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FINAL REPORT

PREPARATION OF FLUOROELASTOMERS FOR USE  
WITH CRYOGENIC STORABLE PROPELLANTS

For the Period  
1 February 1968 - 31 January 1969

UNDER CONTRACT NAS7-668  
TO  
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

by

Eugene C. Stump  
Stephen E. Rochow

PENINSULAR CHEMRESEARCH, INC.  
POST OFFICE BOX 1466  
GAINESVILLE, FLORIDA 32601

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## FOREWORD

This report was prepared by Peninsular ChemResearch, Inc., under Contract NAS 7-668 for National Aeronautics and Space Administration. Mr. D. D. Lawson was NASA Technical Manager and Mr. Frank E. Compitello was NASA Project Manager. This is the Final Report under this program and covers the period 1 February 1968 through 31 January 1969. Laboratory work was carried out only through September, 1968 due to insufficient funding.

Personnel who were engaged in this research were Eugene C. Stump, Project Director, and Stephen Rochow, Research Chemist. Dale A. Warner was in charge of analytical services. Drs. Paul Tarrant and George Butler of the University of Florida Department of Chemistry were acting consultants.

## ABSTRACT

The preparation and polymerization of tetrafluoroethylene oxide (TFEO) was investigated.

Carboxy-terminated polyperfluoroethers were extended and cross-linked with chromium trifluoroacetate and dicyclopentadiene dioxide.

Initial attempts to prepare an acid fluoride-terminated prepolymer by reaction of TFEO and perfluoroglutaryl fluoride were unsuccessful.

Hexafluoropropylene oxide (HFPO) could not be prepared using glow discharge and ultraviolet irradiation techniques.

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## I. INTRODUCTION

Advances in space technology and capabilities have focused increasing attention on the necessity for development of materials with highly unusual properties. A particular area where this problem has become evident is the development of elastomeric materials for use as expulsion bladders, seals, and gaskets in contact with cryogenic storable propellants.

A suitable material has not yet been fully developed to meet this requirement. Highly fluorinated materials, such as polytetrafluoroethylene, offer a potential solution to the problem due to the demonstrated chemical resistance of compounds of this class. However, polytetrafluoroethylene, while it can be fabricated into seals, gaskets, and O-rings, is extremely difficult to process as an expulsion bladder.

A nitroso terpolymer, originally prepared by 3M Company<sup>1</sup> and developed by Thiokol<sup>2</sup>, has demonstrated high resistance of  $N_2O_4$ . However, a recent report<sup>4</sup> indicates that this elastomer (a terpolymer of trifluoronitrosomethane, tetrafluoroethylene, and 4-nitrosoperfluorobutyric acid) has a high permeation rate for liquid  $N_2O_4$  and gases.

The object of this work is the development of other highly fluorinated systems which should exhibit elastomeric properties and resistance to liquid oxygen, liquid hydrogen, and other similar cryogenic fuels and oxidizers.

Under an earlier contract<sup>5</sup>, of which the present work is an extension, we investigated the preparation of perfluoroether prepolymers containing functional terminal groups and their conversion to solid, cross-linked polymers. These polymers were derivatives of prepolymers prepared from hexafluoropropylene epoxide.

Because of the exceptional thermal stability<sup>6</sup> which has been attributed to poly(tetrafluoroethylene oxide), and because of the desirability of incorporating the  $-CF_2CF_2O-$  group in the polymer chain along with other previously prepared polyperfluoroethers, work during this phase of the program was directed toward the preparation of tetrafluoroethylene oxide and its conversion to polymers.

TABLE I  
PREPARATION OF TFEO

Run. No.	Lamp <sup>a</sup>	TFE Used(g.) <sup>b</sup>	Product		Conv(%)	Purity%	Remarks
			Crude(g)	Purified(g)			
165.4	A		5	trace			
.5	A		1	"			
.6	A		1	"			
.7	A		1	"			
.8	A		25	"			
.9	A		7	"			
.10	A		104	8		98	
.11	B		119	9		86	
.12	B		219	5		99	
.13	B		139	trace			
.14	B		479	61		83	
.15	C		183	19		95	
.16	C		376	trace			insufficient Br <sub>2</sub> in mixture
.17	C		288	8		85	
.18	C		260	91		95	
.19	C		224				
.20	D		746	86		97	
.21	D	121	162	12		54	
.22	B	212	250	45		70	
.23	B	615	695	67		36	
.24	B	289	321	105		52	
.25	B	545	670	154	24.3	98-99	Fresh FC-43
.26	B	517	607	170	28.3	99	"
.27	B	417	530	95	-	62	Used FC-43
.28	B	570	700	136	20.5	99	"
.29	B	610	800	23	~9	95	"
				26		35	
				90		35	

(a) A - 2 x 450 watt  
 B - 1200 watt  
 C - 2 x 450 watt + 1200 watt  
 D - 450 watt + 1200 watt

(b) Based on flowmeter readings



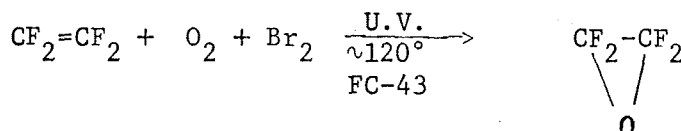
## II. DISCUSSION

### A. Monomer Synthesis

#### 1. Tetrafluoroethylene Oxide (TFEO)

The major portion of work under this contract consisted of an investigation of the preparation and purification of tetrafluoroethylene oxide (TFEO).

Toward the end of the program preceeding this work small quantities of TFEO were prepared in low conversion and purity<sup>5</sup> using a procedure reported by chemists at duPont<sup>7</sup>. This method consists of the direct oxidation of tetrafluoroethylene using ultraviolet irradiation and bromine as initiators.



During the present program this process was utilized to prepare TFEO in quantities as high as 170 g. per day of 99% pure material. Conversions, based on tetrafluoroethylene (TFE) used, were as high as 28%.

Table I summarizes 29 runs carried out under slightly varying conditions. Runs 1-3 were carried out by irradiation of the gaseous mixture without a liquid phase and gave only a trace of pure TFEO. The remainder of the runs were carried out by irradiation of the mixture as it bubbled through FC-43 at 90-150°. Best results were obtained when the temperature was maintained at 125-150°.

Two types of ultraviolet lamps were used. These were 2 x 450 watt Hanovia 679 A lamps and a single 1200 watt GE U-11 lamp. Higher conversions were obtained with the 1200 watt lamp.

Runs 1-25 were carried out using tubes made of Vycor 7913, which was inadvertently obtained from the manufacturer rather than Vycor 7910. Vycor 7913 transmits only a few percent of the ultraviolet spectrum and this, coupled with the use of the 450 watt lamps, probably accounts for the low conversions obtained in the early experiments. After the error was detected the tubes were exchanged for quartz tubes, which transmit 80-95% of the ultraviolet spectrum produced by the 1200 watt U-11 lamp.

