SECOND ANNUAL SUMMARY REPORT
CONTRACT NO. NAS8-5352
CONTROL NO. TP 3-84117 (IF)
CPB 02-1163-63
GEORGE C. MARSHALL SPACE FLIGHT CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

FOR THE PERIOD

MAY 9, 1964 TO MAY 8, 1965

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

JUNE 8, 1965

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

CORRECTION TO QUARTERLY REPORT NUMBER 5

Figure 7 should be titled "Infrared Spectrum of $CF_3CH{=}CFCl$ (H cis to F) (76 and 14 mm)"

Figure 8 should be titled "Infrared Spectrum of $CF_3CH{=}CFCl$ (H trans to F)

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

SECOND ANNUAL SUMMARY REPORT
CONTRACT NO. NAS8-5352

FOR THE PERIOD
MAY 9, 1964 TO MAY 8, 1965

CONTRIBUTING STAFF:

Eugene C. Stump
Paul D. Schuman
T. W. Brooks, Senior Research Chemist
Geraldine Westmoreland, Research Chemist
Vince D. McGinniss, Research Chemist
Larry Sapp, Technician

PREPARED BY: Paul D. Schuman
Paul D. Schuman
Senior Research Chemist

APPROVED BY: Eugene C. Stump
Eugene C. Stump
Project Director

FOREWORD

This report was prepared by Peninsular ChemResearch, Inc., under Contract NAS 8-5352. "Development of Vulcanizable Elastomers Suitable For Use in Contact With Liquid Oxygen", with the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratory, Materials Division of the George C. Marshall Space Flight Center with Mr. J. T. Schell acting as Project Manager and Mr. Jim Curry acting as the Contracting Officer's Technical Representative.

Other personnel who have contributed to this research effort are Mr. Van A. May, Analytical Director, and Drs. Paul Tarrant and George Butler acting as consultants. In addition, Dr. Wallace Brey of the University of Florida supplied valuable assistance in interpretation of NMR spectra and Dr. R. J. Hanrahan also of the University of Florida assisted in our polymerization studies.

ABSTRACT

15770

Selected references have been compiled concerning polymer structure as related to thermal properties with major emphasis placed on fluorine containing polymers. Glass transition temperature as related to polymer structure is discussed.

Several new monomers have been prepared: $CF_3OCH = CF_2$, $CF_3OCF = CHF$, $(CF_3O)_2C = CF_2$ and $SF_5OCF = CF_2$. Elastomeric copolymers have been prepared from $CH_2 = CF_2$ and the first three monomers. Transition temperatures of a number of polymers have been determined by DTA and the extension of our present knowledge concerning structure-thermal properties relationship is discussed.

The previously unreported CHFBrCHFBr was synthesized. Optimum conditions for the preparation of CF_3OF, COF_2 and $(CF_3O)_2$ have been determined. $(CF_3O)_2$ has been added to $CFCl = CFCl$ to give mainly telomers. An attempt to prepare $(CH_3O)_2C = CF_2$ and $(CF_3CH_2O)_2C = CF_2$ by the Wittig synthesis was not successful. Reaction of $(CF_3)_2C = O$ with C_2F_4 in the presence of CsF gave a low conversion to a complex liquid mixture. A low molecular weight siloxane polymer $-\left[C(CF_3)_2OSi(CH_3)_2O\right]-_x$ and a poly(carbonate), $-\left(OCH_2(CF_2)_3CH_2OCO\right)-_x$ were prepared. Attempts to prepare C_2F_5OF by reaction of AgF_2 with CF_3COF and by indirect reaction through the intermediate $CF_3OOC_2F_5$ were not successful. An attempt to prepare $CsOCF_3$ resulted in only limited success.

Author

TABLE OF CONTENTS

TABLE OF CONTENTS (cont.)

DISCUSSION (cont.)

C. Synthesis (cont.)

TABLE OF CONTENTS (cont.)

EXPERIMENTAL (cont.)

B. Synthesis (cont.)

TABLE OF CONTENTS (cont.)

TABLES

FIGURES

TABLE OF CONTENTS (cont.)

FIGURES (cont.)

INTRODUCTION

This report describes work carried out during the second year of Contract NAS8-5352. It is proceeded by sixteen monthly reports, six quarterly reports, and an annual summary report.

Past efforts and the ultimate goal of this project, to develop elastomeric polymer systems which are vulcanizable and suitable for use in contact with liquid oxygen, make it quite evident that the required systems will be polymeric systems containing large proportions of fluorine and/or chlorine.

Due to the lack of data concerning low temperature properties of halocarbon polymers, in particular that of the fluorocarbons, it is necessary to at least initially attempt to relate structural features of the hydrocarbon and available halocarbon polymer systems which enhance low temperature properties. Obviously the desired low temperature properties which may be directly related to a polymer's usefulness at cryogenic temperatures are mechanical properties. Unfortunately a thorough search of the literature reveals little information in this area. In lieu of this information other thermal properties which are more readily available in the literature have been chosen for comparison. These properties are the crystalline melting point (Tm) and the glass transition temperature (Tg). A correlation between Tm and Tg has been recognized[1-3] which permits an approximation of Tg from a knowledge of the more readily available Tm. Thus, for symmetrical crystalline polymers as poly(ethylene) Tm = 2Tg and for unsymmetrical crystalline polymers as poly(propylene) Tm = 1.4Tg in °K.

(1) R. R. Boyer, "Changements de Phases" p. 383, pub. by Soc. de Chemie Physique, Paris, 1952.

(2) R. G. Beaman, J. Polymer Sci. 9, 472 (1953).

(3) E. Jenkel, Kolloid-Z., 130, 64 (1953).

Unfortunately, the usefulness of this relationship is limited in the present investigation since non-crystalline polymers, such as the elastomers desired in this work, melt over a considerable range allowing the possibility of only an extremely crude approximation of Tg from the melting range. It would thus appear that any extensive correlation of polymer properties with structure without resorting to actual temperature-property-structure determination must necessarily rely on literature references to Tg data. The relationship of glass transition temperatures to mechanical properties slightly above and below Tg is not known at this point but in the present investigation a good correlation between Tg and modulus of rigidity and also the Clash-Berg stiffness test has been obtained for the copolymer system, $CH_2 = CF_2/CF_3OCF = CF_2$. Boyer[4] has, in addition, proposed a possible correlation between the area under the curve of transitions occurring below Tg and impact strength.

As discussed in previous reports in attempting to correlate low temperature properties of polymers with polymer structure, the most notable characteristic found in literature references is the lack of consistency in data for low temperature transitions. This inconsistency is most pronounced in references to proposed glass transition temperatures for polytetrafluoroethylene (PTFE). In view of the recent extensive review of Boyer[4] covering multiple transitions occurring in polymers and their relation to polymer structures, it is understandable how interpretive errors may occur. McCrum[5] found transitions occurring at 127° and -97° for PTFE calling these Glass I and GlassII transitions. Boyer points out that in amorphous polymers three types of transitions are observed. Transitions occur below, above and at Tg ($T < Tg$, $T > Tg$, $T = Tg$), while crystalline polymers may exhibit two additional transitions $Tg < T < Tm$.

---

(4) R. F. Boyer, Rubber Chem. and Tech., 36 (5) 1303-1421 (1963).

(5) N. G. McCrum, Makromol. Chem., 34 (1) 50 (1959).

A tabulation of Tg (Ref. 4, p. 1405) for both linear and branched polyethylene (PE) shows a rather wide range of values depending on the method of determination. Although most of the values for linear PE were between -70° and -88° two extremes were noted at -48° (specific heat method) and -130° (specific volume studies). Similarly for branched PE the extremes were -63° (dilatometer method) and -101.5° (beta ray method). Boyer proposes that the most probable Tg for PE is -85° ± 20°.

Although these great variations would appear to preclude the usefulness of Tg as a criteria for determining structure-low temperature properties, reproducibility within a given test method is believed to be good.

In this study glass transition temperatures have thus far been determined by differential thermal analysis.

DISCUSSION

A. Glass Transition Temperatures as Related to Polymer Structure

Recognizing that possible erroneous conclusions may be drawn from existing Tg values, some selected values were tabulated (Table I and II) for a number of different homopolymers to note any possible general trends which might be beneficial in predicting low temperature properties. By considering all polymers in Table I as substituted polyethylenes (PE) and tabulating Tg in column 2 and the net change in Tg (Δ Tg, on substitution of H) some rather pronounced differences may be noted.

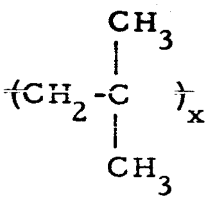
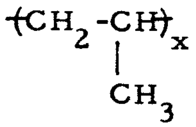
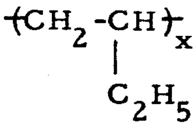
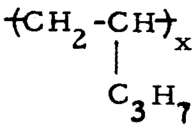
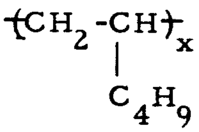
1. Symmetry of Substitution

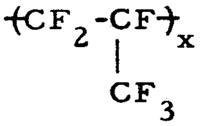
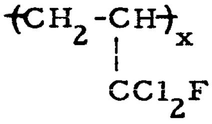
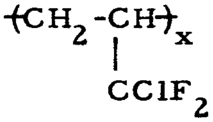
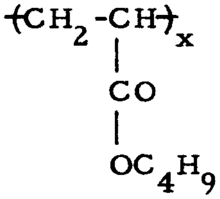
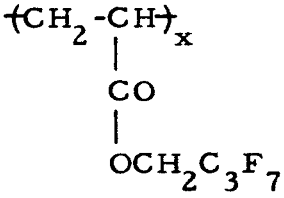
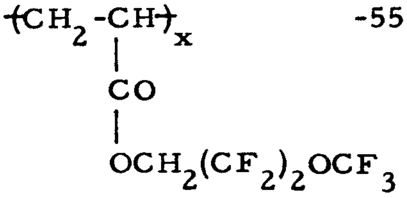
With symmetrical substitution of two H by two CH_3 groups, as in poly(isobutylene), Δ Tg is 15° whereas substitution of a single H with CH_3 as in poly(propylene) causes quite a drastic increase, Δ Tg is 68°. This same effect is carried over to the halocarbon series where replacement of two H with F increases Tg by 40°, as in vinylidene fluoride, whereas replacement of a single H by F, as in vinyl fluoride, gives a Δ Tg of 125°. With similar replacement of 2 chlorine atoms for H, as in poly(vinylidene chloride), Δ Tg is 100° and the unsymmetrical replacement of one H by Cl, as in poly(vinylchloride), gives Δ Tg of 180°.

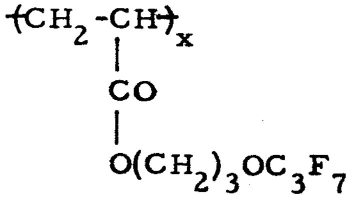
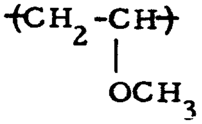
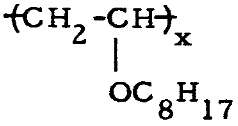
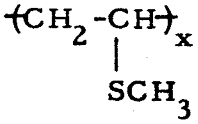
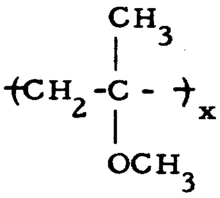
We may in addition note that comparing total replacement of H for F as in poly(tetrafluoroethylene) with partial but symmetrical replacement as in poly(vinylidene fluoride) little change occurs in Tg (assuming Tg for PTFE is -50°).

TABLE I

Glass Transition Temperatures of Selected Polymers
Substituted Poly(ethylenes)

Polymer	Tg °C**	△ Tg from PE*	Reference
$(CH_2-CH_2)_x$	$\underline{-85}$, -165, -125	-	a, b, c
 $(CH_2-C(CH_3)_2)_x$	-70	+15	d
 $(CH_2-CH(CH_3))_x$	-17	+68	e
 $(CH_2-CH(C_2H_5))_x$	-25, -43 (atactic)	+42	f, e
 $(CH_2-CH(C_3H_7))_x$	-24	+61	b
 $(CH_2-CH(C_4H_9))_x$	-117 (calc.)	-32	g
$(CH_2-CCl_2)_x$	+$\underline{15}$, -17	+100	h, i
$(CH_2-CHCl)_x$	+95	+180	h
$(CF_2-CF_2)_x$	127, 110, 30, $\underline{-50}$, -95, -112	+35	j, k, l, m, j, n
$(CH_2-CF_2)_x$	-45	+40	o

Polymer	Tg °C**	Δ Tg from PE*	Reference
$(CH_2-CHF)_x$	+40	+125	h
 $(CF_2-\underset{\substack{\vert\\ CF_3}}{CF})_x$	+165, +11	250°	p, d
$(CF_2-CFCl)_x$	-80, 45	+130	q, r
 $(CH_2-\underset{\substack{\vert\\ CCl_2F}}{CH})_x$	47	+132	s
 $(CH_2-\underset{\substack{\vert\\ CClF_2}}{CH})_x$	25	+110	s
	Vinyl Esters and Ethers		
 $(CH_2-\underset{\substack{\vert\\ CO\\ \vert\\ OC_4H_9}}{CH})_x$	256	+29	d
 $(CH_2-\underset{\substack{\vert\\ CO\\ \vert\\ OCH_2C_3F_7}}{CH})_x$	-30	+55	t
 $(CH_2-\underset{\substack{\vert\\ CO\\ \vert\\ OCH_2(CF_2)_2OCF_3}}{CH})_x$	-55	+30	t

Polymer	Tg °C**	Δ Tg from PE*	Reference
 $\left(CH_2-\underset{\substack{\mid\\ CO\\ \mid\\ O(CH_2)_3OC_3F_7}}{CH}\right)_x$	-68	+17	t
 $\left(CH_2-\underset{\substack{\mid\\ OCH_3}}{CH}\right)$	-31	+54	u
 $\left(CH_2-\underset{\substack{\mid\\ OC_8H_{17}}}{CH}\right)_x$	-80	+5	u
 $\left(CH_2-\underset{\substack{\mid\\ SCH_3}}{CH}\right)_x$	-1	+84	u
 $\left(CH_2-\overset{\substack{CH_3\\ \mid}}{\underset{\substack{\mid\\ OCH_3}}{C}}-\right)_x$	+67	+152	u

* Net change in Tg from that of poly(ethylene).
** Underlined value considered to be most reliable.

REFERENCES TO Tg DATA IN TABLE I

a. B. M. Brieveson, Polymer, 1, 499 (1960).

b. F. P. Reding, J. A. Faucher, and R. D. Whitmen, J. Polymer Sci., 57, 483 (1962).

c. R. F. Boyer, Rubber Chem. and Tech., 36 (5), 1303-1421 (1963).

d. "Property and Structure of Polymers", A. V. Tobolsky, John Wiley and Sons, New York, 1960.

e. R. Zannetti, P. Manaresi, and L. Baldi, J. Polymer Sci., 62, 174 (1962).

f. F. P. Reding, J. Polymer Sci., 21, 547 (1956).

g. F. P. Reding, J. Polymer Sci., 21, 547 (1956).

h. K. Schmieder and K. Wolf, Kolloid-Z., 134, 149 (1953).

i. "Physical Chemistry of High Polymeric Systems", H. Mark and A. V. Tobolsky, Interscience Publishers, New York, 1950.

j. N. G. McCrum, Makromol. Chem., 34 (1), 50 (1959)

k. A. V. Tobolsky, J. Polymer Sci., Part A, 1, 483 (1963)

l. B. Ke, J. Polymer Sci., Part B, 1, 167 (1963).

m. R. F. Boyer, Rubber Chem. and Tech., 36 (5), 1354 (1963).

n. M. Bacareda and E. Butta, J. Polymer Sci., 31, 189 (1958).

o. L. Mandelkern, G. M. Martin, and F. H. Quinn, Jr., J. Res. Nat'l Bureau of Standards, 58, 137 (1957)

p. H. S. Eleuterio and E. P. Moore, Second International Symposium on Fluorine Chemistry, Estes Park, Colo., July 17-20, 1962.

q. T. Nakajima and S. Saito, J. Polymer Sci., 53, 764 (1958).

r. A. W. Meyers, V. Tammela, V. Stannett, and M. Szwarc, Modern Plastics, 37 (10), 139 (1960).

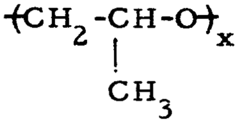
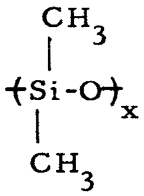
s. G. S. Kolesnikov and N. G. Mateeva, Vysokomolekulyarne Soediniya, 1, 1733 (1959).

t. Minnesota Mining and Manufacturing Co., WADC Tech. Report 52-197 Part 3, Sept. 1953.

u. J. Lal and G. Trick, J. Polymer Sci., Pt. A, 2 (10) 4559-72 (1964).

TABLE II

Glass Transition Temperatures of Some Polyethers

Polymer	Tg	Reference
$\left(CH_2-O\right)_x$	-76	a
$\left(CH_2-CH_2-O\right)_x$	-56, -27	b, c
 $\left(CH_2-CH(CH_3)-O\right)_x$	-62, -74, -50	b, e, f
$\left(CH_2CH_2CH_2-O\right)_x$	-64	f
 $\left(Si(CH_3)_2-O\right)_x$	-123	d

REFERENCES TO DATA IN TABLE II

a. B. E. Read and G. Williams, Polymer, 2, 239 (1961)

b. B. E. Read, Polymer, 3, 529 (1962)

c. N. G. McCrum, J. Polymer Sci., 54, 561 (1961)

d. "Property and Structure of Polymers", A. V. Tobolsky, John Wiley and Sons, New York, 1960.

e. G. Allen, et. al., Polymer, 5 (11), 547-52 (1964)

f. J. Stratta, F. P. Reding and J. Faucher, J. Polymer Sci., Pt. A 2 (11), 5017-23 (1964); C.A., 62, 6578h (1965)

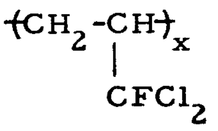
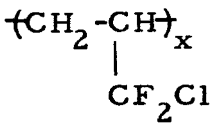
It would appear from the consistency within this series that symmetry along the polymer chain is vital in allowing low temperature mobility. This data is also supporting evidence for the Tm/Tg correlation previously noted for symmetrical and unsymmetrical systems. This effect of symmetry would appear to be eliminated when increased flexibility is introduced into the polymer chain such as noted for the polyether series in Table II. Comparing ethylene and propylene oxide transitions, no great change in Tg is noted. This also appears to be true for unsymmetrical substitution where flexibility is provided in the side chain as in the acrylate esters.

In addition to these observations concerning symmetry it is interesting to note the apparent effect of replacing F with the larger halogen Cl. With the replacement of F by Cl in the polyvinyl halides a change of 55° occurs and replacement of 2F by 2Cl in the vinylidene halides causes an increase of 60°. In view of this the presence of chlorine on the polymer backbone would be detrimental to low temperature properties with the possible exception as presented before where chain flexibility is provided by inclusion of oxygen in the polymer chain. In the case of the vinyl halides symmetry appears to exhibit the more pronounced effect if we may in addition compare $(CF_2\text{-}CF_2)_x$ with a Tg of -50 to that of $(CF_2\text{-}CFCl)_x$ with a Tg of 45°.

Based on the foregoing discussion indications are that $(CFH\text{-}CF_2)_x$ and $(CFH\text{-}CFH)_x$ (prepared under this contract) would have a higher Tg than $(CF_2\text{-}CF_2)_x$ and the latter one would probably have a higher Tg than $(CF_2\text{-}CFCl)_x$ (see Table III). This prediction is substantiated by the approximate value of 85° for Tg of poly(vinylene fluoride) as determined by heat distortion using a Vicat type penetration apparatus and by DTA analysis which gave a Tg of 102°. In addition, Tg of $(CHFCF_2)_x$ was estimated from two DTA determined crystalline transitions to be 31°, 49°.

2. Side Chain Effects

The adverse effect of unsymmetrical substitution on Tg apparently decreases as the length of the side chain is increased. Reding[6] found for isotactic 1-olefins that Tm goes through a minimum for poly(1-hexene) at a crystalline melting point (Tm) of -55° and a calculated Tg of -117° (where Tm = 1.4 Tg). An excellent demonstration of this same effect is given by Lal and Trick[7] where Tg determined on a series of vinyl ethers was found to go through a minimum value with a side chain length of C_8. The Tg for n-octyl vinyl ether was -80°, a ΔTg of 5° (Table I). An extreme change in Tg was also noted for the unsymmetrical isopropenyl methyl ether, Δ Tg 152°. In addition they also found that replacement of oxygen by sulfur in the vinyl ethers increased Tg by 30° or more.

Although the effect of symmetrical replacement once again is evident in  $-\!\left(CH_2-\underset{\underset{\displaystyle CFCl_2}{|}}{CH}\right)_x$ where Tg is +47° and  $-\!\left(CH_2-\underset{\underset{\displaystyle CF_2Cl}{|}}{CH}\right)_x$ where Tg is 25°, the effect of changing F for Cl is less pronounced than when directly on the polymer backbone.

Flexibility in the side chain as in the acrylate polymers appears to offset considerably the effect of unsymmetrical substitution. However, substitution of a C_3F_7 group for a C_3H_7 in poly(butyl acrylate) increases Tg by 26°. Although appreciable, the increase is less than a similar substitution of H for F on the polymer chain. Also the replacement of a CF_3 by a OCF_3 group in the alcohol group of the esters reduces Tg by 25°.

We may also compare Tg values of the homopolymer of perfluoropropene (HFP), 165°, with that of poly(perfluoromethyl vinyl ether), -5°, (Table III) and note a rather dramatic difference of 170°. Unfortunately,

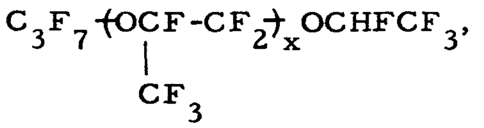
(6) F. P. Reding, J. Polymer Sci., 21, 547 (1956).
(7) J. Lal and G. Trick, J. Polymer Sci., Pt. A 2 (10), 4559-72 (1964)

once again widely differing values are reported for HFP (ref. p and d, Table I) but this higher value is considered to be more reliable and has also been accepted by Tobolsky[8].

In an attempt to construct this homopolymer from Stuart and Briegleb models[9] it became quite apparent that this polymer is extremely hindered since only three monomer units could be joined. A fourth unit could not enter without breaking the structure. In comparing models by replacement of the CF_3 by a OCF_3 group, the polymer chain is still highly hindered but may be constructed and some rotation of the pendent OCF_3 groups is possible.

3. Heteroatoms in the Polymer Chain

It is interesting to note in Table II that introduction of oxygen in the polymer chain has no apparent beneficial effect on lowering Tg. In fact Tg for the series of polyethers shown in this table range from a low of -76° to a doubtful high of -27° with little effect noted for symmetry. Most notable is the fact that none of these polymers have a Tg equal to that of poly(ethylene). It would appear that the beneficial effect of added flexibility imparted to the polymer chain by the presence of oxygen is counteracted by hydrogen bonding. With fluorocarbon polyethers this would not occur. Unfortunately no references to Tg of high molecular weight fluorocarbon polyethers have been found. One reference which would tend to support this view, however, is the extreme liquid range, about 290°, and low pour point of series E Freons[10] which are understood to have the ether structure. Structure shown below.



$C_3F_7(OCF(CF_3)-CF_2)_xOCHFCF_3$, when x is 1 to 5.

---

(8) M. C. Shen and A. V. Tobolsky, ONR Technical Report RLT-75, April, 1964

(9) A. S. LaPine and Co., Chicago, Ill.

(10) E. I. du Pont de Nemours and Co., Tech. Bul. EL-4 and EL-8.

4. Copolymers

No copolymer systems have been included in the tables since for purposes of comparison Tg values must be related to copolymer composition. Any extensive table of this nature would become unwieldy and complicated. In addition, since few values for fluorocarbon copolymers are available no broad comparison could be made. Two fluorocarbon copolymer systems for which limited Tg values have been determined are copolymers of $CH_2=CF_2$ with $CF_2=CFCl$ (Kel-F elastomer)[11] and $CF_3CF=CF_2$ (Viton A)[8]. Fairly well established Tg values are known for homopolymers of $CF_2=CH_2$ and $CF_2=CFCl$ but unfortunately only a single copolymer Tg for Viton A is given which lends little support to the widely divergent values shown in Table I for a homopolymer of poly(HFP).

In a mathematical treatment for copolymer systems presented by Gordon-Taylor[12] and the equivalent by Wood[13] and others, Tg depends on the composition of copolymers according to a weighted average of the Tg of the two homopolymers. These equations imply that a copolymer Tg cannot be less than the Tg of the homopolymer having the lowest Tg. Although this has been found to be a good approximation for a number of polymer systems, many exceptions have also been noted. Beevers and White[14] found a minimum in Tg for random copolymers of acrylonitrile and methyl methacrylate. Illers[15] presented data on 17 copolymer pairs. Curves of Tg against composition showed maxima, minima and both plus and minus deviations from a linear curve between the Tg of the two homopolymers. Hence, Tg data must necessarily be obtained on our present polymer systems to determine the validity of our reasoning in the above discussion and to characterize our new

(11) L. Mandelkern, G. M. Martin and F. A. Quinn, Sr., J. Research Nat'l. Bur. Std., 58, 137 (1951)
(12) M. Gordon and J. S. Taylor, J. Appl. Chem. (London), 2, 493 (1952).
(13) L. A. Wood, J. Polymer Sci., 20, 319 (1958)
(14) R. Beevers and E. White, Trans. Faraday Soc., 56, 1529 (1960)
(15) K. H. Illers, Kolloid Z, 190, 16 (1963).

copolymer systems.

B. New Polymers

Since our present study is mainly concerned with polymers which are oxidatively stable, hence containing large proportions of halogen, an extension of Table I was prepared containing some repetitions of values but using poly(tetrafluoroethylene)(PTFE) as a basis for comparison. Table III lists the structure, Tg and ΔTg of known and new fluorine containing polymers with Δ Tg based on Tg of PTFE as -50°. Although considerable doubt still exists concerning Tg of PTFE the most likely value is -50°. Recent work of Durrell[16] lends additional support to this value. During the course of the present study, additional data will become available to firmly establish Tg for PTFE.

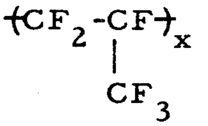
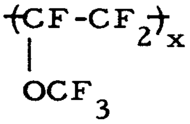
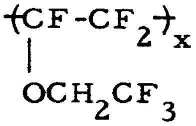
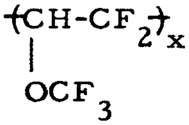
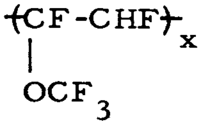
In Table VI in the experimental section are shown transition temperatures of three copolymers of $C_2F_4/CF_3OCH{=}CF_2$. In submitting these samples for thermal analysis it was hoped to establish Tg for PTFE. Unfortunately, the results of these analysis are quite inconsistent and appear to be of little value for establishing this point.

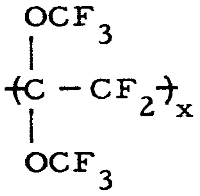
Glass transition temperatures have been determined for $-\!(CHFCHF)\!-$ and $-\!(CHFCF_2)\!-$. These polymers were submitted for DTA analysis as polymerized and were presumed to be highly crystalline. No attempt was made to reduce crystallinity by melting and quenching since absolute Tg values for these polymers are not necessary. The values do provide, however, further corroborative evidence for the detrimental effect on Tg by the presence of the CHF group in the polymer chain. The thermogram of $-\!(CHF{-}CF_2)\!-_x$ did not reveal any transition occurring below two crystalline melting points, necessitating Tg for this polymer to be estimated from the Tm values by the Tm= 1.4 Tg relationship. It is of interest to note also that onset of decomposition for this polymer occurs at 320°. The added increase in Tg when the CHF group is repeated as in the $-\!(CHF{-}CHF)\!-_x$ is substantial (Tg=102°).

(16) W. S. Durrell, Burke Research Co., unpublished work concerning Tg of copolymers of C_2F_4.

TABLE III

Glass Transition Temperatures of Fluorine Containing Polymers

Polymer	Tg °C*	Δ Tg from PTFE**	Reference
$\left(CF_2-CF_2\right)_x$	127, 110, 30, $\underline{-50}$ -95, -112	-	a, b, c, d, a, e
$\left(CHF-CF_2\right)_x$	31, 49 (calc. from Tm)	81, 99	n
$\left(CH_2-CF_2\right)_x$	-45	5	f
$\left(CFH-CFH\right)_x$	85, $\underline{102}$	152	g, n
$\left(CH_2-CHF\right)_x$	+40	90	h
 $\left(CF_2-\underset{\displaystyle CF_3}{\underset{\vert}{CF}}\right)_x$	+$\underline{165}$, +11	215	i, j
$\left(CF_2-CFCl\right)_x$	-80, $\underline{45}$	95	k, l
 $\left(\underset{\displaystyle OCF_3}{\underset{\vert}{CF}}-CF_2\right)_x$	-5	45	Fig. 1
 $\left(\underset{\displaystyle OCH_2CF_3}{\underset{\vert}{CF}}-CF_2\right)_x$	28°	82	Fig. 3
 $\left(\underset{\displaystyle OCF_3}{\underset{\vert}{CH}}-CF_2\right)_x$	0	50	Fig. 2
 $\left(\underset{\displaystyle OCF_3}{\underset{\vert}{CF}}-CHF\right)_x$	***		Fig. 2

Polymer	Tg °C*	Δ Tg from PTFE**	Reference
 $-\!\!\left(\overset{\displaystyle OCF_3}{\underset{\displaystyle OCF_3}{C}}-CF_2\right)_{\!x}\!\!-$	-60	Crude estimate from best DTA analysis obtained.	

* Underlined value considered most reliable.
** Net change in Tg from that of PTFE.
*** Thus far indicated to be close to 0°. See Discussion.

