Final Report

THERMALLY RESISTANT POLYMERS

FOR FUEL TANK SEALANTS

AUTHOR

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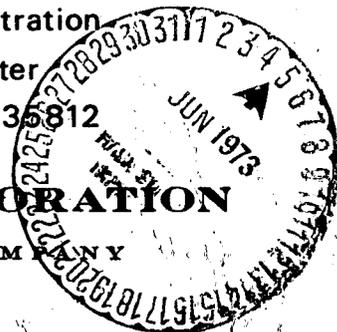
28 June 1971 — 31 December 1972

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

MONSANTO RESEARCH CORPORATION

A SUBSIDIARY OF MONSANTO COMPANY

DAYTON
Monsanto   LABORATORY

DAYTON, OHIO 45407

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FOREWORD

This report is the Final Report prepared by Monsanto Research Corporation, under Contract NAS8-21401, "Thermally Resistant Polymers for Fuel Tank Sealants" for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Astronautics Laboratory, Materials Division, with Mr. W. J. Patterson as principal Contracting Officer's Representative.

The work was performed at the Dayton Laboratory of Monsanto Research Corporation during the period from 28 June 1971 to 31 December 1972 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

New imide-linked perfluoroalkylene ether polymers, that have been
developed for the high temperature fuel tank sealant application,
are discussed. Modifications of polymer structure and properties
were realized through use of a new aromatic dianhydride intermedi-
ate containing an ether-linked perfluoroalkylene segment. Tests
of thermal, oxidative and hydrolytic stability, fuel resistance
and adhesion are discussed along with tensile strength and elonga-
tion results. Efforts to effect a low temperature condensation of
"amic" acid prepolymer to form imide links inside are described.

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I.   INTRODUCTION AND SUMMARY

The objective of this program was the development of improved thermally and oxidatively stable polymers for use as sealants in advanced aerospace structures. The major requirement that the polymer must satisfy is the ability to maintain a seal within a fuel tank for an extended period of time (up to 25,000 hr) while subjected to a variety of adverse conditions. The conditions include exposure to high and low temperatures (-45 to 260°C) in the presence of oxygen, hydrocarbon fuel and moisture. These conditions necessitate a high level of thermal, oxidative, and hydrolytic stability. The polymer must also exhibit adequate physical and chemical characteristics including tensile strength and elasticity, good adhesion, and freedom from stress corrosion of titanium alloys.

The approach to satisfying the severe high temperature and long term serviceability requirements was to achieve a significant advance in thermal and oxidative stability. To accomplish this, perfluoroalkylene ether chain segments were terminated by aryl amine groups and then incorporated into a polymer by coupling through high stability aromatic imide linkages. The manner in which this was done was designed to maximize thermal, oxidative, and hydrolytic stability while imparting elasticity and improved fuel resistance.

During this report period, structure modification and extension of perfluoroalkylene ether segment has been accomplished with significant property improvement. Fluorocarbon segments were also incorporated in the dianhydride component of the polyimide in an effort to improve the low temperature properties of the polymer. Polyimides were prepared from perfluoroalkylene and perfluoroalkylene ether-containing aromatic dianhydrides and the aromatic amine-terminated fluorocarbon ether. Mellitic trianhydride was incorporated into the linear polymers to improve high temperature properties. The resulting polymers exhibited excellent thermal, oxidative, and hydrolytic stability and good tensile strength and elongation from -45 to 260°C. The polymer modifications also increased the fuel resistance, lowered the transition temperature, and improved the high temperature capabilities of the polymer.

Study of the imide-forming reactions was carried out in an effort to effect low temperature cures of polyimides. Rapid formation of imide structures from simple dianhydride and amine derivatives at moderate to low temperatures (25 to 65°C) was shown but efforts to extend the reactions to polymer systems were not successful.

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Further tests will be required to determine if the combination of polymer properties will satisfy the fuel tank sealant polymer requirements. Evaluation of a test configuration under conditions simulating fuel tank sealant use conditions is planned and results will be forwarded to NASA when complete.

The fluorocarbon intermediates and products developed under this contract could be adapted to applications other than fuel tank sealant use. Suggested applications might include other elastomer uses, matrix resins for composites, molding resins, and films.

II.   RESULTS AND DISCUSSION

A.   BACKGROUND AND APPROACH

The Third Annual Summary Report under Contract NAS8-21401 described the development of a synthesis route to high stability aromatic imide-linked perfluoroalkylene ether polymer of the type

$$\left[\begin{array}{c} O \\ \| \\ C \end{array} \cdots R \cdots \begin{array}{c} O \\ \| \\ C \\ | \\ C \\ \| \\ O \end{array} N \cdots O \left(CF_2CF O \atop \overset{|}{C}F_3\right)_x -(CF_2)_5 \left(O\overset{|}{C}FCF_2 \atop CF_3\right)_y O \cdots N \right]_n \quad I$$
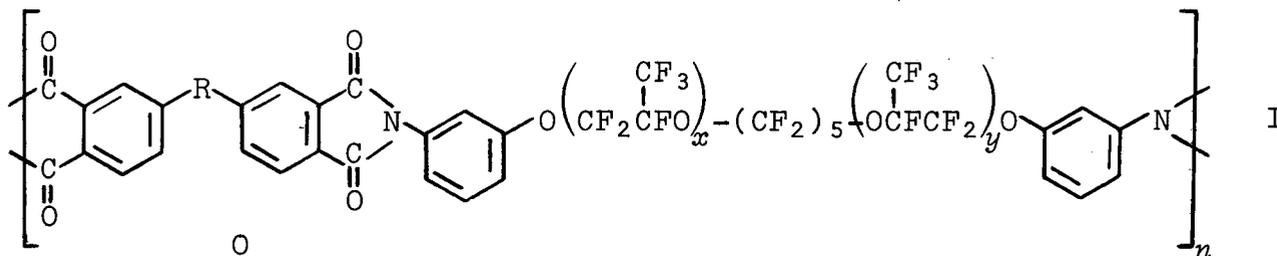
where $R = -\overset{O}{\underset{\|}{C}}-$ and $x + y = 2$ (Ref. 1). The limited evaluation results that were available at that time indicated high stability, fuel resistance and freedom from stress corrosion of titanium alloy. The results were sufficiently encouraging to warrant continuation of this approach.

The objectives during the past year have been to improve the elastomeric character of the polymer through structure modification and extension of the fluorocarbon segment, to characterize and evaluate the physical and chemical properties of the polymer with respect to fuel tank sealant requirements, and to overcome limitations in utilization of the polymer for the fuel tank sealant application. The severe high temperature requirements (up to 260°C) and long-term serviceability (25,000 hr) appeared to necessitate a significant advance in thermal and oxidative stability over currently available sealant polymers. These requirements ruled out aliphatic C-H containing structures, which are more susceptible to oxidative attack than aromatic hydrocarbon moieties. The objective, therefore, was to utilize the perfluoroalkylene ether chain structure to provide chain flexibility and the aromatic imide structure as the chain linking moiety.

A continuing objective this year was to provide a polymer with increased elasticity, and a lower glass transition temperature, in effect, to increase the temperature range over which the polymer exhibits elastomeric properties. Although it is difficult to define the physical property characteristics required for a polymer to function satisfactorily as a sealant, knowledgeable opinion and past experience indicate a need for low temperature elasticity. The relatively high glass transition temperature (~80°C) of the imide-linked fluorocarbon structure shown above and reported previously was suspected of being too high for adequate low temperature service. It is recognized,

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of course, that other factors such as the adhesive strength, ductility, and modulus of a specific polymer could also affect the T_g requirement.

One approach to lowering the T_g was to increase the length of the fluorocarbon ether chain segment in the diamine. A second approach was to incorporate the fluorocarbon segment and ether linkages into the dianhydride. The combination of these modifications resulted in lower T_g and improved flexibility with no adverse effects on stability. Appreciable synthesis effort was involved in this tailoring of polymer structure to this specific application.

B.   SYNTHESIS OF POLYMER INTERMEDIATES

1.   Synthesis of Aminophenoxy-Terminated Perfluoroalkylene Ether

a.   3:1 Oligomer Diamine

Development of the synthesis route for preparation of aromatic amine-terminated perfluoroalkylene ether intermediates of the type

$$H_2N-\bigcirc-O\left[CF_2\underset{\underset{CF_3}{|}}{C}FO\right]_x(CF_2)_5\left[O\underset{\underset{CF_3}{|}}{C}FCF_2\right]_yO-\bigcirc-NH_2 \qquad II$$
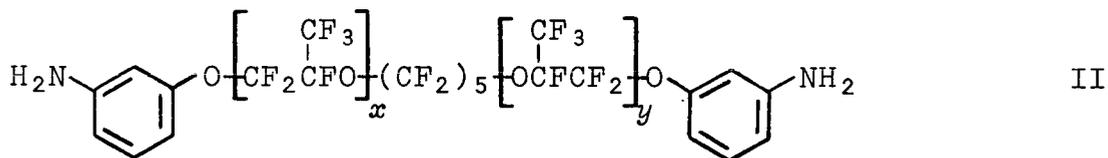
shown by structure II, where $x + y$ = 0, 1 and 2, was summarized in the Third Annual Summary Report (Ref. 1). Briefly, the synthesis route involved preparation of the nitrophenyl ester of a perfluoroalkylene ether dicarboxylic acid, SF_4 fluorination of the ester to form the ether structure, and subsequent catalytic

$$O_2N-\bigcirc-O\underset{\underset{O}{\|}}{C}R_f\underset{\underset{O}{\|}}{C}O-\bigcirc-NO_2 \xrightarrow{SF_4} O_2N-\bigcirc-OCF_2R_fCF_2O-\bigcirc-NO_2$$
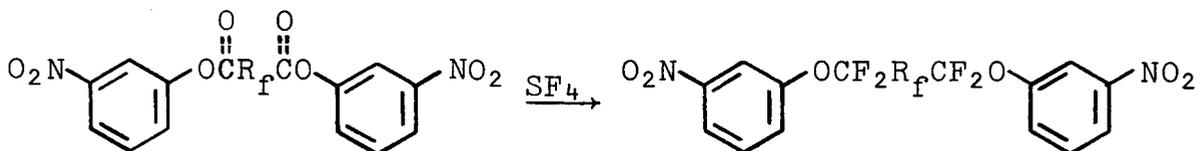
reduction of the nitro groups to form the diamine.

Each step in the synthesis of the diamine was relatively straightforward and gave high yields (>80%) with the exception of the SF_4 fluorination step. Although considerable progress in the fluorination step was achieved and reported in the previous report, we were not confident that a comparable yield would be assured upon scale-up of this fluorination step. Because of the limited supply of the perfluoroalkylene ether intermediates, it was essential that as high a yield as possible be obtained.

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Consequently, scale-up of the fluorination reaction was approached conservatively by carrying out additional fluorination experiments with the ester derived from the 2:1 acid (i.e., the ester that would give the diamine II where $x + y = 2$). A somewhat larger supply of this intermediate was available. The results obtained in these experiments are summarized in Table 1 and discussed below.

Experiment 139660 represents the maximum yield (50% purified product) previously reported (Ref. 1). When the quantity of reactants was increased slightly, the proportion of HF doubled, and a 10°C higher temperature employed, (139694) the yield decreased considerably and an appreciable quantity of polymeric residue was formed. When a similar charge of reactants was heated at 80°C in a larger reactor (142704), very little product was formed and there was an appreciable recovery of unreacted ester, indicating incomplete reaction. This experiment was repeated at 90°C (142707) with the result that a low yield of viscous, tarry product was obtained. The poor results obtained in the larger reactor were attributed to the lower reaction pressure that undoubtedly prevailed, and insufficient anhydrous HF to maintain a liquid phase. Rough calculations indicated a need for more than 15 g HF to ensure presence of a liquid phase at 80°C in the reactor having a volume of 1370 ml. The quantity of HF was increased significantly in experiment 142713 and the result was a reasonable yield (42%) of purified, distilled nitrophenoxy intermediate. Finally, in experiment 142716 the charge of ester, sulfur tetrafluoride, and fluorocarbon solvent was increased several times but with only a minor increase in the quantity of hydrogen fluoride. A significant increase in the yield of the product suggested that an increase in pressure also favored higher yields.

Two additional experiments were carried out in an attempt to determine whether the perfluorotributylamine solvent, FC-43, might give a significantly better yield than the perfluorobutyl-tetrahydrofuran solvent, FC-75. A previously reported comparison of these solvents suggested a slight advantage in yield obtained with the appreciably more expensive FC-43, and experiments 142708 and 142709 appeared to confirm the earlier results.

With the above experiments providing additional insight into the variables affecting the ester fluorination reactions, scale-up of the 3:1 ester fluorination reaction was carried out in 49% yield as shown in Table 2. The purification in each example included hydrolysis of unreacted ester and isolation of the nitro-phenoxy product by distillation.

An additional 1500 g of perfluoroalkylene ether dicarboxylic acid fluoride was subsequently purchased from PCR, Inc. as a mixture of 1:1, 2:1, 3:1, and 4:1 oligomer products. The 3:1 intermediate was isolated by distillation and converted to

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Table 1

SF$_4$ FLUORINATION OF 2:1 NITROPHENYL ESTER INTERMEDIATES[1]

Experiment No.	Ester Wt, g	Wt SF$_4$, g	Wt HF, g	Reactor Volume, ml	Solvent ml	Time, hr	Temp, °C	Results
139660	12	12	10	330	100 FC-75	56	80	40-50% purified
139694	15	15	25	330	150 FC-75	91	90	<20% crude
142704	15	15	15	1370	150 FC-75	66	80	12% crude
142707	10	15	15	1370	150 FC-75	62	90	tar and solids
142713	10	15	60	1370	100 FC-75	60	80	42% distilled
142716	50	50	75	1370	500 FC-75	66	80	65% yield of distilled 2:1 product
142708	5	5	10	330	57 FC-75	60	80	34% distilled
142709	5	5	10	330	57 FC-43	60	80	42% distilled

[1]Ester derived from 2:1 oligomer of hexafluoropropylene epoxide and perfluoroglutaryl fluoride

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Table 2

COMPARISON OF SF$_4$ FLUORINATIONS OF 3:1 ESTER

	142719[1]	142774	142784	147215	147232
Experiment No.					
Reactor Volume	1340[2]	3470[3]	3470[3]	1340[2]	1340[2]
Relative Volume	1	2.5	2.5	1	1
Charge of 3:1 Ester, g	40	123	100	40	40
Charge of HF, g	75	134	209	75	75
Charge of SF$_4$, g	50	122	125	50	50
FC-75, ml	500	1250	1250	500	500
Reaction Time, hr	89	95	84	89	89
Reaction Temperature, °C	80	80	80	80	80
Yield, fluorination reaction, %	49	39	34	42	45
n_D^{25}, Nitro Compound	1.3941-1.3944	1.3931	1.3941-1.3944	1.3916-1.3941	1.3939
n_D^{25}, Amine Compound	1.3919-1.3922	1.3915	1.3919-1.3921	1.3919	

[1]Previously reported.
[2]Hastelloy C
[3]Stainless Steel

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nitrophenyl ester. Results of five fluorination experiments with the 3:1 ester are summarized in Table 2. Fluorination experiments performed in a 3400 ml stainless steel reactor resulted in somewhat lower yield (39% vs 49%) than the experiment carried out in a 1380 ml Hastelloy reactor. The relative amounts of each reactant used in the scale-up were reasonably close to those previously used although the HF was decreased to a proportion that had given good results in a 330 ml pressure vessel. We have suggested the importance of reactor volume and ratio of reactants, for we believe these factors affect or determine the nature of the liquid phase, the quantity of ester and/or SF_4 in solution, and reaction pressures. Although these factors still seem valid, the inability to duplicate the yield shown by the first experiment in Table 2 suggested that additional variables were not identified. The low yields in the fluorination step were accompanied by the formation of appreciable by-product. While much of the by-product appears as tarry residues, an effort to isolate specific products was made in an attempt to resolve the poor yield problem.

