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MRC-DA-301

Third Annual Summary Report

THERMALLY RESISTANT POLYMERS FOR FUEL TANK SEALANTS

Authors

James A. Webster
Thomas J. Morrow

1 July 1970 — 28 June 1971

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

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DAYTON LABORATORY
DAYTON, OHIO 45407

July 1971

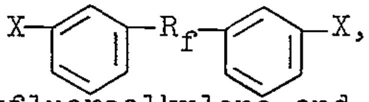
FOREWORD

This report is the Third Annual Summary 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 Astronautics Laboratory, Materials Division, with Mr. W. J. Patterson as principal Contracting Officer's Representative and D. E. Morris and W. P. Lewis as alternate Contracting Officer's Representatives.

The work was performed at the Dayton Laboratory of Monsanto Research Corporation during the period from 1 July 1970 to 28 June 1971 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

The development of imide, isocyanate and siloxane linked fluorocarbon polymers is described. Synthesis and polymerization of polymer intermediates of the type



where R_f represents perfluoroalkylene and perfluoroalkylene ether segments, and X represents amine, isocyanate, or silyl groups is discussed. Polymer evaluations including thermal and oxidative stability, fuel resistance, and stress corrosion of a titanium alloy are discussed.

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I. 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. This task requires development of new polymer systems that exhibit improved properties to satisfy tensile strength and elongation, adhesion, thermal and oxidative stability requirements, and resistance to hydrocarbon jet fuels. In addition, the sealant must give long-term service--up to 25,000 hours and at temperatures to 260°C (500°F) and not contribute to stress corrosion of titanium alloys.

During this past year the work has been concentrated on the development of fluorocarbon polymer systems as the most promising approach to meeting both the high stability requirements and the necessary physical property characteristics. Two objectives toward this goal have been pursued simultaneously. These objectives were (1) the development of synthesis methods enabling conversion of fluorocarbon and fluorocarbon ether intermediates to polymerizable polymer intermediates, and (2) the preparation and evaluation of prototype and candidate polymer systems.

II. SUMMARY

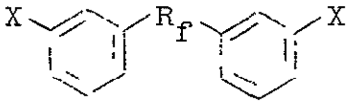
Considerable progress toward development of a fluorocarbon based sealant polymer was made during the past year. The work was a continuation of our previously reported efforts to develop high stability polymer linkages by coupling fluorocarbon polymer segments via reactive end groups. A portion of the first year's effort demonstrated the synthesis and polymerization of α,ω-bis(isocyanatophenyl) perfluoroalkylenes to form the thermally stable polyisocyanurate polymers. During the second year the emphasis was placed on improving the physical properties of the polymers by extending the fluorocarbon segment through incorporation of a polyperfluoroalkylene ether segment between polymerizable end groups. A major portion of that effort was devoted to overcoming synthesis problems. A promising method, the fluorination of nitrophenyl perfluoroalkylene dicarboxylates, was demonstrated as a potential route to intermediates terminated with stable functional groups although initial experiments gave low yields.

During this past year the ester fluorination route was greatly improved and then extended to the synthesis of perfluoroalkylene ether dicarboxylic acid intermediates. These reactions enabled preparation and evaluation of high stability polyimide and polyisocyanurate polymers. An elastomeric fluorocarbon-modified silicone polymer was also prepared. More recently a decision to concentrate the effort on one of the three polymer-linking reactions was made in an effort to develop a candidate product during the next year. The imide-forming reaction was chosen for this concentrated effort.

III. DISCUSSION

A. BACKGROUND AND APPROACH

The primary requirement for the development of an improved fuel tank sealant is a long service life under severe operating conditions including exposure to hydrocarbon fuels, air, and water at temperatures as high as 260°C (500°F). These severe conditions were the primary reasons for emphasizing the development of a fluorocarbon-based polymer for this application. The approach has been to develop polymerizable polymer intermediates containing reactive terminal functional groups, X, that are linked through phenylene transitional moieties to perfluoroalkylene or perfluoroalkylene ether chain segments, R_f. Together these units make up the polymer intermediate, which may be represented schematically by the structure



The perfluoroalkylene and perfluoroalkylene ether segments (R_f) are those derived from the available fluorocarbon intermediates indicated below:

Perfluoroalkylene, $(CF_2)_n$

(a) Dicarboxylic acids $HOOC(CF_2)_nCOOH$ n = 3 to 8

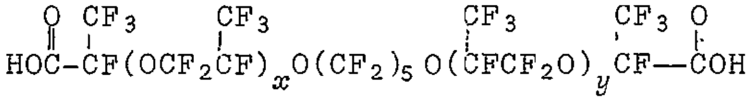
(b) Diiodides $I(CF_2)_nI$ n = 2 to 8

Perfluoroalkylene Ethers

(a) Perfluoroglutaryl fluoride-hexafluoropropylene epoxide adducts

1:1 $HOOCCFCF_3O(CF_2)_4COOH$

2:1 $HOOCCFCF_3O(CF_2)_5OCFCF_3COOH$

>2:1 

$$HO\overset{O}{\overset{\|}{C}}-\overset{CF_3}{\overset{|}{C}}F(OCF_2\overset{CF_3}{\overset{|}{C}}F)_xO(CF_2)_5O(\overset{CF_3}{\overset{|}{C}}FCF_2O)_y\overset{CF_3}{\overset{|}{C}}F—\overset{O}{\overset{\|}{C}}OH$$

$x + y = 1\text{-}5$

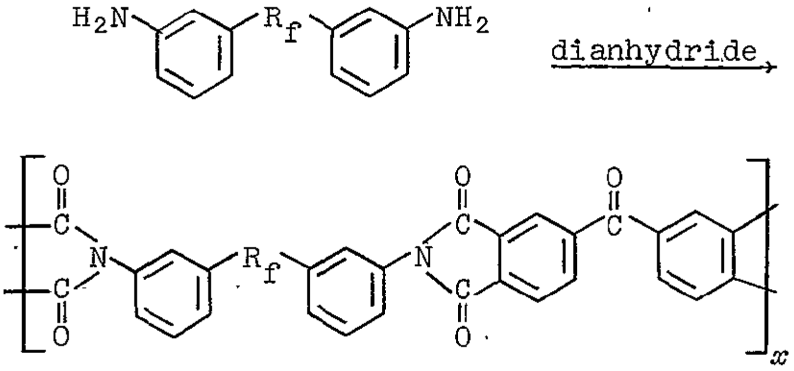
(b) Perfluorobutylene oxide

$HOOC(CF_2CF_2OCF_2CF_2)_nCOOH$

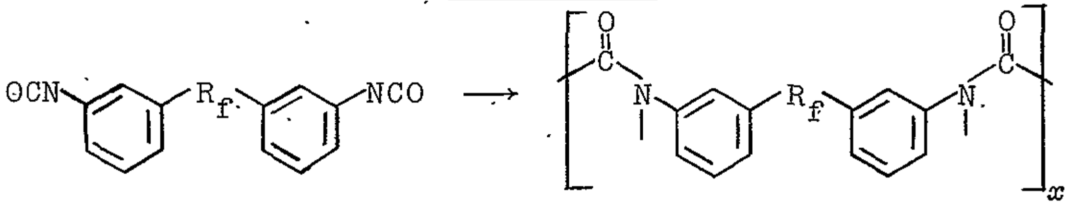
Dicarboxylic acids based on the linear structure have been reported and may even be preferred but have been unavailable to us (Ref. 1,2).

The terminal functional groups, X, that have been investigated in polymer coupling reactions are the amino, isocyanato, and dimethylsilanol groups. Reactions of these groups have formed the imide, isocyanurate, siloxane, and azo-linked polymers shown below.

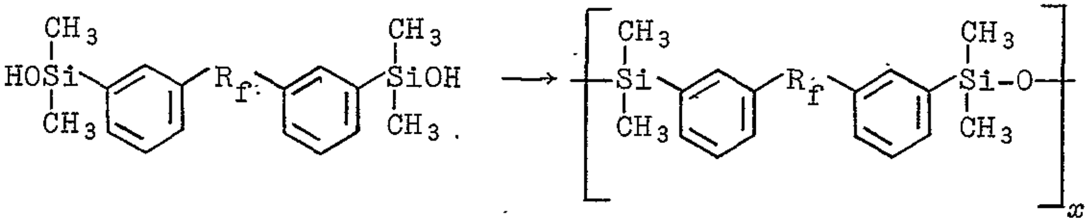
Imide



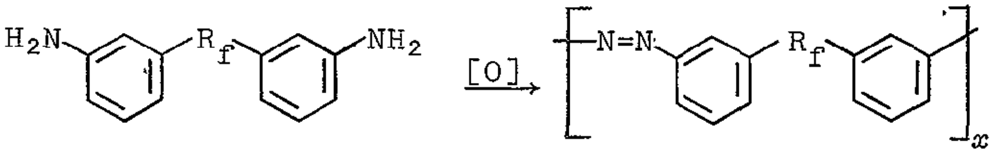
Isocyanurate



Siloxane



Azo

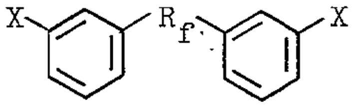


Each of these reactions provides a means of linking the basic phenyl-terminated fluorocarbon chain segment to form high stability polymers.

The major effort of the past year's work has been concentrated in two areas. The first has been the development of synthesis methods to allow incorporation of the perfluoroalkylene ether chain segment into polymer intermediates of the types shown above. The second objective was the preparation and evaluation of prototype and candidate polymers to establish stability, fuel resistance and stress corrosion potential of representative polymer structures.

B. SYNTHESIS OF INTERMEDIATES

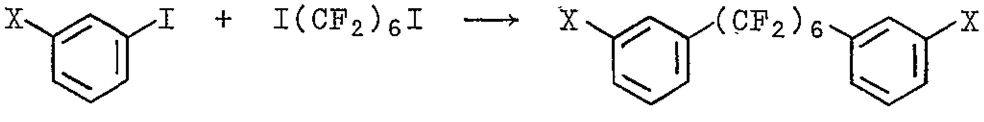
The objective of the synthesis work has been to develop suitable synthesis methods that would provide a satisfactory preparation of polymer intermediates represented by the generalized structure,



with particular emphasis on extending the fluorocarbon chain length to include the perfluoroalkylene ether intermediates. Separation of the fluorocarbon segment (R_f) from the terminal functional groups (X) by the phenylene moiety has been considered an important aspect in the development of high stability polymer systems. The phenylene isolates the functional group from the electron-withdrawing effect of the fluorocarbon segment while the phenylene itself preserves the high thermal and oxidative stability characteristics of the remaining portion of the molecule.

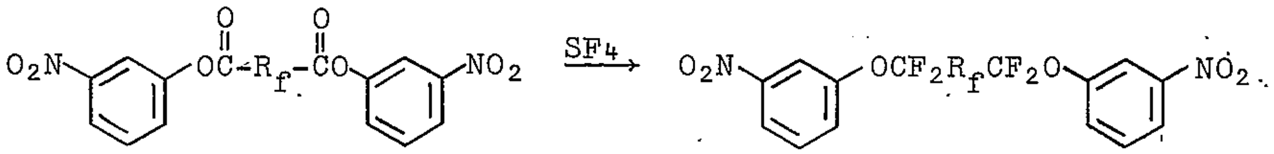
The synthesis methods that have been developed are variations or extensions of the following three types of phenyl coupling reactions.

via Direct Coupling

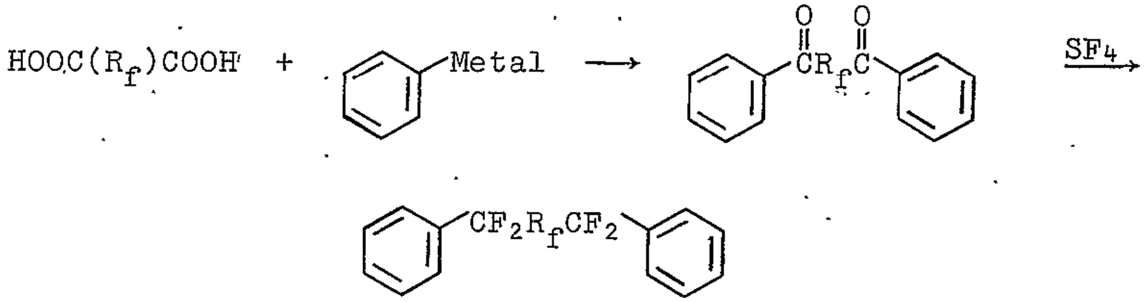


$X = -H, -NO_2, -Br$

via Ester Fluorination



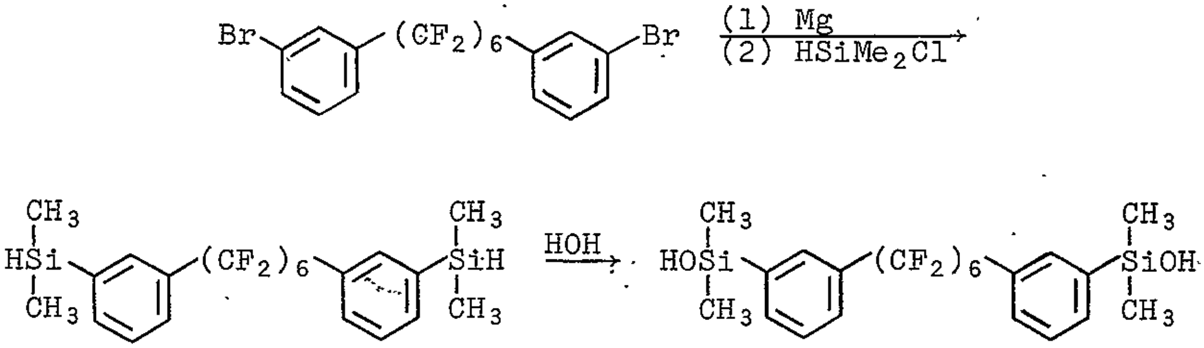
via Ketone Synthesis



Each of these reactions has given high yields of product, but until recently, attempts to extend the reactions beyond short chain segments and to include the perfluoroalkylene ether segment, have given poor results.

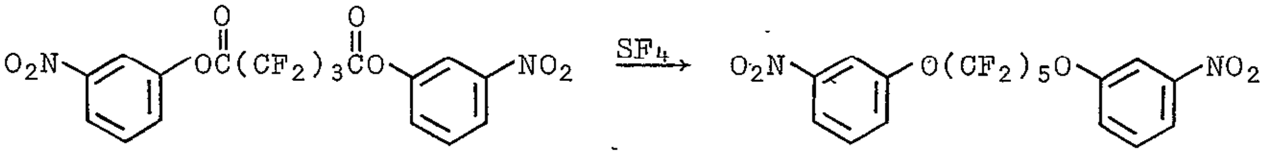
1. Direct Phenyl-Fluorocarbon Coupling

The direct coupling reaction is an effective synthesis route that has been described previously (Ref. 3,4). It is applicable to the limited range of primary perfluoroalkylene iodides that are available. This reaction, for example, provided a convenient synthesis of the 1,6-bis(*m*-bromophenyl)perfluorohexane intermediate that was subsequently converted to the dimethylsilanol derivative for polymer synthesis.



2. Ester Fluorination Route

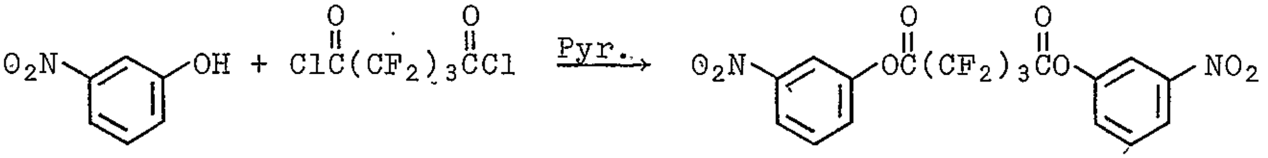
The second route, the ester fluorination, was demonstrated toward the end of last year's effort by the reaction



This reaction was particularly attractive for several reasons: (a) the polymer intermediate could be formed from the dicarboxylic acid or halide by a minimum number of steps, (b) with the exception of the fluorination, each step could be carried out in high yield, (c) the phenyl-O-CF_2 linkage not only was a high stability linkage but also added increased molecular chain flexibility and further isolated the functional group from adverse effects of the fluorocarbon segment. Efforts this year improved the yields and extended the reaction to include the perfluoroalkylene ether segment.

a. Ester Synthesis

Synthesis of nitrophenyl esters of perfluoroalkylene dicarboxylic acids was generally straightforward. This synthesis was accomplished in good yields by pyridine-catalyzed reaction of nitrophenol with the diacyl chloride. Employing the acyl halide for ester synthesis is



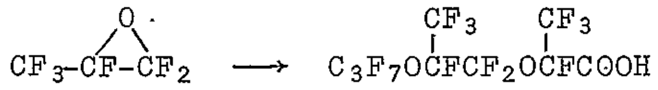
probably necessary because the ease with which the ester hydrolyzes suggests that the equilibrium favors the free acid.

The perfluoroalkylene ether dicarboxylic acid intermediates are obtained as the acyl fluorides. Although the nitrophenyl ester was formed in 80% yield from perfluoroglutaryl fluoride and nitrophenol, similar reaction of the 1:1 acyl fluoride, $FOCCFCF_3O(CF_2)_4COF$, with nitrophenol gave a 40% yield of ester at best (Table 1). When the 1:1 acid fluoride was hydrolyzed and distilled as the carboxylic acid, two products were obtained. One was the expected dicarboxylic acid (50% yield), but the second product was a monocarboxylic acid, presumably the homopolymer by-product of hexafluoropropylene epoxide.

Table 1

REACTIONS OF PERFLUOROALKYLENE ETHER INTERMEDIATES

NBP	Acid Derivative $X\overset{\underset{\|}{O}}{C}-R_f-\overset{\underset{\|}{O}}{C}X$	Solvent	Time hr	Temp °C	Product	Yield %
	$R_f = (CF_2)_3$					
139601	$F\overset{\underset{\|}{O}}{C}R_f\overset{\underset{\|}{O}}{C}F$ + Nitrophenol + KF	CH_3CN	1	25	Nitrophenyl ester	80
	$R'_f = -\overset{CF_3}{\overset{\vert}{C}}FO(CF_2)_4-$					
139602	$F\overset{\underset{\|}{O}}{C}-R'_f-\overset{\underset{\|}{O}}{C}F$ + Nitrophenol + KF	CH_3CN	16	25	Nitrophenyl ester	40
139625	$F\overset{\underset{\|}{O}}{C}-R'_f-\overset{\underset{\|}{O}}{C}F$ + Nitrophenol + Et_3N	CH_2Cl_2	20	35-40	Nitrophenyl ester	32
139633	$F\overset{\underset{\|}{O}}{C}R'_f\overset{\underset{\|}{O}}{C}F$ + H_2O + $CaCl_2$				Distilled $HOOC-R'_f-COOH$ $C_3F_7OCF_2CFCF_3OCFCF_3COOH$	53 30
139635	$HOOCR'_fCOOH$ + $SOCl_2$		21	80	$Cl\overset{\underset{\|}{O}}{C}R'_f\overset{\underset{\|}{O}}{C}Cl$	68
139637	$Cl\overset{\underset{\|}{O}}{C}R'_f\overset{\underset{\|}{O}}{C}Cl$ + Nitrophenol		18	110	Nitrophenyl ester	95
	$R''_f = -\overset{CF_3}{\overset{\vert}{C}}FO(CF_2)_5O\overset{CF_3}{\overset{\vert}{C}}F-$					
139640	$F\overset{\underset{\|}{O}}{C}R''_f\overset{\underset{\|}{O}}{C}F$ + H_2O + $CaCl_2$				Distilled $HOOCR''_fCOOH$	87
139653	$HOOCR''_fCOOH$ + $SOCl_2$		30	80	Distilled $Cl\overset{\underset{\|}{O}}{C}R''_f\overset{\underset{\|}{O}}{C}Cl$	85
139658	$Cl\overset{\underset{\|}{O}}{C}R''_f\overset{\underset{\|}{O}}{C}Cl$ + Nitrophenol		19	155-160	Nitrophenyl ester	94
	$R'''_f = -\overset{CF_3}{\overset{\vert}{C}}FO(CF_2)_5O\overset{CF_3}{\overset{\vert}{C}}F-CF_2O\overset{CF_3}{\overset{\vert}{C}}F-$					
139674	$F\overset{\underset{\|}{O}}{C}R'''_f-\overset{\underset{\|}{O}}{C}F$ + H_2O + $CaCl_2$				Distilled diacid	92
139676	$HOOCR'''_fCOOH$ + $SOCl_2$		64	80	Acid chloride	87
139680	$Cl\overset{\underset{\|}{O}}{C}R'''_f\overset{\underset{\|}{O}}{C}Cl$ + Nitrophenol		54	160-165	Distilled ester	89



$$CF_3\text{-}CF\text{-}CF_2 \longrightarrow C_3F_7O\overset{CF_3}{C}FCF_2O\overset{CF_3}{C}FCOOH$$

In effect, what initially appeared to be a poor reaction yield with this 1:1 acyl fluoride was the result of a separation of product from by-products.

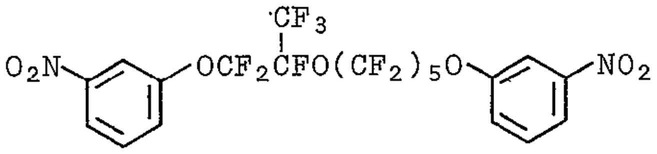
The conversion of acid fluoride to acid is essentially quantitative. Reaction with thionyl chloride and subsequent ester formation both can be carried out in excellent yield (Table 1). The purification thus accomplished by this three-step ester synthesis route appeared to justify the additional work.

b. Fluorination

Initially the fluorination of nitrophenyl esters of monocarboxylic acids was investigated because of ease in work-up and identification of products. This was followed by further study of the nitrophenyl ester of perfluoroglutaric acid as shown by experiments summarized in Table 2.

