QUARTERLY REPORT NO. 9

CONTRACT NO. DA 19-129-AMC-152(N)(OI9116)
WITH
U. S. ARMY NATICK LABORATORIES
Report Period: 1 July 1965 - 26 November 1965

SYNTHESIS AND POLYMERIZATION OF FLUORINATED SULFUR MODIFIED NITROSO RUBBER

By
Eugene C. Stump, Ward H. Oliver
and Calvin D. Padgett

21 December 1965

Code 1

Peninsular ChemResearch, Inc.
Post Office Box 14318
Gainesville, Florida

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FOREWORD

This report was prepared by Peninsular ChemResearch, Inc. under Contract No. DA 19-129-(AMC)-152(N)(OI9116) for the U. S. Army Natick Laboratories with Mr. C. B. Griffis as Project Officer. This is the ninth Quarterly Report under this contract and covers the period 1 July 1965 through 26 November 1965.

Personnel engaged in this research are Eugene C. Stump, Project Supervisor (174 hours), Ward H. Oliver, Senior Research Chemist (184 hours), Calvin D. Padgett, Research Chemist (716 hours). Analytical work was performed under the supervision of Van A. May. Drs. Paul Tarrant and George Butler are acting consultants.

It is estimated that 76% of the work is completed and that 78.6% of the estimated costs have been incurred to date. To the contractor's best knowledge the funds remaining unexpended are sufficient to complete the work called for in the contract.

ABSTRACT

Terpolymer samples containing 3 and 6 mole percent $ONCF_2CF_2CO_2CH_3$ with CF_3NO and $CF_2{=}CF_2$ have been prepared. A larger amount (280 g.) of 1, 1, 2-trifluorobutadiene terpolymer with CF_3NO and $CF_2{=}CF_2$ was prepared. Terpolymers of $CF_2{=}CFCF_2NO$, $CF_2{=}CFCH_2CF_2CF_2CH_2CF{=}CF_2$ and $ONCF_2CF_2CF_2COOH$ with CF_3NO and $CF_2{=}CF_2$ were prepared. Attempted copolymerization of carbonyl fluoride and hexafluoroacetone with CF_3NO was unsuccessful. A 2-l. reactor equipped with stirrer and cooling coils has been procured and is being fitted with a refrigeration system.

TABLE OF CONTENTS

FIGURES

I. INTRODUCTION

The research described in this report is part of a continuing program sponsored by the U. S. Army Natick Laboratories and concerned with the development of so-called "nitroso rubber", a 1:1 copolymer of trifluoronitrosomethane and tetrafluoroethylene. A list of references describing prior research was given in the First Quarterly Report.

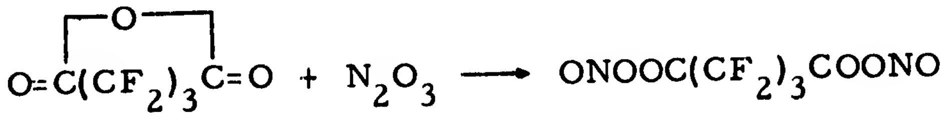
The primary objective of this contract was to enhance the desirable properties, in particular the low-temperature flexibility, of nitroso rubber by the incorporation of sulfur atoms in a modified polymer structure. Secondary objectives included the synthesis of desirable monomers, including monomers not containing sulfur, and their polymerization in the nitroso rubber system. This research has been described in previous reports.

During the course of the contract the objectives were modified and increased in scope. During this quarter, major emphasis was placed upon the incorporation of termonomers in the nitroso polymer system. The objective of this work is to provide a cross-linking site along the polymer chain which would not require the use of the usual diamine cure.

II. DISCUSSION

A. Monomer Synthesis

The synthesis of 4-nitrosoperfluorobutyric acid has been reported[1,2]. In order to prepare a reference sample of this monomer and its terpolymer with CF_3NO and $CF_2{=}CF_2$, the following sequence of reactions was carried out:



$$O{=}C(CF_2)_3C{=}O + N_2O_3 \longrightarrow ONOOC(CF_2)_3COONO$$

$$ONOOC(CF_2)_3COONO \xrightarrow{u.v.} ON(CF_2)_3COONO + CO_2$$

$$ON(CF_2)_3COONO + H_2O \longrightarrow ON(CF_2)_3COOH$$

The first reaction proceeded without difficulty, giving 90% of the solid, yellow dinitrite. Photolysis was carried out in a Pyrex tube containing a Vycor immersion well with Hanovia lamp Type 30620. Product was removed under vacuum as formed in about 50% conversion and was hydrolyzed to the acid by pouring into crushed ice. The blue aqueous solution was extracted with ethyl ether which apparently complexes with the product. An infrared spectrum of this complex is shown in Figure 1. NMR analysis also indicates the presence of other, as yet unidentified, fluorine-containing impurities. A green polymeric residue was also formed in the photolysis reaction. An infrared spectrum of this material is shown in Figure 2.

An attempt has been made to prepare a functional nitroso compound by the reaction of 1, 3-diiodohexafluoropropane with nitric oxide. This

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(1) 3M Co., Summary Report under Contract DA-19-129-QM-1684, 23 December 1962.