Work-up and distillation of a benzene-insoluble fraction led to isolation of two products which were identified as

$$O_2N-\text{C}_6\text{H}_4-OCF_2\overset{\overset{\displaystyle CF_3}{|}}{CF}O(CF_2)_5O\overset{\overset{\displaystyle CF_3}{|}}{CF}CF_2O\overset{\overset{\displaystyle CF_3}{|}}{CF}CF_3$$

and

$$O_2N-\text{C}_6\text{H}_4-OCF_2\overset{\overset{\displaystyle CF_3}{|}}{CF}O(CF_2)_5O\overset{\overset{\displaystyle CF_3}{|}}{CF}CF_2O\overset{\overset{\displaystyle CF_3}{|}}{CF}COOH$$
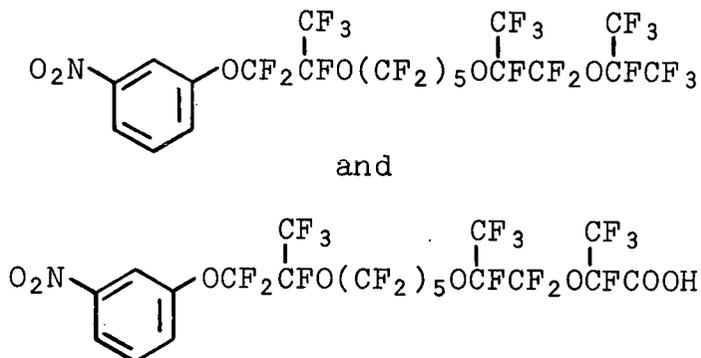
The first product is presumed to have formed by hydrofluorinolysis of the ester followed by fluorination of the resulting acid fluoride as shown below

$$\sim\sim O-\overset{\overset{\displaystyle CF_3}{|}}{CF}-\overset{\overset{\displaystyle O}{\parallel}}{C}-O-\text{C}_6\text{H}_4-NO_2 \xrightarrow{HF} \sim\sim O-\overset{\overset{\displaystyle CF_3}{|}}{CF}-\overset{\overset{\displaystyle O}{\parallel}}{CF} + HO-\text{C}_6\text{H}_4-NO_2$$

$$\sim\sim O-\overset{\overset{\displaystyle CF_3}{|}}{CF}-\overset{\overset{\displaystyle O}{\parallel}}{CF} + SF_4 \longrightarrow \sim\sim O-\overset{\overset{\displaystyle CF_3}{|}}{CF}-CF_3$$

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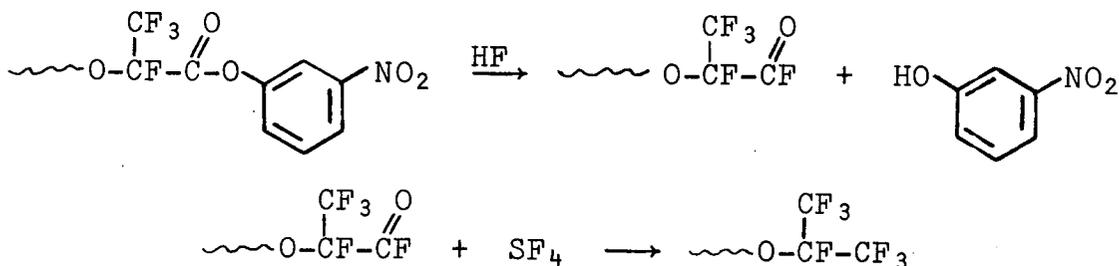
The carboxylic acid product probably was formed subsequent to the fluorination step by hydrolysis of the partially fluorinated ester with aqueous alkali.

$$O_2N\!-\!\langle\text{ring}\rangle\!-\!OCF_2R_fC(\!=\!\!O)O\!-\!\langle\text{ring}\rangle\!-\!NO_2 \quad \xrightarrow[\text{(2) H}^+]{\text{(1) NaOH}} \quad O_2N\!-\!\langle\text{ring}\rangle\!-\!OCF_2R_fCOOH$$
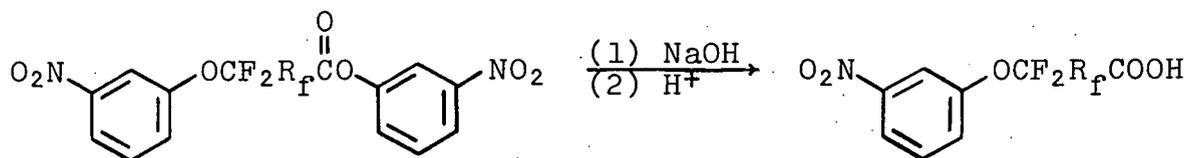
In effect the products suggest both incomplete or insufficient fluorination and competing side reactions, explaining to some extent why reaction conditions appear to be so critical.

b.   Assay and Purification of the 3:1 Diamine

High purity and a high degree of difunctionality were considered essential for optimum polymer properties but required an accurate assay of the diamine preparations. The assay method previously described was a potentiometric titration of the diamine in glacial acetic acid using perchloric acid in glacial acetic acid as the titrant (Ref. 1). Originally the titrating solution was standardized against potassium acid phthalate as a base. Titration of the diamine resulted in high neutral equivalent values. Subsequent standardization of the perchloric acid against purified p-chloroaniline along with refinements in the method gave more acceptable results but left doubt as to which results were more accurate. Further verification of the titration results was carried out by standardization of the perchloric acid solution against a second aromatic amine, 2-aminobiphenyl, purified by two recrystallizations. Titrations were performed potentiometrically in glacial acetic acid. Standardization results obtained with the two aromatic amines showed good agreement with less than 0.5% average difference whereas the results obtained using KHP as the standard differed by about 3%. The average concentration value of $HClO_4$ obtained with p-chloroaniline (distilled and recrystallized three times) and the 2-aminobiphenyl was then accepted. Neutral equivalents of two fluorocarbon diamine preparations were found to be 490 and 493 compared to the calculated value of 482. The 3:1 diamine fractions were then combined and redistilled. The neutral equivalent values of the center fraction were then found to be 483 and 484 compared to the calculated value of 482.

c.   Attempted Preparation of 4:1 Oligomer Diamine

The 4:1 oligomer acid fluoride intermediate was also converted to dicarboxylic acid, and then in turn to the acid chloride and the nitrophenyl ester with 92%, 89% and 89% yields of the respective distilled products. A small-scale trial fluorination of the ester intermediate resulted in incomplete reaction as determined by IR spectrum. No further attempts were made to develop proper conditions for conversion of this ester to diamine intermediate.

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2. Dianhydride Modifications

a. 1,6-Diphenylperfluorohexane-3,3',4,4'-tetracarboxylic Dianhydride

Characterization and evaluation of polyimide prepared from the 3:1 diamine (II) and benzophenonetetracarboxylic dianhydride indicated a need for increased solvent resistance and lower glass transition temperature (T_g). One approach for lowering the T_g was to increase the length of the fluorocarbon ether segment in the diamine. The present amine synthesis route, however, shows diminishing returns as the fluorocarbon content is increased. A second approach, the modification of the di-anhydride, appeared to be more easily accomplished.

Introduction of a fluorocarbon segment into the dianhydride reactant appeared to offer two possible advantages. One was an unexpected increase in molecular mobility resulting from substitution of a linear aliphatic chain segment for the single carbonyl moiety while the second was the introduction of an electron withdrawing fluorocarbon substituent. Although the latter effect was thought to be small, it was expected to increase the acidity of the tetracarboxylic acid and, as a consequence, the stability of resulting imide linkage. For these reasons the dianhydride, III, was synthesized by the following sequence of reactions. The synthesis route has been reported by Critchley, et al. (ref. 2).
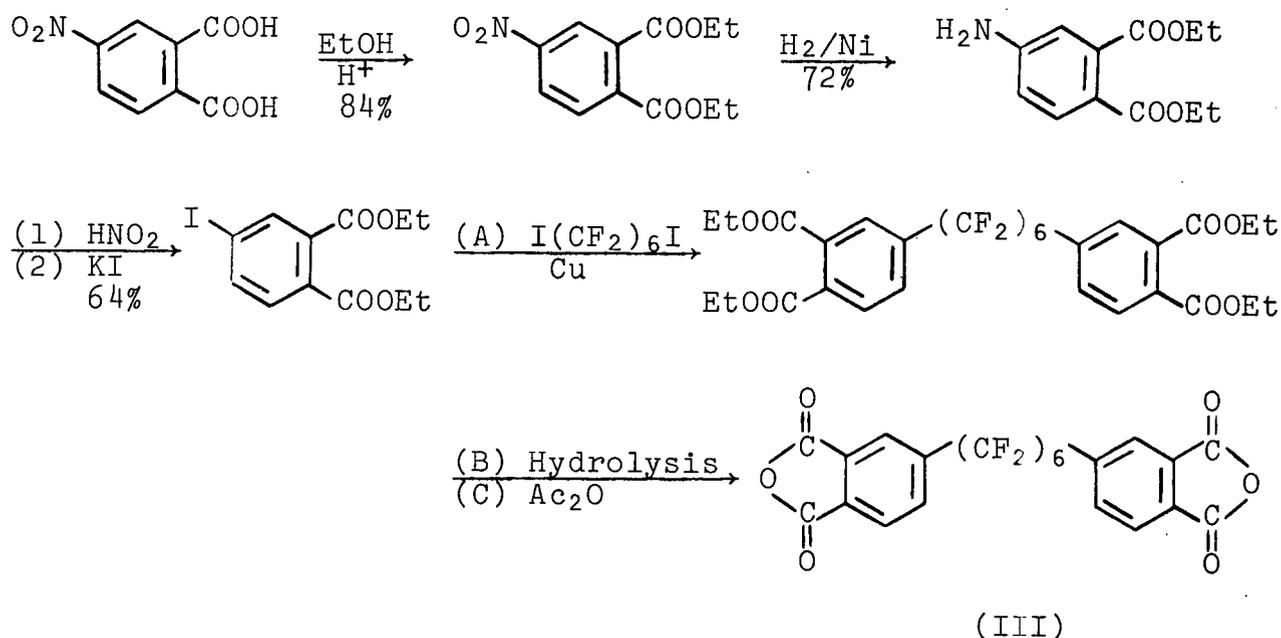

Yield of steps A→C = 65%

Synthesis of the iodophthalic acid intermediate by direct iodina-
tion of phthalic acid has been reported (ref. 3, 4) but several
attempts to carry out this reaction were without significant
success. The alternative route reported by Blicke and shown above
was therefore employed for synthesis of the iodophthalic ester
(ref. 5).

The decrease in polymer glass transition temperature gained by
employing the above dianhydride in polyimide preparation was
approximately 20°C. A further decrease in T_g was anticipated if
the aryl and fluorocarbon moieties of the above dianhydride could
be linked through an ether oxygen. This additional structural
modification of the dianhydride was undertaken as described below
in an attempt to improve the low temperature properties of the
polymer.

> b.   1,5-Diphenoxydecafluoropentane-3,3',4,4'-tetracarboxylic
>   Dianhydride

The proposed synthesis route to an aryl ether perfluoroalkylene
linked dianhydride of the type
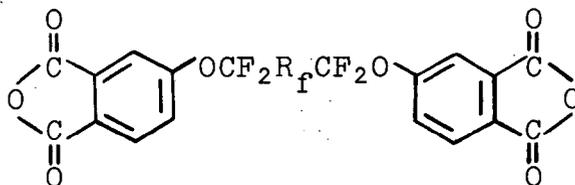
depended on preferential hydrolysis of $-CF_3$ substitutents of an
aryl ring without attack on a perfluoroalkoxy substituent. This
reaction was demonstrated in a trial experiment by hydrolyzing
the $-CF_3$ of m-trifluoromethylphenyl perfluorooctyl ether to the
corresponding benzoic acid without attacking the perfluoroalkoxy-
linkage.
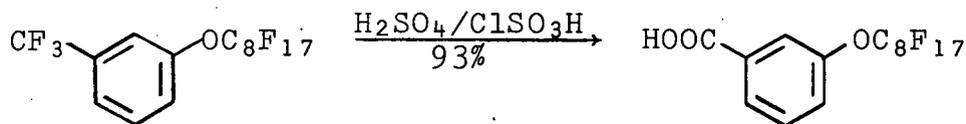
Success with this reaction was followed by synthesis of the
ether-linked tetracarboxylic dianhydride shown by the sequence of
reactions in Figure 1. In the first step, fluorination of nitro-
phthalic acid with SF_4 afforded a relatively high yield (70%) of
3,4-bis(trifluoromethyl)nitrobenzene. When an increased propor-
tion of anhydrous hydrogen fluoride was employed in a subsequent

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Figure 1.   Reaction Sequence for Synthesis of 1,5-Diphenoxydecafluoropentane-3,3',4,4'-tetracarboxylic Dianhydride

preparation of this intermediate there was an increase in the formation of a close-boiling by-product, which was subsequently identified as 5-nitro-1,1,3,3-tetrafluorophthalan,

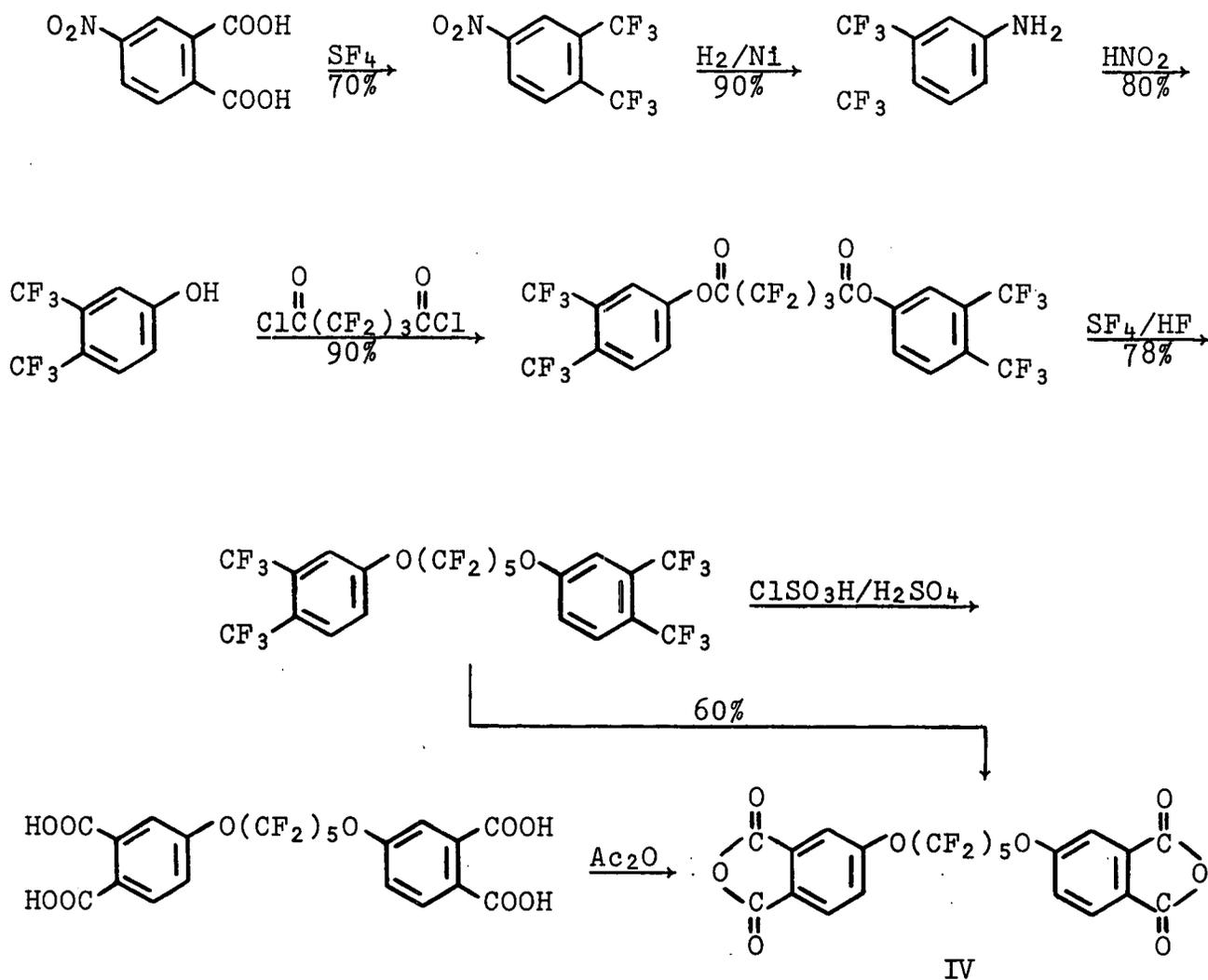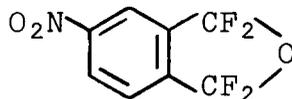$$O_2N-\underset{CF_2}{\overset{CF_2}{\bigcirc}}O$$

Use of a fraction containing this impurity was an unfortunate decision because it appears to have been responsible for lower yields and increased difficulty in purifying products in succeeding steps. This difficulty probably could be avoided or minimized by more careful purification of this first intermediate by distillation.