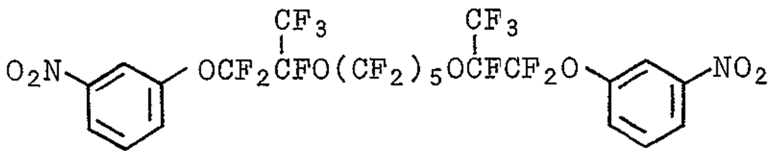
The yield in this latter reaction was gradually increased from 20% of crude product to 87% of distilled product. These results were accomplished through a combination of factors, including optimization of reaction conditions, use of a large excess of anhydrous hydrogen fluoride as a solvent and purification of commercial SF_4 reagent. The SF_4 obtained from the Matheson Company was found to contain an appreciable bromine content. Removal of bromine by reaction with mercury (Ref. 5) resulted in a very significant improvement in yield.

Fluorination of the nitrophenyl esters of the 1:1, 2:1, and 3:1 adducts of perfluoroglutaryl fluoride and hexafluoropropylene epoxide formed the corresponding nitrophenyl ether derivatives (Table 3).



50-60% yield

1:1

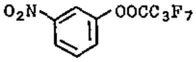
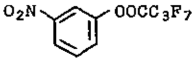
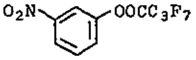
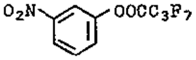
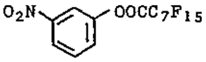
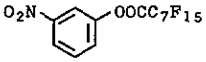
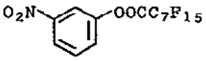
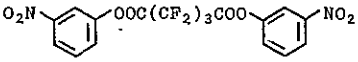
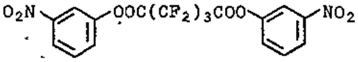
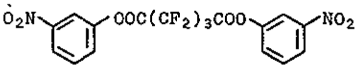
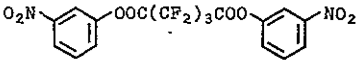
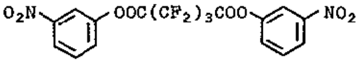
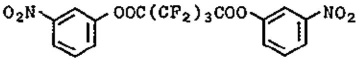
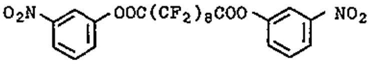


18-50% yield

2:1

Table 2

SULFUR TETRAFLUORIDE FLUORINATION OF ARYL ESTERS OF PERFLUOROALKYLENE DICARBOXYLIC ACIDS

NBP	Ester Reactant	g (moles)	SF_4 g (moles)	HF g	Time hr	Temp °C	% Yield (Distilled)
132810		15 (0.047)	20 (0.2)	5	23 24 18	100 125 150	39
132816		10 (0.031)	4 (0.04)	20	1 2 2.5	100 150 175	<45
138821		10 (0.031)	4 (0.04)	20	2.0 2.0 2.5	100 125 150	44
132823		10 (0.031)	6 (0.06)	20	3	150	<36
132826		10 (0.019)	8 (0.07)	20	5 24 2	100 125 150	41
132837		10 (0.019)	8 (0.07)	20	10	100	43[1]
132839		10 (0.019)	8 (0.07)	20	10	80	69[2]
132829		20 (0.042)	12 (0.1)	40	6 17 2	100 125 150	40
132833		40 (0.083)	26 (0.24)	80	6 11 2	100 125 150	42
125095		10 (0.019)	10 (0.09)	10	19 24 8	100 125 150	<20
132842		20 (0.042)	12 (0.11)	40	5	100	59
132857		90 (0.182)	56 (0.52)	190	5	100	42
137089		73 (0.155)	50 (0.46)[3]	157	12	100	87
132855		40 (0.055)	16 (0.15)	80	5.5[4]	110[4]	--[5]

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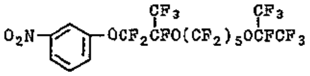
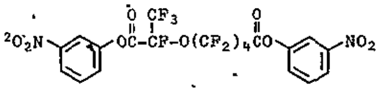
[1] Isolated as amine·HCl
[2] Incomplete reaction C=O evident in the IR
[3] Purified SF_4 was used
[4] Possible temperature control failure, may have overheated
[5] Recovered 50% unreacted ester

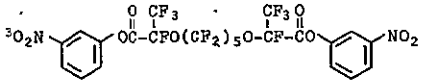
Table 3

SF_4 FLUORINATION OF NITROPHENYL ESTERS OF PERFLUOROALKYLENE ETHER DICARBOXYLIC ACIDS

NBP	Ester	Wt g	SF_4[1] Wt g	HF Wt g	Solvent Wt, g	Time hr	Temp °C	% Yield	Product
139604	Nitrophenyl ester, 1:1 acid[2]	5.7	7	12	--	18 6	100 120	65	Nitrophenoxy perfluoroalkylene ether
139614	Nitrophenyl ester, 1:1 acid	11.4	14	24	--	17 20	100 125	55	Nitrophenoxy perfluoroalkylene ether
139639	Nitrophenyl ester, 1:1 acid	9.6	10	20	--	21 20	100 125	52	Nitrophenoxy product
139620	Nitrophenyl ester, 2:1 acid[3]	10.2	10	20	--	17 20	100 125	18	Nitrophenoxy product
139636	Nitrophenyl ester, 2:1 acid	5.0	5	10	benzene	38	100	--	Recovered ester
137463	Nitrophenyl ester, 2:1 acid	5.4	14	13	dimethoxy-ethane	18	100-110	--	Black, infusible solid
139645	Nitrophenyl ester, 2:1 acid	5.0	5	10	FC 43[4]	20 20	100 125	36	Nitrophenoxy perfluoroalkylene ether
139651	Nitrophenyl ester, 2:1 acid	5.0	5	10	$C_6H_5NO_2$	18	125	--	30% recovery of ester
139654	Nitrophenyl ester, 2:1 acid	5.0	5	10	FC 75[5]	30 - 16	100 125	38	Contained carbonyl impurity
137464	Nitrophenyl ester, 2:1 acid	5.0	10	10	FC 43	32 20	75 100	42	
139657	Nitrophenyl ester, 2:1 acid	5.0	5	10	FC 75	24	60	--	Recovered ester, largely unreacted
139659	Nitrophenyl ester, 2:1 acid	5.0	5	10	FC 43	57	80	47	
139660	Nitrophenyl ester, 2:1 acid	12.0	12	10	FC 75	56	80	50	Contained carbonyl impurity
139677	Nitrophenyl ester, 2.1 acid	15.0	12	15	FC 75	66	80	35	Purified nitrophenoxy product, also isolated
								15	
139686	Nitrophenyl ester, 3:1 acid	10	10	8	FC 75	90	80	50	Nitrophenoxy product

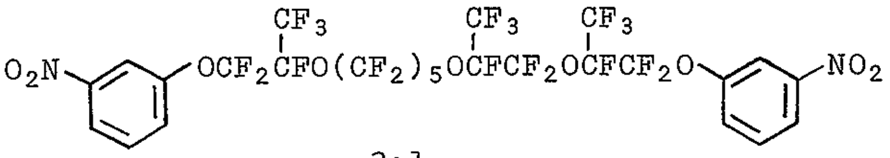
[1] Purified SF_4

[2] 

[3] 

[4] FC 43 = perfluorotributylamine

[5] FC 75 = perfluorobutyltetrahydrofuran



3:1

50-60% yield

The yields in the fluorination reactions appeared to decrease with increasing molecular weight. An attempt to overcome the low yield initially obtained in fluorination of the nitroester of the 2:1 acid adduct through the use of various solvents was not successful until the fluorocarbon solvents, FC 43 and FC 75 (3M Company) were used. These permitted a substantial improvement, with yields up to 50%. This reaction is still being studied in an attempt to gain further improvement in yields. The products still showed evidence of the ester carbonyl. Brief hydrolysis in aqueous alkaline solution destroyed the ester. The desired product, which was soluble in benzene, was separated from benzene-insoluble residues. Distillation afforded the nitrophenyl ether product.

Conversion of the nitrophenoxy-fluorocarbon intermediates to amines by catalytic hydrogenation over Raney nickel was essentially quantitative. Conversion of several of the simple amine products to isocyanates by phosgenation was also accomplished in high yield.

Attempts to extend the ester fluorination to bromophenyl and xylyl esters of perfluoroglutaric acid were not successful. Upon fluorination with SF_4 the xylyl ester formed insoluble, infusible solid products indicating attack on the methyl groups even at temperatures as low as 40°C when anhydrous HF was employed. In the absence of hydrogen fluoride, the ester was recovered unchanged at 120°C. Formation of an infusible product from the bromo compound at 100°C was considered evidence of attack on the aromatic ring. The ring-deactivating effect of the nitro substituent probably protects the ring in the nitrophenyl ester fluorination reactions. These experiments are summarized in Table 4.

The bromophenyl ether product was of interest for conversion to the phenoxyfluorocarbon silanol intermediate while the intention was to convert xylyl ether product to the corresponding dianhydride

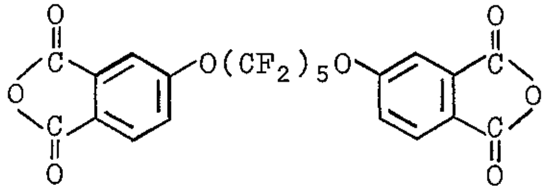
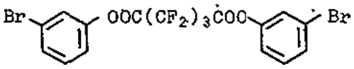
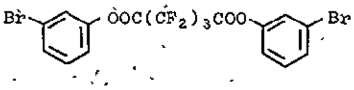
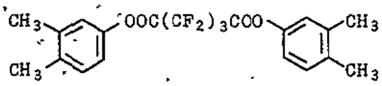
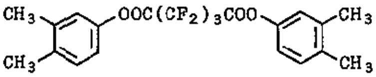
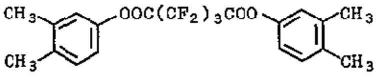
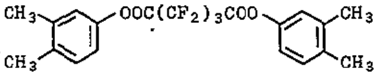
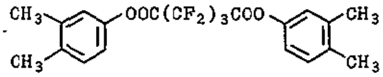
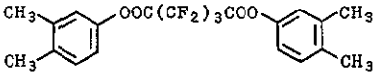
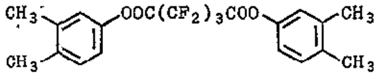


Table 4

ATTEMPTED SF₄ FLUORINATION OF ARYL ESTERS

NBP	Ester	Weight g	SF_4[1] Wt. g	HF Wt. g	Solvent	Time hr	Temp. °C	Results
137036		14	10	30	--	10	100	viscous black liquid no product isolated
139619		12.4	10	25	--	18 20	100 120	nonfusible black solid
139648		10	10	20	--	24	100	refractory black solid
137462		10	10	8	$C_6H_5NO_2$	17	75	black viscous liquid C=O evident in IR
139662		10	10	2	FC-75	22	100	refractory black solid
139664		5	5	--	FC-75	19	50	ester recovered
139666		5	5	--	FC-75	19	120	ester recovered
139667		5	5	4	FC-75	21	25-30	ester recovered
139673		5	5	10	FC-75	18	40	black solid + sulfur

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[1] Purified SF_4 used except 137036

intermediate to gain further lowering of the glass transition temperature of the resulting polyimide polymers.

3. Ketone Fluorination

The third approach, the development of phenyl-fluorocarbon coupling via ketone synthesis and subsequent SF_4 fluorination, was an area of concentrated effort during the previous year's work. While dibenzoyl perfluoropropane and perfluorobutane derivatives were made in high yield by Grignard or acylation reactions, the attempts to extend these reactions to the perfluoroalkylene ether intermediate were largely unsuccessful because of insolubility of organo-metallic salts and intermediate products of the Grignard reactions.

a. Ketone Syntheses

Further efforts were made this year to synthesize the ketone derivatives via direct coupling between organometallic reagents and acyl halides. Experiments with aryl zinc reagents were relatively unsuccessful, but reaction of phenyl copper with perfluorooctanoyl chloride resulted in a surprisingly high yield (83%) of the corresponding ketone. These experiments are included in Table 6 along with a series of related miscellaneous coupling experiments discussed later. Because this encouraging result came at a time when significant improvement in the ester fluorination was being obtained, this ketone approach was not pursued further.

b. Ketone Fluorination

Further study of the SF_4 fluorination of diketones was carried out also, because of the need for a better source of α,ω-diphenylperfluoroalkylene intermediates. The limited availability of the diiodide intermediate $I(CF_2)_6I$ made the ketone route an attractive alternative route to the direct coupling reaction. Further study of the dibenzoylhexafluoropropane fluorination was prompted also by our inability to obtain the high yield diphenyl perfluoropentane reported in the literature (ref. 6). The fluorinated product obtained was a varying mixture of the expected product and the cyclic ether by-product shown below.

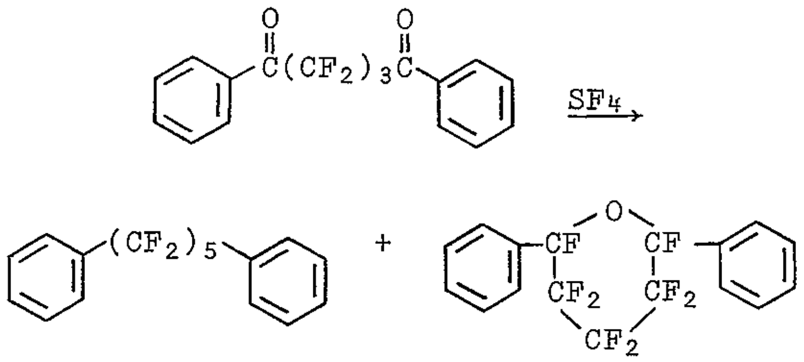
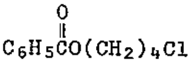


Table 6

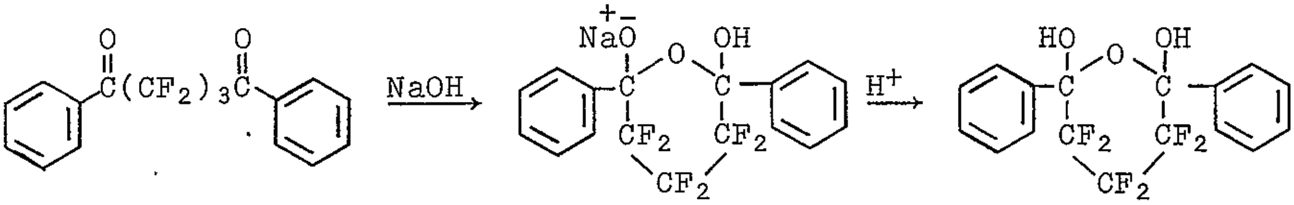
COUPLING REACTIONS

NBP	Reactants	Solvent[1]	Time hr	Temp. °C	Results
132832	$C_7F_{15}COCl + IC_7F_{15} + Zn$	THF	0.3	-10 to 0 0 to 25	R_fI added to R_fCOCl, Zn and THF, ∿35% diketone
137065	$C_3F_7I + C_7F_{15}COCl + Zn$	THF	2	-10 to 20	exothermic reaction, $C_3F_7COC_7F_{15}$ formed
137053	$C_3F_7ZnI + C_3F_7COCl$	DME	18	25	IR evidence of ketone product
137050	$C_6H_5COCl + IC_3F_7 + Zn$	THF	1 0.7	-10 0 to 10	 $C_6H_5\overset{\overset{O}{\|}}{C}O(CH_2)_4Cl$
137055	$C_6H_5COCl + C_3F_7ZnI$	DME pyr.	0.5 16	-10 to -15 25	no ketone product (benzoic acid isolated)
137081	$C_3F_7I + Cu$ C_6H_5COCl added	DMF DMF	7	110 25	exothermic, no ketone product
123897	$C_6H_5I + C_7F_{15}COCl + Zn^2$	THF	22	25	no evidence of phenyl coupled product
137047	$C_6H_5COCl + I(CF_2)_4I + Zn$	THF	2.5 16	-10 to -5 25	no evidence of phenyl coupling, $C_6H_5CO(CH_2)_4Cl$ tentatively identified
137049	$C_6H_5COCl + I(CF_2)_4I + Zn$	THF	2.5	-10 to -5	no evidence of phenyl coupling, $C_6H_5CO(CH_2)_4Cl$ tentatively identified
137435	$C_6H_5I + Ni(CO)_4 + C_7F_{15}COCl$	--	3 3	75 150	no products identified
123899	$C_6H_5MgBr + ZnCl_2 + C_7F_{15}COCl$	ether	0.5 1.0 16	-5 to 0 0 to 10 10 to 25	no ketone product recovered R_fCOOH
137438	$C_6H_5Cu + C_7F_{15}COCl$	ether		-30 to -40	83% yield, $C_6H_5COC_7F_{15}$

[1] THF = Tetrahydrofuran
DME = Dimethoxyethane
DMF = Dimethylformamide

[2] Activated Zn/Cu couple

The successful use of HF as a solvent and catalyst in the ester fluorination reactions prompted a similar approach in the SF_4 fluorinations of the ketone. The experiments summarized in Table 5 show that polymeric sulfone products were obtained at 125°C. In the absence of the HF no reaction occurred at 125°C. The cyclic ether and a brominated product were isolated when a similar experiment was carried out at 50°C. These products provided a clue to impurities in the SF_4 reactant. After purification of the SF_4 to remove elemental bromine (a consistent impurity in the SF_4 obtained from Matheson Co.), the product obtained in the presence of anhydrous HF was a high yield of the cyclic ether. When the reaction was repeated with 1,4-dibenzoyloctafluorobutane, a high yield of diphenylperfluorohexane was formed, indicating that the cyclization was peculiar to the C_5 diketone. The ease of this cyclization was made even more apparent when aqueous titration of the diketone showed a sharp end point upon addition of one equivalent of NaOH and formation of a cyclic diol upon subsequent acidification, as shown by the following equations.



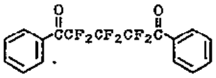
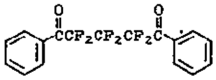
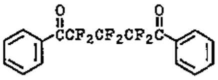
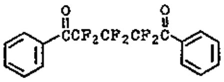
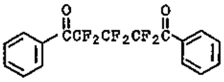
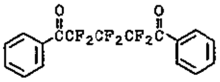
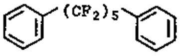
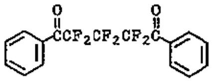
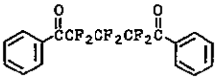
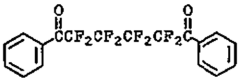
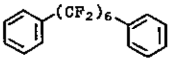
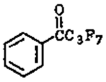
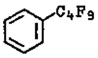
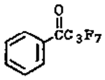
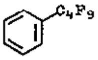
Attempts to demonstrate a similar intermolecular coupling reaction between mono ketone intermediates in the presence of excess HF was not successful. The products were the fluorinated alkyl benzenes shown in Table 5.

4. Miscellaneous Phenyl Coupling Reactions

Dicarboxylic acid derivatives are probably the best potential sources of perfluoroalkylene and perfluoroalkylene ether chain segments. Although the short-chained 1,3-dibenzoylhexafluoropropane intermediate was readily prepared by acylation of benzene with perfluoroglutaryl chloride or by reaction of phenyl Grignard on the dicarboxylic acid, neither route gave satisfactory results with polymeric perfluoroalkylene ether dicarboxylic acid (Ref. 4). As a result, the development of methods for incorporating the longer-chained intermediate into a phenyl-terminated product was a continuing objective.

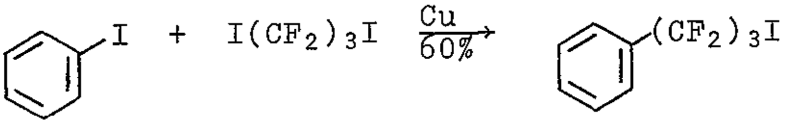
Table 5

SF$_4$ FLUORINATION OF KETONE INTERMEDIATES

NBP	Reactant	Weight g (moles)	SF$_4$ g (moles)	HF g	Time hr	Temp °C	% Yield	Results
132865		10 (0.029)	10 (0.093)	20	3 21 19	100[1] 125 150		polymer[2]
137063		10 (0.029)	12 (0.11)	20	20	125	--	11 g polymer (sulfone)
137062		10 (0.029)	20 (0.185)	none	20	125	0	recovered diketone
137067		10 (0.029)	10 (0.092)	20	6 12	25 50	--	cyclic ether[3], + brominated derivative and polymer
137069		10 (0.029)	10 (0.092)	20	2.5 0.5 2.0	25 50 50-25	0	recovered diketone
132881		19.8 (0.055)	50 (0.464)	none	12 34	175 220	41	
137090		19.8 (0.055)	40[4] (0.37)	none	2 18 24	125 175 220[5]	0	high recovery of starting ketone
137087		10 (0.029)	10[4] (0.092)	20	12	75	>80	cyclic ether[3]
137098		10 (0.024)	10[4] (0.092)	20	12	75	76	
137007		13.7 (0.050)	6 (0.056)	20	10	100	54	
137026		55 (0.2)	24 (0.22)	80	11	100	62	

[1] May have exceeded recorded values
[2] Polymer identified on a sulfone $\{\phi C_5 \phi - SO_2\}_x$
[3] Diphenylperfluorotetrahydropyran
[4] Purified SF$_4$
[5] These were the conditions reported to give high yield of diphenyldecafluoropentane (Ref. 6)

Alternate methods for linking fluorocarbon segments through phenyl moieties were investigated. Synthesis of a phenyl perfluoroalkyl iodide in reasonably good yield was reported by McLoughlin and Thrower (Ref. 3).



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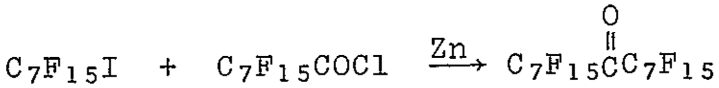
The possibility of linking this product to a perfluoroacyl chloride was suggested by the following reaction



$$C_7F_{15}I + C_7F_{15}COCl \xrightarrow{Zn} C_7F_{15}\overset{\overset{O}{\|}}{C}C_7F_{15}$$

The above coupling, which was carried out in anhydrous tetrahydrofuran, was found to be exothermic at -10 to 0°C and formed 35% yield of diperfluoroheptyl ketone. This reaction suggested that coupling of (I) with fluorocarbon dicarboxylic acid halides could be used to prepare the desired phenyl-terminated products.

