

UNCLASSIFIED

AD. 246 784

*Reproduced
by the*

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

CATALOGED BY ASTIA
AS AD NO. 246 784

RESEARCH REPORT

October 15, 1957 to August 15, 1960
Contract DA-19-129-QM-1043

Central Research Dept.
Minnesota Mining and Mfg. Co.
St. Paul 19, Minnesota

XEROX

583 500

ASTIA
RECEIVED
DEC 2 1960
RESOLVED
TIPDR C

CENTRAL RESEARCH DEPARTMENT

RESEARCH REPORT

ARCTIC RUBBER

U.S. Army Contract DA-19-129-QM-1043

For the Period October 15, 1957 to August 15, 1960

Astia Availability Notice: "QUALIFIED
REQUESTORS MAY OBTAIN COPIES OF THIS
REPORT FROM ASTIA."

Central Research Department
Minnesota Mining & Mfg. Company
St. Paul, Minnesota

RESEARCH REPORT

Subject: U. S. Army Contract DA-19-129-QM-1043


For the Period October 15, 1957 to August
15, 1960.

Staff: J. W. Copenhaver, B. F. Landrum, G. H. Crawford,
C. L. Sandberg, D. E. Rice, W. J. Fraser, A. W.
Rankin, R. G. McCrea, J. M. Mullins.

(The above list includes all persons who have been
associated with the project at some time during
the contract period.)

Authors: G. H. Crawford
D. E. Rice
W. J. Fraser

This report has been read and approved.


J. W. Copenhaver

OUTLINE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION.....	6
A. Purpose of the Project	6
B. Research Program	6
C. Past Progress	6
II. SUMMARY AND CONCLUSIONS	7
III. RECOMMENDATIONS	8
IV. EXPERIMENTAL DATA AND DISCUSSION	8
A. Monomer Procurement	8
1. Sources	8
2. Monomer List	9
3. Monomers and Precursors Received	9
4. Conversion of Precursors to Monomers	9
5. Equipment	9
B. Polymerization Research - Immediate Range	10
1. Exploratory Polymerizations	10
a. Discussion	10
b. Experimental	10
1. Polymers based on $\text{CF}_3\text{CH}=\text{CH}_2$ (35) ...	10
2. Polymers based on $\text{C}_2\text{F}_5\text{CF}=\text{CH}_2$ (125) ..	10
3. Saturated Fluorohydrocarbon interpolymers	10
4. Polyolefin/ $\text{CF}_2=\text{CFCH}=\text{CH}_2$ Systems'	10
5. Diene Systems, Misc.	11
2. Continued Work on Promising Systems	11
a. Discussion	11
b. Experimental.....	11
1. $\text{CH}_2=\text{CHCH}=\text{CH}_2/\text{CF}_2=\text{CFCH}=\text{CH}_2$ (3/56) Copolymers	11
2. $\text{CF}_2=\text{CHCF}=\text{CH}_2/\text{CF}_2=\text{CFCH}=\text{CH}_2$ (51/56) Copolymers	11
3. Evaluation Data	12

C.	Polymerization Research-Long Range	13
1.	Exploratory Polymerizations	13
a.	Discussion	13
b.	Experimental	14
2.	Nitroso Polymerizations - $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ (24/127) Copolymers	14
a.	Discussion	14
b.	Experimental	14
1.	Polymerization techniques	15
2.	Vulcanization and Properties	15
3.	Polymerization kinetics/Postulated Mechanisms.....	15
3.	Nitroso Polymerizations - Other Systems based on CF_3NO	20
a.	Discussion	20
b.	Experimental	20
1.	$\text{CF}_3\text{NO}/\text{Olefin}$ Copolymerizations	20
2.	CF_3NO Diene Copolymerizations	20
4.	Nitroso Polymerizations - Nitrosos Other Than CF_3NO	21
a.	Discussion	21
b.	Experimental	21
1.	$\text{O}_2\text{NCF}_2\text{CF}_2\text{NO}$ Copolymerizations	21
2.	$\text{ClCF}_2\text{CF}_2\text{NO}$ Copolymerizations	22
5.	Structure-Property Relationships Among Nitroso Polymers	22

I. INTRODUCTION

A. Purpose of the Project

The development of solvent-resistant fluorine-containing rubbers having good to excellent elastomer properties and serviceability at temperatures between 160°F. and -70°F.; the investigation and solution of accompanying problems of polymer structure prediction, monomer procurement and purification, and polymerization technique.

B. Research Program

In order to achieve the above objectives, the Quartermaster Research and Development Command authorized the Minnesota Mining and Manufacturing Company to conduct a broad investigation into fluorine-containing polymers. This investigation divided itself into two phases; "immediate range" and "long range". The former consisted mainly of the interpolymerization of fluoro olefins, dienes and other ethylenically unsaturated monomers to give new polymers having structures which, based on earlier observation and theoretical considerations, were expected to approach or meet the requirements. Many of the systems studied in this category were previously unobtainable; due either to non-availability of monomers, or lack of a method of making the desired monomers polymerize to the needed polymeric structure.

Early in the program, emphasis shifted to the "long range" category into which fall macro molecules resulting from more unorthodox polymer syntheses. Polymers prepared in this category contain other elements in addition to carbon in the backbone.

Generally, the group has sought to arrive at new polymer structures by making use of functionalities previously unexploited for elastomer preparation. Frequently, interpolymerizations with comonomers reacting via conventional vinyl polymerization mechanisms have been employed. Since in this area little background exists for prediction of the properties of a given structure, emphasis has been placed upon the discovery of structures which can be made to polymerize by the aforesaid unique mechanisms. Under the terms of the contract, this "long range" phase of the polymerization program has generally involved moieties containing fluorine.

C. Past Progress

The present contract was preceded by contracts awarded to the M. W. Kellogg Company.* Under these contracts a large number

* U. S. Army Contracts DA-44-109-qm-222
DA-44-109-qm-1580
DA-19-129-qm-736

of polymers containing fluorine were prepared and evaluated. Out of this work came the copolymers $\text{CH}_2=\text{CF}_2/\text{CF}_2=\text{CFC1}$ (Kel-F 5500 and 3700 Elastomer) and $\text{CH}_2=\text{CF}_2/\text{CF}_3\text{CF}=\text{CF}_2$ (FLUOREL) which are now commercially available. These saturated, highly fluorinated elastomers were unequaled in thermal stability and resistance to corrosive chemicals and fuels but fell far short of the low temperature objectives. The system $\text{CF}_2=\text{CHCF}=\text{CH}_2/\text{CF}_2=\text{CFCH}=\text{CH}_2$ was found to have the best balance of properties, but was not outstanding in any one respect.

II. SUMMARY AND CONCLUSIONS

In the "immediate range" category; saturated copolymers related to "FLUOREL," $\text{CF}_2=\text{CH}_2/\text{CF}_3\text{CF}=\text{CF}_2$, (developed under the above mentioned contract) were prepared in an effort to improve the low-temperature serviceability of this class of polymers without sacrifice of solvent resistance.

Copolymers of partially fluorinated dienes were also prepared. A polymerization process for the most promising of these, $\text{CF}_2=\text{CHCF}=\text{CF}_2/\text{CF}_2=\text{CFCH}=\text{CH}_2$, was developed which gave gel-free polymer of optimum mole ratio and molecular weight. Under a separate contract, (O.I. 3108-59), 25 lbs of this copolymer were prepared for evaluation by the Q.M.C.

Catalyst research led to the successful polymerization of some previously unworkable monomer systems. The best of the "immediate range" systems were found to offer only marginal improvements over existing materials.

In the "long range" category, heteroatomic chain formation via copolymerization of aldehydes, ketone, azomethines and nitroso compounds was studied. The most significant discovery has been that when CF_3NO and C_2F_4 are copolymerized to high molecular weights, the resultant - $\text{N} - \text{O} - \text{CF}_2\text{CF}_2 -$ chain is elastomeric, CF_3

having an excellent combination of chemical-solvent resistance and low-temperature utility. This system was developed into a rubber for which preparative procedures from monomer synthesis to compounding and curing techniques have been studied intensively.

A large number of nitroso copolymers have been prepared and tested. Of particular interest are those of $\text{C1CF}_2\text{CF}_2\text{NO}$, $\text{O}_2\text{NCF}_2\text{CF}_2\text{NO}$, and CF_3NO . The kinetics of polymerizations through the NO linkage have been studied and a mechanism proposed. Determinations of thermal stability and solution properties of nitroso copolymers have been carried out. The effect of substituents other than F in the basic structure - $\text{NO}-\text{CF}_2\text{CF}_2-$ CF_3

has been studied, providing information of general use in polymer chemistry.

The original objectives of the contract have been exceeded from the standpoint of thermal stability and chemical-solvent resistance and closely approached from the standpoint of utility at low temperatures. However, higher average molecular weights and better curing and filling techniques are needed for improved tensile properties.

The nitroso rubbers demonstrate that elastomers comprising heteratomic chains of high fluorine content provide hitherto unrealized combinations of properties. Nitroso rubbers will have much utilitarian value as well as significance in polymer science and technology.

III. RECOMMENDATIONS

1. No extensive work in the "immediate range" category should be undertaken since little in the way of breakthroughs can be expected.
2. Research should embrace non-fluorocarbon as well as fluorocarbon systems.
3. The nitroso systems can be considered as of proven merit. They should be developed to their fullest extent. This involves two jobs:
 - a. Enhance M_w to ca. 6×10^6 .
 - b. Provide structure modifications to aid in reinforcement.
4. Emphasize the "long range" approach, i.e., realization of structures comprising heteratomic backbones through the discovery of totally new polymerization reactions or adaptation of known reactions to polymer formation.
5. #4 will often entail the synthesis of monomers which are totally new. The efforts of the supporting monomer synthesis groups outside 3M should be supplemented, particularly in cases of proven systems such as the nitroso polymers where more practical monomer syntheses are needed in order to provide the larger quantities of polymer for further evaluation by the Armed Forces.

IV. EXPERIMENTAL DATA AND DISCUSSION

A. Monomer Procurement

1. Sources

a. Outside Purchase

Fluorocarbon monomers or precursors for the project have been purchased from the following companies:

Peninsular ChemResearch, Inc., Gainesville, Florida
Columbia Organic Chemicals, Inc., Columbia, South Carolina
Chemicals Procurement Company, New York, New York
E. I. DuPont De Nemours, Inc., Wilmington, Delaware

b. Academic Monomer Synthesis Research

Purchase of monomers from commercial houses has been confined to the replacement of stocks as they are depleted. The program has relied to a great extent upon the academic suppliers for new monomers. Two groups, under Dr. J. D. Park, University of Colorado, and Dr. Paul Tarrant, University of Florida, have pursued lines of research aimed at providing new monomers for the project.

c. Internal Procurement

Other projects at Central Research and elsewhere within the company have produced monomers of potential use on this project. Research samples have been obtained for the project at no cost to the government.

2. Monomer List

For reference purposes, a complete monomer list, showing synthetic route and physical properties, is included. The list includes all monomers used both on the current project and on the preceding projects at M.W. Kellogg.

3. Monomers and Precursors Received

In Table I are shown the monomers and precursors procured during the contract period.

4. Conversion of Precursors to Monomers

In Table II is summarized the precursor conversion effort at 3M during the contract period.

5. Equipment

In Table III are shown the special or non-expendable items of equipment constructed or purchased during the contract period.

B. Polymerization Research - Immediate Range1. Exploratory Polymerizationsa. Discussion

The polymerizations reported in this category represent attempts to improve the low temperature properties of saturated fluorohydrocarbon elastomers through concentration of fluorine atoms in the side-chains rather than in the backbone. Also represented are attempts to achieve a good balance of properties in diene systems through judicious placement of fluorine atoms and fluoroalkyl groups. The polymerizations reported are representative. Confirmatory experiments or repeat runs made to provide more polymer of a given type have been deleted where possible in this report.

Only those polymers which on the basis of analytical results and preliminary tests contained sufficient fluorine and had promising physical characteristics were forwarded to QMC for evaluation.

b. Experimental1. Polymers Based on $\text{CF}_3\text{CH}=\text{CH}_2$ (35)

This monomer should provide the crystallinity disruption and solvent-resistance attributable to the CF_3 side-group while enabling more CH_2 groups to be incorporated into the backbone. Several attempts to prepare $\text{CF}_3\text{CH}=\text{CH}_2/\text{CF}_2=\text{CH}_2$ copolymers (not shown) produced poor yields although $\text{CF}_3\text{-CH}=\text{CH}_2$ copolymerized readily with $\text{CF}_2=\text{CF}_2$. Terpolymers containing $\text{CF}_2=\text{CH}_2$ were, however, achieved. (See Table IV.) Properties were poor.

2. Polymers Based on $\text{CF}_3\text{CF}_2\text{CF}=\text{CH}_2$ (125)

These systems were examined for the same reason as 1. It was found that (125) copolymerized readily with $\text{CF}_2=\text{CH}_2$. Rubbery polymers having excellent solvent resistance and thermal stability were obtained, but Gehman T values were higher than corresponding values for $\text{CF}_2=\text{CH}_2/\text{CF}_3\text{CF}=\text{CF}_2$. (See Tables V and XII.) Increased CH_2 in the backbone does not necessarily bring about improved low-temperature properties.

3. Other Saturated Fluorohydrocarbon Interpolymers

In Table VI appear miscellaneous exploratory polymerizations having the objectives of 1 and 2.

4. Polyolefin/ $\text{CF}_2=\text{CFCH}=\text{CH}_2$ Systems

In Table VII appear polymers prepared by combining $\text{CF}_2=\text{CF-CH}=\text{CH}_2$ (56) with ethylene, propylene, and butene-1 in the presence of Ziegler catalysts. Some of the polymers so obtained warranted

evaluation. Test results appear in Table XII. While the results were comparatively good, these systems did not have sufficient promise to indicate further investigation.

5. Fluorohydro Diene Systems, Misc.

In Table VIII appear some diene systems which were studied briefly.

2. Continued Work on Promising Systems

a. Discussion

Two systems in the "immediate range" class showed enough promise to justify a concerted effort at attaining optimum system properties through composition study and recipe development. These were both based on the highly reactive diene, $\text{CF}_2=\text{CFCH}=\text{CH}_2$. In both cases problems of excessive microgel content and scorch during fabrication had to be overcome.

b. Experimental

1. $\text{CH}_2=\text{CHCH}=\text{CH}_2/\text{CF}_2=\text{CFCH}=\text{CH}_2$ (3/56) Copolymers

Recipe and composition studies appear in Tables IX and X. From the evaluation data it was concluded that optimum properties were obtained at 13/87 combined mole ratio. Anomalous Gehman curves were caused by 1st order transitions occurring during the determination. This was alleviated by modification with $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CF}_3$ or $\text{C}_3\text{F}_7\text{CH}_2\text{OCOCH}=\text{CH}_2$. See runs 8071-8-1 and 7924-31-2, Tables IX and XII. Again, this system had comparatively good properties, but in general offered only marginal, if any, advantages over existing materials such as Neoprene. It was abandoned in favor of more promising "long range" systems.

2. $\text{CF}_2=\text{CHCF}=\text{CH}_2/\text{CF}_2=\text{CFCH}=\text{CH}_2$ (51/56) Copolymers

This system, which offered the best balance of properties of all materials studied under the aforementioned earlier contracts at M.W. Kellogg, was prepared in a 25 lb. lot for detailed curing and evaluation studies by the QMC as well as other branches of the armed services. The work was done under a separate contract (O.I. 3108-59) but involved project personnel, hence the results are summarized here. Recipe studies appear in Table XI. Early samples submitted to QMC for evaluation were highly cross-linked and difficult to compound. A recipe was developed which was controllable, yet yielded gel-free polymer in a stable latex at high conversion. Monomer syntheses were carried out in the laboratory (See Table II.) The

polymerization was upscaled rather abruptly from 60cc ampoules to a 5 gal. autoclave with a 1 litre autoclave run intervening. The large scale runs were carried out in the 3M Central Research Pilot Plant. Disappointingly poor yields obtained in the precursor conversions made it necessary to re-order precursors from Peninsular ChemResearch, Inc. and repeat the entire process before enough polymer to fill the order could be obtained. The polymerization recipe finally employed in two 5 gal. autoclave runs was as follows:

Monomers	100 parts
H ₂ O	200 parts
TDDM (Modifier)	0.6 parts
K ₂ S ₂ O ₈	0.2 parts
K ₂ HPO ₄	3.0 parts
C ₇ F ₁₅ COONH ₄	6.0 parts
Reaction Temp.	40° C.
Reaction Time	20 hrs.
Conversion	70%

The cure employed by C. B. Griffis of QMR & E Center on this material and the properties on the cured stocks obtained therefrom appear below:

Cure

51/56 raw gum	100 parts
Stearic acid	.5
ZnO	5
Philblack HAF	30
TP 90 B (plasticizer)	10
Di Cup	4
30 Minutes @ 307°F	

Properties

Gehman T ₁₀	-38°C
ASTM Fluid 3 swell	16%
TR ₁₀	-36°C
TR ₇₀	+70°C
F300	1700
Hardness Shore A	51
F break	2600 psi
Elongation	380%

3. Evaluation Data

Elastomer evaluation data obtained on those immediate range systems selected for forwarding to QMR & E Center appear in Table XII.

C. Polymerization Research - Long Range

1. Exploratory Polymerizations

a. Discussion

The fluorocarbon polymer chain is inherently stiff, too stiff for good low temperature properties, e.g., T_g for the $-\text{CF}_2-\text{CF}_2-$ chain comprising polytetrafluoroethylene is ca 80°C . In fluorocarbon polymers prepared by addition polymerization, rubbery properties have been achieved through compromise-dilution of the CF_2-CF_2 chain with CH_2 groups. The commercial elastomers Kel-F 5500 ($\text{CH}_2=\text{CF}_2/\text{CF}_2=\text{CFC1}$) and FLUOREL ($\text{CH}_2=\text{CF}_2/\text{CF}_2=\text{CFCF}_3$) were achieved through compromise between the "fluorocarbon" characteristics, i.e., thermal stability, chemical-solvent resistance, and stiff but non-interacting chains; and "hydrocarbon" characteristics (i.e. comparative thermal instability, vulnerability to oxidative and solvent attack) and flexible chains with freely rotating segments necessary for elastomeric properties. In Kel-F 5500 and FLUOREL, this compromise is such that both materials are somewhere between hydrocarbons and fluorocarbons in all respects with a definite leaning toward the fluorocarbon side -(particularly in the case of FLUOREL). This leaning hurts chiefly in low temperature properties. Experiments to date have shown that attempts to become more hydrocarbonlike out of deference to low-temperature serviceability have resulted in rapid degeneration of the desirable fluorocarbon features.