With each succeeding run the build-up of a white solid material in the FC-43 was observed. Higher conversions to TFEO were obtained when fresh FC-43 was used rather than material from a previous run, probably due to the decrease in irradiation of the gas phase caused by the solid suspension. A quantity of this material was isolated by filtration and an infrared spectrum made. Based upon a comparison of the spectrum of this material with a spectrum of a polymer formed in the reaction of TFE with oxygen using ultraviolet irradiation in the gas phase<sup>8</sup>, this material appears to be poly(carbonyl fluoride),  $\{CF_2O\}_n$ . Poly(carbonyl fluoride) may be prepared by irradiation of poly(tetrafluoroethylene peroxide),  $\{CF_2CF_2OO\}$ , by ultraviolet irradiation<sup>9</sup>, which may account for the presence of this polymer in our system. The polymer is apparently unstable, slowly decomposing to carbonyl fluoride monomer at room temperature.

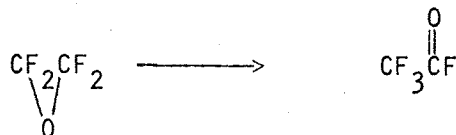
Best conversions were obtained using a combination 1200 watt-lamp and fresh FC-43 heated to 125-150°.

Since the crude product consisted primarily of unreacted TFE in addition to TFEO,  $COF_2$ , hexafluorocyclopropane (trace) and  $CO_2$ , purification present a problem. The procedure which was developed consisted of two steps. In the first step TFE was removed by bubbling through bromine (25% in  $CF_2BrCF_2Br$ ) in a 3" x 3' tube containing Raschig rings. A fluorescent light was set parallel to the tube. Exit gases were collected in a LOX cooled trap and condensed into an evacuated cylinder. Most of the remaining impurities were then removed by scrubbing the gas through two 3" x 3' tubes containing aqueous KOH. Purity of 99% may be obtained.

In handling the crude material caution should be exercised since TFE and oxygen may form explosive peroxides. After isolation of the pure TFEO it should not be allowed to become contaminated with oxygen since explosions have been experienced in other laboratories<sup>10</sup>.

Pure TFEO has been stored for short periods ( 1 week ) at -73° with no appreciable decomposition. At room temperature, however, the monomer rearranges rapidly and exothermically to trifluoroacetyl fluoride.

Consequently, pure TFE0 should be used as prepared or stored at LOX temperature, since rearrangement does occur at  $-78^{\circ}\text{K}$ .



Purity is determined by GLC analysis using a column packed with 35% PFOX\* on acid-washed Chromosorb W. The sample is withdrawn at cylinder pressure at -20% into a Hewlett-Packard gas sampling valve with a 0.1 ml. sample loop. The injection port and column is maintained at room temperature. As prepared, the main components of the crude product mixture are TFE0, tetrafluoroethylene, carbonyl fluoride, and carbon dioxide. Hexafluorocyclopropane is also present in trace amounts. Bromination of the mixture, followed by scrubbing through aqueous base, removes most of these impurities with the exception of hexafluorocyclopropane. Purities of 98-99% are generally obtained. A typical gas chromatogram of purified TFE0 shows 3-4 peaks with relative retention times (corrected for air) of 0.4 ( $\text{CO}_2$ ), 1.0 (TFE0), 2.5, and 3.4.

An attempt to prepare TFE0 by the procedure used to prepare hexafluoropropylene oxide, low temperature epoxidation using basic hydrogen peroxide, was unsuccessful.

An infrared spectrum of 99% pure TFE0 is shown in Figure 1.

A total of 478 g. of purified TFE0 was shipped to JPL for polymerization studies.

## 2. Attempted Preparation of Hexafluoropropylene Oxide (HFPO) by Glow Discharge and Ultraviolet Irradiation

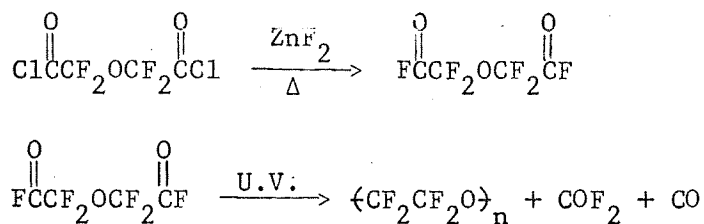
HFPO used in the proceeding program<sup>5</sup> was prepared by reaction of hexafluoropropylene with basic hydrogen peroxide in methanol at low temperature ( $\sim -40^{\circ}$ ). During this contract we examined the preparation of HFPO by two other methods.

In the first, hexafluoropropylene was passed through the reactor used for the preparation of TFE0 and under similar conditions. No HFPO was detected in the effluent.

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\* A perfluorinated polyether with the repeating unit  $\{\text{CF}(\text{CF}_3)\text{CF}_2\text{O}\}_n$  manufactured by Montecatini-Edison.





difficulties, particularly low conversions, encountered in the preparation of the intermediate 1,2-dichloroperfluoro-4-oxacyclopentene, and because of the arrival of the necessary ultraviolet equipment, this synthesis was not pursued.

## B. Polymers

### 1. Polytetrafluoroethylene Oxide (PTFEO)

TFEO was homopolymerized by irradiation using a cobalt-60 source<sup>15</sup>. The monomer samples were sealed in glass ampoules and irradiated at liquid nitrogen temperatures. Two sources were used. Nineteen hours irradiation in the first source, with a strength of about 540 curies, produced polymer in very low conversion. Two other polymerizations, carried out by the NASA Technical Manager, Mr. D. D. Lawson, using a 10,000 curie source at Jet Propulsion Laboratories, gave (after ~3 hours) conversions of 25 and 75%. The first sample (from the low intensity source) was apparently of low molecular weight. An infrared spectrum of this sample is shown in Figure 3. Infrared spectra of the two samples polymerized at JPL were obtained as solutions in FC-43 and by the attenuated total reflectance method. These spectra are shown in Figures 3 and 4, respectively.

DSC analysis of the poly(TFEO) samples prepared at JPL revealed  $T_g$ 's of  $-50^\circ$  and  $-40^\circ$  and  $T_m$ 's of  $32.5^\circ$  and  $30^\circ$ , respectively. Determination of intrinsic viscosity using FC-43 gave values of 0.25 and 0.21. Hexafluorobenzene gave values of 0.18 and 0.12, respectively.

2. Reaction of Chromium Trifluoroacetate with Carboxy-Terminated Polyperfluoroethers

In order to prepare stable, cured polymers from samples prepared under the previous program<sup>5</sup>, we investigated the reaction of MEDA and poly(DEDA) with chromium trifluoroacetate. Chromium trifluoroacetate has been used as a curing agent for carboxy-pendent nitroso rubber<sup>16</sup> and it was felt that a similar cure might occur. The reactions, described in Table II, produced polymers ranging from sticky semi-solids to hard lumps. One sample (171.3) was found to have a Tg of  $-41^{\circ}$  by DSC. None of the samples, although several were somewhat rubbery, exhibited any appreciable tensile strength or elongation. An infrared spectrum of Sample 171.8 is shown in Figure 5.

After the work on the reactions with chromium trifluoroacetate had been completed, a report<sup>17</sup> describing an attempt to cure a similar carboxy-terminated poly(fluoroether) was received. Although no experimental details or properties were given, it appears that results similar to ours were obtained.

