.7-2.2\text{mm}$., m.p. $40-45^\circ$, glc 89.7% pure, neutralization equivalent 656 (theory 586), molecular weight by vapor pressure osmometry 548 (theory 586). These data are congruent with the production of desired ester, contaminated with 10-12% of lower molecular weight, non-acidic material; for example, unesterified secondary alcohol.

Treatment of the n=5 alcohol with excess trifluoroacetic anhydride gave a 74% yield of $\text{CF}_3\text{CO}_2\text{CH}_2(\text{CF}_2\text{CF}_2)_5\text{H}$, b.p. $85-104^\circ/0.2\text{mm}$. Attempted transesterification with glacial acrylic acid, by distilling off $\text{CF}_3\text{CO}_2\text{H}$ as liberated, only resulted in polymer formation.

b. Hexafluoropropylene oxide oligomers

Carefully dried diglyme and 34 g. of cesium fluoride were introduced into a 2-liter, 2-neck flask equipped with gas inlet and liquid sampling port. An atmosphere of hexafluoropropylene oxide was supplied at 2 1/2 - 5 psig, while the diglyme-CsF slurry was stirred magnetically. Samples of the lower liquid layer (oligomers) were withdrawn at 2-hour intervals for examination by gas-liquid chromatography. At the end of

two hours, the chromatogram showed more than 30% dimer, with decreasing amounts of higher boilers. After 4 hours, the product distribution had shifted to that usually encountered. A plot of relative abundance vs x-mer size approached a normal distribution curve. Thus, from 350 g. of hexafluoropropylene oxide, Reaction 1 gave 30 g. of dimer, 68 g. of trimer, and the remainder higher oligomers.

The crude product of Reaction 2 weighed 315 g. After separation from the diglyme layer, it was allowed to stand overnight at room temperature in contact with the whole charge of CsF. Gas chromatographic analysis at the end of the reaction period (4 hours) and after the 18-hour holding period, showed that all the dimer and trimer had disappeared overnight. Distillation of the diglyme afforded 22 g. of dimer and 9 g. of trimer.

In the continuous-batch operation, a 1000-ml., 3-neck round bottom flask was fitted with a bottom drain having a fritted glass disc at the point of connection and a stopcock to give on-off control of liquid flow. One neck was sealed, one carried a thermometer dipping into the liquid, and one carried a gas inlet tube. The flask was cooled in a ice bath and its contents stirred magnetically.

Diglyme (150 ml.) was refluxed over CaH_2 and distilled into the flask; CsF was oven-dried and transferred into the flask in a dry box. The flask was flushed with dry nitrogen while cooling in the ice bath. Then a pressure of 2 1/2 psig of hexafluoropropylene oxide was established in the head space. To remove samples of the lower, oligomer, layer, the ice bath was lowered and the drain stopcock opened. Hexafluoropropylene oxide pressure forced the liquid oligomers through the fritted disc into a collection bottle.

A very small scale run was carried out wherein three 50-ml. flasks were charged with 0.1 g. of CsF and 10 ml. of diglyme, and exposed to 2 1/2 psig hexafluoropropylene oxide pressure for various times. The contents of the flasks were analyzed gas chromatographically.

The results of the continuous-batch and small runs are shown below in Table IV.

TABLE IV

Oligomerization of Hexafluoropropylene Oxide

		Relative Abundance				
		Dimer	Trimer	Tetramer	Pentamer	Hexamer
A. SMALL-SCALE RUNS						
<u>Contact Time</u>						
	2 hours	77	8	3	1.0	0
	5 hours	10	4.0	6.2	3.7	1.0
	8 hours	1	4.3	8.2	5.6	1.7
B. CONTINUOUS-BATCH						
<u>Total Time</u>	<u>Interval</u>					
2 hours	2 hours	1	1.3	2.2	2.6	1.8
4 hours	2 hours	1	1.4	2.6	2.4	1.04
5 hours	1 hour	1	2.0	4.6	5.3	2.7

c. Reduction of hexafluoropropylene
oxide oligomers

A solution of 40 g. (0.08 mole) of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COF$ in 30 ml. of $CF_2Cl \cdot CFCl_2$ (Freon 113) was added dropwise during 2 1/2 hours to 6 g. (0.16 mole) of $NaBH_4$ in 110 ml. of rigorously dried monoglyme. The temperature was kept below $50^\circ C$ during the addition, and then kept at $60-65^\circ C$ for 2 hours. The mixture was then cooled below room temperature and 150 ml. of water added slowly to destroy excess $NaBH_4$ and complex borates. The layers were separated and the upper (aqueous) layer extracted three times with 45 ml. of ether. The combined organic layers were dried over $MgSO_4$ and the solvent stripped off. There remained 37 g. (100% yield) of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CH_2OH$. Its infrared spectrum is shown in Figure 4.

B. Cyclic Polymers

1. Perfluoroglutaraldehyde

a. Polymerization

Polymerization of perfluoroglutaraldehyde (PFGA) was carried out in anhydrous Et_2O solution, at room temperature, using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ initiation. Polymerization occurred rapidly.

Copolymers of perfluoroglutaraldehyde and trifluoroacetaldehyde were prepared by adding the dialdehyde, as a 33(wt/vol %) in Et_2O , to a 13-ml. capacity Carius tube. The tube was cooled to -196° , the solution deaired several times by warming to room temperature and refreezing, then gaseous CF_3CHO was measured volumetrically, and condensed into the evacuated tube. The $\text{BF}_3 \cdot \text{Et}_2\text{O}$ initiator, 0.1 ml., was added as a 5% solution in Et_2O , by puncturing the rubber connecting tubing with a hypodermic needle. The reactants were mixed thoroughly on liquéfaction, then allowed to warm to room temperature. After two hours at room temperature, the tubes were opened to the vacuum line and the Et_2O was distilled from the polymer.

Polymerization of PFGA, in the absence of solvents, occurred exothermically with a rapid increase in viscosity. The viscosity continued to increase, over several hours at room temperature, resulting in brittle, tacky polymer. This polymer, as well as other PFGA polymers shown in Table V, are soluble in polar organic solvents.

The molecular weights of polymers PC 43-1, 2, and 3 (Table V) were determined on MEK solutions using a Model 302 Mechrolab vapor pressure osmometer.

TABLE V

Perfluoroglutaraldehyde (PFGA) Polymers*

<u>Polymer Number</u>	<u>PFGA (mM)</u>	<u>CF₃CHO (mM)</u>	<u>BF₃·Et₂O (mM)</u>	<u>MW</u>	<u>Polymer Character</u>
PC 42-2	44.0	-	7.8	-	Dark, viscous liquid.
PC 43-1	24.0	-	0.78	609	Viscous, clear liquid.
PC 43-2	12.0	-	0.78	581	Viscous, clear liquid, lower visc. than PC 43-1.
PC 43-3	2.4	-	0.78	283	Viscous, clear liquid, lower visc. than PC 43-2.
MH 11-1	7.2	7.2	0.78	-	Viscous liquid.
MH 11-2	7.2	17.4	0.78	-	Viscous liquid.
PS 1-2	24.0	-	1.55	-	Brittle, tacky solid.

*Polymerization run in Et₂O solution (approximately 30% solution) with the exception of PS 1-2, which was run neat.

b. Acylation of
poly(perfluoroglutaraldehyde)

Polymer PC 42-2, 4.0 g., a dark, viscous liquid, was refluxed in 25 ml. of acetic anhydride for 18 hours. The acetic anhydride and acetic acid were removed under vacuum and the polymer residue was dissolved in Et₂O. The ether solution was washed with water and then dried over MgSO₄. The Et₂O was removed under vacuum leaving a dark, viscous residue. Infrared spectra of this polymer before and after acylation are shown in Figures 5 and 6.

c. Monomer preparation

To a 500-ml., 3-neck flask was added 300 ml. of anhydrous Et_2O and 20 g. (0.53 mole) of LiAlH_4 . While continuously sweeping with dry N_2 , the reaction mixture (at room temperature) was stirred for three hours.