REFERENCES TO Tg DATA IN TABLE III

a. N. G. McCrum, Makromol. Chem., 34 (1), 50 (1959).

b. A. B. Tobolsky, J. Polymer Sci., Part A, 1, 483 (1963).

c. B. Ke, J. Polymer Sci., Part B, 1, 167 (1963)

d. R. F. Boyer, Rubber Chem. and Tech., 36 (5), 1354 (1963).

e. M. Bacareda and E. Butta, J. Polymer Sci., 31, 189 (1958)

f. L. Mandelkern, G. M. Martin, and F. H. Quinn, Jr., J. Res. Nat'l Bureau of Standards, 58, 137 (1957).

g. Determined by Vicat type penetration apparatus by G. F. L. Ehlers, Air Force Materials Laboratory, Wright-Patterson A. F. B., Ohio.

h. K. Schmieder and K. Wolf, Kolloid-A., 134, 149 (1953)

i. H. S. Eleuterio and E. P. Moore, Second International Symposium on Fluorine Chemistry, Estes Park, Colo., July 17-20, 1962

j. "Property and Structure of Polymers", A. V. Tobolsky, John Wiley and Sons, New York, 1960

k. T. Nakajima and S. Saito, J. Polymer Sci., 53, 764 (1958)

l. A. W. Meyers, V. Tammela, V. Stannett, and M. Szwarc, Modern Plastics, 37 (10), 139 (1960)

m. DTA Analysis, Sadtler Research Laboratories, Philadelphia, Pa., During the period covered by this report, several Tg values have been determined for copolymer systems containing $CF_3CH_2OCF{=}CF_2$ and the new vinyl ethers $CF_3OCF{=}CF_2$, $CF_3OCH{=}CF_2$, $CF_3OCF{=}CHF$ and $(CF_3O)_2C{=}CF_2$. These values were determined by DTA and are shown in Table VI in the Experimental section. Since it was not possible to prepare homopolymers of these ethers, with the exception of $CF_3CH_2OCF{=}CF_2$, it was necessary to obtain homopolymer Tg by extrapolation of copolymer values. The values obtained in this way for copolymers of $CF_3OCF{=}CF_2$, $CF_3OCH{=}CF_2$ and $CF_3CH_2OCF{=}CF_2$ are shown in Figures 1, 2 and 3 and the extrapolated values for the ether homopolymers are included in Table III.

It is interesting to note the close agreement of modulus of rigidity values[17] shown in Figures 1 and 2 to Tg values determined by DTA. In addition two other points shown in Figure 1 are values obtained[18] by the Clash-Berg stiffness test (ASTM D1043-51). These values are also very close to the values determined by DTA. This good agreement lends support to the use of Tg as a criteria for estimating low temperature properties of polymers.

1. Copolymers of $CF_3OCH{=}CF_2$ and of $CF_3OCF{=}CHF$

In contrast to the large increase in Tg noted above where CHF is present in the polymer chain, as in $-(CHFCHF)-$ with Tg = 102°, a single Tg determined for the copolymer $CF_2{=}CH_2/CF_3OCF{=}CHF$ (single point on Figure 2) indicates little change in Tg from that of copolymers of the isomeric ether $CF_3OCH{=}CF_2$. In view of the foregoing discussion this would appear to be contrary to what might be expected. Symmetry has such a pronounced effect, (compare also Tg of $-(CF_2-CH_2)_x-$, -45°, to $-(CFH-CH_2)_x-$, +40°, or

---

(17) Determined by the Materials Division of the Propulsion and Vehicle Engineering Laboratory, Marshall Space Flight Center, the points correspond to the mid-point in the stiffness curve vs. temperature.

(18) J. R. Albin, U. S. Patent 3, 136, 745, (June, 1964).

Figure 1.

Tg of Copolymers of

$CH_2=CF_2/CF_3OCF=CF_2$

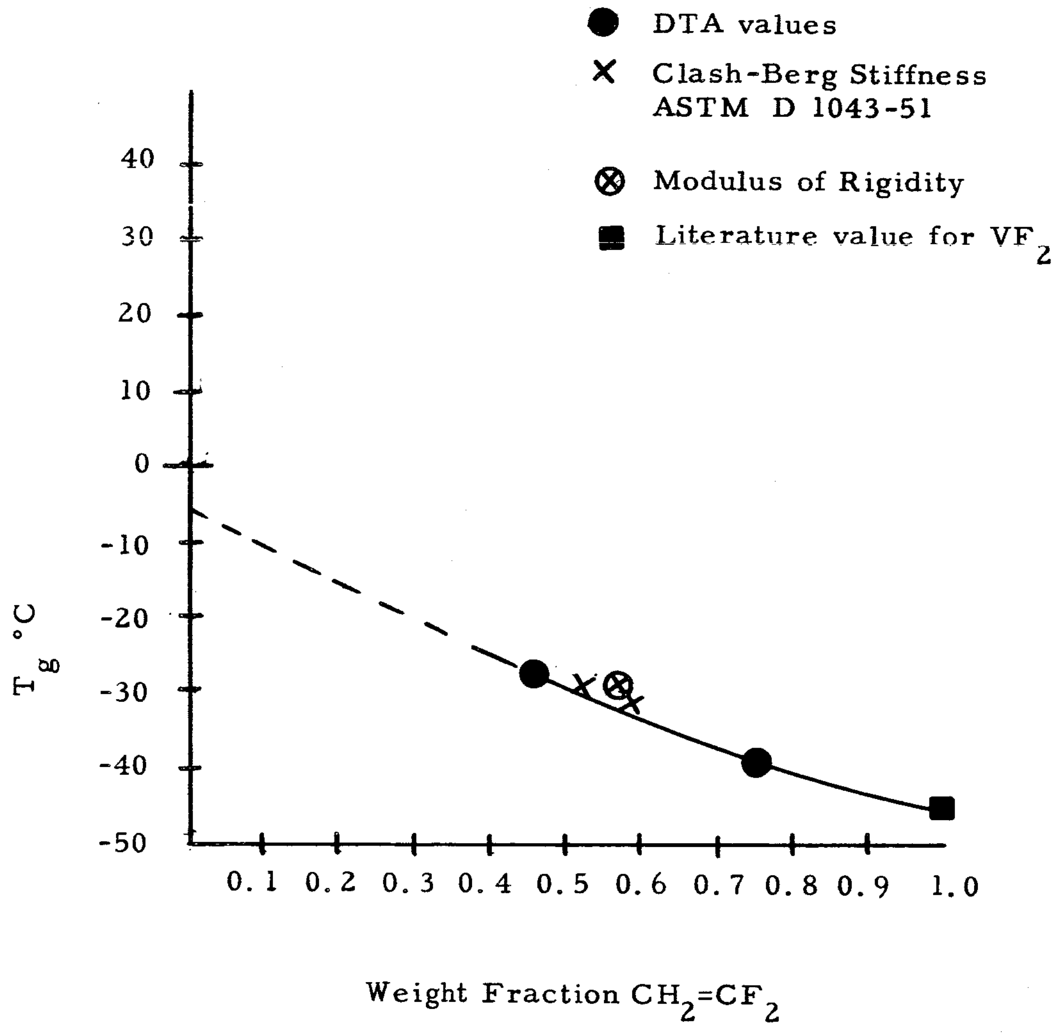


Figure 2

Tg of Copolymers of Vinylidene Fluoride with $CF_3OCH=CF_2$ and $CF_3OCF=CFH$

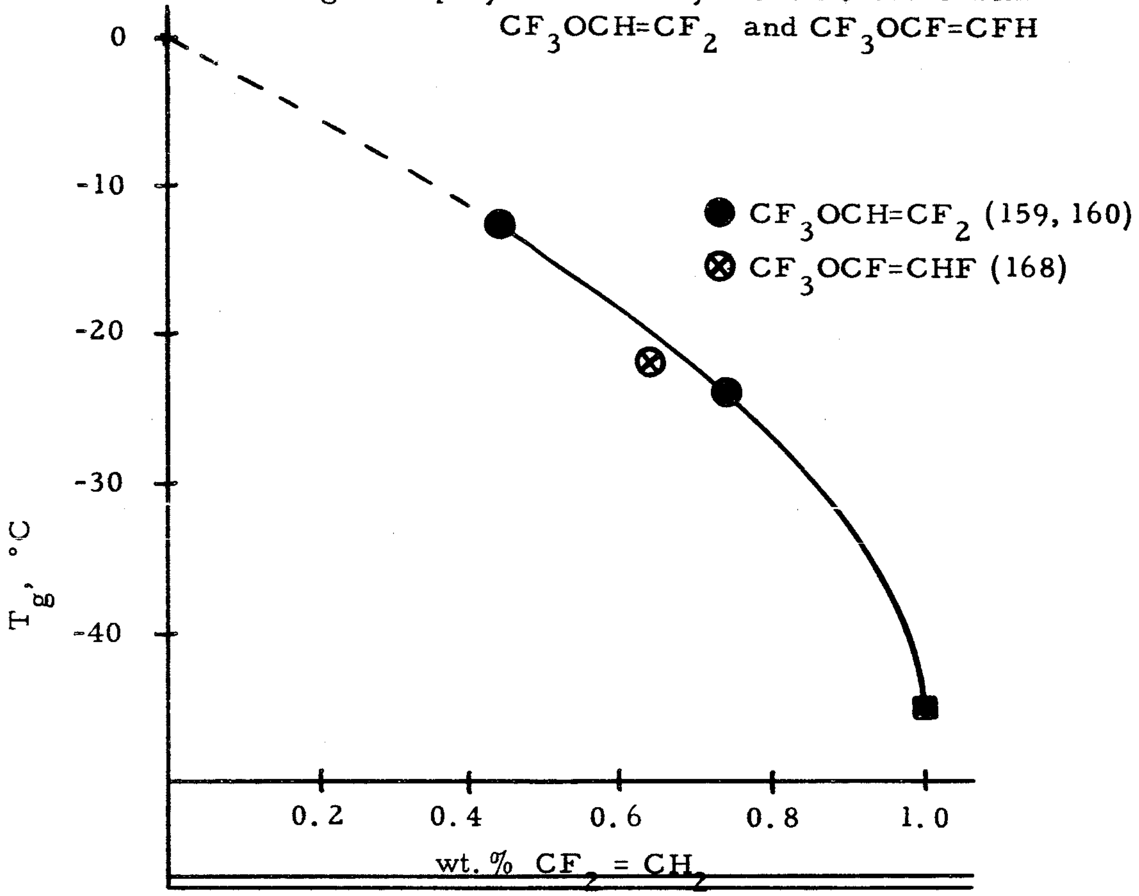
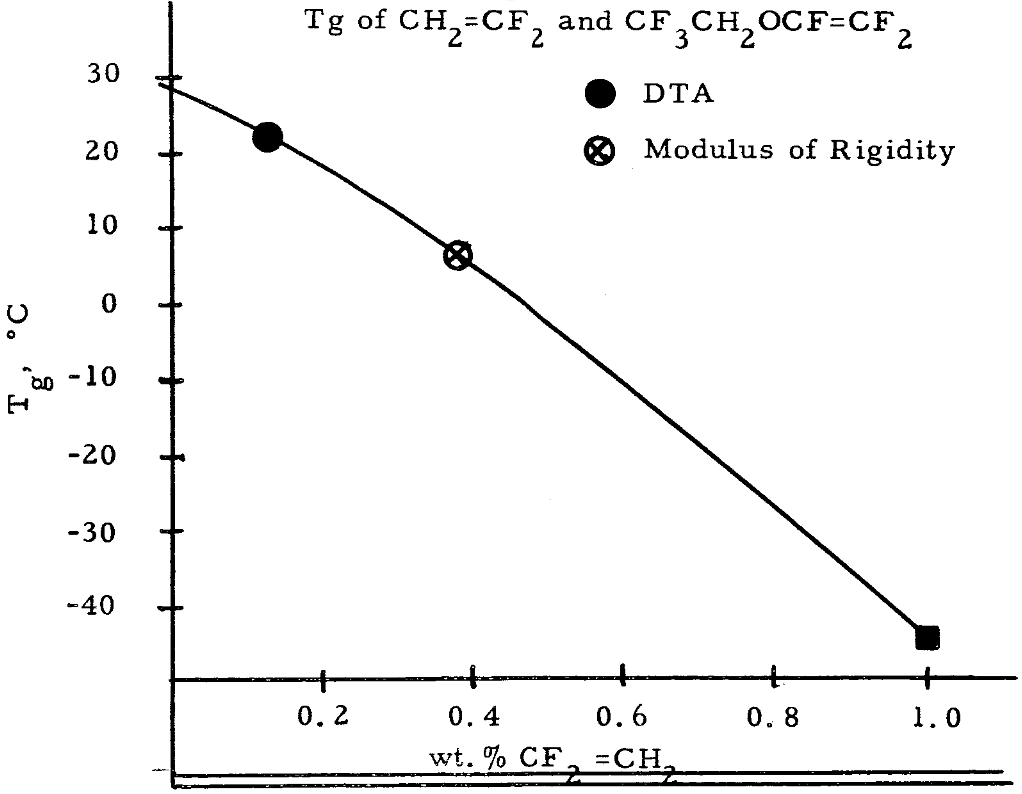
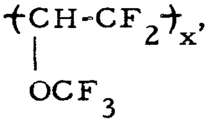


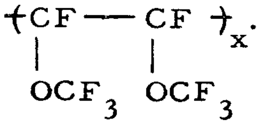
Figure 3

Tg of $CH_2=CF_2$ and $CF_3CH_2OCF=CF_2$



$(CFH{-}CFH)_x$, 102°) that it would suggest that the Tg value is in error. Structural assignment of this isomer was based on NMR data obtained on its dichloro precursor, $CF_3OCFClCFHCl$, and there appears to be little doubt with regard to structure. A second polymer sample of this ether was in preparation but unfortunately this ampule burst. In view of this suggested anomalous Tg value, additional copolymers were prepared but have not as yet been evaluated. This will be of particular interest since, if this Tg is found to be a true value, it indicates that the presence of the trifluoromethoxy group on the adjacent carbon completely offsets the demonstrated detrimental effect of the asymmetric CHF group in the polymer chain.

The isomeric ether,  $(\underset{\underset{\displaystyle OCF_3}{|}}{CH}{-}CF_2)_x$, has a Tg value quite close to that of the perfluoro analog. This result is also surprising in view of the numerous examples of the invariable increase in Tg when hydrogen is substituted by F either on the polymer chain or on a side group. We may compare $(CH_2{-}CH_2)_x$ (Tg -85°) with $(CF_2{-}CF_2)_x$ (Tg -50°) or $(CH_2{-}CF_2)_x$ (Tg -45°). This Tg would indicate an additional beneficial effect of the pendent CF_3O group and further indicate some promise for the low temperature properties of the proposed polymers of the 1, 2-bis(trifluoromethoxy)difluoroethylene,



$(\underset{\underset{\displaystyle OCF_3}{|}}{CF}{-\!-}\underset{\underset{\displaystyle OCF_3}{|}}{CF})_x$.

In addition to the copolymerization experiments an attempt was made to prepare a homopolymer of $CF_3OCH{=}CF_2$. Similar to previous attempts to prepare homopolymers of $CF_3OCF{=}CF_2$, irradiation of this vinyl ether (gamma dose of 3.87×10^7 rep) resulted in a tacky liquid polymer. Since equally hindered polymers have been homopolymerized when the polymerization has been carried out at extremely high pressures it seems reasonable that this would also be true for these vinyl ethers. Some thought has been given to this method of polymerization due to the advantage of being able to directly determine Tg for the homopolymers.

Since considerably increased flexibility of the polymer chain is noted when Stuart and Briegleb models of $CF_3OCF=CF_2/CH_2=CH_2$ were constructed it was felt that inclusion of small amounts of $CH_2=CH_2$ may have a marked effect on Tg. Three experimental polymers were attempted containing varying proportions of C_2H_4 in terpolymers of $CH_2=CH_2/CH_2=CF_2/CF_3OCH=CF_2$. Two of the polymer ampules burst and the third containing 32.0 mole % $CH_2=CH_2$, 35.0 mole % $CH_2=CF_2$ and 33.0 mole % $CF_3OCH=CF_2$, after a gamma dose of 4.12×10^7 rep, yielded only a trace of a viscous oil.

2. Copolymers of $(CF_3O)_2C=CF_2$ (PVM)

During the latter part of this period sufficient monomer was available to prepare a number of copolymers of the new monomer 1, 1-bis(trifluoromethoxy)-difluoroethylene or perfluorovinylidene methoxide (PVM), Table V. It was found that PVM copolymerizes readily with both $CH_2=CF_2$ (VF_2) and C_2F_4(TFE) when exposed to ionizing radiation. The physical state of the copolymers VF_2/PVM ranged from a liquid, where monomer ratios of reacted VF_2/PVM were <2, to a solid flexible polymer, when the ratio was 4. The change in solubility characteristics of these copolymers with increase in total gamma dose suggests the possibility that some crosslinking has occurred. At 1.4×10^6 rep. (exp. 188 and 189) solid polymers were obtained in low conversion (11%) which were totally soluble in acetone. Equivalent polymers 185 and 192, which had a total dose of 13.2×10^6 rep. were swollen by and only slightly soluble in acetone. Other factors seem to contradict or minimize the possibility that crosslinking has occurred in that the insoluble polymers were fusible and that monomer ratios of VF_2/PVM of 2.4 gave low molecular weight polymers at very high total dose of 33.6×10^6 rep. which were completely soluble in acetone.

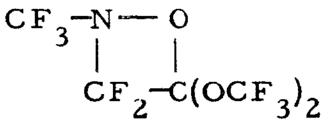
Based on the information gained in the preparation of copolymers of VF_2/PVM, a single copolymer of TFE/PVM was prepared using a monomer ratio of TFE/PVM of 4. A high conversion to polymer was obtained at a total gamma dose of 4.5×10^6 rep. Examination of the polymer after removal from the Carius tube revealed it to be paste-like, similar to that of a homopolymer of TFE. A very small sample molded into a film didn't appear to have elastomeric properties. The copolymer also exhibited a crystalline transition identical with that observed for poly(TFE) at 322°, Table VI. The ease with which this polymerization occurred would indicate that it should be possible to incorporate a greater proportion of PVM into a copolymer and possibly obtain an elastomer.

The initial copolymer sample VF_2/PVM submitted for thermal analysis, sample 185, showed a very pronounced endotherm at -50° attributable to Tg (Table VI). A crude extrapolation of this value would indicate a Tg of -60° for the homopolymer of PVM. Unfortunately, two additional samples which were submitted for analysis, samples 190 and 192, gave inconsistant results. Sample 192 showed a somewhat doubtful Tg at -26° and sample 190 showed no transitions occurring below ambient temperature. In view of this inconsistancy it is not possible at present to establish Tg for the homopolymer of PVM.

The preparation and evaluation of copolymer samples of this new monomer has thus far been limited by the availability of chromatographically pure samples. Although approximately 49% of the PVM is present in the crude mixture from the dehydrochlorination of $(CF_3O)_2CHCF_2Cl$, the separation has been hampered by the presence of two unidentified trace impurities which have retention times very close to that of the desired PVM monomer.

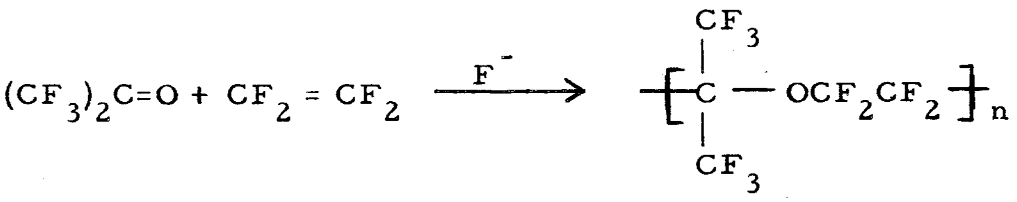
a. Attempted Copolymerization of PVM with CF_3NO.

In our initial attempt to copolymerize PVM with CF_3NO under conditions similar to that used in the copolymerization of C_2F_4/CF_3NO no reaction appeared to occur. Even after an extended period at ambient temperature the intense blue nitroso color remained. However, upon exposure to ionizing radiation to a total dose of 7.56 x 10^6 rep. only a slight blue color remained. After removal of residual PVM and CF_3NO a mixture of a high boiling, cloudy, viscous liquid and a lower boiling clear liquid remained. These reaction products have not been characterized but the lower boiling component, boiling above that of either starting monomers, is believed to be the cyclic perfluoro-2-methyl-4, 4-dimethoxy-1, 2-oxazetidine,



3. Attempted Copolymerization of $(CF_3)_2C{=}O$ with C_2F_4

Since the incorporation of a heteroatom such as oxygen into the backbone of a fluorocarbon polymer chain should enhance low temperature flexibility, we have attempted the copolymerization of hexafluoroacetone and tetrafluoroethylene as shown. Reaction of carbonyl fluoride with perfluoroolefins using



$$(CF_3)_2C{=}O + CF_2 = CF_2 \xrightarrow{F^-} \left[\overset{CF_3}{\underset{CF_3}{C}} - OCF_2CF_2 \right]_n$$

CsF as catalyst has been reported to give perfluoroacid fluorides[19]. Since hexafluoroacetone could not react in this manner it was hoped that an anionic polymerization initiated by fluoride ion would take place to give the polymer shown above. After heating the reactants as high as 150° a small amount of higher boiling product was obtained. This material was shown to be a complex

---

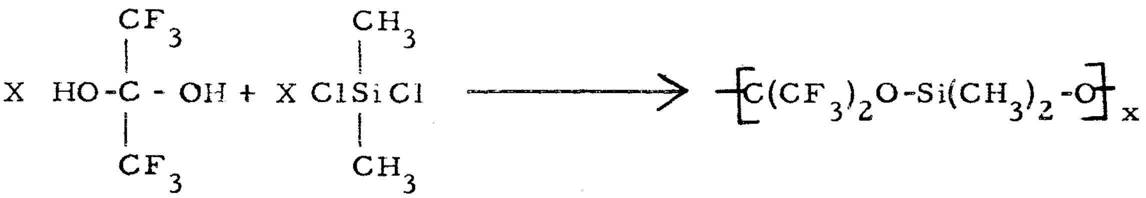
(19) F. S. Fawcett, A. W. Tullock and D. C. Coffman, J. Am. Chem. Soc., 84, 4275(1962).

mixture of at least five components and was not examined further.

4. Attempted Preparation of Polymers Containing Heteroatoms in the Polymer Chain

In an attempt to utilize the demonstrated excellent low temperature properties of the siloxanes (dimethylsiloxane, Tg -123°) and of the polyesters [poly(ethylene)adipate, Tg -70°][20], a siloxane polymer was prepared from hexafluoroacetone monohydrate and dimethyldichlorosilane and a polyester was prepared from 2, 2, 3, 3, 4, 4-hexafluoropentanediol and phosgene.

This initial attempt to prepare a siloxane polymer



$$X\ HO-\overset{CF_3}{\underset{CF_3}{C}}-OH + X\ Cl\overset{CH_3}{\underset{CH_3}{Si}}Cl \longrightarrow \left[C(CF_3)_2O-Si(CH_3)_2-O \right]_x$$

resulted in a low molecular weight liquid polymer which appears, from an NMR analysis, to be composed of randomly occurring units. The NMR spectrum indicates CF_3, CH_3 combinations to occur in three sequences.

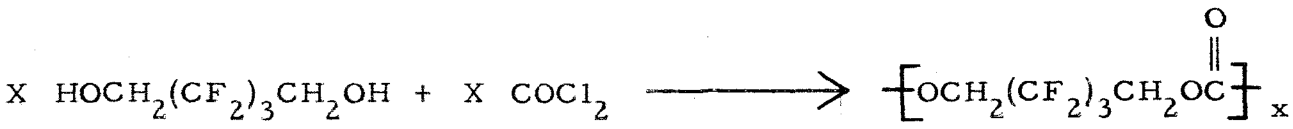
CF_3	CF_3	CF_3
CF_3	CF_3	CH_3
CH_3	CF_3	CH_3

An infrared spectrum of the polymer was superimposable on that of an authentic sample of poly(dimethylsiloxane) with the exception of a single strong absorption maximum at $8.11\,\mu$. In addition to the polymer both octamethyltetrasiloxane and decamethylpentasiloxane were identified as side products.

---

(20) "Textbook of Polymer Science", F. W. Billmeyer, Interscience Publishers, New York, 1962.

The polycarbonate which was obtained in essentially quantitative yield, by reaction of the diol with phosgene, had an intrinsic viscosity of



$$x\ HOCH_2(CF_2)_3CH_2OH + x\ COCl_2 \longrightarrow \left[OCH_2(CF_2)_3CH_2O\overset{O}{\overset{\|}{C}} \right]_x$$

0.18 (in methyl ethyl ketone at 30°). Infrared and end group analysis confirmed the expected hydroxy terminated structure and the molecular weight, as indicated by end group analysis, was 6,600. The polymer was a waxy pliable solid suggesting possible elastomeric properties if a higher molecular were obtained.

C. Synthesis

1. $CF_3OCH{=}CF_2$ and $CF_3OCF{=}CHF$

The overall reaction sequence in the preparation of these monomers is

$$(1.)\quad CF_3OF + CHCl{=}CFCl \longrightarrow \begin{array}{l} (a)\ CF_3OCHClCF_2Cl \\ \qquad + \\ (b)\ CF_3OCFClCHFCl \end{array}$$

The expected proportions of the two isomers were observed, namely 66% isomer (a) and 34% isomer (b). The structure of the two isomers was confirmed by NMR analysis and an infrared spectrum of each is shown in Figures 4 and 5.

$$(2.)\quad (a) + (b) \xrightarrow[DMSO]{Zn} \begin{array}{l} (c)\ CF_3OCH{=}CF_2 \\ \\ (d)\ CF_3OCF{=}CHF \end{array}$$

Dehalogenation of the mixed isomers occurred readily giving the desired vinyl ethers. The structure of the major isomer (c) was confirmed by NMR and the structural assignment of the minor isomer (d) was based on infrared analysis and on NMR analysis of its dichloro precursor. Infrared spectra of these compounds are shown in Figures 6 and 7.

2. $\underline{(CF_3O)_2C{=}CF_2}$ (PVM)

During this period synthesis of PVM has been successfully completed and, as previously described, several copolymers were prepared. The overall reaction sequence is

$$1.\quad CF_3OF + CHCl{=}CCl_2 \longrightarrow \begin{array}{l}(a)\ CF_3OCHClCFCl_2 \\ \qquad + \\ (b)\ CF_3OCCl_2CHFCl\end{array}$$

$$2.\quad a + b \xrightarrow[DMSO]{Zn} \begin{array}{l}(c)\ CF_3OCH{=}CFCl \\ \qquad + \\ (d)\ CF_3OCCl{=}CHF\end{array}$$

$$3.\quad c + d + CF_3OF \longrightarrow \begin{array}{l}(e)\ (CF_3O)_2CHCF_2Cl \\ \qquad + \\ (f)\ CF_3OCFClCHFOCF_3\end{array}$$

$$4.\quad e + f \xrightarrow{KOH} \begin{array}{l}(g)\ (CF_3O)_2C{=}CF_2 \\ \qquad + \\ (h)\ CF_3OCF{=}CFOCF_3\end{array}$$

In the initial synthesis only crude purification steps were taken and in steps 2, 3 and 4, as shown above, the mixed isomers plus impurities were reacted. As discussed earlier, this method presented problems in isolation of the pure PVM for polymer preparation. Additional monomer is now being prepared and the first step of the synthesis has been completed. Distillation of this adduct gave 98% pure $CF_3OCHClCFCl_2$, b.p. 84-85°. The major impurity was the isomeric adduct. Infrared spectra of these two compounds and the dechlorination products of the major isomer, cis and trans $CF_3OCH{=}CFCl$, are shown in Figures 8 through 11.

It is interesting to note that all steps in this reaction sequence occur quite readily and as predicted. Although it was predicted, on the basis of the empirical method of Lovelace[21], that reaction 3 should give predominantly the desired 1, 1-isomer, there were some reservations concerning this prediction since no reference is available concerning a radical addition to a trifluoromethoxy substituted olefin. Judging from the isomer ratio obtained in the first step in this sequence (reaction 1, about 90% $CF_3OCHClCFCl_2$ and 10% CF_3OCCl_2CHFCl) and comparing numerical values indicative of isomer ratios expected, the isomer ratio $(CF_3O)_2CHCF_2Cl/CF_3OCHFCFClOCF_3$ should have been better than 90/10. The isomer ratio found appears at present to be 79/21. Although this is a smaller ratio of the 1, 1 adduct than might have been predicted, the predominance of $(CF_3O)_2CHCF_2Cl$ in the reaction product does clearly establish the relative intermediate free radical stabilities as $-\dot{C}FCl > CF_3O\dot{C}H-$.

Dehydrochlorination also occurs surprisingly well by simple contact of solid, powdered KOH with $(CF_3O)_2CHCF_2Cl$ at 100°. The structure of $(CF_3O)_2C{=}CF_2$ and its precursor, $(CF_3O)_2CHCF_2Cl$ have been confirmed by NMR. Infrared spectra of these two compounds are shown in Figures 12 and 13. The isomeric adduct $CF_3OCHFCFClOCF_3$ and its dehydrohalogenation product have not been characterized as yet.

3. $\underline{SF_5OCF{=}CF_2}$

A considerable amount of difficulty has been encountered in attempts to prepare this monomer. Initially, this difficulty was due to problems involved in the preparation of SF_5OF. Early attempts to dechlorinate $SF_5OCFClCF_2Cl$ resulted mainly in decomposition of the compound with only trace amounts, indicated by IR analysis, of the desired olefin produced.

Using the following reaction sequence below a small amount of $SF_5OCF{=}CF_2$ has been prepared.

---

(21) Lovelace et al, "Aliphatic Fluorine Compounds", Reinhold Publishing Corp., 1958, p. 38.

1. $CHF = CHF + Br_2 \longrightarrow CHFBrCHFBr$

2. $CHFBrCHFBr \xrightarrow{KOH} CHF = CFBr$

3. $$CHF = CFBr + SF_5OF \longrightarrow \begin{array}{c} SF_5OCHFCF_2Br \\ + \\ SF_5OCFBrCHF_2 \end{array}$$

4. $$\begin{array}{l} SF_5OCHFCF_2Br \xrightarrow{KOH} \text{Decomposition} \\ SF_5OCFBrCHF_2 \xrightarrow{KOH} SF_5OCF = CF_2 \end{array}$$

A survey of the literature has shown that the product of the first reaction, $CHFBrCHFBr$, is a new compound. An infrared spectrum of this compound is shown in Figure 14.

The addition of SF_5OF to the olefin was carried out on a small scale by repeatedly reacting small amounts of olefin with SF_5OF (about 50% pure) on the vacuum system. The crude reaction product was shown by GLC analysis to be composed of two major products, $SF_5OCHFCF_2Br$, 82.7% and $SF_5OCFBrCHF_2$ 17.3%. An infrared spectrum of the major isomer is shown in Figure 15. This isomer ratio is surprisingly high (82.7/17.3) in view of the reaction of CF_3OF with $CHCl = CCl_2$, where a 90/10 $CF_3OCHClCFCl_2/CF_3OCCl_2CHFCl$ ratio was obtained.