3. Reaction of Dicyclopentadiene Dioxide with Poly(DEDA)

Since carboxy-pendent nitroso rubber can also be cross-linked with diepoxides, the reaction of poly(DEDA), prepared under the preceding program<sup>5</sup>, with dicyclopentadiene dioxide was also investigated. Several reactant ratios were investigated producing solid polymers which ranged from hard sheets (after press-curing) to weak, sticky elastomers. Glass transition temperatures ranging from  $-77^{\circ}$  to  $-32^{\circ}$  were observed. These reactions are summarized in Table III. An infrared spectrum of one of the samples (174.4) is shown in Figure 6.

4. Attempted Preparation of Acid Fluoride-Terminated Polymers from TFEO and Perfluoroglutaryl Fluoride

Since diacid fluorides from TFEO and perfluoroglutaryl fluoride (PFGF), analogous to those prepared earlier from HFPO and PFGF, would be of considerable interest in further polymerizations, the reaction of TFEO and

TABLE II  
Cr(CF<sub>3</sub>COO)<sub>3</sub> Cured Polymers

Reaction No.	Diacid	Ratio	Reaction System	Temp.	Time	Molding	Appearance	T <sub>g</sub>	T <sub>d</sub>	Remarks
		Cr(CF <sub>3</sub> COO) <sub>3</sub> /diacid								
171.1	MEDA	1/1.05	100-ml. flask	110°	1/2 hour	-	hard, green lumps	-	-	
171.2	Poly(DED A)	1/.82	100-ml. flask	75°	overnight	105°, 1 1/4 hr. 500 psi	rubber-like olive green polymer	-	-	
171.3	Poly(DED A)	1/3.16	250-ml. flask acetone solvent	reflux	overnight	110°, 2 min. 500 psi	dark, green polymer	-41°	132° 162° 312°	T <sub>d</sub> depended on thermal history of sample.
171.4	Poly(DED A)	1/3.5	100-ml. flask	115°	3 hours	110°, 5 min. 500 psi	hard, green polymer	-	-	
171.5	Poly(DED A)	1/4.2	on plates in press	110°	2 hours	100 psi	flakes of dark green in starting material.	-	-	
171.6	Poly(DED A)	1/4	100-ml. flask	75°	20 min.	110° 1/2 hr. 100 psi	sticky semi-solid	-	-	
171.7	Poly(DED A)	1/4	Teflon coated aluminum sheets in vacuum oven	82°	2 hours	-	specks of polymer in semi-solid	-	-	
171.8	Poly(DED A)	1/4.3	Reactants dissolved in acetone, acetone removed, then same as 171.7	80°	2 hours	-	sticky, rubbery	-	-	Infrared spectrum Figure 5
171.9	MEDA	1/4	as above in 171.8	80°	2 hours	-	sticky, rubbery	-	-	

TABLE III

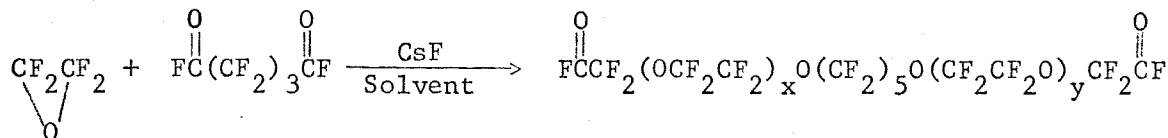
## Dicyclopentadiene Dioxide Cured Polymers

<u>Reaction No.</u>	<u>Ratio</u> Poly(DED A)/Dioxide	<u>Reaction System</u>	<u>Tg</u>	<u>Hardness*</u>	<u>Appearance</u>
174.1	1/1	test tube	-64°	96	Hard sheet
174.2	2/1	100-ml. flask		31	Flexible, sticky sheet
174.3	2/1	200-ml. flask 100 ml. acetone	-77°	41	Slightly sticky, elastomeric sheet
174.4	1.5/1	200-ml. flask 100-ml. acetone	-32°	60	Weak elastomeric sheet

\*Shore type A-2.

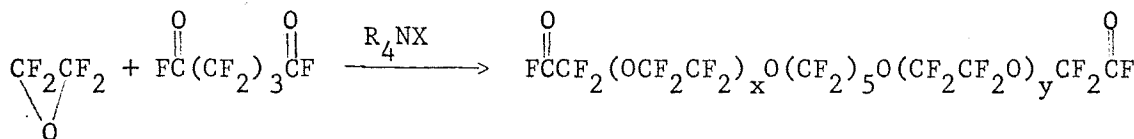


PFGF was investigated.



The procedure was the same as used earlier for HFPO and PFGF; i.e., CsF catalyzed addition of epoxide to PFGF in diglyme (Ansul Ether 141). A small amount (~10 g.) of higher boiling material was isolated by distillation. An infrared spectrum (Fig. 7) of this material exhibits the expected acid fluoride carbonyl absorption of 5.3 microns, and is very similar to the spectrum of PFGF.

The reaction of TFEO with perfluoroglutaryl fluoride was repeated except that tetraethylammonium bromide and 1,2-dichloroethane were used as the catalyst and solvent. According to the patent literature<sup>18</sup>, TFEO and perfluoroglutaryl fluoride will react in a variety of halogenated solvents using any quarternary ammonium salt which forms a quarternary ammonium fluoride in situ by reaction of the salt with either the acid fluoride or TFEO. Tetraethylammonium bromide and 1,2-dichloroethane are both described



as a suitable catalyst and solvent, respectively. In practice, the catalyst is converted to the quarternary ammonium fluoride by the initial addition of a small amount of TFEO to the system. The diacid fluoride is then added, followed by addition of TFEO. Initial consumption of the TFEO indicates the catalyst to be active.

In attempting to carry out this reaction in our laboratories, it appeared that very little, if any, TFEO was consumed initially by the system. Since it was felt that the catalyst might be converted to the fluoride by the acid fluoride, perfluoroglutaryl fluoride was added to the solvent-catalyst mixture. TFEO was then added to the closed system at 7 psig but only a very small amount of TFEO was consumed.

The failure of this reaction to proceed as expected might be explained by failure to form the quaternary ammonium fluoride. Although the bromide was heated at 170° under vacuum overnight, this treatment may not be adequate to provide an active catalyst. Also, an atmosphere of air was inadvertently allowed in the flask. Should future work be desired in this area, a series of small scale experiments using various catalysts and solvents should be carried out to determine their reactivity with TFE. Tetraethylammonium cyanide appears to be a preferred catalyst according to examples given in the patent literature<sup>18</sup>. Air should also be excluded from the reactor in future reactions.

Investigation of this reaction was terminated due to depletion of supporting funds.

