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13. ABSTRACT (Maximum 200 words)

Environmentally durable high temperature polymer matrix resins are critical in the design of near-term high performance supersonic aircraft. Currently available 6F based polymers are thermally stable, but are expensive and difficulty processable into void-free laminates. 3F polymers have demonstrated equivalent thermal stability and processability, but are amenable to more facile, environmentally acceptable synthetic procedures. In the current program, Semi-Interpentrating Polymer Network (SIPN) blends of ethynyl and phenylethynyl terminated 3F polymers have been formulated and evaluated. A series of test panels were fabricated, using dielectric monitoring procedures, from a 1:1 3F SIPN blend of phthalic anhydride terminated thermoplastic 3F oligomer with a phenylethynyl terminated thermosetting 3F oligomer. Solution prepregging techniques were used to prepare IM7 fiber prepreg tape. The void content of these laminates was somewhat higher than acceptable, probably due to the high melt viscosity. To address this problem, the remainder of the Program will be devoted to a powder prepreg evaluation by Lockheed and Virginia Tech.

14. SUBJECT TERMS High Temperature Polymers; Matrix Resins; Semi-Interpenetrating Polymer Network (SIPN). 3F Polyimide; 3F Diamine; Phenylethynyl Termination; Dielectric Cure Monitoring

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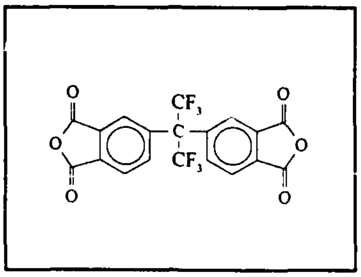
THERMALLY STABLE ORGANIC POLYMERS (TSOPS)
U.S. ARMY RESEARCH OFFICE CONTRACT NUMBER DAAL03-92-C-0021
INTERIM TECHNICAL REPORT

STATEMENT OF THE PROBLEM

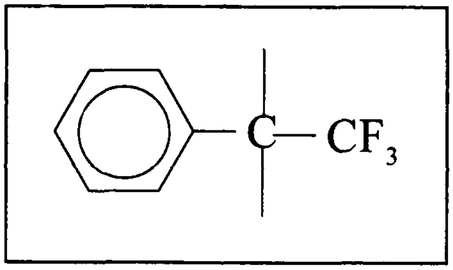
High temperature polymers for use as matrix resins in processible high performance composite materials are of critical importance in the design of near-term high performance military and commercial supersonic aircraft. Utilization of composite materials in place of metals in aircraft structures results in higher specific strength and stiffness, reduced corrosion, and, in the case of military aircraft, supressed radar signature. Current NASA sponsored developmental research at Boeing, McDonnell Douglas, Northrop and Lockheed is directed toward composite matrix resins and adhesives for application on primary and secondary structures for the High Speed Civil Transport (HSCT), a commercial transport to be manufactured by Boeing with a projected cruising speed of Mach 2.4, capable of carrying 300 passengers. The elevated service temperatures of the HSCT carry a long-term durability requirement of 60,000-120,000 hours. Since "real-time" data on composite service for these extended time periods does not currently exist, high performance materials are currently being subjected to accelerated testing. In the NASA Advanced Composite Technology (ACT) and High Speed Research (HSR) Programs, state of the art powder prepreg and towpreg techniques, including advanced towpreg, prepreg tape and powder preforms are being utilized in fabrication of complex composite structures.

Composite matrix resins for elevated temperature service, particularly in the temperature range from 400°F(204°C) to 700°F(371°C), are all polyimides. Polyimides with the highest thermooxidative stability generally contain the hexafluoroisopropylidene group, CF_3CCF_3, (6F) as a connecting entity between aromatic structural groups in the polymer backbone. Recently reported work has shown that substitution of the phenyltrifluorethylidene moiety, $C_6H_5CF_3$, (3F) for the 6F group results in a polyimide matrix resin with comparable thermooxidative stability and processability, but with less expensive prepolymer materials and with synthetic procedures that are less labor intensive and more environmentally acceptable.

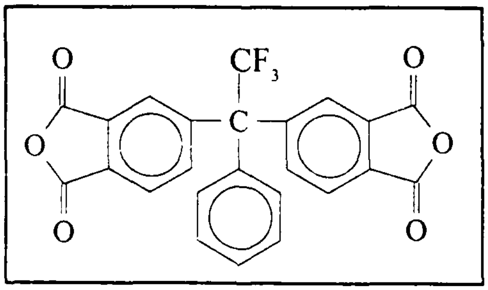
The most stable commercial organic matrix composite materials all contain the (6F) moiety as a key portion of the polymer backbone. These materials are represented by Avimid N, PMR-II, and AFR700B. An essential monomer for all of these products is the 6F anhydride I. A key intermediate in the manufacture of this anhydride is hexafluoroacetone, which is expensive, toxic, and available in limited supply. To preclude the necessity for utilization of 6F anhydride, intermediates containing the phenyltrifluoroethylidene (3F) group (II) have been synthesized. Thus, in earlier work at United Technologies, the 3F anhydride (III) has been synthesized.