Several attempts were made to dehydrobrominate $SF_5OCHFCF_2Br$. The use of dry KOH was suggested by the ease with which dehydrochlorination of $(CF_3O)_2CHCF_2Cl$ occurred. In the first attempts using dry KOH no reaction was indicated but subsequent attempts using Me_3N, Et_3N and also dry KOH apparently were successful in that the reaction product in these experiments showed strong infrared absorption at 5.61 μ which was indicative of the presence of the trifluorovinyl group.

Reaction of $SF_5OCHFCF_2Br$ with Et_3N appears to occur quite readily, as indicated by an immediate exotherm and intense color change. The reaction appears to either proceed slowly or a side reaction occurs over a long period of time as indicated by a continued color change of the liquid reaction product after clarifying by trap to trap distillation.

Reactions with the amines provided qualitative evidence that dehydrobromination could be effected, while reaction with KOH provided sufficient product for separation and identification of the desired olefin.

Initial attempts to dehydrobrominate the adduct mixture by simple contact with KOH gave low conversions to a low boiling product which showed strong IR absorption at 5.61 μ. This product was separated by GLC and its structure, $SF_5OCF = CF_2$, assigned on the basis of M. Wt. determination and IR analysis showing C = C and strong absorption at 10.6 to 12.1 μ attributed to SF_5 absorption. Preliminary NMR analysis confirmed this assignment. An infrared spectrum of this compound is shown in Figure 16.

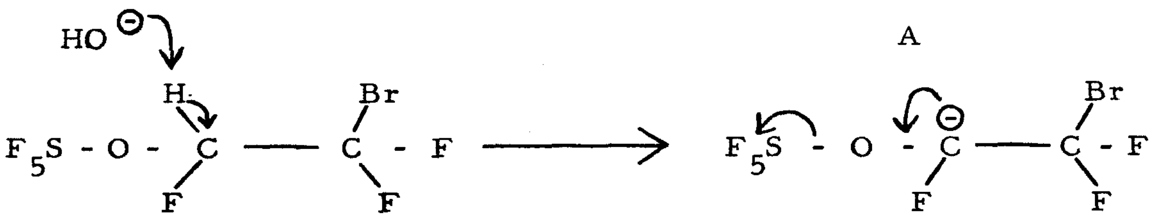
In order to determine if one of the isomers was preferentially dehydrobrominating, the progress of the reaction of the mixed isomers with KOH was followed chromatographically. It was found that the ratio of the GLC areas of the two starting materials $SF_5OCHFCF_2Br/SF_5OCFBrCF_2H$ increased after repeated reactions with KOH indicating that the quantity of the minor isomer was diminishing.

In substantiation of this observation a small quantity of GLC pure minor component was found to react vigorously with KOH at about 50-60° to give mainly the producted isolated from the earlier reactions with the mixed isomers and assigned the structure $SF_5OCF = CF_2$.

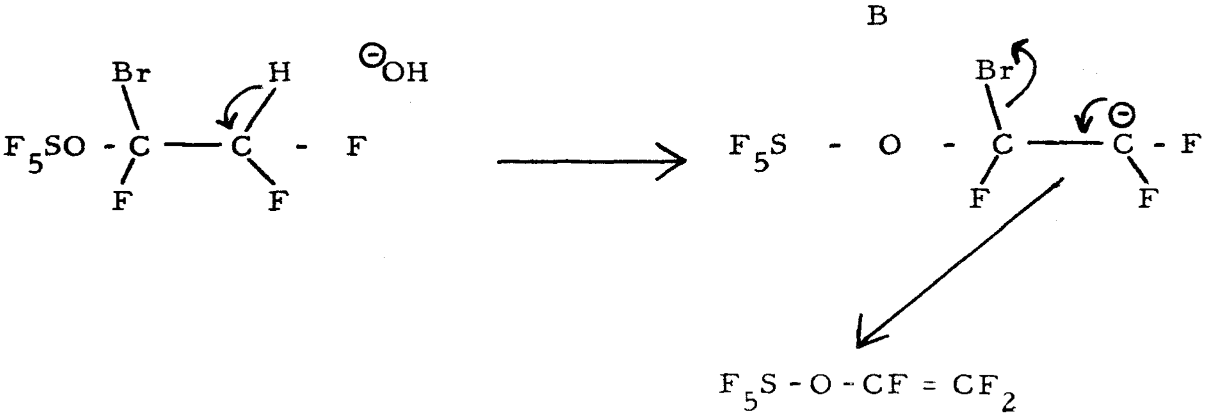
In contrast, when GLC pure $SF_5OCHFCF_2Br$ was reacted with KOH under more severe conditions only a trace amount of reaction product resulted. An infrared spectrum of the overgases from this reaction showed absorption maxima attributable to a reaction product or products at 5.28, 5.47, 7.42, 7.73 and 12μ. The remaining maxima correspond to absorption due to starting material. GLC analysis showed mainly starting material and a trace (2.5%) of a low boiling component. Unfortunately, insufficient material was available to characterize the minor component. Continued contact with KOH increased the intensity of the maxima of 5.28 and 5.47μ.

From a mechanistic standpoint the contrast in reactivity is interesting but from the preparative standpoint it is quite disturbing since the desired $SF_5OCF = CF_2$ is derived only from the minor isomer which is present to the extent of 17 to 20% in the reaction (3) of SF_5OF with CHF=CFBr.

If we may presume the initial reaction of each isomer is proton abstraction then the following two intermediate carbanions result, A and B.

(1) 

Since the major isomer gives rise to a product or products other than the dehydrobromination product, then it is reasonable to presume that elimination of SF_5^- occurs preferentially. No products of this reaction were identified but reaction of the mixed isomers showed $SO_4^{=}$, F^- and Br^- to be present.

(2) 

The minor isomer obviously gives the normal HBr elimination.

4. Reaction of $(CF_3O)_2$ with CFCl = CFCl

In the course of preparation of vinyl ethers the unsymmetrical olefin, $CF_3OCF{=}CFOCF_3$, appeared to be a possible monomer candidate. This monomer appeared to have some special interest in view of the discussion, under copolymers of $CF_3OCH{=}CF_2$, when it appeared that the presence of a pendent OCF_3 group reduced the detrimental effect associated with unsymmetrical substitution. The similarity of this compound to unpolymerizable internal olefins is obvious. However, Cleaver[22] has claimed polymers were prepared from similar compounds, ROCF=CFOR, where R was secondary or tertiary alkyl groups.

Several routes to this compound are possible, including a by-product in the preparation of $(CF_3O)_2C{=}CF_2$. However, since bis(trifluoromethyl) peroxide is readily available, it appeared attractive to prepare this compound in a two step process by the homolytic cleavage of $(CF_3O)_2$ and addition to CFCl=CFCl.

$$1.\quad (CF_3O)_2 + CFCl = CFCl \longrightarrow CF_3O(CFClCFCl)_xOCF_3$$

$$2.\quad CF_3O(CFClCFCl)_xOCF_3 \xrightarrow{-xCl_2} CF_3O(CF{=}CF)_xOCF_3$$

This method presented the additional desirable feature in the possibility of preparing the second addition product which would be the precursor to the interesting perfluoro-1, 4-dimethoxy butadiene.

Early attempts to prepare these compounds on a small scale, by reacting the olefin with an excess of peroxide at elevated temperatures, gave encouraging results. GLC analysis showed three major peaks which were attributed to α, ω-trifluoromethoxy substituted products where x (above) was 1, 2 and 3. Attempts to distill subsequent larger scale preparations on a

---

(22) C. S. Cleaver, U.S. Patent 2, 853, 531 (1958)

28 plate spinning band column gave no constant boiling fraction over a temperature range of 53 to 190°.

GLC analysis of samples taken at intervals over this boiling range showed each to be composed of a number of compounds.

An explanation for this complex mixture probably lies in the fact that at the temperature at which this reaction was run (200 to 210°) decomposition of the trifluoromethoxy radical is also occurring giving rise to fluorination products as well as the simple addition and telomerization products.

$$(CF_3O)_2 \rightleftharpoons 2CF_3O\cdot$$

$$2CF_3O\cdot \rightleftharpoons 2COF_2 + F_2$$

No attempt was made to determine the presence or amount of COF_2 after reaction but on one occasion it was quite obvious that fluorination had occurred since the recovered peroxide was colored yellow suggesting the presence of Cl_2. In addition, washing the recovered peroxide with a KI solution removed the color, thus

$$\begin{tikzcd} (CF_3O)_2 + x\ CFCl = CFCl \arrow[r] & CF_3O(CFClCFCl)_xOCF_3 \arrow[dl, "nF\cdot"] \\ CF_3O(CF_2)_n(CFCl)_{2x-n}OCF_3 & \end{tikzcd}$$

It is quite obvious that even for low values of x and n numerous products are possible plus, of course, low boiling materials such as COF_2, CF_2ClCF_2Cl, CF_3CF_2Cl, etc. Roberts[23] recently reported a similar reaction in which he obtained telomers by reaction of $(CF_3O)_2$ with C_3F_6. In this

(23) H. L. Roberts, J. Chem. Soc., 4538-40 (1964)

reaction fluorination would not have been a problem.

5. Attempted Preparation of $(CH_3O)_2C = CF_2$

A recent publication[24] has shown that the Wittig synthesis may be used in preparing difluoroethylenes as illustrated by the example below.

$$ClCF_2COONa \xrightarrow[\Delta]{sol.} :CF_2 \xrightarrow{\Phi_3P} \Phi_3P = CF_2 \xrightarrow{RCHO}$$
$$RCH = CF_2$$

In an attempt to extend this reaction to the synthesis of 1, 1-dialkoxydifluoroethylenes, we have reacted dimethyl carbonate with sodium chlorodifluoroacetate and triphenyl phosphorous in a refluxing solution of diglyme. The desired reaction is shown below. However, the desired

$$ClCF_2COONa \xrightarrow[\Delta]{sol.} :CF_2 \xrightarrow{\Phi_3P} \Phi P = CF_2 \xrightarrow{(CH_3O)_2C = O}$$
$$(CH_3O)_2C = CF_2$$

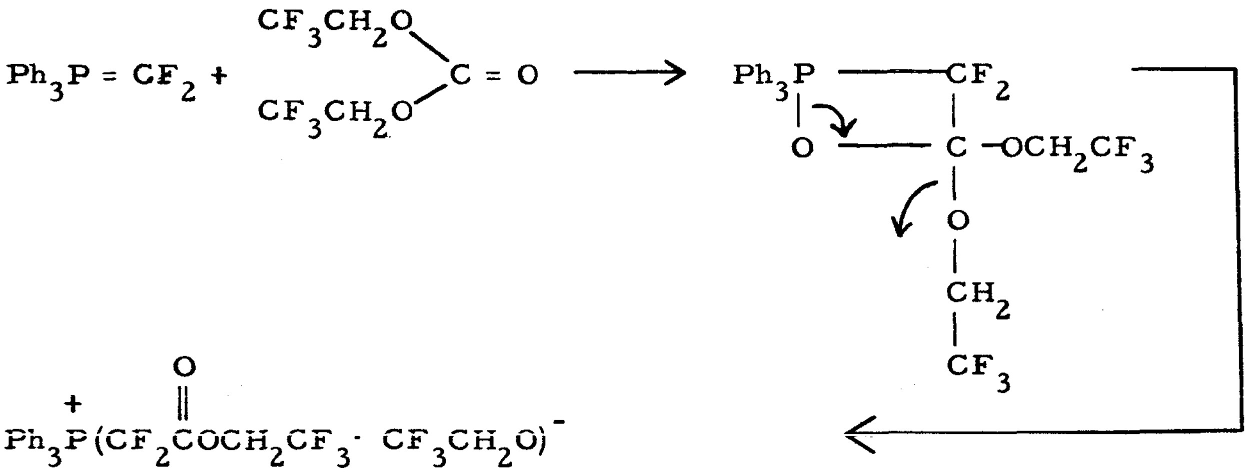
product was not obtained. Apparently, dimethyl carbonate decomposes under these conditions. Most of the triphenyl phosphorous was recovered unchanged. This reaction was also attempted with $(CF_3CH_2O)_2C = O$, which was synthesized by the reaction of phosgene and CF_3CH_2ONa in dioxane.

6. Attempted Preparation of $(CF_3CH_2O)_2C = CF_2$

A similar attempt, as described above, was made in an effort to prepare the titled ether. However, as before, no distillate boiling lower than the solvent was isolated.

The failure of this reaction to proceed in the desired way can be attributed to the following sequence of reactions:

(24) S. A. Fugua, W. G. Duncan and R. M. Silverstein, Tetrahedron Letters, 23, 1461 (1964).



"A phosphonium alkoxide"

Precedence for this type of reaction has been reported [25]. Thus, it has been shown that reaction of phosphoranes with esters gives alkoxide displacement from the ester with subsequent formation of the triphenyl β-keto alkyl or aryl phosphonium alkoxide.

7. Attempted Preparation of C_2F_5OF

Some exploratory experiments have been run in attempts to prepare longer chain hypofluorites. Preparation of these compounds will extend our present evaluation of the low temperature properties of vinyl ether polymers having pendant OCF_3 to polymers having increased side chain length. By analogy to hydrocarbon polymers increased length of the side chain should decrease Tg.

In the first attempts to prepare these longer chain hypofluorites two approaches were taken. The first was that of indirect fluorination of trifluoroacetyl fluoride with AgF_2.

$$CF_3COF + AgF_2 \xrightarrow[\Delta]{} [C_2F_5OF]$$

At 100° no apparent reaction occurs but when heated to 200° only cleavage products were noted.

[25] G. Wittig and U. Schollkopf, Ber., 87, 1318 (1954)

A second approach, suggested by the relative ease of preparing $(CF_3O)_2$ by reaction of CF_3OF and COF_2, was that of reaction of CF_3OF with an acid fluoride and subsequent fluorination of the peroxide with either F_2 or a less reactive fluorinating agent.

$$\begin{tikzcd}
CF_3OF + R_fCOF \arrow[r] & CF_3OOCF_2R_f \arrow[d, "F_2 \text{ or } MF"] \\
& CF_3OF + R_fCF_2OF
\end{tikzcd}$$

Similar to the results experienced with the AgF_2 fluorination of CF_3COF, attempted addition of CF_3OF to CF_3COF at elevated temperatures resulted in cleavage of the acid fluoride with no apparent methyl ethyl peroxide formation.

Apparently, in both of these experiments, conditions were much too severe since Prager and Thompson[26] have shown that C_2F_5OF decomposes between 110 to 200° and have also indicated that preparation of these longer chain hypofluorites may be carried out by direct fluorination under mild conditions.

8. Attempted Preparation of $CsOCF_3$

In a recent publication Bradley[27] revealed the first synthesis of trifluoromethoxide of the heavier alkali metals through reaction of the metal fluoride with COF_2, i.e., $CsOCF_3$, $RbOCF_3$ and $KOCF_3$.

By analogy to the addition of hydrocarbon alkoxides to fluoroolefins, Bradley's research suggested several

$$CH_3ONa + CF_2 = CF_2 \longrightarrow CH_3OCF = CF_2 + NaF$$

---

(26) J. H. Prager and P. G. Thompson, J. Am. Chem. Soc., 87, 230 (1965)

(27) D. C. Bradley, M. E. Redwood and C. J. Willis, Proc. Chem. Soc., 416 (1964).

reactions which would be applicable to our present study.

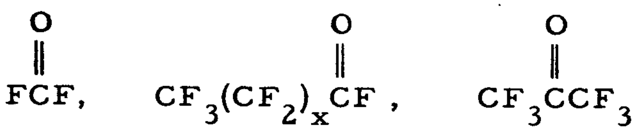
$$CsOCF_3 + CF_2 = CF_2 \longrightarrow CF_3OCF = CF_2 + CsF$$

Conceivably a second addition and elimination may occur, similar to the hydrocarbon alkoxides, to give our new monomer PVM.

$$CsOCF_3 + CF_3OCF = CF_2 \longrightarrow (CF_3O)_2C = CF_2 + CsF$$

Extending beyond this reaction we may compare reactions of COF_2 and $(CF_3)_2C = O$ both of which are subject to nucleophilic attack and addition across the carbonyl group.

Numerous examples of additions to the carbonyl of $(CF_3)_2C = O$ may be cited in the literature[28-30] and in view of Bradley's work the character of the carbonyl in R_fCOF should be intermediate between that of $(CF_3)_2C = O$ and COF_2.



$$\overset{O}{\overset{\|}{FCF}}, \quad CF_3(CF_2)_x\overset{O}{\overset{\|}{C}}F, \quad CF_3\overset{O}{\overset{\|}{C}}CF_3$$

If the reasoning thus far is valid, it should be possible to prepare the longer chain alkyl ethers required in the next phase of our research, the overall reaction being

$$R_fCOF + CsF \longrightarrow R_fCF_2OCs$$

$$R_fCF_2OCs + C_2F_4 \longrightarrow R_fCF_2OCF = CF_2 + CsF$$

(28) N. Fukuhara and L. A. Bigelow, J. Am. Chem. Soc., 63, 788 (1941)
(29) I. I. Knunyants, et al. Khim. Nauka i. Prom., 4, 802 (1959)
(30) H. E. Simmons and D. W. Wiley, J. Am. Chem. Soc., 82, 2288 (1960)

Reacting COF_2 with anhydrous CsF in dry CH_3CN over a period of several days at R. T. and subsequent recovery of unreacted COF_2 indicated some reaction to have occurred. Attempted reaction of the salt with C_2F_4 and infrared analysis of the overgases gave no indication of the presence of a vinyl ether. The infrared analysis showed mostly C_2F_4 and only a trace of COF_2 to be present.

Bradley indicated $CsOCF_3$ decomposes at 80 to 100°

$$CsOCF_3 \rightleftharpoons CsF + COF_2$$

suggesting a method for determining whether the salt was still present. The ampule was heated to the reflux temperature of the CH_3CN (82°) and an infrared spectrum of the overgases taken. No COF_2 was detected.

9. $\underline{CF_3OF, (CF_3O)_2 \text{ and } COF_2}$

Preparation of relatively large quantities of CF_3OF are now possible using our new fluorination apparatus shown in Figure 17. The data presented in Table VII is a summary of the reactions run in attempts to optimize conditions. The product composition was roughly calculated from the product areas obtained by Cady co-distillation analysis[31]. In current preparations, however, using essentially the conditions shown as run No. 6 in Table VII, indications are that the CF_3OF purity is approximately 70%. The major impurities are COF_2, CF_4 and $(CF_3O)_2$.

By varying the proportions of CO and F_2 either CF_3OF, $(CF_3O)_2$ or COF_2 may be favored in the reaction product. It was found that COF_2 may be prepared in essentially quantitative conversions by reacting an excess of CO with fluorine. Similarly, as shown in Table VII

(31) G. H. Cady and D. P. Siegworth, Anal. Chem., 31, 618 (1959)

CF_3OF may be prepared in good yield by reversing the reactant concentrations. Intermediate or stoichiometric concentrations of CO and F_2 do not, however, give good yields of $(CF_3O)_2$, 21% max.[32]

Porter and Cady[32] and more recently Roberts[23] have shown that the peroxide may be prepared by reacting CF_3OF with COF_2 at elevated temperatures.

Several attempts were made to repeat this reaction but initially the major product was COF_2, an obvious loss of F_2. Porter and Cady[33] report that CF_3OF undergoes a reversable decomposition starting at 327°.

$$CF_3OF \rightleftharpoons COF_2 + F_2$$

At this time it is not known if our original reaction was run in a stainless steel bomb but subsequent reactions have been run in mild steel bombs below 327° with apparent decomposition of the CF_3OF occurring.

In more recent reactions indications are that the peroxide also decomposes to COF_2 and F_2 in the probable following sequence.

$$(CF_3O)_2 \rightleftharpoons 2CF_3O\cdot \qquad (1)$$

$$2CF_3O\cdot \longrightarrow 2COF_2 + F_2 \qquad (2)$$

Since the $CF_3O\cdot$ radical is presumably an intermediate common to CF_3OF and $(CF_3O)_2$ at elevated temperatures, it is not surprising that the peroxide also decomposes to COF_2 and F_2. This was qualitatively substantiated in the reaction of $(CF_3O)_2$ with $CFCl = CFCl$, as previously discussed.

Attempted preparation of the peroxide in a glass reactor by heating or by ultraviolet initiation through the addition of CF_3OF to COF_2 was

(32) R. S. Porter and G. H. Cady, U. S. Patent 3, 100, 803 (1963).
(33) R. S. Porter and G. H. Cady, J. Am. Chem. Soc., 79, 5628 (1957).

not successful but when run in a Monel cylinder yields were good, giving a product containing 70% $(CF_3O)_2$. Later preparations gave higher yields, and subsequent washing with basic KI solution and drying through P_2O_5 gives 98% pure $(CF_3O)_2$.

10. SF_5OF

The direct fluorination of SOF_2 was initially attempted in our large reactor previously used only for the preparation of CF_3OF. The fluorination product obtained, about 200 g., was found to be composed mainly of SO_2F_2. Following these runs it appeared that the AgF_2 catalyst was spent since subsequent attempts to prepare CF_3OF were not successful at previously established conditions. Due to this, the large reactor was dismantled and repacked and a separate reactor built specifically for the fluorination of SOF_2. This reactor was constructed from a 2" x 8' stainless steel pipe with essentially the same design used in the large reactor.

Fluorination of SOF_2 at 200° with a large excess of undiluted fluorine, after repeated short runs, produced a maximum of 18 mole % SF_5OF in the reaction product. The major impurity in most experiments was SO_2F_2, the hydrolysis product of SOF_4. On repeated short runs the SF_5OF concentration rose from zero to 18 mole %.

An additional modification was made in the reactor. The 2" stainless steel reactor was lined with a copper tube and the tube packed alternately with silver plated copper gauze and cesium fluoride. The use of the additional catalyst was dictated by the success of a static reaction of F_2 with SOF_2 carried out by Ruff and Lustig[34]. Using this reactor the fluorination product obtained contains greater than 34% SF_5OF.

During this period a relatively simple method has been developed for determining the mole % SF_5OF in SOF_2 fluorination product. By reacting the fluorination product directly with C_2H_4 on a calibrated vacuum system the concentration of SF_5OF in the reaction product may be determined in a matter of minutes.

(34) John F. Ruff and Max Lustig, Inorg. Chem., 3, 1422 (1964).

EXPERIMENTAL

A. Polymer Preparation

1. Copolymers of $CF_3OCH = CF_2$, $CF_3CF = CHF$ and $(CF_3O)_2C = CF_2$

In all polymerization reactions summarized in Tables IV and V the vinyl ethers were chromatographically pure. Separation was made on a 16 or 40' column, at R. T., packed with HMDS chromosorb with Kel-F ester as the stationary phase. Allied Chemical Company Genetron 1132A (vinylidene fluoride) was used as received, tetrafluoroethylene was used as prepared from the debromination of 1, 2-dibromo-1, 1, 2, 2-tetrafluoroethane. Monomer proportions shown in these Tables were measured volumetrically on a calibrated vacuum system, condensed into a 13 ml. capacity Carius tube and sealed under vacuum. The reaction tubes while still frozen were placed in a sample holder containing six copper tubes concentrically spaced 1. 91 cm. from the center of a central 1. 78 cm. I. D. tube. The samples and sample holder were warmed to room temperature, then placed in the radiation chamber and the Co^{60} capsule lowered into the central tube. The radiation flux was approximately 7×10^5 r/hr. and the total gamma dose for each sample is shown in Table IV and V. Irradiation of these samples was carried out at the University of Florida, Gainesville, Florida, through the assistance of Dr. R. J. Hanrahan of the Department of Chemistry.

Polymer samples which were considered to be homogeneous and suitable for further characterization were heated to 100° under vacuum to remove any residual monomer before being submitted for analysis.

Glass transition temperatures were determined by Sadtler Research Laboratories on a du Pont Model 900 differential thermal analyzer. The following conditions were used over a temperature range of -100 to 500°.

TABLE IV

Copolymers of $CF_3OCH = CF_2$ and $CF_3OCF = CHF$

Experiment Number	Monomer, m. moles $CF_3OCH=CF_2$	 $CF_2=CH_2$	Gamma Dose (10^7 rep)	Mole % Ether in Polymer[a]	Tg °C	Polymer wt. grams	Polymer Characteristics
158	8.9	6.9	1.35	41.3		0.578	Tacky gum
169	8.6	7.1	1.21	-		-	Tacky gum
159	4.7	11.2	1.35	35.1	-13	0.690	Elastomeric
160	2.3	13.8	1.35	13.5	-24	0.193	Elastomeric
162	-	5.8	0.86	-		0.097	-
161	10.7		3.87	-		0.59	Viscous liquid
	$CF_3OCF=CHF$	$CF_2=CH_2$					
168	13.8	2.1	1.21	19.3	-22	0.149	Elastomeric
	$CF_3OCH=CF_2$	$CF_2=CF_2$					
164	10.4	5.2	2.52	20.0		0.647	Tacky paste
165	6.4	9.07	2.52	-		0.095	-
166	0.29	12.9	2.52	2.2		1.29	Friable wax m.p. 295°
170	6.4	9.4	1.21	37.6		1.33	Elastomeric

(a) Based on elemental analysis, with the exception of 166 which was based on residual monomer recovered.

TABLE V

COPOLYMERS OF

$(CF_3O)_2C = CF_2$

Experiment Number	Monomer $(CF_3O)_2C=CF_2$	M. Moles $CF_2=CH_2$	Gamma Dose (REPS)	Mole % PVM in Polymer	% Conv. to Polymer	Polymer Charac.
184	5	4.2	$3.32(10^7)$	34.8[a]	57	High viscosity liquid or tacky gum
185	3.1	12.1	$2.76(10^7)$	11.2[b]	85.6	Flexible polymer, insoluble in common solvents
186	4	9.5	$3.36(10^7)$	16.7(b)	69	Sl. tacky, translucent gum
187	6	9	$3.36(10^7)$	---	85.8	Viscous liquid, lower visc. than 184
188	3.75	11.25	$0.14(10^7)$	---	---	Elastomer sol. in acetone, approx. mp and decomp. temp. 140, 270°
189	3	12	$0.14(10^7)$	21.0(b)	11	Elastomer sol. in acetone, approx. mp and decomp. temp. 160, 265°
190	2.3	12.65	$1.32(10^7)$	4.4(b)	---	Elastomer, swollen by and sl. sol. in acetone decomp. 340°, did not melt
192	3.75	11.25	$1.32(10^7)$	11(b)	80.6	Elastomer, swollen by and sl. sol. in acetone, decomp. 375°

TABLE V

COPOLYMERS OF

$(CF_3O)_2C{=}CF_2$ (Cont'd.)

Experiment Number	Monomer $(CF_3O)_2C{=}CF_2$	M. Moles $CF_2{=}CH_2$	Gamma Dose (REPS)	Mole % PVM in Polymer	% Conv. to Polymer	Polymer Charac.[c]
193	5	10	$3.19(10^7)$	27.1[(a)]	70.7	Tacky gum, sol. in acetone
194	3	$CF_2{=}CF_2$ 12	$0.45(10^7)$	4.2[b]	80.7	Molded to a weak flexible film. Tc 320°, decomp. 395°

(a) Indicated polymer composition from GLC analysis of recovered monomers. (PVM) poly(perfluorovinylidene methoxide).

(b) By elemental analysis

(c) Polymer character after heating for 24 hrs. under vacuum.

TABLE VI

POLYMER TRANSITION TEMPERATURES

Sample	Ether (mole %)[a]	Comonomer	Transitions[b]	
			T_g	Other Transitions[c] Observed
144	$CF_3CH_2OCF=CF_2$ (52.2)	CH_2CH_2	-56°	-45° En., -23 En, 188° En. 280° En.
152	$CF_3OCF=CF_2$ (36.4)	"	-13°	-50 En., 48° En.
159	$CF_3OCH=CF_2$ (35)	CF_2CH_2	-13°	
160	" (13.5)	"	-24°	
164	" (21.7)	CF_2CF_2	-60°[d]	130° decomp.
166	" (29)	"	-27 to -60[e]	147° En., 292-299° decomp.
170	" (37.6)	"	-32[f]	-57° Ex., -25 En., 169° En., 266° decomp.
168	$CF_3OCF=CHF$ (19.3)	CF_2CH_2	-22°	
185	$(CF_3O)_2C=CF_2$ (11.2)	"	-50°	122° En., 187° En., 253° En., 300° Ex. decomp.
190	" (4.4)	"	none observed	60° En., 141° En., 360 Ex. Decomp.
192	" (11)	"	-26	441° Ex. decomp.
194	" (4.2)	CF_2CF_2	none observed	314° En., 322° En. decomp.
100	$CF_3CH_2OCF=CF_2$ (70)	CF_2CH_2	+22	
102	" (50)	"	-1	
135	" (39.7)	"	[g]	
	-------- -----	$CFHCF_2$	31, 49[h]	
	-------- -----	CHFCHF	102	

TABLE VI (Cont'd)

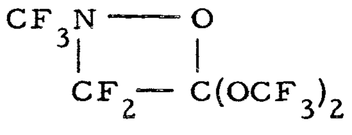
(a) By elemental analysis.
(b) Values determined by Sadtler Research Laboratories by DTA.
(c) En., Endotherm; Ex., Exotherm.
(d) Questionable T_g.
(e) Low temperature transition distinct but base line extrapolation not possible for estimate of T_g.
(f) Change in scale on thermogram occurred at inflection in curve attributed to T_g.
(g) An apparent crystalline melting point occurred at +133°, T_g not detected due to temperature scale change over at 0°. Interpolation of T_g copolymer data indicates this would be the temperature range expected for T_g of this copolymer.
(h) Calculated from two separate crystalline transitions occurring at 152 and 178° where $T_m = 1.4\ T_g$.