### III. EXPERIMENTAL

#### A. Monomer Synthesis

##### 1. Tetrafluoroethylene Oxide (TFEO)

Two quartz tubes (41 mm i.d. x 3') with one closed end were filled 2/3 full with FC-43. An 8 mm. glass bubble tube pulled to a point and a thermocouple well were inserted through a rubber stopper at the top of the tube. The FC-43 was heated to about 125° with a heating tape wrapped around the lower end of the tube. Heating was controlled by a pyrometer. A mixture of air, TFE, oxygen and Br<sub>2</sub>/N<sub>2</sub> were passed through the tubes while being irradiated by a 1200 watt G.E. U-11 ultraviolet lamp. Flow rates were adjusted as nearly as possible to those described in the literature<sup>7a</sup>, using flowmeters connected to a manifold. Air was passed

air:	700 ml./min.
oxygen:	130 ml./min.
bromine:	(0.3% in 99.7% N <sub>2</sub> ): 26 ml./min.
TFE:	500 ml./min.

first through a LOX-cooled trap to remove oil and water and TFE was passed through a packed trap at -70° to remove inhibitor. Due to heating caused by the lamp it was necessary to cool the tubes with a stream of air to maintain the temperature at 125-150°. The exit gases passed through condensers cooled to -78°, then through a finger trap at -40° and into a LOX-cooled trap. The flow was continued for as long as desired, usually 5-6 hours.

As a safety precaution inhibitor (dipentene) was placed in the collection trap and in the cylinder into which the crude product was then condensed. This operation was carried out behind a shield. After the crude product is condensed into the storage cylinder at LOX temperature a vacuum is pulled on the cylinder to remove any oxygen which may be present.

The crude product was then purified by bubbling through a 25% mixture of bromine in CF<sub>2</sub>BrCF<sub>2</sub>Br in a 3" x 3' glass tube containing Raschig rings. The tube was irradiated by a fluorescent light. The existing gases were passed through a -40° trap, collected in a LOX-cooled trap, and condensed into a new, mild steel cylinder. Any bromine which is retained reacts with the steel and is removed.

The crude product from which tetrafluoroethylene had been removed was then passed through two tubes (3" x 3') containing aqueous base (250 g. KOH in 650-750 ml. water) and packed with Raschig rings and glass helices. The tubes were kept in ice water. The purified TFEO (98-99%) was passed through a packed trap at  $-40^{\circ}$  and into a LOX-cooled trap backed up with another LOX-cooled trap to keep  $\text{CO}_2$  out of the product trap.

Cylinders containing TFEO (both crude and pure) were kept cold at all times, generally at  $-78^{\circ}$  and then at  $-20^{\circ}$  when venting from a cylinder to a scrubber or when sampling for GLC analysis.

2. Attempted Preparation of Hexafluoropropylene Oxide (HFPO) by Glow Discharge and Ultraviolet Irradiation

a. Hexafluoropropylene was passed through the reactor described above, using two-thirds flow rates of TFEO at  $70-80^{\circ}\text{C}$ . No epoxide was detected in the product mixture.

b. A mixture of one-half perfluoropropylene and one-half  $\text{O}_2$  was bled at 5-10 mm through the glow-discharge reactor. A 15,000 volt transformer was used, producing a blue to violet glow in the gases between the electrodes. Tap water cooling was used. No epoxide was formed.

3. Perfluorooctadiene-1,7 Diepoxide

The reactor consisted of a 12 x 200 mm Pyrex tube with gas bubbler and condenser. Oxygen (1000 cc/min.) was dried by passing through a LOX trap and a  $\text{H}_2\text{SO}_4$  bubbler; chlorine (10 cc/min.) was dried by passing through a drying tube and a  $\text{H}_2\text{SO}_4$  bubbler. Gases exiting from the reactor were collected in a LOX trap. A Hanovia 30620 UV lamp was used for irradiation. Perfluorooctadiene-1,7 (20 g., 0.055 mole) was added and the reaction was run one hour. The condenser was cooled with ice water. Liquids from reactor and trap were combined and added cautiously to 50 ml. ice water, and neutralized with  $\text{NaHCO}_3$ . The organic layer was washed twice with water, and dried with  $\text{MgSO}_4$ . This was stirred overnight with excess bromine. Mercury was added to remove excess  $\text{Br}_2$ , filtered, leaving 8 g. of liquid that had less diepoxide (IR, GLC analysis) than before bromination.

The crude product from the second reaction (30 g. of diene) was brominated directly, without neutralization, and distilled, giving 13 g. of material (b.p. 40°/16mm-48°/1.2mm). This was cautiously neutralized with sodium bicarbonate, leaving 10 g. of 95% pure (by GLC) material identified by NMR as  $\text{CF}_2\text{CF}(\text{CF}_2)_4\text{CFBrCF}_2\text{Br}$ .

#### 4. 1,2-Dichlorotetrafluoro-4-oxacyclopentene

Using a reported procedure<sup>14</sup>, a 3-liter autoclave was loaded with 325 g. of dichloromaleic anhydride (1.94 moles) and 868 g. of  $\text{SF}_4$  (8 moles) with 10 g. of  $\text{BF}_3$ . The clave was heated to 300°C overnight and stopped after 20 hours. After cooling,  $\text{SF}_4$  was vented. A fuming, black liquid was poured out and flash distilled to a LOX trap. The resulting pale yellow liquid was distilled on a micro column, giving 158 g. of impure 1,2-dichloroperfluoro-4-oxacyclopentene, b.p. 71-77° (rptd. b.p. 73°).

### B. Polymers

#### 1. Polytetrafluoroethylene Oxide (PTFEO)

Eight grams of 98% pure TFEO were condensed in an ampoule and irradiated for 19 hours with a  $\text{Co}^{60}$  source (strength ~540 curie) while frozen in liquid nitrogen. No observable change occurred. Upon opening, a small amount of white, waxy polymer remained in the tube after removal of monomer. This had a Tg of -46°C, and m.p. 40°C.

Another sample of 8 g. TFEO (95%) was irradiated with a  $\text{Co}^{60}$  source of 10 kilocuries for ~3 hours, giving 2 g. solid, waxy, spongy polymer (Tg -40°, m.p. 30°) and 6 g. of TFEO. Another 8 g. sample gave 6 g. of polymer and 2 g. of TFEO.

#### 2. Reaction of Chromium Trifluoroacetate with Carboxy-Terminated Polyperfluoroethers

For most experiments the diacid and chromium trifluoroacetate were placed in a 100-ml. flask, stirred, and heated under vacuum. The product was removed and pressed. Pressing did not extend the product and a sheet could not be formed. When a solvent was used (acetone), polymer

precipitated out. The reactants were spread out on Teflon-surfaced aluminum plates and heated in a vacuum oven or press. This produced sticky, semi-solids. These experiments are summarized in Table II.

### 3. Reaction of Dicyclopentadiene Dioxide with Poly (DEDA)

Poly(DEDA) (10 g., 8 mmoles, m.w. 1230) and dicyclopentadiene dioxide (0.67 g., 4 mmoles) were placed in a 200-ml., 3-neck flask with 100 ml. dry acetone, equipped with condenser, thermometer, and stirrer. The acetone was pumped off. The mixture was heated slowly to 80° with stirring over one-half hour, causing a decided increase in viscosity. The product was removed and pressed 10 minutes at 110-150° at 600 psi, forming a slightly elastomeric, sticky sheet, hardness 41 [Shore type A-2], Tg -77°C. These experiments are summarized in Table III.

