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PERFLUOROETHER TRIAZINE ELASTOMERS

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I. INTRODUCTION

Aerospace progress can often be measured in terms of material development as advanced aerospace applications place more stringent requirements on the thermal and mechanical properties of materials. This is especially true of elastomers and sea....ts. The weakest link in high performance equipment is often an elastomeric component. Seals, gaskets, diaphragms and couplings are inherently less stable than structural metals and composites. This is true of such diverse applications as fuel tank sealants in high speed aircraft, couplings for drill bits used in geothermal formations, deep wells and wells exposed to sour gas, electrical connectors, firewall seals, and tough-service parts in automobile engines, pumps, compressors, pipelines and scientific equipment. All of these applications require elastomeric materials with outstanding thermal and environmental stability.

Development of high temperature elastomers has concentrated on the fluorocarbons and fluorosilicones. Fluorocarbons are generally superior to fluorosilicones in thermal stability and fluid resistance. However, most fluorocarbons are not useful as elastomers at low temperatures (less than -40°C) because of their high glass transition temperatures. In particular, perfluoroalkylene-triazine elastomers have promised a clear superiority over other known elastomers in thermal and oxidative stability. Their reduction to practice has been frustrated by the complex nature of the chemical system used for polymerization and the non-availability of desirable synthetic intermediates (1).

In order to obtain high performance elastomers with the high thermal stability and chemical inertness of perfluoroalkylene triazine and a low glass transition temperature, I have been examining perfluoroether triazine elastomers. These materials were proposed as potentially superior high performance elastomers in 1975 (2). However, perfluoroether synthesis was limited to low molecular weight polymers. Elastomers with good mechanical properties such as high tensile strength and with a low glass transition temperature were not produced at this time. Before an improved high performance elastomer could be produced, high molecular weight linear perfluoroether triazine polymers were required that could be quantitatively crosslinked by a stable linkage. Average chain length between crosslinks must be controlled in order to achieve desired mechanical properties such as modulus.

Measurement of molecular weight distributions of fluorinated polymers is difficult because of their insolubility in organic solvents. So fluorinated
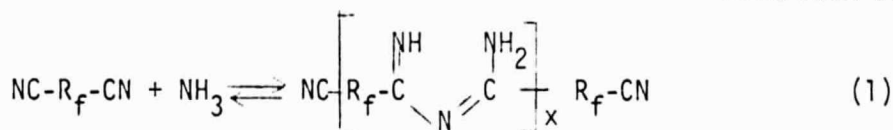
solvents must be used. To determine molecular distribution of perfluoroether polymers, I have used exclusion chromatography with small particle silica column packing (3). This rigid packing is compatible with fluorinated solvents whereas the polystyrene gel packings shrink in the presence of fluorinated solvents.

We have recently produced thermally stable perfluoroalkylether oxidiazole elastomers crosslinked by tri-functional triazine (4). This stable triazine crosslink is also used in the synthesis of perfluoroether triazine elastomers.
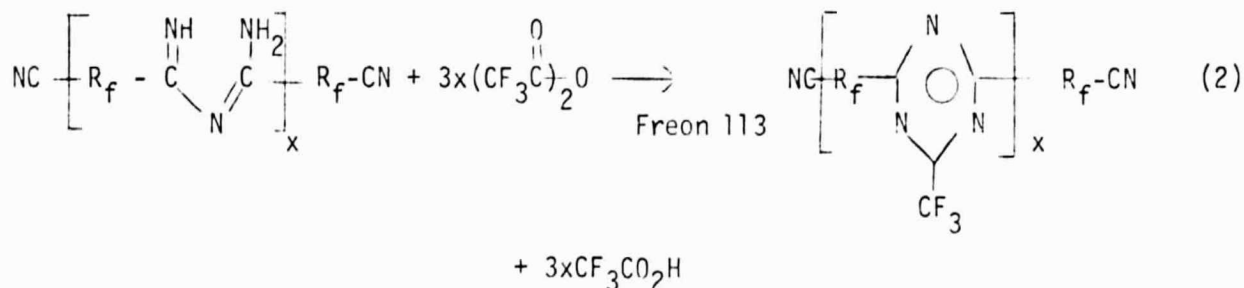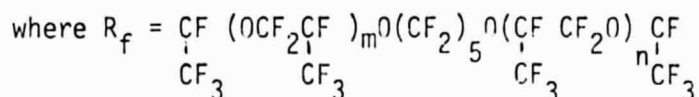
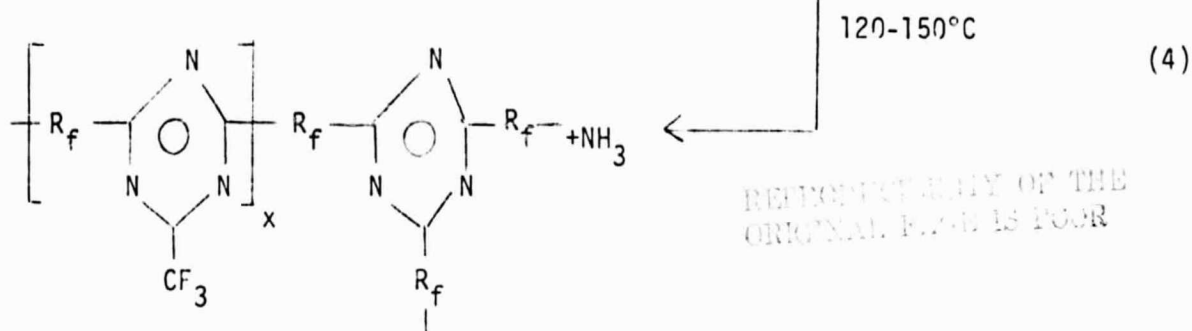## II. SYNTHESIS OF PERFLUOROETHER TRIAZINE ELASTOMERS