Condensation polymers, silicones, and other systems prepared under previous QM contracts and elsewhere have shown the soundness of the principle of introducing heteroatoms about whose bonds rotation of adjoining chain segments is facilitated. UNFORTUNATELY, CONVENTIONAL APPROACHES TO THE INTRODUCTION OF HETEROATOMS INTO BACKBONES, BY THEIR NATURE, OR BY THE RESTRICTIONS IMPOSED BY FLUOROCARBON CHEMISTRY, COMPLETELY MISS THE MOST SALIENT POINT, WHICH IS THAT BACKBONE HETEROATOMS MUST HAVE THE SAME CHARACTER THAT THEY HAVE WHEN INCORPORATED INTO SIMPLE, COMPLETELY FLUORINATED MOLECULES. Thus, a backbone nitrogen must not be amine-like but rather a "Nitride" nitrogen as in 3M's FC-43 which has the structure $(\text{C}_4\text{F}_9)_3\text{N}$. Likewise, backbone oxygens must not be "ether" oxygens but rather "Oxide" oxygens as in FC-75, a high temperature stable fluid containing the linkage $-\text{CF}_2-\text{O}-\text{CF}_2-$. Both FC-43 and FC-75 are utterly lacking in amine or ether properties, respectively. In the past, comparative thermal-oxidative instability and frequently great susceptibility to hydrolytic attack by acids and bases has been encountered. Lopsided structures offer no advantage, e.g., $-\text{CH}_2-\text{O}-\text{CH}_2-$ is bad, $-\text{CH}_2-\text{O}-\text{CF}_2-$ is worse.

The "long range" research reported below has had the objective of finding new reactions which can be used to put "nitride" nitrogens and/or "oxide" oxygens as well as other heteroatoms into the completely fluorinated backbones of high polymers.

b. Experimental

In Table XIII appear exploratory polymerizations following the objectives set forth above. Because of the relative emphasis which has been placed on nitroso polymerizations, all work in this category appears below. It will be noted that fluorocarbon aldehydes were polymerized in conjunction with other monomers in attempts to produce elastomeric polymers. Homopolymerization of fluorocarbon aldehydes is well known, having been discovered in these laboratories some years ago. Polymerization occurs across the carbonyl group and gives a polymer which is either amorphous or crystalline, depending upon whether anionic or cationic initiation is employed. These polymers are thermally unstable due to the presence of the hydrogen on the ex-carbonyl carbon. By studying the aldehyde polymerization, it is hoped that techniques can be found whereby fluorocarbon ketones and acid fluorides, as well as carbonyl fluoride itself, can be made to undergo polymerization.

2. Nitroso Polymerization - CF₃NO/C₂F₄ (24/127)
Copolymers

a. Discussion

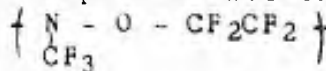
In the work described below, the writers have been able to prepare a considerable variety of polymers containing the N-O linkage in the backbone. Inasmuch as both the nitrogen and oxygen are attached to perfluoroalkyl groups, they are of the aforementioned nitride and oxide types. This fact undoubtedly accounts for surprisingly high stability of the bond connecting the nitrogen and oxygen in the structure.

The system CF₃NO/C₂F₄ represents the first true fluorocarbon elastomer and conclusively demonstrates the soundness of the principle of incorporating heteroatoms whose bonds have low rotational energy barriers into the backbone of a high molecular weight polymer.

b. Experimental

The system CF₃NO/C₂F₄ has thus far been the most promising of the nitroso polymers and has received the most emphasis during the current period.

Elemental analysis, IR and NMR spectra have shown the structure of the copolymer to be



1. Polymerization Techniques

In the early stages of development of this system, approximately 60 polymerizations were run in an attempt to determine optimum conditions for the polymerization. The results of these experiments were inconclusive due to impure monomer. When pure monomer became available, these experiments were repeated. Therefore, only the latter set of experiments will be reported.

The copolymer has been prepared in solution, emulsion, and suspension systems as well as in bulk. Only one solvent, $(C_4F_9)_3N$, was found suitable for obtaining polymer of molecular weight and conversion comparable to a bulk polymerization (Table XIV). The optimum monomer concentration for polymerization in this solvent was found to be in the range of 30 - 50% (Table XV). The results of some emulsion, suspension, and bulk polymerizations are shown in Table XVI.

Molecular weight of the polymer decreases with increasing temperature (Table XVII), and is highest for a 1:1 charged mole ratio (Table XVIII). The addition of catalysts has little effect on the polymerization while amines, phenols, and free radicals such as NO, NO₂, and DPPH lower the molecular weight (Table XIX). A study of the effect of additives on the polymerization is complicated since many substances (bases, Hg, C, etc.) react with CF₃NO itself producing chiefly CF₃NO₂ and $CF_3N=N-CF_3$.

2. Vulcanization and Properties

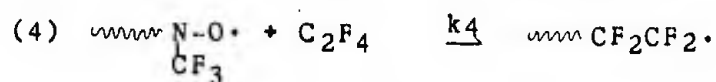
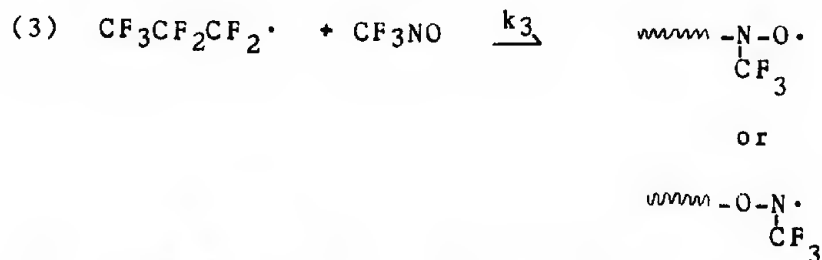
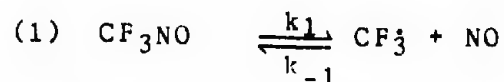
Molecular weight values (determined by light scattering) of the copolymer run as high as 2×10^6 . The relationship between $\langle \eta \rangle$ and MW is shown in Figure 1, and the MW distribution in Figure 2.

Typical gumstock properties of CF₃NO/C₂F₄ copolymer along with the curing recipe developed by the QMR & E Center appear in Table XX and Figure 3.

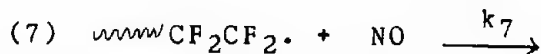
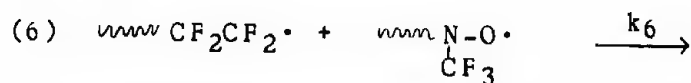
3. Polymerization Kinetics/Postulated Mechanisms

The dependence of initial polymerization rate on the concentration of CF₃NO and C₂F₄ was determined approximately by polymer isolation techniques. The rates obtained (Table XXI) best fit a reaction which is first order in [CF₃NO] and one-half order in [C₂F₄] (Figure 4). The fact that the polymerization rate was reproducible using different batches of CF₃NO (Runs 1 & 2) is strong evidence against a mechanism in which initiation is due to impurities present in the monomer. This conclusion is supported by another experiment in which the two monomers were allowed to polymerize for a time (gas phase) and then half of the remaining unreacted monomer mixture transferred to another vessel. Further polymerization occurred at the same rate in both vessels.

Another possible mechanism involves the homolytic cleavage of CF_3NO . According to this mechanism, the polymerization would involve the following steps.



Termination could occur by one or more of the following reactions:



Under steady state conditions,

$$(8) \frac{d(\text{CF}_3^\cdot)}{dt} = 0$$

so that

$$(9) k_1 (M_1) = k_{-1} (\text{CF}_3^\cdot)(\text{NO}) + k_2 (\text{CF}_3^\cdot)(M_2)$$

or

$$(10) (\text{CF}_3^\cdot) = \frac{k_1(M_1)}{k_{-1}(\text{NO}) + k_2(M_2)} \quad \begin{array}{l} \text{where } M_1 = \text{CF}_3\text{NO} \\ \text{and } M_2 = \text{C}_2\text{F}_4 \end{array}$$

Because the polymer is known to be alternating, under steady state conditions,

(11) $k_3(M_2^\cdot)(M_1) = k_4(M_1^\cdot)(M_2)$ where M_1^\cdot is a chain ending in $\begin{array}{c} -\text{N}-\text{O}^\cdot \\ | \\ \text{CF}_3 \end{array}$ or $\begin{array}{c} -\text{O}-\text{N}^\cdot \\ | \\ \text{CF}_3 \end{array}$ and M_2^\cdot is a chain ending in $-\text{CF}_2\text{CF}_2^\cdot$

so that

$$(12) \quad \frac{(M_2^\cdot)}{(M_1^\cdot)} = \frac{k_4}{k_3} \cdot \frac{(M_2)}{(M_1)}$$

or

$$(13) \quad \frac{(M_1^\cdot)}{(M_2^\cdot)} = \frac{k_3}{k_4} \cdot \frac{(M_1)}{(M_2)}$$

If termination occurs by reaction (5), then

$$(14) \quad k_2(\text{CF}_3^\cdot)(M_2) = k_5(M_2^\cdot)^2$$

or

$$(15) \quad (M_2^\cdot) = \left[\frac{k_2}{k_5} (\text{CF}_3^\cdot)(M_2) \right]^{1/2}$$

Substituting the value of (CF_3^\cdot) from (10),

$$(16) \quad (M_2^\cdot) = \frac{(k_1 k_2 / k_5)^{1/2} (M_1)^{1/2} (M_2)^{1/2}}{[k_{-1}(\text{NO}) + k_2(M_2)]^{1/2}}$$

The rate of polymerization is given by

$$(17) \quad \text{Rate} = k_3 (M_2^\cdot)(M_1)$$

Substituting the value of (M_2^\cdot) from 16,

$$(18) \quad \text{Rate} = \frac{k_3 (k_1 k_2 / k_5)^{1/2} (M_1)^{3/2} (M_2)^{1/2}}{[k_{-1}(\text{NO}) + k_2(M_2)]^{1/2}}$$

and the initial rate will be proportional to $[\text{CF}_3\text{NO}]^{3/2}$ and independent of $[\text{C}_2\text{F}_4]$.

If termination occurs by reaction (6),

$$(19) \quad k_2(\text{CF}_3^\cdot)(M_2) = k_6 (M_2^\cdot)(M_1^\cdot)$$

Substituting the value of (M_1^\cdot) from (13),

$$(20) \quad k_2(\text{CF}_3^\cdot)(M_2) = \frac{k_3 k_6}{k_4} \cdot \frac{(M_1)}{(M_2)} (M_2^\cdot)^2$$

$$(21) \quad (M_2^{\cdot}) = \left(\frac{k_2 k_4}{k_3 k_6} \right)^{1/2} \frac{(M_2)(CF_3^{\cdot})^{1,2}}{(M_1)^{1/2}}$$

Substituting the value of (CF_3^{\cdot}) from (10).

$$(22) \quad (M_2^{\cdot}) = \left(\frac{k_2 k_4}{k_3 k_6} \right)^{1/2} \frac{(M_2)}{[k_{-1}(NO) + k_2(M_2)]^{1/2}}$$

(23) Rate of polymerization =

$$k_3 \left(\frac{k_2 k_4}{k_3 k_6} \right)^{1/2} \frac{(M_2)(M_1)}{[k_{-1}(NO) + k_2(M_2)]^{1/2}}$$

and the initial rate is proportional to $[C_2F_4]^{1/2} [CF_3NO]$

If termination occurs by (7),

$$(24) \quad k_7 (M_2^{\cdot})(NO) = k_2 (CF_3^{\cdot})(M_2)$$

or

$$(25) \quad (M_2^{\cdot}) = \frac{k_2}{k_7} \frac{(CF_3^{\cdot})(M_2)}{(NO)}$$

Substituting this value into the rate equation, (17).

$$(26) \quad \text{Rate of polymerization} = k_3 \frac{k_2}{k_7} \frac{(CF_3^{\cdot})(M_2)(M_1)}{(NO)}$$

Substituting the value of (CF_3^{\cdot}) from (10).

$$(27) \quad \text{Rate of polymerization} = \frac{k_1 k_2 k_3 (M_2)(M_1)^2}{k_7 (NO) [k_{-1}(NO) + k_2(M_2)]}$$

The value of (NO) is given approximately by

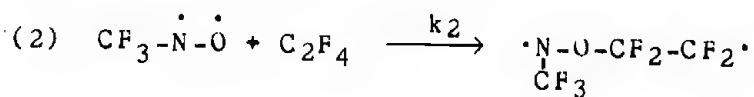
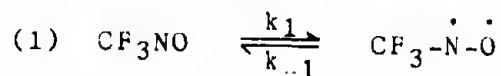
$$(28) \quad (NO) \approx k_1 (M_1) \dagger$$

The initial rate will then be proportional to $[CF_3NO]$ and to something less than the 1st power of $[C_2F_4]$

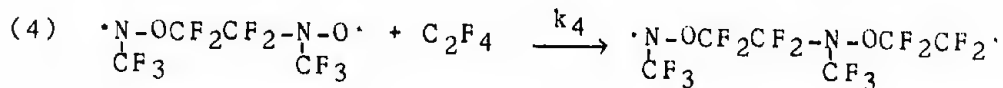
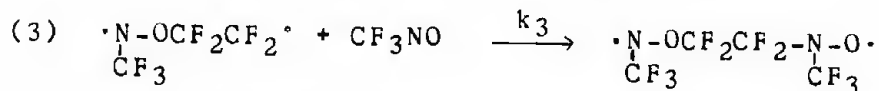
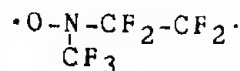
While the rate data fit this mechanism fairly well, particularly for termination by reaction (6), there are serious objections to it. CF_3NO , in the absence of light, is quite stable. The IR spectra and vapor chromatographic analyses of pure samples kept at room temperature for as long as two months do not show any change. Attempts to detect cleavage products by means of triphenylmethyl and diphenylpicrylhydrazyl have been unsuccessful.

Another possible mechanism is one in which initiation is due to the radical character of the nitroso compound itself, i.e., some of the molecules of the nitroso compound exist in the triplet or biradical state as postulated by Lewis and Kasha,¹

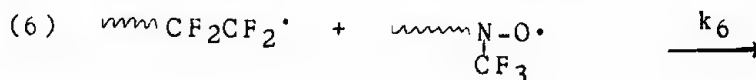
A partial kinetic scheme for this mechanism is:



or



Possible termination steps include



This scheme is not complete. It is not known if initiation occurs at both sites of the biradical. Since the polymer chains contain unpaired electrons, some other type of termination must eventually occur.

By derivations similar to those used for the cleavage mechanism the polymerization rate will be proportional to $[\text{CF}_3\text{NO}]^{3/2} [\text{C}_2\text{F}_4]^{0 \text{ to } .5}$ and $[\text{CF}_3\text{NO}] [\text{C}_2\text{F}_4]^{.5 \text{ to } 1}$ for termination by (5) and (6) respectively. Similar calculations for initiation at both sites of the biradical result in greater rate dependencies on $[\text{CF}_3\text{NO}]$ and $[\text{C}_2\text{F}_4]$. This biradical mechanism is the most plausible on the basis of existing data and is compatible with the stability of CF_3NO and the formation of $\text{CF}_3-\text{N}-\text{Q}$ rather than CF_2-CF_2

polymer under certain conditions, (usually higher temperatures.)

1. G. N. Lewis and M. Kasha, J. Am. Chem. Soc., 67, 994 (1945).

3. Nitroso Polymerizations - Other Systems Based on CF₃NO

a. Discussion

CF₃NO does not homopolymerize. However, its copolymerization is quite general. With careful monomer purification, i.e., exclusion of radical transfer agents, and selection of polymerization conditions a useful variety of high copolymers can be prepared.

b. Experimental

1. CF₃NO Olefin Copolymerizations

Copolymerizations of CF₃NO with ethylenically-unsaturated materials are listed in Table XXII. The reactivity of CF₃NO with substituted ethylenes follows the order C₂F₄ > C₂F₃H > C₂F₂H₂ > C₂FH₃ > C₂H₄. Polymers obtained by copolymerization through -CH=CH₂ double bonds are, as predicted, comparatively unstable.

2. CF₃NO/Diene Copolymerizations

CF₃NO reacts readily with dienes. In preliminary screening experiments with the following compounds,

- 1) CH₂=CHCH=CH₂
- 2) CH₂=C(C₁)CH=CH₂
- 3) CH₂=C(CH₃)CH=CH₂
- 4) CH₂=C(CH₃)C(CH₃)=CH₂
- 5) CH₃CH=CH-CH=CH₂
- 6) CH₃CH=CHCH=CHCH₃
- 7) CF₂=CFCH=CH₂
- 8) CF₂=CHCF=CH₂
- 9) CH₂=C(OCH₂CF₃)CH=CH₂

only (7), 1,1,2-trifluorobutadiene was found to react with CF₃NO to give polymer. The other dienes yielded Diels-Alder adducts. The 1:1 copolymer of CF₃NO/CF₂=CF-CH=CH₂ was found to have a Tg of -55°C., which led to an extensive study of the reaction. However, the results of this study of polymerization conditions and modifiers in the reaction were inconclusive due to the reaction being extremely rapid and uncontrollable.

The experiments have been grouped (Table XXIII) according to the results obtained, i.e., polymerization, cyclic adduct formation, and detonation. No definite factor seemed common to any particular one of the three phenomena.

4. Nitroso Polymerizations - Nitrosos Other Than CF₃NO

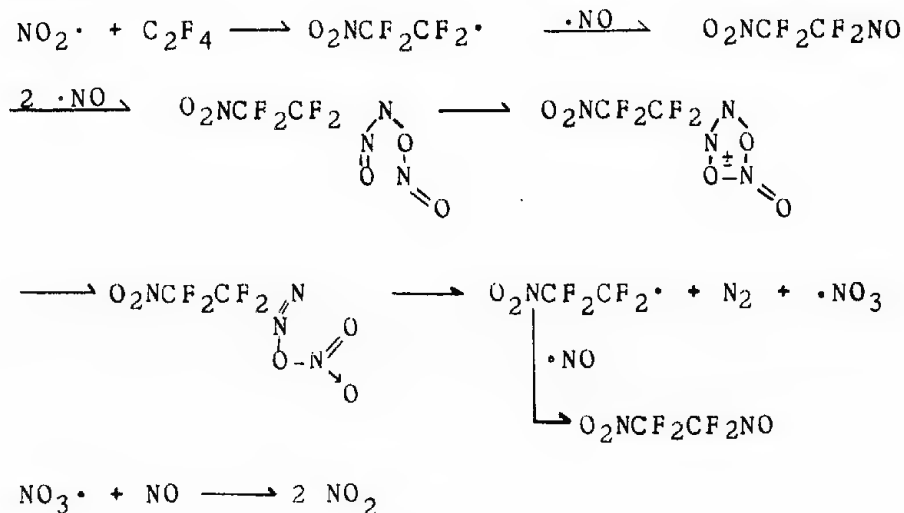
a. Discussion

Insofar as the attainment of desirable properties in the nitroso field is concerned, the information obtained to date indicates that modification of the nitroso monomer, which of course means alteration of the side group rather than alteration of the comonomer which would directly affect the backbone, is to be preferred. Of particular interest are the copolymers obtained with O₂NCF₂CF₂NO and ClCF₂CF₂NO as copolymerized with tetrafluoroethylene. Copolymerizations involving nitroso compounds other than CF₃NO are listed in Table XXIV.

b. Experimental

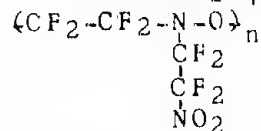
1. O₂NCF₂CF₂NO Copolymerizations

When nitric oxide is combined with C₂F₄ in the vapor phase, O₂NCF₂CF₂NO (136) is formed by the following postulated mechanism.



Preparative work is summarized in Table II. Nitro-nitroso adducts have also been obtained with CF₂=CFC1, CF₂=CCl₂ and C₃F₆. This work is dealt with in detail in the quarterly progress reports and is the subject of a paper by one of the authors.* As a result of this work, (136) becomes quite readily available for study.