Catalytic reduction of fluoroalkyl nitro aromatic compounds has generally given near quantitative yields of the corresponding amines. Unexpected difficulty and the poor yield that was experienced in a resynthesis of the bis(trifluoromethyl)aniline intermediate was attributed to catalyst poisons, incomplete reduction, and thermal decomposition with concommitant formation of acidic products during distillation. In a subsequent experiment the nitro compound was slurried first with Raney nickel to remove catalyst poisons, filtered, and then reduced over fresh catalyst without difficulty. Thermal decomposition and formation of acidic products occurred once again during distillation. After washing the crude product with aqueous alkali, the distillation was continued without difficulty. The product had an appreciably higher refractive index suggesting that the difficulty may be associated with the presence of the cyclic by-product impurity discussed above.

Initially, low yields ($\sim$25%) were obtained in the conversion of the amine derivative to phenol, presumably because of the low base strength and insolubility of the fluoroaliphatic aromatic diamine in aqueous acid. A modified diazotization procedure, in which sodium nitrite dissolved in concentrated sulfuric acid was added to a solution of the amine in concentrated sulfuric acid, afforded an 80% yield of the phenol derivative.

Esterification and ester fluorination steps resulted in good yields. An attempt to extend the fluorocarbon segment by incorporating the 2:1 perfluoroalkylene ether segment into the dianhydride was not successful, however. Although the ester of the 2:1 acid was prepared in high yield, the fluorination of the ester failed. Success with this reaction probably can be achieved through modification of reaction conditions.

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Significant improvement in the final step, the hydrolysis of
3,3',4,4'-tetrakis(trifluoromethyl)-1,5-diphenoxydecafluoropentane,
isolation and purification of the tetracarboxylic acid and sub-
sequent conversion to dianhydride, IV, raised the 25% yield
obtained initially to ∿60%. Extensive purification, including
repeated recrystallization of the tetra acid as well as a second
sublimation of the dianhydride product, resulted in a product
considered to be of high purity.

3. Miscellaneous Syntheses

The possibility that a new fluorinating agent, MoF_6, available
as a methylene chloride solution under the name Fluoreeze could
be used to fluorinate the nitrophenyl esters was investigated.
The results of a single experiment were not encouraging. The
reagent, which is considered less powerful than SF_4, showed no
evidence of ester fluorination.

An attempt was made also to convert a simple bis(aminophenoxy)-
perfluoroalkylene to the corresponding bromophenoxy derivative
via the Sandmeyer reaction. Apparently the amine was not
diazotized under the conditions that were employed despite success-
ful conversion of bis(trifluoromethyl)aniline to the bromo deriva-
tive. The reaction appears potentially useful, however, and the
bromo compound could be of interest in other polymer syntheses.

C. CHARACTERIZATION AND EVALUATION OF IMIDE-LINKED PERFLUORO-ALKYLENE ETHER POLYMERS

1. Fluorocarbon Polyimide Preparation

The polyimide polymers were prepared in a conventional manner
(ref. 6) by addition of aromatic dianhydrides to diamine
dissolved in dimethylacetamide. Formation of the fluorocarbon
polyamic acids takes place more slowly than with conventional
polyimides, presumably because of the lower base strengths of
the fluorocarbon aromatic diamines. An appreciable increase
in solution viscosity became apparent only after stirring over-
night whereas with conventional polyimides a maximum viscosity
is normally attained within a few hours. Evaporation of solvent
and gradual heating to 150-200°C (resulted in condensation of
the polyamic acid to the cyclic imide.

The variations in the polyimide polymer composition that were
investigated are represented by the polyimide structure

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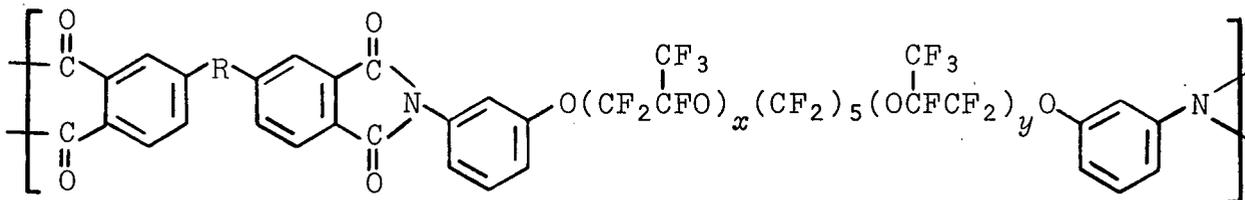
	R	$x + y$	T_g °C
Composition A	C=O	2	∿110
Composition B	C=O	3	∿80
Composition C	$-(CF_2)_6-$	3	∿60
Composition D	$-O(CF_2)_5O-$	3	∿40

As the R group of the dianhydride was varied from $-\overset{\overset{\text{O}}{\|}}{\text{C}}-$ to $-(CF_2)_6-$ to $-O(CF_2)_5O-$, the T_g of the polymers decreased from ∿110 to ∿40°C. Increased molecular flexibility was accompanied by increasing solubility in solvents, such as acetone and dimethylacetamide, and lower softening points.

Solutions of the polyimide in acetone or dimethylacetamide could be recast to produce films which exhibited high strength and elongations. Compression molding of the linear polymers at 150°C was demonstrated also. These characteristics indicated a non-crosslinked high polymer. Because of the tendency to flow at 150°C a small proportion of a trifunctional crosslinking agent was incorporated into polymers C and D to impart high temperature mechanical stability and increased solvent resistance. The resulting crosslinked polyimide exhibited high stability and appreciable tensile strength and elongation at temperatures as high as 300°C.

The diamine and dianhydride reactants were usually employed in stoichiometric proportions. Small deviations from 1:1 proportions showed little apparent changes in physical or mechanical properties. Purity of the difunctional intermediates was more important and significant improvement in tensile strength and elongation was achieved through careful purification of the diamine and dianhydride intermediates.

2. Tensile Strength and Elongation

Tensile strength and elongation measurements were determined using microtensile test specimens. The specimens were cut with the aid of a non-standard die, similar in shape but smaller than that designated by ASTM procedure D-412-64T. The die dimensions, designated by the ASTM procedure as A, C, L, and W, were 8, 44, 17 and 2.6 mm, respectively.

The tensile strength measurements carried out using microtensile test specimens approximate but may differ from values obtained using standard tensile test specimens. The reported elongation

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values are based on crosshead travel because of the inability
to use an extensiometer. If the length of the necked-down
portion of the die is considered the gauge length, the results
will be too high when appreciable elongation occurs within the
entire length of the specimen, between the grips. On the other
hand, inspection of elongated, cold drawn specimens showed that
the elongation of some specimens occurred primarily within the
necked-down portion. Because of this, maximum and minimum
elongation values are shown in Table 3. The maximum elongation
results are based on the 17 mm gauge length, and minimum values
are those based on 23 mm, the specimen length between grips.

The tensile data in group A, Table 3, show relatively small
variation in tensile strength and elongation values as a
consequence of small changes in stoichiometry. The proportions
of the reactants in this group were based on calculated equiva-
lent weights. The equivalent weight of the 2:1 diamine used in
these experiments as determined by titration was 411 whereas the
calculated value was 399. Part of the discrepancy in calculated
and experimental equivalent weight values probably rests with
inaccuracy in the earlier titration method already discussed,
but the results no doubt also indicate amine impurities. Thus
the significance of the results is reduced by a degree of
uncertainty in the stoichiometry. Relative viscosities of the
polyamic acid solutions from which these polymer samples were
prepared decreased in a consistant manner as the proportion of
diamine was increased. It may be significant that the maximum
tensile and elongation values correspond to a 1.03 ratio of amine
to anhydride based on theoretical equivalent weights and that this
ratio corresponds to 1:1 proportions if based on the experimental
equivalent weight (assay) values.

Tensile and elongation results in group B of Table 3 are those of
the polyimide prepared from the 3:1 oligomer diamine with benzo-
phenonetetracarboxylic dianhydride. The data show high elonga-
tions and low strengths at the elevated temperatures, particularly
at 200°C.

Polyimide polymers prepared from 1,5-diphenyldodecafluorohexane-
tetracarboxylic dianhydride, shown in Table 3 as group C, included
∿10% of the anhydride as mellitic trianhydride to overcome the
low melting point of the linear polymer. The lower tensile
strengths of polymer preparations 147204 and 142958 reflect the
effects of impurities in the diamine and dianhydride intermediates.
Higher purity intermediates used for experiments 149229 to 149231
resulted in significantly higher tensile strength.

Replacement of the fluorinated anhydride by the analog contain-
ing ether oxygens between the aryl ring and the perfluoroalkylene
segment gave the polyimide represented by data in group D.
Specimen 149669 was prepared by pouring the polyamic acid
solution into a film mold 1 hour after mixing the reactants.

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Table 3

TENSILE STRENGTH AND ELONGATION OF POLYIMIDE

$$\left[\begin{array}{c} \text{O} \\ \text{C} \\ \text{C} \\ \text{O} \end{array} R \begin{array}{c}\text{O}\\\text{C}\\\text{C}\\\text{O}\end{array} N \right] O\left(CF_2CFO\right)_x(CF_2)_5\left(OCFCF_2\right)_y O \cdots N \Bigg]$$

$$x + y =$$
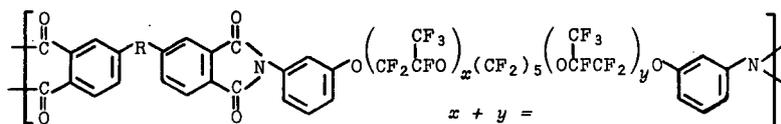
	Composition (Equiv. Fraction of Reactants)								% Elongation	
	Anhydride, R =			Amine x + y =		Mellitic	Cure Temp.	Test Temp.	Tensile Strength,	0.9	0.65
Sample No.	C=O	$(CF_2)_6$	$O(CF_2)_5O-$	2	3	Trianhydride	°C	°C	psi	gauge	gauge[4]
COMPOSITION A											
142742	1.0			0.98			180	25[2]	6300	110	160
142745	1.0			0.99			180	25[3]	6100	100	150
142746	1.0			1.00			180	25[3]	6300	90	120
142743	1.0			1.01			180	25[3]	7300	140	200
142744	1.0			1.03			180	25[3]	7600	150	215
COMPOSITION B											
142731A	1.0				1.0		260	25[3]	8000	250	350
								100[2]	2700	550	750
								200[1]	100	360	500
142731B	1.0				1.0	70 hr @	260	25[3]	6900	210	290
COMPOSITION C											
147204		0.9 (impure)			1.0	0.1	180	25[2]	3300	700	1000
								100[2]	90		
								200[1]	10	310	430
							250	25[2]	3200	250	265
								100[1]	210	900	1200
142958		0.9			1.0	0.1	230	25[3]	5100	240	360
142965		0.85			1.0	0.15	180	25[2]	3700	200	280
								100[1]	200	400	550
142968		0.9			1.0	0.1	200	25[2]	3700	280	400
								100[1]	250	430	600
147229		0.9			1.0	0.1	250	25[2]	6800	270	375
147230		0.9			1.0	0.1	250	25[2]	6200	240	340
147231A		0.85			1.0	0.15	250	25[2]	6400	230	320
								-43[2]	7200	60	90
								288[2]	80	85	120
COMPOSITION D											
149669			0.9		1.0	0.1	200	-43[3]	5900	60	80
								25[2]	5200	230	320
								288[2]	165	70	100
149670			0.9		1.0	0.1	200	-43[2]	7000	140	190
								25[2]	8500	290	400
								288[2]	190	50	65
149676			0.92		1.0	0.1	200	-43[2]	7300	130	180
								25[3]	6100	300	420
								288[2]	130	50	70

[1] Single specimen
[2] Two specimens
[3] Three specimens
[4] Range – depending on effective gauge length

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Specimen 149670 was prepared from the same polyamic acid solution but after it had been stirred overnight at 25°C. The higher tensile strengths of the latter indicate an advantage in allowing sufficient time for the polyamic acid to attain maximum molecular weight. The properties of polymer 149676 prepared with 2% excess anhydride were not significantly different from 149670.

3.   Polymer Stability Evaluation

Resistance to jet fuel and to effects of oxidation products and water that might be formed in fuel tanks subjected to aerodynamic heating is essential if a material is to function as a fuel tank sealant. Evaluation of thermal, oxidative, and hydrolytic stability, therefore, was considered an important and continuing part of the polymer development. The evaluation results reflect the quality of the intermediates and their effect on molecular weight, the composition of the polymer, and the degree of crosslinking. Because some of the test data were obtained earlier in the testing program on specimens prepared from intermediates that may have been of less than optimum quality, some of the results may represent less than optimum properties. Consequently, the comparison of evaluation results versus polymer compositions shown in Table 3 may not be entirely valid.

High thermal and oxidative stability of the imide-linked fluorocarbon polymers is indicated by the thermogravimetric analyses (Figure 2). The plot of weight loss as a function of time and temperature of polymer compositions B, C, and D were very similar and showed little or no weight loss below 450°C.

Qualitative evaluation of polymer films exposed to high temperatures, to fuel environments, and to hydrolysis conditions showed varying degrees of adverse effects. The non-crosslinked composition B after refluxing for 7 days in jet fuel under conditions of air oxidation was severely degraded. Weight increases of 20 to 30% and formation of gummy residues of low strength resulted. In the absence of air the same conditions resulted in little apparent change to the polymer film and only small weight gain (<5%). Aldehydic and ketonic oxidation products that are formed in the fuel were probably responsible for some adverse effects. Fuel-air degraded polymer was found to be fairly soluble in acetone. Evaporation of the solvent from dissovled polymer left a film of polyimide indistinguishable by infrared analysis from the original polymer. These observations suggested that the polymer had degraded by occasional rupture of the polyimide chain with resultant formation of lower molecular weight, acetone soluble polyimide fragments and consequent loss of the desired mechanical properties. These characteristics could represent hydrolytic degradation but could also be the consequence of an occasional fault or imide bonding failure in the original polymer chain giving rise to a less stable linkage. The crosslinked
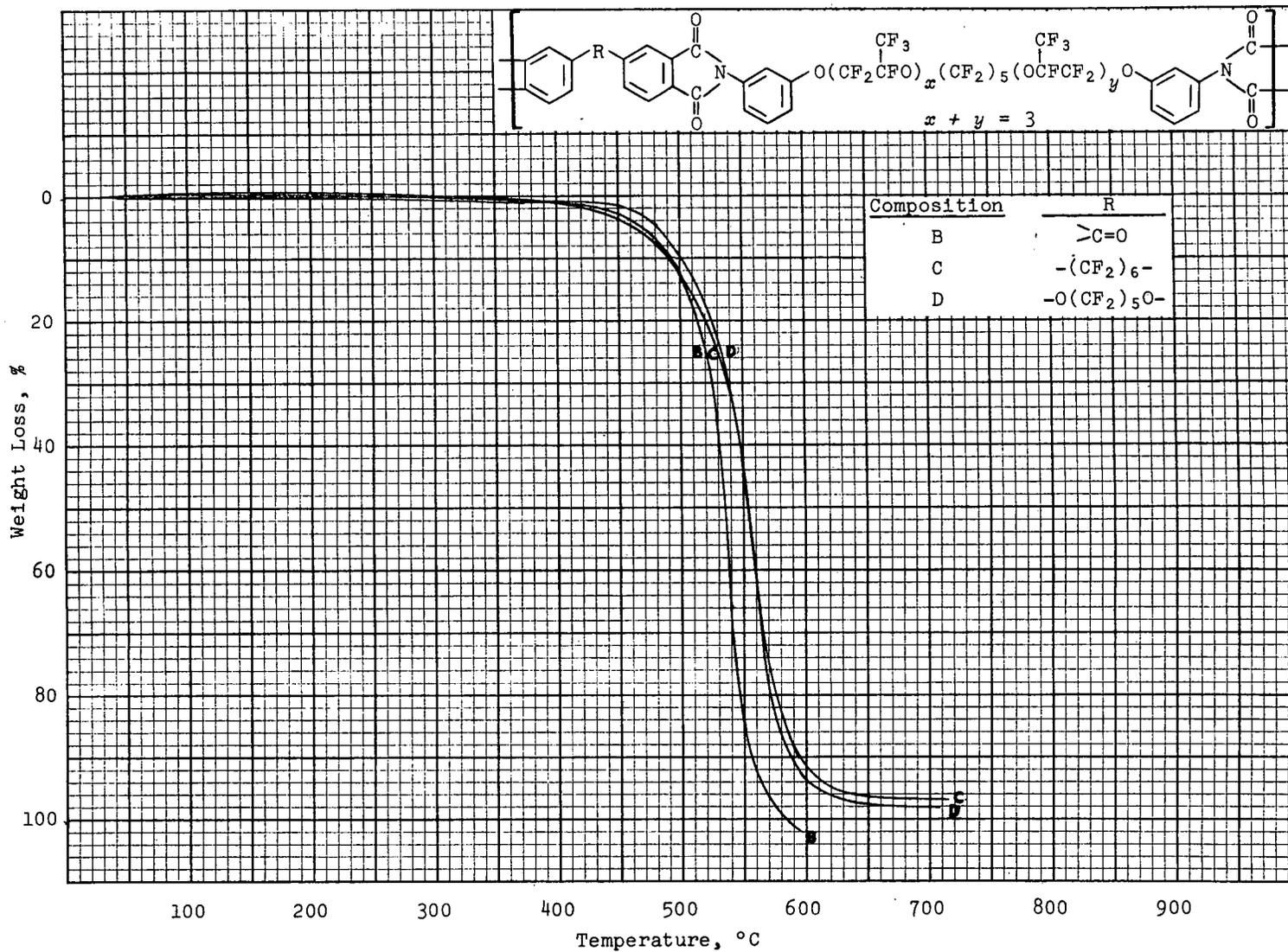
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Figure 2.   Thermogravimetric Analysis of Polyimide in Air, 2.8°C/minute

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polymer, D, when refluxed in fuel exposed to air, showed appreciable resistance to degradation.