Formation of the perfluorodialkyl ketone in the above experiment was not immediately recognized because the boiling point and infrared spectrum of the product were nearly the same as that of perfluorooctanoic acid (the ketone formed the hydrate very rapidly in contact with air). The fact that the ketone was formed from the acyl halide contrasted with the poor results previously obtained with acyl halides and Grignard reagents. Several experiments were carried out in an attempt to expand upon this coupling reaction, but the results for the most part were negative (Table 6). Attempted coupling of diidooctafluorobutane with benzoyl chloride in presence of zinc and THF at -10°C, for example, formed γ-chlorobutyl benzoate as a major product even though these were the conditions that formed the ketone when the perfluorooctanoyl chloride was used with the perfluoroalkyl iodide. When perfluorooctanoyl chloride was used in a third experiment, once again no ketone was isolated. Possibily the clue to what appears to be a discrepancy in these results is Miller's (Ref. 7) speculation that a bimolecular reaction occurs on the surface of the zinc rather than an initial formation of perfluoroalkylzinc iodide followed by reaction with the acyl halide. In the original experiment that resulted in formation of the ketone, the vigorous exothermic reaction occurred after all the reactants had been added.

Finally, in a further attempt to utilize the organozinc coupling reaction, anhydrous zinc chloride was added to phenyl Grignard followed by addition of perfluorooctanoyl chloride. This method also failed to give more than a trace of ketone. This experiment was based on a procedure which with alkyl Grignards is reported to give excellent yields of aliphatic ketones (Ref. 8).

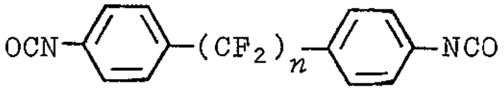
The attempted coupling of iodobenzene with perfluorooctanoyl chloride in the presence of a stoichiometric quantity of $Ni(CO)_4$ was based on the $Ni(CO)_4$-catalyzed reactions of perfluoroaryl chlorides with benzene in which 40% yield of perfluoroalkyl benzene product was reported (Ref. 9). By substituting iodobenzene for benzene, a higher conversion to perfluoroalkyl benzene product was anticipated. None of the desired product was isolated, however.

C. POLYMER SYNTHESES AND EVALUATIONS

1. Fluorocarbon Isocyanurate Polymers

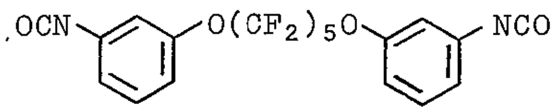
The development of the isocyanate cyclotrimerization reaction for linking of fluorocarbon polymer intermediates through the formation of high stability isocyanurate polymers has been pursured for three reasons: (1) the polymerizations occur under mild temperature conditions, (2) the reaction is an addition rather than a condensation reaction thereby avoiding formation of volatile side products, and (3) the isocyanurate structure has been shown to have high thermal and oxidative stability. The objective has been to determine whether the fluorocarbon polymers linked through the isocyanurate ring system have the necessary stability and freedom from stress corrosion to satisfy the requirements of a fuel tank sealant application.

Small quantities of fluorocarbon isocyanurate polymers were prepared during the previous year's effort from intermediates of the type

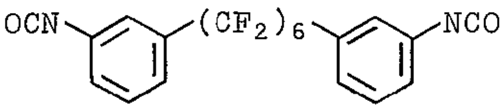


where n = 3 and 8. The high glass transition temperature of these polymers indicated a need for greater fluorocarbon chain length and flexibility.

The synthesis effort of this past year provided larger quantities of two polymer intermediates, I and II, for further study of isocyanurate polymer properties.



I



II

Because the fluorocarbon chain lengths were too short to impart the desired physical properties, the two compounds were considered prototype intermediates. Nevertheless, these compounds permitted evaluation of polymerization and stability characteristics of the basic fluorocarbon isocyanurate polymer structures.

a. Polymerization

Polymerization of 1,5-bis(isocyanatophenoxy)decafluoropentane, I, proceeds at room temperature upon addition of catalytic amounts of N,N,N',N'-tetramethylbutanediamine and allyl glycidyl ether. Upon post cure at 100°C a hard, clear, somewhat brittle polymer was formed.

The high melting point of the second compound, bis(isocyanatophenyl)perfluorohexane, II, necessitated heating the monomer above 75°C at which temperature the polymerization was too rapid to permit mixing of catalyst. Polymer formed essentially instantaneously as the catalyst was added. To overcome this problem created by the high melting point of the monomer and to effect a change in polymer properties by decreasing the degree of crosslinking, the monofunctional nonafluorobutylphenyl isocyanate intermediate was prepared as a diluent for the diisocyanate. A liquid solution of the two components could be cooled to less than 40°C at which temperature catalyst could be added and mixed before polymerization occurred to any appreciable degree.

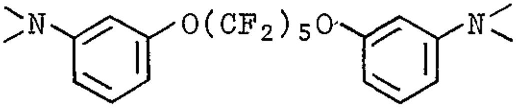
b. Thermal Stability

Evidence of high thermal stability of the isocyanurate-linked fluorocarbon polymer structures formed from intermediates I and II, was obtained in two ways. TGA analyses of the polymers (Figure 1) showed low weight losses below 300°C. The loss in weight of the phenyl-O-CF_2 linked polymer was less than 5% at temperatures up to 400°C when the heating rate in air was 2.7°C/minute. Whether the appreciably greater weight loss of the ϕ-CF_2 linked polymer below 400°C represents optimum performance is questionable.

A more sensitive measure and comparison of the thermal stabilities of the two analogous fluorocarbon isocyanurate structures was obtained by the isoteniscope method (Ref. 10). Two isocyanurate compounds were prepared by cyclotrimerization of perfluorobutylphenyl- and perfluorobutoxyphenyl isocyanates and were purified by recrystallization. The thermal stability values shown in Table 7 indicate comparable stability levels. The values shown are the temperatures at which the rate of vapor pressure change, dp/dt, resulting from thermal decomposition was equal to 0.014 torr/sec or 500 torr/10 hr. This temperature corresponds to a slow but measurable rate of decomposition. The 370°C thermal stability values suggest that the isocyanurate structure has adequate thermal stability for long-term service at temperatures of 260°C (500°F) and possibly above.

c. Stress Corrosion Potential

Stress corrosion test samples were prepared by casting the fluorocarbon isocyanurate polymers on the test surface of titanium stress corrosion specimens. The samples were then evaluated under Task B program (Ref. 11), by heating for 1000 hours at 260°C (500°F) under a tensile load of 75% of the test bar yield strength. Initial tests of the polymer showed failure of the metal, resulting from stress corrosion after 100 and 270 hours. At the same time the identical fluorocarbon structure,



incorporated into an imide showed no evidence of stress corrosion during a similar 1000-hour test.

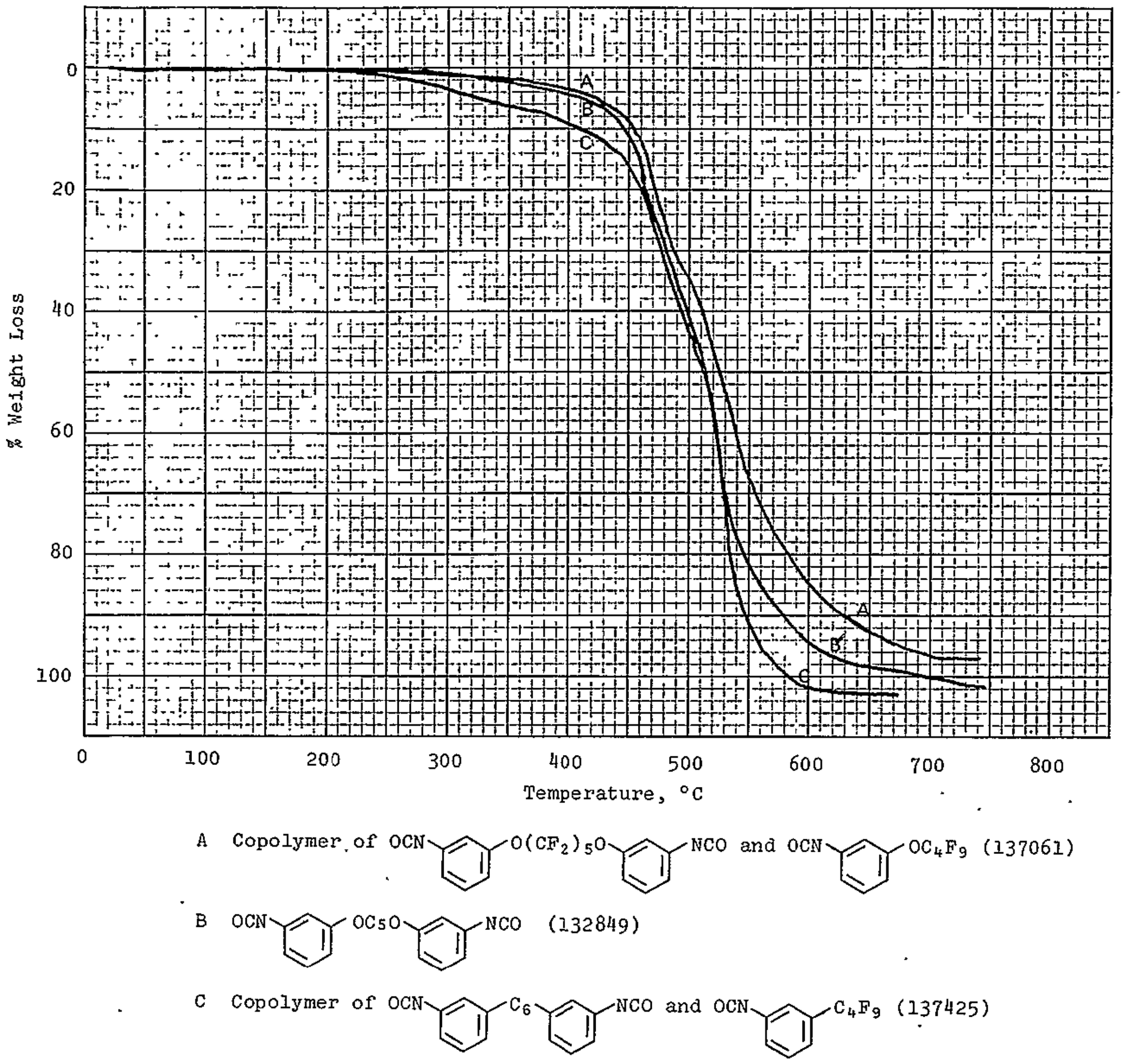
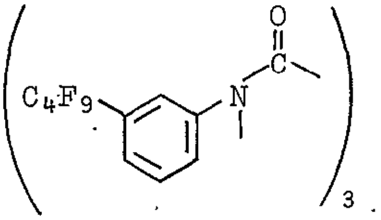
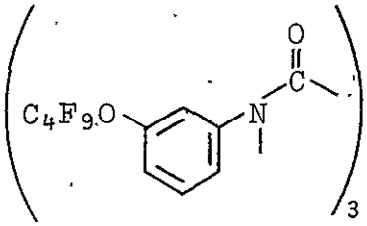


Figure 1. Thermal Gravimetric Analysis of Fluorocarbon Isocyanurate Polymers in Air, Heating rate 2.7°C/minute

Table 7

ISOCYANURATE STABILITY

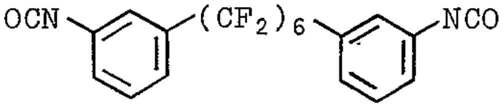
Compound	Melting Point, °C	Thermal Stability	Hydrolytic Stability 95° over Water
 I	121.5-123	373°C	--
 II	124.5-125.5	370°C	15 days no degradation

These test results prompted further study of the isocyanurate cure reactions, the monomer purity, and hydrolytic stability of the isocyanurate polymers. These studies, which are described further in the following sections, indicate that the failure was not an inherent characteristic of the isocyanurate structure but the result of impurities or inadequate cure. Further test specimens coated with fluorocarbon isocyanurate polymer were prepared from the two prototype intermediates under improved conditions and then reevaluated. These tests showed no evidence of stress corrosion after 1000 hours at 260°C (500°F).

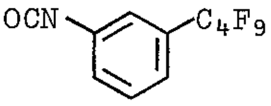
d. Hydrolytic Stability

The hydrolytic stability testing of prototype isocyanurate polymers was carried out by suspending solid polymer specimens over water in a closed system at 95°C. Initial tests under these conditions with a sample of the copolymer of $OCN\phi(CF_2)_6\phi NCO$ and $C_4F_9\phi NCO$ resulted in formation of a gummy liquid within three days, and the residual polymer was found to be soluble in warm ethanol. Under the same conditions, nonfluorinated isocyanurate polymer samples were unaffected after several weeks. These results prompted further study to determine whether poor hydrolytic stability was an inherent defect of fluorocarbon-containing polymer or the result of some other factor that might be overcome. Infrared analysis of hydrolyzed polymer material showed strong -NH absorption at 3.0 µ and no longer showed the isocyanurate absorption at 5.8 µ. Further infrared analysis of the original polymer samples showed evidence of amidic -NH absorption suggesting impurities in the polymer prior to subjection to hydrolytic conditions. While evidence of this -NH impurity in the isocyanurate polymers had been observed previously, it was thought to have resulted from reaction, prior to cure of thin film specimen, with traces of moisture rather than from an inherent deficiency of the bulk polymer.

Further study of the curing reaction by infrared spectra analysis was carried out to determine whether the -NH containing impurity in the polymer may have resulted from incomplete cure and subsequent hydrolysis of residual isocyanate groups. A polymerization mix of



and



and the catalysts was prepared under conditions carefully controlled to exclude moisture. The bulk of the reaction mixture polymerized to a solid within 10 minutes upon mild heating. A small portion of the mixture between salt crystals was simultaneously used for IR study. Gradual conversion of free NCO to isocyanurate was shown by periodic determination of infrared spectra. Surprisingly, the conversion was not complete even after the sample had been heated to 150°C for about 3 hours. After five hours, however, the -NCO absorption was nearly eliminated. Upon heating at 185°C overnight no free -NCO absorption could be detected. The relatively long time and high temperature needed to eliminate the -NCO absorption from the infrared spectrum suggested that previously prepared samples may have been incompletely cured and that residual -NCO groups may have resulted in subsequent hydrolysis and formation of less stable urea linkages.

When precautions were taken during preparation and polymerization of the polymer to ensure adequate cure conditions, (i.e. -NH free intermediates, moisture-free catalysts, and strictly anhydrous conditions) very little or no -NH absorption was evident in the infrared spectra of the polymers. Isocyanurate polymer prepared in this manner from $OCN\phi O(CF_2)_5O\phi NCO$ showed no evidence of hydrolytic instability after 5 weeks over water at 95°C. Also, this polymer did not cause stress corrosion of the titanium alloy in 1000 hr at 260°C. The copolymer of $OCN\phi(CF_2)_6\phi NCO$ and $C_4F_9\phi NCO$ also showed greatly improved hydrolytic stability, although evidence of degradation was observed after 2 weeks at 95°C, $\sim$95% RH. Again no evidence of stress corrosion of titanium alloy was observed with this polymer after 1000 hr at 260°C (500°F).

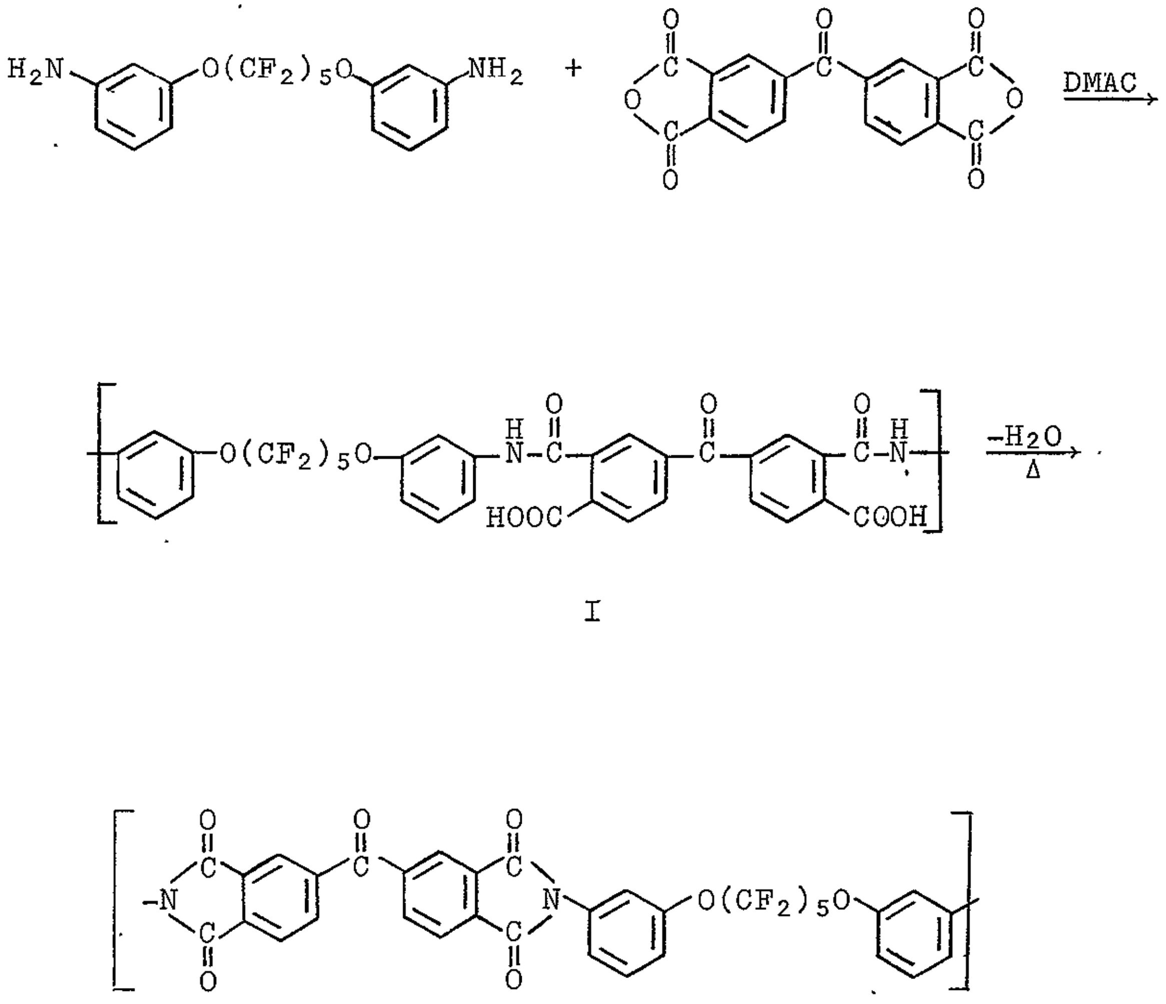
A comparison of the two prototype polymer structures suggests that while the fluorocarbon segment may tend to decrease the hydrolytic stability of the isocyanurate-linked polymers, the polymer containing the oxygen link between the phenyl and perfluoroalkylene exhibited appreciably greater hydrolytic stability. It was concluded that the oxygen helps to stabilize the structures against the adverse effects of the fluorocarbon segment on hydrolytic stability.

While these tests suggest that the isocyanurate linked polymers have reasonably good hydrolytic stability, it is difficult to assess, at this state, the relationship of these hydrolytic stability tests to long-term polymer stability under conditions that might prevail in a fuel tank.

2. Fluorocarbon Polyimide Polymers

a. Polymer Synthesis

The aminophenyl and aminophenoxyperfluoroalkylene compounds that were synthesized for conversion to isocyanate intermediates also provided intermediates for preparation of polyimide polymers. A prototype polyimide was prepared from 1,5-bis(*m*-aminophenoxy)decafluoropentane and benzophenonetetracarboxylic dianhydride.

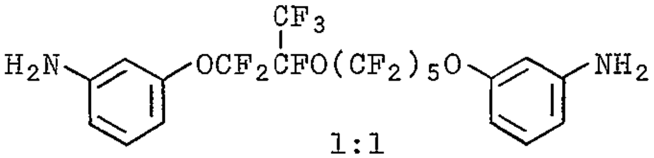


I

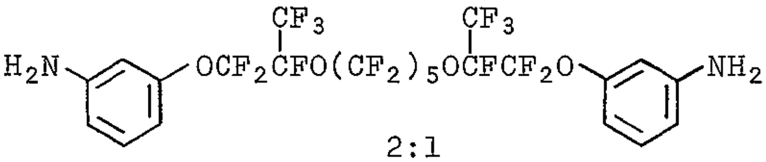
II

Synthesis of the polyamic acid (I) was simply a matter of adding the stoichiometric quantity of the dianhydride to an anhydrous solution of the diamine in dimethylacetamide. A clear, amber colored film of polyamic acid was formed upon evaporation of the solvent. Upon further heating, the film was converted to polyimide II through condensation and elimination of water.

Additional polyimide homologs were prepared in a similar manner from the diamines prepared from the 1:1 and 2:1 perfluoroalkylene ether intermediates shown below, and discussed previously under synthesis of intermediates.



