General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

Produced by the NASA Center for Aerospace Information (CASI)

Seventh Quarterly Progress Report

NI CR-102951

THERMALLY RESISTANT POLYMERS FOR FUEL TANK SEALANTS

AUTHOR

James A. Webster

1 July 1970 — 30 September 1970

CONTRACT NO. NAS8-21401

DCN 1-0-50-09657(IF)

to

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

MONSANTO RESEARCH CORPORATION

A SUBSIDIARY OF MONSANTO COMPANY

DAYTON LABORATORY

DAYTON, OHIO 45407

N71-14054

(ACCESSION NUMBER)	(THRU)
33	G3
(PAGES)	(CODE)
CR-102951	18
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

FACILITY FORM 602

RECEIVED NOV 1970 MSFC ST MAILING BRANCH

THERMALLY RESISTANT POLYMERS FOR FUEL TANK SEALANTS

Quarterly Report No. 7

1 July 1970 - 30 September 1970

Contract No. NAS8-21401

DCN 1-0-50-09657 (1F)

MRC Job No. 5512

to

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

Author

James A. Webster

MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO 45407

22 October 1970

FOREWORD

This report is the Seventh Quarterly Progress Report prepared by Monsanto Research Corporation, under Contract NAS8-21401, "Thermally Resistant Polymers for Fuel Tank Sealants" for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratory, Materials Division with Mr. W. J. Patterson as principal Contracting Officers Representative and D. E. Morris and W. P. Lewis as alternate Contracting Officers Representatives.

The work was performed at the Dayton Laboratory of Monsanto Research Corporation under the direction of Dr. John Mann Butler, Research Manager of Polymer and Organic Synthesis, by James A. Webster, Project Leader and Principal Investigator, with technical assistance provided by Mr. Thomas J. Morrow.

ABSTRACT

Experimental polyisocyanurate- and polyimide-linked fluorocarbon polymers for high temperature sealant applications are described. Preliminary thermal stability and titanium stress corrosion evaluations are discussed.

TABLE OF CONTENTS

I. SUMMARY

A practical synthesis for preparation of research quantities of isocyanatophenoxy-ended fluorocarbon polymer intermediates based on SF_4 fluorination of phenyl esters was developed. The intermediates polymerize readily forming isocyanurate polymers having reasonably good thermal stability. Stress corrosion of titanium at 500°F (260°C) was observed, however.

A polyimide based on the corresponding aminophenoxy intermediate was prepared and evaluated. The thermal gravimetric analysis indicated a significantly higher stability than the corresponding isocyanurate.

Silicone polymers having a fluorocarbon segment within the polymer chain were prepared. Evaluation of these is in progress.

II. INTRODUCTION

The objective of this program is the development of improved thermally and oxidatively stable polymers for use as sealants in fuel tanks of advanced high speed aircraft. More specifically the task is to develop and tailor new polymer systems to provide adequate tensile strength and elongation, adhesion, solvent resistance to hydrocarbon fuels and sufficient oxidative and thermal stability for long term service at temperatures up to 500°F. In addition the application requires a polymer system that does not contribute to stress corrosion of titanium alloys.

The chain structure that can be employed in the polymer system is largely determined by the high thermal and oxidative stability requirements. Long term stability at temperatures as high as 500°F, for example, would preclude incorporation of polymers containing significant aliphatic alkylene content whereas fluorocarbon and aromatic structures generally have sufficient stability at this temperature. Polysiloxanes can be expected to have reasonably good oxidative stability but could prove inadequate for long service life. As a result development of polymer systems based on fluorocarbon and aromatic moieties has been emphasized.

The approach being taken in the development of high temperature polymers deals with three aspects of the polymer system

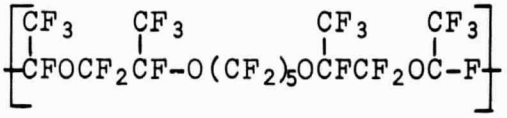
(a) The linear chain segment, $-R_f-$
(b) The reactive functional group, f
(c) The functional-group-to-chain-segment linking moiety, -X-

Together these make up the total polymerizable polymer intermediate which can be represented diagrammatically as

$$f\text{-}X\text{-}R_f\text{-}X\text{-}f$$

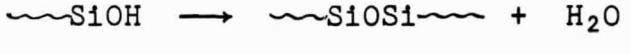
While the $-R_f-$ implies a difunctional fluorocarbon segment it may also represent a siloxane or fluorocarbon modified siloxane chain.

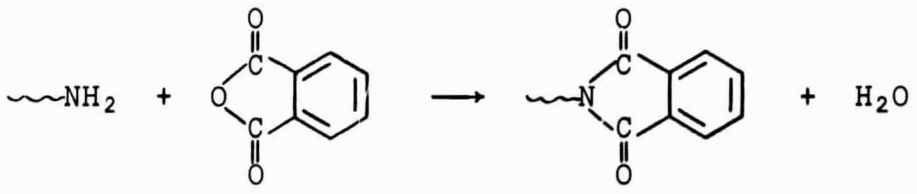
The chain segment in the fluorocarbon polymers, $-R_f-$, so far has been limited to low molecular weight perfluoroalkylene chains, $-(CF_2)_n-$ where n is 3 to 8. The intermediates are derived from available dicarboxylic acids or perfluoroalkylene diiodides. The ultimate objective, however, is the incorporation of a polymeric perfluoroalkylene ether segment which is considered to represent the preferred chain structure. This segment



is presently available in limited quantities as the dicarboxylic acid and is potentially commercially available.

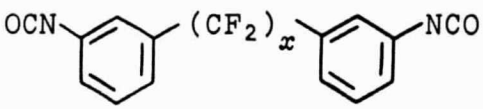
The functional group, f, is ideally one that undergoes reaction under mild conditions to form a high stability linkage, preferably without elimination of a volatile fragment, i.e., by an addition reaction. Since the cyclotrimerization of the isocyanate group appears to meet these criteria, this reaction has been emphasized. Alternative linking reactions being investigated include siloxane and polyimide formation even though volatile fragments are formed





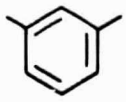
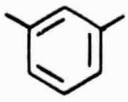
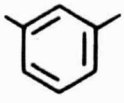
Silane addition provides a linkage that may be acceptable, however this reaction forms an aliphatic alkylene segment that could be a point of oxidative instability.

The third aspect and possibly a major factor in successful incorporation of a fluorocarbon segment into a sealant composition is the chemical bonding or the moiety, X, linking the functional group and chain segment. One of the first fluoro isocyanate intermediates investigated was $OCN(CF_2)_3NCO$, where the absence of a linking group X, to separate the perfluoroalkylene chains from the isocyanate group had an adverse effect on functional group reactivity. Failure of this intermediate to cyclotrimerize was attributed to the electron withdrawing effect of the fluorocarbon. Insertion of a phenylene group gave the isocyanatophenyl compound



which polymerized readily and formed a polymer having good oxidative and thermal stability.

In summary then, the problem is the linking of the fluorocarbon chains to functional groups and the definition of the optimum combination of functional groups, linking structures and chain segments to develop optimum stability and physical characteristics. During this past quarter evaluation of polymers as well as synthesis of intermediates containing the following structural components was emphasized.

Functional Group (f)	Linking Group (-X-)	Chain Segment R_f	Polymer Type Formed
OCN-		$\leftarrow CF_2 \rightarrow_5$	fluorocarbon isocyanurate
H_2N-		$\leftarrow CF_2 \rightarrow_5$	fluorocarbon polyimide
Me HOSi- Me		$\leftarrow CF_2 \rightarrow_3$ $\leftarrow CF_2 \rightarrow_6$	fluorocarbon modified siloxane

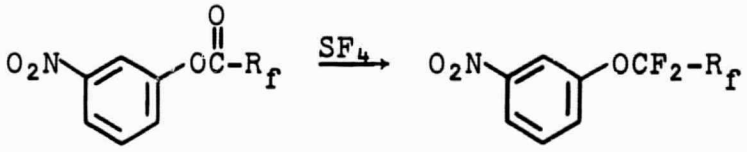
The results are discussed in the following section.