Determination of tensile strengths and elongations before and after exposure to various environmental conditions, as shown in Table 4, provided a more quantitative indication of the adverse effects of the conditions. The results parallel the qualitative results already described. Thermal exposure of the non-crosslinked polymer composition B at 260°C for 70 hours resulted in relatively little decrease in tensile strength or elongation. Refluxing for 70 hours in hydrocarbon fuel (∿180°C) under dry nitrogen and also with water added, resulted in significantly lower tensile strength. When air was present under the same conditions the fuel oxidation products caused severe loss of strength. Under the same conditions the jet fuel alone oxidized forming tars and residues as well as water.

The addition of mellitic trianhydride to form the crosslinked polyimide compositions C and D increased the stabilities of the resulting polymers. Polymer C after 70 hours of exposure to jet fuel vapor under its own vapor pressure (about 60 psi) suffered a moderate decrease in tensile strength and a sizable decrease in elongation. In contrast, polymer D exposed to fuel vapor at atmospheric pressure for 200 hours at 288°C showed a significant increase in elongation with a moderate decrease in tensile strength. Similar properties were observed after a specimen of the polyimide D was refluxed for 64 hours at 180°C while exposed to air. The latter result contrasted with the severe degradation of the linear polymer B.

The hydrolytic stability of the polyimide composition B was investigated. Refluxing polymer film in water for 7 days resulted in essentially no weight gain, although the surface of the film became hazy and the film became less flexible. Heating for 10 minutes at 150°C, however, restored the clarity of the film and much of the original toughness. It is not known whether the hydrolytic conditions caused some hydrolytic degradation or merely resulted in physical changes.

Further study of hydrolytic stability was carried out with the aid of a simple diimide compound synthesized for that purpose.
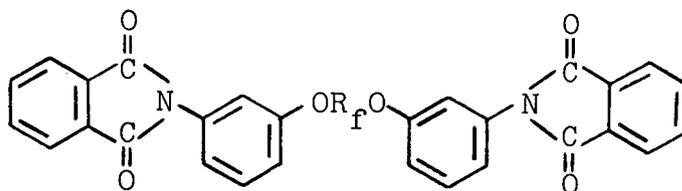
Table 4

POLYIMIDE STABILITY

Polymer Composition	Sample No.	Exposure Conditions	Tensile Strength, psi	Elongation, %[1] 0.65 gauge
B	142731	none	8000	350
		70 hr, 260°C	6900	290
		70 hr, reflux in water	5200	250
		70 hr, 180°C, in fuel, N_2	3800	150
		70 hr, 180°C, fuel, N_2, H_2O	3260	60
		70 hr, 180°C, fuel, air	polymer degraded severely	
C	147229	none	6800	375
		70 hr, 260°C, fuel vapor at 60 psia	4000	120
		70 hr, 260°C, fuel vapor, air	polymer degraded	
	147231	none	6400	320
		70 hr, 260°C, fuel vapor at 60 psia	3800	40
		70 hr, 260°C, fuel vapor, air	polymer degraded	
	147204	none	3200	265
		70 hr, 180°C, reflux in fuel, N_2	1600	350
D	149676	none	6100	420
		200 hr, 288°C, fuel vapor at 15 psia	4500	810
		64 hr, 180°C, reflux fuel, air	4400	730

[1]Based on gauge length of 0.65 in.

This compound was prepared from the 2:1 diamine (i.e., where $x + y = 2$, structure II) and phthalic anhydride. The compound was purified by recrystallization from ethanol. Upon boiling this compound in water for 72 hours the compound was recovered unchanged with respect to the infrared spectrum and melting point.

The model imide compound was subjected to hydrolytic conditions at 200°C. After 20 hours the imide was recovered unchanged with respect to the infrared spectrum, although a small decrease in melting point (128-132°C vs 136-138°C) was observed. Recrystallization from ethanol resulted in near quantitative recovery of pure diimide melting 136-138°C. A second sample heated with water for 47 hours at 200°C (225 psi) in a sealed glass tube showed evidence of hydrolysis. Approximately 10% of the phthalic moiety was isolated as the diacid. A minimum of 65% of the diimide was recovered unchanged (mp 133-134°) and an oily liquid product having an infrared spectrum identical to that of the diamine, except for presence of carbonyl absorption, was isolated. Although these experiments indicate susceptibility to hydrolysis, the conditions of steam at 200°C and 225 psi must also be considered relatively severe. It may be more significant that a major portion of the material did not hydrolyze. Also, the fact that no evidence of degradation of the fluorocarbon ether or phenoxy-fluorocarbon linkages was detected suggests that improvements in stability of the imide linkage will result in overall polymer stability.

The diimide model compound was refluxed for 96 hours at 200°C in *n*-pentylbenzene to simulate a pure hydrocarbon component in place of jet fuel. Air oxidation was permitted. A 95% recovery of purified diimide (mp 136-137°C) was isolated. When the polyimide (structure B) was similarly treated, the polymer became gummy and a minor portion dissolved in a *n*-pentylbenzene solution.

4.   Adhesion

Adhesion of polyimide film to stainless steel and titanium metal test strips was investigated. The metal specimens were cleaned by three different procedures and then coated with polyimide polymer composition B and cured at 180°C. The strips were then refluxed for 70 hours in JP-4 jet fuel at 180°C under a nitrogen atmosphere except for one example which was carried out in contact with air. Significant differences were observed even though the exposure was the same. The conclusion was that the substrate cleaning procedure had significant effect on the ability of the polyimide film to resist damage by the fuel. The alkaline cleaning of stainless steel resulted in good adhesion in contrast to chromic acid treatment of the stainless steel substrate.

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Improved substrate preparation and use of crosslinked polyimide formulations C and D resulted in good adhesion and resistance to refluxing jet engine fuel.

An attempt was made to obtain a rough quantitative indication of adhesion by preparation and testing of three T-peel specimens. Although valid testing requires 5 to 10 specimens, the limitation of polymer intermediates necessitated appreciable compromise in the testing of single specimens at three temperatures. The presence of 25 to 50% voids between the two surfaces was a further limitation of the test procedure. Aluminum strips were cleaned by the procedure recorded in experimental section C and then coated with polyimide prepolymer and bonded with further cure by heating to 180°C.

The T-peel results are shown below:

Temperature °C	Peel Strength, lb/inch		
	Maximum	Minimum	Average
-43	11	1.5	6.5
25	17	0.2	6.9
288	1.9	0.1	0.8

5. Dynamic Evaluation Test

The ultimate test of a fuel tank sealant is how well it seals a fuel tank which is subjected to a combination of adverse circumstances over long periods of time. A dynamic test facility is presently being developed by Dow-Corning Corporation under Air Force contract F33615-70-C-1422 to simulate use conditions for sealant evaluation. The test facility will permit evaluation of a test joint consisting of a fillet seal between a circular cup and a titanium sheet metal surface. The test configuration (Figure 3) will then be subjected to thermal cycling in the presence of fuel as the joint is subjected to torsional and/or joint opening deflections until failure occurs. Arrangements have been made with Air Force Materials Laboratory to include the testing of one or two test configurations of the polyimide sealant. Test data are not available in time for inclusion in this report but will be forwarded to NASA, MSFC later.

D. IMIDE FORMATION AT LOWER TEMPERATURES

1. Silazanes and Aminosilanes as Curing Agents

The relatively high temperatures normally employed in the formation of the polyimide polymers (120 to 200°C) is a deficiency of the imide-linking reaction for the fuel tank sealant application. One of the objectives of the fuel tank sealant program
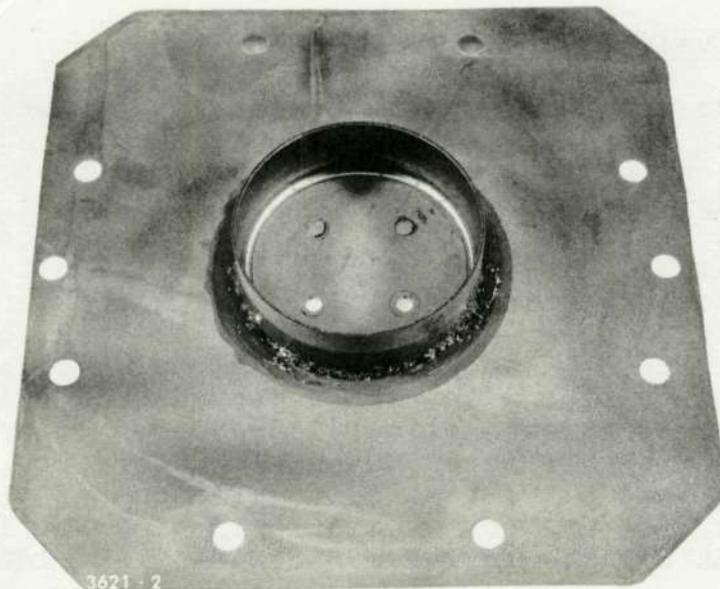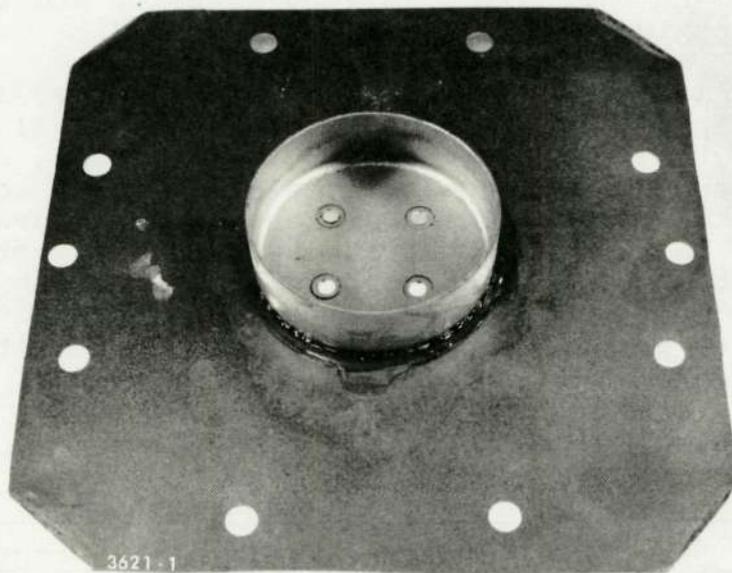
23

Figure 3.   Test Specimens for Dynamic Tests

this year was to develop cure capabilities at moderate temperatures, preferably below 100°C. One approach was to effect low temperature cure through use of catalysts, or dehydrating agents. A second approach was to develop or utilize an alternative imide-forming reaction. Both of these approaches were investigated in an effort to develop an effective low-temperature curing system.

Reaction of bis(trimethylsilyl)aniline with phthalic anhydride was investigated as a way of providing a reactive, aprotic derivative of the aromatic amine. In the presence of a tertiary amine catalyst, reaction of these materials formed the corresponding imide and hexamethyldisiloxane at moderate temperatures according to the equation
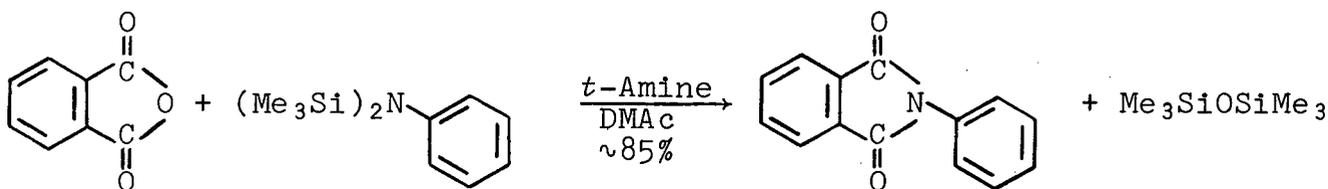

The bis(trimethylsilyl)aniline intermediate was prepared by lithiation of aniline and reaction with trimethylchlorosilane (ref. 7). Although the compound is thermally stable (>200°C) it is quite sensitive to reaction with active hydrogen compounds.

The monosilyl amine derivative, which is more easily prepared, was found to react with phthalic anhydride to form imide in relatively high yield. The imidization reaction was followed by infrared analysis and appeared essentially complete within 20 minutes. The NH absorption of the $Me_3Si-NHC_6H_5$ in the infrared disappeared almost immediately. The anhydride absorptions at 5.4 and 5.6 μm also disappeared within 20 minutes and were replaced by a strong C=O absorption at 5.85-5.95 μm. Evaporation of the solvent from half of the reaction mixture left a residue that by infrared analysis, corresponded to impure imide. The other half was refluxed overnight with t-amine added as catalyst. The residue remaining upon evaporation of solvent from this portion was similar to the first half. These experiments showed that the reactions of either N-trimethyl silyl or N,N-bis(trimethylsilyl)aniline with phthalic anhydride formed imide at temperatures well below 100°C although there was some question as to how quantitative the reactions might be.

A somewhat different approach was taken in a series of experiments aimed at low temperature imidizations of the preformed amic acid. Addition of phthalic anhydride to aniline in tetrahydrofuran forms the amic acid, phthalanilic acid, V.

