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WITH

U. S. ARMY NATICK LABORATORIES

Report Period: 26 February 1966 - 26 May 1966

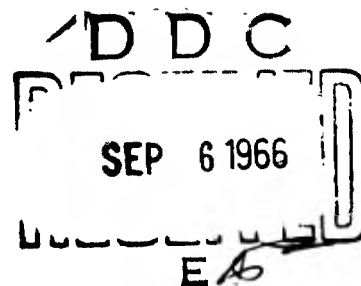
SYNTHESIS AND POLYMERIZATION OF
FLUORINATED SULFUR MODIFIED
NITROSO RUBBER

By

Eugene C. Stump, Calvin D. Padgett
and Charles R. Wetzel

26 June 1966

Peninsular ChemResearch, Inc.
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Gainesville, Florida 32601



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⑫ 13 p.

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FOREWORD

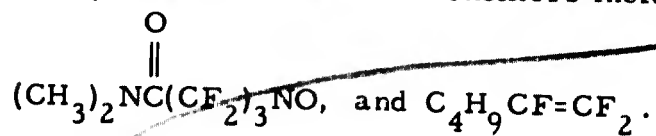
This report was prepared by Peninsular ChemResearch, Inc. under Contract No. DA 19-129-AMC-152(N)(OI9116) for the U. S. Army Natick Laboratories with Mr. C. B. Griffis as Project Officer. This is the eleventh Quarterly Report under this contract and covers the period 26 February 1966 through 26 May 1966.

Personnel engaged in this research are Eugene C. Stump, Project Supervisor (140 hours), Calvin D. Padgett, Research Chemist (517-1/4 hours), and Charles R. Wetzel, Research Chemist (518-3/4 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 90% of the work is completed and that 85% 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

Additional quantities (245 g.) of $\text{ON}(\text{CF}_2)_3\text{CO}_2\text{CH}_3$ have been prepared and polymerized with CF_3NO and $\text{CF}_2=\text{CF}_2$. A total of 526 g. of nitroso ester terpolymer (NET) in charged compositions of 2-10 mole % has been submitted for compounding and curing studies. Investigation of the synthesis of other termonomers includes $\text{CH}_3\text{OCF}_2\text{CF}_2\text{NO}$,



The high boiling material formed in the pyrolysis of $\text{ONOOC}(\text{CF}_2)_3\text{CO}_2\text{CH}_3$ has been identified as $(\text{CH}_3\text{OC}(\text{CF}_2)_3)_2\text{NO}(\text{CF}_2)_3\text{CO}_2\text{CH}_3$.

A new copolymer was prepared from CF_3NO and $\text{CF}_2=\text{C}=\text{CH}_2$ but was found to decompose at room temperature.

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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 Quarterly Report No. 1, dated 21 October 1963.

The original 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. Recent work, and work described in this report, has been directed toward the preparation of nitroso terpolymers containing a reactive site for cross-linking.

II. DISCUSSION

A. Monomer Synthesis

In order to prepare larger quantities of $\text{CF}_3\text{NO}/\text{CF}_2=\text{CF}_2/\text{ON}(\text{CF}_2)_3\text{CO}_2\text{CH}_3$ (N. E. T.) terpolymer for testing, it was necessary to synthesize additional samples of the nitroso ester. A total of 245 g. of fractionated monomer was prepared in an average conversion of 21%. Passage of pure nitric oxide through the pyrolysis chamber at 5 mm. pressure produced no increase in conversion as desired. As previously reported,¹ pyrolysis of the nitrite ester gives a higher boiling material in addition to the nitroso ester. On the basis of its infrared spectrum this material was believed to be a diester, which could presumably result from coupling of the $\text{CH}_3\text{O}_2\text{C}(\text{CF}_2)_3\cdot$ radical. Recent NMR and elemental analysis have identified this compound, however, as $[\text{CH}_3\text{O}_2\text{C}(\text{CF}_2)_3]_2\text{NO}(\text{CF}_2)_3\text{CO}_2\text{CH}_3$. The NMR spectrum is described below. Tetramethyl silane and trifluoroacetic acid were used as reference.