III. RESULTS AND DISCUSSION

A. ISOCYANURATE-LINKED FLUOROCARBON POLYMERS

1. Isocyanatophenoxy Perfluoroalkylene Intermediates

a. Synthesis. Isocyanatophenoxy-ended fluorocarbon intermediates have been investigated as alternative structures for isocyanatophenyl-linked intermediates. The synthesis route involving SF_4 fluorination of a nitrophenyl ester was outlined in the Second Annual Progress Report (Ref. 1).



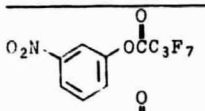
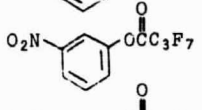
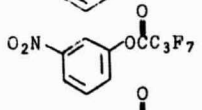
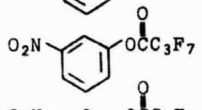
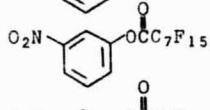
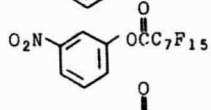
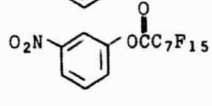
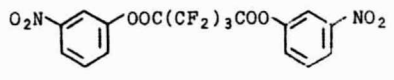
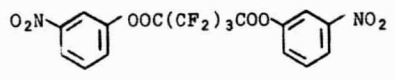
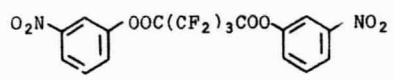
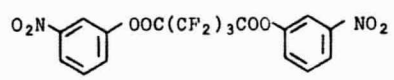
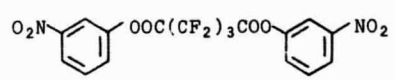
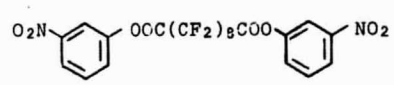
Although the initial experiments gave discouragingly low yields the route was sufficiently attractive to warrant further effort.

During the past quarter the yields have been increased from 20% yield of crude product to 60-70% yield of distilled nitrophenoxy perfluoroalkane (Table 1). The improvement was accomplished by increasing the proportion of anhydrous hydrogen fluoride used as solvent and decreasing the time and temperature. This improvement enabled synthesis of intermediates for subsequent conversion to diamine and diisocyanate derivatives from which polyimide and polyisocyanurate polymers were prepared for evaluation.

b. Polymerization and Evaluation. Polymerization of 1,5-bis(isocyanatophenoxy)decafluoropentane proceeds at room temperature upon addition of catalytic quantities of N,N,N',N'-tetramethylbutanediamine and allyl glycidyl ether. Upon post cure at 100° a hard, clear, somewhat brittle polymer was formed. Preliminary thermal gravimetric analysis evaluation indicated that the

Table 1

SULFUR TETRAFLUORIDE FLUORINATION
OF NITROPHENYL ESTERS OF PERFLUOROCARBOXYLIC ACIDS
TO FORM NITROPHENOXYPERFLUOROALKANES

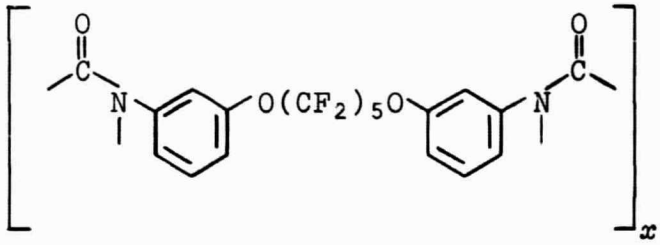
NBP	Ester Reactant, g (moles)	SF_4 g (moles)	HF g	Time hr	Temp °C	% Yield Crude	% Yield Distilled
132810	 15 (0.047)	20 (0.19)	5	23 24 18	100 125 150	54	39
132816	 10 (0.031)	4 (0.037)	20	1 2 2.5	100 150 175	45	--
138821	 10 (0.031)	4 (0.037)	20	2.0 2.0 2.5	100 125 150	66	44
132823	 10 (0.031)	6 (0.055)	20	3	150	36	--
132826	 10 (0.019)	8 (0.074)	20	5 24 2	100 125 150	61	41
132837	 10 (0.019)	8 (0.074)	20	10	100	73	--[1]
132839	 10 (0.019)	8 (0.074)	20	10	80	81	69[2]
132829	 20 (0.042)	12 (0.11)	40	6 17 2	100 125 150	63	40
132833	 40 (0.083)	26 (0.24)	80	6 11 2	100 125 150	78	42
125095	 10 (0.019)	10 (0.092)	10	19 24 8	100 125 150	20	--
132842	 20 (0.042)	12 (0.11)	40	5	100	85	59
132857	 90 (0.182)	56 (0.52)	190	5	100	85	--
132855	 40 (0.055)	16 (0.15)	80	5.5[3]	110[3]	0	--[4]

[1]Crude product reduced affording amine hydrochloride in 43% yield
[2]Evidence of incomplete reaction
[3]Possible failure of temperature controller
[4]Recovered ~50% unreacted ester

thermal stability below 450°C was equal or superior to the analogous isocyanurate having an isocyanatophenyl linkage (Figure 1). The weight loss increased rapidly above 500°C and finally exceeded 100%, perhaps because the polymer decomposition products attacked the crucible. The polymer showed no apparent change upon prolonged refluxing in water or jet fuel. Castings of the polymer around a titanium alloy test specimen were prepared for stress corrosion evaluation. These specimens were submitted for testing under Task B, Contract NAS8-21399. The results indicate that this polymer caused stress corrosion at 500°F. Details will be reported under the Task B contract.

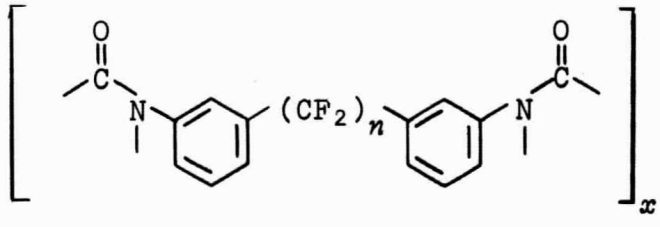
2. Isocyanatophenylperfluoroalkylene Intermediates

Since the isocyanatophenoxy-derived polymer, I,



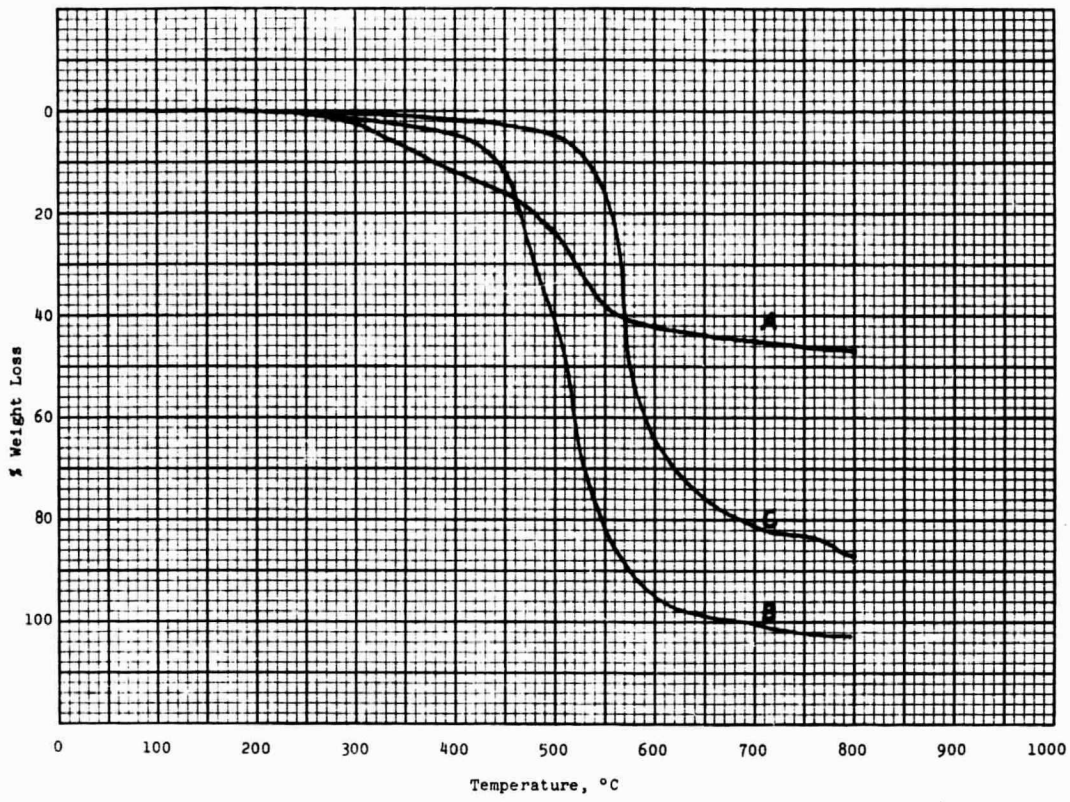
I

caused stress corrosion of titanium at 500°F, further evaluation of the phenylperfluoroalkylene isocyanurate polymer, II, became more critical.