To a 1-liter, 3-neck flask equipped with a condenser and an addition funnel, was added 156.8 g. (0.53 mole) of $(\text{CF}_2)_3(\text{COOEt})_2$ and approximately 300 ml. of anhydrous Et_2O . The reaction mixture was cooled to -78° . The LiAlH_4 solution plus undissolved solids was transferred to the addition funnel. The LiAlH_4 solution was added slowly, over a three-hour period, to the ester solution. At this point 65 ml. of 76% aqueous EtOH was added to the reaction mixture and the mixture was warmed to room temperature. The mixture was then poured over ice containing 75 ml. of H_2SO_4 .

The aqueous layer was separated and extracted twice with Et_2O . The combined ether portions were distilled to remove the Et_2O and EtOH . The residual higher boiling product was added slowly to an excess of P_2O_5 contained in a 250-ml., 3-neck flask equipped with a Vigreux distilling column.

Distillation yielded the following cuts:

<u>Cut</u>	<u>b.p.</u>	<u>Wt.</u>
1	50-55°	3.7 g.
2	75-79°	11.1 g.
3	100-105°	61.4 g.

An infrared spectrum of cut 3, $(\text{CF}_2)_3(\text{CHO})_2$, is shown in Figure 7.

2. Perfluoroglutaryl Fluoride

a. Attempted polymerization

Perfluoroglutaryl fluoride (12 g., 50 mmoles) was placed in a Carius tube, degassed, evacuated, sealed, and exposed to gamma radiation

for 24 hours at ambient temperature. The diacid fluoride was recovered unchanged. Similarly no change occurred when 12 g. (50 mmoles) of perfluoroglutaryl fluoride was heated at 90°C for 18 hours with 0.1 ml. of triethylamine.

b. Monomer preparation

To each of two 2-liter steel cylinders equipped with pressure gauges was added 440 g. (7.6 moles) of KF. The cylinders were evacuated and heated to 230-250° for 18 hours. The cylinders were then cooled and 250 g. (1.17 moles) of $(CF_2)_3(COCl)_2$ was added. The reaction mixture was heated to 280-290° and maintained at this temperature for 96 hours. The reaction mixture was transferred to a vapor take-off low temperature distillation apparatus and distilled, yielding two cuts: 77 g., b.p. 36.5-42°; and 124 g., b.p. 46-47°. Chromatographic analysis (6'; 10% PFOX on HMDS treated Chromosorb) indicated both cuts to be 95+% perfluoroglutaryl fluoride. An infrared spectrum of perfluoroglutaryl fluoride is shown in Figure 8.

3. Poly(perfluoro-3-oxaheptadiene-1,6)

a. Attempted polymerization

VAZO* initiator. - Six grams of perfluoro-3-oxaheptadiene-1,6 was vacuum transferred into an evacuated Carius tube containing 12.2 mg. of VAZO, and degassed. After evacuating and sealing, the ampoule was held at 68°C for 16 1/4 hours, and at 89°C for four days. There was no evidence of polymerization.

A mixture of 16 g. of diene and 17.3 mg. of VAZO was degassed and placed in an autoclave under a nitrogen atmosphere. The autoclave was heated to 84°C and then pressurized to 4000 psig with nitrogen. The tube was removed and opened after 18 hours at temperature; no polymerization had occurred.

*Registered trademark of E. I. duPont deNemours & Co.

Emulsion. - The following recipe was used:

Perfluoro-3-oxaheptadiene-1,6	6 g.
$K_2S_2O_8$.03 g.
Sodium laurylsulfate	0.18 g.
Water	24 g.

A stable emulsion was readily obtained. After six hours at 80°C, the emulsion was broken by centrifugation. The organic layer consisted of unreacted diene.

b. Monomer preparation

Perfluoro-2-methyl-3-oxaoctanedioyl fluoride. - Three hundred ml. of diglyme was distilled from CaH_2 directly into a 1-liter flask containing 24 g. of CsF which had been dried in vacuo at 190° overnight. One hundred seventy-four g. (0.71 mole) of perfluoroglutaryl fluoride was charged to the flask. While cooling was continued, 5 psig of hexafluoropropylene oxide pressure was established in the flask and maintained, with stirring, for four hours. Epoxide uptake was 239 g. (1.39 mole). The crude product was distilled through a 1-meter column, giving 51 g. (30.6% yield based on perfluoroglutaryl fluoride) of $FCOFCF(CF_3)O(CF_2)_4COF$, 90% pure by GLC.

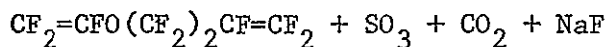
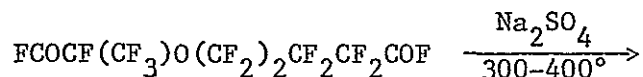
Disodium perfluoro-2-methyl-3-oxaoctanedioate. - Two hundred grams of the acid fluoride from Step 1 above (0.49 mole) was dissolved in 200 ml. of acetone containing 20 ml. of water, in a polyethylene bottle. Cooling was supplied by an ice bath. Phenolphthalein (0.5 ml.) was added, followed by 10% aqueous NaOH until a pink color persisted. The salt was recovered by evaporation of solvents. Yield, 154 g. (70%).

Perfluoro-3-oxaheptadiene-1,6. -

i. - By pyrolysis of disodium perfluoro-2-methyl-3-oxaoctanedioate. - Five-gram portions of the disodium salt were pyrolyzed in a 100-ml. flask using a small hand torch. The clear liquid product weighed 84 g. (88% yield); it was shown to be >95% pure by GLC.

Subsequent re-examination of the infrared spectrum (Figure 9) showed that the double bond absorption was due to C-CF=CF₂. The NMR spectrum confirmed this, and disclosed the presence of a proton attached to a CF group. On this evidence the structure was deduced to be CF₃CFHO CF₂CF₂CF=CF₂.

ii. - By pyrolysis of perfluoro-2-methyl-3-oxaocanedioyl fluoride. - In an effort to apply the apparently facile decomposition of simple acid fluorides to olefins having one less carbon atom, as claimed in the patent literature,¹⁵ to the problem of preparing perfluoro-3-oxaheptadiene-1,6, perfluoro-2-methyl-3-oxaocanedioyl fluoride was passed over Na₂SO₄ at elevated temperature. The expected reaction was:



The diacid fluoride was dripped from a funnel into a vaporizer, from which it entered a Vycor tube held at the desired temperature by a tube furnace. Products were collected in traps arranged in series, and cooled in ice water, Dry Ice, and liquid oxygen, respectively. The sodium sulfate was dried at reaction temperature in a stream of nitrogen for one hour prior to introduction of the diacid fluoride; the nitrogen purge was maintained throughout the first attempt only. Table VI summarizes the results obtained.

An infrared spectrum of the diacid fluoride taken for Run 1 showed the presence of some acid; the recovered diacid fluoride did not show these absorptions.

TABLE VI

Pyrolysis of $\text{FCOCF}(\text{CF}_3)\text{O}(\text{CF}_2)_4\text{COF}$

<u>Run</u>	<u>Rxn Temp.</u>	<u>Diacid Fluoride</u>		<u>Diene</u>	<u>Conversion</u>	<u>Yield</u>	<u>Other Products</u>
		<u>Starting</u>	<u>Recovered</u>				
1	300°	34 g.	28 g.	trace ^a	18%	0	SiF_4
2	320°	42 g.	34 g.	trace ^a	20%	0	SiF_4
3	320°	14 g.	9 g.	trace ^a	30%	0	SiF_4
4 ^b	350°	24 g.	14 g.	trace ^a	40%	0	SiF_4

- (a) Total contents of LOX-cooled trap gave enough material for one gas phase infrared spectrum which showed the absorptions expected of the product, along with others.
- (b) In Run 4 only, the tube was arranged vertically in an effort to improve contact between vapors and solid Na_2SO_4 .

C. Linear Polymers

1. Polyanhydrides

a. Polyadipic anhydride

A solution of 10 g. (34.5 mmoles) of perfluoroadipic acid in 20 ml. of acetic anhydride was heated under reflux for 24 hours. When the excess acetic anhydride was stripped off in vacuo, only an intractable black, tarry residue remained.

b. Tetrafluoroterephthalic anhydride

A solution of 20 g. (80 mmoles) of tetrafluoroterephthalic acid in 50 g. of acetic anhydride was refluxed for 24 hours. Upon stripping off the acetic anhydride in vacuo, a black syrup remained which was not investigated further.

c. Perfluoro-2-methyl-3-oxaoctanedioic anhydride

A mixture of 30 g. (80 mmoles) of perfluoro-2-methyl-3-oxaoctanedioic acid and 15 g. (150 mmoles) of acetic anhydride was placed in a still pot under a Vigreux column with a fraction cutter attached. Heat was applied to the pot, and distillate taken over when the head reached 118°. When no more acetic acid could be driven off, the residue was heated for four hours in vacuo, to remove excess acetic anhydride. There remained only a black syrup which could not be characterized.