### 4. Attempted Preparation of Acid Fluoride-Terminated Polymers from TFEO and Perfluoroglutaryl Fluoride

#### a. with CsF

Cesium fluoride (10 g., 0.065 mole) was dried overnight by heating at 190°C in a 1-liter, 30-mm O-ring neck flask under vacuum. After cooling, 100 ml. redistilled diglyme (Ansul Ether 141) and perfluoroglutaryl fluoride (44 g., 0.180 mole) were added. The flask was cooled in ice, and tetrafluoroethylene oxide was added to 4 psig with stirring. Only 15 g. TFEO was taken up. Distillation gave 27 g. of unreacted PFGF, and 14 g. of higher boiling fractions which exhibited a distinctive infrared absorption at 5.3 microns.

#### b. with Tetraethylammonium Bromide

Tetraethylammonium bromide (0.5 g., 0.0042 mole) was added to a 1-liter, 30-mm. O-ring flask with magnetic stirring bar and heated overnight at 170° under vacuum. The flask was then cooled to -75°, and 38 g. of 1,2-dichloroethane (freshly distilled) was added. Air was inadvertently admitted to the flask due to a leaking spring-loaded stopcock. The flask was pressurized with TFEO to 7 psig at -75°C and allowed to warm up to -20°. No consumption of TFEO was observed. The flask was then cooled to -75° and PFGF (65 g., 0.376 mole) was added. TFEO was added at 7 psig. at -20 to -30°. No more than 15 g. of TFEO was consumed, indicating the catalyst to be inactive.

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## APPENDIX A

### Infrared Spectra

#### Figure

1. TFEO
2. Poly(TFEO)
3. Poly(TFEO)
4. Poly(TFEO)
5. Poly(DED) - Chromium Trifluoroacetate Polymer
6. Poly(DED) - Dicyclopentadiene Dioxide Polymer
7. Product from TFEO - PFGF Reaction

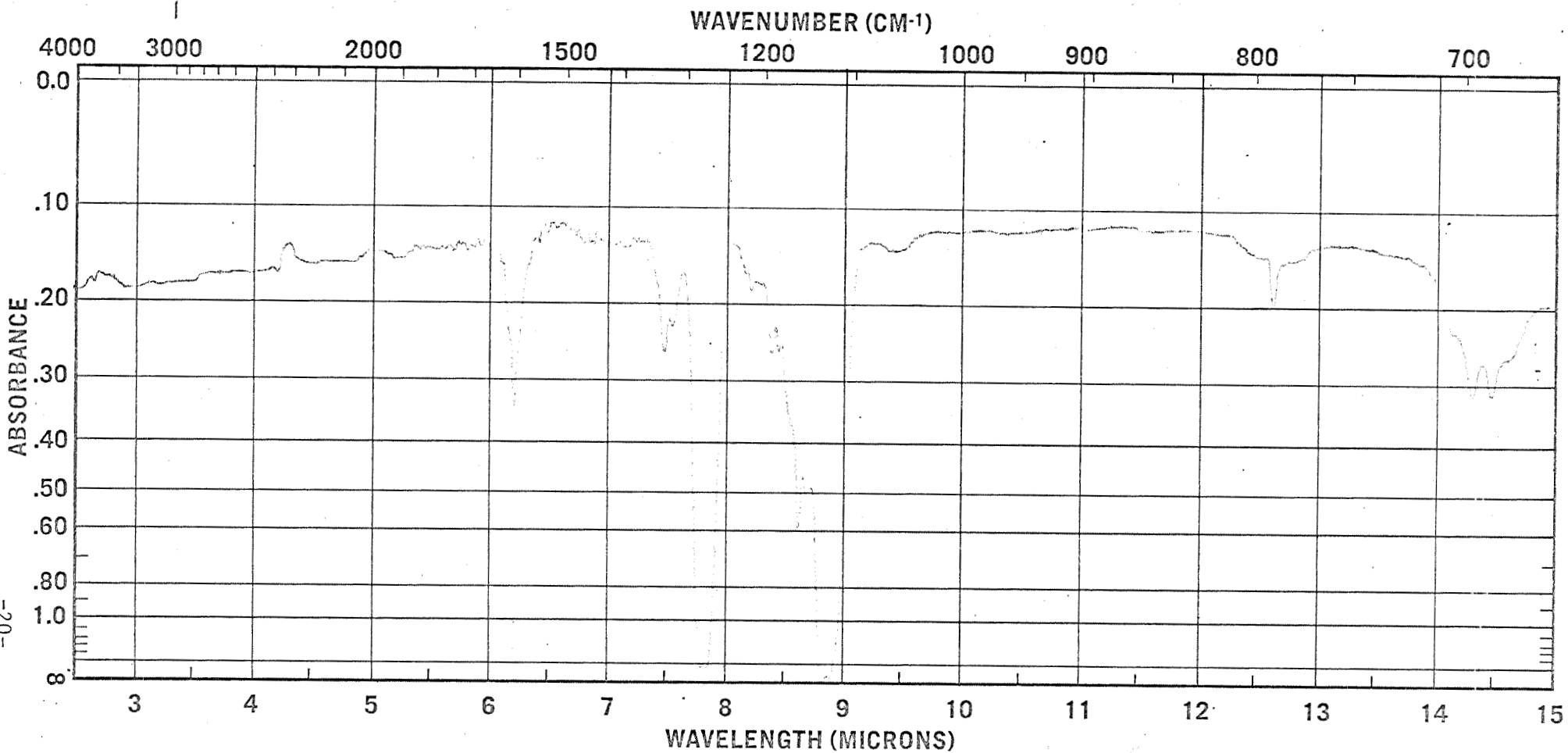


FIGURE 1

Infrared Spectrum of TFEO  
(Gas, 10 mm, 10 cm. cell)