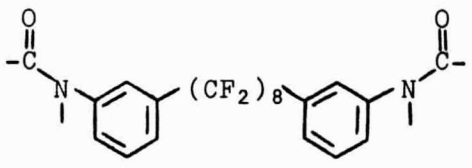


II

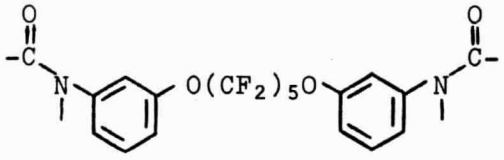
The stress corrosion potential of the latter structure had not been included in the earlier evaluation of this polymer. Synthesis of sufficient diisocyanate intermediate to carry out the evaluations, however, is hampered by limited availability of



A Sample 113265 in Helium



B Sample 132849 in Air



C Sample 132873-A in Air

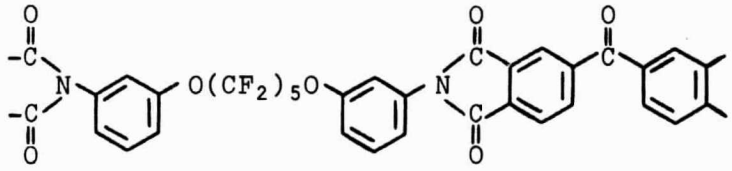
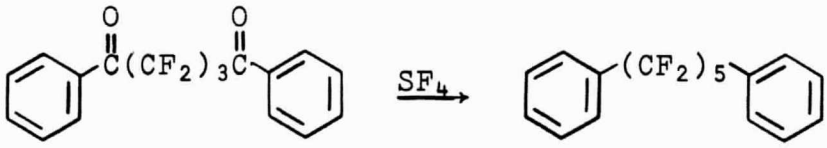


Figure 1. Thermal Gravimetric Analysis of Isocyanurate and Polyimide Polymers, 2.7°C/min

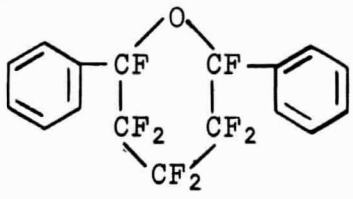
necessary intermediates. As a result structure of II is effectively limited to n = 3,5 and 6 unless extensive synthesis effort is undertaken. Chain lengths of at least n = 5 or 6 are preferred. The intermediate where n = 3 may be too short and rigid for satisfactory formation of the highly crosslinked isocyanurate polymer. Intermediates where the value of n is 5 can be made from one of the most readily available intermediates, perfluoroglutaric acid, by Route B outlined in the Second Annual Progress Report (Ref. 1). This route involves SF_4 fluorination of the diketone



III

for which optimum conditions, as previously indicated (Ref. 1) were not determined.

Additional investigation of the SF_4 fluorination of dibenzoylperfluoropropane was therefore begun to provide material for the isocyanurate evaluation. The previous work resulted in a good yield of a mixture of the desired diphenylperfluoropentane and cyclic ether (IV) products



IV

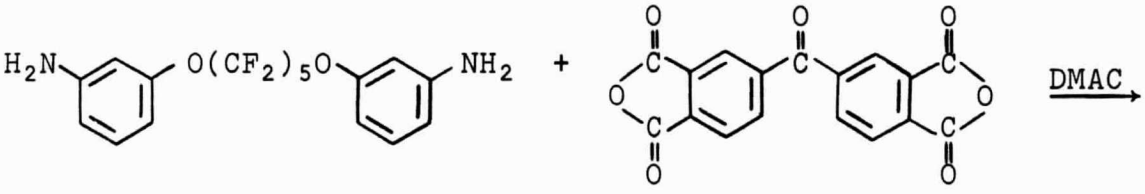
which were difficult to separate. The recent success using anhydrous hydrogen fluoride as a solvent for the SF_4 fluorination of the nitro ester prompted a trial of similar reaction conditions. Surprisingly, a polymeric product was formed under mild

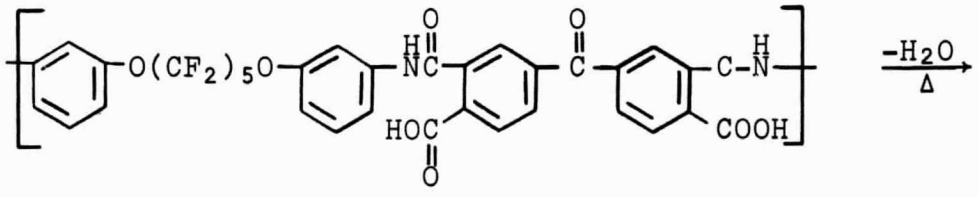
conditions, presumably by an intermolecular condensation. Further investigation of this product is being carried out.

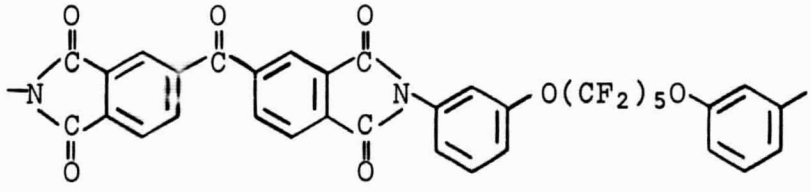
A simpler route, the coupling of nitroiodobenzene with 1,6-diiodoperfluorohexane telomer intermediate could provide a convenient synthesis, but the supply of the diiodide is limited and is contaminated with iodobenzene. Nevertheless, synthesis by this route is being investigated also.

B. FLUOROCARBON POLYIMIDE

A polyimide was prepared by reaction of the diamine, formed by reduction of 1,5-bis(*m*-nitrophenoxy)decafluoropentane, with benzophenonetetracarboxylic dianhydride.







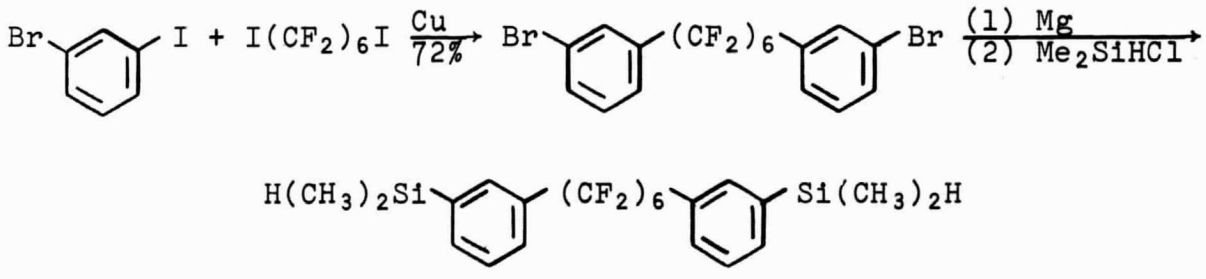
A clear, amber-colored film was formed upon elimination of solvent and further heating to complete the condensation.

Thermal gravimetric analysis of the polyimide indicates the polymer has high stability (Figure 1) with a weight loss of 5% at 500°C in air. Evaluations of compatibility with fuel and stress corrosion potential with titanium are in progress under Task B, Contract NAS8-21399.