2. Polyesters from gem-Diols

a. Polymerizations

Heptafluorobutyraldehyde hydrate (ca. 95% pure by GLC) was added slowly to tetrafluoroterephthaloyl chloride at 40°C. After an hour, a small amount of ammonium sulfate was added and the temperature raised to 90°C. After 2 1/2 days under reflux at about 90°C, there was no discernible evidence for polymerization.

To 4.0 g. (0.015 mole) of tetrafluoroterephthaloyl chloride in 3 g. (0.038 mole) of pyridine there was added 4.0 g. (0.019 mole) of heptafluorobutyraldehyde hydrate. The temperature was slowly raised to 80° with stirring. The material in the reaction vessel became steadily blacker and thicker; at 24 hours it had solidified. An infrared spectrum showed no major difference from tetrafluoroterephthaloyl chloride.

An aqueous solution of 13 g. (0.11 mole) of trifluoroacetaldehyde hydrate was covered with a benzene solution of 17 g. (0.04 mole) of tetrafluoroterephthaloyl chloride at room temperature. When no polymer film was noted at the interface after one hour, the mixture was transferred to a blender and agitated at slow speed (ca. 1000 rpm) for ten minutes. A mustard-colored precipitate was obtained, which was shown by its infrared spectrum and melting point to be identical with the starting acid chloride.

b. Monomer synthesis

Tetrafluoroterephthaloyl chloride was prepared from 5 g. (21 mmoles) of tetrafluoroterephthalic acid and 5 g. (42 mmoles) of thionyl chloride in the presence of a few drops of pyridine. The product was freed of SO_2 and HCl by warming under vacuum.

3. Miscellaneous

a. Polyethers by a
Williamson-type synthesis

Disodium salt of hexafluoropentanediol. - Hexafluoropentanediol (50 g., 0.24 mole) and sodium methylate (26 g., 0.48 mole) were mixed thoroughly and heated in the absence of solvent for five days at 75° in vacuo. Ten grams (0.31 mole) of methanol was recovered in a LOX-cooled trap. On the fifth day the pot charge exploded on contact with the atmosphere.

b. Reaction of $\text{C}_3\text{F}_7\text{I}$ with O_2

To a 60 x 300 mm Pyrex reactor was added 25 g. (0.08 mole) of $\text{C}_3\text{F}_7\text{I}$. While irradiating the iodide with a 450-watt Hanovia 679A UV lamp for one hour, 0.05 mole of O_2 was passed through the reactor. At the end of this period GLC analysis of the reaction mixture (1/8" x 6', 10% Silicone Rubber on 80-100 mesh Chromatoport, 30°C) showed a single major peak which corresponded to the retention time for $\text{C}_3\text{F}_7\text{I}$. An infrared spectrum of the crude product showed a strong maximum at 5.6 microns and a broad maximum between 3.1 and 3.5 microns. A water wash of the reaction product was highly acidic.

- c. $\text{FOC}(\text{CF}_2)_4\text{OCF}(\text{CF}_3)\text{COF}$ (A),
 $\text{FOCCF}(\text{CF}_3)\text{O}(\text{CF}_2)_5\text{OCF}(\text{CF}_3)\text{COF}$ (B),
and $\text{FOC}(\text{CF}_2)_4\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{COF}$ (C)

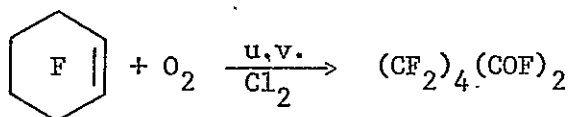
To a 2-liter, 3-neck flask was added 80 g. (0.53 mole) of CsF . The flask was evacuated, then heated for 72 hours at $290-300^\circ$.

The flask was then cooled to room temperature and 200 ml. of freshly distilled diglyme was added. The flask was then equipped with a gas inlet tube, a pressure gauge, and the ground glass connectors were securely clamped to the flask. While stirring with a magnetic stirrer, 199 g. (0.73 mole) of perfluoroglutaryl fluoride was added. The reaction mixture was cooled to 0° and 252 g. (1.54 moles) of hexafluoropropylene oxide was added at a pressure of 4 to 5 psi. After addition of the epoxide, which required four hours, the reaction mixture was transferred to a separatory funnel, and the diglyme decanted. Distillation through a 1-meter column packed with 3/16" glass helices gave the following cuts. Purity of each cut was determined chromatographically on a 6' column with 10% PFOX (fluorocarbon ether) on HMDS treated Chromosorb W and the temperature programmed at 10°/min. from ambient to 190°C.

<u>Cut</u>	<u>Weight</u>	<u>b.p./mm</u>	<u>Product</u>
1	56	49-60°/760	Mostly C ₃ F ₇ OCF(CF ₃)COF
2	13	60-106°/760	-
3	47	106-109°/760	84% A
4	49	59°/17	74% B, 10 to 15% C
5	48	90-102°/24-29	Higher oligomer

Infrared spectra of A and B are shown in Figures 10 and 11.

d. Preparation of perfluoroadipoyl fluoride



The method of Baranauckas and Golfund¹⁶ was used in this oxidation. To a 60 x 300 mm Pyrex reactor equipped with a bottom gas inlet tube, an upper gas exit tube, and a water-cooled UV immersion well, was added 300 g. (1.15 moles) of perfluorocyclohexene. The gas exit tube was connected to a LOX cooled trap. The reactor was immersed

in an ice bath and while irradiating the cyclohexene with a 450-watt Hanovia 670A UV lamp, a mixture of 153.5 ml./min. of O₂ and 50 ml./min. Cl₂ was bubbled through the cyclohexene. After 3 1/4 hours the O₂ rate was doubled and the reaction was continued until 4.14 moles of O₂ and 0.641 mole of Cl₂ had been added.

The crude product was rectified on a 60-cm. vacuum jacketed distillation column packed with 6 mm. Rashig rings, yielding the following distillation cuts:

<u>Cut</u>	<u>Temperature</u>	<u>Wt. g.</u>
1	53-71	95.0
2	71-71.9	78.1
3	73-94	3.5

Infrared analysis indicated Cut 2 to be pure perfluoroadipoyl fluoride. An infrared spectrum of this product is shown in Figure 12.