I have used the following synthetic route to obtain perfluoroether triazine elastomers:

$$NC-R_f-CN + NH_3 \rightleftharpoons NC \left[R_f-C \underset{N}{\overset{NH}{\diagdown}} \overset{NH_2}{\underset{}{}} C \right]_x R_f-CN \qquad (1)$$

poly(imidoyl amidine)

where $R_f = \underset{CF_3}{CF} (OCF_2 \underset{CF_3}{CF})_m O(CF_2)_5 {}^n (\underset{CF_3}{CF} CF_2O)_n \underset{CF_3}{CF}$

$$NC \left[R_f - C \underset{N}{\overset{NH}{\diagdown}} \overset{NH_2}{\underset{}{}} C \right]_x R_f-CN + 3x(CF_3C)_2O \xrightarrow[\text{Freon 113}]{} NC \left[R_f \overset{N}{\diagdown} \bigcirc \underset{N}{\diagdown} \right]_x R_f-CN \qquad (2)$$

$$+ 3xCF_3CO_2H$$

$$NC \xrightarrow{\hspace{0.3cm}} R_f \xrightarrow{\hspace{0.3cm}} \left[\begin{array}{c} N \\ \bigcirc \\ N \quad N \end{array} \right]_x R_f\text{-CN} + NH_3 \rightleftarrows \quad R_f \xrightarrow{\hspace{0.3cm}} \left[\begin{array}{c} N \\ \bigcirc \\ N \quad N \end{array} \right]_x R_f\text{-}\underset{N}{\overset{NH}{\underset{\|}{C}}}\underset{}{\overset{NH_2}{\underset{}{C}}} \xrightarrow{\hspace{0.3cm}} \quad (3)$$

	120-150°C

$$\left[\begin{array}{c} \\ R_f \xrightarrow{} \end{array} \begin{array}{c} N \\ \bigcirc \\ N \quad N \end{array} \right]_x R_f \xrightarrow{} \begin{array}{c} N \\ \bigcirc \\ N \quad N \end{array} R_f \xrightarrow{} +NH_3 \quad \longleftarrow \quad (4)$$

CF_3 beneath first ring, R_f beneath second ring.
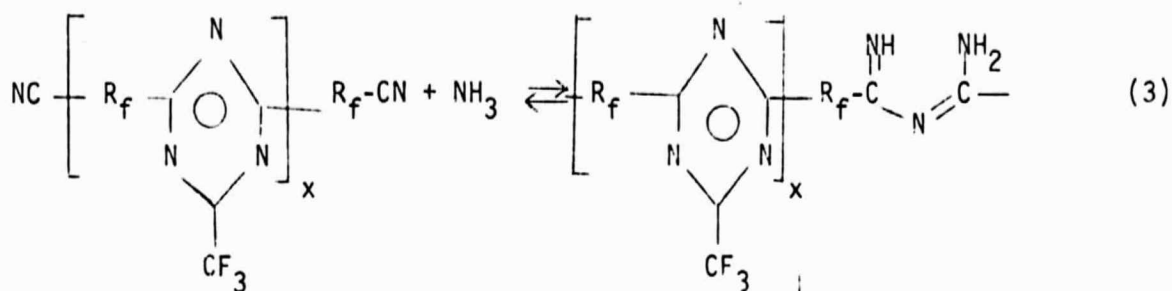
A. Procedure for Elastomer Synthesis

Perfluoroalkylether dinitrile was weighed into a three neck, round bottom flask. One neck of the flask was connected to a Dewar condenser, one neck to a nitrogen cylinder and one neck to an ammonia lecture bottle. The flask was placed in a water bath on a magnetic stirrer. Reactions were run at room temperature.

The flask was purged with nitrogen and the condenser loaded with dry ice. All gases were purified by passage through drying tubes packed with calcium oxide and pyrex glass wool. Air and moisture were carefully excluded from the reaction flask. Ammonia was introduced with refluxing. After two to eight hours, the ammonia was vented and the viscous polymer dissolved in Freon 113. During this reaction period samples were withdrawn from the reaction flask for infrared spectroscopic analysis in order to determine extent of reaction. The polymer solution was added dropwise to trifluoroacetic anhydride in an amber bottle with the weight of trifluoroacetic anhydride at least 0.3 times the weight of the polymer. An amber bottle is necessary to prevent photoinitiated decomposition of the anhydride. Slow addition of poly (imidoyl amidene) to the trifluoroacetic anhydride solution is required in order to maintain a high concentration of the anhydride

during ring closure. The anhydride acts as a dehydrating agent, and prevents hydrolysis products, expecially amides, from forming. Amides act as a polymer chain terminator and are formed if water is not excluded from this reaction. The resultant solution was allowed to stand overnight. Freon 113 was then removed by distillation. After solvent removal a two phase, poly (perfluoroalkyether triazine) and trifluoroacetic acid, system resulted. The poly (perfluoroalkyl- ether triazine) was separated and placed in a three neck, round bottom flask. Ammonia was introduced to reflux as before. After two hours the flask was sealed and left overnight. The resultant polymer was heated in vacuum (ca 2/3 atm) for one day period at 100°C, 130°C and 150°C to form an elastomer.

B. General Experimental Methods

Infrared (IR) spectra were recorded on the Perkin-Elmer Model 180 infrared spectrophotometer. Thermogravimetry (TG) measurements were obtained with the DuPont Instruments 951 Thermogravimetric Analyzer and 990 Thermal Analyzer. Glass transition temperatures (T_g) were measured with a DuPont Differential Scanning Calorimetry (DSC) cell. All high performance liquid chromatography (HPLC) measure- ments were made with the Waters ALC-GPC 202/401 liquid chromatograph (3, 4). De- tection by UV absorption was at 254 nm and DuPont prepacked size exclusions (SE) columns were used. Viscosities were determined at several concentrations with Freon 113 as solvent in a Cannon-Ubbelohde size 50 viscometer at 30°C. Intrinsic viscosity was calcualted by the relationship

$$[n] = \left(\frac{t_s - t_o}{ct_o} \right)_c \rightarrow 0$$

where t_s = flow time of polymer solution, t_o = flow time for Freon 113, and c is the polymer concentration in g/ml.

1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113) was purchased from E.I. DuPont deNemours and Co. Perfluoroalkylether dinitriles were obtained from PCR, Inc.