I. 6F DIANHYDRIDE



II. PHENYLTRIFLUOROETHYLIDENE GROUP



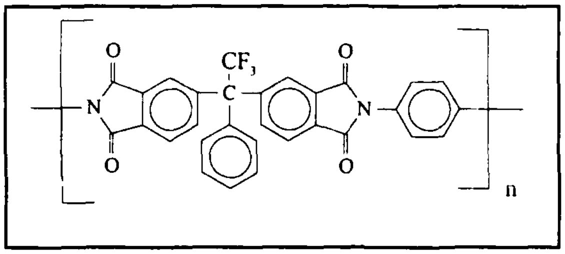
III. 3F DIANHYDRIDE

The 3F anhydride III has been used to provide a portion of the backbone in a polyimide polymer (IV), analogous to the duPont Avimid N (V). Polymer IV, with the 3F group II substituted for the 6F group in Avimid N (V), has been shown to have a thermooxidative stability comparable with (V).

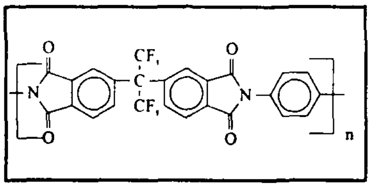
RESULTS OF PROGRAM STUDIES

The very high melt viscosities and process temperatures of linear thermoplastic polymers such as IV and V make it very difficult to process high quality laminates of these materials, due to the restricted resin flow and fiber wetting created by the low flow characteristics of these polymers. To address this problem, a two component semiinterpenetrating polymer network (SIPN), consisting of a thermosetting, ethynyl terminated component VII, blended with a thermoplastic component VIII was initially proposed for the current program. The thermoset component oligomer VII has a backbone structure made up of the 3F diamine VI and the commercially available biphenyldianhydride (BPDA), endcapped with 3-aminophenylacetylene, a commercial product of National Starch and Chemical Corporation. In work performed at Virginia Tech and more recently at Maxdem, Inc., synthetic procedures for 3F monomers, particularly 3F diamine (VI), have evolved which are amenable to large scale production of 3F polyimides. The synthetic procedures for the key 3F intermediate, trifluoroacetophenone, and its conversion into 3F diamine VI, have been modified and scaled up by Maxdem, Inc., one of the subcontractors on this Program. These procedures are summarized in Figure 1 and in the appendix of this report.

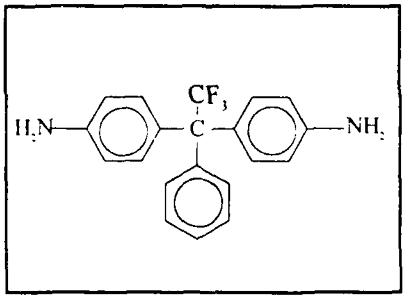
In addition, a summary of the preparation of four batches of 3F polyimides VII and VIII, synthesized from diamine VI and biphenyl dianhydride (BPDA), is included.