C. FLUOROCARBON-MODIFIED SILICONE

Incorporation of a linear fluorocarbon segment within the silicone polymer chain to improve the solvent resistance was discussed previously (Ref. 1). The steps in the synthesis of the intermediate, 1,3-bis(chlorodimethylsilylphenyl)hexafluoropropane, were also described in the previous report. The quantity of the product was considered inadequate for further work. Moreover synthesis of a longer chained homolog was highly desirable. Therefore the efforts this quarter included the synthesis of a perfluorohexylene-containing disilane intermediate.

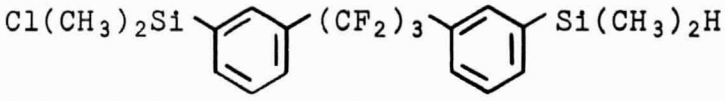
A small quantity of pure 1,6-diiodoperfluorohexane was isolated from a mixture of telomer diiodides, $I(CF_2CF_2)_nI$. Copper catalyzed coupling of diiodoperfluorohexane (n = 3) with bromoiodobenzene followed by Grignard reaction provided a dimethylsilylphenyl derivative



Hydrolysis of a portion of the above disilane formed a viscous polysiloxane which cured upon further heating forming a weak

elastomeric material. A titanium stress corrosion specimen coated with this material was prepared for subsequent evaluation under the Task 3 contract. Additional trial hydrolysis experiments using a platinum catalyst suggest that the monomeric diol can be obtained.

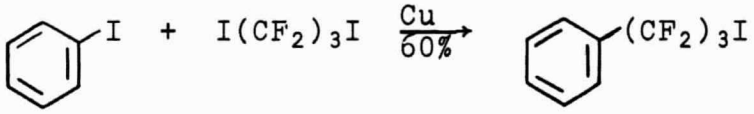
Hydrolysis of the previously prepared chlorosilane



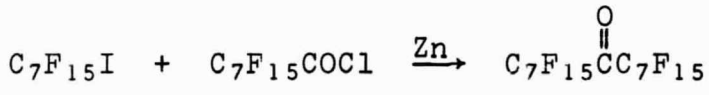
was also carried out forming a fluorocarbon modified siloxane.

D. MISCELLANEOUS COUPLING EXPERIMENTS

Efforts to develop alternate methods for linking fluorocarbon segments through phenyl moieties continue. Synthesis of a phenyl perfluoroalkyl iodide in reasonably good yield was reported by McLoughlin and Thrower (Ref. 2).



The possibility of linking this product to a perfluoroacyl chloride was shown by the following reaction



The above coupling was carried out in anhydrous tetrahydrofuran and was found to be exothermic at -10 to 0°C.

IV. EXPERIMENTAL

A. ISOCYANURATE-LINKED FLUOROCARBON POLYMERS

1,5-Bis(*m*-nitrophenoxy)decafluoropentane

The following experiment is representative of numerous reactions of SF_4 with nitrophenyl esters shown in Table 1.

132842

A 300 ml stainless steel autoclave was charged with bis(*m*-nitrophenyl)hexafluoroglutarate (20 g, 0.0415 mole). The vessel was evacuated and charged with (40 g, 2.0 moles) anhydrous hydrogen fluoride and 12 g, (0.11 mole) of sulfur tetrafluoride. The bomb was heated to 100° for 5 hours then cooled and vented. The contents of the bomb was poured onto ice and washed with sodium bicarbonate. The organic material was extracted with benzene. Evaporation of the solvent gave 18.5 g residue from which 12.8 g (59% yield) of 1,5-bis(*m*-nitrophenoxy)decafluoropentane was recovered by distillation, bp 200°/0.06 mm, n_D^{25} 1.4724. The infrared spectrum (Figure 2) was consistent with this structure.

1-(*m*-Nitrophenoxy)nonafluorobutane

132810
132821

Reaction of SF_4 with *m*-nitrophenyl heptafluorobutyrate under the conditions shown in Table 1 gave 38-44% yields of 1-(*m*-nitrophenoxy)perfluorobutane, bp 56°/0.05 mm, n_D^{25} 1.4028-31.

m-Nitrophenyl Perfluorooctoate

132812

Reaction of perfluorooctanoyl chloride (86.5 g, 0.2 mole) with *m*-nitrophenol (34.8 g, 0.25 mole) in the presence of a few drops of pyridine and at 110-125° for 18 hours gave a 57% yield of ester, bp 91-95°/0.03 mm, mp 36-38.5°.

1-(*m*-Nitrophenoxy)perfluorooctane 132826
132839

Fluorination of *m*-nitrophenyl pentadecafluorooctanoate with SF_4 under the condition shown in Table 1 formed 1-(*m*-nitrophenoxy)perfluorooctane in 69% yield, bp 103°/0.1 mm, n_D^{25} 1.3804. The infrared spectrum (Figure 3) substantiates the nitrophenyl ether structure.

m-Nitrophenyl Perfluorosebacate 132854

Pyridine catalyzed reaction of 30 g (0.057 moles) of perfluorosebacoyl chloride with 28 g (0.2 mole) of *m*-nitrophenol over a period of 18 hours at 110° formed 42 g of *m*-nitrophenyl perfluorosebacate. Excess phenol was removed under vacuum leaving 42 of crude crystalline solid, mp 91-94.5°. The infrared spectrum (Figure 4) was consistent with the diester structure.

m-Perfluorooctyloxyaniline Hydrochloride 132864

m-Nitrophenyl perfluorooctyl ether (9.4 g, 0.0168 mole) was catalytically reduced over Raney nickel at 48 psi hydrogen. The solution was filtered and the solvent evaporated. The residue was dissolved in ether and saturated with anhydrous hydrogen chloride to form the amine hydrochloride. The yield of crude product was 8.1 g, 85.5%, mp 195-217°C.

1,5-Bis(*m*-aminophenoxy)decafluoropentane 132838
132861

Hydrogenation of 1,5-bis(*m*-nitrophenoxy)decafluoropentane (19.5 g, 0.037 mole) in ethanol over Raney nickel gave a 98% yield of the corresponding diamine, mp 45-47°. The amine, dissolved in ether was precipitated as the hydrochloride upon addition of anhydrous hydrogen chloride. The melting point of a small portion recrystallized from isopropanol water solution was 264°C.

132863

Free amine was isolated from a larger quantity of the amine hydrochloride (22 g) by treatment with aqueous sodium hydroxide. Distillation afforded 17 g of 1,5-bis(*m*-aminophenoxy)decafluoropentane, bp 162°/0.03 mm, n_D^{25} 1.4755, mp 45.5-47° (Figure 5).

m-Perfluorooctyloxyphenyl Isocyanate 132871

A slurry of *m*-perfluorooctyloxyaniline hydrochloride (12 g, 0.021 mole) in 200 ml of dry *o*-dichlorobenzene, as a reaction medium, was stirred and heated slowly as phosgene was passed into the mixture. All solid material had dissolved by the time the temperature was 110°C. Heating was continued to a temperature of 170°. Distillation gave 6.6 g of *m*-perfluorooctyloxyphenyl isocyanate, bp 77°/0.05 mm, n_D^{25} 1.3790-1.3799.

1,5-Bis(*m*-isocyanatophenoxy)decafluoropentane 132844

Phosgene was passed into a slurry of 1,5-bis(*m*-aminophenoxy)-decafluoropentane hydrochloride (25.6 g, 0.0475 mole) in 400 ml of *o*-dichlorobenzene as the mixture was gradually heated to 125°C. Heating was continued to a temperature of 170°. Distillation then afforded an 83% yield of 1,5-bis(*m*-isocyanatophenoxy)decafluoropentane, bp 153°/0.03 mm, n_D^{25} 1.4690, isocyanate equiv. 261, 259; Calcd 259.1 (Figure 6).

Polyisocyanurate Polymer from 1,5-bis(*m*-isocyanatophenoxy)-decafluoropentane 132846

A two gram portion of the 1,5-bis(*m*-isocyanatophenoxy)decafluoropentane intermediate was mixed with 0.02 g quantities of allyl glycidyl ether and N,N,N',N'-tetramethyl-1,3-pentanediamine. The mixture solidified upon standing for a few hours at 25°C. A post cure at 100° completed the reaction of isocyanate groups. A clear, amber-colored hard polymer resulted.