Sample Size ------------------------ 15 mg
Reference material ---------------- glass beads
Heating rate ------------------------ 20° minute
Starting temperature --------------- 100°C
Atmosphere ------------------------ N_2 at 760 mm
Temperature scale ----------------- 50°/inch, 10°/inch
ΔT scale --------------------------- .5°/inch
Thermocouples -------------------- chromel-alumel

Transition temperatures of a variety of polymers and copolymers prepared under this contract are shown in Table VI.

a. Attempted Copolymerization of $(CF_3O)_2C{=}CF_2$ with CF_3NO

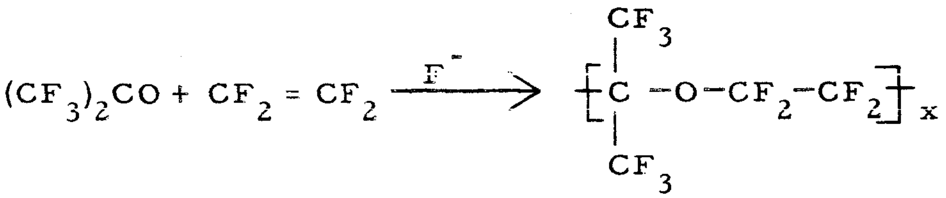
Into a small evacuated Carius tube (about 3 ml.) was added equal molar amounts (4.5×10^{-3} moles) of CF_3NO and $(CF_3O)_2C{=}CF_2$. The ampule was placed in an ice water bath and allowed to slowly warm to R. T. (18 hrs.). After this period of time no signs of reaction were observable. The ampule was then placed in the Co^{60} source and exposed to a total dose of 7.56×10^6 rep. When removed from the source only a faint trace of blue color remained indicating reaction to have occurred. The ampule was reopened to the vacuum system and the lowest boiling, transferable, materials removed. Chromatographic analysis of a gas sample of the volatiles (40', Kel-F ester on HMDS Chromosorb) showed three major components. The first two peaks were identified as unreacted CF_3NO and $(CF_3O)_2C{=}CF_2$. The higher boiling component, which was the predominant peak after successive gas samples were taken, was tentatively assigned the oxazetidine structure,



perfluoro-2-methyl-4,4-dimethoxy-1,2-oxazetidine by its lower volatility than the starting materials and by infrared analysis. The IR spectrum of a GLC pure sample of this material showed a maxima at 7.27 μ which appears to be characteristic of the oxazetidines.

Remaining in the ampule, after transfer of volatiles was a cloudy viscous oil. The products of this reaction have not been further characterized.

2. Attempted Copolymerization of $(CF_3)_2CO$ and $CF_2=CF_2$



$$(CF_3)_2CO + CF_2=CF_2 \xrightarrow{F^-} \left[\overset{\displaystyle CF_3}{\underset{\displaystyle CF_3}{\overset{|}{\underset{|}{C}}}} -O-CF_2-CF_2 \right]_x$$

A 120 ml. autoclave was charged with 14 ml. of acetonitrile, 1.0 g. (0.13 mole) of hexafluoroacetone, and 15 g. (0.15 mole) of tetrafluoroethylene. The mixture was rocked in an autoclave for 4 hrs. at 100° and for 11 hrs at 150°. After cooling to room temperature and releasing the overgases, the residual brown liquid was poured into water. The resulting two phase mixture was extracted with ether and the ether extract was dried over anhydrous sodium sulfate. Evaporation of the ether left 2.1 g. of a brown liquid which was found by GLC to be a complex mixture containing at least five components. An infrared spectrum of this mixture was suggestive of a fluorinated alcohol. Because of the complexity of this mixture and the absence of polymeric material in the product mixture the experiment was not pursued further.

3. Attempted Polycondensation of $(CF_3)_2C(OH)_2$ with Me_2SiCl_2

A 500 ml. 3-neck flask was equipped with a stirrer, gas inlet tube, and a condenser which was connected to a dry ice-acetone cold trap. The entire apparatus was protected from atmospheric moisture by means of a $CaCl_2$ drying tube connected to the outlet side of the cold trap. The flask was then charged with 150 ml. of dry toluene and 9.0 g. (0.5 mole) of distilled water and 110 g (0.66 moles) of hexafluoroacetone was bubbled into the rapidly stirred toluene-water mixture. The temperature of the reaction mixture was controlled by means of an ice water bath. During the addition a white slurry developed as the hexafluoroacetone hydrate formed. When all of the hexafluoroacetone had been added the material which was caught in the cold trap was recycled through the reaction mixture. Upon warming the reaction mixture to room temperature most of the hexafluoroacetone hydrate dissolved. Introduction of 64.5 g (0.50 mole) of dimethyldichlorosilane at room temperature produced no evolution of hydrogen chloride. Heating the reaction mixture to gentle reflux also produced no hydrogen chloride although some evolution of hexafluoroacetone was noted. The mixture was cooled back to room temperature and treated with 0.5 mole of dry pyridine whereupon an exothermic reaction ensued with evolution of hydrogen chloride. When the reaction mixture began to cool it was heated to gentle reflux for 30 minutes and then allowed to cool to room temperature. A cloudy lower liquid layer separated upon cooling. The mixture was extracted with 100 ml. of water and the organic layer which separated was dried over sodium sulfate and distilled to remove toluene. During distillation of the solvent some hexafluoroacetone evolution was again observed. The clear viscous residue left after removal of the toluene was distilled under reduced pressure through a spinning band column. Two fractions were obtained which were identified as octamethyltetrasiloxane (2.9 g.) and decamethylpentasiloxane (1.9 g.). The viscous pot residue had an infrared spectrum which was superimposable on that of authentic poly(dimethylsiloxane) with the exception of a single strong band at 8.11μ. A sample of the pot residue was submitted for NMR analysis and the following results were obtained. The chemical shifts for hydrogen and fluorine are given with respect to external CH_3CHO and CF_3COOH respectively.

NMR Data for $\left[C(CF_3)_2\text{-O-}Si(CH_3)_2\text{-O-} \right]_x$

Designation	Chemical Shift	Pattern and Splitting	Rel. Area	Assignment
H	10.17 tau	Singlet	-	CH_3Si-
F	1.25 ppm	Broad	1.0	CF_3C-
F	2.00 ppm	Broad	2.1	CF_3C-
F	4.45 ppm	Broad	0.9	CF_3C-
F	4.65 ppm	Broad		

4. Preparation of 2, 2, 3, 3, 4, 4-Hexafluoropentane-1, 5-Polycarbonate

A 500 ml. 3-neck flask fitted with thermometer, stirrer, gas inlet tube, and condenser was flamed out under dry N_2 and charged with 350 ml. of reagent grade pyridine (distd. from KOH) and 53 g. (0.25 mole) of hexafluoropentanediol. Phosgene 32 g. (0.32 mole) was then bubbled into the reaction mixture from a small cylinder while the temperature was maintained at 25-30° by means of an ice bath. After about 12 g. of the phosgene had been added (30-40 min.) the reaction mixture became cloudy and the rate of addition was reduced. The remaining phosgene was added over a 1.5 hr. period after which the mixture was vigorously stirred for 5-10 min. The mixture was then poured into 1200 ml. of distilled water at which time the polycarbonate precipitated as a white gummy mass. The polymer was precipitated from acetone with water twice and dried at 50° under vacuum. When free of solvents the polymer changed slowly to a flexible, white, opaque, waxy-textured solid. The crude polymer was obtained in essentially quantitative yield and had an intrinsic viscosity of 0.18 (methyl ethyl ketone at 30°). Infrared and end group analysis confirm the expected hydroxy terminated structure. Thus, the polymer has an acid number of 0.66 and an OH number of 18.45. These values correspond to a molecular weight of 6,600.

Anal. Calcd. for $C_6H_4F_6O_3$: C, 30.3; H 1.6; F, 47.9
Found: C, 30.32; H 1.98; F, 45.59.

B. Synthesis

1. $CF_3OCH = CF_2$ and $CF_3OCH = CHF$

a. Reaction of CF_3OF with $CHCl = CFCl$

(1) Subatmospheric Gas Phase Reaction

A 5-l. flask was evacuated and charged with CF_3OF (156 mm, 0.45 moles, 40% pure) and He (90 mm). Into a second evacuated 5-l. flask was added 100 mm (0.03 moles) of $CHCl = CFCl$. The olefin/He mixture was allowed to bleed, at a very low rate, into the flask containing the CF_3OF until the pressure in each flask was equal (3 hrs.). After remaining at room temperature for 40 hours the reaction product and unreacted gases were condensed into a trap. An infrared spectrum of the mixture indicated no residual CF_3OF.

Chromatographic separation (GLC) (Kel-F ester on HMDS Chromosorb, on a 16' column, at room temperature) gave six major peaks, three of which were identified as unreacted cis and trans olefin and original impurities.

(2) Vapor Phase Fluorojet Reaction

A very short run, approximately 20 minutes, was made using the Mark IV Fluorojet reactor. A procedure was followed similar to that described in the first Annual Summary Report. No attempt was made to optimize conditions.

Approximately 0.48 g. (4.2×10^{-3} moles)/min. of $CHCl = CFCl$ was entrained in a sweep of N_2 (142 cc/min) and carried to the jet reactor where it was mixed with a deficiency of CF_3OF (approx. 3.5×10^{-4} moles/min). The reactor was at room temperature and the reaction products and unreacted materials were collected in a dry-ice cooled trap. Analysis by GLC showed four major peaks, the first two being unreacted olefin. The latter two peaks were found to be the two possible products of addition; $CF_3OCHClCF_2Cl$ and $CF_3OCFClCHFCl$.

(3) Reaction in Solution

Into a 3-neck, 200 ml. flask fitted with a gas addition tube, a mechanical stirrer and an exhaust outlet was added a solution of 5.75 g. (0.05 moles) of CHCl = CFCl in 150 cc. of Kel-F Oil No. 1. While at room temperature 5.20 g. (0.05 moles) of CF_3OF was bubbled slowly into the solution. On addition, during approximately a one hour period, the solution temperature rose slowly to 52°. The flask was then fitted with a distillation condenser and the reaction mixture heated. At a pot temperature of 105° the reaction mixture turned yellow and on continued heating became progressively darker with no distillation occurring up to a pot temperature of 160°.

A second run was made altering the above procedure. To similar apparatus, as described above, was added 100 cc. of Kel-F Oil No. 1 and CF_3OF bubbled in until saturation occurred (by starch iodide paper test of exit gases). At saturation it was found that about 1 g. of CF_3OF remained in solution at 0°C. The flask was then fitted with a volumetric addition funnel containing a solution of 20 g. of CHCl = CFCl made up to a volume of 100 cc with Kel-F Oil No. 1. While continuously bubbling CF_3OF into the reaction flask, maintaining a saturated solution, the olefin/Kel-F Oil solution was added very slowly. The reaction mixture was allowed to warm to room temperature during addition. The reaction was terminated when 13 g. (0.12 moles) of CF_3OF and 16 g. (0.13 moles) of CFCl = CHCl were added. On distillation 4.8 g. of material boiling at 50 to 55° was obtained. GLC analysis of the crude product was identical in retention times to those obtained from the jet reactor and showed two major product peaks. A Dumas molecular weight was determined on a GLC pure fraction, which represented the major peak, and was found to be 215 g./mole. Calculated for $CF_3OCHClCF_2Cl$ 218 g./mole. The crude product distribution, as determined by GLC, was 46.1% as the major peak, ($CF_3OCHClCF_2Cl$), and 19.1% as the second largest peak ($CF_3OCFClCFHCl$).

or a 71/29 isomer ratio. The other remaining major peaks were attributed to starting olefin. Conversion to the combined addition products was 39.4% with a yield of 62% (by GLC).

Distillation of two runs totaling 58.6 g. of crude product gave 17 g. of product distilling at 52 to 55°. GLC showed this fraction to be composed of 81% $CF_3OCHClCF_2Cl$, 11.0% of the isomeric product $CF_3OCFClCHFCl$ and the major portion of the remainder unreacted olefin.

Subsequent preparations gave similar product distributions with a combined total crude product yield of 162.6 g. from three runs.

It should be noted that on two occasions minor explosions occurred. In both instances trace amounts of CF_3OF and olefin vapor were inadvertantly allowed to mix. In the first instance the flash occurred when the dropping funnel was being filled and the second occurred when attempting to add 5 cc. of a 50 W/V% olefin/Kel-F oil mixture to the Kel-F oil saturated with CF_3OF.

A final run similar to the above described run was set up such that the added olefin - Kel-F oil solution was introduced below the surface of the Kel-F oil in the reaction flask. This reduced the possibility of accumulating olefin vapor above the reaction mixture and no explosion occurred with this technique.

An infrared spectrum of the two isomers are shown in Figures 4 and 5. The structure of these compounds were further substantiated by the following NMR analysis.

The chemical shifts for fluorine are given with respect to external CF_3COOH and the chemical shifts for hydrogen are given with respect to external CH_3CHO.

NMR Data for $CF_3OCHClCF_2Cl$

Peak	Chemical Shift	Pattern and Splitting (cps.)	Assignment
H	4.28 tau	2° x 3.5, 2° x 5.2	$C\underline{H}Cl$
F	-15.60 ppm	Singlet	CF_3O
F	-11.45 ppm	2° x 172, 2° x 3.5	One F in CF_2Cl
F	-8.73 ppm	2° x 172, 2° x 5.2	Other F in CF_2Cl

NMR Data for $CF_3OCFClCHFCl$

H	3.85 tau	2° x 48.6, 2° x 4.3	$C\underline{H}FCl$
F	-14.75 ppm	Singlet	CF_3O
F	-8.65 ppm	2° x 22.2, 2° x 4.0	CFCl
F	+58.6	2° x 22.4, 2° x 48.8	CHFCl

b. Dechlorination of $CF_3OCHClCF_2Cl$

Into a 250 ml. 3-neck flask fitted with a mechanical stirrer, a dropping funnel and an ice-water cooled reflux condenser was placed 150 ml. of dimethyl sulfoxide, 30 g. of zinc dust and several crystals of $ZnCl_2$.

The mixture was heated to 80° and while stirring vigorously 81 g. of a mixture of $CF_3OCHClCF_2Cl$ and $CF_3OCFClCHFCl$ were added slowly. (This mixture was a combined distillate from several preparations of the olefin-hypofluorite addition containing greater than 90% of the isomeric ethers in an approximate 70/30 ratio of $CF_3OCHClCF_2Cl/CF_3OCFClCHFCl$). The crude product, 54 g., was collected in the dry-ice cooled trap.

Due to the difficulty encountered in attempted separation of the starting dichloroethers by distillation, no attempt was made to fractionate this crude dehalogenation product.

The crude product was separated by GLC on a 40' column (Kel-F ester on Chromosorb) giving 15 g. (0.101 moles) of $CF_3OCH = CF_2$, 10 g. (0.067) moles of $CF_3OCF = CHF$ and 20 g. of starting material. A vapor density molecular weight determined on the major product was 152 (MW Calc. 148).

An infrared spectrum of the two isomers, $CF_3OCH = CF_2$ and $CF_3OCF = CHF$ are shown in Figures 6 and 7. The structure of the major isomer, $CF_3OCH = CF_2$, was further substantiated by the following NMR analysis.

The chemical shifts for fluorine and hydrogen are given with respect to CF_3COOH and CH_3CHO.

NMR Data for $CF_3OCH = CF_2$

Peak	Chemical Shift	Pattern and Splitting (cps.)	Assignment
H	4.91 tau	2• x 13.1, 2• x 3.18	$C\underline{H}OCF_3$
F	-11.6 ppm		OCF_3
F	+ 18.0 ppm	2• x 57.8, 2• x 12.9, 4• x 2.0	One CF in $=CF_2$
F	+ 37.2 ppm	2• x 50.1, 2• x 3.0	Other CF in $=CF_2$

2. $(CF_3O)_2C = CF_2$

a. Addition of CF_3OF to $CHCl = CCl_2$

Into a 460 ml. capacity steel cylinder equipped with a maximum indicating pressure gauge was added 19.0 g. (0.146 moles) of $CHCl = CCl_2$. The lower portion of the cylinder was cooled to -183° and the cylinder evacuated, freezing the olefin entirely in the lower part of the cylinder. Freon 113 ($CFCl_2CF_2Cl$), 50 cc, was condensed on top of the olefin and maintained as a frozen barrier while CF_3OF, 11.1 g. (0.106 moles) was added, [calc. on the basis of 75 mole % CF_3OF, the remainder being 14.4% COF_2 and 12% $(CF_3O)_2$]. The cylinder valve was closed, the cylinder removed from the liquid oxygen, and placed behind a barrier and allowed to warm slowly. Within an hour the reaction was complete. In several identical preparations the maximum pressure which occurred during the reaction was 400 psig. Generally the maximum pressure was less than 200 psig. The temperature rise was not determined but the cylinder temperature shortly after reaction had occurred was estimated to be about 50 - 70°.

Combined product mixtures from several identical runs where 51.2 g. (0.492 moles) of CF_3OF and 89.0 g. (0.685 moles) of $CHCl = CCl_2$ were used gave on simple distillation 102 g. of crude product. Analysis of the crude product by GLC at 25° on a 8' column packed with HMDS chromosorb with Kel-F ester as the stationary phase gave four peaks. The first two peaks were identified by retention time as 33.8% Freon 113 and 9.6% $CHCl = CCl_2$ and the second two as 51.3% $CF_3OCHClCFCl_2$ and 5.3% of the isomeric adduct CF_3OCCl_2CHFCl, an isomer ratio of 91/9.

An attempt to rectify this mixture resulted in a major fraction boiling at 84 to 85° which was composed of 77.6% $CF_3OCHClCFCl_2$, 17.4% $CHCl = CCl_2$ and 3.0% CF_3OCCl_2CHFCl, initially considered to be an azeotropic mixture. In the earlier preparations this mixture was used without further purification in subsequent steps. In more recent preparations, however, the $CHCl = CCl_2$ is totally reacted with CF_3OF and the reaction mixture rectified on a 35 plate spinning band column to give > 98% pure $CF_3OCHClCFCl_2$ b.p. 84-85°; d_{25}, 1.5884; n_D^{20}, 1.3622. Elemental analysis calc. for $C_3Cl_3F_4HO$: C, 15.28; H, 0.42; Cl, 45.22.

Found: C, 15.10; H, 0.43; Cl, 45.09.

The structural assignment is further confirmed by the following NMR analysis. Fluorine and hydrogen chemical shifts are given with respect to CF_3COOH and CH_3CHO.

NMR Data for $CF_3OCHClCFCl_2$

Peak	Chemical Shift	Pattern and Splitting (cps.)	Rel. Area	Assignment
H	3. 84 (approx. tau)	2° x 3. 7; 4° x 0. 5	-	CHCl
F	-16. 7 ppm		3	CF_3O
F	-10. 8 ppm		1	$CFCl_2$

An infrared spectrum of this compound is shown in Figure 8.

The isomeric adduct CF_3OCCl_2CHFCl 70. 3% pure, major impurity its isomer, distilled at 87°; n_D^{20}, 1. 3685. An infrared spectrum of this compound is shown in Figure 9.

b. Dechlorination of $(CF_3O)_2CHCF_2Cl$

Into a 500 ml. 3-neck flask fitted with a mechanical stirrer, a dropping funnel and a gas outlet tube was added 250 ml. of Baker analytical grade dimethyl sulfoxide, 50 g. of zinc dust and several crystals of $ZnCl_2$.

The reaction mixture was heated to 80° and 133 g. crude adduct (83. 8 mole % $CF_3OCHClCFCl_2$, 10. 9% CF_3OCCl_2CHFCl and 4. 8% $CHCl = CCl_2$) was added slowly. After a short induction period a vigorous reaction started and on continued addition of the adduct the exotherm was sufficient to maintain the temperature at 80-90°.

The crude dehalogenation product, 74 g., was collected in a trap cooled to -78°. GLC analysis (8' column at RT, Kel-F ester on Chromosorb) indicated 65% $CF_3OCH = CFCl$, 29. 8% $CF_3OCCl = CHF$, 2. 7% $CF_3OCHClCFCl_2$ and 0. 9% CF_3OCCl_2CHFCl. GLC on a longer column (40') further split the two major peaks into the expected cis-trans isomers of the two vinyl ethers. Infrared spectra of $CF_3OCH = CFCl$ (F cis to H) and its trans isomers are shown in Figures 10 and 11. A gas density molecular weight determined on the cis and trans isomers gave 165 and 161 g/mole. Calculated for C_3ClF_4HO, 164. 5. In Quarterly Report No. 5 the trans isomer was erroneously identified as the positional isomer $CF_3OCCl = CHF$. Subsequent NMR analysis has identified this compound as $CF_3OCH = CFCl$ (H trans to F). Fluorine and hydrogen shifts are given with respect to CF_3COOH and CH_3CHO, $CFCl_3$ solvent.

NMR Data for $CF_3OCH = CFCl$ (trans)

Peak	Chemical Shift	Pattern and Splitting	Assignment
H	4.12 tau	2° x 13.4 cps	
F B	TFAA -15.6 ppm $CFCl_3$ +62.7 ppm	Singlet	CFCl (F trans to H)
F C	TFAA +15.0 ppm $CFCl_3$ +93.3 ppm	2° x 13.5 cps	OCF_3

c. <u>Addition of CF_3OF to $CF_3OCH = CFCl$</u>

Into an evacuated 460 ml. steel cylinder, equipped with a maximum indicating pressure gauge, was condensed 0.045 moles of an olefin mixture composed of 58% $CF_3OCH = CFCl$, 35% $CF_3OCCl = CHF$ and 7% of an unidentified impurity. While maintaining the olefin mixture at -183°, approximately 8 mmoles of CF_3OF [estimated purity 70% with the major impurities COF_2, $(CF_3O)_2$ and CF_4] was slowly added. The cylinder valve was closed and the cylinder was removed from the vacuum system and allowed to warm to room temperature. No excessive pressure rise was noted during reaction. The addition of CF_3OF was repeated six times until 0.049 moles of the CF_3OF/impurities mixture was added. Infrared analysis of the over gases showed the presence of CF_3OF indicating that all of the olefin had reacted. Subsequent infrared analysis of the higher boiling residue, however, showed the presence of $C = C$ indicating that the reaction had not gone to completion.

Chromatographic analysis (Kel - F ester on HMDS chromosorb, 8 ft. column at room temperature) of the higher boiling components showed four major product peaks. The major peak separated chromatographically had a vapor density molecular weight of 266. Molecular weight calculated for $(CF_3O)_2CHCF_2Cl$, 268.5. The structure of this compound was further substantiated by the following NMR data. The chemical shifts for fluorine are given with respect to external CF_3COOH.

NMR Data for $(CF_3O)_2CHCF_2Cl$

Designation	Chemical Shift (ppm)	Pattern and Splitting (cps.)	Assignment
H	---	triplet	$-CHCF_2-$
F	-16.5	3° x 2.1; 2° x 0.5	CF_3O-
F	- 6.5	2° x 3.3; 7° x 2.0	$-CF_2Cl$

No attempt was made to further purify the crude reaction product by distillation. The boiling point and other physical properties of GLC pure $(CF_3O)CHCF_2Cl$ were determined by measuring the vapor pressure of the compound over a temperature range of -5 to 17.3°. The vapor pressure approximates the following equation.

$$\log P = 8.30 - \frac{1719}{T}$$

Assuming ideal gas behavior the following data were calculated for $(CF_3O)_2CHCF_2Cl$. Boiling point, 44°; Trouton constant, 24.8; and the heat of vaporization, 8.41 Kcal/mole. An infrared spectrum of this compound is shown in Figure 12.

A vapor density molecular weight of the second major product peak was found to be 279, calc. for $C_4ClF_8HO_2$, 268. Preliminary NMR analysis supports the structural assignment of this compound as $CF_3OCHFCFClOCF_3$.

In order to determine the relative proportions of the two possible adducts obtainable under the reaction conditions described above, an initial small scale reaction of CF_3OF with GLC pure $CF_3OCH = CFCl$ was run. The two isomers, $(CF_3O)_2CHCF_2Cl/CF_3OCHFCFClOCF_3$ were obtained in the ratio of 71/29.

d. <u>Dehydrochlorination of $(CF_3O)_2CHCF_2Cl$</u>

In an initial attempt at dehydrochlorination of $(CF_3O)_2CHCF_2Cl$, 1.9 mmoles of GLC pure adduct was added to a 25 ml. capacity stainless steel cylinder containing 0.45 g. (8 mmoles) of powdered KOH. The cylinder was heated for 2 hours at 100°. GLC analysis (40' column, Kel-F ester on HMDS Chromosorb at RT) showed one major peak 98%, 1.9% starting material and trace amounts of two other unidentified impurities. An infrared spectrum of the reaction mixture showed absorption at 5.5μ indicating dehydrochlorination had occurred. The structure of this compound was substantiated by the following NMR data. The chemical shifts for fluorine are given with respect to external CF_3COOH.

NMR Data for $(CF_3O)_2C = CF_2$

Designation	Chemical Shift ppm	Pattern and Splitting cps.	Rel. Area	Assign.
F	-13.9	triplet, 2.3	6.7	CF_3O-
F	+31.1	heptet, 2.4	2.0	$=CF_2$

Subsequent dehydrochlorination runs were made on a larger scale using crude $(CF_3O)_2CHCF_2Cl$.

The boiling point and other physical properties of GLC pure $(CF_3O)C = CF_2$ were determined by measuring the vapor pressure of the compound over a temperature range of -13 to 7°. The vapor pressure of this compound approximates the following equation

$$\log P = 6.74 - \frac{1117}{T}$$

Assuming ideal gas behavior the following data was calculated for $(CF_3O)_2C = CF_2$. Normal boiling point, 11.9°; Trouton constant, 17.9; and a heat of vaporization of 5.11 Kcal/mole. An infrared spectrum of this compound is shown in Figure 13.

3. $SF_5OCF = CF_2$

a. Addition of SF_5OF to CFCl = CFCl

A glass ampule was charged with SF_5OF (0.027 moles) and CFCl = CFCl (0.027 moles) and stored at -28° for 24 hours. The contents were allowed to warm slowly to room temperature and the unreacted overgas removed on the vacuum line leaving 5 g. (0.017 moles) of $SF_5OCFClCF_2Cl$. The conversion was 63%. Two attempts to repeat this reaction resulted in explosions immediately upon condensation of SF_5OF into the ampule.

This reaction was also carried out in the gas phase by charging a 1-l flask with SF_5OF (200 mm, 5 mmoles) and helium (100 mm). A second flask was charged with CFCl = CFCl (190 mm, 10 mmoles) and helium (570 mm). This mixture was slowly added to the SF_5OF until the pressure in the two flasks were equal. The reaction mixture was then placed in the sunlight for 8 hours. Infrared analysis showed that the desired product had been produced. Due to the small size of the reaction the product was not separated, however.

An infrared spectrum of this compound was reported in the first Annual Report under this contract. The structure of this compound has since been substantiated by the following NMR data. Chemical shifts for fluorine are given with respect to external CF_3COOH.

NMR Data for $SF_5OCFClCF_2Cl$

Designation	Chemical Shift ppm	Pattern and Splitting cps.	Rel. area	Assign.
A	Approx. -148	Complex multiplet	5.0	SF_5
B	-7.3	doublet	2.06	CF_2Cl
C	+0.3	Complex multiplet	1.0	CFCl

b. Addition of SF_5OF to CHF = CFBr

Into a finger trap on a calibrated vacuum system was condensed 64.3 mmoles of a gas mixture containing approximately 50 mole % SF_5OF (major impurities SOF_4 and SO_2F_2). While maintaining the SF_5OF mixture frozen in the bottom of the trap, 1.5 moles of CHF = CFBr was added. The reactants were allowed to warm slowly until a sudden surge in pressure indicated reaction had occurred. Additional olefin was added in small amounts until no further reaction occurred (32 mmoles). Volatiles were removed by trap to trap distillation giving 8 to 9 g. of crude product per run. Chromatographic analysis (16' column, 59°, U.C. L-45 silicon grease on Chromosorb) showed two product peaks. Preliminary NMR analysis indicates the major product (82.7%) to be the desired $SF_5OCHFCF_2Br$, b.p. 74° (micro determination); n_D^{20}, 1.3163; d_4^{20}, 1.99. Preliminary NMR analysis also supports the structure of the isomeric addition product as $SF_5OCFBrCHF_2$, b.p., 77-78; n_D^{20}, 1.3332. An infrared spectrum of the major isomer is shown in Figure 15.

c. Attempted Dechlorination of $SF_5OCFClCF_2Cl$.

In Tetramethylene Sulfone

A mixture of tetramethylene sulfone (50 ml.), powdered zinc (10 g.) and a trace of $ZnCl_2$ was placed in a 3-neck, 100 ml. flask fitted with a mechanical stirrer, a condenser and a dropping funnel. The mixture was heated to 70-90° and while stirring vigorously $SF_5OCFClCF_2Cl$ (5.0 g., 0.017 moles) was added slowly. Volatile products were caught in a trap at -78°. Infrared analysis indicated the presence of H_2S, CFCl = CFCl, CF_2 = CFCl, SO_2F_2 and SF_6. An unidentified compound absorbing at 5.59 microns was also detected.

In Dioxane

In apparatus similar to the above a mixture of dry dioxane (45 ml.) and powdered zinc (5 g.) was heated to 50° and $SF_5OCFClCF_2Cl$

(3 g., 0.01 moles) added dropwise with stirring. No apparent reaction occurred as the temperature was raised to 90°. After 2 hours several drops of liquid were collected in a trap at -78°. Infrared analysis showed it to be mainly CFCl = CFCl containing dissolved SO_2F_2 and SOF_4.

d. Dehydrobromination of $SF_5OCHFCF_2Br$ With $(C_2H_5)_3N$

Into an evacuated 250 ml. capacity pyrex glass reactor, fitted with a Fisher-Porter stopcock, was added 5.8 g. of crude $SF_5OCHFCF_2Br$. While at room temperature 2.55 g. (25.0 mmoles) of Et_3N was added. Immediately, on addition of the amine, a slight exotherm was noted and a dark brown solid formed as a precipitate and as a deposit on the reactor walls. After 15 minutes reaction time the remaining liquid was transferred (colorless) to the vacuum system. An infrared spectrum taken shortly after transfer showed absorption at 5.6 μ indicating the presence of CF = CF_2.

The solids remaining in the reactor, 3.5 g., were found to be almost entirely soluble in water and gave a positive test for Br^- and a negative test for $SO_4^=$.

The initially clear reaction product on standing overnight again formed a dark brown precipitate. The product was transferred colorless two additional times with the same result. The product was finally washed with aqueous HCl and a liquid layer separated which no longer showed C = C in its IR spectrum. An additional run was made in which an attempt was made to remove the dehydrobromination product as formed.

Into a 100 ml. 3-neck flask fitted with a dropping funnel, mechanical stirrer and a water cooled condenser connected to a LOX cooled trap was added a solution of 4.5 g. (14.7 mmole) $SF_5OCHFCF_2Br$ in 30 ml. of Freon 113. To the solution at room temperature was aded 1.5 g. (14.9 mmoles) of $(C_2H_5)_3N$. On addition of the amine a small amount of solids formed and no volatiles were collected in the LOX cooled trap.

The solution was heated to reflux and three crude cuts were taken at a solution temperature of 89 to 91°. An infrared spectrum of each showed no unsaturation and indicated starting adduct in the last two cuts.