Designation	Chemical Shift	Pattern and Splitting	Rel. Area	Assignment
H	6.22 tau	Sharp singlet		$-\text{OCH}_3$
F A	+10.2 ppm	Broad	2.6	$-\text{CF}_2\text{O}$
B, C	+17.2	Non-equiv. quartet, broad	4.7	$-\text{CF}_2\text{N}$
D	+41.2	Broad, overlapping peaks	9.0	$-\text{CF}_2\text{CO}_2$
E	+43.5	Broad	5.1	$-\text{CF}_2-$
F	+47.8	Broad	2.5	$-\text{CF}_2-$

A similar compound, $(\text{C}_3\text{F}_7)_2\text{NOC}_3\text{F}_7$, has been reported² and was prepared by pyrolysis of $\text{C}_3\text{F}_7\text{NO}$. The NMR spectrum of this compound

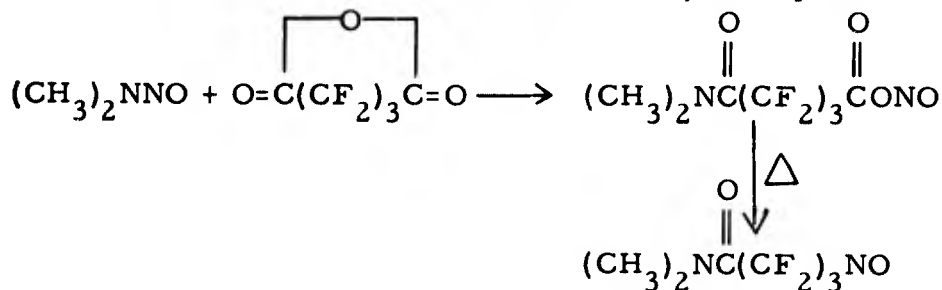
(1) Quarterly Report No. 10, this contract.

(2) R. E. Banks, et al., J. Chem. Soc., 7203(1965).

exhibited the same chemical shift and non-equivalence of the fluorine atoms in the CF_2N groups as the triester. In addition, the infrared spectra of the two compounds exhibited a peak, attributed to C-N stretch, at 10.25 microns.

In an attempt to prepare an alkoxy-substituted nitroso compound, methyl nitrite and tetrafluoroethylene were combined and irradiated with an ultraviolet lamp. The only nitroso compound isolated from the reaction mixture was identified as $\text{ONCF}_2\text{CF}_2\text{NO}_2$. This reaction will be repeated using sunlight.

N-Nitrosodimethylamine was combined with perfluoroglutaric anhydride in an attempt to prepare a nitrite amide and subsequently a nitroso amide as shown. The experiment was terminated by an explosion and will be repeated



using other conditions.

Tetrafluoroethylene has been reacted with butyl lithium to give $\text{C}_4\text{H}_9\text{CF}=\text{CF}_2$. Difficulty was encountered in separating the olefin from the hexane solvent. Purification by bromination, followed by distillation and debromination, will be examined.

The reaction of nitrosyl chloride with pentafluorophenyl lithium³ has been reexamined using tetrahydrofuran as a solvent. As before, no $\text{C}_6\text{F}_5\text{NO}$ was obtained. In order to determine the stability of $\text{C}_6\text{F}_5\text{NO}$ in the presence of lithium reagent, perfluoronitrosobenzene was dissolved in THF and butyl lithium added at -78° . An immediate reaction occurred, giving an unidentified light brown solid. Due to this apparent instability in the presence of lithium reagent, this approach will be discontinued.

(3) Quarterly Report No. 4, this contract.

B. Polymerization

As indicated in Table 1, several explosions occurred during the bulk polymerization of $\text{CF}_3\text{NO}/\text{CF}_2=\text{CF}_2/\text{ON}(\text{CF}_2)_3\text{CO}_2\text{CH}_3$. Since these runs were larger than those previously carried out, without incident, it is felt that these explosions are due to the inability of the system to conduct heat from the vessel rapidly enough to prevent an uncontrolled, exothermic polymerization. This problem could probably be resolved by carrying out the polymerization in suspension in the 2-l., stirred autoclave, but due to the possibility of hydrolysis of the ester group by this method, it was felt desirable to use the bulk method. Batches of about 200 g. or less can be polymerized without difficulty.

During this period a new polymer was prepared from CF_3NO and $\text{CF}_2=\text{C}=\text{CH}_2$. This copolymer is surprisingly unstable and decomposes at room temperature with the evolution of an unidentified fluorine-containing gas. A terpolymer containing $\text{CF}_2=\text{C}=\text{CH}_2$ was also found to have very low thermal stability as it decomposed at 70° .

An attempt to copolymerize CF_3NO and CF_3CFCF_2 with activated charcoal was unsuccessful.