C. Results and Discussion

Perfluoroalkylether dinitrile and ammonia combine to form poly (imidoyl amidine) as shown in reaction 1. The extent of this reaction was followed by viscosity measurements and infrared (IR) spectroscopy. A typical IR spectrum is shown in Figure 1. This figure shows nitrile absorption at 2260 cm^{-1} and imidoyl amidine absorption at 1520 cm^{-1}, 1600 cm^{-1} and 1650 cm^{-1}. Size exclusion chromatography was attempted on the poly (imidoyl amidine) polymers using both

WAVELENGTH (MICRONS)
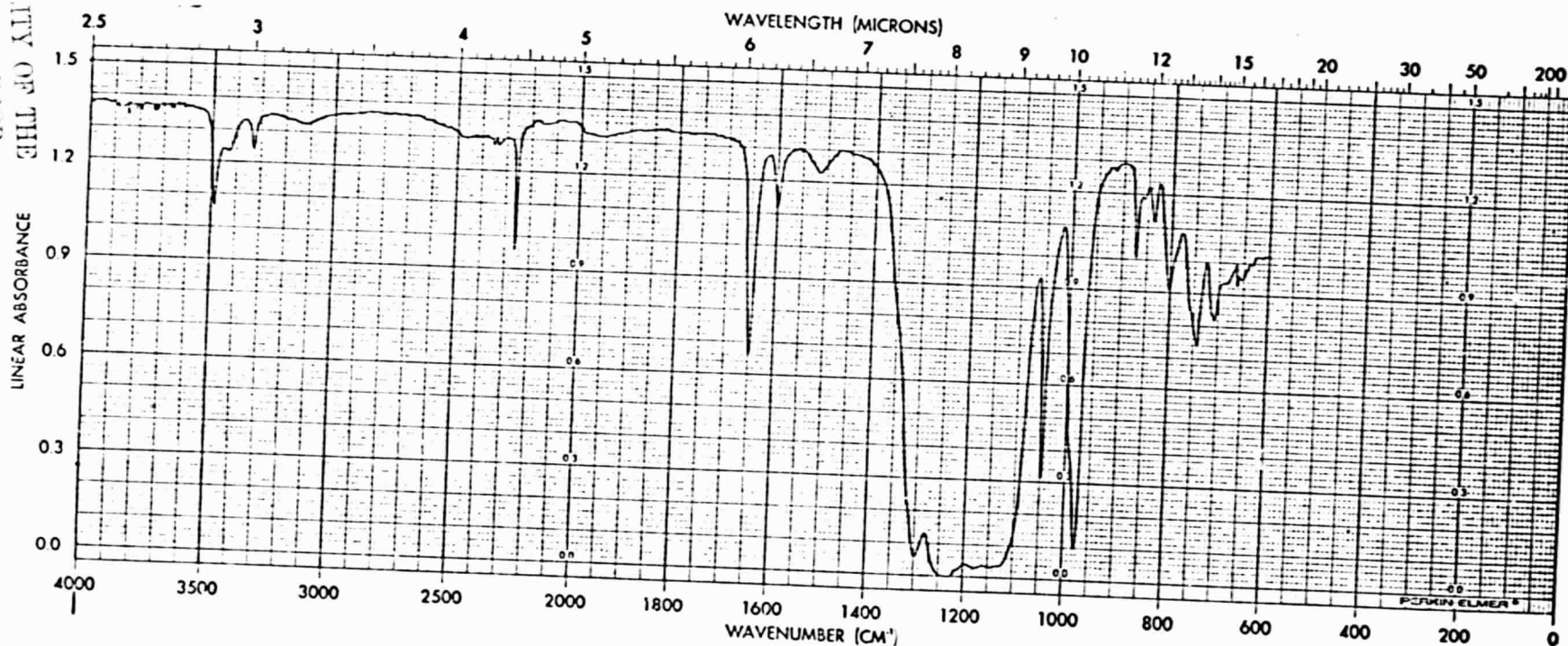
WAVENUMBER (CM⁻¹)

FIGURE 1: Infrared spectrum of reaction product from reaction 1 - Nitrile band is at 2260 cm^{-1}, imidoyl amidine bands are at 1520 cm^{-1}, 1600 cm^{-1} and 1650 cm^{-1}.

DuPont SE columns and Waters μ BONDAGEL columns. The poly (imidoyl amidine) polymers were adsorbed on both column types, and molecular weight distributions could not be determined at this stage of the synthesis. After ring closure to linear polytriazine polymers, reaction 2, adsorption was no longer a problem, and molecular weight distributions were determined on the linear perfluoroether triazine polymers. Since the degree of polymerization is not affected by reaction 2, molecular weight measurements on the linear perfluoroether triazine polymers can be correlated with the viscosity and IR measurements on the corresponding linear poly (imidoyl amidine) polymers (see Table I). Molecular weight measurements of perfluoroalkylether triazine polymers by HPLC gave weight average molecular weights as high as 28,000 for eight hour exposure to ammonia in reaction 1. However, it was difficult to control molecular weight according to NH_3 exposure time in reaction 1 because rate of reaction was dependent on many factors such as amount of dinitrile used, stirring rate, NH_3 concentration and reflux rate. For these reasons, the extent of reaction 1 was periodically measured as a function of reaction time. Infrared spectroscopy was used to measure extent of reaction, or equivalently the degree of poly (imidoyl amidine) polymerization. Subsequent reactions 2, 3 and 4 are all carried out to completion. In reaction 2 excess trifluoroacetic anhydride is used so that the ring closure of linear poly (imidoyl amidine) to linear polytriazine is driven to completion. An IR spectrum of a linear polytriazine formed by reaction 2 is shown in Figure 2. Triazine shown bands at 1550 cm^{-1} and 1430 cm^{-1}. The nitrile band can still be seen at 2260 cm^{-1}. There is no evidence of imidoyl amidine. In reaction 3 excess ammonia is used to convert the remaining nitrile to imidoyl amidine. The resultant polymer is an insoluble gum that is converted to a triazine elastomer at 110-150°C.

Using similar synthetic methods, high molecular weight perfluoroalkyl triazine polymers have been synthesized by Dorfman, et. al. (1, 5). These linear polymers were crosslinked to form tough, rubbery elastomers with glass transition temperatures from -17 to -5°C (5). Young has said that the materials made by Dorfman, et. al. represent the closest approaches to practicable perfluoroalkylene-triazine elastomers (1). This method differs from mine in several important aspects. First, only perfluoroalkyl inter-ring monomers were used by Dorfman whereas I have used perfluoroalkylether inter-ring monomers. Using perfluoroalkylether groups produces much improved low temperature properties. Perfluoroalkylether triazine elastomers have glass transition temperatures of approximately -45°C or about 35

TABLE I. CHARACTERIZATION OF PERFLUOROALKYLETHER TRIAZINE ELASTOMERS

Sample	Absorbance Ratio[1]	Intrinsic Viscosity (ml/g)	$\bar{M}_w$ by HPLC	Modulus[2] (N_m^{-2})	Description
1	1.5	6.2	8600	10^7-10^8	cheesy
2	3	5.95	7000	10^7-10^8	cheesy
3	10	7.4	12000	10^6	rubbery
4	35	7.8	14500	10^5	gum
5	41	10.0	23000	10^5	gum
6	44	8.96	18000	10^5	gum
7	50	9.9	19000	10^6	rubbery
8	60	11.2	28000	10^4	gum

[1]Absorbance ratio is the ratio of IR absorbance at 1600 cm^{-1} (imidoyl amidine) to IR absorbance at 2260 cm^{-1} (nitrile) after reaction 1.