With KOH

Into an evacuated 100 ml. capacity Fisher-Porter pyrex reactor containing 10 g. of KOH was added 4.5 g. of $SF_5OCHFCF_2Br$. After 16 hrs. at room temperature an infrared absorption spectrum of the over-gases showed a strong absorption at 5.61 μ, indicative of the presence of the $CF = CF_2$, and C-H stretch absorption at 3.3 μ. The reactants were heated at 50° and infrared analysis of the over-gases was determined after 1 and 4 hours at temperature. The ratio of intensities of IR absorption at 5.61 and 3.33 μ increased with time at temperature indicating additional dehydrobromination was occurring. After an additional 16 hrs. at room temperature the ratio of intensities $C = C/C - H$ decreased.

The volatiles were transferred and the residual solids dissolved in distilled water. The water solution gave a positive test for Br^-, F^- and $SO_4^=$.

In an attempt to remove the dehydrobromination product before hydrolysis could occur 70 g. of KOH was heated to 80° in a 300 ml. 3-neck flask fitted with a mechanical stirrer, a dropping funnel, and a condenser connected to a LOC cooled trap. While stirring the LOX, 6.1 g. of $SF_5OCHFCF_2Br$ was slowly added. During addition of the adduct only a small amount of material was collected in the LOX cooled trap. Additional material was collected by sweeping the flask with N_2. The volatile reaction product, 2.2 g. was transferred to the vacuum system and enrichment of the lowest boiling portion was carried out by trap to trap distillation.

Further separation of the lowest boiling component (vapor pressure > 200 mm at RT) by GLC (16' U.C. L-45 Silicone grease on Chromosorb at RT) showed three major peaks. The material having the longest retention time, representing 57.3% of the total, was identified by IR and retention time as the starting adduct $SF_5OCHFCF_2Br$. The first peak, 20% of the total, is identified as $SF_5OCF = CF_2$ by vapor density MW of 216;225 (calc. 224) and by a strong IR absorption maximum at 5.61 μ indicating absorption due to $CF = CF_2$ stretch. In addition, strong absorption maxima found between 10.7 and 11.6 μ are attributable to the SF_5 group, Figure 16. Preliminary NMR analysis further substantiates the structure of this compound as $SF_5OCF = CF_2$.

An infrared spectrum of the second peak, 22.4% of the total, showed absorption at 3.34 μ (C-H stretch) and no unsaturation. Further analysis will be necessary for identification of this material.

In view of the probably hydrolysis of the $SF_5OCF = CF_2$ an additional dehydrobromination was attempted using a KOH/BaO mixture.

Into a 100 ml. capacity Pyrex Fisher-Porter reactor was added a mixture of 20 g. KOH and 20 g. BaO. The reactor was evacuated and 10 g. of an approximate 80/20 mixture of $SF_5OCHFCF_2Br/SF_5OCFBrCF_2H$. was added. The reaction mixture was left at room temperature for 16 hrs. An infrared spectrum of the overgases after this time showed a maximum at 5.61 indicating $-CF = CF_2$ and also a maximum at 3.3 μ (C-H).

The reactor was heated to 50° and after a short time at this temperature an explosion occurred.

A flow system was set up such that the adduct mixture could be passed over KOH pellets while maintaining the system under vacuum. Through a 2 x 80 cm Pyrex tube, wrapped with nichrome wire and packed with KOH pellets was passed 4.4 g. of the 80/20 mixture of $SF_5OCHFCF_2Br/SF_5OCFBrCF_2H$. An infrared spectrum after a single pass showed a maximum at 5.61 μ and also at 3.3 μ (C-H). The column was heated to progressively higher temperatures and an infrared spectrum taken after each pass and the change in absorption maxima noted at 3.33 (C-H), 7.22 μ (characteristic of the starting material) and at 5.61, 7.4 μ (characteristic of the reaction product). On successive passes at temperatures ranging to about 70° the ratio of the intensities at 5.61/3.33 μ and 7.4/7.22 μ increased. A final pass was made with the KOH heated to 90 - 100°. When the adduct was passed at this temperature the KOH initially became slightly yellow and on continued flow of the adduct became molten. An infrared spectrum of the material passed through the molten KOH showed 5 maxima of varying intensity between 5 and 6 μ (5.1, 5.18, 5.29, 5.47 and 5.6 μ).

An additional run was made similar to the above and the change in isomer ratio determined after repeated passes over KOH at room temperature. The starting isomer ratio was 91:9. After a single pass through the KOH column (in this experiment powdered KOH was used) the isomer ratio changed to 92.5:7.5. After a total of three passes the isomer ratio was 95:5 indicating progressive loss of the $SF_5OCFBrCF_2H$.

A GLC pure sample of the minor isomer $SF_5CFBrCHF_2$, 0.3 g., was condensed into an evacuated ampule containing 0.5 g. of powdered KOH. While still open to the vacuum system the ampule was heated slowly.

At a temperature estimated to be 50-60° a sudden surge in pressure occurred. An infrared spectrum of the overgases showed strong absorption at 5.61 and 7.4 μ and very weak absorption at 3.33 and 7.22 μ indicating that the reaction product was mainly $SF_5OCF = CF_2$.

A chromatographically pure sample, 0.3 g., of $SF_5OCHFCF_2Br$ was heated in contact with 5 g. of powdered KOH, similar to the previous reaction, to the reflux temperature of the compound with no pressure surge occurring. An infrared spectrum taken after heating for 5 min. at reflux showed maxima attributable to a reaction product or products at 5.28, 5.47, 7.42, 7.73 and 12 μ. The remaining maxima correspond to the starting compound.

GLC analysis (16' U.C. L-45 Silicone grease on Chromosorb at RT) of an overgas sample of the reaction product indicated mainly starting material to be present with a small additional peak 2.5%.

On continued contact with heated KOH the intensity of the infrared maxima at 5.28 and 5.47 μ increased slightly.

4. CFBr = CFBr

a. Bromination of CHF = CHF

Bromine (68 g., 0.43 moles) was placed in a 3-neck flask fitted with a stirrer, a gas inlet tube and a water cooled condenser. Gaseous CHF = CHF, (29 g., 0.43 moles) was bubbled into the bromine over a 6 hour period. The solution color turned from red-brown to pale yellow during the addition. Distillation of the crude product on an 18" spinning band column gave a fraction (33.5 g.) boiling at 107 - 108° and a fraction (40.0 g.) boiling at 108 - 110°. Conversion to CHFBrCHFBr was 72.6%. An infrared spectrum of the compound is shown in Figure 14. Analysis calculated for $C_2H_2F_2Br_2$: C, 10.72%; H, 0.90%; F, 16.97%; Br, 71.39%.

Found: C, 10.92%; H, 0.98%; F, 16.92%; Br, 71.36%.

b. Dehydrobromination of CHFBrCHFBr

Into a 100 ml. 3-neck flask fitted with a mechanical stirrer, ice water cooled condenser, and a dropping funnel was placed CHFBrCHFBr (40 g., 0. 1 moles). While vigorously stirring, KOH (10 g., 0. 18 moles in about 30 cc of Nujol) was added slowly. The reaction was run at room temperature but on addition of the KOH an exothermic reaction was noted. Upon complete addition of the KOH the reaction mixture was heated to distill off residual dissolved dehalogenated product. The volatile products (21 g.) were trapped at 0° and found by GLC (Kel-F ester on HMDS Chromosorb) to be composed of about 60% CHF = CFBr and about 40% of the saturated starting compound. Conversion was 41%. This material was used in the following preparation without further purification.

c. Bromination of CHF = CFBr

Bromine (23. 4 g., 0. 146 moles) was added to a 100 ml. 3-neck flask equipped with an ice water cooled condenser and a gas bubbler tube. The bromine was maintained at 0° by an ice bath and the CHF = CFBr/CHFBrCHFBr mixture from the previous experiment (0. 273 moles contained in a Fisher-Porter valve-equipped ampule) was slowly added through the gas inlet tube. After complete addition the flask was warmed to room temperature and the excess bromine was flushed with helium into a trap at -28°. The crude product remaining (29. 5 g.) was distilled on an 18" spinning band column yielding $CHFBrCFBr_2$ (26. 6 g.) boiling at 144 - 146°. (Literature 146°).

d. Dehydrobromination of $CHFBrCFBr_2$

Into a 100 ml. flask equipped with a mechanical stirrer, a distilling head with thermometer, and ice water cooled condenser was placed an excess of powdered KOH dispersed in Nujol. The reaction mixture was heated to 100° and $CHFBrCFBr_2$ (26. 6 g., 0. 088 moles) was added slowly. The crude dehydrohalogenation product (113. 0 g.) distilled into an ice water cooled receiver. Yield of CFBr = CFBr was 69%.

5. Reaction of $(CF_3O)_2$ with CFCl = CFCl

a. Thermal Reaction

Into a 300 ml. Monel cylinder was condensed 40.3 g. (0.237 moles) of $(CF_3O)_2$ and 17.3 g. (0.131 moles) of CFCl = CFCl. The reactor was heated to 213° for a period of about 19 hrs. The reactor was cooled and the volatiles passed through a series of traps at 0°, -78° and -183°. The combined volatiles collected at -78 and -183° was 0.15 moles and remaining in the cylinder was 28.1 g. of higher boiling liquid. Several runs were combined to give 102 g. of crude product. (Apparently fluorination also occurred on one occasion since the reaction product when transferred to the vacuum system had the color of Cl_2. GLC analysis on a 16' column (U.C. Silicone L-45 on chromosorb) showed six major products present in addition to a number of minor products appearing as individual peaks or as shoulders on the major product peaks. Resolution in this analysis was considerably improved over that reported previously where the separation was effected on a 8' column at 150° with diisodecylphthalate on PTFE.

Similar to the results obtained in earlier attempts to isolate the desired 1:1 and 1:2 addition products by distillation, distillation through a 16" spinning band column over a range of 53 to 190° gave no constant boiling cuts. GLC analysis of ten samples taken over the entire range showed each to be composed of numerous products.

b. U. V. Initiated Addition

Into a evacuated 1.2 l. volume system consisting of a 1 l. Vycor flask equipped with a vacuum gauge was added 22.4 mmoles of $(CF_3O)_2$ and 22.4 mmoles of CFCl = CFCl. The Vycor flask was irradiated at a distance of 3" and for a period of 3 days with a 140 watt Hanovia type 30620 U. V. lamp. At the end of this time a pressure drop of 80 mm occurred and a higher boiling liquid was present. The volatiles were passed through an ice cooled trap and 0.6 g. of low boilers were collected leaving about 1.0 g. of higher boiling material in the reaction flask. GLC analysis (123°, 16' col., U.C. Silicone L-45 on Chromosorb) of the lower boiling material showed five products, in addition to residual starting olefin. The higher boiling fraction also showed five products but the two having the longest retention times were only slightly more than trace amounts. In both GLC separations the product peaks were well resolved indicating a fairly simple mixture.

A second run was made similar to that described above with the exception that a 5/1 molar ratio of $(CF_3O)_2/CFCl = CFCl$ was used. After 22 hours irradiation 0.2 g. of liquid product was obtained. Chromatographic analysis showed three well resolved symmetrical peaks in addition to some starting olefin and trace low boilers.

6. Attempted Preparation of $(CH_3O)_2C = CF_2$

A 250 ml. 3-neck flask was equipped with a nitrogen inlet tube, stirrer, and condenser to which was attached a CO_2 absorption tube and liquid oxygen trap. The flask was charged with 9 g. (0.1 mole) of dimethyl carbonate, 28.6 g. (0.11 mole) of triphenyl phosphorus, 16.8 g. (0.11 mole) of sodium chlorodifluoroacetate, and 50 ml. of dry diglyme. The mixture was stirred under a slow N_2 sweep at 85-90° for 16 hr. No evidence was obtained for formation of the desired olefin. Failure of the desired reaction to occur was further demonstrated by isolation of 64% recovery of triphenyl phosphorus m.p. 79-80° (lit. m.p. 79°).

7. $(CF_3CH_2O)_2C = O$

Aldrich and Shepard[35] have reported the synthesis of the desired carbonate by reaction of Cl_2CO with CF_3CH_2OH in the presence of pyridine using ether as the solvent. In the synthesis reported here the method of Choppin and Roberts [36] was employed in that CF_3CH_2ONa was reacted with Cl_2CO in dioxane solvent. Thus, a 1-liter 3-neck flask was fitted with condenser, stirrer, gas inlet tube, and thermometer well and charged with 600 ml. of freshly distilled dioxane and 23 g. (1.0 g. atoms) of freshly cut

---

(35) Aldrich and Shepard, J. Org. Chem., 29, 11 (1964).
(36) Choppin and Roberts, J.A.C.S., 70, 2937 (1948).

sodium. To this mixture was added all at once 100 g. (1.0 mole) of CF_3CH_2OH. After the initial exothermic reaction was subdued (with the aid of an ice bath) the mixture was stirred for 30 minutes without heating and then at reflux for 4 hours. At the end of this period all of the sodium had reacted. The temperature of the reaction mixture was adjusted to 70° and a cylinder containing 53 g. (0.53 mole) of Cl_2CO was attached to the gas inlet tube and opened. An exothermic reaction began immediately upon introduction of the gaseous Cl_2CO and the temperature rose to 94°. At the same time precipitation of the sodium chloride caused the mixture to become a white viscous slurry. The exothermic reaction persisted, holding the temperature at 94° until all of the Cl_2CO had been bubbled in. No unreacted Cl_2CO was found in a dry ice-acetone trap which was connected to the condenser. The mixture was heated at 70° for an additional hour, after which time it was cooled and the white slurry poured into a mixture of ice, water, and 100 ml. of ether. The ether layer was separated and the aqueous phase was extracted with a 100 ml. portion of ether. The ethereal extracts were continued, washed twice with 250 ml. portions of water, and dried over anhydrous sodium sulfate. The ether was stripped off with a rotary film evaporator and the residual straw colored liquid was fractionally distilled to give 42.8g. (37.5%) of a fraction b.p. 58-60°/70 mm., n_D^{20} 1.3152 which was shown by VPC to be about 92% pure $(CF_3CH_2O)_2C{=}O$(lit. b_{75}62.5°). The yield reported by Shepard and Aldrich was 15%.

8. Attempted Preparation of $(CF_3CH_2O)_2C = CF_2$

A 300 ml. 3-neck flask equipped with condenser, nitrogen inlet tube and stirrer, and connected through the condenser to a liquid oxygen trap was charged with 18.2 g. (0.08 mole) of $(CF_3CH_2O)_2CO$, 21.0 g. (0.084 mole) of triphenyl phosphorus, 12.8 g. (0.084 mole) of $ClCF_2COONa$ and 50 ml. of dry diglyme. The stirred mixture was then heated at 95-100° under a slow sweep of nitrogen for a period of 18 hours. During this time the reaction mixture turned dark brown in color. The warm reaction mixture was filtered and an attempt was made to distill the filtrate. No distillate was obtained, however, up to a pot temperature of 165° and, upon cooling, the pot material contained a considerable amount of black tarry material. The solid filtrate from the original reaction mixture was mostly soluble in water indicating that it was mainly sodium chloride from the decomposition of $ClCF_2COONa$. The water insoluble material was a brown sticky mass which was not identified.

9. Preparation of R_fCOF[37]

Into a 460 ml. capacity steel cylinder was placed 50 g. (0.49 moles) anhydrous ZnF_2 and 26.5 g. (0.2 moles) of CF_3COCl. The cylinder was heated to 110°C. and during the reaction period the progress of the reaction was followed by infrared analysis. The carbonyl absorption of the acid chloride at 5.5 μ gradually disappeared and the carbonyl absorption of the acid fluoride at 5.27 μ intensified over a 5 day period. At the end of this time IR analysis and GLC (8' column, fluorosilicone on PTFE) indicated an apparent quantitative conversion to CF_3COF.

In a similar manner C_2F_5COF, 33 g.; C_3F_7COF, 95 g. and $(CF_2)_3(COF)_2$, 24.4 g. were prepared.

10. Attempted Preparation of C_2F_5OF

a. Reaction of CF_3COF with AgF_2

Into a Monel cylinder of 100 ml. capacity was added 30 g. of AgF_2. The cylinder was evacuated, 5.8 g. (50 mmoles) of CF_3COF was condensed in and the cylinder heated to 100°. After 16 hours at 100° an infrared spectrum of the over gases indicated no reaction had occurred. After

---

(37) Organic Reactions Vol. II, p 61, J. Wiley and Sons, New York.

heating the cylinder for an additional 16 hours at 200° an infrared spectrum showed the presence of CF_4 and COF_2 and the absence of CF_3COF, indicating that cleavage had occurred.

b. Reaction of CF_3OF with CF_3COF

Into an evacuated 100 ml. capacity Monel cylinder equipped with a pressure gauge was condensed 20.6 mmoles of CF_3OF mixture containing COF_2, CF_4 and $(CF_3O)_2$ and 10.6 mmoles of CF_3COF. The cylinder was heated to 228° for 16 hrs. and during this period the pressure remained essentially constent at 195 psig. After heating for an additional 5 days at 195° up to 320° with no observable abrupt pressure change occurring, heating was stopped. Examination of the reaction products by IR and by GLC showed no evidence that the methyl ethyl peroxide had formed and also that no CF_3OF or CF_3COF was present. The remaining gases identified were COF_2, CF_4 and $(CF_3O)_2$.

11. Attempted Preparation of $CsOCF_3$

Into a 50-ml. heavy-wall Carius tube having a double constriction was placed 3.1 g. (20.4 mmoles) CsF which was dried by heating under vacuum for 36 hrs. at 200°. Approximately 5 ml. of CH_3CN was distilled from P_2O_5 into the tube followed by 25.6 mmoles of COF_2. The tube was sealed at the upper constriction and warmed to room temperature. On standing over a period of 8 days with occasional shaking the upper portion of the originally granular CsF changed to a finer particle size. On reopening the tube to the vacuum system residual COF_2 was removed (estimated to be 8.7 mmoles). The tube was cooled in liquid N_2, 12.5 mmoles of C_2F_4 added and the ampule resealed. After 24 hrs. at room temperature the ampule was reopened to the vacuum system and the lower boiling volatiles removed. Infrared analysis of the volatiles showed mostly C_2F_4 with a trace of COF_2. The ampule was then heated to the reflux temperature of CH_3CN and an infrared spectrum of the overgases taken. No COF_2 was present.

12. Preparation of CF_3OF

The results tabulated in Table VII are a summary of the attempts to optimize the new fluorination reactor. The operation of this reactor is similar to that reported in the First Annual Summary Report. Fluorine and nitrogen are mixed in the proportions shown in Table VII then mixed with carbon monoxide. The gas mixture is passed through a 14.4 l. heated reactor packed with 2500 g. silver plated copper gauze. The exit gases are collected in a series of liquid oxygen cooled traps. The reactor is constructed of black iron pipe (6' x 4" I.D.). A schematic diagram of the reactor is shown in Figure 17.

Although fluorine is not condensable at -183° some fluorine dissolves in the collected product. The major portion of the dissolved fluorine is removed at reduced pressures through a water aspirator. The product containing approximately 70% CF_3OF is used for subsequent reactions without further purification.

At the point where the N_2/F_2 mixture contacts the incoming CO it was noted that the temperature of the "T" was about 140°. Trapping the gases after this point but prior to the reactor gave a product distribution of 27.8% CF_3OF and 72.2% COF_2 and no $(CF_3O)_2$.

13. $(CF_3O)_2$

Into a 2-l. Monel cylinder was condensed 132 mmoles of COF_2 and 181 mmoles of a gaseous mixture containing approximately 70 mole % CF_3OF [impurities were COF_2, $(CF_3O)_2$ and CF_4]. The reactor was heated to 230-240° for 39 hrs. The reactor was cooled to RT and the product washed with basic KI solution and collected in a trap at -78°. After drying the product by passing through P_2O_5, chromotographic analysis (40' column, Kel-F ester on HMDS Chromosorb) indicated a purity of better than 98% with only one small contaminant present. The combined pure product from two runs, where a total of 246 mmoles of COF_2 and 357 mmoles of CF_3OF mixture was used,

TABLE VII

Fluorination of CO

Run No.	Flow Rate Moles/hr			Total Reaction Time hr	Reactor Temp °C	Crude Prod. Wt. g./hr	Product Composition %	Yield of CF_3OF based on CO
	F_2	N_2	CO					
1	1.34	4.90	0.57	-	250	-	COF_2, $(CF_3O)_2$ No CF_3OF	
2	3.20	4.90	1.42	-	250	-	COF_2, $(CF_3O)_2$ No CF_3OF	
3	4.90	4.90	0.57	-	238	-	COF_2, CF_3OF	
4	3.10	0.54	0.57	0.5	238	48g	CF_3OF, 88%; COF_2 8% $(CF_3O)_2$, 4%	70.6%
5	3.10	0.54	0.57	1.0	155	47g	CF_3OF, 64.5%; COF_2, 17.1% $(CF_3O)_2$, 18.4%	51.0%
6	3.10	0.54	0.57	1.5	210	48g	CF_3OF, 91%; COF_2, 3% $(CF_3O)_2$, 6%	73.5%
Small Jet Reactor	0.34	0.31	0.06	1.0	238	3 g	CF_3OF, 50%; remainder $(CF_3O)_2$ and COF_2	24.0%
7	3.10	0.54	0.57	1.5	210	46.7g	Product distribution undetermined	
8	3.10	0.54	0.57	3.0	210	65 g	84% CF_3OF, 16% $(CF_3O)_2$	93.0%
9*	3.10	0.54	0.57	-	300		Little $(CF_3O)_2$, 127 g, mainly CF_3OF	

* Attempted prep. of $(CF_3O)_2$

yielded 36 g. or 212 mmoles of $(CF_3O)_2$. The indicated yield based on the COF_2 used was 86.3%. The actual yield is indeterminant since the amount of COF_2 and $(CF_3O)_2$ in the CF_3OF is not known.

14. SOF_2

Preparation of SOF_2 was done according to the method of Tullock and Coffman[38].

Into a 3-l. 3-neck flask fitted with a reflux condenser a mechanical stirrer and a dropping funnel was placed 943 g. of CH_3CN, 672 g. (16 moles) NaF. The NaF was held in suspension by vigorous stirring and the mixture heated to 90° (heating mantle temp.). $SOCl_2$, 476 g. (4 moles), was added slowly over a period of 7 hours. The crude reaction product (268 g.) was collected in a dry-ice/acetone cooled trap. Analysis by Cady codistillation technique showed the product to be 90% SOF_2 or 70% yield.

15. SF_5OF

$$SOF_2 + 2F_2 \longrightarrow SF_5OF$$

A new reactor was constructed for the preparation of SF_5OF. The reactor was constructed from a 2" x 8' stainless steel pipe with essentially the same design used in the larger CF_3OF reactor. This reactor was also packed with silver plated copper gauze and prior to use the reactor was heated to 200° and swept with F_2 to convert the Ag to the AgF_2 catalyst.

Initial attempts to prepare SF_5OF at 200° with a large excess of undiluted F_2 produced, after repeated small runs, SF_5OF having a maximum purity of about 18%. The major impurity in these experiments was SO_2F_2, the hydrolysis product of SOF_4. Only very slow rates and small quantities of reactants were used, hence trace amounts of water were sufficient to hydrolyze the initial fluorination product, SOF_4. The reactor was kept continuously at 200° and capped between runs. On repeated short runs the SF_5OF concentration in the reaction product increased from zero to 18 mole %.

(38) C. W. Tullock and D. D. Coffman, J. Org. Chem., 25, 2016 (1960)

After a series of small runs were made the reactor was dismantled and rebuilt using a 1-1/2" I. D. 8-1/2' long copper pipe. Unlike the stainless steel reactor the copper reactor was packed alternately with silver plated copper gauze and CsF.

Several runs were made in the new reactor using a 1:10:4 molar ratio of SOF_2:F_2:N_2 with a reactor temperature of 150-170°. A typical run where 27 g. (0.314 moles) SOF_2 was fluorinated at a rate of 0.125 moles/hr. using the above conditions gave 39.7 g. of reaction product. Analysis by Cady codistillation and infrared analysis of the individual components showed the final and major peak to contain 75% SF_5OF (estimated from the IR spectrum) and 25% SOF_4. The first and second distillation components were mixtures of SO_2F_2 and SOF_4. Analysis by direct reaction with C_2H_4 gave a SF_5OF purity of 38%.

In the most recent SF_5OF preparations the crude reaction product of SOF_2 with F_2 containing approximately 38% SF_5OF is refluorinated to convert the remaining SOF_4 to SF_5OF. In this way SF_5OF purity of 50% or greater is obtained.

Analysis by direct reaction was carried out using a small measured quantity (6 mmoles) of the crude SF_5OF and condensing it into the bottom of a trap connected to the vacuum system, then 6 mmoles of $CH_2 = CH_2$ in increments of 1 mmoles was condensed into the trap at a level above the SF_5OF. The reactants were allowed to warm to room temperature and expend into the calibrated vacuum system. Since SF_5OF reacts rapidly and quantitatively with the olefin and the usual contaminants (SO_2F_2, SOF_4, and SOF_2) do not react, then the concentration of SF_5OF present was calculated from the number of moles present before and after reaction.

16. COF_2

A simple reactor consisting of a 4' long 3/8" copper tubing was used to fluorinate CO with F_2 to give COF_2 in high purity. The only impurity detected by infrared analysis and by Cady codistillation analysis was a trace amount of SiF_4.

The apparatus consisted of a 3/8" brass tee, heated to 150°C., into which was metered 1.42 moles/hr. of CO and a mixture of 1.34 moles/hr. N_2 and 0.67 moles/hr. F_2. Reaction apparently occurred at the point of mixing at the tee as indicated by a rise in temperature of the tee to 260°C. The reaction product was passed through the 3/8" copper tubing and was collected in a LOX cooled trap.

A typical 5 hr. run using the above amounts of CO, N_2 and F_2 gave 220 g. of high purity COF_2, 100% yield based on F_2.

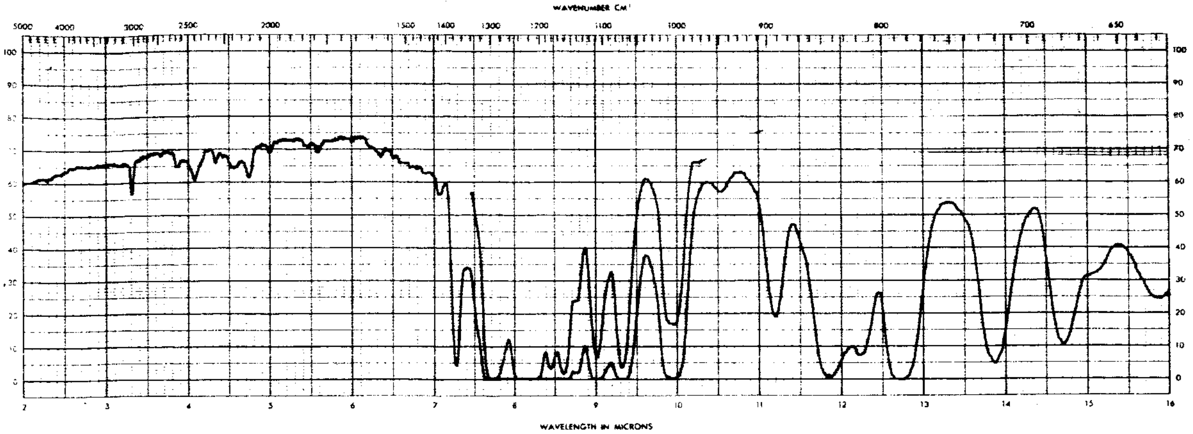


Figure 4. Infrared Spectrum of $CF_3OCHClCF_2Cl$ (gas, 25 and 7 mm).

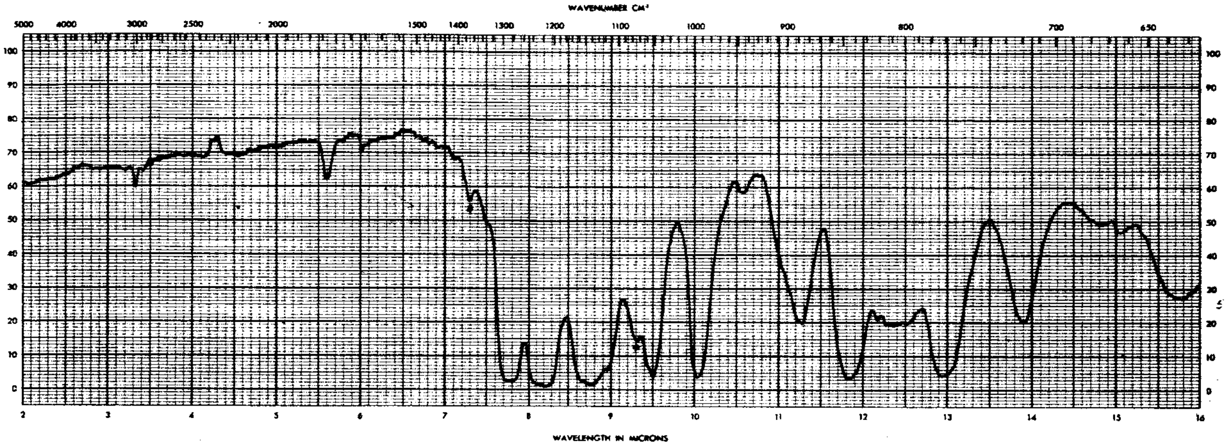


Figure 5. Infrared Spectrum of $CF_3OCFClCHFCl$ (5 mm)
*5 to 10% isomeric compound, Figure 4.

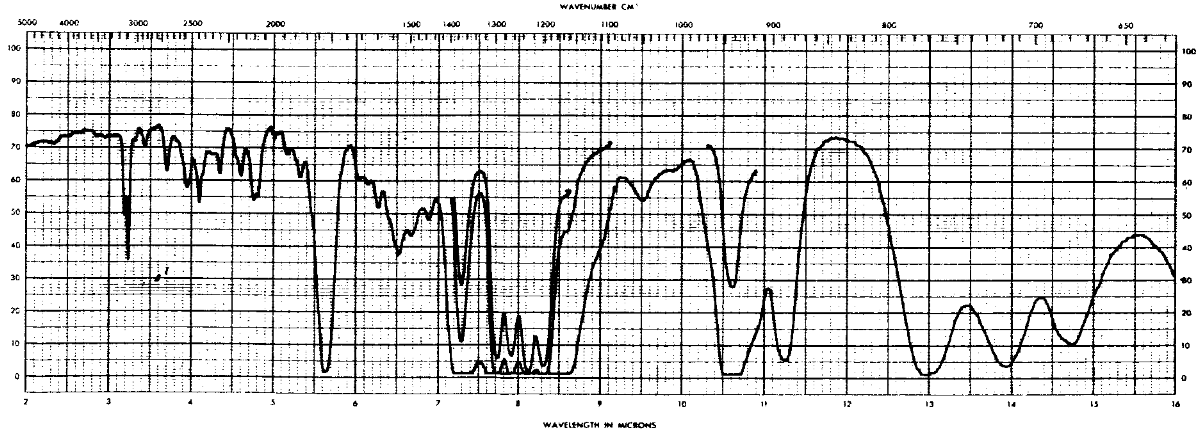


Figure 6. Infrared Spectrum of $CF_3OCH = CF_2$ (gas, 50, 5 and 2 mm).