(2) Thiokol Chemical Corp., Summary Report under Contract DA-19-129-AMC-69(X) For the period 27 February 1963 to 28 February 1965.

reaction could give either an iodonitroso propane, which could be used as a reactive termonomer, or a dinitroso propane, which might be valuable as a cross-linking agent. This reaction was attempted both with and without

$$ICF_2CF_2CF_2I + NO \longrightarrow ICF_2CF_2CF_2NO \text{ and/or } ONCF_2CF_2CF_2NO$$

mercury in the presence of sunlight but no evidence for the formation of a nitroso compound was obtained in either case.

An attempt has been made to prepare CF_2BrCF_2NO using the procedure previously described[3] but with a shorter period of irradiation. Very little product was obtained. This reaction will be repeated using both gas phase and solution for the addition of the nitrosyl bromide to tetrafluoroethylene.

Perfluoropropylene epoxide, which was also previously prepared under this contract[4] by a reported procedure[5], is potentially of value in low temperature elastomers due to the possible incorporation of an oxygen atom into the backbone of the polymer chain. Since it has recently been shown that perfluoropropylene can be reacted directly with oxygen in the liquid phase by ultraviolet irradiation[6] we attempted the reaction in the gas phase using sunlight. Infrared analysis after one month exposure indicated that no reaction had occurred.

B. Polymerization

During this period terpolymer samples containing 3 and 6 mole % $ONCF_2CF_2CO_2CH_3$ were prepared with CF_3NO and $CF_2{=}CF_2$. Incorporation of the ester was definitely established by infrared analysis (Figures 3 and 4) after reprecipitation of the polymer from Freon 113. The samples

(3) Quarterly Report No. 7, this contract, 23 April 1965.

(4) Quarterly Report No. 6, this contract, 25 January 1965.

(5) British Patent 904, 877 (5 September 1962)

(6) D. Sianesi, A. Pasetti, and C. Corti, Makromol. Chem., 86, 308 (1965).

were submitted to the U. S. Army Natick Laboratory for curing studies.

A larger sample of 1, 1, 2-trifluorobutadiene terpolymer containing 10 mole % diene (charged) was also prepared and submitted. A total of 500 g. was prepared in several batches ranging from 25 to 100 g. per batch. Explosions occurred with one 50 g. and one 100 g. batch. The crude polymer was reprecipitated from Freon 113 using methanol and dried to give 280 g. of terpolymer.

A terpolymer was also prepared from $ONCF_2CF_2CF_2COOH$ as a reference sample. The infrared spectrum of this polymer is shown in Figure 5.

Two new terpolymers were prepared from CF_3NO and $CF_2=CF_2$ with $CF_2=CFCF_2NO$ and $CF_2=CFCH_2CF_2CF_2CH_2CF=CF_2$. The polymer with $CF_2=CFCF_2NO$ gave, in addition to material soluble in Freon 113, a small amount of insoluble gel, indicating that some cross-linking had taken place, most likely through the pendent $CF_2=CF-$ group. The infrared spectrum of the reprecipitated polymer (Figure 6) verifies the incorporation of the termonomer by the appearance of a peak at 5. 58 microns attributed to the double bond absorption in the pendent $CF_2=CFCF_2-$ group. In addition, a peak at 6. 2 microns indicates that some polymerization occurred through the $CF_2=CF-$ group, giving pendent $-CF_2NO$ groups. The polymer containing the diene was insoluble in Freon 113, forming a gel. This behavior is unusual in that a previous attempt to incorporate a similar compound, $CF_2=CFCF_2CFClCF_2CF=CF_2$, gave a soluble polymer. An infrared spectrum (Figure 7) of the insoluble polymer shows $CF_2=CF$ absorption at 5. 55 microns.

Terpolymerization with $CF_2ClCF(NO)CH_2CH=CH_2$ resulted in a low molecular weight polymer which did not contain the unsaturated pendent group as desired.

During this period a number of polymerizations have been attempted at greatly increased pressures. These polymerizations were run by condensing monomer into a 5-ml. nickel tube which was then sealed, placed in a high pressure reactor, and pressurized by a hydraulic pump. A control polymerization with $CF_3NO/CF_2=CF_2$ produced a sudden surge as the pressure reached 8000 psi. Apparently a very rapid, exothermic reaction takes place under these conditions since carbonization occurred.

The high pressure polymerization of CF_3NO with $CF_2=CFBr$ was also examined. In one run a white, sticky polymer was formed which reacted with acetone, releasing extremely lachrymatory fumes. An orange solution was formed which was completely miscible with water. This behavior is unusual since earlier samples prepared in bulk at -30° gave no reaction when dissolved in acetone.

High pressure polymerization of CF_3NO was also attempted with both COF_2 and $(CF_3)_2C=O$. Incorporation of either of these compounds would result in an additional heteroatom in the backbone, which would lead to improved low temperature properties. In neither case, however, did a reaction occur.

During this period a Parr No. 4501 pressure reactor fitted with stirrer and internal cooling coils has been procured and is now being fitted with a refrigeration system using $CaCl_2$ brine in order to carry out future polymerizations on a larger scale. A control run using $CF_3NO/CF_2=CF_2$ will be made in suspension followed by the preparation of a larger batch of 1, 1, 2-trifluorobutadiene terpolymer. Additional samples of the nitroso ester terpolymers will also be prepared.