The (136)/C₂F₄ copolymer has the interesting structure



*G. H. Crawford, "Nitric Oxide Addition to Tetrafluoroethylene - Copolymerization of the Adducts." J. Poly. Sci. (in press)

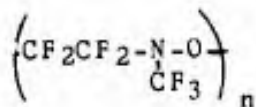
In spite of the dangling $-NO_2$, its T_g is $-41^\circ C$. Its solvent resistance is comparable to CF_3NO/C_2F_4 .

2. $C_1CF_2CF_2NO$ Copolymerizations

The chloronitroso has been the subject of some synthetic work by Dr. J. D. Park who has developed a method which promises to make this material quite readily available. $C_1CF_2CF_2NO/C_2F_4$ copolymer is surprisingly like CF_3NO/C_2F_4 copolymer. Its T_g is $-48^\circ C$. Its solvent resistant properties are comparable to CF_3NO/C_2F_4 and it is stable in air to at least $300^\circ F$.

5. Structure - Property Relationships Among Nitroso Polymers

The systems which illustrate the effect of placement of moieties other than F atoms in the basic structure,




are shown in Table XXV. All of the systems shown are elastomeric. Since low temperature serviceability is a prime objective, T_g is the property treated. Measurements were made on materials of MW such that $T_g \neq k \bar{M}_w$. Although the table is incomplete, the results thus far show that the nature of the side chain resulting from the nitroso moiety has a comparatively small effect, while modification of the olefin moiety has a large effect. A single H in the backbone of the polymer is disastrous in its effect upon low temperature serviceability.

[Handwritten signature]

[Handwritten signature]

[Handwritten signature]

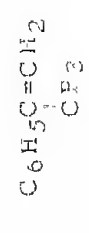

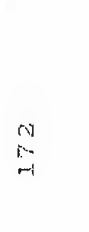
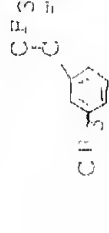
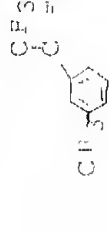
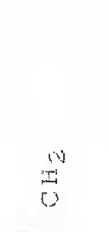
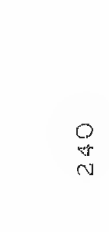
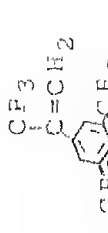
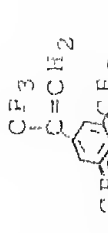

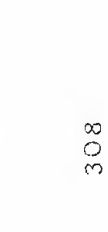
COMPLETE MONOMER LIST

Monomer	Molecular Weight	Density	Boiling Point	Preparation
1 $CF_2=CFC1$	116	1.61	-27°	**
2 $CF_2=CH_2$	64	1.392	-84°	**
3 $CH_2=CHCH=CH_2$	54	0.741	-3°	**
4 $CF_2=CFCF=CF_2$	162	1.671	6°	$CF_2=CFC1 + CF_2CFC1 \xrightarrow{Zn} CF_2=CFCF=CF_2$ $CF_2=CFCFC1CF_2Cl \xrightarrow{Zn} CF_2=CFCF=CF_2$
5 $CH_2=CH(CH_3)CH=CH_2$	68	0.683	34°	**
6 $CH_2=C(CH_3)_2$	56	0.71	-6°	**
7 $CF_2CF=CFCF_2$	162	1.841	1°	$CF_2=CFC1 \xrightarrow{500^\circ} \begin{matrix} CF_2CFC1 \\ \\ CF_2CFC1 \end{matrix}$
8 $CH_2=CHC1$	62	0.961	-14°	**
9 $CF_2=CC1_2$	133	1.661	19°	**
10 $CH_2=CHCH_3$	42	0.61(-47°)	-47°	**
11  -CH=CH ₂	104	0.913	145°	**
12 $CH_2=CC1_2$	97	1.23	32°	**
13 $CH_2=CC1CH=CH_2$	88	0.93	59°	**
14 $CF_2=CFCF_3$	150	1.711	-28°	**
15 $CF_2=CFCN$	107	1.481	16°	$CF_2C1CF=CF_2 \xrightarrow{NH_3} CF_2=CFCN$
16 $CH_2=CHCN$	53	0.803	78°	**
17 $CH_2=CHCO_2C_4H_9(n)$	128	0.93	145°	**
17A $CH_2=CHCO_2CH_3$	86	0.953	80°	**
18 $CF_2=CHC1$	98	1.471	-17°	**


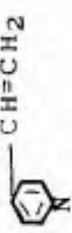
Monomer	Molecular Weight	Density	Boiling Point	Preparation
19 CF ₃ CCl=CClCF ₃	233	1.57 ³	67°	Cl ₂ C=CClCCl=CCl ₂ $\xrightarrow{\text{SbF}_3\text{Cl}_2}$ [CCl ₃ CCl=CClCCl ₃] $\xrightarrow{\text{SbF}_3}$ CF ₃ CCl=CClCF ₃
20 CF ₃ C≡CCF ₃	162	1.54 ¹	-24°	CF ₃ CH=CH-CF ₃ $\xrightarrow{\text{Br}_2}$ CF ₃ CHBrCFBrCF ₃ $\xrightarrow{\text{KOH}}$ CF ₃ CH=CBBrCF ₃ $\xrightarrow[\text{-HBr}]{\text{Br}_2}$ CF ₃ CBBr=CBBrCF ₃ $\xrightarrow{\text{Zn}}$ CF ₃ C≡CCF ₃
21 CF ₂ =CFH	82	1.64 ²	-51°	**
22 CH ₂ =CFC1	80	1.25 ¹	-22°	CH ₂ =CCl ₂ $\xrightarrow{\text{Br}_2}$ CH ₂ BrCCl ₂ Br $\xrightarrow{\text{SbF}_3}$ CH ₂ ClCCl ₂ F $\xrightarrow{\text{Zn}}$ CH ₂ =CFC1
23 CF ₃ CH=CHCF ₃ (cis)	164	1.59 ¹	32°	CCl ₂ =CClCCl=CCl ₂ $\xrightarrow{\text{SbF}_3\text{Cl}_2}$ CF ₃ CCl=CClCF ₃ $\xrightarrow{\text{Zn}}$ CF ₃ C≡CCF ₃ $\xrightarrow{\text{H}_2}$ CF ₃ CH=CHCF ₃
24 CF ₂ =CF ₂	100	1.90 ²	-78°	CF ₂ BrCF ₂ Br $\xrightarrow[\text{THF}]{\text{Zn}}$ CF ₂ =CF ₂
25 CF ₃ CH=CHCF ₃ (trans)	164	1.57 ¹	6-9°	CCl ₂ =CClCCl=CCl ₂ $\xrightarrow{\text{SbF}_3\text{Cl}_2}$ CF ₃ CCl=CClCF ₃ $\xrightarrow[\text{HC}\equiv\text{O}]{\text{Zn}}$ $\xrightarrow{\text{NH}_2}$ CF ₃ CH=CHCF ₃
26 CH ₂ =CHC6H ₄ CH=CH ₂	130	0.91 (40°C)	31° (m.p.)	**
27 CF ₃ C=CH ₂ CH ₃	110	1.19 ¹	6°-7°	CF ₃ CO ₂ C ₂ H ₅ $\xrightarrow[\text{CH}_3]{\text{CH}_3\text{MgBr}}$ CF ₃ -C(CH ₃)-OH P ₂ O ₅ $\xrightarrow{\text{CF}_3-\text{C}=\text{CH}_2}$
28 CH ₂ =CFCH=CH ₂	72	0.88 ¹	12°	HC≡CCH=CH ₂ $\xrightarrow[\text{Hg salts}]{\text{HF}}$ CH ₂ =CFCH=CH ₂
29 (CF ₃) ₂ C=CF ₂	200	1.79 ¹	7°	HCF ₂ -CCl-CF ₃ $\xrightarrow[\text{CF}_3]{\text{Zn}}$ (CF ₃) ₂ C=CF ₂

Monomer	Molecular Weight	Density	Boiling Point	Preparation
44 $\text{CF}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$	104	1.09 ¹	38°	$\text{CF}_2\text{BrCH}(\text{CH}_3)\text{CHBrCH}_3 \xrightarrow{\text{R}_3\text{N}}$ $\text{CF}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$
45 $\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	86	0.9 (20°C)	72°	**
45A $\text{CH}_2=\text{CHOCCH}_2\text{CH}_2\text{CH}_3$	114			**
45B $\text{CH}_2=\text{CHOCCH}_2\text{C}_1$	120			**
46 $\text{C}_6\text{H}_5\text{CH}=\text{CHCOOCH}_3$	162	1.09 ³	262°	**
47 $\text{CH}_2=\text{CHOC}_2\text{H}_5$	72	0.75 ³	36°	**
48 $\text{CH}_2=\text{CHOCCH}_2\text{CH}_2\text{C}_1$	106	1.05 ³	108°	**
49 $\text{CH}_2=\text{CHOCCH}_2\text{CH}(\text{CH}_3)_2$	100	0.76 ³	83°	**
50 $\text{CF}_2=\text{C}(\text{CH}_3)\text{CF}=\text{CH}_2$	122	1.10 ³	51°	$\text{CF}_2\text{BF}_2\text{CH}(\text{CH}_3)\text{CFBr}-\text{CH}_3$ $\text{CF}_2=\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CF}=\text{CH}_2 \xrightarrow{(\text{C}_4\text{H}_9)_3\text{N}}$
51 $\text{CF}_2=\text{CHCF}=\text{CH}_2$	108	1.28 ¹	17-19°	$\text{CF}_2\text{BrCH}_2\text{CFBrCH}_3$ $\text{CF}_2=\text{CHCF}=\text{CH}_2 \xrightarrow{(\text{C}_4\text{H}_9)_3\text{N}}$
52 $\text{C}_2\text{H}_5\text{O}_2\text{CCH}=\text{CHCO}_2\text{C}_2\text{H}_5$ (trans)	172	1.05 ³	218°	**
53 $\text{C}_2\text{H}_5\text{O}_2\text{CCH}=\text{CHCO}_2\text{C}_2\text{H}_5$ (cis)	172	1.16	205°	**
54 $\text{CH}_2=\text{CH}-\text{Si}(\text{OC}_2\text{H}_5)_3$	190	0.93	160°	**
55 $\text{CF}_2=\text{CFC}_6\text{H}_5$	158	1.22 ³	68°/75mm	**
56 $\text{CF}_2=\text{CF}-\text{CH}=\text{CH}_2$	108	1.31	5-8°	$\text{CF}_2\text{BrCFClCH}_2\text{CH}_2\text{Br} \xrightarrow{\text{KOH}}$ $\text{CF}_2\text{BrCFClCH}=\text{CH}_2 \xrightarrow[\text{BuOH}]{\text{Zn}}$ $\text{CF}_2=\text{CFCH}=\text{CH}_2$
57 $\text{CH}_2=\overset{\text{CN}}{\underset{\text{CN}}{\text{C}}}-\text{CF}_3$	120	1.32 ¹	73-78°	$\text{CF}_3\overset{\text{CH}_3}{\underset{\text{CN}}{\text{C}}}\text{O}_2\text{CCH}_3 \xrightarrow{\Delta} \text{CH}_2=\overset{\text{CN}}{\underset{\text{CN}}{\text{C}}}-\text{CF}_3$

Monomer	Molecular Weight	Density	Boiling Point	Preparation
58 $CF_2=CFCH=CF_2$	144	1.441	15°	$CF_2=CFCl \xrightarrow{Br_2} CF_2BrCFClBr \xrightarrow{CH_2=CF_2} CF_2BrCFClCH_2CF_2Br \rightarrow CF_2BrCFClCH=CF_2 \rightarrow CF_2=CFCH=CF_2$
59 $CH_3(CH_2)_{16}COOCH=CH_2$	310			**
60 $CF_2Cl(CFC1CF_2)_2CF=CF_2$	399		92°C/8mm	$CF_2Cl(CFC1CF_2)_2CFC1-CF_2Cl \xrightarrow{Zn} CH_3COOH$
61 $CF_2C1CF=CFCF_2C1$	233		64-66°	$CF_2C1CC1IF \xrightarrow{hv} CF_2C1CFC1CFC1CF_2C1$ $\xrightarrow{Zn, HOAc} CF_2C1-CF=CFCF_2C1$
62 $CF_2CFC=CF_2$	158	1.273	37-38°	$CF_2C1CC1FI + CF_2=CHCH_3 \xrightarrow{1. KOH, 2. Zn} CF_2C1CFC1CH(CH_3)CF_2I$ $CF_2=CFC(CH_3)=CF_2$
63 $CH_2=CH-(C_6H_4)_2-(CF_3)_2$ 3,4 & 3,5 isomers	240	1.353	60-70°C/20mm	$C_6H_4(CF_3)_2 \xrightarrow{hv, Cl_2} C_6H_4(CF_3)_2 \xrightarrow{LA} C_6H_4(CF_3)_2$ $C_6H_4(CF_3)_2 \xrightarrow{BuLi, OH} C_6H_4(CF_3)_2$ $CH_3CHO \xrightarrow{H^+} C_6H_4(CF_3)_2$ $(CF_3)_2C=CH_2 \xrightarrow{P_2O_5} C_6H_4(CF_3)_2$
64 $CH_2=CCO_2CH_3$	154		107-8°	$CH_2=C(CN)CF_3 \xrightarrow{H_2O, NaOH} CH_2=C(COOH)CF_3$ $CH_2=CCO_2CH_3$
65 $CF_2=CFC_2H_2CH=CH_2$	122	1.043	38°	$CF_2BrCFClBr + CH_3CH=CH_2 \xrightarrow{1. KOH, 2. Zn} CF_2BrCFClCH_2CHBrCH_3$ $CF_2=CFC_2H_2CH=CH_2$

Monomer	Molecular Weight	Density	Boiling Point	Preparation
66 (CN) ₂	52	0.87	-20°	CuSO ₄ + KCN → Cu(CN) ₂ Cu(CN) ₂ $\xrightarrow{\text{aqFeCl}_3}$ (CN) ₂
67 CF ₃ CF=CH ₂	114	1.31	-34 to -26°	C ₂ F ₅ CO ₂ H → C ₂ F ₅ CO ₂ C ₄ H ₉ → C ₂ F ₅ CH ₂ OH $\xrightarrow{\text{Zn/HOAc}}$ C ₂ F ₅ CH ₂ OTs → C ₂ F ₅ CH ₂ I $\xrightarrow{\text{Zn/HOAc}}$ CF ₃ CF=CH ₂
68 CF ₂ =CFCH=CFH	126	1.441	17°	CF ₂ =CFC1 $\xrightarrow{\text{BzI}_2}$ CF ₂ BrCFC1Br $\xrightarrow{\text{CH}_2=\text{CHF}}$ CF ₂ BrCFC1CH ₂ CH ₂ CFBr $\xrightarrow[2. \text{Zn}]{1. \text{KOH}}$ CF ₂ =CFCH=CHF
69 C ₆ H ₅ C=CH ₂ CF ₃	172	1.48-9°	148-9°	 $\xrightarrow[\text{Et}_2\text{O}]{\text{Mg}}$  $\xrightarrow{\text{CF}_3\text{COCH}_3}$ 
70 	240	1.35 30°C	58°C/20mm	 $\xrightarrow[\text{Et}_2\text{O}]{\text{Mg}}$  $\xrightarrow{\text{P}_2\text{O}_5}$ 
71 	308	1.453	59-61°/15mm	 $\xrightarrow[\text{Et}_2\text{O}]{\text{Mg}}$  $\xrightarrow{\text{P}_2\text{O}_5}$ 
72 CH ₂ =CHOCHF ₂ CF ₂ H	144	1.401	39°	CH ₃ -CH ₂ OH+CF ₂ =CF ₂ $\xrightarrow{\Delta}$ CH ₃ -CH ₂ -O-CF ₂ -CF ₂ H $\xrightarrow{\text{Cl}_2}$ CH ₃ -CHCl-O-CF ₂ -CF ₂ H $\xrightarrow{\text{KOH}}$ CH ₂ =CH-O-CF ₂ -CF ₂ H

Monomer	Molecular Weight	Density	Boiling Point	Preparation
73 $\text{Cl}(\text{CF}_2\text{CFCl})_2\text{CF}_2\text{CO}_2\text{CH}_2\text{CH}=\text{CH}_2$	403	1.62	100°/10mm	$\text{Cl}(\text{CF}_2\text{CFCl})_2\text{CF}_2\text{CO}_2\text{Na} + \text{Cl}-\text{CH}_2-\text{CH}=\text{CH}_2$ $\longrightarrow \text{Cl}(\text{CF}_2\text{CFCl})_2\text{CF}_2\text{CO}_2-\text{CH}_2-\text{CH}=\text{CH}_2$
73A $\text{Cl}(\text{CF}_2\text{CFCl})_3\text{CF}_2\text{CO}_2\text{CH}_2\text{CH}=\text{CH}_2$	519			Same procedure for this telomer ester as #73
74 $\text{CH}_2=\text{C}(\text{CF}_3)\text{CH}=\text{CH}_2$	122	1.211	35-6°	$\text{CF}_3-\overset{\text{O}}{\text{C}}-\text{CH}_3 + \text{CH}_2(\text{CO}_2\text{H})_2 \xrightarrow{\text{CF}_3}$ 1. red'n 2. P205 $\longrightarrow \text{CH}_2=\text{C}(\text{CF}_3)\text{CH}=\text{CH}_2$
75 $\text{CH}_2=\text{CHCH}_2\text{CO}_2\text{CF}_2(\text{CF}_2\text{CFCl})_2\text{CF}_2\text{O}_2\text{CCl}_2\text{CH}=\text{CH}_2$	520		160°/6mm	$\text{NaO}_2\text{CCF}_2(\text{CF}_2\text{CFCl})_2\text{CF}_2\text{COONa} +$ $\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl} \xrightarrow{\text{Et}_2\text{O}}$ $\text{CH}_2=\text{CH}-\text{CH}_2\text{O}_2\text{CCF}_2(\text{CF}_2\text{CFCl})_2\text{CF}_2\text{O}_2\text{CH}_2-\text{CH}=\text{CH}_2$
76 $\text{CF}_2=\text{CFCF}_2\text{CFCl}_2$	233		68°	$\text{CFCl}_2-\text{CF}_2-\text{CFCl}-\text{CF}_2\text{Cl} \xrightarrow[\text{EtOH}]{\text{Zn}}$ $\text{CFCl}_2-\text{CF}_2-\text{CF}=\text{CF}_2$
77 $\text{CF}_2=\text{CH}-\overset{\text{CF}_3}{\text{C}}=\text{CH}_2$	158	1.51	31°	$\text{CF}_3\text{CO}_2\text{C}_2\text{H}_5 \xrightarrow[2. -\text{H}_2\text{O}]{1. \text{CH}_3\text{MgBr}}$ $\text{CH}_2=\text{C}(\text{CF}_3)\text{CH}_3$ $\text{CCl}_3\text{Br} \longrightarrow \text{CCl}_3\text{CH}_2\text{C}(\text{Br})(\text{CF}_3)\text{CH}_3 \xrightarrow[2. -2\text{H}^+]{1. \text{SbF}_3\text{Cl}_2}$ $\text{CF}_2=\text{CHC}(\text{CF}_3)=\text{CH}_2$
77A $\text{CF}_3\text{CH}=\text{C}(\text{CF}_3)\text{CH}_3$	178	1.51	31°	Same procedure as above. Product is HF adduct of #77
78 $\text{CH}_2=\text{CHOCHF}_2\text{CHClF}$	160	1.243	73-75°	$\text{CF}_2=\text{CFCl} + \text{CH}_3-\text{CH}_2\text{OH} \longrightarrow \text{CH}_3-\text{CH}_2\text{O}-\text{CF}_2\text{CFHCl}$ $\text{Cl}_2 \xrightarrow{\text{hv}}$ $\text{CH}_3-\text{CHClO}-\text{CF}_2-\text{CFHCl}$ $\xrightarrow[\text{R}_3\text{N}]{\text{KOH}}$ $\text{CH}_2=\text{CH}-\text{O}-\text{CF}_2-\text{CFHCl}$
78A $\text{CHCl}=\text{CHOCHF}_2\text{CHClF}$	194		120°-125°C	$\text{CH}_3\text{CH}_2-\text{O}-\text{CF}_2-\text{CFHCl} \xrightarrow[\text{amine}]{\text{KOH}}$ $\text{CHCl}=\text{CH}-\text{O}-\text{CF}_2-\text{CFHCl}$