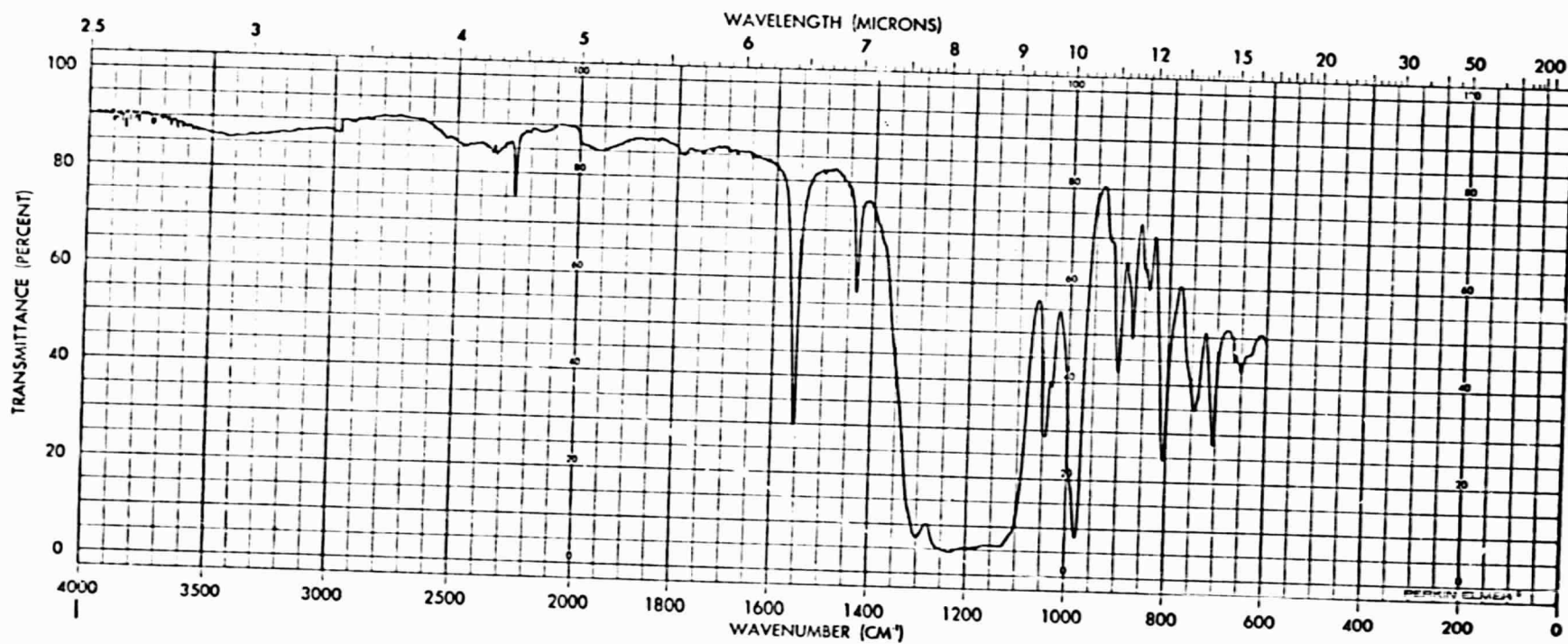[2]Modulus is dependent on the curing conditions used in reaction 3 so approximate values are given.

FIGURE 2: Infrared spectrum of reaction product from reaction 2. Triazine bands are at 1430 cm^{-1} and 1550 cm^{-1}.

degrees less than the corresponding perfluoroalkyl triazine elastomers.

Secondly, my method of crosslinking (reactions 3 and 4) appears to be novel. Dorfman, et. al. do not even discuss crosslinking methods. Young discusses possible ways for incorporating sites for crosslinking in a linear triazine polymer. The methods that he discusses are considerably more complex, require higher curing temperatures, and are not as clean as crosslinking by reactions 3 and 4.

Several batches (30 to 50 g each) of perfluoroether triazine elastomers have been prepared. Infrared spectroscopy was used to moniter extent of reaction and was found to be a good indicator of the final elastomer properties. A summary of the results obtained in the characterization of eight perfluoroalkylether triazine polymers and elastomers in given in Table 1. These elastomers and polymers were all synthesized from 8-EDAF perfluoroether dinitriles (m + n = 6, see reaction 1). Modulus measurements were obtained using the DuPont 943 Thermomechanical Analyzer with the stress relaxation accessory (part no. 943169-000). With one exception (sample 7) the properties of the elastomers correlate well with each of the three measurements of the extent of polymerization.

Glass transition temperatures were measured with a DuPont differential scanning calorimetry cell on the DuPont 990 Thermal Analyzer. The 8-EDAF perfluoroalkyether triazine elastomers had a glass transition temperature of -45°C.

Thermogravimetric analysis measurements were obtained with the DuPont Instruments 951 Thermogravimetric Analyzer and 990 Thermal Analyzer. Five-25 mg. of sample were placed on the microbalance and weight was recorded either as a function of temperature (thermogram) as the temperature was raised 10°C/min or as a function of time (isothermal) at a constant temperature.

A thermogram of a perfluoroether triazine elastomer in a nitrogen atmosphere is shown in Figure 3. Thermograms of oxadiazole and fluorosilicone elastomers are shown in Figure 4 for comparison. Maximum weight losses occur at 570°C for the triazine, 540°C for the fluorosilicone, and 510°C for the oxadiazole elastomers. However, the fluorosilicone elastomer shown significant weight loss from 250-350°C. The perfluoroether elastomers shown no appreciable weight loss up to 400°C.