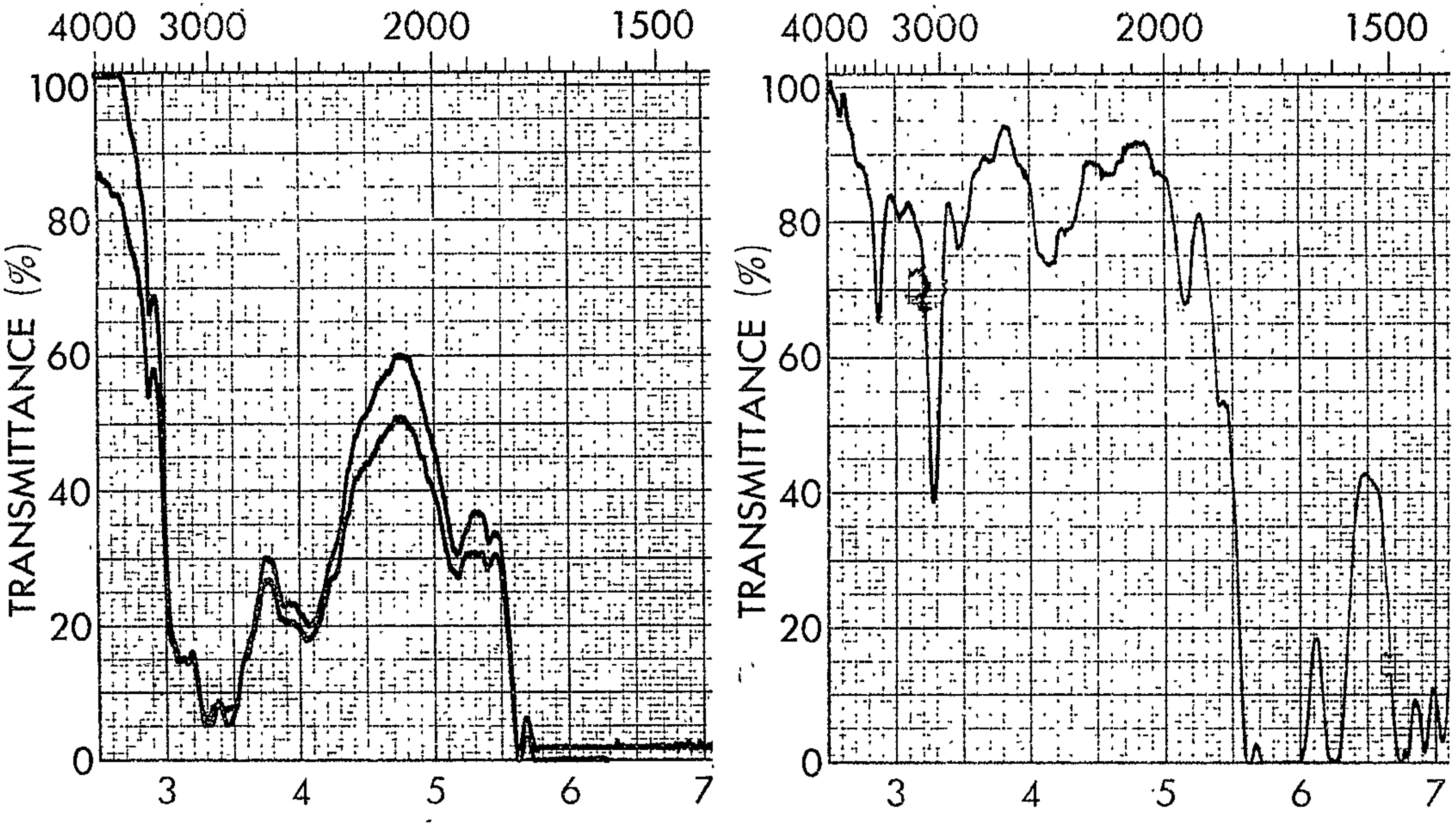
1:1



2:1

b. Cure Temperature

The first samples of fluorocarbon polyimide were cured by gradual heating to 300°C. An attempt was made to determine the minimum temperature at which polyimide formation occurs. The infrared spectrum of a film of polyamic acid showed strong absorption between 3.0 and 4.5 μ. The infrared spectrum was run periodically as the film was heated above 130°C. After heating for one-half hour at 150°C, the strong absorption originally evident between 3.0 and 4.5 μ had largely disappeared, leaving relatively weak absorption peaks at 2.87, 3.30 and 3.46 μ as shown by the spectrum in Figure 2. No further change was observed upon further heating at 150°C or at higher temperatures.



A

B

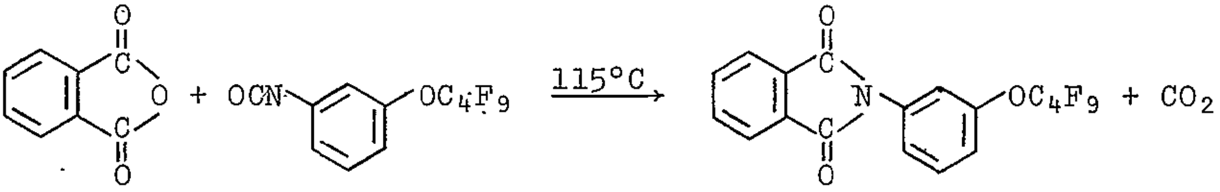
Figure 2. Infrared Spectra, 137409

A Polyamic Acid Film

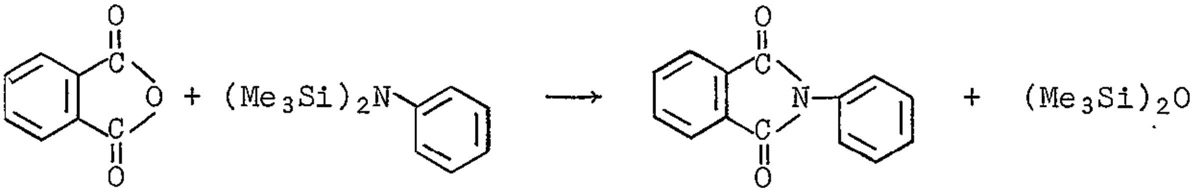
B Polyimide Cured 0.5 hr at 150°C

A qualitative test of solvent effects of dimethylacetamide and jet fuel at room temperature showed only small differences between polyimide cured at 150° and 300°C. All of the samples swelled moderately in dimethylacetamide and none appeared to be affected by jet fuel. The samples that were cured at higher temperatures swelled somewhat less than those cured at 150°C. It was concluded that while the major cure reaction in polyimide formation occurs at or below 150°C as evidenced by the infrared spectra, additional condensation occurs at elevated temperatures.

The high cure temperature (130-150°C) of the polyimide formation represents a deficiency of this cure system with respect to a fuel tank sealant application. Two alternative imide-forming reactions were investigated very briefly. One, the reaction between the anhydride and an isocyanate derivative of the diamine (Ref. 12), was demonstrated by a single experiment.



The second reaction represented by the equation,



gave a low yield of phthalanil. Both reactions suggest possibilities for further development.

c. Fluorocarbon Polyimide Evaluation

The high thermal and oxidative stability of the fluorocarbon polyimide is shown by thermal gravimetric analysis of the polymer (Figure 3), wherein the weight loss in air was less than 5% until the temperature reached 500°C.

Stress corrosion evaluation of this polymer was carried out under the Task B contract NAS8-21399. No evidence of corrosion of the titanium alloy was evident after heating at 260°C (500°F) for 1000 hours. Similar evaluation of the imide based on the 1:1 ether structure also showed no evidence of corrosion in 1000 hours at 260°C (500°F).

Fuel resistance evaluation of polyimide polymers structures I and II were carried out under the Task B polymer evaluation program. Lap shear test results of structure I polyimide were little affected by a 70-hour heating in jet fuel at 260°C (500°F). Qualitatively a similar exposure of the 1:1 polyimide (Structure II) showed adverse effects of water and fuel oxidation products (ketones and aldehydes) although fuel alone appeared not to affect the polymer (Table 8).

One of the objectives of the synthesis effort has been to increase the length of the fluorocarbon segment to decrease the glass transition temperature of the polymer. A rough indication of the transition temperature was obtained by the ADL-Ball Rebound test. The results are shown in Figure 4 and given as approximate T_g in Table 8. Because of varying film thickness a direct comparison of percent rebound is probably less significant than the temperature at which the percent rebound begins to decrease most rapidly.

All of the polyimide evaluation results must be considered minimum performance levels since polymer properties have not been optimized. Larger quantities of the diamine intermediates will be prepared before this is done.

3. Fluorocarbon Modified Polysiloxane

Siloxane-linked fluorocarbon polymers represent a third type of polymer that was investigated. The siloxane linking reaction is readily applicable to the cure-in-place formation of a high stability sealant material. If, in the structure shown below, the R_f represents a polymeric fluorocarbon segment, the silyl phenylene end groups can be considered merely the linking groups for polymer formation.

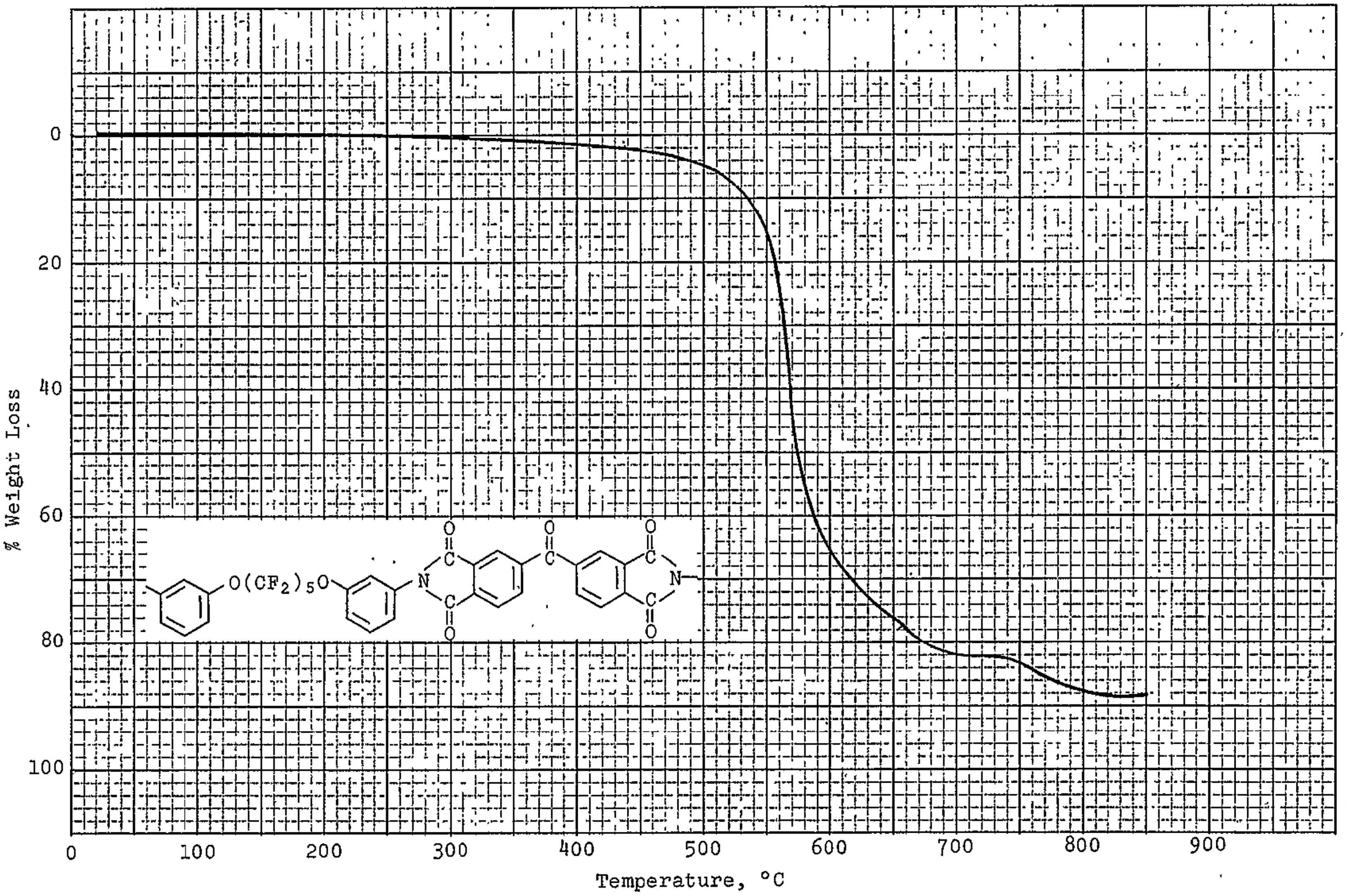
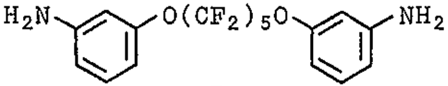
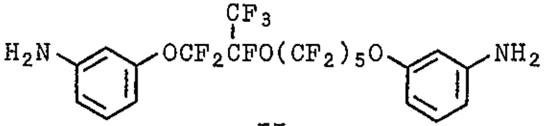
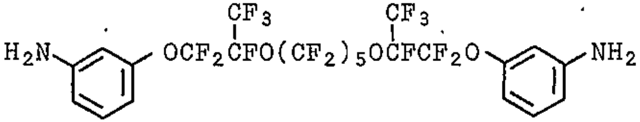


Figure 3. Thermal Gravimetric Analysis, Sample 132873
2.7°C/minute in Air

Table 8

POLYIMIDES PREPARED FROM BENZOPHENONETETRACARBOXYLIC DIANHYDRIDE AND FLUOROCARBON AROMATIC DIAMINES

NBP	Amine Intermediate	1000 hr 260°C Stress Corrosion	T_g, °C	Fuel Resistance, 70 hr 260°C		
				Fuel-N_2	Fuel-N_2/H_2O	Fuel Air
132873	 I	none	120-130	good	good	softened
137458	 II	none	95-110	good	softened	flowed became brittle
139670	 III	--	85-95	--	--	--

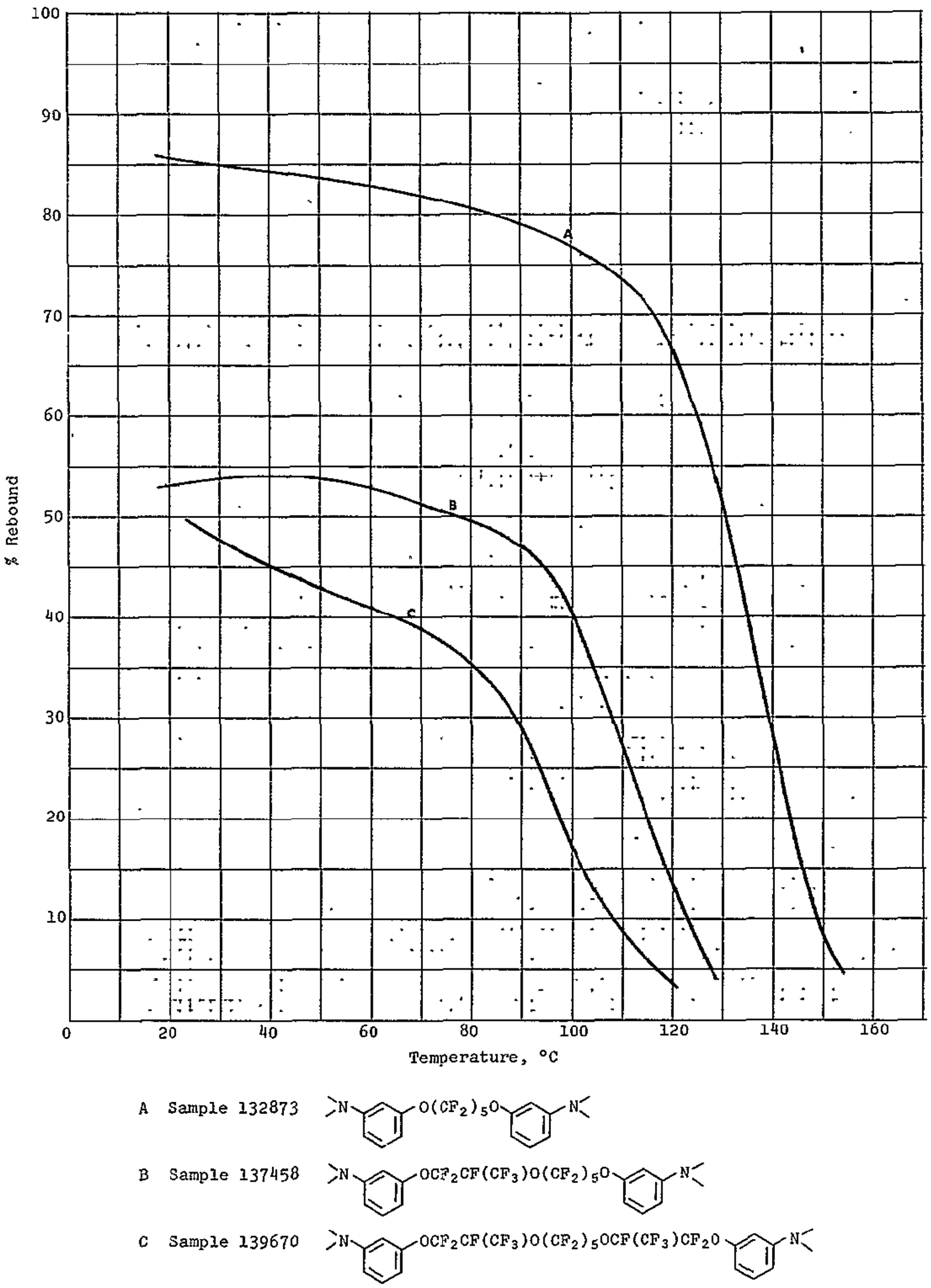
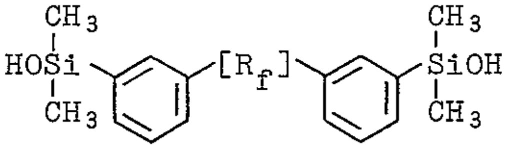


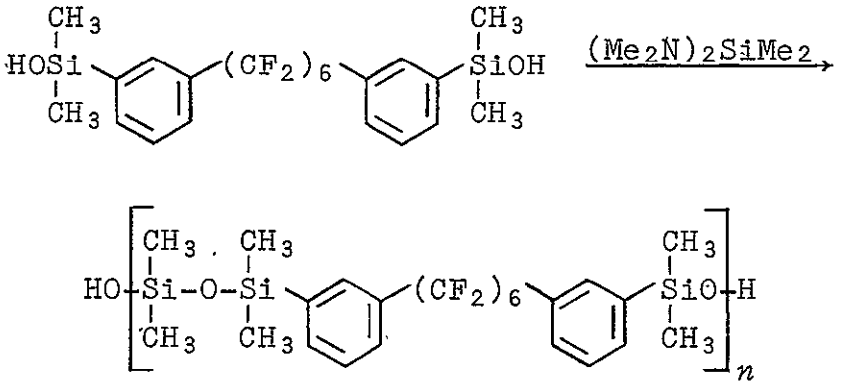
Figure 4. ADL-Ball Rebound Test Comparison of Polyimide Polymers



I

Synthesis of the silanol intermediate of the type shown above, where $R_f = (CF_2)_3$ or $_6$ was discussed earlier. Although the silanol intermediates offer several advantages in terms of ease of polysiloxane formation under mild temperature conditions, the resulting polymer structure (e.g., the siloxane linkage) may be marginal for long-term use under the fuel tank sealant conditions at temperatures of 260°C. For this reason less emphasis has been placed on this route for linking the fluorocarbon intermediates and the results obtained must be thought of as preliminary or tentative.

An elastomeric fluorocarbon modified siloxane polymer gum was prepared by reaction of the diol, I, with bis(dimethylamino)dimethylsilane.



This product was lightly crosslinked by reaction with ethyl silicate. The stress corrosion evaluation of a titanium alloy specimen coated with this polymer showed no evidence of corrosion after 1000 hours at 260°C. Thermal gravimetric analysis of this crude polymer (Figure 5) shows reasonably good (less than 5%) weight loss to 350°C.

4. Azo Linked Fluorocarbon Polymer

The possibility that the aminophenyl-terminated fluorocarbon intermediates could be linked through an oxidative coupling reaction to form stable azo polymers was investigated very briefly. Aromatic amines can be oxidized in air at 25°C in the presence of a copper catalyst (Ref. 13, 14).

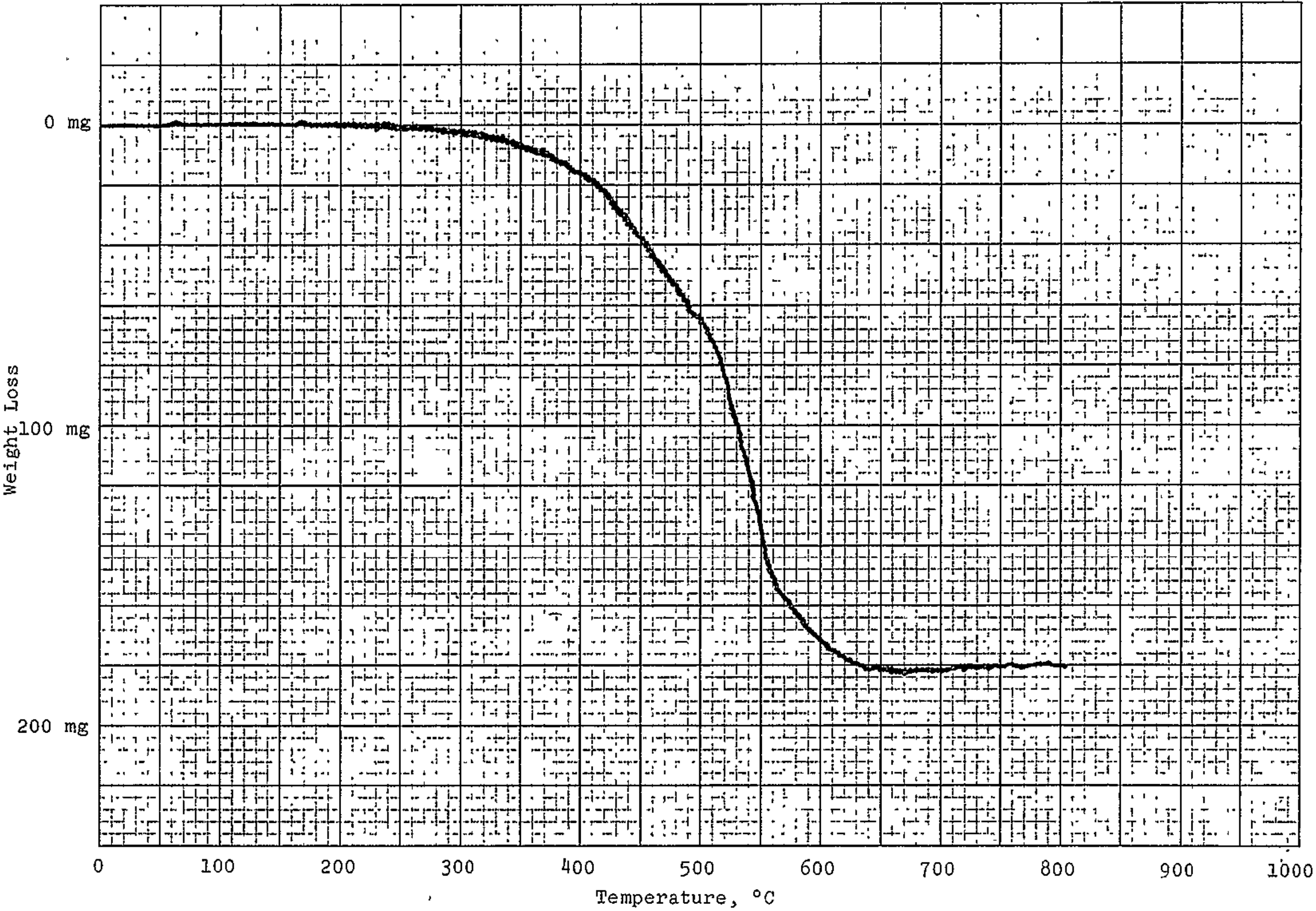
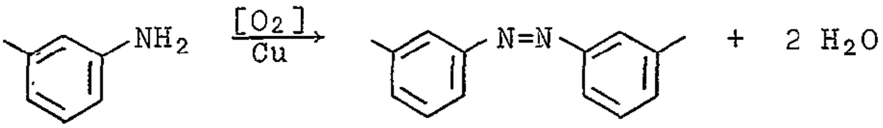


Figure 5. Thermal Gravimetric Analysis of Fluorocarbon Modified Silicone 2.7°C/minute in air



Bach and Black reported that thermogravimetric analyses of the resulting polymers show no weight loss up to 325°C (Ref. 14).

