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AFML-TR-70-153

SYNTHESIS OF ELASTOMERIC POLYMERS, POLYMER INTERMEDIATES AND CURING AGENTS

Harold R. Ringler
Eugene C. Stump

PENINSULAR CHEMRESEARCH
GAINESVILLE, FLORIDA

TECHNICAL REPORT AFML-TR-70-153

August 1970

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FOREWORD

This report was prepared by Peninsular ChemResearch, Gainesville, Florida, under Contract No. F33615-68-C-1349, Project No. 7340 "Nonmetallic and Composite Materials," Task No. 734005, "Elastomeric and Compliant Materials." This work was administered by the Elastomers and Coatings Branch (MANE), Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, with Mr. Tom L. Graham as Project Engineer for the Air Force.

This Technical Report covers work from 1 March 1968 through 28 February 1970.

Personnel who have contributed to this research are Dr. Eugene C. Stump, Project Director; Harold R. Ringler and Howard Holtzendorf, Research Chemists; Dr. T. W. Brooks, Director of Development; Marvin Hamlin and Joe Dykes, Technicians. Analytical services were performed under the direction of Dr. Dale A. Warner, Director of Analytical Services. Dr. Paul Tarrant and Dr. George B. Butler are acting consultants.

This report was released by the authors February 1970.

This technical report has been reviewed and is approved.

W. P. Johnson, Chief
Elastomers and Coatings Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

Preparation of both high and low molecular weight triazine polymers was investigated. Block copolymers of the ABA type containing polyethylene B blocks and A blocks of polyisoprene and polystyrene were prepared. A nitroso terpolymer containing CF_3NO, $CF_2{=}CF_2$ and $CF_2{=}CFOCH(CH_3)_2$ was prepared.

Fluorine-containing diepoxides were prepared by reaction of fluorine-containing diols with an epihalohydrin and by direct oxidation of a perfluorodiolefin using a halogen-sensitized photochemical reaction.

Fluoroalkylmethylchlorosilanes were prepared by reduction of the corresponding dichlorosilane to the fluoroalkylmethylsilane followed by reaction with silver chloride.

A perfluorinated dinitroso compound, $CF_3CF(NO)(CF_2)_4CF(NO)CF_3$, was prepared by addition of nitrosyl fluoride to perfluorooctadiene-1,7. Several perfluorinated diisocyanates containing ether oxygen atoms were prepared from their corresponding diacid fluorides using the Curtius reaction.

The reaction of perfluoroisobutylene oxide with several perfluorinated acid fluorides was investigated.

The synthesis of perfluoroisobutyronitrile and perfluorosebaconitrile is described.

4-Cyanoperfluorobutyryl chloride was prepared by a new method.

A wide variety of intermediates was prepared including perfluoroisobutylene epoxide, perfluorosuberyl fluoride and its dimethyl ester, pentafluoronitrobenzene, perfluorooctadiene-1,7, perfluoroisobutyryl fluoride and its amide, and 4,4'-dihydroxyoctafluorobiphenyl.

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I. INTRODUCTION

The objective of this contract is to supply otherwise unobtainable monomers, polymers, curing agents and certain chemical intermediates to the Air Force Materials Laboratory or its contractors in support of new and improved elastomer development programs.

Polymer samples are characterized by sufficient analytical data to reflect composition, molecular weight, monomer block lengths of block copolymers and other pertinent data as applicable. Monomers, curing agents, and intermediates are characterized by usual methods including elemental, infrared, and NMR analysis.

A schedule of materials shipped to the Air Force Materials Laboratory is given in Appendix I. Infrared spectra and NMR data on certain compounds and polymers are given in Appendix II and III, respectively.

II. DISCUSSION

A. Triazine Polymers

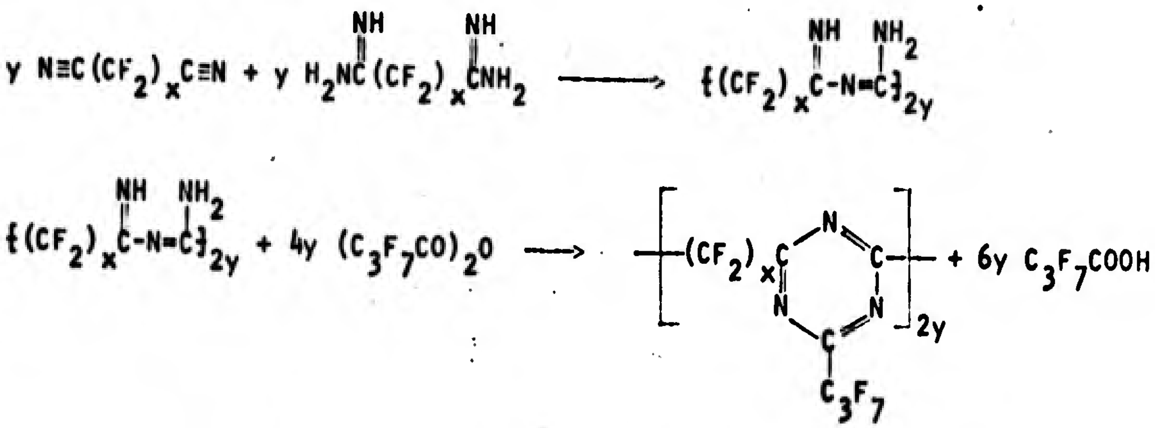
1. Polymer Synthesis

Perfluorinated triazine polymers consisting of a repeating unit containing a triazine ring and a perfluoroalkylene group have been of considerable interest to the Air Force because of their elastomeric nature, high thermal stability and chemical resistance.

First prepared and reported by Brown[1] at the University of Florida, the synthesis and cross-linking of triazine elastomers has been extensively investigated by workers at Hooker[2], Dow Corning[3], and the Air Force Materials Laboratory[4,5].

The initial objective of our work in this area was to consist of a study of reaction variables leading to an optimization of conditions for the reproducible preparation of high molecular weight triazine elastomers. Due to the requirements for triazine polymer which would be suitable for use as a potting compound, however, emphasis was shifted to the preparation of low molecular weight, fluid triazine polymer containing terminal and pendent nitrile groups which could be used for crosslinking.

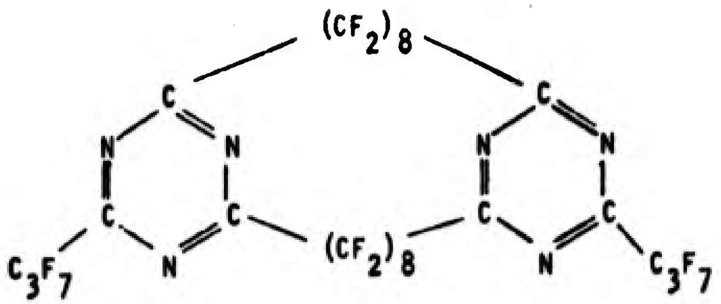
Preparation of high molecular weight triazine polymer was investigated using the method developed by workers at Hooker[2]. This procedure consists of the slow addition of powdered diamidine to a concentrated solution of dinitrile at room temperature to form an imidoylamidine polymer. As the polymerization progresses to increasingly higher molecular weights, with attendant viscosity increases, more solvent is added to keep the viscosity within tolerable limits. The last amounts of diamidine are added in increasingly smaller increments because of the decreasing rate of reaction with the nitrile end groups. Toward the end of the polymerization large polymer chains are being coupled by diamidine units which result in very large molecular weight increases. The imidoylamidine polymer can then be converted to the triazine polymer by the addition of the imidoylamidine polymer solution to perfluoroalkanoic anhydride[6]. These reactions may be summarized by the following equations.



$$y\ N{\equiv}C(CF_2)_xC{\equiv}N + y\ H_2N\overset{NH}{\overset{\|}{C}}(CF_2)_x\overset{NH}{\overset{\|}{C}}NH_2 \longrightarrow \{(CF_2)_x\overset{NH}{\overset{\|}{C}}{-}N{=}\overset{NH_2}{\overset{|}{C}}\}_{2y}$$

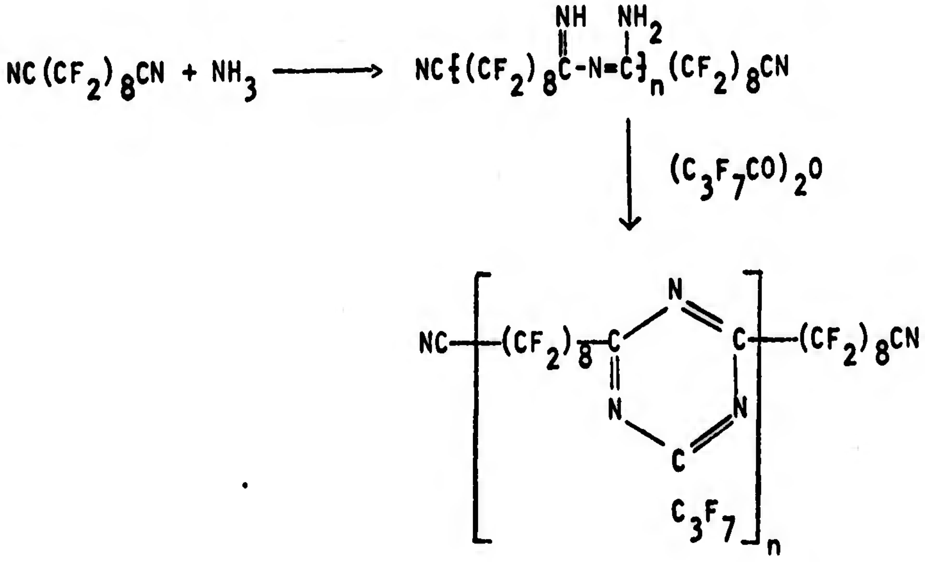
By this method workers at Hooker[2] were able to attain an imidoylamidine polymer molecular weight of 104,000 (intrinsic viscosity 1.10) using perfluorosuberonitrile and perfluorosuberamidine in dimethoxyethane (glyme) solvent. The reaction required 37 days. Later larger scale reactions were run using perfluorosebaconitrile and perfluorosebacamidine to prepare the imidoylamidine polymer for conversion to the triazine polymer using trifluoroacetic and perfluorobutyric anhydrides. Triazine polymer molecular weights of 90,000 to 200,000 were reached. Tensile strengths up to 2,490 psi were reported.

Imidoylamidine polymerization in dilute media was one of the reaction variables explored in the earlier work.[2] Using perfluorosebaconitrile and the derived diamidine with perfluorobutyric anhydride a cyclic, volatile triazine compound was isolated in 20% yield having the following proposed structure. For this reason this method was believed to be unsuitable.



In another variation, the reaction temperature was increased to 50-55°C. The molecular weight of the resulting imidoylamidine polymer was about half that attained in the analogous reaction run at room temperature.

The direct synthesis of imidoylamidine polymer by the addition of gaseous ammonia to dinitrile offered attractive possibilities in simplification of the reaction in by-passing the troublesome synthesis of the diamidine. However, it was found that when 90% of the theoretical amount of ammonia was added to the dinitrile in glyme solvent, the imidoylamidine polymer gelled and became insoluble. This method was attempted, in pyridine solvent, for making high molecular weight polymers. There was considerably less gel formation but there was difficulty in removing the pyridine and the derived triazine polymers had poor thermal stability. The addition of anhydrous ammonia to perfluorosebaconitrile in glyme solvent has been used successfully to prepare low molecular weight imidoylamidine precursor polymers of up to about 20 monomer units.



$$NC(CF_2)_8CN + NH_3 \longrightarrow NC\{(CF_2)_8\overset{NH}{\overset{\|}{C}}\text{-}N\text{=}\overset{NH_2}{\overset{|}{C}}\}_n(CF_2)_8CN$$

Still another approach, to avoid the diamidine synthesis and attendant deleterious evolution of ammonia accompanying its use, was an imidoylamidine polymerization using dinitrile and "prepolymer." Dinitrile was treated with a slight excess of ammonia in glyme to form a low molecular weight amidine terminated prepolymer. The polymer chain was then developed by the controlled addition of more dinitrile until the desired molecular weight was obtained and was finally nitrile terminated by the rapid addition of excess dinitrile. Some problems in control of the reaction were encountered but this method was reported as promising for the preparation of high molecular weight polymers.

In the initial work with imidoylamidine polymerization in this laboratory, perfluorosebacamidine was added to perfluorosebaconitrile in glyme solvent. This polymerization proceeds very slowly, since the longer chain perfluorosebacamidine is less reactive than the shorter chain diamidines. In an effort to reproduce the imidoylamidine polymerization of Dorfman, et al.[2], it was anticipated that about 97% of the stoichiometric amount of diamidine should be added, dependent upon the solution viscosity. This deficiency of diamidine should result in a nitrile terminated polymer. Amidine end groups could have a deleterious effect upon the polymer by hydrolysis to amide groups since the ammonia evolved would result in triazine degradation. After 49 days only 91.7% of the amidine had been added. At this time, due to the extremely slow consumption of the diamidine, the reaction was stopped and the imidoylamidine cyclized with excess perfluorobutyric anhydride. Properties of the polymer (Exp. No. 1105.40) are shown in Table I.

In order to determine the most suitable conditions for preparation of a low molecular weight, fluid triazine polymer suitable for potting applications, a series of experiments was carried out in which the dinitrile/diamidine ratio, solvent, and method of addition of diamidine were varied. Results are summarized in Table I (Exps. No. 1105.41-49.2).

Since nitrile termination is necessary to provide cross-linking sites in the potting compound (in addition to nitrile pendent groups which were to be added in later work), the ratio of dinitrile to diamidine was at least 2 and went as high as 5. No advantage was found in using ratios

TABLE I

Perfluoroalkylenetriazine Polymers[1]

Exp. No.	Dinitrile/ Diamidine Ratio	Solvents	Reaction Conditions	η_{red}[2]	(η)[3]	Mol. Wt.[4]	Appearance
1105.40	1.09/1	1,2-Dimethoxyethane	A	0.13	0.18	32,400	Brownish gum.
.41	2.0/1	1,2-Dimethoxyethane	B	0.03	0.03	2,840	Light tan, very viscous liquid.
.43	2.0/1	1,2-Dimethoxyethane	C	0.05	0.07	3,900	Brown, very viscous liquid.
.44	2.0/1	1,2-Dimethoxyethane	D	0.04	0.04	3,600	Dark brown, very viscous liquid.
.45	2.0/1	Dimethylformamide	E	0.10	0.10	7,360	Yellow, very viscous liquid.
.46	2.0/1	N-Methyl-2-pyrrolidone	E	-	-	-	Insoluble, brown solid.
.47	3.0/1	1,2-Dimethoxyethane	C	0.02	0.02	2,700	Light colored, free flowing liquid.
.48	4.0/1	1,2-Dimethoxyethane	C	0.02	0.03	2,820	Light colored, free flowing liquid.
.49.1	5.0/1	1,2-Dimethoxyethane	C	0.03	0.03	1,910	Light colored, free flowing liquid.
.49.2	2.0/1	1,2-Dimethoxyethane	C	0.03	0.03	2,230	Light colored, free flowing liquid.
.52	1.1/1	Dimethylformamide	E	.08	.08	32,400	Light yellow, clear gum.

---

(1) From perfluorosebaconitrile, perfluorosebacamidine, and heptafluorobutyric anhydride at ambient temperature.
(2) 0.50 g/100 ml. in hexafluoroxylene at 30.0°C.
(3) Hexafluoroxylene at 30.0°C.
(4) Measurement by vapor phase osmometer in hexafluoroxylene.

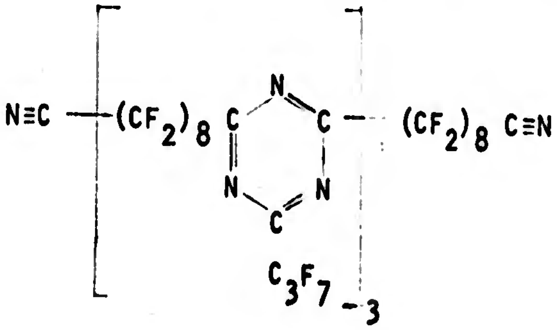
A Incremental powdered diamidine addition, 49 days reaction.
B Powdered diamidine added over 11 hours.
C Powdered diamidine added in one shot.
D Powdered diamidine added in one shot. 50% excess dinitrile added at end of polymerization.
E Diamidine dissolved in solvent and slowly added dropwise to pure dinitrile.

greater than 2 since all the samples appeared to be nitrile terminated (infrared analysis) and had very similar viscosities.

Three solvents were investigated. The most effective solvent was found to be 1,2-dimethoxyethane (glyme), which had been used extensively in the Hooker work[2]. The use of dimethylformamide in one experiment (1105.45) gave polymer which had an appreciably higher molecular weight than those prepared in glyme under the same conditions. For this reason, an attempt was made (1105.52) to prepare a high molecular weight triazine using a low nitrile to amidine ratio and a long period of addition of the diamidine solution. Although this single reaction did not produce a very high molecular weight polymer, the method may be worthy of further investigation as a route to high molecular weight triazine elastomers.

The effect of rate of diamidine addition to the dinitrile on the properties of the polymer was also investigated. Two methods were used, one in which the diamidine was added incrementally over 11 hours and the other in which the diamidine was added all at once. No advantage was observed in the use of incremental addition. Consequently, the single addition method is preferred because of the decreased manipulation involved.

The reaction conditions described in the preparation of 1105.49.2 appear to be suitable for the preparation of the desired low molecular weight polymer. This polymer has a reduced viscosity of 0.03 at 0.50 g/100 ml. in hexafluoroxylene at 30.0°C, an intrinsic viscosity of 0.03, and a molecular weight of 2230. It is quite fluid, has a light color, and was prepared in 78.8% conversion. This molecular weight corresponds to an average degree of polymerization of 2.76, a polymer of DP of 3.0 having the structure:



The polytriazine formed by reaction of two molecules of dinitrile with one molecule of diamidine would have a DP of 2.0 and a molecular weight of 1746; that formed from the reaction of three dinitriles and two diamidines would have a DP of 4.0 and a molecular weight of 3040. This suggests that 1105.49.2 is a mixture of the two with a predominance of the former.

A plot was made of the logarithms of the intrinsic viscosities vs the logarithms of the number average molecular weights, tabulated in Table I, to find if a linear relationship existed between the two. A good linear plot was not obtained, however, probably due to the precision in determining viscosity which can be obtained at these low molecular weights.

Due to a shift in emphasis to another area, this work was not pursued further.

2. Monomer and Intermediate Synthesis

a. Perfluorosebaconitrile

In the initial phase of the triazine elastomer synthesis it was necessary to prepare perfluorosebaconitrile as a starting material. With the availability of a high purity (99.95%) sample obtained from the Air Force Materials Laboratory, this work was later terminated.

Three synthetic routes from perfluorosebacic acid to the dinitrile, all involving diamide dehydration, were explored. In one route, the diacid was converted to the diacid chloride by reaction with thionyl chloride in ethyl acetate solvent using a reported[2] procedure. A good conversion to sufficiently pure diacid chloride without isolation was obtained. The reaction of the diacid chloride with liquid ammonia in methylene chloride solvent, however, produced a diamide product in low yield which was very difficult to purify. Dehydration of the diamide by intimate mixture and heating with phosphorous pentoxide resulted in good conversion to perfluorosebaconitrile in all cases. The overall conversion from diacid to dinitrile was 37.6%.

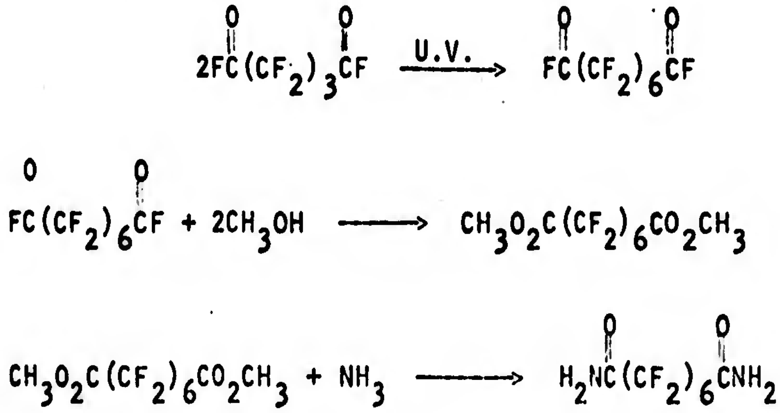
In a second sequence of reactions, the diacid was first converted to the dimethyl ester. The diacid was mixed with dry methanol and a large amount of concentrated sulfuric acid and stirred for 2 hours without heating. The product (92.3% pure) was distilled and collected at 132-150°C at 2.8 mm in a conversion of 54%. These results compare unfavorably with those obtained in the procedure followed[8], i.e., 99% pure dimethyl ester boiling at 129-145°C (12 mm) in a conversion of 89.5%. A possible cause for this difference in results may be the impurity of the perfluorosebacic acid used in our work. The dimethyl ester was easily converted to the diamide of very high purity in high conversion by reaction with liquid ammonia in dry ethyl ether. The overall conversion from diacid to dinitrile of 15.7% is not completely indicative of the utility of this route.

A third synthetic route involved the preparation of the diacid chloride from the diacid as before. The diacid chloride was refluxed with dry methanol 20 hours to form the dimethyl ester (78.3% purity) in 79% conversion. Some difficulty with sulfur contamination was encountered. The product was used to form the diamide and then dinitrile in an overall conversion of 45%.

The products obtained from the three reactions were combined and distilled from P_2O_5 to give a 99.7% pure fraction boiling at 147.8-148°.

b. Perfluorosuberonitrile

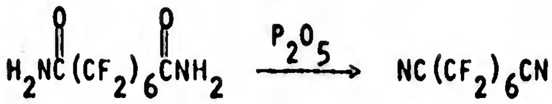
Prior to the availability of perfluorosebaconitrile the synthesis of the shorter chain perfluorosuberonitrile was investigated. The following sequence of reactions was proposed.



$$2F\overset{\overset{O}{\|}}{C}(CF_2)_3\overset{\overset{O}{\|}}{C}F \xrightarrow{U.V.} F\overset{\overset{O}{\|}}{C}(CF_2)_6\overset{\overset{O}{\|}}{C}F$$

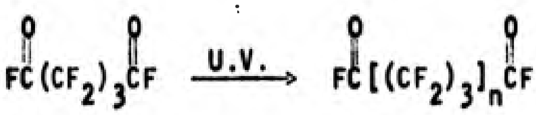
$$F\overset{\overset{O}{\|}}{C}(CF_2)_6\overset{\overset{O}{\|}}{C}F + 2CH_3OH \longrightarrow CH_3O_2C(CF_2)_6CO_2CH_3$$

$$CH_3O_2C(CF_2)_6CO_2CH_3 + NH_3 \longrightarrow H_2N\overset{\overset{O}{\|}}{C}(CF_2)_6\overset{\overset{O}{\|}}{C}NH_2$$



$$H_2N\overset{O}{\overset{\|}{C}}(CF_2)_6\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow{P_2O_5} NC(CF_2)_6CN$$

Perfluoroglutaryl fluoride was coupled to give perfluorosuberyl fluoride by ultraviolet irradiation of the refluxing monomer. The reactor was designed and the temperature controlled so that only perfluoroglutaryl fluoride was exposed to irradiation. GLC analysis indicated a 70% conversion to perfluorosuberyl fluoride which was readily converted to its more stable dimethyl ester. The method is an adaptation of the photolysis reactions of perfluoroacyl fluorides reported[7] by Harris, who obtained solid polymers by the irradiation of perfluoroglutaryl fluoride.



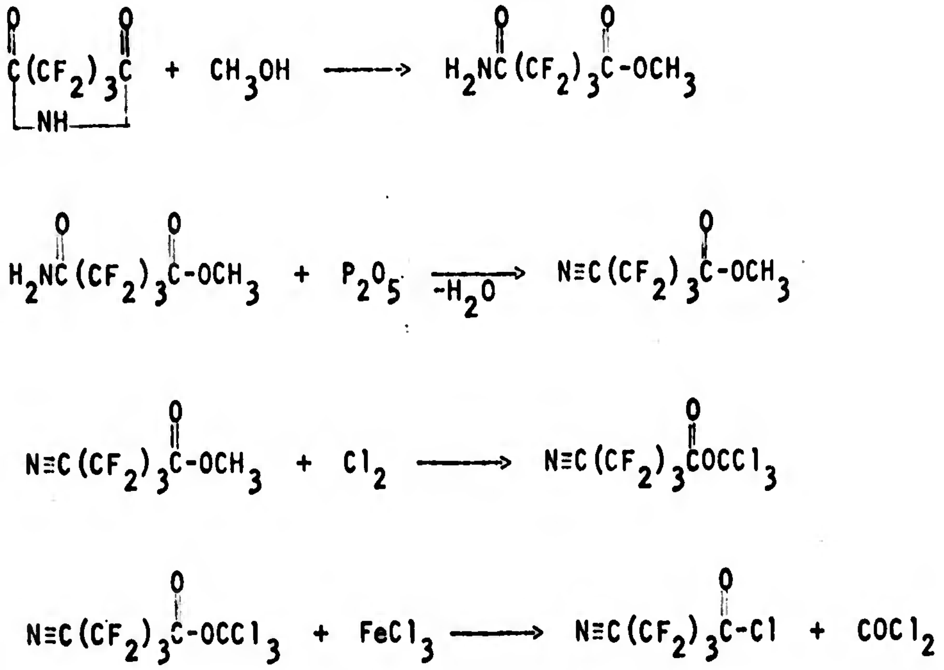
$$F\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}F \xrightarrow{U.V.} F\overset{O}{\overset{\|}{C}}[(CF_2)_3]_n\overset{O}{\overset{\|}{C}}F$$

Because of the availability of high purity perfluorosebaconitrile this sequence of reactions was not carried beyond the preparation of the dimethyl ester.

c. 4-Cyanoperfluorobutyryl Chloride

In order to crosslink gum triazine polymers it is necessary to incorporate functional groups in the polymer chain which, after crosslinking, do not detract from the desirable properties of the raw gum. One of the most promising approaches utilizes 4-cyanoperfluorobutyric anhydride in conjunction with perfluorobutyric anhydride in the cyclodehydration step of the polyimidoylamidine[2]. The amount of 4-cyanobutyl groups incorporated in the polymer can be controlled by varying the ratio of the anhydride mixture. The pendent nitrile groups can then act as crosslinking sites using a variety of curing agents[5].

A reported[2] synthetic route to the required 4-cyanohexafluorobutyryl chloride uses perfluoroglutarimide as the starting material. Reaction of this compound with methanol gives the half amide-methyl ester of hexafluoroglutaric acid. Dehydration of the amide group with phosphorous pentoxide gives good yields of the nitrile-ester. Chlorination of methyl cyanohexafluorobutyrate results in a trichloromethyl ester which is catalytically decomposed with ferric chloride to 4-cyanohexafluorobutyryl chloride.



$$\underbrace{\overset{\overset{O}{\|}}{C}(CF_2)_3\overset{\overset{O}{\|}}{C}}_{NH} + CH_3OH \longrightarrow H_2N\overset{\overset{O}{\|}}{C}(CF_2)_3\overset{\overset{O}{\|}}{C}\text{-}OCH_3$$

$$H_2N\overset{\overset{O}{\|}}{C}(CF_2)_3\overset{\overset{O}{\|}}{C}\text{-}OCH_3 + P_2O_5 \xrightarrow[-H_2O]{} N{\equiv}C(CF_2)_3\overset{\overset{O}{\|}}{C}\text{-}OCH_3$$

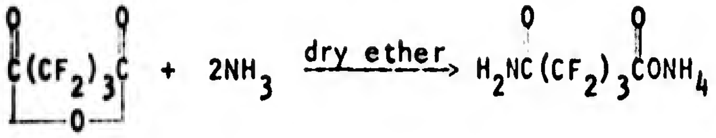
$$N{\equiv}C(CF_2)_3\overset{\overset{O}{\|}}{C}\text{-}OCH_3 + Cl_2 \longrightarrow N{\equiv}C(CF_2)_3\overset{\overset{O}{\|}}{C}OCCl_3$$

$$N{\equiv}C(CF_2)_3\overset{\overset{O}{\|}}{C}\text{-}OCCl_3 + FeCl_3 \longrightarrow N{\equiv}C(CF_2)_3\overset{\overset{O}{\|}}{C}\text{-}Cl + COCl_2$$

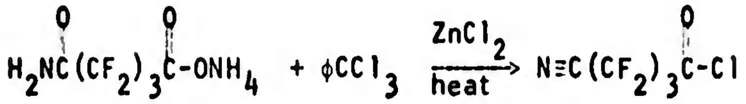
The corresponding anhydride was also prepared by reaction of the acid chloride with silver oxide.

$$2N{\equiv}C(CF_2)_3COCl + Ag_2O \longrightarrow [N{\equiv}C(CF_2)_3CO]_2O + 2AgCl$$

Due to the anticipated requirement for 4-cyanoperfluorobutyryl chloride as a precursor to the anhydride, we investigated its synthesis by another route which, it was anticipated, would be less tedious and result in higher overall conversion. This reaction sequence is as follows:

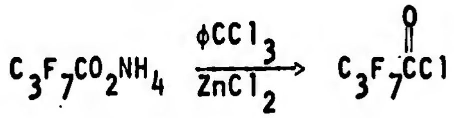


$$\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}\text{(–O– ring)} + 2NH_3 \xrightarrow{\text{dry ether}} H_2N\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}ONH_4$$



$$H_2N\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}\text{-}ONH_4 + \phi CCl_3 \xrightarrow[\text{heat}]{ZnCl_2} N{\equiv}C(CF_2)_3\overset{O}{\overset{\|}{C}}\text{-}Cl$$

Benzotrichloride with zinc chloride has been used by others[9] to dehydrate perfluorosebacamide to perfluorosebaconitrile and resulted in a product mixture of the desired dinitrile and mononitrile-acyl chloride, $N{\equiv}C(CF_2)_8COCl$. On the basis of this information and the suggestion[10] that the acid chloride might result from reaction with an ammonium salt impurity $[H_2N\overset{O}{\overset{\|}{C}}(CF_2)_6\overset{O}{\overset{\|}{C}}ONH_4]$, we initially investigated the reaction of ammonium perfluorobutyrate with benzotrichloride/zinc chloride.



$$C_3F_7CO_2NH_4 \xrightarrow[ZnCl_2]{\phi CCl_3} C_3F_7\overset{O}{\overset{\|}{C}}Cl$$

Since a 71% conversion to perfluorobutyryl chloride was obtained, the procedure was extended to reaction with the half amide-ammonium salt of perfluoroglutaric acid, prepared from perfluoroglutaric anhydride and ammonia.

The initial attempt to prepare 4-cyanoperfluorobutyryl chloride utilized a large excess (30:1 molar ratio) of benzotrichloride to amide-ammonium salt. The amount of zinc chloride used was 30% of the total weight of the other reactants. Crude product was collected over the temperature range of 100-210°. An infrared spectrum (Fig. 5) of this material showed typical nitrile absorption at 4.44 microns, acyl chloride absorption at 5.56 microns and was very similar to a reported spectrum of the desired product[2].

Although a reorientation in research objectives did not allow further investigation of this reaction, the results obtained in the initial experiment are extremely encouraging.

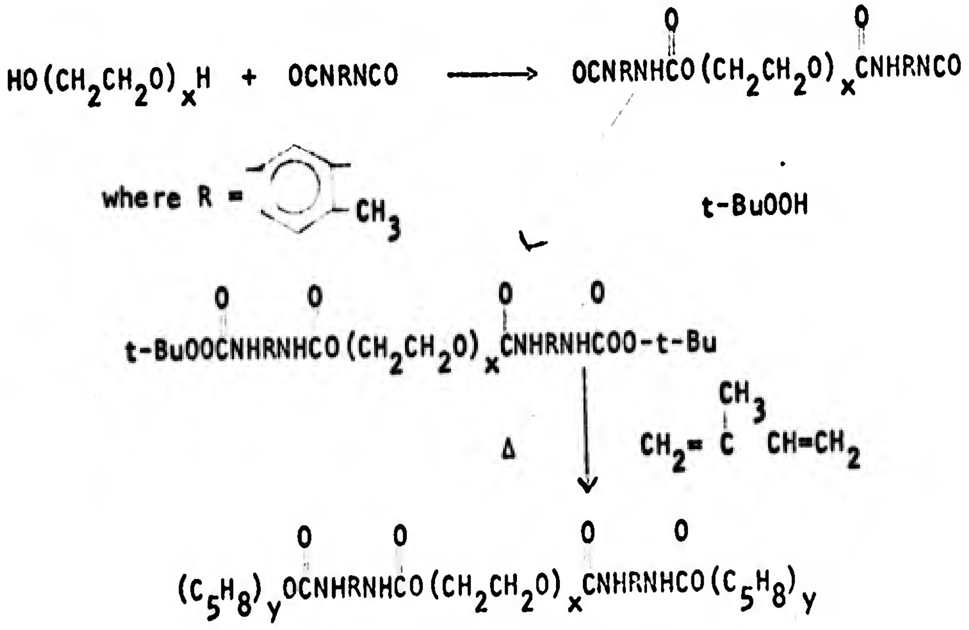
B. Block Copolymers

The objective of one phase of this synthesis program was to supply Air Force investigators with well characterized block copolymers of the ABA type for use in fundamental investigations on the relationship of structure and morphology to mechanical properties.

In earlier work in these laboratories[11], urethane type block copolymers were prepared in which poly(propylene adipate) served as the non-crystallizing segment and poly(ethylene sebacate), poly(decamethylene terephthalate) or poly(ethylene terephthalate) served as crystallizing segments. Block copolymers were also prepared from hydroxyl-terminated ethylene oxide and propylene oxide prepolymers by diisocyanate linking.

In the present work ABA block copolymers containing a polyethylene block of approximately 6000 molecular weight and A blocks of polyisoprene or polystyrene were requested.

These polymers were prepared by utilization of a procedure for the synthesis of block polymers described by Tobolsky and Rembaum[12]. This approach, outlined below, consists of the initial preparation of an isocyanate-terminated prepolymer, followed by reaction with t-butyl hydroperoxide to give peroxycarbamate end groups. These groups are then capable of initiating polymerization of certain vinyl monomers, including isoprene.



$$HO(CH_2CH_2O)_xH + OCNRNCO \longrightarrow OCNRNH\overset{O}{\overset{\|}{C}}O(CH_2CH_2O)_x\overset{O}{\overset{\|}{C}}NHRNCO$$

$$t\text{-}BuOO\overset{O}{\overset{\|}{C}}NHRNH\overset{O}{\overset{\|}{C}}O(CH_2CH_2O)_x\overset{O}{\overset{\|}{C}}NHRNH\overset{O}{\overset{\|}{C}}OO\text{-}t\text{-}Bu$$

$$(C_5H_8)_yO\overset{O}{\overset{\|}{C}}NHRNH\overset{O}{\overset{\|}{C}}O(CH_2CH_2O)_x\overset{O}{\overset{\|}{C}}NHRNH\overset{O}{\overset{\|}{C}}O(C_5H_8)_y$$

The hydroxy-terminated polyethylene oxide (PEO) used in this work had a molecular weight (after drying) of 7160 by VPO and an equivalent weight of 3792 by hydroxyl number determination. Reaction of the PEO with 2,4-toluenediisocyanate in a 2.0/1 isocyanate/hydroxyl equivalent ratio produced a diisocyanate-terminated prepolymer. This intermediate was characterized by free isocyanate analysis which showed essentially complete isocyanate-hydroxyl reaction and no isocyanate-water reaction. A t-butylperoxycarbamate-terminated prepolymer was then formed by reaction with the stoichiometric amount of butyl hydroperoxide in THF solvent using a catalytic amount of pyridine. Decomposition of this intermediate upon heating with isoprene initiated free radical polymerization and formation of the polyisoprene A blocks.

In the initial polymerization (in THF solution) the degree of polymerization of polyisoprene A block appeared to have been very small as indicated by the slight increase in weight of the product over the prepolymer (see Table II). A methanol extraction of the polymerization product removed no methanol soluble PEO, which can be considered as good evidence for block formation. Infrared analysis showed the presence of both polyisoprene and PEO units in the final product (Figs. 6-8). The polymer (1105.61A) is soluble in methylene chloride, which indicates that little or no crosslinking occurred in this polymerization. The polymerizations run without solvent resulted in insoluble reaction products that showed solvent swelling. It appears that these materials have been crosslinked, probably at the double bond sites of the polyisoprene. Tobolski and Rembaum[12] reported a considerable degree of crosslinking in a somewhat similar solvent-free polymerization with a much shorter poly(propylene oxide) B block.

TABLE II

ABA BLOCK COPOLYMERS[1]

Sample No.	A Block	Amt., g.	Conversion,%	Mole % $[CH_2CH_2O]$	[n]	H_2O Extract Amt., g.	H_2O Extract Mole % $[CH_2CH_2O]$	H_2O Extract [n]
1105.65.1[4,6]	Polystyrene	5.7	27.8	22.9	1.29[2]	2.9	96.7	0.49[2]
1105.65.2[5,6]	Polystyrene	10.1	4.9.4	48.9	1.29[2]	1.1	100	0.51[2]
1105.61.A[7]	Polyisoprene	6.4	29.8	53.0	0.43[3]	0.8[8]	--	--

1. PEO; molecular weight 7160 by VPO, equivalent weight 3792 by hydroxyl no. det'n.
2. Benzene at 30.0° C
3. 1,2-Dichloroethane at 30.0° C
   NOTE: [n] of B block in benzene at 30.0°C is 0.18, in 1,2-dichloroethane 0.21
4. Polymerization in benzene solvent
5. No solvent used in polymerization
6. Soluble in benzene and methylene chloride
7. Soluble in methylene chloride
8. Methanol extract

Due to the difficulties encountered with crosslinking, efforts were directed toward the preparation of ABA block copolymers having polystyrene A blocks, less susceptible to crosslinking, using the same B block peroxycarbamate described above. ABA block copolymers having 4750 molecular weight polyethylene oxide B blocks and polystyrene A blocks had been previously prepared by other workers of this laboratory[13]. Block copolymers resulting from ethylene oxide/styrene molar charge ratios of 1:1 and 1:2 contained, respectively, 75 and 56 mole percent ethylene oxide units.

Two samples containing polystyrene A blocks were prepared. The first, 1105.65.1, was prepared in benzene solution. The second, 1105.65.2, was prepared without solvent using the same quantities of reactants. In the latter case an appreciably higher conversion to polymer having more than double the mole % of ethylene oxide was obtained. The infrared spectra of 1105.65.1 (Figure 9) and 1105.65.2 (Figure 10) show intense polystyrene absorption at 6.25 microns and in the 13 and 14 micron regions as well as PEO absorption in the 9 micron region (compare with Figure 6). The intrinsic viscosity of both 1105.65.1 and 1105.65.2 was 1.29 in benzene, which is suggestive of high molecular weight polymer. The PEO had an intrinsic viscosity of 0.18 in benzene. Elemental analyses provided the following data.

	% C	% H
1105.65.1	83.90	7.78
1105.65.2	74.18	8.04
PEO	54.65(54.60 calcd.)	9.29 (9.09 calcd.)

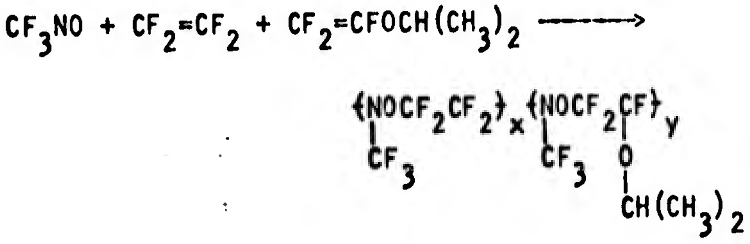
The mole % ethylene oxide was calculated by comparison of the percent oxygen, by difference, with that of the PEO. Both materials are soluble in benzene and methylene chloride and insoluble in cyclohexanone.

The water extracts of 1105.65.1 and 1105.65.2 were shown by infrared analysis (Figures 11 and 12) and elemental analysis to consist primarily of ethylene oxide. The intrinsic viscosities of 0.49 and 0.51 of the 1105.65.1 and 1105.65.2 extracts, compared with 0.18 of the PEO, as well as weak infrared absorption at 14.3 microns, suggest the extracts to be something other than pure PEO. In addition, the extracts were filtered as stable, cloudy suspensions and not as clear aqueous solutions, obtainable from PEO in cold water. Plausible explanations are that the extracts are comprised of ABA block copolymer with very short A blocks or that they consist of two or more PEO chains linked together by 2,4-toluenediisocyanate.

The fact that both 1105.65.1 and 1105.65.2 formed stable, opaque suspensions in methanol is evidence that they are block copolymers. The PEO block of the copolymer solubilizes the polymer in methanol while the polystyrene block is precipitated by this solvent. This phenomenon was observed by Tobolski and Rembaum[12] in their preparation of block copolymers.

C. Nitroso Terpolymers

In support of an AFML program on the study of functional nitroso polymers, we had earlier prepared and submitted terpolymer samples containing trifluorovinyl methyl ether[11]. Since attempts to cure these samples by peroxides were unsuccessful, samples containing a pendent isopropoxy group have been prepared by terpolymerization with trifluorovinyl isopropyl ether.



$$CF_3NO + CF_2{=}CF_2 + CF_2{=}CFOCH(CH_3)_2 \longrightarrow \{\underset{CF_3}{N}OCF_2CF_2\}_x\{\underset{CF_3}{N}OCF_2\underset{\underset{CH(CH_3)_2}{O}}{CF}\}_y$$

Unlike earlier samples containing trifluorovinyl t-butyl ether which decomposed at room temperature[11], the terpolymer samples were stable and did not evolve hydrogen fluoride. The terpolymerization does not appear to proceed normally, however, since two samples prepared under the same conditions and using the same reactant ratios, gave widely divergent elemental analyses.

Since these samples, described in Table III, were not susceptible to curing, they were not further investigated.

D. Fluorine-Containing Diepoxides

Perfluorinated and partially fluorinated diepoxides were required for study as curing agents for carboxy nitroso rubber and other experimental elastomers.