VI
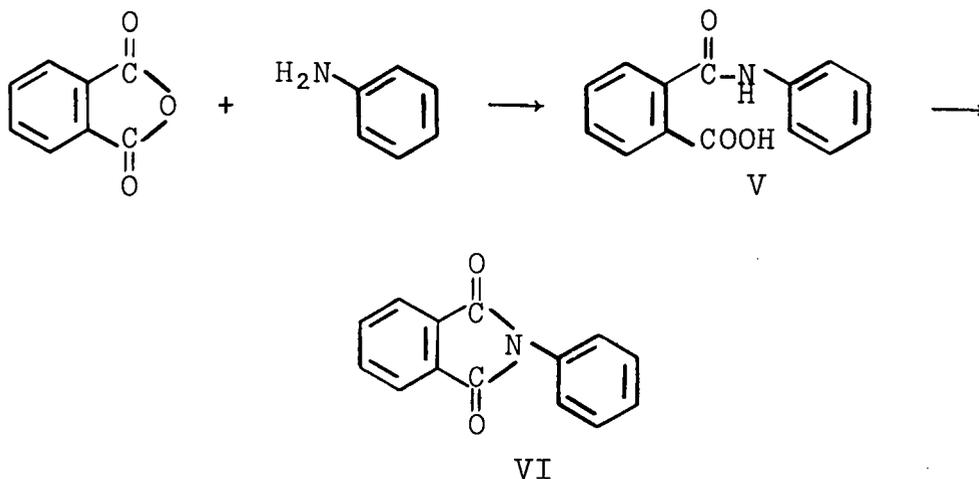
Although continued refluxing at 65°C failed to convert V to imide, addition of a catalytic quantity of the tertiary amine, N,N,N',N'- tetramethylbutanediamine resulted in formation of some imide within two hours at 65°C as indicated by infrared analysis. When one equivalent of hexamethyldisilazane was added to the amic acid at 25°C, an exotherm and evolution of ammonia was observed. The mixture was heated to 65°C and volatiles were then distilled off under vacuum leaving the theoretical weight of residue calculated as imide. The melting point 206-209°C and infrared spectrum corresponded to that of phthalanil, VI. Recrystallization afforded a 75% yield of purified imide. In effect, the silazane acts as a dehydration agent, an effect that has been reported previously for the conversion of amides to nitriles (ref. 8). The simultaneous elimination of ammonia suggests possible formation of by-products such as the following:
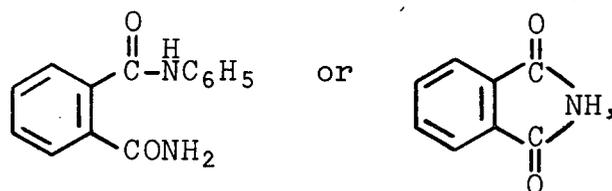
The possibility of evolved ammonia displacing the aromatic amine would be particularly damaging to the formation of high polymers. To preclude this possibility a tertiary aminosilane, diethyl- aminotrimethysilane, was prepared and evaluated for imide forma- tion. This reagent is also a more powerful silylating agent. Addition of this aminosilane reagent to a slurry of purified phthalanilic acid, V, in ether at 25°C (2:1 molar ratio) resulted in a rapid, exothermic imidization reaction. Partial solution of the phthalanilic acid was observed at first followed by rapid copious precipitation of fine crystalline solid, which was identified as high purity N-phenylphthalimide (mp 207-209°C) isolated in 96.5% yield.

Further insight into the action of the diethylaminotrimethyl silane with the amic acid from phthalic anhydride and aniline (e.g., phthalanilic acid) was obtained when a 1:1 ratio of reactants was used. These conditions formed a mixture of the imide and a water soluble product. The latter product when heated was converted to imide, diethylamine and water. It was therefore considered to be the diethylammonium salt of phthalanilic acid. The products of 1:1 reaction then can be explained by equations 1 and 2 in Figure 4, while a 1:2 reaction of phthalanilic acid and trimethyldiethylaminosilane can be represented by equation 4, the sum of equations 1-3.

The isolation of a trace of aniline upon thermal reorganization of the diethylammonium salt of the phthalanilic acid (reaction 3-B, Figure 4) represents a chain-terminating reaction if this step were to occur thermally in a polymer system. To prove that the aniline was formed by thermal reorganization rather than being present as an impurity, purified phthalanilic acid was prepared and the experiment was repeated. Aniline was formed once again.

The fact that the aminosilane and the silazanes effect rapid imidization of the simple "amic" acid at 25°C and in high yields seemed to offer intriging possibilities for high polymer formation. Attempts to utilize these reactions in polymer formation, however, were not successful. Polyamic acid films from which most or essentially all of the solvent had been removed at low temperatures were treated with hexamethyldisilazane and diethylaminotrimethyl-silane in both vapor and liquid states. The films remained glassy or brittle even after additional thermal exposure at 100°C. Whether this suggest that the polyamic acid films contained linkages other than amic acid structures, which are not imidized by these reagents, or that side reactions limit polymer formation, is not known. The fact that subsequent thermal exposure of the silane-treated polyamic acid film at 180°C converted the films to the anticipated polyimide suggested that the chemically induced imidization was not effective. Further study would be needed to determine why the aminosilane, which is so highly effective in converting a simple amic acid to imide, is so ineffective with polyamic acid film and whether these reactions could be used to effect low temperature polymer formation.

2. Imides from Isocyanates

The known reaction of isocyanates with anhydrides (ref. 9, 10) offered an alternative route to polyimide polymers. Several experiments were performed to determine the ease of imide formation in the simple phthalic anhydride-phenyl isocyanate system. Although N-phenylphthalimide was formed at 100-110° in reasonably good yields in the presence of a tertiary amine catalyst, an unidentified higher melting by-product was also

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1. [structure: phthalanilic acid with CONHC$_6$H$_5$ and COOH] $+$ 0.5 Me$_3$SiNEt$_2$ $\longrightarrow$ 0.5 [structure with CONHC$_6$H$_5$ and COOSiMe$_3$] $+$ 0.5 [structure with CONHC$_6$H$_5$ and COO$^-$ $^+$NH$_2$Et$_2$]

2. 0.5 [structure with CONHC$_6$H$_5$ and COOSiMe$_3$] $+$ 0.5 Me$_3$SiNEt$_2$ $\longrightarrow$ 0.5 [N-phenylphthalimide structure] $+$ 0.5 Me$_3$SiOSiMe$_3$ $+$ 0.5 Et$_2$NH

3. A   0.5 [structure with CONHC$_6$H$_5$ and COO$^-$ $^+$NH$_2$Et$_2$] $+$ Me$_3$SiNEt$_2$ $\longrightarrow$ 0.5 [N-phenylphthalimide structure] $+$ 0.5 Me$_3$SiOSiMe$_3$ $+$ 1.5 Et$_2$NH

   B $\xrightarrow[\Delta]{130-150°}$ [N-phenylphthalimide structure] $+$ H$_2$O $+$ Et$_2$NH $+$ trace of amine

4. [structure with CNHC$_6$H$_5$ (C=O) and COOH] $+$ 2 Me$_3$SiNEt$_2$ $\longrightarrow$ [N-phenylphthalimide structure] $+$ Me$_3$SiOSiMe$_3$ $+$ 2 Et$_2$NH
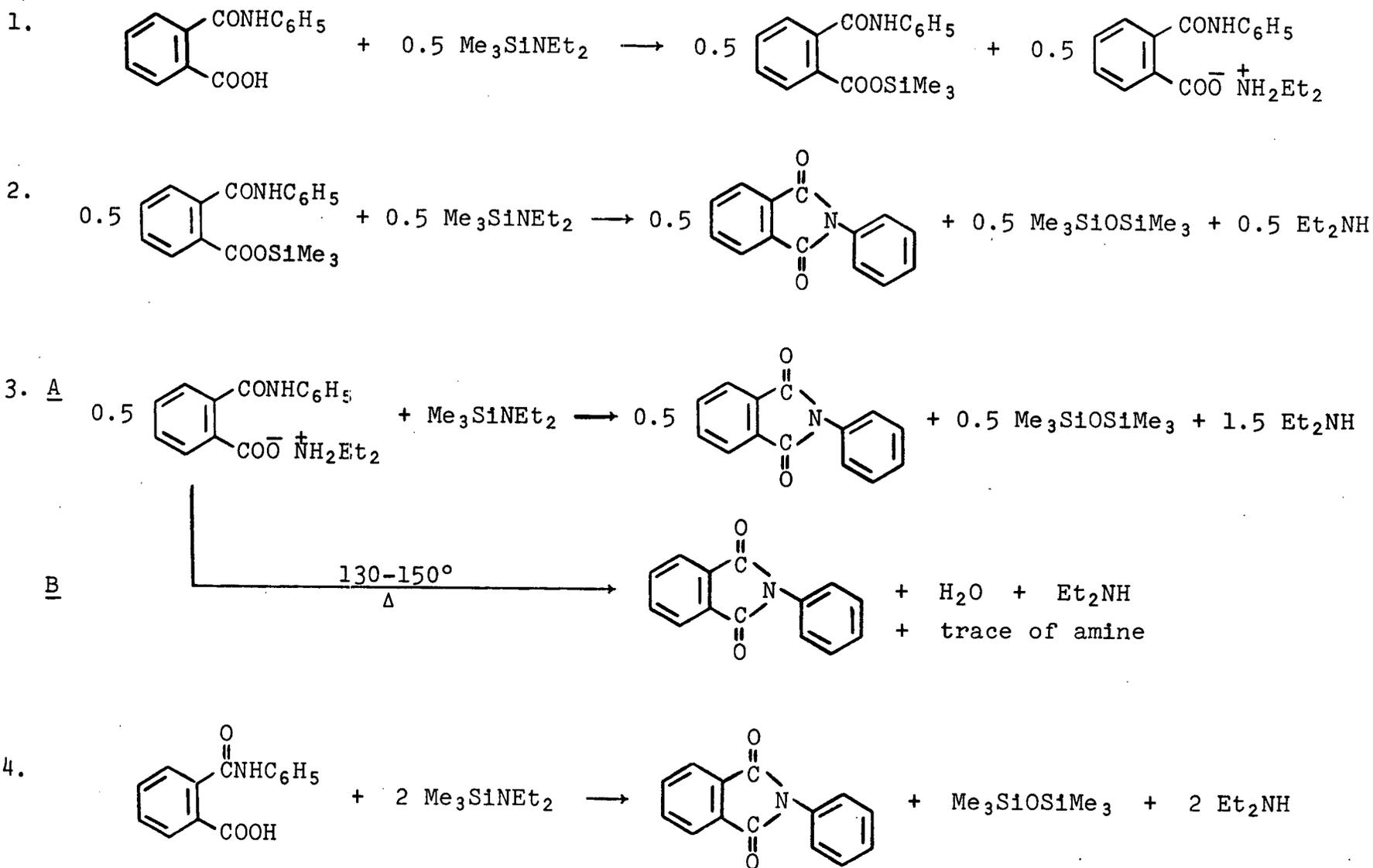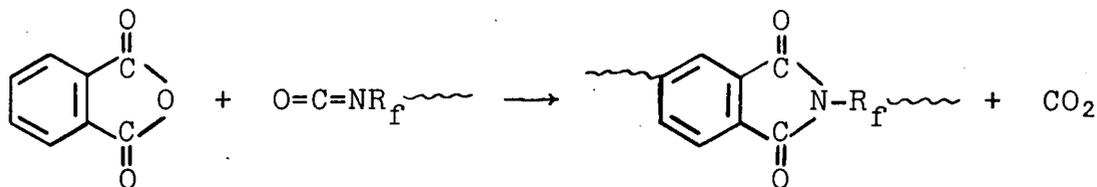
Figure 4.   Phthalanilic Acid-Diethylaminotrimethylsilane Reaction Sequence

formed. Although additional effort might suggest more reason
for optimism, this approach was not pursued further.

A related reaction that has been suggested for the preparation
of imide-linked fluorocarbon polymers is that of a perfluorinated
isocyanate with a dianhydride, e.g.

Jones and Cassey touched on this in their work under Air Force
contract (ref. 11). The advantage that would be gained in being
able to convert the perfluoroalkylene ether dicarboxylic acid
halide directly to the diisocyanate polymer intermediate would
be appreciable but would be offset by an imide structure sus-
pected of exhibiting poor hydrolytic stability. There are
numerous examples of unstable structures resulting from per-
fluoro groups adjacent to functional groups. In an effort to
prove or disprove our contention of poor hydrolytic stability,
perfluoroheptyl isocyanate was prepared for conversion to the
N-perfluoroheptyl phthalimide. Several attempts to prepare
the phthalimide by the reaction shown above were not successful.
This, together with past experience in trying to cyclotrimerize
a perfluoroalkyl isocyanate under conditions that readily cyclo-
trimerize alkyl isocyanates suggests that the perfluoro substitu-
ent deactivates the isocyanate group in these reactions, although
the perfluoroalkyl isocyanates are quite reactive toward hydroly-
sis. On the basis of the rather limited effort expended it was
concluded that the perfluoroalkyl isocyanate reacts sluggishly
at best with the dianhydride. No assessment of the hydrolytic
stability was possible.

III.   EXPERIMENTAL

A.   SYNTHESIS OF POLYMER INTERMEDIATES

1.   Diamine Synthesis

Details of perfluoroalkylene ether aryldiamine syntheses were described previously in the Third Annual Report (ref. 1). Additional fluorination experiments were carried out in an attempt to improve the yield and reliability of the procedure. These experiments were summarized earlier in Tables 1 and 2. Further description of the conversion of the nitrophenyl ester of the 3:1 oligomer acid to the corresponding aminophenoxy derivative is given below.

a.   3:1 Diamine   142719

Synthesis of the *m*-nitrophenyl ester of the 3:1 oligomer acid product of hexafluoropropylene epoxide and perfluoroglutaryl fluoride was described previously (ref. 1). A 40-g quantity of this ester (0.041 mole) was charged to a 1370 ml Hastelloy autoclave along with 50 g (0.463 mole) of purified sulfur tetrafluoride (ref. 12), 75 g (3.75 moles) of anhydrous hydrogen fluoride, and 500 ml of fluorocarbon solvent FC-75 (3M). The autoclave was heated at 80°C for 89 hours. The gases were then released. The contents of the reactor were poured into ice water and neutralized with $NaHCO_3$. Essentially pure FC-75 liquid phase separated from the product and aqueous phases and was recovered for reuse. The product was extracted from the aqueous phase with ether and was washed with water. Evaporation of solvent left 38.8 g of a dark oily product that by infrared spectral analysis showed carbonyl-containing product. The oil was redissolved in ether and stirred for 45 minutes with 100 ml of 0.5 N NaOH to hydrolyze unreacted ester. The ester phase was separated and washed to neutrality with water. Evaporation of solvent left 35.9 g of dark oil that showed no carbonyl absorption in the infrared spectrum. The crude product was extracted with benzene leaving 7.2 g of an insoluble brown gum. Distillation of the benzene extract gave 24.0 g of crude distilled product. Redistillation afforded 20 g of *m*-nitrophenoxy perfluoroalkylene ether ($x + y = 3$), bp 179°C/0.03 torr, n_D^{25} 1.3941, representing a 49% yield.

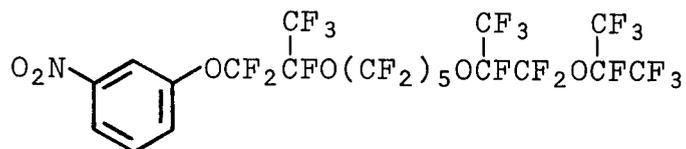   142725

Catalytic reduction of the above product in benzene using Raney nickel at 40 psi hydrogen formed the diamine. Distillation of 18.7 g of crude product gave 17.2 g (93% yield), bp 160°C/0.01 torr, n_D^{25} 1.3722. Titration against 0.1 N standard perchloric acid in glacial acetic acid showed a neutralization equivalent to 482 (calc'd 482.2).
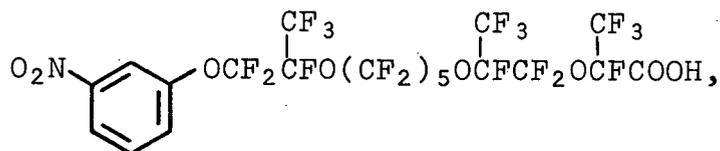
30

Elemental Analysis for $C_{26}H_{12}F_{28}N_2O_5$

	C	H	N	F
Calc'd	32.38	1.25	2.91	55.17
Found	32.45	1.08	3.20	55.53

142950

By-product of ester fluorination was separated as a viscous, black, tarry residue of benzene-insoluble material. The residue (18.7 g) was investigated further by dissolving in ether and acidifying with 6 N HCl, and then extracting with water. The ether solution was dried over MgSO$_4$ and evaporated to dryness. Extraction with benzene left a 5-g residue. Distillation of the extract gave two fractions; the first, boiling at ∿102°C/0.1 torr, n_D^{25} 1.3510, by IR appeared to be a nitrophenyl ether derivative.

$$O_2N\text{-}\underset{}{\bigcirc}\text{-OCF}_2\overset{\overset{\text{CF}_3}{|}}{\text{C}}\text{FO(CF}_2)_5\text{OC}\overset{\overset{\text{CF}_3}{|}}{}\text{FCF}_2\text{OC}\overset{\overset{\text{CF}_3}{|}}{}\text{FCF}_3$$

The second fraction, bp 160-165°C/0.01 torr, n_D^{25} 1.3635, was identified as a mono carboxylic acid,

$$O_2N\text{-}\underset{}{\bigcirc}\text{-OCF}_2\overset{\overset{\text{CF}_3}{|}}{\text{C}}\text{FO(CF}_2)_5\text{OC}\overset{\overset{\text{CF}_3}{|}}{}\text{FCF}_2\text{OC}\overset{\overset{\text{CF}_3}{|}}{}\text{FCOOH},$$

neutral equiv. found 887, calc'd. 887.