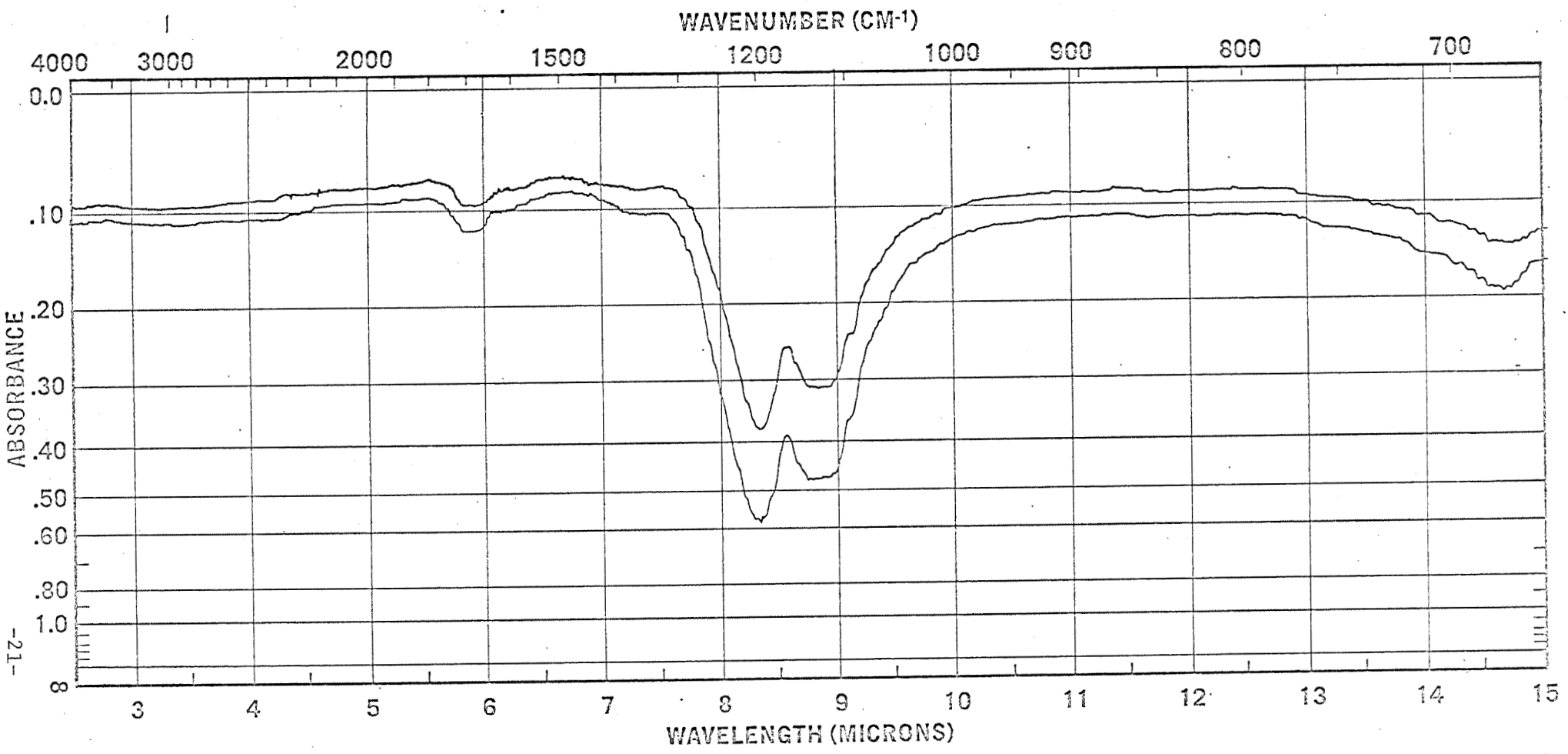


Figure 2 Infrared Spectrum of Poly(TFEO)- low intensity source  
Film from FC-43

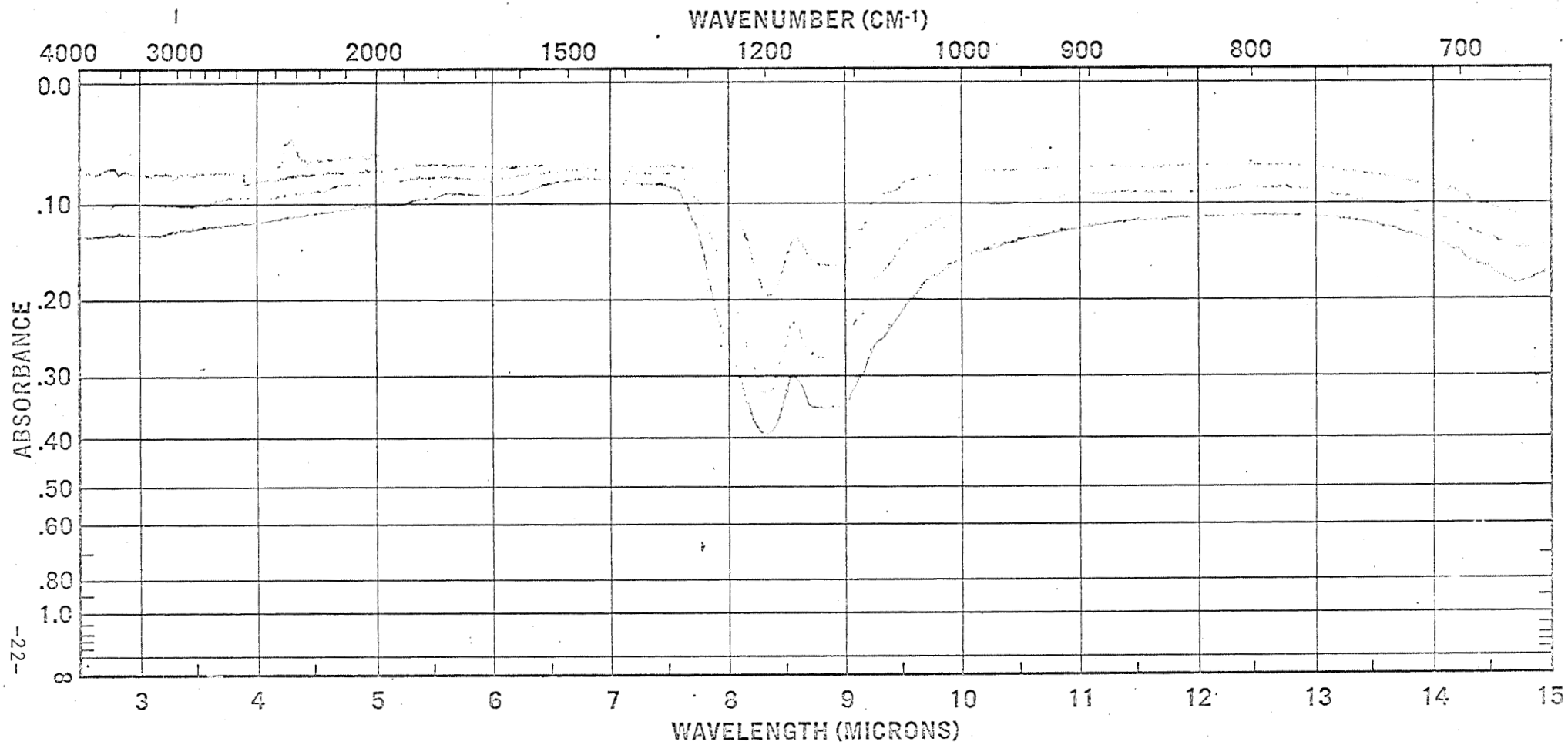


Figure 3 Infrared Spectrum of Poly(TFEO) - JPL Source  
Film from FC-43