Isothermal weight losses of Sample 8 (see Table I) were determined in nitrogen and in air (Table II). The perfluoroalkylether triazine elastomer shown lower isothermal wieght losses than poly(trifluoropropylmethane siloxane), a thermally stable polyester sealant, and perfluoroalkylether oxadiazole elastomers (4). The high temperature oxidative stability of the perfluoroether triazine elasto-
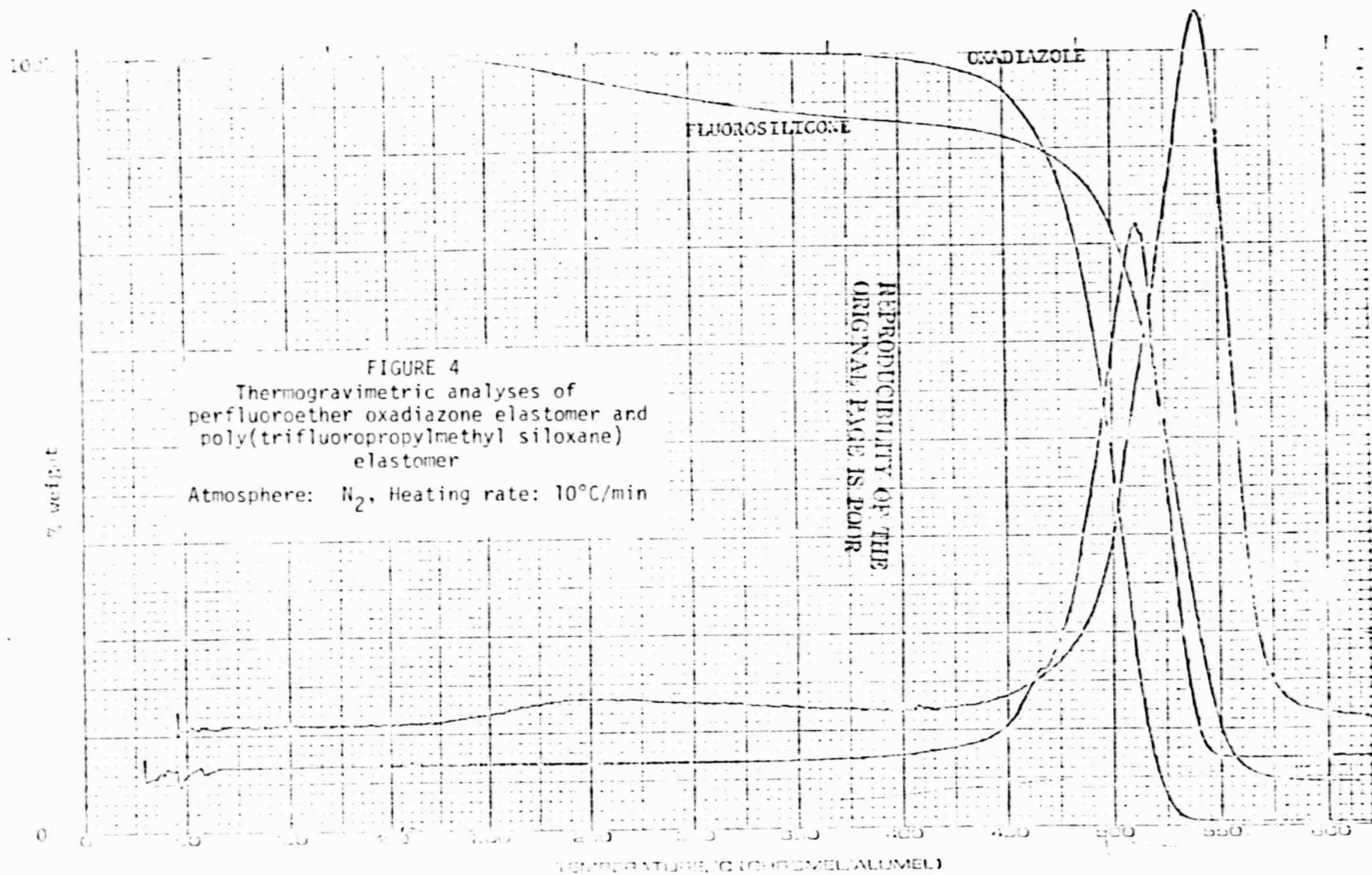
FIGURE 3

Thermogravimetric analysis of
perflouroether traizine elastomer

Atmosphere: N_2, Heating rate: $10°C/min$

TEMPERATURE, °C (CHROMEL/ALUMEL)

FIGURE 4

Thermogravimetric analyses of
perfluoroether oxadiazone elastomer and
poly(trifluoropropylmethyl siloxane)
elastomer