The first product was reduced over Pd/C and distilled, bp 100°C/0.07 torr, n_D^{25} 1.3480. The neutral equivalent by titration with HClO$_4$ in glacial acetic acid was 840, calc'd. 875.

b.   4:1   Diamine   142766

A 230-g fraction (bp 123-125°C/24 torr) of 4:1 oligomer dicarboxylic acid fluoride (0.25 mole) (PRC, Inc.), derived from perfluoroglutaryl fluoride and perfluoropropylene epoxide, was hydrolyzed in water (800 ml) containing calcium ion. The dicarboxylic acid was extracted with ether, dried over MgSO$_4$, and distilled to

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give 209 g (92% yield) of the dicarboxylic acid, bp 125-127/0.17 torr, n_D^{25} 1.3131, neut. equiv. found 434, calc'd. 452.

142768

The acid was converted to acid chloride by refluxing for 72 hours with a two-fold excess of thionyl chloride and a few drops of pyridine as catalyst. Distillation gave an 89% yield of the acid chloride, bp 135°C/16 torr, n_D^{25} 1.3054.

Nitrophenyl Ester of 4:1 Oligomer Acid   142772

Reaction of 4:1 oligomer acid chloride with excess *m*-nitrophenol afforded 200 g (89% yield) of the corresponding ester, bp 185-190°C/0.01 torr, n_D^{25} 1.3938-42.

Attempted Fluorination of 4:1 Ester   142918

Attempted fluorination of an 11.8 g portion of the above ester using 12 g SF_4, 14 g anhydrous HF, and 100 ml of FC-75 solvent at 80°C for 88 hours gave a mixture of ester and ether product indicating incomplete fluorination. The synthesis was not pursued further.

2. Dianhydride Modifications

   a. 1,6-Diphenyldodecafluorohexane-3,3',4,4'-tetracarboxylic Dianhydride (Dianhydride III)

Diethyl 4-Nitrophthalate   147201

Esterification of 4-nitrophthalic acid (292 g, 1.38 moles) by azeotropic removal of water from a solution of the acid dissolved in 500 ml ethanol, 500 ml benzene, and 10 ml sulfuric acid formed the ester in 83% yield, bp 156-160°C/0.06 torr, n_D^{25} 1.5250, mp 33-34°C (Lit. 34°C, ref. 5).

Diethyl 4-Aminophthalate   142963

Catalytic reduction of an ethanol solution of the above nitro ester (50 g) over Pd/$BaSO_4$ formed the corresponding diethyl 4-aminophthalate (37 g) mp 96-97.5°C (Lit. 97-98°C, ref. 5).

Diethyl 4-Iodophthalate   142964

The procedure of Blicke and Smith was followed (ref. 5). Diethyl 4-aminophthalate (52 g, 0.22 mole) was dissolved in a cold solution of 88 ml conc. hydrochloric acid dissolved in 44 ml water. Ice was added and diazotization was carried out by adding to the stirred solution 15.4 g (0.22 mole) of sodium nitrite in 66 ml of ice water. The solution was stirred for 30 minutes at 0-15°C whereupon 53 g of potassium iodide in 440 ml water was

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added and stirring was continued for 30 minutes. Organic product was extracted with ether, washed, dried, and distilled affording 50 g of diethyl 4-iodophthalate, bp 135-140°C/0.1 torr, n_D^{25} 1.5608, yield 65%.

Tetraethyl 1,6-Diphenyldodecafluorohexane-3,3',4,4'-tetracarboxylate

147212

A mixture of 23.2 g (0.042 mole) of 1,6-diiodododecafluorohexane, 36.4 g (0.106 mole) of diethyl 4-iodophthalate, and 32.8 g (0.052 mole) of activated copper in 100 ml of dry dimethylformamide was gradually heated with stirring (2 hr) to 115°C. This temperature was maintained for 8 hours. Solids were removed by filtration. Water was added to the filtrate and the product was extracted with ether. The residue remaining upon evaporation of ether was heated to 220°C at 0.04 torr to remove mono coupled by-product. The residue of crude product weighed 30.1 g, n_D^{25} 1.4656. The saponification equivalent was 180, calc'd. 185.5.

1,6-Diphenyldodecafluorohexane-3,3',4,4'-tetra-carboxylic Dianhydride

The crude product above was hydrolyzed by heating for two hours with a solution of 10 g sodium hydroxide in 200 ml water and 125 ml ethanol. Ethanol was then removed under vacuum and the tetra-acid was precipitated by adding a cold solution of 40 ml conc. hydrochloric acid in 100 ml water. The dry weight of recovered, washed crude product was 23.9 g, partially melting at ∿205°C. The neutralization equivalent was 166, calc'd. 157. This crude product was refluxed for 2 hours with 200 ml acetic anhydride, then evaporated to dryness under vacuum, wt 20.7 g, mp 175-183°C. Sublimation under vacuum at 180-200°C gave 15.1 g (60% overall yield) of 1,6-diphenyldodecafluorohexane-3,3',4,4'-tetracarboxylic dianhydride, mp 186-188°C, neut. equivalent 147.6, calc'd. 148.6.

b. 1,5-Diphenoxydecafluoropentane-3,3',4,4'-tetracarboxylic Dianhydride (Dianhydride IV)

147214

Synthesis of this compound was contingent upon the preferential hydrolysis of trifluoromethyl groups without adverse effect on perfluoroalkoxy groups as demonstrated by the following three experiments.

m-Trifluoromethylphenyl Pentadecafluorooctoate

142973, 147226

Reaction of m-trifluoromethylphenol (24 g, 0.15 mole) with per-fluorooctanoyl chloride (43.2 g, 0.1 mole) at reflux temperature in the presence of 5 drops of pyridine afforded an 85% yield of m-trifluoromethylphenyl pentadecafluorooctoate, bp 73°C/0.08 torr, n_D^{25} 1.3555. The infrared spectrum was consistent with the expected compound.

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m-Trifluoromethylphenyl Heptadecafluorooctyl Ether   147227

Fluorination of m-trifluoromethylphenyl pentadecafluorooctoate (22.0 g, 0.039 mole) was carried out by heating for 14 hours at 80°C in a stainless steel autoclave in the presence of 18.0 g (0.17 mole) of sulfur tetrafluoride and 40 g of anhydrous hydrogen fluoride (2.0 moles). Work-up in the usual manner and distillation gave an 83% yield of m-trifluoromethylphenyl heptadecafluorooctyl ether, bp 95-97°C/4 torr, n_D^{25} 1.3439 (IR, Figure 1 in Appendix).

m-Heptadecafluorooctoxybenzoic Acid   147234

Hydrolysis of the trifluoromethyl group was carried out by adding m-trifluoromethylphenyl heptadecafluorooctyl ether (6.6 g, 0.011 mole) to a mixture of 100% sulfuric acid (7.5 g) and chlorosulfonic acid (7.5 g). The mixture was stirred for two hours at 100° and then poured over ice. Crystalline product was isolated by filtration, washed with water and dried, 7.2 g, mp 108-118°C. Recrystallization from benzene gave 5.2 g of white crystals, mp 123-125°C, representing a 93% yield of m-heptadecafluorooctoxybenzoic acid. Neut. equivalent found: 542, calc'd. 556 (IR, Figure 2 in Appendix).

3,4-Bis(trifluoromethyl)nitrobenzene   147259

A 3-liter stainless steel autoclave was charged with 120 g of 4-nitrophthalic acid (0.57 moles), 307 g of purified sulfur tetrafluoride (2.84 moles), and 50 g of anhydrous hydrogen fluoride. The autoclave was rocked for 15 hr at 80°C and then for 14 hr at 150°C. Gases were released and the residue was poured over ice and acid was neutralized with sodium carbonate solution. Products were extracted with ether, washed, and distilled, giving 105 g (70% yield) of 3,4-bis(trifluoromethyl) nitrobenzene, bp 96-98°C/17 torr, n_D^{25} 1.4380-1.4397. This was followed by a 5.5 g fraction, bp 98-110°C/18 torr, n_D^{25} 1.4552 which crystallized upon standing and 5 g of crystalline solid, bp 110-113°C/17 torr, mp 55-57.5°C. Recrystallization of the solid from ethanol-water raised the melting point to 58-58.5°C. The infrared spectrum, higher boiling point and higher refractive index suggested the cyclic compound, 5-nitro-1,1,3,3-tetrafluorophthalan. The literature reports a melting point of 57-58°C for this compound (ref. 13).

3,4-Bis(trifluoromethyl)aniline   147249

Catalytic reduction of 3,4-bis(trifluoromethyl)nitrobenzene (45.5 g, 0.175 mole) in 150 ml of ethanol over Raney nickel at 50 psi hydrogen gave 36 g (89% yield) of 3,4-bis(trifluoromethyl)-aniline, bp 111°C/17 torr, n_D^{25} 1.4504.

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3,4-Bis(trifluoromethyl)phenol   147270

3,4-Bis(trifluoromethyl)aniline (24 g, 0.15 mole) was dissolved
in 120 ml of concentrated sulfuric acid. A solution prepared
by dissolving sodium nitrite (12.0 g, 0.174 mole) in 120 ml
of cold concentrated sulfuric acid was added to the amine over
a period of 75 minutes. The temperature was then permitted to
rise to 25°C and stirring was continued for 2 hours. The reac-
tion mixture was then poured over excess ice and the resulting
aqueous solution was steam distilled until 2 liters of distillate
was collected. Extraction of this aqueous solution with ether
and distillation of the extract afforded 19.3 g (80% yield) of
3,4-bis(trifluoromethyl)phenol, bp 116°C/50 torr, n_D^{25} 1.4286.
Additional experiments are listed in Table 5.

3,4-Bis(trifluoromethyl)phenyl Hexafluoroglutarate   149604

Pyridine catalyzed reaction of 3,4-bis(trifluoromethyl)phenol
(7.8 g, 0.034 mole) with perfluoroglutaryl chloride (4.7 g,
0.017 mole) at 75 to 120°C formed the corresponding diester in
90% yield, bp 155°C/0.15 torr, n_D^{25} 1.4123-28.

3,3',4,4'-Tetrakis(trifluoromethyl)-1,5-diphenoxydeca-   149606
fluoropentane

A 300 stainless steel autoclave was charged with 8.0 g (0.012
mole) of 3,4-bis(trifluoromethyl)phenyl hexafluoroglutarate,
38 g (1.9 moles) hydrogen fluoride and 24 g (0.22 mole) sulfur
tetrafluoride. The bomb was heated for 3 hr at 80°C and 21 hr
at 85°C. The pressure was released after the bomb had cooled
and the contents was poured over ice and neutralized with $NaHCO_3$.
The product was extracted with chloroform, washed, dried. Dis-
tillation gave 8.5 g of product considered to be 3,3',4,4'-
tetrakis(trifluoromethyl)-1,5-diphenoxydecafluoropentane, bp 115,
122°C/0.15 torr, n_D^{25} 1.3895. Infrared analysis showed no carbonyl
absorption (IR, Figure 3 in Appendix).

1,5-Diphenoxydecafluoropentane-3,3',4,4'-   149656
tetracarboxylic Acid

A mixture of 3,3',4,4'-tetrakis(trifluoromethyl)-1,5-diphenoxy-
decafluoropentane (28.5 g, 0.049 mole), 100% sulfuric acid (25 g,
0.25 mole), and chlorosulfonic acid (29 g, 0.25 mole) was heated
with stirring in a flask under a condenser with dry nitrogen
atmosphere. The temperature was held at 90°C for 48 hours, 100°C
for 16 hours, and 120°C for 24 hours. During this time HCl
evolved slowly. The mixture was then poured over ice, extracted
with ether, washed, and dried. Evaporation of ether left a brown
gummy solid. This was dissolved in 300 ml water at 85°C, decolor-
ized with charcoal, and filtered hot. Upon cooling, 19 g of white
solid was collected by filtration, neut. equiv. found 160; calc'd.
for tetracarboxylic acid, 153. (IR, Figure 4 in Appendix).

Table 5

CONVERSION OF 3,4-BIS(TRIFLUOROMETHYL)ANILINE TO BIS(TRIFLUOROMETHYL)PHENOL
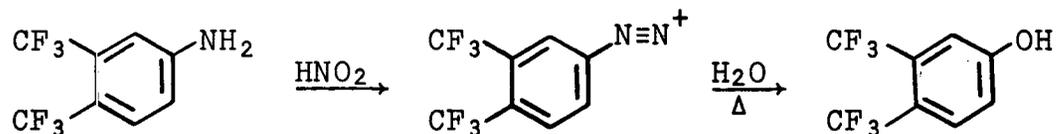
Experiment No.	Amine Weight g	Solvent	Diazotization Addition	Conditions		Phenol Weight g	n_D^{25}	% Yield
				Time hr	Temp °C			
147241	3	glac. HOAc	amine to $NaNO_2/H_2SO_4$	3	10-15	0.9		2
147253	30	glac. HOAc	amine to $NaNO_2/H_2SO_4$	1 3	10-15 10-35	8.2	1.4309	25
147266	5	conc. H_2SO_4	$NaNO_2/H_2SO_4$ to amine	1 1	5-10 10-25	3.9	1.4292	78
147268	5	conc. H_2SO_4	$NaNO_2/H_2SO_4$ to amine	0.5 3	5-10 25	4.1	1.4283- 1.4296	82
147270	24	conc. H_2SO_4 (120 ml)	$NaNO_2/H_2SO_4$ to amine	1.5 2.0	5-10 10-25	19.3	1.4286	80
147279	54	conc. H_2SO_4 (280 ml)	$NaNO_2/H_2SO_4$ to amine	1.5 2.5	∿5 5-25	33.2	1.4275- 1.4302	61

This product was refluxed with excess acetic anhydride and then devolatilized. Sublimation of the solid residue at 160°C/<0.01 torr afforded 17.3 g of dianhydride, mp 94-97°C (60% yield).

Attempts to purify the dianhydride further by recrystallization failed for lack of a suitable solvent. The anhydride (17.3 g) was finally dissolved in water and recrystallized as the acid, mp 145-155°C, neut. equiv. 159. The acid was then recrystallized from 27% (by volume) acetic acid/water solution and a second time from 35% acetic acid solution. The melting point was raised to 151-153° with very little loss in material. Neut. equiv. found 159, calc'd. 153. NMR analysis showed an equal proportion of labile and aromatic protons suggesting that the tetracarboxylic acid crystallized as the monohydrate with a calculated equivalent weight of 157.5.

The above tetraacid was then converted once again to dianhydride and sublimed. Three fractions of sublimed material were collected.

	Weight g	mp °C	Neut. Equiv. Found	Neut. Equiv. Calc'd
1.	4.4	97-99	145.5	144.0
2.	6.5	97.5-99	146	
3.	2.9	99-100	–	

Titration was carried out by dissolving in excess standard alkali and back titrating with acid. The infrared spectrum (Figure 5 in Appendix) and elemental analysis substantiated the structure of the product.

Analysis for $C_{21}H_6F_{10}O_8$

	C	H	F
Calc'd	43.77	1.05	32.97
Found	43.53	0.96	33.10

c.   Attempted Synthesis of 2:1 Perfluoroalkylene
   Ether-Oligomer-Containing Dianhydride

3,4-Bis(trifluoromethyl)phenyl Ester of   147283
2:1 Oligomer Acid

Reaction of 10.2 g (0.044 mole) of 3,4-bis(trifluoromethyl)phenol with 13.2 g (0.022 mole) of 2:1 oligomer perfluoroalkylene ether-dicarboxylic acid chloride at 140°C/18 hr gave upon distillation a 85% yield of the corresponding ester, bp 152°C/0.1 torr, n_D^{25} 1.3735.