1. Perfluorinated Diepoxides

In earlier work in these laboratories both 4-chloroperfluorohepta-diene-1,6 diepoxide and perfluorooctadiene-1,7 diepoxide[14] had been prepared

TABLE III

$CF_3NO/CF_2=CF_2/CF_2=CFOCH(CH_3)_2$ Terpolymers

	Sample No.		
	1095.62	1095.65	1095.75
Charge Ratio (Mole %) $CF_3NO/CF_2=CF_2/CF_2=CFOCH(CH_3)_2$	51.7/25.9/22.4	50/40/10	50/40/10
Wt., g.	0.0305/0.0154/0.0181	3.4/2.74/0.96	2.52/2.06/0.72
mmoles	0.308/0.154/0.133	34.3/37.4/6.85	25.75/20.6/5.15
Total Weight of Reactants	0.0645 g.	6.4 g.	5.3 g.
Reaction Time (hours at -35°C)	43	40	40
Weight of Polymer Recovered	0.060 g.	5.5 g.	4.3 g.
Conversion, %	93	86	81

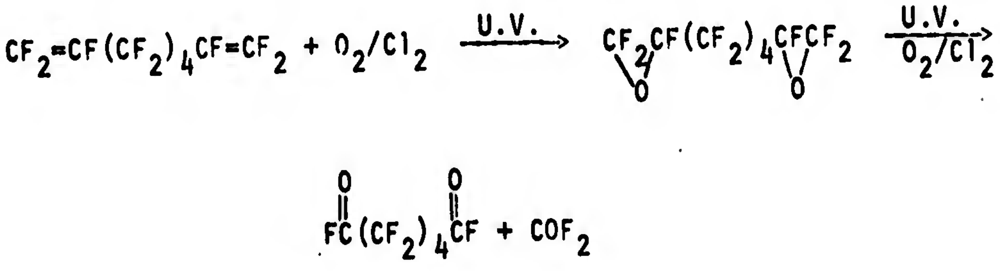
by chlorine-sensitized photochemical oxidation of the corresponding diolefins[11]. Because of the low conversions (∿8%) obtained in our initial work, the synthesis of perfluorooctadiene-1,7 diepoxide by basic hydrogen peroxide oxidation was reexamined. Although perfluoroheptene-1 could be converted to its epoxide by this method, only very small quantities of the diepoxide could be detected in the crude product mixture. The major product of the reaction appeared to be perfluoroadipic acid, which would be formed by complete oxidation of both olefinic groups.

$$CF_2{=}CF(CF_2)_4CF{=}CF_2 + KOH + H_2O_2 \longrightarrow$$

$$HOOC(CF_2)_4COOH$$

Because of the difficulty in controlling the reaction to give reasonable amounts of the desired diepoxide, the photochemical epoxidation was reexamined. Improvements in reactor design and reaction conditions resulted in significant improvement in conversion (∿19%). Specifically, a much higher intensity ultraviolet lamp (450 watts) was used together with a Vycor 7910 (ultraviolet transmitting grade) reaction cell. Better gas dispersion in the reactor was achieved by use of a fritted glass gas dispersion tube. An improved condenser system, including a wide diameter cold finger that cools the reaction and decreases the path length through which U.V. must pass, was employed.

A rapid degradation reaction of the product to the acid fluoride and carbonyl fluoride appears to occur during the irradiated oxidation and afterwards, before work-up. Large quantities of carbonyl fluoride



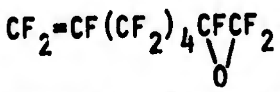
$$CF_2{=}CF(CF_2)_4CF{=}CF_2 + O_2/Cl_2 \xrightarrow{U.V.} \underset{\diagdown O \diagup}{CF_2CF}(CF_2)_4\underset{\diagdown O \diagup}{CFCF_2} \xrightarrow[O_2/Cl_2]{U.V.}$$

$$F\overset{O}{\overset{\|}{C}}(CF_2)_4\overset{O}{\overset{\|}{C}}F + COF_2$$

are evolved and the crude reaction mixture reacts vigorously with water with the formation of a solid acid. Immediate work-up of the crude mixture, after an optimum period of oxidation, is thereby suggested for achieving a maxiumum yield of diepoxide. The optimum period of epoxidation may be judged by the relative increase in infrared perfluoroepoxide absorption at 6.5 microns and decrease in trifluorovinyl absorption at 5.6 microns, and also by GLC in the relative increase of diepoxide peak height. An infrared spectrum of the pure compound is shown in Fig. 13a.

The relative retention times, t_R component/t_R diepoxide, (measured from the air peak) are diene 0.14, monoepoxide 0.64, diepoxide 1.0 (t_R = 0.87 min.) and acid fluoride 1.23.

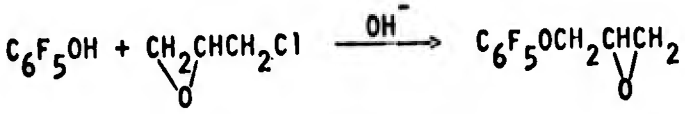
Conditions: Stationary liquid phase: Silicone gum
U.C. W-98 10% 6 feet
Support - Diatoport S, 80-100 mesh
Carrier gas: Helium 25 cc/min.
Temperature: Injection 150°
Column 27°
Detector 230°
Detection: T.C. - WX filaments

After 10 hours reaction time GLC analysis of the crude product indicated that about 54% conversion to the diepoxide had occurred. Three other components were also detected: 7.2% unreacted diolefin, 15.9% monoepoxide  $CF_2{=}CF(CF_2)_4\underset{O}{CF{-}CF_2}$ and 12.1% of an acid fluoride, probably perfluoroadipyl fluoride. An appreciable amount of product is apparently lost in work-up of the product mixture, since only 20.41 g. of pure product was obtained after distillation. Even with this loss, however, an overall conversion of about 19% was obtained compared to 8% obtained in an early preparation[11].

2. Partially Fluorinated Diepoxides

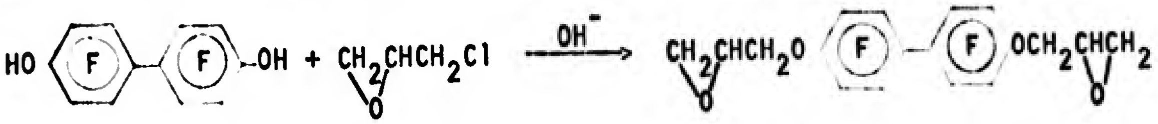
In order to compare the reactivity and effectiveness as curing agents of the perfluorinated diepoxides mentioned previously with other fluorine-containing diepoxides, the synthesis of several diglycidyl ethers containing fluorine was investigated.

The initial successful synthesis of pentafluorophenyl glycidyl ether[13] by reaction of pentafluorophenol with epichlorohydrin



$$C_6F_5OH + CH_2CHCH_2Cl \xrightarrow{OH^-} C_6F_5OCH_2CHCH_2$$

prompted the investigation of this method using several fluorine-containing diols, particularly tetrafluorohydroquinone, perfluorophenylenebis-(dimethyl carbinol) and 4,4'-dihydroxyoctafluorobiphenyl. Only in the latter case was the desired product isolated in a state sufficiently pure to allow characterization. Early attempts to prepare this



compound gave impure material whose infrared spectrum exhibited strong hydroxyl absorption and which contained an appreciable amount of chlorine, indicating the presence of chlorohydrin groups. Polymeric products decomposing above 200° were also obtained. Although stoichimetric amounts of base are used in these reactions, it appears that the formation of polymeric material is very difficult to prevent even when the base is added incrementally over a period of time. Small quantities of impure product were isolated from the reaction mixture by extraction with ethanol, followed by sublimation. Reaction of the impure product with a stoichiometric amount of KOH (based upon chlorine content) gave reasonably pure product which melted at 74-75° (rptd.[17] m.p. after six recrystallizations, 75-77°) and gave a good analysis for the desired compound. An infrared spectrum of this material exhibited the peaks reported[17] as well as hydroxyl absorption at 3.0 microns (Fig. 14).

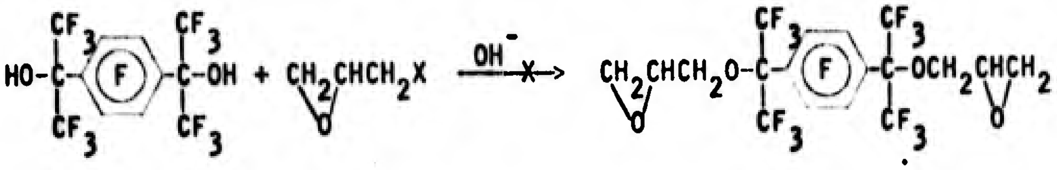
Several base-catalyzed methods were investigated in the unsuccessful attempt to prepare tetrafluoro-p-phenylene diglycidyl ether by reaction of tetrafluorohydroquinone with excess epichlorohydrin or epibromohydrin.

In one method, the sodium salt of the diol was prepared by reaction with sodium hydride and was mixed with an 8:1 excess of epichlorohydrin. The small quantity of product which was isolated was found by NMR to contain oxirane rings but no fluorine. The molecular weight of this material (492) suggested that it may have been formed in a base catalyzed polymerization of epichlorohydrin.

Similar results were obtained when sodium hydroxide (aqueous) was added to a mixture of the diol and epichlorohydrin. The solid product would not melt, was insoluble in water, acetone, ethyl acetate and DMSO. Several difficulties appear to be attendant in the synthesis of the diglycidyl ether of tetrafluorohydroquinone. A hydroquinone is oxidized to the quinone very readily in a basic medium. The difunctional diglycidyl ether, if formed, appears to polymerize readily to higher molecular weight products. This poses a serious problem during isolation and purification of the product, since during distillation on several occasions the probable product was observed to have polymerized in the receiver. Since this compound is probably a liquid, a fractional crystallization from the inevitably formed higher condensation products is not possible. Difficulty in obtaining high purity tetrafluorohydroquinone may have been still another complicating factor.

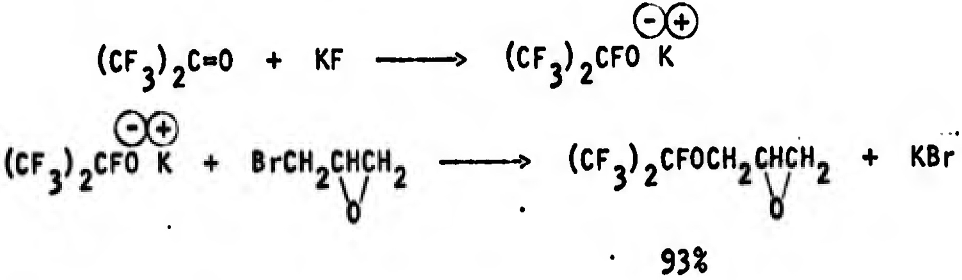
A method of synthesis reported[15] for the preparation of the diglycidyl ether of hydroquinone was applied to the preparation of the subject diglycidyl ether. The conditions of this method were such as to optimize an S_N2 displacement of bromine by aryloxide ion and minimize the possibilities for condensation of higher molecular weight materials. The condensing agent, $LiOH \cdot H_2O$ was slowly added to tetrafluorohydroquinone dissolved in a 2-to-1 molar excess of epibromohydrin at methanol reflux temperature. At any time during the reaction only a small amount of base was present. This feature was intended to prevent, in this case, the well known base catalyzed condensation reactions of epihalohydrins with aromatic diols, e.g., the reactions of epichlorohydrin and bisphenol-A with an alkaline catalyst in the manufacture of epoxy resins. Unfortunately, this method was also unsuccessful.

Attempts to prepare perfluoro-1,4-phenylenebis(dimethyl carbinol) diglycidyl ether by reaction of the diol with the halohydrins



were also unsuccessful. The diol was recovered unreacted in experiments using both sodium methoxide in methanol and the sodium salt of the diol. Reaction of the lithium salt of the diol with epibromohydrin produced what appeared to be an epibromohydrin polymer.

A final attempt to prepare a diglycidyl ether was based upon the reported preparation of heptafluoroisopropyl glycidyl ether by reaction of potassium perfluoroisopropoxide (prepared from hexafluoroacetone and KF) with epibromohydrin in diglyme[20].

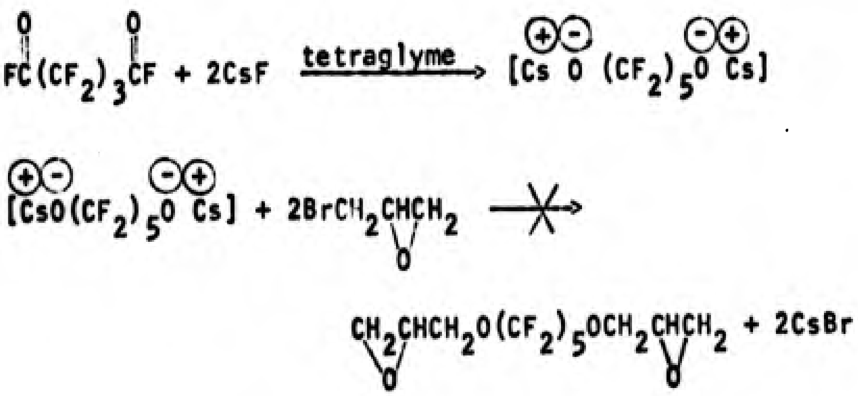


$$(CF_3)_2C{=}O + KF \longrightarrow (CF_3)_2CF\overset{\ominus\oplus}{O\ K}$$

$$(CF_3)_2CF\overset{\ominus\oplus}{O\ K} + BrCH_2\underset{O}{CHCH_2} \longrightarrow (CF_3)_2CFOCH_2\underset{O}{CHCH_2} + KBr$$

93%

Since the formation of the dicesium salt of perfluoropentanediol is indicated by the reaction of perfluoroglutaryl fluoride and cesium fluoride with hexafluoropropylene oxide to form compounds having an internal $-O(CF_2)_5O-$ group[21], we attempted the reaction of perfluoroglutaryl fluoride and cesium fluoride in tetraglyme with epibromohydrin.



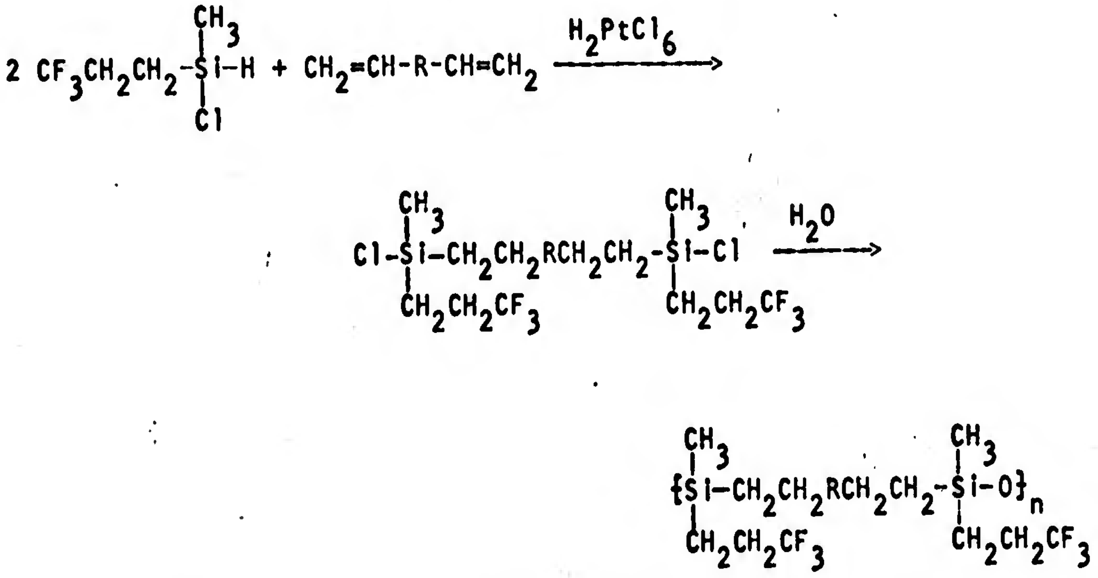
$$F\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}F + 2CsF \xrightarrow{\text{tetraglyme}} [\overset{\oplus\ominus}{Cs\ O}\ (CF_2)_5\overset{\ominus\oplus}{O\ Cs}]$$

$$[\overset{\oplus\ominus}{CsO}(CF_2)_5\overset{\ominus\oplus}{O\ Cs}] + 2BrCH_2\underset{O}{CHCH_2} \not\longrightarrow \underset{O}{CH_2CH}CH_2O(CF_2)_5OCH_2\underset{O}{CHCH_2} + 2CsBr$$

In two runs, perfluoroglutaryl fluoride was added to cesium fluoride and tetraglyme under anhydrous conditions. Nearly complete solution of the salt resulted. Epibromohydrin was then added. The reaction mixture, at this point, was strongly acidic and the product showed infrared absorption characteristic of a hydroxy ester. A similar infrared spectrum was obtained from the product of the reaction between perfluoroglutaric acid and epibromohydrin. The desired diglycidyl ether was not isolated.

E. Fluorine-Containing Silanes

Fluoroalkylmethylchlorosilanes are desirable intermediates in the synthesis of a variety of polymers. They may, for example, be added to vinyl-terminated monomers and hydrolyzed to give polymers containing siloxane links.



$$2\ CF_3CH_2CH_2-\overset{CH_3}{\underset{Cl}{Si}}-H + CH_2{=}CH-R-CH{=}CH_2 \xrightarrow{H_2PtCl_6}$$

$$Cl-\overset{CH_3}{\underset{CH_2CH_2CF_3}{Si}}-CH_2CH_2RCH_2CH_2-\overset{CH_3}{\underset{CH_2CH_2CF_3}{Si}}-Cl \xrightarrow{H_2O}$$

$$\{\overset{CH_3}{\underset{CH_2CH_2CF_3}{Si}}-CH_2CH_2RCH_2CH_2-\overset{CH_3}{\underset{CH_2CH_2CF_3}{Si}}-O\}_n$$

3,3,3-(Trifluoropropyl)methylchlorosilane and 3-(heptafluoroisopropoxy)propylmethylchlorosilane were prepared using an oxidation-reduction reaction of silver chloride with $CF_3CH_2CH_2Si(CH_3)H_2$ and $(CF_3)_2CFOCH_2CH_2CH_2Si(CH_3)H_2$, respectively. The procedure utilized in this synthesis was similar to that used in a reported[22] method for the preparation of dialkylmonohalosilanes from the corresponding dialkylsilanes using salts such as AgCl, $HgCl_2$, $CoCl_2$, and $HgBr_2$. A stoichiometric amount of silver chloride was added in small increments to the neat silane followed by distillation of the product. Conversions of 51 and 84%, respectively, were obtained.

$$R_fSi(CH_3)H_2 + AgCl \longrightarrow R_fSi(CH_3)ClH$$

$$R_f = CF_3CH_2CH_2 \text{ and } (CF_3)_2CFOCH_2CH_2CH_2$$

The intermediate dialkyl silanes, $R_fSi(CH_3)H_2$, were prepared by reduction of the corresponding dialkyldichlorosilanes, $R_fSi(CH_3)Cl_2$, using lithium aluminum hydride.

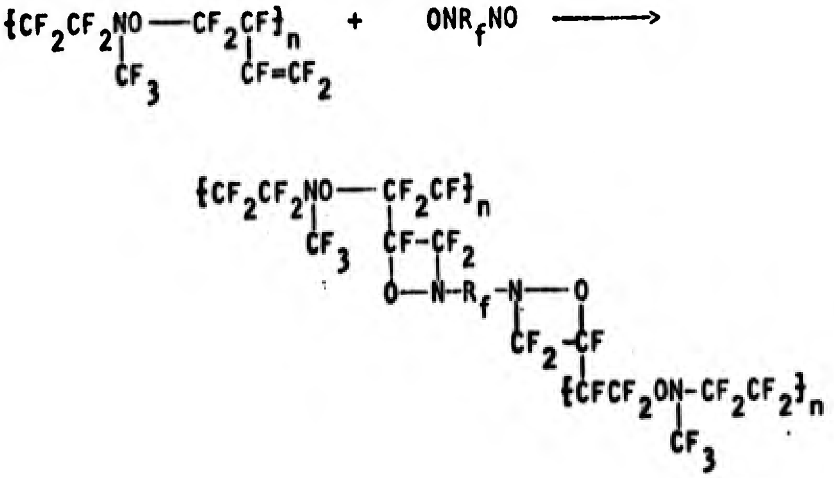
$$2\ R_fSi(CH_3)Cl_2 + LiAlH_4 \longrightarrow 2\ R_fSi(CH_3)H_2$$

The first reduction was carried out by addition of $CF_3CH_2CH_2Si(CH_3)Cl_2$ to $LiAlH_4$ in dry ethyl ether. The product was isolated by destruction of unreacted reducing agent with water and acid, followed by distillation of the ether solution. Since very low conversions (20.4%) to the desired product was obtained, this procedure was modified in the reduction of $(CF_3)_2CFOCH_2CH_2CH_2Si(CH_3)Cl_2$ by utilization of a high boiling solvent (tetraglyme) so that a higher reaction temperature could be maintained and the product could be distilled directly from the reaction mixture without further treatment. A conversion of 74% was obtained using this method.

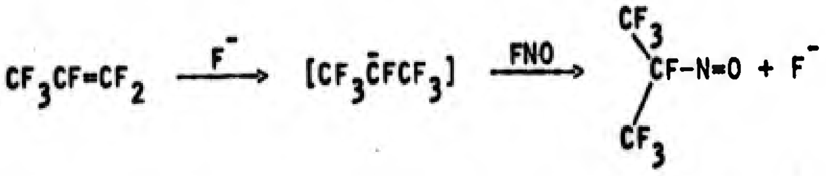
The low conversion to $CF_3CH_2CH_2Si(CH_3)H_2$ obtained in the first reduction may be due to incomplete reaction because of the low reaction temperature (35°) and time (2 hours), azeotropic loss of product during stripping of the ether, or conversion of the intermediate to a higher molecular weight by-product resulting from hydrolysis and condensation to a cyclic siloxane. Hydrolysis of dialkyldichlorosilanes by water to linear and cyclic intermediates is well known, while hydrolysis of dialkylsilanes by base to siloxanes is also reported[24]. An infrared spectrum of this unidentified by-product is shown in Fig. 16.

F. Nitroso Compounds

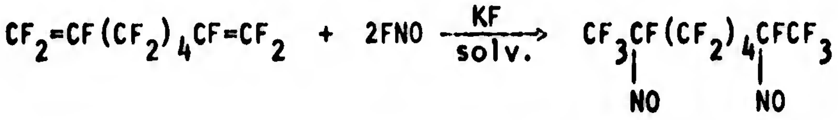
Difunctional perfluorinated nitroso compounds are desired for evaluation as crosslinking agents for oxidatively stable nitroso elastomers. Reaction of the nitroso group with pendent trifluorovinyl groups to form stable oxazetidine linkages was anticipated.



A novel dinitroso compound was prepared, in a low conversion, using a method reported[5] by Knunyants, et. al. These workers have reported the successful addition of nitrosyl fluoride to hexafluoropropene in tetrametnyllenesulfone (Sulfolane) with KF. This reaction was described as a nucleophilic type nitrosyl fluoride addition giving 2-nitrosoperfluoropropane in about 90% yield. This reaction was repeated and infrared analysis indicated the presence of the product as well as unreacted olefin in the distilled reaction mixture. Further attempts at resolution of the pure nitroso product were not made.



The desired dinitroso compound was prepared in 16.5% conversion (after preparative GLC purification) by the addition of nitrosyl fluoride to perfluorooctadiene-1,7 in tetraglyme solvent with KF under anhydrous conditions in an autoclave.



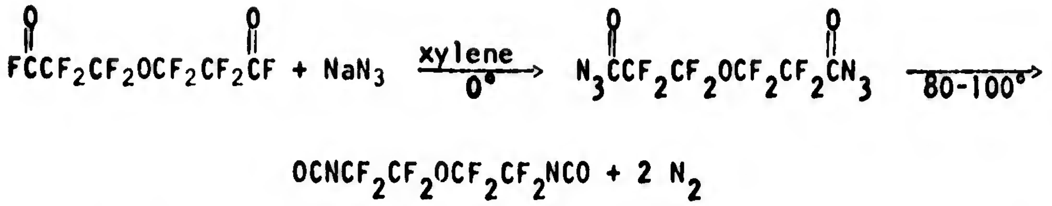
$$CF_2{=}CF(CF_2)_4CF{=}CF_2 + 2FNO \xrightarrow[\text{solv.}]{KF} CF_3\underset{\substack{|\\ NO}}{CF}(CF_2)_4\underset{\substack{|\\ NO}}{CF}CF_3$$

Preparative chromatography was necessary for isolation of pure 2,7-dinitrosoperfluorooctane since fractional distillation, even under mild conditions, resulted in decomposition. Proof of structure was obtained by infrared analysis (Fig. 20), NMR analysis (Appendix III) and elemental analysis. In addition to the desired product a novel monoaddition production, $CF_2{=}CF(CF_2)_4CF(NO)CF_3$, was isolated by preparative GLC. An infrared spectrum (Fig. 21) of this compound showed the expected $CF_2{=}CF$ absorption at 5.6 microns and N-O absorption at 6.2 microns. NMR analysis (Appendix III) was consistent with the assigned structure.

G. Perfluorinated Diisocyanates

Perfluorinated diisocyanates containing ether links in the molecule were required for use as intermediates in the preparation of elastomeric polyurethanes and polyimides.

Three perfluorinated diisocyanates, $OCNCF_2CF_2OCF_2CF_2NCO$, $OCNCF(CF_3)O(CF_2)_5OCF(CF_3)NCO$, and $OCNCF(CF_3)OCF_2CF(CF_3)O(CF_2)_5OCF(CF_3)NCO$, were prepared from their corresponding diacid fluorides using the Curtius reaction. The first diisocyanate, perfluoro-di-(β-isocyanoethyl) ether, was prepared from perfluorooxydipropionyl fluoride supplied by the Air Force Materials Laboratory. The sample was supplied as approximately 77% pure, which was corroborated in our laboratories by GLC. The material was distilled into six fractions over a b.p. range of 65.0-69.2° but very little purification was achieved. Consequently, the sample was used in the impure state and converted to the diazide using sodium azide. The diazide was then decomposed thermally to the diisocyanate.



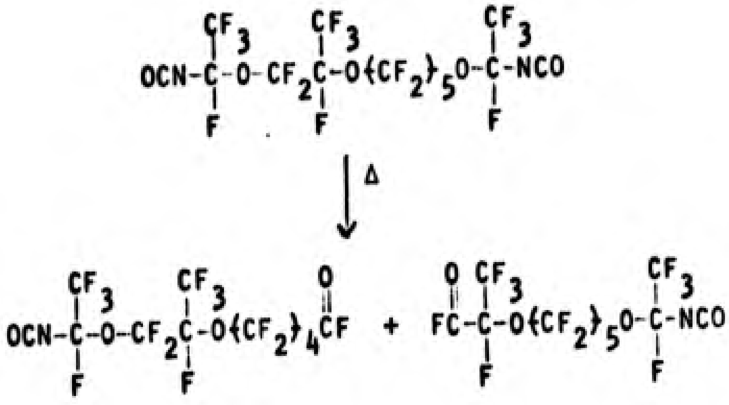
$$F\overset{\overset{O}{\|}}{C}CF_2CF_2OCF_2CF_2\overset{\overset{O}{\|}}{C}F + NaN_3 \xrightarrow[0^\circ]{xylene} N_3\overset{\overset{O}{\|}}{C}CF_2CF_2OCF_2CF_2\overset{\overset{O}{\|}}{C}N_3 \xrightarrow{80\text{-}100^\circ}$$

$$OCNCF_2CF_2OCF_2CF_2NCO + 2\ N_2$$

Distillation of the crude product gave a small quantity of 96-98% pure material. The major product was found to be material containing both acid fluoride and isocyanate groups, indicating incomplete conversion to the diazide. This material was allowed to react again with sodium azide using benzonitrile rather than xylene as a solvent. The reaction was allowed to proceed for a longer period of time until the acid fluoride carbonyl absorption peak at 5.3 microns had become very weak. Decomposition of the diazide gave additional product boiling at 99-100°. The structure was confirmed by infrared (Fig. 22), NMR (Appendix III), and elemental analysis.

The second and third diisocyanates had been previously prepared in our laboratories under another contract[17]. In this method Freon 113 was used as a cosolvent with acetonitrile to provide adequate contact of the diacid fluoride with sodium azide. The precursor diacid fluorides were prepared as described in a previous report[11] from reaction of hexafluoropropylene oxide and perfluoroglutaryl fluoride. The existence of structural isomers has also been established[11,29].

During the slow distillation of TEDI, $OCNCF(CF_3)OCF_2CF(CF_3)O(CF_2)$-$OCF(CF_3)NCO$, it was observed that an apparent thermal decomposition was occurring. Although GLC analysis of the crude TEDI before distillation showed only very small amounts of impurities eluting before the product peak and the infrared spectrum showed only barely detectable acid fluoride absorption, an appreciable amount of low boiling material was detected in the first fractions from the distillation. The first fraction, boiling at 56-60°/6mm (∿40° lower than TEDI at the same pressure), was found by GLC to be 92% one peak eluting on a GLC column before TEDI. An infrared spectrum (Fig. 27) of this material exhibited both acid fluoride peaks (5.3 microns) and isocyanate peaks (4.35 microns). On the basis of NMR analysis (Appendix III) it appears that cleavage occurs at the C-O bond adjacent to the isocyanate group to give the compounds shown. Molecular weight determination



$$OCN\text{-}\underset{F}{\overset{CF_3}{C}}\text{-}O\text{-}CF_2\underset{F}{\overset{CF_3}{C}}\text{-}O(CF_2)_5O\text{-}\underset{F}{\overset{CF_3}{C}}\text{-}NCO \xrightarrow{\Delta} OCN\text{-}\underset{F}{\overset{CF_3}{C}}\text{-}O\text{-}CF_2\underset{F}{\overset{CF_3}{C}}\text{-}O(CF_2)_4\overset{O}{\overset{\|}{C}}F + F\overset{O}{\overset{\|}{C}}\text{-}\underset{F}{\overset{CF_3}{C}}\text{-}O(CF_2)_5O\text{-}\underset{F}{\overset{CF_3}{C}}\text{-}NCO$$

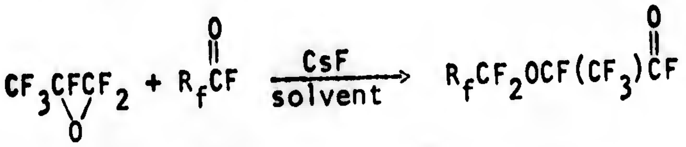
by VPO gave a value of 632 (calc. 571). Elemental analysis was as follows:

	Found	Calculated
% C	23.00	23.10
% N	3.38	2.45

Since this work was carried out at the end of the contract period, no further investigation of this decomposition was possible. It would be of interest to isolate and identify the lower boiling fragments resulting from the decomposition as well as to determine if the two compounds shown could further cleave to give $F\overset{O}{\overset{\|}{C}}CF(CF_3)O(CF_2)_4\overset{O}{\overset{\|}{C}}F$ (MEDAF).

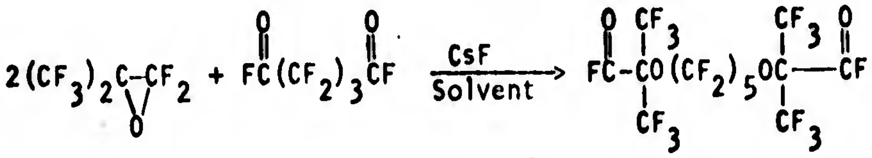
H. <u>Reactions of Perfluoroisobutylene Oxide</u>

Hexafluoropropylene oxide reacts with a variety of perfluorinated acid fluorides and diacid fluorides in the presence of fluoride ion and a suitable solvent[30] to give

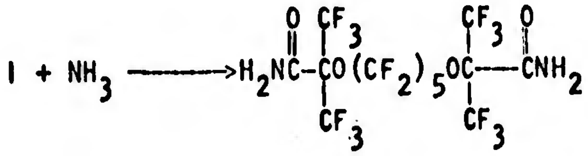


$$CF_3\underset{\backslash O /}{CFCF_2} + R_f\overset{O}{\overset{\|}{C}}F \xrightarrow[\text{solvent}]{\text{CsF}} R_fCF_2OCF(CF_3)\overset{O}{\overset{\|}{C}}F$$

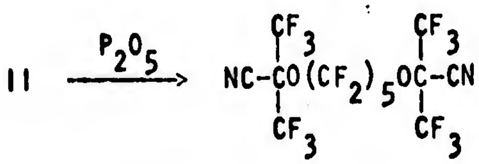
perfluoroalkoxy-substituted acid fluorides (as shown) and diacid fluorides, respectively. In an attempt to prepare sterically hindered perfluorinated dinitriles containing ether links to be used in research on perfluorinated triazine polymers, the following reaction sequence was proposed:



$$2(CF_3)_2\underset{\diagdown O \diagup}{C{-}CF_2} + F\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}F \xrightarrow[\text{Solvent}]{CsF} F\overset{O}{\overset{\|}{C}}-\underset{CF_3}{\overset{CF_3}{C}}O(CF_2)_5O\underset{CF_3}{\overset{CF_3}{C}}-\overset{O}{\overset{\|}{C}}F \qquad \text{(I)}$$



$$I + NH_3 \longrightarrow H_2N\overset{O}{\overset{\|}{C}}-\underset{CF_3}{\overset{CF_3}{C}}O(CF_2)_5O\underset{CF_3}{\overset{CF_3}{C}}-\overset{O}{\overset{\|}{C}}NH_2 \qquad \text{(II)}$$



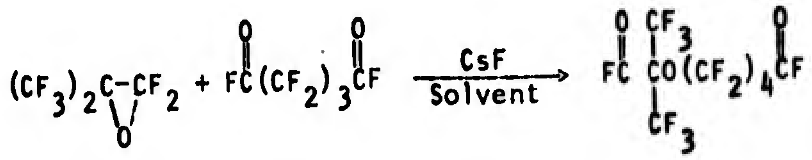
$$II \xrightarrow{P_2O_5} NC-\underset{CF_3}{\overset{CF_3}{C}}O(CF_2)_5O\underset{CF_3}{\overset{CF_3}{C}}-CN \qquad \text{(III)}$$

Although hexafluoropropylene oxide reacts readily with perfluoroglutaryl fluoride to form the analogous compound $F\overset{O}{\overset{\|}{C}}CF(CF_3)O(CF_2)_5OCF(CF_3)\overset{O}{\overset{\|}{C}}F$, it was not known if perfluoroisobutylene oxide (PFIO) would be sufficiently reactive to undergo a similar nucleophilic substitution or, if it did react, at which carbon atom substitution might occur.

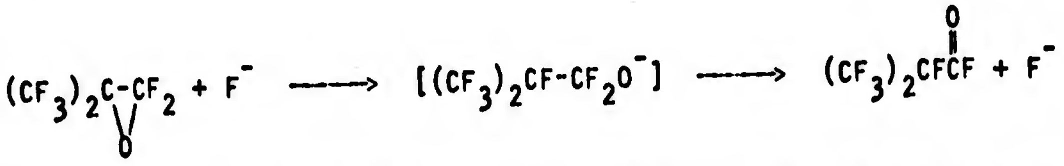
In attempting this reaction it was found that PFIO is considerably less reactive than hexafluoropropylene epoxide, as might be expected, but that nucleophilic substitution does take place at the carbon atom substituted with the trifluoromethyl groups.

The first attempt to carry out this reaction was run under conditions similar to the normal addition of hexafluoropropylene oxide to the diacid fluoride; i.e., by the addition of the epoxide under slight pressure to the stirred mixture of cesium fluoride, diacid fluoride and solvent. No reaction was observed under these conditions. When sealed in a glass reactor under pressure, however, the epoxide did react as evidenced by a decrease in pressure. After the uptake of PFIO ceased, the product was observed as a distinct, clear lower layer in the reactor.

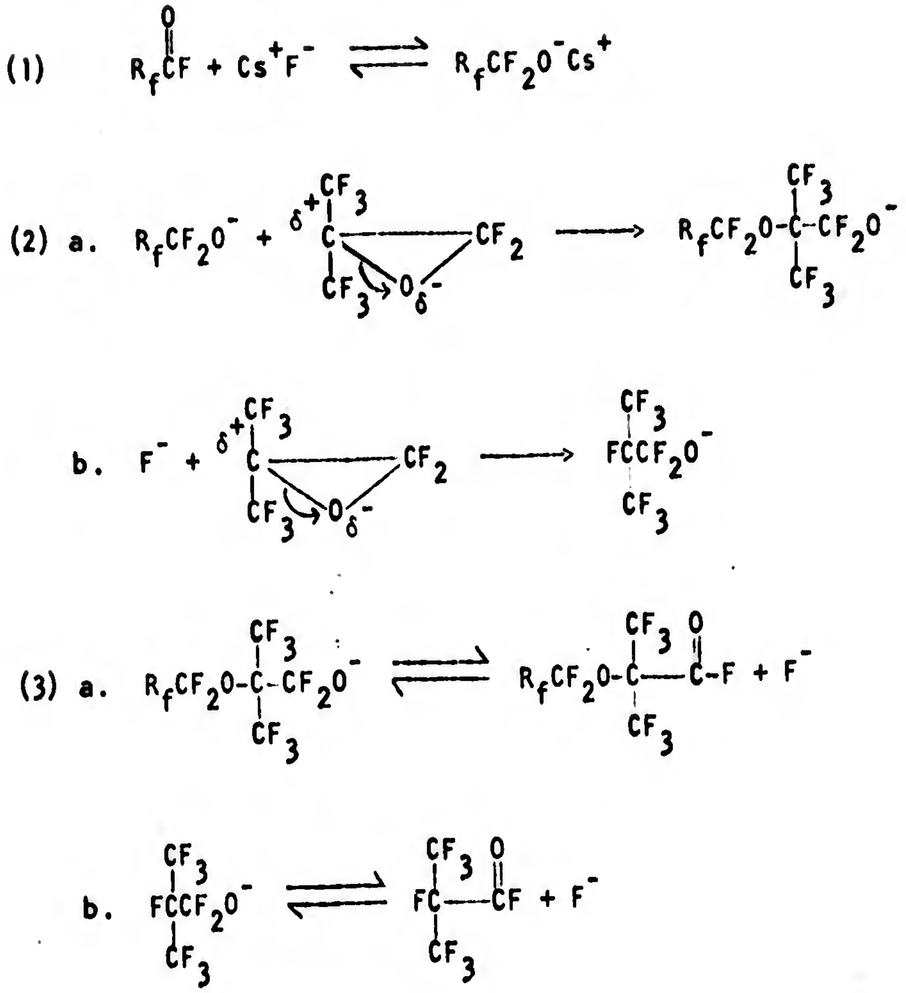
The only higher boiling product isolated from this reaction was identified by infrared (Fig. 28) and NMR (Appendix III) as the 1-to-1 diacid fluoride, resulting from the reaction of one molecule of PFIO with perfluoroglutaryl fluoride. The major volatile product was found to be



perfluoroisobutyryl fluoride, resulting from reaction of PFIO with fluoride ion. Attempts to bring about further reaction between the 1-to-1 diacid fluoride and additional PFIO were not successful.



The reaction of PFIO with both carbonyl fluoride and trifluoroacetyl fluoride was investigated. The desired products, perfluoro-α-methoxyisobutyryl and perfluoro-α-ethoxyisobutyryl fluoride, were required for use in making perfluoro(alkoxy-substituted anhydrides) for cyclodehydration of polyimidoylamidines to polytriazines. The reactions were run in diglyme solvent using cesium fluoride catalyst at 75°. Under these conditions carbonyl fluoride and trifluoroacetyl fluoride react readily with hexafluoropropylene oxide (HFPO) to give the corresponding perfluoroalkoxy-substituted propionyl fluorides[30] as shown above. In each case with PFIO, however, the major product was perfluoroisobutyryl fluoride. Although a small quantity of higher boiling material was obtained in the reaction with trifluoroacetyl fluoride, NMR analysis showed that it did not contain the C_2F_5O-group. A possible explanation for these observations may be found by consideration of the reaction mechanism of the attempted reaction.



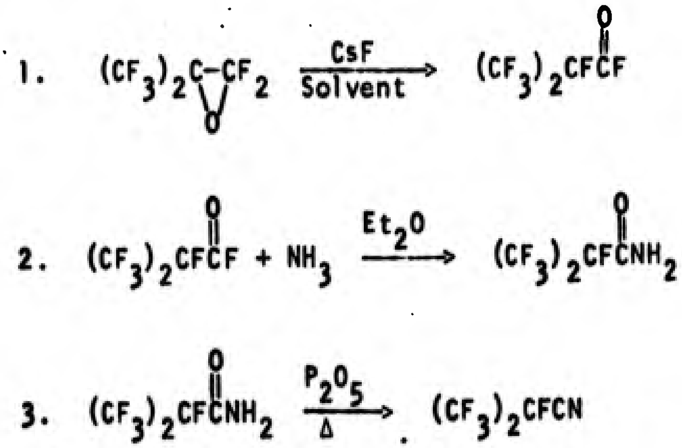
$R_f = F, CF_3$, and $F\overset{O}{\overset{\|}{C}}(CF_2)_3$

Possibly because of steric considerations in the substitution step, the competing attack of the fluoride anion (2b) upon the hindered epoxide ring takes preference over that of the perfluoroalkoxide nucleophile (2a) and results in the formation of perfluoroisobutyryl fluoride. The corresponding reaction of the less hindered perfluoropropylene epoxide with carbonyl fluoride using the same reaction conditions has been reported[30] and resulted in a 77% conversion to perfluoro-2-methoxy-propionyl fluoride[11]. Perhaps this same effect is involved in the formation of only small amounts of the 1-to-1 adduct and none of the 2-to-1 adduct in the reaction of perfluoroisobutylene oxide with perfluoroglutaryl fluoride. The same reaction conditions were used and perfluoroisobutyryl fluoride was a major product.

I. Nitriles

Perfluoroisobutyronitrile was required for use in the study of triazine elastomers in order to compare the effect of the two trifluoromethyl groups upon the chemical properties of triazines derived from it.

