$$E=mc^2$$
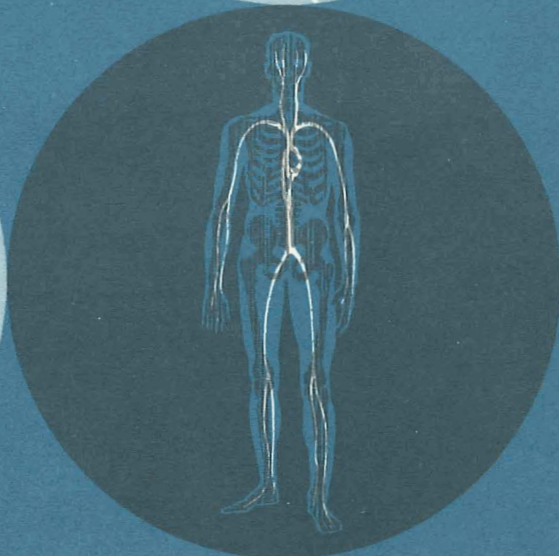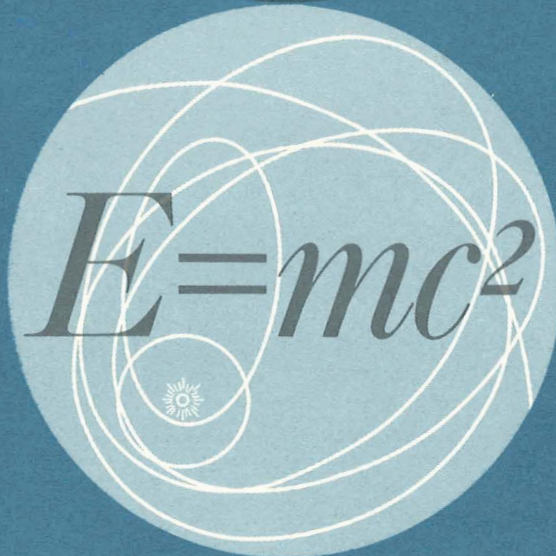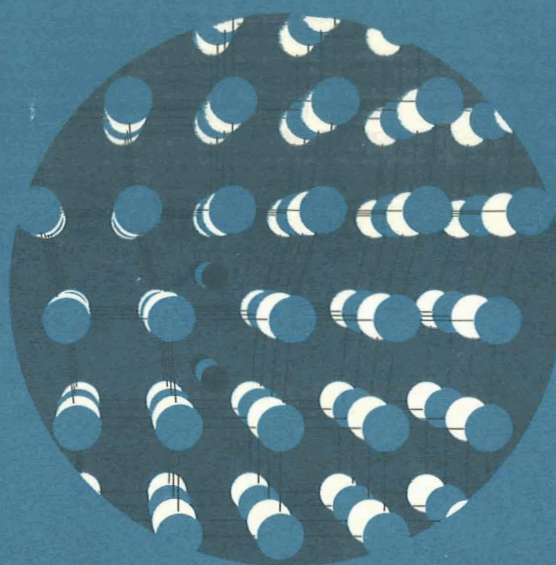
NEW FLUORINE-CONTAINING ELASTOMERS FOR SPACE-PROPULSION APPLICATIONS

**FINAL TECHNICAL REPORT
FOR PERIOD 3 MARCH 1969 TO 31 MARCH 1970
UNDER CONTRACT NAS 7-723**

JULY 1970

MCDONNELL DOUGLAS
CORPORATION

DOUGLAS ADVANCED RESEARCH LABORATORIES

MCDONNELL DOUGLAS

CORPORATION

REPORT MDC-Q0018

(DAC-61000-F)

NEW FLUORINE-CONTAINING ELASTOMERS FOR SPACE -PROPULSION APPLICATIONS

CONTRACT NAS 7-723

FINAL TECHNICAL REPORT
FOR PERIOD 3 MARCH 1969 TO 31 MARCH 1970

BY

M.S. TOY, Ph.D.

FOREWORD

This final technical report represents the results accomplished during the past year in a program on New Fluorine-Containing Elastomers for Space-Propulsion Applications carried out at McDonnell Douglas for the National Aeronautics and Space Administration, Jet Propulsion Laboratory, under Contract NAS 7-723.

The contract is administered by the NASA Chief, Liquid Propulsion Technology, Code RPL, Washington, D.C., with Mr. J. D. Ingham and Dr. R. A. Rhein of the Polymer Research Section at Jet Propulsion Laboratory as Technical Managers.

This report covers work started out at Douglas Astropower Laboratory on 3 March 1969 and continued at Douglas Advanced Research Laboratory since 20 October 1969 to 31 March 1970 with the same Principal Investigator, Dr. M. S. Toy. She and her assistant, Mr. J. M. Newman, were both transferred from Astropower to DARL during October 1969. The cooperation of Mr. D. D. Lawson of Jet Propulsion Laboratory in the conduct of the program has been of great value.

ABSTRACT

The goal of this program is to develop low temperature elastomers which are resistant to strong oxidizers. The reasons for selecting perfluorobutadiene as the monomer and bis(trifluoromethyl) peroxide as catalyst and the theoretical considerations on the method of approach and reactions of polyperfluorobutadiene with fluorine and oxygen difluoride were discussed.

The first significant accomplishment was the discovery of novel utilization of oxygen difluoride for fluoropolymer syntheses applicable to three areas: (1) chain extension of unsaturated perfluoropolymers, (2) insertion of functional groups into fluoropolymers, and (3) addition copolymerication with terminally—unsaturated per— fluorodienes or diolefins to form inert perfluoroalkylene oxide polymers.

The second significant accomplishment was the larger scale homo- polymerizations of perfluorobutadiene under autogenous pressure (i. e. about 2 atm) at ambient temperature by CF_3OOCF_3 catalysis to reach molecular weight of 17, 000.

The third significant accomplishment was the selective reaction of oxygen difluoride and polyperfluorobutadiene to increase molecular weight by forming inert ether linkages without insertion of functional groups into the polymer chain. Preliminary results also indicated that the increase of number of ether linkages tends to increase solubility with increase molecular weight and the products become more gummy.

The fourth accomplishment was the invention of a novel vulcanization
and graft-copolymerization process, which involves the exposure of
polyperfluorobutadiene to low concentration of gaseous fluorine
under controlled conditions in order to create reactive sites on the
polymer chains. Successful graft copolymerization and vulcanization
by monomeric species such as tetrafluoroethylene, perfluorobutadiene
and hexafluoropropylene epoxide were achieved. The three dimensional
fluoropolymers by the former two monomers contain only carbon and
fluorine but the latter monomer also contains oxygen in the form
of inert ether linkages.

CONTENTS

CONTENTS (Continued)

CONTENTS (Continued)

CONTENTS (Continued)

ILLUSTRATIONS

ILLUSTRATIONS (Continued)

TABLES

Section 1

INTRODUCTION AND SUMMARY

The objective of this investigation is to synthesize and evaluate new fluorine-containing polymers having elastomeric properties and oxidative stability. This work was initiated to meet a need for a highly inert resilient material to use in expulsion bladders, seals, gaskets, and O-rings in contact with strong oxidizers for space-propulsion applications.

A suitable elastomer had not yet been fully developed to meet the requirements. Perfluorinated polymers, such as polytetrafluoroethylene (PTFE), offer the highest resistance to chemical oxidants but it is extremely difficult to process PTFE as an expulsion bladder and the bladders have serious drawbacks due to permeation of propellants. While fabrication of PTFE into seals, gaskets, and O-rings is successful, cold flow of the polymer requires a special design of the seals and housings so that leaks do not develop.

The properties of nitroso elastomers (i. e. , the $CF_3NO/CF_2{=}CF_2/ON(CF_2)_{2,3}{-}COOH$ terpolymer systems) have received considerable attention (References 1 and 2). These materials are susceptible to chemical attack in direct contact with strong oxidizers such as fluorine. The infrared spectrum indicated the absence of carbonyl group after fluorine exposure. Its impact sensitivity in liquid fluorine was reduced somewhat, but not significantly, by compounding with calcium difluoride (Reference 3).

This work describes further investigation into the syntheses of polyperfluorobutadiene under low pressure and temperature. The selected catalyst for scale-up preparation is bis(trifluoromethyl)peroxide. The molecular weight of the homopolymer at current-state-of-the-art reaches 17,000. From the various larger batches of polyperfluorobutadiene preparations by CF_3OOCF_3 catalysis, the polymer yield, molecular weight and structure are found to be dependent upon monomer-catalyst ratio, polymerization temperature and time, agitation and photolysis.

The chain extension process of polyperfluorobutadiene by means of oxygen difluoride to form inert ether linkages without insertion of functional groups into the polymer chain has been achieved. The novel utilization of oxygen difluoride was discovered for fluoropolymer syntheses applicable to three areas:

(1) Chain extension of unsaturated perfluoropolymers.

(2) Insertion of functional groups such as epoxide and acyl fluoride groups into fluoropolymers.

(3) Addition copolymerization with terminally unsaturated perfluorodienes or diolefins to form inert perfluoroalkylene oxide polymers.

The mechanism of reactions of oxygen difluoride with the two types of unsaturated bonds of polyperfluorobutadiene were presented and discussed.

Preliminary results on low temperature properties of polymers indicated that OF_2-chain extended polyperfluorobutadienes are superior to homopolymers of identical molecular weight range. Experimental results showed that by adding ether linkages one can

2

go from a hard elastomeric homopolymer to a gum, even though the overall molecular weight increases. Furthermore, the solubility of the polymer also increases. It would appear that OF_2 affects the crystallinity and morphology of the polymer, which tends to become more gummy. The glass transition temperatures of two OF_2-chain extended polymers of approximately the same molecular weight range (25,000) were compared. The one formed from molecular weight of starting homopolymer in the 7,000 range showed Tg at $-42°C$, while one formed from starting homopolymer in the 15,000 range is about 50°C higher. These preliminary data indicate that further investigation in this area will clarify the most effective approach to reach the ultimate goal of the program.

In contrast to saturated perfluoropolymers, the vulcanization of polyperfluorobutadiene can be accomplished under very mild conditions. A new vulcanization process based on the reaction between gaseous fluorine and polyperfluorobutadiene was originated. The method involves two steps:

1. Exposure of solid polyperfluoropolyene to very low concentration of gaseous fluorine under controlled conditions to create reactive sites on the polymer chains, followed by evacuation to remove the gaseous fluorine also under carefully controlled conditions.

2. Introduction of monomer to graft-copolymerize, and crosslink onto the polymer chains under controlled conditions.

This fluorine-polyperfluoropolyene process has been successfully applied to achieve vulcanized and graft-copolymerized polymers containing only carbon and fluorine or carbon, fluorine and oxygen as inert perfluorinated ether linkages.

Section 2

THEORETICAL CONSIDERATIONS

2.1 POLYPERFLUOROBUTADIENE

This work was initiated to meet a need for a highly inert resilient
material in contact with strong oxidizers. Originally, there were
several reasons for selecting perfluorobutadiene as the monomer
which is commercially available and can be polymerized in the
presence of certain catalysts under low pressure at relatively low
temperature (Reference 4). To ensure satisfactory stability in
strong oxidizers, a highly fluorinated elastomer was regarded as
necessary and polyperfluorobutadiene contains only carbon and
fluorine. It was also considered that the mechanical properties of
perfluorobutadiene high polymer might be superior to those of
commercial polytetrafluoroethylene and the perfluorinated copolymer
of ethylene and propylene. This was based on the consideration that
the introduction of double bonds and the reduction in symmetry of
polymer chains would be favorable in diminishing the ease of
crystallization of perfluorinated polymers to give elastomeric
properties.

Although the macromolecular conformations of perfluoropolymers
have been reported for polytetrafluoroethylene (References 5 and 6)
and polytetrafluoroallene (References 7 and 8), the structural con-
figurations and conformations for polyperfluorobutadiene have not
been investigated elsewhere to our knowledge. Free radical poly-
merizations of perfluorobutadiene were shown to involve one or both

double bonds to give 1,2- and 1,4-polymers, which may have varied steric configurations as well as head-to-tail and head-to-head arrangements in the former case and cis and trans vinylene groups in the latter (References 9 and 10). For uncontrolled propagation of the monomer, one would expect the products to contain a mixture of these features, thus being copolymers.

$$nCF_2=CFCF=CF_2 \begin{cases} +CF_2CF=CFCF_2 +_n & \text{1,4-polymer (cis and trans forms)} \\ \\ +CF_2CF +_n \\ \quad | \\ \quad CF=CF_2 & \text{1,2-polymer (atactic and tactic forms as well as head-to-tail and head-to-head arrangements)} \end{cases}$$
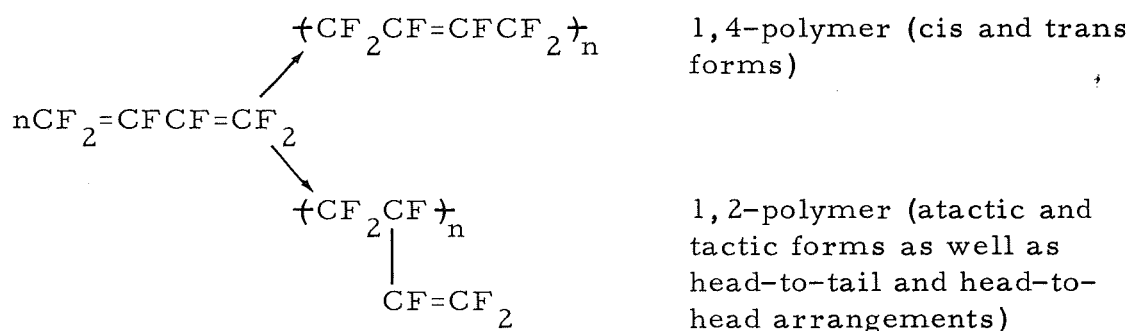
Straight and relatively smooth chains are undesirable for development of high elasticity (Reference 11). The copolymers of perfluoro-1,2- and 1,4-butadiene provide chemical irregularity to the polymer chains to reduce the tendency to crystallize. Also, the double bonds having the cis-configuration lower the attainable density of packing to give a similar effect of enhancing elastomeric properties.

For a polymer to be potentially useful as a synthetic elastomer, it is desirable to crosslink in such a way as to bond a macroscopic sample into a continuous network (Reference 12). The unsaturated bonds in polyperfluorobutadiene chains are potential crosslinking sites. Saturated fluoropolymers require drastic methods such as high energy irradiations, or reaction with aliphatic amines and peroxides (Reference 13), whereas vulcanization of polyperfluorobutadiene can be accomplished under very mild conditions. The

6

danger of carbon-carbon bond scission, which occurs during high energy irradiations (Reference 14), and the introduction of reactive sites into the polymer network by amine and peroxide crosslinking methods are thus eliminated. The need for maximum obtainable purity of the polymers is obvious, since their use requires compatibility with strong oxidizers. Polymer vulcanization will aim at lower degrees of crosslinking, because networks of lower degrees of vulcanization consist of longer chains, which are less susceptible to orientation by elongation than the shorter ones occurring in networks of high degrees of crosslinking. Experimental evidence bears out the fact that crystallization begins at lower elongations for higher degrees of crosslinking (Reference 15); therefore widely-spaced crosslinking should give the dimensional stability to polyperfluorobutadiene without restricting chain mobilities for elastomeric properties.

Finally, the residual double bonds of vulcanized polyperfluoro-butadiene can be saturated by direct fluorination to increase the chemical resistance. Bond saturation of polyperfluorobutadiene after vulcanization will decrease the ease of crystallization, and provide lower attainable density of packing and an increase of free-volume compared to saturated linear chains. Also any 1,2-addition units in the polymer chain should be bulky enough to provide the chain irregularity desirable to enhance elastomeric properties within the loose network. Thus, we outlined our general scheme of approach as three steps:

1. Polymerization of perfluorobutadiene to flexible fluorocarbon chains.

2. Low density crosslinking for permanence of structure or dimensional stability.

3. Fluorination of the unsaturated network for greater chemical resistance.

The present state-of-the-art preparation methods of polyperfluoro-butadiene under low pressure and temperature in the presence of free radical catalysts is at molecular weight about 5000 to 17,000. In general, an elastomer of high tensile strength and extensibility requires the primary molecular weight of a vulcanizate to be about 100,000 to give good mechanical properties. Therefore, emphasis was placed on chain extension of the homopolymer. The utilization of OF_2 as chain extender of polyperfluorobutadiene (Appendix D) is one means to increase the molecular weight. Then vulcanization to low crosslink density and fluorination of the residual unsaturation should give us good inert elastomers.

2.2 REACTION WITH FLUORINE

There are two types of unsaturated bonds in the copolymer of perfluoro-1,2- and 1,4-butadiene: (1) the internal double bonds (vinylene), $-CF=CF-$, as a result of 1,4-addition polymerization to form the cis and trans perfluorovinylene groups in the chain; and (2) the pendant double bonds (vinyl), $-CF=CF_2$, as a result of 1,2-addition polymerization (References 10 and 16). The chemical reactivities of these two types of perfluoroolefinic bonds are different.

8

The saturation addition reactions with gaseous fluorine were shown to occur more rapidly and completely in the vinylene groups than in the vinyl groups. In contrast, the preferred reactions with amines such as hexamethylenediamine and piperidine were with the vinyl groups (Reference 9). This can be explained by the two crosslinking agents, fluorine and hexamethylene diamine, involving different mechanisms. The former, being a free radical type, favors the vinylene bonds ($-CF=CF-$), while the latter, being an ionic type, favors the pendant vinyl bonds ($-CF=CF_2$) due to increased polarity of the olefinic bonds, as well as the fact that hexamethylene diamine and piperidine are more sterically hindered molecules (Reference 17).

The reaction of fluorine molecule with olefinic bond was reported by Miller and Koch to produce a fluorinated free radical and a fluorine atom (Reference 18). The reactions of fluorine and polyperfluoro-butadiene are more complex, and produce a series of reactions as follows:

$$-CF_2CF=CFCF_2- + F-F \rightarrow -CF_2CF_2\overset{.}{C}FCF_2- + F\cdot \qquad (1)$$

$$-CF_2CF=CFCF_2- + F\cdot \rightarrow -CF_2CF_2\overset{.}{C}FCF_2- \qquad (2)$$

$$-CF_2CF_2\overset{.}{C}FCF_2- + F-F \rightarrow -CF_2CF_2CF_2CF_2- + F\cdot \qquad (3)$$

$$-CF_2CF_2\overset{.}{C}FCF_2- + -CF_2CF=CFCF_2- \rightarrow -CF_2CF_2CFCF_2- \qquad (4)$$
$$\overset{|}{\underset{-CF_2\overset{.}{C}FCFCF_2-}{}}$$

$$2\text{-}CF_2CF_2\overset{\cdot}{C}FCF_2- \;\rightarrow\; -CF_2CF_2\underset{\displaystyle -CF_2CF_2CFCF_2-}{\overset{|}{C}FCF_2-} \tag{5}$$

$$-CF_2CF_2\overset{\cdot}{C}FCF_2- + F\cdot \;\rightarrow\; -CF_2CF_2CF_2CF_2- \tag{6}$$

$$-CF_2CF_2\overset{\cdot}{C}FCF_2- + nCF_2=CF_2 \;\rightarrow\; -CF_2CF_2-\underset{\displaystyle (CF_2CF_2)_{n-1}CF_2\overset{\cdot}{C}F_2}{\overset{|}{C}FCF_2-} \tag{7}$$

$$2\text{-}CF_2CF_2\overset{\cdot}{C}FCF_2- + nCF_2=CF_2 \;\rightarrow\; -CF_2CF_2-\underset{\displaystyle (CF_2CF_2)_{n-1}CF_2\underset{\displaystyle -CF_2CF_2-CF-CF_2-}{\overset{|}{C}F_2}}{\overset{|}{C}F-CF_2-} \tag{8}$$
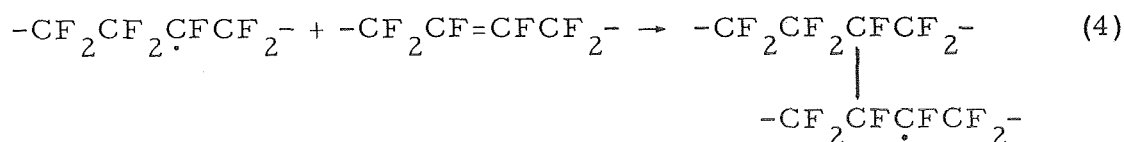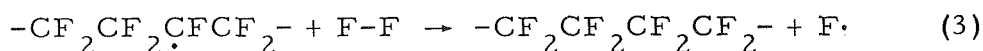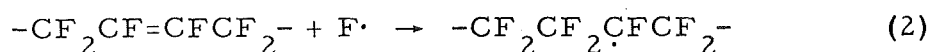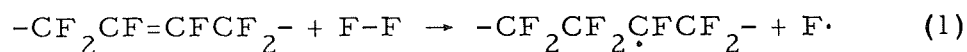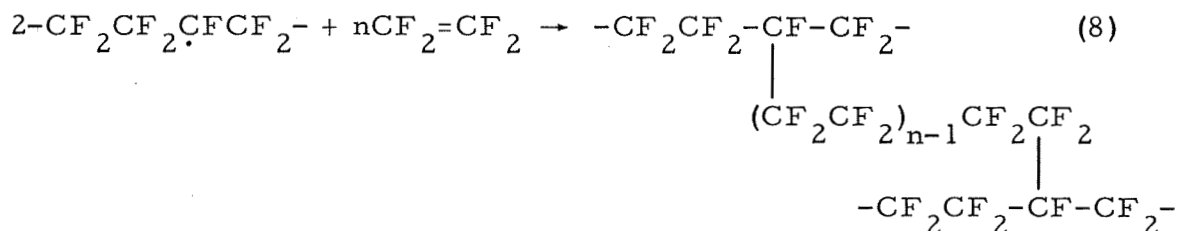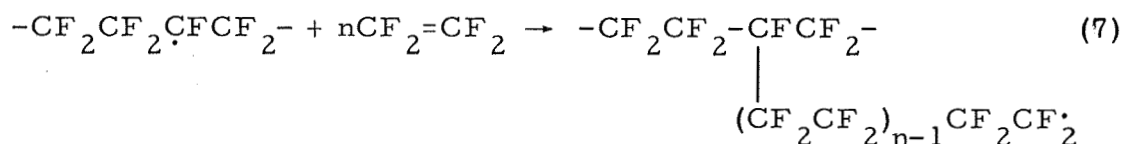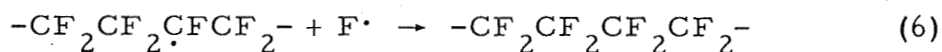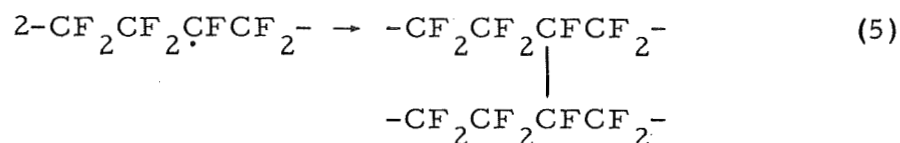
The advantage of fluorine exposure to solid polyperfluorobutadiene is that the fluorocarbon radicals thus produced and trapped in the solid matrix should be fairly stable (Step 1). The high stability of fluorocarbon radicals has been previously reported by other workers (References 19 and 20). The fluorine atom and fluorocarbon radicals of Step 1 can serve as free radical initiators (Steps 2 to 4), dimerize (Step 5), saturate (Step 6) or graft (Step 7), and crosslink (Step 8) in the presence of excess monomer.

Vulcanization and graft copolymerization in the presence of monomeric species such as tetrafluoroethylene, perfluorobutadiene and

hexafluoropropylene oxide were achieved (see Appendix A). The purpose of low concentration vapor fluorination of the solid homopolymer is to favor formation of radical sites on the polymer chain rather than saturation reactions (Reference 21). The electron spin resonance (ESR) spectra of polyperfluorobutadiene, curves 1 and 2 of Figure 1, Appendix A, show the dependence of radical concentrations on the fluorine pressure after identical length of evacuation. The difference of radical concentrations between curves 2 and 3 may be explained by possible crosslinking (Step 8), in addition to graft copolymerization (Step 7).

The polyperfluorobutadiene–tetrafluoroethylene and –perfluorobutadiene systems led to elastomers containing only carbon and fluorine and the polyperfluorobutadiene–hexafluoropropylene epoxide system contained pendant poly(perfluoropropylene ether).

A series of new fluoropolymers, which possess yet unknown physical properties, can be obtained as a result of this crosslinking and graft–copolymerization technique.

2. 3 REACTION WITH OXYGEN DIFLUORIDE

A review of the chemistry of hypofluorite, a class of compounds containing the oxygen–fluorine bond (Reference 22), revealed that the rupture of the oxygen–fluorine bond resulted in addition across the double bonds in molecules such as ethylene, perfluorocyclopentene and tetrafluoroethylene (References 23 and 24).

$$CF_3OF + CH_2{=}CH_2 \rightarrow CF_3OCH_2CH_2F$$

$$CF_3OF + \begin{array}{c} CF\underline{\hspace{1cm}}CF_2 \\ \| \quad\quad\quad | \\ CF\diagdown_{}CF_2 \\ CF_2 \end{array} \rightarrow \begin{array}{c} CF_3O{-}CF\underline{\hspace{1cm}}CF_2 \\ | \quad\quad\quad | \\ CF_2\diagdown_{}CF_2 \\ CF_2 \end{array}$$

$$FOCF_2OF + CF_2{=}CF_2 \xrightarrow[N_2]{-184^\circ C} CF_2(OCF_2CF_3)_2$$
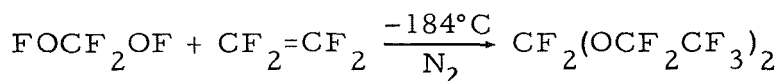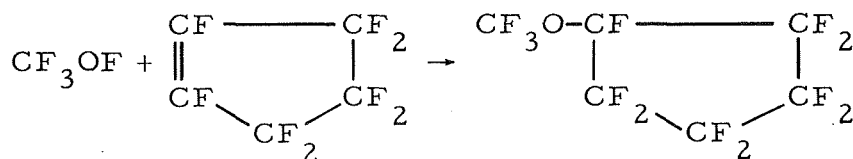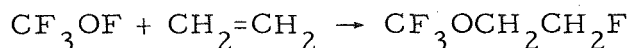
Organic reactions of the fluoroxy compounds, particularly fluoroxytrifluoromethane (CF_3OF), have been studied during recent years. Barton and co-workers discovered that CF_3OF as a versatile electrophilic fluorinating agent, which constitutes a source of "electrophilic fluorine," can selectively and rapidly effect the electrophilic fluorination of activated olefins (Reference 25). These authors precluded homolytic scissions of the O–F bonds of fluoroxy compounds prior to the attack on the ethylenic linkages and free-radical involvements at subsequent stages of the reactions (Reference 26).

In the great majority of chemical reactions of oxygen difluoride, it acts as a powerful fluorinating agent and requires more energy of activation than is needed for elemental fluorine (Reference 27). In contrast to the fluorine reactivity with reducing agents (References 28 and 29), mixtures of OF_2 with hydrogen or methane are stable even at elevated temperatures.

12

Solomon, Bauer and Jaye reported the thermal decomposition of OF_2 proceeding in a complex fashion via a chain reaction. Their analysis has assumed a more equal distribution of bond strengths of OF_2 and the second bond is actually weaker than the first (Reference 30). This thought was supported by electron-impact data (Reference 31), but with Cl_2O, the first ClO bond is considerably weaker than the second (References 32 and 33). It has been pointed out by Dauerman (Reference 34) that if the experimental activation energies are equated with the energy required to dissociate the first bond, then OF should be twice stronger than OF_2. However, according to Arkell (Reference 35), the rapid disappearance of OF in an argon matrix above 40°K coupled with its exothermic reaction with OF_2 (ca. 12 kcal/mole) indicates that OF is very reactive and will not be present in reaction mixture to any appreciable extent. Bauer and Solomon (Reference 36) used computer analysis to deduce the mechanism of thermal dissociation of OF_2. The following reaction mechanism was assumed in their calculations:

$$OF_2 + M \rightarrow OF + F + M \qquad (\Delta H_{298} = 43 \text{ kcal}) \qquad (1)$$

$$OF + OF + M \rightarrow O_2 + 2F + M \qquad (\Delta H_{298} = -23 \text{ kcal}) \qquad (2)$$

$$F + F + M \rightarrow F_2 + M \qquad (\Delta H_{298} = -38 \text{ kcal}) \qquad (3)$$
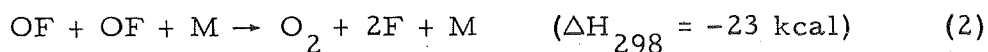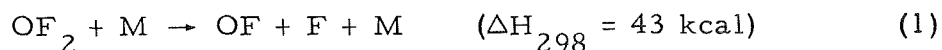
The heats of formation 5.8 and 29.7 kcal are used for OF_2 and OF respectively. Bauer and Solomon found that no combination of Steps 1-3 could give any apparent acceleration in reaction rate unless the activation energy of Step 1 was in the region of

100 kcal/mole, and thus they concluded that the reaction is autocatalytic and proceeds by a chain mechanism.

Besides its fluorine-like reactions, there are a few instances where OF_2 has been reported to form products resulting from simple OF_2 addition to the substrate, such as the addition to SO_2 and SO_3 (References 37 and 38).
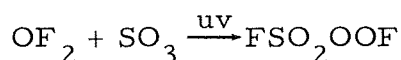
$$OF_2 + 2SO_2 \xrightarrow{\text{uv}} FSO_2OSO_2F$$

$$OF_2 + SO_3 \xrightarrow{\text{uv}} FSO_2OOF$$

The addition of OF_2 to carbonyl fluoride was reported to produce bis(trifluoromethyl)trioxide, and a polar mechanism was suggested (Reference 39). CF_3OOOCF_3 is quite stable at room temperature (References 39 and 40).

$$OF_2 + 2COF_2 \xrightarrow{\text{MF}} CF_3OOOCF_3$$
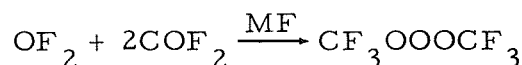
The addition of OF_2 to olefinic bonds were reported to follow by decomposition or rearrangement (References 41 and 42). The reactions of OF_2 and fluoroolefins were reported to occur only when irradiated or heated, and the products did not contain any fluoroalkoxy compound but chiefly acid fluorides and fluorocarbons arising from fragmentation of the intermediates (References 42 and 43). However, low temperature addition of OF_2 to allene was reported to give two products arising from an initial adduct (Reference 44). Sheppard and Sharts stated their doubts of the

14

general utility of OF_2 as a synthetic reagent due to handling hazards (Reference 45).

The utility of OF_2 in addition reactions for chain extensions, modifications of terminal and pendant perfluorovinyl groups of fluoropolymers to introduce functional groups, graft-copolymerizations and addition copolymerizations with perfluorodienes or perfluorodiolefins as new route to synthesize perfluoroalkylene oxide polymers has not been reported in the literature. This original concept of OF_2 as a versatile synthetic reagent and its technology are of particular significance in the field of organofluorine chemistry for syntheses of new fluorine-containing polymers, compounds or monomers, and to achieve previously unobtainable fluoropolymer products and reagents.

The OF_2 reactions with polyperfluorobutadienes can selectively function as chain extenders or introduce functional groups to pendant and terminal perfluorovinyl groups depending upon the reaction temperature. We are currently exploring the scope of this reaction, both in this program and under our company sponsored projects. For this program, we are attempting to establish the factors that favor chain extension over introduction of functional groups, to serve as one of the means to increase the molecular weights of polyperfluorobutadiene without introducing unstable groups or linkages in the presence of fluorine.

The results of reaction of OF_2 with polyperfluorobutadiene indicate the selectivity of the reactions under controlled conditions, as shown in Table I of Appendix D. Temperature appears to be an important

15

factor to increase the molecular weight of polyperfluorobutadiene without introducing acyl fluoride groups. Prolonged exposure of OF_2 extends chemical attack to the vinylene groups to cause chain scission.

Due to the complex reactions of OF_2 with polyperfluorobutadiene (Figure 1 of Appendix D) perfluoro-n-heptene-1 was selected as the model compound to demonstrate some of the suggested reactions and intermediates (see Section 3.2.4).

Section 3

DISCUSSION AND RESULTS

3.1 HOMOPOLYMERIZATION OF PERFLUOROBUTADIENE

The polymerization of perfluorobutadiene was reported by Miller to give rubbery high polymer, when subjected under very high pressure with oxygen or peroxide promotion (Reference 46). In this work, attention is focused on using practical and commercially useful methods of preparing the homopolymer.

From our previous study on a variety of methods to polymerize perfluorobutadiene, we achieved a procedure, which involved homogeneous bulk polymerization in the presence of free radical catalysts under low pressure (i.e., about 2 atm) at ambient temperature or slightly above to obtain solid polyperfluoro-1,2- and 1,4-butadiene (Reference 9). Our major effort for this year was to select one free radical catalyst for this low pressure and temperature method to work out optimum conditions for larger scale preparations.

Optimization was based on consideration of yield, polymer properties, and conditions needed to cause the polymerization to occur. Following the choice of the optimum procedure larger batches were initiated by the selected method (see Appendix C). This was done in order to obtain more material for studies of the properties of polymer, to explore the chain extension process and to learn the factors that influenced the yield in larger scale operations.

Bulk polymerization of perfluorobutadiene under low pressure and temperature by means of bis(trifluoromethyl)peroxide as catalyst was the selected method. The common free radical catalysts such as the alkyl or inorganic peroxides are not free from disadvantages especially in introducing reactive end groups into the polymer chain. The principal advantages of bis(trifluoromethyl)peroxide, CF_3OOCF_3, as initiator is that the polymers are free of end groups to impart chemical and thermal instability and it is also miscible with the monomer to give good yield of the polymer. Thus, the compatibility of CF_3OOCF_3-initiated polyperfluorobutadiene in fluorine was studied to confirm the selection of CF_3OOCF_3 as initiator over other organic peroxides for scale-up preparations of polyperfluorobutadiene (Appendix A).

In order to help define the optimum conditions for preparations of polyperfluorobutadiene using CF_3OOCF_3 as initiator, the screening of process variables such as by means of thermal or photopolymerizations, monomer-catalyst ratio, polymerization time and temperature, etc., were investigated (see Appendixes B and C).

Although a polymer tumbling apparatus capable to produce 1 to 2 pounds of polyperfluorobutadiene by the selected method and catalyst were designed (Figure 1) and built (Figure 2 of Appendix C) to provide agitation, modifications are continuously being introduced to improve yields and properties of the homopolymer before full-scale operations. Each of the twelve large ports of Figure 1 is capable of holding a sealed polymerization tube containing about 100g of the monomer.