III. EXPERIMENTAL

A. Monomer Synthesis

1. 4-Nitrosoperfluorobutyric Acid

Perfluoroglutaric anhydride (44.4 g., 0.2 mole) was placed in a 2-neck flask and cooled to slightly above its freezing point. This was followed by the addition of N_2O_3 (61 g., 0.2 mole) cooled to -78°. After the addition of the N_2O_3 the mixture was allowed to warm to room temperature with stirring. It was then placed under full vacuum for several hours. After the first few minutes the product became solid. This solid product, $ONOOC(CF_2)_3COONO$ (54.7 g., 90% conversion), was transferred to a large Pyrex tube containing a Vycor immersion well. A full vacuum was maintained and the product was irradiated with ultraviolet light. The volatile product was condensed as a solid in a -183° trap. After all of the dinitrite had reacted a green polymeric material (9.5 g.) was left in the photolysis vessel. The product trapped at -183° was warmed to room temperature and degassed to remove CO_2 and nitrogen oxides. The final product weighed 23 g. representing a 50% yield of $ONOOC(CF_2)_3NO$. This material was poured over crushed ice and a blue solution resulted. The solution was extracted with ethyl ether which removed all of the blue color from the aqueous layer. The ether extract was dried over Na_2SO_4, and then the ether was removed under vacuum. A chromotogram of the blue product showed only one peak, but an infrared spectrum (Figure 1) showed the presence of ethyl ether. NMR analysis confirmed the presence of ethyl ether as well as other impurities.

2. Reaction of $ICF_2CF_2CF_2I$ with Nitric Oxide

A magnetic stirring bar, Hg (5 ml.), NO (0.10 g., 0.035 moles). and $I(CF_2)_3I$ (14.1 g., 0.035 mole) were placed in a 1-l. Vycor flask and the mixture was stirred in sunlight for 8 hours. During this time a large amount of red solid deposited on the walls of the flask. The volatile were removed to a trap in liquid air, forming a white solid with a trace of blue coloring. An infrared spectrum gave no evidence for any R_fNO absorption.

The reaction was repeated without the presence of Hg. The only difference in the product was that crystals of I_2 were deposited on the walls of the flask. There was still no evidence for any R_fNO.

3. Reaction of Tetrafluoroethylene with Nitrosyl Bromide

Two identical reactions were run and the products were combined. A 12-l. flask was charged with C_2F_4 (19 g., 0.19 mole) and BrNO (21 g., 0.19 mole) and irradiated for 4 hours with an ultraviolet lamp. At the end of this time the originally brown gas had turned green. The product was transferred to a small flask and distilled. Only a small amount (~2 g.) of a blue product was obtained and approximately 50% of the C_2F_4 was recovered unreacted.

4. Reaction of Perfluoropropylene and Oxygen in Sunlight

A 1-l. Vycor flask was charged with $CF_3CF{=}CF_2$ (2.7 g., 0.018 mole) and O_2 (0.58 g., 0.018 mole) and placed in sunlight. Infrared spectra were made periodically for one month but the only absorption shown was for $CF_3CF{=}CF_2$.

B. Polymerization

Polymers prepared during this period are described in Tables 1 and 2. Procedures for preparing and working up the terpolymers are the same as previously reported. Polymerization described in Table 2 was accomplished by condensing monomers into a 5-ml. nickel tube, which was sealed and placed in a high pressure reactor, which was then pressurized by an hydraulic pump.

C. Synthesis of Intermediates

1. Preparation of $ICF_2CF_2CF_2I$

A 300-ml. autoclave was charged with perfluoroglutaryl chloride (100 g., 0.36 moles) and potassium iodide (130 g., 0.78 mole) and heated at 200° for 20 hours. A red liquid product was removed and washed several times with water. This was followed by washings with $Na_2S_2O_3$, then dilute NaOH, and finally several more washings with water. The product was then dried over Na_2SO_4 and distilled. This gave 52 g. (36% yield) of $ICF_2CF_2CF_2I$ boiling at 126-132°.

2. Preparation of Nitrosyl Bromide

A 500-ml., 3-neck flask was fitted with a stirrer, a gas inlet tube, and an outlet tube vented to traps at -78° and -183°. Water (80 ml.) and $NaNO_2$ (383 g., 5.5 moles) were stirred in the flask as HBr was bubbled in. It appears that no reaction takes place until the HBr concentration reaches a certain point. The product was caught in the -78° trap and distilled on a glass-packed column to give 42 g. of material boiling at 8°.

It was found that the following is the better method of producing NOBr. A 1-liter flask containing 567 ml. of concentrated HBr solution (7 moles) was fitted with a stirrer, gas outlet vented to -78° and -183° traps, and an addition funnel containing 345 ml. of a solution of $NaNO_2$ (3 moles). The flask was maintained at ambient temp. with a water bath and the $NaNO_2$ solution was slowly added. The product was trapped at -78°.

TABLE 1

TERPOLYMERS[a]

No.	Monomers	Amount Grams	Amount Moles	Time Hours	Temp. °C	Yield Grams	Conversion %	Remarks
1.	CF_3NO	1.6	0.016	108	-35	2.7	69	Colorless gum; fractionated polymer shows CF_2=CF— infrared absorption.
	$CF_2=CF_2$	1.9	0.019					
	$CF_2=CFCF_2NO$	0.4	0.002					
2.	CF_3NO	3.1	0.031	48	-35	4.5	61	White gum; appears cross-linked; infrared shows CF_2=CF—.
	$CF_2=CF_2$	2.5	0.025					
	$(CF_2=CFCH_2CF_2)_2$	1.8	0.006					
3.	CF_3NO	2.5	0.025	114	-38	~2	~35	Viscous, brown polymer; infrared shows unsaturation.
	$CF_2=CF_2$	2.8	0.028					
	$CF_2ClCF(NO)CH_2CH=CH_2$	0.5	0.002					
4.	CF_3 NO	3.0	0.003	48	-35	~2.5	~44	White gum; infrared indicates no ester incorporated
	$CF_2=CF_2$	2.7	0.0027					
	p-$CF_2=CFC_6H_4CO_2C_2H_5$	0.7	0.0003					
5.	CF_3NO	20.0	0.200	18	-35	16.5	34	Colorless gum; fractionated.
	$CF_2=CF_2$	22.5	0.225					
	$ONCF_2CF_2CF_2COOH$	5.6	0.025					

(a) All polymerizations were run in bulk.