Preliminary experiments have shown a rapid initial absorption of oxygen by 1,5-bis(aminophenoxy)perfluoropentane but a decreasing rate as the product became insoluble. A brown, waxy product, apparently of low molecular weight, was obtained. Further work will be needed to define the potential of this curing reaction for fuel tank sealant applications.

IV. EXPERIMENTAL

A. ARYL-FLUOROCARBON COUPLING REACTIONS

1. Via Direct Phenyl Coupling

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 long column packed with glass helices. Careful fractionation of the C_6 fraction resulted in separation of 200 g of an azeotrope of diiodoperfluorohexane-iodobenzene, bp 112°C/99 torr, n_D^{25} 1.5018, from 88 g of pure 1,6-diiodoperfluorohexane, bp 117°C/99 torr, n_D^{25} 1.4030.

Attempted Separation of Iodobenzene-1,6-Diiododecafluorohexane Azeotrope 123862

The azeotropic mixture (n_D^{25} 1.5018) of iodobenzene (n_D^{25} 1.6180, mp -31°C) and 1,6-diiodododecafluorohexane (n_D^{25} 1.4029, mp 20°C) was cooled to -30°C 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 glass filter. Three liquid fractions were taken as the crystalline mass gradually melted.

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

Fractions 1 and 2 were combined as iodobenzene-enriched mixture. The crystalline solid was considered to be a 1,6-diiodododecafluorohexane-enriched mixture from which the pure diiodide can be obtained by redistillation. The two compounds appear to have co-crystallized, making this method only partially effective for separation of the iodobenzene and the diiodo fluorocarbon.

1,6-Diphenyldodecafluorohexane 132883

An azeotropic mixture (120 g) containing about 70 g of iodobenzene and 50 g of 1,6-diiodoperfluorohexane was added to 70 g of additional iodobenzene in dimethylformamide. The mixture and activated copper were gradually heated to 120°C over a period of 6 hours. Work-up of the product as previously described (Ref. 4) followed by distillation afforded 42 g of 1,6-diphenylperfluorohexane, bp 104°C/0.03 torr, n_D^{25} 1.4358, infrared spectrum, Figure A-1.*

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

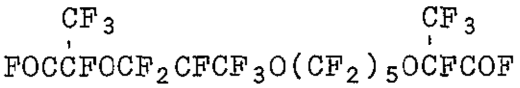
A copper-catalyzed coupling of *m*-bromoiodobenzene (90.5 g, 0.32 mole) with 1,6-diiodododecafluorohexane by the method previously reported (Ref. 4) resulted in a 71% yield of 1,6-bis(*m*-bromophenyl)-perfluorohexane, bp 154-156°C/0.05 torr.

2. Via Ester Fluorination

a. Intermediates and Ester Synthesis

Isolation of Hexafluoropropylene Epoxide Perfluoroglutaryl Fluoride Addition Products 137099 139605

A mixture of oligomerization products of hexafluoropropylene epoxide and hexafluoroglutaryl fluoride was purchased from PCR, Inc. Distillation of 403 g of the mixture gave the following:

Fraction	Wt %	bp °C/press torr	Product
1	0.5	30-55/atm	
2	14.0	55/atm	$C_3F_7OCFCF_3COF$
3	1.6	55-105/atm	
4	13.2	105-108/atm	$FOCCFCF_3O(CF_2)_4COF$ (1:1)
5	3.6	108-155/atm	
6	41.4	155-165/24	$FOCCFCF_3O(CF_2)_5OCFCF_3COF$ (2:1) IR, Figure A-2
7	1.0	65-96/24	
8	18.8	96-98/24	 $FOC\overset{CF_3}{C}FOCF_2CFCF_3O(CF_2)_5O\overset{CF_3}{C}FCOF$ (3:1)

Residue 3.5%

The structures were assigned by comparison of boiling points with those reported by Schuman, (Ref. 15) and by neutral equivalents (Table 9).

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*Infrared spectra, Figures A1-A27 are shown in the Appendix.

Conversion of Acyl Fluoride to Acyl Chloride

The three oligomer acid fluoride addition products of hexafluoropropylene epoxide and perfluoroglutaryl fluoride were converted to the corresponding acid chloride derivatives by hydrolyzing to the acid and then forming the acid chloride by reaction with thionyl chloride. Hydrolysis of the acid fluoride (10 g) was carried out in aqueous solution using four equivalents of calcium chloride for precipitation of fluoride ion as insoluble CaF_2. The acid was extracted with ether, dried, and freed of solvent. The acid was refluxed for 20 hours with excess thionyl chloride and then distilled affording high yields of the acid chlorides. The individual experiments are summarized in Table 9 with physical properties of products.

The aryl esters were all prepared by reaction of the appropriate phenol and acyl halide. A representative example is described below. Physical properties and yields of the esters similarly prepared are shown in Table 10.

m-Nitrophenyl Heptafluorobutyrate 137006

Reaction of 53.1 g (0.23 mole) of perfluorobutanoyl chloride with 37.1 g (0.27 mole) of *m*-nitrophenol in the presence of pyridine afforded 65 g (89% yield) of *m*-nitrophenyl heptafluorobutyrate, bp 63°/0.14 torr, n_D^{25} 1.4281.

m-Nitrophenyl Perfluoro-2-methyl-3-oxa-octanedioate 139602

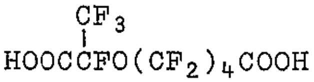
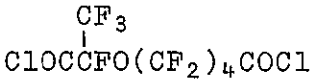
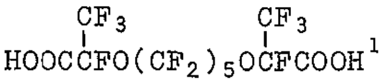
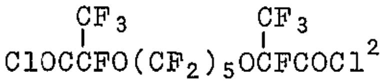
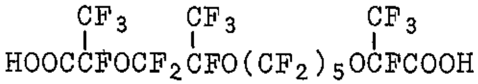
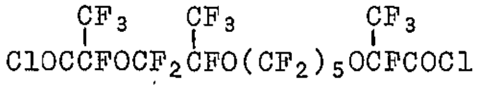
The 1:1 oligomer, perfluoro(2-methyl-3-oxa-1,8-octanedioyl) fluoride, (10 g, 0.0244 mole) was added rapidly with stirring to a mixture of *m*-nitrophenol (89.5 g, 0.065 mole), potassium fluoride (3.8 g, 0.065 mole), and 10 ml acetonitrile (distilled from P_2O_5). The temperature rose to 45°C. The mixture was stirred 16 hours, diluted with 30 ml of methylene chloride, and then filtered. The solution was distilled. Solid material formed in the pot as the excess nitrophenol was being distilled. The solid (2.5 g) was removed by filtration and distillation was resumed. The nitrophenyl ester was obtained in 40% yield; bp 190-200°C/0.03torr, n_D^{25} 1.4587, infrared spectrum Figure A-6. The high melting point by-product (mp ∿180°C) isolated by filtration was not identified.

Preparation of *m*-Nitrophenyl Ester of 2:1 Acid 139618

The 2:1 fluorocarbon diacid chloride (9.1 g 0.015 mole), *m*-nitrophenol (5.5 g, 0.04 mole) and 2 drops of pyridine as catalyst was heated 18 hours at 110-120°C. The two-phase mixture indicated incomplete reaction. Heating was continued for 20 hours at 145°C

Table 9

PHYSICAL PROPERTIES OF PERFLUOROALKYLENE ETHER DICARBOXYLIC ACIDS AND ACID CHLORIDES

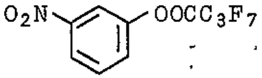
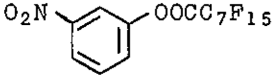
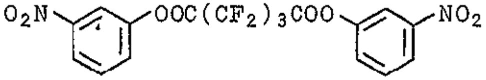
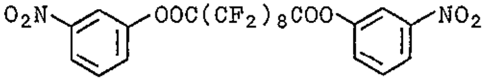
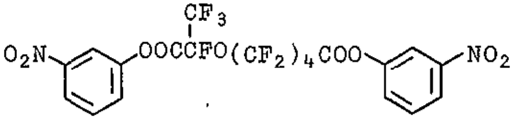
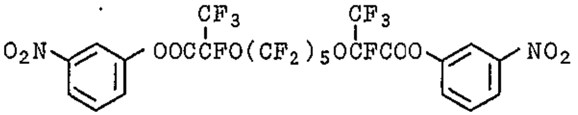
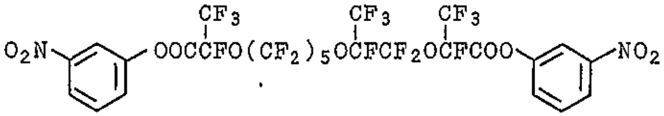
NBP	Acid	% Yield	bp °C/torr	n_D^{25}	Neut. Equiv. Found	Neut. Equiv. Calc'd
139633	 $HOOC\overset{CF_3}{C}FO(CF_2)_4COOH$ 1:1	47	93-95/0.02	1.3372	208.5	203
139635	 $ClOC\overset{CF_3}{C}FO(CF_2)_4COCl$	68	157/740			
139633	$C_3F_7OCFCF_3CF_2OCF(CF_3)COOH$	30	85/12	1.3058	506	496
139640	 $HOOC\overset{CF_3}{C}FO(CF_2)_5O\overset{CF_3}{C}FCOOH$[1] 2:1	87	126/0.04	1.3229	294	286
139616	 $ClOC\overset{CF_3}{C}FO(CF_2)_5O\overset{CF_3}{C}FCOCl$[2]	87	60/15	1.3224		
139674	 $HOOC\overset{CF_3}{C}FOCF_2\overset{CF_3}{C}FO(CF_2)_5O\overset{CF_3}{C}FCOOH$ 3:1	92	135/0.11	1.3179	363	368
139679	 $ClOC\overset{CF_3}{C}FOCF_2\overset{CF_3}{C}FO(CF_2)_5O\overset{CF_3}{C}FCOCl$	87	114/14	1.3176		

[1] Infrared spectrum Figure A-3

[2] Infrared spectrum Figure A-4

Table 10

PHYSICAL PROPERTIES OF ARYL ESTER INTERMEDIATES

NBP	Ester	% Yield	bp °C/torr	mp °C	n_D^{25}	Infrared Spectrum Figure
137006		89	63/0.14		1.4281	
132812		57	91-95/0.03	36-38.5	--	
139601		80	197-205/0.04	97-100	--	A-5
132854		100	--	91-94.5	--	
139602		40	190-200/0.03		1.4587	A-6
139618 139624	 [1]	90 93	200/0.005	60-80	--	A-7
139680		89	189/0.04	~35	1.4080	A-8

[1] Analysis Calc'd for $C_{23}H_8F_{18}N_2O_{10}$: %C 33.95, %H 0.99, %N 3.45
(139624) Found: %C 34.57, %H 1.06, %N 3.34

HCl was evolved more vigorously at the higher temperature. Distillation gave 11.0 g of waxy solid (90% yield) bp ~200°C/0.005 torr, mp 60-80°C infrared spectrum Figure A-7.

Preparation of *m*-Nitrophenyl Ester of 3:1 Acid 139680

Reaction of 61 g (0.079 mole) of the 3:1 acid chloride with excess nitrophenol (28 g, 0.2 mole) at 160-165°C; 84 hours gave on distillation 68.6 g (89% yield) of the corresponding *m*-nitrophenyl ester; bp 189°C/0.04 torr, n_D^{25} 1.4080.

b. Ester Fluorination Reactions

Sulfur Tetrafluoride Purification 137086

A one-liter Hastelloy-D autoclave was charged with 100 g of mercury and 440 g of sulfur tetrafluoride (Matheson). The autoclave was rocked for 72 hours at ambient temperature. The SF_4 (397 g) was recovered by condensation in an evaculated pressure cylinder cooled in dry ice. The bomb contained 132 g of a grey powder mixed with excess mercury.

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

The following experiment is representative of numerous reactions of SF_4 with nitrophenyl esters shown in Table 3. Use of purified SF_4 resulted in significant improvement in yields.

137089

A 300-ml stainless steel autoclave was charged with bis(*m*-nitrophenyl)hexafluoroglutarate (70 g, 0.155 mole). The vessel was evacuated and charged with 154 g (7.7 mole) anhydrous hydrogen fluoride and 50 g (0.46 mole) of purified sulfur tetrafluoride. The bomb was heated to 100°C for 12 hours then cooled and vented. The contents of the bomb were poured onto ice and washed with sodium bicarbonate. The organic material was extracted with benzene, washed and dried. Distillation afforded an 87% yield, (71 g) of 1,5-bis(*m*-nitrophenoxy)decafluoropentane, bp 190°C/0.05 torr, n_D^{25} 1.4729. The infrared spectrum Figure A-9 was consistent with this structure. The ester fluorination products listed in Table 11 were prepared in a similar manner.

A modification of the above procedure was necessary for the higher perfluoroalkylene ether derivatives where fluorination of the ester was incomplete. Distillation did not remove a carbonyl containing (ester) impurity. The product was then stirred with 1 N NaOH to hydrolyze the ester and washed with additional dilute alkali. The bis nitrophenoxy product was extracted from less soluble byproducts with benzene and redistilled. This eliminated the carbonyl impurity.

SF_4 Fluorination of Nitrophenyl Ester of Polymeric Perfluoroalkylene Oxide Dicarboxylic Acid 132897

An early attempt to fluorinate the nitrophenyl ester of the polymeric perfluoroalkylene oxide dicarboxylic acid using the crude SF_4 as received was not successful. A portion of the recovered product, examined by infrared, appeared to correspond to perfluoroalkylene ether indicating cleavage of the aryl group and fluorination of the carboxylic group.

3. Via Ketone Fluorination

a. Ketone Syntheses

Syntheses of several phenyl ketone derivatives of perfluoroalkanes by Friedel-Crafts acylation or Grignard reactions were described in previous reports (Ref. 4). One example of the Grignard synthesis is described below. Previous attempts to prepare the ketone derivatives by reaction of organometallic reagents with acid chloride intermediates were largely unsuccessful. A recent, promising exception is the synthesis using phenyl copper also described below.

1,4-Dibenzoyloctafluorobutane 137095

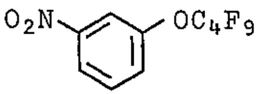
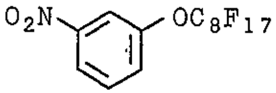
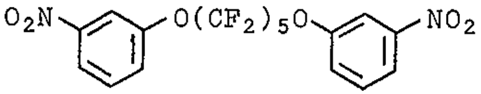
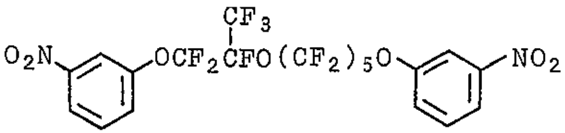
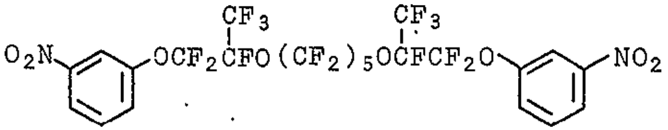
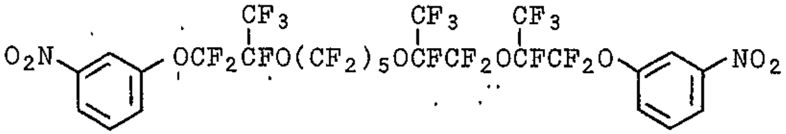
Phenyl Grignard prepared from 1.5 moles of bromobenzene was added over 1 hour to 50 g (0.1725 mole) of distilled perfluoroadipic acid, obtained from 3M Company (bp 150°C/9 torr) dissolved in 500 ml of ether at 0°C. The mixture was stirred two hours while warming to 25°C and then refluxed for two hours before pouring over acidified ice. Distillation, after the ususal washing, extraction and drying, gave 49 g (69%) of 1,4-dibenzoyloctafluorobutane, bp 134°C/0.06 torr, n_D^{25} 1.4929, lit. bp 143.5-144°C/0.47 torr, n_D^{20} 1.4922 (Ref. 6).

Phenylcopper in Synthesis of Perfluoroalkyl Phenyl Ketone 137438

Phenyllithium was prepared in ether from bromobenzene(5 g, 0.032 mole) and lithium (0.5 g; 0.072 mole). Phenyllithium (0.025 equiv. of 0.5N solution) was added dropwise, at -10 to 0°C to a slurry of purified cuprous bromide (0.028 mole in ether) to form phenylcopper (Ref. 16). A yellow-brown solid formed after ~90% of the phenyllithium had been added. To this mixture, at -30 to -40°C, was added 0.022 equivalent of perfluorooctanoyl chloride. The mixture was permitted to warm to 25°C overnight. The reaction mixture was filtered and the filtrate was poured over acidified ice. The organic phase was washed, dried and distilled giving 8.6 g (83%) of phenyl perfluoroheptyl ketone, bp 100°C/4 torr, n_D^{25} 1.3820, identified by the infrared spectrum and comparison of physical properties of the same compound previously prepared from phenyl Grignard and perfluorooctanoic acid (bp 130°C/25 torr, n_D^{25} 1.3794).

Table 11

PHYSICAL PROPERTIES OF ESTER FLUORINATED PRODUCTS

NBP	Compound	% Yield	bp °C/torr[1]	n_D^{25}	Infrared Spectrum Figure
137010		62	67/0.2	1.4027	
132826 132839		69	103/0.1	1.3804	
137089		87	190/0.05	1.4729	A-9
139604 139614		65 55	205-210/0.015 195-200/0.06	1.4355 1.4332	A-10
139677	 [2]	~50	177/0.06	1.4095	A-11
139690		~50	194/0.04	1.3874	A-12

[1] Boiling points of the high boiling products are only approximate

[2] The fluorocarbon segment is derived from the mixture of the symmetrical (shown) and unsymmetrical adducts of perfluoroglutaryl fluoride and hexafluoropropylene epoxide

b. Ketone Fluorinations

The ketone fluorination experiments were summarized in Table 5. Representative experiments are described below.

m-Nonafluorobutylbenzene

137007
137026

Fluorination of heptafluorobutyrophenone (13.7 g, 0.05 mole) was carried out by heating the ketone for 10 hours at 100°C with 20 g (1.0 mole) of hydrogen fluoride and 6 g (0.056 mole) of crude sulfur tetrafluoride. This procedure resulted in a 54% yield of nonafluorobutylbenzene, bp 90°C/98 torr, n_D^{25} 1.3717-26. A 62% yield was obtained in a second experiment.

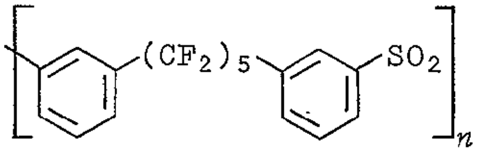
SF_4 Fluorination of 1,5-Diphenylhexafluoropentane-1,5-dione

Several experiments, summarized in Table 5 were performed in an attempt to improve the synthesis of 1,5-diphenylperfluoropentane.

132865

Reaction of 10 g (0.0925) of crude sulfur tetrafluoride with 10 g (0.0278 mole) of 1,5-diphenylhexafluoropentane-1,5-dione in the presence of 20 g of hydrogen fluoride formed a polymeric product upon heating 3 hr at 100°C, 21 hr at 125°C and 19 hr at 150°C. A benzene solution of the polymer was washed, dried, and evaporated to dryness.

A partially purified product was obtained by extraction with pentane and isolation of an insoluble solid residue. This was analyzed and found to correspond closely to a polysulfone.



Anal. calc'd for $C_{17}H_8F_{10}O_2S$: C 43.79; H 1.73; F 40.75; S 6.87
Found: C 43.78; H 1.59; F 40.50; S 6.52

Infrared and NMR spectra were consistent with the above structure. Polymeric products from the other two experiments were similar and were considered to be sulfones also. Elemental sulfur was also identified as a product of experiment 132876.

SF_4 Fluorination of 1,3-Dibenzoylhexafluoropropane 137087

Reaction of 1,3-dibenzoylhexafluoropropane (10 g, 0.029 mole) with purified SF_4 (10 g, 0.185 mole) in the presence of hydrogen fluoride (20 g, 1.0 mole) at 75°C for 12 hours resulted in a high conversion (>80%) to 2,6-diphenyl-perfluorotetrahydropyran with no evidence of polymer formation, bp 163°C/9 torr, mp 68-70.5°C.

Anal. Calc'd. for $C_{17}H_{10}F_8O$: C, 53.41; H, 2.64; F, 39.76
Found: C, 53.71; H, 2.60; F, 39.42

Similar experiments shown in Table 5 that were carried out without addition of hydrogen fluoride gave no fluorinated product even after heating to 220°C. When the SF_4 was not purified, the ketone was converted to polymeric product as in the above experiment.

2,6-Diphenyl-2,6-dihydroxyperfluorotetrahydropyran 137441

Titration of a 1-gram sample of 1,5-dibenzoylhexafluoropropane with 0.1 N NaOH showed an equivalent weight of 360, the molecular weight of the diketone. Addition of an equivalent quantity of 0.1 N hydrochloric acid caused precipitation of a white crystalline solid, which was recovered in 92% yield by filtration, mp 89-91°C. The infrared spectrum (Figure A-13) showed no carbonyl absorption but strong -OH absorption at 2.9 and 3.0 μ. The compound is considered to be 2,6-diphenyl-2,6-dihydroxyperfluorotetrahydropyran.