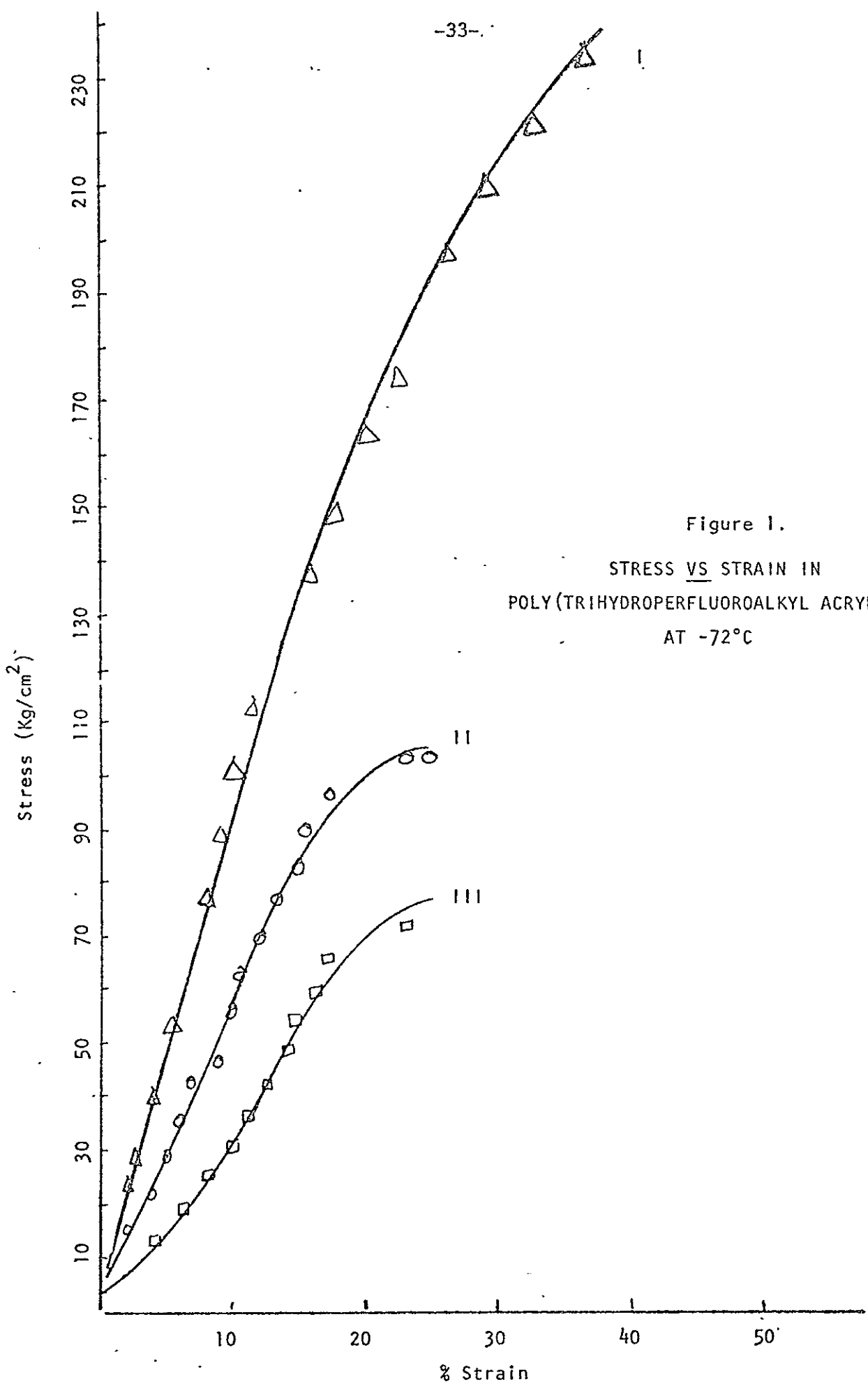
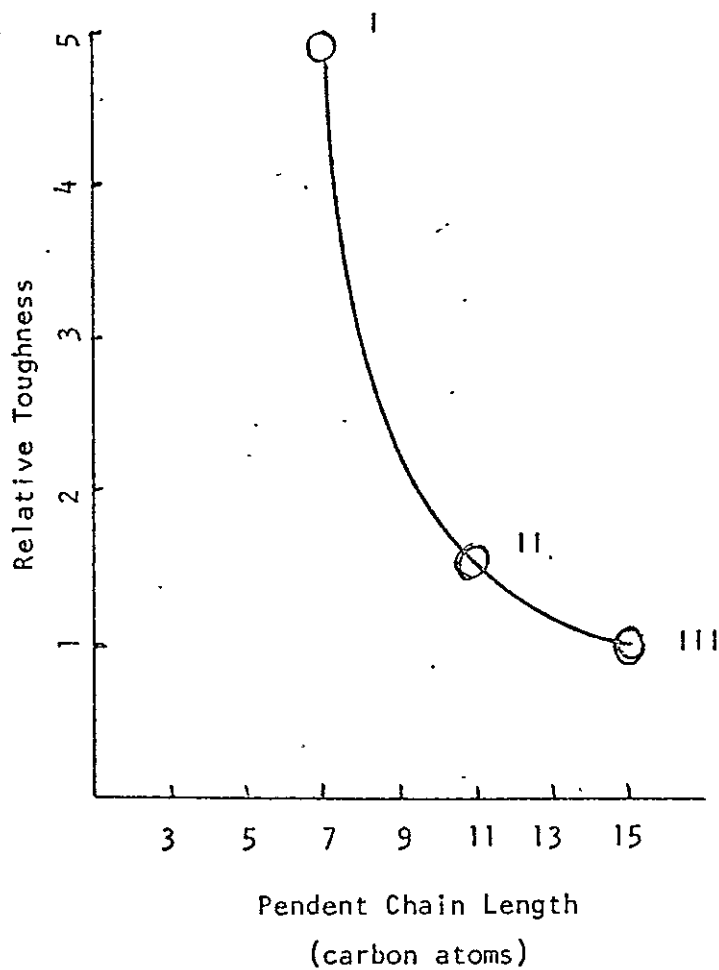


Figure 1.
STRESS VS STRAIN IN
POLY(TRIHYDROPERFLUOROALKYL ACRYLATES)
AT -72°C

Figure 2.

TOUGHNESS VS PENDENT CHAIN LENGTH
IN POLY(TRIHYDROPERFLUOROALKYL ACRYLATES)



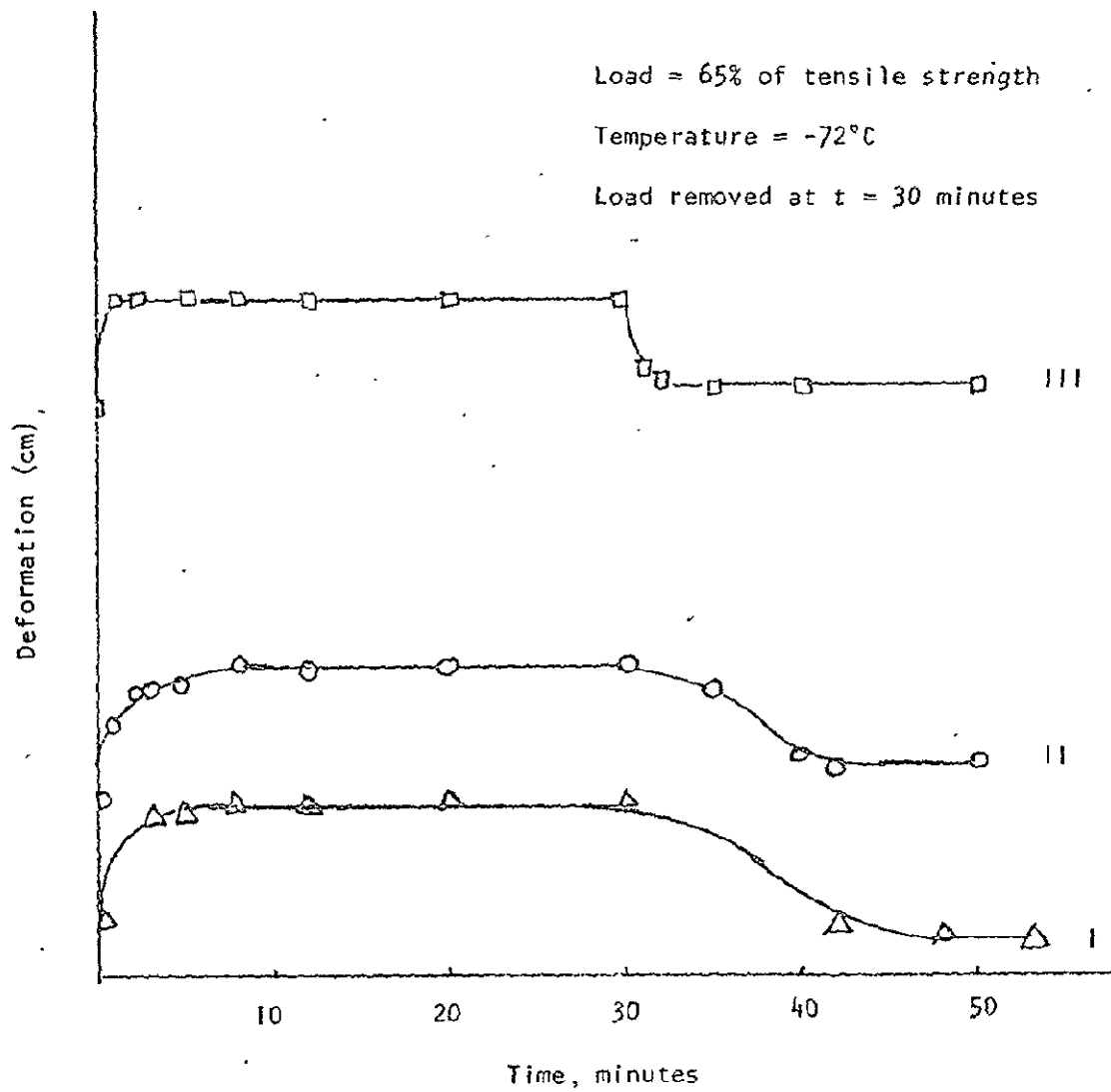


Figure 3.