TABLE 1 (Continued)

TABLE 1 (Continued)

TERPOLYMERS[a]

No.	Monomers	Amount		Time	Temp.	Yield	Conver-sion	Remarks
		Grams	Moles	Hours	°C	Grams	%	
6.	CF_3NO	6.0	0.060	18	-38	—	—	Brown low m. wt. fluid.
	$CF_2=CF_2$	3.0	0.030					
	$CF_2=CFCH_2CH=CH_2$	3.7	0.030					
7.	CF_3NO	49.5	0.50	15	-35	40	40	White gum; fractionated
	$CF_2=CF_2$	40.0	0.40					
	$CF_2=CFCH=CH_2$	11.0	0.10					
8.	CF_3NO	25.0	0.25	48	-30	42	71	White gum.
	$CF_2=CF_2$	14.0	0.14					
	$CF_2=CFBr$	19.8	0.12					
9.	CF_3NO	16.6	0.16	48	-30	25	66	Gum; fractionated; $[\eta] = 0.32$
	$CF_2=CF_2$	17.1	0.17					
	$ONCF_2CF_2CO_2CH_3$	3.8	0.02					
10.	CF_3NO	16.6	0.16	48	-30	15	42	Gum; fractionated; $[\eta] = 0.36$
	$CF_2=CF_2$	17.1	0.17					
	$ONCF_2CF_2CO_2CH_3$	2.0	0.01					

(a) All polymerizations were run in bulk.

TABLE 2

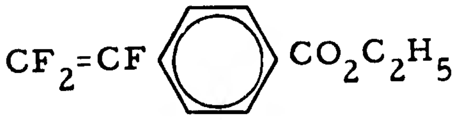
COPOLYMERS WITH CF_3NO^a

No.	Monomers	Amount		Hours	Yield	Conversion	Remarks
		Grams	Moles		Grams	%	
1.	CF_3NO	2.5	0.025	48	0	0	Under 18, 000 psi; starting material recovered.
	COF_2	1.7	0.025				
2.	CF_3NO	1.1	0.011	5	0	0	Same
	$(CF_3)_2C=O$	1.8	0.011				
3.	CF_3NO	1.8	0.018		~ 0.1	~3	Under 13, 000 psi; pressure surge at 8000 psi; carbon and some white gum polymer formed.
	$CF_2=CF_2$	1.8	0.018				
4.	CF_3NO	1.8	0.018	1	0	0	Pressure surge at 8000 psi; no solid products
	$CF_2=CFBr$	2.9	0.018				
5.	CF_3NO	1.8	0.018	20	~ 2.5	~53	Under 18, 000 psi; white, sticky polymer which reacts with acetone
	$CF_2=CFBr$	2.9	0.018				

(a, All polymerizations carried out in 5-ml. nickel tube at ambient temperature.

IV. MONOMER PROCUREMENT

During this report period the following samples were received from outside sources:

	5 g.	University of Florida
$CF_2ClCF(NO)CH_2CH=CH_2$	1 g.	University of Florida
$CF_2=CFCF_2NO$	0.5 g.	University of Florida

V. SAMPLES SUBMITTED

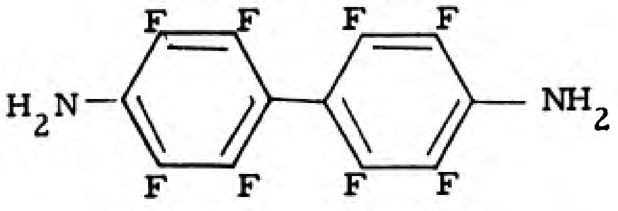
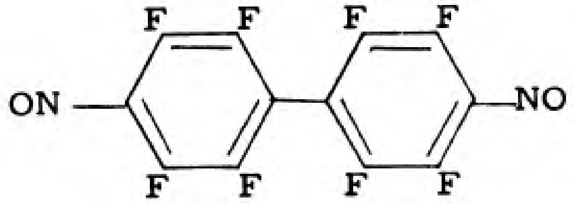
During this quarter the following samples were submitted to the U. S. Army Natick Laboratories for evaluation:

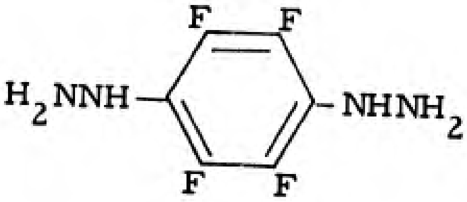
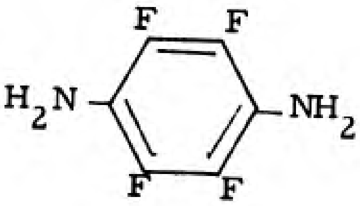
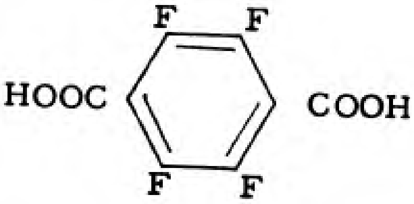
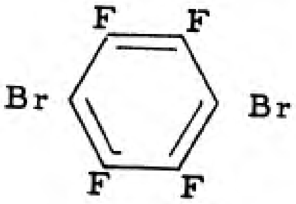
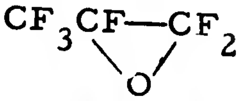
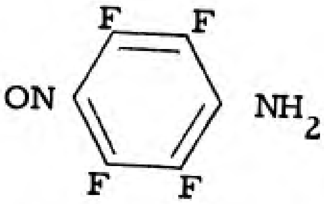
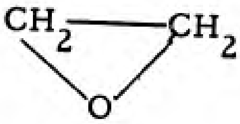
Designation	Charged Composition	Amount (g.)
W. O. 17. 3	$CF_3NO(5)/CF_2{=}CF_2(4)/CF_2{=}CFCH{=}CH_2$ (1)	280
QC-8. 12	$CF_3NO(2)/CF_2{=}CF_2(1)/CF_2{=}CFBr$ (1)	41.6
W. O. 81. 1	$CF_3NO(8)/CF_2{=}CF_2(9)/ONCF_2CF_2CO_2CH_3$ (1)	25
W. O. 81. 2	$CF_3NO(16)/CF_2{=}CF_2(17)/ONCF_2CF_2CO_2CH_3$ (1)	15
W. O. 80. 2	$CF_3NO(17)/CF_2{=}CF_2(18)/$ $ONCF_2CF_2CF_2CO_2CH_3$ (2)	20
W. O. 80. 3	$CF_3NO(17)/CF_2{=}CF_2(18)/$ $ONCF_2CF_2CF_2CO_2CH_3$ (1)	23

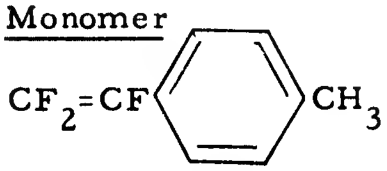
In addition to these samples, 150 g. of ICF_2CF_2I was prepared as an intermediate for use in the monomer synthesis program at the University of Florida.

VI. MONOMER LIST

The monomers listed below have been assigned the identification numbers shown. These numbers will be used frequently throughout future reports in place of cumbersome nomenclature or structures. A complete list of monomer number assignments will be given in each report.

Number	Monomer
400	$F_2C=S$
401	C_6F_5NO
402	$SF_5CH=CH_2$
403	$CF_3SCF=CF_2$
404	$(CF_3)_2C=S$
405	$CF_3N=SF_2$
406	C_6H_5NO
407	$[CF_3CF_2CH_2CH_2Si(CH_3)O]_3$
408	$[CF_3CF_2CH_2CH_2Si(CH_3)O]_4$
409	$CF_3SCF(NO)CF_2Cl$
410	
411	

Number	Monomer
412	
413	
414	
415	
416	$SF_5CF=CF_2$
417	 $CF_3CF{-}CF_2$ (epoxide, O bridging)
418	
419	 $CH_2{-}CH_2$
420	$(NC)_2C=C(CN)_2$

Number	Monomer
421	
422	CF_2BrCF_2NO
423	$CH_3OOCCF_2CF_2NO$
424	$CH_3O_2CCF_2CF_2CF_2NO$
425	$CF_2{=}CFI$
426	$(CH_3)_2NNO$