Monomer	Molecular Weight	Density	Boiling Point	Preparation
79 $CF_3CH=CClCF_3$	198	1.67 ¹	31-33°	$CF_3-CBr=CF_3 \xrightarrow{Zn} CH_3COOH$ $CF_3-C\equiv C-CF_3 \xrightarrow{HCl}$ catalyst $CF_3-CH=CCl-CF_3$
80 $CF_3CF_2CF_2CHO$	198	1.50 ³	28-29°	**
81 $C_4F_9N=CF_2$	283	1.84 ¹	37-39°	$(C_4F_9)_3N \xrightarrow{\Delta} C_4F_9N=CF_2$
82 $CF_2=CFCF_2Cl$	166	1.71	8°	$C1CF_2CFC1CF_2CO_2Na \xrightarrow{\Delta} CF_2=CFCF_2C1$
83 	105	1.0; 0°C	79-82°C/29mm	**
84 	105		59°C/12mm	**
85 $CF_2=CFCF_2OCH_2CF_3$	230		55-56°	$CF_2=CFCF_2Cl + CF_3CH_2OH \xrightarrow{KOH}$ $CF_3CH_2OCF_2CFCF_2Cl \xrightarrow{KOH} CF_3CH_2OCF_2CF_2$
86 $CF_2=CC1CF=CF_2$	178			$CF_2Cl-CFC1_2 + CF_2=CC1_2 \xrightarrow{press}$ $CF_2Cl-CFC1-CC1_2-CF_2Cl \xrightarrow{Zn} CH_3COOH$ $CF_2=CF-CC1=CF_2$
87 $CF_2=CFCC1=CH_2$	142	1.03 ¹	49°	$CF_2Br-CFC1-CC1H-CH_2Cl \xrightarrow{KOH} alc$ $CF_2BrCFC1-CC1=CH_2 \xrightarrow{Zn} acid$ $CF_2=CF-CC1=CH_2$
88 $CF_2=CC1CH=CF_2$	160			M.S. did not support structure
89 $C1CF_2CFC1CF_2CO_2CH=CH_2$	273	1.51 ³	82°/94mm	$C1CF_2CFC1CF_2CO_2H + HC\equiv CH \xrightarrow{HgO}$ $C1CF_2CFC1CF_2CO_2CH=CH_2$

Monomer	Molecular Weight	Density	Boiling Point	Preparation
90 $\text{CF}_2=\text{CFCF}_2\text{CFCICF}_2\text{Cl}$	283		91°	$\text{CF}_2\text{Cl}-\text{CFC1}=\text{CF}_2 + \text{CF}_2=\text{CFC1} \xrightarrow{\text{Zn, EtOH}} \text{CF}_2\text{Cl}-\text{CFC1}-\text{CF}_2-\text{CFC1}-\text{CF}_2\text{Cl}$ $\text{CF}_2=\text{CF}-\text{CF}_2-\text{CFC1}-\text{CF}_2\text{Cl}$
91 $\text{CF}_2=\text{CFCF}_2\text{CF}_3$	200	1.751	0-1°	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CO}_2\text{Na} \xrightarrow{\Delta} \text{CF}_2=\text{CFCF}_2\text{CF}_3$
92 $\text{CF}_3\text{CH}=\text{CHCH}=\text{CHCF}_3$	190		87°	
93 $\text{CFC1}_2\text{CF}=\text{CH}_2$	146	1.353	55°	$\text{CH}_3-\text{CFC1}-\text{CC1}_3 \xrightarrow{\text{SbF}_5} \text{CH}_3\text{CFC1}-\text{CFC1}_2$ $\text{KOH} \rightarrow \text{CH}_2=\text{CF}-\text{CFC1}_2$
94 CF_3CHO	98		-19 to -18°	$\text{CF}_3\text{CH}(\text{OH})\text{OCH}_3 \xrightarrow{\text{P}_2\text{O}_5} \text{CF}_3\text{CHO}$
95 $\text{CF}_2=\text{CFC}=\text{CF}_2$	212	1.661	29-30°	$\text{CF}_3-\text{CC1I}-\text{CF}_2\text{Cl} + \text{CHF}=\text{CF}_2 \xrightarrow{\text{Bz, 202, 200°C, press}} \text{CF}_2=\text{CFC}=\text{CF}_2$ $\text{CF}_2\text{C1CC1}-\text{CHF}-\text{CF}_2 \xrightarrow{\text{KOH, alc}} \text{CF}_2=\text{CFC}=\text{CF}_2$ $\text{CF}_2\text{C1}-\text{CC1}-\text{CF}=\text{CF}_2 \xrightarrow{\text{Zn, CH}_3\text{COOH}} \text{CF}_2=\text{CFC}=\text{CF}_2$
96 $\text{CF}_2=\text{CCH}=\text{CH}_2$	158	1.361	30-31°	$\text{CF}_2=\text{C}-\text{CF}=\text{CF}_2$ $\text{CF}_2\text{Br}_2 + \text{C}_n=\text{CHCH}_3 \rightarrow \text{CF}_2\text{Br}-\text{CHBr}-\text{CH}_3$ $(\text{C}_4\text{H}_9)_3\text{N} \rightarrow \text{CF}_2=\text{C}-\text{CH}=\text{CH}_2$
97 $\text{CF}_2=\text{CFCF}_2\text{CF}_2\text{H}$	182	1.741	20-25°	$\text{HCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{COONa} \xrightarrow{\Delta} \text{CF}_2=\text{CFCF}_2\text{CF}_2\text{H}$
98 $\text{CF}_2=\text{CF}(\text{CF}_2)_4\text{H}$	282	1.721	53°	$\text{H}(\text{CF}_2)_6\text{COONa} \xrightarrow{\Delta} \text{CF}_2=\text{CF}(\text{CF}_2)_4\text{H}$
99 $\text{CF}_2=\text{CFCF}_2\text{CO}_2\text{C}_2\text{H}_5$	204	1.343	72-74/207mm	$\text{CF}_2\text{C1CFC1CF}_2\text{CO}_2\text{C}_2\text{H}_5 \xrightarrow{\text{Zn, MeOH}} \text{CF}_2=\text{CFCF}_2\text{CO}_2\text{C}_2\text{H}_5$
100 $\text{CF}_2=\text{CFCF}_2\text{CF}=\text{CF}_2$	212	1.771	34-36°	$\text{CF}_2=\text{CFCF}_2\text{CFC1CF}_2\text{Cl} \xrightarrow{\text{Zn}} \text{CF}_2=\text{CFCF}_2\text{CF}=\text{CF}_2$

Monomer	Molecular Weight	Density	Boiling Point	Preparation
101 C ₂ F ₅ CH=CH ₂	146	1.34	22°C	C ₂ F ₅ I + CH ₂ =CH ₂ → C ₂ F ₅ CH ₂ CH ₂ I R ₃ N → C ₂ F ₅ CH=CH ₂
102 C ₃ F ₇ CH=CH ₂	208	1.26	31°	C ₃ F ₇ I + CH ₂ =CH ₂ → C ₃ F ₇ CH ₂ CH ₂ I R ₃ N → C ₃ F ₇ CH=CH ₂
103 CF ₃ CH ₂ CH ₂ CH=CH ₂	124	1.0	49-53°C	CF ₂ Br ₂ + 2CH ₂ CH ₂ → CF ₂ BrCH ₂ CH ₂ CH ₂ CH ₂ Br SbF ₃ / SbCl ₅ → CF ₃ (CH ₂) ₄ Br → KOH → CF ₃ CH ₂ CH ₂ CH=CH ₂
104 CF ₃ (CH ₂ CH ₂) ₂ CH=CH ₂	152	1.1	98°C	CF ₃ (CH ₂) ₅ CH ₂ I → KOH / alc → CF ₃ (CH ₂) ₂ CH=CH ₂
105 CH ₂ =CH-CF(CF ₂) ₂	224	1.46 ³	82-84°	CF ₂ -CF ₂ -CH ₂ -CH ₂ Br → KOH / alc → CF ₂ -CF ₂ -CH=CH ₂ CF ₂ -CFCI
106 CF ₃ CH-C(CH ₃) ₂	112	1.31 ³	39°	CF ₃ CH(OH)CH ₂ Br → NaOH → CF ₃ CH-C(CH ₃) ₂
107 C ₃ F ₇ CH ₂ OCH=CH ₂	202	1.23 ³	54-60°	C ₃ F ₇ -CH ₂ -O-Na+CH ₂ Br-CH ₂ Br (C ₂ H ₅) ₂ O → C ₃ F ₇ -CH ₂ -O-CH ₂ -CH ₂ Br C ₃ F ₇ -CH ₂ -O-CH ₂ -CH ₂ Br → KOH / alc → C ₃ F ₇ -CH ₂ -O-CH=CH ₂
108 CF ₃ CF=CFCF ₃	200	1.53(0°)	0°	CF ₃ CF ₂ CF ₂ CO ₂ K → CF ₃ CF=CFCF ₃
109 CF ₂ -CF-CH ₂ -CH	108	1.41 ¹	30°	CF ₂ =CFCI + CH ₂ =CHBr → Press → CF ₂ -CF-CH ₂ -CH CF ₂ -CFCI → Zn / HOAc → CF ₂ -CF-CH ₂ -CH

103
104
105

Monomer	Molecular Weight	Density	Boiling Point	Preparation
110 $\text{CF}_3\text{CH}_2\text{OCH}=\text{CH}_2$	125	1.123	42-48°	$\text{CF}_3\text{CH}_2\text{OH} + \text{CH}_2=\text{CH}_2 \xrightarrow{\text{O}} \text{CF}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$
111 CF_2O	66	1.14 (-114°)	-83°	$\text{CF}_3-\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \xrightarrow{\text{PCl}_5}$ $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{KOH}}$ $\text{CF}_3-\text{CH}_2\text{OCH}=\text{CH}_2$ $\text{CO} + \text{F}_2 \xrightarrow{\text{activated carbon}} \text{COF}_2$
112 $\text{CF}_3\text{CH}_2\text{CH}=\text{CH}_2$	110		10.5°	$\text{CF}_3-\text{CH}_2\text{I} + \text{CH}_2=\text{CH}_2 \xrightarrow[500^\circ\text{C}]{\text{press}} \text{CF}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{I}$ $\text{CF}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{I} \xrightarrow[\text{alc}]{\text{KOH}}$ $\text{CF}_3-\text{CH}_2-\text{CH}=\text{CH}_2$
113 $\text{C}_3\text{F}_7\text{CH}_2\text{CH}=\text{CH}_2$	210	1.30	60°-65°C	$\text{C}_3\text{F}_7\text{CH}_2\text{I} + \text{CH}_2=\text{CH}_2 \xrightarrow{\text{press}} \text{C}_3\text{F}_7\text{CH}_2-\text{CH}_2-\text{CH}_2\text{I}$ $\text{C}_3\text{F}_7\text{CH}_2-\text{CH}_2-\text{CH}_2\text{I} \xrightarrow[\text{alc}]{\text{KOH}}$ $\text{C}_3\text{F}_7\text{CH}_2-\text{CH}=\text{CH}_2$
114 $(\text{CF}_3)_2\text{C}=\text{CH}_2$	164		11-13°	$\text{CF}_3-\overset{\text{CH}_3}{\text{C}}=\text{CF}_2 \xrightarrow{\text{Cl}_2} \text{CF}_3-\overset{\text{CH}_3}{\text{C}}\text{Cl}-\text{CF}_2\text{Cl}$ $\xrightarrow[\text{alc}]{\text{KOH}} (\text{CF}_3)(\text{CF}_2\text{Cl})\text{C}=\text{CH}_2 \xrightarrow{\text{SbF}_3\text{Cl}_2} (\text{CF}_3)_2\text{C}=\text{CH}_2$
115 $\text{CH}_2=\text{CHCF}_2\text{OCF}_3$	162			
116 $\text{CH}_2=\text{CHCF}_2\text{OC}_3\text{F}_7$	262			
117 $\text{CF}_2=\text{CHCF}_2\text{OCF}_3$	198			
118 $\text{CF}_2=\text{CHCF}_2\text{OC}_3\text{F}_7$	298			
119 $\text{CF}_2=\text{CFCF}_2\text{OCF}_3$	216			
120 $\text{CF}_2=\text{CFCF}_2\text{OC}_3\text{F}_7$	316			
121 $\text{CH}_2=\text{CHOCHF}_2\text{CF}_3$	162			

No samples of monomers 115-124 were actually received.

Monomer	Molecular Weight	Density	Boiling Point	Preparation
122 CF ₂ =CFOCF ₃	166			
123 CF ₂ =CFOC ₃ F ₇	266			
124 CF ₂ =CHOCH ₂ CF ₃	162			
125 CF ₃ CF ₂ CF=CH ₂	164	1.4 ¹	7°	CF ₃ CF ₂ CF ₂ CH ₂ OH → CF ₃ (CF ₂) ₂ CH ₂ OTs → CF ₃ (CF ₂) ₂ CH ₂ I $\xrightarrow[\text{FOAc}]{\text{Zn}}$ CF ₃ CF ₂ CF=CH ₂
126 C ₅ F ₁₁ CF ₂	366		85°-90°C	3M Stock
127 CF ₃ N=O	99	1.80 ²	-84°	CF ₃ Br $\xrightarrow[\text{NO}]{\text{h}\nu/\text{Hg}}$ CF ₃ NO
128 CF ₂ =CFC ₆ H ₄ CO ₂ H	202		m.p. 156-157°	CF ₂ BrCFC ₆ H ₄ CO ₂ H $\xrightarrow{\text{Zn}}$ CF ₂ BrCFC ₆ H ₄ CO ₂ H $\xrightarrow{\text{Zn}}$ CF ₂ =CFC ₆ H ₄ CO ₂ H
129 CFC ₁ =CFOCH ₃	128			
130 C ₃ F ₇ NO	199		-12°	C ₃ F ₇ I $\xrightarrow[\text{NO}]{\text{h}\nu/\text{Hg}}$ C ₃ F ₇ NO
131 C ₂ F ₅ NO	149		-42°	C ₂ F ₅ I $\xrightarrow[\text{NO}]{\text{h}\nu/\text{Hg}}$ C ₂ F ₅ NO
132 C ₃ F ₇ N=CF ₂	156		12°	(C ₃ F ₇) ₃ N $\xrightarrow{\Delta}$ C ₃ F ₇ N=CF ₂
133 C ₈ F ₁₇ NO	449		53°/48 m.m.	C ₈ F ₁₇ I $\xrightarrow[\text{NO}]{\text{h}\nu/\text{Hg}}$ C ₈ F ₁₇ NO
134 CF ₂ CFC ₁ (NO)(NO ₂)	192			CF ₂ =CFC ₁ + NO → CF ₂ CFC ₁ (NO)(NO ₂)
135 CF ₂ CC ₁₂ (NO)(NO ₂)	208			CF ₂ =CC ₁₂ +NO → CF ₂ CC ₁₂ (NO)(NO ₂)

Monomer	Molecular Weight	Density	Boiling Point	Preparation
136 ONCF ₂ CF ₂ NO ₂	176	1.74 ¹	21°	CF ₂ =CF ₂ $\xrightarrow{\text{NO}}$ ONCF ₂ CF ₂ NO ₂
137 CF ₂ C1CFC1NO	181			CF ₂ =CFC1 $\xrightarrow[\text{FeCl}_3]{\text{NO}}$ CF ₂ C1CFC1NO
138 CF ₂ C1CF ₂ NO	165	1.59 ¹	- 7°	CF ₂ =CF ₂ $\xrightarrow[\text{FeCl}_3]{\text{NO}}$ CF ₂ C1CF ₂ NO
139 CF ₃ CC1=C(OCH ₃)CF ₃	228			CF ₃ -CC1=CC1-CF ₃ +NaOCH ₃ \longrightarrow CF ₃ -CC1-C(OCH ₃)CF ₃ \longrightarrow
140 CH ₂ =C(OCH ₂ CF ₃)CH=CH ₂	132	1.10 ³	92-93°	CH ₂ =CHCH ₂ CH ₂ + HOCH ₂ CF ₃ \longrightarrow CH ₂ =CHCH(OCH ₂ CF ₃)CH ₂ OH $\xrightarrow{\text{PCl}_5}$ CH ₂ =CH-CH(OCH ₂ CF ₃)CH ₂ Cl $\xrightarrow[\text{a.i.c.}]{\text{KOH}}$ CH ₂ =CHC(OCH ₂ CF ₃)=CH ₂
141 C ₃ F ₆ (NOXNO ₂)	226	1.62 ³	42-44°	CF ₃ CF=CF ₂ $\xrightarrow{\text{NO}}$ C ₃ F ₆ (NOXNO ₂)
142 CF ₂ =CFCF ₂ CO ₂ H	176	1.49 ³		CF ₂ C1CFC1CF ₂ COOH $\xrightarrow{\text{Zn}}$ CF ₂ =CFCF ₂ CO ₂ H
143 CF ₃ CF ₂ CF ₂ COF	216		6°-8°C	CF ₃ CF ₂ CF ₂ COOH $\xrightarrow{\text{NaF}}$ CF ₃ CF ₂ CF ₂ COF

¹Dry ice - acetone temperature

²Liquid nitrogen temperature

³Room temperature

**Monomer commercially available

Continued

TABLE I

<u>No. Code</u>	<u>Monomer</u>	<u>Amount</u>	<u>Source</u>	<u>No. Code</u>	<u>Precursors</u>	<u>Amount</u>	<u>Source</u>
15 129	CFCl=CF-O-CH ₃	71 gm	Univ. of Florida (Tarrant)				
16 130	C ₃ F ₇ NO	15 gm	Univ. of Florida (Tarrant)				
130	C ₃ F ₇ NO	47 gm	Univ. of Colo. (Park)				
17 131	C ₂ F ₅ NO	100 gm	3M stock				
18 133	C ₈ F ₇ NO	20 gm	3M stock				
19 137	CF ₂ ClCFClNO	25 gm	Univ. of Florida (Tarrant)				
20 138	CF ₂ Cl-CF ₂ NO	208 gm	Univ. of Colo. (Park)				
21 141	CF ₃ -CF(NO)CF ₂ NO ₂	6 gm	Univ. of Colo. (Park)				
22 51	CF ₂ -CHCF-CH ₂	2 lbs.	Peninsular Chem Res				