Resiliency of
Poly(trihydroperfluoroalkyl acrylates)

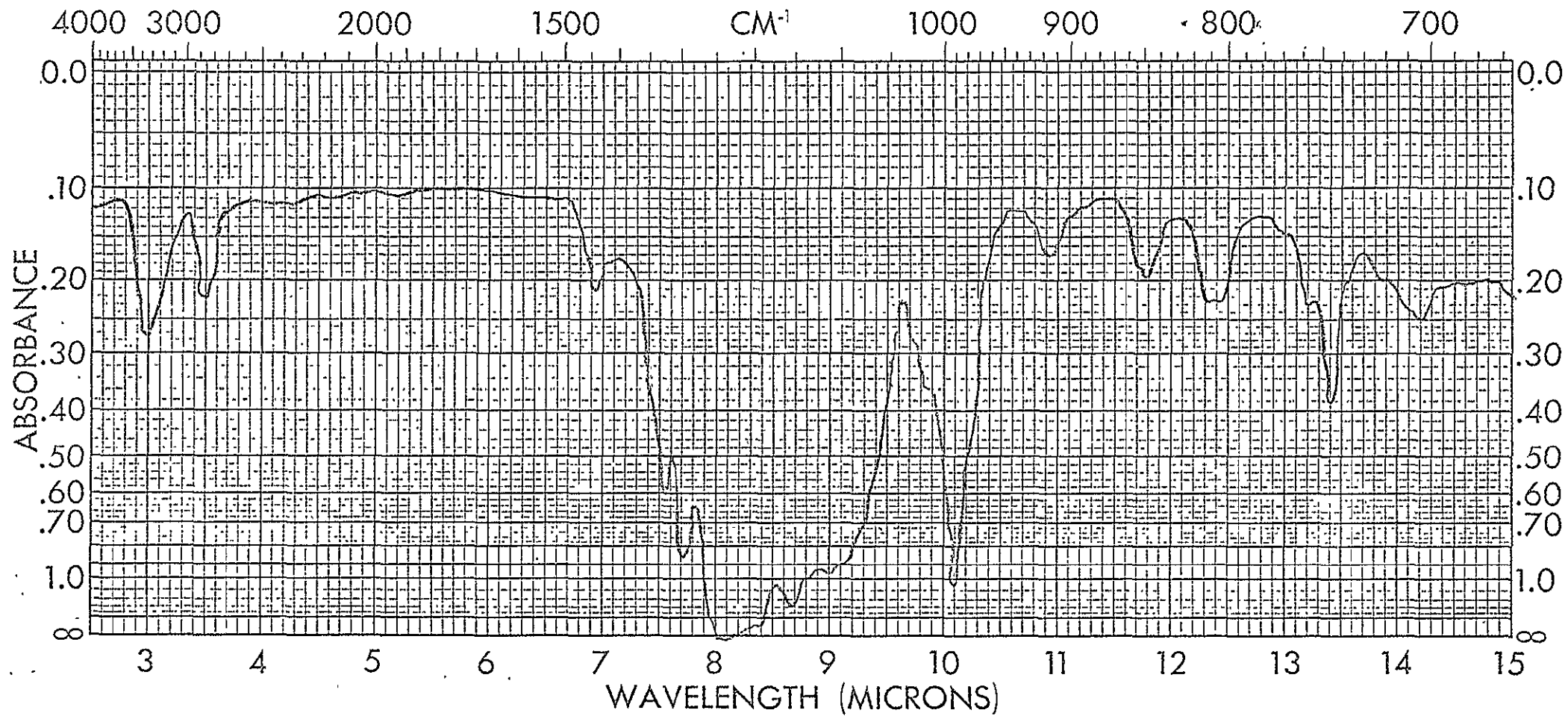


Figure 4.

Infrared Spectrum of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CH_2OH$

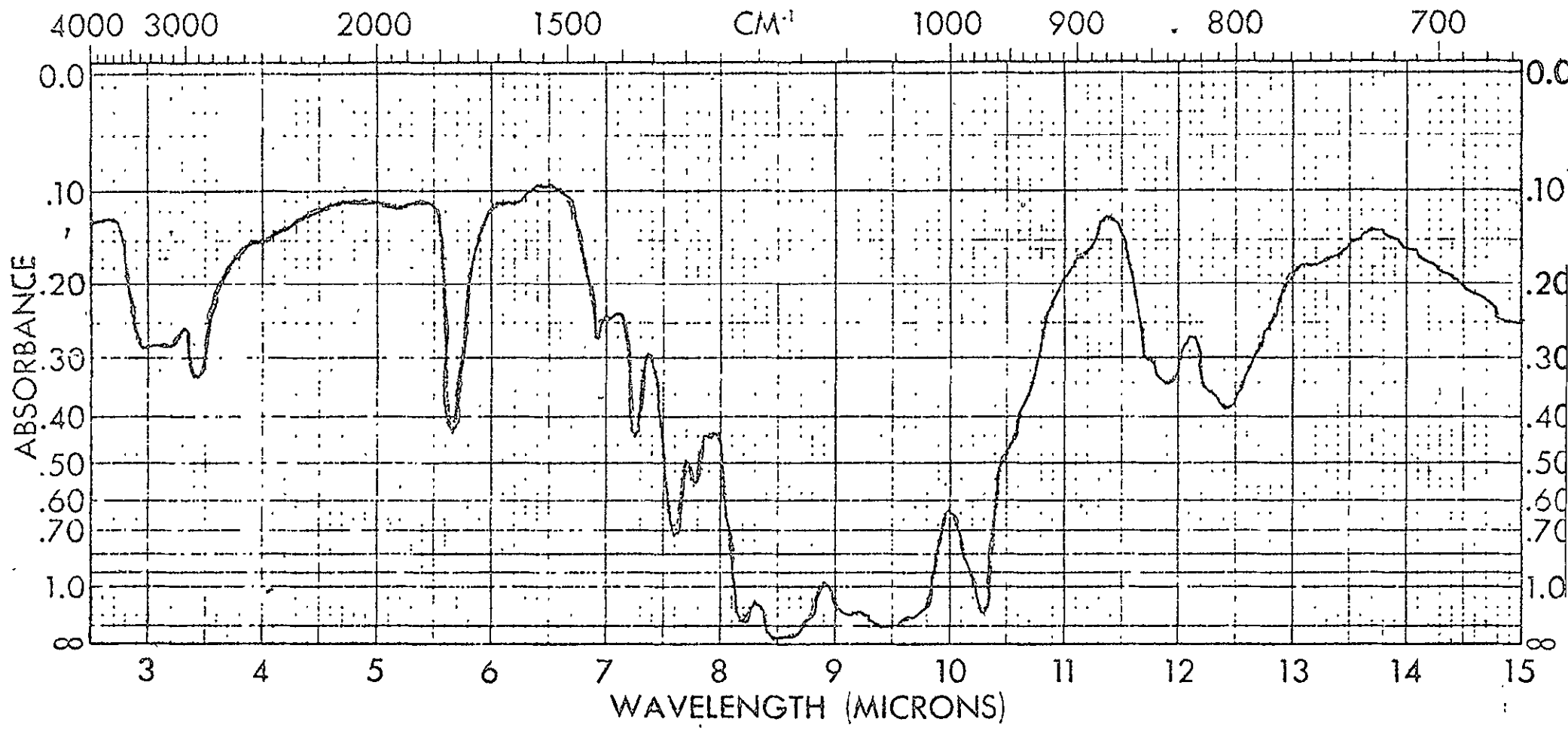


Figure 5.