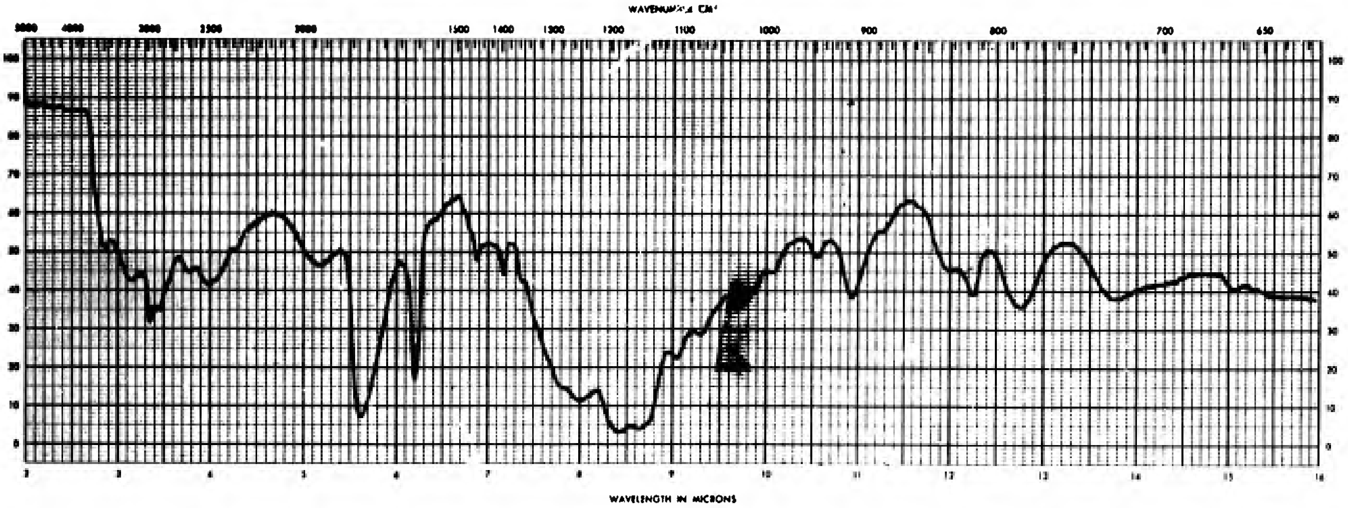


Figure 1. Infrared Spectrum of $ONCF_2CF_2CF_2COOH$/Ether Complex

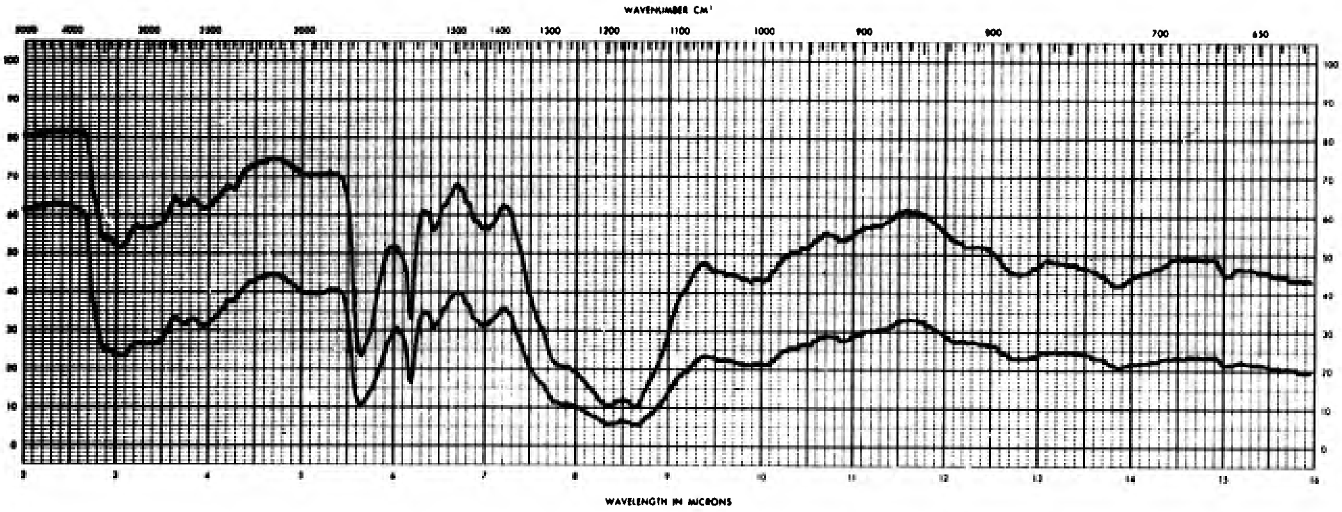


Figure 2. Infrared Spectrum of Residue from Photolysis of $ONOOC(CF_2)_3COONO$

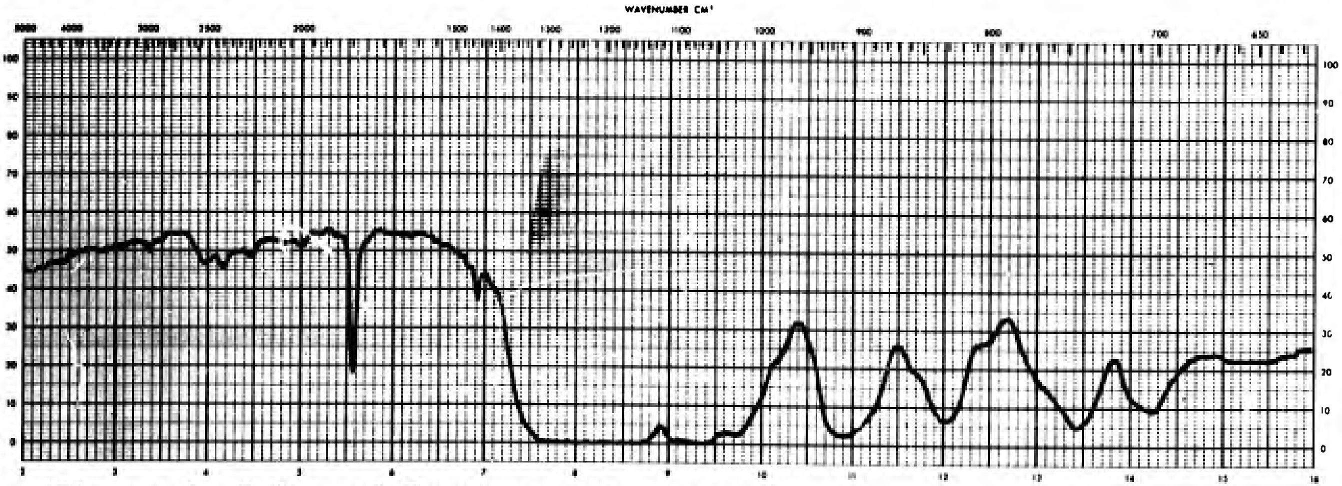


Figure 3. Infrared Spectrum of $CF_3NO/CF_2{=}CF_2/CH_3O_2C(CF_2)_2NO$ (3%) Terpolymer