The following sequence of reactions was used in the preparation of perfluoroisobutyronitrile:



$$1.\quad (CF_3)_2C{-}CF_2\ (\text{epoxide, }O) \xrightarrow[\text{Solvent}]{\text{CsF}} (CF_3)_2CF\overset{O}{\overset{\|}{C}}F$$

$$2.\quad (CF_3)_2CF\overset{O}{\overset{\|}{C}}F + NH_3 \xrightarrow{Et_2O} (CF_3)_2CF\overset{O}{\overset{\|}{C}}NH_2$$

$$3.\quad (CF_3)_2CF\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow[\Delta]{P_2O_5} (CF_3)_2CFCN$$

Perfluoroisobutylene oxide is readily converted to perfluoroisobutyryl fluoride of high purity in an autoclave reaction in the presence of cesium fluoride and diglyme solvent. The preparation of the pure amide derivative by the reaction of its precursor with liquid ammonia in ethyl ether is accomplished only with difficulty and appears to be the limiting step in the sequence. Once obtained in pure form, however, the amide is easily dehydrated with phosphorous pentoxide to its nitrile in good yield and high purity. An overall conversion of 22.5% was obtained. Infrared spectra of the acid fluoride, amide, and nitrile are shown in Figs. 29-31, respectively. NMR analysis of the nitrile is given in Appendix III.

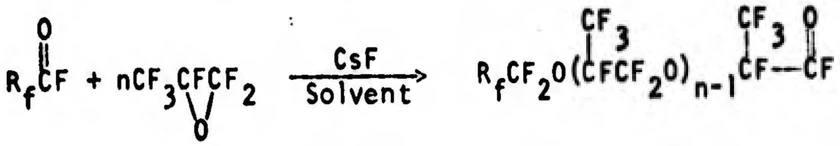
The synthesis of perfluorosebaconitrile and 4-cyanoperfluorobutyryl chloride is discussed in Part A of this section.

J. Miscellaneous Reactions

During the period of this contract several short-term projects were assigned to determine feasibility of certain syntheses or to provide intermediates for other reactions.

1. Reaction of Pentafluorobenzoyl Fluoride with Hexafluoropropylene Oxide

Perfluoroalkanoic acid fluorides have been shown to react with hexafluoropropylene oxide (HFPO) to give polyfluoroethers containing an acid fluoride end group.[6] As yet, no reference to the use of perfluoroaromatic acid fluorides has been found in our review of the literature.

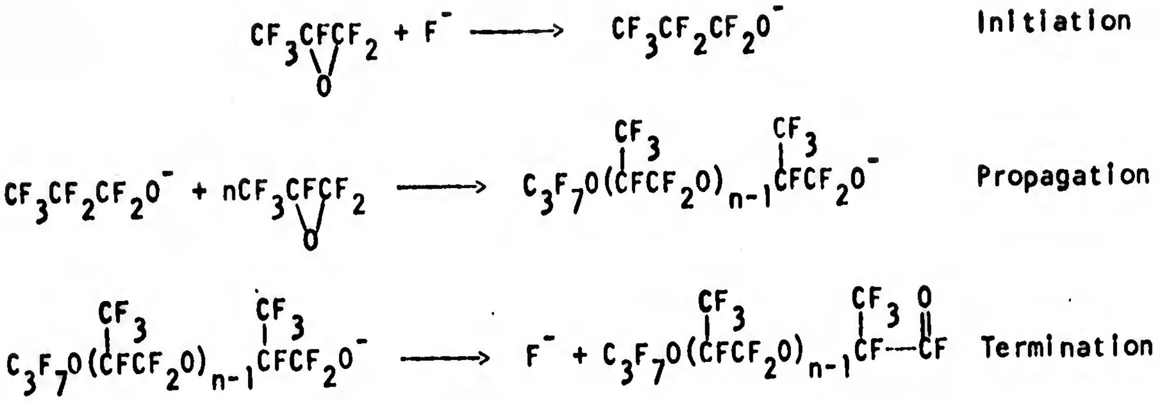


$$R_f\overset{O}{\overset{\|}{C}}F + nCF_3\underset{\diagdown O \diagup}{CFCF_2} \xrightarrow[\text{Solvent}]{\text{CsF}} R_fCF_2O(\overset{CF_3}{\overset{|}{C}}FCF_2O)_{n-1}\overset{CF_3}{\overset{|}{C}}F-\overset{O}{\overset{\|}{C}}F$$

During this period we investigated the reaction of pentafluorobenzoyl fluoride with HFPO using cesium fluoride as catalyst in diglyme and tetraglyme solvents. The desired reaction was as shown.

$$C_6F_5\overset{O}{\overset{\|}{C}}F + CF_3\underset{\diagdown O \diagup}{CFCF_2} \xrightarrow[\text{Solvent}]{\text{CsF}} C_6F_5CF_2O\overset{CF_3}{\overset{|}{C}}F-\overset{O}{\overset{\|}{C}}F$$

The reaction was attempted three times. The first experiment was carried out at room temperature in diglyme. After a slight excess of the epoxide had been added the reaction was stopped. Two layers were observed, both of which contained unreacted acid fluoride as determined by infrared analysis. The lower layer was found to consist primarily of oligomers of the epoxide formed by fluoroanion initiation.

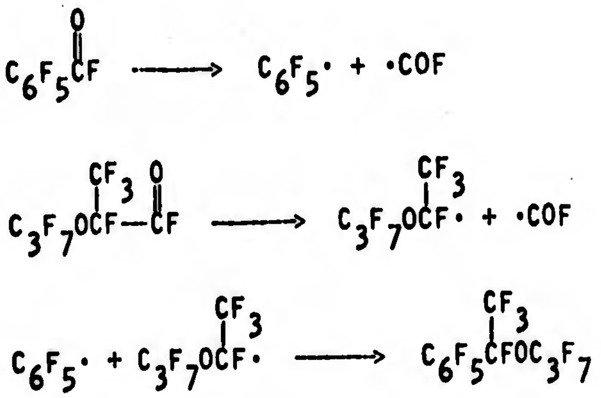


$$CF_3\underbrace{CFCF_2}_{O} + F^- \longrightarrow CF_3CF_2CF_2O^-$$

$$CF_3CF_2CF_2O^- + nCF_3\underbrace{CFCF_2}_{O} \longrightarrow C_3F_7O(\overset{CF_3}{C}FCF_2O)_{n-1}\overset{CF_3}{C}FCF_2O^-$$

$$C_3F_7O(\overset{CF_3}{C}FCF_2O)_{n-1}\overset{CF_3}{C}FCF_2O^- \longrightarrow F^- + C_3F_7O(\overset{CF_3}{C}FCF_2O)_{n-1}\overset{CF_3}{C}F{-}\overset{O}{\overset{\|}{C}}F$$

Distillation of the mixture gave a small amount of higher boiling material which appears, on the basis of NMR analysis (see Appendix III), to be $C_6F_5CF(CF_3)OCF_2CF_2CF_3$. Formation of this ether might occur by a radical coupling process similar to the ultraviolet catalyzed coupling of other perfluorinated acid fluorides[31].



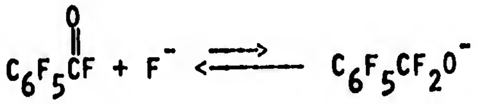
$$C_6F_5\overset{O}{\overset{\|}{C}}F \longrightarrow C_6F_5\cdot + \cdot COF$$

$$C_3F_7O\overset{CF_3}{C}F{-}\overset{O}{\overset{\|}{C}}F \longrightarrow C_3F_7O\overset{CF_3}{C}F\cdot + \cdot COF$$

$$C_6F_5\cdot + C_3F_7O\overset{CF_3}{C}F\cdot \longrightarrow C_6F_5\overset{CF_3}{C}FOC_3F_7$$

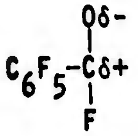
Attempts at effecting the desired reaction by carrying out the experiment at both lower (-5 to -10°) and higher (70-80°) temperatures and in another solvent (tetraglyme) were likewise unsuccessful.

Since the success of this reaction depends upon the formation of the perfluoroalkoxy anion, which then participates in the nucleophilic substitution and ring opening of the epoxide, the reaction of pentafluorobenzoyl fluoride with cesium fluoride in diglyme has been studied by NMR which indicates that the mixture contains (within the limits of detection) only the acid fluoride with no indication of the perfluorobenzyloxy anion or cesium salt. In contrast, very little of the acid fluoride is seen in the NMR spectrum of perfluoroglutaryl fluoride, which reacts readily with HFPO. NMR analyses of mixtures of CsF with both perfluorobenzoyl fluoride and perfluoroglutaryl fluoride are shown in Appendix III. If an equilibrium exists between the perfluoroacid fluorides and their corresponding anions, it is apparent that in this case it is predominately to the left.



$$C_6F_5\overset{O}{\overset{\|}{C}}F + F^- \rightleftharpoons C_6F_5CF_2O^-$$

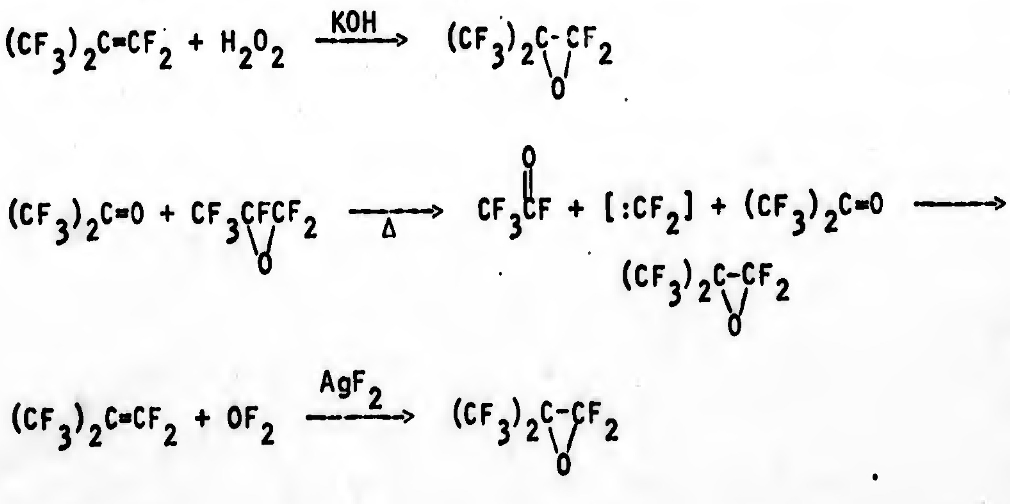
This might be accounted for by a destabilization of the positive charge on the carbonyl carbon atom by electron withdrawal from the site by the pentafluorophenyl group, effectively suppressing formation of the intermediate shown below.



$$C_6F_5-\overset{O\delta-}{\overset{|}{\underset{F}{\underset{|}{C}}}}\delta+$$

2. Preparation of Perfluoroisobutylene Oxide

Perfluoroisobutylene oxide (PFIO), required as an intermediate for reaction with perfluoroglutaryl fluoride, has been prepared by the reaction of perfluoroisobutylene with basis hydrogen peroxide[32,33] by the addition of difluorocarbene (generated from hexafluoropropylene oxide) to hexafluoroacetone[34], and by reaction of perfluoroisobutylene



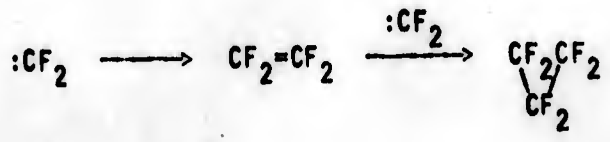
with oxygen difluoride in the presence of silver difluoride[35].

Of the three reported procedures the second, reaction of hexafluoroacetone and hexafluoropropylene oxide, appeared to be the most attractive since it avoided the synthesis and handling of highly toxic perfluoroisobutylene and both reactants were readily available.

In carrying out this reaction it was found that the rate of decomposition of hexafluoropropylene oxide to difluorocarbene and trifluoroacetyl fluoride is relatively slow at 150°, the reaction temperature reported. Consequently, the reaction was run at 225-230° using an excess of hexafluoroacetone. The reaction was monitored by infrared, which indicated complete disappearance of the hexafluoropropylene oxide after 42-68 hours.

It was found that the most convenient way of separating the pure PFIO from the reaction mixture was to bubble the volatile mixture through a column of water and trap the effluent PFIO. Both trifluoroacetyl fluoride and unreacted hexafluoroacetone, the major impurities, are removed by this treatment.

The presence of small quantities of tetrafluoroethylene and hexafluorocyclopropane was also detected in the reaction mixture. These were removed by distillation. Formation of tetrafluoroethylene could be accounted for by combination of difluorocarbene, which might be generated by decomposition of either hexafluoropropylene oxide or PFIO. The cyclopropane could then be formed by addition of another molecule of difluorocarbene.



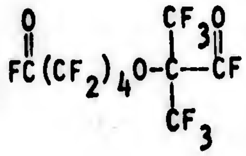
It is interesting to note that PFIO is considerably more thermally stable than hexafluoropropylene epoxide since it is isolated in reasonable conversion (up to 66%) after being heated to 200° for 48 hours.

3. Preparation of Pentafluoronitrobenzene

The preparation of pentafluoronitrobenzene was carried out following a reported[7] procedure. Pentafluoroaniline was oxidized by trifluoroacetic acid formed in situ with 30% hydrogen peroxide and trifluoroacetic anhydride. The reaction was run at the reflux temperature (41°C) of the methylene chloride solvent. The oxidation appeared to proceed only to the green colored nitroso compound. The use of 90% hydrogen peroxide possibly would have resulted in the oxidation going to completion to the nitro compound.

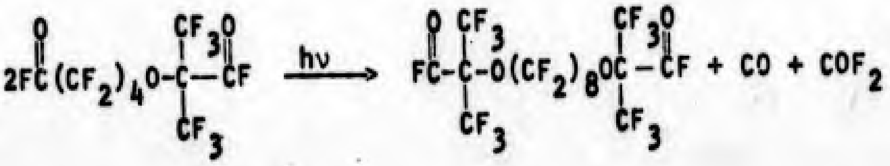
More vigorous oxidizing conditions were used to complete the oxidation. A method reported[8] for the preparation of 3,5-dichloro-4-nitrobenzonitrile from the corresponding aniline was followed. The methylene chloride solvent was removed and glacial acetic acid was added with concentrated sulfuric acid and additional 30% hydrogen peroxide. The reaction mixture was heated to 75-90°C for 9 hours and after one hour the color of the mixture turned to a golden yellow. After cooling and the addition of water, about 48 g. of a golden-yellow, oily product settled to the bottom of the flask. The infrared spectrum (Fig. 32) of this material dried over magnesium sulfate corresponds to that of pentafluoronitrobenzene.

4. Attempted Photochemical Dimerization of



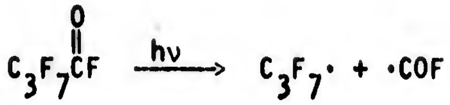
$F\overset{O}{\overset{\|}{C}}(CF_2)_4O-\underset{CF_3}{\overset{CF_3}{C}}-\overset{O}{\overset{\|}{C}}F$

In an effort to make a highly hindered diacid fluoride containing ether linkages, the photochemically induced coupling dimerization (1) was attempted.

(1) 

$$2F\overset{O}{\overset{\|}{C}}(CF_2)_4O-\underset{CF_3}{\overset{CF_3}{C}}-\overset{O}{\overset{\|}{C}}F \xrightarrow{h\nu} F\overset{O}{\overset{\|}{C}}-\underset{CF_3}{\overset{CF_3}{C}}-O(CF_2)_8O\underset{CF_3}{\overset{CF_3}{C}}-\overset{O}{\overset{\|}{C}}F + CO + COF_2$$

The photolysis of perfluorobutyryl fluoride has been reported[31] to form perfluoro-n-hexane in 58% yield. The following sequence of reactions was proposed.

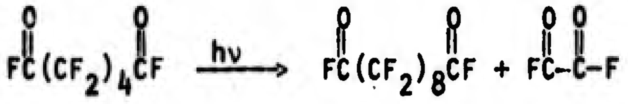
(2) 

$$C_3F_7\overset{O}{\overset{\|}{C}}F \xrightarrow{h\nu} C_3F_7\cdot + \cdot COF$$

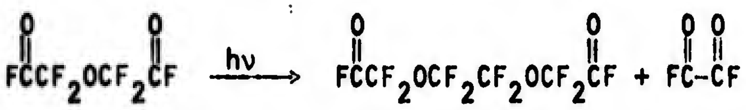
(3) $$2C_3F_7\cdot \longrightarrow n\text{-}C_6F_{14}$$

(4) $$2\cdot COF \longrightarrow COF_2 + CO$$

The photodimerization of perfluoroadipyl fluoride to perfluorosebacyl fluoride (5) and of perfluorooxydiacetyl fluoride (6) has also been reported[6].

(5) 

$$F\overset{O}{\overset{\|}{C}}(CF_2)_4\overset{O}{\overset{\|}{C}}F \xrightarrow{h\nu} F\overset{O}{\overset{\|}{C}}(CF_2)_8\overset{O}{\overset{\|}{C}}F + F\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-F$$

(6) 

$$F\overset{O}{\overset{\|}{C}}CF_2OCF_2\overset{O}{\overset{\|}{C}}F \xrightarrow{h\nu} F\overset{O}{\overset{\|}{C}}CF_2OCF_2CF_2OCF_2\overset{O}{\overset{\|}{C}}F + F\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}F$$

Varied attempts with and without a solvent did not result in any conclusive indication that a dimerization had occurred. GLC analysis showed a proliferation of minor quantities of new components in the irradiated mixture. No evidence was obtained of the formation of carbonyl fluoride or carbon monoxide as by-products of the desired coupling.

III. EXPERIMENTAL

A. Triazine Polymers

The perfluoroalkylenetriazine polymers prepared together with their characterization data are summarized in Table I. All polymers were prepared by polymerization of perfluorosebaconitrile and perfluorosebacamidine in a solvent to the imidoylamidine followed by triazine ring closure with heptafluorobutyric anhydride at room temperature. The perfluorosebaconitrile used in all reactions, except 1105.40, was used as received from Air Force Materials Laboratory and had an analyzed purity of 99.95% (GLC) (Fig. 1). The perflurorosebacamidine used in all reactions was also used as received from Air Force Materials Laboratory and has high purity (Fig. 2). The heptafluorobutyric anhydride (PCR) had an analyzed purity of 98+% (GLC) and all solvents were dried, distilled and stored over molecular sieves. The weighing of reactants and transfer of materials were carried out in a dry box and the reactions were run under a prepurified nitrogen atmosphere. The experimental details of the preparation of 1105.49.2 and 1105.52 will be described as successful and typical examples of Reaction Conditions C and E (Table I).

1. Preparation of Low Molecular Weight Triazine Polymer (1105.49.2)

Perfluorosebaconitrile (9.30 g., 0.0205 mole) followed by 10.0 ml. 1,2-dimethoxyethane (glyme) were placed in a 100-ml., 1-neck flask. Perfluorosebacamidine (5.00 g., 0.0103 mole) was added in one batch, the flask filled with prepurified nitrogen, and the mixture rapidly stirred with a magnetic stirrer for about 2 days. Several hours were required for complete solution of the powdered diamidine. The molar ratio of dinitrile to diamidine was 2.0/1. The infrared spectrum of the glyme solution of a similar polyimidoylamidine may be seen in Fig. 3. The polyimidoylamidine solution was then added to a 5 to 1 molar ratio of heptafluorobutyric anhydride (42.3 g., 0.103 mole) by dropwise addition over an interval of 15-20 minutes. An exotherm increased the temperature to about 40° and the solution remained clear. Stirring was continued overnight. A rotovac at full pump vacuum at room temperature was cautiously used for removal of the glyme solvent, followed by use of an oil bath at temperatures finally up to 175° for 30-45 minutes for removal of excess heptafluorobutyric anhydride and its acid derivative. A light colored, fluid triazine polymer (14.1 g.) was obtained. The infrared spectrum (Fig. 4) showed strong nitrile absorption at 4.40 microns, indicative of nitrile end groups, triazine absorption at 6.45 microns and similarity to the reported[2] spectrum of poly(perfluoropropylperfluorooctamethylenetriazine). The reduced viscosity at 0.50 g./100 ml. in hexafluoroxylene at 30.0° was 0.03 and the intrinsic viscosity 0.03. The molecular weight by vapor phase osmometer measurement was 2230.

2. Preparation of High Molecular Weight Triazine Polymer (1105.52)

Perfluorosebacamidine (5.00 g., 0.0103 mole) was dissolved in 20.0 ml. dimethylformamide with slight warming and added dropwise over about 15 hours to pure perfluorosebaconitrile (5.11 g., 0.0113 mole) with stirring. The mixture was allowed to react for 45 hours. The molar ratio of dinitrile to diamidine was 1.1/1. Triazine ring closure was accomplished by dropwise addition of the polyimidoylamidine solution to an excess of heptafluorobutyric anhydride (42.3 g., 0.103 mole) in a 5 to 1 molar ratio over an interval of 30 minutes. The mixture was stirred for 18 hours. The solvent, excess anhydride and acid were removed by use of a rotovac under full pump vacuum and an oil bath at 175-180° for 30-45 minutes. The triazine product (13.0 g.) was a light yellow, clear gum. Its infrared spectrum was identical to that of 1105.49.2 with the exception that nitrile absorption at 4.40 microns was much less intense. The reduced viscosity at 0.50 g/100 ml. in hexafluoroxylene at 30.0° was 0.08 and the intrinsic viscosity 0.08. The molecular weight by vapor phase osmometer measurement was 32,400.

3. Preparation of High Molecular Weight Triazine Polymer (1105.40)

The reaction apparatus and all materials and reactants were placed in a Hydrovoid (Air Control, Inc.) dry box in order to maintain anhydrous reaction conditions. The dry box was filled and kept under a slight pressure with prepurified nitrogen which was circulated by pump through a liquid oxygen cooled trap and two 1 1/2 x 24 inch drying tubes filled with silica gel.

A 500-ml., 3-neck flask was fitted with a stirrer, addition funnel and viscometer. The viscometer consisted of a 10-ml. pipette with the fine portion of its tip removed and attached to a vacuum system via a trap. The pipette was attached to the flask with a threaded Teflon adapter which permitted the tip to be raised or lowered inside the flask while keeping a tight seal. Relative increases in solution viscosity could be measured by drawing the solution to slightly above the etched marking of the pipette, raising the tip out of the solution in the flask, and noting the efflux time required for the miniscus to drop to a second marking.

Perfluorosebaconitrile (21.60 g., 0.0478 mole) was added to the flask followed by 20.0 ml. glyme (1,2-dimethoxyethane). The stoichiometric amount of perfluorosebacamidine (23.23 g., 0.0478 mole) was weighed out and kept in a stoppered flask for the slow stepwise addition as the imidoylamidine polymerization proceeded. Over the interval of the first 6 days, 77% of the diamidine (17.94 g., 0.0369 mole) was added in increments averaging 1.8 g. At this time the viscosity of the polymer solution increased to such an extent as to preclude good mixing of the added diamidine and 20.0 ml. more of glyme solvent was added. The incremental addition of diamidine was continued together with glyme addition using decreasing amounts of diamidine until after 49 days 91.7% of the diamidine has been added and 80.0 ml. of glyme had been used. At this time a white precipitate, identified as unreacted diamidine by infrared analysis, was observed. The solid was removed using a sintered glass filter. The filtrate showed no nitrile absorption in the infrared. The filtered solution was added to heptafluorobutyric anhydride (177.1 g., 0.432 moles) as described earlier and the triazine polymer isolated as before, giving 50.3 g. of a light brown gum. Viscosity and molecular weight are given in Table I.

4. Reaction of N'-(Perfluorobutyrimidoyl) Perfluorobutyramidine with Perfluorobutyryl Chloride and Trifluoroacetic Anhydride

Perfluorobutyronitrile (18.1 g., 0.093 mole) and excess ammonia (13.0 g., 0.764 mole) were condensed into a 100-ml. Fischer-Porter tube having a magnetic stirrer. After 3 hours, the excess ammonia was bled off through a drying tube. The white, crystalline perfluorobutyramidine left in the tube was placed under full pump vacuum overnight for removal of the last traces of ammonia. N'-(Perfluorobutyrimidoyl) perfluorobutyramidine was prepared by adding 20 ml. glyme solvent (1,2-dimethoxyethane), under anhydrous conditions, and then condensing in perfluorobutyronitrile (25.2 g., 0.129 mole) and allowing reaction with stirring overnight at room temperature. The excess nitrile was then bled off through a drying tube. Perfluorobutyryl chloride (25.0 g., 0.107 mole) was condensed into the tube. After allowing to warm to room temperature, the solid reaction product came out of solution and was removed quickly from the tube and mixed with a high excess of trifluoroacetic anhydride (100 g., 0.476 mole). The solid immediately went into solution and a strong exotherm was observed. The solution was stirred overnight. Fractional distillation was used for isolation of the triazine products; a constant boiling fraction (57.3 g.) was collected at 130.0° C and a second fraction (33.5 g.) at 131-155° C. GLC and infrared analysis indicated the first fraction to be an azeotropic mixture of perfluorobutyric acid and triazine product. This material was washed with K_2CO_3 solution and water and dried for removal of the acid. Fractional distillation yielded 18.9 g. of pure triazine collected at 147° C. GLC analysis using a standard of tris-(perfluoropropyl)-s-triazine (b.p. 165° C) showed that the major triazine formed was not the desired symmetrical triazine but probably 2,4-bis-(perfluoropropyl)-6-trifluoromethyl triazine.

B. Block Copolymers

1. Polyisoprene-Poly(ethylene Oxide)-Polyisoprene

The hydroxy-terminated polyethylene oxide (Matheson, Coleman & Bell), after drying, had an analyzed molecular weight of 7161 by vapor phase osmotic measurement and an equivalent weight of 3792 by hydroxyl number determination. A diisocyanate-terminated prepolymer was prepared by reaction of a 1:2 equivalent ratio of PEO (268.1 g., 0.0707 equiv.) with 2,4-toluenediisocyanate (12.3 g. 0.1414 equiv., Monomer-Polymer Laboratories) in 40 parts toluene solution. The mixture was stirred under nitrogen for 6 hours at 80°C. Complete reaction was indicated by an analyzed free isocyanate content of 0.42% (theoretical, 0.48%) after addition of dry tetrahydrofuran solvent. The diisocyanate-terminated prepolymer (598 g. sol'n., 0.0684 equiv.) was, in turn, mixed with a stoichiometric amount of t-butylhydroperoxide (6.2 g., 0.0687 equiv.) based upon the theoretical free isocyanate content of 0.48% to form t-butyl peroxycarbamate end groups. Additional tetrahydrofuran (1370 g.) was added to make a 20.2% solution. Pyridine (2.8 g.) was added as a mild catalyst for the isocyanate-hydroxyl reaction and the mixture was stirred under nitrogen for 24 hours at room temperature. The t-butyl hydroperoxide (Monomer-Polymer Labs), originally 74.3% pure by iodometric titration, was distilled through a packed column and collected at 22-23°C/11mm and found to be 100% pure. The impurities, t-butyl alcohol and water, upon reaction with the isocyanate end groups would result in termination of the B block preventing linkage to the A blocks.

Three polymerizations were carried out with the t-butylperoxycarbamate-terminated B block prepolymer and freshly distilled isoprene.

a. Prepolymer solution (24.8 g., 5.0 g. prepolymer, isoprene (16.4 g., 0.252 mole), and _ca._ 0.5 g. t-butyl hydroperoxide were placed in a 100-ml. Fischer-Porter tube. The tube was heated in a silicone oil bath at 90°C for 14 hours and 125°C for 4 hours. After cooling, _ca._ 0.5 g. 2-5-di-t-butylhydroquinone inhibitor was added and the solvent was removed under vacuum. The polymer (7.2 g.) was subjected to a Soxhlet extraction with methanol for removal of any unreacted prepolymer and 6.4 g. (29.8% conversion) of product was obtained. The methanol extract was shown by infrared analysis to contain no polyethylene oxide B block material. The polymer was soluble in methylene chloride and insoluble in ethyl ether. Absorption peaks attributable to both polyethylene oxide and polyisoprene blocks were observed in the infrared spectrum of the polymer (Figs. 6-8).

b. Prepolymer solution (24.8 g.) was stripped of solvent under vacuum in a 100-ml. Fischer-Porter tube and isoprene (16.4 g., 0.252 mole) and *ca*. 0.5 g. t-butyl hydroperoxide were added under nitrogen. The reactants became homogeneous upon heating to 95°C, which was continued for 18 hours. The mixture was then heated at 135°C for 26 hours. Inhibitor was added and the polymer (21.4 g.) was Soxhlet extracted first with methanol and then with hexane. The product was insoluble in all solvents tried, showing swelling and appears to be crosslinked.

c. Prepolymer solution (24.8 g.) was stripped of solvent under vacuum in a 100-ml. Fischer-Porter tube and isoprene (16.4 g. 0.252 mole) was added under nitrogen. The contents of the tube became homogeneous upon heating and were heated at 95°C for 48 hours. Inhibitor was added and the polymer (12.1 g.) was extracted first with methanol and then hexane. The product was insoluble, solvent swollen and, as in the preceding run, appears to be crosslinked.

2. Polystyrene-Poly(Ethylene Oxide)-Polystyrene

The 1105.65.1 polystyrene A block material was prepared in a 100-ml. Fischer-Porter tube using 20.0 g. solution (4.0 g. prepolymer). The THF solvent was removed under vacuum without warming. Freshly distilled styrene (99+ % purity by GLC and n_D^{25} 1.5432; reported n_D^{25} 1.5439) was added in an amount (16.4 g.) calculated to yield a copolymer having 33 1/3 mole % ethylene oxide. Benzene solvent (20 ml.) was added and the mixture was covered with nitrogen. The contents of the tube were heated in an oil bath for 24 hours at 80°C. Pentane was added for precipitation of the polymer from solution. A methanol extraction for removal of any unreacted PEO B block was attempted by shaking with methanol; a stable suspension resulted. After removal of the methanol, the material was extracted with cold water. The 1105.65.2 material was prepared in the same way with the exception that no benzene solvent was used.

C. Nitroso Terpolymers

1. Terpolymer of Trifluoronitrosomethane, Tetrafluoroethylene, and Trifluorovinyl Isopropyl Ether

Three polymerizations were attempted, using identical procedures. Specific reactant charges and results are listed in Table III. The reactants were condensed into glass ampoules, sealed and held at -35 to -30°C for the times indicated. The ampoules were then cooled in liquid air, opened, and the volatile materials removed on a vacuum line. The products were clear, rubbery gums which were insoluble in FC-43, FC-75, cyclohexanone, and only slightly soluble in hexafluorobenzene, indicating that some cross-linking may have occurred during polymerization.

<u>Anal</u>. Sample 1095.65. Found: %C, 25.97;[a] %H, 1.46;[a] %N, 6.97;[a] %F, 62.90[b]
Sample 1095.75. Found: %C, 18.42;[b] %H, 1.74;[b] %N, 6.86;[b] %F, 56.08[b]

(a) Average of double determination.
(b) Average of triple determination.

An infrared spectrum of the terpolymer is shown in Fig. 13.

D. Fluorine-Containing Epoxides

1. Perfluoroheptene-1 Epoxide

A reaction cell 8 x 2 inches fabricated from Vycor 7910 (U.V. transmitting grade) having a 45-degree upward inclined sidearm was used. The cell had a fritted glass gas dispersion tube and a one-inch diameter cold condenser inserted through a rubber stopper at the top and extended to the bottom of the tube. Oxygen gas (U.S.P.) was dried and purified by bubbling through a concentrated sulfuric acid scrubber and the flow rate was measured using a rotameter. The chlorine gas was bubbled through concentrated sulfuric acid at a rate of flow approximately 1 percent of the oxygen flow rate. Both gases were passed through Mallcosorb acid gas absorbers after leaving the sulfuric acid scrubbers. The two gases were then passed into a 500-ml. flask mixing chamber and thence to the reaction cell. Two Friedricks condensers in series were connected to the sidearm of the cell and a liquid oxygen cooled trap with a drying tube was placed on the other side of the condensers. The apparatus was dried immediately before use by purging nitrogen through the system while heating the mixing flask and reactor. Perfluoroheptene-1 (43.4 g., 0.124 mole) was placed in the cell. Ice water was circulated through the cold finger and the Friedricks condensers; the flow of oxygen and chlorine started and adjusted. A 450-watt Hanovia 679A-36 ultraviolet lamp inserted in a water-cooled Vycor immersion well was placed about 3 inches from the reaction cell. U.V. irradiation was continued until an infrared absorption peak appeared at 6.50 microns indicating formation of perfluoroepoxide and decreased intensity of the peak at 5.6 microns indicating conversion of the olefin. The perfluoroheptene-1 epoxide was not isolated from the mixture.

2. Perfluorooctadiene-1,7 Diepoxide

a. Alkaline Hydrogen Peroxide

Perfluorooctadiene-1,7 (10.0 g.), 50% hydrogen peroxide (15.0 ml.), methanol (20.0 ml.), and 2.4 g. potassium hydroxide dissolved in 5.0 ml. water were reacted using the same procedure as described in the alkaline hydrogen peroxide epoxidation of perfluoroheptene-1. The reaction was run for 8 hours at 0°C. The organic layer was separated and dried over sodium sulfate. A GLC analysis indicated the crude product to contain about 4.5% diepoxide, 12.6% monoepoxide, and 82.5% unchanged diene. Bromination was used to aid in the separation of unreacted olefin in the mixture.

Bromine (2 ml.) was added to and shaken with the mixture and allowed to stand overnight. The excess bromine was removed by shaking with a 10% solution of sodium bisulfite, followed by a water wash and drying over magnesium sulfate. A fractional distillation through a packed, heated column yielded the following three fractions.

Fraction	Boiling Point, °C	Refractive Index
1	95-105	n_D^{20} 1.3459
2	105-110	n_D^{21} 1.6743
3	157 at 44 mm	n_D^{22} 1.6768

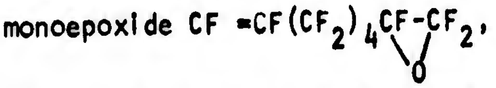
Fraction 1 may contain the desired perfluoro-1,2,7,8-diepoxyoctane (reported[14] b.p. 104°C) although the refractive index differs greatly from that reported, n_D^{20} 1.2900.

When the above described reaction was repeated with extension of the reaction time to 47 hours, the organic layer was indicated by GLC analysis to contain 4.26% diepoxide, 10.1% monoepoxide, and 85.6% unchanged diene. The infrared spectrum showed a relatively weak peak at 6.45 microns. A considerable portion of the starting perfluorooctadiene-1,7 was oxidized to perfluoroadipic acid. The aqueous layer (pH 9) was taken to dryness on a steam bath and the residue was dissolved in dilute hydrochloric acid and the solution extracted with ethel ether. The infrared spectrum of the ether extract corresponded to that of perfluoroadipic acid. About 1.6 g. of solid material was obtained from the extract, which according to determination of the neutralization equivalent was 93% pure perfluoroadipic acid.

b. Chlorine-Sensitized Photochemical Oxidation

Perfluorooctadiene-1,7 (103.4 g., 0.285 mole) was placed in the reaction cell described in Section III. D. 1. and irradiated with ultraviolet light for 10 hours while oxygen containing about 1% chlorine was bubbled through the liquid. The perfluorooctadiene-1,7 had a boiling point of 106-109°C and greater than 99% purity by GLC analysis.

The apparatus was dried immediately before use by purging nitrogen through the system while heating the mixing flask and reactor. After the starting material was added to the reactor, ice water was circulated through the cold finger and the Friedricks condensers; the flow of oxygen and chlorine was started and adjusted. A 450-watt Hanovia 679A-36 ultraviolet lamp inserted in a water-cooled Vycor immersion well was placed about 3 inches from the reaction cell. Ultraviolet irradiation was continued until an infrared absorption peak appeared at 6.50 microns, indicating formation of perfluoroepoxide, and decreased intensity of the peak at 5.6 microns indicated the conversion of the diolefin.

After 10 hours of reaction time, infrared analysis showed the appearance of absorption peaks at 5.3 microns (acid fluoride), 5.6 microns (CF_2-CF-), and 6.45 microns (perfluoroepoxide) in relative intensities of 0.61, 0.70, and 0.73. A GLC analysis of the crude reaction mixture, after standing overnight, showed the presence of about 56 g. (54% conversion) perfluorooctadiene-1,7 diepoxide. The gas chromatogram indicated the presence of three other components in the crude mixture; 7.2% unreacted perfluorooctadiene-1,7, 15.0% of the monoepoxide  $CF{=}CF(CF_2)_4CF{-}CF_2$ (O bridging), and 12.1% of an acid fluoride. Preparative GLC was used to isolate small amounts of the three main components for identification by infrared analysis. The detection of 54.5% diepoxide and 15.9% monoepoxide by GLC was corroborated by NMR analysis, which indicated that approximately 55% of the terminal groups were epoxide groups.

A large amount of gas was evolved during reaction and afterwards before work-up. The volatiles evolved during reaction and caught in the liquid oxygen cooled trap were shown by infrared analysis to be carbonyl fluoride and silicon tetrafluoride.

The crude mixture was treated cautiously with 100 ml. ice water washed with 100 ml. 10% sodium bicarbonate solution, and finally with 100 ml. water, and then dried over sodium sulfate.

Bromination was used to facilitate the separation of the olefin compounds from their epoxide derivatives since their boiling points are very close to one another. Bromine (3 ml.) was added to the mixture, which was allowed to stand 36 hours in the presence of light. The excess bromine was removed by treatment with a sodium bisulfite solution followed by washing twice with water and drying over sodium sulfate.

Distillation of the mixture using an 18 x 2 cm. Vigreaux column provided the five fractions listed below:

Fraction	Boiling Point, °C	Pressure, mm Hg	Amount, g.
1	47.0	144	5.38
2	60-61	142	15.03
3	71-72	22	10.57
4	80-100	20	1.12
5	125	20	2.02

Fractions 1 and 2 were determined by infrared and GLC analysis to be the desired perfluorooctadiene-1,7 diepoxide. The GLC analysis indicated 99+% purity for both fractions. The difference in boiling points is attributed to the distillation of an azeotrope with water in Fraction 1. A gas infrared analysis was made from Fraction 2 and found to be in good agreement with the gas IR spectrum of the same diepoxide previously[11] prepared in this laboratory.

3. Pentafluorophenyl Glycidyl Ether

A 250-ml., 3-neck flask was fitted with a stirrer, reflux condenser and addition funnel. A solution of 5 g. sodium hydroxide in 100 ml. water followed by 18.4 g. (0.1 mole) pentafluorophenol was placed in the reaction flask. The flask was maintained at running tap water temperature throughout the course of the reaction with a circulating water bath. Distilled epichlorohydrin (14.0 g., 0.15 mole) was then slowly added to the stirred reaction mixture over an interval of 45 minutes. The reaction was allowed to continue for 24 hours. Next, the lower organic layer was extracted three times with 100-ml. portions of methylene chloride. The extract was washed once with dilute acetic acid solution (10 g. acetic acid in 50 ml. water) and then three times with water. Following this the extract was dried over magnesium sulfate. The methylene chloride solvent was removed by means of a rotovac at a temperature not exceeding 30°C. The crude product was micro-distilled and 11 g. of 98% pure (GLC) product was recovered boiling at 69°C at 1.2 mm. Identification of the product was confirmed by infrared and elemental analysis.

	%C	%H
Calculated	45.0	2.08
Found	45.0	2.00

4. Tetrafluoro-p-phenylene Diglycidyl Ether

a. The sodium salt of tetrafluorohydroquinone was prepared by the slow addition (3 hours) of tetrafluorohydroquinone (9.1 g., 0.05 mole) dissolved in 100 ml. dry THF to a rapidly stirred suspension of sodium hydride (7.2 g., ~50% oil dispersion, 0.15 mole) in 80 ml. THF. The mixture was stirred an additional 1 1/2 hours after which the excess sodium hydride was removed by the addition of 5.0 ml. methanol. Redistilled epichlorohydrin (74.0 g., 0.80 mole) in an 8:1 molar excess was added with continued stirring for 26 hours at room temperature. After filtration of the brown colored, water soluble salts the THF solvent and excess epichlorohydrin were flashed off using a rotovac. Two layers of immiscible higher boiling liquids remained in the flask and were separated with a separatory funnel. Infrared and GLC analysis suggested that the top layer was largely mineral oil from the sodium hydride dispersion and that the bottom layer was 90.4% pure probable product. A GLC preparative separation of the bottom layer yielded about 700 mg. of 99.4% pure material. An elemental carbon and hydrogen analysis and molecular weight determination (VPO) provided the following data:

	C	H	Mol. Wt.
Theoretical	49.0	3.41	294
Found	39.07	5.22	492

NMR analysis indicated the presence of hydrocarbon protons and of the oxirane ring, but no fluorine. This material was thus shown not to be the desired tetrafluorohydroquinone diglycidyl ether product, but possibly a base catalyzed polymerization product of epichlorohydrin.

b. A procedure reported[15] for the preparation of the diglycidyl ether of hydroquinone was followed. A 300-ml., 3-neck flask was fitted with an ice water cooled reflux condenser, thermometer extended into the reactants, magnetic stirrer and addition funnel. The tetrafluorohydroquinone (19.8 g., 0.1085 mole) was dissolved in a 2-to-1 molar excess of epichlorohydrin (40.2 g., 0.434 mole) in the reaction flask with stirring at room temperature. The stoichiometric amount of NaOH (8.7 g., 0.217 mole) was dissolved in 18 ml. water and added dropwise to the stirred reactants at 60-86°C. A strong exotherm was observed. At the start of the NaOH addition, a reddish purple coloration appeared, which gradually darkened, until after the addition of about three quarters of the NaOH, the reaction mixture solidified. The solid material would not melt, was insoluble in water, acetone, ethyl acetate and DMSO, and appears to have been a polymerization product.

The tetrafluorohydroquinone (Imperial Smelting) was subjected to an attempted purification by sublimation at full pump vacuum. The sublimed material had a broad m.p. range up to 160°C and a DCS curve indicative of low purity. An elemental analysis yielded the following results:

	Found	Theoretical
C	38.88%	39.58%
H	1.13	1.11
F	39.02	41.75

Analysis of the material, as received, yielded the data:

	Found	Theoretical
C	39.11%	39.58%
H	1.18	1.11
F	37.82	41.75
m.p.	155-165°C	168-170°C

A DCS curve corroborated the degree of impurity indicated by this data. NMR analysis indicated 95% purity.

c. A 300-ml., 3-neck flask was fitted with a stirrer, ice water cooled reflux condenser protected with a drying tube, and an addition funnel. Provision was made for a slow purge of nitrogen through the entire system.