The Tg by Vicat softening point was approximately 165°C. Thermal gravimetric analysis showed less than 5% weight loss to 400°C.

Tris(*m*-perfluorooctoxyphenyl)isocyanurate 132875

m-Isocyanatophenoxyperfluorooctane (2.0 g) was mixed with 0.02 g of allyl glycidyl ether and 0.02 g of tetramethyl-1,3-butanediamine. An exothermic reaction was accompanied by increase in viscosity. A viscous residue resulted after further heating at 100° overnight showed no free isocyanate absorption in the infrared spectrum but a strong carbonyl at 5.8 μ

A white solid, mp ∿90°, formed upon mixing the above viscous residue with methanol. This reformed a viscous residue upon air drying. Elemental analysis and infrared spectrum (Figure 7) substantiate the empirical formula for tris(*m*-perfluorooctyloxyphenyl)isocyanurate.

Calcd for $C_{45}H_{12}F_{51}N_3O_6$: %C, 32.58; %H, 0.73; %F, 58.39
Found: %c, 32.56; %H, 0.57; %F, 58.02

SF_4 Fluorination of Dibenzoylperfluoropropane 132865

A 300 ml stainless steel pressure vessel was charged with 10 g of 1,3-dibenzoylhexafluoropropane (0.028 moles) 20 g of anhydrous hydrogen fluoride and 10 g of sulfur tetrafluoride (0.093 mole). The bomb was heated 3 hours at 100°, 21 hr at 125° and 19 hours at 150°. A gummy mass resulted. A portion of this was benzene soluble and the remainder was soluble in methylene chloride. The organic solutions were washed with water, dried and evaporated to dryness. A gummy brown residue (9.6 g) was obtained from the benzene, and 3.6 g from the methylene chloride. Portions of both fractions were redissolved

in the solvent and precipitated with hexane, dried well under vacuum and then analyzed. The infrared spectra showed aromatic and fluorocarbon absorptions but no carbonyl absorption (Figure 8).

B. FLUOROCARBON POLYIMIDE

Polyimide from 1,5-Bis(aminophenoxy)decafluoropentane 132873

A mixture of freshly sublimed benzophenonetetracarboxylic dianhydride (3.22 g, 0.01 mole), and 1,5-bis(*m*-aminophenoxy)decafluoropentane (4.66 g, 0.01 mole) was stirred in 50 ml of freshly distilled dry dimethylacetamide at 10-20° for one hour. The solution was then stirred overnight at room temperature. Evaporation of the solvent from a portion of the solution at ∿135° left a yellow film which was subsequently heated to ∿290-300°C without obvious change in appearance. The weight loss by thermal gravimetric analysis was less than 5% up to 500°C in air. A sample of the polymer was submitted for evaluation under Task B contract.

C. FLUOROCARBON-MODIFIED SILICONE

1,6-Diiodododecafluorohexane 132815

A 1350 g mixture of α,ω-diiodopolytetrafluoroethylene, $I(CF_2CF_2)_nI$, n = 1-5, product was distilled through a one-meter length glass helices packed column. Careful fractionation of the C_6 fraction resulted in separation of 200 g of the diiodoperfluorohexane-iodobenzene azeotrope, bp 112°/99 mm, from 88 g of pure 1,6-diiodoperfluorohexane, bp 117°/99 mm n_D^{25} 1.4030.

Attempted Separation of Iodobenzene-1,6-Diiodo-dodecafluorohexane 123862

The azeotropic mixture (n_D^{25} 1.5018) of iodobenzene (n_D^{25} 1.6180, mp -31°) and 1,6-diiodododecafluorohexane (n_D^{25} 1.4029, mp 20°) was cooled to -30° at which point the liquid had completely crystallized. The solid was permitted to warm slowly and the liquid that formed was drawn off through a fritted filter. Three liquid fractions were taken as the crystalline mass gradually melted.

1	42.5 g	n_D^{25} 1.5490
2	31.1 g	n_D^{25} 1.5427
3	54.4 g	n_D^{25} 1.5100
Residue	67.7 g	n_D^{25} 1.4393

Fractions 1 and 2 were combined as iodobenzene enriched mixture. The crystalline solid was considered to be 1,6-diiodododecafluorohexane enriched mixture from which a portion of the pure diiodide can be obtained by redistillation.

1,6-Bis(*m*-bromophenyl)perfluorohexane 132827

A copper catalyzed coupling of *m*-bromoiodobenzene (90.5 g, 0.32 moles) with 1,6-diiodododecafluorohexane by the method previously reported (Ref. 1) resulted in a 0.71% yield of 1,6-bis(*m*-bromophenyl)perfluorohexane, bp 154-156°/0.05 mm.

1,6-Bis(dimethylsilylphenyl)dodecafluorohexane 123876

1,6-Bis(*m*-bromophenyl)dodecafluorohexane (36 g, 0.059 mole) in tetrahydrofuran was added to excess magnesium in the presence of dimethylchlorosilane (21.7 g, 0.23 mole). The reaction mixture stirred overnight at 25° and was then heated to 40°. An

exotherm with temperature rise to 50° indicated further reaction. The reaction mixture was poured onto ice. Separation of the organic material with the aid of added methylene chloride followed by distillation gave a 57% yield of 1,6-bis(dimethylsilylphenyl)dodecafluorohexane, bp 140°/0.05 mm, n_D^{25} 1.4530-37, d_4^{25} 1.299.

Hydrolysis of 1,6-Bis(dimethylsilylphenyl)dodecafluorohexane

Attempts to hydrolyze the disilane to diol in alkaline aqueous and alcoholic solutions resulted in slow and incomplete reaction or condensation to polysiloxane.

132851

Sodium methoxide in methanol was added to 13 g of crude 1,6-bis(*m*-dimethylsilylphenyl)dodecafluorohexane to convert the disilane to dimethoxy derivative. After reaction at 40°C for 1 hour the solution was added to cold neutral buffered aqueous solution. An oily product was recovered by extraction with ether. The viscous oil left upon evaporation of solvent showed no SiH in the infrared spectrum, but appeared to contain siloxane linkages as well as silanol groups.

132877

Upon heating at 120°C the above residue formed a weak rubbery polymer. A tensile test specimen was coated with this material which was then cured at elevated temperature. The specimen was then submitted for stress corrosion evaluation. The polymer did not flow at 260°C.

Hydrolysis of 1,3-Bis(*m*-chlorodimethylsilylphenyl)-hexafluoropropane 123875

1,3-Bis(*m*-chlorodimethylsilylphenyl)hexafluoropropane (4.2 g) in ether solution was hydrolyzed in cold water at pH 7 maintained by addition of ammonium hydroxide. The product was extracted from the aqueous phase with ether. Evaporation of volatiles left viscous oil showing -OH absorption in the infrared spectrum as well as expected fluorocarbon, siloxane and aromatic moieties. Reaction of this silanol with bis(dimethylamino)dimethylsilane formed a viscous polymeric oil showing almost identical infrared spectrum as the above silanol but without the hydroxyl absorptions.

Bis(dimethylamine)dimethylsilane 132859

Dimethyldichlorosilane (258 g, 2.0 moles) was added dropwise to a cold solution dimethylamine (440 g, 9.9 moles) in pentane. The mixture was warmed to 30° and then filtered. Distillation of the filtrate gave a 74% yield of dimethyl bis(dimethylamino)-silane, bp 126-127°/740 mm, n_D^{25} 1.4160. Lit: bp 128°, (Ref. 3).