TABLE II
Conversion of Precursors to Monomers

Code	Reaction	No. of Runs	Total Monomer	Avg. Yield
14	$C_3F_7COOH \xrightarrow{NaOH} C_3F_7COONa$			
	$C_3F_7COONa \xrightarrow{\Delta} CF_3-CF=CF_2$	2	390 gms	65%
24	$CF_2Br-CF_2Br \xrightarrow{Zn} CF_2=CF_2$	2	450 gms	93%
35	$CF_3-CH_2CH_2I \xrightarrow[C_2H_5OH]{KOH} CF_3-CH=CH_2$	1	130 gms	91.5%
42	$CF_3-CH_2-CF_2Br \xrightarrow[H_2O]{KOH} CF_3-CH=CF_2$	1	40 gms	64.5%
51	$CF_2Br-CH_2-CFBr-CH_3 \xrightarrow{(C_4H_9)_3N} CF_2=CH-CF=CH_2$	20	16.1 lbs	65%
56	$CF_2Br-CFC1-CH_2-CH_2Br \xrightarrow[\text{mineral oil}]{KOH} CF_2Br-CFC1-CH=CH_2$			
	$CF_2Br-CFC1-CH=CH_2 \xrightarrow[C_4H_9OH]{Zn} CF_2=CF-CH=CH_2$	30	13.2 lbs	50%
67	$CF_3-CF_2-CH_2I \xrightarrow[CH_3COOH]{Zn} CF_3-CF=CH_2$	1	37 gms	86%
77	$CF_2C1-CH(CF_3)-CH=CH_2 \xrightarrow[C_2H_5OH]{KOH} CF_2-C(CF_3)-CH=CH_2$	1	25 gms	70%
101	$C_2F_5CH_2-CH_2I \xrightarrow[C_2H_5OH]{KOH} C_2F_5-CH=CH_2$	2	100 gms	50%
103	$CF_3(CH_2)_3CH_2I \xrightarrow[C_4H_9OH]{KOH} CF_3(CH_2)_2-CH=CH_2$	1	95 gms	65%
107	$C_3F_7CH(OH)OCH_3 \xrightarrow{P_2O_5} C_3F_7CHO$	1	100 g	92%
108	$CF_3-CH(OH)OCH_3 \xrightarrow{P_2O_5} CF_3-CHO$	2	130 g	90%

TABLE II

(Continued)

Code	Reaction	No. of Runs	Total Monomer	Avg. Yield
125	$\text{C}_3\text{F}_7\text{CH}_2\text{OH} \xrightarrow[\text{NaOH}]{\text{CH}_3-\text{C}_6\text{H}_4-\text{SO}_2\text{Cl}} \text{C}_3\text{F}_7\text{CH}_2\text{OSO}_2-\text{C}_6\text{H}_4-\text{CH}_3$			
	$\text{C}_3\text{F}_7\text{CH}_2-\text{OSO}_2-\text{C}_6\text{H}_4-\text{CH}_3 \xrightarrow{\text{NaI}} \text{C}_3\text{F}_7\text{CH}_2\text{I}$			
	$\text{C}_3\text{F}_7\text{CH}_2\text{I} \xrightarrow[\text{CH}_3\text{COOH}]{\text{Zn}} \text{C}_2\text{F}_5-\text{CF}=\text{CH}_2$	5	1 lb.	75%
127	$\text{CF}_3\text{I} + \text{NO} \cdot \xrightarrow[\text{Hg}]{\text{u.v.}} \text{CF}_3\text{NO} + \text{HgI}_2$		2 lb.	60%
129	$\begin{array}{c} \text{CF}_2 - \text{CFCI} \\ \\ \text{CH}_2 - \text{CH}_2 \end{array} \xrightarrow[\text{C}_4\text{H}_9\text{OH}]{\text{KOH}} \begin{array}{c} \text{CF}_2 - \text{CF} \\ \\ \text{CH}_2 - \text{CH} \end{array}$		50 g	60%
130	$\text{C}_3\text{F}_7\text{I} + \text{NO} \cdot \xrightarrow[\text{Hg}]{\text{u.v.}} \text{C}_3\text{F}_7\text{NO} + \text{HgI}_2$		20 g	
131	$\text{C}_2\text{F}_5\text{I} + \text{NO} \cdot \xrightarrow[\text{Hg}]{\text{u.v.}} \text{C}_2\text{F}_5\text{NO} + \text{HgI}_2$		20 g	
136	$\text{C}_2\text{F}_4 + 3\text{NO} \longrightarrow \text{O}_2\text{NCF}_2\text{CF}_2\text{NO} + 1/2\text{N}_2$		600 g	65% (based on C ₂ F ₄)
140	$\text{CH}_2\text{Cl}-\text{CH}(\text{OCH}_2\text{CF}_3)-\text{CH}=\text{CH}_2 \xrightarrow[\text{C}_4\text{H}_9\text{OH}]{\text{KOH}} \text{CH}_2=\text{C}(\text{OCH}_2\text{CF}_3)\text{CH}=\text{CH}_2$		30 g	56%

TABLE III

Non-expendable Equipment Constructed or Purchased*

<u>No.</u>	<u>Equipment</u>	<u>Purchased From</u>	<u>Remarks</u>
1	"Micro" series 300 ml stainless steel reaction vessel	American Instrument Co.	Replacement for I.D. #1264-1
1	Shaking mechanism and heating jacket for above	American Instrument Co.	
12	Stainless shields for ampoules	Fabricated in 3M shop	
1	Horizontal multiple shaker and thermostat bath	Fabricated in 3M shop	(Later adapted for low-temp. operation)
1	"Revcon" 8 ft ³ cold storage box	A.S. Aloe Co.	
1	Low Temperature fractionation apparatus	Constructed in laboratory	
1	"Potentiostat" controller for above	Wheelco	
1	5 l. stainless steel resin pot	Chicago Apparatus Co.	
1	Welch vacuum pump	A.S. Aloe Co.	
1	Adams centrifuge	G. T. Walker Co.	
1	Hoffman stainless steel vacuum flask	Air Reduction Co.	
2	Lab jack supports	Emil Greiner Co.	
4	Powerstats	G. T. Walker Co.	
6	HS 150 hi-pressure cylinder outlet threads	Hoke, Inc.	
6	#3002 needle valves	Hoke, Inc.	
2	Hoffman 15 l. liquid air containers	Air Reduction Co.	

*Only purchases of \$50 or more are included

TABLE IV

Copolymers of $\text{CF}_3\text{CH}=\text{CH}_2$

Ref. No.	Comonomer	Charged Mole Ratio $\text{CF}_3\text{CH}=\text{CH}_2/\text{X}$	Recipe	Time (hrs)	Temp (°C)	Conversion (%)	Nature of Polymer	Analysis %F %C	Combined Mole Ratio	Test Results and Remarks
7301-32-1	$\text{CH}_3\text{CH}=\text{CH}_2$	50/50	Ziegler-1	20	50	16.5	Grease	.71	1/99	Insufficient F.
7301-32-2	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	"	"	"	"	6.6	Oil	-	-	Probably polybutene -1
7301-32-3	$\text{C}_3\text{H}_6/\text{C}_4\text{H}_8$	33/33/33	"	1	20	6	Soft rubber	0.1	<1/99	Insufficient F
7301-32-5	$\text{CH}_2=\text{CF}_2/\text{CF}_2=\text{CF}_2$	5/66/29	PBK2	24	50	93	Leathery	-	-	Properties too poor for evaluation.
7301-32-7	"	10/63/27	"	"	"	100	Leathery	-	-	"
7301-32-8-1	"	20/56/24	"	"	"	100	Short rubber	-	-	"
7301-32-8-1	"	40/42/18	"	"	"	42	Grease	-	-	"
7301-32-7	"	30/49/21	"	"	"	Quant.	Leathery	-	-	"
7301-8-1	$\text{CH}_2=\text{CH}_2$	20/80	"	"	40	20	Low M.W.	40	67/33	"
7301-9-1	"	10/90	"	"	35	<2	Semi-rubbery	Contains F	-	Insufficient polymer for evaluation

These solutions combined in
50/50 ratio to form catalyst

1 TiCl_4 (.42 x 10^{-3} molar in heptane)
Al(i - C_4H_9)₃ (1.27 x 10^{-3} molar in heptane)

2 PBK recipe: $\text{K}_2\text{S}_2\text{O}_8$ - - - - 0.75 parts
 K_2HPO_4 - - - - .75 parts
 $\text{C}_7\text{F}_{15}\text{COOK}$ - - - - 1.2 parts
Monomer - - - - 50 parts
 H_2O - - - - -100 parts

TABLE V

Copolymers Based on $C_2F_5CF=CH_2$

Ref No.	Comonomer (X)	Charged Mole Ratio X/C ₂ F ₅ CF=CH ₂	Recipe	Time (hrs)	Temp (°C)	Conversion %	Nature of Polymer	Analysis % C *	Combined Mole Ratio	Test Results and Remarks
7924-15-2	CH ₂ =CH ₂	80/20	PBK ¹	40	55	90	Soft rubber	44.9	28/72	Evaluated.
7924-15-4	CH ₂ =CH ₂	70/30	"	40	55	86	Soft rubber	38.9	17/83	Yield or
7924-20-1	CH ₂ =CH ₂	85/15	"	76	55	56	Soft rubber	45.3	29/71	properties did
7924-20-4	CH ₂ =CH ₂	70/30	"	76	55	50	Sl. rubbery	39.1	17/83	not warrant
7924-20-5	CH ₂ =CH ₂	60/40	"	76	55	40	Sl. rubbery	37.2	14/86	evaluation.
7924-21-1	CH ₂ =CF ₂	80/20	"	24	55	Quant.	Plastic	34.2	60/40	
7924-21-2	CH ₂ =CF ₂	75/25	"	24	55	Quant.	Leathery	33.8	58/42	
7924-21-3	CH ₂ =CF ₂	70/30	"	24	55	Quant.	Very tough rubber	33.6	56/44	
7924-21-4	CH ₂ =CF ₂	65/35	"	42	55-60	Quant.	Tough rubber	33.2	53/47	
7924-21-5	CH ₂ =CF ₂	60/40	"	42	55-60	Quant.	Tough rubber	32.9	52/48	
7301-37-6	CH ₂ =CF ₂	50/50	"	24	45	30	Tough rubber	31.5	26/74	
7301-37-7	CH ₂ =CF ₂	60/40	PBK ²	24	45	40	Tough rubber	31.2	24/76	
7301-42-1	None	0/100	"	48	50	0	-	-	-	
7301-42-2	CH ₂ =CF ₂	70/30	"	48	50	60	Tough, slow rubber	30.8	20/80	Evaluated
7301-42-3	CH ₂ =CF ₂	60/40	"	48	50	94	Tough, slow rubber	32.1	35/65	
7301-42-4	CH ₂ =CF ₂	70/30	"	48	50	42	Tough, slow rubber	38.1	100%VF ₂	

PBK¹ Same as PBK¹ except K₂S₂O₈ .25 parts

PBK²

Monomer
H₂O
C₇F₁₅COOK
K₂HPO₄
K₂S₂O₈
100 parts
200 parts
3 parts
2 parts
.75 parts

*C analyses indicate loss of F

TABLE VI

Saturated Fluorohydrocarbon Copolymer Systems

Ref. No.	A	Monomers	B	Mole Ratio	Recipe	Time (hrs)	Temp (°C)	Conversion(%)	Nature of Polymer	Analysis, Preliminary Test Results, etc.	Disposal
7301-19-1	CH ₂ =CH-CF ₂ CFCl-CF ₂		C ₂ H ₄	15.3/84.7	PBK ¹	20	50	4	White powder	13/87 CMR ²	3
7301-19-2	"		CH ₂ =CF ₂	33/66	"	20	50	Trace	-	-	4
7301-19-3	"		C ₂ F ₄	33/66	"	20	50	7	White powder	20/80 CMR	4
7301-19-4	"		None	100/0	"	20	50	59	Semi-rubbery	Side chain bulk too great	4
7301-22-10	"		C ₄ H ₈	90/10	Ziegler	20	50	6	Soft sticky rubber	1/99 CMR, 2.3% F	5
—	CF ₂ =CF ₂		C ₂ H ₄	50/50	PBK	24	45	5	Intractable powder	-	4
7301-13-1	CH ₂ =CF ₂		C ₂ H ₄	50/50	PBK	17	55	4.45	Sl. rubbery	F, 6.6, 5/95 CMR	4
7301-10-1	CH ₂ =CF ₂		C ₂ H ₄	60/40	PBK	20	58	60	Short rubber	F 13.4 13/87 CMR	4
7301-24-6	CF ₃ CH=CH ₂		C ₂ H ₄	50/50	Ziegler	20	20	55	Wax	-	4
—	C ₃ H ₆		C ₂ H ₄	50/50	"	24	20	100	Short rubber	Scorched on mill	5
7301-22-7	CF ₃ CH=CH ₂		C ₃ H ₆	25/75	"	24	20	33	Wax	C, 42.2; F 38.4 53/47CMR 4	4
7301-22-8	CF ₃ CH=CH ₂		C ₄ H ₈	25/75	"	24	20	32	Wax	C, 40.3; F 39.1 61/7CMR 4	4
8071-16-1	CF ₃ CH ₂ CH=CH ₂		None	100/0	"	24	20-60	0	-	-	3
8071-16-2	"		C ₂ H ₄	12/88	"	1	20	58.5	Polyethylene	-	5
8071-16-3	"		C ₂ H ₄	50/50	"	1	20	17.5	Polyethylene	-	5
8071-16-4	"		C ₂ H ₄	33/67	"	1	20	Trace	Polyethylene	-	5
8071-16-5	"		C ₃ H ₆	40/60	"	3 wks	20	44	Rubber	-	5

(Continued)

TABLE VI

Ref. No.	Monomers		Mole Ratio	Recipe	Time (hrs.)	Temp (°C)	Conversion (%)	Nature of Polymer	Analysis, Preliminary Test Results, etc.	Disposal
	A	B								
8071-19-1	CF ₃ CH ₂ CH ₂ CH=CH ₂	None	100/0	Szwarc ⁶	3 wks	20	0	-		
8071-19-2	"	None	100/0	BF ₃ Etherate	3 wks	20	0	-		
8071-18-2	CF ₂ -CF=CH-CH ₂	CF ₃ CH ₂ OCH=CH ₂	50/50	PBK	24	50	30	Thermoplastic		4
8071-18-4	"	CH ₂ =CF ₂	30/70	"	24	50	39	Thermoplastic		4
8071-18-5	"	None	100/0	"	24	50	34	Thermoplastic		4
3 runs	"	None	100/0	-Szwarc -BF ₃ Etherate -Ziegler	48	20	0	No polymer		

¹Emulsion Recipe:

K₂S₂O₈ 0.75 pts.
K₂HPO₄ 2
C₇F₁₅COOK 3

⁶Szwarc catalyst: 12 cc THF

.46 g Na

2.56 g Naphthalene

²Combined Mole Ratio
³Insufficient polymer for evaluation

⁴Insufficient elastomeric character for evaluation

⁵Insufficient fluorine for evaluation

TABLE VII

Polyolefin/CF₂=CFCH=CH₂ (56) Systems

Ref No.	Olefin Charge	Mole Ratio Olefin/56	Time (hrs)	Temp (°C)	Conversion (%)	Analysis %C %F	Wt. %56	Nature of Polymer	Disposal
—	C ₃ H ₆	75/25	24	20	30	49.1 44.2	49	Short rubber	Not evaluated
—	C ₄ H ₈	75/25	24	"	13	47.6 45.4	24	Semi rubbery	"
7301-24-3	C ₂ H ₄	50/50	20	"	39	41.2	73	Tough, short rubber	"
7301-26-3	C ₂ H ₄ /C ₃ H ₆	1/1/1	24	"	46	2.8	6	Sticky, soft rubber	Evaluated
7301-26-4	C ₂ H ₄ /C ₃ H ₆	1/1/.5	24	"	63	35.1	68	Tough, short rubber	"
7301-26-5	C ₂ H ₄ /C ₃ H ₆	1/1/1	24	"	83	40	77	Leathery	"
7301-26-6	C ₂ H ₄ /C ₃ H ₆	1/8/1	24	"	67	40.5	77	Soft rubber	"
7301-24-4	C ₂ H ₄ /C ₃ H ₆	1/1/1	20	"	72	35	675	Tough, short rubber	"
7301-24-5	C ₂ H ₄ /C ₄ H ₈	1/1/1	20	"	43	40.5	77	Tough, short rubber	"
7301-27-1	C ₂ H ₄ /C ₃ H ₆	1/8/1	24	"	14.4			Rubber	Not evaluated
7301-27-2	C ₂ H ₄ /C ₄ H ₈	1/8/1	24	"	9.4			Short Rubber	"
7301-27-3	C ₂ H ₄ /C ₃ H ₆	1/8/1	24	"	2.2			Rubber	"
7301-28-1	C ₂ H ₄ /C ₃ H ₆	1/8/1	48	"	24.1	21.2	40	Hetero, Rubbery	"
7301-28-2	C ₂ H ₄ /C ₃ H ₆	1/8/1	"	"	15.0	31.7	61	Short Rubber	"
7301-28-3	C ₂ H ₄ /C ₄ H ₈	1/8/1	"	"	6.0	41.8	77	Soft rubber	"
7301-28-4	C ₂ H ₄ /C ₃ H ₆	.5/9/.3	"	"	21.6	16.3	30	Soft Sticky Rubber	"
7301-28-5	C ₂ H ₄ /C ₄ H ₈	.5/9/.5	"	"	9.9	31.7	61	Short Rubber	"

All Runs made with "Ziegler Catalyst"

$$\left(\begin{array}{c} 3:1 \text{ mole ratio} \\ (i - C_4H_9)_3Al/TiCl_4 \end{array} \right)$$

TABLE VIII
Fluorohydro Diene Polymerizations

Ref. No.	Monomers See monomer list	Chg. Mole Ratio	Time (hrs)	Temp. (°C)	Conversion (%)	Combined Mole Ratio	Nature of Polymer	Disposal
7301-14-1	2/56	50/50	4	75	12		Intractable	Prepared by special QMC request for non-Arctic rubber use.
7301-15-1	2/56	76/24	18	60	27		Plastic	
7301-15-2	2/31/56	50/25/25	64	45	69		Plastic	
7301-16	56 homo	100/0	.73	45	100	100/0	Leathery	
7924-31-2	3/56/110	12/88/12	48	35-45	90	contains 110 (I.R.)	Rubber	E
7924-31-3	3/56/FBA	12/88/12	48	35-45	68	contains FBA (I.R.)	Rubber	E
8071-8-1	3/56/FBA	88/12/12	48	35-45	91.7	contains FBA (I.R.)	Rubber	E
8071-18-1	109/56	10/90	24	50	61		Thermoplastic	X
8071-18-3	109/3	30/70	24	50	77		Thermoplastic	X
7924-43-1	51/110	90/10	12	40	50		Tough rubber	E

PBK recipe was used in all runs.

For full polymerization and workup details,
see quarterly progress reports.