18
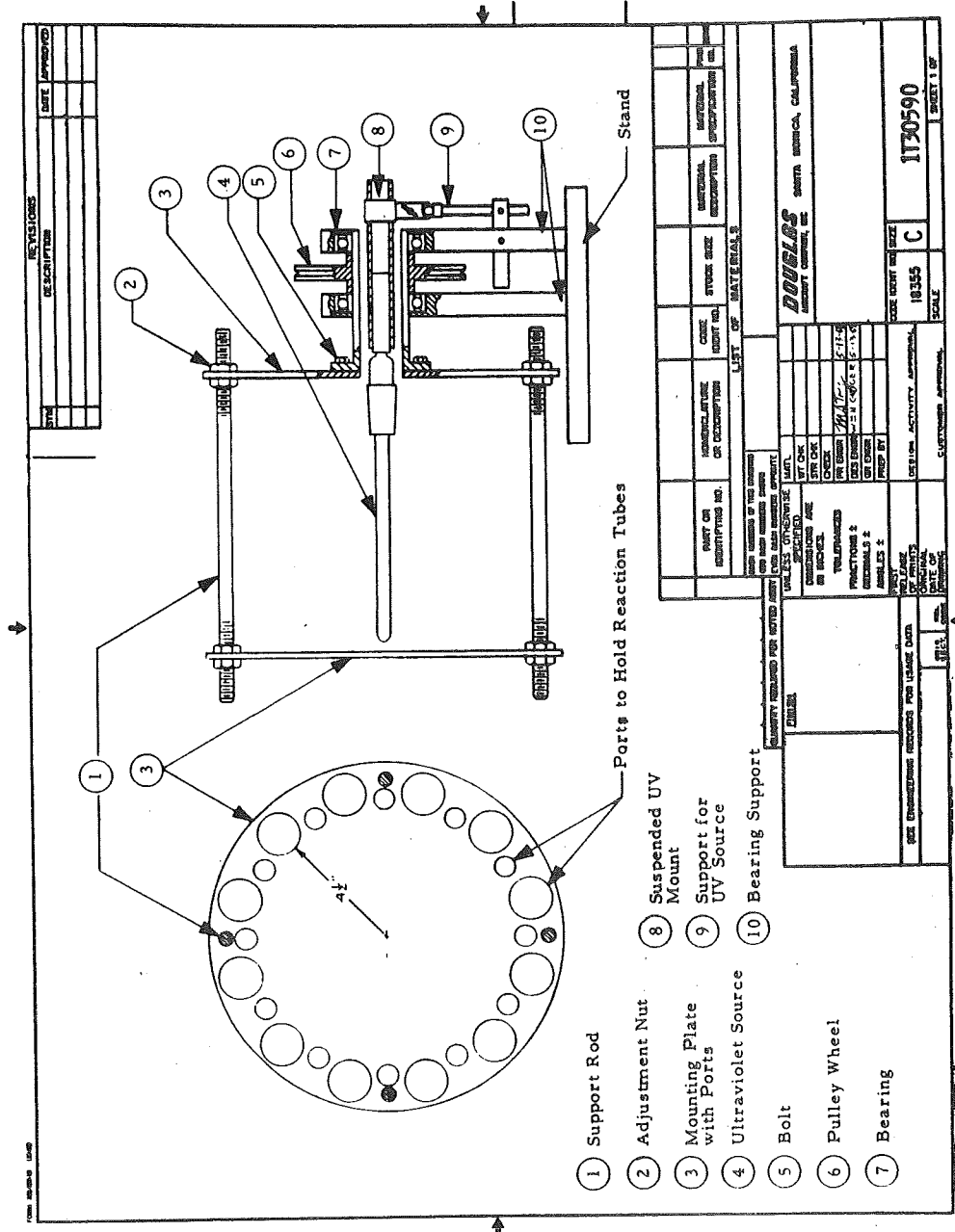
Figure 1. Polymer tumbling apparatus.

Currently, the varied parameters of the selected procedure with CF_3OOCF_3 catalysis are carried out under scale-up operations with the purpose to define optimum and reproducible scale-up conditions and also provide linear homopolymers for chain extension and vulcanization studies.

3.1.1 Larger Scale Polymer Preparation

A polymer tumbling apparatus was designed to provide agitation for larger scale bulk polymerizations under radiation. The centered low pressure mercury arc lamp at 4-1/2 inches distance from the quartz reaction tubes as described in the original design (Figure 1) was too weak and was replaced by two 275-watt sun lamps, which in turn were replaced by a General Electric 400-watt mercury lamp (H400-R33-1) above the apparatus. Currently, a medium pressure mercury arc lamp and cooling system are being designed and built to be installed in the center of the tumbling apparatus. The data described below used the 400-watt mercury lamp.

Table I shows that the infrared absorbance ratio $5.6\mu/5.8\mu$ of the homopolymer increases with an increase of concentration of CF_3OOCF_3 catalyst. Since the pendant perfluorovinyl bonds ($-CF=CF_2$) as a result of 1,2-addition polymerization and the internal perfluorovinylene bonds ($-CF=CF-$) as a result of 1,4-addition polymerization in the polymer structure are signified by the relative intensities of absorptions at 5.6μ for the former and 5.8μ for the latter, the results indicate that under ultraviolet irradiation the 1,2-addition polymerization of perfluorobutadiene can be enhanced by increasing CF_3OOCF_3 concentration.

20

Table I

LARGER SCALE BULK POLYMERIZATION OF PERFLUOROBUTADIENE[a]

Batch No.	Perfluoro-butadiene (g)	CF$_3$OOCF$_3$ as Catalyst (g)	CF$_3$OOCF$_3$ as Catalyst (%)	Product			
				Yield (g)	Conversion[b] (%)	IR Absorbance Ratio 5.6μ/5.8μ	T$_m$[c] (°C)
10222-6-2 (quartz)	52.5	2.5	4.7	20.3	38.7	2.2	132-158
10222-6-4[d] (quartz)	52.4	5.0	9.5	25.4	48.4	3.1	125-158
10222-6-1 (Vycor)	52.6	2.5	4.7	18.8	35.7	2.2	132-160
10222-6-3 (Vycor)	60.3	5.0	8.3	27.6	45.8	2.5	133-157

(a) Under agitation and exposure to a 400-watt mercury lamp at ambient temperature for 2 months.

(b) Based on grams of polymer recovered.

(c) From differential scanning calorimeter of Perkin-Elmer Model DSC-1B.

(d) See Table II for fractionation and properties of fragments.

Table I also shows that the quartz reaction vessels give slight higher yield of the product than Vycor and at higher concentration of CF_3OOCF_3 catalyst the increase of infrared absorbance ratio at $5.6\mu/5.8\mu$ of the homopolymer is also more intensified than using Vycor reaction vessels.

The white solid polymers are not completely soluble in boiling hexafluorobenzene, but are in octafluorotoluene at elevated temperature.

3.1.2 Polymer Fractionation and Characterization of Scale-Up Batch of Polyperfluorobutadiene

One illustrative scale-up batch of polyperfluorobutadiene was selected to fractionate into three fragments for further investigations. The results of the fractionations and viscosity findings were summarized in Table II. A considerable portion (65 wt. % of the total sample) is of medium molecular weight range about 5000 and is soluble in hexafluorobenzene. The lowest molecular weight fraction (10 wt. %) is wax-like and soluble in n-hexane. In particular, the infrared absorption spectrum of this fraction indicates that the wax-like product is ten times richer in 1, 2-moieties than the major fraction.

$$\begin{array}{c} CF \\ \parallel \\ CF_2 \\ \mid \\ \sim\sim\sim(CFCF_2)_x(CF_2CF{=}CFCF_2)_y\sim\sim\sim \end{array}$$
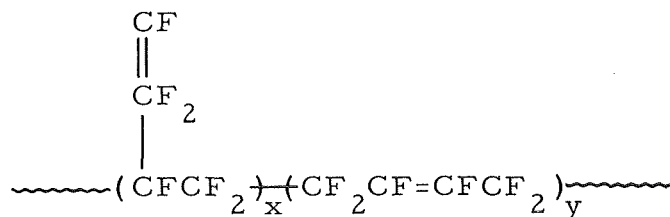
Polyperfluorobutadiene

Table II

FRACTIONATION OF POLYPERFLUOROBUTADIENE[a] BY SOLVENT EXTRACTIONS

Fraction	Condition of Extraction	Method of Drying	Product						
			Yield (g)	Weight (%)	IR Absorbance Ratio 5.6μ/5.8μ	T_m[b] (°C)	[η] (dl/g)	Mw	DP
n-Hexane-soluble fraction (Fraction I)	Soxhlet extraction by n-hexane for 1 hour	Evacuation at ambient for 24 hours	2.2	9.9	4.0	<40	0.008[c]	1,720	10
Hexafluorobenzene-soluble fraction (Fraction II)	Soxhlet extraction by hexafluorobenzene for 10 days	Freeze-drying	14.7	65.2	0.4	79-127	0.021[c]	5,200	32
Hexafluorobenzene-insoluble fraction (Fraction III)		Evacuation at ambient for 48 hours	5.6	25.0	0.6	153-166	0.045[d]	17,000	105

(a) Batch No. 10222-6-4 of Table I.

(b) From differential scanning calorimeter of Perkin-Elmer Model DSC-1B.

(c) In hexafluorobenzene at 65.0°C.

(d) In octafluorotoluene at 90.0°C.

In other words, the numbers of 1,2-polymer repeating unit (x) in the lowest molecular weight fraction is the highest in the integral, while the ratios of x/y for the remaining fractions are approximately the same.

For the last 25 wt. % fractions, the intrinsic viscosity is 0.045 dl/g in octafluorotoluene at 90.0°C. The estimated molecular weight is 17,000 (see Section 3.3.4).

3.1.3 Polymer Initiation Study

During this contract period, a very minor effort was devoted to polymer initiation study, which was carried out in a small scale sealed polymerization tube containing approximately 2 to 3 ml of monomer. Among the initiators explored at ambient temperature were 1% gaseous oxygen, oxygen difluoride and fluorine under ultraviolet irradiation and the former two were also carried out in the dark for 28 days. Commercial cobalt trifluoride, rhodium trichloride and iridium trichloride at 3 to 5% level were placed in a 50 to 60°C bath with the monomer for a month. The yields were 1 to 2% and below, except for fluorine as initiator showed the highest yield of 5% conversion of solid polymer. Due to the ease of flammability for the latter and very poor yields for the others, none of these initiators will be further studied for polymerizations.

The infrared spectra of polyperfluorobutadienes initiated by means of O_2, OF_2 and F_2 are of interest. Figures 2 and 3 show the infrared spectra of oxygen-initiated polyperfluorobutadienes in the dark and under ultraviolet light respectively. The intensity of

24
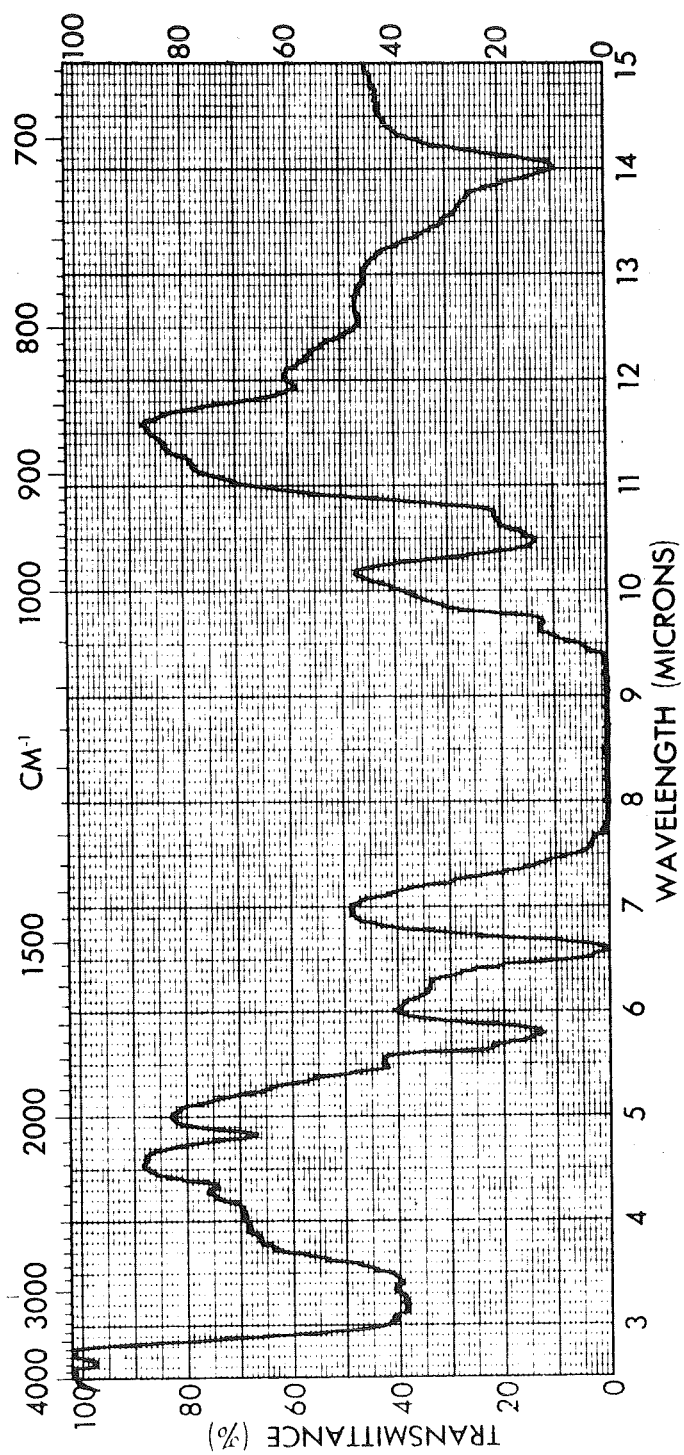
Figure 2. Infrared spectrum of polyperfluorobutadiene initiated by oxygen in the dark.
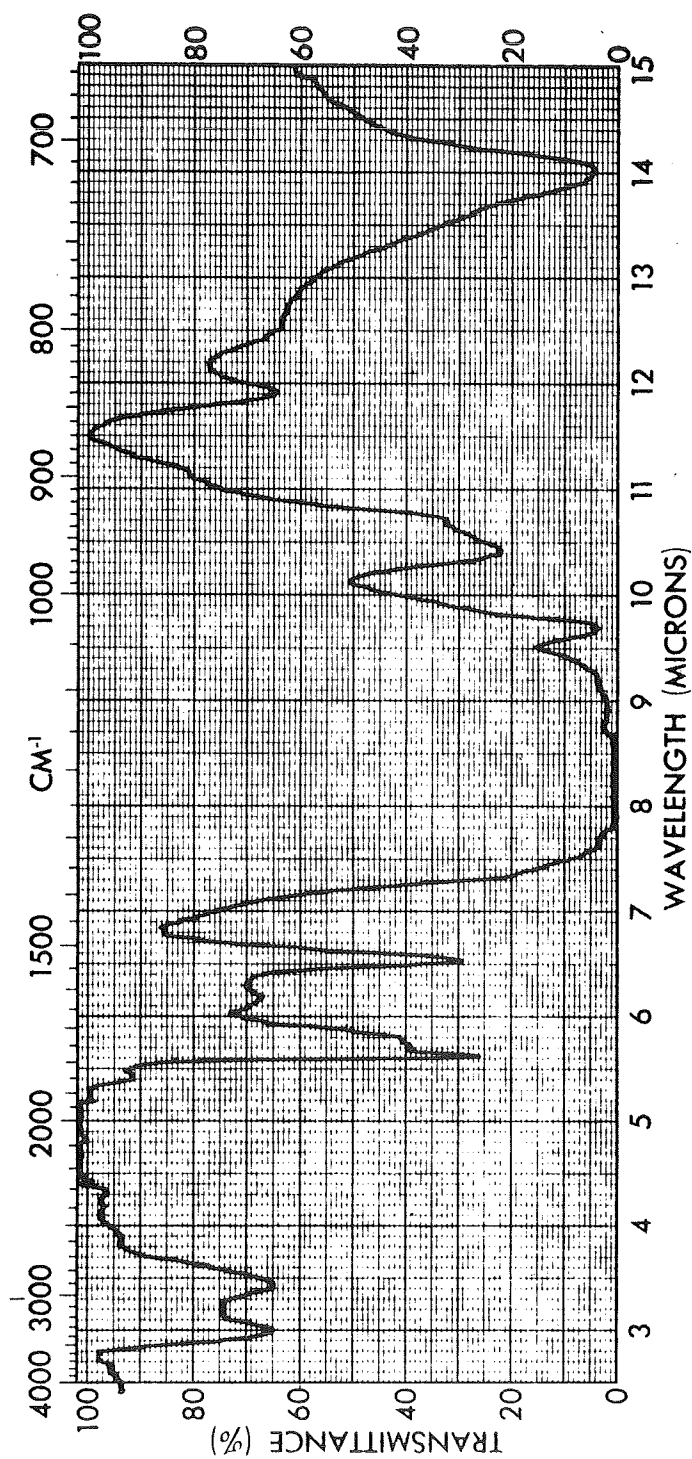
Figure 3. Infrared spectrum of polyperfluorobutadiene initiated by
oxygen under ultraviolet irradiation.

absorbance at 5.6μ is higher for Figure 3 under ultraviolet irradiation and 5.8μ is higher for Figure 2 in the dark. A possible explanation is under ultraviolet irradiation there is higher radical formation and the preference of radical reactions is at perfluoro-vinylene bond; therefore 5.8μ peak is lower for irradiated sample. Both spectra showed the presence of epoxide groups at 6.55μ, but no epoxide groups were detected for OF_2 and F_2 as initiators (Figures 4 and 5).

3.1.4 Photopolymerization of Perfluorobutadiene

See Appendix B.

3.1.5 Thermal Versus Photopolymerization of Perfluorobutadiene by CF_3OOCF_3 Catalysis

See Appendix C.

3.2 UTILIZATION OF OXYGEN DIFLUORIDE FOR FLUORO-POLYMER SYNTHESES

The utilization of oxygen difluoride can be summarized into three categories for fluoropolymer syntheses (see Appendix D):

(1) Chain extension of unsaturated perfluoropolymers

$$2 \sim\!\!\sim\!\!\sim CF{=}CF_2 + OF_2 \rightarrow \sim\!\!\sim\!\!\sim CF_2CF_2OCF_2CF_2 \sim\!\!\sim\!\!\sim$$
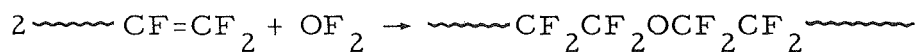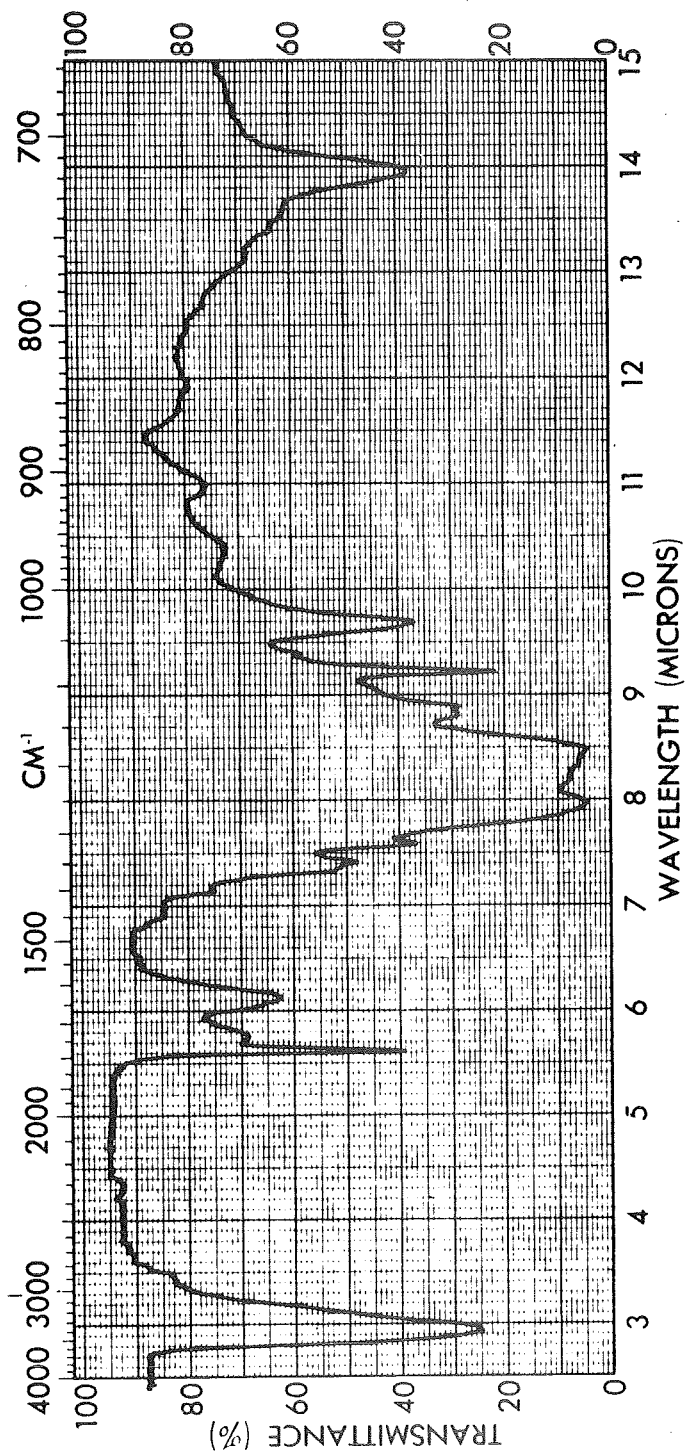
Figure 4. Infrared spectrum of polyperfluorobutadiene initiated by oxygen difluoride under ultraviolet irradiation.
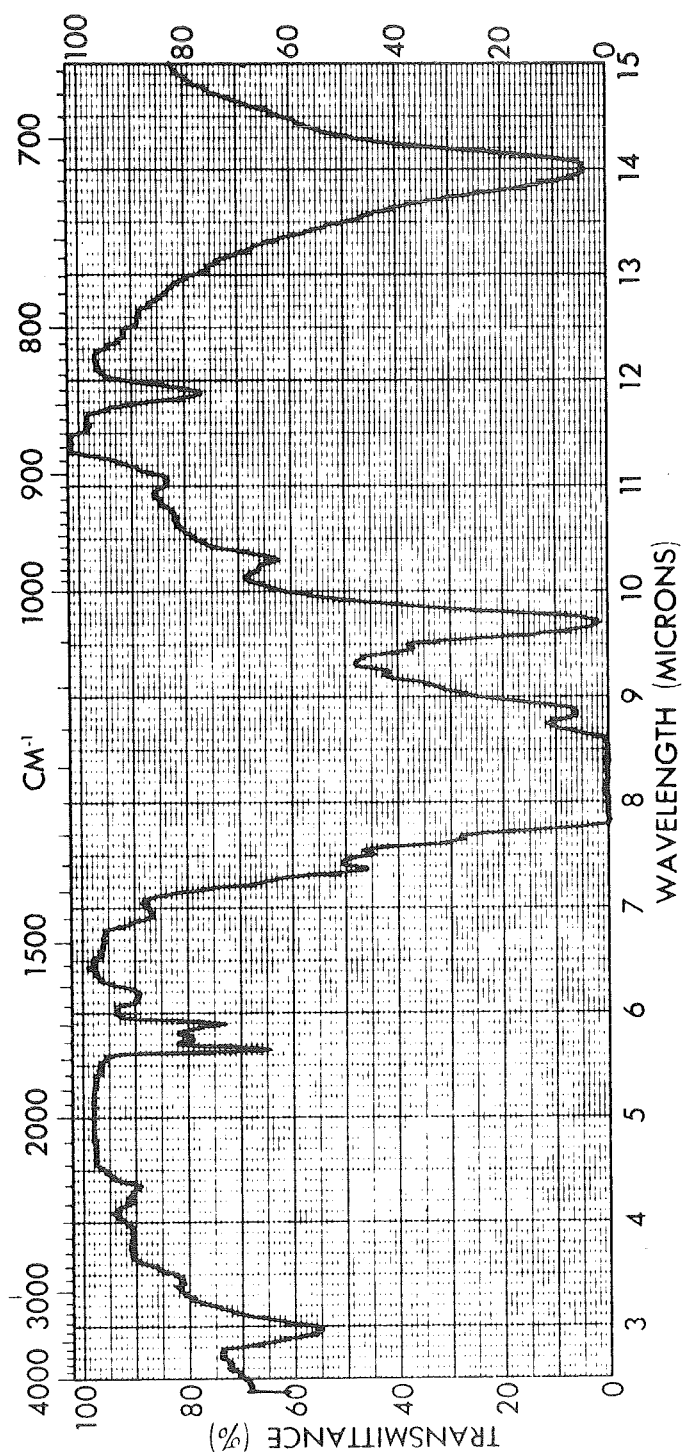
Figure 5. Infrared spectrum of polyperfluorobutadiene initiated by fluorine under ultraviolet irradiation.

29

(2)   Insertion of functional groups into fluoropolymers

$$CF=CF_2 + OF_2 \longrightarrow \left[CF_2CF_2OF \right] \xrightarrow{-F_2} CF_2\overset{\overset{\displaystyle O}{\|}}{C}F + CF-CF_2$$

and
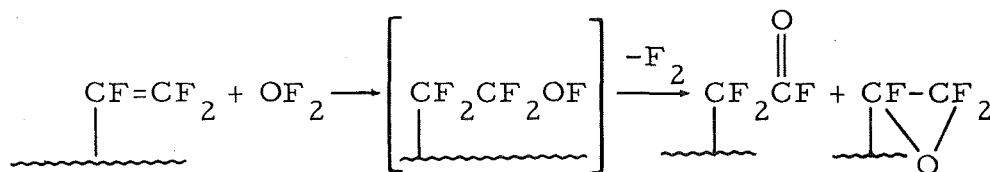
(3)   Addition copolymerization with perfluorodienes or perfluorodiolefins

$$CF_2=CFCF=CF_2 + OF_2 \longrightarrow \left(CF_2CF_2CF_2CF_2O \right)_n$$
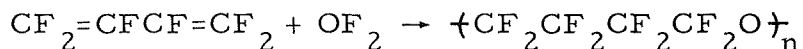
3.2.1   Chain Extension and Insertion of Functional Groups into Polyperfluorobutadiene

The reactions of OF_2 and polyperfluorobutadiene are under study to investigate the effect of experimental parameters such as temperature, molecular weight and condition of starting polymer as freeze-dried solid or as suspension in Freon solvent, the concentration of OF_2 and as static or flow state on changes of properties, molecular weights and functionalities of the products for selection of optimum procedures.   It was thought that a thorough understanding of the process would benefit in establishing guidelines for controlling the selective reactions to occur as chain extender by ether formation or insertion of functionality, range of molecular weight and molecular weight distribution.

Table I of Appendix D established the process as selective under controlled conditions.   Temperature appears to be an important

30

factor in applying the reaction to function exclusively for chain extension or for insertion of acyl fluoride groups into polyperfluoro-butadiene. The presence of acyl fluoride groups in the polymer is detected by infrared absorption at 5.3μ peak. Lower temperatures (0°C and below) favor chain extension without insertion of acyl fluoride groups, while higher temperatures (ambient and above) introduce acyl fluoride groups into the polymer structure without chain extension. The intermediate temperatures modify the products by both increasing chain length and insertion of acyl fluoride and epoxide groups. Upon prolonged OF_2-exposure (usually over one day period at ambient or higher temperatures) chain scission of the polymer with high degree of functionality (acyl fluoride groups) occurs.

Hydrolysis of acyl fluoride polyperfluorobutadiene gives carboxyl polyperfluorobutadiene, which exhibits adhesive properties and is a castable and vulcanizable unsaturated perfluoropolymer between ambient to 100°C

$$\begin{array}{c} \overset{O}{\overset{\|}{C}}-F \\ | \\ CF_2 \\ | \\ +CFCF_2\,\overline{)_x}\,(CF_2CF{=}CFCF_2\,)_y \end{array} \quad \cdot \quad \longrightarrow \quad \begin{array}{c} COOH \\ | \\ CF_2 \\ | \\ +CFCF_2\,\overline{)_x}\,(CF_2CF{=}CFCF_2\,)_y \end{array}$$

| Acyl Fluoride | Carboxyl |
| Polyperfluorobutadiene | Polyperfluorobutadiene |
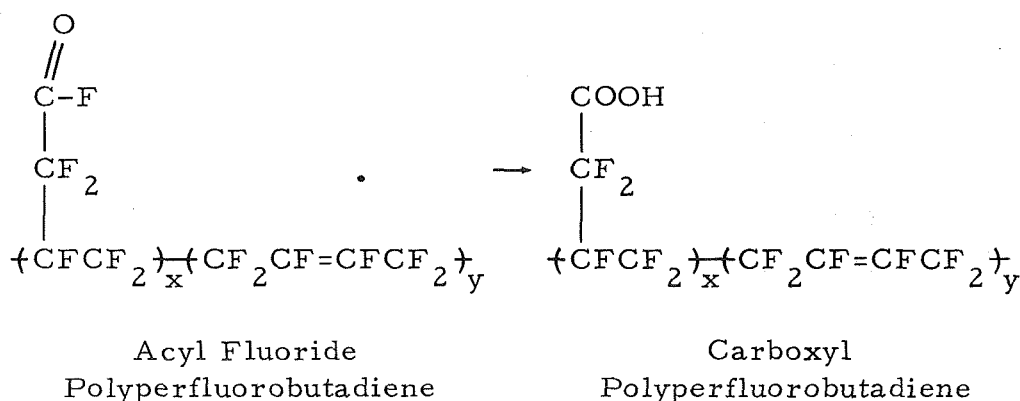
depending on the molecular weight and degree of functionality of the polymer. Figure 6 shows the infrared spectrum of carboxyl poly-perfluorobutadiene, which sticks tenaciously to all surfaces on which it has been tried, including surface-untreated Teflon. When carboxyl polyperfluorobutadiene was used to bond two pieces of surface-untreated Teflon for tensile strength measurement of a composite test piece of aluminum (with 1-in. grit-blasted overlap area)-adhesive-untreated Teflon sheet-adhesive-aluminum for lap shear strength measurement under our company sponsored project, the parting line was in the bulk of adhesive due to cohesional failure, but not at the adhesive-Teflon and adhesive-metal interfaces due to adhesional failure.

In this program, the objective is to establish the factors and conditions that favor chain extension over introduction of functional groups, to serve as one of the means to increase molecular weight of polyperfluorobutadiene without adding groups or linkages to polymers incompatible with liquid fluorine.

The experiments summarized in Table III used the selected conditions to favor chain extension reactions described in Table I of Appendix D, but current scale-up batches of polyperfluorobutadienes, which had been fractionated and characterized, were used as starting polymers. Results described in Table III confirmed that oxygen difluoride can extend current scale-up batches of polymer chain without introducing functional groups, except the reaction temperature will have to be maintained at $0°C$ or lower for over an hour.

32
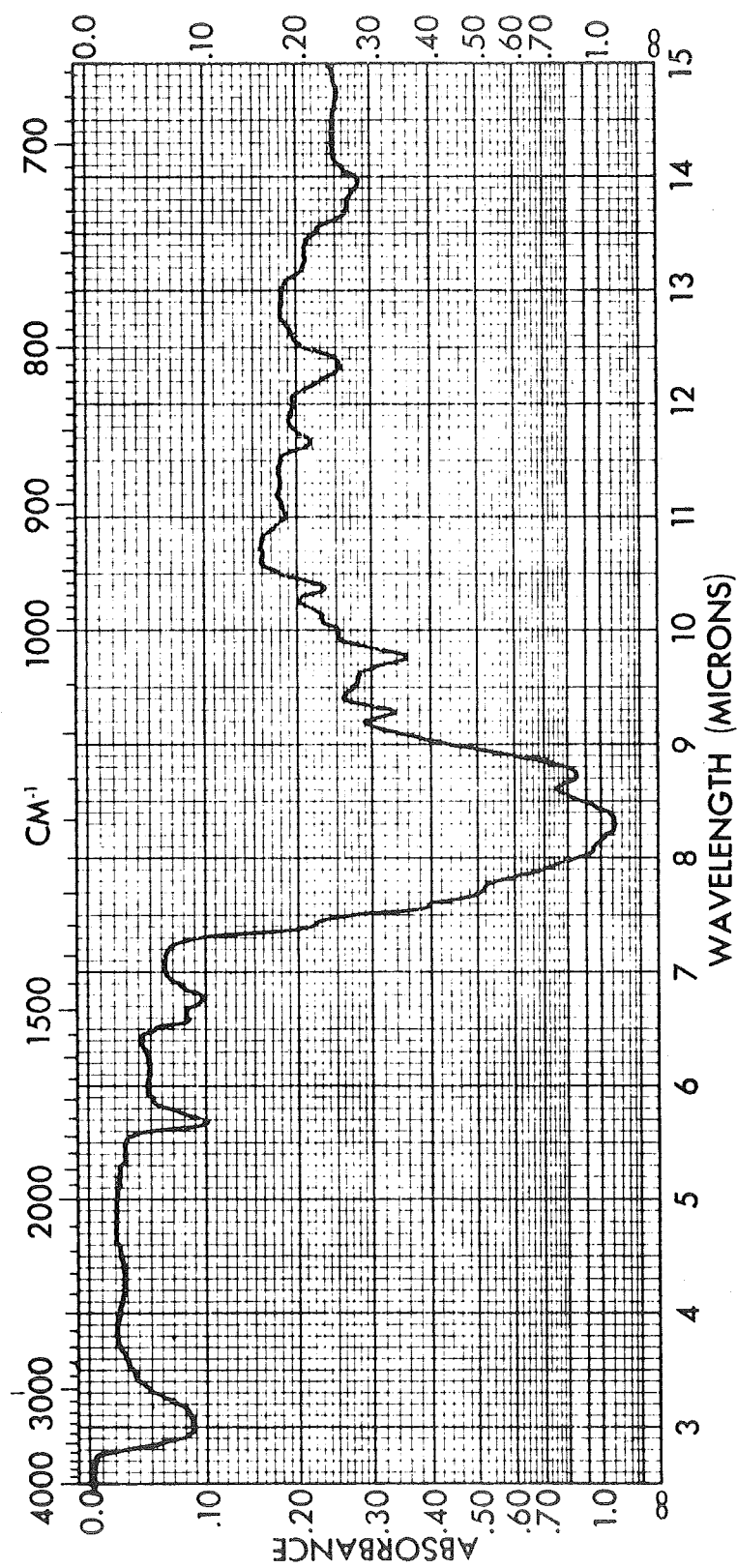
Figure 6. Infrared spectrum of carboxyl polyperfluorobutadiene.

33

Table III

REACTIONS OF OF$_2$ WITH POLYPERFLUOROBUTADIENE

Starting Polymer(a)	OF$_2$				Product						
	Concentration, Flow or Static	Pressure (atm)	Temperature (°C)	Time (hr)	Relative Infrared Peak Among			T$_m$(b) (°C)	$[\eta]$(c) (dl/g)	Mn	DP
					5.3μ O=CF	5.6μ -CF=CF$_2$	5.8μ -CF=CF-				
Freon 113-stirred suspension of batch 10222-5-1B	50% OF$_2$-He, flow	1-1/3	0	1	None	Strong	Medium	107-143	0.021	7,200	44
Ditto	ditto	1-1/3	0	6	Very very weak	Strong	Medium	110-140	0.028	10,000	62
Ditto	ditto	1-1/3	0 to 13	17	Medium	Strong	Strong	98-136	—		
Freon 113-stirred suspension of batch 10222-6-4A	50% OF$_2$-He, flow	1-1/3	0	6	None	Strong	Medium	130-170	0.053	24,000	148

(a) Both are solvent fractionated scale-up batches of polyperfluorobutadiene by CF$_3$OOCF$_3$ catalysis: No. 10222-5-1B as hexafluorobenzene-soluble fraction, Tm 118-145°C, $[\eta]$.021 in octafluorotoluene at 90°C, Mol. wt. 7,200 and No. 10222-6-4A as hexafluorobenzene-insoluble fraction (Fraction III of Table II), $[\eta]$.045, Mol. wt. 17,000.