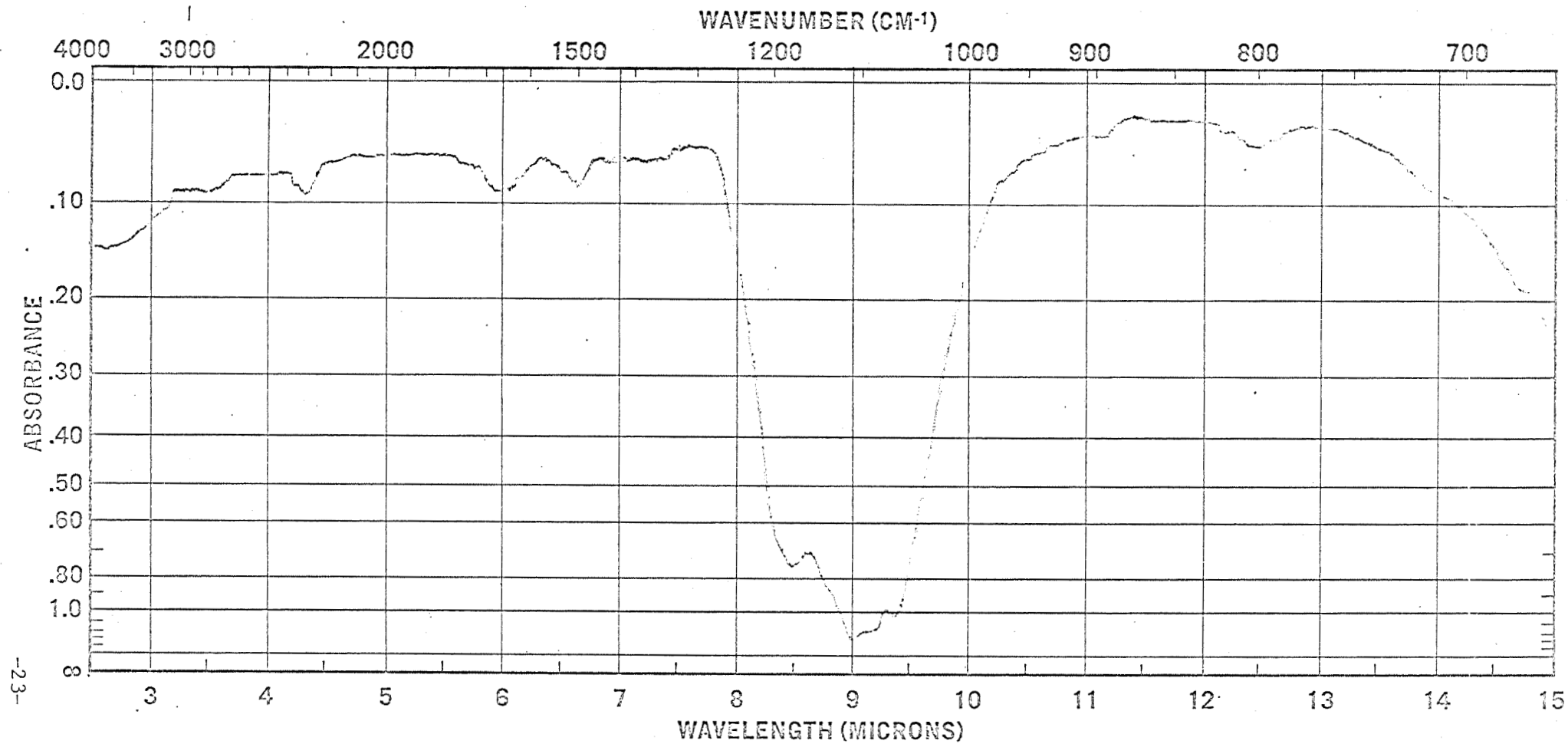


Figure 4. Infrared Spectrum of Poly(TFEO) - ATR - 45° angle - 3 reflections

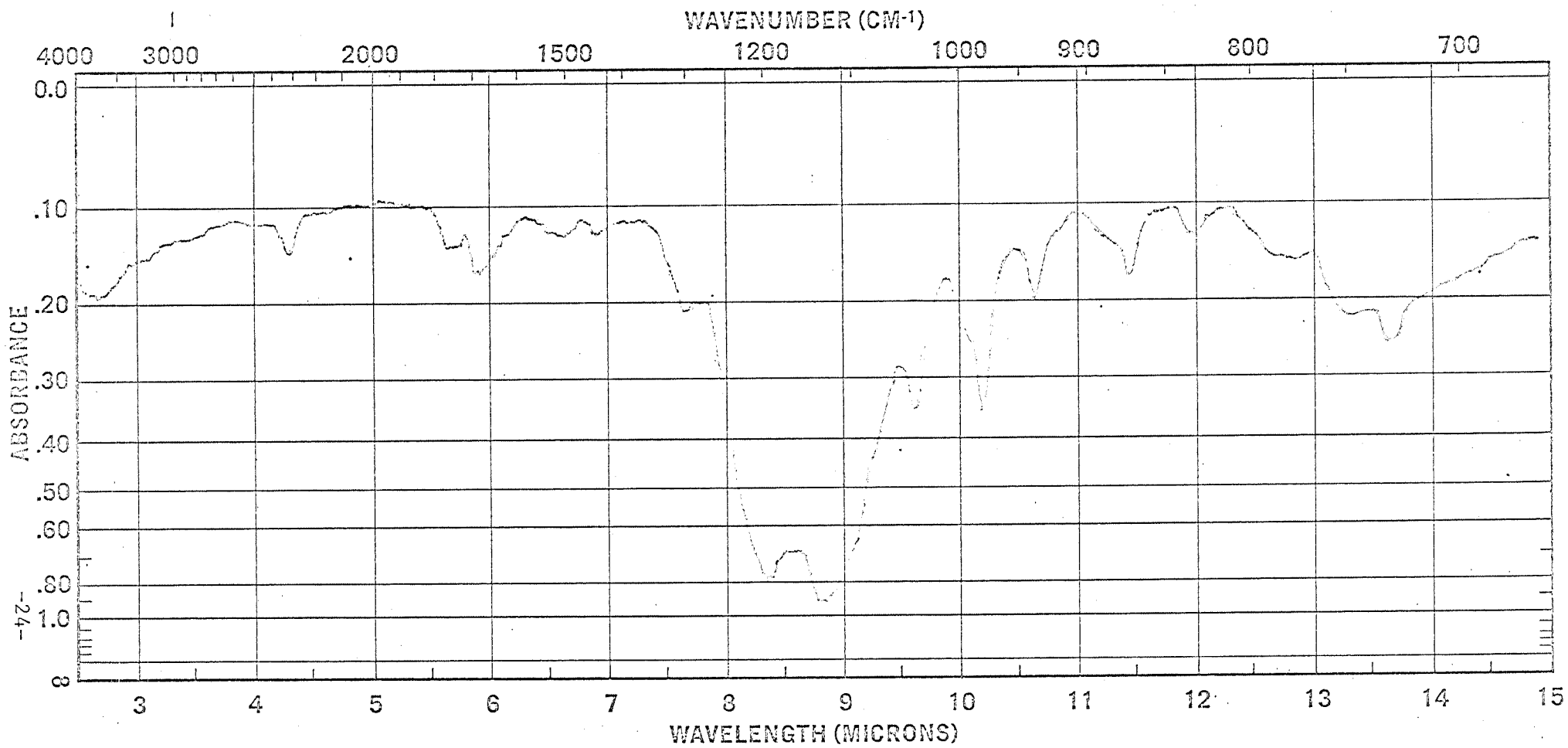


Figure 5. Infrared Spectrum of Poly(DEDA) - Chromium Trifluoroacetate  
ATR - 50° angle - 3 reflections