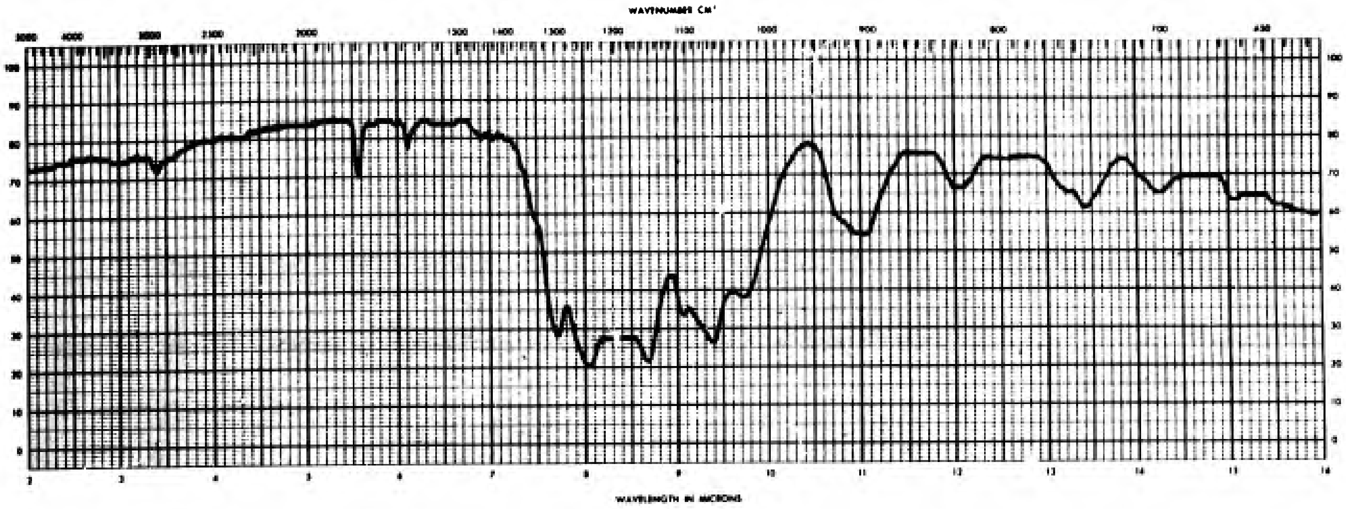


Figure 4. Infrared Spectrum of $CF_3NO/CF_2{=}CF_2/CH_3O_2C(CF_2)_2NO$ (6%) Terpolymer

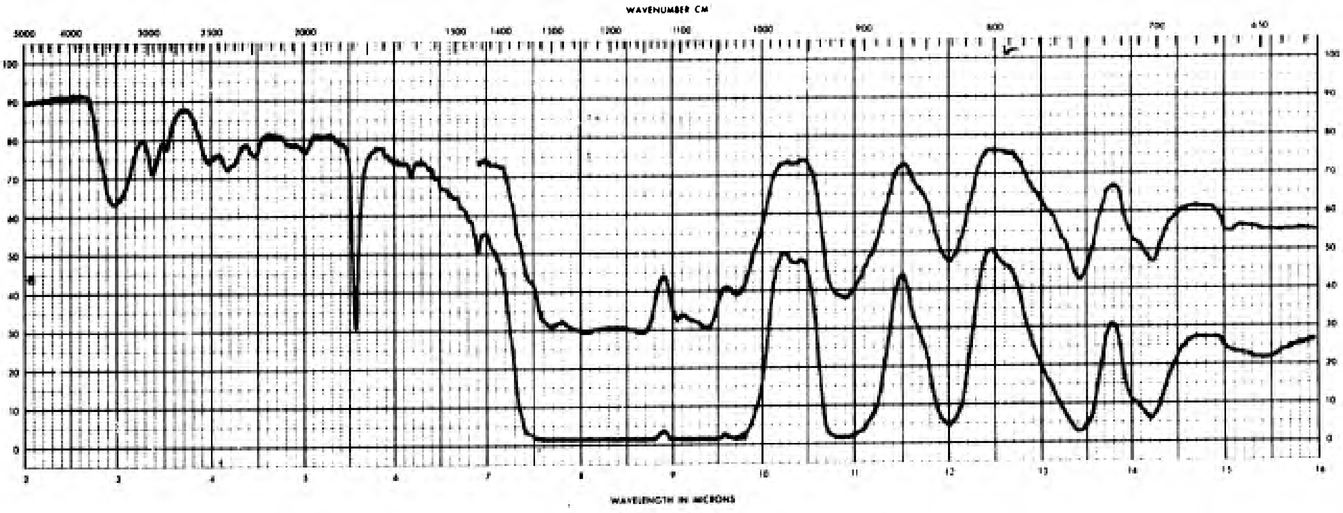


Figure 5. Infrared Spectrum of $CF_3NO/CF_2{=}CF_2/ONCF_2CF_2CF_2COOH$ Terpolymer