Infrared Spectrum of a Liquid Polymer of $(CF_2)_3(CHO)$ (Liquid)

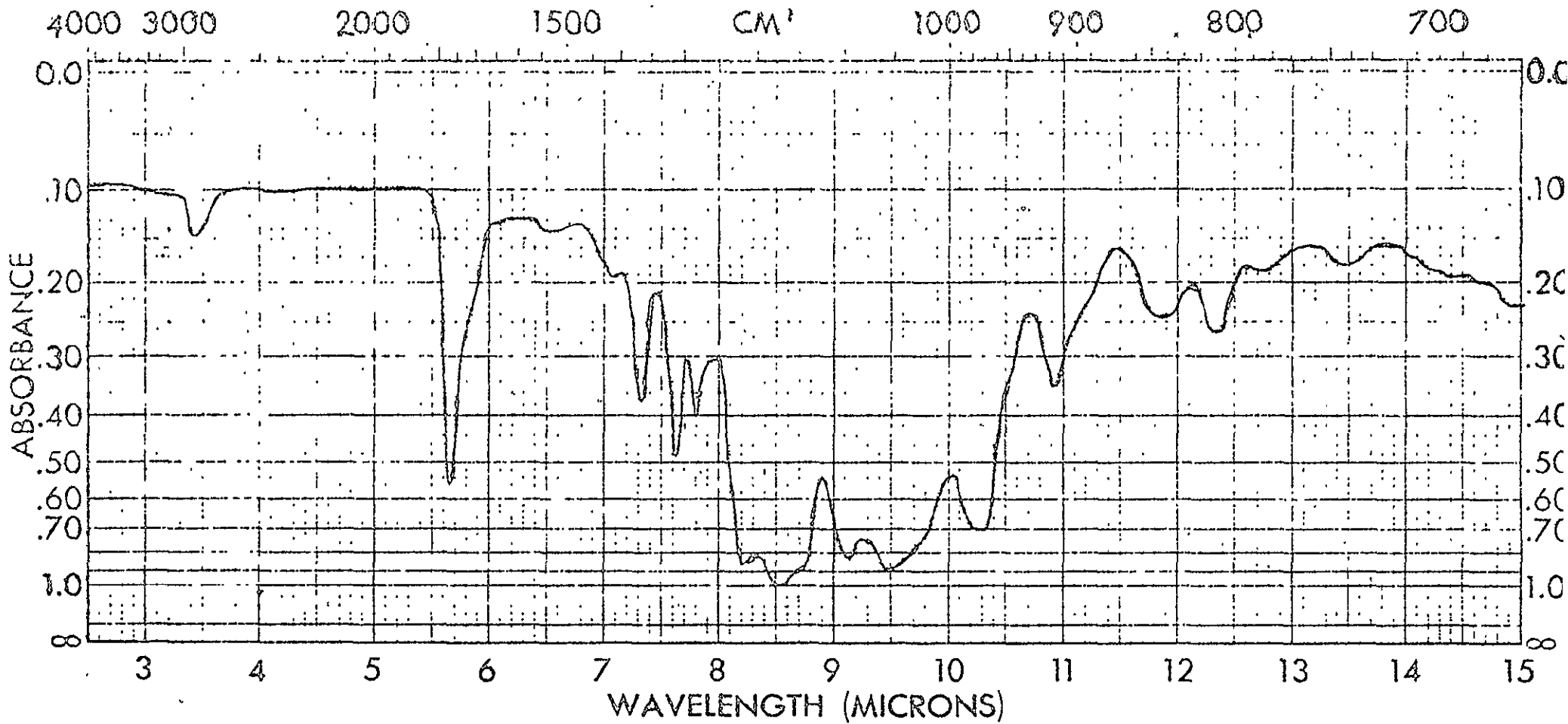


Figure 6.

Infrared Spectrum of a Liquid Polymer of $(CF_2)_3(CHO)$
After Acylation (Liquid)

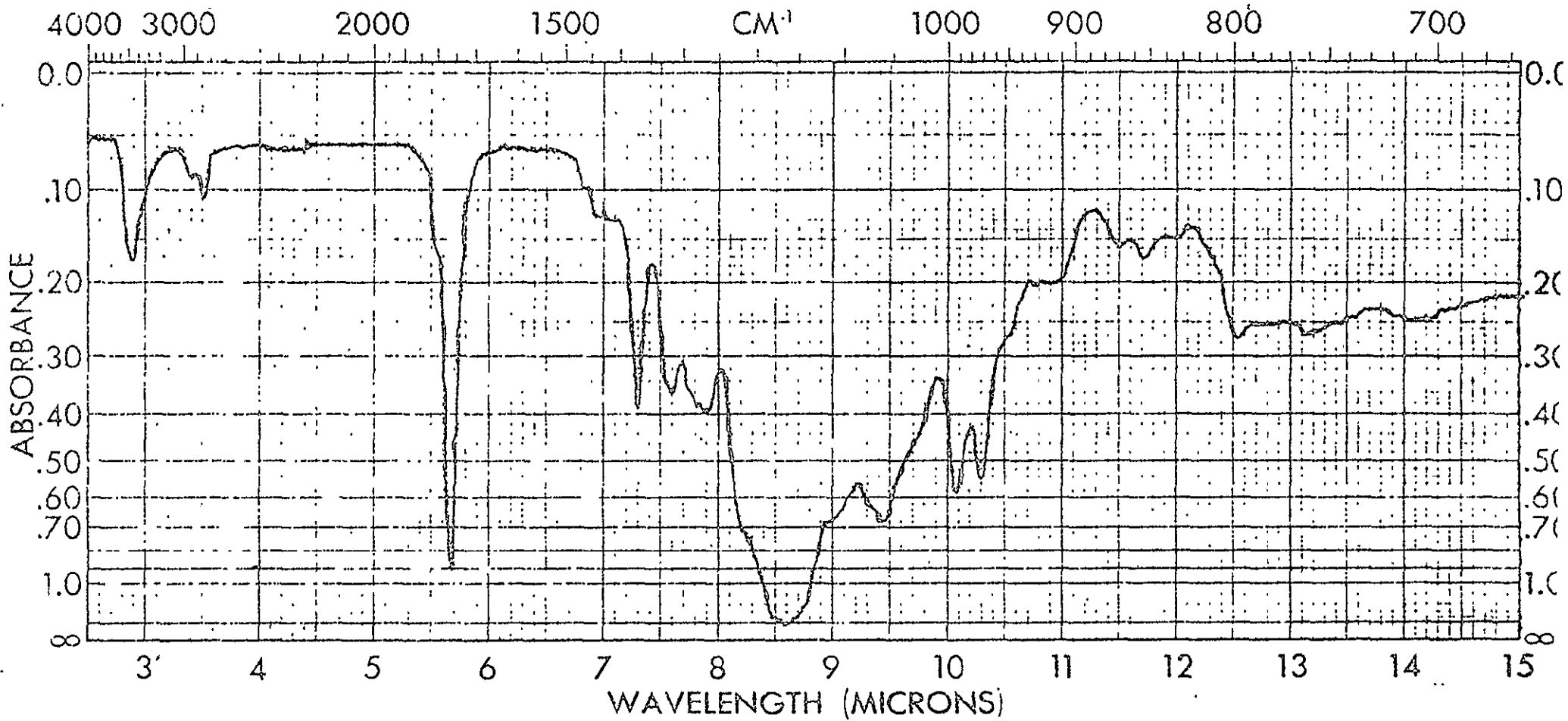


Figure 7.