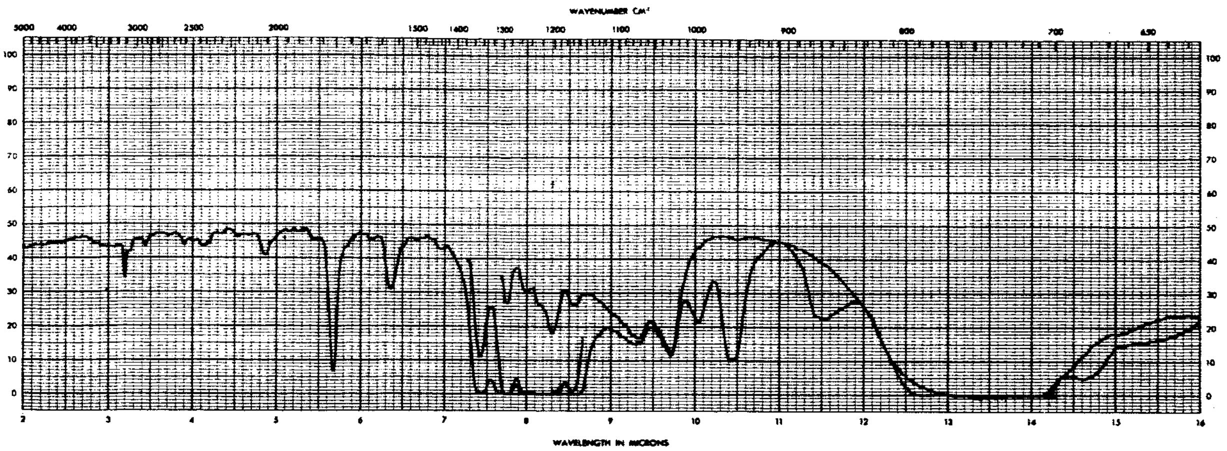


Figure 7. Infrared Spectrum of $CF_3OCF = CHF$

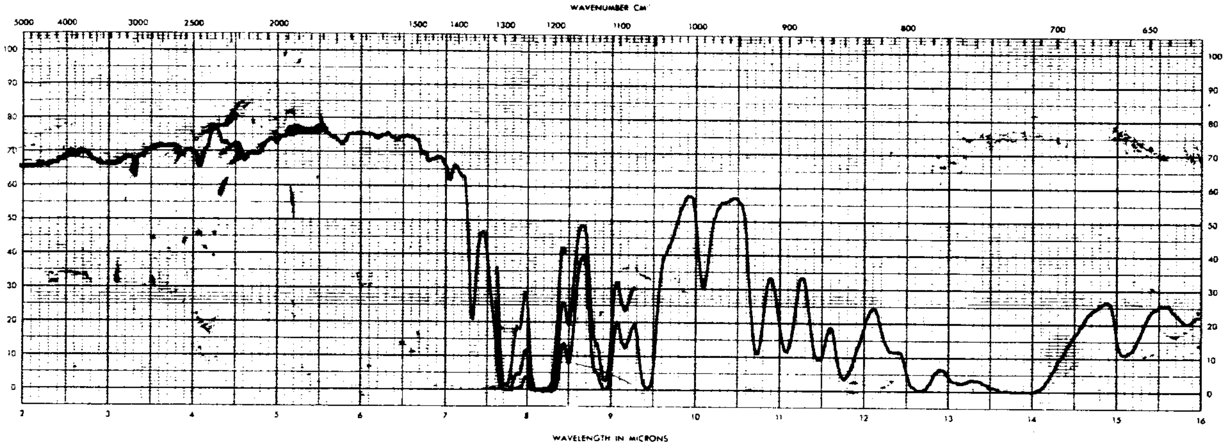


Figure 8. Infrared Spectrum of $CF_3OCHClCFCl_2$
(20, 15 and 8 mm)

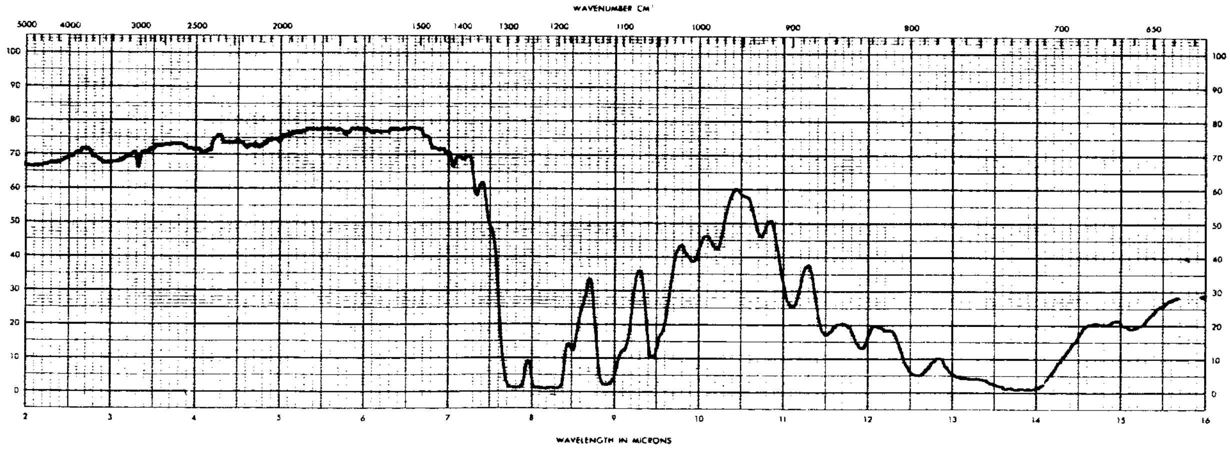


Figure 9. Infrared Spectrum of CF_3OCCl_2CFHCl

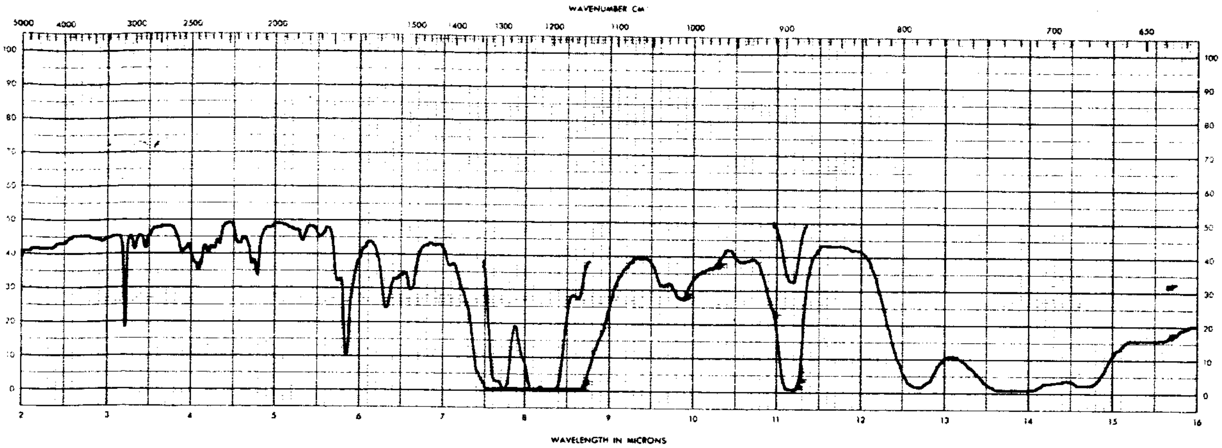


Figure 10. Infrared Spectrum of $CF_3OCH = CFCl$ (H cis to F) (76 and 14 mm)

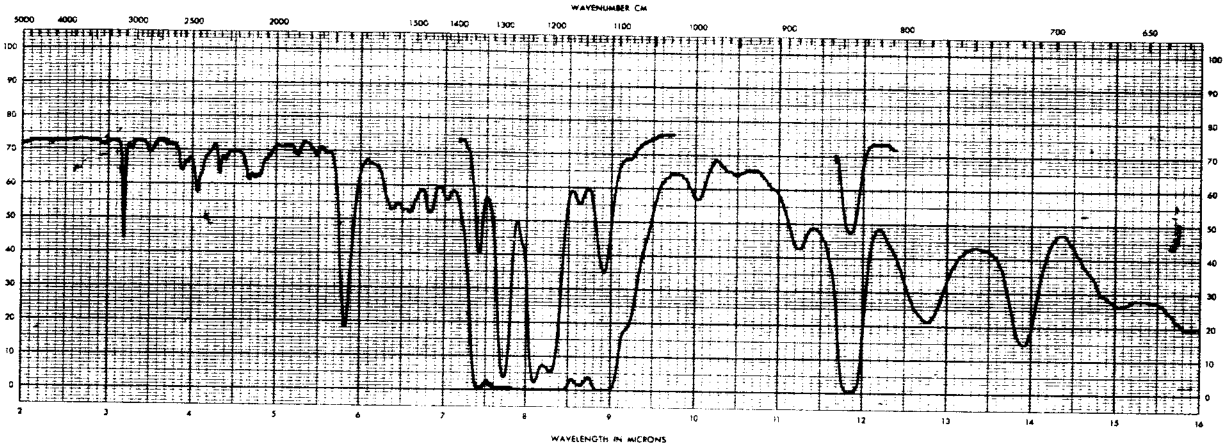


Figure 11. Infrared Spectrum of $CF_3OCH = CFCl$ (H trans to F) (cis-trans mixture)

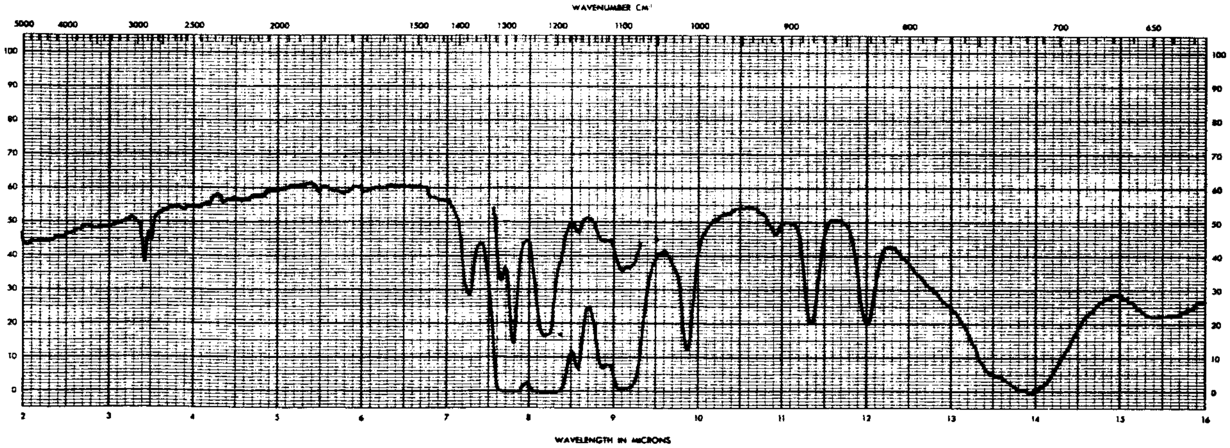


Figure 12. Infrared Spectrum of $(CF_3O)_2CHCF_2Cl$ (gas, 4 and 15 mm)

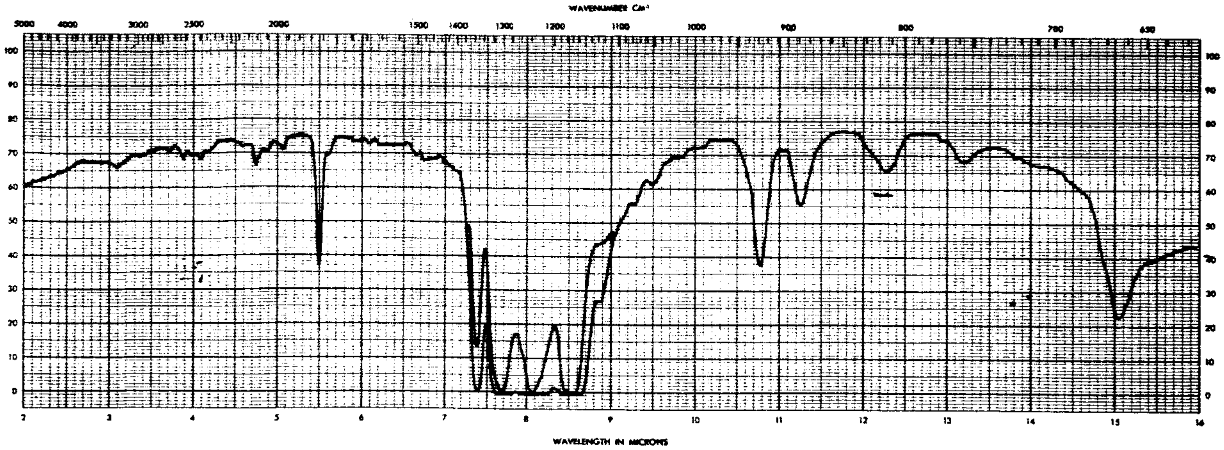


Figure 13. Infrared Spectrum of $(CF_3O)_2C = CF_2$ (gas, 5 and 35 mm)

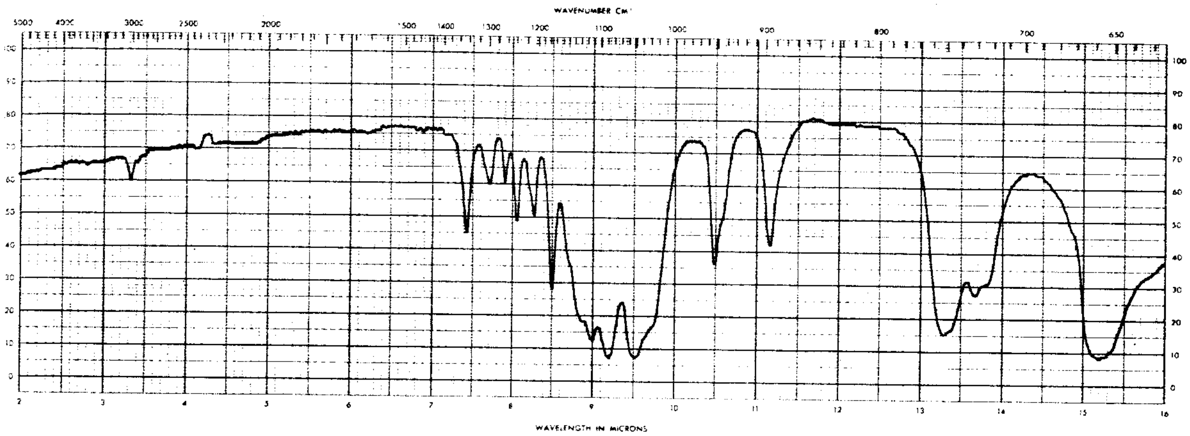


Figure 14. Infrared Spectrum of CHFBrCHFBr (liquid)

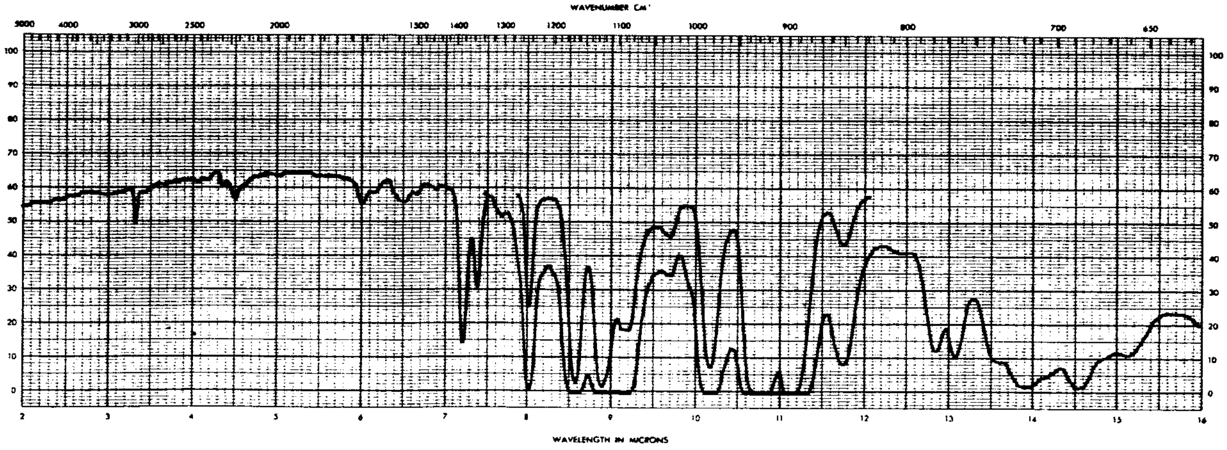


Figure 15. Infrared Spectrum of $SF_5OCHFCF_2Br$ (gas, 4 and 29 mm)

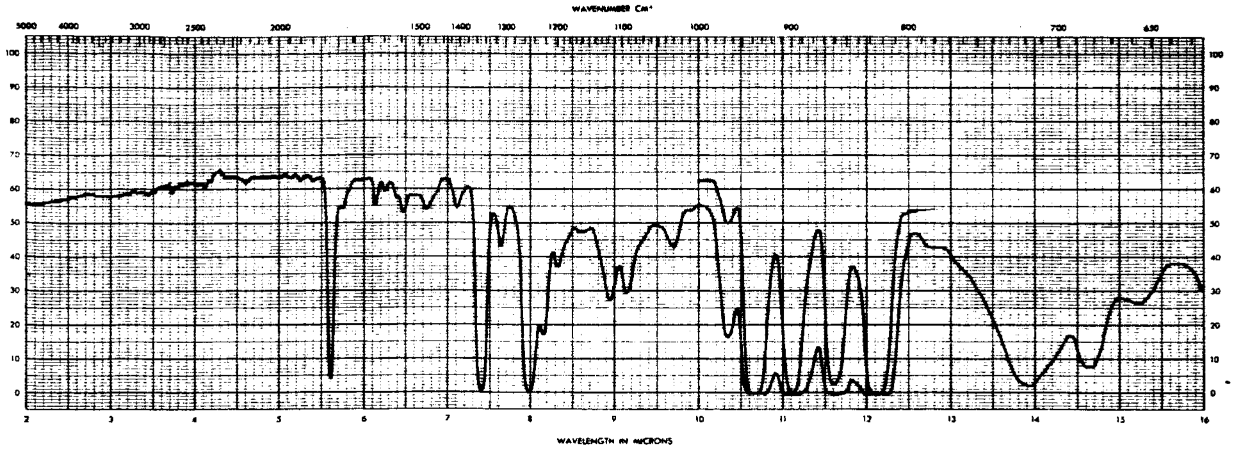
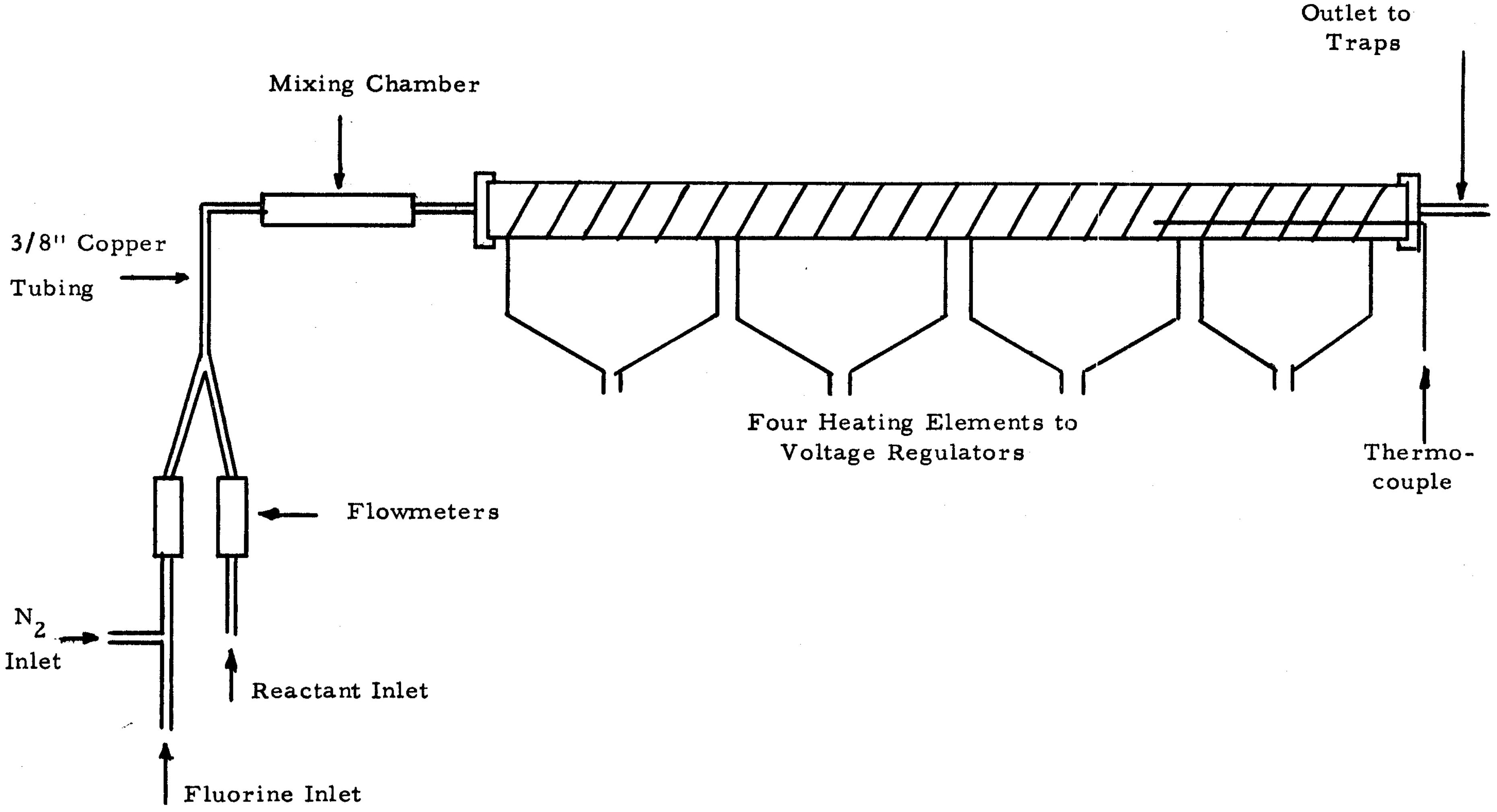


Figure 16. Infrared Spectrum of $SF_5OCF_5OCF = CF_2$ (gas, 5 and 32 mm)

Figure 17

Elemental Fluorination Reactor



APPENDIX

ANNOTATED BIBLIOGRAPHY

1957 to March 15, 1965

INTRODUCTION

This bibliography was prepared mainly through a rather intensive scanning of Chemical Abstracts plus numerous additional primary sources. Major emphasis was placed on references to fluorine containing monomers and polymers and to thermal properties of all classes of polymers.

Due to the great number of references in these categories it was considered advisable to limit the references reported here to those which were considered to be of most significance to the present investigation. The choice of references unfortunately is somewhat subjective but it is felt that the cross-section given is a useful representation of the literature to date.

The references listed from 1957 forward have been categorized with respect to the general subdivisions shown below. Once again for the sake of brevity no cross-referencing has been done, hence where a paper was concerned with more than one subdivision the reference, in general, was placed in the category of greatest importance. Copolymers were placed in the earliest listed monomer category with the exception of the vinyl ethers and thioethers, the copolymers of which were included under the main heading of vinyl ethers.

INDEX TO APPENDIX

APPENDIX

Annotated Bibliography 1957 to March 15, 1965

I. Reviews on Fluorine-containing Polymers

1958

Szurrat, J., C. A. 52, 16777d (1958)
Fluoro elastomers as construction material

Tatlow, J. C., Rubber and Plastics Age 39, 33 (1958)
Organic fluorine rubbers

Vaillant, M., Chem. and Ind. (Paris) 80, 429-36 (1958). C.A. 53, 9030a (1959)
Chlorofluorinated polymers and their derivatives. I. Generalities and properties

1959

Fitzgerald, J. E., Prod. Eng. 30, No. 6, 23-5 (1959). C.A. 53, 23049e (1959)
Soviet plastics

Gall, J. F., ARSJ 29, 95-103 (1959). C.A. 53, 14811a(1959)

Postelnek, W., Coleman., L. E., and Lovelace, A. M., Fortschr. Hochpolymer Forsch. 2, 75-113 (1959). C.A. 54, 10385b (1960)
Fluorine-containing polymers. I. Fluorinated vinyl polymers with functional groups, condensation polymers, and styrene polymers

1961

Banks, R. E., Birchall, J. M., and Haszeldine, R. N., Monograph 13, 207-94 (1961). C.A., 56, 7483e (1962)
Polymers containing fluorine

Kubouchi, Y., C. A. 55, 26807b (1961)
Fluorine resins and fluorine rubbers

I. Reviews on Fluorine-containing Polymers

1961 (continued)

Lamm, Mme. G., C. A. 55, 20475i (1961)
Fluorinated elastomers

Minoura, Yuji, and Saito, Kozo, C. A. 55, 9934f (1961)
Fluorine-containing polymers

Sperati, C. A., and Starkweather, H. W., C. A. 55, 19316f (1961)
$(CF_2CF_2)_n$

Montermoso, J. C., Rubber Chem. Technol. 34, 1521-52 (1961). C.A. 57, 1010g
Fluorine-containing elastomers

1962

Fischer, H., C. A. 56, 6161g (1962)
Fluorine chemistry. V. Poly(tetrafluoroethylene)

Le Guellec, G., C. A. 57, 13942g (1962)
Processing and application of fluoro elastomers

1963

Coulter, D. J. B., C. A. 59, 14179f (1963)
Viton-a fluoroelastomer: properties and applications

Kormity, P., C. A. 59, 15463 (1963)
Application of halogenated elastomers in chemical engineering

Seymour, R. B., I and EC 55 (9), 56 (1963)
Polyfluorocarbons (among others)

1964

Chenchung Ma, C.A. 61, 12089b (1964)
Free radical addition polymerization of fluoroalkenes. 39 ref.

Hsi-Chun Hung, C. A. 61, 16279a (1964)
Chemistry of nitroso rubbers, 58 references.

II. Fluorine-containing Vinyl Polymers

A. Vinyl Fluoride

1960

Kalb, G. H., et al., J. Appl. Polymer Sci. 4, 55 (1960)
Vinyl fluoride, brittleness temp. for 200 gauge film is between -196 and -130°C

1963

Usmanov, et al., C. A. 59, 11666b (1963)
Radiation polymerization of vinyl fluoride

James, V. E., Belg. 614,581. C. A. 58, 9253f (1963)
Polyvinyl fluoride, using azo catalyst in water

du Pont, Brit. 940, 176, October 23, 1963. C. A. 60, 6953g (1964)
Vinyl fluoride polymers

Proctor, J. S., (to du Pont), U. S. 3, 096, 299. C. A. 59, 8949f (1963)
Poly(vinyl fluoride) film soluble in DMSO

Usmanov, Kh. U., et al., C. A. 59, 11666a (1963)
Radiation polymerization of CH_2CHF

B. Vinylidene Fluoride

1962

Hauptschein, M., (to Pennsalt Chemicals Corp.), U.S. 3, 012, 021. C.A. 57, 2428f (1962)
Poly(vinylidene fluoride)

Iserson, Hyman, (to Pennsalt Chemicals Corp.), U.S. 3, 031, 437. C.A. 57, 3638f (1962)

Vinylidene fluoride polymers and copolymers, emulsion recipe at 25-60 atom (approximately 375-840 psi)

Volkova, Ye. V., et al., Zhur. vsesoy. khim. obsheh. . im. D. I. Mendeleeva, 7, 593 (1962)
CH_2CF_2 polymerization by gamma radiation

II. Fluorine-containing Vinyl Polymers (continued)

B. Vinylidene Fluoride

1964 (continued)

Pennsalt Chemicals, Brit. 942, 956. C.A. 60, 70039g (1964)
Polyvinylidene fluoride films and coatings

1. Copolymers

1949

McBee, E. T., Hill, H. M., and Bachman, G. B., I and EC 41, 70 (1949)
Polymerization of CH_2CF_2 and CF_2CCl_2

1957

Dixon, S., Rexford, D. R., and Rugg, J. S., Ind. Eng. Che. 49, 1687-90 C.A. 52, 4237f (1958)
Synthesis of viton

1958

Rugg, J. S. and Stevenson, A. C., Rubber Age (N. Y.) 82, 102-4 (1958). C. A. 52, (1958)
Viton A, a new fluorine-containing rubber

1959

Gabris, T., C.A. 53, 751d (1959)
Viton A, a fluorine-containing elastomer

Stivers, D.A., Honn, F. J., and Robb, L.E., IEC, 51, 1465 (1959). C.A. 54, 8139f (1960)
Properties of $CF_2=CH_2/C_3F_6$ copolymer

1960

3 M, Brit. 823, 974. C.A. 54, 9368g (1960)
Copolymers of hexafluoropropene and $CH_2=CF_2$ showed good low-temp. flexibility

II. Fluorine-containing Vinyl Polymers

B. Vinylidene Fluoride

1. Copolymers (continued)

1960

Wilson, A., Griffis, C.B., and Montermoso, J.C., C.A. 54, 12632c (1960)

Evaluation of copolymer of $CH_2=CF_2$ and $CF_3-CF=CF_2$ showed good resistance to heat, acid, fuels, and oil but poor resistance to cold

1962

Lo, E. S., (to 3 M), U.S. 3,023,187. C.A. 56, 15651f (1962)

Copolymerizing hexafluoropropene with vinylidene fluoride in the presence of silica. Improves tensile

1963

Coulter, D.J.B., C.A. 59, 14179f (1963)

Viton -a fluoroelastomer: properties and applications

Krigbaum, W.R., and Kaneko, M., J. Poly. Sci. Pt A, 1, 1 (1963)

Concerned with dielectric constant, stress, and birefringence

1964

Sianesi, D., et. al. Belg. 626,289; C.A. 60, 10885c (1964).

CH_2CF_2/CF_2CHCF_3, elastomers with 10 to 70% propene.