1,6-Diphenyldodecafluorohexane 137098

Reaction of 10 g (0.024 mole) of 1,4-dibenzoylperfluorobutane with sulfur tetrafluoride (10 g, 0.072 mole) and hydrogen fluoride (20 g, 1.0 mole) at 75°C for 12 hours formed a 76% yield of 1,6-diphenyldodecafluorohexane, bp 97-100°C/0.02 torr, n_D^{25} 1.4363-68, previously reported n_D^{25} 1.4361, from iodobenzene and diiodoperfluorohexane (Ref. 4).

Zinc-Catalyzed Coupling of Perfluorooctanoyl Chloride with Perfluoropropyl Iodide 137065

Perfluorooctanoyl chloride (17.3 g, 0.04 mole) was added rapidly to tetrahydrofuran (25 ml) and zinc granules at -10°C. No evidence of reaction was observed. Perfluoropropyl iodide (4.8 g, 0.05 mole) was added rapidly and was followed by a highly exothermic reaction with a temperature rise to 20°C despite cooling. Two layers formed. The reaction mixture was poured over acidified ice, washed, and dried. Distillation gave a 4 g fraction considered to be impure perfluoropropylheptyl ketone bp 110-112°C/30 torr, n_D^{25} 1.3143.

Coupling of Perfluoroheptyl Iodide with Perfluorooctanoyl 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°C 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°C/7 torr, n_D^{25} 1.3016.

Attempted Coupling of Benzoyl Chloride and Iodoperfluoroalkanes

Several attempts to couple acid chlorides with perfluoroalkyl zinc reagents were unsuccessful. The following is a representative example of the experiments summarized in Table 6.

137047

A mixture of powdered zinc (13 g, 0.2 g atoms) and freshly distilled tetrahydrofuran (THF) was cooled to -10°C under dry nitrogen. Benzoyl chloride (21.1 g, 0.15 mole) was added and then a mixture of 1,4-diiodooctafluorobutane dissolved in 35 ml THF was added over 2.5 hr while the exothermic reaction was maintained at -5 to -10°C. The mixture was filtered, and most of the THF was removed under vacuum. The mixture was poured onto ice, washed with dilute hydrochloric acid, extracted with ether, dried and distilled. The products did not appear to be an aryl perfluoroaliphatic ketone. The infrared spectrum indicated o-chlorobutylbenzoate formed by reaction of the acyl halide with the THF.

Attempted Coupling of Benzoyl Chloride with Perfluoropropyl Iodide.

137050

An equimolar mixture of benzoyl chloride and perfluoropropyl iodide was added over a period of 1 hour to a slurry of zinc dust in tetrahydrofuran at 10 to 0°C. An exothermic reaction occurred but was easily controlled. After 0.75 hour at 0-10°C the reaction mixture was poured over ice containing sodium bicarbonate and was then extracted with ether, dried and distilled. The major product, by IR and refractive index (n_D^{25} 1.5187) appeared to be δ-chlorobutyl benzoate, the reaction product of benzoyl chloride with THF.

137055

In a similar experiment, benzoyl chloride was added dropwise to a preformed solution of perfluoropropylzinc iodide in dimethyoxyethane (Ref. 7) at -10 to -15°C. The refractive index of the liquid product was too high to be perfluoroalkyl aryl ketone. Benzoic acid was identified as a product.

B. CONVERSION OF α,ω-ARYL PERFLUORO COMPOUNDS TO POLYMER INTERMEDIATES

1. Nitration Reactions

m-Nonafluorobutylnitrobenzene 137002
137028

Nonafluorobutylbenzene (28.6 g, 0.096 mole) was nitrated at 50-60°C using a mixture of 38.5 ml of nitric acid (70%) and 61 ml of sulfuric acid (95%). The reaction mixture was quenched in 250 ml water. The product was extracted with chloroform, washed, dried and distilled to give 30.9 g (94% yield) of *m*-nonafluorobutylnitrobenzene, bp 113-114°C/17 torr, n_D^{25} 1.4114-1.4116.

1,6-Bis(*m*-nitrophenyl)dodecafluorohexane 132888

Nitration of 1,6-diphenylperfluorohexane (25 g, 0.055 mole) at 55°C with a mixture of 44 ml of conc. nitric acid and 70 ml of sulfuric acid gave 29.1 g of crude 1,6-bis(*m*-nitrophenyl)perfluorohexane, lit. mp 94-95° (Ref. 17). Recrystallization from methanol gave 25.5 g, mp 100-102°C, representing an 85% yield. A second fraction (1 g) recovered from the methanol melted 70-77°C.

2. Catalytic Reduction of Nitro Compounds

The nitrophenyl intermediates prepared by fluorination of ketones and esters were reduced catalytically over Raney nickel to form the corresponding amines in near quantitative yields. Evaporation of the solvent left the crude amine which, in several instances, was converted to the hydrochloride as a means of purification.

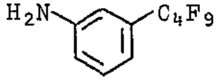
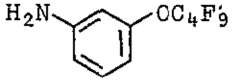
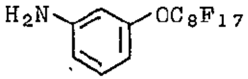
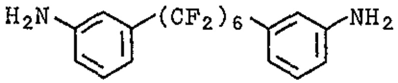
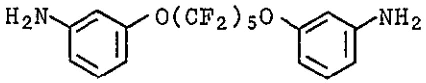
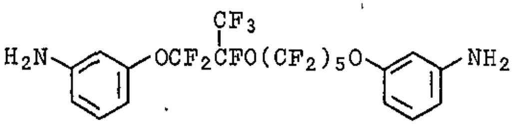
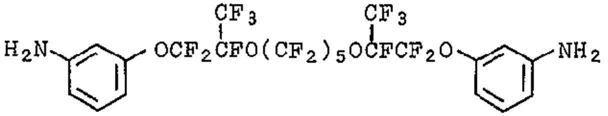
A representative example is described below. Properties of other amines similarly prepared are shown in Table 12.

1,5-Bis(*m*-nitrophenoxy)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°C. 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.

Table 12

PROPERTIES OF AMINOPHENYL FLUOROCARBON INTERMEDIATES

NBP	Compound	% Yield	bp °C/torr	mp °C	n_D^{25}	Amine·HCl mp, °C
137005		91	--	--	1.4107	150-152
137012		>86	--	--	1.3958	215-220
132864		85	--	--		195-217
132891		93	--	82-86	--	261-268
132838 132861		95	162/0.03	47-47.5	1.4755	264
139607	 [1]	72	--	--	1.4368	
139668	 [2]	95	157/0.007	--	1.4082	

[1] Neut. Equiv. Calc'd 316, found 331; IR Figure A-15
[2] Neut. Equiv. Calc'd 399, Found 410; IR Figure A-16

132863

Free amine was isolated from a larger quanity 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°C/0.03 mm, nD^{25} 1.4755, mp 45.5-47° (Figure A-14). After recrystallization from hexane the melting point was 47-47.5°C.

3. Phosgenations

m-(Dodecafluorohexamethylenebis)phenyl Isocyanate 132892

Phosgenation of 23 g (0.041 mole) of (dodecafluorohexamethylenebis)aniline hydrochloride afforded an 86% yield of *m*-(dodecafluorohexamethylenebis)phenyl isocyanate, bp 152-153°C/0.03 torr, mp 72.5-74.5; isocyanate equivalent: Found 268.2, calc'd 268.1.

m-Nonafluorobutylphenyl Isocyanate 137031

137008

Phosgenation of a slurry of *m*-nonafluorobutylaniline hydrochloride (37.9 g, 0.165 mole) in xylene at gradually increasing temperature from 25 to 137°C gave, upon distillation, a 73% yield (26.6 g) of nonafluorobutylphenyl isocyanate, bp 145°C/133 torr, n_D^{25} 1.4111, infrared spectrum, Figure A-17. Isocyanate equivalent: calc'd 337, found 343.

m-Nonafluorobutoxyphenyl Isocyanate 137013

Phosgenation of a slurry of 35 g of *m*-nonafluorobutoxyaniline hydrochloride (0.097 mole) in *o*-dichlorobenzene formed the corresponding isocyanate. This product was difficult to separate from the solvent, however. A portion (~18 g, 50% yield) was isolated by careful fractionation, bp 152°C/150 torr, n_D^{25} 1.4009 and identified by the infrared spectrum, Figure A-18.

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°C. Distillation gave 6.6 g of *m*-perfluorooctyloxyphenyl isocyanate, bp 77°C/0.05 torr, 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°C. Distillation then afforded an 83% yield of 1,5-bis(*m*-isocyanatophenoxy)decafluoropentane, bp 153°C/0.03 torr; n_D^{25} 1.4690, isocyanate equiv: Found 261, 259; calc'd 259.1, infrared spectrum, Figure A-19.

4. Silylation and Synthesis of Organo Silicon Intermediates

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 was stirred overnight at 25°C and was then heated to 40°C. An exotherm with temperature rise to 50°C 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°C/0.05 torr, n_D^{25} 1.4530-37, d_4^{25} 1.299.

Dodecafluorohexamethylenebis(3-phenyldimethylsilanol) 137402

1,6-Bis(*m*-dimethylsilylphenyl)dodecafluorohexane, 10.2 g (0.0175 mole) was dissolved in 70 ml of tetrahydrofuran. A buffered aqueous solution at pH 7 (13 ml) was added along with 0.1 g of 5% palladium/carbon catalyst (Ref. 18). The mixture was heated to reflux until gas evolution ceased (<1 hour). The mixture was filtered and concentrated under vacuum and then the product was extracted with ether. Evaporation of the solvent extract under vacuum left 10.2 g of waxy solid. This was slurried with pentane to give 9.2 g (87.5%) of crystalline solid, mp 92-94.5°C, infrared spectrum, Figure A-20. Recrystallization from hexane gave pure dodecafluorohexamethylenebis(3-phenyldimethylsilanol), mp 94.5-96°C.

Anal. Calc'd for $C_{22}H_{22}F_{12}O_2Si_2$: C 43.85; H 3.68; F 37.84
Found: C 43.20; H 3.40; F 38.47

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.

2 4

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°C and then filtered. Distillation of the filtrate gave a 74% yield of dimethyl bis(dimethylamino)silane, bp 126-127°C/740 torr, n_D^{25} 1.4160. Lit: bp 128°C (Ref. 19).

Methylphenylvinylchlorosilane 137042

Vinyl Grignard prepared in tetrahydrofuran from vinyl bromide (53 g, 0.5 mole) and magnesium (12 g, 0.5 mole) was added to cold ether solution of phenylmethyldichlorosilane (100 g, 0.5 mole) initially at -20°C and later at temperatures increasing to 25°C. The mixture was finally heated to 40°C for 1.5 hours. The solid was filtered off and washed with ether. The filtrate was then distilled and the fractions boiling at 107°C/30 torr were considered to be impure methylphenylvinylchlorosilane, n_D^{25} 1.5194-1.5198, equivalent weight 163-174, theory 183, estimated yield ~50%.

(Dimethylamino)methylphenylvinylsilane 137046

A mixture of fractions approaching the methylphenylvinylchlorosilane composition (58 g, 0.32 mole) was treated with excess dimethylamine in hexane at -30°C, and allowed to warm to 25°C overnight. Filtration and extraction with hexane followed by distillation gave two product fractions. The fraction boiling at 115-117°C/30 torr appears to be the desired methylphenylvinyldimethylaminosilane though the product was not cleanly separated from close boiling by-products, n_D^{25} 1.5085-1.5095, neutral equiv. 202, calc'd 191. The overall yield in the above two steps was less than 20%.

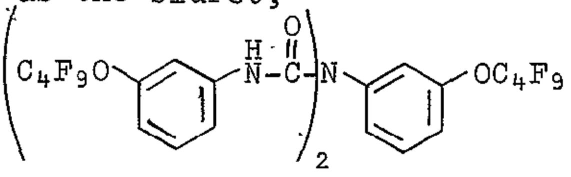
C. POLYMERIZATION

1. Isocyanurate-Linked Polymers Preparation

a. Cyclotrimerization of Monofunctional Compounds

m-Nonafluorobutoxyphenyl Isocyanate Trimerization 137014
137405

An allyl glycidyl ether-tetramethylbutanediamine cocatalyst system was added to a distillate fraction containing an unknown quantity of *m*-nonafluorobutoxyphenyl isocyanate in dichlorobenzene in the phosgenation solvent. After 18 hours at 90°C two products were isolated. One melting at 158-159°C was identified by infrared and elemental analysis as the biuret,



Anal. Calc'd for $C_{32}H_{14}F_{27}N_3O_5$: C 37.18; H 1.37; F 49.60
Found: C 37.29; H 1.48; F 49.58

Molecular weight Calc'd: 1033
Found: 975

Infrared spectrum, Figure A-21.

A second, lower-melting product had an infrared spectrum that corresponded to that of the expected isocyanurate.

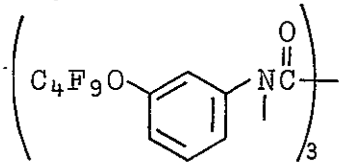
137422

Purified *m*-nonafluorobutoxyphenyl isocyanate (3.5 g) was polymerized in freshly distilled *o*-dichlorobenzene (for comparison with above results) under the same conditions. The infrared spectrum showed only a trace of -NH before and after cyclotrimerization. Evaporation of the solvent and recrystallization of the residue from hexane gave four fractions.

Fraction Weight, g	Appearance	mp °C	IR
1. 0.9	white crystalline solid	113-121	isocyanurate
2. 1.0	crystalline solid	113-117	isocyanurate
3. 0.7	gummy solid	109-114	isocyanurate
4. 0.3	gum	gum	isocyanurate

The first fraction upon recrystallization from hexane melted at 120-123.5°C (infrared spectrum, Figure A-22) and finally on further purification 124.5-125.0°C.

Chemical and infrared analysis indicated that this product was the cyclic trimer isocyanurate,



Anal. Calc'd for $C_{33}H_{12}F_{27}N_3O_6$: C 37.41; H 1.14; F 48.42
Found: C 37.08; H 1.20; F 48.72

Molecular weight by VPO in $HCCl_3$: 1050, 1070
Calc'd: 1059.5

m-Nonafluorobutylphenyl Isocyanate Trimerization 137039

Cyclotrimerization of nonafluorobutylphenyl isocyanate resulted in both isocyanurate and biuret-like products as in the above experiments. The isocyanurate product upon repeated recrystallization melted at 121.5-123°C and was identified by comparison of the infrared spectrum (Figure A-23) with that of the nonafluorobutoxyphenyl isocyanurate.

The second product melting at 134-135°C appears to be an amide-type compound and may be a biuret. The infrared spectrum, Figure A-24, showed two absorptions at 2.9 and 3.14 μ and a weak carboxyl absorption at ~5.8 μ. NMR indicated approximately seven aromatic protons for each labile proton. No further effort was made to identify this product.

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°C overnight showed no free isocyanate absorption in the infrared spectrum but a strong carbonyl at 5.8 μ.

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

Calc'd 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

b. Isocyanurate Polymer Preparations

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

A 2-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°C completed the reaction of isocyanate groups. A clear, amber-colored hard polymer resulted.

Isocyanurate Copolymer 137035

A mixture of dodecafluorohexanemethylenebis(*m*-phenyl isocyanate) (5.36 g) and *m*-nonafluorobutylphenyl isocyanate (2.26 g) was warmed to 70°C to dissolve the solid diisocyanate. Allyl glycidyl ether and tetramethylbutanediamine catalysts were added upon cooling the isocyanate mixture to about 40°C. The mixture solidified (polymerized) within 30 minutes at 50°C. Heating was continued for 19 hours at 100°C. A yellow brittle polymer was formed.

2. Polyimide Formations

a. Polymer Preparation

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 evaluated under Task B contract.

Polyimide from 1,8-bis(aminophenoxy)perfluoro-2-methyl-3-oxaoctane (1:1 acid derivative) 137458

Benzophenonetetracarboxylic dianhydride (0.656 g, 2.04 mmole) was added in portions to a solution of the diamine, 1,8-bis(aminophenoxy)perfluoro-2-methyl-3-oxaoctane, (1.347 g, 2.04 mmole at 95%) in dimethylacetamide. The mixture was stirred overnight and a portion of the solvent was removed, leaving a viscous solution. A film was cast on a plate glass surface; solvent was allowed to evaporate at ambient temperature. The polymer film was placed in an oven at 100°C and gradually heated to 170°C over a period of 6 hours. The infrared spectrum, Figure A-25, indicated a polyimide structure.

Polyimide from the α,ω-Aminophenoxy Derivative of the 2:1 Acid 137670

Addition of benzophenonetetracarboxylic dianhydride (0.192 g, 1.19 meq) to a DMAC solution of the diamine,

$$H_2NC_6H_4O(CF_2CFCF_3O)_x(CF_2)_5(OCFCF_3CF_2)_yOC_6H_4NH_2$$

where $x + y = 2$ (0.497 g, 1.19 meq) over a period of one hour followed by stirring overnight, gave a viscous polyamic acid solution. Evaporation of solvent from a film of this solution followed by gradual heating to 180°C gave a tough film of polyimide.

b. Reaction of Phthalic Anhydride with *m*-(nonafluorobutyl)phenyl Isocyanate

137078

Phthalic anhydride (1.45 g, 0.01 mole) and *m*-nonafluorobutylphenyl isocyanate (3.37 g, 0.01 mole) were added to 5 ml of dry pyridine under a dry nitrogen atmosphere. The mixture was gradually heated to 100°C over a period of 2 hours. Infrared analysis showed evidence of strong -NCO absorption. After heating the mixture an additional 3.5 hours at 100-110°C IR analysis showed only a trace of -NCO absorption. Evolution of gas was observed. From 3 g of tacky crystalline solid was isolated 0.9 g of purified solid considered to be the *N*-(*m*-perfluorobutylphenyl)phthalimide, mp 107.5-108°, IR, Figure A-26.

c. Reaction of Phthalic Anhydride with N-Phenylhexamethyldisilazane

137455

N-Phenylhexamethyldisilazane (2.5 g, 0.0122 mole) was mixed with 1.8 g of phthalic anhydride and heated at 100°C. The mixture was heated to 135°C for a few minutes to melt the anhydride. Finally, 10 ml anhydrous dimethylacetamide was added and heating over a steam bath was continued overnight.

The mixture was poured into water, extracted with alkali leaving 0.9 g (33%) crude phthalamide. Recrystallization from ethanol gave the imide, mp 208-209.5°C, lit. 208°C (Heilbron, Ref. 20).

3. Siloxane-Linked Fluorocarbon Polymers

Condensation of Silanediol with Bis(dimethylamino)dimethylsilane

137408

A mixture of dodecafluorohexamethylenebis(3-phenyldimethylsilanol) (1.205 g, 2.0 mmoles), bis(dimethylamino)dimethylsilane (0.278 g, 1.9 mmoles) and dry benzene (10 ml) was stirred at 25°C and finally refluxed until evolution of dimethylamine ceased. Solvent was removed under vacuum leaving a viscous residue containing a small amount of -OH absorption in the infrared spectrum. One drop of ethyl silicate and a catalytic quantity of dibutyltin dioctoate was added to this residue. The polymer slowly cured at elevated temperatures (100°C) forming a lightly crosslinked elastomeric material. The polymer swelled in chloroform or toluene.

137413

A second condensation using 1.2 g of the disilanol (2 mmoles) with 0.15 g (1.0 mmole) of the bis(dimethylamino)dimethylsilane formed a viscous, clear polymer containing appreciable residual silanol content.

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 remaining 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.

4. Azo-linked Fluorocarbon Polymers

Oxidative Coupling of 1,5-Bis(aminophenoxy)perfluoropentane 137445

Copper (I) chloride (0.5 g) freshly prepared by reduction of copper II chloride with ascorbic acid (Ref. 21) was added to 25 ml of pyridine in a gas tight apparatus connected to a gas burette. The solution was stirred and equilibrated in an oxygen atmosphere. 1,5-Bis(*m*-aminophenoxy)perfluoropentane (1.96 g, 4.21 mmole) was added. Initial oxygen absorption was rapid but gradually decreased and ended with absorption of approximately half the calculated volume. Heating to 50-60°C redissolved the precipitated material and temporarily increased the rate of gas absorption. A brown, waxy solid that showed little N-H absorption in the infrared compared to the diamine was isolated, infrared spectrum, Figure A-27.