Tetrafluorohydroquinone (18.2 g., 0.1 mole) was dissolved in a 2-to-1 molar excess of epibromohydrin (54.8 g., 0.4 mole) in the reaction flask and 75 ml. dry methanol was added. The tetrafluorohydroquinone was used as received. The stoichiometric amount of $LiOH \cdot H_2O$ (8.4 g., 0.2 mole) was then dissolved in 130 ml. dry methanol and added dropwise to the stirred reactants at methanol reflux temperature. After the addition of the base had been completed, the mixture was stirred and refluxed for 5 hours. The methanol solvent was stripped off using a rotovac and the residue was washed twice with water until neutral. The first washing had a pH of 10. The excess epibromohydrin was removed by distillation up to 40°C/0.1mm. Distillation of the reaction products was then attempted using a micro distillation apparatus. Fraction #1 (4.8 g.) was collected at 120-135°C/.075mm. and Fraction #2 (6.0 g.) at 140°-200°C/.1mm. Decomposition occurred suddenly at 200° C with some polymerization in the receiver and the distillation was stopped.

Fraction #1 solidified and had a sharp melting point at 86-87°C. The IR showed strong hydroxyl absorption at 2.9 microns. A titration of the oxirane oxygen content using HCl, pyridine and NaOH gave a value of 6.92%. This suggested that the identity of Fraction #1 was the monoglycidyl ether of tetrafluorohydroquinone which has a theoretical oxirane oxygen content of 6.70%. However, an elemental analysis did not provide additional corroboration for this supposition. The results were the following:

	Found	Theoretical
C	48.10%	45.5%
H	3.42	2.5

Fraction #2 was found to have an oxirane oxygen content of 2.88%, far below the theoretical value of 10.85% of the desired diglycidyl ether. Fraction #2 slowly solidified to a brownish tar.

d. Because of the indication of formation of the monoglycidyl ether of tetrafluorohydroquinone in the preceding reaction, the reaction was repeated, using an increased reaction time of 24 hours. The use of no excess of $LiOH \cdot H_2O$ was indicated by the first wash giving a neutral reaction to litmus paper. Infrared analysis of the crude reaction mixture isolated from solvent, bases and salts and excess epibromohydrin showed strong hydroxyl absorption at 3.0 microns. A titration for epoxide content showed the absence of oxirane oxygen. A GLC analysis showed fair purity with two major components. The presence of strong hydroxyl absorption in the infrared and the absence of epoxide groups suggested the possibility of bromohydrin groupings. The crude product was found to contain 22% bromine. However, the di(bromohydrin) derivative of the desired product has a theoretical bromine content of 35.0%.

5. Perfluoro-1,4-phenylene bis(dimethyl carbinol) Diglycidyl Ether

a. Perfluoro-1,4-phenylene bis(dimethyl carbinol)* (18.5 g., 0.0385 mole), m.p. 95-96°C, was dissolved in a 5:1 molar excess of epichlorohydrin (35.6 g., 0.385 mole) in a 250-ml., 3-neck flask equipped with a drying tube. Sodium methoxide (4.6 g., 0.084 mole) in 10% excess of the stoichiometric amount was dissolved in 80 ml. dry methanol and added over 15 minutes with rapid stirring to the diol-epichlorohydrin mixture. The mixture was stirred for 1 additional hour at room temperature. No solids formation or exotherm was noted and it was assumed that no reaction had occurred. This was confirmed by the recovery of the starting diol which melted at 85-95°C.

b. The sodium salt of the recovered diol of the preceding section was prepared by reaction with sodium hydride. The diol was dissolved in 150 ml. dry THF in the reaction flask of the apparatus described in the preceding

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*Received from Air Force Materials Laboratory.

section. Sodium hydride (3.7 g. of ca. 50% oil dispersion, 0.077 mole) in 50 ml. dry THF was slowly added with rapid stirring to the diol solution. A vigorous evolution of hydrogen gas resulted. The mixture was stirred an additional 2-3 hours at room temperature after which the excess sodium hydride was removed by the addition of 10 ml. dry methanol. The last part of this addition caused no further evolution of gas. Epibromohydrin (42.2 g., 0.308 mole) in a 4:1 molar excess was added via the dropping funnel with rapid stirring. The mixture was stirred for 15 hours at room temperature. A small amount of solids were filtered off, the THF solvent was stripped with a rotovac and the remaining material was washed twice with water. The excess epibromohydrin was removed using a rotovac at high vacuum with a water bath up to 75°C. The remaining material consisted of two immiscible liquids, the clear, high boiling mineral oil from the sodium hydride dispersion and a viscous colored material. The clear liquid was decanted off and the viscous residue was washed with petroleum ether. After the last amounts of petroleum ether were removed under vacuum with warming, the material was dissolved in ethyl ether, filtered, and submitted for infrared and GLC analysis. The results indicated the presence of any of the desired product to be unlikely. The water washings were then acidified with dilute sulfuric acid to find if they contained the unreacted sodium salts of the starting diol. Upon acidification a large amount of white solids precipitated out of solution, which were filtered, washed, dried, and sublimed. This material (11.4 g.) was shown by infrared analysis and melting point (85-92°C) to be the unreacted starting diol.

c. The lithium salt of the title dicarbinol was prepared according to the method of Tamborski[18]. 1,2,4,5-Tetrafluorobenzene (26.2 g., 0.175 mole), hexafluoroacetone (133 g., 0.80 moles) and n-butyl lithium (21 g., 0.33 mole) in a 15% n-hexane solution (220 ml.) were used. Without isolation, the solution of the lithium salt was added to a 4.65 to 1 molar excess of epibromohydrin with rapid stirring. The mixture was stirred for 4 days at room temperature. A large quantity of lithium bromide (36.3 g.)

precipitated out of solution. This was removed by filtration and the THF solvent and hexane were flashed off using a rotovac. The mixture was washed with water, benzene added, and subjected to rotovac treatment at reduced pressure up to 85°C for removal of the benzene-water azeotrope and epibromohydrin. A yellowish solid material was recovered from the flask as an ether solution. Infrared and GLC analyses indicated similarity of this material to that obtained earlier in a reaction between the sodium salt of the title dicarbinol and epibromohydrin. The main GLC peak of the impure mixture was not that of epibromohydrin and may possibly be due to a base catalyzed epibromohydrin polymerization product.

6. Perfluoro-1,5-Pentanediol Diglycidyl Ether

Cesium fluoride (15.2 g., 0.10 mole) was dried overnight at 130°C under full pump vacuum in a 250 ml. 3-neck reaction flask. Dry tetraglyme solvent (100.0 ml., 0.015% H_2O) was added and perfluoroglutaryl fluoride (24.4 g., 0.10 mole) was added dropwise with stirring. The mixture was allowed to stir overnight at room temperature. This did not result in complete solution of the CsF. The excess perfluoroglutaryl fluoride was removed by subjecting the mixture to full pump vacuum for 2-3 hours. Epibromohydrin (13.7 g., 0.10 mole) was then added dropwise with stirring at room temperature and then heated to 80-90° for 8 hours with stirring. After cooling and removal of the solids by filtration, 250 ml. ice water was added and a viscous, orange colored bottom layer was separated (19.6 g.). This was washed twice with 20 ml. portions of water and dried over $MgSO_4$. Infrared analysis indicated this material not to be the desired diglycidyl ether but was suggestive of the hydroxy ether reaction product between the acid and epibromohydrin. A second run of the same reaction yielded similar results.

7. 4,4'-Bis (glycidoxy) octafluorobiphenyl

a. 4,4'-Dihydroxyoctafluorobiphenyl[19]

A 3-liter, 3-necked flask was equipped with a magnetic stirrer, heating mantle, Vigreaux column and Erlenmeyer flask connected with rubber

Gooch tubing. Decafluorobiphenyl (150 g., 0.45 mole) was stirred in 720 ml. of refluxing t-butyl alcohol (82.9°C) while powdered 90% potassium hydroxide (135 g., 2.0 moles) was cautiously added from the Erlenmeyer flask over an interval of 2 hours. A vigorous reaction resulted. The stirred mixture was heated at reflux an additional hour and then one liter of distilled water was added. The mixture was left standing overnight after which the t-butyl alcohol was distilled off under reduced pressure and 350 ml. of conc. hydrochloric acid was added. The resulting solution was ether extracted, the extracts dried over $MgSO_4$, and the ether flashed off using a rotary evaporator. The amount of crude product obtained was 156.1 g. with m.p. 202-208°C. This material was recrystallized twice from toluene to give 4,4'-dihydroxyoctafluorobiphenyl (73.5 g., 0.224 mole) with an m.p. 204-207°C in 49.7% conversion. The reported[3] m.p. is 202.5-205.5°C. An infrared spectrum of the product was consistent with the structure of the desired compound. Elemental analysis yielded the following results.

	Found	Theoretical
%C	43.76	43.70
%H	0.63	0.61

Only a single spot was observed when this material was analyzed by thin layer chromatography. An additional 20.8 g. of less pure material was obtained from the filtrate of the first recrystallization.

b. 4,4'-Bis(glycidoxy)octafluorobiphenyl

A 500-ml., 3-neck flask was fitted with a Vigreaux column, addition funnel, and magnetic stirrer. 4,4'-Dihydroxyoctafluorobiphenyl (33.0 g., 0.1 mole), epichlorohydrin (92.5 g., 1.0 mole), acetone (92.5 g.) and water (12 g.) were added to the flask. A 20% aqueous solution of NaOH (8.8 g., 0.22 mole) was added in six equal increments with stirring at reflux with 15 min. reaction time between each addition. After the fifth and sixth additions, the aqueous phase was separated and discarded. The excess epichlorohydrin was removed using a rotary evaporator at full pump vacuum up to 80°C.

Attempts at recrystallization of the oil residue from methanol and ethanol were not successful. The infrared spectrum of the crude product, after removal of the alcohol, showed strong hydroxyl absorption at 3.0 microns, indicative of the presence of chlorohydrin. The material finally obtained (11.5 g.) was insoluble in methanol or ethanol and decomposed at 235-245°C, indicating that polymerization had occurred.

A 250 ml., 1-necked flask was fitted with a Vigreaux column, addition funnel and magnetic stirrer. 4,4'-Dihydroxyoctafluorobiphenyl (14.8 g., 0.045 mole), epichlorohydrin (41.6 g., 0.45 mole), acetone (45 g.) and water (100 g.) were added to the flask. The mixture was brought to reflux with stirring and a 20% aqueous solution of NaOH (4.0 g., 0.10 mole) was added in six equal increments with 15 min. reaction time between each addition. After the fifth addition and reaction period, the aqueous phase was separated and discarded and after the final caustic addition and reaction, 100 ml. of water was added, shaken with the mixture and separated. The aqueous phase had a neutral pH. The excess epichlorohydrin was removed using a rotary evaporator up to 160°C at 1 mm. Ethyl alcohol was added to the residual oil in an attempt to crystallize the product. A small amount of white, waxy precipitate was obtained with m.p. 65-66°C and intense infrared hydroxyl absorption at 2.95, 7.92 and 9.10 microns. Further purification by sublimation was carried out and 1.0 g. of material with m.p. 65-66°C (the reported[17] m.p. is 75-77°C) was obtained. Infrared analysis again showed intense hydroxyl absorption at 2.95 microns as well as absorption bands reported[17] for the desired product. Oxirane and elemental analyses yielded the following results.

	Found	Theoretical
%C	46.23	48.88
%H	2.21	2.28
% Oxirane O_2	4.68	7.24
%Cl	6.20	0.00

A thin layer chromatogram showed two large spots and two smaller ones.

The ethanol filtrate containing the major portion of the crude material was stripped of ethanol. A separation of the desired product from hydroxyl containing material was attempted, without success, by chromatography using a column of neutral aluminum oxide for adsorption of hydroxyl containing components. Finally, the crude material was sublimed twice and 5.7 g. of white solid was obtained with m.p. 55-60°C and infrared absorption at 3.0 microns. This material was allowed to react with a stoichiometric amount of powdered KOH (1.0 g.) in ethylene glycol, based upon an analyzed chlorine content of 6.2%. After reaction for 30 min. at 70-80°C, full pump vacuum was applied and the product (4.6 g.) was collected from a sublimation cold finger. The infrared spectrum showed the absorption bands reported for the product as well as hydroxyl absorption at 3.0 microns. The melting point was 74-75°C; reported 75-77°C. Elemental analysis yielded the following data.

	Found	Theoretical
%C	48.03	48.88
%H	2.26	2.28
% Oxirane O_2	6.70	7.24
%Cl	0.00	0.00

E. Fluorine-Containing Silanes

1. 3,3,3-(Trifluoropropyl)methylsilane

A 500-ml., 3-neck flask was equipped with a magnetic stirrer, addition funnel and reflux condenser protected with a drying tube. Anhydrous ethyl ether (100 ml.) was placed in the flask and small increments of $LiAlH_4$ were added with stirring for removal of trace amounts of water. A 2-to-1 molar excess of $LiAlH_4$ (14.8 g., 0.39 mole) was dissolved in the ether. 3,3,3-(Trifluoropropyl)methyldichlorosilane (83.2 g., 0.394 mole, 96% purity by GLC) was added dropwise with stirring. After the addition was completed, the mixture was stirred at reflux for an additional 2 hours. Small amounts of water were cautiously added for the removal of the excess $LiAlH_4$ followed by addition of 88 ml. of 50% H_2SO_4. The lower aqueous layer was extracted with 200 ml. of ethyl ether and the extracts were combined with the upper ether layer. The ether solution was distilled through a 24 inch, packed, silvered column. The system was kept under a nitrogen atmosphere. 3,3,3-(Trifluoropropyl)methylsilane (7.9 g., 0.0556 mole) of 99+% purity (GLC) was collected in a conversion of only 14.1%. The product had a boiling point of 58.2°C and refractive index n_D^{20} 1,3410; the reported[23] physical data are b.p. 58.2°C/758mm, n_D^{20} 1.3408 and d_D^{20} 1.3408. GLC analysis indicated that the pot residue had six major components which eluted at temperatures up to 230°C.

A distillation of this material using a 12" packed, heated column with a micro distillation head yielded an additional 3.5 g. (at 58-59°C) of 3,3,3-(trifluoropropyl)methylsilane of 98+% purity (GLC) having an IR spectrum (Fig. 15) identical to that of the product obtained in the first distillation. A total of 11.4 g. (0.0803 mole) of product was obtained in a conversion of 20.4%. A compound (5.7 g.) of 99+% purity (GLC) was collected at 81°C/24mm and was found to have 33.22% carbon, 5.40% hydrogen, and a molecular weight of 392. The infrared spectrum of this compound (Fig. 16), which remains unidentified, is very similar to that of the desired product.

2. 3,3,3-(Trifluoropropyl)methylchlorosilane

Following a reported[22] method, powdered, dried AgCl was slowly added to 3,3,3-(trifluoropropyl)methylsilane. The stoichiometric amount of AgCl (7.90 g., 0.0556 mole) was added in small increments over a period of 5 hours with stirring at room temperature to 3,3,3-(trifluoropropyl)methylsilane (7.90 g., 0.0556 mole). Both reactants were kept under a nitrogen atmosphere. The product was isolated by distillation using a micro-Vigreaux distillation column and head. 3,3,3-(Trifluoropropyl)methylchlorosilane (5.0 g., 0.0284 mole) of 99.0% purity (GLC) was collected in a conversion of 51.0%. An elemental analysis yielded the following data.

	Found	Theoretical
C	27.51%	27.20%
H	4.35	4.52

The product had a boiling point of 94°C, refractive index n_D^{21} 1.3674, and infrared absorption (Fig. 17) at 4.58 microns. The reported constants for this compound are b.p. 96.5°C/746mm, n_D^{20} 1.3651.

3. 3-(Heptafluoroisopropoxy)propylmethylsilane

$(CF_3)_2CFOCH_2CH_2CH_2Si(CH_3)Cl_2$ was reduced using lithium aluminum hydride by the slow addition of the silane to a stirred solution of $LiAlH_4$ in tetraglyme solvent.

A 200-ml., 3-neck flask was fitted with an immersion thermometer, addition funnel, an ice-water cooled reflux condenser with drying tube, and a slow purge of nitrogen was maintained throughout the reaction. The $LiAlH_4$ (3.9 g., 0.1024 mole) in about 20% excess was added to the reaction flask followed by the cautious addition of 75.0 ml. of dry tetraglyme (0.019% H_2O). After the $LiAlH_4$ was dissolved in the solvent, 3-(heptafluoroisopropoxy)-propylmethyldichlorosilane (57.6 g., 0.1685 mole) was added dropwise with stirring over an interval of 45 minutes at 60 to 90°. The mixture was stirred at 60-70° for an additional 3 hours. The product was isolated by distillation from the reaction flask using a micro-Vigreaux column and reduced pressure. Apiezon grease was used on all ground glass joints. 3-(Heptafluoroisopropoxy)-propylmethylsilane (33.6 g., 0.124 mole, M.W. 272) was collected at 53.0°C/68mm in 99%+ purity (GLC) in a conversion of 74.0%. The refractive index of this previously unreported compound is n_D^{25} 1.3325. An elemental analysis yielded the following data:

	Found	Theoretical
%C	31.06	30.9
%H	4.00	4.05

Strong Si-H absorption appeared in the infrared spectrum at 4.69 microns (Fig. 18). NMR analysis (Appendix C) confirms the identity of this compound.

4. 3-(Heptafluoroisopropoxy)propylmethylchlorosilane

The title monochlorodialkylsilane was prepared from 3-(heptafluoroisopropoxy)propylmethylsilane, described in the preceding section, by a displacement of hydrogen by chlorine using AgCl.

Silver chloride (16.45 g., 0.1148 mole) was added in small increments over an interval of about 10 hours at room temperature with stirring to 3-(heptafluoroisopropoxy)propylmethylsilane (31.2 g., 0.1148 mole). Stirring was continued overnight. The AgCl was powdered and dried immediately before use. Anhydrous conditions were maintained and a nitrogen atmosphere was kept over the reaction. Apiezon grease was used on all ground glass joints.

The product was isolated by fractional distillation at reduced pressure. 3-(Heptafluoroisopropoxy)propylmethylchlorosilane (29.5 g., 0.0963 mole) was collected at 75.0°C/50mm in a conversion of 84.0%. GLC analysis indicated 98.9% purity and the infrared spectrum (Fig. 19) showed strong Si-H absorption at 4.62 microns. An elemental analysis yielded the following data:

	Found	Theoretical
%C	27.8	27.4
%H	2.84	3.26

The refractive index of this previously unreported compound is n_D^{25} 1.3526. NMR analysis provides confirmation of the structure of this compound (Appendix C).

F. Nitroso Compounds

1. 2-Nitrosoperfluoropropane

Following a reported[25] procedure, hexafluoropropene (32 g., 0.213 mole) was condensed into an 80-ml. autoclave which contained 7 g. KF and 25 ml. tetramethylene sulfone (Sulfolane). The KF was powdered and dried and the Sulfolane was purified using a reported[25] procedure. Caution was taken to maintain anhydrous conditions. After the hexafluoropropene was condensed into the liquid oxygen cooled, evacuated autoclave, nitrosyl fluoride (13.5 g., 0.28 mole) was added. The contents were shaken for 9 hours at 30-35°C. The volatile reaction products were bubbled through a concentrated sulfuric acid gas scrubber into an evacuated, liquid oxygen cooled, evacuated cylinder. The amount of volatile reaction products collected was 26.8 g. Purification was attempted by distillation through a 24" packed column using Dry Ice-acetone coolant in the condenser of the distillation head. A quantity of material was collected having the dark blue color characteristic of nitroso compounds. Infrared analysis of the distilled material showed strong nitroso absorption at 6.30 microns and also trifluorovinyl absorption at 5.65 microns. Attempts at further separation were not made.

2. 2,7-Dinitrosoperfluorooctane

a. Purified, dry tetramethylene sulfone (Sulfolane, 30 ml.), powdered, dry KF (8 g.), and perfluorooctadiene-1,7 (44.5 g., 0.123 mole) were placed in an 80-ml. autoclave under anhydrous conditions. Nitrosyl fluoride (21.1 g., 0.43 mole) was then condensed into the evacuated, LOX cooled autoclave. The reactants were shaken at 30-35°C for 9 hours. After venting the volatiles from the autoclave, the liquid phase was filtered for removal of the KF and the upper light blue solvent layer and bottom dark blue product layer (43.0 g.) were separated. Infrared analysis indicated that the layers were, in fact, immiscible and that the dark blue product layer had strong nitroso absorption at 6.25 microns and also trifluorovinyl absorption at 5.60 microns. A careful fractional distillation at reduced pressure through a 12" packed, heated column was used in an attempt at isolation of pure compounds. The pressure was adjusted so that the distillation temperature was never higher than 55°C. Infrared and GLC analyses were made immediately after the distillation to minimize the effects of degradation upon the analytical results. Evolution of a brownish gas, suggestive of decomposition, was observed in two of the fractions; the materials were stored in brown bottles and refrigerated for increased stability. GLC indicated many components, e.g., 5 or 6, to be present in each of the 7 fractions, and IR showed nitroso and trifluorovinyl absorption in varying degrees in each fraction. Fraction #6 with b.p. 50-55°C/44mm was subjected to preparative GLC for isolation of its three major components. The third peak was isolated in 87% purity (GLC). Its IR spectrum showed strong nitroso absorption at 6.20 microns and strong trifluorovinyl absorption at 5.60 microns. NMR analysis (Appendix C) indicated the compound to be 90% pure 2-nitrosoperfluorooctene-7. The infrared spectra of the three components isolated by preparative GLC showed decreasing nitroso absorption and increasing trifluorovinyl absorption in order of peak elution, suggesting that the dinitroso compound may be eluted from this column (W-95) before the mononitroso adduct.

b. Powdered, dry KF (7 g.) and dry tetraglyme (25 ml., 0.03% H_2O) were added to an 80-ml. autoclave under anhydrous conditions. Perfluorooctadiene-1,7 (38.4 g., 0.106 mole) was added and nitrosyl fluoride (13.5 g., 0.276 mole) was condensed into the autoclave after cooling to liquid oxygen temperature and evacuating. The reactants were shaken at 30-35° for 14 hours. After venting the volatiles from the autoclave, the KF was filtered from the liquid, which formed two immiscible layers. The lower, dark blue product layer (34.4 g.) was shown by infrared and GLC analysis to be immiscible with the upper, light blue tetraglyme layer. The IR spectrum of the crude product showed intense nitroso absorption at 6.23 microns and only weak trifluorovinyl absorption at 5.60 microns. The relative absorption intensities of the respective peaks were in a ratio of about 20 to 1. Improved GLC resolution of the three major components of the crude product was achieved using a 15% PFOX column. Preparative GLC was used in the separation of these components since fractional distillation in the preceding run suggested that distillation caused extensive decomposition.

2,7-Dinitrosoperfluorooctane (8.04 g., 0.01745 mole) was collected as the third peak in a conversion of 16.5%. GLC analysis indicated a purity of 96.6% and NMR (Appendix C) analysis 96-98%. The infrared spectrum showed (Fig. 20) intense nitroso absorption at 6.23 microns. NMR analysis provided confirmation of the structure of this compound (Appendix C).

Characterization of the compound as 2,7-dinitrosoperfluorooctane was further corroborated by elemental analysis:

	Found	Theoretical
%C	20.37	20.85
%N	6.58	6.10

NMR and GLC analyses were not in agreement in regard to the purity of the components eluted as the first two peaks and their identity has not been established.

G. Perfluorinated Diisocyanates

1. $OCNCF_2CF_2OCF_2CF_2NCO$

a. Perfluorooxydipropionyl fluoride (79.6 g., 0.256 mole) was added dropwise to an "activated" sodium azide suspension in dry xylene with rapid stirring at ice bath temperature. Stirring was continued at room temperature for about 18 hours. The reaction flask was then fitted for a simple distillation with an ice water cooled condenser and receiver immersed in a dry ice-acetone bath. The mixture was then heated cautiously, using a hot water bath, until at 80-100°C rapid evolution of nitrogen was observed, indicating rearrangement of acyl azide to isocyanate. Finally, the temperature of the pot was increased to 125° to obtain the last amounts of crude product (81.6 g.). This material was subjected to fractional distillation for purification.

Infrared and GLC analysis indicated the major impurity in the last collected fractions to be the monoisocyanate-acyl fluoride compound. The last five fractions were redistilled and 5.1 g. of material, indicated by infrared and GLC analysis to be the desired product, was collected at 95°C as a second fraction. The purity was 96.8% by GLC analysis and 98% by NMR analysis (Appendix C). An infrared spectrum of this compound is shown in Fig. 22. Elemental analysis is shown below.

	Found	Calculated
%C	25.98	23.95
%H	0.34	0.00
%N	9.02	9.35

b. Partially reacted material recovered from the above experiment (37.4 g.) and containing both acid fluoride and isocyanate groups was dissolved in Freon 113 (15 ml.). The solution was added dropwise with stirring at 0° over 30 min. to activated sodium azide (7.8 g., 0.12 mole) suspended in benzonitrile (40 ml.). Stirring was continued at room temperature for 41 hours until acyl fluoride carbonyl infrared absorption at 5.3 microns was weak and acyl azide carbonyl absorption at 5.75 microns was strong. The acyl azide-isocyanate rearrangement was then carried out in an apparatus set up for a simple distillation, using an ice-water cooled condenser and receiver immersed in a dry ice-acetone cold bath. Rapid evolution of nitrogen occurred upon heating to 110-120°C with stirring and the crude product was distilled over into the receiver. Fractional distillation gave product (13.7 g.) boiling at 99-100°. Purity by GLC was 95.9%. Elemental analysis is shown below.

	Found	Calculated
%C	24.39	23.95
%H	0.00	0.00
%N	9.50	9.35

2. $OCNCF(CF_3)O(CF_2)_5OCF(CF_3)NCO$ and Isomer

Sodium azide was activated immediately before using according to a reported[28] procedure as follows: sodium azide (60 g.) was moistened with 2.5 ml. of 90% hydrazine hydrate and ground in a mortar until homogeneous. After standing overnight it was dissolved in a minimum amount of hot water (ca. 120 ml.). About 2.5-3.0 l. of cold acetone was added and the mixture was allowed to stand for one hour. The precipitated NaN_3 was filtered, washed with acetone and air dried. The cake was crushed in a mortar and dried for a short time under full pump vacuum. The yield was 50.3 g.

DEDAF (134.9 g., 0.234 mole, 87% purity) was dissolved in 117 ml. Freon 113 and added dropwise with stirring over 2 1/2 hours to activated NaN_3 (38.0 g., 0.585 mole) in 117 ml. dry acetonitrile in a cold water bath. Infrared analysis showed azide absorption at 4.6 microns and azide carbonyl absorption at 5.8 microns with no acyl fluoride carbonyl absorption at 5.3 microns. The NaF was removed by washing with 100 ml. water, 100 ml. saturated $NaHCO_3$ solution and again with 100 ml. water. The azide solution was dried overnight over $MgSO_4$. The infrared spectrum of the DiEther DiAzide (DEDAZ) is shown in Figure 23.

The azide solution was slowly added to 100 ml. toluene at reflux with stirring. As the rearrangement proceeded with evolution of nitrogen, the lower boiling solvents were distilled off. After the addition of the azide solution was completed, the reaction was heated to 100-110°C for 1 hour. After cooling, the lower product layer (69.3 g.) was separated from the upper toluene layer. Distillation through a Vigreaux column yielded an isomer mixture of only 73.9% purity (GLC). A second distillation using a heated, packed column increased the purity to 87.7%. A final distillation through the same column yielded a third fraction (b.p. 66.0-67.0° C/4.0 mm, 95.1% purity) of 27.6 g. (0.0488 mole). Conversion based on this fraction was 20.8%. The isomer ratio was 7:1 sym:unsym. The infrared spectrum (Figure 24) shows isocyanate absorption at 4.35 microns. The following elemental analyses were obtained:

	Found	Theoretical
%C	22.51	23.3
%N	4.72	4.94

3. $OCNCF(CF_3)OCF_2CF(CF_3)O(CF_2)_5OCF(CF_3)NCO$ and Isomer

A 3-necked, 1-l flask was fitted with a 500 ml. addition funnel, stop-cock vent with drying tube and magnetic stirrer. Freshly "activated" dry sodium azide (51.2 g., 0.788 mole) in a 5% molar excess and 200 ml. dry, redistilled acetonitrile solvent were placed in the dried apparatus. TEDAF (TriEther DiAcid Fluoride, 278.5 g., 0.375 mole) in 200 ml Freon 113 was added dropwise with rapid stirring over 7.5 min. at ice bath temperature. The TEDAF was purified by fractional distillation and collected at 118-119°C/55 mm. GLC analysis indicated 95.8% purity. The ice bath was removed and stirring continued for 10 hours. Infrared analysis showed complete acid fluoride-sodium azide reaction, i.e., azide absorption at 4.58 microns and azide carbonyl absorption at 5.7 microns. Sodium fluoride and unreacted sodium azide were removed by washing with water, saturated sodium bicarbonate solution and twice more with water. After drying over $MgSO_4$, a water analysis indicated 0.07% water in the reaction mixture. The infrared spectrum of the TEDAZ (TriEther DiAzide) intermediate is shown in Figure 25. The reaction flask was fitted with an immersion thermometer, simple distillation head with ice-water cooled condenser and stop-cock vent with drying tube; the take-off was connected to a liquid oxygen cooled trap and then to a nujol bubbler. The TEDAZ solution was placed in the dried flask along with 400 ml. toluene and the mixture was heated cautiously with stirring. Rapid evolution of nitrogen occurred around 100°C, after the Freon 113 had distilled into the receiver. Heating was stopped and the mixture was cooled after evolution of nitrogen had stopped. The contents of the flask separated into two layers, a bottom product layer (197.3 g.) and an upper toluene layer, shown by GLC analysis to contain little product. Fractional distillation was used for purification of the crude product giving 120.0 g. of product boiling at 91°/6 mm; indicated by GLC analysis to be 91.3% pure. A second fractional distillation of this material gave a fraction boiling at 95.0-95.5°/6 mm. (74.8 g.) and a fraction boiling at 95.5-96.0°C/6 mm. (19.9 g.). GLC analysis indicated that the 95-95.5° fraction was 94.8% pure and the 95.5-96° fraction 96.2% pure. The infrared spectra of these two fractions were identical. The spectrum of the higher boiling fraction is shown in Fig. 26. A vapor phase osmotic molecular weight determination of this fraction gave a result of 726; the calculated molecular weight of TEDI, $C_{14}F_{24}O_5N_2$, is 732. Elemental analysis of the same fraction yielded the following results:

	Found	Theoretical
%C	23.08	22.98
%N	3.95	3.82

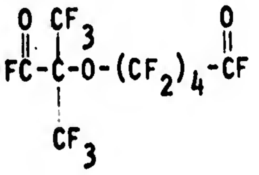
H. Reactions of Perfluoroisobutylene Oxide

1. With Perfluoroglutaryl Fluoride

a. Cesium fluoride (0.38 g.) was added to a 50-ml., one-neck flask containing a magnetic stirring bar. The CsF was dried under vacuum at 200°C overnight. The flask was cooled and dry diglyme (10 ml.) and perfluoroglutaryl fluoride (PFGF) (3.2 g., 13.1 mmoles) were added in a glove bag. The flask was connected to a glass manifold and hexafluoropropylene oxide (HFPO) was charged at room temperature into the stirred flask contents via a low-pressure regulator at 5-6 psig delivery pressure. The HFPO was taken up rapidly, indicating the system to be reactive. The HFPO cylinder was replaced by a cylinder containing 19 g. perfluoroisobutylene oxide (PFIO). The PFIO was charged at a delivery pressure of 5-6 psig into the flask, but was not taken up by the system. The flask temperature was varied from 0° to 50° and the delivery pressure varied from 2 to 8 psig, but no reaction took place, as evidenced by the absence of pressure drop in the closed system and negligible weight loss from the PFIO cylinder.

b. Cesium fluoride (2 g.) was dried overnight under vacuum at 200° in a 200-ml., Fischer-Porter bottle containing a magnetic stirring bar.

Dry diglyme (50 ml.) and PFGF (16.8 g., 0.069 mole) were added and PFIO (16 g., 0.074 mole) was condensed into the bottle. The contents were stirred at room temperature for 14 hours. The pressure dropped from 10 psig to 0 psig. Additional PFIO (10 g., 0.0463 mole) was condensed in and the mixture stirred for 7 hours at room temperature. The pressure dropped only slightly from 3 psig. Infrared analysis of the reaction overgas showed no epoxide remaining. The volatile portion (6.5 g.) was removed on a vacuum line and was found to contain carbonyl fluoride by infrared analysis. The lower (product) layer (17 g.) was separated from the upper (diglyme) layer. Analysis of the crude product by GLC revealed one major peak, greater than 90% purity (47% conversion based on PFGF). Infrared analysis showed typical acid fluoride absorption at 5.32 microns, but differing from the infrared spectrum of perfluoroglutaryl fluoride. Distillation of the crude product under dry N_2 yielded a fraction (8.73 g.) boiling at 106-111° (no higher boilers removed), which was identified by NMR (Appendix C) as the 1-to-1 adduct,

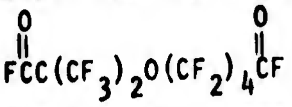


$$F\overset{O}{\overset{\|}{C}}-\overset{CF_3}{\underset{CF_3}{C}}-O-(CF_2)_4-\overset{O}{\overset{\|}{C}}F$$

(F.W.=460)

Anal. Calcd. for $C_9F_{16}O_3$: %C, 23.48. Found: %C, 23.50.

An infrared spectrum of this compound is shown in Fig. 28.

c. Cesium fluoride (5.8 g., 0.038 mole) was dried overnight under vacuum at 190°C in a 200-ml. Fischer-Porter bottle having a magnetic stirring bar and a 100 psi pressure gauge. Dry diglyme (50 ml.) and perfluoroglutaryl fluoride (PFGF, 27.7 g., 0.1135 mole) were added to the cooled bottle under nitrogen in a glove bag. A 3-to-1 molar ratio of PFGF to cesium fluoride was used. Perfluoroisobutylene oxide (PFIO, 60 g., 0.278 mole) was condensed into the bottle in increments over an interval of 8 hours until infrared analysis indicated unreacted PFIO continued to be present in the overgas. A maximum pressure of 25 psi was reached and the final pressure was 10 psi. The primary volatile product recovered was 97% pure (GLC) perfluoroisobutyryl fluoride (40.6 g., 0.188 mole). A lower product layer (44.5 g.) was separated from the diglyme layer and distilled under nitrogen. The 1-to-1 adduct  $F\overset{\overset{O}{\parallel}}{C}C(CF_3)_2O(CF_2)_4\overset{\overset{O}{\parallel}}{C}F$ (17.7 g., 0.0385 mole, ~90% by GLC) was separated in a fraction boiling at 103-110°C. The infrared spectrum of this material was identical with that of an earlier sample of this compound. Another reaction in a 300-ml. autoclave yielded 95 g. perfluoroisobutyryl fluoride (0.44 mole) and 9.5 g. of the 1-to-1 adduct (0.0205 mole) of 78.5% purity by GLC. The quantities of reactants used were 99.5 g. (0.46 mole) PFIO, 56.1 g. (0.23 mole) of PFGF, and 7 g. cesium fluoride.

2. With Carbonyl Fluoride

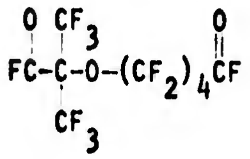
Cesium fluoride (30 g.) was dried overnight at 250°C under vacuum and placed together with dry diglyme (75 ml.) into a 300-ml. autoclave under anhydrous conditions. The autoclave was evacuated and charged with carbonyl fluoride (65 g., 1.0 mole) followed by perfluoroisobutylene oxide (100 g., 0.46 mole). The reactants were heated to 75°C for 5 hours with rocking. The volatile products were then removed from the autoclave and purified by a trap-to-trap distillation followed by a low temperature fractional distillation of the contents of the ice water and dry ice-acetone traps. A 60-g. quantity of perfluoroisobutyryl fluoride (96% purity by GLC) boiling at 11-18°C was isolated. Identification of the material was confirmed by infrared and NMR analysis. No other products from the reaction were identified.

3. With Trifluoroacetyl Fluoride

Dry cesium fluoride (30 g.) and dry diglyme (75 ml.) were placed in a 300-ml. autoclave under anhydrous conditions The autoclave was then charged with perfluoroisobutylene oxide (129 g., 0.5 mole) followed by trifluoroacetyl fluoride (120 g., 1.0 mole). The reactants were heated to 75°C with rocking for 7 hours until the disappearance of epoxide was indicated by infrared analysis. The volatile materials from the reaction were condensed into a cylinder and subjected to a trap-to-trap distillation. infrared analysis indicated that the contents of the -25°, -75° and -183°C traps consisted of a mixture of perfluoroisobutyryl fluoride and trifluoroacetyl fluoride. A low temperature distillation (head temperature -40°C) of the combined mixtures of the three traps resulted in the isolation of 121 g. of a mixture of trifluoroacetyl fluoride and perfluoroisobutyryl fluoride and 50 g. perfluoroisobutyryl fluoride. The liquid contents of the autoclave were removed and separated into two layers, an upper diglyme layer and a bottom layer (17 g.). The bottom layer was subjected to a distillation using a micro Vigreaux column and separated into three fractions boiling at 56, 62, and 64°C, each having 87% purity (GLC). Identification of the fraction boiling at 62°C as perfluoro-α-ethoxyisobutyryl fluoride is suggested by its infrared spectrum, but NMR analysis indicated that the grouping C_2F_5O- is not present in the sample.

4. With $F\overset{O}{\overset{\|}{C}}C(CF_3)_2O(CF_2)_4\overset{O}{\overset{\|}{C}}F$

An attempt was made to add perfluoroisobutylene oxide to the previously prepared 1-to-1 adduct of perfluoroglutaryl fluoride and perfluoroisobutylene oxide,



$$F\overset{O}{\overset{\|}{C}}-\underset{CF_3}{\overset{CF_3}{C}}-O-(CF_2)_4\overset{O}{\overset{\|}{C}}F$$

(F.W. = 460)

The epoxide (15 g., 0.0695 mole) was condensed into a 100-ml. Fischer-Porter tube containing the 1-to-1 adduct (8.73 g., 0.019 mole), cesium fluoride (0.87 g.), and diglyme (30 ml.). The tube was shaken at room temperature for 7 hours, after which time infrared analysis showed no epoxide remaining in the reaction overgas. The volatile portion (9.0 g.) which was separated from the diglyme layer was shown by GLC to consist of three compounds. These were tentatively identified by their infrared spectra as perfluoroisobutyryl fluoride (major component), perfluorocyclopropane, and carbonyl fluoride. The liquid product mixture (7.07 g.) was separated from the diglyme layer and distilled to give 5.73 g. of the 1-to-1 adduct starting material along with

0.66 g. of material boiling from 60 to 130°C at 20 mm. pressure, which appeared by infrared analysis to be hydrolyzed starting material.

I. Nitriles

1. Perfluoroisobutyronitrile

a. Perfluoroisobutyryl Fluoride

Perfluoroisobutylene epoxide (103 g., 0.477 mole) was heated in an autoclave for 5 hours at 75°C in the presence of cesium fluoride (1 g.) and diglyme solvent (5 ml.). Appropriate precautions were taken for the maintenance of anhydrous reaction conditions. The cesium fluoride was dried overnight at 200°C under vacuum, dry diglyme was used and transfer to the autoclave was done in a glove bag under nitrogen. The reaction was continued until the disappearance of the epoxide infrared absorption peak at 6.52 microns. After 4 hours this infrared peak was still present. Perfluoroisobutyryl fluoride (89.4 g., 0.414 mole) was recovered from the autoclave having 97.5% purity (GLC) without purification. Conversion was 84.7%. An infrared spectrum is shown in Fig. 29.

b. Perfluoroisobutyramide

Perfluoroisobutyramide was formed by the reaction of perfluoroisobutyryl fluoride with liquid ammonium in ethyl ether solvent. Perfluoroisobutyryl fluoride (87.6 g., 0.404 mole) was condensed (b.p. 12-18°C) into a cylinder in which 300 ml. of dried ethyl ether had been placed. The liquid ammonia (335 g., 20 moles) was placed in a 1-liter, 3-neck reaction flask cooled in a dry ice-acetone bath and equipped with an inlet tube above the liquid, stirrer and dry ice-acetone cooled reflux condenser. The acid fluoride solution was slowly added to the flask over a period of 3 hours with stirring, after which the cooling bath was removed and reflux was permitted for 1 hour. The ether solution was then filtered for removal of the solid ammonium fluoride and the solvent removed by stripping using a Rinco evaporator. About 63.5 g. of orange brown residue was obtained which had an m.p. range of 66-135°C. This material was recrystallized from benzene-toluene solution and yielded 25.4 g. (0.119 mole) of perfluoroisobutyramide in a conversion of 29.5%. The melting point of the product was 50.0°C and the purity was indicated by GLC to be 98+%. The infrared spectrum (Fig. 30) had strong absorption peaks at 3.0 (doublet) and 5.8 (broad) microns, indicating an amide group. An elemental analysis provided the results listed below:

	%C	%H	%N
Calculated	22.2	0.92	6.57
Found	20.4	0.92	6.44

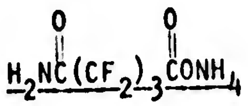
Conclusive proof of structure was obtained by the use of this compound to prepare the nitrile derivative described below.

c. Perfluoroisobutyronitrile

Phosphorous pentoxide (85.2 g., 0.60 mole) was intimately mixed with dry, powdered perfluoroisobutyramide (25.3 g., 0.119 mole) and placed in a 250-ml., 1-neck reaction flask in a glove bag under nitrogen. The apparatus was set up as in a simple distillation and a dry ice-acetone cooled condenser and receiver bath were used. The reactants were heated at 225-250°C for 2 1/2 hours after which the product (20.9 g., 0.107 mole) was condensed into an evacuated cylinder. Without further purification, GLC analysis (35% PFOX) indicated a purity of 99.6%. The infrared spectrum (Fig. 31) showed strong absorption peaks at 7.61, 7.91, 8.59, 9.30 and 10.11 microns, as well as nitrile absorption at 4.39 microns. A molecular weight determination by vapor density resulted in a measurement of 195 coinciding exactly with the theoretical value. The identification of the product as perfluoroisobutyronitrile is further established by NMR analysis (see Appendix C) consistent with the postulated structure. Conversion was 90% (17.5 g.).

2. 4-Cyanoperfluorobutyryl Chloride

a.