Coupling of Perfluoroheptyl Iodide with Perfluoro-octanoyl Chloride 132832

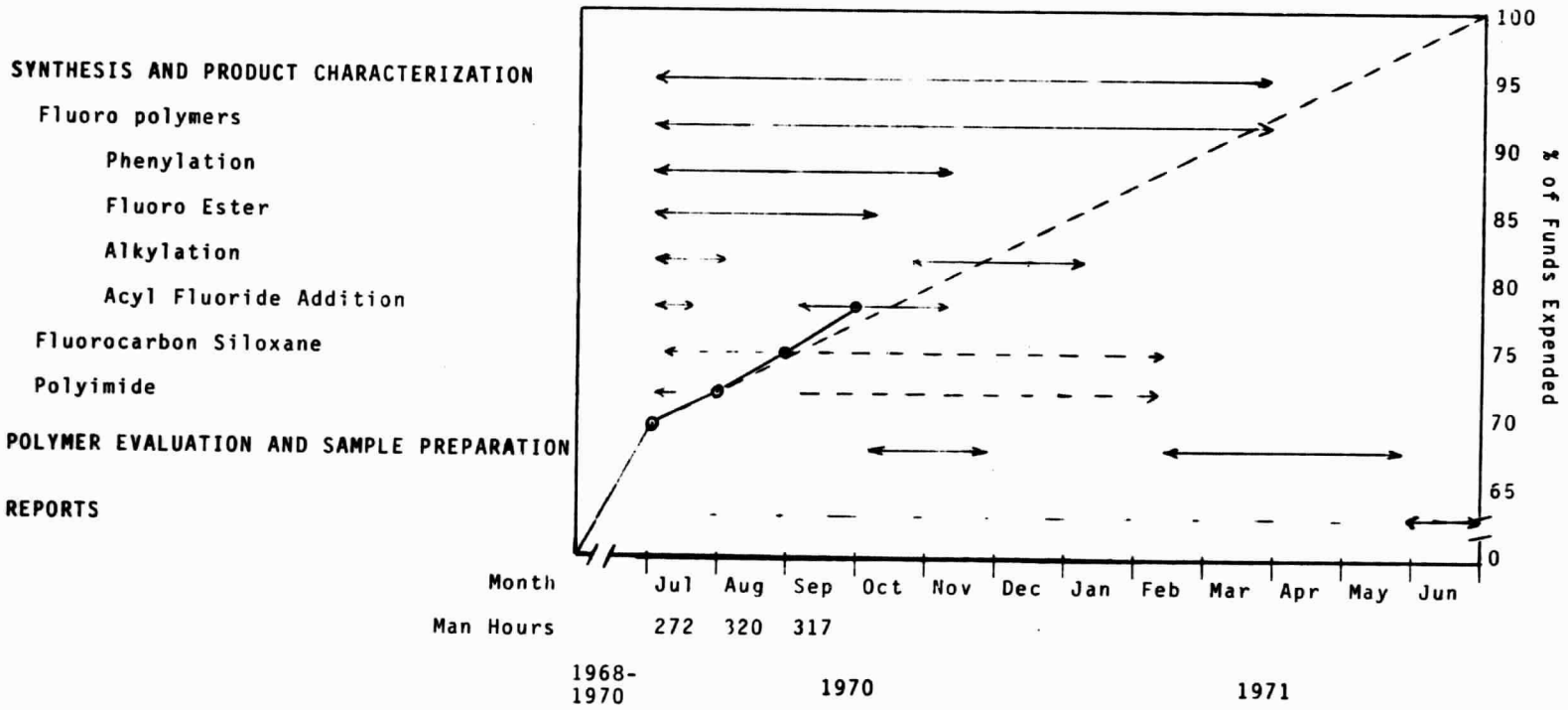
A mixture of perfluorooctanoyl chloride (8.7 g, 0.022 mole) and dry tetrahydrofuran (20 ml) was added to zinc granules at -10°. Perfluoroheptyl iodide (10.0 g, 0.022 mole) was added dropwise. An exothermic reaction occurred with formation of a white precipitate. The mixture was poured onto ice. The organic phase was separated and distilled yielding a 4.4 g fraction believed to be bis(perfluoroheptyl)ketone, bp 88°/7 mm, n_D^{25} 1.3016.

V. FUTURE PLANS

Prepare and evaluate stress corrosion of the isocyanurate polymer prepared from $OCNC_6H_4(CF_2)_6C_6H_4NCO$.

Continue preparation and evaluation of fluorocarbon modified siloxane polymers.

PROGRAM PLANNING CHART



VI. REFERENCES

1. John Mann Butler, C. E. Hathaway, R. P. Quill, J. A. Webster, "Thermally Resistant Polymers for Fuel Tank Sealants", Second Annual Progress Report, 1 July 1969 - 30 June 1970, Contract No. NAS8-21401.