Infrared Spectrum of $(\text{CF}_2)_3(\text{CHO})_2$ (Liquid)

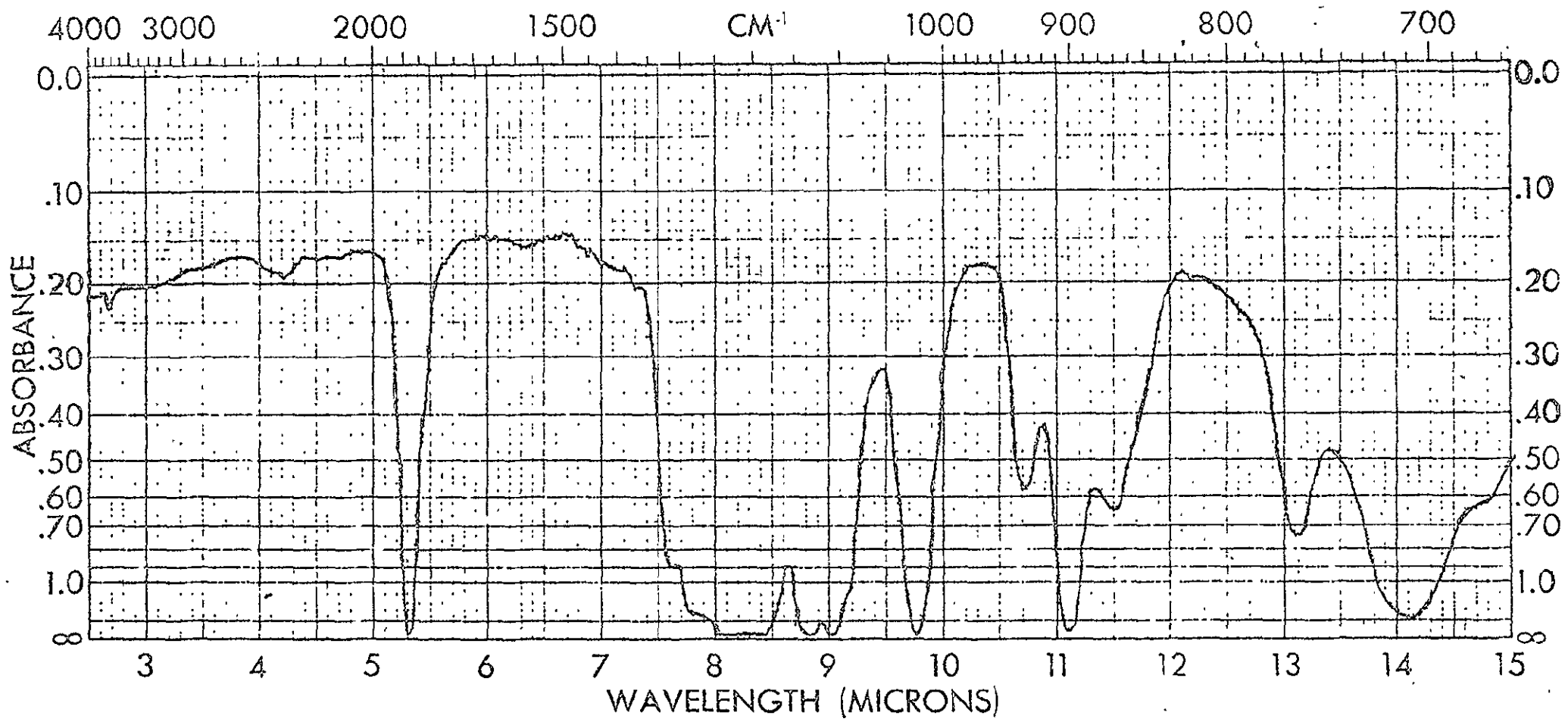


Figure 8.

Infrared Spectrum of Perfluoroglutaryl Fluoride (Gas)

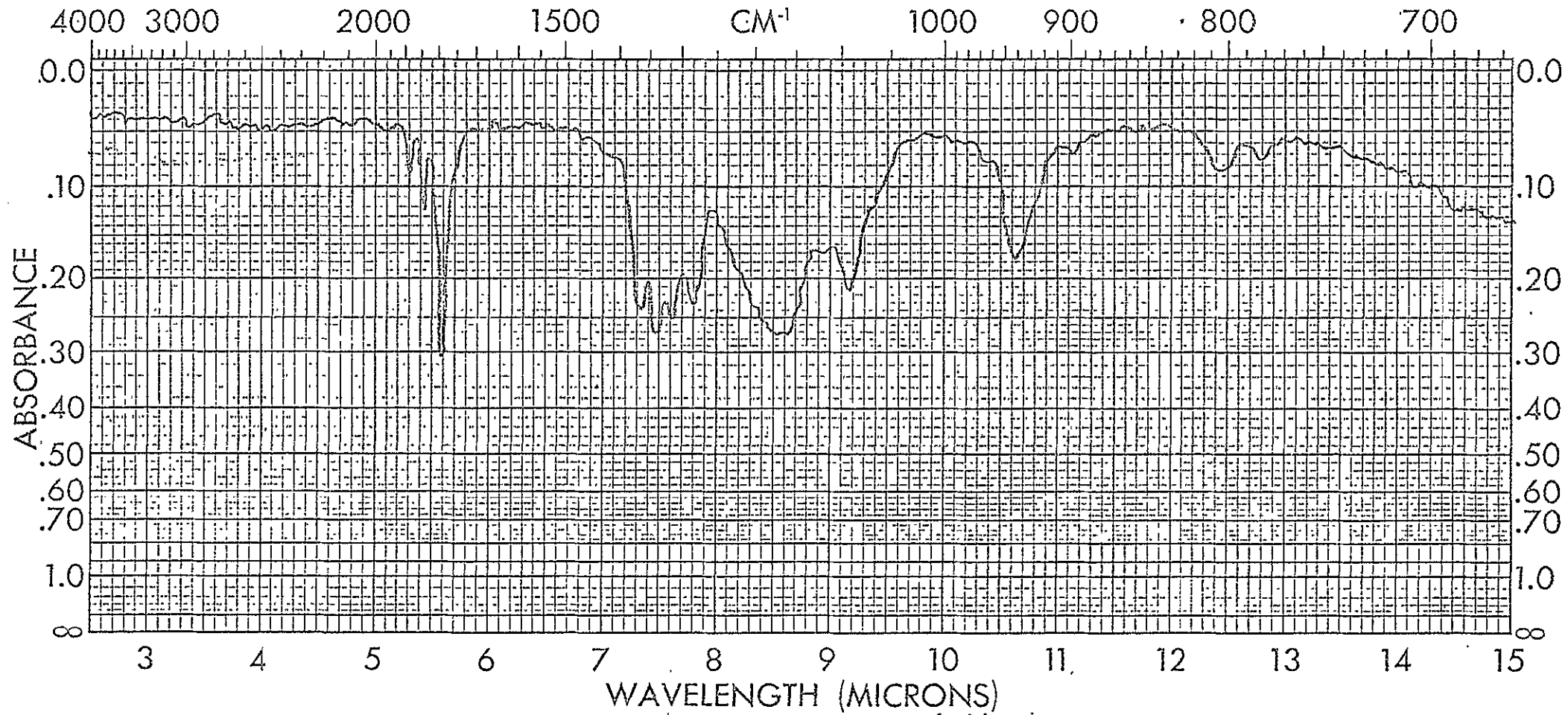


Figure 9.

Infrared Spectrum of

Presumed $\text{CF}_2=\text{CFO}(\text{CF}_2)_2\text{CF}=\text{CF}_2$

Actual $\text{CF}_3\text{CFHO}(\text{CF}_2)_2\text{CF}=\text{CF}_2$

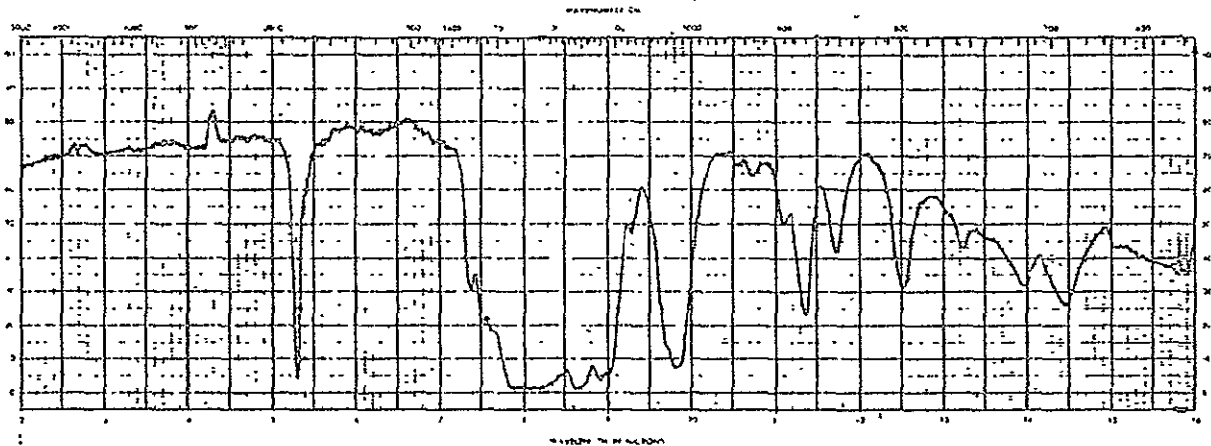


Figure 10. Infrared Spectrum of $\text{FC}(\text{CF}_2)_4\text{OCF}(\text{CF}_3)\text{CF}$
(Gas, 5 mm)