III. EXPERIMENTAL

A. Monomer Synthesis

1. Methyl γ -Nitrosoperfluorobutyrate

The reaction of methyl nitrite with perfluoroglutaric anhydride was carried out ten times as previously described.⁴ A total of 432 g. of methyl nitrite and 1579 g. of perfluoroglutaric acid gave $\text{ONOOC}(\text{CF}_2)_3\text{CO}_2\text{CH}_3$ in an average conversion of 90%. Decarboxylation to the nitroso ester was accomplished by both ultraviolet irradiation and pyrolysis as before.⁵ A total of 245 g. of pure $\text{ON}(\text{CF}_2)_3\text{CO}_2\text{CH}_3$ was prepared in an average conversion of 21%.

2. Tetrafluoroallene

Tetrafluoroallene was prepared as previously reported.⁵ A total of 275 g. of $\text{CF}_2\text{BrCH}_2\text{CF}_2\text{Br}$ was obtained by the addition of CF_2Br_2 to $\text{CH}_2=\text{CF}_2$. Dehydrobromination in two steps, with the second step being carried out according to the method described by Jacobs and Bauer,⁶ gave 24 g. of $\text{CF}_2=\text{C}=\text{CF}_2$. Conversion was 24% based on $\text{CF}_2\text{BrCH}_2\text{CF}_2\text{Br}$.

3. Reaction of Methyl Nitrite with Tetrafluoroethylene

Tetrafluoroethylene (25 g., 0.25 moles) and methyl nitrite (13.7 g., 0.225 moles) were charged to a 12 l. flask equipped with a quartz immersion well. After u.v. irradiation for 48 hours with a No. 8A36 Hanovia lamp, trap to trap distillation gave mostly unreacted tetrafluoroethylene. A higher boiling blue product was also partially purified. Further purification of this product on VPC gave a pure sample. The compound was identified as $\text{ONCF}_2\text{CF}_2\text{NO}_2$ by NMR and infrared analysis.

(4) Quarterly Report No. 8, this contract.

(5) Quarterly Report No. 10, this contract.

(6) T. L. Jacobs and R. S. Bauer, J. Am. Chem. Soc., 81, 608 (1959).

4. Reaction of N-Nitrosodimethylamine with Perfluoroglutaric Anhydride

Perfluoroglutaric anhydride (22.2 g., 0.1 mole) and N-nitrosodimethylamine (7.4 g., 0.1 mole) were charged to a Fischer-Porter tube cooled to -183. After melting had occurred the reactants were mixed thoroughly by shaking. Soon after this the tube exploded.

5. Reaction of Methyl Lithium and Butyl Lithium with Tetrafluoroethylene⁷

Dry ether (500 ml.) and butyl lithium (195 ml., 0.30 mole) in hexane solution were placed in a 1-l. flask fitted with an air driven stirrer and inlet with a helium sweep. The flask was cooled by a Dry-Ice/acetone bath. Tetrafluoroethylene (36 g. 0.36 moles) was condensed into the flask by means of a cold finger condenser at -96°. After stirring for two hours, the flask was allowed to warm slowly to room temperature. After washing with dilute HCl and drying over anhydrous CaSO₄, the mixture was fractionated and the 65°-75° cut was collected. An IR spectrum and VPC indicated that the product (b. p. 70°) was obtained but its separation from hexane (b. p. 69°) could not be effected on a large scale.

A similar preparation of CH₃CF=CF₂ was attempted using 5% CH₃Li in ether (1.3 moles) and tetrafluoroethylene, (100 g., 1.50 moles) with reaction time of 4 hours at -78°. Work up yielded no material boiling at 18°. Most of the CH₃Li appeared to be unreacted.

6. Reaction of Nitrosyl Chloride with Pentafluorophenyl Lithium

A reaction run in an earlier report³ between nitrosyl chloride and pentafluorophenyl lithium was repeated using tetrahydrofuran as a solvent. The reaction again failed to give perfluoronitrosobenzene.

In order to determine the stability of perfluoronitrosobenzene in the presence of excess lithium reagent the following experiment was run.

Perfluoronitrosobenzene (2.0 g., 0.01 moles) was dissolved in 30 ml.

(7) S. Dixon, J. Org. Chem., 21, 400 (1956).

of tetrahydrofuran and cooled to -78° . Butyl lithium in hexane (6.5 ml., 0.01 mole) was added slowly. Immediate discoloration took place. After 2 hours the black solution was warmed to room temperature, washed with dilute HCl, dried and evaporated to a tarry material. Washing with methanol gave a light brown material with typical fluoroaromatic absorption in the infrared, as well as an absorption at 5.92 microns.

In light of the above experiment, inverse addition of the reactants at -96° was tried; however, work up gave no nitrosobenzene.