2. V. C. R. McLoughlin, J. Thrower, *Tetrahedron* 25, 5921 (1969).

3. H. H. Anderson, *J. Am. Chem. Soc.* 74, 1421 (1952).

APPENDIX

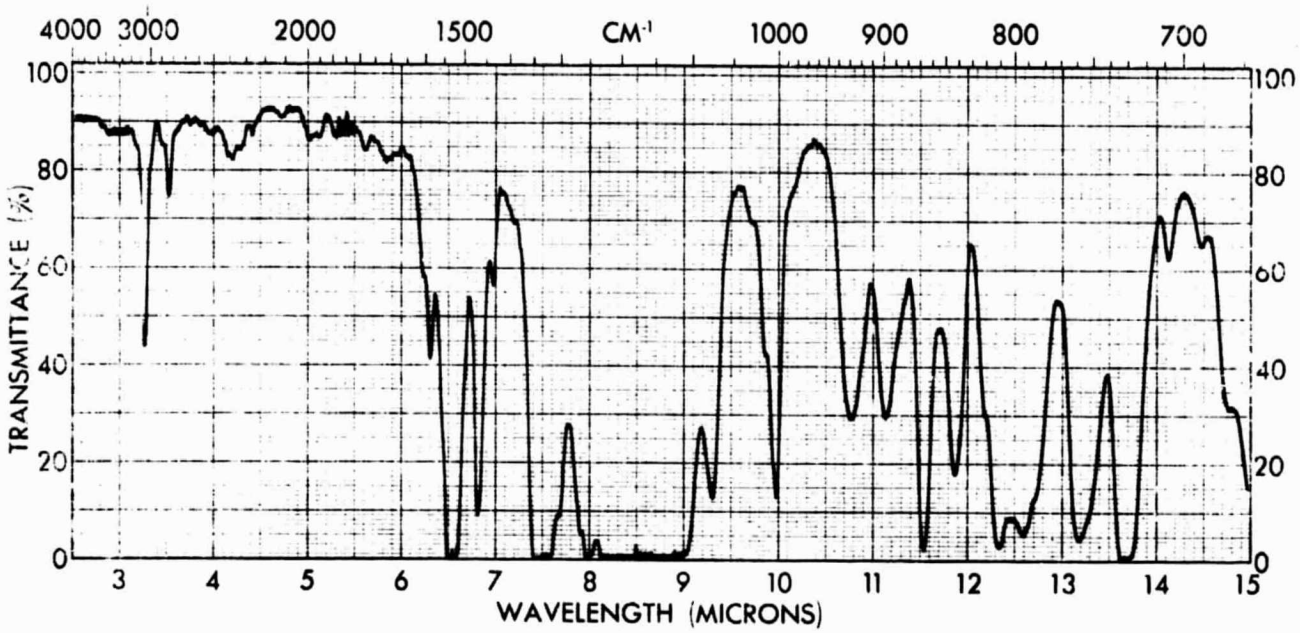


Figure 2. Sample 132834 O_2N–C$_6$H$_4$–$O(CF_2)_5O$–C$_6$H$_4$–NO_2

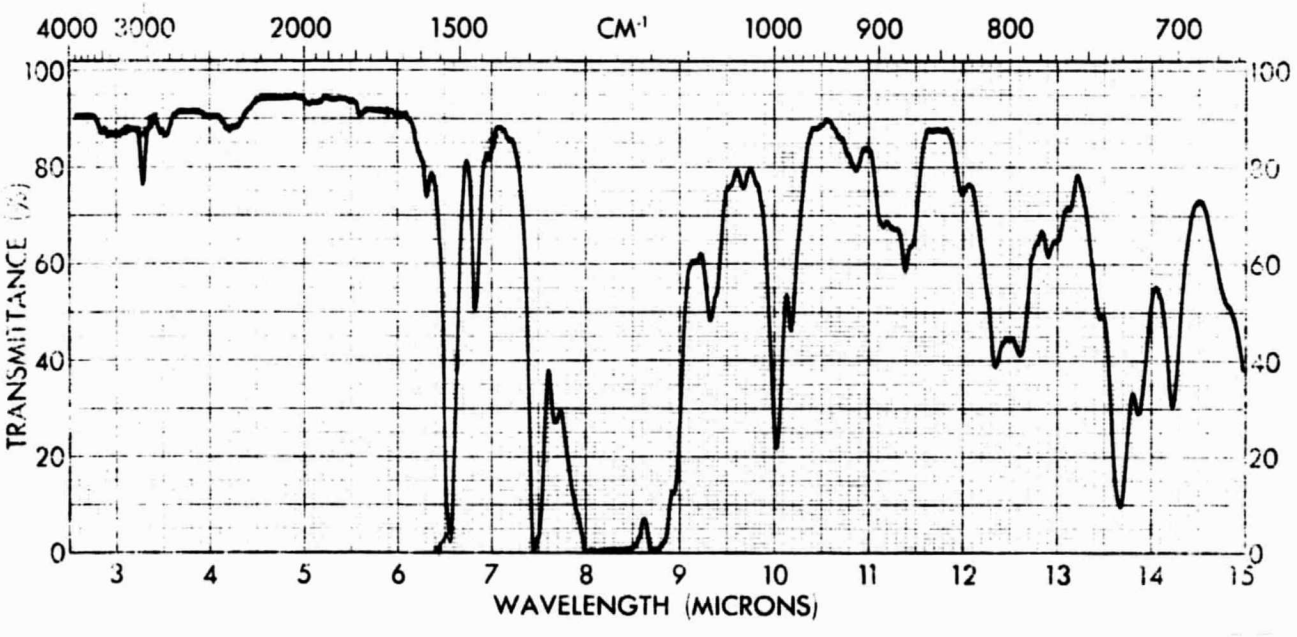


Figure 3. Sample 132830-2 O_2N–C$_6$H$_4$–OC_8F_{17}

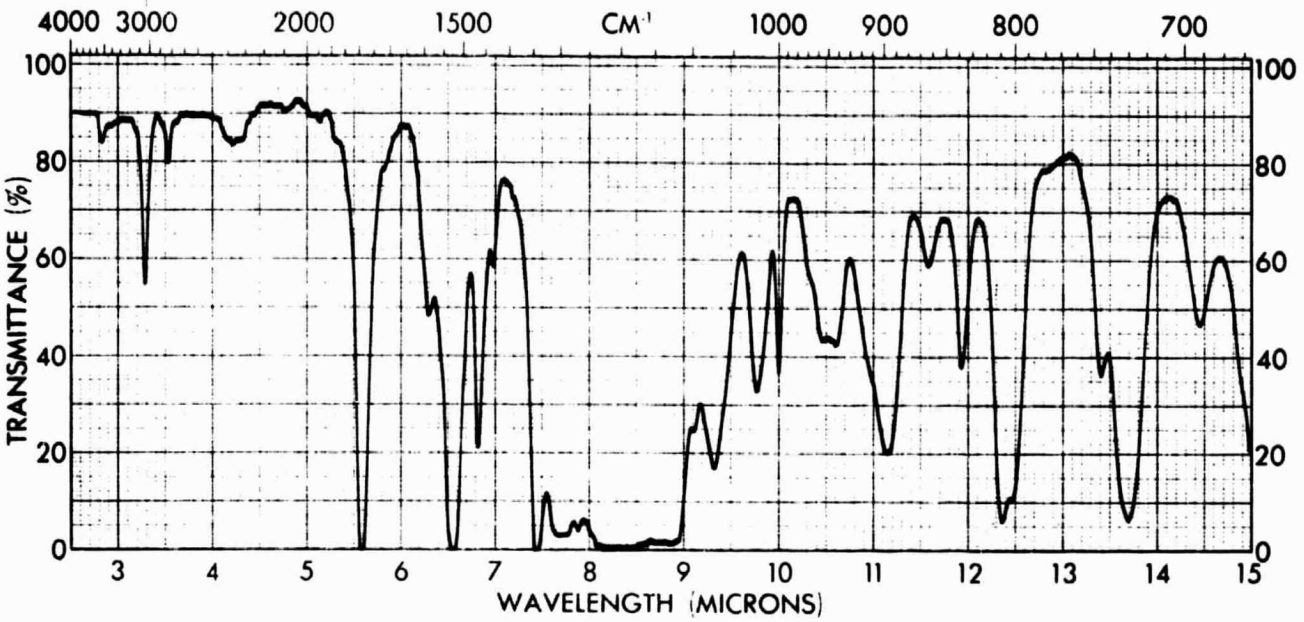


Figure 4. Sample 132854 O_2N-⟨⟩-$OOC(CF_2)_8COO$-⟨⟩-NO_2

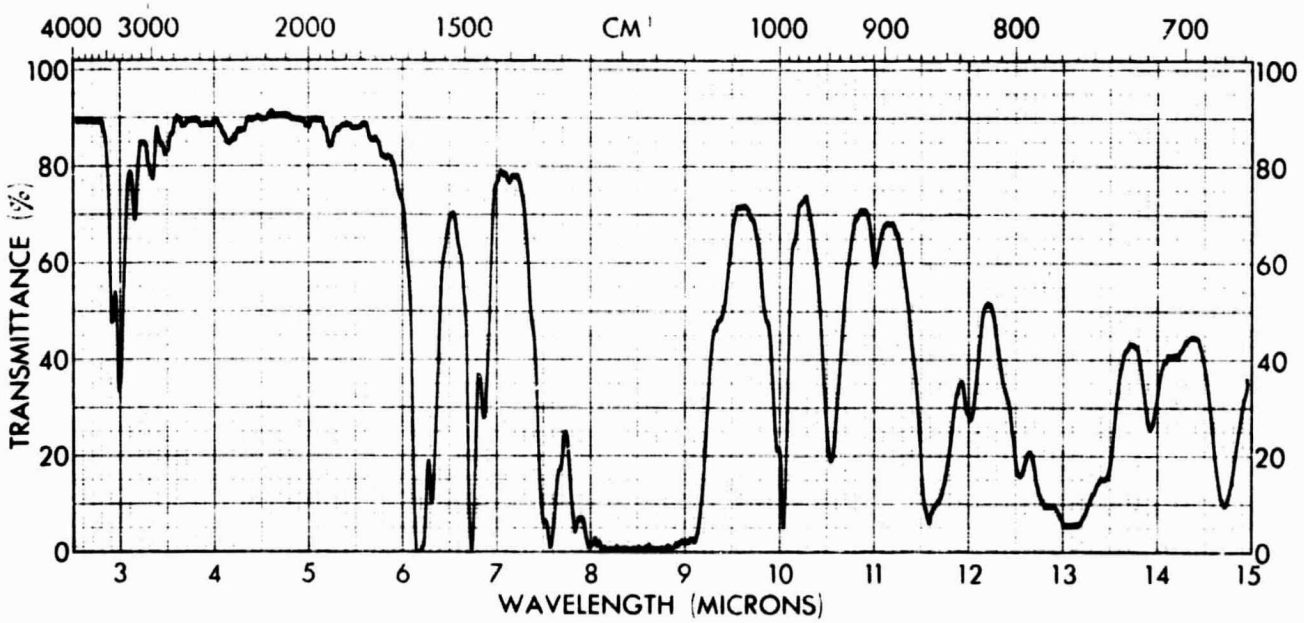