C. Trifluoroethylene

1958

Dittman, A. L., Passino, H. J. and Wrightson, J.M., (to 3M), U.S. 2,837,505. C.A. 52, 15130b (1958)

Polymerization of $CHF=CF_2$ in H_2O

Hoyt, J. M., (to 3M), U.S. 2,836,582. C.A. 52, 14223f (1958)

Redox system used

D. Tetrafluoroethylene

1961

Arvia, A. J., Aymonino, P. J., and Schumacher, H. J., C. A. 55, 21759h (1961)
Kinetics of the polymerization of gaseous C_2F_4 with $(CFO)_2O_2$

1962

Roberts, H. L., (to ICI), U.S. 3,063,922, November 13, 1962
Polymerizing C_2F_4 with SF_5Cl and u. v. irradiation

1963

Bruk, M.A., *et al.*, C. A. 59, 4039 (1963)
Radiation polymerization of CF_2CF_2 in the solid state

1964

Halliwell, R. H., (to du Pont), U. S. 3,110,704. C.A. 60, 6950h (1964)
Low pressure TFE polymerization

Sobue, H. Tabata, Y. and Shibano, H., C.A. 60, 686c (1964)
$(CF_2CF_2)_n$ by gamma radiation

1. Copolymers

1960

Krespan, C. G., (to du Pont), U.S. 2,938,889. C.A. 54, 20327g (1960)
Use of PbF_4, AgF_2, COF_3 in ASF_3 to polymerize CF_2CF_2 and copolymerize with $F(CF_2)_nCF=CF_2$.

Bro, M. I., (to du Pont), U.S. 2,943,080. C.A. 54, 20339c (1960)
Copolymers of tetrafluoroethylene and fluorinated olefins

1963

Tabata, Y., *et al.*, C. A. 58, 6931f (1963)
Gamma-induced polymerization of C_2F_4 and C_3H_6 at low temperature

1. Copolymers (continued)

1963 (continued)

Sobue, H., Tabata, Y., and Shibano, H., C.A. 59, 15404b (1963)
Copolymer of tetrafluoroethylene and ethylene

S. Sherratt, Brit. 929,990 (to Imperial Chemical Industries, Ltd.), C.A. 59, P6536g (1963).
Copol. of $SF_5CF{=}CF_2/C_2F_4$ T_c, 331°.

1964

Montecatini, Belg. 624,205; C.A. 60, 13344c (1964)
C_2F_4/CF_3CHCF_2

A.N. Bolstad, U.S. 3,163,628 (to 3M); C.A. 62, 6587h (1964)
Copolymer of $CHFCCl_2/C_2F_4$ claimed to be elastomeric

Y. Tabata et al., J. Polymer Sci. 2 (4), 1977-86 (1964); C.A. 62, 728b (1964) also C.A. et at, 61, 7105b (1964)
Copol. C_2F_4/C_2H_4 induced by ionizing radiation

E. Chlorotrifluoroethylene

1953

Elliot, J.R., Myers, R. L., and Roedel, G.F., I and EC 45, 1786 (1953)
Polymer of CF_2CFCl

Hamilton, J.M., Jr., I and EC 45, 1347 (1953)
Polymer of CF_2CFCl

Thanos, W. M., and O'Shaughnessy, M. T., J. Polymer Sci. 11, 455 (1953)
Kinetics of $(CF_2CFCl)_n$ formation

1955

Dittman, A. L., Passino, H. J., and Wrightson, J. M., U.S. 2,689,241 C.A. 49, 11681a (1955)
Redox system for CF_2CFCl

E. Chlorotrifluoroethylene (continued)

1958

Lazar, M., J. Polymer Sci. 29, 573 (1958)
Effect of solvent on the polymerization of chlorotrifluoroethylene

1959

Dennstedt, I., and Becker, W., Ger. 959,060. C.A. 53, 13670e (1959)
Polymerization of CF_2CFCl

1960

Fokin, A. V., et al., U.S.S.R. 125,678. C.A. 54, 14791c (1960)
Gamma radiation in Cl containing solvent

1962

Muramatsu, H., Iwasahi, M., and Baba, H., C.A. 57, 13975c (1962)
Polymerization of trifluorochloroethylene. Carboxylic end groups in poly(trifluorochloroethylene)

1963

Hann, F.J., and Hoyt, J.M., U.S. 3,053,818. C.A. 58, 3584e (1963)
CF_2CFCl interpolymers

1. Copolymers

1960

Kliman, N., and Lazar, M., C.A. 54, 10390d (1960)
Copolymers of CTFE with vinyl chloride and vinylidene chloride

Kahrs, K.H., et al., U.S. 2,919,263. C.A. 54, 7237i (1960)
CTFE polymerized with $CF_3\text{-}CH{=}CH_2$

1961

Landrum, B.F., and Herbst, R.L., Jr., (to 3M), U.S. 2,951,783. C.A. 55, P 1090h (1961)
CTFE - diallyl maleate copolymers as adhesives

F. Propenes

1951

Goldschmidt, A., J. Am. Chem. Soc. 73, 2940 (1951)
Low polymers formed, CF_3CHCH_2

1958

Bolstad, A.N., (to 3M), U.S. 2,842,529. C.A. 52, 16790c (1958)
3,3,3-Trifluoropropene polymers

1960

Kolesnikov, G.S., and Mateera, N.G., C.A. 54, 17941b (1960)
Polymers of CH_2CHCF_2Cl

3 M, U.S. Army Contract No. DA-19-129-QM-1043. Report for period October 15, 1957 - August 15, 1960
Studies included C_3F_6 and $CF_3CH=CH_2$

1961

Eleuterio, H.S., (to du Pont), U.S. 2,958,685. C.A. 55, P6041c (1961)
C_3F_6 polymers

Lo, E.S., (to 3M), U.S. 2,970,988. C.A. 55, 12938a (1961)
Polymers of $CF_3CF=CH_2$

1962

Eleuterio, H.S., and Moore, E.P., 2nd International Fluorine Symposium, Estes Park, Colorado, July 17-20, 1962
$(C_3F_6)_n$

1964

H. L. Roberts, J. Chem. Soc. 4538-40 (1964)
Addition of $(CF_3O)_2$ to C_3F_6 to give mainly telomers.

F. Propenes (continued)

1. Copolymers

1962

Brehm, W. J., and Millian, A. S., (to du Pont), U.S. 3,053,823. C.A. 57, 16890d (1962)

Copolymers of hexafluoropropylene and fluoranil, basically $(C_3F_6)_n$

1963

Sterling, G. B., (to Dow Chemical Co.), U.S. 3,069,388. C. A. 58, 5852b (1963)

$CF_3CH{=}CH_2$ copolymers

G. Dienes

1951

Wakefield, L. B., IEC 43, 2363 (1951)

$CH_2CFCFCH_2$, Synthesis, polymerization, $T_g = 1°C$

1956

3M, WADC TR 52-197. Pts 1-6. 1952 → 1956.

Polymers from $CH_2CFCHCH_2$, $CF_2CFCHCF_2$, $CF_2CFCFCF_2$, $CF_2CClCFCF_2$, $CH_2C(C_3F_7)CHCH_2$

1957

Pennsalt, WADC TR 57-436. ASTIA Doc. No. AD 142116, November, 1957

Polymerization studies with $CF_2CFCFCF_2$, $CF_2CFCClCH_2$, $CF_2CFCFCH_2$, $CF_2CFCClCHCl$, $CF_2{=}CF\underline{C{=}CFCF_2CF}_2$

last three polymerize with difficulty

G. Dienes (continued)

1960

Iserson, I. I., Hauptschein, M., Lawlor, F. E., J. Am. Chem. Soc. 81, 2676 (1959). C.A. 54, 7528d (1960)
$CF_2=CFCF=CH_2$ elastomeric below 0°

Klebanskii, A. L., and Timofeev, O. A., C.A. 54, 8131e (1960)
Polymerization of hexafluorobutadiene

1961

Honn, F. J., (3M), Ger. 1,089,973. C.A. 55, 16000b (1961)
Polyfluoro-substituted butadienes

1962

Klebanskii, A. L., and Timofeev, O.A., J. Polymer Sci. 52, 23-9 (1961). C.A. 56, 6162b (1962)
Relative activity of hexafluoro-1,3-butadiene in polymerization and copolymerization reactions with other dienes

1963

Iserson, H., Lawlor, F. E., and Hauptschein, M., (to Pennsalt Chemicals Corp.), U.S. 3,062,794. C.A. 58, 3583e (1963)
$CF_2=CFCF=CH_2$

Fern, J.E., and Wall, L. A., SPE Trans. 3, (3), 231-4 (1963)
Polymers of $CF_2=CFCF_2CFClCF_2CF=CF_2$

1964

J. E. Fearn and Leo Wall, U.S. Gov. Research Reports AD 435087.
Preparation and polymerization of some perfluorodienes.

I. L. Knunyants et al., C.A. 60, 11883g
Preparation and polymerization of some perfluorodienes.
Dienes as $CH_2=CH(CF_2)_nCH=CH_2$ polymerize readily.

1964 (continued)

E. Frisch and O. Steward, Fr. 1, 361, 256, (to Dow Corning Corp.); C.A. 61, 13445b

u. v. initiated polymerization of $CF_3CF=CFCH=CH_2$ gave a tough flexible polymer with a softening point of 170°.

1. Copolymers

1957

Jones, F.B., and Coleman, L.E., J. Polymer Sci. 28, 242 (1957). C.A. 55, 6025f (1961)

Copolymerization of $CF_2CHCF_2CHCF_2$, $CF_2=CFCF_2CFClCF_2Cl$.

$CF_2=CFCF_2CF=CF_2$,

$EtOC=CFCF_2CF_2$

Pennsalt, WADC TR 57-436. ASTIA Doc. No. AD 142116, November 1957

1959

Lo, E. S., (to 3M), U.S. 2, 837, 503. C.A. 53, 1805b (1959)

1, 1, 1-Trifluoro-3-trifluoromethyl-2-butene elastomers copolymerized with 1, 1, 2-trifluorobutadiene and 1, 1, 3-trifluorobutadiene. Flexible at -28°C.

Hoyt, J.M., (to 3M), U.S. 2, 843, 575. C.A. 53, 26756 (1959)

Copolymer of fluoroprene and perhalogenated ethylene

1960

Druesedow, D., (to B.F. Goodrich), Ger. 1, 031, 968. C.A. 54, 13744d (1960)

Copolymers of 1, 3-butadiene and 1, 1-difluoro-2, 2-dichloroethylene. Increase of $CF_2=CCl_2$ diminishes flexibility.

Klebanskii, A. L., and Timofeev, O.A., C. A. 54, 22317a (1960)

Copolymerization of hexafluorobutadiene with diene compounds in solution

Lo, E. S., (to 3M), U.S. 2, 938, 888. C.A. 54, 20276d (1960)

Chloroprene copolymers with $CF_2CFCHCH_2 + CF_2CHCFCH_2$

I. Copolymers (continued)

1960 (continued)

3M, U.S. Army Contract No. DA-19-129-QM-1043. Report for the period October 15, 1957-August 15, 1960
Polymers from $CF_2CHCFCH_2$ and $CF_2CFCHCH_2$

1961

Bolstad, A.N., and Lo, E.S., (to 3M), U.S. 2,951,063. C.A. 55, P 1047d (1961)
Copolymers of $CF_2CHCFCH_2$ with $CH_2CFCHCH_2$

Honn, F. J., (to 3M), U.S. 2,949,446. C.A. 55, P 1048f (1961)
Copolymers of styrene with fluorinated dienes

Lo, E.S., (3M), U.S. 2,979,489. C.A. 55, 19276b (1961)
Copolymers of 2-trifluoromethyl butadiene

Lo, E.S., (to 3M), U.S. 2,951,064. C.A. 55, P 1047f (1961)
Copolymerization of CH_2CClCF_3 with $CH_2CFCHCH_2$

Lo, E.S., and Crawford, G.H., (to 3M), U.S. 2,951,065. C.A. 55, P 1047h (1961)
Elastomeric 2-(trifluoromethyl)butadiene copolymers

H. Polymers and Copolymers of Vinyl Ethers and Thioethers

1956

3M Company, WADC TR 52-197. Pts 1-6. 1952-1956
Polymers of CH_2CHOR, where $R=CH_2CF_3$, CF_2CF_2H, CF_2CFHCF_3, $CH_2C_3F_7$, and $CH_2C_5F_{11}$

1957

Perry, R. W., (to Firestone Tire and Rubber Co.), U.S. 2,799,025. C.A. 51, 7054a (1957)
Copolymer of monochlorotrifluoroethylene and an alkyl vinyl ethers

1957 (continued)

Pennsalt Chem. Co., WADC TR 57-436. ASTIA Doc. No. AD 142116, November 1957
Polymers of $CF_3CH_2OCHCH_2$

1958

Barr, J.R., (to Pennsalt Chem. Co.), U.S. 2, 813, 848. C.A. 52, 3406e (1958)
Copolymers of $CF_2CH_2OCHCH_2$ and CF_2CHCl

Schildknecht, C.E., (to Air Reduction), U.S. 2, 820, 025. C.A. 52, 5872c (1958)
($CF_3CH_2OCHCH_2$)

Vandenberg, E. J., Heck, R.F., and Breslow, D.S., J. Polymer Sci., 28, 249 (1958). C.A. 54. 11552b (1960)
Crystalline polymers of $CF_3CH_2OCHCH_2$ from Ziegler catalysts

1959

Air Reduction Co., Brit. 811, 037. C.A. 53, 10849g (1959)
Copolymer of $CF_3CH_2OCHCH_2$ and vinyl esters

Gorden, J., and Woolf, C., (to Allied Chem. Co.) U.S. 2, 870, 222. C.A. 53, 8709h (1959)
Low polymers from BF_3 + CF_2CHOCH_3

Harris, J.F., Jr., and McCane, E.I., (to du Pont), Brit. 812, 116, April 15, 1959. C.A. 53, 14585f (1959)
Polymers from CF_2CFOR

Schildknecht, C.E., (to Air Reduction Co.), Brit. 810, 515. C.A. 53, 23044h (1959)
Copolymers of $CF_3CH_2OCHCH_2$ and chloroolefins

Schildknecht, C.E., (to Air Reduction Co.), U.S. 2, 851, 449. C.A. 53, 2694h (1959)
Copolymers of $CF_3CH_2OCHCH_2$ and vinyl esters

1959 (continued)

Folt, V. L., (to B. F. Goodrich), Ger. 1, 003, 447. C. A. 53, 23016e (1959)
Copolymers of CF_2CCl_2 and vinyl alkyl ethers

1960

3M Company, U. S. Army Contract No. DA-19-129-QM-1043. Report for the period October 15, 1957 - August 15, 1960
Polymers of $CF_3CH_2OCH=CH_2$

Bovey, F. A., Smith, S., and Abere, J. F., (to 3M), Ger. 1, 040, 248. C. A. 54, 25939a (1960)
Rubbery copolymers of $CF_2CFCFCF_2$ and 1, 1-dihydroperfluoroalkyl vinyl ethers

Holly, E. D., and Nummy, W. R., (to Dow Chem.), U. S. 2, 947, 730. C. A. 54, 26010h (1960)
Polymers of vinylpentachlorophenylsulfide

Robertson, James J., (to Firestone Tire and Rubber Co.), U. S. 2, 905, 660 C. A. 54, 2823b (1960)

Copolymers of CF_2CFCl with vinyl alkyl ethers

1961

Abramo, J. G., and Reinhard, R. H., (Monsanto), U. S. 2, 975, 161. C. A. 55, 17101i (1961)
Copolymers of allyl fluoroalkyl ethers

Crawford, G. H., and Lo, E. S., (3 M), U. S. 2, 975, 164. C. A. 55, 15999f (1961)
Polymers of $CH_2=CHOCF_2CF_2H$

Lo, E. S., (3 M), U. S. 2, 975, 163. C. A. 55, 16004i (1961)
Copolymers of $CF_2=CFCF_2OCH_2R_f$

Schildknecht, C. E., (to Air Reduction Co.), U. S. 2, 991, 278. C. A. 55, P 27988g (1961)
Copolymers of $CF_3CH_2OCH=CH_2$ with haloolefins

H. Polymers and Copolymers of Vinyl Ethers and Thioethers (cont'd.)

1962

Barr, J.T., U.S. 3,025,279. C.A. 57, 1013a (1962)
Copolymers of trifluoroethylvinyl ether and fluoroalkyl acrylates

Harris, J.F., Jr., (to du Pont), U.S. 3,048,569. C.A. 57, 16886i (1962)
Vinyl perfluoroalkylsulfides and their polymers

Okuhara, K., Baba, H., and Kojima, R., C.A. 57, 5784c (1962)
Preparation and properties of alkyl trifluorovinyl ethers and related compounds.

1963

Brown, D.W., and Wall, L.A., SPE Trans, 3 (4), 300 (1963). C.A. 60, (1964)
Low polymers from $\phi CFCF_2$ and $\phi_f OCFCF_2$ by α irradiation

du Pont, Brit. 926,573 (1963). C.A. 60, 1596b (1964)
Polymers of vinylperfluoroalkyl sulfides

Khomutov, A.M., C.A. 59, 11670g (1963)
Reactivity of vinyl ethers in copolymerization

Ray, N.H., Brit. 931,919. C.A. 59, 10258b (1963)
Polymers of $SF_5CH{=}CH_2$

1963

Pummer, W.J., and Wall, SPE Trans. 3 (3), 220 (1963)
$CF_2CFO\phi$ and $CF_2CFOC_6F_5$

1964

du Pont de Nemours and Co., Brit. 953,098. C.A. 61, 16275a
Terpolymers of $CF_3OCF{=}CF_2/C_2F_4/CF_2CH_2$ using persulfate-aq. emulsion system.

H. Polymers and Copolymers of Vinylethers and Thioethers (cont'd)

1964 (continued)

W. Pummer and L. Wall, C.A. 61, 2999d
Preparation and polymerization of $C_6H_5CFCF_2$ and $C_6F_5CFCF_2$. Polymerization required high pressure (10,000 atm), gamma initiation.

D. McCane, U.S. 3,132,123 (to E.I. du Pont de Nemours and Co.), C.A. 61, 1968h also Brit. 953,152 and U.S. 3,159,609.
Copolymers of $CF_3OCF{=}CF_2$. 11.3 wt % C_2F_4, tough film; 27% CH_2CF_2 rubber.

Darby, R.A., Fr. 1,341,087 (to E.I. du Pont de Nemours and Co.); C.A. 60, 9151a (1964)
Copolymer of C_2F_4 with $CF_3CF_2CF_2OCF(CF_3)CF_2OCF{=}CF_2$ using N_2F_2 as initiator gave a high MW polymer

II. Fluorine-containing Vinyl Polymers

I. Styrenes

1958

Coleman, L.E., Jr., and Durrell, W.S., J. Org. Chem. 23, 1211-13 (1958) C.A. 53, 2124a (1959)
Reactivity ratios of trifluoromethyl substituted styrenes with methyl methacrylate and styrene

1961

Malkevich, S.G., and Chereshkwich, L.V., C.A. 55, 2176a (1961)
p-Fluorostyrene and 2,5-difluorostyrenes

Coleman, L.E., and Durrell, W.A., C.A. 55, 18173f (1961)
Synthesis and characteristics of new vinyl polymers. Substitution of CF_3 on styrene increased polymerization reactivity.

1963

Yakubovich, A. Ya., et al., C.A. 59, 11377c (1963)
Polymers and copolymers of $CF_2CF\phi$

J. Miscellaneous Polymers

1950

Prober, M., J. Am. Chem. Soc. 72, 1036 (1950)
Decreasing reactivity to polymerization in the series:
CF_2CFCl, CF_2CCl_2, $CFClCFCl$, CCl_2CClCF_3,
$CF_3CClCClCF_3$, $C\text{-}C_4F_6$, $\overline{CF_2CF_2CF_2CCl{=}C}Cl$

1956

Jacobs, T. L., and Bauer, R.S., J. Am. Chem. Soc. 78, 4815-16 (1956)
C. A. 51, 2525c (1957)
Tetrafluoroallene. Prep and polymerization

Haas, H. C., Emerson, E. S., and Schuler, N. W., J. Polymer Sci., 22, 291-302 (1956). C. A. 51, 3179d (1957)
Poly(vinyl trifluoroacetate) homopolymers and copolymers with vinylacetate

1956

3 M, WADC TR 52-197, Pts 1-6. 1952-1956
Polymers containing $CF_2{=}CFH$, CF_2CFBr, $1\text{-}C_4F_8$, $1\text{-}C_9F_{18}$

1957

Knobloch, F. W., J. Polymer Sci. 25, 453-64 (1957). C.A. 52, 6267b (1958)
Polymers and copolymers of N-(1, 1-dihydroperfluoroalkyl)acrylamides

Rausch, D. A., Coleman, L. E., Jr., and Lovelace, A. M., J. Am. Chem. Soc. 79, 4983-4 (1957)
The preparation and polymerization of perfluoroalkyl propenyl ketones. Polymers containing CH_2CFCl, $CHFCFCl$, CF_2CHCl, CF_2CCl_2, $C\text{-}C_4F_6$, CF_2CMe_2, vinyl and trifluorovinyl halocyclobutanes (which copolymerized only with reluctance)

1958

Coleman, L. E., Jr., Rausch, D. A., and Griffin, W. R., Chem. and Eng. Data Ser. 3, 113-15 (1958). C. A. 53, 12734d (1959)
Polymerization of some 1-alkyl-1-hydroperfluoroalkyl acrylates

1959

Kolesnikov, G. S., and Avetyan, M. G., C. A. 53, 19941i (1959)
$CCl_2{=}CHF$

Koleshikov, G. S., Avetyan, M. G., C. A. 53, 6056h (1959)
$CHF{=}CCl_2$, $CHFCHCl$, $CHFCBr_2$ polymers

Borland, J. W., Miller, C. B. and Pearson, J. H., (to Allied Chem. Co.), U. S. 2, 865, 824. C. A. 53, 5749c (1959)
Produces polymers for resistance to corrosive substances.
CF_2CFCl, CH_2CFCl, CH_2CF_2, CF_2CFH, CF_2CHCl

Jacobs, T. L., and Bauer, R. S., J. Am. Chem. Soc., 81, 606-10 (1959) C. A. 53, 16952d (1959)
Synthesis and polymerization of tetrafluoroallene

1960

Skinner, W. A., Bishop, E., Tieszen, D., and Johnston, J. D., Ind. Eng. Chem. 51, 1359-60 (1959)
Synthesis and polymerization of 3, 3, 3-trichloro-1-propene

3M, U. S. Army Contract No. DA-19-129-QM-1043. Report for the period October 15, 1957-August 15, 1960
Polymers containing CF_2CF_2, CH_2CF_2 and CF_2CHCl, $CF_2CH{=}CFCF_2$, $CH_2CH\overline{CH_2CH_2C}F_3$, $CH_2{=}CH\overline{CFCF_2CF_2C}FCl$, $CH_2CFCF_2CF_3$

1961

Anspon, H. D., (to GAF) U. S. 2, 956, 939. C. A. 55, P 6923a (1961)
Methyl α -fluoroacrylate

Bolstad, A. N., and Honn, F. J., (to 3M), U. S. 2, 966, 482. C. A. 55, 8916e (1961)
$CF_3C{\equiv}CCF_3 : CH_2CFCl$ copolymers

Brown, H. C., and Gewanter, H. L., J. Org. Chem. 25, 2071 (1960). C. A. 55, 14283i (1961)
Polymerization of $CF_3C{\equiv}CCF_3$

J. Miscellaneous Polymers (continued)

1962

Harris, J.F., Jr., (to du Pont), U.S. 3,037,010. C.A. 57, 7465e (1962)
Polymeric perfluoro-2-butyne

Overberger, C.G., and Davidson, E.B., J. Poly. Sci. 62, 23 (1962)
Monomer and polymers containing the CF_3-group. $CF_3CH=CH_2$, $CF_3CH_2CH=CH_2$, $CF_3(CH_2)_2CH=CH_2$, $CH_3CH(CF_3)CH=CH_2$, and $CH_3CH(CF_3)CH_2CH=CH_2$

1963

Krbekyan, G.E., Sinanyam, E.G., and Akopyan, A.N., C.A. 59, 12927e (1963)
Copolymerization of trans-2, 3, 4, 5-tetrachlorohexa-1, 3, 5-triene

1964

E. Rostonskii and L. Rubinovitch, C.A. 61, 1950c
Acrylates with omega-H fluoro-alcohols.

III. Condensation Polymers

A. Fluorine-containing Polysiloxanes

1960

Holbrook, G.W. Gordon, A.F., and Pierce, O.R., J. Am. Chem. Soc. 82, 825-6 (1960). C.A. 54, 12641f (1960)
Cyclodimerization of vinyl silicon compounds with CF_2CFCl and subsequent polymerization

Pierce, O.R., Holbrook, G.W., Johannson, O.K., Saylor, J.C., and Brown, E.D., Ind. Chem. Eng. 52, 783-4 (1960). C.A. 54, 25933a (1960)
Polymerization of $(RCH_2CH_2SiMeO)_3$ where R is CF_3-, C_2F_5-, or C_3F_7- wide temp. range.

Pierce, O.R., et al., I.E.C. 52, 783 (1960). C.A. 54, 25933a (1960)
Synthesis and polymerizations. LS-53 $T_{brittle}$ -90°F

A. Fluorine-containing Polysiloxanes (continued)

1961

Steward, O. W., Pierce, O. R., J. Org. Chem. 26, 2943 (1961)
3-(Fluoroalkoxy)propylpolysiloxanes

1962

Schweiker, G. C. and Robitschek, Paul, U.S. 3,016,360. C.A. 56, 7480c (1962)
Stable carboxylic elastomers containing fluorine

Kanner, B., and Reid, W. G., Am. Chem. Soc., Div. Polymer Chem., Preprints 2, No. 1, 99-104 (1961). C.A. 57, 15349c (1962)
Graft copolymers of fluoroolefins with dimethylsilicones

Polmanteer, K. E., et al., U.S. 3,050,492 (to Dow-Corning Corp.), C.A. 57, 13948i (1962)
Incorporation of fluoroalkyl substituted organosiloxane units into conventional organosiloxane rubbers low temp. flex retained.

1964

Dolgoplosk, et al., C.A. 60, 745h (1964)
SiO- or SiϕSiO in backbone, $-CH_2CH_2CF_3$ side group. Amyl groups raise T_g (from -70 to + 10°), increase tensile strength

G. W. Holbrook, (to Dow-Corning Corp.) Fr. 1,359,397; C.A. 62, 4181c
Siloxane polymers containing trifluoropropyl substituents.

S. Fuqua and R. Silverstein, C.A. 61, 10849b
Rigid polymer obtained from 1,2-bis [p-(ethoxydimethylsilyl)phenyl]-tetrafluoroethane.

B. Fluorine-containing Polyesters

1957

Schweiker, G. C., and Robitschek, P., J. Polymer Sci. 24, 33-41 (1957)
Increase in fluorine content raises brittle temperature

B. Fluorine-containing Polyesters (continued

1959

Gouinlock, E.V., Jr., Verbanic, C.J., and Schweiker, G.C., J. Appl. Polymer Sci. 1, 361-70 (1959). C.A. 53, 23035g (1959)
Dibasic acids with hexafluoropentanediol

1962

Freeman, Ronald R., U.S. Dept. Com. Office Tech. Service. AD 275,520, 17 pp (1962). C.A. 60, 739e (1964)
Aromatic diacids (or chloride) and hexafluoro-1,5-pentanediol-, rubbery polymer

Ottmann, G.F., (to Olin Mathieson Chem. Co.) U.S. 3,044,988. C.A. 57, 12724i (1962)
Fluorinated glycol polyesters

Schweiker, G.C., and Robitschek, P., U.S. 3,016,360. C.A. 56, 7480c (1962)
Stable carboxylic elastomers containing fluorine

IV. Polymers with Heteroatom Chains

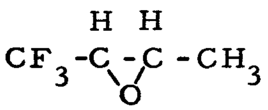
A. C-O

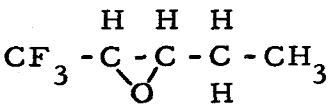
1957

Etienne, Y., C.A. 51, 15992e (1957)
Polymerization of 3,3-bis(fluoromethyl)oxetane

1958

Jones, F.B., Stickney, P.B., Coleman, L.E., Jr., Rausch, D.A., and A.M. Lovelace, J. Polymer Sci., 26, 81-8 (1957). C.A. 52, 5875d (1958)
Polymerization of some fluorine-containing olefin oxides





Cairns, T.L., Cline, E.T., and Grahm, P.J., (to du Pont), U.S. 2,828,287 C.A. 52, 10641e (1958)
Fluoroaldehyde-modified polyoxymethylene

A. <u>C-O</u> (continued)

1959

du Pont, Brit. 809,754. C.A. <u>53</u>, 19452 g (1959)
Produced an acetylated fluorinated (by copolymerizing with CF_3CHO) polyoxymethylene with good mech. prop. from -78 to 200°

1960

3M Company, U.S. Army Contract No. DA-19-129-QM-1043. Report for the period October 15, 1957-August 15, 1960
Polymerization of CF_3CHCH_2O, $C_5F_{11}CFCF_2O$, C_3F_7CHO

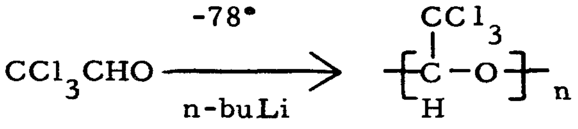
1962

Case, L.C., and Todd, C.C., J. Poly. Sci. <u>58</u>, 633 (1962)
Polyperfluoroalkyl oxetanes

1963

Barney, Arthur L., U.S. 3,067,173. C.A. <u>59</u>, 10310b (1963)
Hydroperfluorovaleraldehyde polymer

Ilyina, D.E., Krentsel, B.A., and Seminido, G.E., Int'l. Symposium of Macromolecular Chemistry, Paris July 1-6, 1963. Paper No. 38



$$CCl_3CHO \xrightarrow[n\text{-}buLi]{-78^\circ} \left[\overset{CCl_3}{\underset{H}{C}} - O \right]_n$$

V. Ginsburg, <u>et al</u>, C.A. <u>59</u>, 5008f

$$C_2F_4 + O_2 + (CF_3)_2N_2 \longrightarrow (C_2F_4O)_n \quad \text{oil}$$

1964

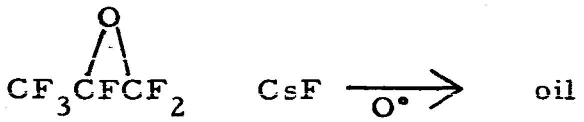
Pummer, W.L. and Wall, L.A., J. Research Nat'l. Bur. Ltd. A68(3)277-86(1964); C.A. <u>61</u>, 1951g (1964)
Perfluorophenylether and related polymers

A. C-O (continued)

1964 (continued)

V. McLaughlin and J. Thrower, Chem. Ind. (London) 1557 (1964), C.A. 62, 5347f.
Polymers of p-$CF_3C_6F_4OK$

E.P. Moore (to E.I. du Pont de Nemours and Co.), Fr. 1,359,426; C.A. 62, 4181a



N. Madison and D. Miller, Research on the Synthesis of Fluorine-containing Polymers. Part 1 Apr. 1964. Dow Chemical Co.
AF 33(657)11254
Copolymerization of CH_2O with $CF_3CF{=}CF_2$, $(CF_3)_2C{=}CF_2$, $(CF_3)_2C{=}O$ and C_2F_4.