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Attempted Fluorination of 3,4-Bis(trifluoromethyl)-   147283
Ester of 2:1 Oligomer Acid

A 300 ml autoclave was charged with 17 g (0.017 mole) of the above
ester, 40 g (0.37 mole) of purified SF_4, and 80 g of anhydrous
HF (4.0 moles). The autoclave was rocked and heated at 80°C
for 20 hours. Work-up of reaction products in the usual manner
gave 15.2 g of a dark colored oil. Distillation gave ∿4.5 g
of recovered phenol, bp 42°C/0.2 torr, n_D^{25} 1.4290 and a small
quantity of material that may be the monofluorinated product.

$$F_3C-C_6H_3(CF_3)-OCF_2CFO(CF_2)_5OCFCOOH$$
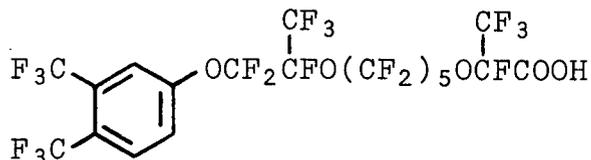
None of the desired product was isolated.

3.   Miscellaneous Syntheses

Attempted Ester Fluorination Using MoF_6 147237

A 0.8 molar solution of MoF_6 in CH_2Cl_2 was added at -10 to -15°C
to 0.1 mole of *m*-nitrophenyl pentadecafluorooctoate (53.5 g) in
100 ml of methylene chloride. There was little or no evidence
of reaction. The mixture was stirred and warmed to 17°C over
a period of three hours. The mixture was poured onto ice,
neutralized with sodium carbonate, washed, and dried. Evapora-
tion of solvents left 47 g of liquid and crystalline material.
Distillation gave only recovered ester, and acid and phenol
hydrolysis products.

Attempted Synthesis of 3,3'-Dibromo-1,5-   149653
diphenoxydecafluoropentane

1,5-Bis(aminophenoxy)decafluoropentane (ref. 1) (7 g, 30 meq)
dissolved in 75 ml of concentrated H_2SO_4, was treated with 2.2
g of sodium nitrite (0.031 mole) in 50 ml of concentrated sulfuric
acid at 0-5°C. Stirring was continued for an hour at 5°C and
2 hours at 25°C. This mixture was added to a solution of cuprous
bromide (20 g) dissolved in 50 ml of concentrated hydrobromic acid
and maintained at <10°C by addition of ice during addition of the
diazonium solution. The total slurry was gradually warmed to
30-40°C. Ether extraction of products from the aqueous solution
followed by distillation failed to give brominated material.
Appreciable recovery (35%) of amine starting material was
indicated by IR and refractive index. The diamine apparently
did not diazotize under these conditions.

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Reaction of phthalic anhydride (3.4 g, 0.02 mole) with 2:1
diamine (structure II where $x + y = 2$) (9.2 g, 0.02 mole) in
30 ml dimethylacetamide, followed by evaporation of solvent
and heating at 170°C for three hours gave a solid product melting
at 128-132°C. Recrystallization from ethanol raised the melting
point to 135-139°C. The structure was substantiated by the
infrared spectrum.

Diimide Hydrolysis at Elevated Temperature   142915
and Pressure

A 1.26 g quantity of the above diimide compound was sealed in a
glass tube with 10 ml water. The tube was placed in a 300 ml
bomb with 25 ml water to equalize the vapor pressure on both
sides of the glass tube. The bomb was heated to 200°C for
47 hr. Upon opening the tube, solid (1.23 g) was recovered by
filtration. Recrystallization from ethanol gave 0.80 g of
product (65%), mp 133-134°C, that was identified by IR as
starting material.

Approximately 0.04 g of solid phthalic acid (by IR) was isolated
from the aqueous filtrate, while 0.38 g of waxy solid was isolated
from the alcoholic filtrate. The latter showed both N-H and
imide absorptions in the IR suggesting a half imide, amine pro-
duct. Extraction with cyclohexane and evaporation of the cyclo-
hexane filtrate left an oily residue that was nearly identical
(except for a carbonyl absorption) to the 2:1 diamine from which
the diimide had been made.

B.   CURE REACTIONS AND REACTANTS

1.   Silazanes and Aminosilane Curing Agents

N,N-Bis(trimethylsilyl)aniline   137499

Phenyllithium was prepared from bromobenzene (78.5 g, 0.5 mole)
and lithium (7 g, 1.0 g atom) in refluxing ether. Aniline (20 g,
0.215 mole) dissolved in ether was added dropwise to the phenyl-
lithium stirred for an hour at reflux and allowed to stand over-
night. (The latter may have been detrimental). Trimethylchloro-
silane (54 g, 0.5 mole) dissolved in ether was added. An exotherm
was observed after half of the solution was added. The mixture
was allowed to reflux for half an hour before adding the remaining
chlorosilane. The mixture was then refluxed for 8 hours - filtered
and distilled. After stripping off most of the solvent and low
boiling material, considerable solid had formed. This was
removed by filtration. There was some indication that the solid
might be an organometallic material.

Distillation of the liquid phase gave 19 g (38%) N,N-bis(trimethyl-silyl)aniline, bp 220-225°C/740 torr, n_D^{25} 1.4844. The infrared spectrum showed no N-H absorption. Lit. bp 98-99°C/11 torr, n_D^{20} 1.4855 (ref. 7).

Reaction of N,N-Bis(trimethysilyl)aniline   142903
with Phthalic Anhydride

N,N-Bis(trimethylsilyl)aniline (3.55 g, 0.015 mole), was added to phthalic anhydride (2.22 g, 0.015 mole) dissolved in 10 ml of dimethylacetamide. Three drops of N,N,N',N'-tetramethyl-1,3-butanediamine was added. The mixture was heated to 80-90°C under reduced pressure to remove hexamethyldisiloxane. A total of 1.2 g of the latter (50% of theory) was collected after several hours. The solvent was then removed under vacuum without exceed-ing a temperature of 90° leaving a pale yellow crystalline solid weighing 3.7 g. Titration of a sample of the crude solid with 0.1 N NaOH indicated an equivalent weight of 750, equivalent to 16% of the phthalic anhydride used. A 1.0 g aliquot of the solid was slurried with 20 ml of water and then with a 20 ml alcohol. The crystalline solid residue weighed 0.9 g and melted at 207-209°C. The infrared spectrum corresponded closely to that of N-phenylphthalimide. On this basis there was a 80-85% conversion of phthalic anhydride to imide.

Formation of N-phenylphthalimide   142910

Phthalic anhydride (1.0 g, 7 meq) was dissolved in 20 ml of dry, purified tetrahydrofuran. N-Trimethylsilylaniline (1.1 g, 7 meq) was added. Disappearance of the anhydride carbonyl absorp-tions in the infrared at 5.4 and 5.6 μ and of the -NH was observed over the first 20 minutes along with evidence of exothermic reac-tion. A portion of the solution was heated overnight with 2 drops of tetramethyl-1,3-butanediamine added as a catalyst. Upon cool-ing, a crystalline solid formed. This was identified as N-phenyl-phthalimide by IR and melting point (208-209°C). Comparison of infrared spectra indicated that the major reaction occurred within the first half hour.

Diethylaminotrimethylsilane   149623

Trimethylchlorosilane (108.5 g, 1.0 mole) was added to a hexane solution of diethylamine (150 g, 2.05 mole). The mixture was heated to reflux, cooled, filtered and distilled giving 80 g (0.55 mole), 54% yield, of diethylaminotrimethylsilane, bp 127°C/740 torr, n_D^{25} 1.4095 (Lit. bp 126°C, n_D^{20} 1.4109, ref. 14).

Preparation and Purification of Phthalanilic Acid   149634

Aniline (31.4 g, 0.34 mole) dissolved in 100 ml of chloroform was added to phthalic anhydride (50 g, 0.34 mole) in 500 ml of chloroform. The mildly exothermic reaction precipitated

phthalanilic acid, which after stirring overnight, was
collected by filtration and washed with more chloroform, dry
weight 72 g, mp 166-167°C. A 40 g quantity of crude phthalanilic
acid was recrystallized from a mixture of 600 ml acetone and
150 ml hexane. The first crop of 17 g melted at 171.5-172°C,
neutral equiv. 238, calc'd. 241.

Reaction of Phthalanilic Acid with Diethylamino-trimethylsilane   149633

Addition of 8.6 mmoles of diethylaminotrimethylsilane to a
slurry of 4.2 mmoles of phthalanilic acid in ether caused an
appreciable portion of the solid to dissolve. Upon standing
overnight 4.0 mmoles of N-phenylphthalanilic acid, mp 207-209°C,
was recovered by filtration.

1:1 Ratio   149642

To a slurry of purified phthalanilic acid (2.41 g, 0.010 mole)
in ether was added diethylaminotrimethylsilane (1.45 g, 0.010
mole) in 8 ml of ether. Partial solution of solid, slight exo-
therm and precipitation of solid product was observed. Filtra-
tion after 1.5 hr gave 2.71 g of solid product. Theory for
0.005 mole of imide and 0.005 mole of diethylamine salt = 2.69 g.
Gradual heating of this solid under vacuum resulted in vigorous
bubbling at 120-140°C and distillation of a trace of aniline as
well as diethylamine and water. The residue that remained was
extracted with methanol. The insoluble portion, mp 207-210°C,
was identified as N-phenylphthalimide. A small quantity of
methanol soluble material, melting at 95-115°C was isolated.
The infrared spectrum of the latter suggested an aliphatic amide
structure, possibly a diethylamide derivative.

Diethylaminotrimethylsilane as a Polyimide Curing Agent   149635

A polyamic acid solution was prepared in tetrahydrofuran using
3:1 oligomer diamine and 1,6-diphenyldodecafluorohexane-3,3',4,4'-
tetracarboxylic dianhydride. A portion of this prepolymer was
cast on a Teflon surface and cured thermally by gradual heating
to 200°C, thereby forming a tough plastic film. Solvent was
evaporated from a second film of polyamic acid. The film was
then wet with Me_3SiNEt_2 and warmed in an atmosphere saturated
with the aminosilane. After 10 hours the polymeric material
was heated for an additional 16 hr in air at 50°C. The
resulting film was very brittle and not at all like that formed
thermally.

A portion of the brittle material was redissolved in tetrahydro-
furan and treated with Et_2NSiMe_3. Evaporation of volatiles from
a film of this solution also failed to form a tough polyimide
polymer film, yet subsequent heating of any of the Me_3SiNEt_2

treated prepolymer films at 200°C formed the normal tough film of polyimide. The polyimide, once formed, was not adversely affected by the aminosilane.

A similar series of experiments using polyamic acid dissolved in DMAc indicated ineffectiveness of the aminosilane.

2. Imides from Isocyanates

Reaction of Phthalic Anhydride and Phenyl Isocyanate   147289

A few small crystals of triethylenediamine were added to a mixture of phthalic anhydride (1.5 g) and phenyl isocyanate. The test tube was heated to ∿100°C for 20 hr. After 90 minutes the mixture had solidified to a mass of crystals. Recrystallization from methanol gave 1.6 g of N-phenylphthalimide, mp 207-209°C, and a small quantity of higher melting solid mp 236-240°C. The infrared spectrum suggested that this by-product might be diphenylurea (mp 241-243°C). Comparison with a reference spectrum and a mixed melting point failed to confirm this tentative identification although the spectra were similar.

The above experiment was repeated using N,N,N',N'-tetramethyl-butane-1,3-diamine as the catalyst. Solids formed as soon as the solution of anhydride in isocyanate was complete. Imide (1.2 g) was isolated.

A similar experiment using DMF as the solvent and catalyst gave 1.2 g of imide. The high melting unidentified by-product described above was formed in each of these experiments.

Pentadecafluoroheptyl Isocyanate   142992

Perfluorooctanoyl chloride, 43 g (0.1 mole) was added over a period of 1 hour to a cold mixture of sodium azide (8 g, 0.12 mole) dissolved in 22 ml of water, and xylene. Stirring was continued for 3 hours during which time the mixture was permitted to warm to 20°C. An attempt was made to wash the nonaqueous phase with water. This caused formation of solids (amide) and emulsion problems. A low yield of isocyanate was finally isolated and distilled, bp 119°C, n_D^{25} 1.305. The infrared spectrum confirmed the isocyanate structure (IR, Figure 7 in Appendix).

Attempted Synthesis of N-perfluoroheptylphthalimide   142994
from Pentadecafluoroheptyl Isocyanate

A mixture of phthalic anhydride, (1.5 g, 0.001 mole) pentadeca-fluoroheptyl isocyanate (4.1 g, 0.01 mole) and dry dimethyl-acetamide was heated for three hours at 100°C. IR showed disappearance of the -NCO. Isolated solid material (1 g) appeared by IR to be phthalic anhydride, ∿70% recovery.

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In a second experiment the same reactants were heated for 2 hours at 100°C in 5 ml of dry pyridine as the solvent. Removal of volatiles under vacuum left a 4 gram residue. Extraction with benzene removed 1.5 of material, that was identified as phthalic anhydride by its infrared spectrum.

An equimolar mixture of perfluoroheptyl isocyanate (1.46 g) and phthalic anhydride (0.525 g) was heated at 110-120°C for 20 hours. Distillation resulted in a 80% recovery of the perfluoroheptyl isocyanate.

Phthalic anhydride (25 g, 0.017 mole) and perfluoroheptyl isocyanate (3.0 g, 0.007 mole) and one drop of N,N,N',N'-tetramethyl-1,3-butanediamine were heated at 110-120°C for 20 hours. The mixture was subjected to vacuum to remove volatiles leaving a residue weighing 3.0 g. The IR corresponds to phthalic anhydride with little or no indication of C-F absorption.

C. SUBSTRATE CLEANING PROCEDURES

Aluminum (ref. 15) - The aluminum specimens were cleaned by immersion for 10-12 minutes in the following solution at 65°C:

Water	3000 g
Sulfuric acid (conc)	1000 g
Sodium dichromate	100 g

The metal specimens were rinsed with deionized water and dried at 60-65°C.

Stainless Steel - Stainless steel specimens were immersed for 8-12 minutes in the following solution at 75°C and then rinsed well and dried at 65°C (ref. 15).