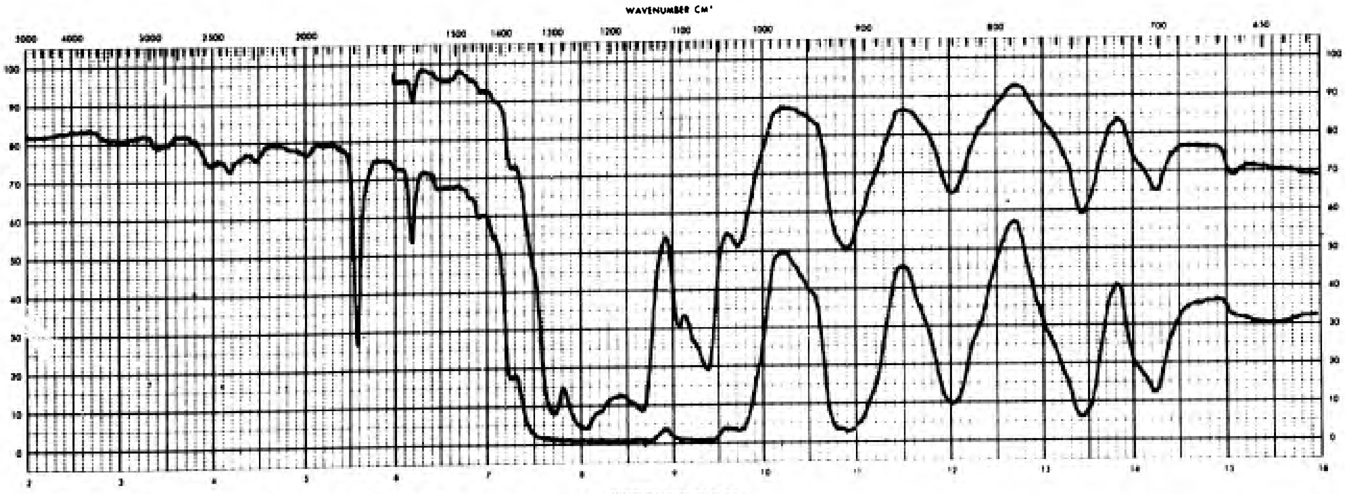


Figure 6. Infrared Spectrum of $CF_3NO/CF_2{=}CF_2/CF_2{=}CFCF_2NO$ Terpolymer

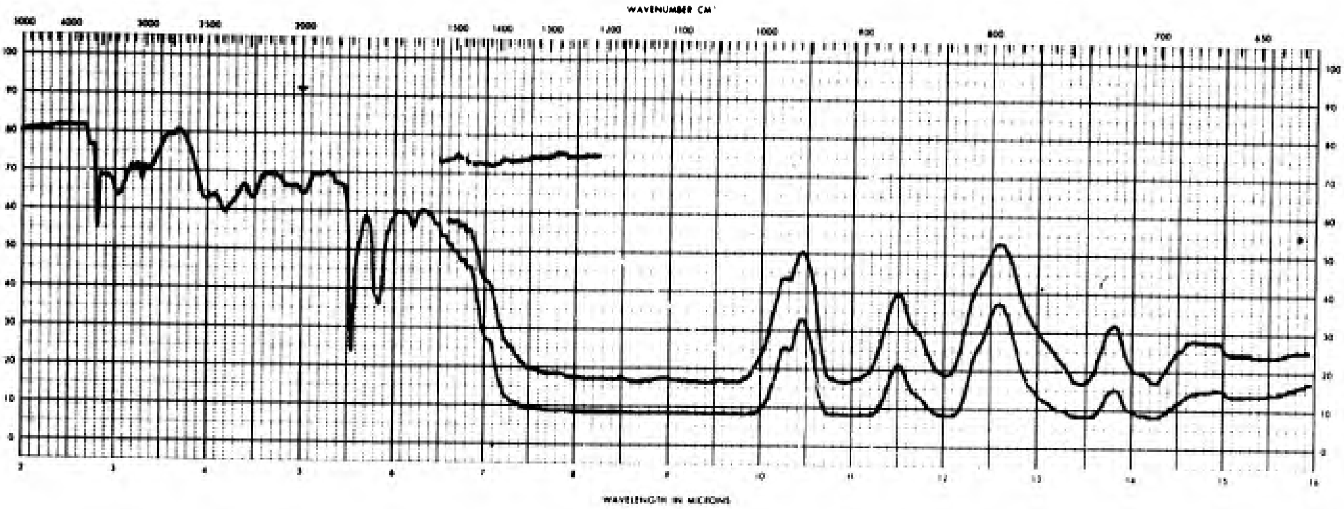


Figure 7. Infrared Spectrum of $CF_3NO/CF_2{=}CF_2/CF_2{=}CFCH_2CF_2CF_2CH_2CF{=}CF_2$ Terpolymer

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Natick, Massachusetts 01760

13. ABSTRACT

Terpolymer samples containing 3 and 6 mole percent $ONCF_2CF_2CO_2CH_3$ with CF_3NO and $CF_2{=}CF_2$ have been prepared. A larger amount (280g) of 1,1,2-trifluorobutadiene terpolymer with CF_3NO and $CF_2{=}CF_2$ was prepared. Terpolymers of $CF_2{=}CFCF_2NO$, $CF_2{=}CFCH_2CF_2CF_2CH_2CF{=}CF_2$ and $ONCF_2CF_2CF_2COOH$ with CF_3NO and $CF_2{=}CF_2$ were prepared. Attempted copolymerization of carbonyl fluoride and hexafluoroacetone with CF_3NO was unsuccessful. A 2-l. reactor equipped with stirrer and cooling coils has been procured and is being fitted with a refrigeration system.

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KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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