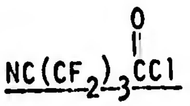
$H_2N\overset{\overset{O}{\|}}{C}(CF_2)_3\overset{\overset{O}{\|}}{C}ONH_4$

A 1-l. filter flask was fitted with a 1/2 inch diameter gas inlet tube extending nearly to the bottom. A drying tube was connected to the side arm of the flask. After drying the apparatus, perfluoroglutaric anhydride (263.7 g., 1.185 moles) and 500 ml. dry ether were added and anhydrous ammonia (41.4 g., 2.43 moles) was bubbled through the solution with stirring at room temperature. After removal of the ether and excess ammonia, the solid mass was broken into a white granular solid. Infrared analysis showed characteristic amide absorption peaks at 2.95 and 5.90 microns and ammonium absorption peaks in the 7.0 micron region. Elemental analysis yielded the following results:

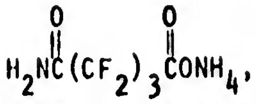
	Found	Theoretical
%C	23.19	23.4
%H	2.34	2.34
%N	10.14	10.92

The desired compound, $H_2N\overset{O}{C}(CF_2)_3\overset{O}{C}ONH_4$, (197.1 g., 0.771 mole) was obtained in 65.0 % conversion.

b.



$NC(CF_2)_3\overset{\overset{O}{\|}}{C}Cl$

A 1-liter, 1-neck flask was fitted with a 14" Vigreaux column, Claisen head and downward inclined ice-water cooled condenser. A liquid oxygen cooled trap was connected to the receiver. The receiver was cooled to about -15°. Zinc chloride (102 g.), 30% by weight of the other reactants, was dried overnight at 200° under full pump vacuum in the reaction flask. Benzotrichloride (326 g., 1.665 mole) was added followed by the half amide-ammonium salt,  $H_2N\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}ONH_4$, (14.2 g., 0.0555 mole). The molar ratio of benzotrichloride to the amide-ammonium salt was 30 to 1. The reaction mixture was heated to 210° and kept at that temperature for one hour. An evolution of gas or apparent reaction was observed below 100°. Crude product (5.9 g.) was collected which showed strong nitrile absorption at 4.44 microns, acyl chloride absorption at 5.56 microns and other similarities (see Fig. 5) to the reported infrared spectrum of this compound.[2]

Due to a reorientation in research effort, this material was not further purified.

3. Perfluorosebaconitrile

a. Perfluorosebacoyl Chloride

Perfluorosebacic acid (50.5 g., 0.10 mole), pyridine (1 g.), and dry ethyl acetate (250 ml.), in order, were charged into a 500-ml., 3-neck flask equipped with an addition funnel, tap water cooled reflux condenser, immersion thermometer, and magnetic stirrer. Thionyl chloride (47.6 g., 0.40 mole) in a 2:1 molar excess was added dropwise with stirring. Afterwards the mixture was heated and maintained at 80°C reflux temperature for 21 hours with stirring. The mixture at this time had a dark brown appearance and contained insoluble tars. After quickly filtering, the unreacted thionyl chloride and ethyl acetate were removed by distillation, leaving 59 g. of crude diacid chloride.

A second reaction run under the same conditions gave 50 g. of 86.5% pure product. Conversion was 74%.

b. Dimethylperfluorosebacate

Perfluorosebacic acid (50.5 g., 0.10 mole) and 50 ml. dry methanol were placed in a 250-ml., 1-neck reaction flask. Concentrated sulfuric acid (50 ml.) was slowly and cautiously added. A tap water cooled reflux condenser was used. The reaction was stirred for 2 hours using a magnetic stirrer after which the mixture was transferred to a separatory funnel. The lower product layer was then washed with an equal volume of water and subjected to a vacuum fractional distillation. Dimethyl perfluorosebacate (28.7 g., 0.054 mole) was collected at 132-150°C at 2.8 mm in a conversion of 54%. GLC analysis indicated that the purity was 92.3%.

Perfluorosebacoyl chloride (50.0 g., 0.095 mole) and 100 ml. dry methanol were charged into a 500-ml., 1-neck reaction flask equipped with a tap water cooled reflux condenser. The reaction was heated and stirred at reflux for 20 hours. After reaction the mixture was fractionally distilled using an 18 x 2 cm Vigreaux column. Dimethyl perfluorosebacate (40.0 g., 0.075 mole) was collected at 90-105°C at ∿2.5mm. Suction filtration through a sintered glass filter was necessary to remove some elemental sulfur contamination. A 79% conversion to 78.3% pure product was realized.

c. Perfluorosebacamide

Crude perfluorosebacoyl chloride (59 g., 0.112 mole) and 200-ml. methylene chloride were placed in a 500-ml., 3-neck reaction flask equipped with a gas inlet tube, dry ice-acetone cooled reflux condenser and magnetic stirrer. Ammonia (227 g., 13.3 moles) was condensed into the flask using a dry ice-acetone coolant bath. The mixture was allowed to reflux and stir, using an ice water bath, for 5 hours, after which the excess ammonia was permitted to escape through the reflux condenser. The material remaining in the flask had a dark brown tarry appearance and proved to be difficult to purify. Extractions and washings with ethyl ether, THF, and water produced 30 g. (0.062 mole) of product melting at 240-243°C. The reported[2] melting point is 240-241°C.

Dimethyl perfluorosebacate (23.5 g., 0.044 mole) was placed in a 300-ml., 3-neck reaction flask equipped with a dry ice-acetone cooled reflux condenser, gas inlet tube, and magnetic stirrer. After purging the system with dry nitrogen, dry ethyl ether (125 ml.) was added. Ammonia (47 g., 2.76 mole) was condensed into the flask using a dry ice-acetone coolant bath. The bath was removed and the mixture was allowed to reflux for 3 hours after which the ammonia was permitted to escape through the reflux condenser. The nearly white crystalline product was filtered, washed with ether and without further purification, melted at 242-245°C. The amount of perfluorosebacamide produced was 20.8 g. (0.426 mole) in a conversion of 96.9%.

Perfluorosebacic acid (284.3 g., 0.56 mole) was treated with excess thionyl chloride in ethyl acetate solvent in the presence of pyridine. The mixture was refluxed and stirred at 80°C for 22 hours. After filtering and distilling off the excess thionyl chloride and solvent, the crude perfluorosebacoyl chloride was treated with excess dry methanol at reflux for 7 hours. Dimethyl perfluorosebacate (198.6 g., 0.384 mole) of 86% purity was collected in a vacuum distillation in a conversion of 68.5% from the acid. This material was converted to perfluorosebacamide by reaction by reaction with anhydrous ammonia in dry ethyl ether. The product (188.5 g., 0.34 mole) was obtained in 61% overall conversion from the acid.

d. Perfluorosebaconitrile

Perfluorosebacamide (30.1 g., 0.062 mole) and phosphorous pentoxide (87 g., 0.613 mole) were intimately ground together and placed in a 500-ml., 1-neck reaction flask in a glove bag under a dry nitrogen atmosphere. The apparatus was set up as in a simple distillation using a downward slanted tap water cooled condenser. The flask was heated to 230°C and the product distilled over at 146°C, after which an additional amount was obtained by raising the flask temperature to 250°C and using reduced pressure (10 mm). Infrared and GLC analysis indicated the material to be perfluorosebaconitrile of 97.0% purity. Conversion to product (17 g., 0.0376 mole) was 60.7%.

The dinitrile preparation above was repeated using 20.8 g. (0.426 mole) perfluorosebacamide and 75.3 g. (0.53 mole) phosphorous pentoxide. A glove bag was not used and the reactants were mixed in a different manner. Perfluorosebaconitrile (7.1 g., 0.0157 mole) was obtained in a conversion of 36.8%.

The diamide dehydration using the procedure of the two preceding reactions was repeated with 30 g. (0.0615 mole) perfluorosebacamide and 70 g. (0.493 mole) phosphorous pentoxide. A glove bag was used and the reactants were intimately mixed. The flask was heated for 6 hours and 20.3 g. (0.045 mole) perfluorosebaconitrile was collected at 95-115°C in a conversion of 73.2%. GLC analysis indicated a purity of 94.3%.

J. Miscellaneous Reactions

1. Preparation of Perfluorooctadiene-1,7

1,2,7,8-Tetrachloroperfluorooctane (721 g.) was obtained in 98% purity (GLC, W-98, 40-160°) as a fraction boiling at 70-75°/5mm. from approximately 6 liters of methylene chloride solution from a previous synthesis. To a vigorously stirred suspension of 577 g. Zn dust in 2600 ml. acetic acid and 865 ml. acetic anhydride was added dropwise 721 g. (1.43 moles) tetrachloroperfluorooctane. Dehalogenation occurred almost immediately, and product was removed through a take-off head as it formed. After addition was completed, the distillation was continued until no more water insoluble material distilled over.

The distillate was washed with two volumes of water, then with sodium bicarbonate solution, followed by two more washings with water. The crude diene (471 g.) was dried over Na_2SO_4 and distilled under N_2, yielding 347 g. (67% conversion) of perfluorooctadiene-1,7, boiling at 106-109°, 99% pure by GLC (W-98, 25°C). Infrared analysis (Fig. 32) showed a characteristic trifluorovinyl absorption peak at 5.6 microns.

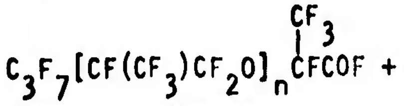
2. Reaction of Pentafluorobenzoyl Fluoride with Hexafluoropropylene Epoxide

a. Cesium fluoride (0.71 g.) was dried under vacuum overnight at 190-200° in a 50-ml. flask containing a magnetic stirring bar. Diglyme (3 ml.) and pentafluorobenzoyl fluoride* (4.68 g., 0.0219 mole) were added to the cooled, evacuated flask using a hypodermic syringe. The flask was stirred for 1/2 hr., then connected to a glass manifold through which hexafluoropropylene epoxide (HFPE) was charged via a low-pressure regulator at 5.25 psig delivery pressure. After about one hour, 5 g. (0.03 mole) of HFPE had added to the reaction mixture at room temperature. Infrared analysis of the two resulting layers indicated pentafluorobenzoyl fluoride (PFBF) present in both layers, and peaks characteristic of oligomers of HFPE present in the

---

*Sample from AFML.

lower layer. Major GLC peaks of the upper layer were those of PFBF and diglyme. Analysis by GLC of the lower layer showed a mixture of oligomers of HFPE together with some unreacted PFBF. The total reaction mixture was distilled to give the following fractions:

Fraction No.	b.p.°C	P, mmHg	Wt.,g.	Probable Structure/Anal.Method
1095.87.1	60	760	0.40	$CF_3CF_2CF_2OCF(CF_3)COF$/infrared
1095.87.2	49	28	0.47	 $C_3F_7[CF(CF_3)CF_2O]_n\overset{CF_3}{\overset{\vert}{C}}FCOF$ + C_6F_5COF/infrared
1095.87.3	61-63	28	5.10	C_6F_5COF + diglyme/NMR + infrared
1095.87.4	66-85	28	2.25	$C_6F_5COF + C_6F_5CF(CF_3)OCF_2CF_2CF_3$/ NMR
1095.87.5	22	0.45	0.60	$C_6F_5CF(CF_3)OCF_2CF_2CF_3$/NMR

NMR analysis (see Appendix C) of the higher boiling fractions (4 and 5) indicated the presence of a fluorinated aromatic compound, probably C_6F_5-$CF(CF_3)CF_2OCF_2CF_2CF_3$ (II) in a concentration ratio of 1/3 with pentafluorobenzoyl fluoride (I) in fraction 1075.87.4. Fraction 1095.87.5 dissolved in Freon 113 was too dilute for area measurement or determination of fine structure, but wa. postulated to be (II) on the basis of similar chemical shifts.

b. Cesium fluoride (0.71 g.) was dried overnight under vacuum at 190-200° in a 50-ml. flask. Tetraglyme (Ansul Ether 181, 5 ml.) and PFBF (8.46 g., 0.0396 mole) were added as before. After stirring for 1/2 hr., HFPE was charged into the flask at 2.75 psig delivery pressure. The flask temperature was held at -5° to -10°. In 1 1/2 hrs., 10.6 g. (0.0638 mole) HFPE was added. Infrared analysis showed that the upper layer contained unreacted PFBF and tetraglyme and that the lower layer contained oligomers of HFPE.

c. Cesium fluoride (0.71 g.), tetraglyme (5 ml.), and PFBF (5.76 g., 0.027 mole) were added to a 50-ml. flask as before. HFPE was charged in at 2.75 to 5.0 psig. with the reaction flask at 70-80°. HFPE (2.8 g., 0.017 mole) was added very slowly over a period of 5 hrs., during which the tetraglyme (upper) layer turned dark brown. Infrared analysis of the lower (clear) layer showed unreacted PFBF present with oligomers of HFPE. The upper (tetraglyme) layer contained more unreacted PFBF.

3. Preparation of Perfluoroisobutylene Oxide (PFIO)

Hexafluoropropylene oxide (HFPO) (254 g., 1.53 moles) and hexafluoroacetone (395 g., 2.38 moles) were condensed into a 1.4-liter autoclave fitted with a pressure gauge and rupture disc. The cylinder was heated to 200°C (1000 psi) and kept at that temperature for 48 hours. Infrared analysis of the cooled gaseous reaction mixture showed the desired product (6.66 microns) present with unreacted hexafluoroacetone (5.5 microns) and trifluoroacetyl fluoride (5.3 microns) resulting from HFPO decomposition. The absence of HFPO indicated completion of the reaction and greatly facilitated purification of the product. The reaction mixture was bubbled through a 1-meter distilled water column packed with Raschig rings to remove hexafluoroacetone and trifluoroacetyl fluoride. The product was passed from the water absorption column through a calcium chloride drying tube into a cold condenser where it was refluxed at -15 to -25°C, allowing impurities to pass into a liquid oxygen cooled trap. Perfluoroisobutylene oxide (216 g.) of 99.5% purity (GLC, PFOX at 40°C) was produced in 66% conversion.

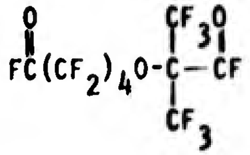
4. Preparation of Pentafluoronitrobenzene

A 5-liter, 3-neck flask was fitted with a stirrer, addition funnel, and reflux condenser. Methylene chloride (1000 ml.) and trifluoroacetic anhydride (250 ml.) were placed in the flask and 30% hydrogen peroxide (200 ml.) was cautiously added. The mixture was refluxed and stirred 30 minutes. Pentafluoroaniline (103 g., 0.56 mole) dissolved in 500 ml. methylene chloride was added slowly with stirring at reflux temperature. The mixture became green in a few minutes. After one hour another 100 ml. of 30% hydrogen peroxide was added and 3 hours later an additional 100 ml. of 30% hydrogen peroxide and 50 ml. trifluoroacetic anhydride was added. The mixture was refluxed and stirred for 18 hours. The mixture at this time still had a dark green color. After cooling one liter of water was added slowly, the methylene chloride layer separated and was washed with another one liter of water. The methylene chloride layer was again separated and dried over anhydrous magnesium sulfate.

Distillation through a 45 x 2 cm. packed column was used to remove the methylene chloride and the reaction products were distilled through a 30-cm. Vigreaux column. The primary product appeared to be the green colored nitroso compound.

After a second reaction was run for 18 hours and the reaction mixture still had the characteristic dark green nitroso color, 500 g. additional trifluoroacetic anhydride and 1200 ml. of 30% hydrogen peroxide were added and the mixture was refluxed and stirred for 14 hours. At the end of this interval the reaction mixture still had a dark green color, suggesting that little oxidation to the desired yellow-colored nitro compound had occurred. In order to permit a higher reaction temperature, the methylene chloride solvent was removed by distillation. The distilled reaction products of the first run were added to the flask. Glacial acetic acid (2300 ml.), 30% hydrogen peroxide (700 ml.), and concentrated sulfuric acid (50 ml.) were cautiously added to the flask. The reaction was stirred and heated to 70-85°C for 9 hours. Within one hour the color of the reaction mixture had changed from a dark green to a light yellow color. After 3 hours an additional 1000 ml. acetic acid and 350 ml. of 30% hydrogen peroxide were added. The golden yellow colored oil (48 g.) that settled to the bottom of the flask was removed and dried over anhydrous magnesium sulfate. Purity was 96.6% by GLC (∿98, 110°). The principal impurity was water.

5. Attempted Photochemical Dimerization of



$$F\overset{O}{\overset{\|}{C}}(CF_2)_4O-\underset{CF_3}{\overset{CF_3}{C}}-\overset{O}{\overset{\|}{C}}F$$

a. The apparatus used in the ultraviolet irradiation consisted of a reaction cell (8 x 2 inches) fabricated from Vycor 7910 (U.V. transmitting grade) having a 45-degree upward inclined sidearm. The cell had a one-inch diameter cold finger inserted through a rubber stopper at the top and extended to the bottom of the tube, and a sampling port at the top. A magnetic stirrer was used. A Friedricks condenser was connected to the sidearm and a liquid oxygen cooled trap with a drying tube was placed on the other side of the condenser. Immediately before use, the apparatus was dried by purging nitrogen through the system while heating the reactor. A 450-watt Hanovia 679A-36 ultraviolet lamp inserted in a water cooled Vycor immersion well was placed about 3 inches from the reaction cell.

The title diacid fluoride (6.3 g., 0.0137 mole), dissolved in 125 g. dry Freon 113, was placed in the reaction cell. The starting diacid fluoride had a boiling point of 102-112°C and was about 80% pure as measured by GLC. Freon 113 (1,2,2-trifluoro-1,1,2-trichloroethane) has a boiling point of 47°C. Irradiation was started with stirring and ice water was circulated through the cold finger and condenser. Samples were withdrawn for infrared and GLC analysis after 0, 8, 13 and 20 hours irradiation.

The gas chromatograms showed the appearance of no new peaks eluted after the peak of the starting material that could be attributed to the desired higher molecular weight coupled product. Little change was observed in the infrared spectra over the period of 20 hours irradiation. Infrared analysis of the trap contents showed the presence of only silicon tetrafluoride.

b. Infrared and GLC analysis of the starting diacid fluoride, after 24 hours irradiation, had shown it to be unchanged and usable for another attempt to achieve the coupling reaction. For this purpose, the Freon 113 solvent was replaced with FC-75 (3M), perfluorobutylfuran. The dry FC-75 solvent (68.7 g.) was added after removal of Freon 113 with a notavac. The apparatus used is the same as described in the preceding section and infrared and GLC analyses were made after 0, 20 hours, and 4 1/2 days irradiation. GLC analysis indicated that no higher molecular weight coupled dimer had formed. A gas IR of the LOX trap contents showed that no gas had been collected.

c. Another attempt at coupling involved the use of a purer sample of diacid fluoride and irradiation without any solvent. The starting material had a purity of 95.8% (GLC) and a boiling point of 103-110°C. The same Vycor 7910 cell was used as before with a reflux condenser attached to the top ofthe tube using a Teflon sheet wrapped rubber stopper. A LOX cooled cold trap was connected to the other end of the condenser. A heating mantle was fitted around the bottom of the reaction tube. After drying the apparatus, the diacid fluoride (17.1 g., 0.037 mole) was placed in the cell and brought to reflux temperature. The liquid was irradiated by the same U.V. source, as in the preceding attempts, as it condensed down the sides of the cell.

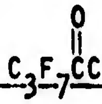
After 7 hours the material had changed from a clear, water white appearance to a very dark brown colored liquid with solid tar deposits on the sides of the cell. The gas chromatogram indicated that no new components had been formed in the mixture. After 35 hours a new peak appeared, considerably past that of the starting material, at 145°C on the temperature programmed chromatogram. This peak could be due to the formation of the desired dimer diacid fluoride. The infrared spectrum showed virtually no change over the 35 hour period of irradiation. No gas had been collected in the cold trap.

d. The effort described in Section 3 was continued using the same material with a modification. The heating mantle was removed and replaced with a magnetic stirrer so that the entire liquid phase was irradiated at ambient temperature. Irradiation was continued for an additional 30 hours.

The appearance of the liquid had changed from dark brown to a clear light yellow color. The GLC analysis indicated some increase in relative peak size at 145°C to the major peak compared with the GLC analysis after 35 hours irradiation in the previous experiment. However, a considerable amount of impurities was indicated. Infrared analysis again showed no change over the period of irradiation. A gas IR of the LOX cooled trap indicated that no gaseous products had been formed.

6. Attempted Preparation of Hexafluoropropylene Oxide Using Osmium Tetroxide

A new synthetic route to hexafluoropropylene epoxide was attempted which had been reported[37] for the conversion of propylene to propylene oxide. Hexafluoropropene (13.6 g., 0.09 mole) was transferred to a Fischer-Porter tube in an ice bath which contained 2.5 ml. aqueous $NaClO_3$ and 2.5 ml. 0.1M OsO_4 in glacial acetic acid. The reactants were stirred with a magnetic stirrer at ice bath temperature; the pressure reached 100 psi. Infrared analyses of the gas after 30 minutes, 1, 5 and 21 hours, showed no epoxide absorption at 6.6 microns. Hexafluoropropylene oxide, which has a typical strong peak at this wave length, apparently is not formed under these conditions.



7. Preparation of $C_3F_7\overset{\overset{O}{\|}}{C}Cl$ from $C_3F_7CO_2NH_4$

The ammonium salt of perfluorobutyric acid was prepared by the cautious addition of aqueous ammonia to perfluorobutyric acid (53.5 g., 0.25 mole) until a pH of 8 was reached. A rotovac with an aspirator and hot water bath was used to remove the water, followed by the addition of 100 ml. benzene, to azeotrope off the last amounts of water.

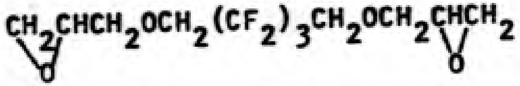
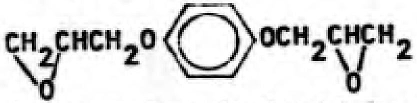
A 1-liter, 1-neck flask was fitted with a 14" Vigreaux column, Claisen head and downward inclined ice-water cooled condenser. A liquid oxygen cooled trap was connected to the receiver. The receiver was cooled to about -15°. Benzotrichloride (293.2 g., 1.5 mole) and 94.9 g. zinc chloride were added to the flask followed by ammonium perfluorobutyrate (23.1 g., 0.1 mole). The molar ratio of benzotrichloride to ammonium perfluorobutyrate was 15 to 1 and 30% by weight zinc chloride of these reactants was used. As the pot was heated, an evolution of gas or apparent reaction started at about 70°. Heating was continued at 210-215°C for 2 hours. Heptafluorobutyryl chloride (16.5 g., 0.071 mole) of 97.6% purity (GLC) was collected in a conversion of 70.9%.

8. Preparation of Dimethyl Perfluorosuberate

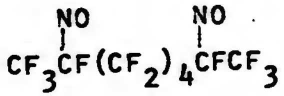
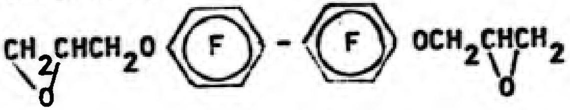
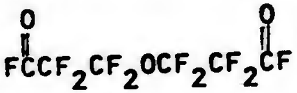
As a possible route to perfluorosuberonitrile for use in triazine polymer work dimethyl perfluorosuberate was prepared in a U.V. coupling reaction of perfluoroglutaryl fluoride followed by esterification with methanol. Perfluoroglutaryl fluoride (24.4 g., 0.1 mole) of 97.0% purity (b.p. 47-50°C) was placed in a 50-ml., 1-neck flask. A 2-foot length of fused quartz tubing (2 cm. dia.) was fitted tightly to the flask using a Teflon sleeve and the other end was connected to a liquid oxygen cooled trap protected with a drying tube. The starting material was refluxed up into the quartz tube and, while in the vapor phase and condensing upon the quartz walls, was irradiated with ultraviolet light. A 450-watt Hanovia 679A-36 ultraviolet lamp inserted in a water-cooled Vycor immersion well was placed about 2 inches from the quartz reaction tube. After 62 hours of irradiation, GLC analysis indicated a 69.7% conversion to perfluorosuberyl fluoride. Dry methanol (25 ml.) was cautiously added to the flask and the mixture was refluxed and stirred. The excess methanol was removed by distillation. Infrared and GLC analysis showed the presence of 58.2% dimethyl perfluorosuberate in the mixture of two main components. The infrared spectrum of the product separated by preparative GLC was identical to the reported[2] spectrum of dimethyl perfluorosuberate.

APPENDIX I

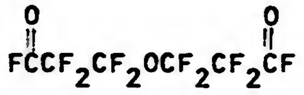
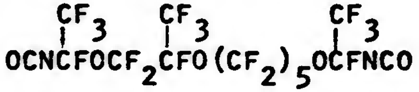
Schedule of Materials Submitted

Material	Sample No.	Quantity Delivered, g.	Delivery Date	Remarks
 $CH_2CHCH_2OCH_2(CF_2)_3CH_2OCH_2CHCH_2$	1072.76	74.4	12 Mar 68	Crude (68% by GLC)
$CF_3NO/CF_2=CF_2/CF_2=CFOCH(CH_3)_2$ Terpolymer	1095.65	2.5	"	5:4:1 charge ratio
"	1095.75	2.4	"	" " "
Fluoranil	-	10	27 June 68	
 (p-phenylenediglycidyl ether)	1105.16	5	22 Aug 68	IR shows -OH
$C_6F_5NO_2$	1105.17	45	4 Oct 68	97% (~3% H_2O)
$(CF_3)_2CFCN$	1118.30.A	17.5	16 Oct 68	99.6% by GLC (IR shows $>C=O$)
 $CF_2CF_2(CF_3)_4CFCF_2$	1105.19	20.0	28 Oct 68	99 + % (contains trace of H_2O)
$CF_2=CF(CF_2)_4CF=CF_2$	-	20.0	22 Nov 68	99 + %

APPENDIX I (Cont'd.)

Material	Sample No.	Quantity Delivered, g.	Delivery Date	Remarks
$CF_3CH_2CH_2Si(CH_3)ClH$	1118.89	5.0	11 Mar 69	99%
$(CF_3)_2CFO(CH_2)_3Si(CH_3)ClH$	1105.39	28.0	7 Apr 69	98.9%
 $CF_3\overset{NO}{C}F(CF_2)_4\overset{NO}{C}FCF_3$	1118.93.3	8.0	26 May 69	97%
Low molecular weight C_3F_7 triazine polymer	1105.47	1	4 June 69	Nitrile term. $[\eta]$=.02 MWt 2700
"	1105.48	1	"	" $[\eta]$=.03 MWt 2820
"	1105.49.1	1	"	" " =.03
"	1105.49.2	1	"	" " =.03
Triazine polymer	1105.52	1	"	"
DEDI [$OCNCF(CF_3)O(CF_2)_5OCF(CF_3)NCO$ & isomer]	1105.67.3	27	22 Oct 69	95% pure, 7:1 isomer ratio
	1105.63.1	0.6	22 Oct 69	impure, m.p. 65-66°
"	1105.63.2	4.6	31 Oct 69	m.p. 70-71°
 $F\overset{O}{\overset{\parallel}{C}}CF_2CF_2OCF_2CF_2\overset{O}{\overset{\parallel}{C}}F$	1105.67.1	10.9	3 Nov 69	From fractionation of 3 M sample b.p. 65-66°

APPENDIX I (Cont'd.)

Material	Sample	Quality Delivered, g,	Delivery Date	Remarks
 $F\overset{O}{\overset{\|}{C}}CF_2CF_2OCF_2CF_2\overset{O}{\overset{\|}{C}}F$	1105.67.2	19.0	3 Nov 69	b.p. 66-67°
"	1105.69.3	40.9	"	b.p. 67-67.8°
"	1105.69.4	7.4	"	b.p. 69.1-69.2°
Polystyrene-Polyethylene Oxide-Polystyrene Block Copolymer	1105.65.1	5.7	16 Oct 69	$[\eta]$=1.29 (benzene 30°), 22.9 mole % EO
" " "	1105.65.2	10.1	"	$[\eta]$=1.29 (benzene 30°), 49.4 mole % EO
Polyisoprene-Polyethylene Oxide-Polyisoprene Block Copolymer	1105.61.A	6.4	"	$[\eta]$=0.43 (1,2-dichloroethane at 30°), 29.8 mole % EO
$OCNCF_2CF_2OCF_2CF_2NCO$	1105.69A	3.5	2 Dec 69	96.8%
"	1105.69B	13.3	"	95.9%
 $OCN\overset{CF_3}{\overset{\|}{C}}FOCF_2\overset{CF_3}{\overset{\|}{C}}FO(CF_2)_5O\overset{CF_3}{\overset{\|}{C}}FNCO$ (TEDI)	1105.75.3	74.3	18 Dec 69	94.8% (GLC)
" (TEDI)	1105.75.4	19.2	"	96.2% (GLC)

APPENDIX II

Infrared Spectra

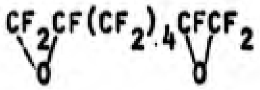
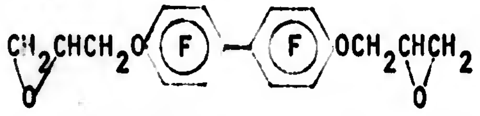
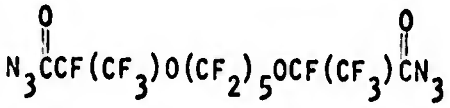
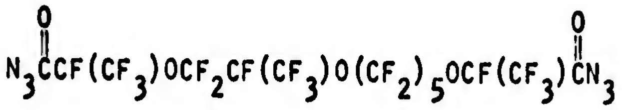
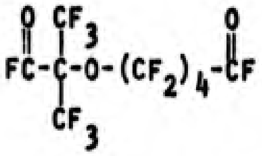
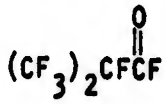
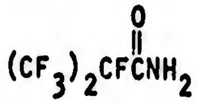
Figure	Compound
1.	Perfluorosebaconitrile
2.	Perfluorosebacamidine
3.	Polyimidoylamidine
4.	Poly(perfluoropropylperfluorooctamethylenetriazine)
5.	Crude 4-Cyanoperfluorobutyryl Chloride
6.	Hydroxy-Terminated Poly(Ethylene Oxide)
7.	Polyisoprene
8.	PEO/Isoprene Block Copolymer
9.	PEO/Styrene Block Copolymer (1105.65.1)
10.	PEO/Styrene Block Copolymer (1105.65.2)
11.	Water Extract of Block Copolymer 1105.65.1
12.	Water Extract of Block Copolymer 1105.65.2
13.	$CF_3NO/CF_2{=}CF_2/CF_2{=}CFOCH(CH_3)_2$ Terpolymer
13a.	
14.	
15.	$CF_3CH_2CH_2Si(CH_3)H_2$
16.	Unidentified Product Obtained in Preparation of $CF_3CH_2CH_2Si(CH_3)H_2$
17.	$CF_3CH_2CH_2Si(CH_3)ClH$
18.	$(CF_3)_2CFOCH_2CH_2CH_2Si(CH_3)H_2$

Figure	Compound
19.	$(CF_3)_2CFOCH_2CH_2CH_2Si(CH_3)ClH$
20.	$CF_3CF(NO)(CF_2)_4CF(NO)CF_3$
21.	$CF_2{=}CF(CF_2)_4CF(NO)CF_3$
22.	$OCNCF_2CF_2OCF_2CF_2NCO$
23.	 $N_3\overset{\underset{\|}{O}}{C}CF(CF_3)O(CF_2)_5OCF(CF_3)\overset{\underset{\|}{O}}{C}N_3$ and Isomer (DEDAZ)
24.	$OCNCF(CF_3)O(CF_2)_5OCF(CF_3)NCO$ and Isomer (DEDI)
25.	 $N_3\overset{\underset{\|}{O}}{C}CF(CF_3)OCF_2CF(CF_3)O(CF_2)_5OCF(CF_3)\overset{\underset{\|}{O}}{C}N_3$ and Isomer (TEDAZ)
26.	$OCNCF(CF_3)OCF_2CF(CF_3)O(CF_2)_5OCF(CF_3)NCO$ and Isomer (TEDI)
27.	Decomposition Product from TEDI
28.	 $F\overset{\underset{\|}{O}}{C}-\underset{CF_3}{\overset{CF_3}{C}}-O-(CF_2)_4-\overset{\underset{\|}{O}}{C}F$
29.	 $(CF_3)_2CF\overset{\underset{\|}{O}}{C}F$
30.	 $(CF_3)_2CF\overset{\underset{\|}{O}}{C}NH_2$ (Nujol mull)
31.	$(CF_3)_2CFCN$
32.	$CF_2{=}CF(CF_2)_4CF{=}CF_2$
33.	$C_6F_5NO_2$

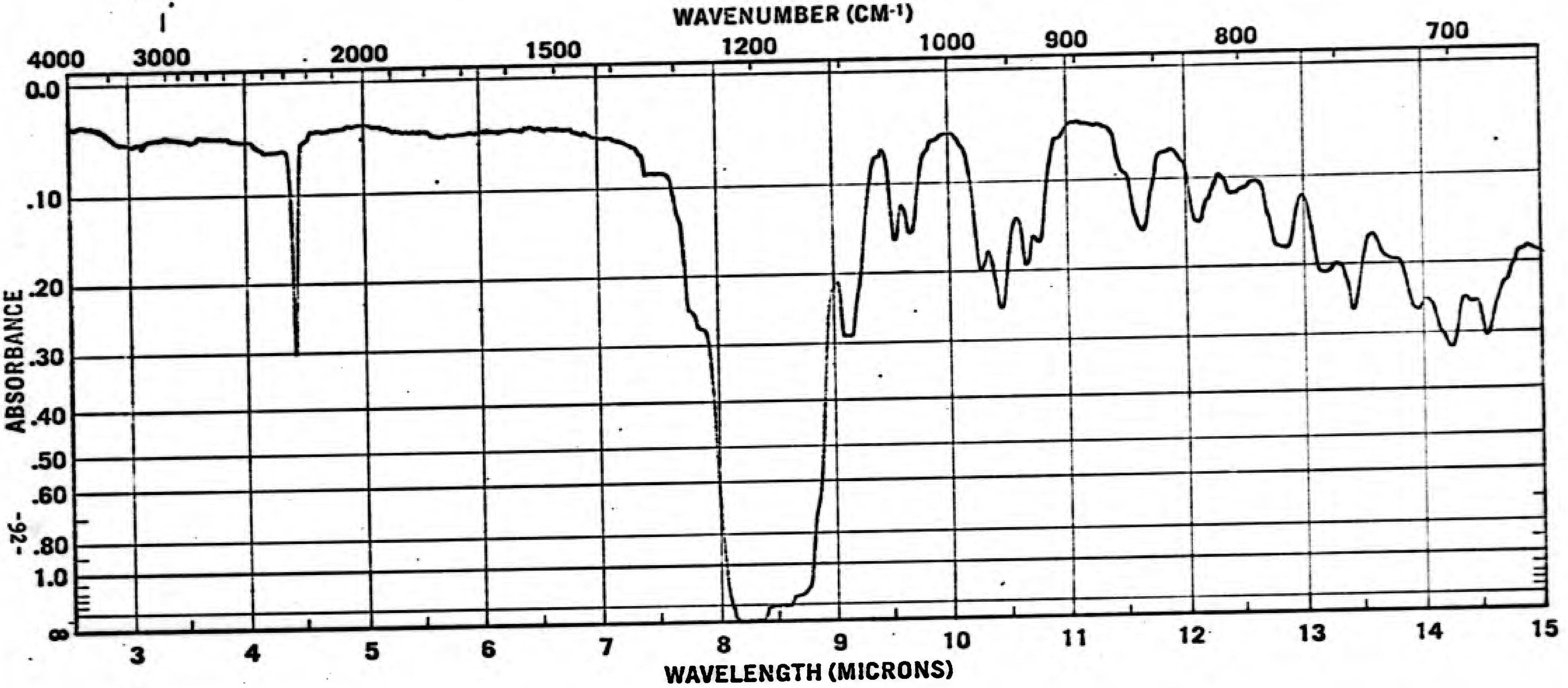


Figure 1.

Infrared Spectrum of Perfluorosebaconitrile

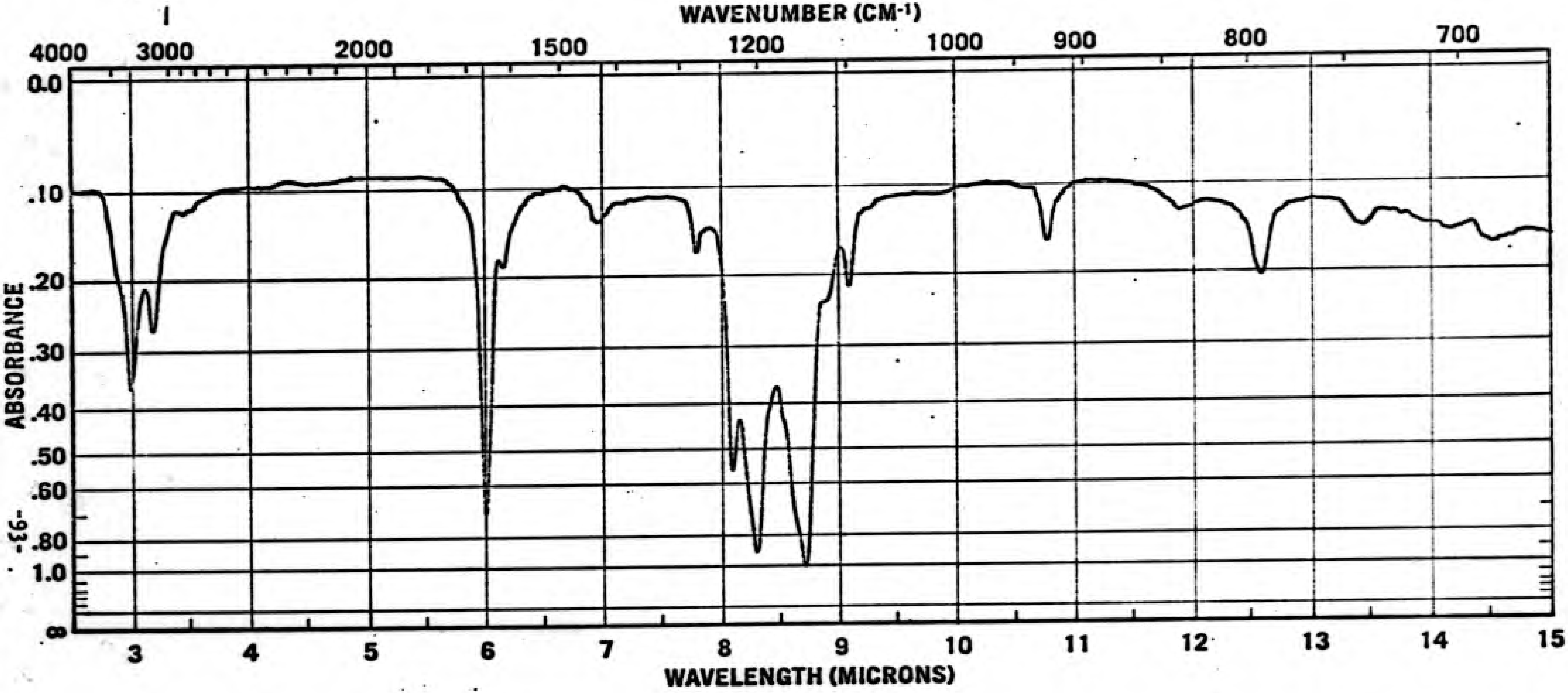


Figure 2.

Infrared Spectrum of Perfluorosebacamidine

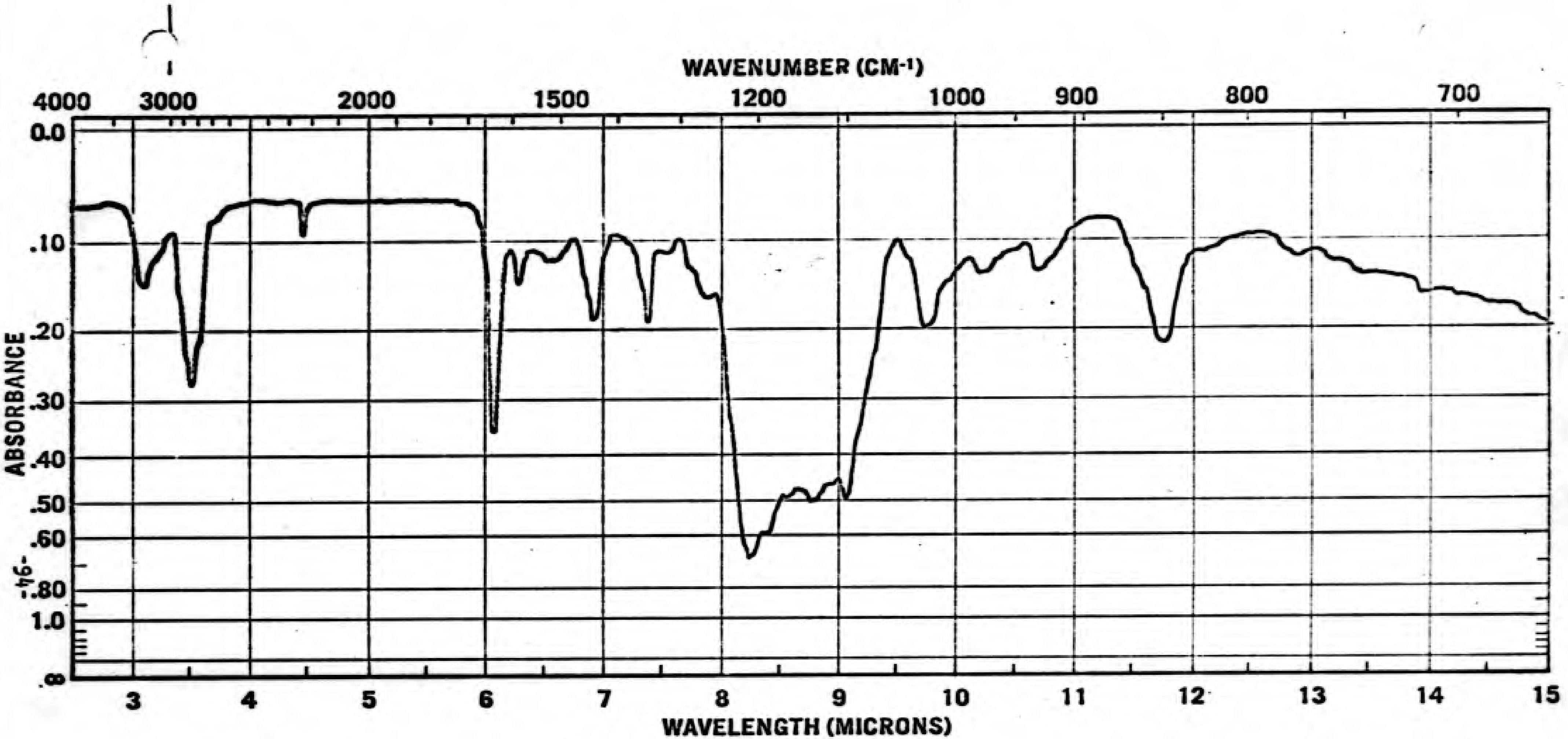


Figure 3.