Atmosphere: N_2, Heating rate: 10°C/min
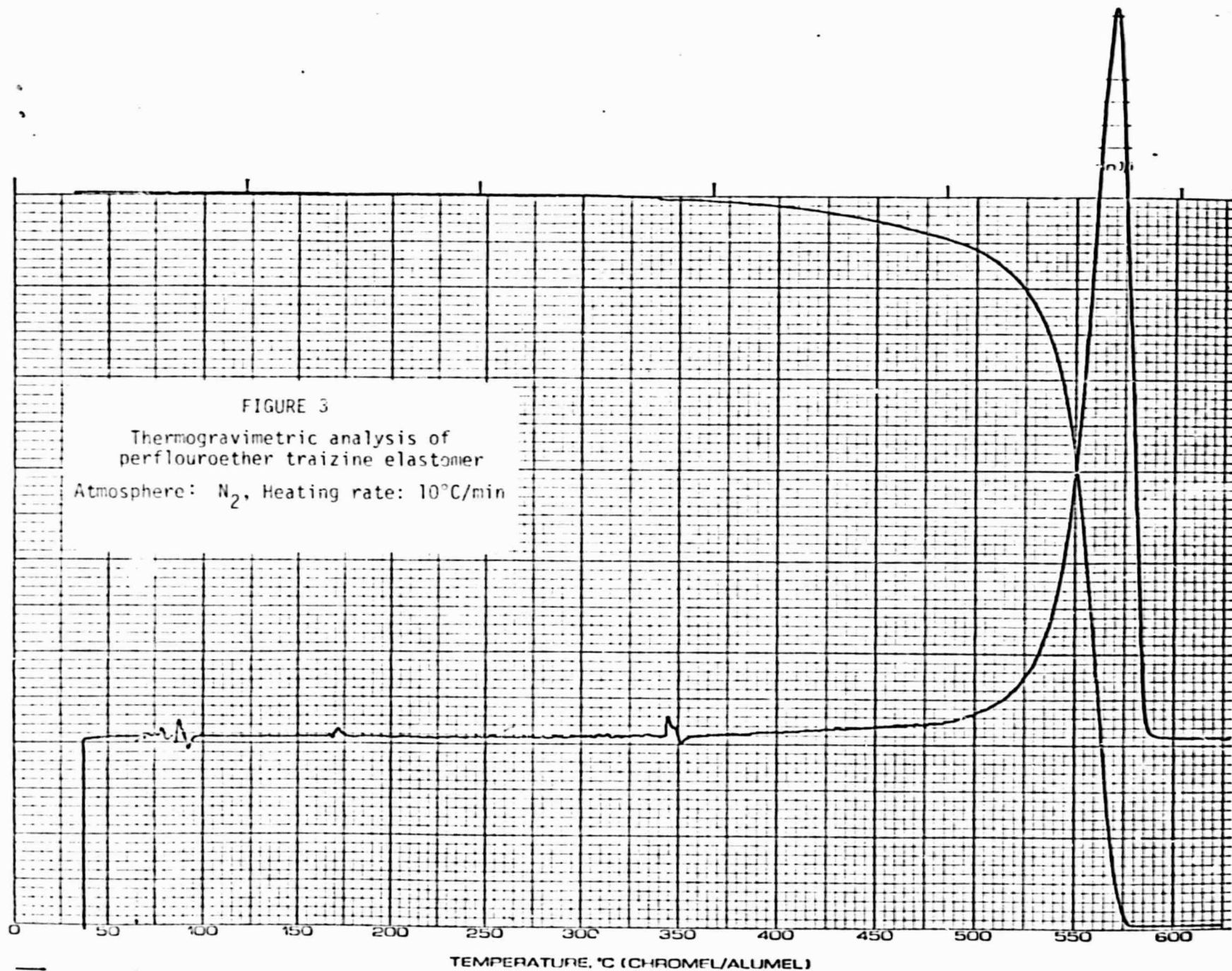
FIGURE 4

THERMOGRAVIMETRIC ANALYSIS

ATMOSPHERE: N_2 HEATING RATE: 10°C/min

TABLE II. ISOTHERMAL WEIGHT LOSS STUDIES

Conditions			% Weight Loss	
Atmosphere	Temperature (°C)	Time (hr)	Poly(trifluoropropylmethane siloxane) elastomer	Perfluoroalkylether triazine elastomer
Nitrogen	300	1	7.5	1.0
Nitrogen	300	10	9.5	2.1
Nitrogen	300	65	17.5	6.5
Nitrogen	325	1	10.4	1.5
Nitrogen	325	10	11.8	3.7
Nitrogen	325	65	19.2	9.6
Air	300	4	42.5	0.8
Air	300	8	73.7	1.3
Air	300	16	77.0	2.3
Air	325	4	75.5	8.5
Air	325	8	76.2	12.5
Air	325	16	77.5	17.5

mers shows a very marked improvement over state-of-the-art thermally stable elastomers.

No problems were encountered in scaling up elastomer synthesis to 50 g batches. In fact synthesis control was somewhat easier on this larger scale because of easier mixing. Control of modulus so as to give a modulus of approximately 10^4 Pa (10^5 dynes/cm^2) was readily achieved with IR monitoring of the synthesis. This is the approximate modulus required for fuel tank sealant applications. Several batches of uncured perfluoroether triazine elastomer (synthesis through reaction 3) have been sent to Ames Research Center for further testing.

III. Dehydration of Perfluoroether Diamide

The starting material for the synthesis of perfluoroether triazine elastomers is a difunctional nitrile (see reaction 1). This dinitrile is prepared from a diacyl fluoride as follows:

$$Cl \overset{O}{\underset{}{\diagdown}} C - R_f - C \overset{O}{\underset{Cl}{\diagup}} + 2NH_3 \rightarrow H_2N \overset{O}{\underset{}{\diagdown}} C - R_f - C \overset{O}{\underset{NH_2}{\diagup}} + 2HCl \qquad (5)$$

$$H_2N \overset{O}{\underset{}{\diagdown}} C - R_f - C \overset{O}{\underset{NH_2}{\diagup}} \rightarrow N \equiv C - R_f - C \equiv N + 2H_2O \qquad (6)$$
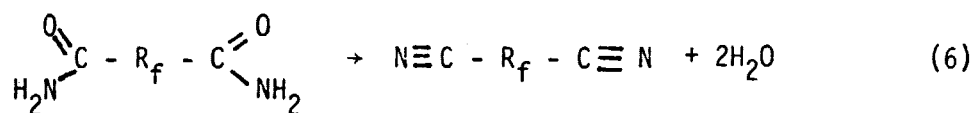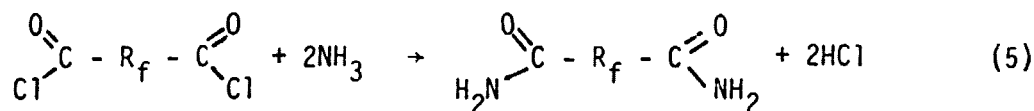
Reaction 5 occurs readily with addition of ammonia to a solution of acid fluoride in Freon 113. This reaction is very exothermic and temperature control will be very important on a large scale. The procedure used for reaction 5 was:

Perfluoroether diacyl fluoride is placed in a 3-neck round bottom flask together with approximately two times as much Freon 113. Nitrogen and ammonia gas cylinders are connected to the flask and a Dewar condenser connected in the same manner as for reactions 1 and 3. Nitrogen was bubbled through the solution for 10 minutes while the condenser was loaded with dry ice. Ammonia was introduced and the reaction complete within one-half hour as evidenced by IR spectroscopy. The resultant solution is cloudy because of the low solubility of tne diamide in Freon 113. Methanol is added in volume equal to the Freon 113 used. The resultant solution is clear in this mixed Freon 113-methanol solvent. This solution is filtered through a 0.5 µm Millipore filter. Methanol and Freon 113 were removed by distillation leaving perfluoroether diamide.

Reaction 6 occurs at appreciable rates only in the presence of dehydrating agents or dehydrating catalysts. It is possible to carry out this reaction in the presence of P_2O_5 in a batch operation followed by distillation to remove dinitrile from the reaction mixture. Dehydration yields are low (60-70%), distillation of the P_2O_5/dinitrile viscous slurry is difficult and must be done under vacuum, and scale-up to a commercial scale does not appear economically feasible.