(b) From differential scanning calorimeter of Perkin-Elmer Model DSC-1B.

(c) In octafluorotoluene at 90°C.

The effect of reaction time versus increments of chain-length, the molecular weight of starting polymer versus the glass transition temperature of chain extended polymer and the vulcanized chain-extended product will definitely warrant investigations in order to select optimum parameters and recommend procedures to obtain desirable chain length, molecular weight distribution and flexibility of the primary polymer chains for elasticity of the vulcanized products.

3.2.2 Mechanism of Reaction Between Oxygen Difluoride and Polyperfluorobutadiene

There is excellent supporting experimental evidence reported in the literature to help clarify the importance of inductive effect of perfluoroalkyl groups in a highly fluorinated aliphatic system, where fluorine or anion hyperconjugation is not important. Andreades (Reference 47) showed that the rate of deuterium exchange varied by a factor of 1 to 10^9 from a series of compounds in the order of CF_3H, $C_6F_{13}CF_2H$, $(CF_3)_2CFH$ to $(CF_3)_3CH$. Streitwieser and Holtz (Reference 48) added another fluorocarbon hydride to the list and showed

$$
\begin{array}{c}
\overleftarrow{\quad} \\
CF_2 \\
FC \qquad CH \\
CF_2\text{-}CF_2 \\
CF_2\text{-}CF_2
\end{array}
$$
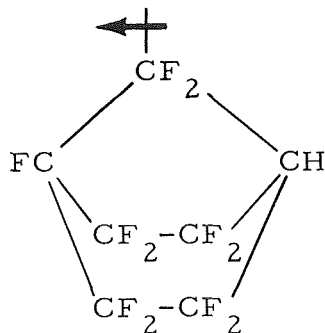
a five-fold increase of the relative rate of proton exchange to 5×10^9. The bridgehead fluorocarbon hydride can be viewed as the "inductive" model of Andreade's $(CF_3)_3CH$. The increase of its acidity confirms the significant influence of inductive effect of perfluoroalkyl group over fluorine or anion hyperconjugation effect in a highly fluorinated aliphatic system.

Consequently, according to inductive effect the carbon constituting the more nucleophilic terminus of the pendant perfluorovinyl groups of polyperfluorobutadiene is not the terminal difluoromethylene carbon $(CF_2=)$ but the carbon atom attached to the terminal difluoromethylene carbon, where the nucleophilic receptive (or electrophilic) fluorine of OF_2 should be linked to afford fluoroxy polyperfluorobutadiene as the product.

(1)

Fluoroxy Polyperfluorobutadiene
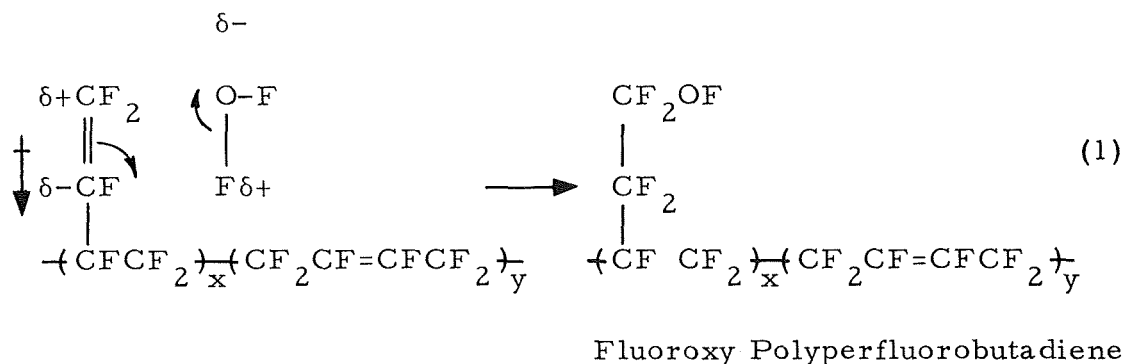
The results from the ESR study of reaction between oxygen difluoride and polyperfluorobutadiene (Figure 7) indicate that the formation of polyperfluorobutadiene radicals by means of OF_2 is likely due to secondary reaction. We believe that the primary reaction is an addition reaction without free-radical involvement by polar mechanism as shown by Equation 1.
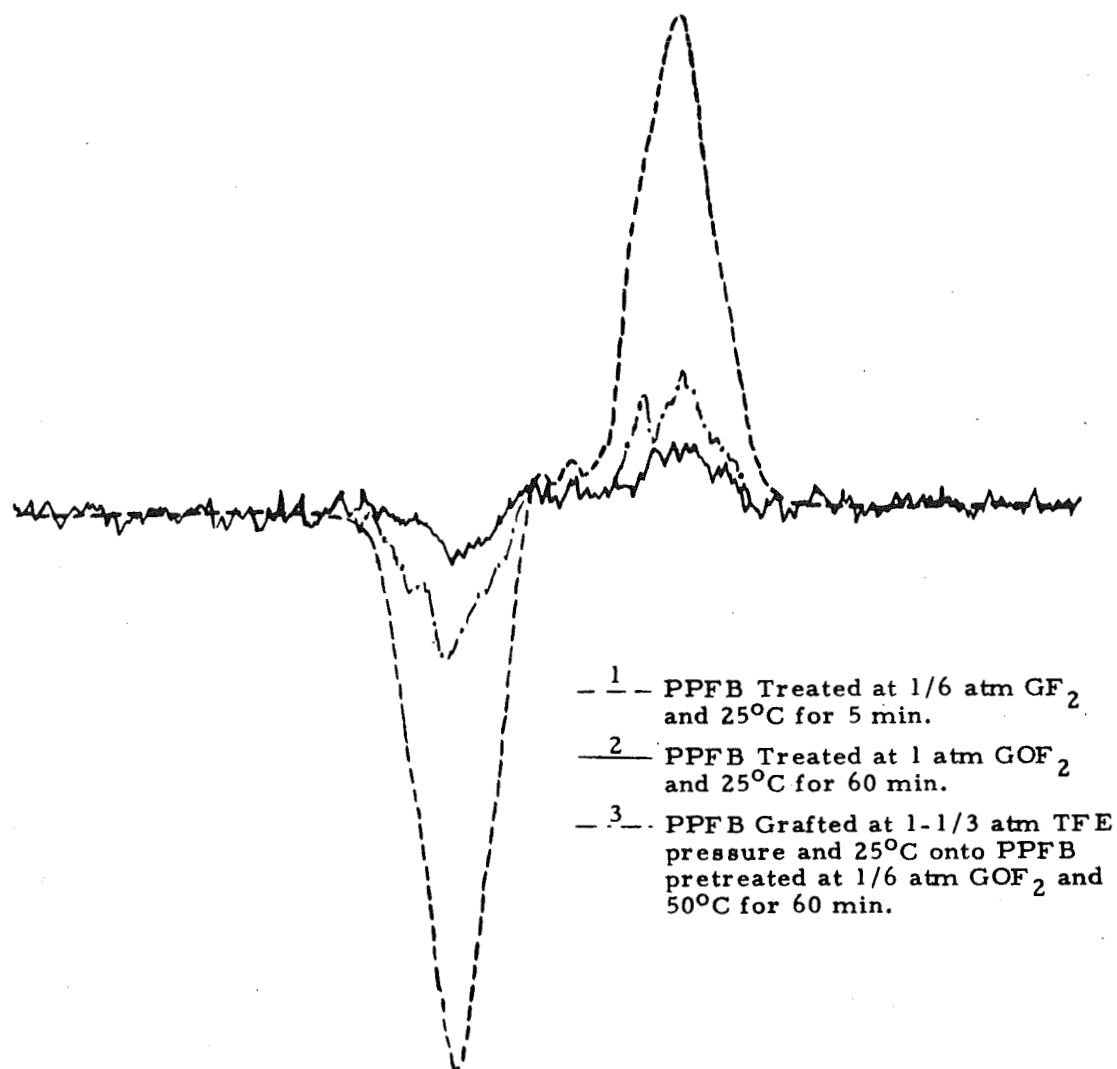
Figure 7. ESR spectra of F_2 and OF_2 treated polyperfluorobutadiene (PPFB) and polytetrafluoroethylene (PTFE) grafted PPFB.

Legend:

— 1 — PPFB Treated at 1/6 atm GF_2 and 25°C for 5 min.

— 2 — PPFB Treated at 1 atm GOF_2 and 25°C for 60 min.

— 3 —. PPFB Grafted at 1-1/3 atm TFE pressure and 25°C onto PPFB pretreated at 1/6 atm GOF_2 and 50°C for 60 min.

The radical-initiator is the fluorine molecule as a result of elimination reaction of pendant fluoroxy to acyl fluoride groups (Equation 2).

$$\text{Fluoroxy Polyperfluorobutadiene} \xrightarrow{50°C} \begin{array}{c} C \diagdown^O \\ | \diagdown^F \\ CF_2 \\ | \\ \end{array} + F_2 \qquad (2)$$

$$+CFCF_2)_x (CF_2CF=CFCF_2)_y$$

Acyl Fluoride Polyperfluorobutadiene
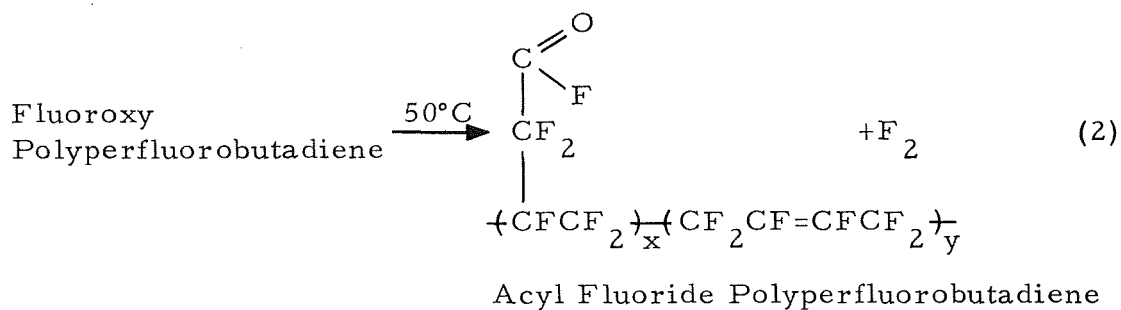
The assumed fluoroxy-containing polyperfluorobutadiene, which acts as a potential fluorine source at ambient or above 0°C, eliminates molecules of fluorine after the ESR tube has been evacuated or vacuum-sealed.

The reaction of fluorine molecule with olefinic bond was reported by Miller and Koch (Reference 18) to produce a fluorinated free radical and a fluorine atom. Thus, the eliminated fluorine molecule from Equation 2 also generates fluorocarbon radical from unsaturated bonds of the polymer (Equation 3) to graft-copolymerize with tetrafluoroethylene (Equation 4) as well as to homopolymerize

tetrafluoroethylene to form polytetrafluoroethylene radical and
fluorine atom (Equation 5).

$$\text{Acyl Fluoride Polyperfluorobutadiene} + F_2 \longrightarrow \begin{array}{c} C\overset{\displaystyle O}{\underset{\displaystyle F}{\diagup\!\!\diagdown}} \\ | \\ CF_2 \\ | \\ \!\!-\!\!(CFCF_2)_x\!\!-\!\!(CF_2CF_2\overset{\bullet}{C}FCF_2)_y\!\!- \end{array} \quad +F\!\cdot \quad (3)$$

Acyl Fluoride Polyperfluorobutadiene
Radical

$$\text{Acyl Fluoride Polyperfluorobutadiene Radical} + nCF_2\!=\!CF_2 \longrightarrow \begin{array}{c} C\overset{\displaystyle O}{\underset{\displaystyle F}{\diagup\!\!\diagdown}} \\ | \\ CF_2 \\ | \\ \!\!-\!\!(CFCF_2)_x\!\!-\!\!(CF_2CF_2CFCF_2)_y\!\!- \\ | \\ (CF_2CF_2)_{n-1}CF_2\overset{\bullet}{C}F_2 \end{array} \quad (4)$$

$$F_2 + nCF_2\!=\!CF_2 \longrightarrow F(CF_2CF_2)_{n-1}CF_2CF_2\!\cdot\, + F\!\cdot \quad (5)$$
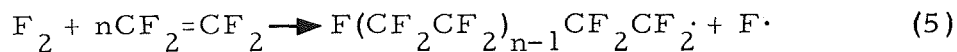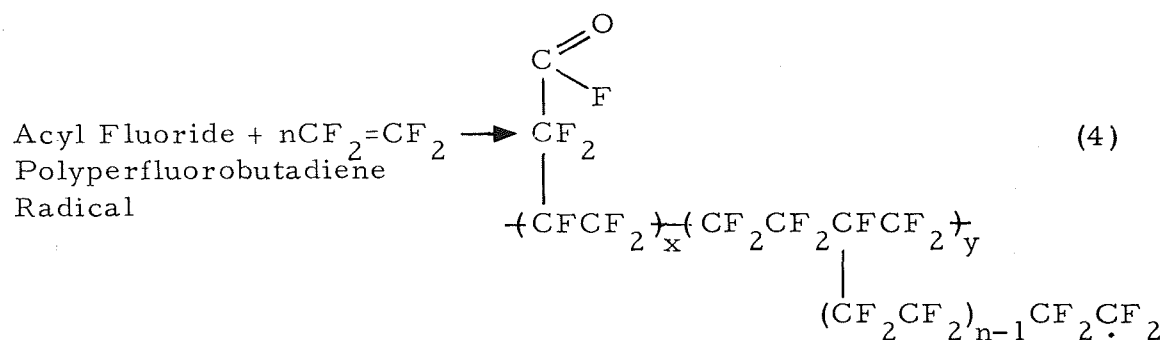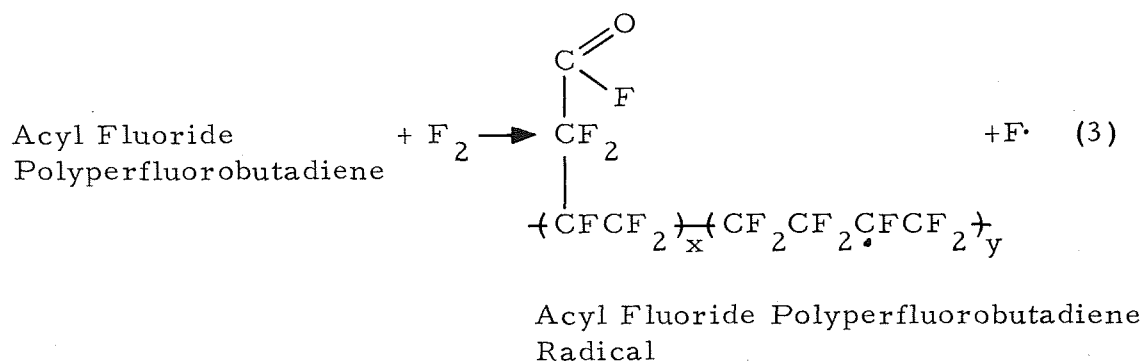
The generated fluorine atoms that result from Equations 3 and 5
are also initiators of fluorocarbon radicals (Equations 6 and 7).

$$F\!\cdot\, + nCF_2\!=\!CF_2 \longrightarrow F(CF_2CF_2)_{n-1}CF_2CF_2\!\cdot \quad (6)$$

$$F\cdot + \text{Acyl Fluoride}$$

$$\text{Polyperfluorobutadiene} \longrightarrow \begin{array}{l} \text{Acyl Fluoride} \\ \text{Polyperfluorobutadiene} \\ \text{Radical} \end{array} \qquad (7)$$
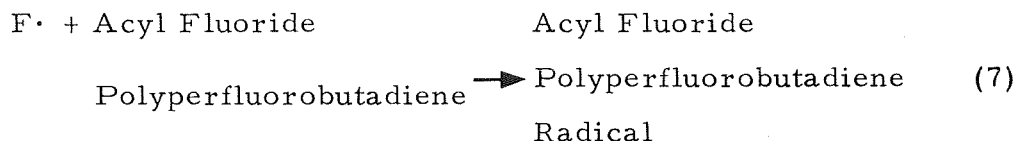
The Equations 3 and 5 followed by 6 and 7 may explain an increase of radical content of curve 3 of Figure 7, after exposure to tetra-fluoroethylene. Otherwise, a decrease (due to crosslinking) or equivalent radical content after tetrafluoroethylene vapor-exposure is expected. When low concentration of elemental fluorine (1/6 atm) was directly exposed to polyperfluorobutadiene, followed by evacuation, exposure to tetrafluoroethylene vapor and evacuation, the decreased ESR signal was reported (Reference 17).

The results of no ESR signal after exposure of polyperfluorobutadiene to 1/6 atm gaseous OF_2 at 25°C for 5 minutes and slight ESR signal after prolonged exposure of polyperfluorobutadiene to 1 atm gaseous OF_2 for 60 minutes at 25°C to a slight increase at 50°C indicate that prolonged reaction time and an increase of temperature increase the radical content. However, the degree of radical content formed by eliminated fluorine molecules as result of secondary reaction cannot compare with the high radical content after direct exposure to 1/6 atm of elemental fluorine for 5 minutes (Figure 7).

The fluorine elimination reactions involve the removal of two fluorine atoms. One fluorine atom is from the fluoroxy group and the other fluorine atom is either from α-carbon to give acyl fluoride or from β-carbon to give epoxide group as shown by Equations 8 and 9 respectively.

40

$$R_f-\underset{\beta}{C}F_2-\underset{\alpha}{C}F_2OF \overset{-F_2}{\longrightarrow} R_f-CF_2-\overset{\overset{\displaystyle O}{\|}}{C}F \qquad (8)$$

$$\alpha-F \text{ elimination}$$

I

$$\overset{-F_2}{\longrightarrow} R_f-CF\underset{\diagdown \underset{O}{\diagup}}{}CF_2 \qquad (9)$$

$$\beta-F \text{ elimination}$$
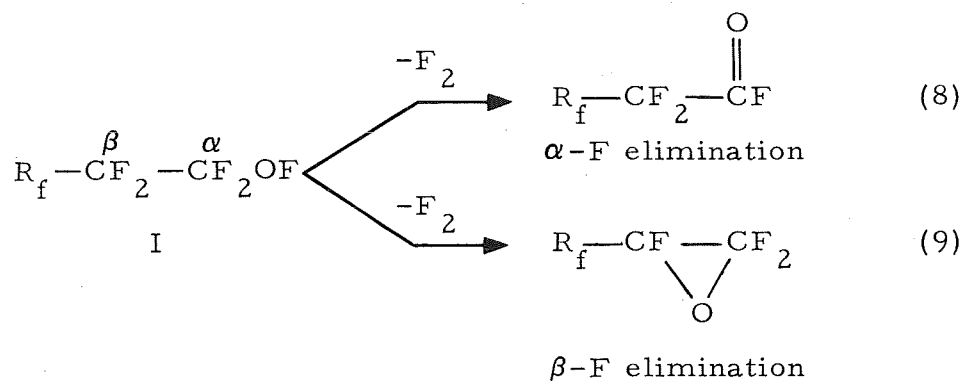
In consideration of the steric factors involved, the preferred conformation of structure (I) is with the two bulky groups, OF and R_f, trans to each other as $R_f-C_\beta-C_\alpha-OF$ lying in one plane. The trans-configuration:

or
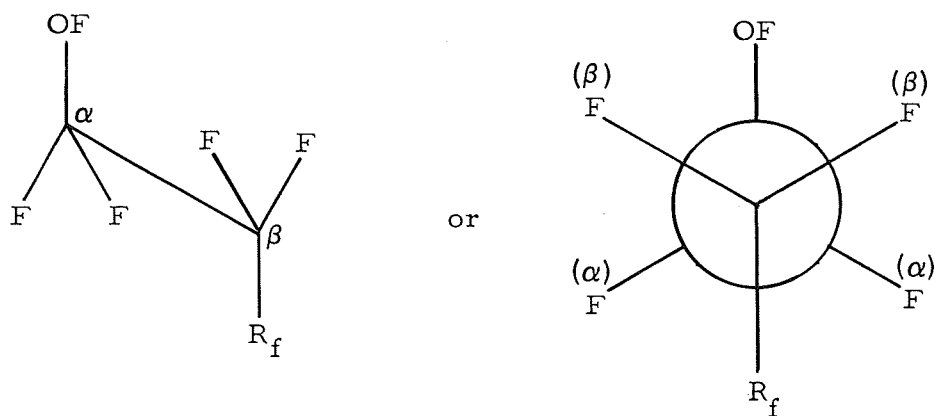
is the most probable orientation corresponding to the lowest energy.

The assumed fluoroxy group of the planar trans configuration exists in two conformations (Ia and Ib):
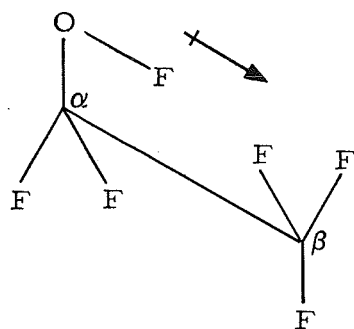
Ia
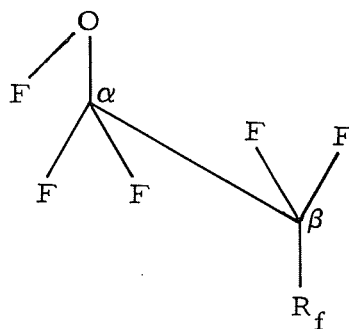
Ib

The maximum ease of fluorine elimination for structure Ia is β–F elimination to form epoxide compound (Equation 9 or 10) and for structure Ib is α–F elimination to form acyl fluoride compound (Equation 8 or 11).

Ia   Epoxide

$$+ F_2 \qquad (10)$$

α-F elimination

+F$_2$

(11)

Ib   Acyl Fluoride
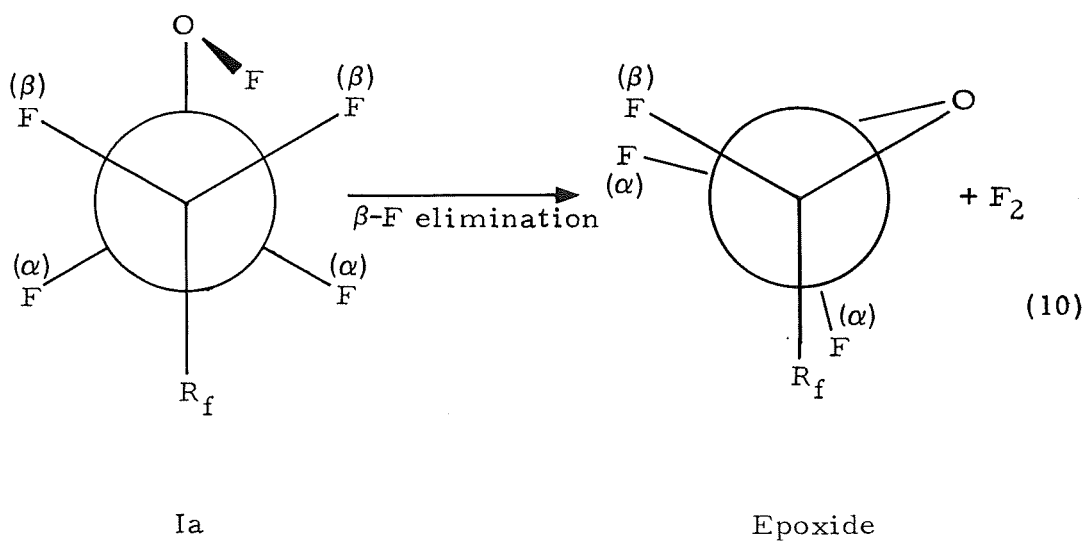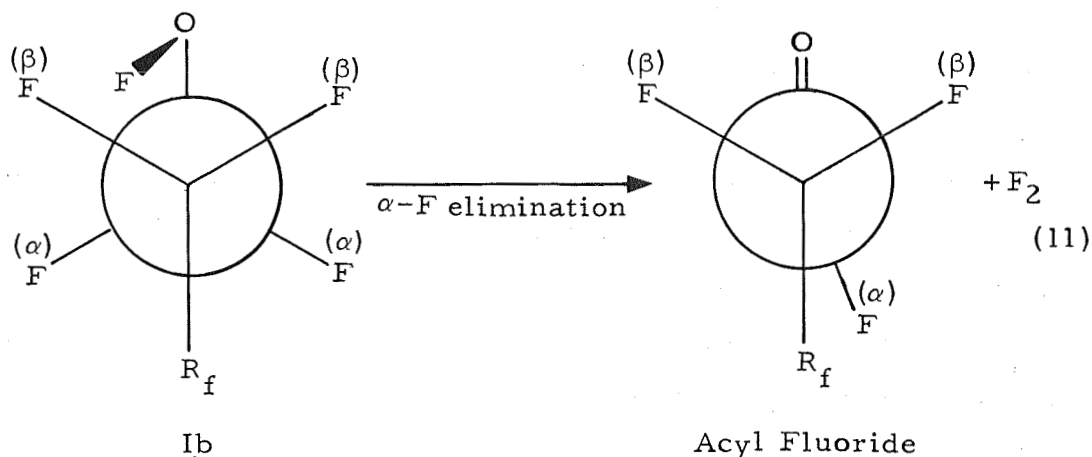
In the reaction of the two conformations of the planar five-centered $(R_f-C_\alpha-C_\beta-O-F)$ trans configuration, the ratio of the rates of reaction of each individual conformation depends upon the free energy difference between the two conformational structures (Ia and Ib). It would be expected that the free energy of Ia would be less than that of Ib because of the strong inductive effect exerted by the perfluoroalkyl group on the nucleophilic receptive fluorine of the fluoroxy group.

From the conformational concept and the demonstrated strong inductive effect of the perfluoroalkyl groups (Reference 48), one can predict the relative rates of epoxide formation, which should occur more readily or at lower temperature than acyl fluoride formation.

Preliminary results from reactions between OF$_2$ and polyperfluoro-butadiene and between OF$_2$ and perfluoro-n-heptene-1 around 0°C indicated selective preference of epoxide formation and for acyl fluoride group at ambient temperature and above.

3.2.3 Addition Copolymerization of Perfluorobutadiene and Oxygen Difluoride

A novel copolymerization reaction, which involves the addition copolymerization of oxygen difluoride with perfluorodiene or perfluorodiolefin, has been originated. Oxygen difluoride reacts with terminal difluoromethylene, $CF_2=$, group by step-wise addition to give the adduct of two moles of perfluoro-α-olefin with one mole of OF_2. By controlling the reaction temperature at 0°C and below, chain extension of polyperfluorobutadiene has been achieved (Table III).
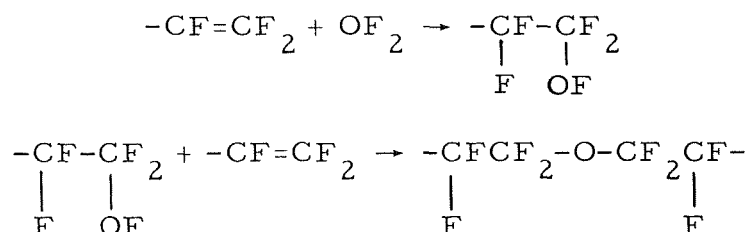
$$-CF=CF_2 + OF_2 \rightarrow -\underset{\underset{F}{|}}{C}F-\underset{\underset{OF}{|}}{C}F_2$$

$$-\underset{\underset{F}{|}}{C}F-\underset{\underset{OF}{|}}{C}F_2 + -CF=CF_2 \rightarrow -\underset{\underset{F}{|}}{C}FCF_2-O-CF_2\underset{\underset{F}{|}}{C}F-$$

The foregoing example strengthens our contention that oxygen difluoride behaves as a difunctional reagent with perfluoroalkenes, it seems likely that copolymerization of OF_2 with perfluorobutadiene would be feasible as shown below:

$$nCF_2=CFCF=CF_2 + nOF_2 \rightarrow n\left[CF_2=CF\underset{\underset{F}{|}}{C}F-\underset{\underset{OF}{|}}{C}F_2\right] \rightarrow +CF_2CF_2CF_2CF_2O \xrightarrow{}_n$$
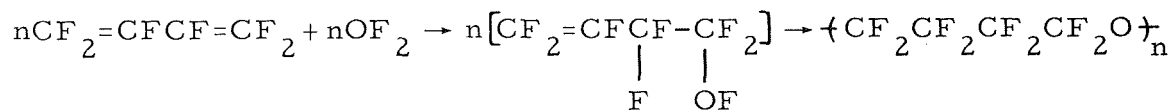
The product of such intermolecular additions is poly(perfluorotetramethylene oxide).

The 3M Company reported the synthesis of poly(perfluorotetramethylene oxide) by photopolymerization of perfluorooxydipropionyl

fluoride under Air Force contracts. The perfluoroalkylene oxide polymers containing $+OCF_2CF_2CF_2CF_2 +$ units showed excellent low- and high-temperature properties: Tg was below -65°C (-85°F), no change was noted below 380°C (716°C) and 10% weight loss in air was observed thermogravimetrically at 515°C (959°F) (Reference 49). However, the crude monomer $FCCF_2CF_2OCF_2CF_2CF$ was unable to be purified beyond 73% purity by distillation; thus a chemical purification scheme was employed by the 3M workers involving alkaline hydrolysis, precipitation, distillation of the acid form, chlorination by thionyl chloride, and finally treatment with anhydrous potassium fluoride to reach a 99% purity of isomeric mixtures of their monomer. In the case of the addition copolymerization approach, both oxygen difluoride and perfluorobutadiene are commercially available in 99% purity.

When addition copolymerization of perfluorobutadiene (m. p. -132°C and b. p. 6. 6°C) and oxygen difluoride (m. p. -223. 8°C and b. p. -145. 3°C) was carried out by repeated alternate condensations of small amounts of reactants followed by warming to -70°C and ambient temperature. The oxygen difluoride was readily miscible and reacted with perfluorobutadiene to form a clear liquid, which had one fraction which was not volatile at ambient temperature. Its infrared spectrum (Figure 2 of Appendix D) is almost identical to 3M Company's acid carboxylic terminated poly(perfluorotetramethylene oxide) as shown in Figure 8, although 3M's poly(perfluorotetramethylene oxide) was synthesized entirely from another route by photopolymerization of perfluorooxydipropionyl fluoride.

POLY(PERFLUOROTETRAMETHYLENE OXIDE)

HOOCCF$_2$CF$_2$[O(CF$_2$)$_4$]$_n$CF$_2$OCF$_2$CF$_2$COOH

m$_n$ =2000

FUNCTIONALITY = 2.2

ABSORBANCE

WAVELENGTH (MICRONS)

CM^{-1}
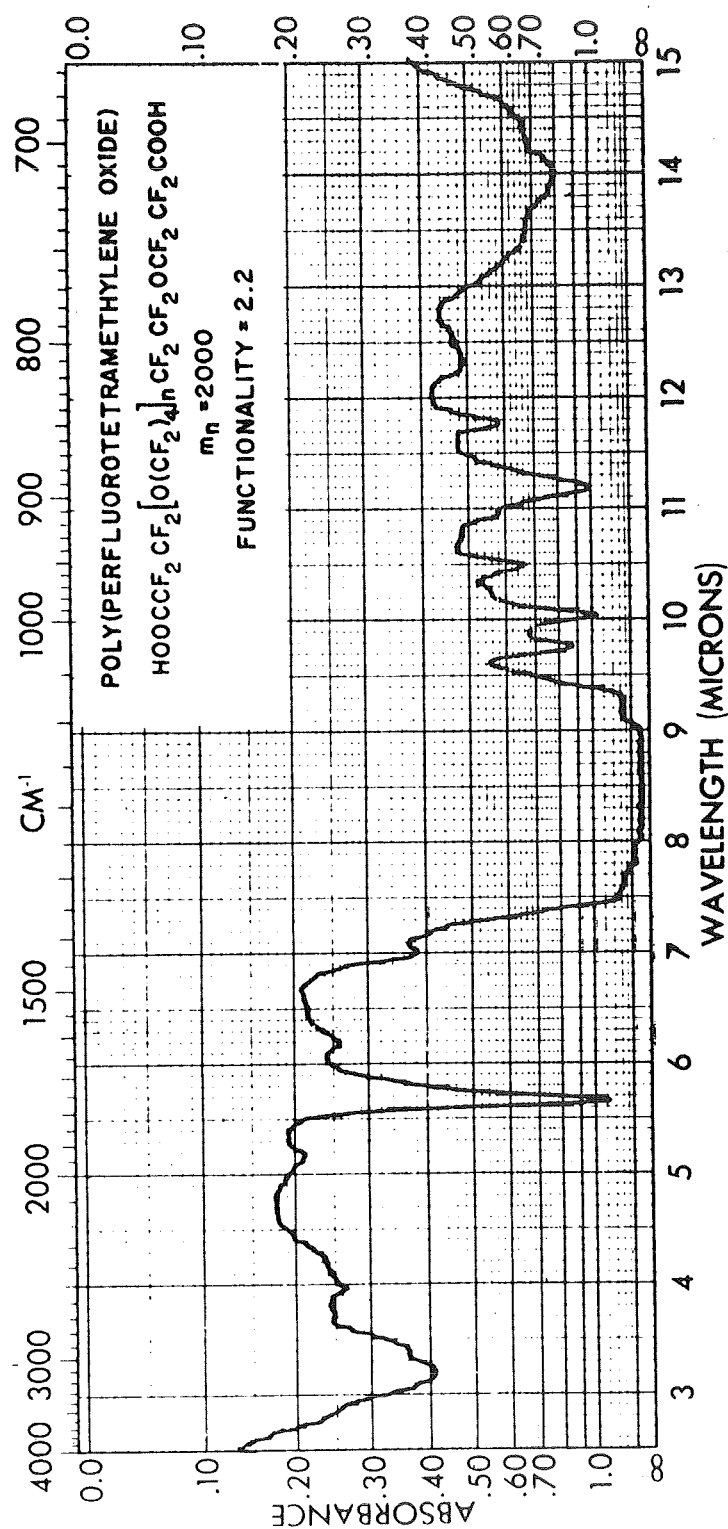
Figure 8.   Infrared spectrum of carboxyl terminated poly(perfluorotetramethylene oxide).

Upon further investigation of the copolymerization reaction using oxygen difluoride as comonomer (see Section 4.2.3), white solid polymer (m.p. 137-167°C dec.) was obtained. Figure 9 shows the infrared spectrum of the copolymer, which is insoluble in hexafluorobenzene and 3M Brand Fluorochemicals FC-75 and FC-43.

3.2.4 Chemistry of Oxygen Difluoride with Terminal and Internal Perfluoroolefinic Bonds

In order to design and recommend scale-up optimum procedure for the OF_2-chain extension process of polyperfluorobutadiene, the chemistry of OF_2 with the polymer's two different types of olefinic bonds: (1) the internal vinylene bonds, $-CF=CF-$, and (2) the pendant vinyl bonds, $-CF=CF_2$, must be completely understood and clarified. Due to the complexity of reactions between the polymer and OF_2, two model compounds were selected to simplify the situation for expedient understandings and to demonstrate the varied reactions actually taken place under the different conditions.