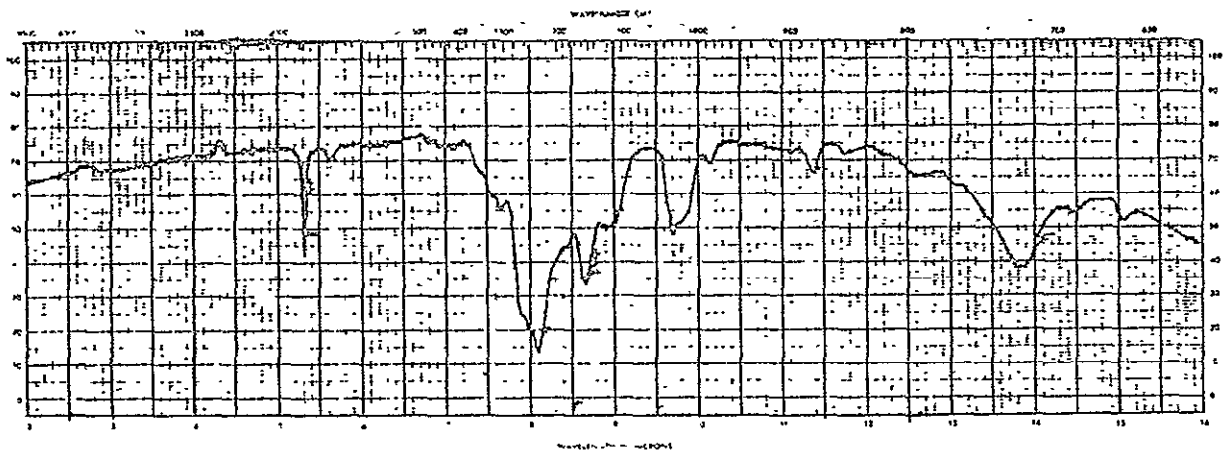


Figure 11. Infrared Spectrum of $\text{FCCF}(\text{CF}_3)\text{O}(\text{CF}_2)_5\text{OCF}(\text{CF}_3)\text{CF}$
(Gas, 2 mm)

APPENDIX

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Report reviews properties of acrylics, fluoroacrylates, fluorocarbons, fluorosilicones and others.

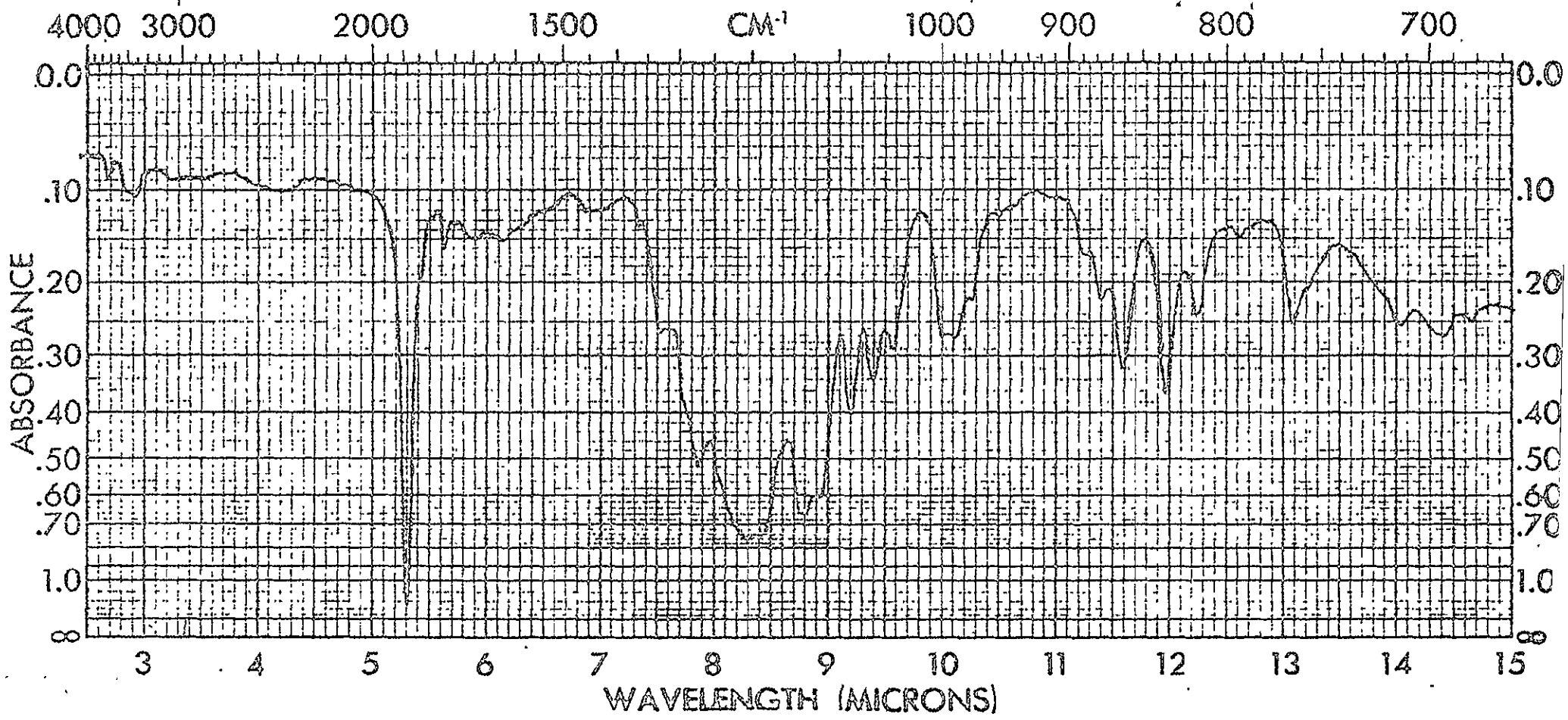


Figure 12.

Infrared Spectrum of $\text{FOC}(\text{CF}_2)_4\text{COF}$ (Liquid)

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INTRODUCTION

This bibliography was prepared from references obtained mainly from Chemical Abstracts but contains, in addition, references taken from a number of primary sources. Major emphasis was placed on references to fluorine-containing monomers and polymers and to thermal properties of all classes of polymers.

In past Annual Summary Reports references covered from 1957 to the date of the report. For the sake of brevity and to eliminate the need for duplicating earlier references, the present bibliography covers only the period of this report - June 1967 through May 1968.

As in the past, the great number of references in the categories covered necessitated selecting references which were considered to be of most significance to the present investigation. The choice of references is somewhat subjective, but it is felt that the cross-section given is a useful representation of the literature to date.

The references listed have been categorized with respect to the general subdivisions shown below. Once again for the sake of brevity, no cross-referencing has been done; hence, where a paper was concerned with more than one sub-division the reference, in general, was placed in the category of greatest importance. Copolymers were placed in the earliest listed monomer category with the exception of the vinyl ethers and thioethers, the copolymers of which were included under the main heading of vinyl ethers.

INDEX TO APPENDIX

	<u>Page</u>
I. Reviews on Fluorine-Containing Polymers.....	3a
II. Fluorine-Containing Vinyl Polymers.....	4a
A. Vinyl Fluoride.....	4a
B. Vinylidene Fluoride.....	4a
C. Tetrafluoroethylene.....	5a
D. Dienes.....	5a
E. Vinyl Ethers and Thioethers.....	5a
F. Miscellaneous Polymers.....	6a
III. Condensation Polymers.....	6a
A. Fluorine-Containing Polysiloxanes.....	6a
B. Fluorine-Containing Polyesters.....	7a
IV. Polymers with Heteroatom Chain.....	7a
A. C-O.....	7a
B. C-S.....	7a
C. N-O.....	8a
D. Miscellaneous.....	9a
V. Thermal Properties of Polymers.....	9a
VI. Polymerization Systems.....	14a
VII. Fluorine-Containing Monomer Synthesis and Miscellaneous Reactions.....	15a
VIII. Vulcanization of Fluorine-Containing Polymers.....	18a

II. Fluorine-Containing Vinyl Polymers

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