E - Submitted for evaluation

X - Not evaluated

TABLE IX

CH₂=CHCH=CH₂/CF₂=CFCH=CH₂ (3/56) Copolymers

(Selected runs illustrating effect of charred and combined mole ratio)

Ref. No.	Charge Mole Ratio (3/56)	Time hrs	Temp °C	Conversion (%)	Analysis %C %F	Combined Mole Ratio	Nature of Polymer
7301-33-7	2.5/97.5	6	45	100		2.5/97.5 ¹	Leathery thermoplastic
7301-33-6	5/95	6	45	100		5/95 ¹	Leathery thermoplastic
7301-33-5	7/93	6	45	100		7/93 ¹	Very tough rubber
7301-34-7	8/92	24	35	100		8/92 ¹	Leathery
7301-33-13A	10/90	20	45	100	47.0 49.0	10/90 (avg.)	Tough rubber
7301-39-5	11/89	20	30	98	47.0	12/88	Very tough rubber
7301-39-4	12/88	20	30	98	47.5	14/86	Tough rubber
7301-39-3	13/87	20	30	97	47.7	15/85	Rubber
7301-39-2A	14/86	17	55	98		14/86	Soft, snappy rubber
7301-39-2	14/86	20	30	87	48.1	17/83	Snappy rubber
7301-39-1	15/85	20	30	85	48.1	17/83	Snappy rubber
7301-33-1	20/80	20	45	100	51.5 43.2	24/76	Snappy rubber
7301-34-567	33/66	20	35/40	100	53	35/65	Snappy rubber

PBK recipe used in all runs

$\frac{1}{4}$ K₂S₂O₈ - - - .75
 K₂HPO₄ - - - 2

C7F15COOK - - - 3
 H₂O - - - 200
 Monomer - - - 100

1 - Quant. yield
 No analysis

TABLE X - RECIPE STUDIES ON 3/56 ELASTOMER

Run #	Monomer (g)	Emulsifier (g)	K ₂ S ₂ O ₈ (g)	DDM (g)	Water (g)	Time (Hrs.)	Temp (°C)	Short-stop (c.c.)	Conversion (g %)	Milling Data and Remarks
7301-40-1	20	Na Stearate .86	.046	.1	36	2.5	25	0.3	15.1	75 Resid. emulsifier interfered. Removed. Scorched on mill.
7301-44-1	18	Na Stearate .86	.046	.1	36	2.5	20	1.0	Trace	G.R.S. recipe does not work at 20°C.
7301-44-2	18	Mixed Alkyl Sulfonate .2	.046	.1	36	5	20	1.0	Trace	Gave a soft rubber which milled to a transparent sheet. Slightly scorched.
7301-44-3	18	Na Stearate .2	.046	.1	36	2.5	20	1.0	Trace	
7301-45-1	18	Mixed Alkyl Sulfonate .15	.015	.75	27	2	30	1.0	2	Too little to mill - soft rubber
7301-45-2	18	Mixed Alkyl Sulfonate .15	.015	.75	27	1.5	60	1.0	18	100 Tough rubber, scorched on mill
7301-45-3	18	Mixed Alkyl Sulfonate .15	.046	.75	27	2.5	30	1.0		
7301-47-1	18	Mixed Alkyl Sulfonate .2	.046	.1	36	3.25	30	1.0	Trace	Something unaccountably wrong with 47-1 - suspect charging error.
7301-47-2	18	Mixed Alkyl Sulfonate .2	.046	.2	36	3.25	30	1.0	4.3	23.9
7301-47-3	18	" .2	.023	.1	36	3.25	30	1.0	11.9	66.0
7301-47-4	18	" .2	.023	.2	36	3.25	30	1.0	11.2	62.4
7301-47-5	18	" .2	.046	.1	36	3.25	30	1.0	13.8	77.0

¹Shortstop Solution (GRS)

Hydroquinone - - - .08 g.
Sodium Sulfite - - - .008 g.
H₂O - - - - - 3 g.

TABLE XI
 $CF_2=CHCF=CH_2/CF_2=CFCH=CH_2$ (51/56) Interpolymerizations

Run #	Chgd. MR 51/56/x	g./g.	Recipe	Time (hrs.)	Temp. (°C)	% Conv.	Remarks
7301-49-1	50/50	40/40	PBK	7	45	72	
8071-31-1	60/40	7.2/4.8	PBK	17.5	32	82	
8071-31-2	70/30	8.4/3.6	PBK	17.5	41	83	
8071-31-3	60/20/20	7.2/2.4/2.8	PBK	17.5	32	69	
8071-31-5	$CF_3CH_2OCH=CH_2$ 70/15/15	8.4/1.5/2.1	PBK	17.5	35	54	
8071-31-6	$CF_3CH_2OCH=CH_2$ 70/25/5	8.4/3.0/0.7	PBK	17.5	35	77	
8071-33-1	50/50	37.5/37.5	UJ4	4	35	44	100% microgel
8071-33-2	70/30	52.5/22.5	UJ4	3	35	29	100% microgel
8071-33-3	50/50	3.5/3.5	UJ4-12cc. + .01cc. DDM	3	35	65	No microgel
8071-33-4	50/50	3.5/3.5	UJ4-12cc. + .01cc. DDM	6	35	78	No microgel
8071-33-5	50/50	3.5/3.5	UJ4-12cc. + .02cc. DDM	3	35	69	No microgel
8071-33-6	50/50	3.5/3.5	UJ4-12cc. + .02cc. DDM	6	35	72	No microgel
8071-36-1	50/50	3.5/3.5	UJ4-12cc. + .02cc. DDM	6	35	81	17% microgel
8071-36-2	50/50	3.5/3.5	UJ4-12cc. + .02cc. DDM	24	35	78	85% microgel
8071-36-3	50/50	3.5/3.5	UJ4-12cc. + .02cc. DDM	6	35	61	56% microgel
8071-36-4	50/50	3.5/3.5	UJ4-12cc. + .01cc. DDM	24	35	73	85% microgel
8071-36-5	50/50	3.5/3.5	UJ4-12cc. + .01cc. DDM	6	35	62	17% microgel, .02 cc. DDM to latex
8071-36-6	50/50	3.5/3.5	UJ4	24	35	74	.02cc. DDM to latex
8071-36-7	50/50	3.5/3.5	UJ4	6	35	88	No microgel; 2 cc. GFS shortstop soln. to latex
8071-36-8	50/50	3.5/3.5	UJ4	24	35	82	Insol. MEK; 2 cc. GFS shortstop soln. to latex
8071-36-7a	50/50	3.5/3.5	UJ4	6	35	86	shortstop soln. to latex 4% microgel; 2 cc. GFS shortstop soln. to latex
8071-53	60/40	150/150	A	5 3/4	35	53	Polymer gel-free; workup by salt-acid coagulation and H ₂ O-MeOH washing.
PP-1	60/40		B	20	40	70	
PP-2	60/40		B	20	40	70	
	PBK: 4 parts 2 parts 0.4 parts 100 parts	UJ4: 1.3 parts Alkyl Sulfonate 0.15 parts K ₂ S ₂ O ₈ 100 parts H ₂ O	Emulsifier		A: C ₇ H ₁₅ COONH ₄ - 6 parts K ₂ S ₂ O ₈ - 0.2 parts K ₂ HPO ₄ - 1 part H ₂ O - 200 parts Monomers - 100 parts TDDM 3B - 0.6 parts		B: C ₇ H ₁₅ COONH ₄ - 6 parts K ₂ S ₂ O ₈ - 0.2 parts K ₂ HPO ₄ - 3 parts H ₂ O - 200 parts Monomers - 100 parts TDDM - 0.6 parts

TABLE XII

Elastomer Evaluation Data

Sample No.	Monomer Combination	Ratio	Glassman, °C				T ₁₀₀	% Volume Swell *	Mod. of Rigidity, PSI
			T ₂	T ₅	T ₁₀	T ₁₀₀			
7301-24-4	C ₂ H ₄ /C ₃ H ₆ /CF ₂ =CFCH=CH ₂	33/33/33*	+ 3.5	-17.5	-25.4	> -70	42		
7301-24-5	C ₂ H ₄ /C ₄ H ₈ /CF ₂ =CFCH=CH ₂	33/33/33*	-14.0	-29.0	-35.0	> -70	32		
7301-26-3	C ₂ H ₄ /C ₃ H ₆ /CF ₂ =CFCH=CH ₂	45/45/10*	- 4.0	-20.5	-25.0	> -55	48		
7301-26-4	C ₂ H ₄ /C ₃ H ₆ /CF ₂ =CFCH=CH ₂	40/40/20*	- 4.0	-23.0	-27.5	> -70	60		
7301-26-5	C ₂ H ₄ /C ₃ H ₆ /CF ₂ =CFCH=CH ₂	33/33/33*	- 7.0	-24.0	-29.5	> -70	41		
7301-26-6	C ₂ H ₄ /C ₃ H ₆ /CF ₂ =CFCH=CH ₂	10/80/10*	-12.5	-25.0	-28.0-	-38	107		
7301-34-567	CH ₂ =CHCH=C ₂ H ₂ /CF ₂ =CFCH=CH ₂	35.4/64.6	-30.5	-36.0	-37.5	-44	153	114	
7301-33-3A	"	50/50	-34.5	-38.0	-40.0	-44.5	185	66	
7301-33-1	"	15/85	-25	-33.0	-35.0	-41.5	99	253	
7301-33-1	"	24/76	-20.0	-38.0	-40.0	-44.5	126	65	
7301-33-13A	"	10/90	- 4.0	-21.5	-26.5	-44.5	66	942	
7301-33-1	"	24/76	-37	-39	-40	-40.5	57		
7301-33-13A	"	10/90	-	-	-29	-41	7.5	218.3	
7301-35-1	"	18/82	0	-35	-38	-42	50-100%		
7301-35-1A	"	18/82	-30	-38.	-39.5	-44	-		
7301-35-2	"	18/82	-30	-37	-40	-42.5	-		
7301-35-2A	"	20/80	-37	-40	-41	-46.5	-		

*ASTM #II Fuel

↓

TABLE XII

Sample No.	Monomer Combination	Ratio	Gehman, °C			T100	% Volume Swell	Mod. of Rigidity, PSI
			T2	T5	T10			
7301-39-1	CH ₂ =CHCH=CH ₂ /CF ₂ =CFCH=CH ₂	15/85	+11.0	-34.5	-36.5	-42.5	100	270
7301-39-2	"	14/86	+14.0	-	-39.0	-43.5	95	325
7301-39-2A	"	14/86	Sample not moldable			-	112+	-
7301-39-3	"	13/87	+ 9.5	-36.5	-38.0	-44.5	92	589
7301-39-4	"	12/88	+ 8.0	-35.0	-37.5	-45.0	86	803
7301-39-5	"	11/89	+ 4.0	-34.5	-36.5	-46.5	77	1096
8071-8-1	CH ₂ =CHCH=CH ₂ /CF ₂ =CFCH=CH ₂ (Modified with C ₃ F ₇ CH ₂ COCH=CH ₂)	12/88	-	-29.5	-31.5	-	114	-
7924-31-2	CH ₂ =CHCH=CH ₂ /CF ₂ =CFCH=CH ₂ (Modified with CH ₂ =CH-O-CH ₂ CF ₃)	12/88	-	-33.0	-35.0	-	137	-
7301-42-3	CH ₂ =CF ₂ /CF ₃ CF ₂ CF=CH ₂	58/42	-	+14.0	+12.0	-	1.1	-
7924-15-2	CH ₂ =CH ₂ /CF ₃ CF ₂ CF=CH ₂	Charred in mold		-	-	-	-	-
Pilot plant Stock	CF ₂ =CHCF=CH ₂ /CF ₂ =CFCH=CH ₂	60/40	-	-	-38.0	-	16	-

*Charged

TABLE XIII
"Long Range" Exploratory Polymerizations

Ref. No.	Monomers A / B	Charge Mole Ratio	Recipe	Time (hrs)	Temp. (°C)	Conversion (%)	Nature of Polymer	Analysis C / F	Combined Mole Ratio	Remarks
26-4	$\text{CH}_3\text{CH}(\text{O})\text{CH}_2/\text{C}_5\text{F}_{11}\text{CF}(\text{O})\text{CF}_2$	94/6	$\text{Al}(\text{i-OC}_3\text{H}_7)_3 / \text{ZnCl}_2$.37 / 0.070	64	80	57	Soft, waxy	- / -	92/8	All four runs were fractionated.
26-1		95/5	.35	64	80	57	Soft, waxy	- / -	92/8	Presence of copolymer confirmed.
26-2		96/4	.35	64	80	63	Soft, waxy	- / -	95/5	Not rubbery enough for evaluation.
26-3		97/3	.42	64	80	65	Soft, waxy	- / -	97/3	
8071-3-1	None/ $\text{C}_3\text{F}_7\text{CHO}$	0/100	Szwarc1	4	+5	Quant.	Amorphous Plastic	- / -	-	No materials rubbery enough for further testing were obtained.
8071-3-2	None/ $\text{C}_3\text{F}_7\text{CHO}$	0/100	BF_3 Etherate	72	5	83	Crystalline Plastic	- / -	-	
8071-3-3	None/ $\text{C}_3\text{F}_7\text{CHO}$	0/100	None	200	5-R.T.	33	Plastic	- / -	-	
7924-17-1	$\text{CF}_2=\text{CHCF}=\text{CH}_2/\text{C}_3\text{F}_7\text{CHO}$	50/50	Szwarc	48	5-R.T.	40	Powder	23.8 / -	-	
7924-17-2	$\text{CF}_3\text{CH}_2\text{OCH}=\text{CH}_2/\text{C}_3\text{F}_7\text{CHO}$	50/50	Szwarc	48	5-R.T.	20	Powder	- / -	-	
7924-17-3	$\text{CF}_3\text{CH}(\text{O})\text{CH}_2/\text{C}_3\text{F}_7\text{CHO}$	50/50	Szwarc	48	5-R.T.	40	Wax	- / -	-	
7924-17-4	$\text{CF}_3\text{CF}=\text{CF}_2/\text{C}_3\text{F}_7\text{CHO}$	50/50	Szwarc	48	5-R.T.	40	Pow	- / 62.6	-	
7924-18-1	$\text{CF}_2=\text{CHCF}=\text{CH}_2/\text{C}_3\text{F}_7\text{CHO}$	50/50	BF_3 Etherate	48	-11°C	60	Wax	- / 57.9	-	
7924-18-2	$\text{CF}_3\text{CH}_2\text{OCH}=\text{CH}_2/\text{C}_3\text{F}_7\text{CHO}$	50/50	BF_3 Etherate	48	-11°C	60	Grease	25 (avg.) / -	-	
7924-18-3	$\text{CF}_3\text{CH}(\text{O})\text{CH}_2/\text{C}_3\text{F}_7\text{CHO}$	50/50	BF_3 Etherate	48	-11°C	-	Oil	27.8 / -	-	
7924-18-4	$\text{CF}_3\text{CF}=\text{CF}_2/\text{C}_3\text{F}_7\text{CHO}$	50/50	BF_3 Etherate	48	-11°C	-	Grease	- / -	-	

(Continued)

TABLE XIII

Ref. No.	Monomers A / B	Charge Mole Ratio	Recipe	Time (hrs)	Temp. (°C)	Conversion (%)	Nature of Polymer	Analysis		Combined Mole Ratio	Remarks
								C	F		
8643-31-1	NO/C ₃ F ₇ N=CF ₂	66/33	Vapor Phase No. Cat.	24	20	No Rx	-	-	-	-	
8643-31-2	C ₂ F ₄ /C ₃ F ₇ N=CF ₂	50/50	C ₃ F ₇ NO (Trace)	24	-16	Trace	-	-	-	-	24/C ₃ F ₇ NO Copolymer
8643-31-3	CH ₂ =CF ₂ /C ₃ F ₇ N=CF ₂	50/50	-	24	20						
8643-31-4	CF ₃ NO/C ₃ F ₇ N=CF ₂	50/50	-	48	-20 to +20	No polymer	-	-	-	-	
8643-31-5	CF ₂ -CH ₂ /C ₃ F ₇ N=CF ₂ CF=CH	50/50	Szwarc	48	20	No polymer	-	-	-	-	
8643-31-6	C ₂ F ₄ /C ₃ F ₇ N=CF ₂	50/50	PBK	48	50	No polymer					
8643-31-8	C ₂ F ₄ /C ₃ F ₇ N=CF ₂	50/50	NO	48	20	Trace	-	-	-	-	24/136 Copolymer
9628-42-1	C ₂ F ₄ /ClCF ₂ CF ₂ Cl	50/50	Bulk-irradiated 8 hrs	48	20	< 3%	Plastic	-	-	-	Polytetrafluoroethylene
9628-42-2	C ₂ F ₄ /ClCF ₂ CF ₂ Cl	50/50	(CH ₃) ₂ C(CN) ₂ (CH ₃) ₂ CN CN Irradiated 8 hrs.	48	20	< 3%	Plastic	-	-	-	"
9628-42-3	C ₂ F ₄ /ClCF ₂ CF ₂ Cl	50/50	PBK	20	45	30%	Plastic	-	-	-	"
9628-42-4	C ₂ F ₄ /ClCF ₂ CF ₂ Cl	50/50	BF ₃ Etherate	48	20	0	-	-	-	-	
9628-42-5	C ₂ F ₄ /ClCF ₂ CF ₂ Cl	50/50	Szwarc	48	20	0	-	-	-	-	
9794-3-1	C ₂ F ₄ /C ₃ F ₇ CF	50/50	Irradiation	72	20-50°C	30%	Plastic	-	-	-	Polytetrafluoroethylene

¹Szwarc catalyst

12 cc THF

.46 g Na

2.56 g Naphthalene

TABLE XIV

Solution Copolymerization of CF_3NO/C_2F_4

Run #	Solvent	Chgd. MR	g./g.	Conc. of Monomers	Temp.	Time, hrs.	Conversion(%)	\bar{M}_n (FM 3246)*
9005-11-1	Cl_2FCF_2Cl	1:1	4.0/4.0	30%	-20°	18	42	0.24
9005-11-2	CCl_3F	1:1	4.0/4.0	30%	-20°	18	30	0.21
9005-11-3	C6-C8 fluorocarbons	1:1	4.0/4.0	30%	-20°	18	55	0.32
9005-11-4	$C_8F_{16}O$	1:1	4.0/4.0	30%	-20°	18	56	0.46
9005-11-5	$(C_4F_9)_3N$	1:1	3.0/3.0	25%	-20°	18	75	0.55
9212-12-1	Mixed fluorocarbons	1:1	3.0/3.0	30%	-25°	18	34	0.30
9212-12-2	Mixed fluorocarbons	1:1	3.0/3.0	30%	-25°	18	-	0.36
9212-22-2	Mixed fluorocarbons	1:1	5.0/5.0	50%	-20°	18	49	0.56
9212-14-1	C_3F_7H	1:1	3.0/3.0	30%	-20°	22	23	0.16
9212-14-2	C_3F_7H	1:1	3.0/3.0	30%	-20°	46	35	0.20
9212-14-3	$(C_4F_9)_2O$	1:1	3.0/3.0	30%	-20°	20	30	0.15
9212-14-4	$(C_4F_9)_2O$	1:1	3.0/3.0	30%	-20°	45	37	0.24
9212-15-5	$CF_3CF=CF_2$	1:1	3.0/3.0	30%	-20°	18	17	0.15
9212-15-6	$CF_3CF=CF_2$	1:1	3.0/3.0	30%	-20°	43	23	0.16
9212-19-2	Mixed fluorocarbons	1:1	2.0/2.0	40%	-20°	27	45	0.48
9212-16-1	n-C7H16	1:1	2.0/2.0	33%	-20°	17	45	low MW
9212-16-2	C_6H_6	1:1	2.0/2.0	50%	23°	16	25	low MW
9212-31-5	$(C_4F_9)_3N$	1:1	3.0/3.0	50%	-20°	17	67	0.76
9212-34-2	$(C_4F_9)_3N$	1:1	3.0/3.0	30%	-20°	18	77	0.62
9212-50-1	$(C_4F_9)_3N$	1:1	3.0/3.0	30%	-20°	22	63	1.04
9212-50-4	$(C_4F_9)_3N$	1:1	3.0/3.0	40%	-20°	22	70	0.80
9212-40-1	$(C_4F_9)_3N$	1:1	3.0/3.0	50%	-20°	66	78	0.66
9212-40-2	$(C_4F_9)_3N$	1:1	3.0/3.0	30%	-20°	66	78	0.97

*3M Commercial Fluorocarbon Solvent

TABLE XV

Effect of Monomer Concentration
in FC-43
on MW of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$

<u>Run #</u>	<u>Monomer Conc. (Wt. %)</u>	<u>$\langle \eta \rangle$(FC-43) *</u>
9628-23-1	10	0.23
-2	15	0.30
-3	20	0.30
-4	25	0.30
-5	30	0.33
-7	40	0.49
-8	50	0.39
-9	60	0.31
-10	75	0.37
-12	100	0.40

6 g. monomer charge (1:1 MR) polymerized 22 hrs.
at -15°C .