B. Polymerization

Polymers prepared during this report period are described in Tables 1-3. Procedures for preparing and working up the polymers are the same as previously reported.

C. Cross-Linking

1. $\text{CF}_3\text{NO}/\text{CF}_2=\text{CFCF}=\text{CF}_2$ Copolymer

A small amount (5.0 g.) of the copolymer $\text{CF}_3\text{NO}/\text{CF}_2=\text{CFCF}=\text{CF}_2$ was thoroughly mixed with hexanitrosobenzene, $\text{C}_6(\text{NO})_6$, (0.5 g.). The mixture was placed in a press and heated at 60° for 1 hour with no apparent reaction.

The following materials were placed in a 250-ml. flask and refluxed overnight: $\text{ICF}_2\text{CF}_2\text{I}$ (9.2 g.), $\text{CF}_3\text{NO}/\text{CF}_2=\text{CFCF}=\text{CF}_2$ (5.0 g.), FC-43 (50 ml.), and benzoyl peroxide (1.2 g.). After the reflux was completed the gum could not be recovered. The product was a liquid, apparently from the decomposition of the polymer.

D. Synthesis of Intermediates

1. Perfluoroglutaric Anhydride

(a) Perfluoroglutaric anhydride (822 g.) was prepared as previously reported⁴ from perfluoroglutaric acid in 89% conversion.

TABLE I

Preparation of Nitroso Ester Terpolymers^a

No.	Monomer	Amount		Time Hours	Temp. °C	Yield Grams	Conv. %	Remarks
		Grams	Moles					
1	CF ₃ NO	77.1	0.779	24	-30	168	80	Contained some unreacted nitroso ester which was removed under vacuum, $[\eta] = 0.5^b$
	CF ₂ =CF ₂	94.5	0.945					
	ON(CF ₂) ₃ CO ₂ CH ₃	37.4	0.156					
2	Ditto	91.8	0.928	-	-30	-	-	2 and 3 run simultaneously and exploded after several hours.
		112.6	1.126					
		44.5	0.186					
3	Ditto	106.2	1.073	-	-30	-	-	Exploded after several hours, 145 g. terpolymer recovered, $[\eta] = .25^c$
		130.2	1.302					
		51.3	0.215					
4	Ditto	356	3.60	-	-45	-	-	Exploded after several hours, 145 g. terpolymer recovered, $[\eta] = .25^c$
		400	4.00					
		95.5	0.40					
5	Ditto	43.82	0.443	48	-30			Polymer from 5, 6, and 7 combined, 10 g. unreacted nitroso ester recovered.
		53.68	0.537					
		21.20	0.089					
6	Ditto	41.77	0.422	36	-30	245	72	Polymer from 5, 6, and 7 combined, 10 g. unreacted nitroso ester recovered.
		51.16	0.512					
		20.20	0.085					
7	Ditto	40.18	0.406	36	-30			Polymer from 5, 6, and 7 combined, 10 g. unreacted nitroso ester recovered.
		49.23	0.492					
		19.40	0.081					

- a. All reactions were carried out in bulk in 900-ml. steel cylinders.
 b. In FC-43.
 c. In FC-75.

TABLE 2

Copolymers

No.	Monomer	Amount		System	Time Hours	Temp. °C	Yield Grams	Conv. %	Remarks
		Grams	Moles						
1	F_3NO $\text{CF}_2=\text{CF}_2$	94 95	0.95 0.95	Suspension ^a	48	-25	99	53	Contained insoluble material.
2	Ditto	53.5 54	0.54 0.54	Bulk	22	-35	82	76	$[\eta] = 1.15^b$
3	CF_3NO $\text{CF}_2=\text{CFCF}=\text{CF}_2$	30.7 50	0.31 0.31	Suspension ^c	48	-35	22	27	Brown gum, color removed with HCl, $[\eta] = 0.1^d$
4.	Ditto	59 97.4	0.60 0.60	Bulk	41	-40	45	29	31.4 g. volatiles + 61.2 g. Diels-Alder adduct recovered, $[\eta] = 0.1^d$
5.	CF_3NO $\text{CF}_2=\text{C}=\text{CH}_2$	2.97 2.28	0.03 0.03	Bulk	18	-20	—	—	Gum decomposes at r. t.
6.	Ditto	1.49 1.14	0.015 0.015	Bulk	19	-20	—	—	Decomposes with evolution of unidentified fluorine-containing gas.
7.	CF_3NO CF_3CFCF $\quad \quad \quad \diagdown \quad \diagup$ $\quad \quad \quad \text{O} \quad \text{O}$	5.45 9.6	0.055 0.049	Activated charcoal	720	25-60	0	0	Reactants recovered.

a. In 2-l., stirred autoclave with H_2O (1000 g.), LiBr (530 g.) and MgCO_3 (35 g.).

b. In FC-43.

c. Shaken in 500 ml. cylinder with H_2O (300 g.), LiBr (159 g.) and MgCO_3 (10.5 g.)

d. In FC-75.