Figure 5. Sample 132863 H_2N-⟨⟩-$O(CF_2)_5O$-⟨⟩-NH_2

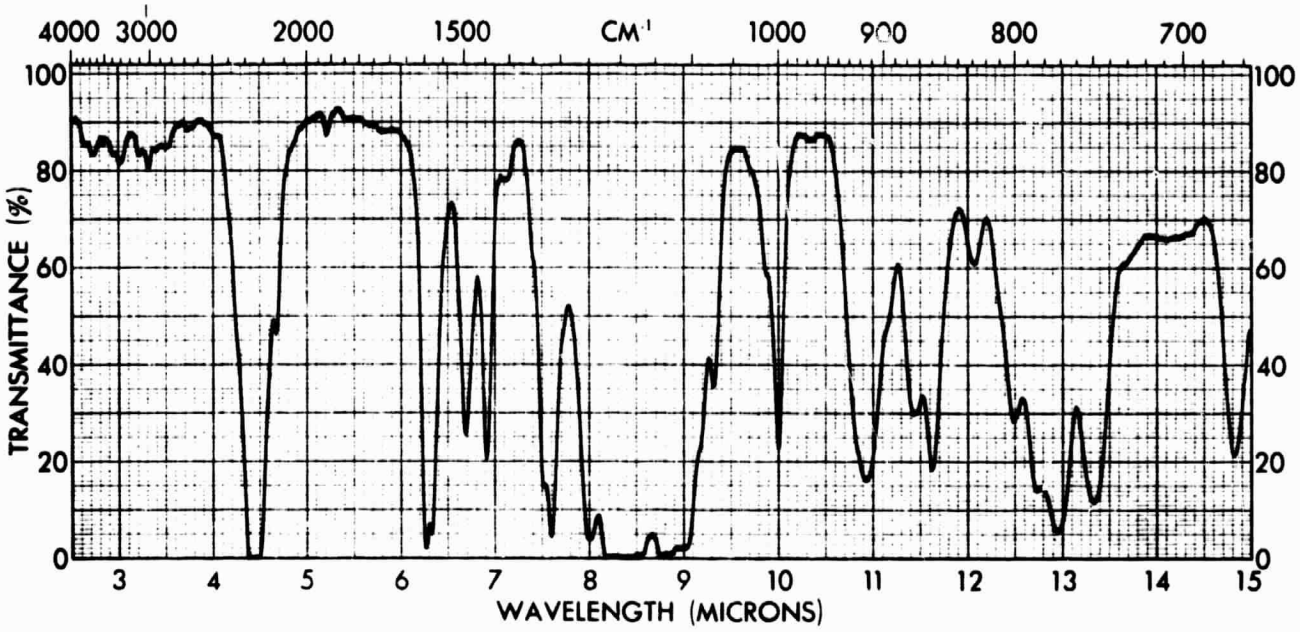
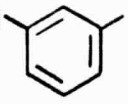
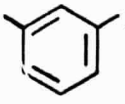


Figure 6. Sample 132845-2 OCN-  -O(CF$_2$)$_5$O-  -NCO

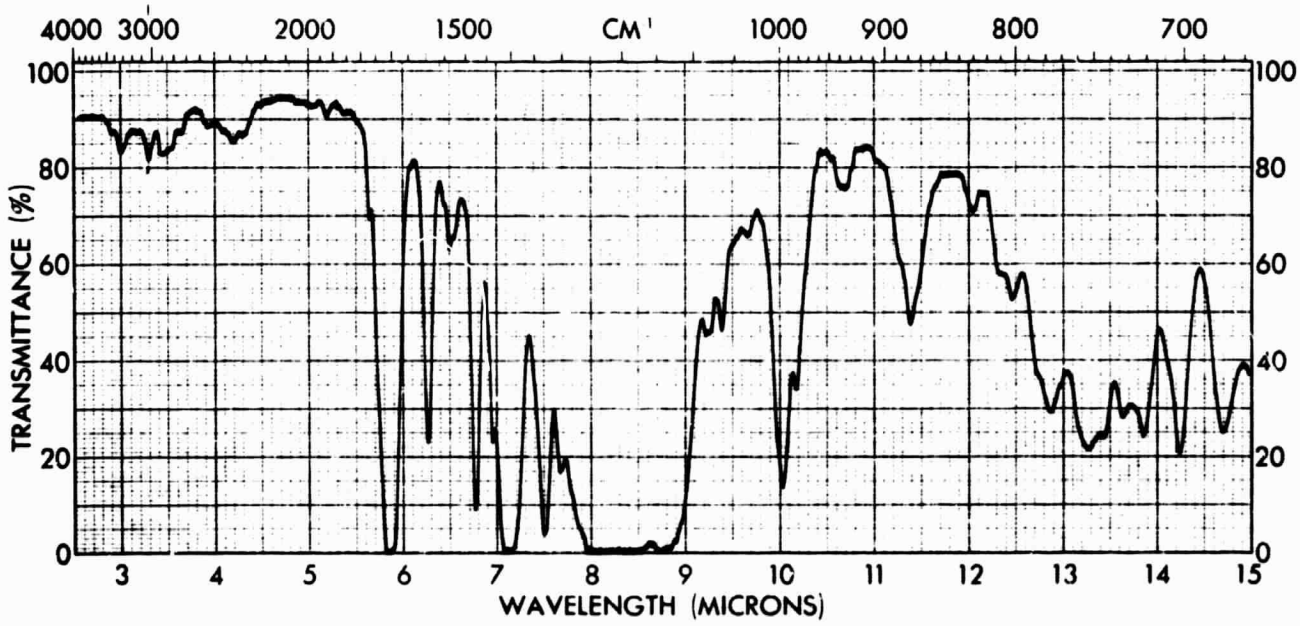
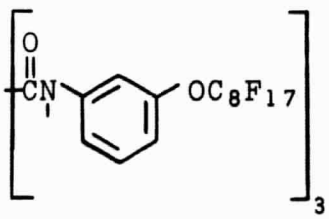


Figure 7. Sample 132875-A 

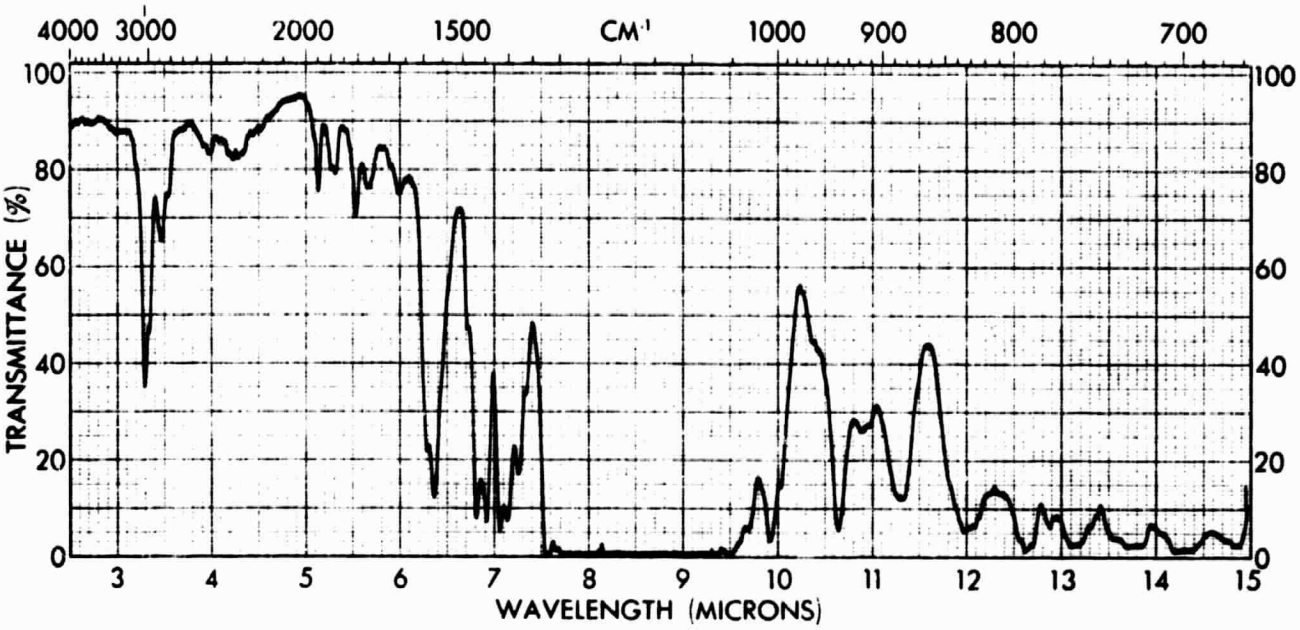


Figure 8. Sample 132869-B Polymeric Product Formed by Reaction of SF_4 with 1,3-Dibenzoylhexafluoropropane