* $(\text{C}_4\text{F}_9)_3\text{N}$

TABLE XVI

Polymerization of CF_3NO/C_2F_4 in Various Media

Run #	Medium	Chgd. MR	G./R.	Temp., °C	Time (hrs.)	Conversion	$\langle \eta \rangle$
9005-35-1	Suspension, 10cc. H_2O	1:1	3.0/3.0	25°	48	40%	.32 ¹
9212-55-1	Suspension, 10cc. H_2O	1:1	3.0/3.0	0°	20	60%	.56 ¹
9212-55-2	Suspension, 7cc. H_2O , 3cc. CH_3OH	1:1	3.0/3.0	0°	20	60%	.37 ¹
8643-4-5	Emulsion, 40% in 3% $C_7F_{15}COOK$	1:1	3.5/3.5	0°	24	30%	.34 ¹ (gum latex)
8643-4-6	Same as 8643-4-5 + H_2SO_4 to pH 2	1:1	3.5/3.5	0°	24	20%	.28 ¹ (gum prefloc)
9628-13-8	5 cc. $(C_4F_9)_3N$ + 5 cc sat. $MgCl_2$ soln. + .001 moles O_2	1:1	2.0/2.0	-22°	22	59%	.28 ²
9628-13-10	5 cc. $(C_4F_9)_3N$ + 5 cc sat. $MgCl_2$ soln. + 0.1 ml. 30% H_2O_2 + 0.5 ml. 10% KOH	1:1	2.0/2.0	-22°	22	47%	.43 ²
9212-6-2	Bulk	1:1	5.0/5.0	-20°	22	78%	.72 ¹
9212-6-3	Bulk	1:1	5.0/5.0	-20°	22	66%	.85 ¹
9212-24-1	Bulk	1:1	50/50	-20°	17	67%	.6 (Agitation used)
9212-24-2	Bulk	1:1	50/50	-20°	17	69%	.6
9212-26-1	Bulk	1:1	50/50	-20°	24	74%	.6
9212-47-1	Bulk	1:1	25/25	-20°	24	61%	.71
9212-47-2	Bulk	1:1	74/78	-20°	24	82%	.71
9628-14-1	Bulk	1:1	75/75	-25°	18	78%	.51 ²
9628-14-2	Bulk	1:1	30/30	-25°	18		
9628-14-3	Bulk	1:1	75/75	-25°	18	86%	.42 ²
9628-14-4	Bulk	1:1	30/30	-25°	18		
9628-14-5	Bulk	1:1	75/75	-25°	18		

1 $\langle \eta \rangle$ determined in FM 32462 $\langle \eta \rangle$ determined in FC-43;ca. 0.85 $\langle \eta \rangle$ (in FM 3246)

(in FC-43)

FM 3246, 3M Commercial Fluorocarbon Solvent
FC-43, $(C_4F_9)_3N$

TABLE XVII

Effect of Temperature on MW for
CF₃NO/C₂F₄ Copolymer

<u>Run #</u>	<u>Temp.</u>	<u>Time</u>	<u>Conversion</u>	<u>$\langle \eta \rangle$(FC-43) *</u>
9212-40-3	-65°	10 days	70%	0.86
9212-37	-20°	16 hrs.	62%	0.70
9212-28-3	-10°	21 hrs.	79%	0.61
9005-35-2	25°	24 hrs.	20%	0.15

6 g. charges (1:1 MR)

Polymerized in bulk

*(C₄F₉)₃N

TABLE XVIII

Effect of Charged MR on MW for

 $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer

<u>Run #</u>	<u>MR</u>	<u>g./g.</u>	<u>$\langle \eta \rangle$(FM 3246) *</u>
9005-6-1	50/50	2/2	0.42
9005-6-2	75/25	3/1	0.18
9005-6-3	25/75	1/3	0.23
9005-6-4	50/50	2/2	0.37
9005-6-5	75/25	3/1	0.23
9005-6-6	25/75	1/3	0.22

Polymerized in bulk

17 hours at -25°

*3M Commercial Fluorocarbon Solvent

TABLE XIX

Modified CF₃NO/CF₂F₄ Polymerizations

Run #	Polymerization Medium	MR	g./g.	Time (hrs.)	Temp. (°C.)	Conversion	$\langle \eta \rangle$	Remarks
8643-4-8	Bulk + .25 cc. BF ₃ etherate	50/50	3.5/3.5	24	-16°	60%	0.56 ¹	Gum
8643-4-9	Bulk + 1 cc. Std. TiCl ₄	50/50	3.5/3.5	48	-16°	54%	0.44 ¹	Gum
8643-4-10	Bulk + 1 cc. Szwarc catalyst	50/50	3.5/3.5	48	-16°	60%	--	Oil
8643-32-10	Bulk + 1 cc. CF ₃ CH ₂ I	66/33	2/1	48	-16°	89%	0.06 ¹	Grease
9628-2-1	Bulk + .15 g. phenylethanol amine	50/50	3.0/3.0	20	-20°	57%	--	Low MW
9628-2-2	Bulk + .15 g. 150 propyl-ethanol amine	50/50	3.0/3.0	20	-20°	65%	--	Low MW
9628-2-3	Bulk + .15 g. m-toluidine	50/50	3.0/3.0	20	-20°	67%	--	Very low MW
9628-2-4	Bulk + .15 g. m-cresol	50/50	3.0/3.0	20	-20°	--	--	Very low MW
9628-20-4	6 g. ϕ CH ₃	50/50	3.0/3.0	19	-20°	46%	--	
9628-20-3	6 g. ϕ CH ₃ + 0.2 g. DPPH	50/50	3.0/3.0	19	-20°	18%	--	Polymer red-brown in color, DPPH lowers conversion
9628-20-5	10 cc. CHCl ₃	50/50	3.0/3.0	17	-20°	33%	--	
9628-20-6	10 cc. CHCl ₃ + 0.2g. DPPH	50/50	3.0/3.0	17	-20°	26%	--	
9628-20-7	10 cc. CHCl ₃	50/50	3.0/3.0	1.5	-20°	20%	--	
9628-20-8	10 cc. CHCl ₃ + 0.2 g. DPPH	50/50	3.0/3.0	1.5	-20°	10%	--	DPPH lowers polymerization rate
9628-21	10 cc. CHCl ₃ + 0.2 g. benzoinone	50/50	3.0/3.0	4	-20°	35%	--	Benzoinone does not affect polymerization
9628-8-1	5 cc. (C ₆ F ₉) ₃ N	50/50	2.0/2.0	19	-10°	46%	0.48 ²	
9628-8-2	5 cc. (C ₆ F ₉) ₃ N + 0.5 Mol% O ₂	50/50	2.0/2.0	19	-10°	46%	0.47 ²	Small amounts of O ₂ have little effect
9628-8-3	5 cc. (C ₆ F ₉) ₃ N + 1.5 "	50/50	2.0/2.0	19	-10°	52%	0.34 ²	
9628-8-4	5 cc. (C ₆ F ₉) ₃ N + 5.0 "	50/50	2.0/2.0	19	-10°	54%	0.18 ²	
9628-9-1	5 cc. (C ₆ F ₉) ₃ N + 2 cc. Hg	50/50	2.0/2.0	19	-20°	75%	0.30 ²	
9628-9-2	5 cc. (C ₆ F ₉) ₃ N + 2cc Hg + 0.5% NO	50/50	2.0/2.0	19	-20°	85%	0.15 ²	Agitation was used. Results inconclusive since Hg reacts with CF ₃ NO
9628-9-3	5 cc. (C ₆ F ₉) ₃ N " + 1.5 "	50/50	2.0/2.0	19	-20°	90%	0.12 ²	
9628-9-4	5 cc. (C ₆ F ₉) ₃ N " + 5.0 "	50/50	2.0/2.0	19	-20°	90%	0.04 ²	
9628-7-1	5 cc. (C ₆ F ₉) ₃ N	50/50	2.0/2.0	19	-5°	52%	0.46 ²	
9628-7-2	5 cc. (C ₆ F ₉) ₃ N + 0.5% mol% NO ₂	50/50	2.0/2.0	19	-5°	82%	0.16 ²	NO ₂ increases rate and lowers MW
9628-7-3	5 cc. (C ₆ F ₉) ₃ N + 1.5 "	50/50	2.0/2.0	19	-5°	85%	0.11 ²	
9628-7-4	5 cc. (C ₆ F ₉) ₃ N + 5.0 "	50/50	2.0/2.0	19	-5°	87%	0.04 ²	
9212-54	Bulk, UV irradiation of 5-140 minutes/day during rx	50/50	3.0/3.0	21 days	-78°	83%		Product was a brown oil

1FM 3246 (3M Commercial Fluorocarbon Solvent)

2FC-43 [(C₆F₉)₃N]

59

Curing Recipe (Developed at QM R & E Center)

CF ₃ NO/C ₂ F ₄ elastomer	100 parts by weight
"Hi Sil-303"	15
TETA	1.25
HMDA carbonate	2.5
Press cure	60 min. @ 250°F
Oven post cure	18 hrs @ 212°F

Properties After Cure

F _{break}	700 psi
Ult. elongation	600 %
Modules @ 300% elong.	270 psi
Shore 'A' Hardness	55
% set after 1 hr @ 100% elong.	
10 sec. reading	20%
30 min. reading	10%

	<u>CF₃NO/C₂F₄</u>	<u>"Fluorel"</u>	<u>"Hycar 1001"</u>
Temperature Retraction 70	-29	- 9	- 9
TR 50	-36	-13	-12
TR 30	-40	-16	-14
TR 10	-46	-19	-18
Gehman Stiffness			
T ₂	-31	-10	- 7
T ₅	-41	-13	-13
T ₁₀	-44	-14	-14
T ₁₀₀	-47	-21	-18
48 hr, 25° swell (%) in:			
70/30 isooctane/toluene	2	3	24
ASTM #2 Fuel	3	3	31
Benzaldehyde	1	75	259
MEK	2	199	175
Benzylalcohol	1	1	179
Ether	2	59	21
Carbon Tet.	5	4	50
Perchloroethylene	3	2	34
Red fuming Nitric Acid	28	70	Decomp.
Acetic Anh.	3	161	108

Special Properties:

Ozone Resistance - No cracks after 24 hr. exposure to 175 ppm
@ 150°F

Sunlight Resistance - No cracks after 2 mo. roof exposure
@ 20% elong.

TABLE XXI
 Polymerization Rates of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$

N.B. Ref.	Ampoule#	Charge Cc. $(\text{C}_2\text{F}_4)_3\text{N}$	CF_3NO^*	C_2F_4^*	Time (mins.)	g. Polymer	Rate (g/min.)
9628-28	1	5.0	4.0	4.0	15	0.10	0.0103
	2	5.0	4.0	4.0	30	0.24	
	3	5.0	4.0	4.0	62	0.58	
9628-31A	1	5.0	4.0	4.0	15	0.08	0.0100
	2	5.0	4.0	4.0	30	0.23	
	3	5.0	4.0	4.0	45	0.40	
	4	5.0	4.0	4.0	60	0.51	
9628-31B	1	3.5	4.0	8.0	15	0.13	0.0122
	2	3.5	4.0	8.0	30	0.31	
	3	3.5	4.0	8.0	45	0.50	
	4	3.5	4.0	8.0	60	0.68	
9628-31C	1	3.5	8.0	4.0	15	0.18	0.0151
	2	3.5	8.0	4.0	30	0.36	
	3	3.5	8.0	4.0	45	0.60	
	4	3.5	8.0	4.0	60	0.84	
9628-33A	1	5.6	2.0	4.0	20	0.06	0.0041
	2	5.6	2.0	4.0	50	0.18	
	3	5.6	2.0	4.0	80	0.30	
9628-33B	1	5.6	4.0	2.0	20	0.07	0.0052
	2	5.6	4.0	2.0	80	0.39	
9628-33C	1	6.2	2.0	2.0	20	0.05	0.0033
	2	6.2	2.0	2.0	50	0.15	
	3	6.2	2.0	2.0	80	0.23	
9628-34A	1	6.8	1.0	1.0	46	0.02	0.00065
	2	6.8	1.0	1.0	90	0.06	
	3	6.8	1.0	1.0	180	0.11	
9628-34B	1	5.0	4.0	4.0	15	0.12	0.0114
	2	5.0	4.0	4.0	35	0.32	
	3	5.0	4.0	4.0	60	0.63	

TABLE XXI

(Continued)

Run #	N. B. Ref.	Ampoule #	CC. (C ₄ F ₉) ₃ N	Charge CF ₃ NO*	C ₂ F ₄ *	Time (mins.)	G. Polymer	Rate (G./min.)
10	9628-34C	1	5.0	4.01	4.0	15	0.11	0.0116
		2	5.0	4.01	4.0	30	0.28	
		3	5.0	4.01	4.0	45	0.44	
		4	5.0	4.01	4.0	60	0.68	
11	9628-34D	1	5.0	4.02	4.0	10	0.07	0.0149
		2	5.0	4.02	4.0	20	0.20	
		3	5.0	4.02	4.0	30	0.38	
		4	5.0	4.02	4.0	50	0.63	
12	9628-34E	1	5.0	4.03	4.0	10	0.07	0.0149
		2	5.0	4.03	4.0	20	0.20	
		3	5.0	4.03	4.0	30	0.38	
		4	5.0	4.03	4.0	50	0.63	

*Each unit equals 0.0052 moles

1 Charge also contained 5.3 x 10⁻⁵ moles CF₃I2 Charge also contained 5.3 x 10⁻⁵ moles NO₂3 Charge also contained 5.3 x 10⁻⁵ moles NO

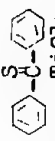
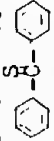
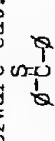
Polymerizations carried out at -30.0 ± 0.2°C.

TABLE XXII
Copolymerizations of CF_3NO

Run #	Comonomer	Medium	MR	E./g.	Temp. °C	Time	Conv.	Nature of Polymer
9628-18-1	$CF_2=CFH$	Bulk	1/1	3.1/2.5	-20°	72 hrs	73%	Elastic gum
8643-18-2A	$CFH=CH_2$	Bulk	2/1	5.4/1.7	-16 to +20°	48 hrs	0	
8643-18-2B	$CFH=CH_2$	Emulsion	2/1	5.4/1.7	+20°	24 hrs	0	
8643-18-3A	$C_2F_5CF=CH_2$	Bulk	2/1	5.4/4.9	-16 to +20°	48 hrs	0	
8643-18-3B	$C_2F_5CF=CH_2$	Emulsion	2/1	5.4/4.9	+20°	24 hrs	0	
8643-18-7A	$C_2F_5CH=CH_2$	Bulk	2/1	5.4/3.9	-20°	48 hrs	0	
8643-18-7B	$C_2F_5CH=CH_2$	Emulsion	2/1	5.4/3.9	+20°	24 hrs	0	
8643-18-9A	$CF_3CH_2OCH=CH_2$	Bulk	2/1	5.4/3.4	-65°	48 hrs	0	
8643-18-9B	$CF_3CH_2OCH=CH_2$	Emulsion	2/1	5.4/3.4	+20°	24 hrs	0	
8643-20-1	$\overline{CF_2CF=CHCH_2}$	Bulk	2/1	5.4/2.9	-20°	48 hrs	0	
8643-18-11	$CF_2=CCl_2$	Bulk	2/1	5.4/3.6	-20°	24 hrs	Quant.	Friable thermoplastic
8071-4-1	$CH_2=CH_2$	Bulk	1/1	1.6/7.0	-15 to +20°	3 weeks	0	
8071-4-2	$CH_2=CF_2$	Bulk	1/1	4.5/7.0	-15 to +20°	3 weeks	37%	Grease
8071-4-3	C_3F_7CHO	Bulk	1/1	6.0/3.5	-15 to +20°	3 weeks	0	
8071-4-4	$CFCl=CFOCH_3$	Bulk	1/1	4.5/3.5	-15°	12 hrs	Quant.	Plastic
8071-4-5	$CF_2=CFCl$	Bulk	1/1	8.1/6.9	-15°	24 hrs	Quant.	Elastic gum
9628-27	$CF_3CF=CF_2$	Bulk	1/2.5	2.0/7.5	+20°	75 days	20%	Elastic gum
9005-2-2	$C_6H_5CH=CH_2$	Bulk	1/1	2.5/2.6	-15°	24 hrs	-	Oil
9005-2-5	$CH_2=C(CH_3)COOClH_9$	Bulk	1/1	2.0/3.0	-15°	24 hrs	80%	Oil

TABLE XXIII

Reactions of CF₃NO and 1,1,2-Trifluoro butadiene (monomer 56)