Perfluorocyclopentene, which contains the internal vinylene bond, and perfluoro-n-heptene-1, which contains the terminal vinyl bond, were reacted with oxygen difluoride under identical conditions at -78°C followed by 0°C. Perfluorocyclopentene was totally recovered and unchanged, but there is a definite reaction taken place in case of perfluoro-n-heptene-1. This experiment affirms our previous deduction that OF_2 reacts more readily with the pendant vinyl bonds in the polymer than the internal vinylene bonds. It also demonstrates that the chain extension of polyperfluorobutadiene can be achieved by stable ether linkages under controlled conditions.
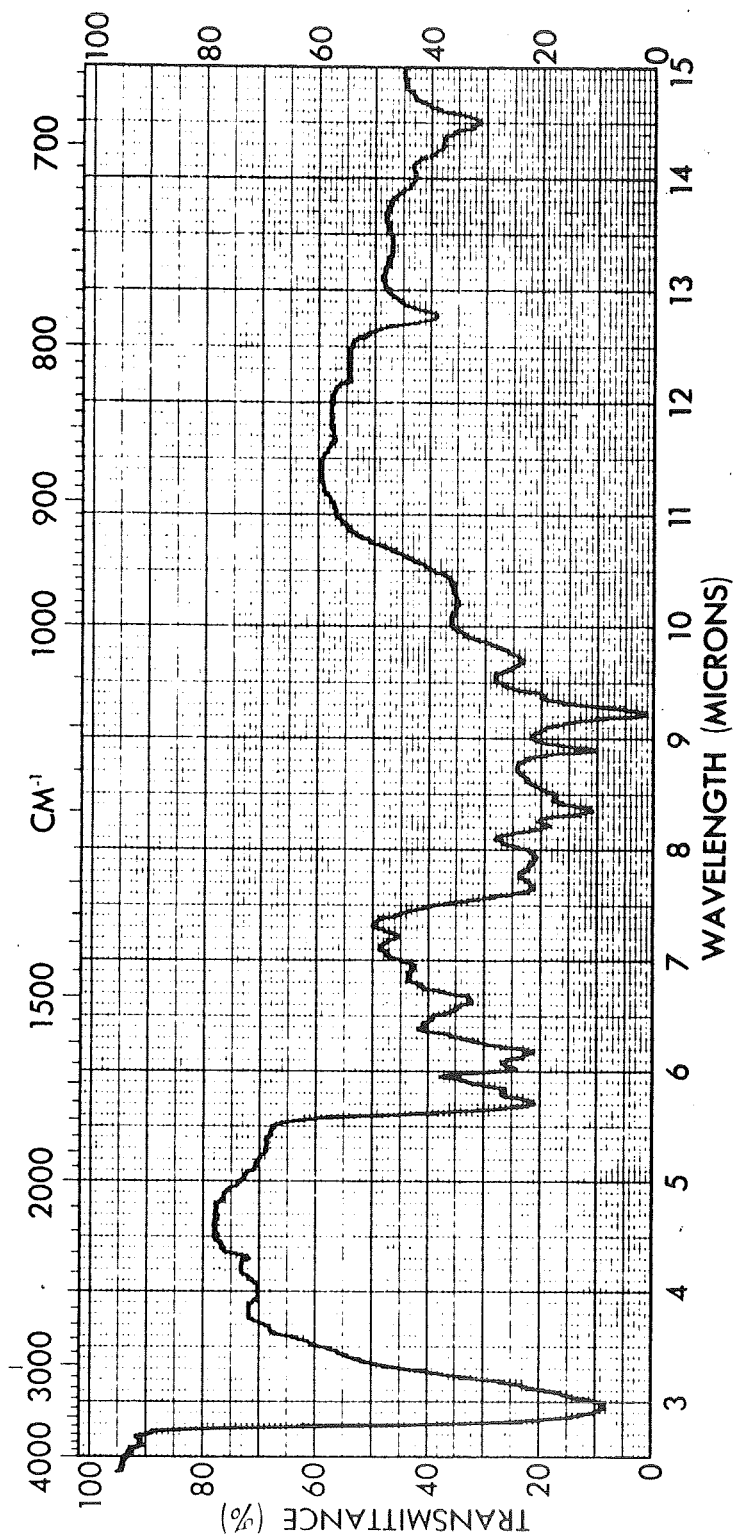
Figure 9. Infrared spectrum of copolymer of perfluorobutadiene and oxygen difluoride.

48

Figure 10 shows the infrared spectrum of the products from reaction of OF_2 and perfluoro-n-heptene-1. Upon fractionations, 1,2-epoxyperfluoro-n-heptane (Figure 11) and bis(perfluoro-n-heptyl) ether (Figure 12) were isolated. The molecular weight of bis(perfluoro-n-heptyl)ether was determined by Dr. D. L. Hildenbrand using his torsion-effusion apparatus (Reference 50) based on vaporization of the material. The reactions of OF_2 and perfluoro-n-heptene-1 are summarized in Figure 13.

3.3 POLYMER CHARACTERIZATION

3.3.1 Glass Transition Temperature

The glass or second-order transition (Tg) is defined as the transformation temperatures of elastomers to brittle glasslike substances on cooling and conversely brittle plastics to elastomers on heating (Reference 51). These transition temperatures (Tg) are dependent on polymer structures (Reference 52). Flexible polymeric chains with small interactions between the chains have the lowest values of Tg and hence retain their elasticity to the lowest temperatures. If Tg is sufficiently low, an elastomer is produced. For example, poly(thiocarbonyl fluoride) is a highly resilient elastomer, which becomes brittle at $-118°C$ (References 53 and 54). Here the C-S chain linkages provide ready rotation and the external field of the CF_2 groupings ensures small polymer-polymer interactions; except at higher temperatures the polymer unzips to regenerate monomer. The Tg of nitroso rubber (one-to-one copolymer of trifluoronitrosomethane and tetrafluoroethylene) is $-51°C$ (Reference 2)
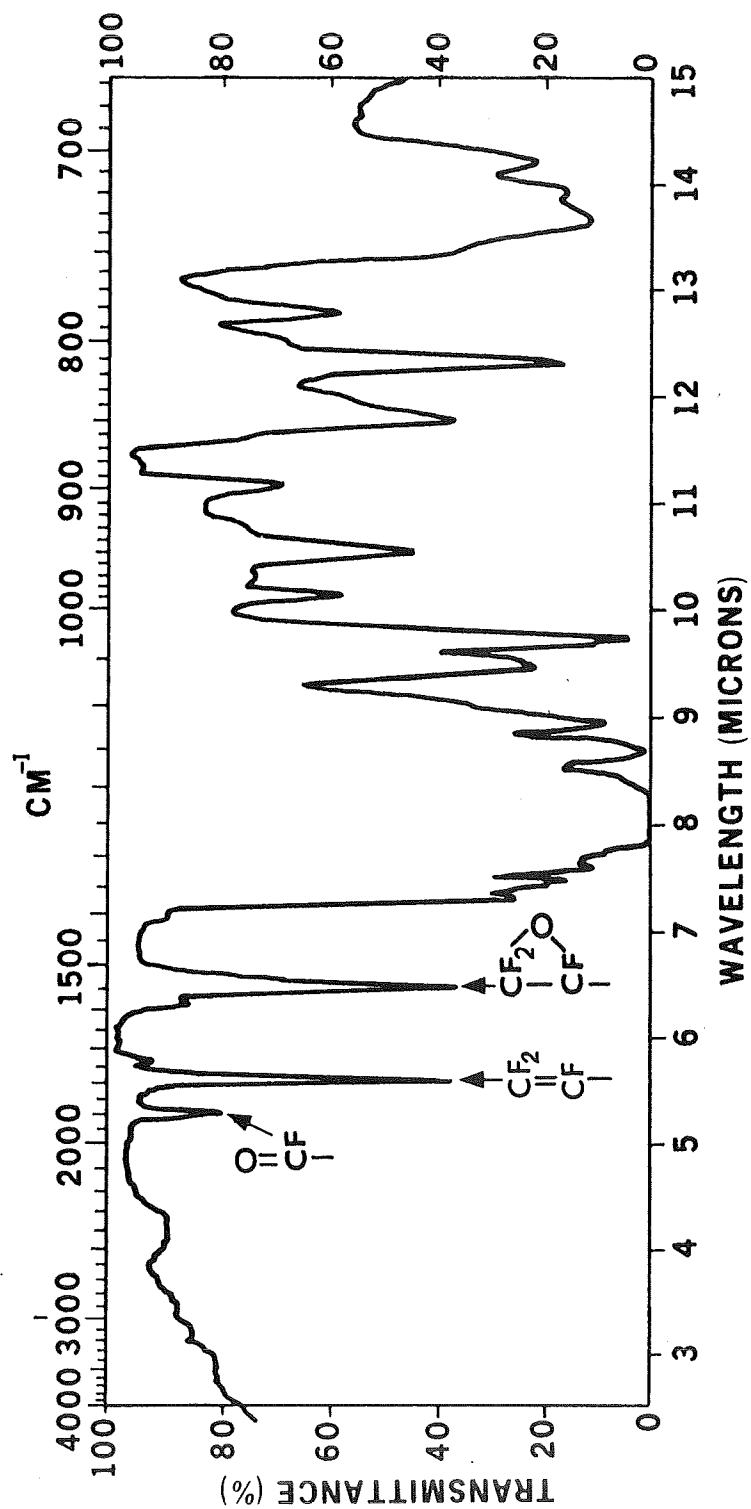
Figure 10. Infrared spectrum of products from reactions of OF_2 and perfluoro-n-heptene-1.

50
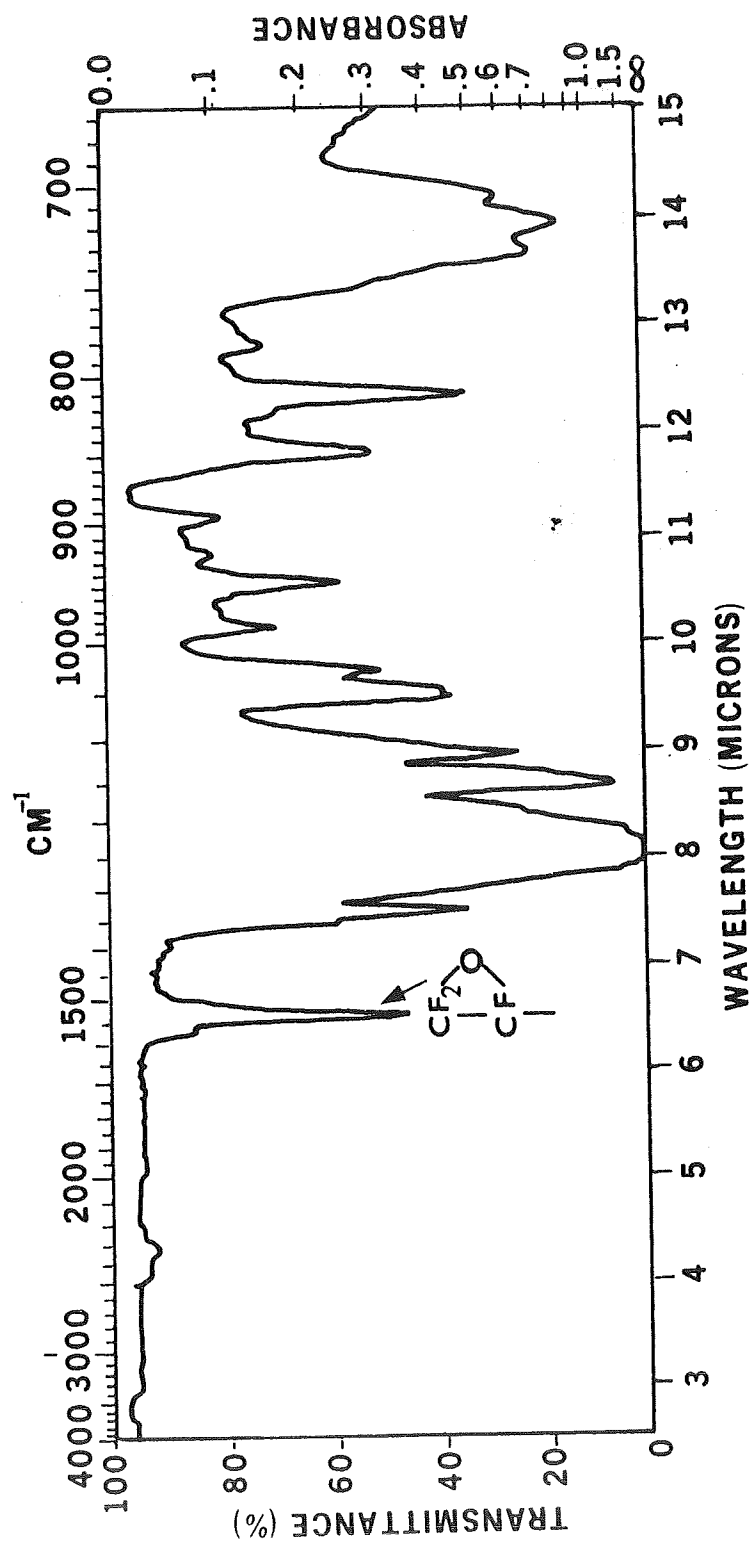
Figure 11. Infrared spectrum of 1,2-epoxyperfluoro-n-heptane.
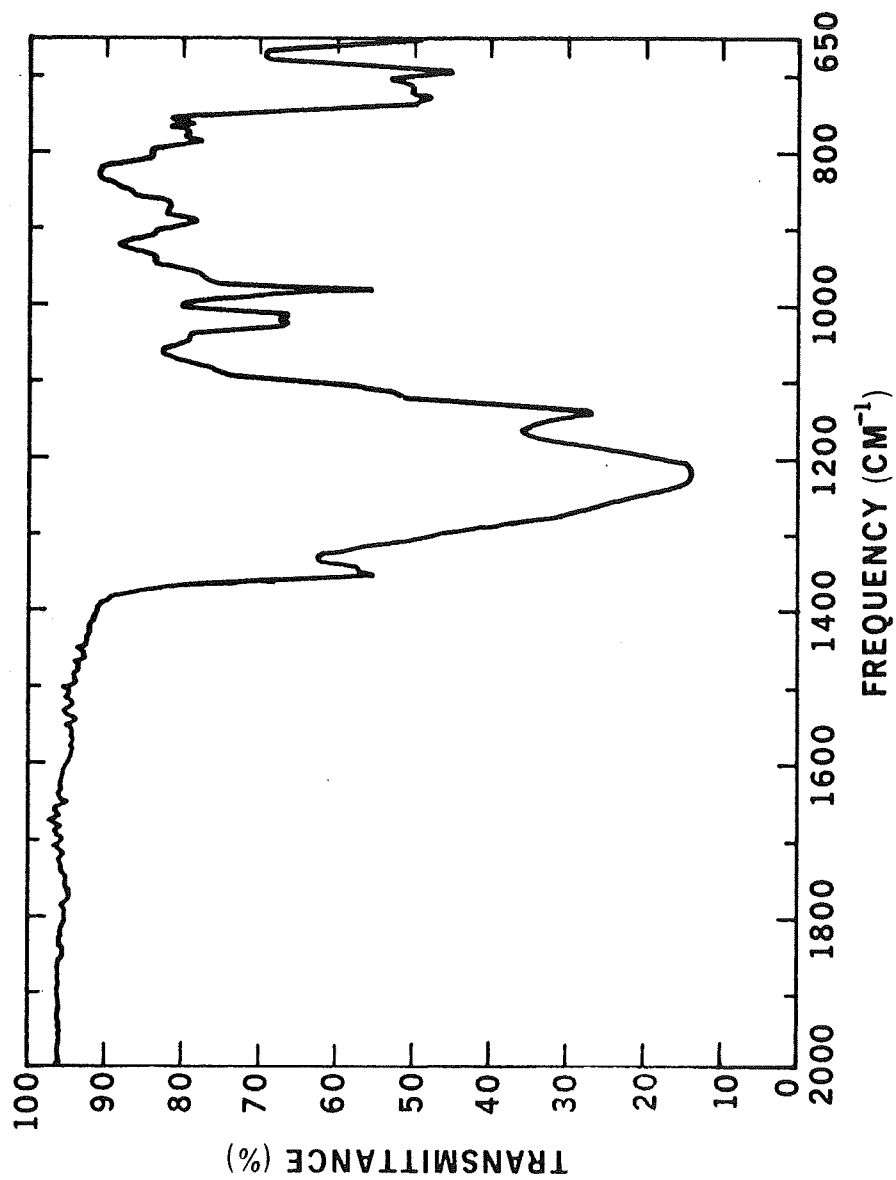
Figure 12.   Infrared spectrum of bis(perfluoro-n-heptyl)ether.

$$CF_3(CF_2)_4CF=CF_2 \xrightarrow{OF_2} \left[CF_3(CF_2)_4CF_2CF_2OF \right] \xrightarrow[\geq 0°C]{-F_2} CF_3(CF_2)_5\overset{\displaystyle O}{\overset{\|}{C}}-F \quad + \quad CF_3(CF_2)_4CF\underset{O}{-}CF_2$$

Perfluoro-n-heptene-1   Perfluoro-n-heptyl hypofluorite   Perfluoro-n-heptanoyl fluoride   1,2-Epoxyperfluoro-n-heptane

$$\Big\downarrow \leq 0°C \quad CF_3(CF_2)_4CF=CF_2$$

$$CF_3(CF_2)_6O\,(CF_2)_6CF_3$$

Bis(perfluoro-n-heptyl)ether
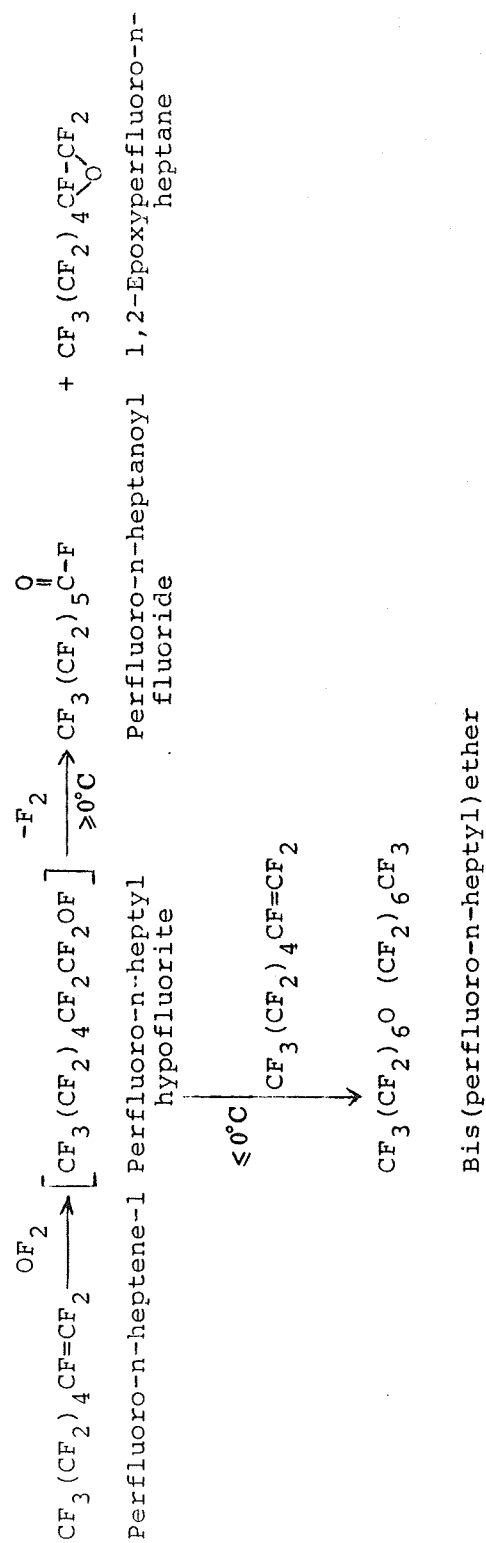
Figure 13. Reactions of OF_2 with perfluoro-n-heptene-1.

and poly(perfluorotetramethylene oxide) is claimed to be flexible at
$-80°C$ (Reference 55). The Tg of homopolymer of 1,1-bis(trifluoro-
methy)difluoroethylene, $(CF_3O)_2C=CF_2$, is about $-60°C$ (Reference 56)
and the copolymer of tetrafluoroethylene and perfluoro(methyl vinyl
ether), $CF_3OCF=CF_2$, is about $-10°C$ (Reference 57).

The Tg of polytetrafluoroethylene has been reported from 130 to
$-112°C$ (Reference 56). Thus some amorphous copolymers of
tetrafluoroethylene and other perfluoroolefins may be rubbers
that are flexible down to quite low temperatures (Reference 58),
but the difficulty of incorporating sufficient amounts of perfluoro-
propylene or other perfluoroolefins into tetrafluoroethylene polymers
to eliminate crystallinity is a problem (Reference 57). Recently
Brown and Wall (Reference 59) reported that rubbery characteristics
below room temperature are possible with polymers containing only
carbon and fluorine. They reported that Tg of
polyperfluoropentadiene-1,3, formed by 1,4-addition, is at $-3°C$
using the differential scanning calorimeter. However, a low Tg
alone is insufficient for high elasticity. The polymeric chains must
also have sufficient irregularity to provide amorphous regions and
to prevent crystallization on standing.

According to the instrument manual of the Perkin-Elmer differential
scanning calorimeter (Model 1B), Tg is taken as the temperature at
which the first evidence of change of increase in heat capacity as
associated with glass transition temperature. The results of each
polyperfluorobutadiene sample curve in Figure 14 show the
temperature region in which the gradual heat capacity change of the
polymer undergoes a discontinuity marked by a sudden increase in

54
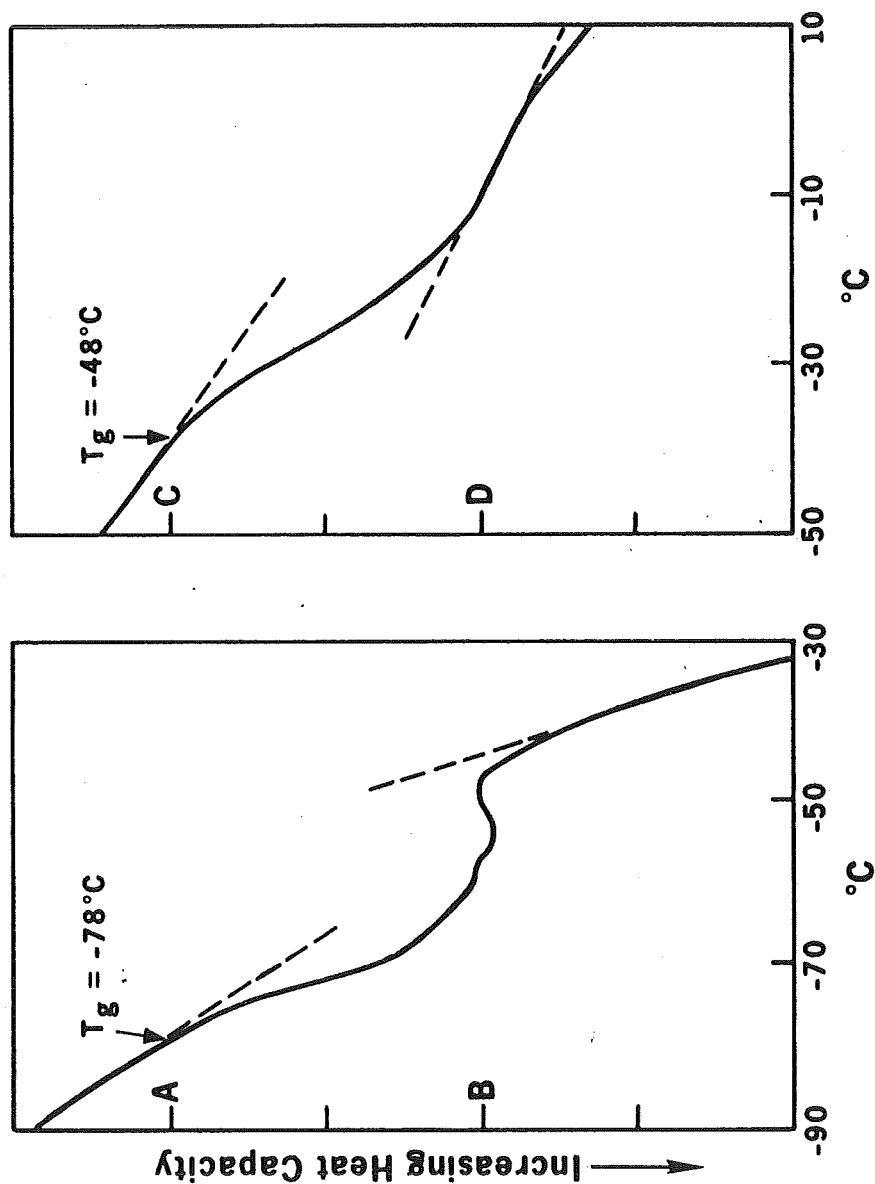
Figure 14. Tracings of records from differential scanning calorimeter for two samples of polyperfluorobutadiene (scanning rate 20°C/min; length of AB represent 0.80 mcal/sec and length of CD represents 1.60 mcal/sec; ordinate values of curves at the start of each scan are arbitrary).

heat capacity. The onset of the discontinuity is difficult to measure precisely. To us the onset of the discontinuity appears to be at −78°C and −48°C for the left and right curves respectively.

3.3.2 <u>Polymer Density</u>

From practical applications as well as a theoretical point of view, the density of a polymer is an important property, but only occasionally are polymer densities mentioned or surveyed in the literature (References 60 and 61). For instance, within a given family of polymers, density is a property closely related to the degree of crystallinity. For the calculation of a number of other properties (e.g., thermodynamic quantities) knowledge of density is essential. Furthermore, polymer density can be easily determined experimentally.

Table IV shows the comparative polymer densities of several commercial fluorocarbons including polytetrafluoroethylene and copolymer of perfluorinated ethylene and propylene, sold by E. I. duPont de Nemours and Company under the trade names Teflon TFE and Teflon FEP, respectively; and polychlorotrifluoro-ethylene, sold by Minnesota Mining and Manufacturing Company under the trade name KEL-F 81 Brand Plastic (Reference 62). Recently Van Krevelen and Hoftyzer have proposed a method to predict densities of linear, amorphous polymers (Reference 63). Their predicted values for amorphous polytetrafluoroethylene and polychlorotrifluoroethylene as 2.000 and 2.015 respectively and the experimental values are also included in Table IV. Van Krevelen

Table IV

COMPARATIVE POLYMER DENSITIES OF SEVERAL FLUOROCARBONS

Polymer	$d^{(a)}$, g/cm^3	$d^{(e)}_{amorph}$, g/cm^3	
		Calculated	Experimental
Polytetrafluoroethylene	2.13–2.20[b]	2.000	2.00
Copolymer of perfluorinated ethylene and propylene	2.14–2.17[c]		
Polychlorotrifluoroethylene	2.10–2.16[d]	2.015	2.032–2.11

[a] Reference 62

[b] "Teflon TFE" from duPont

[c] "Teflon FEP" from duPont

[d] "Kel-F" 81 Brand Plastic from 3M

[e] Reference 63

and Hoftyzer conclude that densities of partly crystalline polymers may be up to 1.2 times the amorphous densities. The density of a polymer in the crystalline state d_{cryst} can be estimated from

$$d_{cryst.} \approx (1 + 0.15\alpha)d_{amorph.}$$

where α is the degree of crystallinity.

Since the greatest source of error in determining the density of a solid polymer is in the adsorption of air by the solid, the pycnometer containing the solid and some inert liquid was set into a Pyrex resin kettle connected to a vacuum pump and evacuated until all air bubbles ceased rising from the solid, before completely filling the pycnometer with liquid and weighing. Water was used as the inert liquid for polyperfluorobutadiene, but for acyl fluoride polyperfluoro-butadiene, water is not an inert liquid due to hydrolysis of the functional groups to cause swelling and bubbling. Water was replaced by n-heptane. For the low melting acyl fluoride polyperfluorobutadiene as Batch No. 9550-32-1 in Table V, no inert liquid was used. The low molecular weight polymer was warmed to a flowing polymer melt to be poured into the pycnometer and cooled to 25.0°C for weighing.

3.3.3 Spectroscopic Investigation

The infrared and fluorine -19 nuclear magnetic resonance spectra of polyperfluorobutadienes indicate that the polymerization reaction by CF_3OOCF_3 catalysis involves one and both double bonds to give a mixture of 1,2- and 1,4-copolymers. The ratio of 1,2- and

Table V

PHYSICAL PROPERTIES OF SOME
POLYPERFLUOROBUTADIENES BEFORE AND AFTER OF$_2$-EXPOSURE

Batch No. of Product	$T_m^{(a)}$ (°C)	d (g/cm^3)	$[\eta]^{(b)}$ (dl/g)	$M_w^{(c)}$	Relative Infrared Absorption Peaks Among		
					5.3μ $-\overset{O}{\overset{\|}{C}}-F$	5.6μ $-CF=CF_2$	5.8μ $-CF=CF-$
7524-24-1 [d]	163–176	2.031	— [e]		None	Weak	Medium
8320-24-1 [d]	132–142	1.990	0.032	7,800	None	Strong	Medium
9588-18-1 [f]	120–135	1.994	0.061	20,000	Medium	Medium	Weak
9550-32-1 [f]	(grease)	1.977			Strong	Weak	None

[a] From differential scanning calorimeter of Perkin–Elmer Model 1B.

[b] In hexafluorobenzene at 30.1°C.

[c] Refer to Figure 17.

[d] Polyperfluorobutadiene prepared by CF$_3$OOCF$_3$ catalysis in the absence (No. 7524-24-1) and in the presence (No. 8320-24-1) of ultraviolet irradiation. No Tg observed.

[e] Insoluble in hexafluorobenzene at 30.1°C but soluble near 80°C.

[f] After flowing OF$_2$ through suspension of polyperfluorobutadiene in Freon 113 for 4 hours (No. 9588-18-1) and for 168 hours (No. 9550-32-1); Tg about –42 to –48°C range.

1,4-polymeric units increases with increase of concentration of catalyst and irradiation.

The infrared spectra of polymers show the usual very strong broad band between 7.5 and 9.1μ (1330 and 1098 cm^{-1}) region for C-F absorption. The two characteristic absorption peaks at 5.6μ (1787 cm^{-1}) indicates pendant perfluorovinyl groups as a result of 1,2-addition and at 5.8μ (1724 cm^{-1}) indicates perfluorovinylene groups from 1,4-addition polymerizations of perfluorobutadiene. Additional peaks for OF_2-treated polyperfluorobutadiene as shown in Figure 15 are at 5.3μ (1888 cm^{-1}) which indicates the presence of acyl fluoride (Reference 64) and at 6.51μ (1536 cm^{-1}) which identifies as perfluorinated epoxide group. The epoxide band in hexafluoropropylene epoxide was reported at 6.45μ (References 43 and 65) and in 2,3-epoxyperfluoropropionyl fluoride at 6.61μ (Reference 66).

The F^{19} NMR spectrum of polyperfluorobutadiene (Figure 16) shows three lines with the signal at -2400 Hz for saturated $+CF_2 +_n$ and pendant perfluorovinyl group and with signals at -1100 and -600 Hz due to 1,4-addition polymerizations (Reference 10).

The ESR spectrum (Figure 7) showed higher radical content for F_2-treated polyperfluorobutadiene than OF_2-treated sample. See Section 3.2.2.
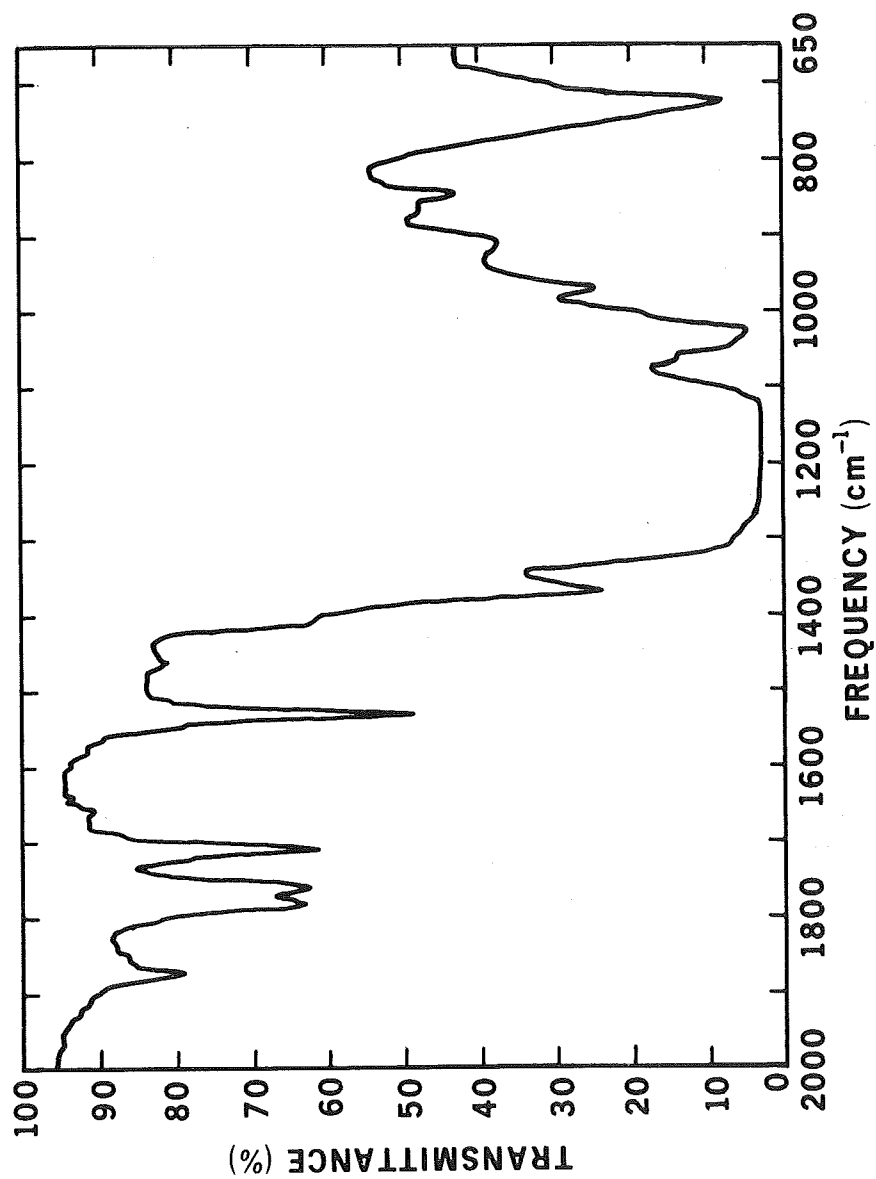
Figure 15. Infrared spectrum of OF$_2$-treated polyperfluorobutadiene at 0 to 13°C for 17 hours.