Dehydration on a commercial scale is almost always done over dehydration catalysts in a continuous flow heterogeneous reactor (6). Dozens of catalysts are commercially available. In order to screen some of these catalysts for activity in reaction 6, the following dehydration catalysts were obtained:

from Aluminum Company of America, Alcoa Technical Center:

    F-1 activated alumina

    XF-100 activated alumina

    F-20 activated alumina

from Filtrol Corporation

    SS-376 grade 49

    SS-376 grade 62 silica-alumina

from Harshaw Chemical Company

    phosphorus catalyst P-0620

    alumina catalyst Al-0104

    alumina catalyst Al-1404

from Chemetron Chemicals Girdler Catalysts Department

    T-311 nickel on activated alumina

from Union Carbide Linde Division

    molecular sieve type 13X

    molecular sieve type SK-400

    molecular sieve type 4A

Initial screening of these dehydration catalysts for activity in reaction 6 was attempted using an Autoclave Engineering Berty spinning basket magnetically stirred catalytic reactor. The catalyst was held in the center of the reactor and the reactant gases were recirculated down through the catalyst by an impeller in the bottom of the reactor. The reactor was heated by a 3 kw heater. Reactor temperatures were measured by a chromel-alumel thermocouple located in the gas stream below the catalyst bed and another thermocouple above the catalyst bed.

The reactant used for all screening experiments was an 8 EDAF mix of amide and nitrile obtained from Technochemie GmbH - Verfahrenstechnik, Germany (sample number H 782-1). An infrared spectrum of H 782-1 is shown in Figure 5.

The operating procedure for screening dehydration catalysts in the Berty reactor was:

1. A few ml of H782-1 were pipeted into a small stainless steel tube. The tube was placed on the screen which supports the catalyst and catalyst was packed around the tube.

2. The reactor was closed and purged with helium for approximately one hour.

3. The outlet and inlet valves were closed and the reactor heated to the desired temperature.

4. After 1 to 4 hours at the desired temperature, the reactor was flushed with helium. The outlet gas was passed through an Erlenmeyer flask which was cooled in an ice bath.

5. The condensate from the reactor was analyzed by IR spectroscopy to determine if amide dehydration had occurred.

The following catalysts were tested in the Berty reactor: Alcoa F1, Alcoa XF-100, Harshaw P-0620, and Harshaw Al-1404. In each case triazine was the predominant reaction product. For the Alcoa F1 catalyst amide disappeared at short reaction times; for the other catlaysts nitrile disappeared before amide. This indicated that the Alcoa F1 catalysts was catalyzing the amide dehydration reaction but the nitrile formed was reacting further to form triazine. Also IR spectra of reaction product remaining in the sample holder at the end of screening experiments showed that much of the sample was polymerizing in the stainless steel sample tube. Both the sample tube and Berty reactor are constructed of 316 stainless steel and polymerization of nitrile to triazine was occuring on stainless steel at 200-250°C.

An all-glass catalytic reactor was constructed in order to avoid the polymerization of nitrile. A schematic diagram and description of this reaction is given in Figure 6. This set-up is similar to a distillation assembly with a packed bed catalytic reactor replacing the condenser. For catalyst screening, catalysts were mixed with glass beads (Kimax 3 mm diameter beads) and the mixture loaded into the reactor. The mixtures were mostly glass beads as it was found that 2 to 7 g. of catalyst were sufficient. The procedure for reaction operation was:

1. A few ml. of H 782-1 were added to the 100 ml. feed flask. Often this was combined with feed from the previous experiment. An infrared spectrum from

ACCY
HI ENERGY
RESOLUTION ✓
OPERATOR RAK DATE 2/27/79
SURVEY
CAL
SPECTRUM NO 8
SAMPLE H 782-1 between 2
salt plates
ORIGIN

MICROMETERS (μm)

3.0   4.0   5   6   7   8   9   10 11 12 13 14 16 18 20 25

FIGURE 5
Infrared spectrum of
Technochemic K 782-1

SAMPLE

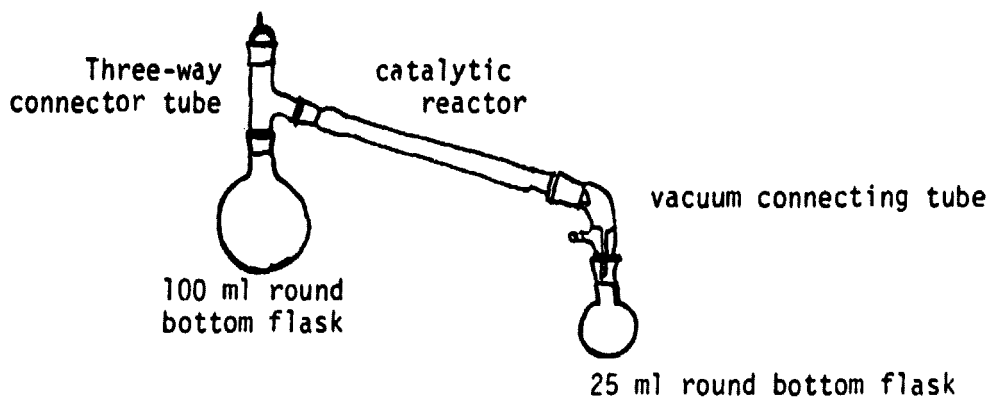SPECTRUM NO.   16

3400 3200 3000 2400 2000 1800 1600 1400 1200 1000 800 600 400

FIGURE 6. Schematic diagram of all-glass catalytic reactor set-up. The
dimension of the catalyst reactor is 3/4 in. ID X 8 in. A chromel-
alumel thermocouple was inserted through a glass tube sealed into
the vacuum connecting tube so that the thermocouple junction is
approximately in the middle of the catalyst bed. The 100 ml round
bottom feed flask is surrounded by a heating mantle which is under
Variac control. A Brisheat heating tape, 1/2 in. X 6 ft., is
wrapped around the catalytic reactor and controlled by another
Variac. Temperatures up to 440°C can be attained in the reactor.
The vacuum connecting tube at the reactor outlet is connected to a
vacuum pump. The 25 ml round bottom product collection flask is
cooled in an ice bath.

experiment D-9 is shown in Figure 7. This feed solution is predominantly amide with some nitrile.

2. The system is closed and the vacuum pump turned on. The catalyst bed is heated approximately 300°C in order to remove adsorbed water from the catalyst.