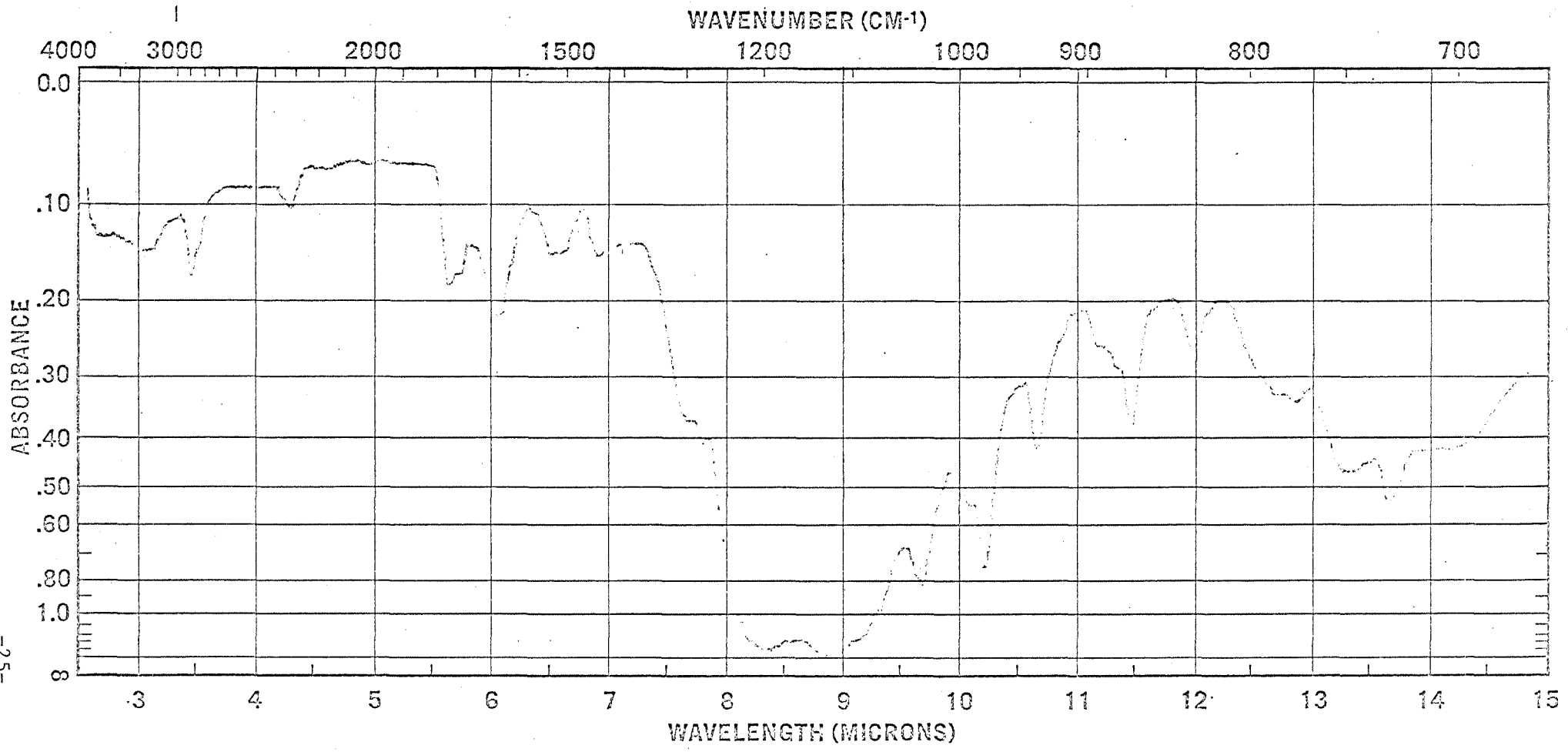


Figure 6. Infrared Spectrum of Poly(DED) - Dicyclopentadiene Dioxide  
ATR - 45° angle - 3 reflections

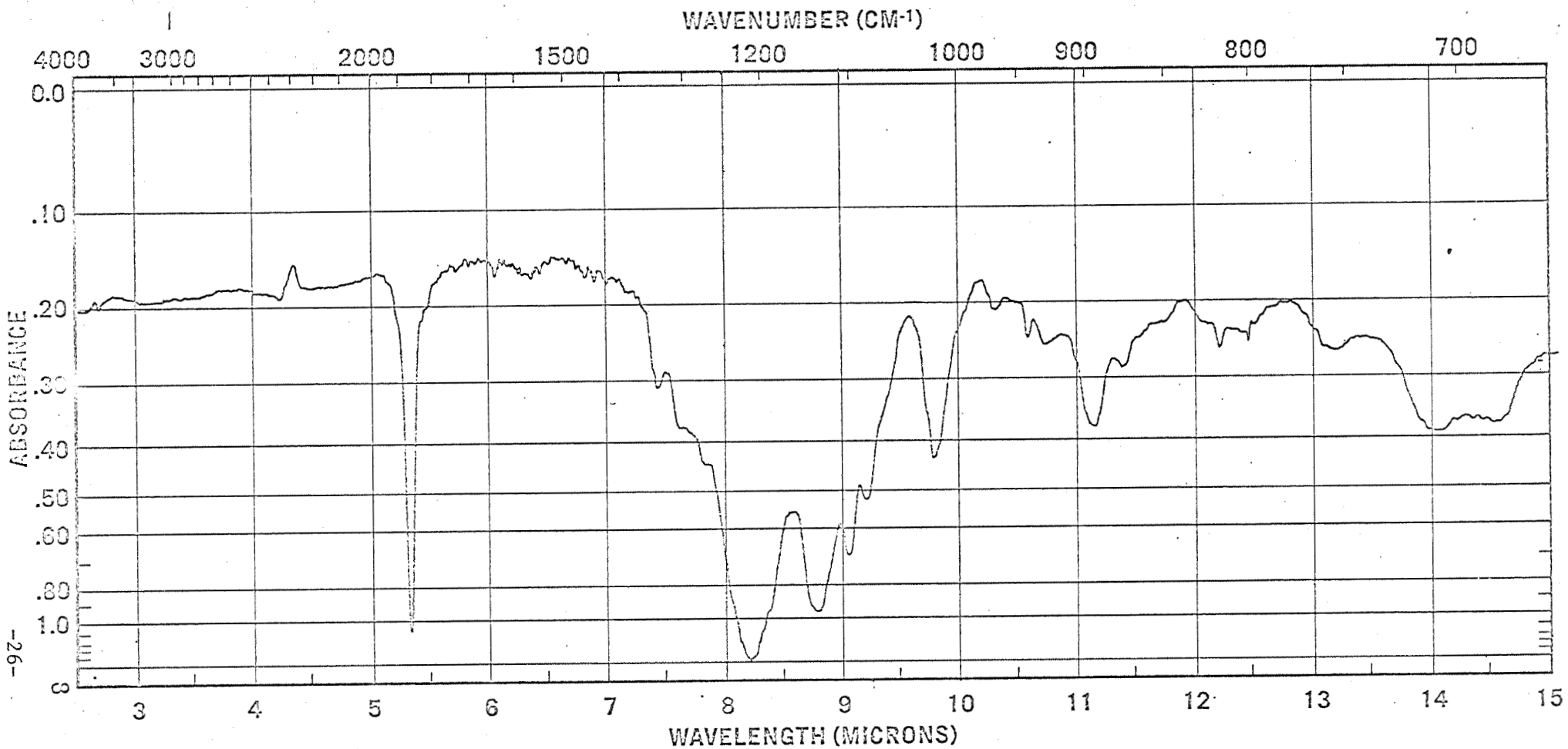


Figure 7.

INFRARED SPECTRUM OF PRODUCT FROM TFEO-PFGF REACTION



## APPENDIX B

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