TABLE 3

Terpolymers

No.	Monomer	Amount		System	Time Hours	Temp. °C	Yield Grams	Conv. %	Remarks
		Grams	Moles						
1.	CF_3NO	85.1	0.859	Suspension ^a	64	-32	43.5	35	$[\eta] = 0.2^b$
	$\text{CF}_2=\text{CF}_2$	63.4	0.634						
	$\text{CF}_2=\text{CFCH}=\text{CH}_2$	24.3	0.225						
2.	Ditto	99	1.00	Bulk	17	-42	120	60	$[\eta] = 0.16^c$
		80	0.80						
		21.6	0.20						
3.	CF_3NO	3.96	0.04	Bulk	120	-20 to r.t.	6.3	84	Decomposes at 70°
	$\text{CF}_2=\text{CF}_2$	2.0	0.02						
	$\text{CF}_2=\text{C}=\text{CH}_2$	1.52	0.02						
4.	CF_3NO	43	0.432	Bulk	72	-30	30	34	White gum; IR shows $=\text{CF}_2$
	$\text{CF}_2=\text{CF}_2$	21.6	0.216						
	$\text{CF}_2=\text{C}=\text{CF}_2$	24.0	0.216						

a. In 2-l., stirred autoclave with H_2O (1000 g.), LiBr (530 g.), and MgCO_3 (35 g.).

b. In FC-43.

c. In FC-75.

(b) Perfluoroglutaric anhydride (502 g.) was prepared directly from perfluoroglutaryl chloride by the following method.⁸ Perfluoroglutaryl chloride (1000 g., 3.6 moles) was charged to a 2-l. flask fitted with Dry-Ice/acetone condensers atop a reflux condenser and protected from moisture by an anhydrous CaSO_4 trap. Water (65 g., 3.6 moles) was added slowly by means of a dropping funnel to the mechanically stirred acid chloride. After the addition was complete, the mixture was refluxed for 10 hours. Lower boiling liquid products were distilled from the mixture leaving 150 g. of residue which was hydrolyzed to perfluoroglutaric acid. Careful fractionation of the liquid products gave 502 g. of material b.p. 71-74° (perfluoroglutaric anhydride) and 110 g. of higher boiling material whose IR spectrum indicated it to be perfluoroglutaryl chloride. Conversion to the anhydride was 63%.

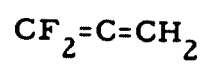
2. Methyl Nitrite

Methyl nitrite was prepared as previously reported.⁴ Two preparations gave 290 g.

(8) E. Dorfman and W. E. Emerson, "Perfluoroalkylenetriazine Elastomeric Polymers," Technical Documentary Report No. ML-TDR-64-249 Part II under Contract AF 33(615)-1636, August 1965, p. 29.

IV. MONOMER PROCUREMENT

During this report period the following sample was received from outside sources:



40 g.

University of Florida



V. SAMPLES SUBMITTED

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

<u>Designation</u>	<u>Charged Composition</u>	<u>Amount</u>
QC-35.2.1	CF ₃ NO(19)/CF ₂ =CF ₂ (14)/CF ₂ =CFCH=CH ₂ (5) (soluble portion)	23 g.
QC-35.2.2	CF ₃ NO(19)/CF ₂ =CF ₂ (14)/CF ₂ =CFCH=CH ₂ (5) (insoluble portion)	20 g.
QC-59.2.2	CF ₃ NO/CF ₂ =CF ₂ /CH ₃ O ₂ (CF ₂) ₃ NO (10 mole %)	34 g.
QC-59.4	CF ₃ NO/CF ₂ CF ₂ /CH ₃ O ₂ (CF ₂) ₃ NO (8 mole %)	165 g.
QC-59.5	" " " "	245 g.
QC-59.6	" " " (2 mole %)	82 g.
QC-60.4	CF ₃ NO/CF ₂ =CF ₂ (suspension)	99 g.
QC-60.5	" " (bulk)	80 g.
CWP-6	CF ₃ NO(2)/CF ₂ =CF ₂ (1)/CF ₂ =C=CF ₂ (1)	19.5 g.