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APPENDIX

Figure

Figure

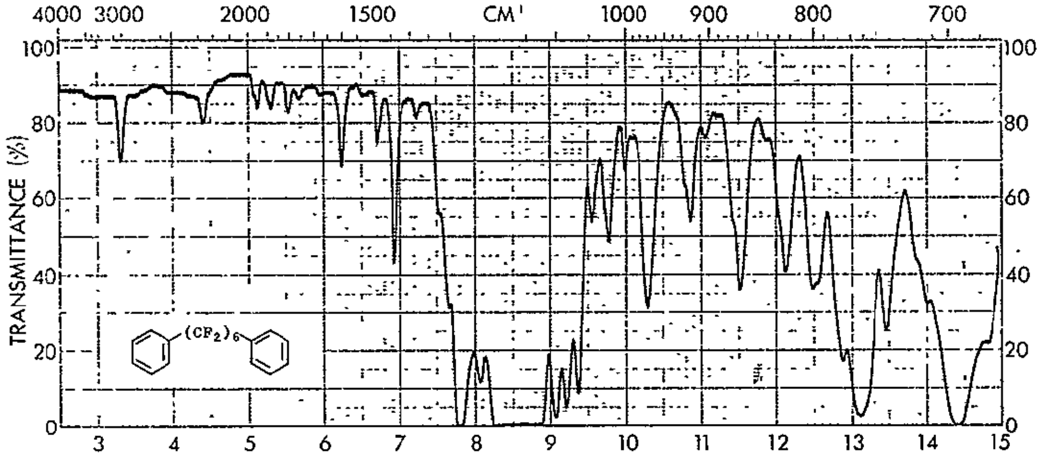

Figure A-1. 1,6-Diphenyldodecafluorohexane (132885-6)

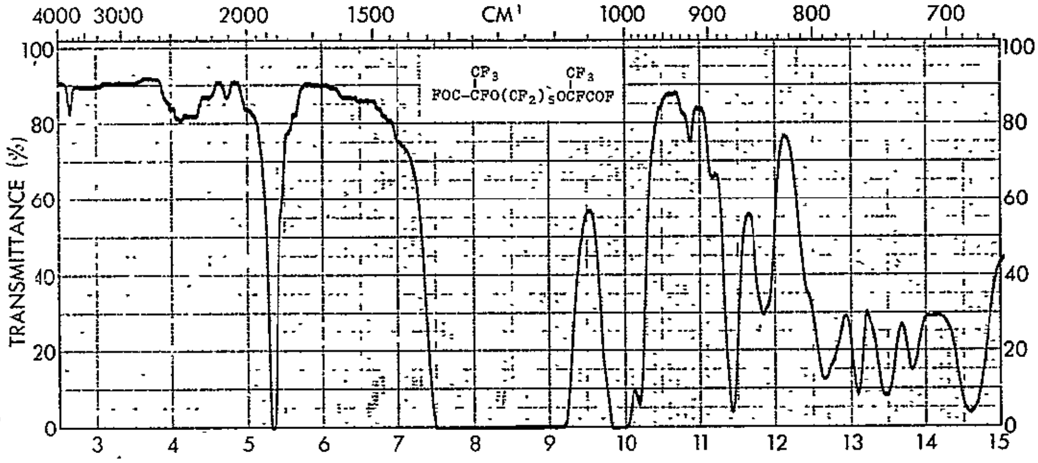

Figure A-2. 2:1 Oligomer Acid Fluoride, Mixture of Symmetrical and Unsymmetrical Products (139605-6)

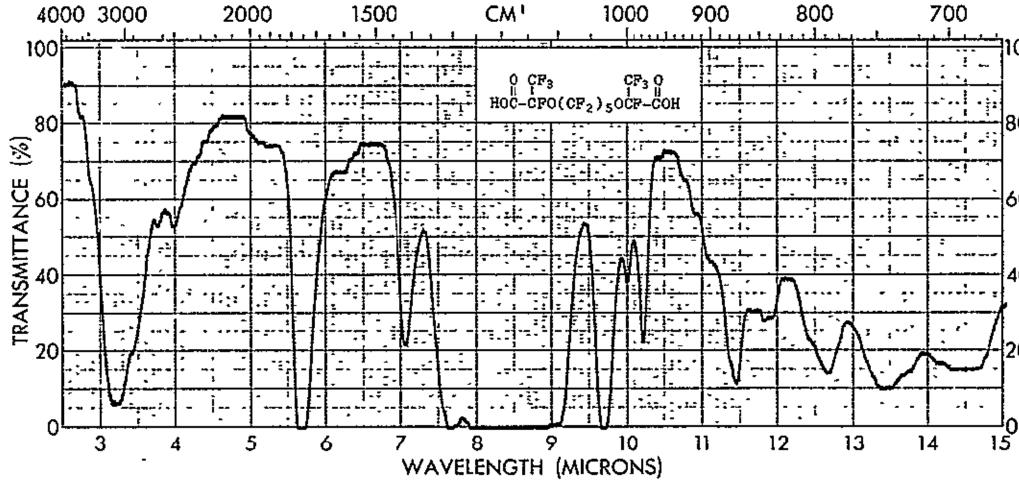

Figure A-3. 2:1 Oligomer Acid, Isomer Mixture (139640)

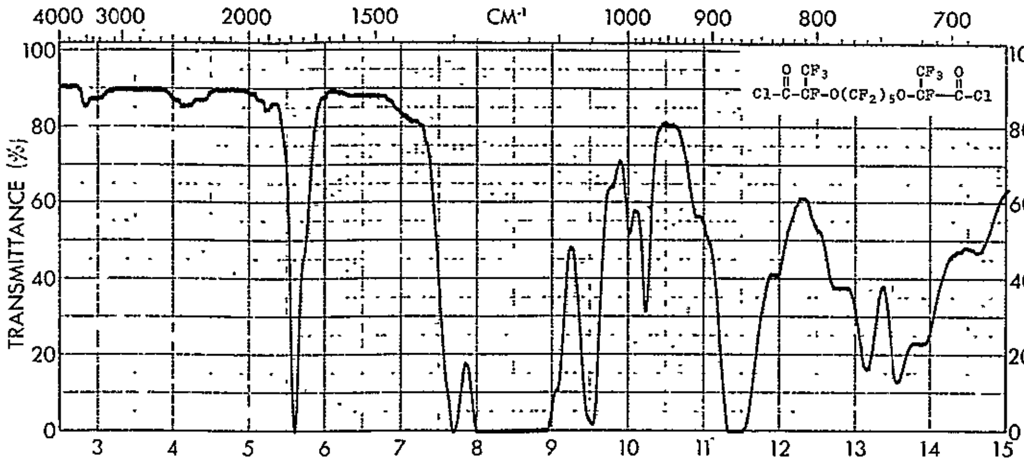

Figure A-4. 2:1 Perfluoroalkylene Ether Acid Chloride (139616-3)

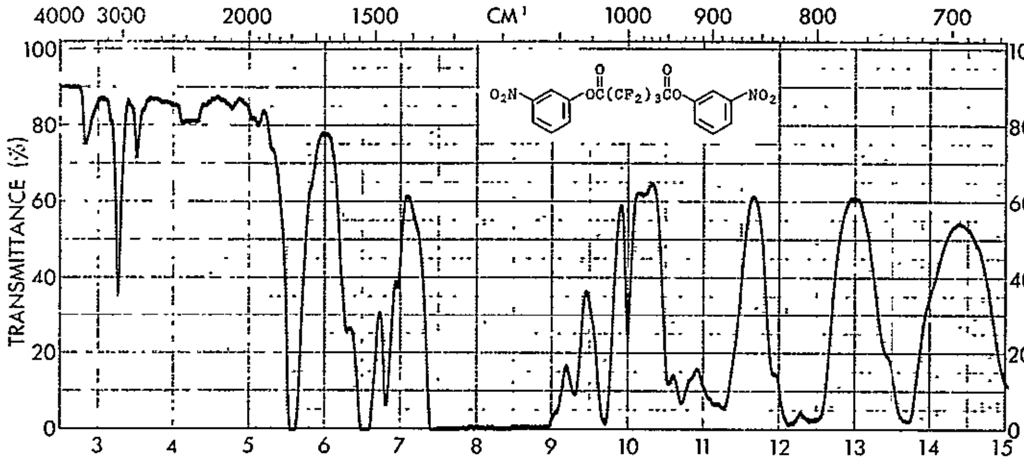

Figure A-5. *m*-Nitrophenyl Hexafluoroglutarate (139601)

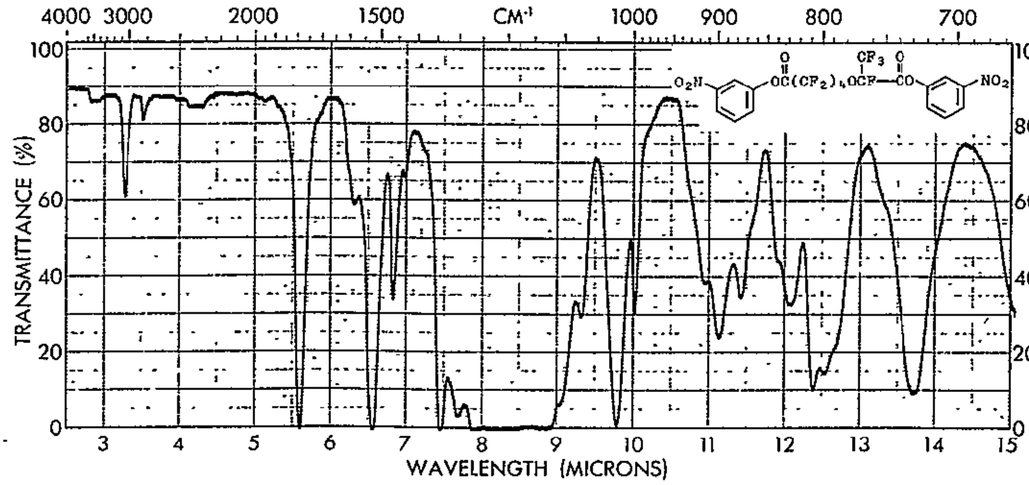

Figure A-6. *m*-Nitrophenyl Perfluoro(2-methyl-3-oxa-1,8-octanedioate) (139603-5)

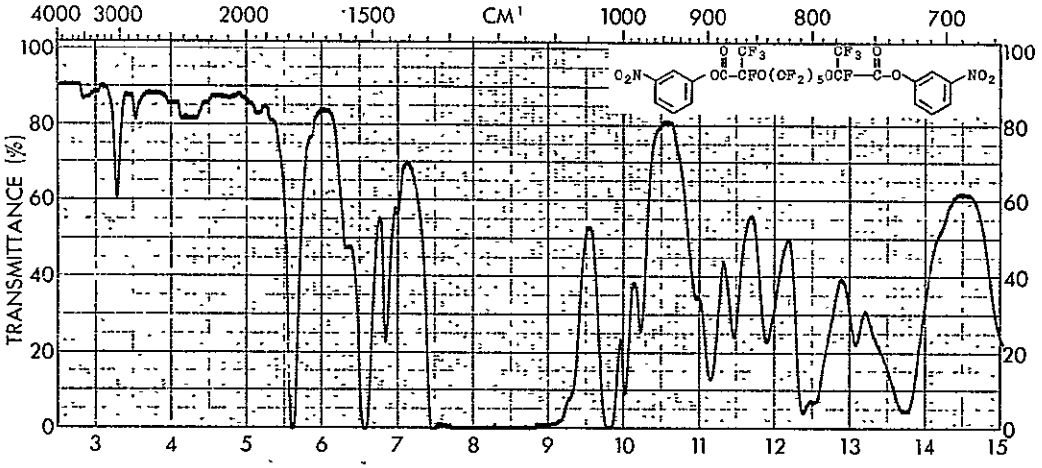

Figure A-7. Nitrophenyl Ester of 2:1 Oligomer Acid (Isomer Mixture) (139618-2)

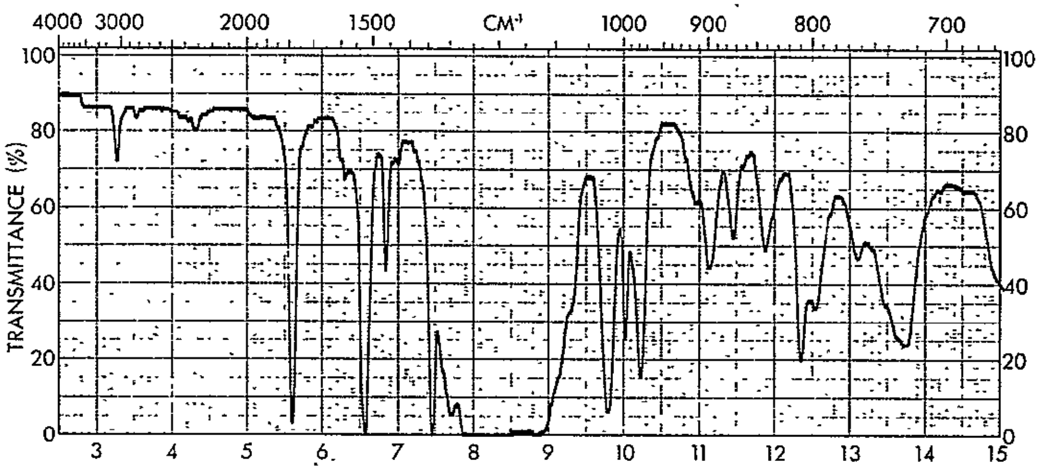

Figure A-8. Nitrophenyl Ester of 3:1 Oligomer Acid (139680)

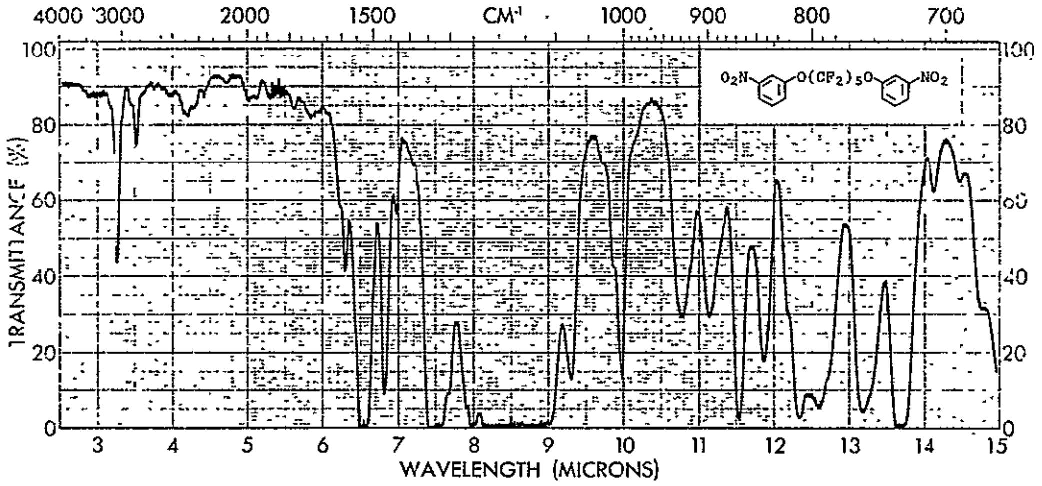

Figure A-9. 1,5-Bis(*m*-nitrophenoxy)decafluoropentane (132834)

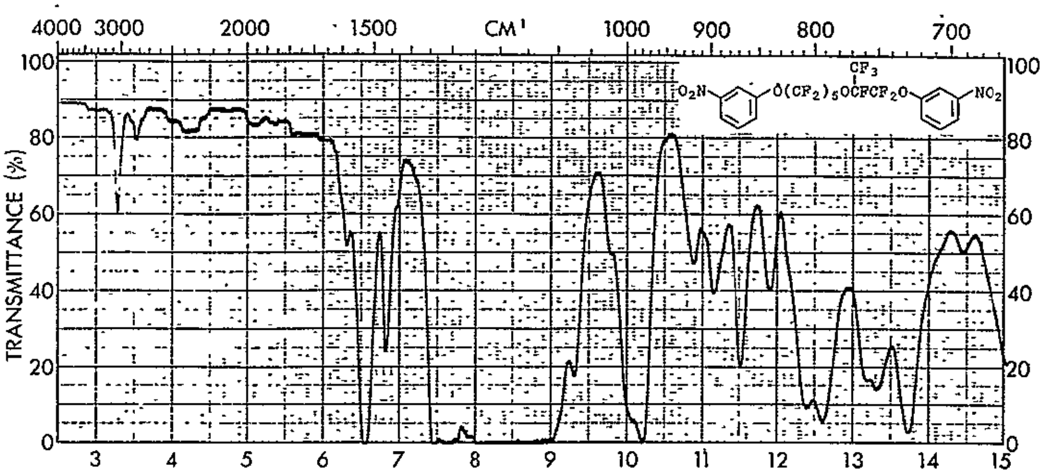

Figure A-10. 1,8-Bis(*m*-nitrophenoxy)perfluoro-2-methyl-3-oxa-octane (139617-2) (1:1 Derivative)

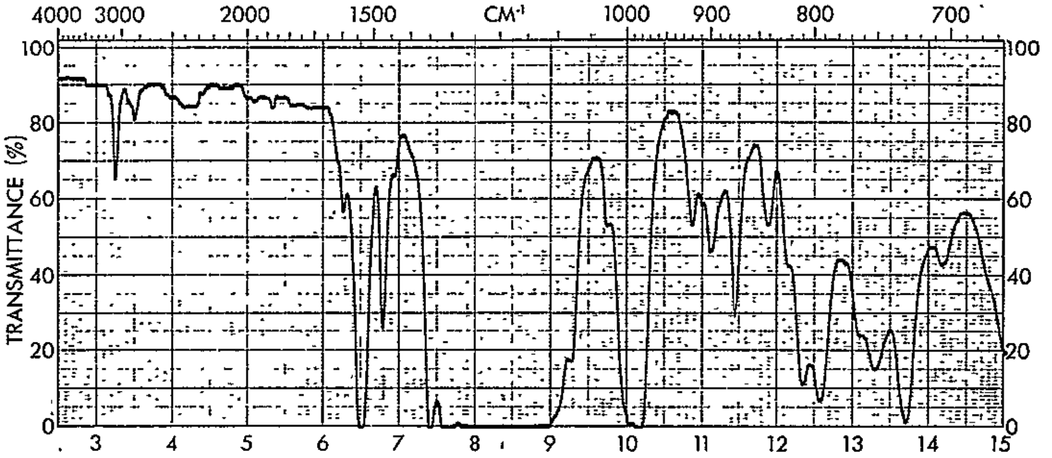

Figure A-11. Nitrophenoxy Derivative of 2:1 Perfluoroalkylene Ether (139665-2)

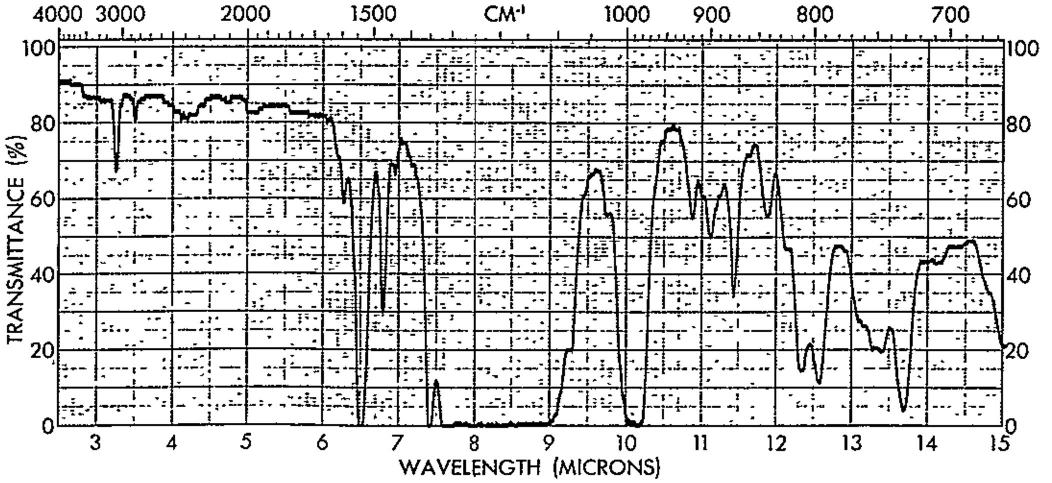

Figure A-12. Nitrophenoxy Derivative of 3:1 Perfluoroalkylene Ether (139697-4)

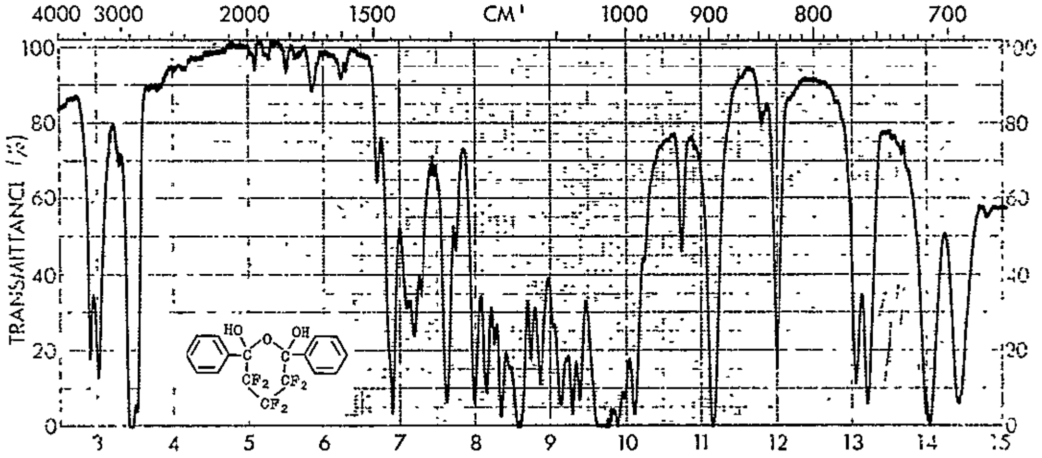

Figure A-13. 2,6-Diphenyl-2,6-dihydroxyperfluorotetrahydropyran (137441)

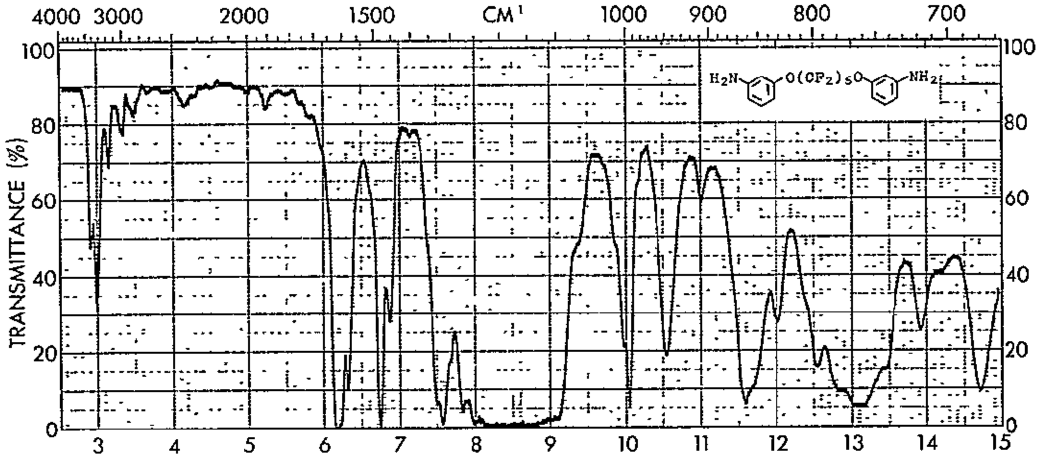

Figure A-14. 1,5-Bis(*m*-aminophenoxy)decafluoropentane (132863)