B. C-S

1961

du Pont, Brit. 857,649. C.A. 55, 11918h (1961)
Low polymer of CF_2S

1962

du Pont, Brit. 877,834. C.A. 56, 4960e (1962)
Thiocarbonyl fluoride polymers

Harris, J.F., Jr., (to du Pont), U.S. 3,047,545. C.A. 57, 13993e (1962)
Polymers of polyfluorothioaldehydes

Walter, H.C., (to du Pont), U.S. 3,032,537. C.A. 57, 7441i (1962)
Anionic polymerization of thiocarbonyldifluoride

1963

Kealy, T.J., (to du Pont), U.S. 3,069,379. C.A. 59, 1489f (1963)
Fluorothioketones and their polymers

B. C-S (continued)

1963 (continued)

Middleton, W. J., U.S. 3,069,395. C.A. 59, 1493g (1963)
Halothioaryl fluorides and polymers

du Pont, U.S. 3,097,236. C.A. 59, 13825f (1963)
Preparation of fluorine-containing thiocarbonyl compounds

C. N-O

1958

Rose, J.B., (to I.C.I.), Brit. 789,254. C.A. 52, 9644a (1958)
A solid rubbery polymer from CF_3NO and C_2F_4

1960

Barr, D.A., Haszeldine, R.N., and Willis, C.J., C.A. 54, 2797e (1960)
$CF_3NO + C_2F_4$

Griffin, C.E., and Haszeldine, R.N., Proc. Chem. Soc., 1959, 369-70 C.A. 54, 10382i (1960)
Trifluoronitrosoethylene and its polymers

Griffin, C.E., and Haszeldine, R.N., J. Chem. Soc., 1960, 1398-1406 C.A. 54, 14217d (1960)
Trifluoronitrosoethylene and its polymers

1961

Haszeldine, R.N., Ger. 1,072,247. C.A. 55, 16015i (1961)
Nitroso polymers, NO + haloolefin → polymer

Haszeldine, R.N., and Willis, C.J., Brit. 843,795. C.A. 55, 4027b (1961)
Nitroso elastomers, CF_3NO and $CF_2{=}CFH$

Barr, D.A. Haszeldine, R.N., and Willis, C.J., J. Chem. Soc., 1961, 1351. C.A. 55, 13404i (1961)
CF_3NO polymers

C. N-O (continued)

1961 (continued)

Montermoso, J.C., Griffis, C.B., Wilson, A., and Crawford, C.H., Rubber and Plastics Age, 42, 514 (1961). C.A. 55, 18158e (1961)
Vulcanization and properties of nitroso rubber

1963

Crawford, G. H., Rice, D.E., and Landrum, B.F., J. Poly. Sci. Pt. A 1, 565 (1963)
R_fNO elastomers

3M, Ger. 1, 153, 173. C.A. 59, 14126f (1963)
CF_3NO-C_2F_4 copolymerized in aqueous suspension at -50° -0° using LiBr solvent

1964

3M, Brit. 943, 224. C.A. 60, 7009c (1964)
Nitroso rubber

G.B. Griffis and M. Henry, Motr. Synys., Nat'l. SAMPE, 7th Los Angeles (1964). C.A. 62, 5418f
Summary of the chemistry of nitroso rubbers.

V. Thermal Properties of Polymers

1952

Gordon, Manfred, and Taylor, J.S., J. Appl. Chem. 2 , 493 (1952)
Conclude that intermolecular forces are weak for polymers in general, thereby allowing equations relating T_g to copolymer composition to be valid

Beaman, R.G., J. Poly. Sci., 9, 470 (1952). C.A. 47, 2573e (1953)
Relation of T_g to T_m

1953

Madorsky, S.L., Hart, V.E., Strauss, S., and Sedlak, V.A., J. Res. NBS 51, 327 (1953)
Thermal degradation of $(CF_2CF_2)_n$, $(CF_2CHF)_n$, $(CF_2CH_2)_n$, $(CFHCH_2)_n$

1954

Swenson, A., Rev. Sci. Instr. 25, 834-5 (1954)
Mechanical properties of teflon at low temperatures

1955

Bunn, C. W., J. Polymer Sci., 16, 323 (1955)
Chain flexibility, effect of doubly bonded atoms

1956

Fox-T. G., Bull. Am. Phys. Soc. [2,] 1, 123 (1956). C.A. 51, 1175le (1957)
Influence of diluent and of copolymer composition on the glass temperature of a polymer system

Kuroda, Toshihiko, Nagoya Kogyo Gijutsu Shikensho Hokoku 5, 257-61 (1956). C.A. 54, 19016c (1960)
Physical properties of fluorocarbon plastics. I. Transition temperature of polytetrafluoroethylene. =330-337°K, 57-63°C

1957

Reevers, R.B., C.A. 51, 9262f (1957)
Mechanical properties of polymers in the glass transition region

Corruccini, R. J., Chem. Eng. Progr. 53, 397-402 (1957). C.A. 51 17267g (1957)
Mechanical properties of metals and alloys, plastics and glass

Gee, G., Proc. Chem. Soc. 1957, 111-18. C.A. 54, 13796f (1960)
The physical properties of polymers in relation to their chemical structure

Griffin, W.R., Rubber World, 136, 687 (1957). C.A. 54, 10369a (1960)
Evaluation of 1 F_4, 2 F_4, Kel F 3700, adipate, Fluorel, Viton A, LS-53

Mandelkern, L., Martin, G.M., and Quinn, F.A., Jr., J. Research Nat'l Bureau Standards 58, 137 (1957)
T_g for $(CF_2CFCl)_n$, $(CF_2CH_2)_n$ and copolymers

1957 (continued)

Rogers, S.S., and Mandelkern, L., J. Phys. Chem. 61, 985-90 (1957) C.A. 52, 31e (1958)

T_g of these polymers decreased as No. of carbon atoms in side chain increased. Change in T_g explained by variation in sp. vol.

Tobolsky, A.V., Scientific American, 197, No. 3, p 121 (1957)

The mechanical properties of polymers

1958

Buchdahl, R., J. Polymer Sci. 28, 239 (1958). C.A. 55, 6014g (1961)

Strength properties below T_g

Dyment, J., and Ziebland, H., J. Appl. Chem. (London) 8, 203-5 (1958). C.A. 52, 15118d (1958)

Tensile strengths of poly (C_2F_4, CTFE, nylon) measured at 20°, -75°, -120°, and -196°. Only teflon retained ductility at -196°.

Gibbs, J.H., and DiMarzio, E.A., J. Chem. Phys. 28, 373-83 (1958)

Quant. predictions are made concerning variations of glass temp. with mol. wt., glass temp. with mole fraction of low-mol.-wt. solvent.

Kambara, S., and Hatano, M., Kogyo Kagaku Zasshi 61, 904 (1958). C.A. 55, 18696a (1961)

Effect of halogen substr on m.p. of poly [3, 3-bis(halomethyl)-oxacyclobutanes]

Keun, Ryum-Sung, Kobunski Kagaku 15, 18-24 (1958). C.A. 53, 8699c (1959)

Relation between composition and glass-transition temperature of non-crystalline copolymer

Kuroda, T., and Sakami, H., Nagoya Kogyo Gyutsa Shikensho Hokoku 7, 315-21 (1958). C.A. 57, 13955f (1962)

III. Relation between crystallinity and molecular weight of poly(tetrafluoroethylene)

V. Thermal Properties of Polymers (continued)

1958 (continued)

Stevens, J. R., and Ivey, D. G., J. Appl. Phys. 29, 1390-4 (1958). C.A. 53, 817g (1959)
Mechanical behavior of a polymer at temperatures through the glass transition temperature

Willbourn, A. H., Trans. Faraday Soc. 54, 717-29 (1958). C.A. 53, 1894f (1959)
Glass transition in polymers with the $(CH_2)_n$ group

Wood, L. A., J. Polymer Sci. 28, 319-30 (1958). C.A. 52, 15110i (1958)
Equation relating T_g of a copolymer to T_g of each of the homopolymers

1959

DiMarzio, E. A., and Gibbs, J. H., J. Polymer Sci. 40, 121 (1959) C.A. 54, 25962a (1960)
T_g relations in copolymer systems

Martin, G. M., and Mandelkern, L., J. Research Nat'l. Bur. Standards 62, 141-6 (1959). C.A. 53, 16574a (1959)
T_g increases from -69° to +90° in vulcanizates as amount of bound S is increased

McCrum, N. G., J. Polymer Sci. 34, 355 (1959)
Transitions in teflon

Muus, L. T., McCrum, N. G., and McGrew, F. C., SPE J. 15, 368 (1959)
Properties below T_g

Nakajuna, T., and Sailo, S., J. Polymer Sci. 31, 764 (1958). C.A. 53, 764a (1959)
$(CF_2{=}CFCl)_n$ T_g extends from -80 to 60 by dielectric prep. measurement

Nivihov, A. S., and Galil-Ogly, F. A., C.A. 53, 13644c (1959)
Heat, Oil, and freezing stability of elastomers

V. Thermal Properties of Polymers (continued)

1959 (continued)

Polmanteer, K. E., and Hunter, M. J., J. Appl. Polymer Sci. 1, 3-10 (1959). C.A. 53, 20877b (1959)
Polymer comp. vs. low-temp. prop. of polysiloxanes. Small amts. of ϕMeSiO increase low temp. flex. dramatically

Robb, L. E., and Wolf, D. R., (to 3M), U.S. 2,849,412. C.A. 53, 756b (1959)
Plasticizers to improve low-temp. prop. of polyperfluorochloroolefins are esters of formula ROX(OR)

Woodward, A. E., and Sauer, J. A., J. Appl. Polymer Sci. 2, 114-58 (1959). C.A. 54, 10385c (1960)
Dynamic mechanical properties of high polymers at low temp.

1960

Belg. 536,033. C.A. 54, 16894e (1960)
Improves the elasticity of natural rubber in the neighborhood of -70°C by adding silicates

Frost, W. M., Advances in Cryogenic Eng. 5, 375 (1960)
The strength of 10 structural adhesives at temperatures down to 20°K

Grieveson, B. M., Polymer 1, 499 (1960). C.A. 55, 9936f (1961)
T_g in homologous series of linear polymers. T_g of methylene found by extrapolation to be -165°

Kalb, G. H., Coffman, D. D., Fort, T. A., and Johnston, F. L. (du Pont), J. Appl. Polymer Sci. 4, 55 (1960). C.A. 55, 3112c (1961)
Polymers from vinyl fluoride. $T_m = 198° = 471°K$

Marei, A. I., C.A. 54, 23395f (1960)
The effect of functional groups on the glass transition temperature of rubber-like polymers

Nielsen, L. E., SPE Journal 16, No. 5, 525-33 (1960). C.A. 54, 1475d (1960)
Dynamic mechanical properties of high polymers

V. Thermal Properties of Polymers (continued)

1960 (continued)

Watanabe, K., Nippon Gomu Kyokaishi, 33, 882 (1960). C.A. 55, 22888h (1961)
Stress relaxation and creep for several elastomers. ...results serve as criteria of usefulness of the elastomers at any temp.

McCrum, N.G., C.A. 54, 2885c (1960)
Internal friction in copolymers of C_2F_4 and C_3F_6

Corrucini, R.J., and Gniewek, J.J. (U.S.) Monograph 29, 1-22 (1961). C.A. 55, 16854h (1961)
Linear coeff. of expansion of 20 plastics and elastomers.

Wall, L.A., and Straus, S., J. Research NBS 65-A, 227 (1961). C.A. 55, 19428f (1961)
Pyrolysis of fluorocarbon polymers. $(CF_2CF_2)_n$, $(C_3F_6)_n$, and $(CF_2CFCl)_n$

Fujimoto, Katsuya, Nippon Gomu Kyokaishi 34, 532-7 (1961)
Resilience of cryst. poly (TFE and CTFE) were detd. in the range -70 to 250°

Gorelik, B.M., and Bukhina, M.F., Kauchuk i. Rezina 20, No. 11, 11-15 (1961). C.A. 57, 3599f (1962)
Crystallization of compressed rubber at low temperatures. An accelerated method for determining crystallizability

Hayes, R.A., J. Appl. Polymer Sci. 5, 318 (1961)
The relationship between T_g, molar cohesion and polymer structure

Mawers, R.E., Advances in Cryogenic Eng. 6, 627 (1961). C.A. 55, 20484b (1961)
Simple hardness test to determine relative crystallinity of fluorinated plastics is correlated with mechanical properties at cryogenic temperatures

Peckner, D., and Riley, M.W., Materials in Design Eng. 54, No. 1, 107 (1961). C.A. 55, 19349c (1961)
The role of materials in cryogenics

1961 (continued)

Weitzel, D. H., et al., Advances in Cryogenic Eng., 6, 219 (1961)
C.A. 55, 25316f (1961)
Elastomers for static seals at cryogenic temperatures

1962

Chernaya, V. V., and Vol'chenko, R. L., Uspekhi Khum. 31, 336 (1962)
English translation p 167-175
Methods for increasing the resistance of polymers to low temperatures

Clark, E. S., and Starkweather, H. W., J. Appl. Polymer Sci. 6, 541-2 (1962)
Crystal structure of quenched poly (C_2F_4)

Eiermann, K., and Hellwege, K. H., J. Polymer Sci. 57, 97-104 (1962). C.A. 56, 15658h (1962)
Thermal conductivity of high polymers from -180° to 90° C

Hertz, J., Advances in Cryogenic Eng. 7, 336 (1962)
Epoxy-nylon adhesives for low-temperature applications

Ludtke, P. R., and Weitzel, D. H., Advances in Cryogenic Eng. 8, 467-77 (1962). C.A. 59, 12998e (1963)
Force and seal evaluation of elastomeric O-rings. O-ring cooled to 76°K; force-temperature curves (for beginning of leaks) recorded; no change in curves at T_g

Miller, R. N., et al., I. and E.C., Product R. and D., 1, 257 (1962)
Properties of foams, adhesives and plastic films at cryogenic temp.

"Montecatini", Italian 611,443. C.A. 57, 15315d (1962)
Copolymers of C_2H_4 and C_3H_6 and C_2H_4 and 1-butene with T_g of -40 and with brittle temperature of -95°

Novikov, A. S., et al., C.A. 57, 12678i (1962)
Structural transformations of fluorine-containing elastomers in thermal treatment

V. Thermal Properties of Polymers (continued)

1962 (continued)

Reding, F.F., Faucher, J.A., and Whitman, R.D., J. Polym. Sci. 57, 483 (1962). C.A. 57, 2399c (1962)
Glass transitions in ethylene copolymers

Robbins, B.F., Weitzel, D.H., and Herring, R.N., Advances in Cryogenic Eng. 7, 343 (1962)
The application and behavior of elastomers at cryogenic temperature

Satokowa, T., and Koisumi, S., Kogyo Kagaku Zosshi 65, 1211 (1962) C.A. 58, 1544h (1963)
Transition at 130° in poly(tetrafluoroethylene)

Sheldon, R.P., J. Appl. Poly. Sci. 6, 543 (1962)
Simple method for determination of glass temperature of amorphous polymers using polarizing microscope

Simha, R., and Boyer, R.F., J. Chem. Phys. 37, 1003-7 (1962) C.A. 57, 15328g (1962)
General relation involving the glass temperature and coefficients of expansion of polymers

Smith, M.B., and Susman, S.E., Advances in Cryogenic Eng. 8, 300 (1962)
Development of adhesives for very low temperature application

Somcynsky, T., and Patterson, D., J. Polymer Sci. 62 (174) S151-S155 (1962)
The glass transition and the reduced temperature of polymeric liquids. Theory of corresponding states tested by lowering of T_g for a polymer by solvents from the n-alkanes homologous series

Zannetti, R., Manaresi, P., and Baldi, L., J. Polymer Sci. 62 (174) S33-S38 (1962). C.A. 66, 4265g (1964)
β-Absorption and glass transitions in polymers

1963

Andrianov, K. A., and Zhdanov, N. A., C. A. 58, 554g (1963)
Poly(borodimethylsiloxanes), T_g approximately -125°

Beck, D. L., Hiltz, A. A., and Knox, J. R., SPE Soc. Plastic Eng. Trans. 3, (4); 279-85 (1963). C. A. 60, 5704d
T_g's in polypropylene

Beevers, R. G., and White, E. F. T., Polymer Letters 1, 171 (1963)
T_g of acrylonitrile-styrene copolymers. Minimum T_g noted

Gerenbaum, M. B., Rosenthal, N. A., and Lecher, H. Z., C. A. 59, 10327d (1963)
Polysulfide rubbers having improved low-temperature properties

Barisov, S. N., Plaste Kautschuek 10, (7), 400-1 (1963). C. A. 60, 1905g (1964)
Cold-resistant polysiloxane elastomers. Phenyls raise T_g, but lower tendency to crystallize

Ellerstein, S. M., (Polymer Letters) J. Poly Sci. Sec. B 1, 223 (1963)
The glass temperature of random addition copolymers

Heller, J., and Layman, D. J., (Polymer Letters) J. Polymer Sci. Sec. B 1, 317 (1963)
T_g by means of differential pressure transducer

Illers, K. H., Kolloid-Z. 190, 16 (1963)
T_g on 17 copolymers, curves of T_g against composition showed maxima, minimum and both plus and minus deviations.

Jendrychowska-Bonamour, A. M., J. Chim. Phys. 60, (9), 1038 (1963). C.A. 60, 1851b (1964)
Graft of styrene on teflon decreased low temperature deformability in contrast to effect on polystyrene

Ke, B., Polymer Letters 1, 167 (1963)
DTA analyses of high polymers. Some low temperature transitions

V. Thermal Properties of Polymers (continued)

1963 (continued)

Kumins, C.A., and Roteman, J., J. Polymer Sci. Sec. Al (1) 527 (1963) C.A. 59, 12935h (1963)

Effect of solid-polymer interaction on transition temperature and diffusion coefficients

Leshchenko, S.S., Karpov, V.L., and Kargin, V.A., C.A. 59, 8937 (1963)

Electrographic study of fluorine-containing copolymers of CF_2CH_2 with C_3F_6 and CF_2CFCl

Robbins, R.R., Oboni, Y., and Weitzel, D.H., Advances in Cryogenic Eng. 8, 287-99 (1963). C.A. 59, 10323a (1963)

Linear Thermal expansion of elastomers in the range 300° to 76°K

Saba, R.G., et al., J. Polymer Sci., PtA, 1, 1483 (1963)

Low temperature transitions in $CH_3\overline{CHCH_2O}$, $(CH_3CH_2OCH{=}CH_2)_n$ has loss maximum at -170

Shetter, J.A., J. Polymer Sci., PtB, 1, 209 (1963)

Effect of stereoregularity on T_g in polyacrylates and polymethacrylates

Sobolevskoya, et al., C.A. 59, 11674d (1963)

Synthesis of poly(methylsiloxanes) with improved low-temperature properties. Inclusion of methyl(trimethylsilyloxy)-silyl units reduced solidification point from -76° to -118°

Tobolsky, A.V. NASA, Doc. N63-13205 (1963). C.A. 60, 1854d (1964)

Aspects of viscoelasticity of polymers

Tobolsky, A.V., and Takohoshi, M., J. Polymer Sci. Pt A, 1, 483 (1963)

Rheology of teflon. $T_g = 110°$ by relaxation time-temperature measurements

Ruby, J.D., NASA, Doc. N63-19809 (1963). C.A. 60, 9456g (1963)

Elastomers for potential use at cryogenic temperatures.

V. Thermal Properties of Polymers (continued)

1963 (continued)

Zannetti, R. Manaresi, P., and Balli, L., Rubber Chem. Technol. 36, (2) 459 (1963)
Determination of phase changes by beta-ray absorption

Boyer, R.F., Rubber Chem. and Tech. 36 (5), 1303-421 (1963)
Excellent review on the relation of transition temperatures to chemical structure. 201 references.

1964

Eisenberg, A., and Rouira, E., J. Polymer Sci. Pt B 2, (3), 269 (1964)
A new method for the rapid determination of glass transition temperatures, using strain gauge

Nielson, L., J. Appl. Sci. 8, 511-20 (1964) C.A. 60, 10900a
Tightly cross-linked rubbers show slight increase in T_g.

Tautz, H., et al., C.A. 61, et al, 735d (1964)
Specific heats of polymers between -150 and 180°. Low pressure PE, T_g 130-3 high pressure PE, T_g 111-4.

Lorant, M., C.A. 61, 735g (1964)
Apparatus for determining T_g. Low temperature gases used in a dilatometer.

Ellerstein, S.M., J. Polymer Sci. Pt. B Pol. Let. 2, 379-80 (1964)
Glass temperature as a function of molecular weight.

Vocrodskaya, M.V. and Bartener, G.M.; C.A. 61, 803g (1964)
Fillers to a 20% loading dosen't change T_g.

Garfield, L.J. and Petri, S., C.A. 61, 5784d
Viscosity and T_g behavior of polymer-diluent systems.

Kovacs, A.J., C.A. 61, 5789a (1964)
T_g in amorphous polymers, a review with 184 references.

Strella, S., J. Polymer Sci. Pt. B, 2 (6) 625-6 (1964), C.A. 61, 5789c
DTA of polymers undergoing T_g.

1964 (continued)

Wunderlich, B.W. and Bodily, D.M. C.A. 61, 7115f
T_g by DTA

Pistorius, C., Polymer 5 (6), 315-17 (1964) C.A. 61, 7181d (1964)
$\left(CF_2CF_2 \right)_n$ transitions

Zutty, H.L. and Whitworth, C.J., J. Polymer Sci. Pt. B, 2 (7), 709-13 (1964)
Correlation of b.p. and H_v of model compounds with T_g.

Manaresi, P. et al., C.A. 61, 12102h (1964)
Determination of transition temperature through measurement of dilation, DTA, X-ray diffraction and beta-ray absorption

McCrum, N.G., J. Polymer Sci., Pt A, 2 (9), 3951-8 (1964); C.A. 61, 13440h
Energy of low-temperature relaxation of PTFE.

Raphael, T. and Armeniades, C.D., C.A. 60, 16054a (1964)
ADL Boll rebound tests on plastics from -200 to 500°F.

Shen, M.C. and Tobolsky, A.V., U.S. Gov. Research Reports AD-434 299
Effect of plasticizer, chain ends and comonomer on the T_g of polymers

Lal, J. and Trick, G., J. Polymer Sci., Pt. A, 2 (10), 4559-72 (1964)
T_g of poly(vinylalkyl sulfides). $CH_3OCH{=}CH_2$, T_g -31; $CH_3SCH{=}CH_2$, T_g -1; $C_8H_{17}CH{=}CH_2$, T_g -80. $CH_3OCH(CH_3)CH_2$, T_g +67°.

1965

Allen, G. et al. C.A. 62, 4190g (1965)
T_g of poly(propyleneoxide) -75°

Di Marzio, E., C.A. 62, 4191a (1965)
Mathematical relation of 2nd order transition to cross-linking in rubber.

V. Thermal Properties of Polymers (continued)

1965 (continued)

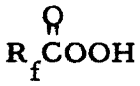
Stratta, J., Reding F. and Faucher J., C.A. 62, 6578h
T_g of $\left(CH_2CH_2CH_2\text{-}O\right)$ -64°, A mechanical loss peak at -128° was attributed to 3 methylene groups in sequence.

VI. Polymerization Systems

1961

3M, Brit. 856,469. C.A. 55, 14990f (1961)
Fluorine-containing vinyl compounds with Ziegler catalysts. CF_2CFCl; 1,1,3-trifluorobutadiene; 1,1-difluorobutadiene, CH_2CF_2

Bro, M.I., Convery, R.J., and Schreyer, R.C., U.S. 2,988,542. C.A. 55, 22917a (1961)
Fluorine-containing 1-olefins polymerized in a halogenated solvent with



$R_f\overset{\overset{O}{\|}}{C}OOH$

Duck, E.W., Brit. 853,355. C.A. 55, 10969f (1961)
Ziegler polymerization of perfluoroolefins

Florin, R.E., and Wall, L.A., J. Research NBS 65-A, 375 (1961)
Gamma irradiation of fluorine-containing polymers

$$CF_2CFH \xrightarrow[60\text{-}80°]{\text{persulfate}} \left[CF_2CFH\right]_n$$

Mantell, R.M. and Hoyt, J.M., (to 3M), U.S. 3,043,823. C.A. 57, 12719b (1962)
Emulsion polymerization of fluorinated monoolefins. Standard **system, except that 5 pts/150 of CS_2** added

1963

Sianesi, D., and Caporiccio, G., C.A. 58, 9237c (1963)
Stereospecific polymerization of perfluoroolefins

Sianesi, D., and Caporiccio, G., Belg. 618,320. C.A. 58, 9247g (1963)
Stereopolymerization of fluoroolefins

VI. Polymerization Systems (continued)

1963 (continued)

Colombo, D., Steinberg, M., and Macehia, D., J. Polymer Sci. Part B 1, (9), 483-8 (1963). C.A. 59, 14116d (1963)
Co^{60} gamma-ray induced copolymerization of ethylene in presence of other monomers

Crawford, G.H., U.S. 3,089,866. C.A. 59, 1776h (1963)
Ziegler polymerization of fluoroolefins

Khramchenkov, V.A., C.A. 59, 4039c (1963)
Radiation-induced polymerization of fluoroolefins. $CF_3CF=CH_2$, $CF_3CH=CF_2$, $CF_3CF=CHF$, CF_3CHCF_2, $CH_2C(CF_3)_2$

1964

E. V. Volkora and A. Shobina, C.A. 61, 5772h (1964)
Polymerization of C_3F_6 by gamma initiation in liquid and solid phases. 50 to 600 rads/sec from 263 to 195°K. Only liquids obtained

A. Gantnikher, et al., C.A. 61, 10786e (1964)
Gamma irradiation of C_2F_4 at -55°. Rate of polymerization $>$ C_2H_4 explained by lower rate of chain rupture.

Manno, P.J., Nucleonics 22 (2), 49 (1964) ibid. 22 (6), 64 (1964)
Radiation polymerization of fluoromonomers. Polymerization rate and yield increases with temp.

Wall, L.A. and Brown, D.W., J. Polymer Sci., Pt C (4), 1151-60 (1964); C.A. 60, 6929h (1964)
Radiation induced polymerization at high pressures.
5 to 17 x 10^3 atm at 20 to 275°, gamma dose rate 0.13 mrad to 3 mrad./hr. Polymers of $C_6H_5OCFCF_2$ and $C_6F_5OCFCF_2$.

VII. Fluorine-containing Monomer Synthesis and Miscellaneous Reactions

1960

Dixon, S., U.S. 2,917,548 (1959). C.A. 54, p 5474e (1960)
$RONa + CF_2CF_2 \rightarrow ROCFCF_2$

1963

Park, J.D. and Lacher, J.R., U.S. Gov. Rept. AD-432-978 (1963)
Synthesis of special fluorine-containing monomers. 3 and 4 membered rings.

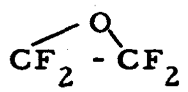
1964

Fritz, C.G., Moore, E.P., Jr., and Selman, S., (to du Pont), U.S. 3,114,778 C.A. 60, 67501 (1964)
Synthesis of perfluoroalkyl trifluorovinyl ethers, including $CF_3OCF{=}CF_2$

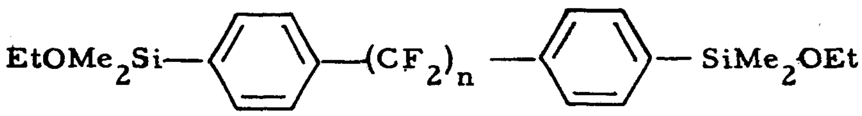
Case, J.R. and Pass, G., J. Chem. Soc. 946-8, (1964); C.A. 60, 10533g (1964)
Pentafluorosulfuroxy derivatives of C_3F_6.
$SF_5O(C_3F_6)_nOSF_5$, n=2, 3 and 4.

Proskow, S., U.S. 3,121,734 (to E.I. du Pont de Nemours and Co.); C.A. 60, 10557b
Prep. of NCCFCFCN

Caglioti, V., Lenzi, M and Mele, A., Nature, 201 (4919), 610-11 (1964); C.A. 60, 11522e (1964)

Prep. of  $\overset{O}{CF_2-CF_2}$ by oxidation of C_2F_4 with O_2

Fuqua, S.A., and Silverstein, R.M., NASA, Doc. N63-15, 280, 39 pp (1962) C.A. 60, 741d (1964), J. Org. Chem. 29 (2), 395 (1964)



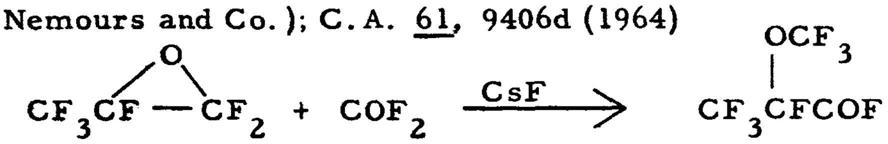
VII. Fluorine-containing Monomer Synthesis and Miscellaneous Reactions (continued)

1964

Lawlor, F.E. et al, U.S. 3, 129, 250 (to Pennsalt Chemicals Corp.); C.A. 61, 2974c (1964).
Preparation of $CF_3(CH_2)_xOCH{=}CH_2$ by pyrolysis of the corresponding acetal.

Frisch, E.E., Fr. 1, 361, 255 (to Dow Corning Corp.); C.A. 61, 9401f (1964)
Preparation of perfluoroisoprene

Frits, C.G. and Moore, E.P., Fr. 1, 342, 515 (to E.I. du Pont de Nemours and Co.); C.A. 61, 9406d (1964)



Haszeldine, R.N., Brit. 963, 634; C.A. 61, 13313d (1964)
Fluorovinyl oxazetidines

1965

Prager, J.H. and Thompson, P.G., J. Amer. Chem. Soc., 87 (2), 230 (1965)
Prep. of fluorocarbon hypofluorites