Infrared Spectrum of Polyimidoylamidine

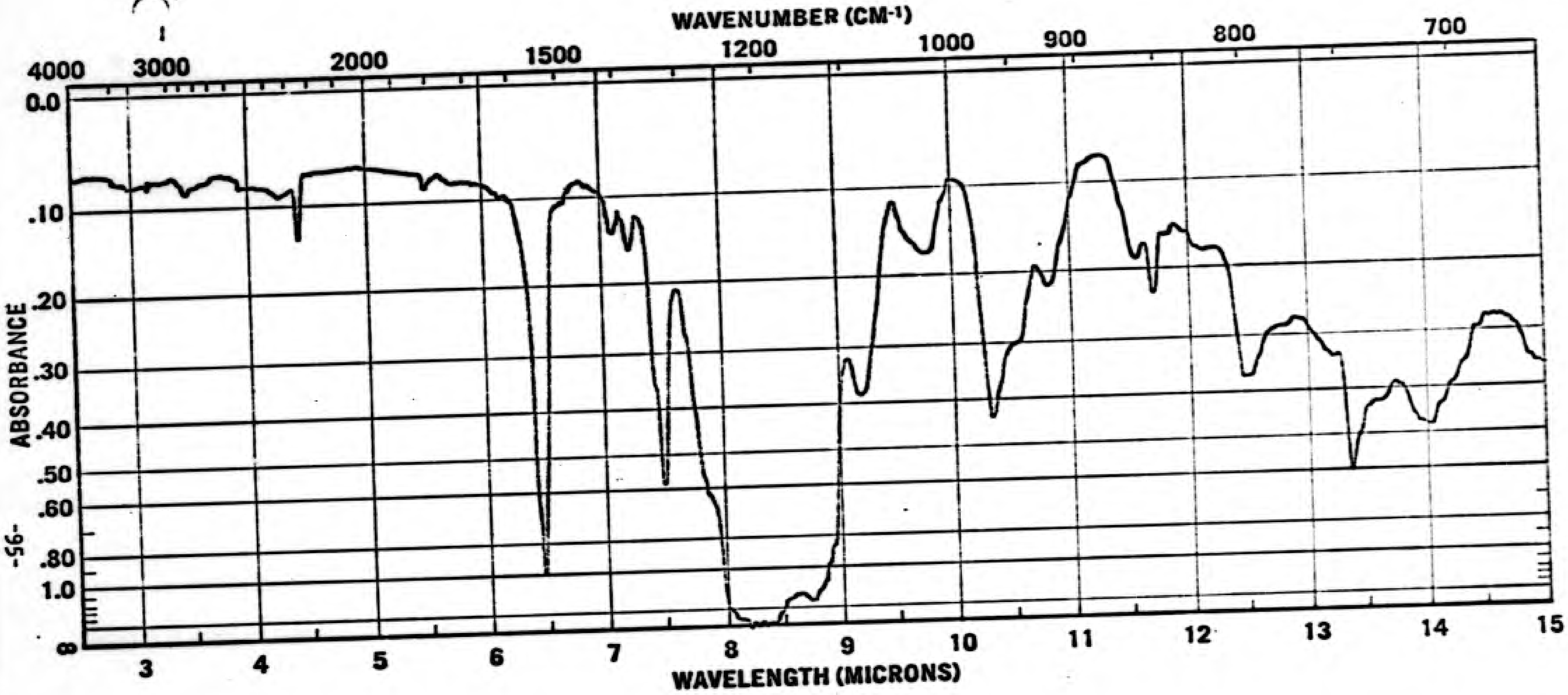


Figure 4.

Infrared Spectrum of

Poly(perfluoropropylperfluorooctamethylenetriazine)

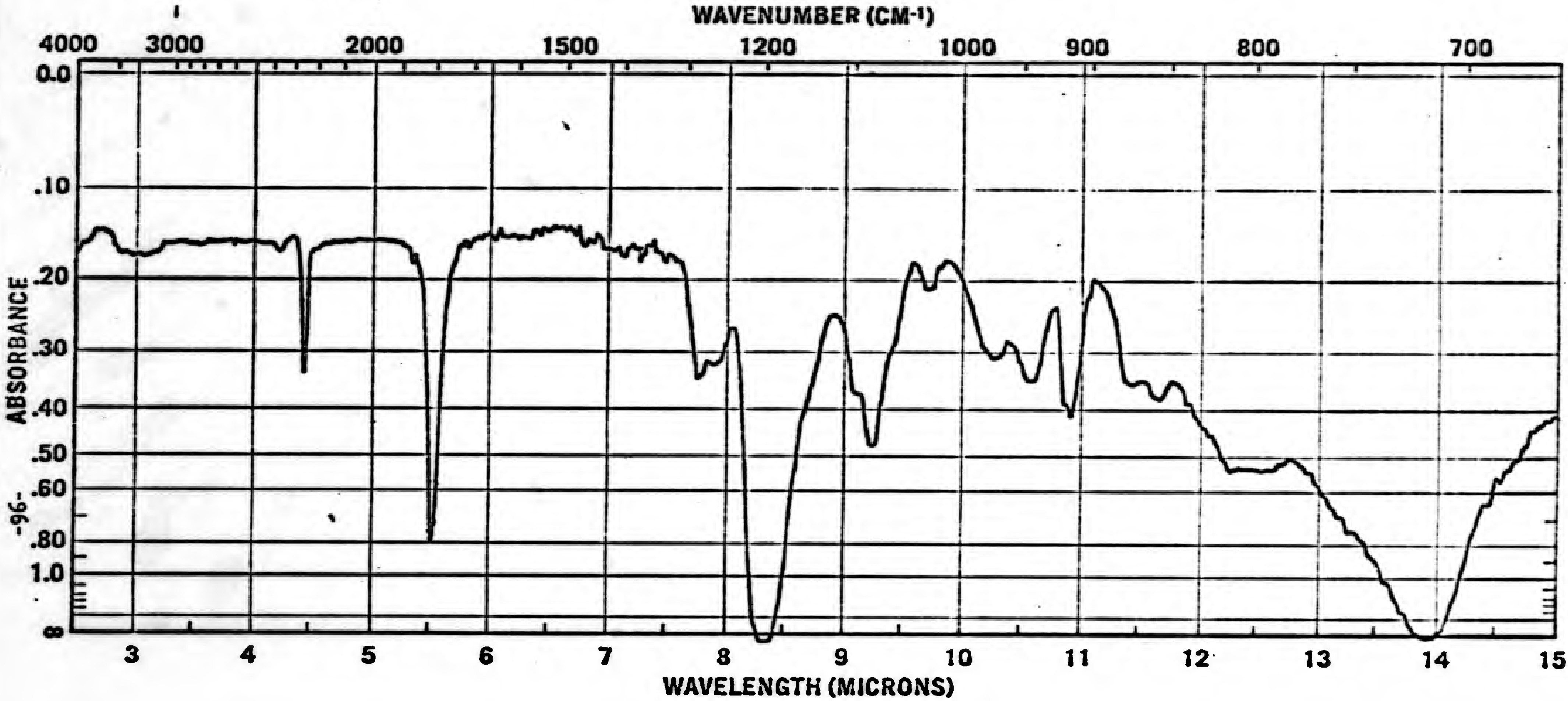


Figure 5.
Infrared Spectrum of
Crude 4-Cyanoperfluorobutyryl Chloride

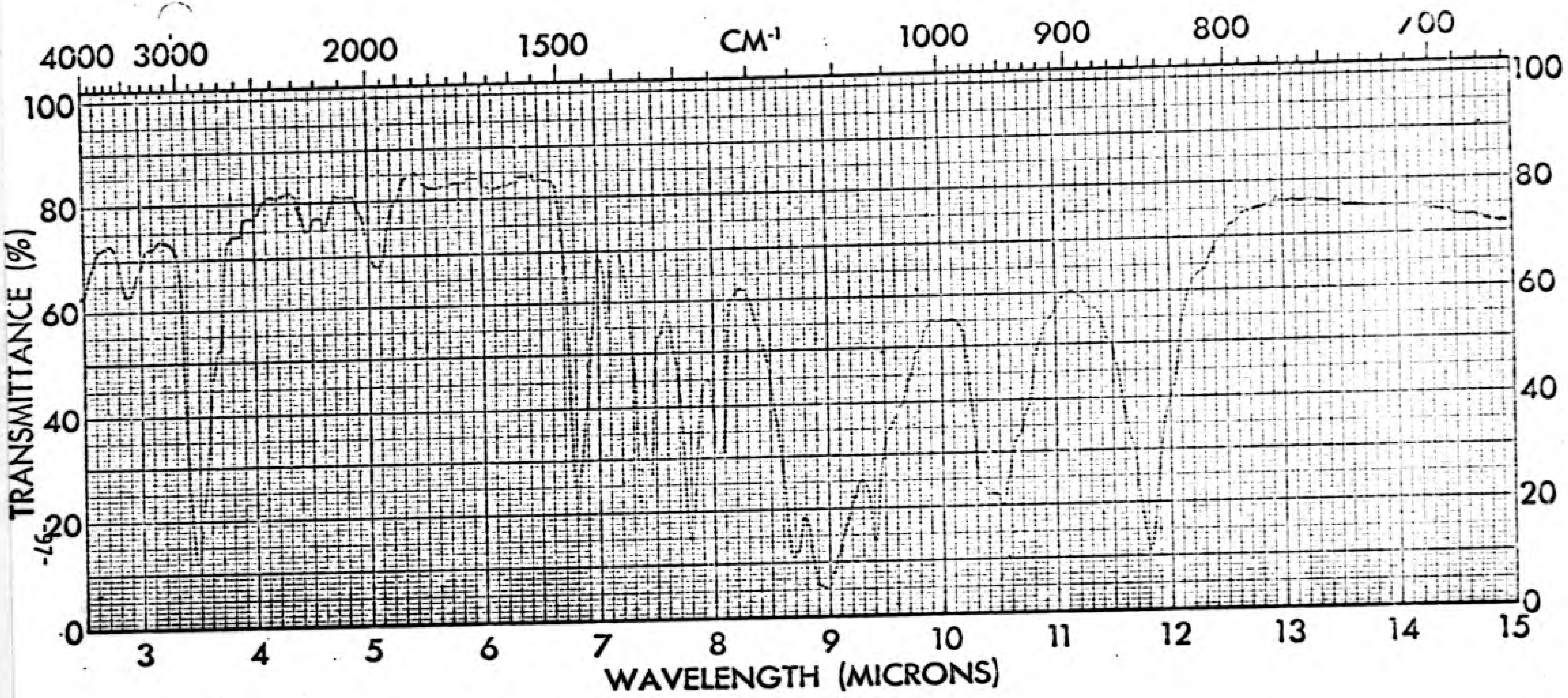


Figure 6.

Infrared Spectrum of

Hydroxy-Terminated Poly(Ethylene Oxide)

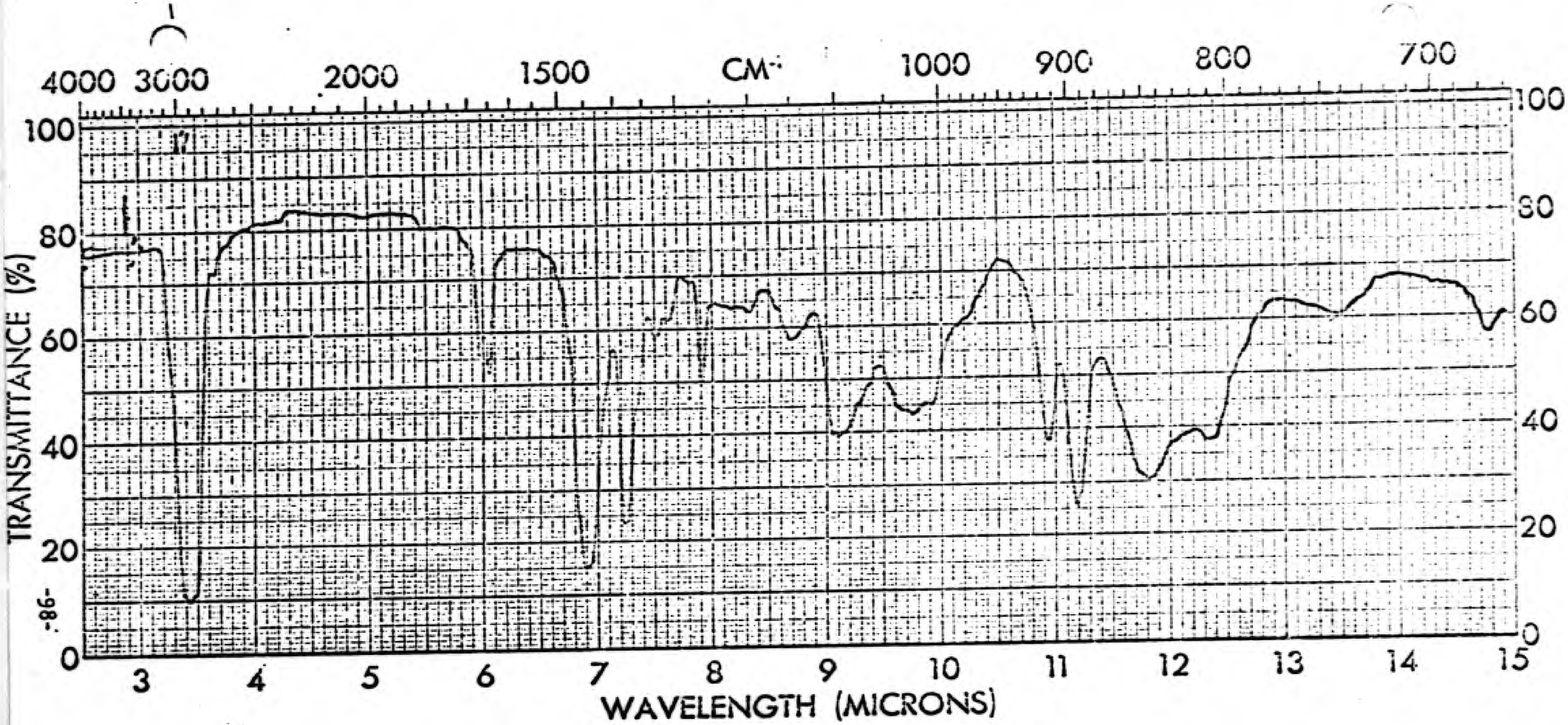


Figure 7.
Infrared Spectrum of Polyisoprene

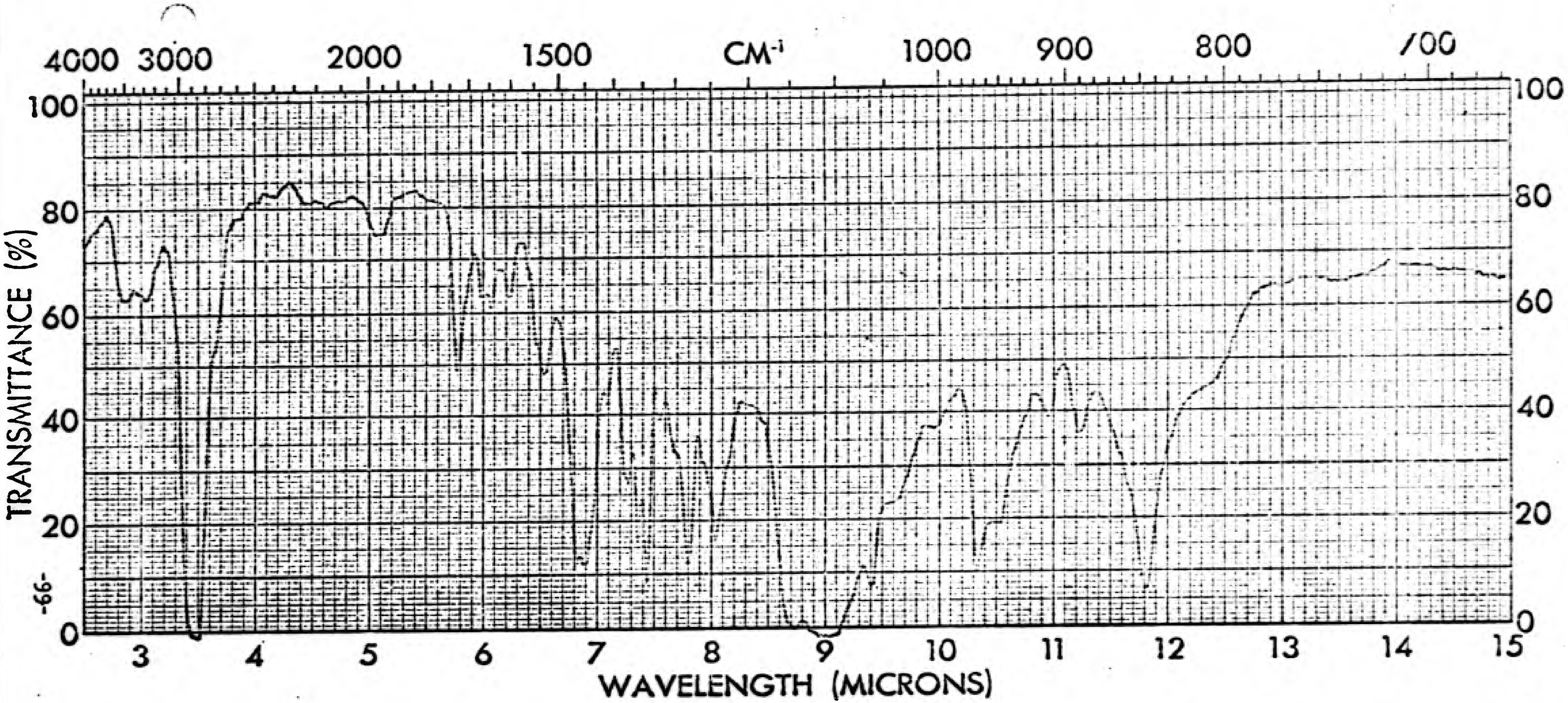


Figure 8.

Infrared Spectrum of PEO/Isoprene Block Copolymer

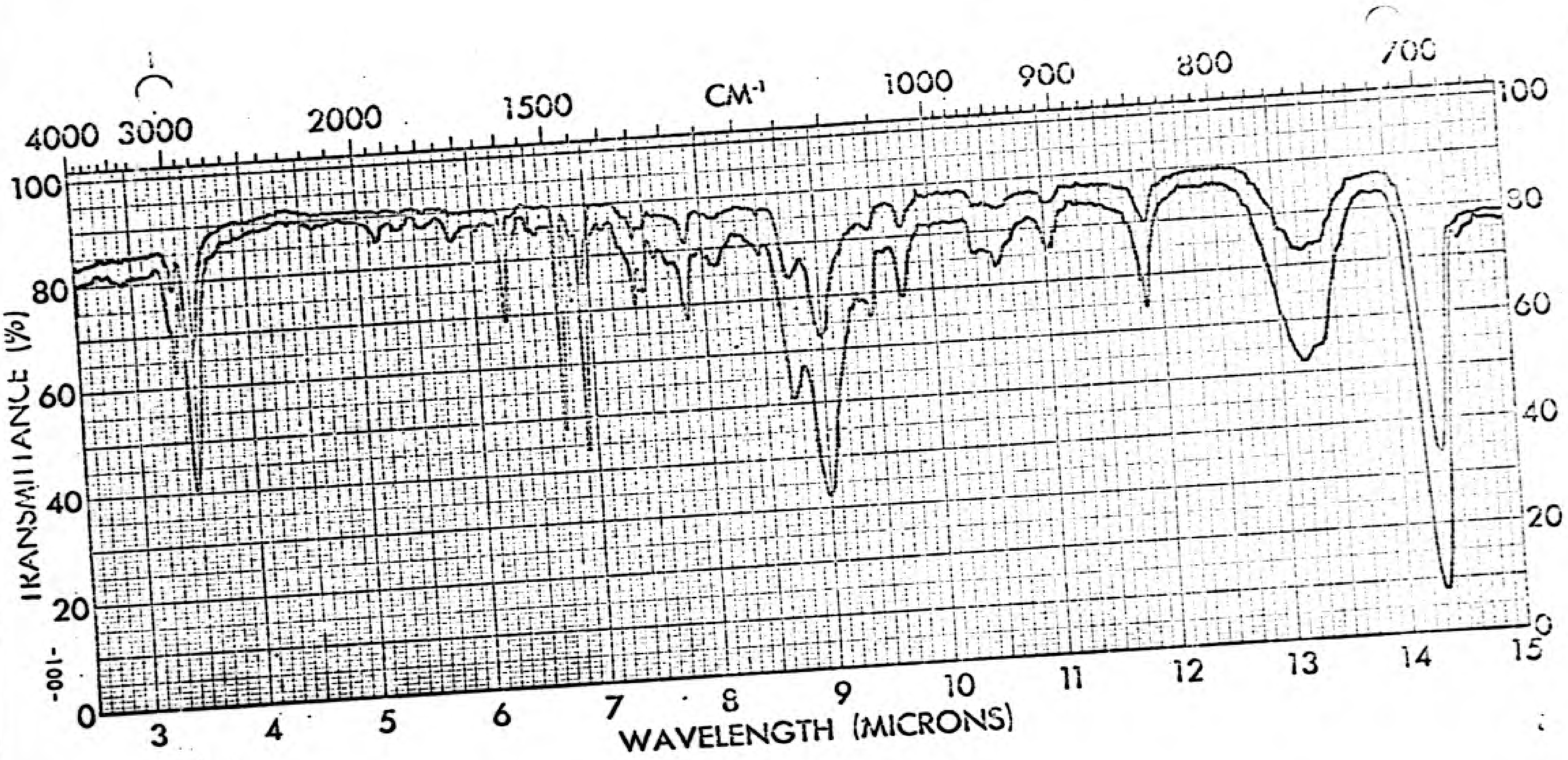


Figure 9.

Infrared Spectrum of

PEO/Styrene Block Copolymer (1105.65.1)

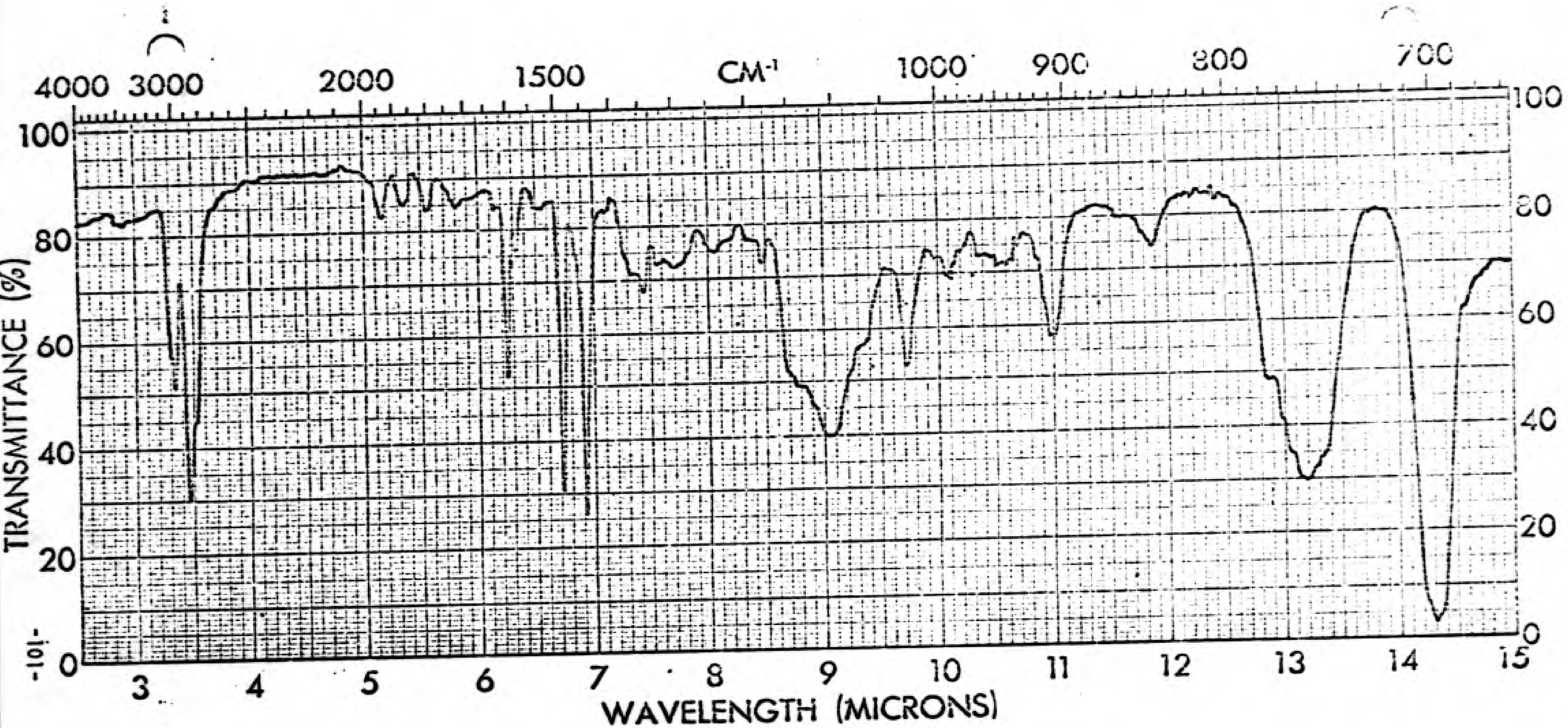


Figure 10.

Infrared Spectrum of

PEO/Styrene Block Copolymer (1105.65.2)

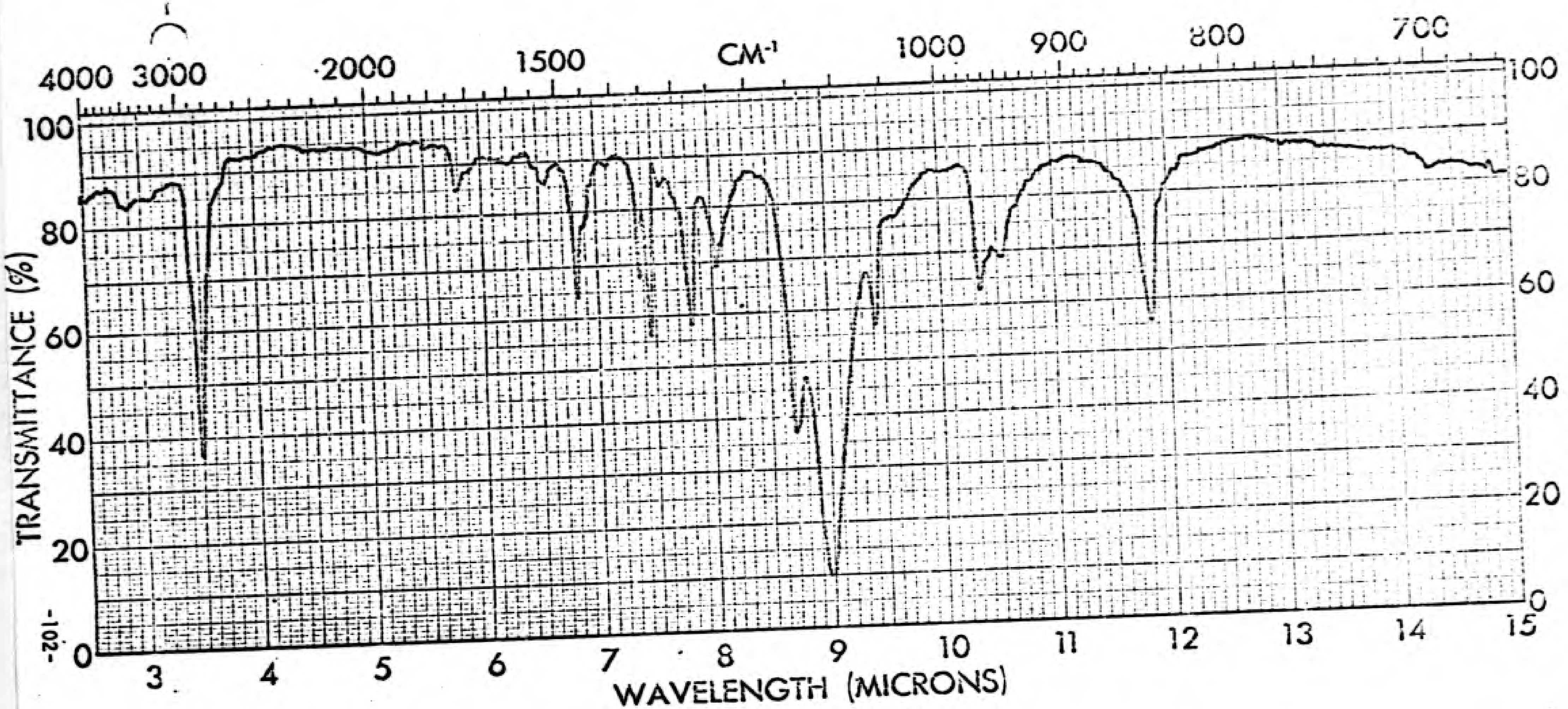


Figure 11.

Infrared Spectrum of

Water Extract of Block Copolymer 1105.65.1

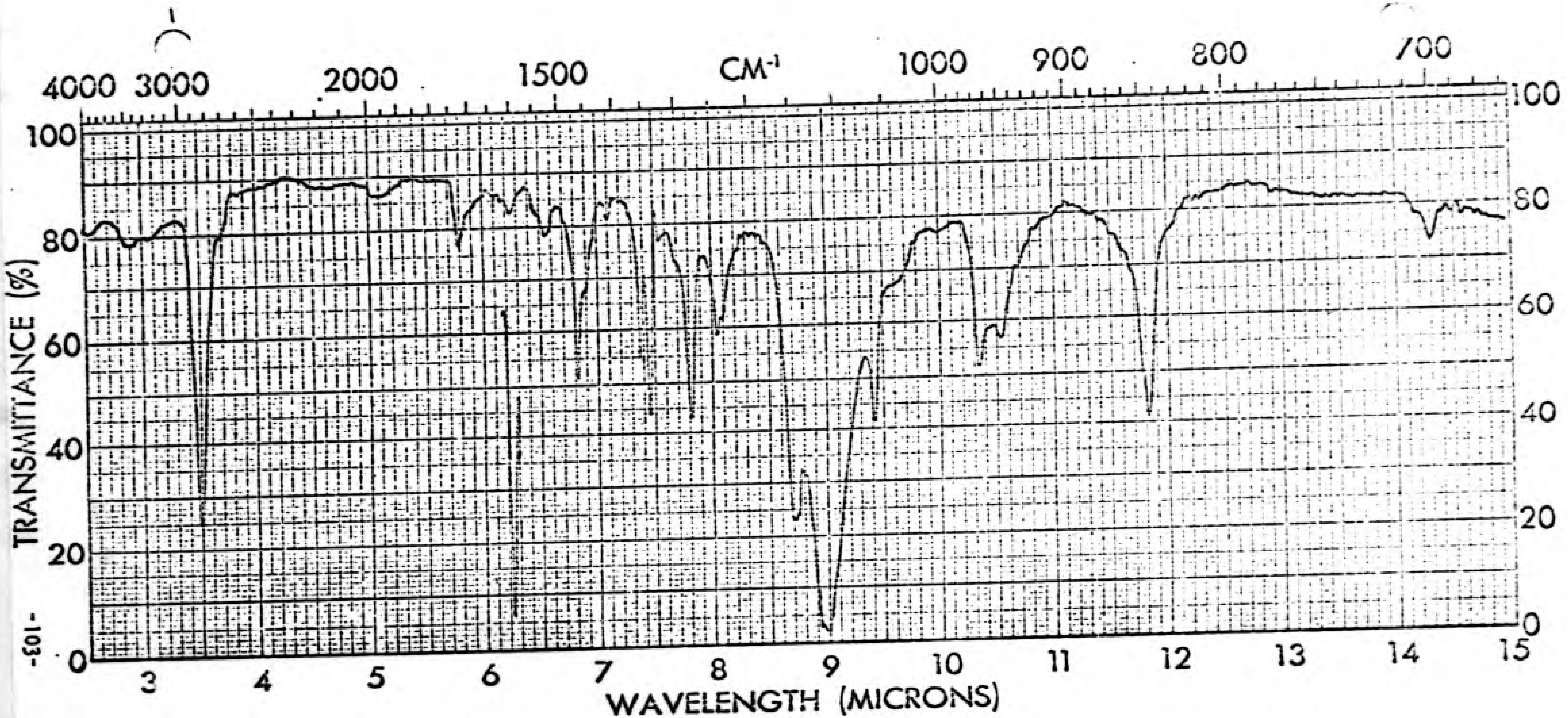


Figure 12.

Infrared Spectrum of

Water Extract of Block Copolymer 1105.65.2

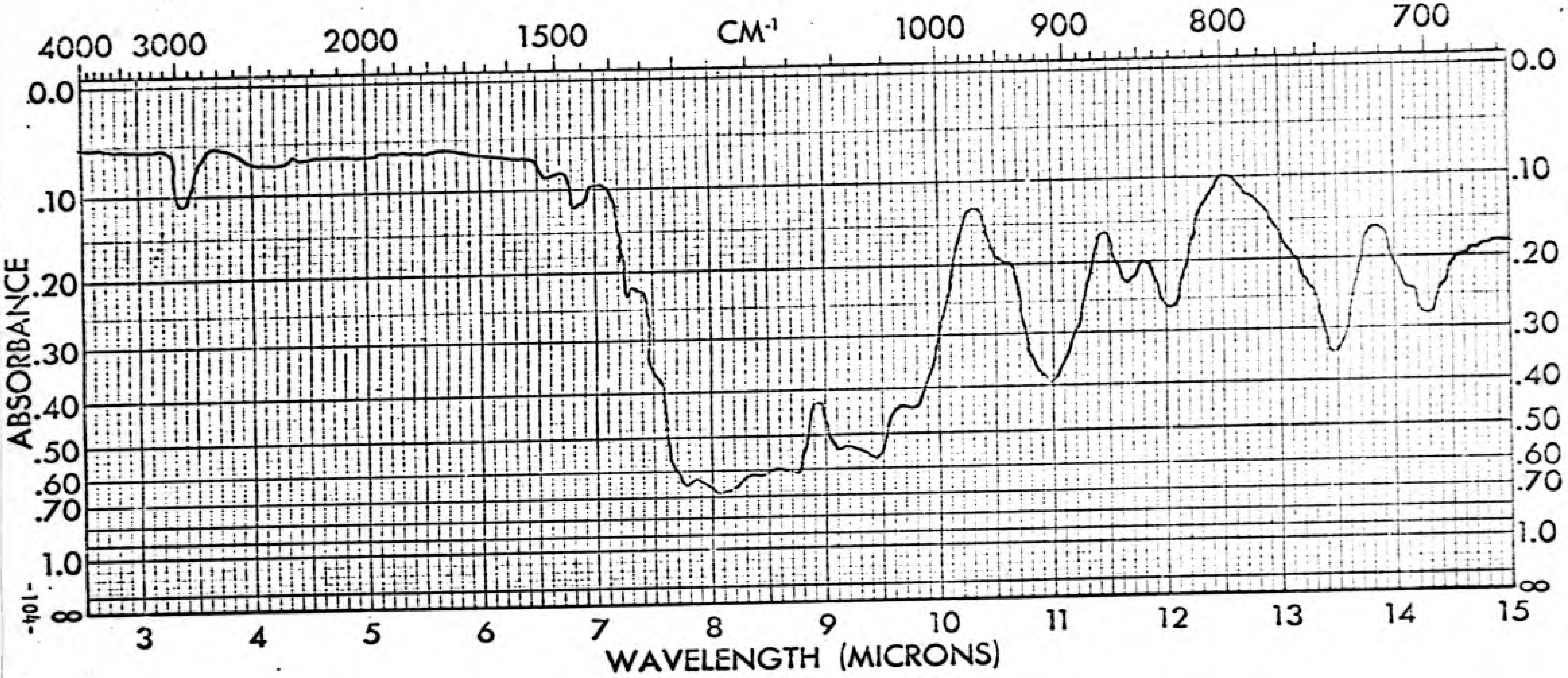


Figure 13.

Infrared Spectrum of

$CF_3NO/CF_2=CF_2/CF_2=CFOCH(CH_3)_2$ Terpolymer

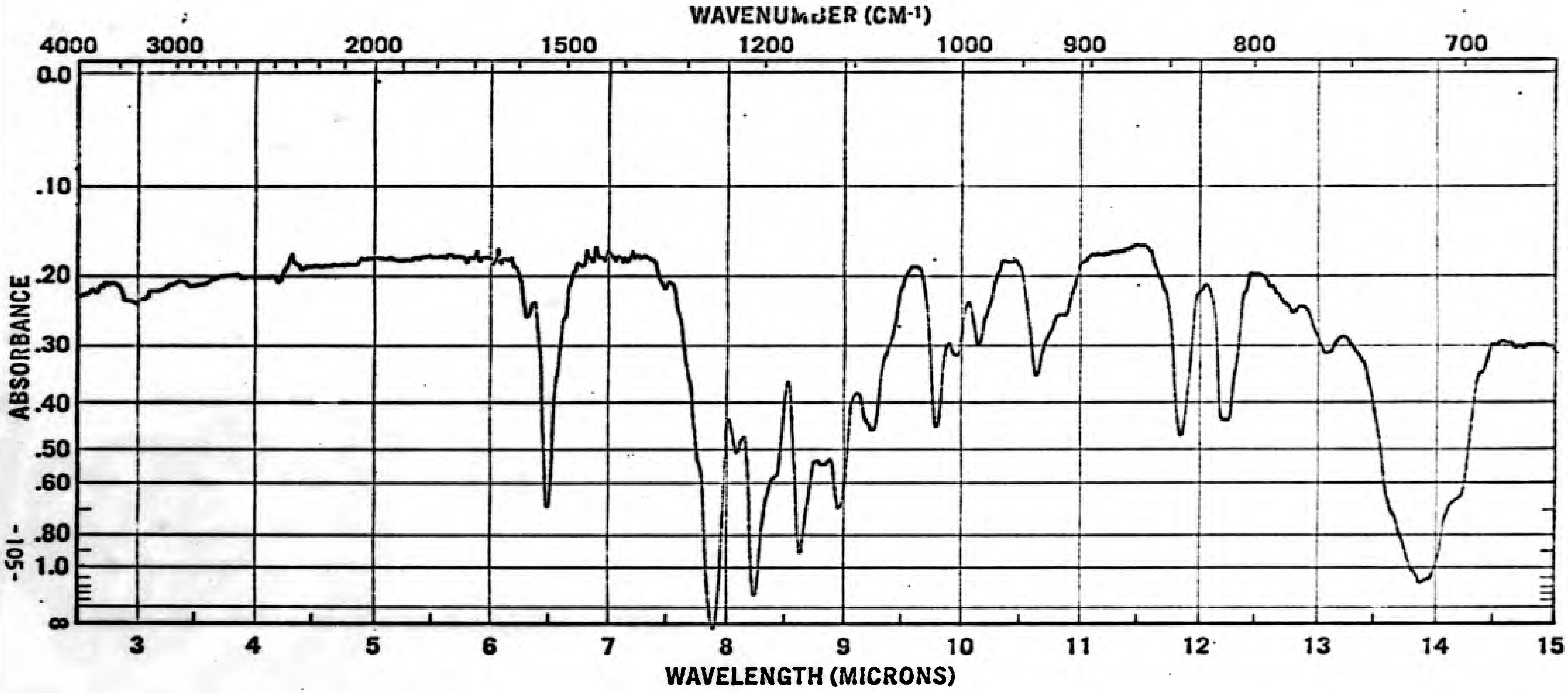


Figure 13a.

Infrared Spectrum of $\underset{\diagdown O \diagup}{CF_2CF}(CF_2)_4\underset{\diagdown O \diagup}{CFCF_2}$

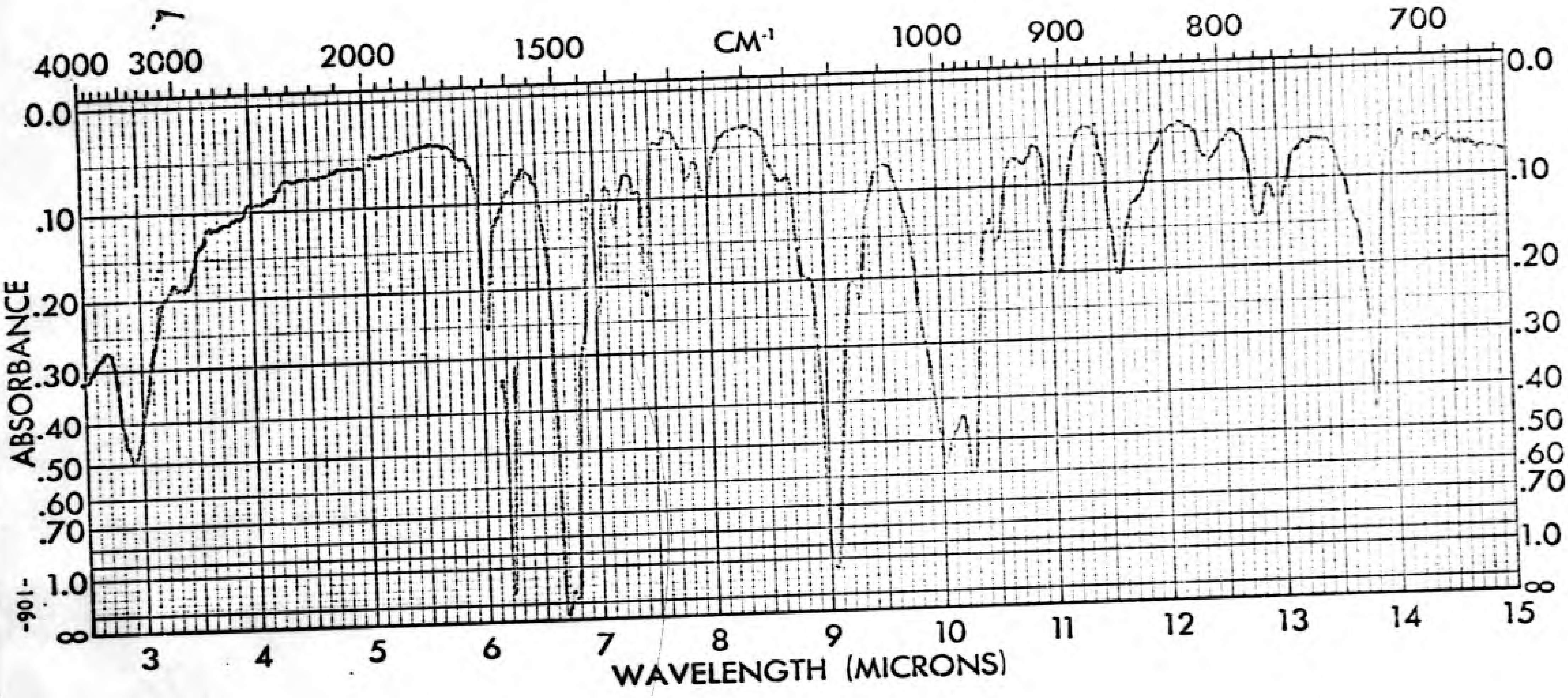
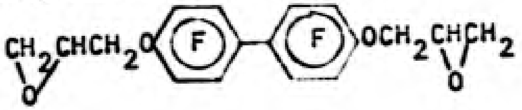


Figure 14.