61
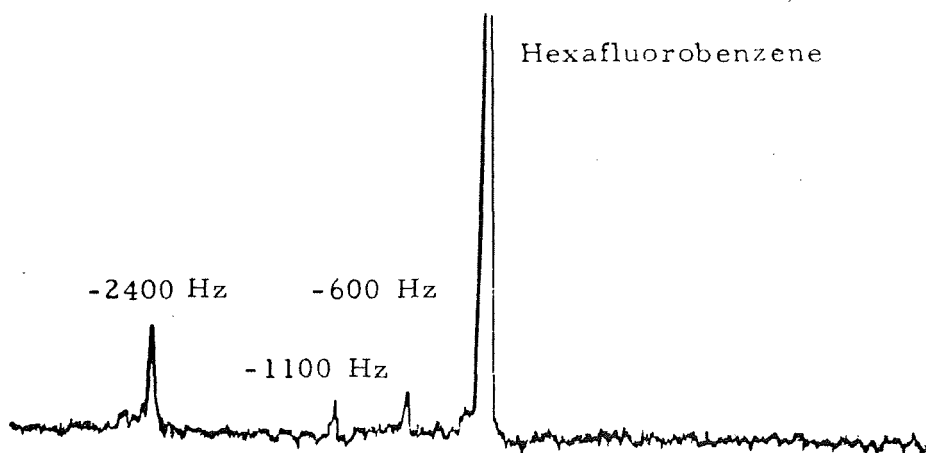
Figure 16. F^{19} NMR spectrum of polyperfluorobutadiene in hexafluorobenzene (56.4 MHz at a field of 14 kilogauss).

3.3.4 Viscosity-Molecular Weight Relationships

The molecular weights of polyperfluorobutadienes were determined by vapor pressure osmometer and Rast Method. The former method uses dilute polymer solutions and benzil as calibrated standard and the latter is a rapid convenient micromethod using melting point lowering measurement of camphor with a few milligrams of solutes that are soluble in camphor (Reference 67). The unexpected solubility of polyperfluorobutadiene of molecular weight below 7000 makes this method particularly useful to determine the lower molecular-weight range of the polymer. The unpredictable solubility characteristics and ease of mixing of perfluoropolymers and polyperfluoropolyenes above their melting temperatures were also noted by other workers (Reference 68).

Physical methods such as osmotic pressure, light scattering, etc.,
are in common use for polymer molecular weight measurements,
but other techniques are also applicable under certain circumstances.
For example, chemical methods and vapor pressure osmometry are
generally reliable for molecular weights about 25,000 and below.

Cryoscopic and ebullioscopic methods are particularly useful in the
lower molecular weight range (100-5000) (Reference 69). The Rast
Method for polymer molecular weight measurement of about 5000
has been reported (Reference 70). A Smith-Menzies ebulliometer
was devised by Ray (Reference 71), who claimed the sensitivity of
the apparatus for the molecular weight measurements of polyethylene
in toluene up to 40,000. Since the sensitivity of both cryoscopic and
ebullioscopic methods decreases with increasing molecular weight,
measurable changes in the boiling and freezing points may be
obtained by increasing the concentration of the solute, in view of
the marked deviations from Raoult's Law the results are likely to
be valueless above 5,000 to 10,000.

The viscosity-molecular weight relationships of CF_3NO/C_2F_4
copolymers were reported (Reference 72):

$$[\eta] = 8.77 \times 10^{-5} \overline{M}_w^{0.66} \tag{6}$$

where $[\eta]$ is intrinsic viscosity in trifluorobutylamine as solvent
at 25°C and $\overline{M}_w$ is weight average molecular weight determined by
light-scattering. The molecular weights of CF_3NO/C_2F_4 copolymer
sample F, which was fractionated into 20 fractions, ranged from
4.9×10^3 to 2.45×10^6. The lowest molecular weight fractions

(F-19 and F-20), which consisted of 25.6% by weight of the whole polymer F (Reference 72), were in the range of melted camphor-soluble polyperfluorobutadiene fractions, whose molecular weights were determined by Rast Method. The intrinsic viscosities were measured at 30.1°C in hexafluorobenzene as solvent. The comparison of viscosity-molecular weight relationships of polyperfluorobutadiene and the CF_3NO/C_2F_4 copolymer is shown in Figure 17.

The molecular weights of hexafluorobenzene-soluble polyperfluoro-butadienes at 65.0°C were estimated by adding an experimentally determined factor of 0.0025 dl/g to convert the intrinsic viscosities of polyperfluorobutadiene in hexafluorobenzene from 65.0°C to 30.1°C. Another experimentally determined factor of 0.0095 dl/g was used to convert the intrinsic viscosities of polyperfluorobutadiene in octafluorotoluene from 90.0°C to hexafluorobenzene at 30.1°C.

3.4 VULCANIZATION AND GRAFT COPOLYMERIZATION OF POLYPERFLUOROBUTADIENE

A new vulcanization and graft copolymerization process based on the reaction between gaseous fluorine and solid polyperfluoropolyenes has been originated to crosslink bulk polyperfluorobutadiene (Reference 17).

This method involves two steps:

1. Exposure of solid polyperfluorobutadiene to low concentration of gaseous fluorine under controlled conditions to create reactive sites on the polymer chains, followed by evacuation to remove the gaseous fluorine also under carefully controlled conditions.
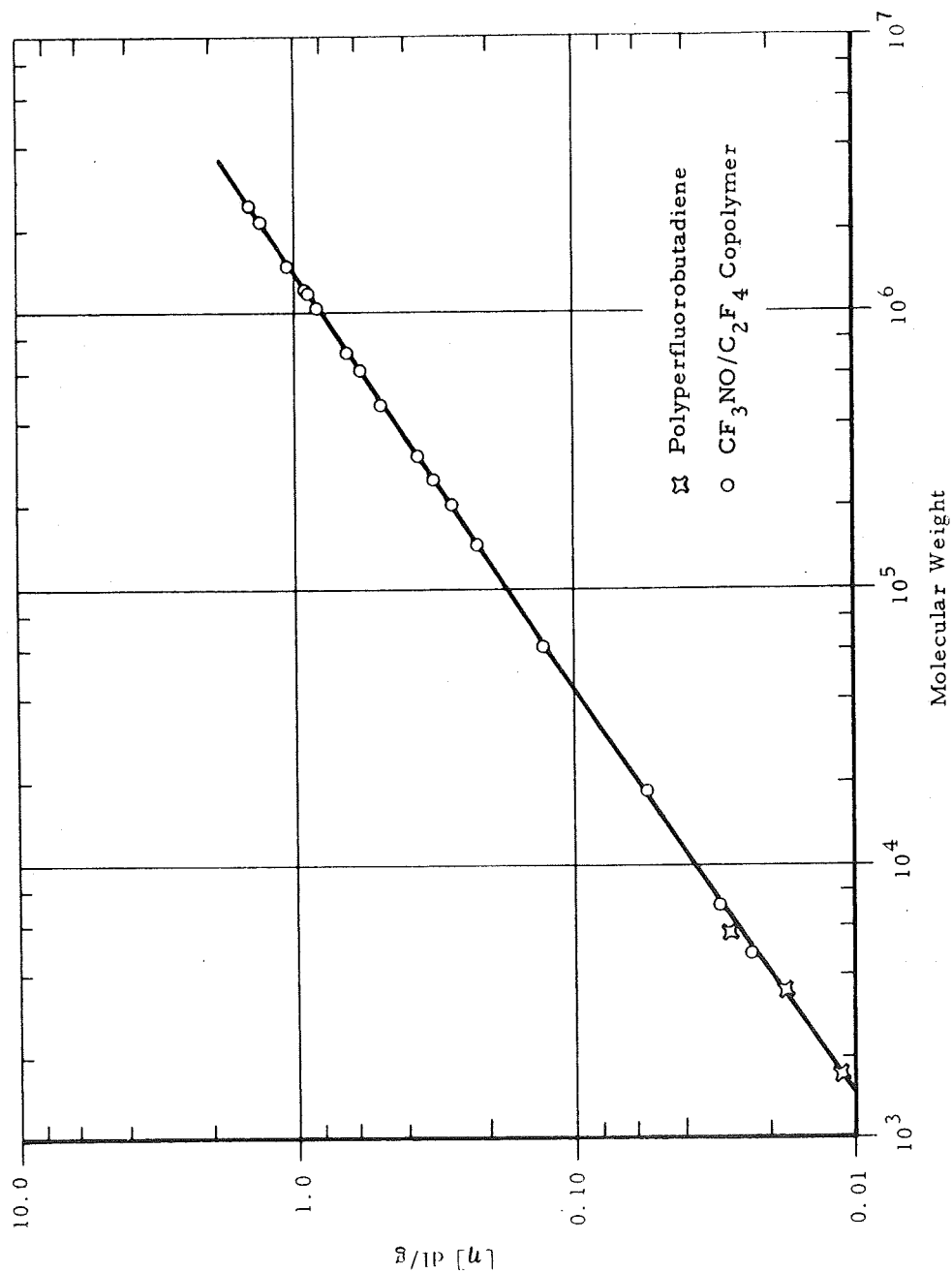
Figure 17. Intrinsic viscosity and molecular weight relationships of polyperfluorobutadiene and copolymer of trifluoro-nitrosomethane and tetrafluoroethylene.

65

2. Introduction of monomer to graft-copolymerize, and crosslink onto the polymer chains under controlled conditions.

Many monomers can be successfully grafted and crosslinked onto the polyperfluoropolyene chains using this fluorine-polyperfluoropolyene process (Appendix A).

This process was investigated for crosslinking polyperfluorobutadiene and the chain-extended homopolymer to achieve vulcanized elastomers containing only carbon and fluorine or carbon, fluorine and oxygen as inert ether linkages. However, the monomers for the second step of the process are not limited to fluoromonomers as shown in Figure 18, where ethylene oxide was graft-copolymerized. Although fluorine readily initiates reactive sites on polyperfluorobutadiene chain (Appendix A), the reaction of oxygen difluoride with poly-perfluorobutadiene is more complex (Figures 19 and 20 and Tables VI and VII) and less efficient for purpose of initiating free radical sites on polyperfluorobutadiene chain (see Section 3.2.2).

The two sizes of plastic molding dies for preparing polymer samples with dimensions of 2-1/2 inches × 3/8 inches and 1-1/2 inches × 1/4 inches as shown in Figures 21 and 22 were designed and constructed for future evaluation of mechanical properties of polymers. These molding dies will be used for pressure process to be performed in hydraulic presses with ram capacities of 1000 to 24,000 pounds load.

66
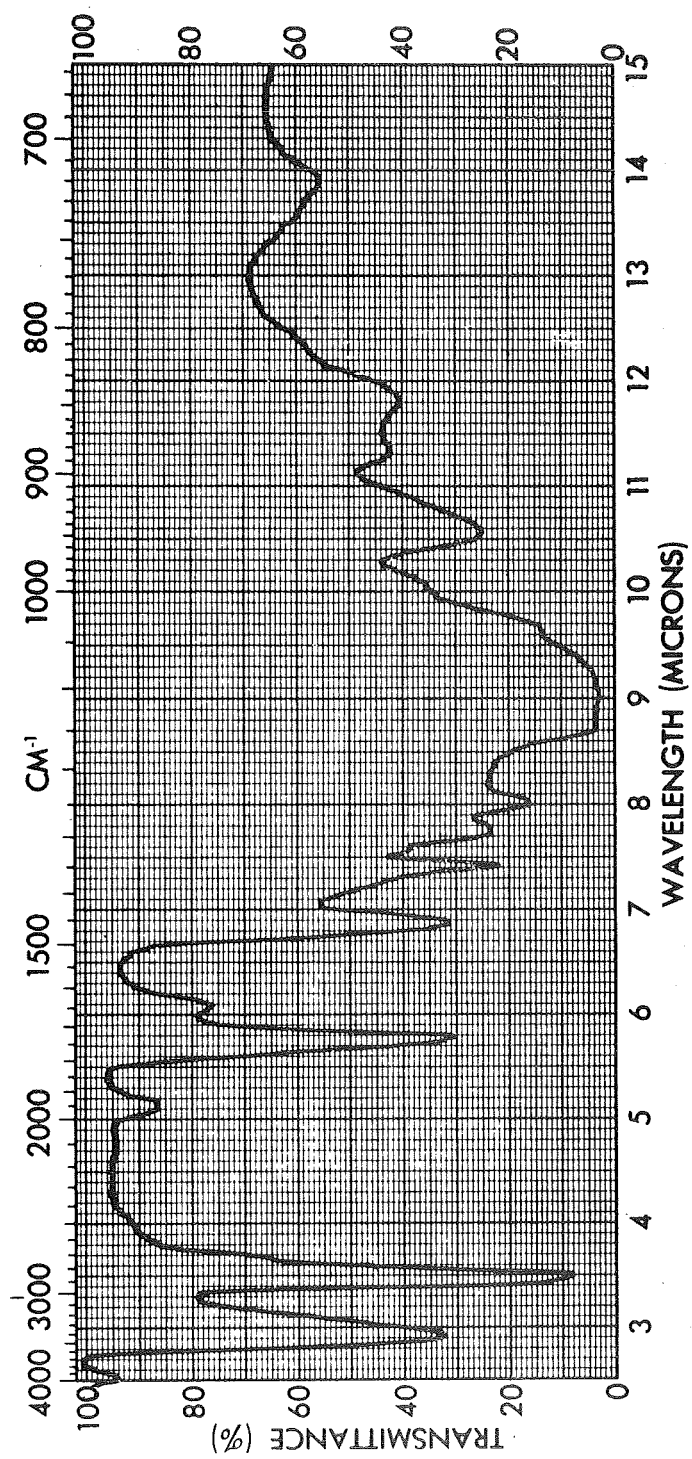
Figure 18. Infrared spectrum of graft copolymerized polyperfluorobutadiene–ethylene oxide by means of GF_2.

67
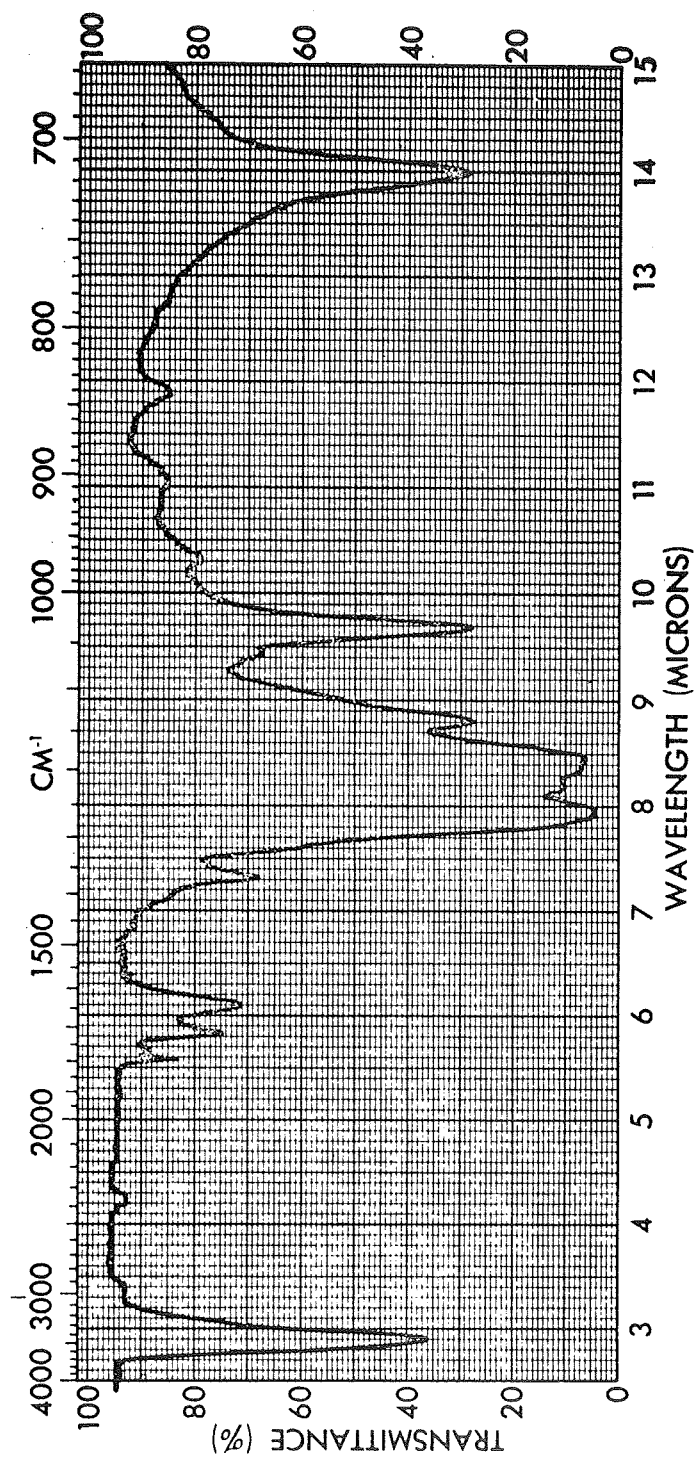
Figure 19. Infrared spectrum of graft copolymerized polyperfluorobutadiene—
tetrafluoroethylene by means of GOF₂ (batch No. 7524-34-1 of
Table VI).
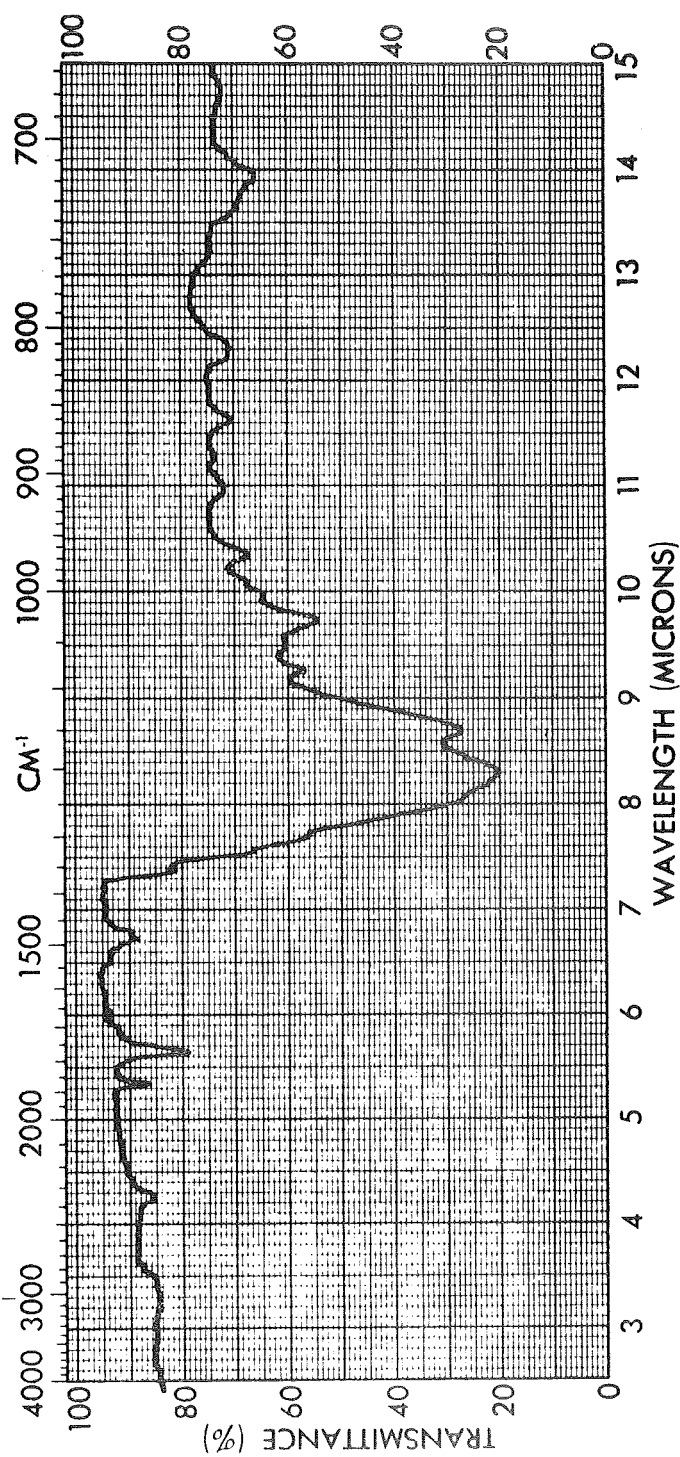
Figure 20. Infrared spectrum of graft copolymerized polyperfluorobutadiene–tetrafluoroethylene by means of GOF_2 (batch No. 8320–11–3 of Table VI).

Table VI

GRAFT COPOLYMERIZATION OF

POLYPERFLUOROBUTADIENE–TETRAFLUOROETHYLENE BY MEANS OF OF_2

Batch No. of Product	Starting Polymer	Static Exposure to OF_2			Static Exposure to C_2F_4			Product				
								Relative Infrared Peaks to Starting Polymer				
		Pres. (atm)	Temp. (°C)	Time (min)	Pres. (atm)	Temp. (°C)	Time (min)	5.3 μ $\overset{O}{\underset{\|}{-C-F}}$	5.6 μ $-CF=CF_2$	5.8 μ $-CF=CF-$	Wt. Change (%)	Tm (°C)
7524-34-1	Freeze-dried solid of Batch 7472-17-1 (Tm 102-130°C)	1/6	0	10	1-1/3[a]	0	15		Decrease	Same	+ 0.9	130-147
8320-6-1	Freeze-dried solid of Batch 7524-10-1 (Tm 138-159)	1	0	30	1-1/3[a]	25	15		Decrease	Same	0	
8320-11-3	Ditto	2	100	60	2-1/3[b]	0	35	New	Decrease	Disappear	+14.7	175-207

(a) A slight decrease of pressure about 0.06 atm was observed at end of 15 min.

(b) A definite decrease of pressure about 2/3 atm was observed at end of 35 min.

70

Table VII

GRAFT COPOLYMERIZATIONS OF POLYPERFLUOROBUTADIENE-
HEXAFLUOROPROPYLENE EPOXIDE AND -PERFLUOROBUTADIENE

Graft Copolymer[a]	Batch No. of Product	Starting Polymer	Static Exposure to OF$_2$			Product				
			Pres. (atm)	Temp. (°C)	Time (min)	Relative Infrared Peaks to Starting Polymer			Wt. Change (%)	Tm (°C)
						5.3 μ $\overset{O}{-C-F}$	5.6 μ -CF=CF$_2$	5.8 μ -CF=CF-		
Polyperfluorobutadiene-Hexafluoropropylene Epoxide	8320-11-1	Freeze-dried solid of Batch 7524-10-1 (Tm 138-159°C)	1	25	60		Slight decrease	Slight decrease	-2.5	90-105
	8320-11-2	Ditto	1	100	90	New	Slight decrease	Disappear	-3.0	<50
Polyperfluorobutadiene-Perfluorobutadiene	9550-14-1	Freeze-dried solid of Batch 8320-19-1 (Tm<50°C)	1	17	60		Slight decrease	Slight decrease		137-150
	9550-14-4	Ditto	1	55	60	New	Slight decrease	Slight decrease		139-148

(a) Both polyperfluorobutadienes after exposure to OF$_2$ were individually immersed in the liquid monomer, vacuum-sealed, kept at ambient temperature for 3 months, evacuated after cooling and dried at 50°C under reduced pressure overnight.

71
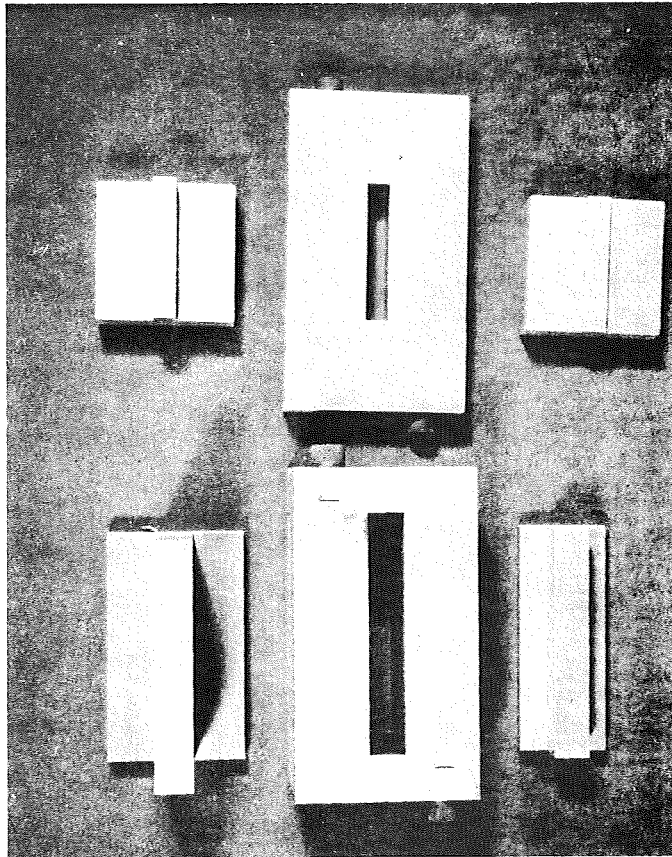
Figure 21.   Two plastic molding dies.
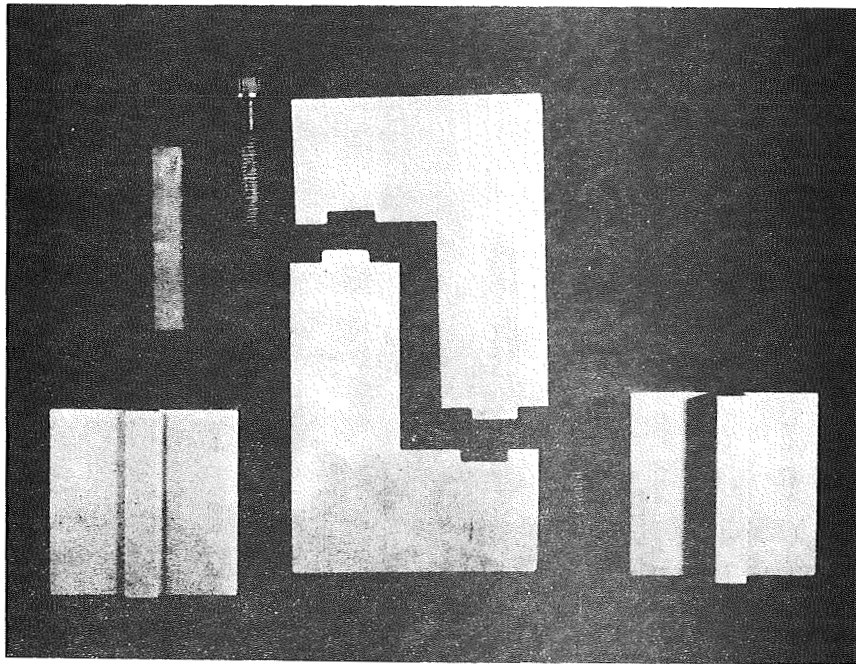
Figure 22. View of plastic molding die construction and polymer sample.

.

Section 4

EXPERIMENTAL

4.1 HOMOPOLYMERIZATION OF PERFLUOROBUTADIENE

Perfluorobutadiene was purchased from Peninsular ChemResearch Company and was shown by Mitsch and Neuvar to be 98-99% pure by vapor phase chromatography (Reference 73). The commercial monomer showed three groups of lines for its F^{19} NMR spectrum as reported by Toy and Lawson (Reference 10), and identical vapor infrared spectrum as reported by Weiblen (Reference 74). Bis(trifluoromethy)peroxide was also obtained from Peninsular ChemResearch and checked for purity by vapor infrared spectrum as reported by Porter and Cady (Reference 75).

Fluorine of 98.9% purity and oxygen difluoride of 99.8% purity were purchased from Allied Chemical. Oxygen of 99.9% purity was obtained from Air Products.

The catalysts and monomer were used directly without further purification, except the vapors of fluorine and oxygen difluoride were passed through columns of sodium fluoride pellets before use.

4.1.1 Polymer Initiation by Means of O_2, OF_2 and F_2 as Catalysts

Perfluorobutadiene (3 ml) was condensed into each of four evacuated Pyrex reaction tubes (4-1/2 in. × 1/2 in. OD with 1/4 in. OD neck) and 1% gaseous O_2 and OF_2 as catalysts were condensed separately

into the tubes (two with each catalyst) and vacuum-sealed. One pair
of tubes containing O_2 and OF_2 as separate catalyst was wrapped
in aluminum foil to prevent access of light. The other pair was
irradiated by a 275-watt sun lamp at the distance of 1 foot. The
unreacted monomer of each tube was discharged into another
container through the vacuum system after cooling the tube.

The set of two tubes under ultraviolet irradiation gave 1 to 2% yields
of brownish solids (Figures 3 and 4) and the unirradiated tubes gave
less than 1% yield of dark brown solid for O_2 as catalyst (Figure 2)
and one drop of brownish liquid for OF_2 as catalyst.

When condensed perfluorobutadiene was exposed to gaseous fluorine
in a similar experiment, a flame was observed. The reaction tube
immersed in liquid nitrogen bath was evacuated for 15 minutes
under 1 mm Hg pressure and the content was condensed into another
tube and vacuum-sealed. The sealed tube was irradiated by sun
lamp as described above at ambient temperature for 28 days. The
yield was about 5% of white solid. Figure 5 shows the infrared
spectrum of the white resin.

4.1.2 Larger Scale Preparation by CF_3OOCF_3 Catalysis

See Appendix C under Experimental.

4.2 UTILIZATION OF OXYGEN DIFLUORIDE FOR FLUOROPOLYMER SYNTHESES

4.2.1 Chain Extension of Polyperfluorobutadiene

See Appendix D under Experimental.

4.2.2 Insertion of Functional Groups into Polyperfluorobutadiene

See Appendix D under Experimental.

4.2.3 Addition Copolymerization of Perfluorobutadiene and Oxygen Difluoride

See Appendix D under Experimental.

Another preliminary experiment was carried out as follows: Perfluorobutadiene (10 mmoles) was condensed into a Pyrex reaction tube through a stainless steel vacuum line, which had been calibrated and passivated in a similar manner as previously described (Section 4.2.1). Gaseous OF_2 (10 mmoles), which had passed through a sodium fluoride scrubber, was brought in contact with liquid perfluorobutadiene at $-70°C$ for 3 hours before an additional 20 mmoles of OF_2 was added into the vapor phase for another 2 hours exposure at $-70°C$. The mixture was cooled to $-196°C$ and evacuated for 15 minutes to remove OF_2 in the system, before the Pyrex tube was vacuum-sealed and brought to ambient temperature. Precipitation of white polymer was observed within an hour at

ambient temperature. Figure 9 shows the infrared spectrum of the white solid polymer (m. p. 137-167°C dec.), which was insoluble in hexafluorobenzene and 3M Brand Fluorochemicals FC-75 and FC-43.

4.2.4 Chemistry of Oxygen Difluoride with Terminal and Internal Perfluoroolefinic Bonds

4.2.4.1 Reaction of OF_2 with Perfluoro-n-heptene-1

Perfluoro-n-heptene-1 (Peninsular ChemResearch; 2 ml; Figure 23) was introduced into a borosilicate reaction tube (5 in. $\times$ 3/4 in. OD with 1/4 in. OD neck) containing a magnetic stirring rod, and connected to a stainless steel vacuum line by Swagelok fitting. The stainless steel manifold for handling oxygen difluoride was similar to that previously described for handling fluorine (Reference 76). The reaction tube was evacuated while the contents were chilling to liquid nitrogen temperature. The first fraction was distilled off at ambient temperature under reduced pressure and discarded. The colorless residual liquid was chilled by a Freon 11-LN_2 bath at -90 to -100°C, before exposure to gaseous OF_2 from 1/3 to 1 atm. A decrease of OF_2 pressure to 0.2 atm was observed, when the temperature was increased gradually from -100°C to ambient temperature, while the liquid was being stirred. The pressure of OF_2 was recharged to 1-1/3 atm at ambient temperature in contact with the stirring liquid for 16 hours. The reaction tube was then evacuated for 10 minutes after chilling the contents to -78°C and for 20 minutes at liquid nitrogen temperature.
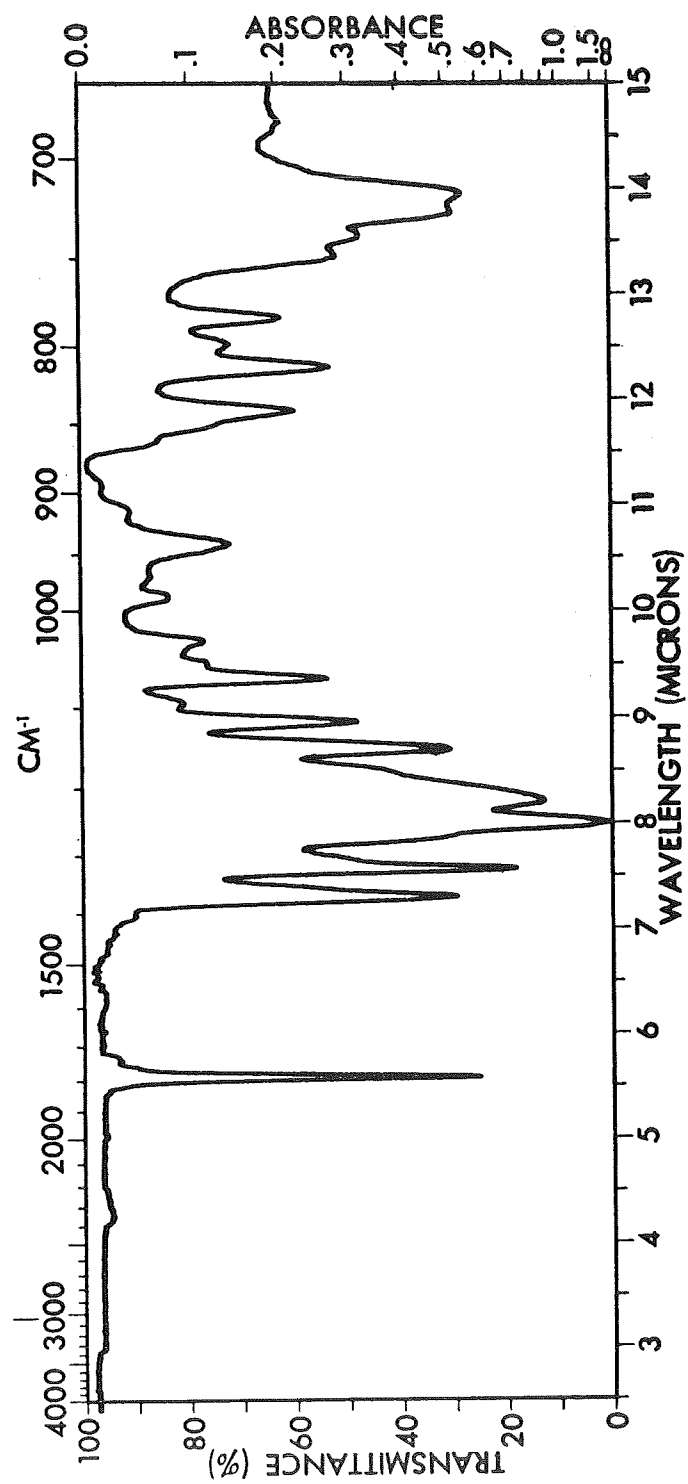
Figure 23. Infrared spectrum of perfluoro-n-heptene-1.