Water	2640 g
Sodium metasilicate	46 g
Trisodium phosphate	23 g
Sodium hydroxide	23 g
Santomerse® #1	8 g

Titanium Alloy - The metal was degreased by refluxing methyl ethyl ketone then immersed in the alkaline cleaning solution used for stainless steel for 10 minutes at 70-80°C. After rinsing with deionized water the metal specimen was immersed for five minutes in acid solution (25°C) containing:

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Sodium fluoride	50 g
Chromium trioxide	25 g
Distilled water	1250 g
Sulfuric acid 96-98%	250 g

The specimens were then rinsed well in deionized water and dried for 10-15 minutes at 70-80°C (ref. 16).
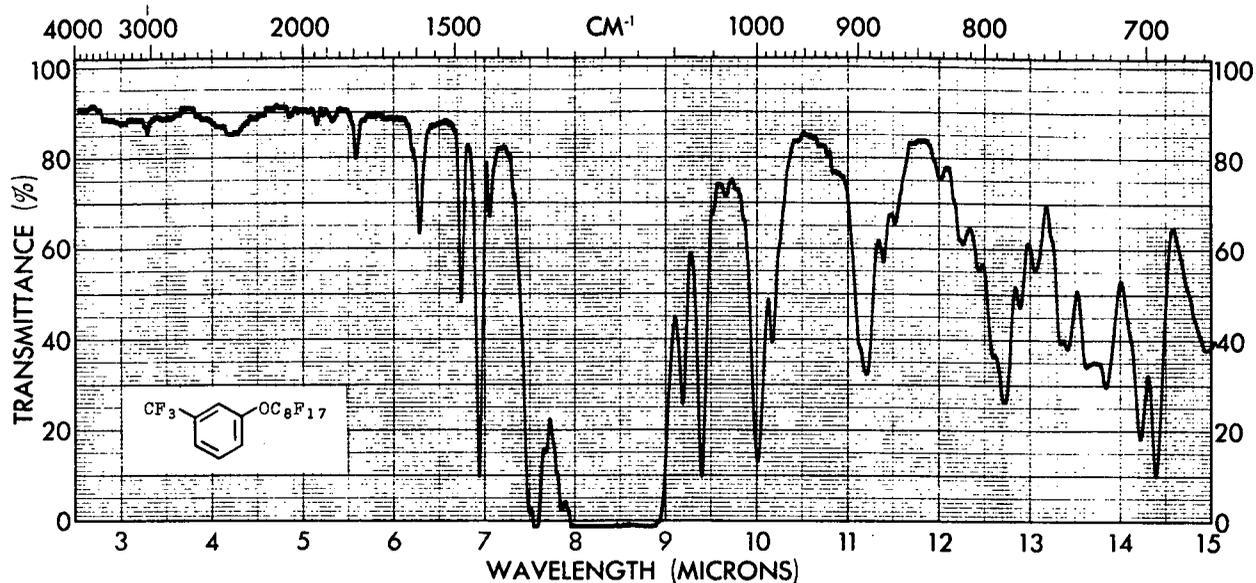
APPENDIX

Infrared Spectra

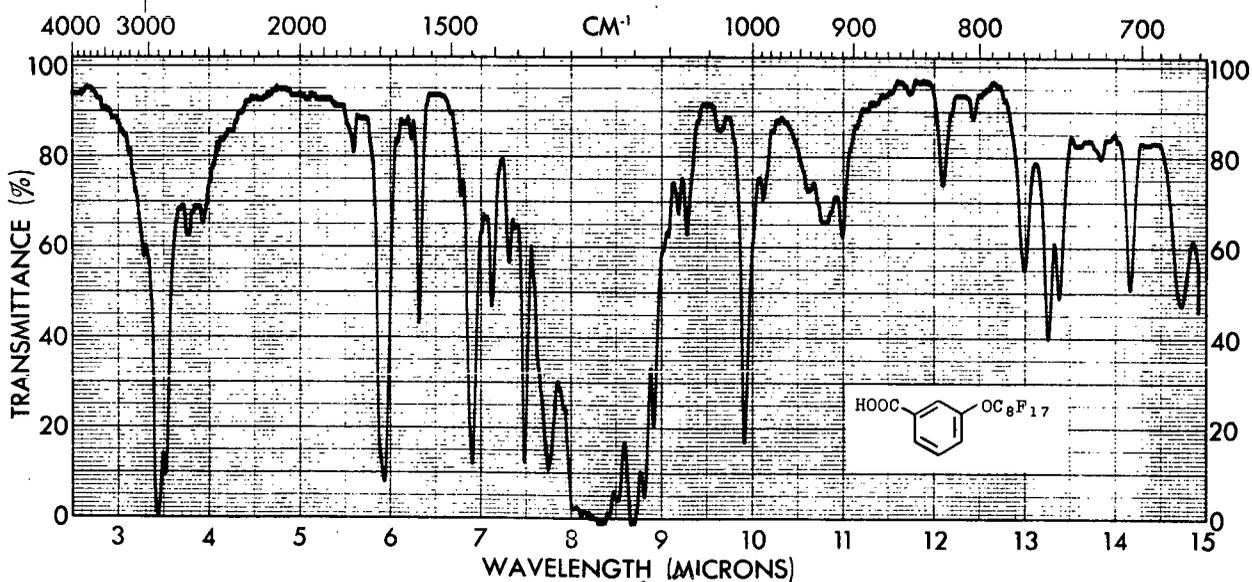Figure 1. *m*-Trifluoromethylphenyl Heptadecafluorooctyl Ether
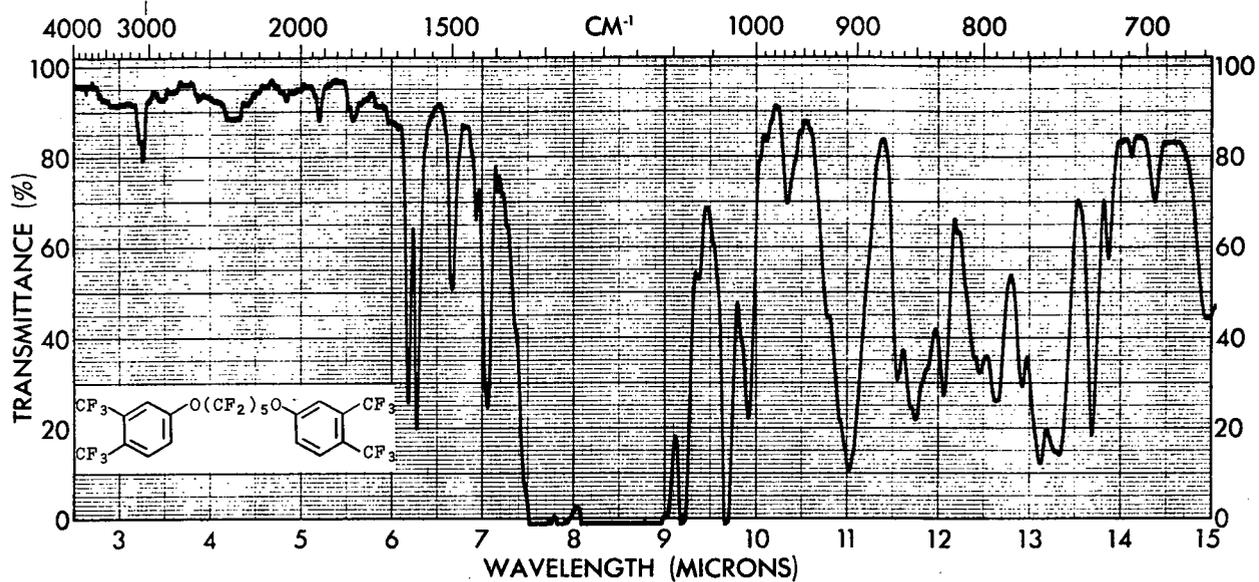

Figure 2. *m*-Heptadecafluorooctoxybenzoic Acid

Figure 3.   3,3',4,4'-Tetrakis(trifluoromethyl)-1,5-diphenoxydeca-
fluoropentane
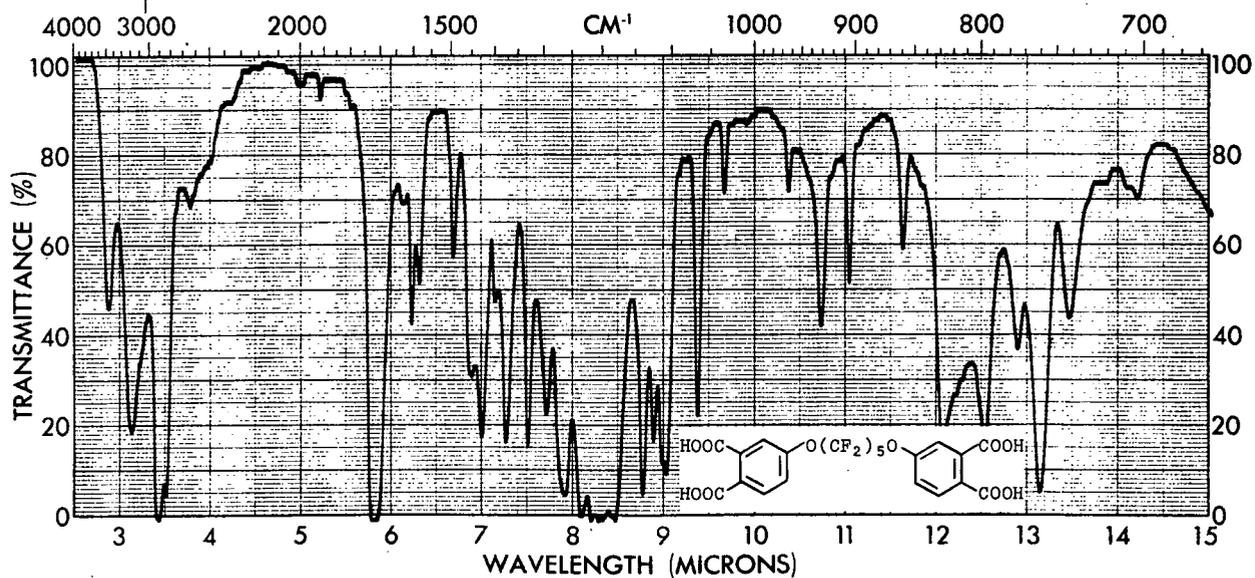
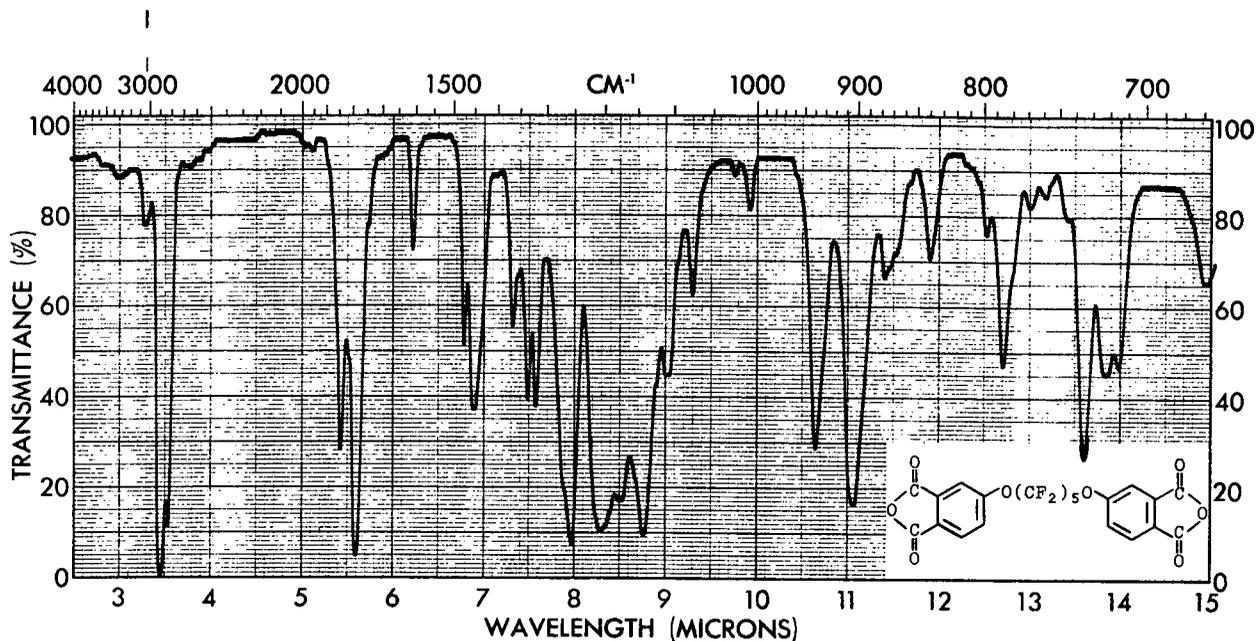Figure 4.   1,5-Diphenoxydecafluoropentane-3,3',4,4'-tetra-
carboxylic Acid

Figure 5.   1,5-Diphenoxydecafluoropentane-3,3',4,4'-tetra-
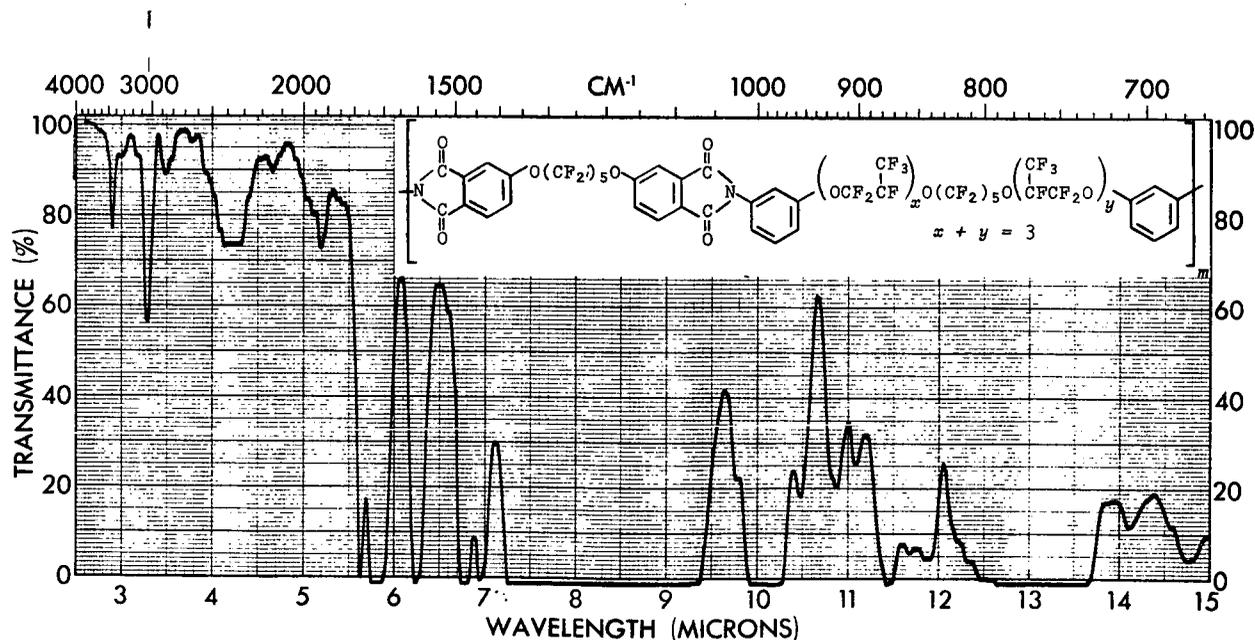carboxylic Dianhydride

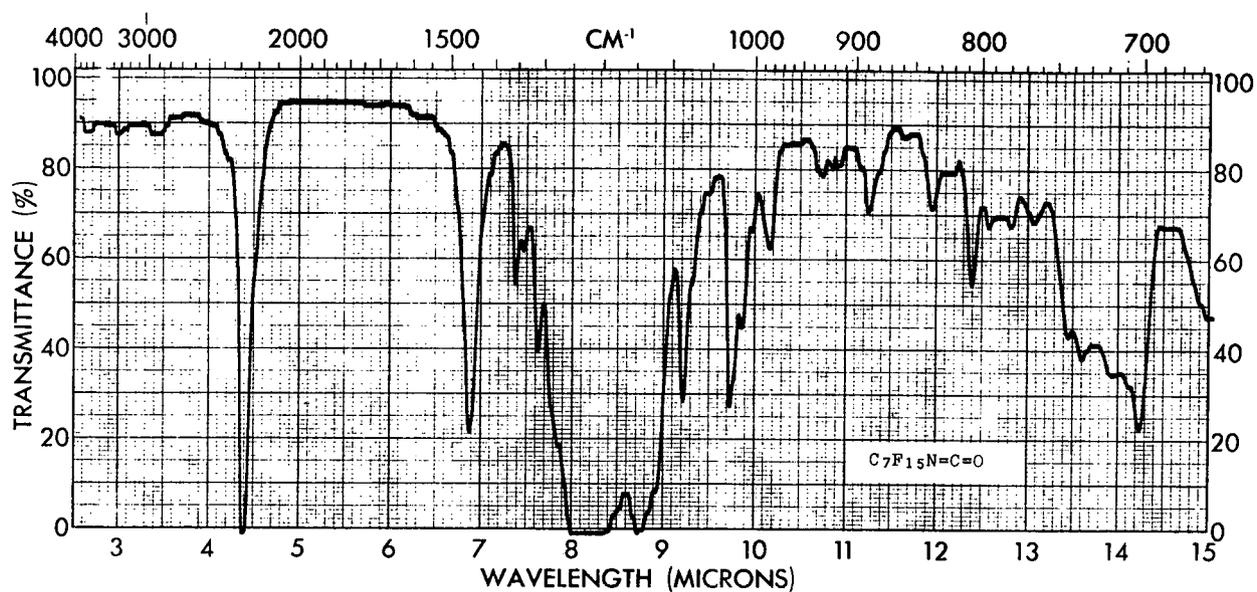Figure 6.   Polyimide Film Containing 10% Mellitic Trianhydride
(149616-B)

Figure 7. Perfluoroheptyl Isocyanate

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