Infrared Spectrum of



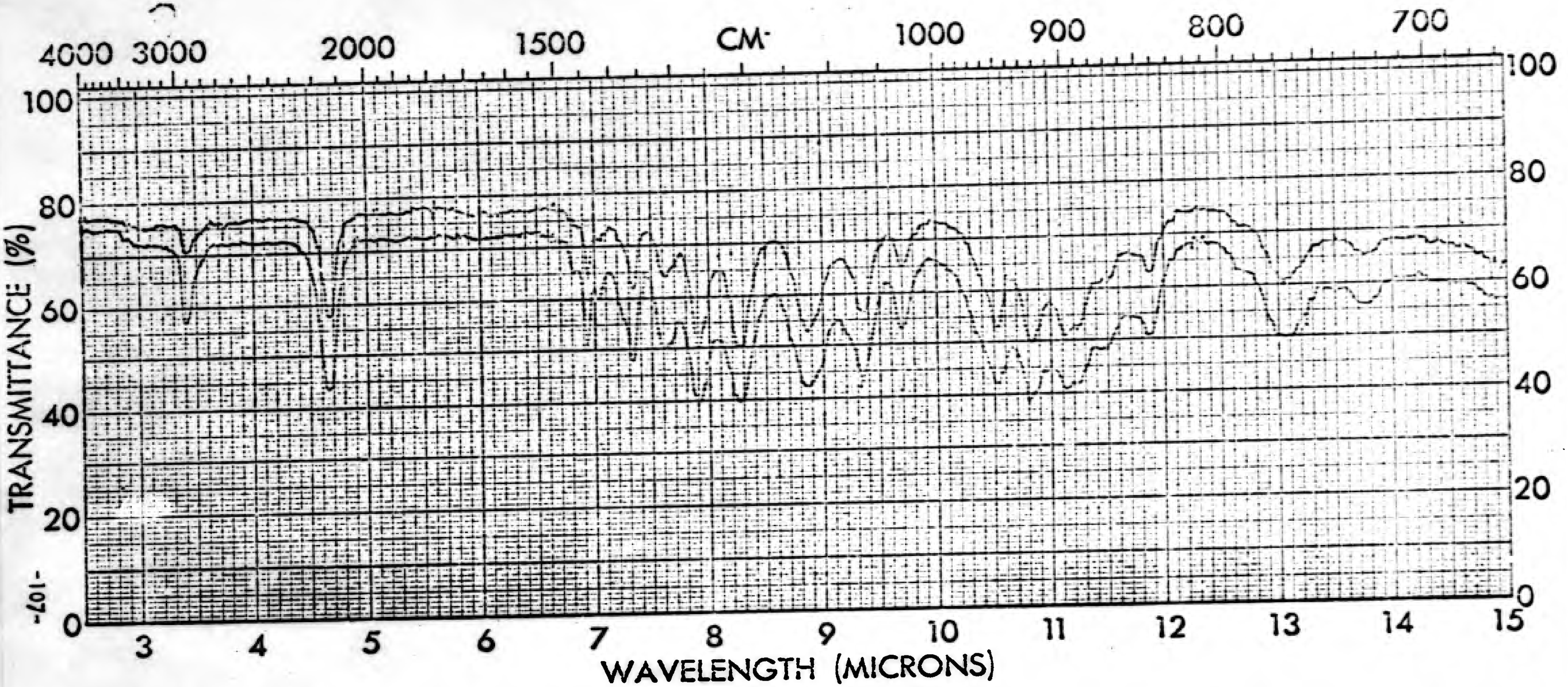


Figure 15.

Infrared Spectrum of $CF_3CH_2CH_2Si(CH_3)H_2$

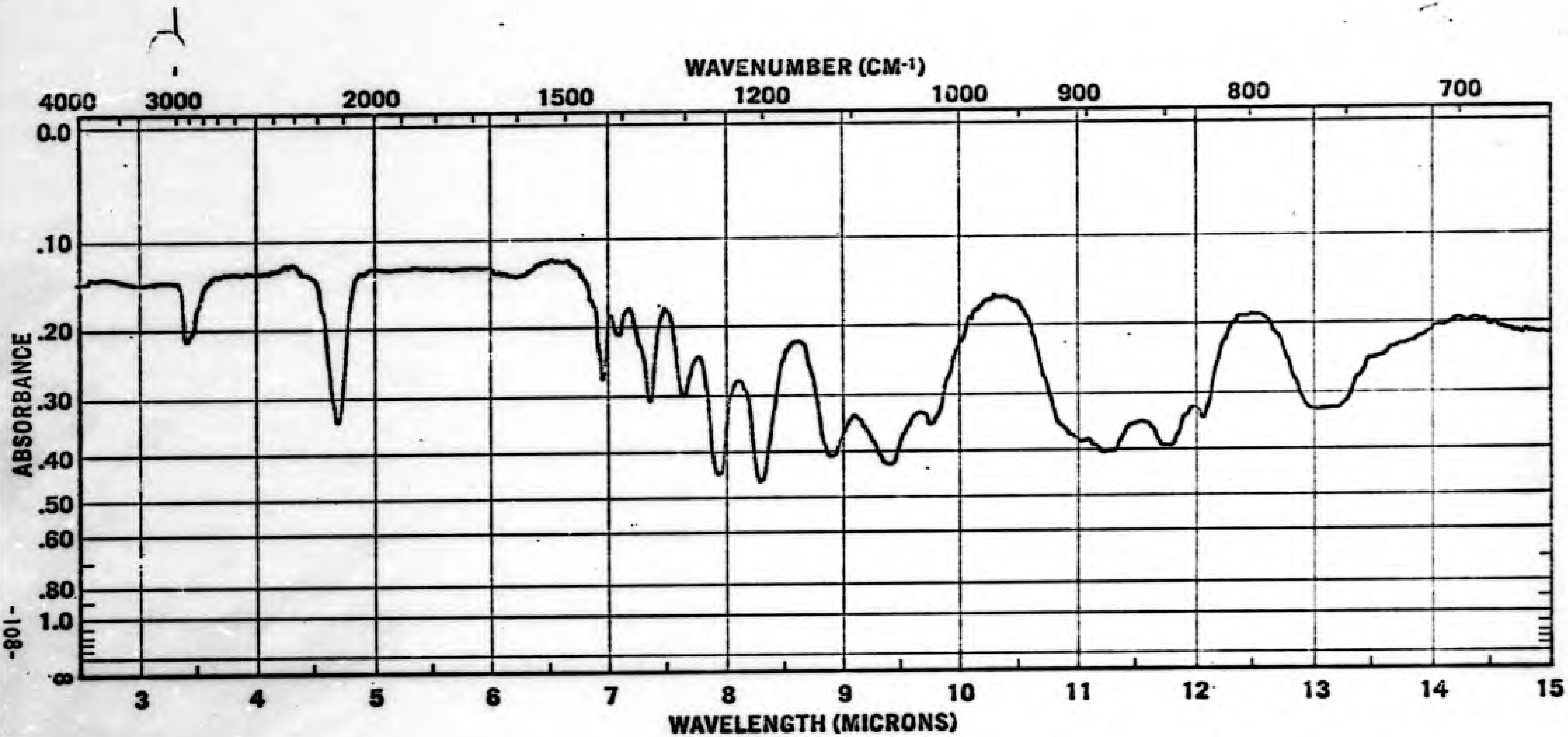


Figure 16.

Infrared Spectrum of Unidentified Product Obtained in Preparation of $CF_3CH_2CH_2Si(CH_3)H_2$

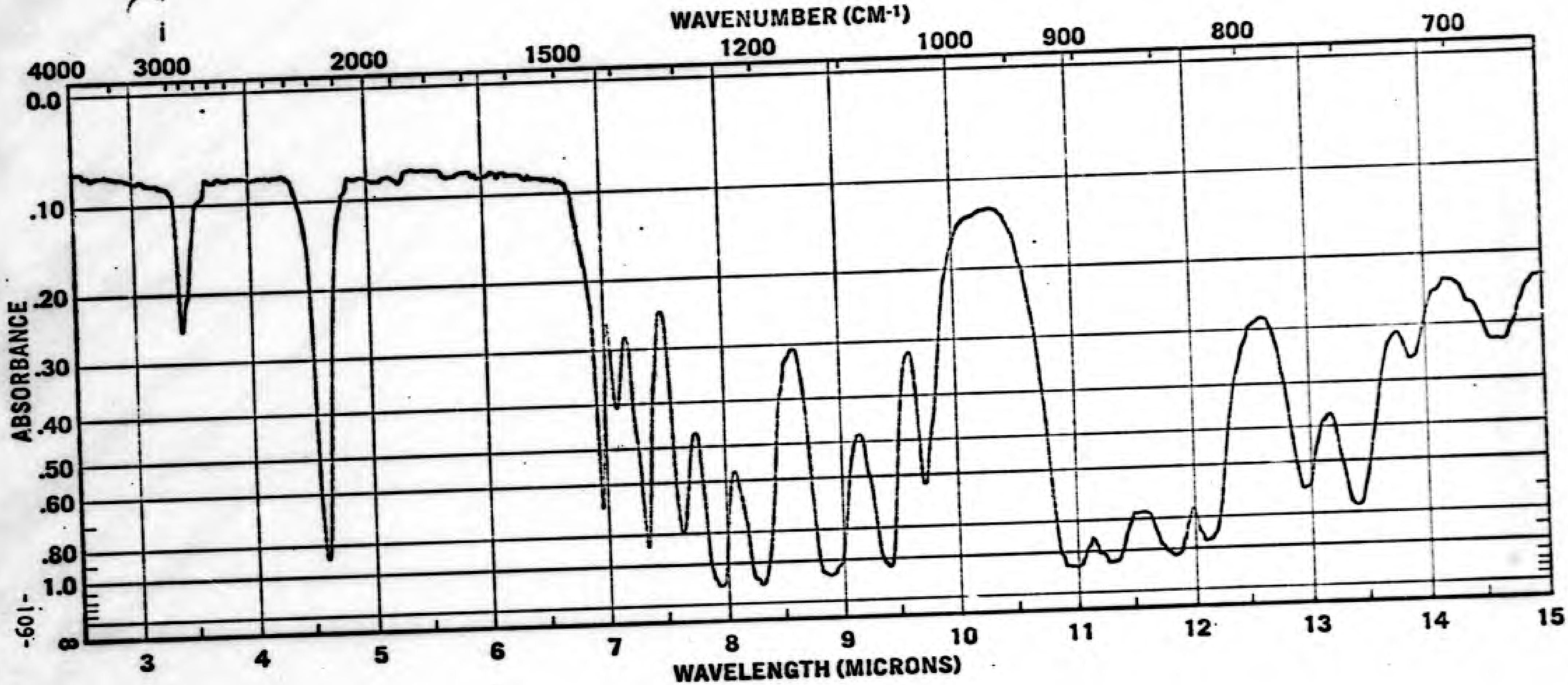


Figure 17.

Infrared Spectrum of $CF_3CH_2CH_2Si(CH_3)ClH$

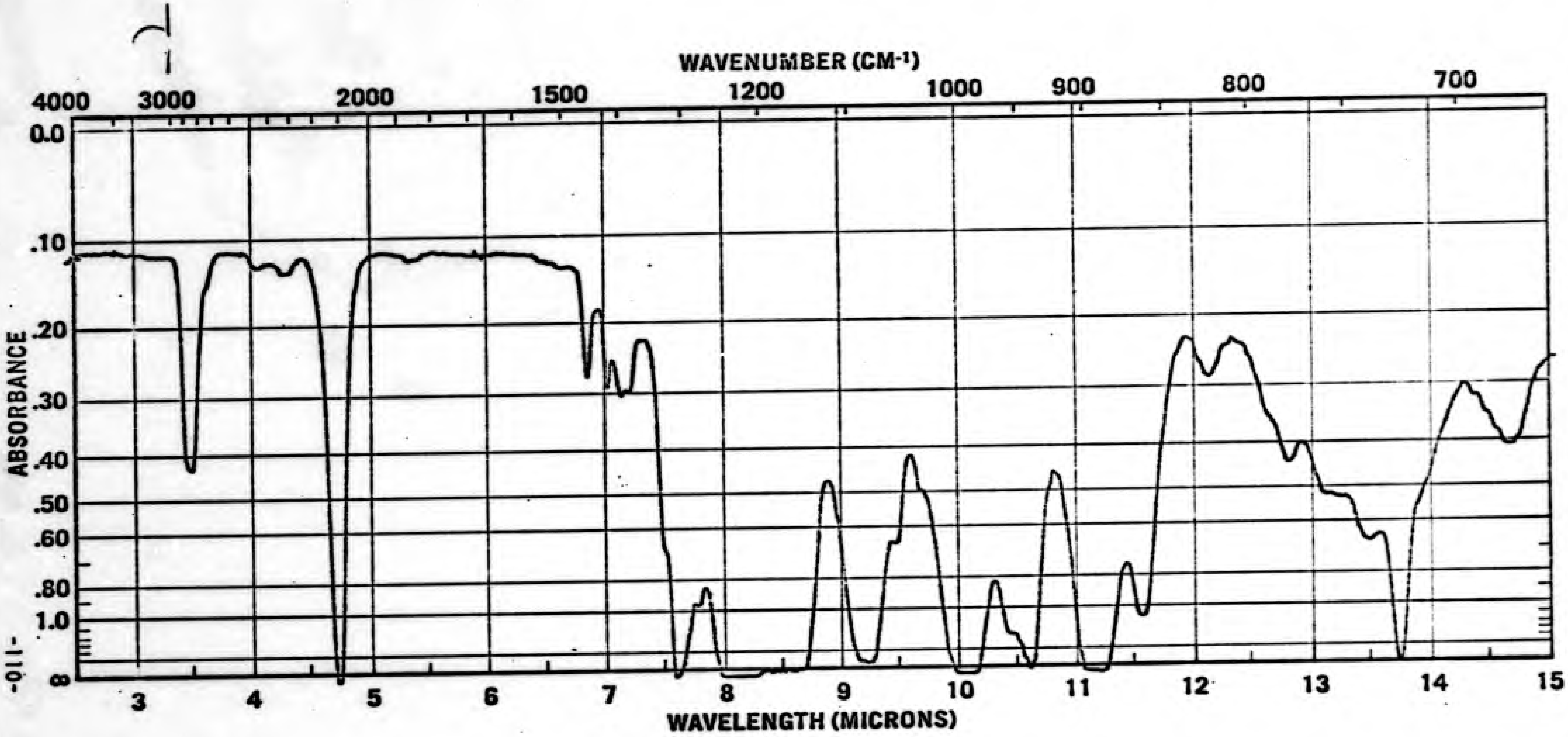


Figure 18.

Infrared Spectrum of $(CF_3)_2CFOCH_2CH_2CH_2Si(CH_3)H_2$

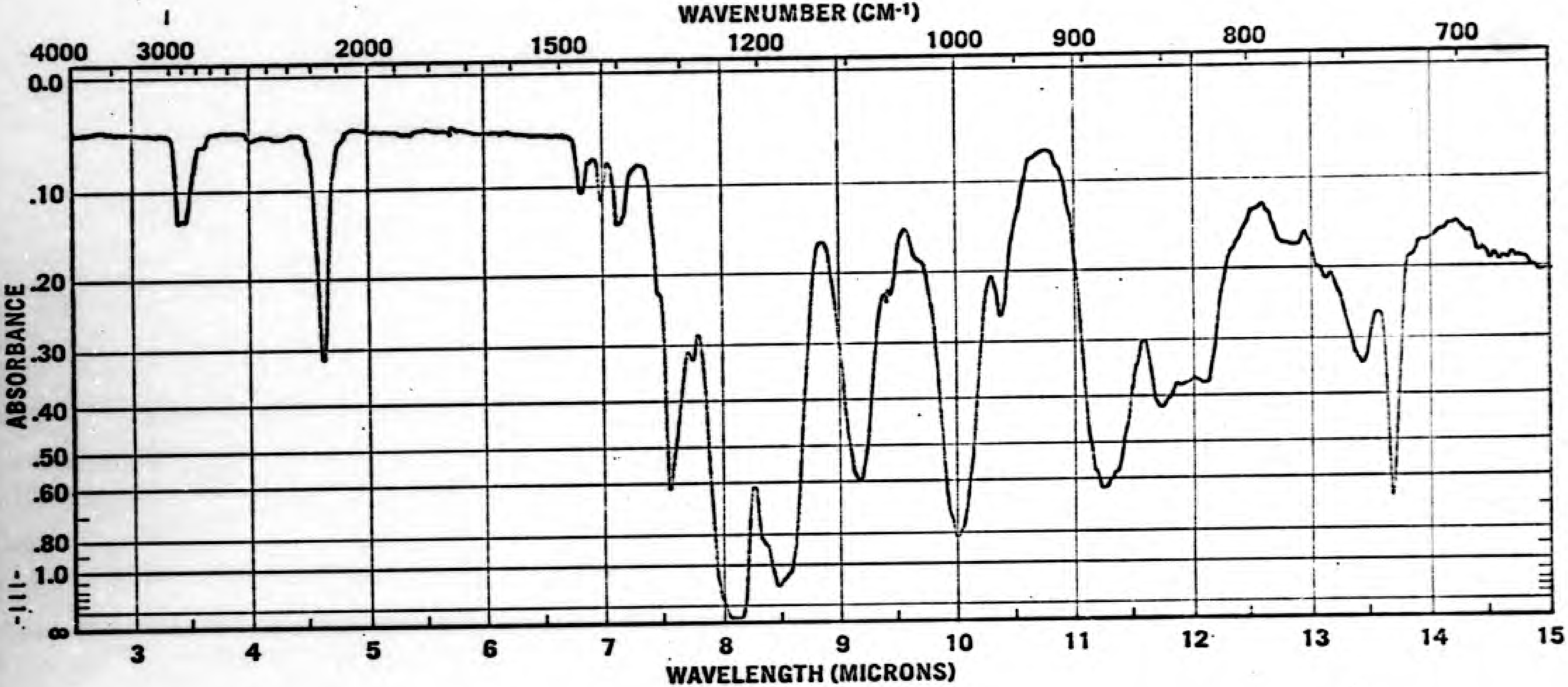


Figure 19.

Infrared Spectrum of $(CF_3)_2CFOCH_2CH_2CH_2Si(CH_3)ClH$

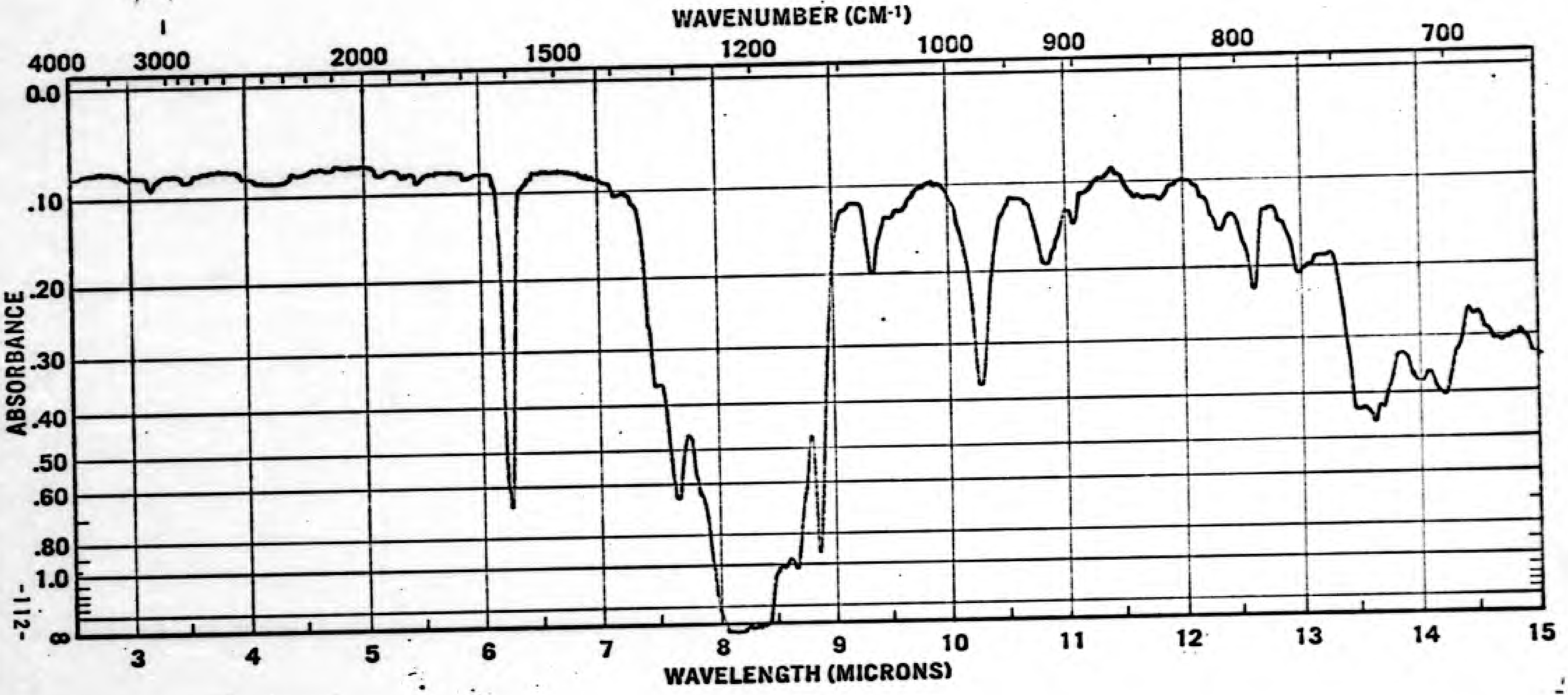


Figure 20.

Infrared Spectrum of $CF_3CF(NO)(CF_2)_4CF(NO)CF_3$

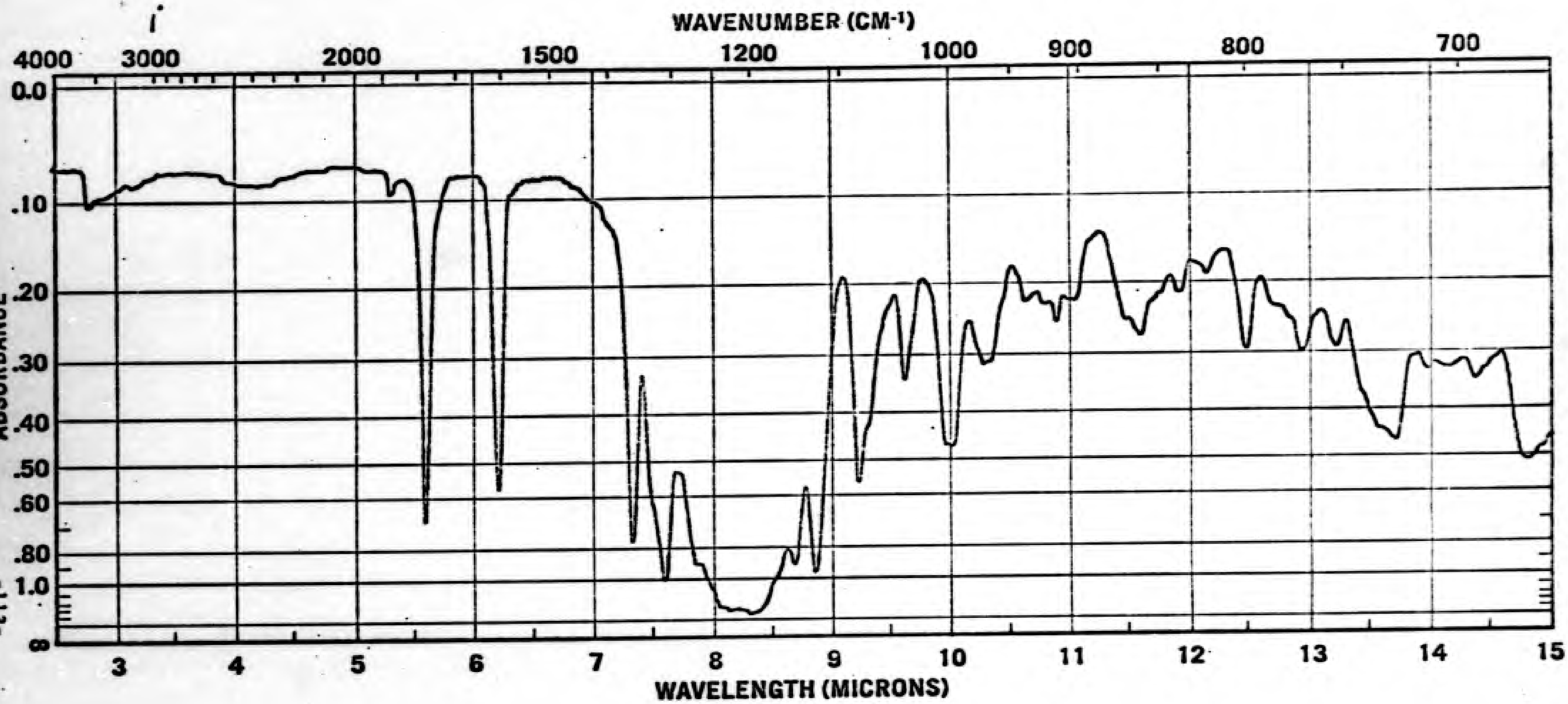


Figure 21.

Infrared Spectrum of $CF_2=CF(CF_2)_4CF(NO)CF_3$

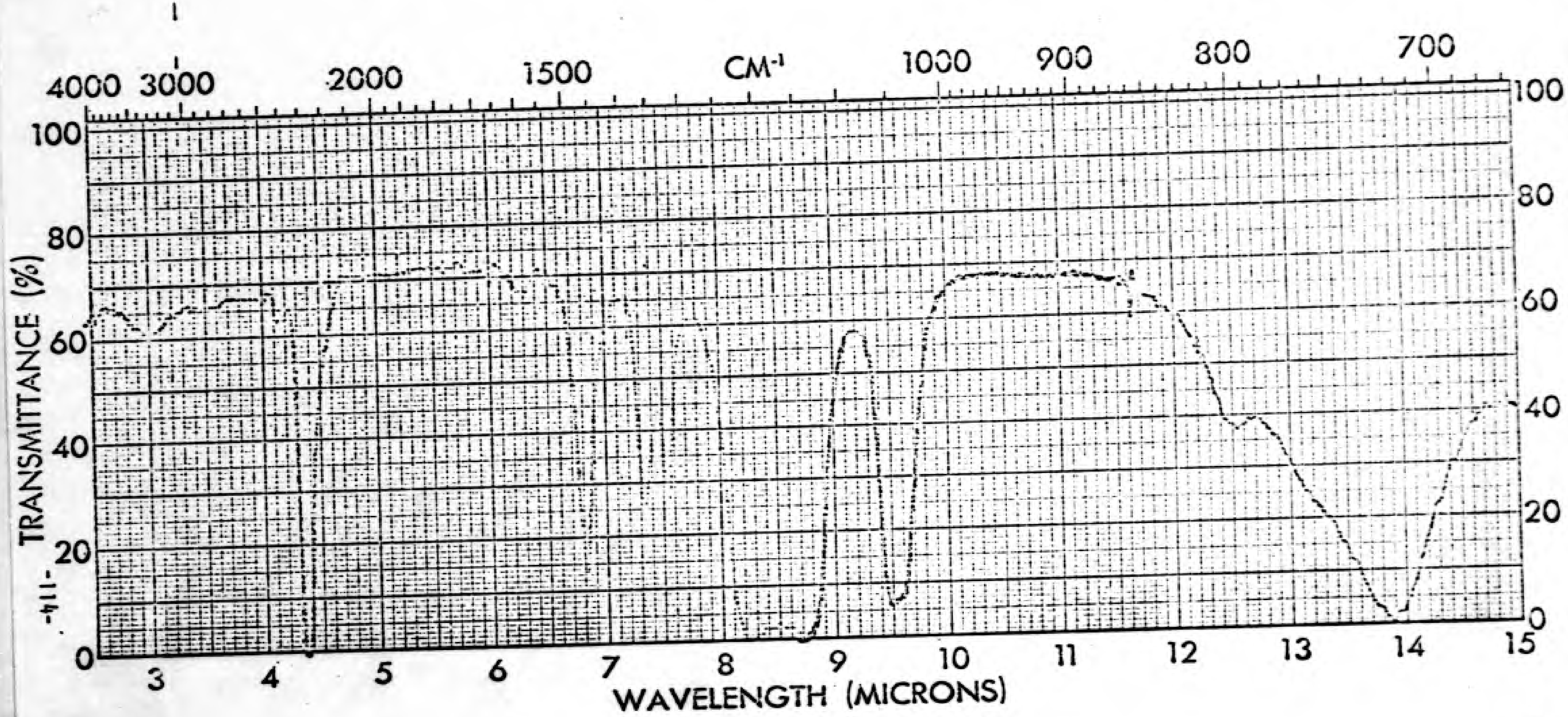


Figure 22.

Infrared Spectrum of $OCNCF_2CF_2OCF_2CF_2NCO$

17-

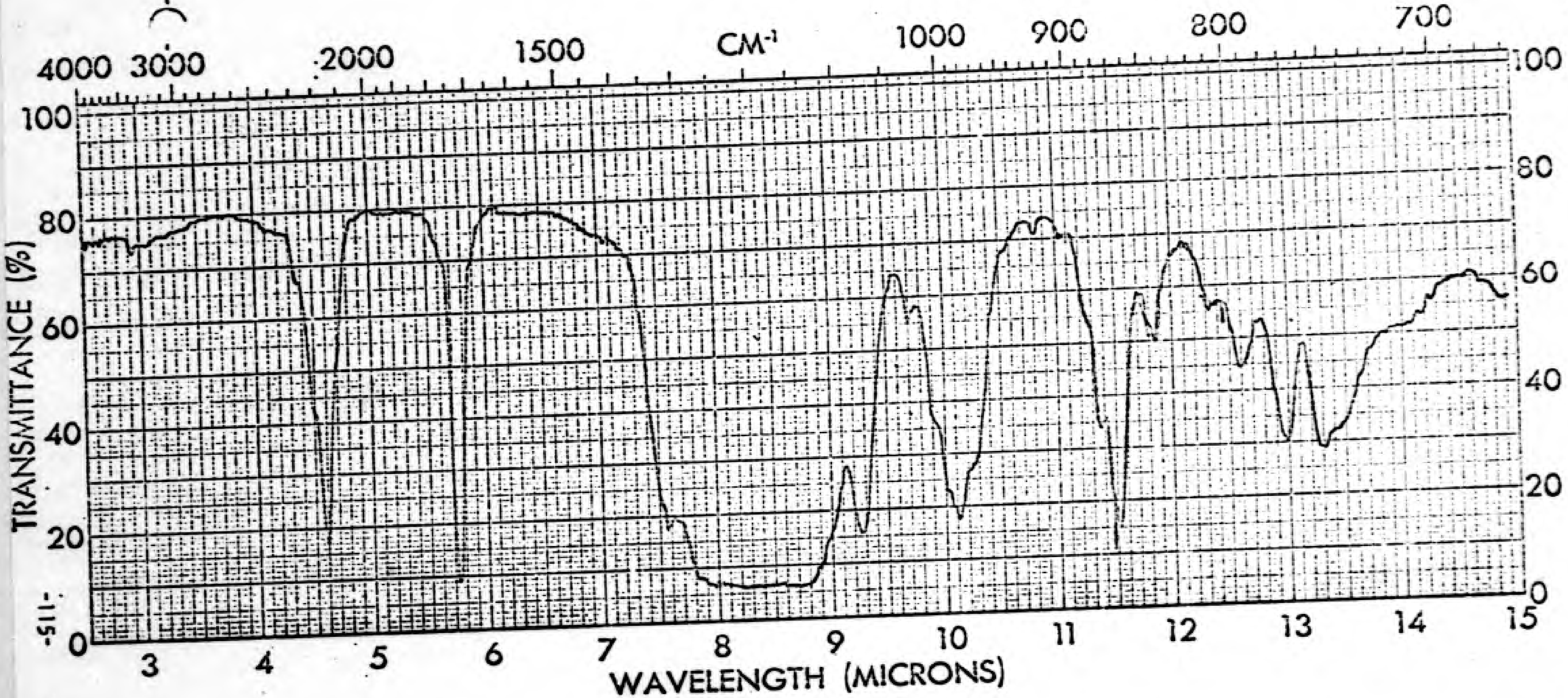


Figure 23.

Infrared Spectrum of $N_3\overset{O}{\overset{\|}{C}}CF(CF_3)O(CF_2)_5OCF(CF_3)\overset{O}{\overset{\|}{C}}N_3$ and Isomer (DEDAZ)

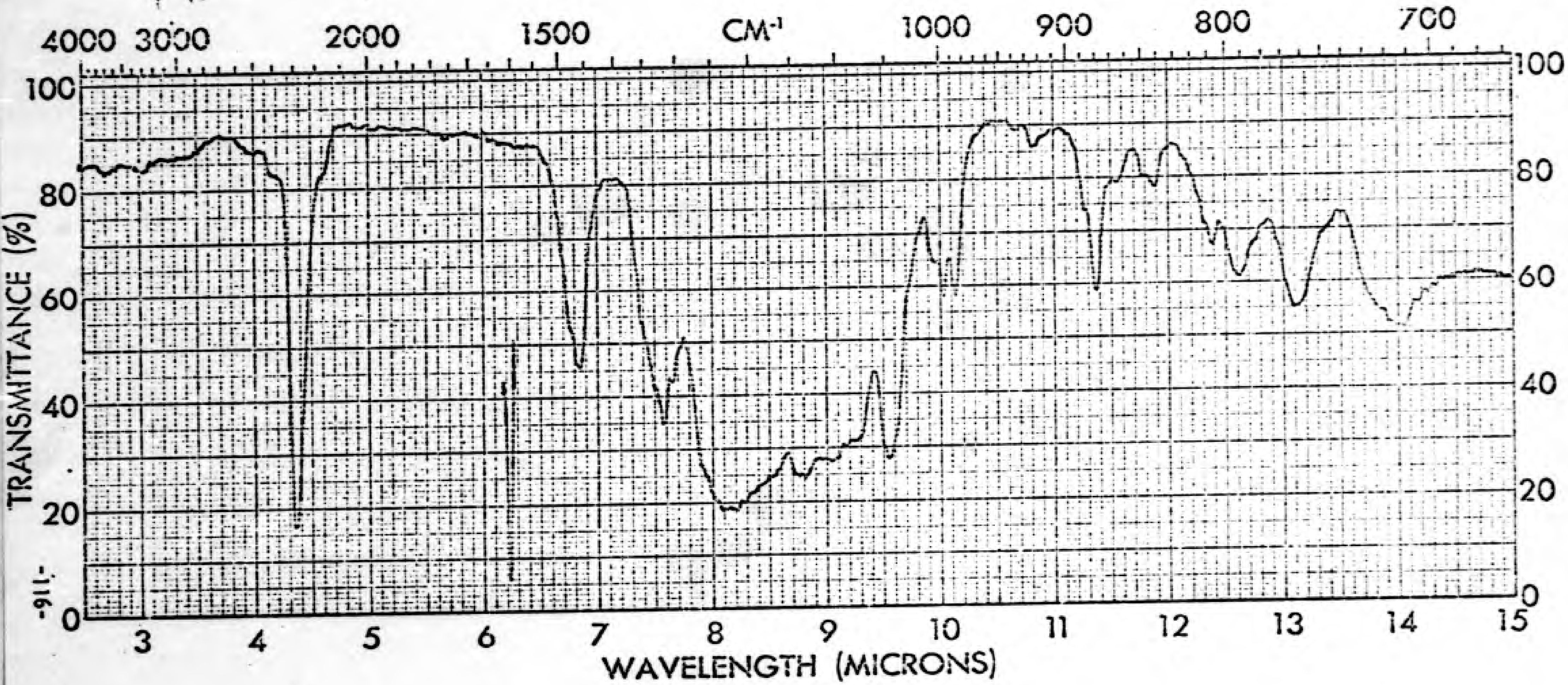


Figure 24.

Infrared Spectrum of $OCNCF(CF_3)O(CF_2)_5OCF(CF_3)NCO$ and Isomer (DEDI)

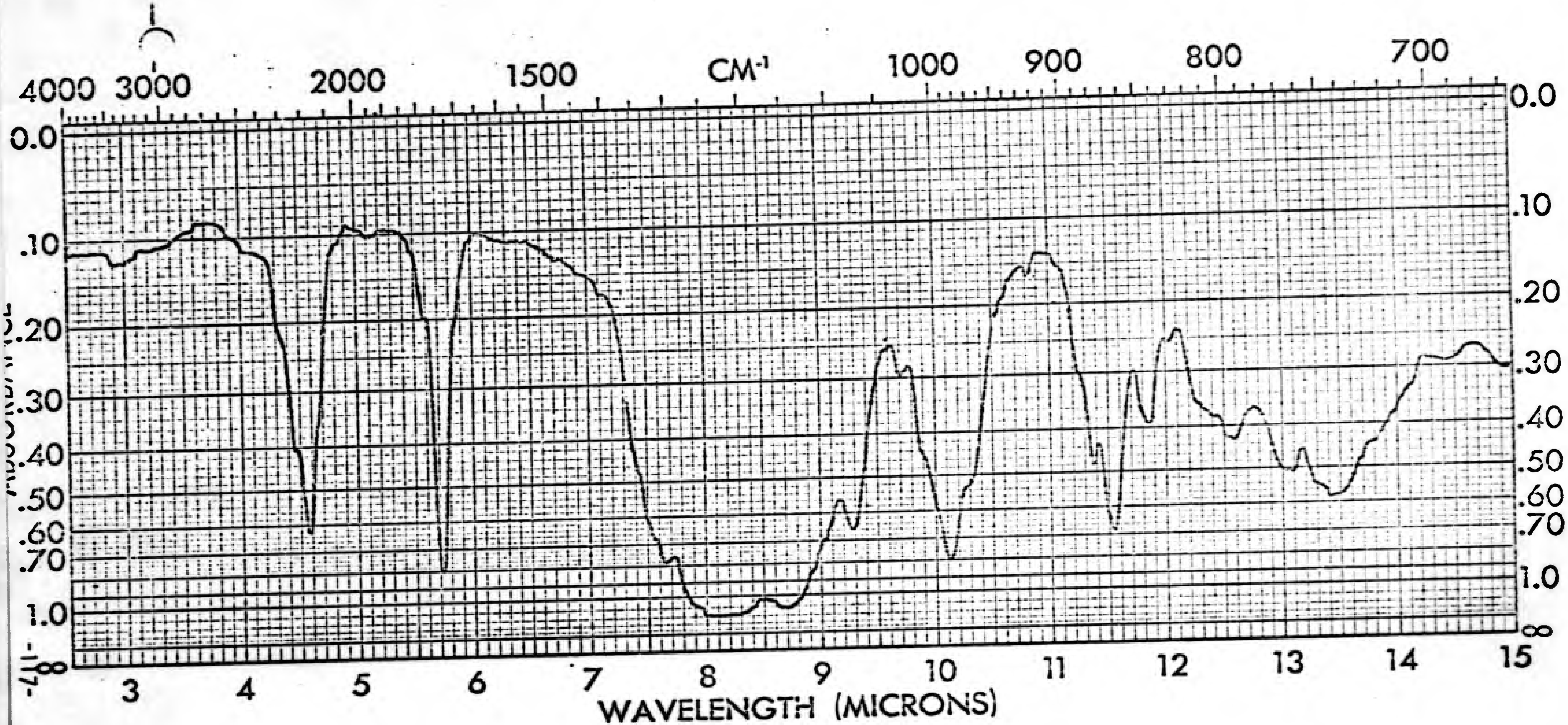


Figure 25.