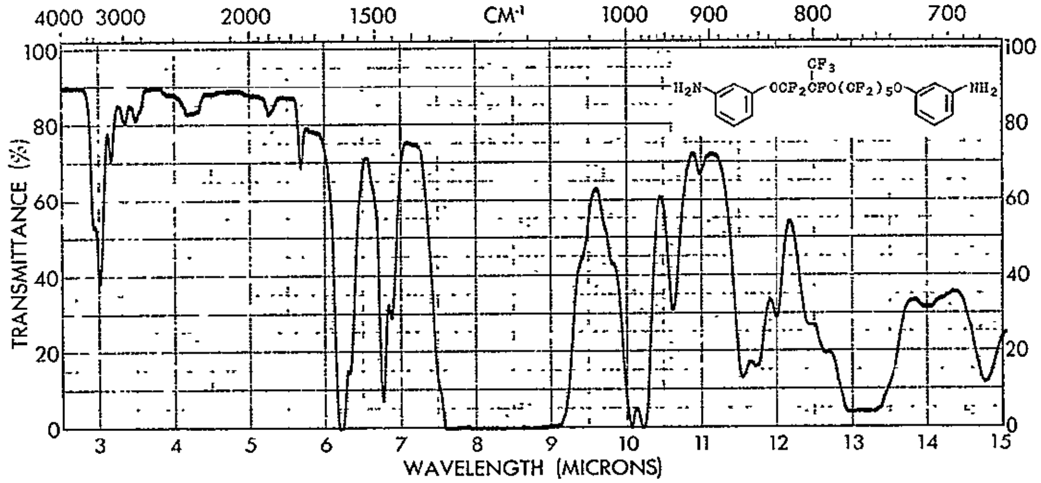

Figure A-15. 1,8-Bis(*m*-aminophenoxy)perfluoro-2-methyl-3-oxa-octane (139607-B)

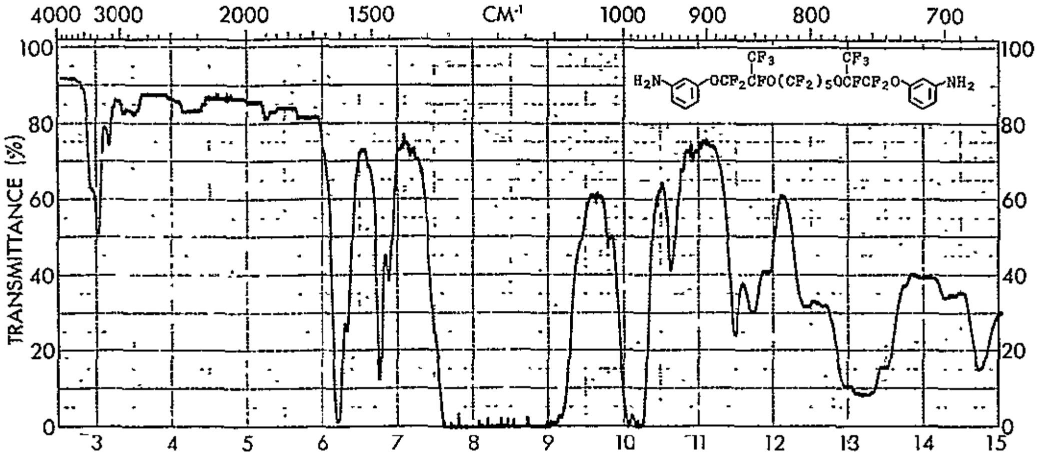

Figure A-16. Aminophenoxy Derivative of 2:1 Perfluoroalkylene Ether (139668)

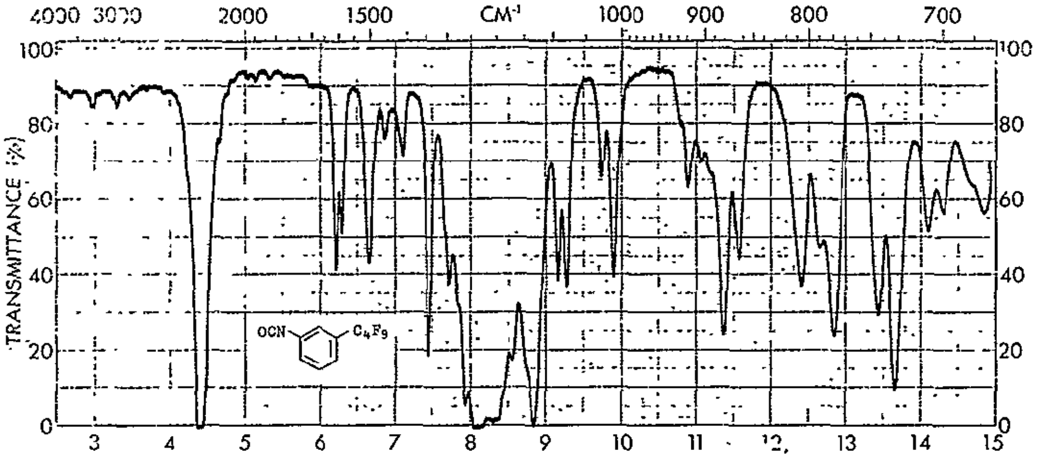

Figure A-17. *m*-Nonafluorobutylphenyl Isocyanate (137032-9)

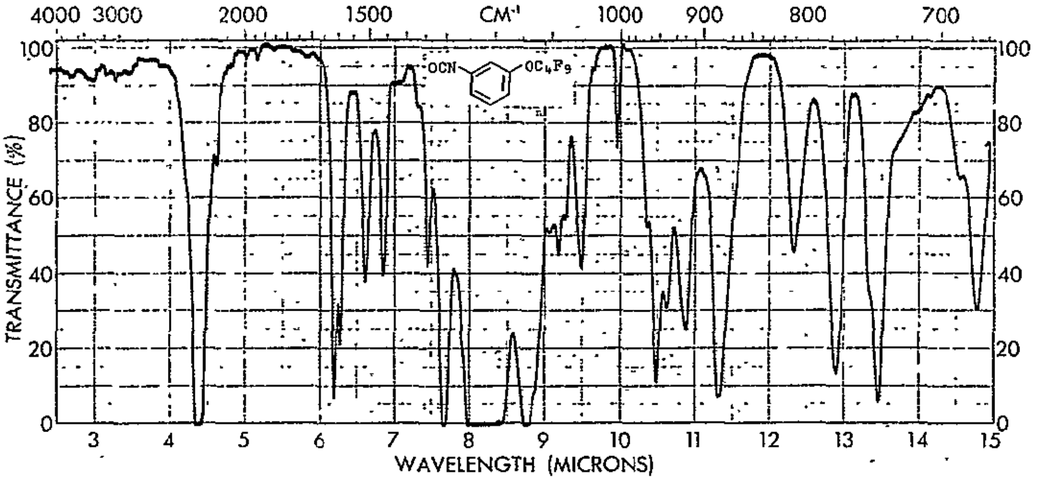

Figure A-18. *m*-Nonafluorobutoxyphenyl Isocyanate (137016)

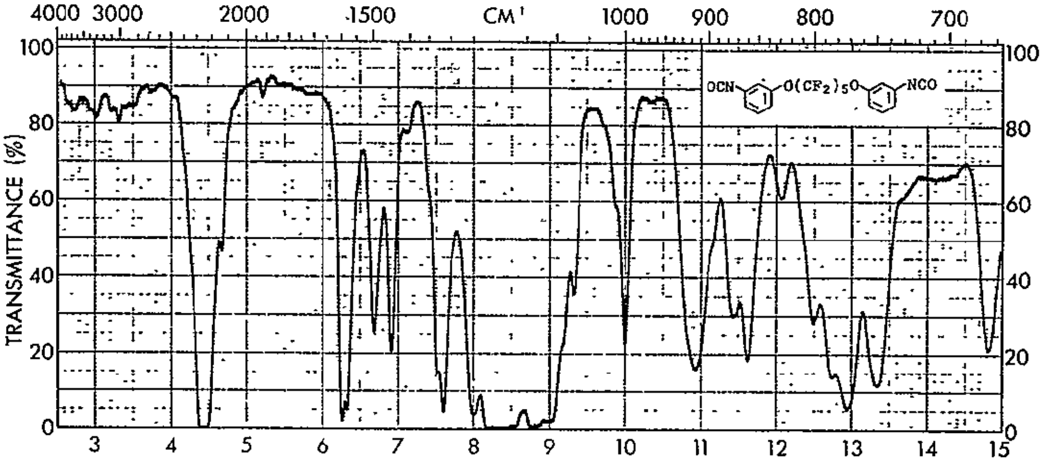

Figure A-19. 1,5-Bis(*m*-isocyanatophenoxy)decafluoropentane (132845-2)

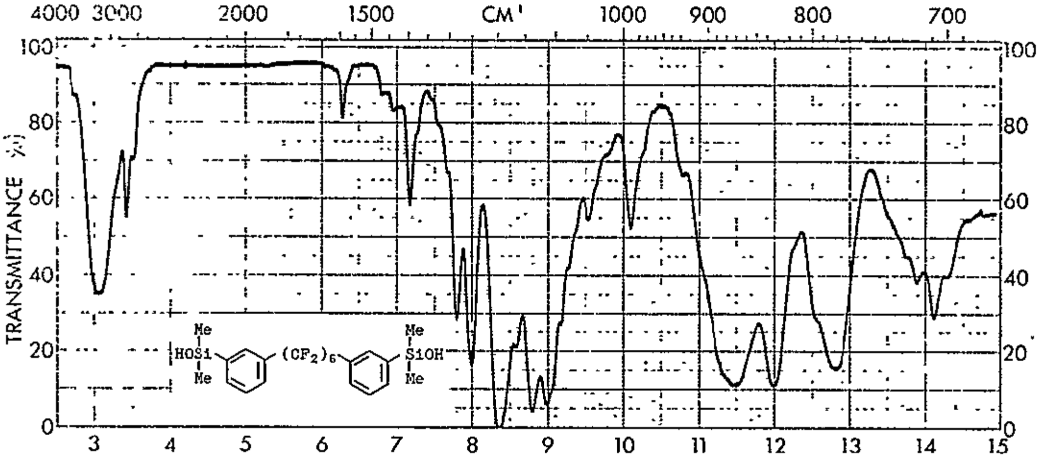

Figure A-20. Dodecafluorohexamethylenebis(3-phenyldimethylsilanol) (123887-B)

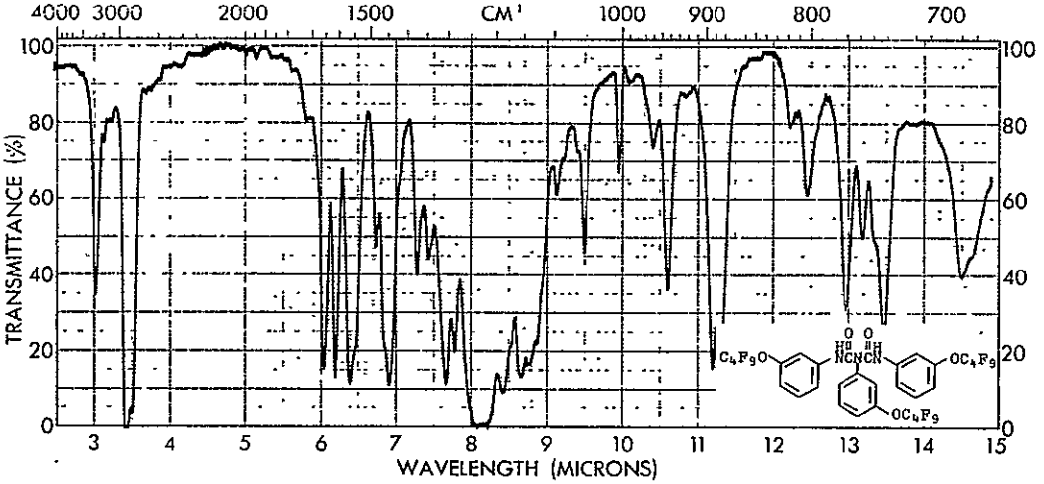

Figure A-21. 1,3,5-Tris(*m*-nonafluorobutoxyphenyl)biuret, Nujol (137014-B)

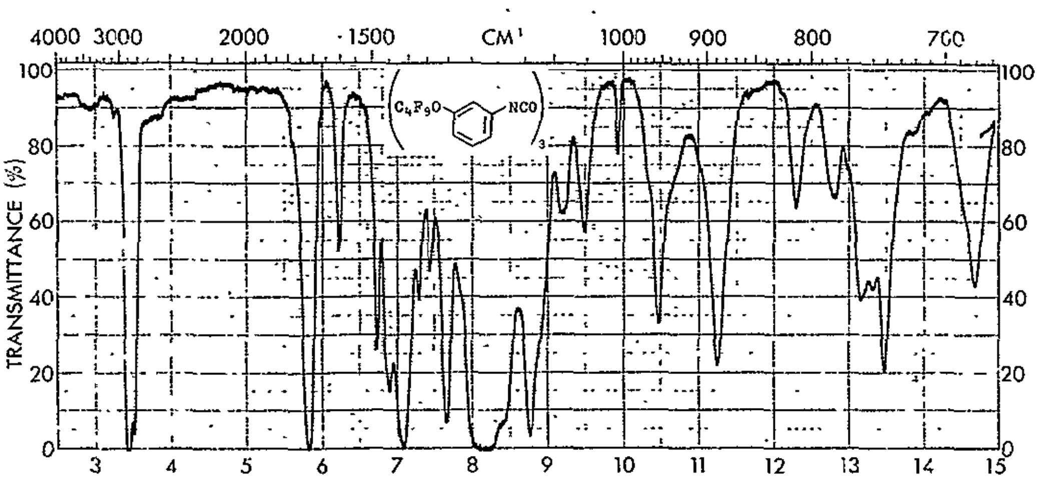

Figure A-22. 1,3,5-Tris(*m*-nonafluorobutoxyphenyl)isocyanurate, Nujol (137041-D)

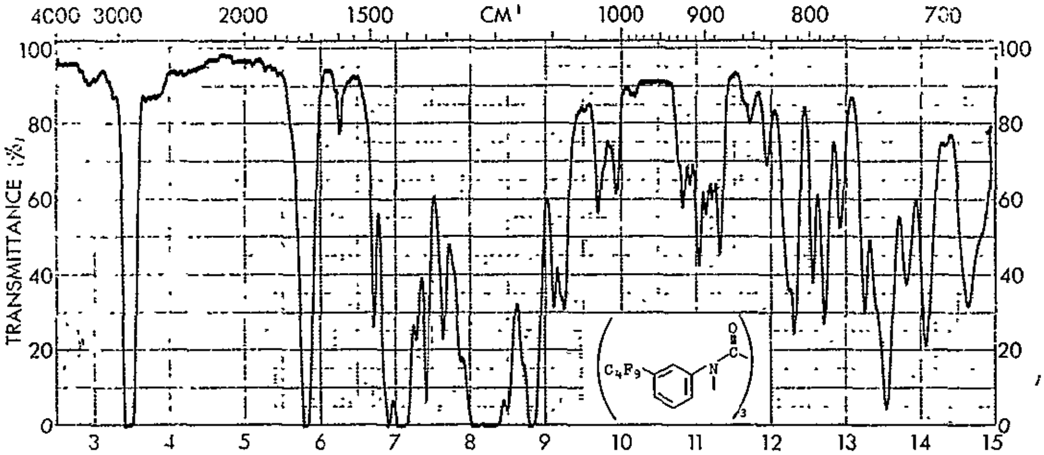

Figure A-23. 1,3,5-Tris(*m*-nonafluorobutylphenyl)isocyanurate, Nujol (137039-D)

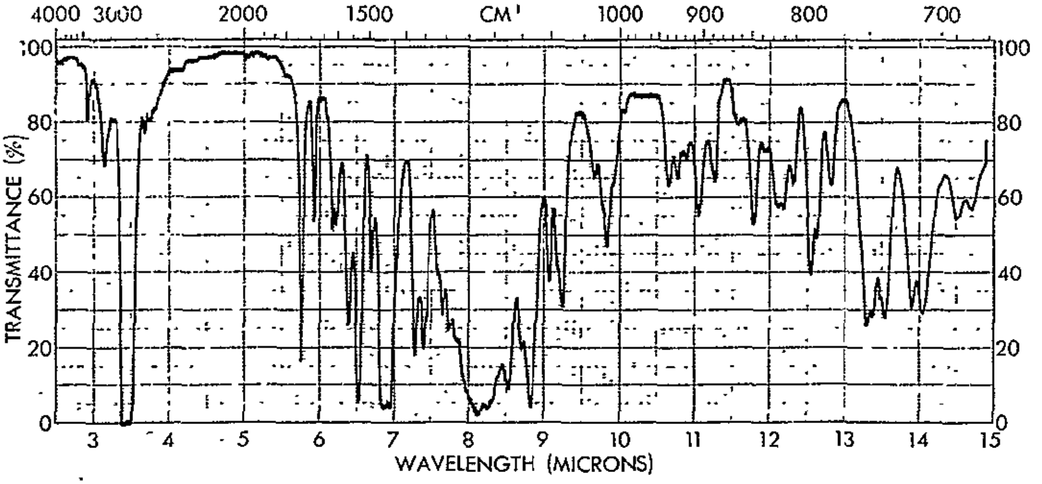

Figure A-24. Isocyanurate By-Product, Nujol (137412)

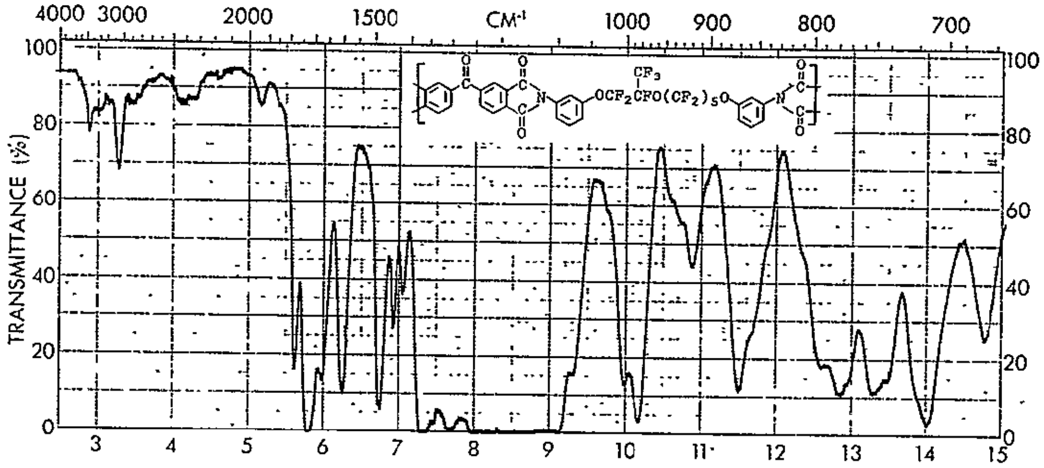

Figure A-25. Imide from 1:1 Amine Derivative (137466)

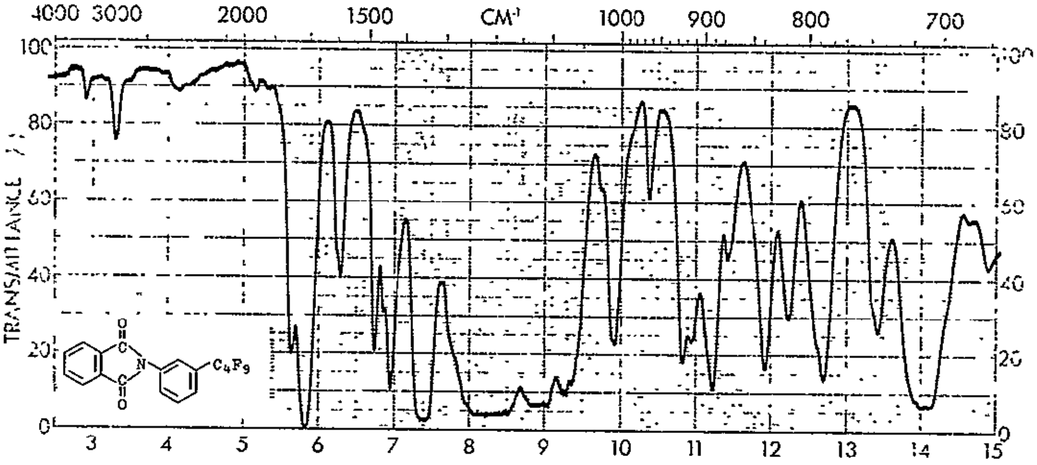

Figure A-26. *N*-(*m*-Nonafluorobutylphenyl)phthalimide

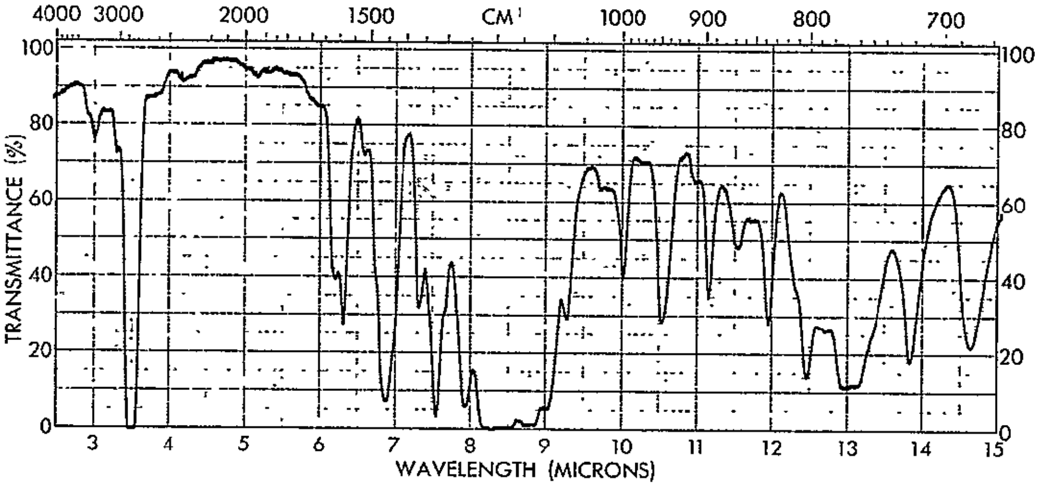

Figure A-27. Azo-coupled 1,5-Bis(*m*-aminophenyl)perfluoropentane (Nujol)

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