The top fraction of the product was condensed into a borosilicate reaction tube containing 1 ml of perfluoro-n-heptene-1, vacuum-sealed, and allowed to remain at ambient temperature for a month. After the content had been chilled to liquid nitrogen temperature, the reaction tube was opened at the neck and connected to the vacuum manifold. The infrared spectrum of the first fraction showed absorption peaks at 5.6μ indicating unreacted perfluoro-n-heptene-1, at 5.3μ indicating acyl fluoride-containing compounds such as perfluoro-n-heptanoyl fluoride and at 6.5μ indicating perfluorinated epoxide such as 1, 2-epoxyperfluoro-n-heptane. The infrared spectra of the second and last fractions are identical with the appearance of a weak new band at 5.8μ which indicates some migration of the terminal perfluorovinyl to internal vinylene bonds and the disappearance of 5.3μ which indicates the absence of acyl fluoride groups. The mass spectrum of this fraction showed the three highest mass fragments as follows: an extremely weak peak corresponds to $CF_3(CF_2)_4CF_2CF_3$ (mass 388), a medium peak corresponds to $CF_3(CF_2)_4\overset{\displaystyle CF-CF_2}{\underset{\displaystyle O}{\diagdown\diagup}}$ or $CF_3(CF_2)_5COF$ (mass 366) and a very strong peak corresponds to $CF_3-(CF_2)_4CF=CF_2$ (mass 350). There is no bis(perfluoro-n-heptyl)ether fragment detected.

The last fraction of the product was only two drops of material. Its infrared spectrum (Figure 11) identifies the material as 1, 2-epoxyperfluoro-n-heptane.

80

4.2.4.2 Perfluorocyclopentene Versus Perfluoro-n-heptene-1

The two perfluoroolefins: (1) perfluorocyclopentene, which contains the internal vinylene bond, and (2) perfluoro-n-heptene-1, which contains the terminal vinyl bond, were reacted separately with OF_2 under a few identical conditions. The reaction of liquid perfluoro-olefin under stirring and gaseous OF_2 at 10% excess in molar ratio was carried out at $-78°C$ under static condition for 24 hours followed by at $0°C$ for 20 hours, before evacuation for 10 minutes after chilling contents to $-78°C$ and for 20 minutes at liquid nitrogen temperature. In case of perfluorocyclopentene, the perfluoroolefin was totally recovered and unchanged, but a definite reaction took place in the case of perfluoro-n-heptene-1. Upon fractionations, the last fraction was identified as bis(perfluoro-n-heptyl)ether (Figure 12). The molecular weight was determined by Dr. D. L. Hildenbrand using his torsion-effusion apparatus (Reference 50) based on vaporization of the material.

The vapor phase reactions of mixtures of the two perfluoroolefins separately with OF_2 at 1:2 and 1:1 molar ratios at the total pressure around 30 mm Hg were carried out at ambient temperature directly in a 7.4 cm gas cell constructed of stainless steel body, sodium chloride windows, and Teflon gaskets. The infrared spectra of mixtures of perfluorocyclopentene and OF_2 showed no reactions for two days, but the infrared spectra of mixtures of perfluoro-n-heptene-1 and OF_2 at 1:2 ratio showed an immediate reaction. The appearance of 6.5μ peak indicating perfluorinated epoxide appears at less than a minute and a 5.3μ peak indicating acyl fluoride group appears between 1 to 2 hours.

81

4.3 POLYMER CHARACTERIZATION

4.3.1 Determination of Glass Transition Temperature

A Perkin-Elmer differential scanning calorimeter Model 1B, was
used to determine Tg. The low temperature accessory was used.
Dry nitrogen at a flow rate of 30 to 40 cc per minute was the purge
gas. The temperature scales of the instrument were calibrated at
two points using n-octane (mp at $-57°C$) and tin (mp at $232°C$). Scans
were made at rates about $20°C/minute$.

For use in the calorimeter polymer was formed into thin discs by
the sample pan crimper. About 40 mg of sample was placed in an
aluminum foil pan and covered with an aluminum foil pan cover and
crimped shut. Proceeding the scan, cooling was at rate of $5°C$ per
minute.

The results of some polymer curves were shown in Figure 14.

4.3.2 Polymer Density Measurement

The pycnometer was weighed empty and filled with distilled water.
Then the pycnometer was dried and weighed with the solid polymer.
After filling with distilled water (plus the solid polymer), it was
weighed again at $25.0°C$, and all the data were then available for
calculating the weight and volume of solid polyperfluorobutadiene
and its density at $25.0°C$. Since the greatest source of error in
determining the density of a solid polymer is in the adsorption of

82

air by the solid, the pycnometer containing the solid and some distilled water was set into a Pyrex resin kettle connected to a vacuum pump and evacuated until all air bubbles ceased rising from the solid; then the pycnometer was completely filled with distilled water before weighing.

For acyl fluoride polyperfluorobutadiene, water is not an inert liquid due to hydrolysis of the functional groups to cause swelling and bubbling. Water was replaced by n-heptane. For the low melting acyl fluoride polyperfluorobutadiene as batch No. 9550-32-1 in Table V, polymer melt was used by slight warming and cooling to 25.0°C for weighing.

4.3.3 Spectroscopic Investigation

The infrared spectrum of the polymer film was investigated between 2.5 and 15μ on the Perkin Elmer Model 137 and 700 spectrophotometers, employing sodium chloride prisms. A 7.4 cm gas cell with stainless steel body, sodium chloride windows and Teflon gaskets were used for vapor samples.

The F^{19} NMR spectrum of the polymer solution utilizing hexafluorobenzene as both solvent and internal standard was investigated at 56.4 MHz at a field of 14 kilogauss on the Varian HR-60 spectrometer system. Chemical shifts are expressed in Hz relative to internal hexafluorobenzene with the negative direction on the low-field side as shown in Figure 16 (Reference 16).

The ESR spectra for radical content was measured by Varian V-4500 electron spin resonance spectrometer which is equipped with a 9 GHz microwave bridge for normal operation and a super-heterodyne attachment for low-power operation. Sample preparations for polyperfluorobutadiene radical studies were described in Appendix A.

Mass spectra of samples were carried out by West Coast Technical Service, San Gabriel, California.

4.3.4 Viscosity and Molecular Weight Measurements

The viscosities of dilute solutions of polymer samples were measured in Ubbelohde viscometers size No. 1 in a Hallikainen Kinematic Viscosity Bath to provide constant temperature to 0.01°F accuracy.

The molecular weight of polymers were determined by Rast Method (Reference 67) and Hitachi-Perkin Elmer Model 115 Vapor Pressure Osmometer.

4.4 VULCANIZATION AND GRAFT COPOLYMERIZATION BY MEANS OF FLUORINE REACTION

4.4.1 Polyperfluorobutadiene - Hexafluoropropylene Epoxide

See Appendix A.

84

4.4.2 Polyperfluorobutadiene – Tetrafluoroethylene

See Appendix A.

4.4.3 Polyperfluorobutadiene – Ethylene Oxide

A hexafluorobenzene solution of 0.33g of polyperfluorobutadiene
(Tm 80–90°C; $[\eta]$ 0.028; Mol. wt. 5700 Rast; Tg–42°C) was freeze-
dried in a borosilicate glass tube, evacuated at 50°C and cooled to
–80°C, before slowly introducing gaseous fluorine, which had been
passed through a sodium fluoride scrubber to 2/3 atm, and warmed
to ambient temperature and kept at the same pressure and temperature
for 5 minutes, then evacuated at ambient temperature. Ethylene
oxide (99.7% purity from Air Products) was condensed into the
reaction tube to cover the solid resin and vacuum-sealed. The
sealed reaction tube was kept at room temperature for two months.
The unreacted ethylene oxide was discharged into another tube
through the vacuum system after cooling the tube. The white resin
was evacuated at 50°C overnight. Its infrared spectrum as a KBr
pellet is shown in Figure 18. The strong absorption peak at 3.5μ
indicates the presence of high content of C–H.

4.5 VULCANIZATION AND GRAFT COPOLYMERIZATIONS BY OXYGEN DIFLUORIDE REACTION

4.5.1 Polyperfluorobutadiene – Tetrafluoroethylene

A hexafluorobenzene solution of 0.346g of polyperfluorobutadiene (Tm 102-130°C) was freeze-dried in a borosilicate glass tube, evacuated at 50°C and cooled to -80°C, before introducing gaseous oxygen difluoride, which had been passed through a sodium fluoride scrubber, to 1/6 atm, warmed to 0°C and kept at 1/6 atm and 0°C for 10 minutes, then evacuated. Tetrafluoroethylene (Thiokol Chemical), which had been passed through a silica gel column to remove its terpene inhibitor, was introduced at 1-1/3 atm at 0°C. A very slight pressure drop was observed at the end of 15 minutes before evacuation. The white resin was evacuated at 50°C overnight and weighed 0.349g and Tm 130-147°C. The infrared spectrum of the resin is almost identical to the starting polymer, except with a definite decrease of 5.6μ peak.

The graft copolymerizations of polyperfluorobutadiene-tetrafluoroethylene were repeated under different conditions following the similar procedure as described above. The results are summarized in Table VI.

4.5.2 Polyperfluorobutadiene – Hexafluoropropylene Epoxide and – Perfluorobutadiene

The similar procedure as described in Section 4.5.1 was followed except under different OF_2 conditions and the monomer

86

(hexafluoropropylene epoxide or perfluorobutadiene) was condensed into the reaction tube and vacuum-sealed. The sealed reaction tube was kept at room temperature for 3 months. The unreacted monomer was discharged into another tube through the vacuum system after cooling the tube. Each white resin was evacuated at 50°C overnight. The results and experimental conditions are summarized in Table VII.

Section 5

REFERENCES

1. Griffis, C. B., and Henry, M. C., Rubber Plastics Age, $\underline{46}$, 63 (1965).

2. Henry, M. C., Griffis, C. B., and Stump, E. E., Fluorine Chem. Rev., $\underline{1}$(1), 1 (1967).

3. Toy, S. M., English, W. D., Crane, W. E., and Toy, M. S., J. Macromol. Sci., $\underline{A3}$(7), 1355 (1969).

4. Toy, M. S., Douglas Report DAC-60524, June 1967.

5. Bunn, C. W., and Howells, E. R., Nature, $\underline{174}$, 549 (1954).

6. Clark, E. S., Z. Krist., $\underline{117}$, 108, 119 (1962).

7. McCullough, J. D., Bauer, R. S., and Jacobs, T. L., Chem. and Ind., 706 (1957).

8. Jacobs, T. L., and Bauer, R. S., J. Am. Chem. Soc., $\underline{81}$, 608 (1959).

9. Toy, M. S., "New Fluorine-Containing Elastomers for Space-Propulsion Applications," Douglas Report DAC-60520-F under Contract NAS 7-603, August 1968.

10. Toy, M. S., and Lawson, D. D., J. Polymer Sci., Part B, $\underline{6}$, 639 (1968).

11. Cooper, W., and Grace, N. S., J. Polymer Sci., $\underline{Part\ C}$, $\underline{No.\ 12}$, 133 (1966).

12. Meares, P., $\underline{Polymer\ Structure\ and\ Bulk\ Properties}$, D. Van Nostrand, N. Y., 1965, p. 163.

13. Bryce, H. G., $\underline{Fluorine\ Chemistry}$, Vol. 5, ed. by H. J. Simons, Academic Press, N. Y., 1964, pp. 469-474.

14. Peffley, W. M., Hannold, V. R., and Binder, D., J. Polymer Sci., Part A-1, $\underline{4}$, 977 (1966).

15. Flory, P. J., $\underline{Principles\ of\ Polymer\ Chemistry}$, Cornell University Press, Ithaca, N. Y., 1953, p. 487.

16. Toy, M. S., and Lawson, D. D., Am. Chem. Soc. Polymer Preprints, 9(2), 1671 (1968).

17. Toy, M. S., and Newman, J. M., J. Polymer Sci., Part A-1, 7, 2333 (1969).

18. Miller, W. T., and Koch, S. D., J. Am. Chem. Soc., 79, 3084 (1957).

19. Wall, L. A., and Florin, R. E., J. Appl. Polymer Sci., 2, 251 (1959).

20. Toy, M. S., J. Electrochem. Soc., 114, 1042 (1967).

21. Toy, M. S., and Newman, J. M., Am. Chem. Soc. Organic Coating and Plastics Chemistry Preprints, 29(1), 206 (1969).

22. Hoffman, C. J., Chem. Rev., 64, 91 (1964).

23. Porter, R. S., and Cady, G. H., J. Am. Chem. Soc., 79, 5625 (1957).

24. Hohorst, F. A., and Shreeve, J. M., Inorg. Chem., 7, 624 (1968).

25. Barton, D. H. R., Ganguly, A. K., Heese, R. H., Loss, S. N., and Pechett, M. M., Chem. Comm., 14, 806 (1968).

26. Barton, D. H. R., Godinho, L. S., Hesse, R. H., and Pechet, M. M., ibid., 14, 804 (1968).

27. Burg, A. B., Fluorine Chemistry, Vol. 1, ed. by J. H. Simons, Academic Press, 1950, p. 83.

28. Levy, J. B., and Copeland, B. K. W., J. Phys. Chem., 71, 3999 (1963).

29. Levy, J. B., and Copeland, B. K. W., ibid., 69, 408 (1965).

30. Solomon, W. C., Blauer, J. A., and Jaye, F. C., ibid., 72, 2311 (1968).

31. Diebler, V. H., Reese, R. M., and Franklin, J. L., J. Chem. Phys., 27, 1296 (1957).

32. Herzberg, G., and Ramay, D. A., Trans. Faraday Soc., 9, 80 (1950).

33. Evans, W. H., Munson, T. R., and Wagman, D. D., J. Res. Nat. Bur. Stand., 55A, 147 (1955).

34. Dauerman, L., Salser, G., and Tajima, Y. A., J. Phys. Chem., 71, 3999 (1967).

35. Arkell, A., Reinhard, R. R., and Larson, P. J., J. Am. Chem. Soc., 87, 1016 (1965).

36. Blauer, J. A., and Solomon, W. C., J. Phys. Chem., 72, 2307 (1968).

37. Franz, G., and Neumayr, F., Inorg. Chem., 3, 921 (1964).

38. Gatti, R., Satricco, E. H., Siere, J. E., and Schumacher, H. J., Angew. Chem., 75, 137 (1963).

39. Anderson, L. R., and Fox, W. B., J. Am. Chem. Soc., 89, 4313 (1967).

40. Thompson, P. G., J. Am. Chem. Soc., 89, 4316 (1967).

41. Merritt, R. F., and Ruff, J. K., J. Org. Chem., 30, 328 (1965).

42. Rhein, R. A., and Cady, G. H., Inorg. Chem., 3, 1644 (1964).

43. Ruff, J. K., and Merritt, R. F., J. Org. Chem., 30, 3968 (1965).

44. Merritt, R. F., J. Org. Chem., 30, 4367 (1965).

45. Sheppard, W. A., and Sharts, C. M., Organic Fluorine Chemistry, W. A. Benjamen, N.Y., 1969, p. 125.

46. Miller, W. T., Preparation, Properties, and Technology of Fluorine and Organic Fluoro Compounds, ed. by C. Slesser and S. R. Schram, McGraw-Hill, N.Y., 1951, pp. 625-626.

47. Andreades, S., J. Am. Chem. Soc., 86, 2003 (1964).

48. Streitwieser, A., and Holtz, D., J. Am. Chem. Soc., 89, 692 (1967).

49. Mitsch, R. A., Throckmorton, J. R., Ting, S. T., Zollinger, J. L., and Gilbert, H., "High Density, High Temperature Binders for Solid Propellants," 3M under Contract AF04611-67-e-0030, August 1968 (AD392757).

50. Hildenbrand, D. L., and Hall, W. F., J. Phys. Chem., 67, 888 (1963).

51. Cooper, W., and Grace, N. S., J. Polymer Sci., Part C, No. 12, 133 (1966).

52. Tobolsky, A. V. , J. Polymer Sci. , <u>Part C. , No. 9</u>, 157 (1965).

53. Barney, A. L. , Bruce, J. M. , Coker, J. N. , Jacobson, H. W. , and Sharkey, W. H. , J. Polymer Sci. , Part A1, <u>4</u>, 2617 (1966).

54. Sharkey, W. H. , ACS Polymer Preprints, <u>7</u>(1), 275 (1966).

55. Minnesota Mining and Manufacturing Co. , Fr. Pat. 1,410,554 (1965).

56. Schuman, P. D. , Stump, E. C. , and Westmoreland, G. , J. Macromol. Sci. Phys. , <u>B1</u>(4), 815 (1967).

57. Barney, A. L. , ACS Polymer Preprints, <u>10</u>(2), 1483 (1969).

58. Tobolsky, A. V. , <u>Properties and Structure of Polymers</u>, John Wiley, 1960, pp. 61-63 and p. 70.

59. Brown, D. W. , and Wall, L. A. , J. Polymer Sci. , Part A-2, <u>7</u>, 601 (1969).

60. Brandrup, J. , and Immergut, E. H. , eds. , <u>Polymer Handbook</u>, Interscience, N. Y. , 1966, pp. III-3/31.

61. Lewis, O. G. , <u>Physical Constants of Linear Homopolymers</u>, Springer, Berlin, 1968.

62. Bringer, R. P. , Paper presented at National Symposium on Effects of Space Environment on Materials, St. Louis, Mo. , May 1962.

63. Van Krevelen, D. W. , and Hoftyzer, P. J. , J. Appl. Polymer Sci. , <u>13</u>, 871 (1969).

64. Haszeldine, R. N. , Nature, <u>168</u>, 1028 (1951).

65. Heicklen, J. , and Johnston, T. , J. Phys. Chem. , <u>71</u>, 1391 (1967).

66. Stuckey, W. , Heicklen, J. , and Knight, V. , Can. J. Chem. , <u>47</u>, 2329 (1969).

67. Shriner, R. A. , and Fuson, R. C. , <u>Identification of Organic Compounds</u>, John Wiley, 1948, pp. 50-51.

68. McIntyre, D. , and Valentine, R. D. , ACS Polymer Preprints, <u>7</u>(2), 1133 (1966).

69. Burnett, G. M. , <u>High Polymers Vol. III, Mechanism of Polymer Reactions, Interscience</u>, 1954, p. 37.

70. Toy, M. S., and Price, C. C., J. Am. Chem. Soc., 82, 2613 (1960).

71. Ray, N. H., Trans. Faraday Soc., 48, 809 (1952).

72. Morneau, G. A., and Roth, P. I., and Schultz, A. R., J. Polymer Sci., 55, 609 (1961).

73. Mitsch, R. A., and Neuvar, E. W., J. Phys. Chem., 70, 546 (1966).

74. Weiblen, D. G., Fluorine Chemistry, Vol. 2, ed. by J. H. Simons, Academic Press, N.Y., 1954, p. 478.

75. Porter, R. S., and Cady, G. H., J. Am. Chem. Soc., 79, 5628 (1957).

76. Schmidt, H. W., "Handling and Use of Fluorine and Fluorine-Oxygen Mixtures in Rocket Systems," NASA SP-3037 (1967).

POLYPERFLUOROBUTADIENE. IV. FLUORINE REACTIONS AND GRAFT COPOLYMERIZATIONS*

INTRODUCTION

Homopolymerization of perfluorobutadiene to solid polymers was recently achieved under low pressure and temperature in the presence of free radical catalysts. The products are copolymers of perfluoro-1,2- and 1,4-butadiene (References A1 and A2). Fluorine reaction with the copolymer was reported to saturate more rapidly and completely the vinylene bonds as a result of 1,4-addition polymerization than the pendant vinyl bonds as a result of 1,2-addition polymerization of the monomer (Reference A3). In this paper, the ease of flammability of bulk polyperfluorobutadienes (PPFB) during fluorine reactions is deduced. Direct fluorination of the bulk polymer by low concentrations of fluorine to initiate fluorocarbon radicals and some graft copolymerizations are described.

RESULTS AND DISCUSSION

Direct vapor phase fluorinations of PPFB were studied in the absence of catalyst. The bulk polymers initiated by $(i\text{-}PrOCO_2)_2$ catalyst

---

were fluorinated without prior solvent extraction. This was not feasible for the bulk polymers initiated by benzoyl peroxide catalyst due to inflammation during fluorination. The difference is probably because $(i-PrOCO_2)_2$ is unstable at ambient temperature (Reference A4). Its volatile decomposition products can easily be removed by evacuation; while excess benzoyl peroxide and its decomposition products remain in the bulk polymer to react vigorously with fluorine. Fluorination reactions also showed that the bulk polymer initiated by CF_3OOCF_3 catalyst could be fluorinated not only without solvent extraction but also at higher initial fluorine pressure without burning than $(i-PrOCO_2)_2$-initiated bulk polymers. This suggests that fluorination reactions are very sensitive to the terminal groups of the polymer chains. The ease of flammability of the bulk polymer during fluorination is dependent upon the initiator used. In the list shown, the catalysts are arranged in the order of decreasing flammability:

$$(C_6H_5COO)_2 \; > \; (i-PrOCO_2)_2 \; > \; CF_3OOCF_3$$
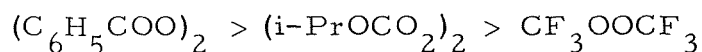
The electron spin resonance (ESR) spectra on prefluorinated PPFB at low fluorine concentrations are shown in Figure A1. The dependence of radical concentrations to prefluorinated fluorine pressures is observed. The stability of fluorocarbon radicals was previously reported (References A5 and A6) and confirmed again by this work. The exposure of solid PPFB to low concentrations of fluorine initiates reactive sites on the unsaturated perfluoropolymer chains. Due to the high stability of these fluorocarbon radicals, graft copolymerizations occur readily by exposure to monomers such as tetrafluoroethylene (TFE) and hexafluoropropylene oxide.

1 —— PPFB Treated at 2/3 atm GF$_2$
2 —— PPFB Treated at 1/6 atm GF$_2$
3 —— PTFE Grafted at 1-1/3 atm TFE
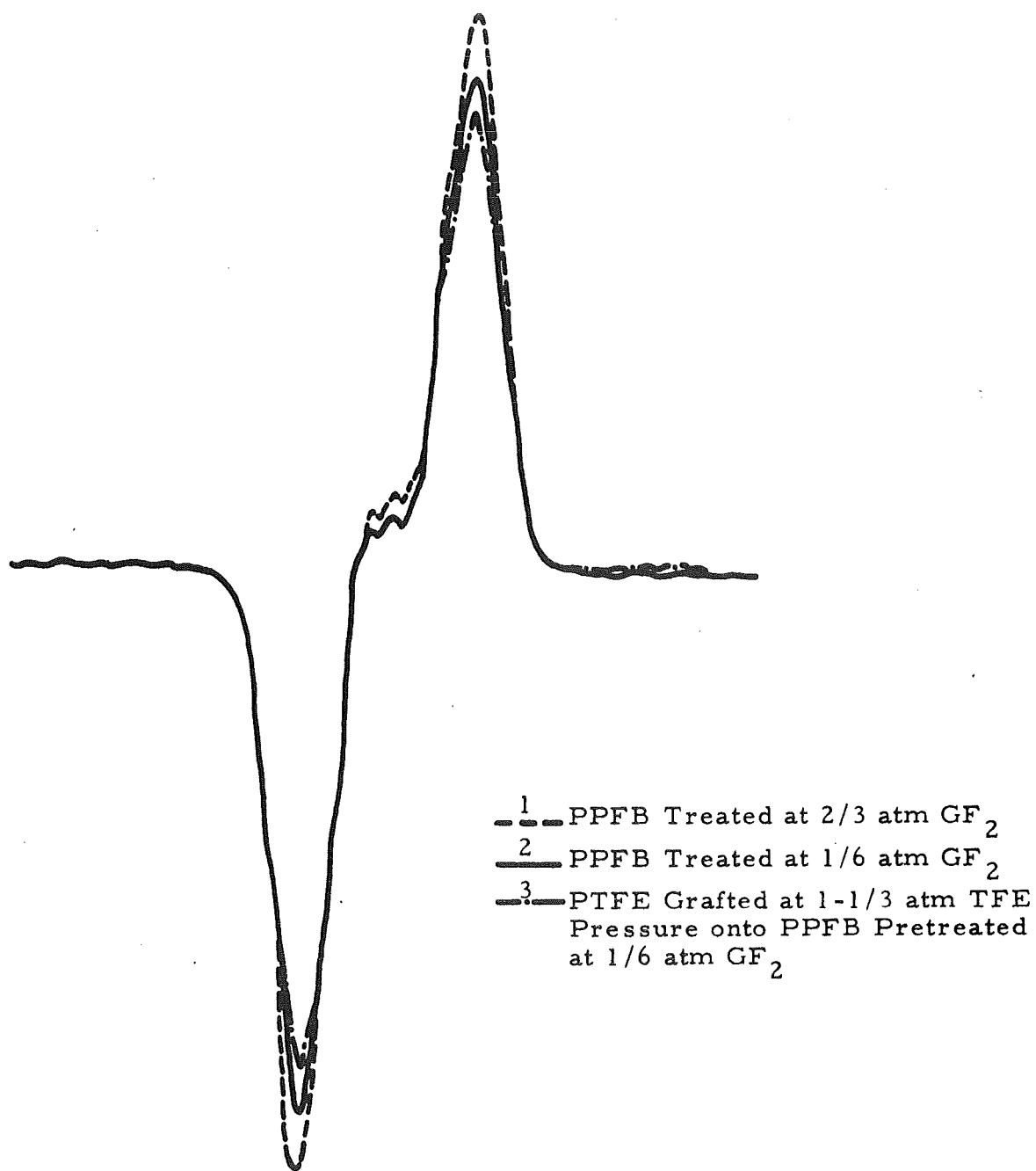Pressure onto PPFB Pretreated
at 1/6 atm GF$_2$

Figure A1. ESR spectra of fluorine treated polyperfluorobutadienes
(PPFB) and polytetrafluoroethylene (PTFE) grafted
PPFB at ambient temperature.

The decrease of radical concentrations of prefluorinated PPFB after exposure to tetrafluoroethylene (Figure A1) may be explained by possible crosslinking besides graft copolymerization.

The infrared spectra of both graft copolymerized PPFB by hexafluoropropylene epoxide (Figure A2) and tetrafluoroethylene (Figure A3) show the very strong broad band between 7.5 and 9.1μ region for C-F absorption (Reference A7). The other two characteristic absorption peaks (Reference A8) at 5.6μ for pendant perfluorovinyl group and 5.8μ for vinylene group are also present. Both graft copolymerized products were insoluble in hexafluorobenzene, dimethyl sulfoxide, dimethyl formamide, concentrated sulfuric acid, and 3M Brand Fluorochemicals FC-43 and FC-75, while both starting PPFB were hexafluorobenzene-soluble (see Experimental).

EXPERIMENTAL

Monomer

Perfluorobutadiene was obtained from Peninsular ChemResearch Company, and was shown by Mitsch and Neuvar to be 98-99% pure by vapor phase chromatography (Reference A9). The commercial monomer showed three groups of lines for its ^{19}F NMR spectrum as reported by Toy and Lawson (Reference A1) and identical infrared spectrum reported by Weiblen (Reference A10).
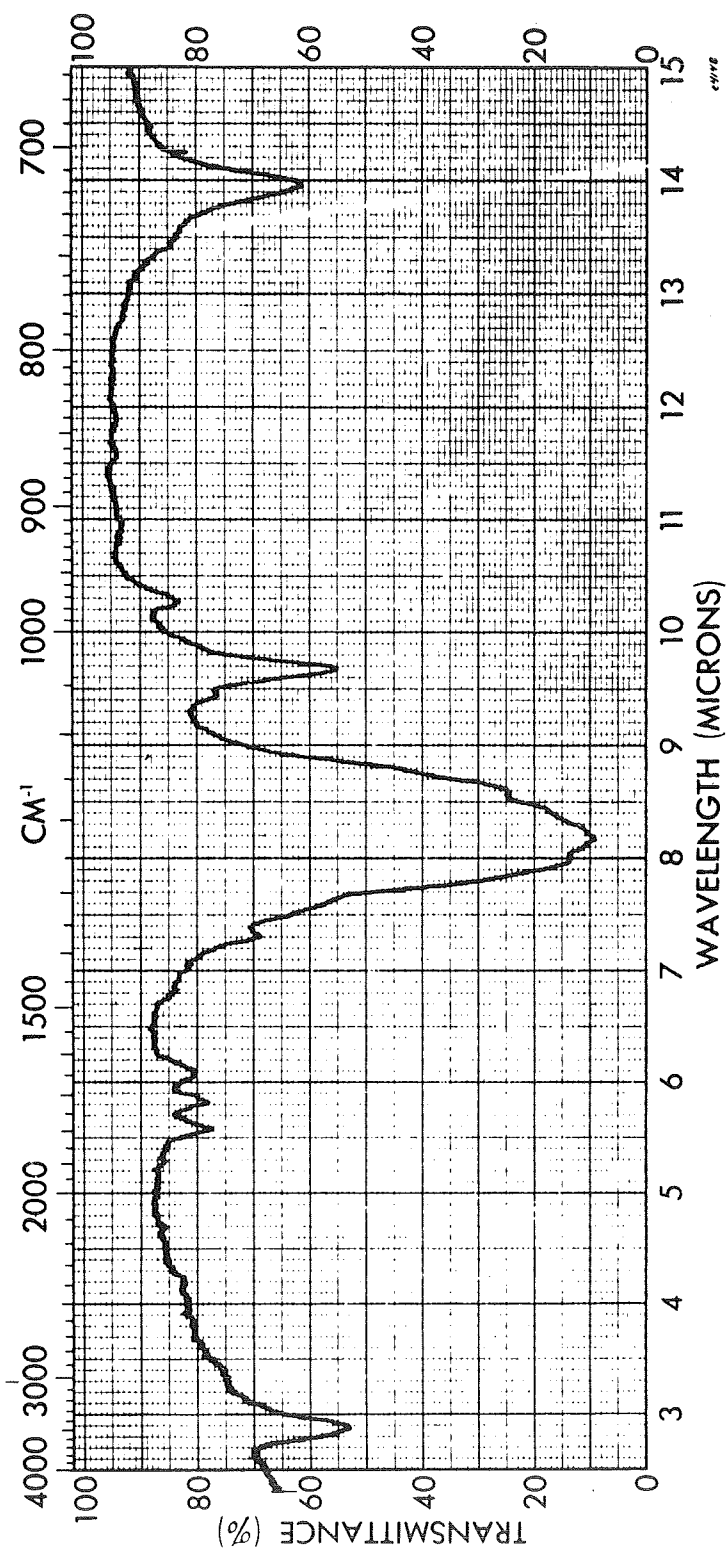
Figure A2. Infrared spectrum of the graft copolymerized and vulcanized polyperfluorobutadiene – hexafluoropropylene epoxide system.
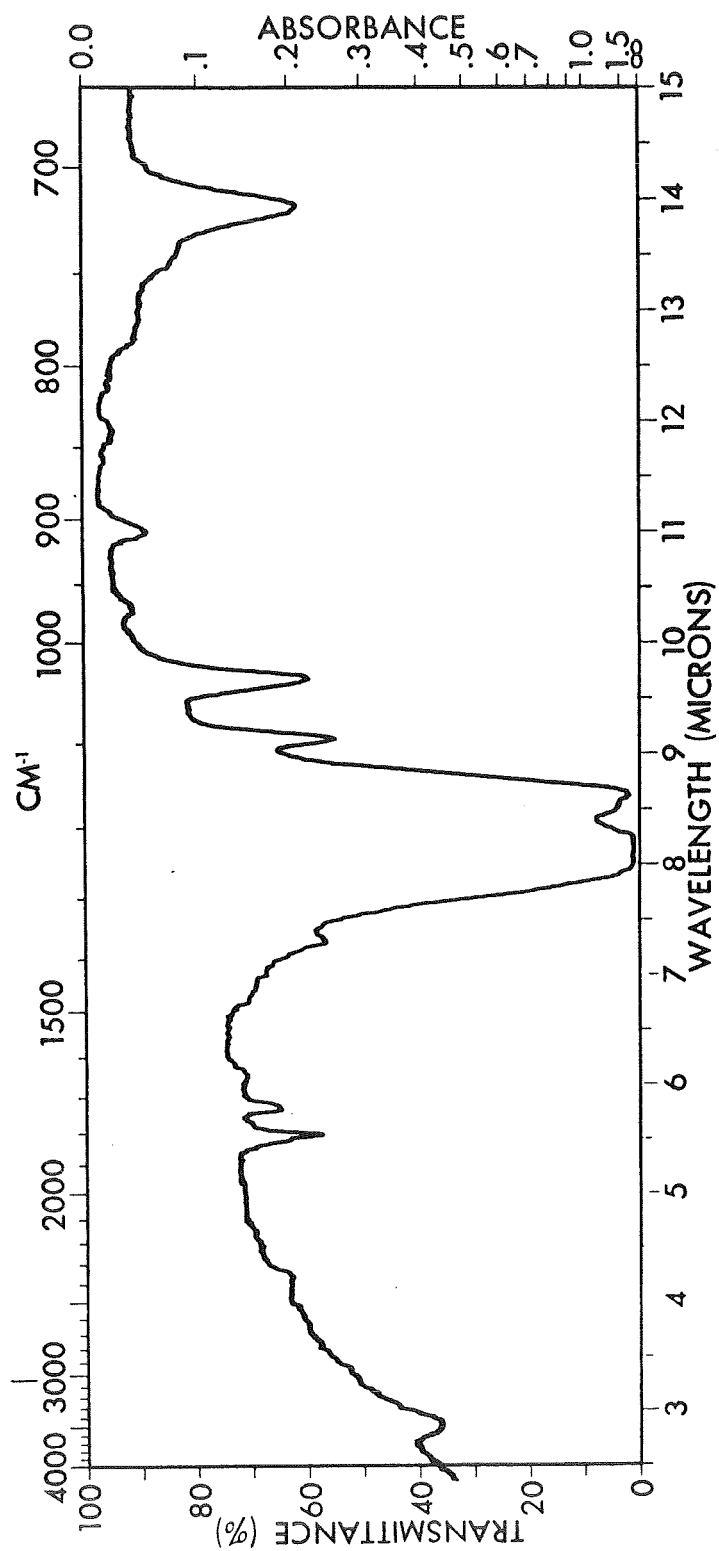
Figure A3. Infrared spectrum of graft copolymerized and vulcanized polyperfluorobutadiene – tetrafluoroethylene system.

Polymer Preparation

Diisopropyl Peroxydicarbonate as Initiator. Solid diisopropyl peroxydicarbonate (1.22g, from Pittsburgh Plate Glass Company) and a magnetic stirring rod were introduced into a zero-degree chilled Pyrex pressure bottle (marketed as Fischer-Porter Aerosol Compatibility Tube) with a metal cap and a valve. The pressure bottle was evacuated through the vacuum system while it was being chilled to liquid nitrogen temperature. The monomer (53.4g of perfluorobutadiene from Peninsular ChemResearch) was condensed into the pressure bottle and the pressure valve was closed under vacuum. The solid catalyst readily dissolved in the monomer to form a clear homogeneous solution. The closed polymerization bottle under autogenous pressure (i.e., about 2 atm) was disconnected from the vacuum and subjected to vigorous stirring for four weeks at ambient temperature. The unreacted monomer was discharged into another container through the vacuum system after cooling the pressure bottle. The white resin was dried at 50°C under reduced pressure overnight to give 23.3g (43.5% conversion) of polyperfluorobutadiene; mp 88–119°C and molecular weight 5,430 (Rast).

Anal. Calcd. for $(C_4F_6)_n$: C, 29.65; F, 70.35; Found: C, 29.62; F, 69.84.