Infrared Spectrum of $N_3\overset{O}{\overset{\|}{C}}CF(CF_3)OCF_2CF(CF_3)O(CF_2)_5OCF(CF_3)\overset{O}{\overset{\|}{C}}N_3$ and Isomer (TEDAZ)

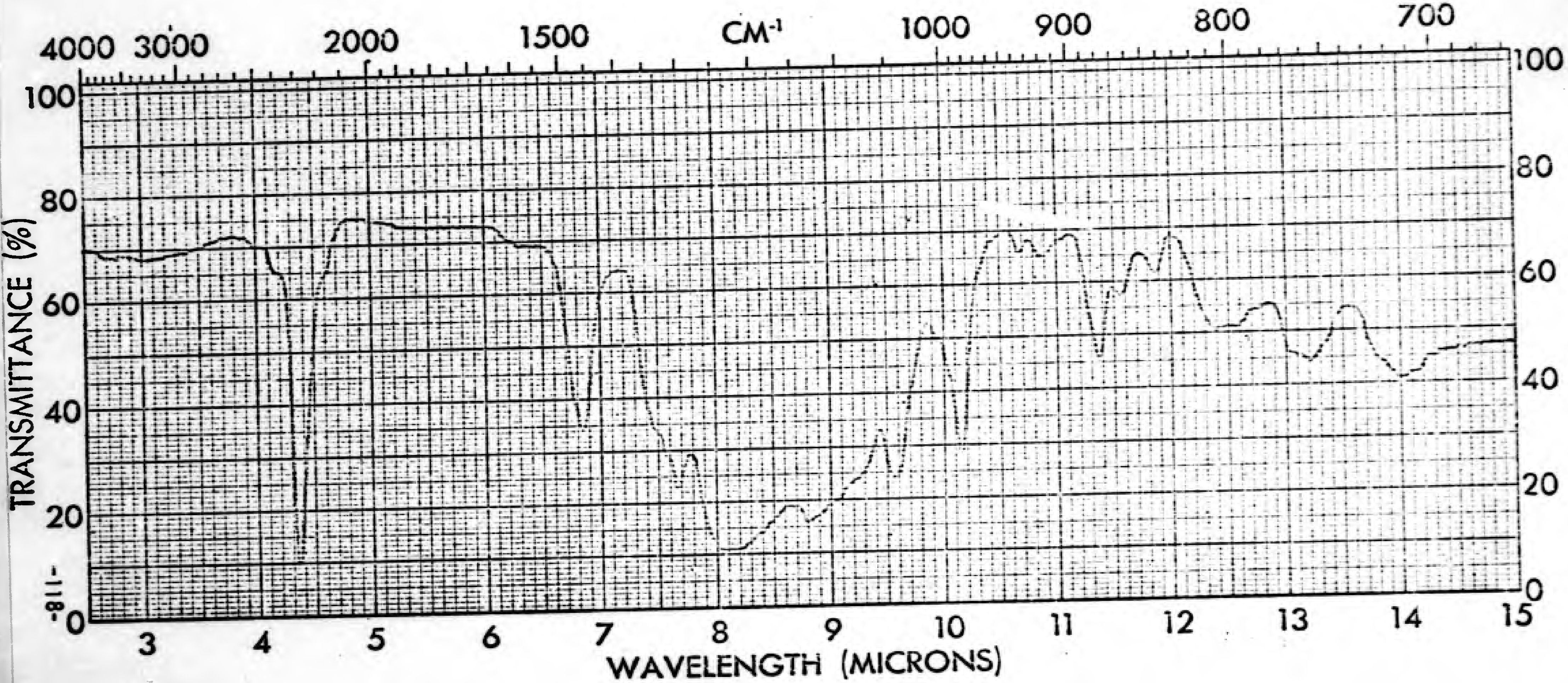


Figure 26.

Infrared Spectrum of $OCNCF(CF_3)OCF_2CF(CF_3)O(CF_2)_5OCF(CF_3)NCO$ and Isomer (TEDI)

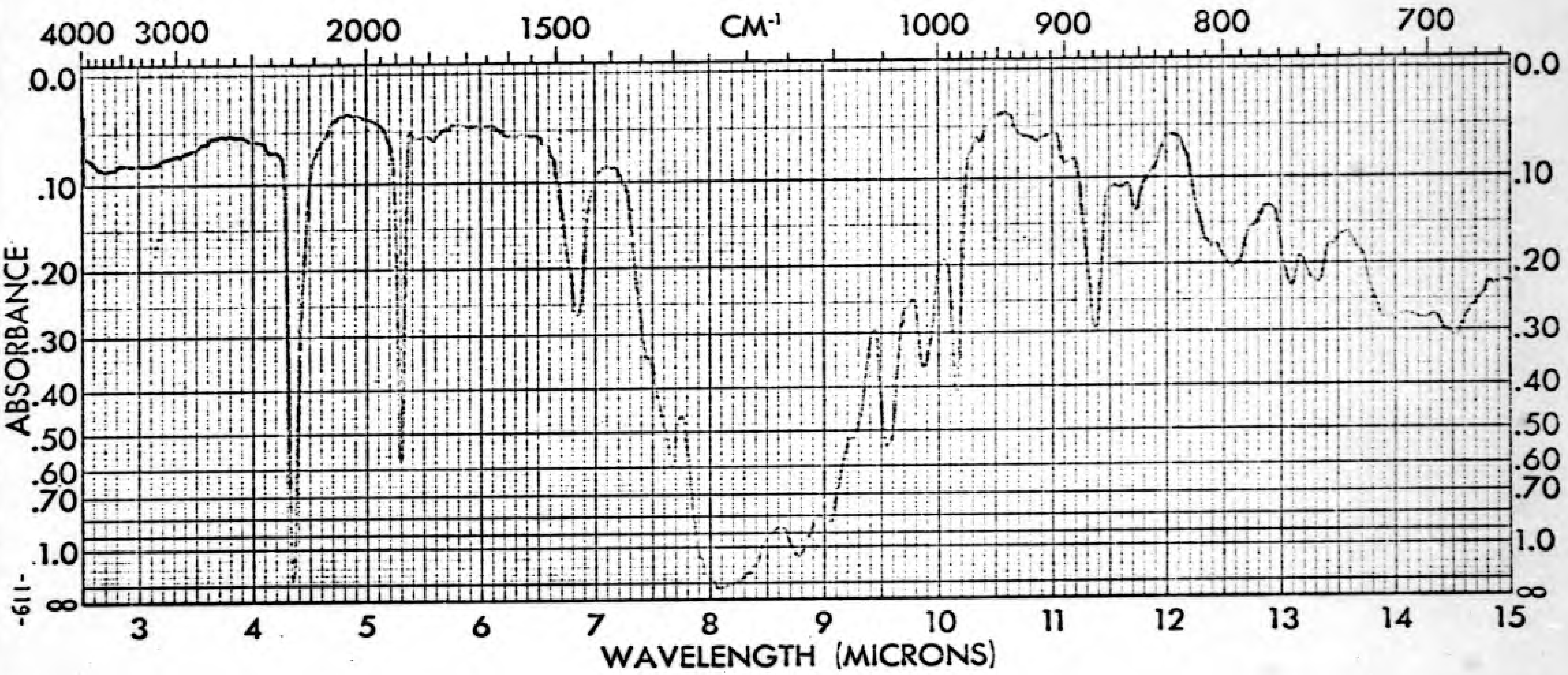


Figure 27.

Infrared Spectrum of Decomposition Product from TEDI

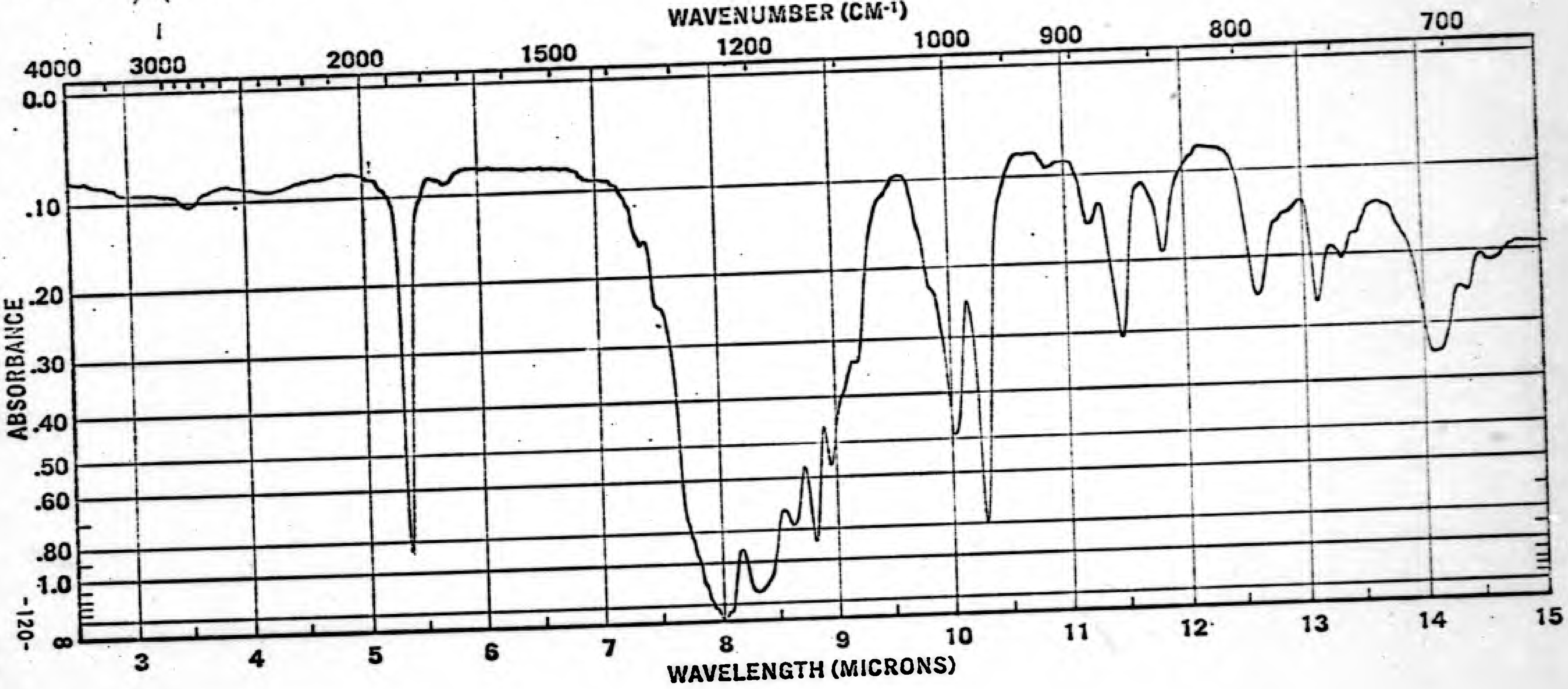
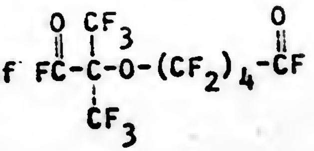


Figure 28.

Infrared Spectrum of



$$FC(=O)-C(CF_3)_2-O-(CF_2)_4-C(=O)F$$

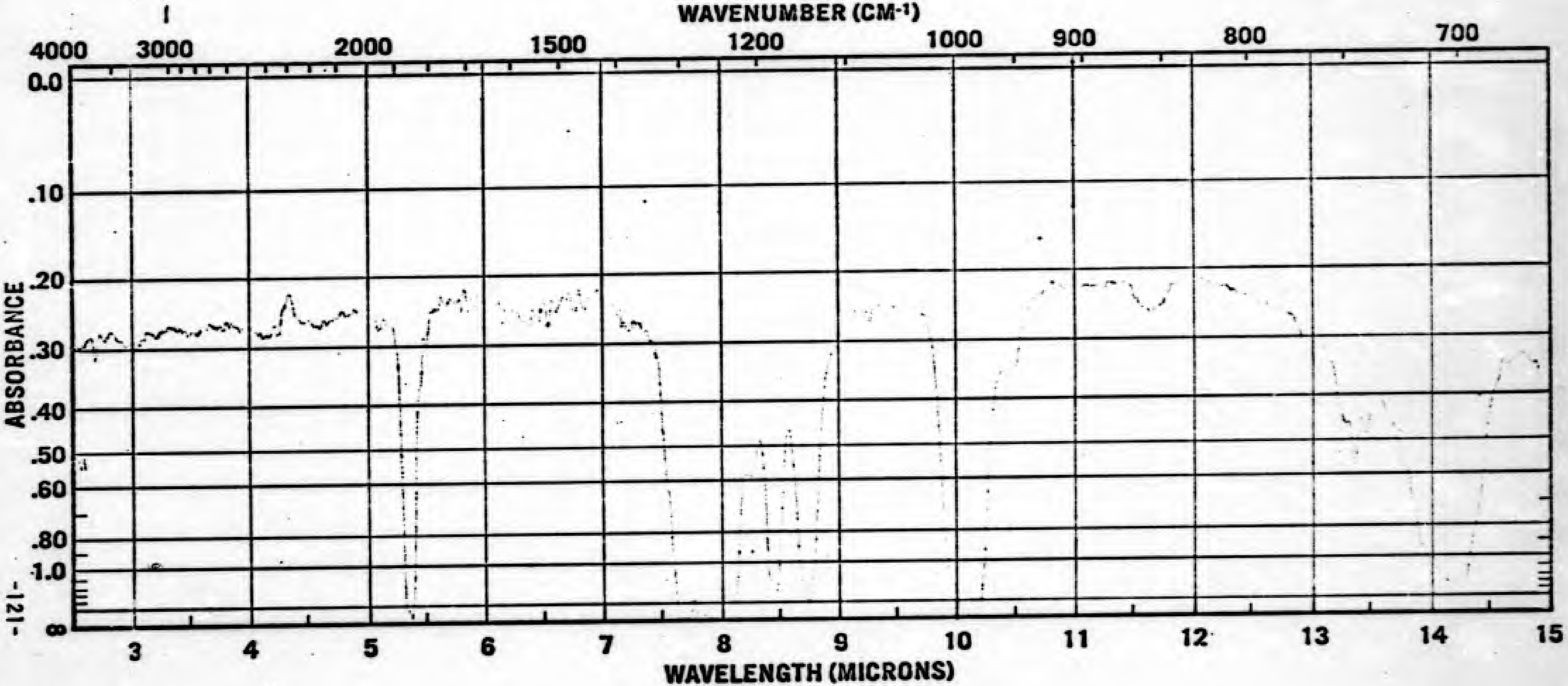


Figure 29.

Infrared Spectrum of $(CF_3)_2CF\overset{O}{\overset{\|}{C}}F$

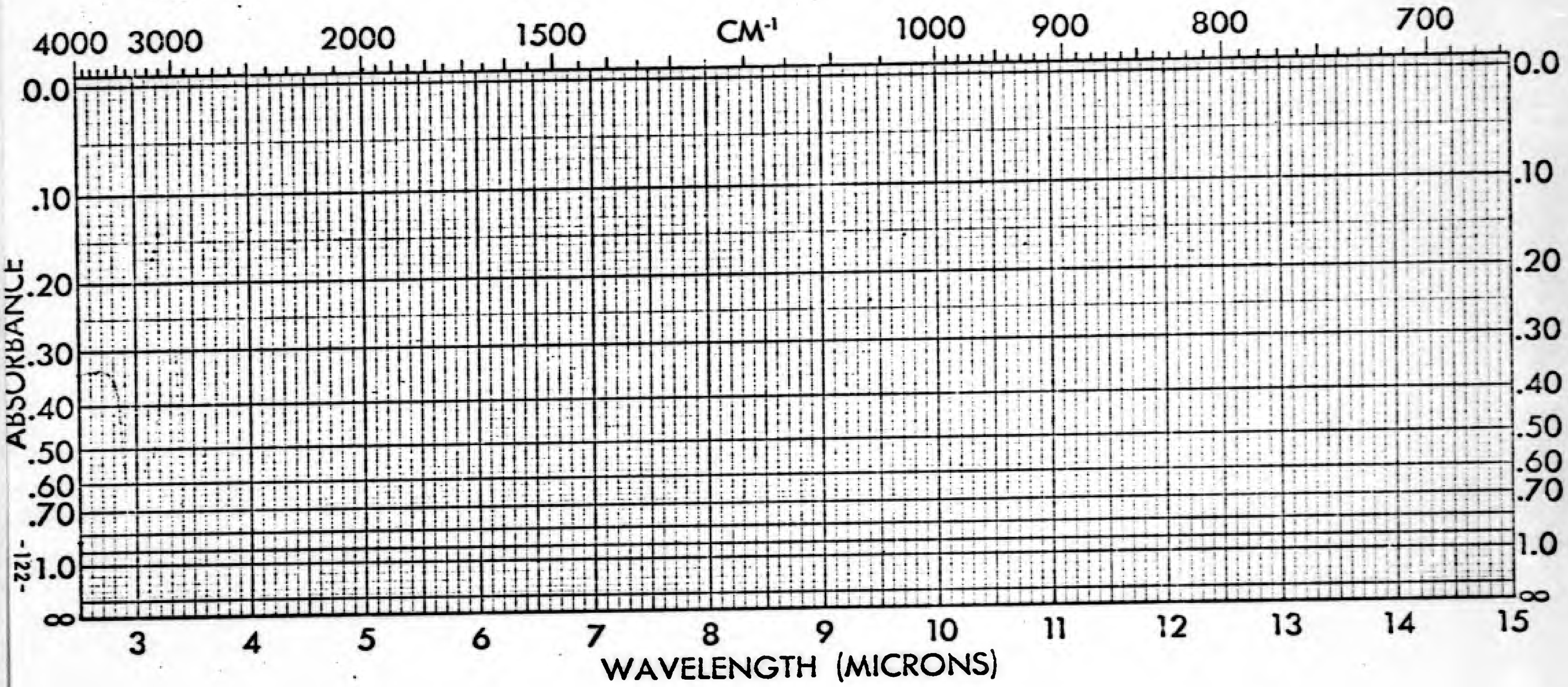


Figure 30.

Infrared Spectrum of $(CF_3)_2CF\overset{\overset{O}{\|}}{C}NH_2$ (Nujol mull)

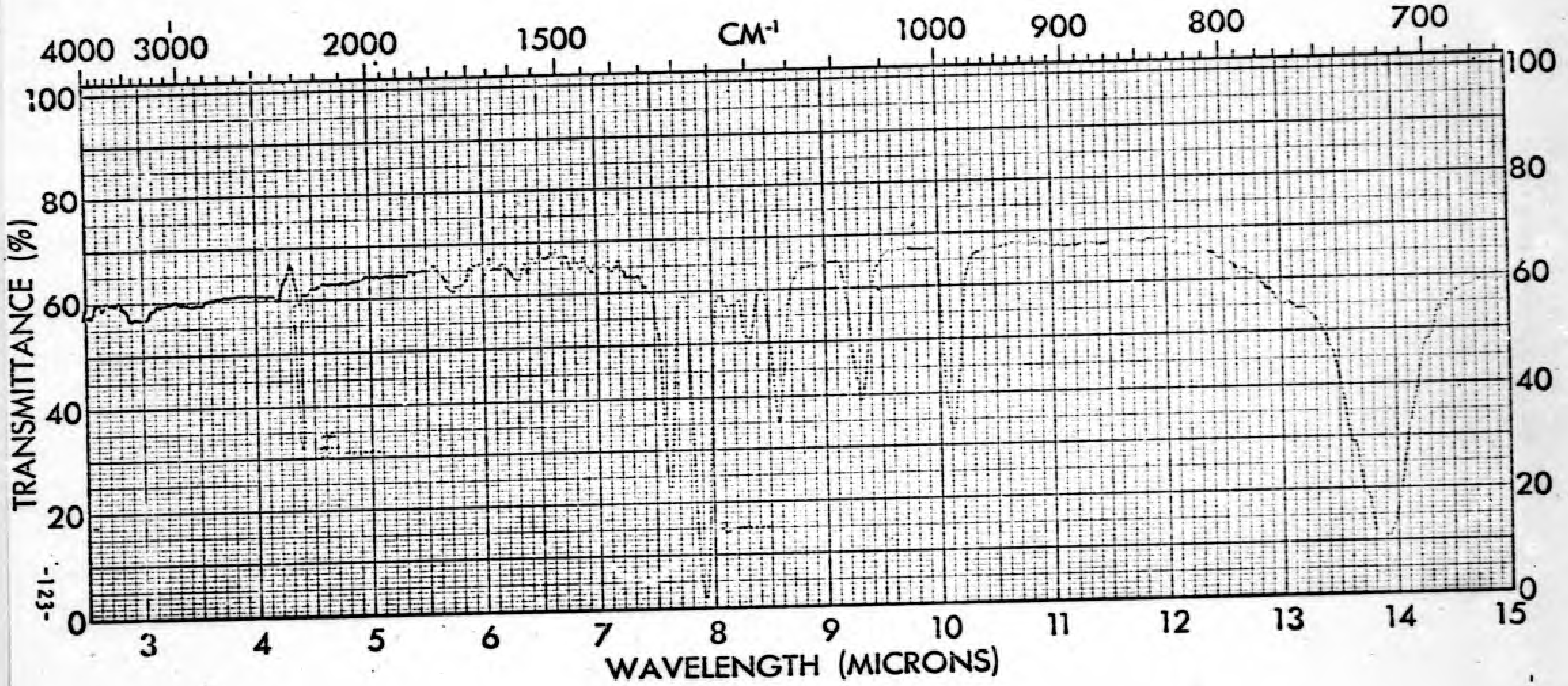


Figure 31.
Infrared Spectrum of $(CF_3)_2CFCN$

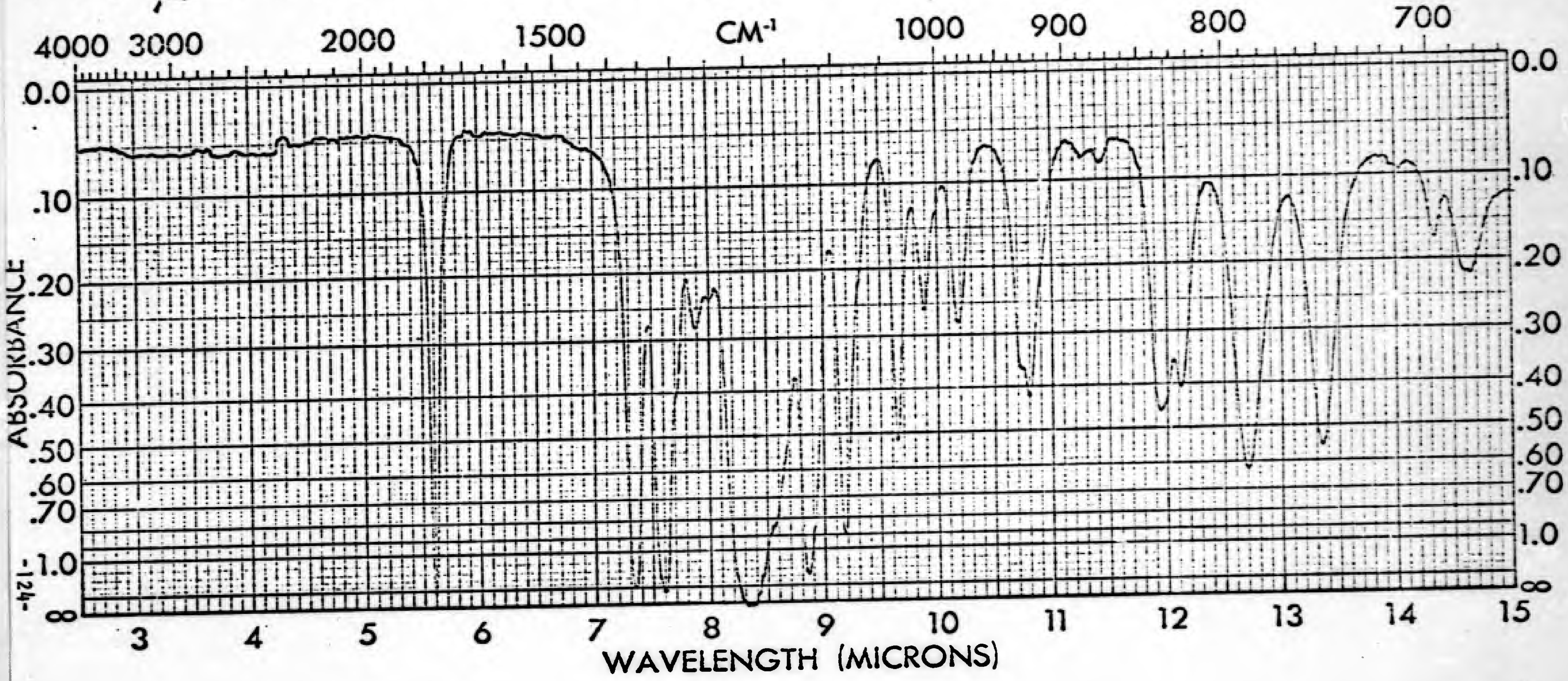


Figure 32.

Infrared Spectrum of $CF_2=CF(CF_2)_4CF=CF_2$

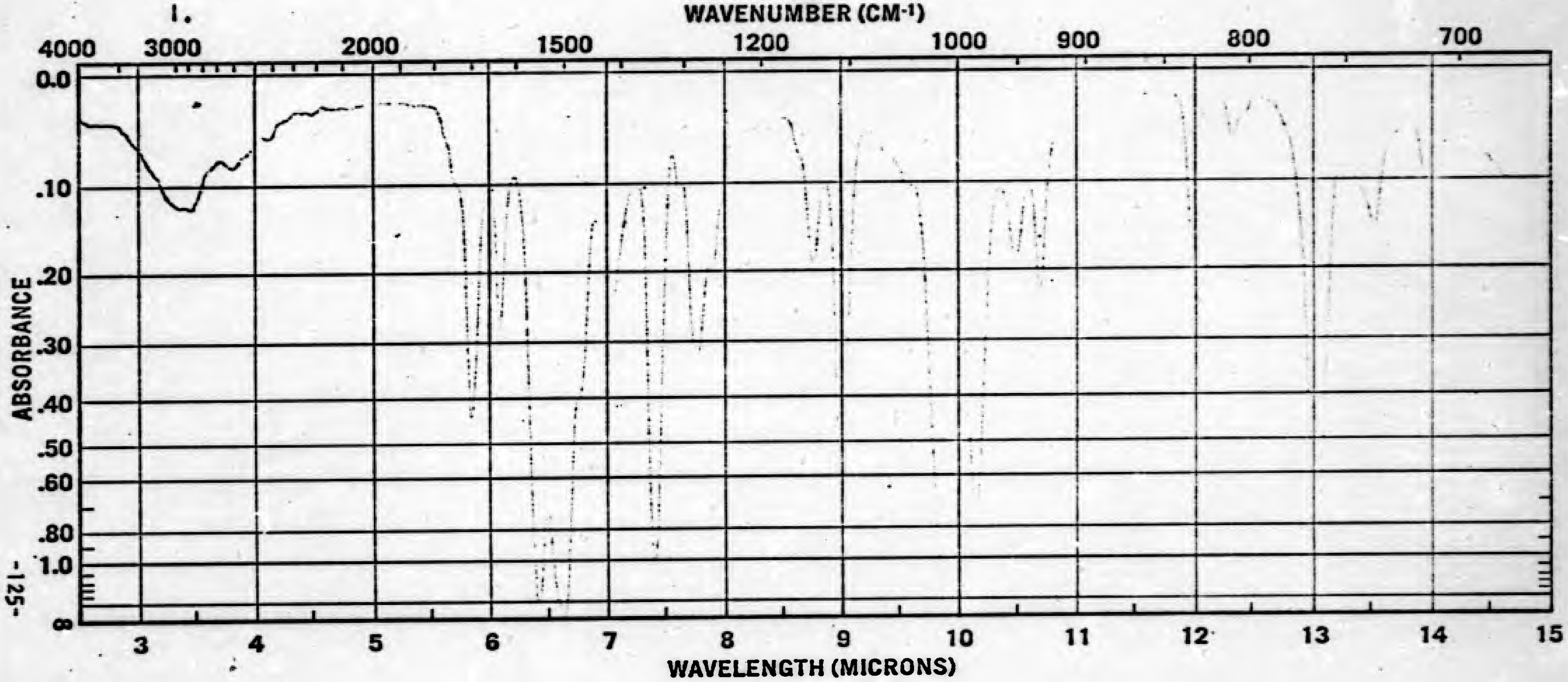


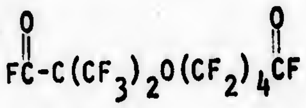
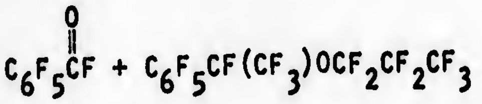
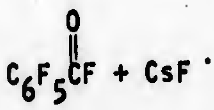
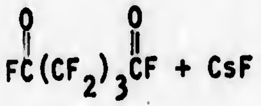
Figure 33.

Infrared Spectrum of $C_6F_5NO_2$

APPENDIX III

NMR Analysis

These spectral results were obtained unless otherwise indicated on a Varian High-Resolution Nuclear Magnetic Resonance Spectrometer Model V-4300-2, provided with field homogeneity control, magnet insulation and Superstabilizer. Chemical shifts were determined by side-bands applied with an audio oscillator for which the frequency is continuously monitored by an electric counter. Unless specified otherwise, the temperature is approximately 30°C. This spectrum was obtained and interpreted by Dr. Wallace Brey of the Department of Chemistry, University of Florida, Gainesville, Florida.

Compound	Page
$(CF_3)_2CFOCH_2CH_2CH_2Si(CH_3)H_2$	127
$(CF_3)_2CFOCH_2CH_2CH_2Si(CH_3)ClH$	128
$CF_2{=}CF(CF_2)_4CF(NO)CF_3$	129
$CF_3CF(NO)(CF_2)_4CF(NO)CF_3$	130
$OCNCF_2CF_2OCF_2CF_2NCO$	131
Decomposition Product From TEDI	132
 $F\overset{O}{\overset{\Vert}{C}}-C(CF_3)_2O(CF_2)_4\overset{O}{\overset{\Vert}{C}}F$	133
$(CF_3)_2CFCN$	134
 $C_6F_5\overset{O}{\overset{\Vert}{C}}F + C_6F_5CF(CF_3)OCF_2CF_2CF_3$	135
 $C_6F_5\overset{O}{\overset{\Vert}{C}}F + CsF$	136
 $F\overset{O}{\overset{\Vert}{C}}(CF_2)_3\overset{O}{\overset{\Vert}{C}}F + CsF$	137

REPORT ON NMR SPECTRUM

Sample Identification 1105.37

Formula

$(CF_3)_2CFOCH_2CH_2CH_2SiH_2CH_3$

Conditions of Spectral Determination

	F	H
Nucleus -	F	H
Solvent -	Neat	
Frequency -	56.4	60.0
Reference -	Subs. tube CF_3COOH	Subs. tube TMS

Peaks Obtained

Designation	Chemical Shift	Pattern & Splitting	Rel. Area	Assignment
F-A	TFAA + 2.4 ppm	Doublet	6.0	CF_3
B	+65.0	Broadened septet	1.0	CFO
H-A	6.5 tau	Overlapping multiplets	4.0	OCH_2 and SiH_2
B	8.6	Complex multiplet	2.0	Middle CH_2
C	9.6	"	2.0	CH_2 next to Si
D	10.15	Triplet	3.0	CH_3

REPORT ON NMR SPECTRUM

Sample Identification 1105.39

Formula

$(CF_3)_2CFO(CH_2)_3SiHClCH_3$

Conditions of Spectral Determination

Nucleus -	F	H
Solvent -	Neat	
Frequency -	56.4	60.0
Reference -	Subs. tube CF_3COOH	Subs. Tube TMS

Peaks Obtained

Designation	Chemical Shift	Pattern & Splitting	Rel. Area	Assignment
F-A	TFAA + 2.2 ppm	Doublet		$2CF_3$
B	+64.2	Septet		CF
H-A	5.33 tau	Sextet	1.0	SiH
B	6.40	Triplet	2.0	CH_2O
C,D	8.88	A_2B_2 pattern	4.0	$2CH_2$
E	9.73	Doublet	3.0	CH_3

REPORT ON NMR SPECTRUM

Sample Identification   2-Nitrosoperfluorooctene-7

Formula CF_3-CFNO-$(CF_2)_4$CF=CF_2

Conditions of Spectral Determination

Nucleus - F
Solvent - Neat
Frequency - 56.4
Reference - Subs. tube CF_3COOH

Peaks Obtained

Designation	Chemical Shift		Pattern & Splitting	Rel. Area	Assignment
A-1	TFAA	-8.6	Broad	0.8	Impurity
A-2	-3.5		Multiplet	2.8	CF_3
B	+13.0		Triplet, with further splitting	0.9	1/2 =CF_2
C	+28.7		Doublet, each a quintet	1.1	1/2 =CF_2
D	+38 to +48		Group of broad peaks	8.1	$(CF_2)_4$
E	+90.8		Somewhat broad	0.9	CFNO
F	+114.5		Doublet, each doubled	0.9	CF

There are a number of other small peaks, indicating about 10% impurity.

REPORT ON NMR SPECTRUM

Sample Identification 1118.94A, Peak #3

Formula

$CF_3CF(NO)CF_2CF_2CF_2CF_2CF(NO)CF_3$

Conditions of Spectral Determination

Nucleus - F
Solvent - Neat
Frequency - 56.4
Reference - Subs. tube CF_3COOH

Peaks Obtained

Designation	Chemical Shift	Pattern & Splitting	Rel. Area	Assignment
A	TFAA -3.4 ppm	Broad	2.92	CF_3
B1	+40.0		1.94	CF_2 next to CFNO
B2	+43.9		2.05	CF_2 in mid-chain
C	+88.7		1.04	CF

Sample looks to be 96-98% pure. Impurity peaks are visible but very small.

REPORT OF NMR SPECTRUM

Sample Identification 1105.69 Fraction #2

Formula

$OCN-CF_2CF_2-O-CF_2CF_2-NCO$

Conditions of Spectral Determination

Nucleus - F
Solvent - Neat
Frequency - 56.4
Reference - Subs. tube CF_3COOH

Peaks Obtained

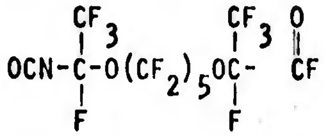
Designation	Chemical Shift	Pattern & Splitting	Rel. Area	Assignment
A	TFAA + 9.1 ppm.	Singlet	1.00	CF_2 next oxygen*
B	+12.1	"	1.00	CF_2 next NCO groups*

*Assignments may be reversed, but this is more probable.

REPORT OF NMR SPECTRUM

Sample Identification 1105.75#1

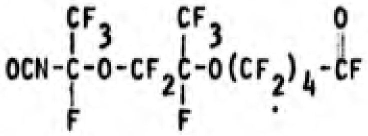
Formula



$OCN-CF(CF_3)-O(CF_2)_5OCF(CF_3)-C(=O)F$

I

+



$OCN-CF(CF_3)-O-CF_2CF(CF_3)-O(CF_2)_4-C(=O)F$

II

Conditions of Spectral Determination

Nucleus - F
Solvent - Neat
Frequency - 56.4
Reference - CF_3COOH

Peaks Obtained

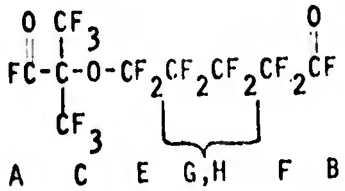
Designation	Chemical Shift	Pattern & Splitting	Rel. Area.	Assignment
A-1	-102.5 ppm.		0.89	CFO in I
A-2	-100.2		0.76	CFO in II
B-2	Near zero	(part of NEQQ, rest of which is at higher field under B-3 to B-5)	0.32	CF_2O in I
B-3	+3.6		2.94	CF_2 + CF_3 in II
B-4	5.7		2.82	CF_3 in I
B-4'	6.0		0.31	?
B-5	7.0		3.76	CF_2 in I, CF_2 in II
B-6	9.1		1.66	CF in I, CF in II
B-6'	10		0.26	?
B-7	11.0		5.79	CF_3 in I, CF_3 in II
C-1	41.6		1.77	CF_2 in II
C-2	46.0		3.89	CF_2 in I, CF_2 in II
C-3	47		0.62	?
C-4	48.5		6.00	2 CF_2 in I, CF in II
C-5	53.4		1.11	CF in I
C-6	68.0		1.15	CF in II

This may be a mixture of the above two molecules with a third component. The areas of peaks obtained are not exactly consistent with the above structure, but the third component, by overlapping the principal peaks, prevents exact measurements.

REPORT ON NMR SPECTRUM

Sample Identification 1095.92

Formula



$\overset{O}{FC}-\overset{CF_3}{\underset{CF_3}{C}}-O-CF_2\underbrace{CF_2CF_2}_{G,H}CF_2\overset{O}{CF}$

Conditions of Spectral Determination

Nucleus - F
Solvent - Neat
Frequency - 56.4
Reference - Subs. tube of CF_3COOH

Peaks Obtained

Designation	Chemical Shift	Pattern & Splitting	Rel. Area	Assignment
A	TFAA -112.2ppm	Broad, unresolved multiplet	1.1	CFO
B	-100.4	5° x 7.2	0.8	CFO
C	-5.0	2° x 8.0, 3° x 6.5	6.2	$2CF_3$
D	-3.1		Trace	
E	+3.9	Broad	2.0	CF_2 next to O
F	+41.9		1.9	CF_2 next to CFO
G	+46.1		1.8	CF_2
H	+47.8		2.1	CF_2

REPORT ON NMR SPECTRUM

Sample Identification 1118.30.A

Formula

$(CF_3)_2CF\text{-}CN$

Conditions of Spectral Determination

Nucleus - F
Solvent - Neat
Frequency - 56.4
Reference - Subs. tube CF_3COOH

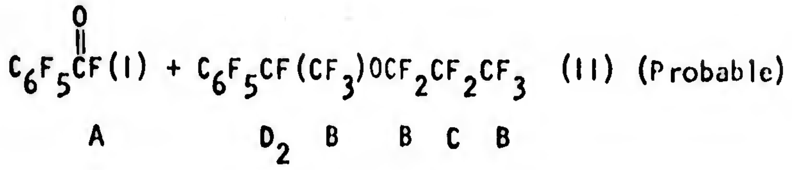
Peaks Obtained

Designation	Chemical Shift	Pattern & Splitting	Rel. Area	Assignment
A	TFAA + 0.9 ppm	2° x 9.9 cps	5.1	$2CF_3$
B	+100.7	7° x 10.2	1.0	CF

REPORT ON NMR SPECTRUM

Sample Identification 1095.87.4

Formula



$$\underset{A}{C_6F_5\overset{O}{\overset{\|}{C}}F}\ (I) + C_6F_5\underset{D_2}{CF}(\underset{B}{CF_3})O\underset{B}{CF_2}\underset{C}{CF_2}\underset{B}{CF_3}\ (II)\ (Probable)$$

Conditions of Spectral Determination

Nucleus - F
Solvent - Neat
Frequency - 56.4
Reference - Subs. tube of CF_3COOH

Peaks Obtained

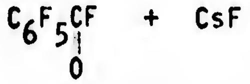
Designation	Chemical Shift	Pattern & Splitting	Rel. Area	Assignment
A	TFAA -122.8ppm	3°	3.1	CFO in I
B	+3 to +4	Overlapping patterns	8.0	OCF_2, CF_3, CF_3 in II
C	+52.3		1.9	CF_2 in II
D_1	+57.5		6.4	Ortho ring F's in I
D_2	+58.7		0.8	CF in II
E	+61.1		1.9	Ortho ring F's in II
F_1	+66.8		3.3	Para ring F in I
F_2	+67.8		1.1	Para ring F in II
G	+82.4		2.2	Meta ring F's in II
H	+83.8		6.5	Meta ring F's in I

Ratio of I/II is approximately 3/1.

REPORT ON NMR SPECTRUM

Sample Identification 1095.95.01

Formula



$C_6F_5\underset{\displaystyle O}{\overset{}{C}}F + CsF$

Conditions of Spectral Determination

Nucleus - F
Solvent - Diglyme
Frequency - 56.4
Reference - Subs. tube CF_3COOH

Peaks Obtained

Designation	Chemical Shift	Pattern & Splitting	Rel. Area	Assignment
F-A	TFAA -122.7 ppm	Triplet	7.3	CFO
B	+57.3	Multiplet	13.4	Ortho fluorines
C	+66.3	Triplet of triplets	6.7	Para fluorine
D	+83.8	Multiplet	13.5	Meta fluorines
Other peaks:				
C'	+64.7	Multiplet	Approx 0.6	Aromatic fluorine
C''	+69.1	Multiplet	Approx 0.3	"

It is not clear what peaks C' and C'' represent. They are probably simply an impurity having no relation to the effect of cesium fluoride.

REPORT ON NMR SPECTRA

Sample Identification 1095.84

Formula

$CFO-(CF_2)_3CFO + 2CsF$

Conditions of Spectral Determination

Nucleus - F
Solvent - Neat
Frequency - 56.4
Reference - Subs. tube CF_3COOH

Peaks Obtained

Designation	Chemical Shift	Pattern & Splitting	Rel. Area	Assignment
A	TFAA -92.6 ppm		Trace	CFO
B	-49.7	Very broad	15.0	Possibly CF_2O^-
C	+38.7	Broad	4	?
D	+42.9	3°	31	Alpha CF_2's
E	+51.2	5°	15	Middle CF_2
F	+52.1	1°	2	?

The peak at approximately -50 ppm is clearly not one expected from the original molecule. On the other hand, its area is not that required for $2 \cdot CF_2O^-$ groups, but only one-half this amount.

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13. ABSTRACT

Preparation of both high and low molecular weight triazine polymers was investigated. Block copolymers of the ABA type containing polyethylene B blocks and A blocks of polyisoprene and polystyrene were prepared. A nitroso terpolymer containing CF_3NO,$CF_2{=}CF_2$ and $CF_2{=}CFOCH(CH_3)_2$ was prepared. Fluorine-containing diepoxides were prepared by reaction of fluorine-containing diols with an epihalohydrin and by direct oxidation of a perfluorodiolefin using a halogen-sensitized photochemical reaction. Fluoroalkylmethylchlorosilanes were prepared by reduction of the corresponding dichlorosilane to the fluoroalkylmethylsilane followed by reaction with silver chloride. A perfluorinated dinitroso compound, $CF_3CF(NO)(CF_2)_4CF(NO)CF_3$, was prepared by addition of nitrosyl fluoride to perfluorooctadiene-1,7. Several perfluorinated diisocyanates containing ether oxygen atoms were prepared from their corresponding diacid fluorides using the Curtius reaction. The reaction of perfluoroisobutylene oxide with several perfluorinated acid fluorides was investigated. The synthesis of perfluoroisobutyronitrile and perfluorosebaconitrile is described. 4-Cyanoperfluorobutyryl chloride was prepared by a new method. A wide variety of intermediates was prepared including perfluoroisobutylene epoxide, perfluorosuberyl fluoride and its dimethyl ester, pentafluoronitrobenzene, perfluorooctadiene-1,7, perfluoroisobutyryl fluoride and its amide, and 4,4'-dihydroxyoctafluorobiphenyl.

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Triazine Polymer						
Block Copolymers						
Nitroso Polymers						
Fluorinated Elastomeric Polymers						
Fluorine-Containing Diepoxides						
Fluorine-Containing Silane						
Nitroso Compounds						
Fluorine-Containing Diisocyanates						
Perfluoroisobutylene Oxide						
Fluorine-Containing Nitriles						