3. The reactor is cooled to the desired operating temperature (150-210°C).

4. The feed flask is heated so that the feed sample refluxes within the three-way inlet adaptor. Product sample appears in the outlet flask approximately 10 minutes after refluxing begins. This reaction product is analyzed by IR spectroscopy.

Two dehydrations catalysts have been examined by this procedure. Initially, the Alcoa F-1 alumina catalyst was tested and found to give a clean perfluoroether dinitrile product. IR spectra of reaction product for two experiments are shown in Figures 8 and 9. The optimum reactor temperature was approximately 150°C. At temperatures less than 110°C or greater than 200°C conversion of amide to nitrile was less than the conversion at 150°C, although the fractional conversion at 200°C approached one.

Screening experimental runs D-8 (product shown in Figure 8) and D-9 (product shown in Figure 9) were made on the same F-1 catalyst. 7.97 g. of catalyst were loaded into the reactor. Between runs the catalytic reactor was flushed with methanol with the reactor temperature set at 110°C to remove any residual amide. In run D-8 the reactor was operated at 150°C, and the initial product was analyzed by IR spectroscopy (Figure 8). This product is a clean nitrile with no trace of amide. In run D-9 the reactor was again operated at 150°C. 4.60 g. of feed was used (see Figure 7 for IR spectrum), and 1.88 g. remained at the end of the experimental run. Of the 2.72 feed weight loss, 1.94 g. or 71% was collected as product. The product is a clean nitrile with no amide band.

The second catalyst tested was the Linde SK-4000 molecular sieve. 6.10 g. of the catlayst was used at 200°C. Conversion of amide to nitrile under these conditions was approximately 70%. The product amide to nitrile ratio was approximately 5 to 1.

Screening of catalysts for dehydration activity will be continued. However, since the Alcoa F-1 catalyst has been shown to given complete conversion of amide to nitrile on a small scale, this reaction should be scaled up to 10 to 50 g batches. At this larger scale yields should be even greater since reactor hold

FIGURE 7
Infrared spectrum of feed to
dehydration reactor in Experiment D-9

SPECTRUM NO. 89

SAMPLE D-8 product

RESOLUTION ✓

DATE 12/18

MICROMETERS (μm)

FIGURE 8
Infrared spectrum of product from
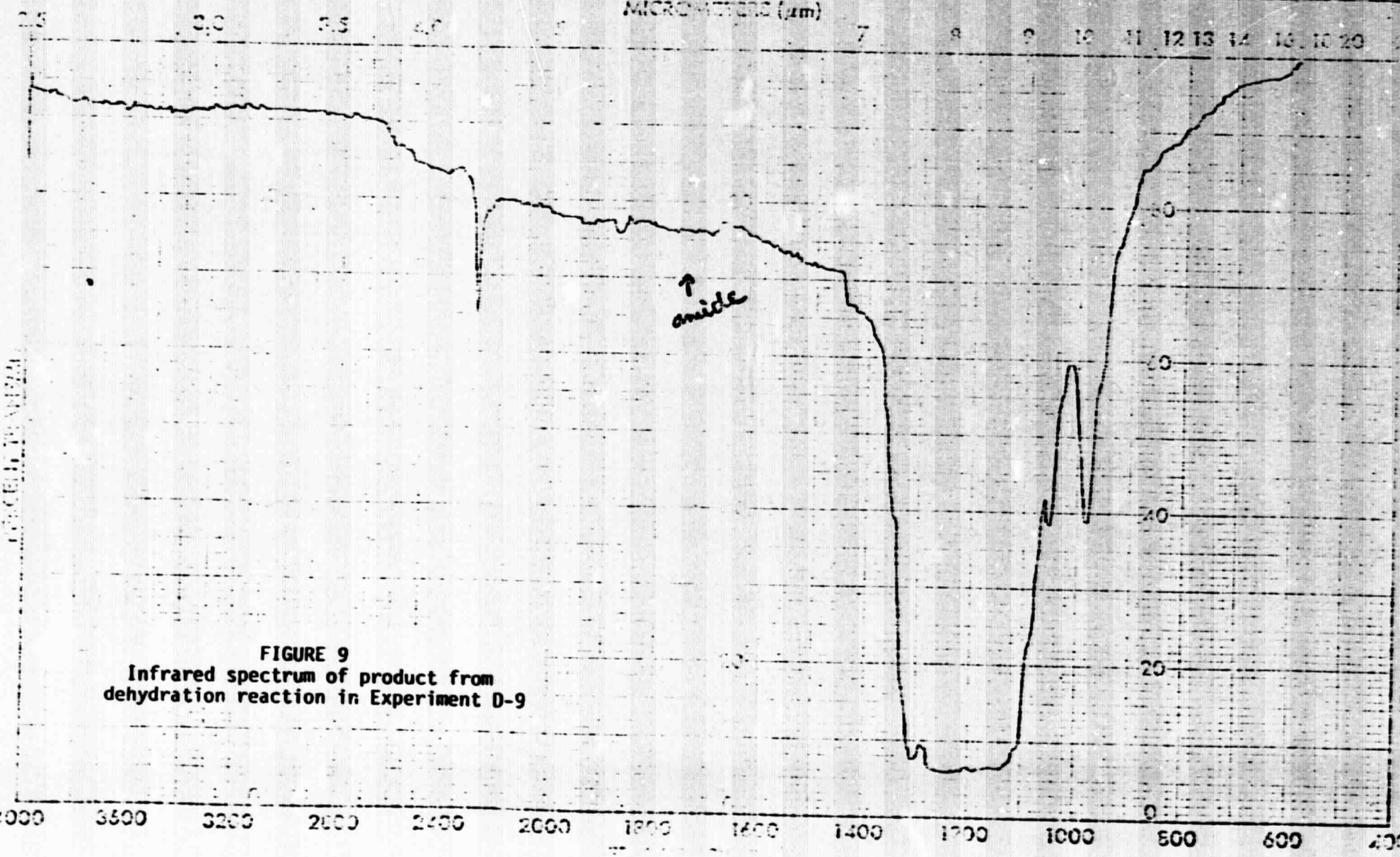dehydration reactor in Experiment D-8

FIGURE 9
Infrared spectrum of product from
dehydration reaction in Experiment D-9

up will not have such a large effect on yield. Dehydration scale up will be studied as soon as sufficient perfluoroether acid fluoride is available.