Bis(trifluoromethyl)peroxide as Initiator. The bulk polymerization reaction was carried out by condensing perfluorobutadiene (43.4g) and bis(trifluoromethyl)peroxide as catalyst (3.9g from Peninsular ChemResearch) in an evacuated quartz pressure bottle with metal

cap and valve. The clear homogeneous solution in the pressure bottle under autogenous pressure (i.e., about 2 atm) was subjected to vigorous stirring under ultraviolet irradiation at ambient temperature for four weeks. The unreacted monomer was discharged into another container through the vacuum system after cooling the container. The white resin was dried at 50°C under reduced pressure overnight to give 17.8g (41.0% conversion) of polyperfluorobutadiene; mp 75-100°C.

Benzoyl Peroxide as Initiator. Bulk polymerization of perfluorobutadiene by benzoyl peroxide as initiator was carried out in a manner similar to previously reported (References A1 and A3).

Compatibility of Bulk Polymers with Fluorine

The bulk polymers, 0.5g, prepared by $(i-PrOCO_2)_2$, CF_3OOCF_3, and $(C_6H_5COO)_2$ as catalysts were partially dissolved and partially suspended in hexafluorobenzene and freeze-dried separately in borosilicate glass tubes with 1/4 in. necks, which were connected to a stainless steel vacuum line by Swagelok fitting. The stainless steel manifold for handling fluorine was similar to previously described (References A11 and A12). The freeze-dried bulk polymer was evacuated at 50 to 60°C for an hour, and cooled to -80°C. Gaseous fluorine, which was passed through a sodium fluoride scrubber to remove the trace amount of hydrogen fluoride impurity, was introduced slowly into the reaction tube to 1/3 atm at -80°C and warmed gradually to ambient temperature. The benzoyl peroxide-initiated bulk polymer was burnt. When gaseous fluorine was initially

102

introduced at 1 atm and ambient temperature, $(i-PrOCO_2)_2$-initiated

bulk polymer, which survived the previous initial fluorination

temperature and pressure treatment, was burnt. Only CF_3OOCF_3-

initiated bulk polymer was compatible to initial fluorination at 1 atm

fluorine pressure and ambient temperature.

Polyperfluorobutadiene Radicals

Polyperfluorobutadiene radicals were measured by freeze-drying a

series of four ESR tubes containing the same suspension of

CF_3OOCF_3-initiated bulk polymer in hexafluorobenzene. The freeze-

dried bulk polymers in ESR tubes were evacuated at 50 to 60°C for

an hour and vacuum sealed the first tube as starting material, which

gave no signals. See Figure A1 for the ESR spectra of polyperfluoro-

butadienes, which were exposed to 2/3 and 1/6 atm of fluorine

pressures at ambient temperature for five minutes, evacuated for

half an hour and vacuum sealed. Another ESR tube of identically

prefluorinated PPFB at 1/6 atm and evacuation was exposed to

1-1/3 atm of tetrafluoroethylene (Thiokol Chemical; a silica gel

column was used to remove terpene inhibitor) monomer pressure

for 20 minutes at ambient temperature and was then evacuated for

half an hour and vacuum sealed (see Figure A1).

Graft Copolymerizations

Polyperfluorobutadiene-Hexafluoropropylene Epoxide. A hexafluoro-

benzene solution of PPFB (0.12g; mp 138-141°C; [η]0.018 in

hexafluorobenzene at 30.1°C and molecular weight 3530) (Reference A1)

was freeze-dried in a borosilicate glass tube, evacuated at 70°C and cooled to -80°C, before slowly introducing gaseous fluorine which had been passed through a sodium fluoride scrubber, to 2/3 atm, and then evacuated at ambient temperature. Hexafluoropropylene epoxide (1.27g; Peninsular ChemResearch) was condensed into the reaction tube and vacuum-sealed. The reaction tube was placed in the refrigerator (0 to 4°C) for 60 days. The unreacted hexafluoropropylene epoxide was discharged into another tube through the vacuum system after cooling the tube. The white residue was evacuated at 50°C for an hour to give 0.87g of polymer; mp 275 to 285°C. The product was insoluble in hexafluorobenzene and its infrared spectrum as a KBr pellet is shown in Figure A2.

Polyperfluorobutadiene-Tetrafluoroethylene. A hexafluorobenzene solution of 1.10g of PPFB (mp 80-90°C, molecular weight 5690) was added to a borsilicate glass tube and freeze-dried. The freeze-dried PPFB in the borosilicate glass tube was evacuated at 45°C and cooled to -80°C, before slowly introducing gaseous fluorine which had been passed through a sodium fluoride scrubber, to 1/3 atm, and evacuated at ambient temperature. Tetrafluoroethylene, which had been passed through a silica gel column, was introduced at 3 atm and ambient temperature. Immediate monomer pressure drop was observed. Three recharges of tetrafluoroethylene to 3 atm were followed for a period of 4 days at ambient. The white product weighed 9.35g. The bulk properties of the product from the top part (mp 320 to 380°C) of the tube was not elastomeric nor did it resemble polytetrafluoroethylene (PTFE), but its infrared spectrum was more similar to that of PTFE than PPFB. The product from

lower part (mp 113 to 120°C) of the tube was flexible. Its infrared
spectrum as a KBr pellet is shown in Figure A3.

ACKNOWLEDGMENT

REFERENCES

A1.   Toy, M. S., and Lawson, D. D., J. Polymer Sci., Part B,
       6, 639 (1968).

A2.   Toy, M. S., and Lawson, D. D., Am. Chem. Soc. Polymer
       Preprints, 9(2), 1671 (1968).

A3.   Toy, M. S., and Newman, J. M., Am. Chem. Soc. Polymer
       Preprints, 9(1), 697 (1968).

A4.   Strain, F., U.S. Patent 2,464,062, March 1949.

A5.   Wall, L. A., and Florin, R. E., J. Applied Polymer Sci.,
       2, 251 (1959).

A6.   Toy, M. S., J. Electrochem. Soc., 114, 940 (1967).

A7.   Bellamy, L. J., The Infrared of Complex Molecules, 2nd
       Ed., John Wiley, New York, 1958, p. 30.

A8.   Fearn, J. E., Brown, D. W., and Wall, L. A., J. Polymer
       Sci., 4, 131 (1961).

A9.   Mitsch, R. A., and Neuvar, E. W., J. Phys. Chem., 70(2),
       546 (1966).

A10.   Weiblen, D. G., Fluorine Chemistry, Vol. 2, H. J. Simons,
       Ed., Academic Press, New York, 1954, p. 478.

A11.   Toy, M. S., and Cannon, W. A., J. Phys. Chem., <u>70</u>, 2241 (1966).

A12.   Toy, M. S., and Cannon, W. A., J. Electrochem., <u>114</u>, 940 (1967).

Appendix B

POLYPERFLUOROBUTADIENE. V. PHOTOPOLYMERIZATION OF PERFLUOROBUTADIENE*

INTRODUCTION

Despite the ease of polymerization of tetrafluoroethylene, the homopolymerization of other perfluoroolefins and perfluorodienes is difficult to accomplish (Reference B1). The homopolymerization of hexafluoropropene to high polymer was brought about under extreme conditions, at a temperature of 210°C and using pressures in the range of 3000-5000 atm (Reference B2). A heavy oil was reported by Roberts, when a mixture of bis(trifluoromethyl)peroxide and hexafluoropropene was irradiated by Hg 2537Å radiation (Reference B3). Wall and his co-workers attacked the polymerization resistance problem using γ-ray initiation and high pressure (up to 20,000 atm). High polymers were obtained from terminally unsaturated perfluoropentadiene (Reference B4), perfluorohexadiene, perfluoro-heptadiene and perfluorooctadiene (Reference B5). The polymerization of perfluorobutadiene was reported by Miller to give high polymer under very high pressure with oxygen and peroxide promotion (Reference B6). Recently Toy and her co-workers reported bulk polymerization of perfluorobutadiene under low pressure and temperature in the presence of free radical catalysts to give polyperfluoro-1,2- and 1,4-butadiene (References B7, B8, and B9).

---

*Presented and published in Symposium Proceedings on "Photochemistry of Macromolecules" Pacific Conference on Chemistry and Spectroscopy, Anaheim, California, October 1969.

In this paper, the photopolymerizations of perfluorobutadiene by γ-ray initiation, ultraviolet light and in the presence of CF_3OOCF_3 are described.

DISCUSSION OF RESULTS

Although the ultraviolet spectrum of perfluorobutadiene (Figure B1a) shows the rapid absorption increase from 260 to 230 mμ to the total absorption below 230 mμ, photolysis of the monomer by ultraviolet light gave very poor yield of the polymer (below 1 to 3%). Radiation induced by γ-rays increased yield to 50% conversion, but similar waxy product of molecular weight between 1500 to 2500 was obtained. The infrared spectra (Figures B2 and B3) show a strong broad band between 7.5 and 9.1μ indicating C-F absorption. The 5.6μ band identifies as pendant perfluorovinyl groups and 5.8μ band as perfluorovinylene groups. The product is thus polyperfluoro-1,2- and 1,4-butadiene.

A substantial increase of yields and molecular weights of polyperfluorobutadiene were obtained, when photolysis of perfluorobutadiene by ultraviolet light was carried out in the presence of free radical catalysts such as benzoyl peroxide, t-butyl hydroperoxide and bis(trifluoromethyl)peroxide. The results of photopolymerization in the presence of CF_3OOCF_3 were summarized in Table BI. The infrared spectra show that the ratio of peak intensity at 5.6μ indicating 1,2-polymer to 5.8μ indicating 1,4-polymer is higher for polyperfluorobutadiene initiated by photolysis in the presence of CF_3OOCF_3 as catalyst than without radiation. The X-ray

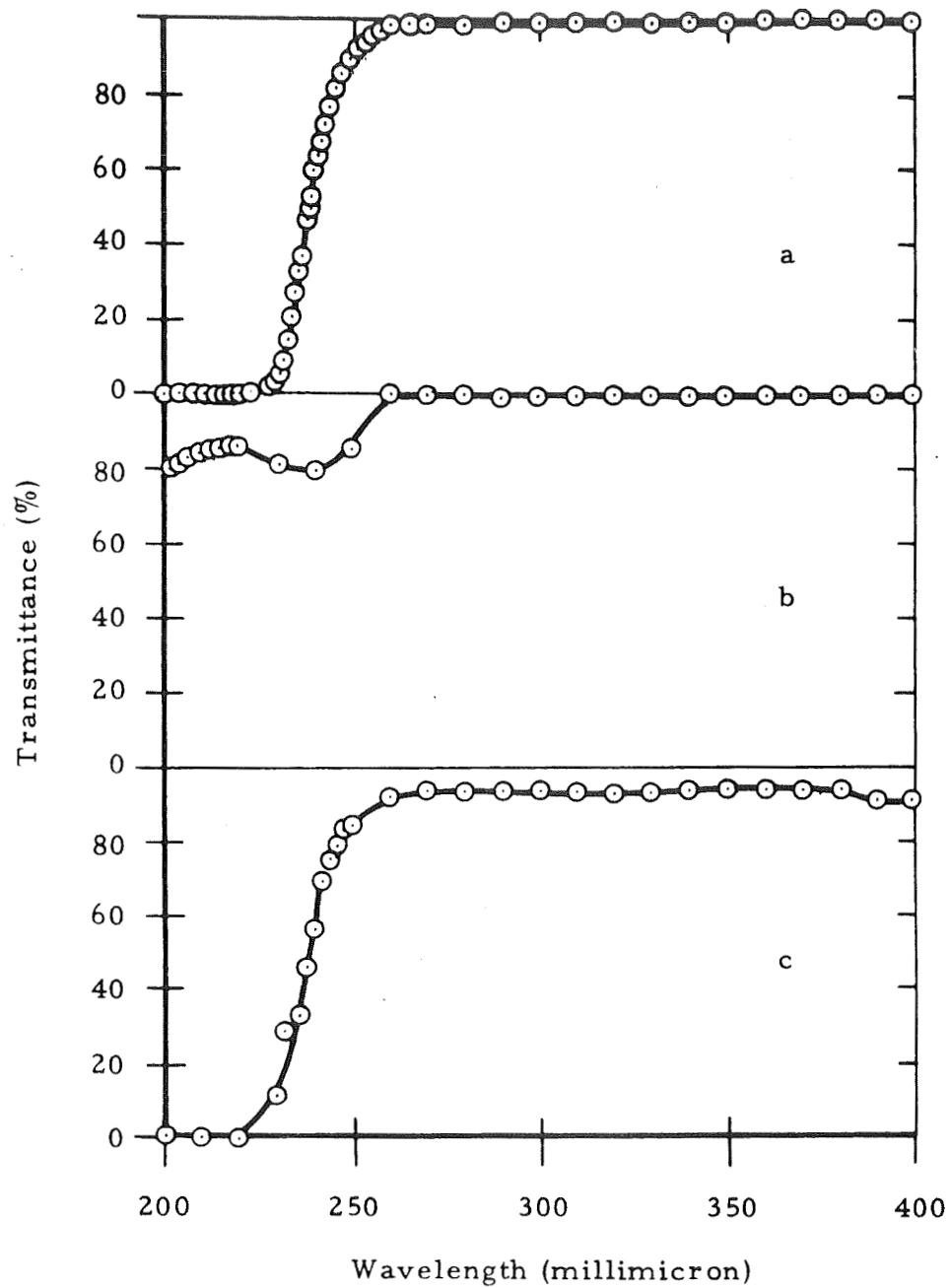Figure B1. Ultraviolet spectra of (a) perfluorobutadiene vapor at 30 mm Hg; (b) CF_3OOCF_3 vapor at 30 mm Hg; (c) mixed vapor of perfluorobutadiene (40 mm Hg) and CF_3OOCF_3 (20 mm Hg) in 1 cm cell at room temperature.
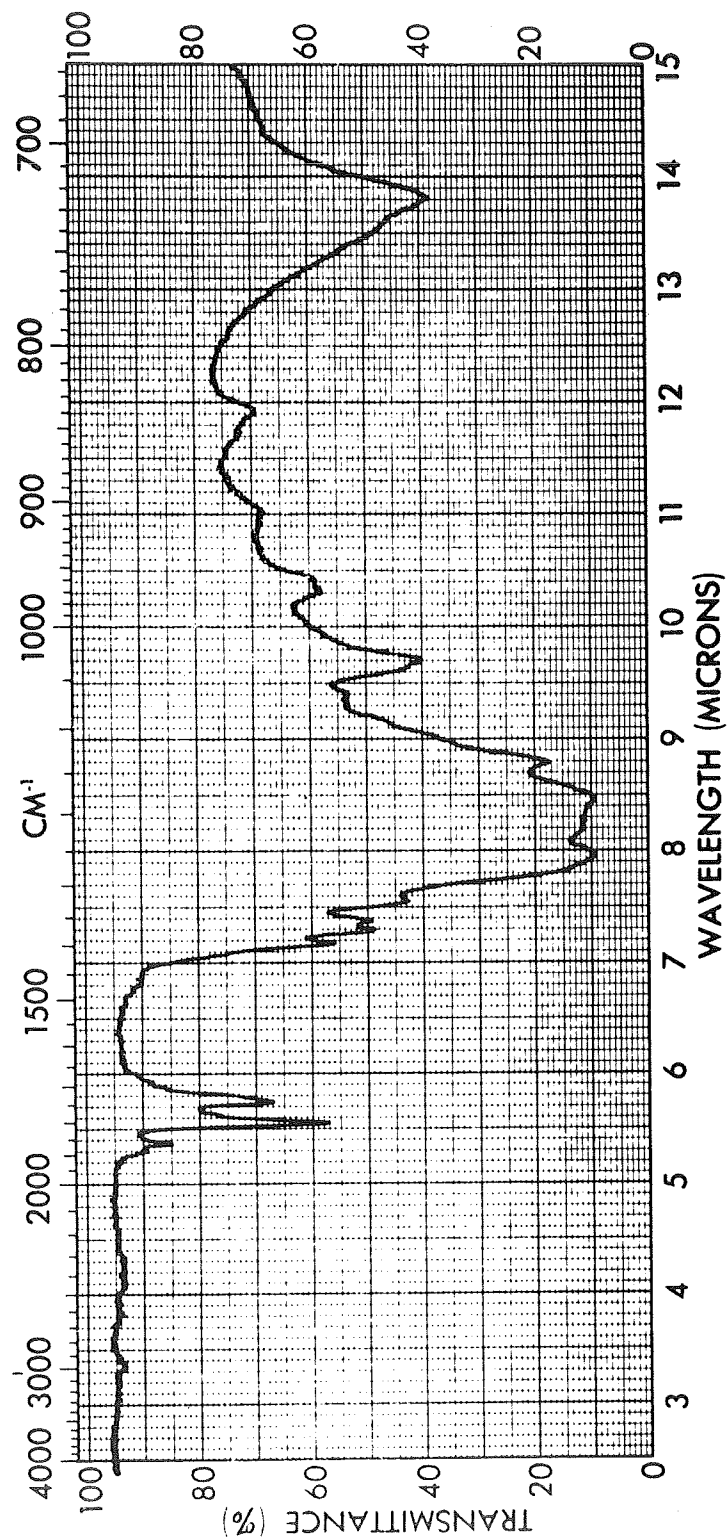
Figure B2. Infrared spectrum of polyperfluorobutadiene initiated by γ-rays.
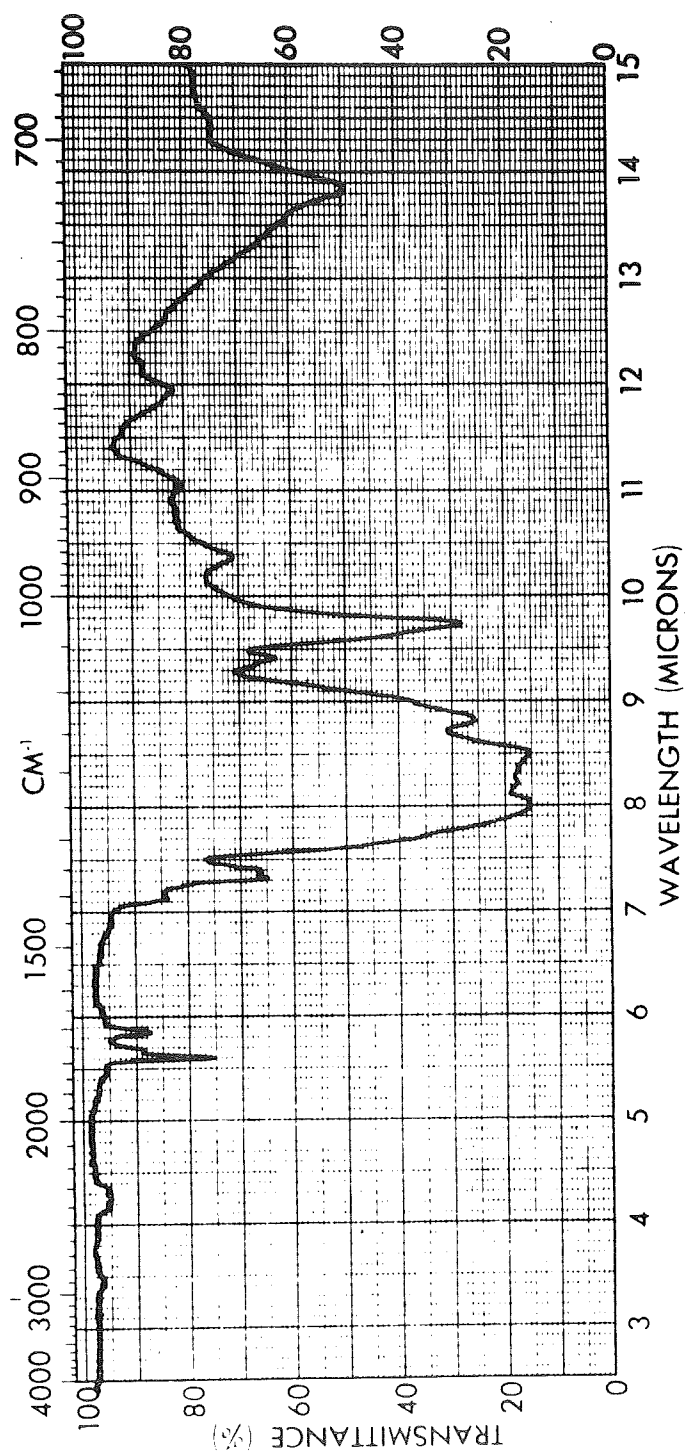
110

Figure B3. Infrared spectrum of polyperfluorobutadiene initiated by CF_3OOCF_3 under ultraviolet irradiation (batch No. 5).

Table BI

POLYMERIZATION OF
PERFLUOROBUTADIENE AT AMBIENT TEMPERATURE

Batch No.	Perfluoro-butadiene (g)	CF$_3$OOCF$_3$ as Catalyst (g)	(%)	Polym. Time (mo)	Exposure to 275-watt Sun Lamp[a]	Product Yield Conversion (g)	(%)	Tm[b] (°C)	[η][c] (dl/g)	M$_n$[d]	DP[e]
1[f]	8.8	1.1	12.5	8.0	No	1.0	11.4	157-160	—		
2	44.9	7.1	15.8	0.9	Yes	23.4	52.1	80-105	0.045	10,300	63
3	43.4	3.9	9.0	0.9	Yes	17.9	41.2	75-100			
4	45.6	6.3	13.8	3.8	Yes	43.0	94.5	<50			
5[f']	93.6	2.4	2.6	3.6	Yes	43.9	46.9	90-100	0.032	7,800	48

(a) From General Electric Company at 9 inches distance from quartz reaction vessel.

(b) In sealed capillary tube.

(c) In hexafluorobenzene at 30.1°C. Sign "—" designates insolubility at 30.1°C.

(d) Refer to Reference 8 for [η] vs. mole. wt. relationship.

(e) Approximate number of repeating units.

(f) See Table II for X-ray diffraction data.

(f') See Figure 3 for infrared spectrum and (f).

diffraction patterns of the two homopolymers were also different as shown in Table BII.

The first step of chain initiation is the breaking of the relatively weak O–O bond to give $CF_3O \cdot$ radicals,

$$CF_3OOCF_3 \rightleftharpoons 2CF_3O \cdot$$
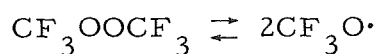
after which a chain mechanism takes place. Table BIII shows an increase of catalyst concentration following an increase in yield of

Table BII

X-RAY DIFFRACTION
PATTERNS OF POLYPERFLUOROBUTADIENE

Line	Batch No. 1[a]		Batch No. 2[a] (Under Ultraviolet)	
	d-Spacing, $\overset{o}{A}$	Intensity	d-Spacing, $\overset{o}{A}$	Intensity
1	5.20	Strong	3.55	Very strong
2	4.40	Medium	3.15	Very weak
3	4.10	Weak	2.90	Strong
4	3.80	Very weak	2.25	Very weak
5	3.55	Very weak	1.73	Weak
6	2.65	Very weak	1.52	Weak
7	2.32	Very weak	1.00	Weak

(a) Refer to Table BI

Table BIII

EFFECT OF CHANGING
MONOMER-CATALYST RATIO ON YIELDS AND
PHYSICAL PROPERTIES OF POLYPERFLUOROBUTADIENE[a]

Monomer, C_4F_6 (mmole)	Catalyst CF_3OOCF_3 (mmole)	Conversion[b] (%)	Tm[c] ($^\circ$C)
93	4.4	10.3	149-161
93	2.2	7.5	151-156
93	0.88	5.5	160-167

(a) Temperature 35°C, 20 days, under autogenous pressure about 2 atm and exposure to a 275-watt sunlamp at 1-foot from quartz reaction tube.

(b) Based on grams of polymer recovered.

(c) From DTA measurements by differential scanning calorimeter of Perkin-Elmer Model DSC-1B.

the homopolymer and a decrease of softening point. A preliminary rate of polymerization curve using CF_3OOCF_3 as catalyst under photolysis is shown in Figure B4.
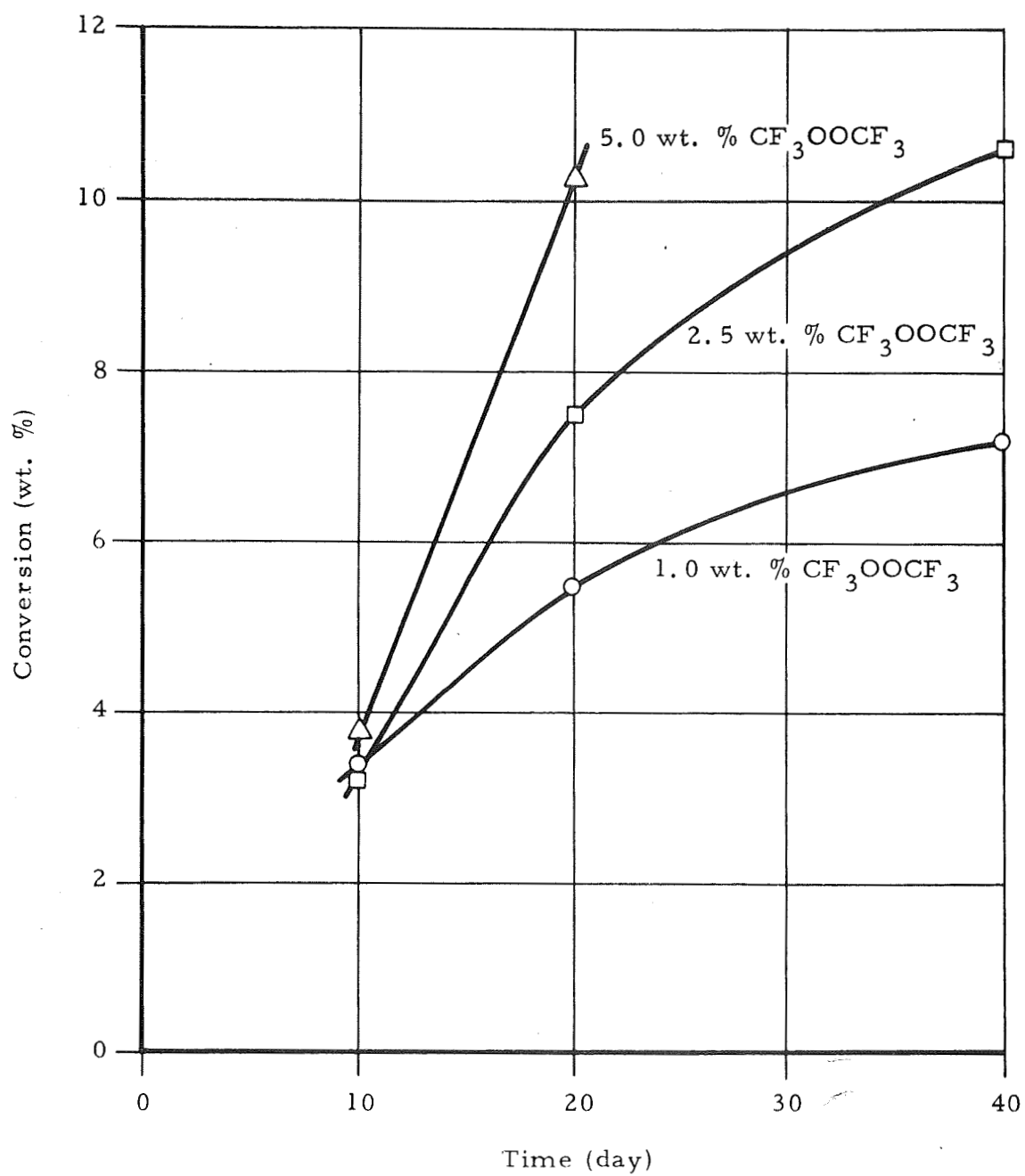
Figure B4.   Polymerization of perfluorobutadiene initiated by
CF_3OOCF_3 under ultraviolet irradiation.

EXPERIMENTAL

Monomer

Perfluorobutadiene was obtained from the Peninsular ChemResearch
Company, and was shown by Mitsch and Neuvar to be 98-99% pure
by vapor phase chromatography (Reference B10). The commercial
monomer showed three groups of lines for its F^{19} NMR spectrum
as reported by Toy and Lawson (Reference B7), and identical infrared
spectrum reported by Weiblen (Reference B11). The ultraviolet
absorption spectrum is shown in Figure B1a.

Photopolymerization Induced by γ-Rays

Perfluorobutadiene (2 ml) was vacuum sealed in a Pyrex ampoule
(3-1/2 in. × 1/2 in. o.d.) and exposed to 9.6 kilocuries of γ-rays
from a cobalt-60 source for 5 days at ambient temperature to give
50% conversion of soft wax. The solid was soluble in hot hexafluoro-
benzene and 3M Brand Fluorochemical FC-43 and partially soluble
in hot 3M's FC-75. The infrared spectrum of the solid is shown in
Figure B2.

Photolysis by Ultraviolet Light

Perfluorobutadiene (2 ml) was vacuum sealed in a quartz ampoule
(3-1/2 in. × 1/2 in. o.d.) and photolyzed by a high mercury arc
lamp (A-H6) between 0° to 5°C for one hour. The liquid was condensed
into a Pyrex reaction tube after photolysis, sealed under vacuum and

116

placed in a 60°C bath. The very small amount of residual solid appearing as a white ring around the quartz tube was insoluble in hot hexafluorobenzene. The infrared spectrum shows the characteristic broad band of C-F as well as the 5.8μ peak for perfluorovinylene groups, but the intensity of 5.6μ peak for perfluorovinyl groups was extremely weak.

The unreacted monomer, which was sealed into a Pyrex reaction tube and placed in a 60° bath, polymerized slowly. After two months, a thin layer of polymeric solid about 1% conversion covered the inside wall of the reaction tube. The infrared spectrum of the waxy solid is similar to Figure B2.

Another sealed quartz reaction tube containing the monomer as described above was placed 9 inches from a 275-watt sun lamp for a week at ambient temperature to give less than 1% conversion of white waxy solid. Its infrared spectrum is also similar to Figure B2.

Radiation Induced by Ultraviolet in the Presence of Bis(trifluoromethyl) Peroxide as Catalyst

The ultraviolet spectra of perfluorobutadiene, bis(trifluoromethyl) peroxide (Peninsular ChemResearch) and the mixed vapor of the monomer and the catalyst are shown in Figure B1.

A series of bulk polymerizations was carried out by condensing monomer into the pressure bottles (Pyrex or quartz) with metal caps and two-way valves. The clear homogeneous solutions in the

pressure bottles under autogenous pressure (i. e., about 2 atm) were subjected to vigorous stirring (except Batch No. 1 of Table BI) at ambient temperature. The source of ultraviolet irradiation was a General Electric 275-watt sun lamp 9 inches from the quartz reaction vessels. The unreacted monomer at the end of each experiment was discharged into another container through the vacuum system after cooling the container. The white resins were dried at 50°C under reduced pressure overnight. The results of polyperfluorobutadiene preparations are summarized in Table BI.

The X-ray diffraction patterns (Table BII) were prepared by the use of CuKα radiation ($\lambda = 1.542$Å) in a camera of 57.3 mm radius. The powder, prepared by grinding in an agate mortar at ambient temperature, was mounted on a quartz fiber about 0.1 mm in diameter, using Vaseline as a binder.

ACKNOWLEDGMENT

REFERENCES

B1. Adams, R. M., and Bovey, F. A., J. Polymer Sci., 9, 481 (1952).

B2. Elenterio, H. S., U.S. Patent 2,958,685 (E. I, duPont de Nemours and Co.), 1960.

118

B3. Roberts, H. L., J. Chem. Soc., 4538 (1964).

B4. Fearn, J. E., Brown, D. W., and Wall, L. A., J. Polymer Sci., Part A-1, 4, 131 (1966).

B5. Wall, L. A., Am. Chem. Soc. Polymer Preprints, 7(2), 1112 (1966).

B6. Miller, W. T., Preparation, Properties and Technology of Fluorine and Organic Fluoro Compounds, ed. by C. Slesser and S. R. Schram, McGraw-Hill, N. Y., 1951, pp. 624-626 and p. 604.

B7. Toy, M. S., and Lawson, D. D., J. Polymer Sci., Part B, 6, 639 (1968).

B8. Toy, M. S., and Lawson, D. D., Am. Chem. Soc. Polymer Preprints, 9(2), 1671 (1968).

B9. Toy, M. S., and Newman, J. M., J. Polymer Sci., Part A-1, in press (1969).

B10. Mitsch, R. A., and Neuvar, E. W., J. Phys. Chem., 70(2), 546 (1966).

B11. Weiblen, D. G., Fluorine Chemistry, Vol. 2, ed. by J. H. Simons, Academic Press, N. Y., 1954, p. 478.

Appendix C

THERMAL VERSUS PHOTOPOLYMERIZATIONS OF
PERFLUOROBUTADIENE BY
CF_3OOCF_3 CATALYSIS*

INTRODUCTION

The thermal polymerization of perfluorobutadiene in the absence of catalyst was reported by Prober and Miller (Reference C1) over the temperature range 150 to 180°C to form perfluorocyclobutene, dimers, trimers, and some high boiling material. The high boiling fractions were viscous liquids which indicated low degree of polymerization. The polymerization of perfluorobutadiene by free radical catalysis under autogenous pressure about 2 atm and at ambient or slightly elevated temperature was reported to give solid polyperfluoro-1,2- and 1,4-butadiene (References C2 and C3).

The use of CF_3OOCF_3 as polymerization initiators at temperatures of 100° to 250°C was reported by Darby and Ellingboc (Reference C4). A heavy oil was reported by Roberts, when a mixture of CF_3OOCF_3 and hexafluoropropene was irradiated by Hg 2537Å radiation (Reference C5). Bulk polymerization of perfluorobutadiene by CF_3OOCF_3 catalysis was recently reported to give solid polyperfluoro-1,2- and 1,4-butadiene of molecular weight around 10,000 and yield from 5 to 95% depending on the monomer-catalyst ratio, polymerization time, photolysis and agitation (References C6

---

*Presented at the 159th ACS Meeting, Houston, Texas, February 1970, and published in ACS Polymer Preprints, 11(1), 121-126 (1970).

121

and C7). This paper describes the thermal polymerization of perfluorobutadiene by CF_3OOCF_3 catalysis and the larger scale preparations of the homopolymer by photolysis.

RESULTS AND DISCUSSION

In the present work, the thermal polymerization of perfluorobutadiene by CF_3OOCF_3 catalysis was studied between 35 to 100°C. Figure C1 shows the isothermal plots of the conversion of polymer recovered versus time of polymerization. An increase of yield followed an increase of temperature (35 to 100°C) and time of polymerization after an initial lag period of 10 days. A substantial increase of yield was shown by an increase of temperature at 75°C and above. White polymeric solids were obtained from all polymerization tubes (see Experimental) except the ones at 100°C for 15 and 20 days period. The former was a semisolid and the latter was a very viscous liquid. The products of polymerization temperature exceeding 75°C show not only a definite decrease of degree of polymerization, but also the presence of low boiling fractions, which probably constituents of dimers, trimers, and cyclic structures as previously reported (Reference C1) in the recovered monomer fraction. The infrared spectra of the recovered monomers from the polymerization temperatures at 75 and 100°C show an additional 7.8μ peak, which is absent in the pure monomer as described by Weiblen (Reference C8).