N.B.	Run #	MR, CF ₃ NO/56	Monomer Concentration (wt.%)	Monomer Charge (grams)	Rx Temp. (°C)	Solvent	m.p. of solvent (°C.)	Monomer first mixed with solvent	Yield of Product	Modifier	Mole %	56 Source Batch No.
8643-16-1	1	60/40	100	6	-14	-	-	-	-	-	-	1
9095-38-7	2	50/50	50	5	-20	(C ₄ F ₉) ₃ N	-50	-	50-60%	-	-	1
9005-46-3	3	20/80	50	6	-20	(C ₄ F ₉) ₃ N	-50	-	50%	-	-	1
9005-46-6	4	50/50	100	6	-65	-	-	-	50-80%	-	-	1
9794-16-2	5	40/60	30	5	-20	(C ₄ F ₉) ₃ N	-50	56	-	-	-	1
9794-28-1	6	50/50	35	4	-25	n-C ₇ H ₁₆	-80	56	33%	-	-	2
9794-29-1	7	50/50	35	4	-65	n-C ₇ H ₁₆	-80	56	11%	-	-	2
9794-29-2	8	50/50	35	4	-78	C ₃ F ₆	-156	56	4%	-	-	2
9794-29-3	9	50/50	35	4	-78	FM 3246*	<-78	56	40%	-	-	2
9794-26-3	10	50/50	20	3	-30	n-C ₇ H ₁₆	-90	56	-	Terpene B	1	2
9794-33-1	11	20/80	30	4	-20	CH ₃ OH	-110	56	low	-	-	2
9794-33-2	12	20/80	30	4	-20	CH ₃ OH	-110	CF ₃ NO	low	-	-	2
-33-3	13	10/90	35	4	-20	FM 3246	<-78	CF ₃ NO	3%	-	-	2
-33-4	14	20/80	35	4	-20	FM 3246	-	CF ₃ NO	6%	-	-	2
-33-5	15	30/70	35	4	-20	FM 3246	-	CF ₃ NO	12%	-	-	2
-33-6	16	10/90	35	4	-20	FM 3246	-	CF ₃ NO	5%	-	-	2
-33-7	17	20/80	35	4	-20	FM 3246	-	56	6%	-	-	2
-33-8	18	30/70	35	4	-20	FM 3246	-	56	11%	-	-	2
9794-34-1	19	50/50	10	4	-24	FC-75**	below-78	56	6%	-	-	2
34-2	20	30/70	35	4	-24	FC-75	-	56	5 to 15%	-	-	2
34-3	21	20/80	35	4	-24	FC-75	-	56	-	-	-	2
34-4	22	50/50	35	4	-24	FC-75	-	56	-	-	-	2
9794-43A-1	23	50/50	35	4	-20	Freon 113	-39	56	29%		1	3
-43A-2	24	50/50	35	4	-20	FM-3246	<-78	56	29%	TiCl ₄	1	3
-43A-3	25	50/50	35	4	-20	FM-3246	<-78	56	18%	Szwarc cat.	1	3
-43B-1	26	50/50	20	4	-20	n-C ₇ H ₁₆	-90	56	15%		1	3
-43B-2	27	50/50	20	4	-20	n-C ₇ H ₁₆	-90	56	6%	TiCl ₄	1	3
-43B-3	28	50/50	20	4	-20	n-C ₇ H ₁₆	-90	56	6%	Szwarc cat.	1	3
-43-C-1	29	50/50	50	4	-78-20	Freon 113	-39	56	29%		1	3
-43-C-2	30	50/50	50	4	-78-20	FM-3246	<-78	56	21%	TiCl ₄	1	3
-43-C-3	31	50/50	50	4	-78-20	FM-3246	<-78	56	19%	Szwarc cat.	1	3

*3M Commercial Fluorocarbon Solvent
 **(3M) Commercial perfluoro Cyclic Oxide Solvent

(Continued)

TABLE XXIII

N.B.	Run #	MR, CF ₃ NO/56	Monomer Concentration (wt.%)	Monomer Charge (grams)	Ex Temp. (°C.)	Solvent	m.p. of solvent first mixed with solvent (°C.)	Monomer first mixed with solvent	Yield of Product	Modifier	Mole % Modifier	56 source Batch No.
9794-21-1	32	50/50	100	6	-40	-	-	-	50%	-	-	1-2
21-2	33	40/60	100	6	-40	-	-	-	50%	-	-	1-2
9794-25-1	34	50/50	30	3	-78 to 0	C ₇ H ₁₆	-90	56	50%	-	-	2
9794-26-1	35	50/50	20	3	-30	C ₇ H ₁₆	-90	56	50%	Ø-N=O	1	2
26-2	36	50/50	20	3	-30	C ₇ H ₁₆	-90	56	50%	TDDM	1	2
9794-44-1	37	50/50	35	4	-20	Freon 11	-	56	44%	-	-	3
-44-2	38	50/50	35	4	-20	C ₃ F ₈	-183	-	45%	-	-	3
-44-3	39	50/50	50	4	-20	C ₃ F ₈	-183	-	94%	-	-	3
-44-4	40	50/50	20	4	-20	C ₃ F ₈	-183	-	75%	-	-	3
9005-46-1	41	50/50	100	6	-20	-	-	-	-	-	-	1
9005-46-2	42	50/50	70	6	-20	(C ₄ F ₉) ₃ N	-50	-	-	-	-	1
9794-23-1	43	80/20	30	5	-30	(C ₄ F ₉) ₃ N	-50	-	-	-	-	1-2
-23-2	44	50/50	30	5	-30	(C ₄ F ₉) ₃ N	-50	-	-	-	-	1-2
9794-16-1	45	50/50	30	5	-20	(C ₄ F ₉) ₃ N	-50	-	-	-	-	1
9794-16-3	46	50/50	-	5	+45	PBK recipe*	-	-	-	-	-	1

Runs 1-31 gave polymer

Runs 32-40 gave Diels-alder adducts (also obtained from gas phase reactions)

Runs 41-46 resulted in detonations

* 4 parts C₇F₁₅COOK
 2 parts K₂HPO₄
 0.1 parts K₂S₂O₈
 100 parts H₂O

TABLE XXIV

Copolymerizations of Nitrosos Other than CF₃NO

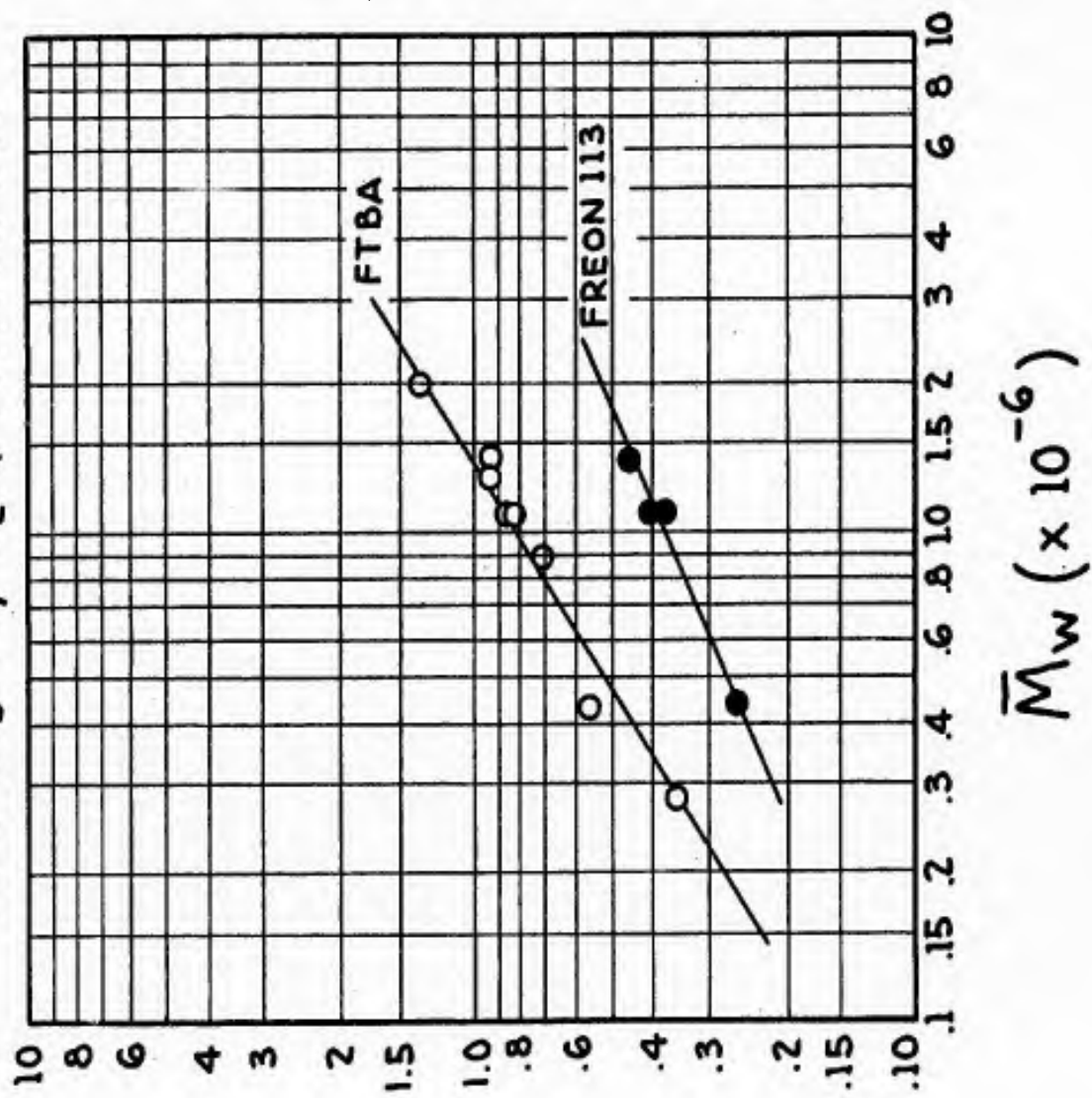
Run #	Nitroso Cpd.	Comonomer	Medium	MR	g./g.	Temp.	Time	Conversion	Nature of Polymer
8643-15-2	C ₂ F ₅ NO	C ₂ F ₄	Bulk	2/1	5.6/1.7	-16°	24 hrs.	Quant.	Rubbery gum
8643-11-1	C ₃ F ₇ NO	C ₂ F ₄	"	2/1	6.5/2.5	-20°	24 hrs.	Quant.	Rubbery gum
8643-32-16	C ₈ F ₁₇ NO	C ₂ F ₄	"	1/1.5	6.0/1.9	-20°	24 hrs.	50%	Gum rubber
8643-32-15	CF ₂ ClCFClNO	CF ₂ CFCl	"	1/1	1.0/0.6	+20°	1 week	ca. 60%	Gum
8643-47-1	O ₂ NCF ₂ CF ₂ NO	CF ₂ CF ₂	"	1/1	2.4/1.5	-25°	24 hrs.	90%	Rubbery gum
8643-47-2	"	CF ₂ CF ₂	"	1/1	1.1/2.9	-25°	24 hrs.	40%	Rubbery gum
8643-47-4	"	CF ₂ CCl ₂	"	1/1	1.0/1.0	-25°	5 days	95%	Brittle - short
8643-52-1	"	CF ₂ CFCl	"	1/1	2.4/1.6	-25°	24 hrs.	92%	Brittle - short
8643-52-2	"	CF ₂ CFH	"	1/1	2.4/1.3	-25°	24 hrs.	80%	Gum - stiff
8643-52-3	"	CF ₃ CH ₂ OCH=CH ₂	"	1/1	2.4/1.7	-25°	24 hrs.	98%	Brown fuming oil
8643-52-6	"	CF ₂ CHCl	"	1/1	2.4/1.5	-25°	24 hrs.	0	
8643-52-7	"	CF ₂ CH ₂	"	1/1	2.4/1.3	-25°	24 hrs.	0	
8643-52-8	"	SO ₂	"	1/1	2.4/0.8	-25°	24 hrs.	0	
8643-52-9	"	C ₂ F ₄	Emulsion	1/1	2.4/1.5	+20°	17 hrs.	95%	Gum
8643-54-3	"	C ₂ F ₄	Bulk	1/1	3.2/1.7	-25°	24 hrs.	82%	Gum
9005-15-1	"	C ₂ F ₄	Bulk	1/1	9.3/5.8	-20°	24 hrs.	75%	
through 7									
9760-22-1	"	C ₂ F ₄	Bulk	1/1	100/59	-20°	24 hrs.	51%	Elastomeric gum
9760-22-2	"	C ₂ F ₄	"	1/1	167/90	-20°	24 hrs.	46%	Elastomeric gum
9760-22-3	"	C ₂ F ₄	"	1/1	100/59	-29°	24 hrs.	54%	Elastomeric gum
9760-22-4	"	C ₂ F ₄	"	1/1	100/59	-29°	24 hrs.		
9760-22-5	"	C ₂ F ₄	"	1/1	100/59	-29°	24 hrs.		
9794-15-1	ClCF ₂ CF ₂ NO	C ₂ F ₄	"	1/1	3.1/1.9	-20°	20 hrs.		Rubbery, transparent
9794-15-2	ClCF ₂ CF ₂ NO	CF ₂ CFCl	"	1/1	2.9/2.1	-20°	20 hrs.		Very short rubber
9794-15-3	"	CF ₂ CFH	"	1/1	3.3/1.7	+20°	20 hrs.		Transparent thermoplastic
9794-15-4	"	CF ₂ CH ₂	"	1/1	3.6/1.4	-20°	20 hrs.		"
9794-15-5	"	CF ₂ CCl ₂	"	1/1	2.8/2.2	-20°	20 hrs.		"
9794-15-6	"	CF ₃ CF=CH ₂	"	1/1	1.8/1.6	-20°	20 hrs.	0	
9794-15-7	"	CF ₃ CH ₂ OCH=CH ₂	"	1/1	2.8/2.2	-20°	20 hrs.		Polymer decomposed on drying
9794-15-8	"	CF ₃ CH=CH ₂	"	1/1	3.1/1.8	-20°	20 hrs.		"
9760-16-1	"	C ₂ F ₄	"	1/1	15.6/9.4	-65 to -35°	8 days	82%	Elastomeric gum
through 7								(av. for 7 runs)	

TABLE XXV
Effect of Structure on T_g

Copolymer	Repeating Unit	n_D^{25}	T _g (°C)
CF ₃ NO/C ₂ F ₄	$\left(\begin{array}{c} \text{NO} - \text{CF}_2\text{CF}_2 \\ \\ \text{CF}_3 \end{array} \right)$	1.317	-51
C ₂ F ₅ NO/C ₂ F ₄	$\left(\begin{array}{c} \text{NO} - \text{CF}_2\text{CF}_2 \\ \\ \text{CF}_2 \\ \\ \text{CF}_3 \end{array} \right)$	1.32	-52
C ₃ F ₇ NO/C ₂ F ₄	$\left(\begin{array}{c} \text{NO} - \text{CF}_2 - \text{CF}_2 \\ \\ (\text{CF}_2)_2 \\ \\ \text{CF}_3 \end{array} \right)$	1.31	-32
C ₈ F ₁₇ NO/C ₂ F ₄	$\left(\begin{array}{c} \text{NO} - \text{CF}_2\text{CF}_2 \\ \\ (\text{CF}_2)_7 \\ \\ \text{CF}_3 \end{array} \right)$	1.32	< -25 *
CF ₃ NO/C ₂ F ₃ H	$\left(\begin{array}{c} \text{NO} - \text{CF}_2\text{CFH} \\ \\ \text{CF}_3 \end{array} \right)$ or HCFCF ₂	1.35	- 9
C1CF ₂ CF ₂ NO/C ₂ F ₄	$\left(\begin{array}{c} \text{NO} - \text{CF}_2\text{CF}_2 \\ \\ \text{CF}_2 \\ \\ \text{CF}_2\text{C1} \end{array} \right)$	1.357	-48
O ₂ NCF ₂ CF ₂ NO/C ₂ F ₄	$\left(\begin{array}{c} \text{NO} - \text{CF}_2\text{CF}_2 \\ \\ \text{CF}_2 \\ \\ \text{CF}_2 \\ \\ \text{NO}_2 \end{array} \right)$	1.36	-41
CF ₃ NO/C ₃ F ₆	$\left(\begin{array}{c} \text{NO} - \text{CFCF}_2 \\ \\ \text{CF}_3\text{CF}_3 \end{array} \right)$ or $\left(\begin{array}{c} \text{NO} - \text{CF}_2\text{CF} \\ \\ \text{CF}_3 \end{array} \right)$	1.323	- 9

*Apparent first order transition interfered with reading.

FIG. 1
 MOLECULAR WEIGHT vs. INTRINSIC VISCOSITY
 FOR CF_3NO/C_2F_4 ELASTOMER



[3]

FIG. 2
MOLECULAR WEIGHT DISTRIBUTION
OF $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ ELASTOMER I

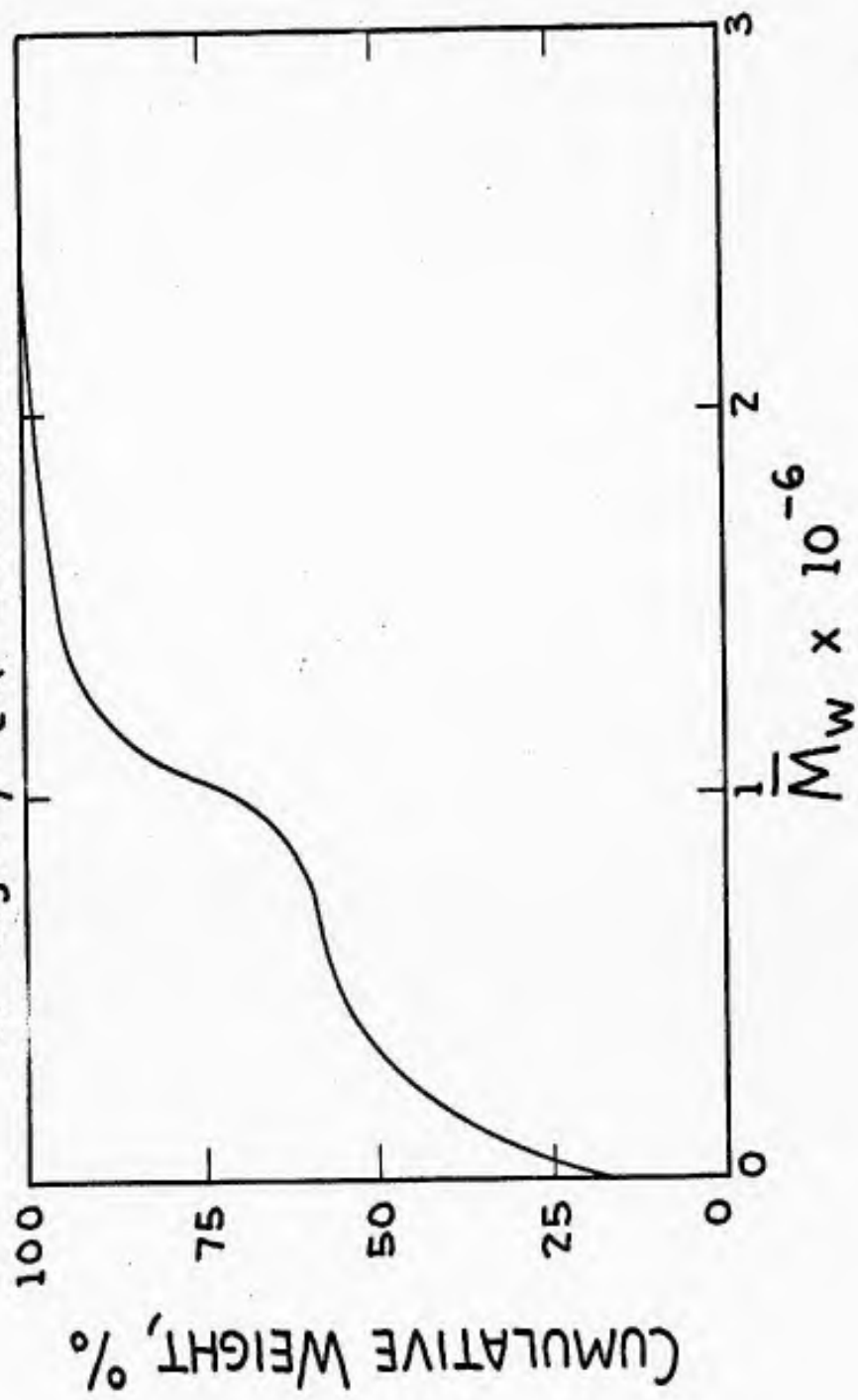


FIG. 3
 THERMAL STABILITY IN AIR
 C_2F_4/CF_3NO ELASTOMER