The comparison of results of polymer preparations under identical monomer-catalyst ratio at 50°C and 35°C under photolysis (Reference C6) without agitation is shown in Table CI. The homopolymers
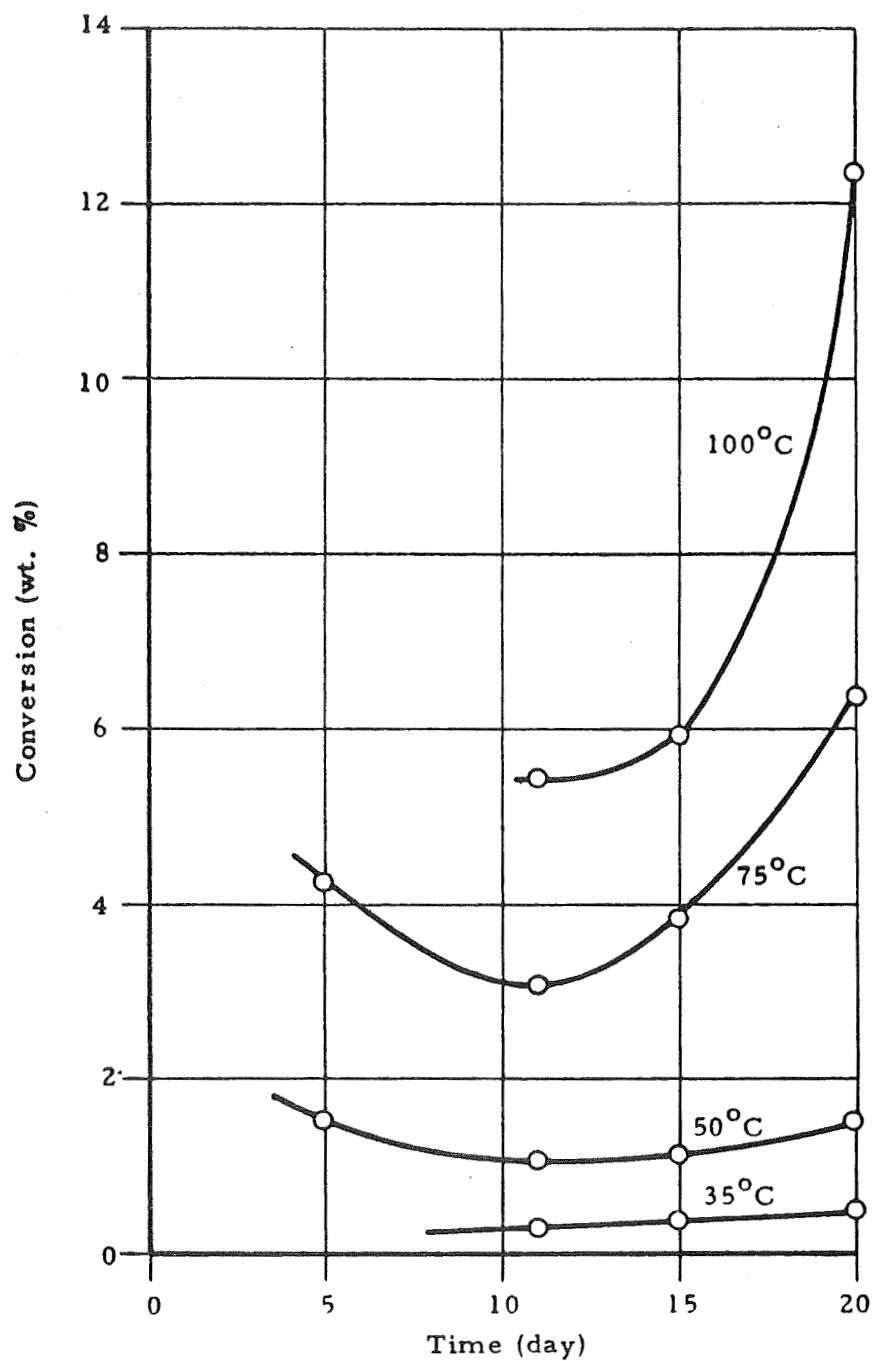
Figure C1. Isothermal plot of PPFB conversion versus time in the presence of CF_3OOCF_3 (3.9 wt. %) as catalyst.

Table CI

EFFECT OF CHANGING
MONOMER-CATALYST RATIO FOR THERMAL
AND PHOTOPOLYMERIZATIONS OF PERFLUOROBUTADIENE[a]

Catalyst CF_3OOCF_3 (mmoles)	Thermal[b]		Photolysis[c]	
	Conversion[d] (%)	Tm (°C)	Conversion[d] (%)	Tm (°C)
0.88	1.09	123–137	5.5	160–167
2.2	1.35	117–147	7.5	151–156
3.5	1.55	127–153		
4.4	1.88	130–158	10.3	149–161

[a] Monomer (93 mmole perfluorobutadiene) under autogenous pressure about 2 atm for 20 days.

[b] Temperature 50°C, no radiation.

[c] Temperature 35°C and exposure to a 275-watt sunlamp at 1-foot distance from quartz reaction tube (Reference C6).

[d] Based on grams of polymer recovered.

under photolysis give better yields at 35°C than without radiation at 50°C. Since low temperatures inhibit side reactions and the properties of a polymer are improved by going to lower polymerization temperatures, photopolymerization rather than thermal polymerization is recommended for larger scale preparations of polyperfluorobutadiene by CF_3OOCF_3 catalysis.

A polymer tumbling apparatus is shown in Figure C2 to provide agitation for larger scale bulk polymerization under ultraviolet irradiation.
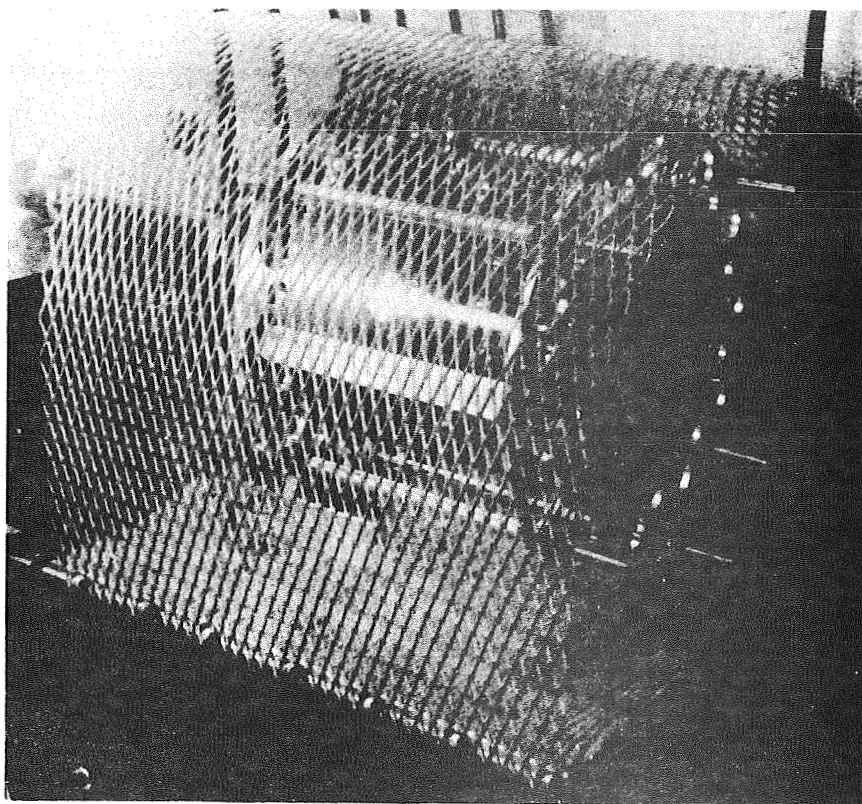
Figure C2. Polymer tumbling apparatus.

EXPERIMENTAL

Effect of Changing Polymerization Temperature and Time. A series
of bulk polymerizations was carried out by condensing 15g
(93 mmole) perfluorobutadiene and 3.9 wt. % (3.5 mmole) of
CF_3OOCF_3 as catalyst into each of fourteen evacuated Pyrex
reaction tubes (4-1/2 in. × 1/2 in. o.d. with a 1/4 in. o.d. neck
connecting to the vacuum line by Cajon ultra-torr union fitting) and
vacuum sealed. Both monomer and catalyst were obtained from
Peninsular ChemResearch and were measured by displacement as
a gas at known volume and pressure according to calculation based

on the perfect gas laws. The two sets of four sealed polymerization tubes were placed separately in a 75°C and 50°C ovens and removed one tube at 75°C and one tube at 50°C at end of each time intervals of 5, 11, 15, and 20 days. Another two sets of three sealed polymerization tubes were placed separately in 100°C and 35°C oven and removed one tube at 100°C and one tube at 35°C at end of each time intervals of 11, 15, and 20 days. The unreacted monomer of each tube and also including some low boiling fractions from polymerization tubes placed at 75 and 100°C ovens were discharged into another container through the vacuum system after first cooling the content of the tube to solid before opening the 1/4 in. o. d. neck of the sealed tube with a file and connected the tube to the vacuum line by Cajon union fitting. The product was continued to evacuate for an hour at ambient temperature.

Effect of Changing Monomer-Catalyst Ratio. A series of bulk polymerizations was carried out in the same manner as described above, except the catalyst concentrations were varied at 0.88, 2.2, and 4.4 mmoles of CF_3OOCF_3 in 93 mmoles of perfluorobutadiene at 50°C for 20 days. The results were summarized in Table CI.

Larger Scale Preparation. The scale-up photopolymerization of perfluorobutadiene was carried out in a vacuum sealed 25 mm o. d. quartz tube of 9 to 12 inches in length, mounted in a polymer tumbling apparatus (Figure C2). Perfluorobutadiene by CF_3OOCF_3 catalysis was exposed to 400-watt mercury lamp to give yield around 50% for 60 days at ambient temperature.

126

ACKNOWLEDGMENT

REFERENCES

C1. Prober, M., and Miller, W. T., J. Am. Chem. Soc., $\underline{71}$, 598 (1949).

C2. Toy, M. S., and Lawson, D. D., J. Polymer Sci., Part B, $\underline{6}$, 639 (1968).

C3. Toy, M. S., and Newman, J. M., J. Polymer Sci., Part A-1, $\underline{7}$, 2333 (1969).

C4. Darby, R. A., and Ellingboc, E. K., (to E. I. duPont DeNemours), U.S. Patent 3,069,404 (December 18, 1962).

C5. Roberts, H. L., J. Chem. Soc., 4538 (1964).

C6. Toy, M. S., Proceedings of Photochemistry of Macromolecules Symposium, J. Macromol. Sci., in press.

C7. Toy, M. S., and Lawson, D. D., Am. Chem. Soc. Polymer Preprints, $\underline{9}$(2), 167 (1968).

C8. Weiblen, D. G., Fluorine Chemistry, Vol. 2, ed. by J. H. Simons, Academic Press, N.Y., 1954, p. 478.

Appendix D

UTILIZATION OF OXYGEN DIFLUORIDE FOR
SYNTHESES OF FLUOROPOLYMERS*

INTRODUCTION

In the great majority of chemical reactions of oxygen difluoride,

the compound acts as a powerful fluorinating agent (Reference D1).

Besides its fluorine-like reactions, there are a few instances where

OF_2 has been reported to form products resulting from simple OF_2

addition to the substrate, such as the addition to SO_2 and SO_3

(References D2 and D3). The addition of OF_2 to carbonyl fluoride

was reported to produce bis(trifluoromethyl)trioxide and a polar

mechanism was suggested (References D4 and D5).

The utilization of OF_2 as chain extender for polyperfluoropolyenes,

to insert functional groups into fluoropolymers and for addition

copolymerizations with perfluorodienes or perfluorodiolefins have

not been investigated to our knowledge. This paper describes some

of our results in using OF_2 as a difunctional reagent for syntheses

of new fluoropolymers.

RESULTS AND DISCUSSION

The reactions of OF_2 are potentially hazardous, because of the high energy content and oxidizing reactivity of OF_2. Suitable protective equipments must be used when working with these reactions, as explosions of considerable force have occurred.

The polymerization of perfluorobutadiene by free radical catalysis to give polyperfluoro-1,2 and 1,4-butadiene has been previously described (References D6 and D7). Bis(trifluoromethyl)peroxide was selected as the initiator (References D8 and D9), because the polymers obtained are free of end groups to impart chemical instability (Reference D10). This is affirmed by the recent compatibility result of CF_3OOCF_3-initiated polyperfluorobutadiene in fluorine (References D7 and D11). The same initiator was selected for the polymer preparation of this study.

The results of reactions of OF_2 and polyperfluorobutadiene (Table DI) indicate that OF_2 under controlled experimental conditions can function as chain extender and insertion of acyl fluoride groups into the polymer structure. Table DII shows the comparison of physical properties of polyperfluorobutadiene before and after OF_2 exposure, where chain extension is accompanied by insertion of acyl fluoride groups (see Experimental for procedure). Prolonged exposure of OF_2 extends chemical attack to the vinylene bonds to cause chain scission (Figure D1 and Table DI).

130

Table DI

REACTIONS OF OF_2 WITH POLYPERFLUOROBUTADIENE

Starting Polymer[a]	OF_2				Product						
	Concentration, Flow or Static	Pressure (atm)	Temperature (°C)	Time (hr)	Relative infrared peaks among			$Tm^{(b)}$ (°C)	$[\eta]^{(c)}$ dl/g	M_n	DP
					5.3 μ $-\overset{\text{O}}{\overset{\|}{C}}-F$	5.6 μ $-CF=CF_2$	5.8 μ $-CF=CF-$				
Freeze-dried Solid of Batch 8320-19-1	100% OF_2,	2	25	25	Strong	Medium	None				
Ditto	100% OF_2, static	2	50	1	Strong	Medium	Weak				
Freon 113-stirred Suspension of Batch 8320-19-1	100% OF_2, flow	1	19	4	Strong	Medium	Weak	<30			
Ditto	100% OF_2, flow	2	25	168	Very Strong	Weak	None	<25			
Ditto	50% OF_2-He, flow	1-1/3	20	4	Weak	Strong	Weak	100-112	0.04	10,100	62
Freeze-dried Solid of Batch 8320-19-1	100% OF_2, static	2	50	18	Strong	Weak	None	53-74			
Freon 113-stirred Suspension of Batch 8320-19-1	50% OF_2-He, flow	1-1/3	25	2	Weak	Strong	Medium	97-106			
Freon 113-stirred Suspension of Batch 8320-24-1	100% OF_2, flow	2	15	144	Weak	Strong	None	<25	0.0125	2,000	12
Ditto	100% OF_2, flow	2	15	4	Medium	Medium	Weak	120-135	0.061	20,000	123
Ditto	50% OF_2-He, flow	1-2/3	0	1	None	Strong	Medium	130-145	—		
Ditto	50% OF_2-He, static	1-1/3	0	1	None	Medium	Weak	117-125	0.032	7,800	48
Ditto	50% OF_2-He, static	1-1/3	20	4	Weak	Strong	Medium	130-145	—		
Ditto	50% OF_2-He, flow	1-1/3	0	1	None	Strong	Weak	127-147	—		

(a) Both polyperfluorobutadidnes, Batch No. 8320-19-1 (Tm <50°C) and Batch No. 8320-24-1 (Tm 90-100°C; $[\eta]$ 0.032; Mol. wt. 7,800) were initiated by CF_3OOCF_3 as catalyst.
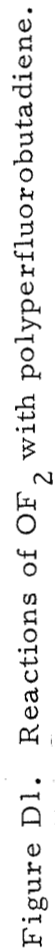
(b) In sealed capillaries.

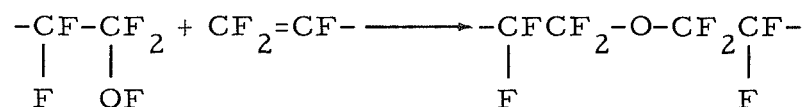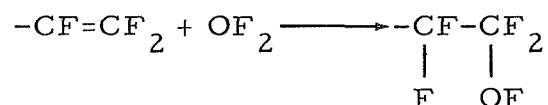(c) In hexafluorobenzene at 30.1°C. Sign "—" designates partial solubility at 30.1°C.

131

Table DII

COMPARISON OF PHYSICAL PROPERTIES OF
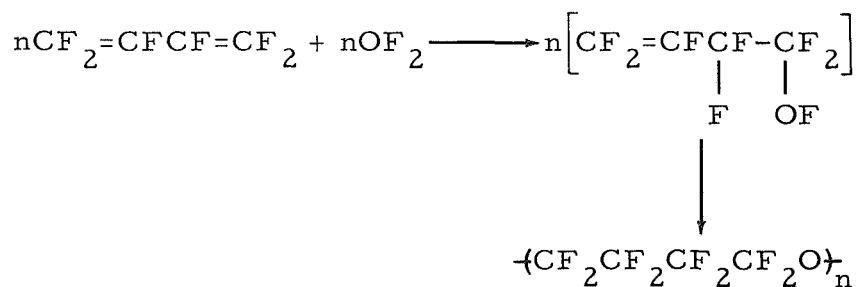
POLYPERFLUOROBUTADIENE BEFORE AND AFTER OF_2-EXPOSURE

	Polyperfluorobutadiene	Same Polymer After OF_2-Exposure[a]
Melting point[b], °C	132-142	120-135
Density, g/cm^3	1.990	1.994
$[\eta]$[c], dl/g	0.032	0.061
M_n	7,800	20,000
DP	48	123
X-ray d-spacing, Å	3.55(vs), 3.15(vw), 2.90(s), 2.25(vw), 1.73(w), 1.52(w), 1.00(w)	5.20(s), 4.40(s), 3.40(w), 3.00(w), 2.60(m), 2.30(m), 2.11(w), 1.91(vw), 1.86(vw), 1.58(vw), 1.50(vw), 1.18(vw), 1.04(vw)
Nature of product	White hard elastomer	Colorless gum

(a) See Polymer Chain Extension Section under Experimental.

(b) From DTA measurements by differential scanning calorimeter of Perkin-Elmer Model DSC-1B.

(c) In hexafluorobenzene at 30.1°C.

(d) With CuKα radiation (λ = 1.542Å) in a camera of 57.3 mm radius.

Figure D1. Reactions of OF_2 with polyperfluorobutadiene.

By controlling the reaction temperature at 0°C and below, chain extension of polyperfluorobutadiene has been achieved without the presence of acyl fluoride groups in the polymer structure (Table DI).

$$-CF=CF_2 + OF_2 \longrightarrow -\underset{\underset{F}{|}}{C}F-\underset{\underset{OF}{|}}{C}F_2$$

$$-\underset{\underset{F}{|}}{C}F-\underset{\underset{OF}{|}}{C}F_2 + CF_2=CF- \longrightarrow -\underset{\underset{F}{|}}{C}FCF_2-O-CF_2\underset{\underset{F}{|}}{C}F-$$

The foregoing example strengthens our contention that oxygen difluoride behaves as a difunctional reagent with perfluoroalkenes, it seems likely that copolymerization of OF_2 with perfluorobutadiene would be feasible as shown below:

$$nCF_2=CFCF=CF_2 + nOF_2 \longrightarrow n\left[CF_2=CFCF-CF_2\underset{\underset{F}{|}}{}\underset{\underset{OF}{|}}{}\right]$$

$$\downarrow$$

$$-(CF_2CF_2CF_2CF_2O)_n$$

The product of such intermolecular additions is poly(perfluorotetramethylene oxide). The infrared spectrum of copolymer of OF_2 and perfluorobutadiene as shown in Figure D2 is almost identical to 3M Company's carboxyl terminated poly(perfluorotetramethylene oxide), $HOOCCF_2CF_2\left[O(CF_2)_4\right]_{7-8}OCF_2CF_2COOH$, which was
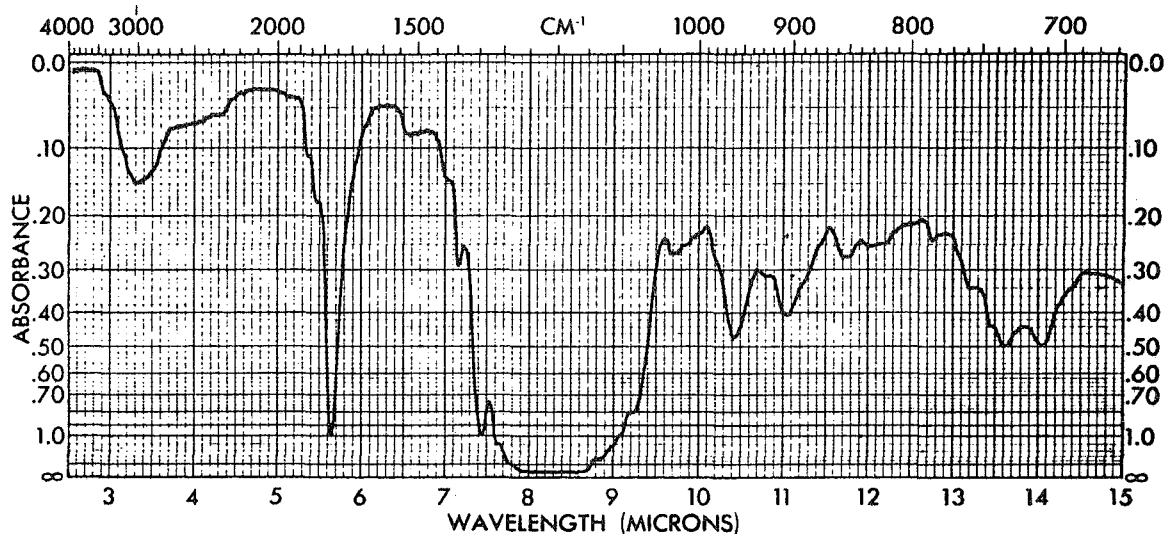
134

Figure D2. Infrared spectrum of carboxyl terminated copolymer of perfluorobutadiene and oxygen difluoride.

synthesized entirely from another route by photopolymerization of perfluorooxydiporpionyl fluoride.

EXPERIMENTAL

Materials

The preparation of polyperfluorobutadiene by bis(trifluoromethyl) peroxide catalysis has been previously described (References D8 and D9). Perfluorobutadiene and bis(trifluoromethyl)peroxide were obtained from Peninsular ChemResearch, fluorine and Freon 113 from Air Products, hexafluorobenzene from Pierce Chemicals and oxygen difluoride from Allied Chemicals. The reagents were used without further purification, except the vapors of oxygen difluoride

and fluorine were passed through sodium fluoride scrubbers to remove possible hydrogen fluoride impurity before use.

Apparatus

A stainless steel vacuum line constructed of Type 304 stainless steel tubing (1/4 in. o.d.) and Types 316 and 321 stainless steel Nupro "BG" bellows valves was employed for manipulation of OF_2 as shown in Figure D3. Careful exclusion of moisture is essential in handling OF_2 reactions. The presence of any water vapor will cause noticeable attack on Pyrex reaction vessel and stainless steel manifold. Pressures were measured with Bourdon gauges, because mercury manometer cannot be used. For precision pressure measurement, the Bourdon gauge was replaced by Seegers Model SS2500A-30 (0 to 60-in. Hg with 600 increments) gauge of accuracy to 0.005-in. Hg. The metal parts of the vacuum system were first washed or soaked for 15 minutes in Oakite-33, and rinsed with distilled water, acetone and Freon 11. Vapor-degreasing with trichloroethane or trichloroethylene (Reference D12) is recommended before the final rinse with Freon 11. The smaller metal parts were dried in a vacuum oven at 100°C for 15 minutes and the larger pieces or long tubings were flushed with a stream of anhydrous oil-free nitrogen. After assembly, the vacuum system was leak-checked, evacuated for 1 hour and passivated with gaseous fluorine at 1 atm and ambient temperature for 1 hour. The system was evacuated and ready for use.
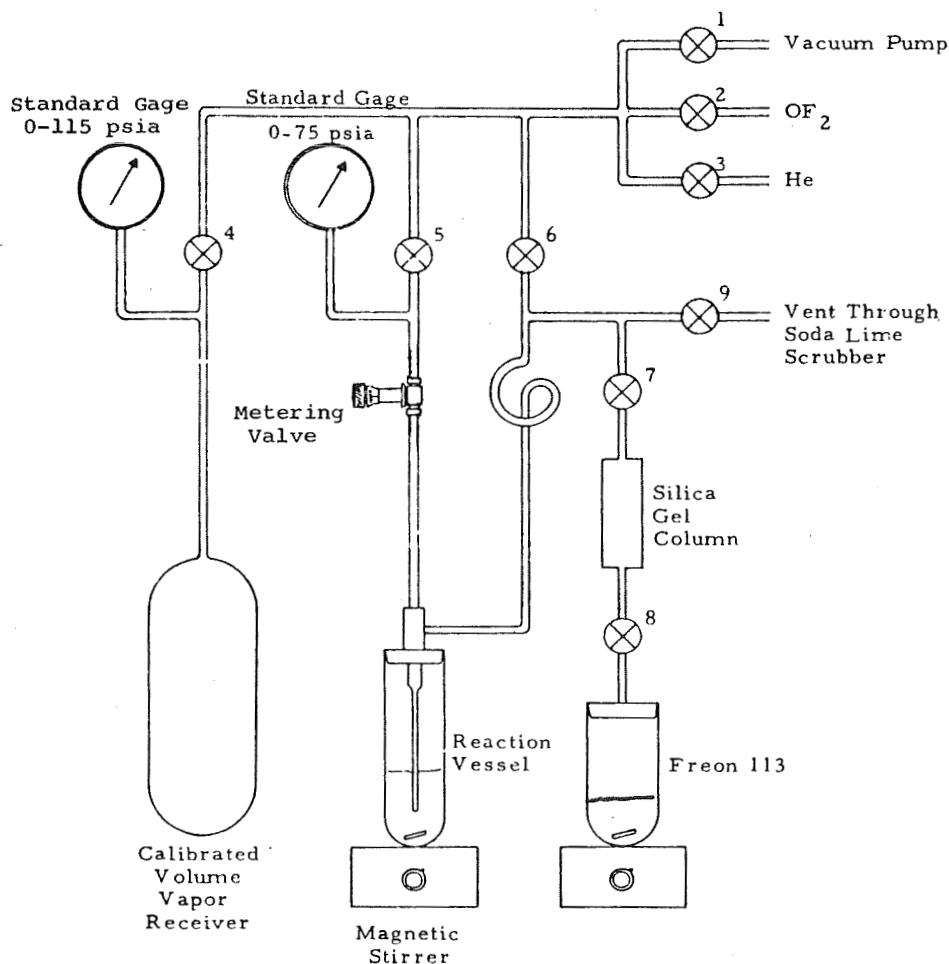
136

Figure D3. The reaction apparatus for oxygen difluoride and
polyperfluorobutadiene.

For static state OF_2 reaction of 1g or less quantity of polyperfluoro-
butadiene, Pyrex tube as shown in Figure D4A was usually selected
as the reaction vessel, while for larger quantity of polymer, Pyrex
pressure bottle (marketed as Fischer-Porter Aerosol Compatibility
Tube) fitted with metal cap and a two-way valve (Figure D4B) was
used. For flow state OF_2 reactions, the two sizes of reaction
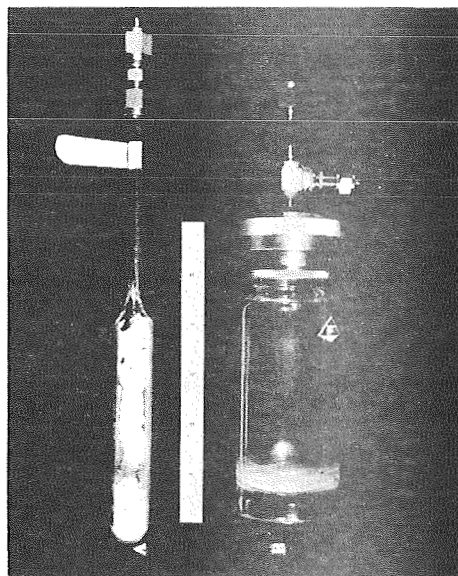vessels were shown in Figure D5.

Figure D4. Reaction vessels for static state OF_2 with polyperfluorobutadiene studies.
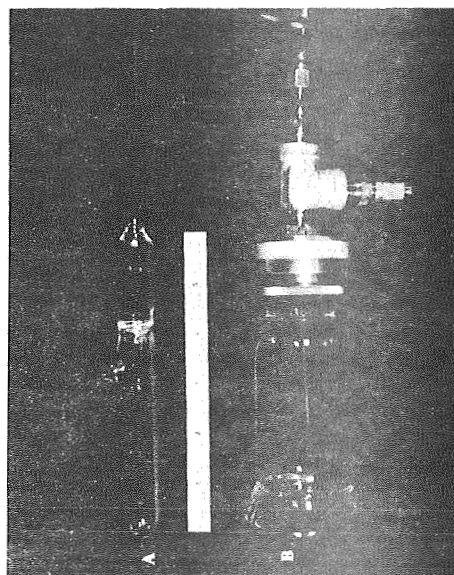

Figure D5. Reaction vessels for flow state OF_2 with polyperfluorobutadiene studies.

138

Polymer Chain Extension

A Pyrex pressure bottle was fitted with a metal cap and a stainless
steel bubbling tube with a welded-on metal syringe tip of 1 mm i. d.
as shown in Figure D5B. Polyperfluorobutadiene (5g, $[\eta]$ 0.032,
Mole. Wt. 7,800 of Table DII) and a magnetic stirring rod were
placed in the pressure vessel. The manifold system (Figure D3)
was evacuated by opening valves 1, 4 to 7, then 8 until Freon had
been boiling off for 30 seconds, then valves 8 and 7 were closed in
sequence. The evacuation was continued and followed by closing
valves 5 and 6 before valve 1. Gaseous OF_2 was introduced into
the vapor receiver by opening valve 2 until the pressure reached
20 psia, then valves 2 and 4 were closed. Valve 1 was opened for
evacuation, then valves 5 to 7 overnight. Anhydrous Freon 113
(50 ml) was condensed into the reaction vessel by closing valves 1,
5 and 6, opening valve 8 and placing a liquid nitrogen bath around
the reaction vessel. Valves 7 and 8 were closed. The polymer was
stirred in Freon 113 after warming to ambient temperature at 15°C
until a polymer suspension was formed. Helium was used to check
the gas bubbling rate by first opening valves 5 and 6, then introducing
helium by opening valve 3 into the system at 20 psia before opening
the vent valve 9 to a flow rate at about one bubble per second.
Oxygen difluoride was bubbled through the reaction vessel at the
same flow rate by closing valve 3 and opening valve 4. Bubbling
OF_2 was continued for 4 hours at 15°C.

At the end of 4 hours, the reaction vessel was purged with helium
by closing valve 4 and opening valve 3 to sweep out oxygen difluoride.
Valves 3 and 9 were closed and 1 opened for evacuation of Freon 113

under stirring. The colorless gum was left in the reaction vessel and evacuated overnight. Valve 1 was closed and valve 3 opened to introduce helium to 1 atm (15 psia). All valves were closed before disconnecting the reaction vessel. The colorless gum product ($[\eta]$ 0.061, Mole. Wt. 20,000 of Table DII) gave quantitative yield.

Insertion of Functional Groups into Fluorpolymer

A solution of 5g of polyperfluorobutadiene (T_m < 50°C) in 25 ml of hexafluorobenzene was freeze-dried in a Pyrex reaction tube (Figure D2A), evacuated overnight, before introducing gaseous OF_2 slowly at ambient temperature to 2 atm, warmed slowly to 50°C and kept at 50°C for 18 hours before evacuation. The vacuum system was then filled with helium to slight positive pressure above 1 atm before disconnecting the reaction tube in order to avoid air and moisture contamination into the system. The product (T_m 53 to 74°C) gave quantitative yield. Its infrared spectrum shows the characteristic strong broad C-F band between 7.5 and 9.4μ, a weak 5.6μ peak for perfluorovinyl groups (Reference D13) the disappearance of 5.8μ peak for perfluorovinylene groups (Reference D13), and the addition of a strong 5.3μ peak for acyl fluoride groups (Reference D14).

Addition Copolymerization of Perfluorobutadiene and OF_2

Perfluorobutadiene (1 ml) was condensed into an evacuated Pyrex reaction tube (4-1/2 in. × 1/2 in. o.d. with a 1/2 in. o.d. neck connecting to the stainless steel manifold by Swagelok fitting), which contained a magnetic stirring rod, at −70°C, and closed the

valve above the reaction tube. Gaseous OF_2 was introduced into the evacuated manifold to 1/3 atm, before the valve above the reaction tube was opened. The initial pressure was recorded after the reaction tube was exposed to OF_2 at $-70°C$ under stirring, warmed slowly to 0°C for a period of 30 minutes and maintained at 0°C for 30 minutes before warming to ambient temperature. A pressure drop to 1/6 atm was observed after cooling the tube back to $-70°C$. Repeated the OF_2-addition to 1/3 atm and followed by the same warming-up steps for three times, except before the last OF_2-addition the manifold was evacuated after cooling the reaction tube to $-70°C$. The reaction mixture was left stirring at ambient temperature overnight, before evacuation after cooling the reaction tube to $-70°C$. Perfluorobutadiene (1 ml) was condensed into the reaction mixture and stirred for 2 hours at 20°C. Upon fractionation of the mixture, the last fraction (the residual liquid) did not boil at 20°C under 1 mm Hg pressure. The infrared spectrum of the liquid is shown in Figure D2.

ACKNOWLEDGMENT

REFERENCES

D1. Stacey, M., Tatlow, J. C., and Sharpe, A. G., ed., Advances in Fluorine Chemistry, Vol. 4, Butterworths, Washington, 1965, pp. 213-214.

D2. Franz, G., and Neumayr, F., Inorg. Chem. 3, 921 (1964).

D3. Gatti, R., Satricco, E. H., Siere, J. E., and Schumaker, H. J., Agnew. Chem. 75, 137 (1963).

D4. Anderson, L. R., and Fox, W. B., J. Am. Chem. Soc. 89, 4313 (1967).

D5. Thompson, P. G., J. Am. Chem. Soc. 89, 4316 (1967).

D6. Toy, M. S., and Lawson, D. D., J. Polymer Sci., Part B, 6, 636 (1968).

D7. Toy, M. S., and Newman, M. J., J. Polymer Sci., Part A-1, 7, 2333 (1969).

D8. Toy, M. S., Proceedings of Photochemistry of Macromolecules Symposium, ACS Western Regional Meeting, Anaheim, Calif., October 1969.

D9. Toy, M. S., and Lawson, D. D., ACS Polymer Preprints, 9(2), 1671 (1968).

D10. Darby, R. A., and Ellingboc, E. K. (to E. I. duPont de Nemours), U.S. Patent 3,069,404 (December 18, 1962).

D11. Toy, M. S., and Newman, J. M., ACS Organic Coating and Plastics Chemistry Preprints, 29(1), 206 (1969).

D12. Schmidt, H. W., Handling and Use of Fluorine and Fluorine-Oxygen Mixtures in Rocket Systems, NASA SP-3037, Scientific and Technical Information Division, National Aeronautics and Space Administration, Washington, D.C., 1967.

D13. Fearn, J. E., Brown, D. W., and Wall, L. A., J. Polymer Sci., Part A-1, 4, 131 (1966).

D14. Haszeldine, R. N., Nature 168, 1028 (1951).

MCDONNELL DOUGLAS

CORPORATION

ADVANCED RESEARCH LABORATORIES · 5251 BOLSA AVENUE · HUNTINGTON BEACH, CALIFORNIA 92647