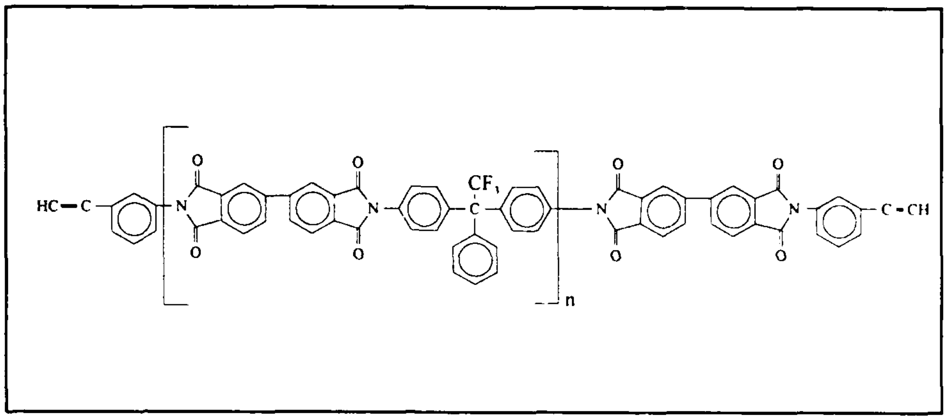
IV. 3F POLYIMIDE POLYMER



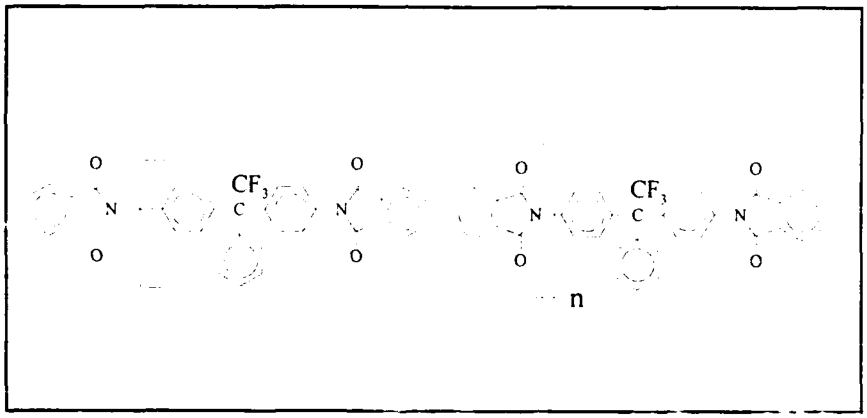
V. DUPONT AVIMID N



VI. 3F DIAMINE



VII. ETHYNYL TERMINATED 3F OLIGOMER



VIII. PHTHALIC ANHYDRIDE TERMINATED
3F OLIGOMER

MONOMER AND PREPOLYMER PREPARATION

Trifluoroacetophenone

Initial work at Maxdem focused on the scale-up of the synthetic procedure for trifluoroacetophenone, which was originally developed by McGrath and coworkers at Virginia Tech. Modifications in the synthesis included elimination of the environmentally unacceptable carbon disulfide as solvent and use of ambient reaction temperature in place of the more cumbersome -40°C. 4 kilograms of trifluoroacetophenone were prepared for use in synthesis of 3F Diamine VI.

3F Diamine

Additional process changes were made in the synthetic procedure for VI to facilitate scale-up procedures. In particular, the hydrochloric acid catalyst was replaced by the more acidic p-toluenesulfonic acid. This change resulted in a reduction of the quantity of by-products and increased yield of purer product. By this procedure, 3 kg of monomer grade 3F diamine was prepared, accompanied by additional material requiring at least one additional recrystallization.

3F Polyimide Oligomers

Four batches of approximately 100g. each of endcapped 3F Polyimide oligomers were prepared in the laboratories at Maxdem, Inc. Two batches were endcapped with aminophenylacetylene, to yield the ethynyl terminated prepolymer VIII, and two batches were endcapped with phthalic anhydride, giving rise to the thermoplastic oligomer IX. Table I shows the calculated and measured (GPC) number average molecular weight, weight average molecular weight, and intrinsic viscosity for each experimental batch.

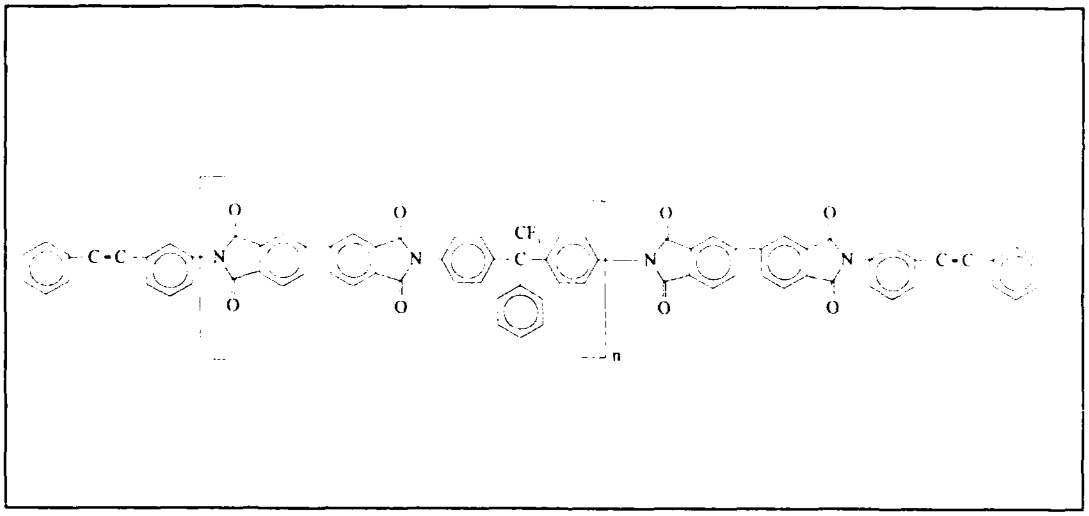
TABLE 1. ENDCAPPED 3F POLYIMIDE POLYMERS

Batch	Endcap	Calculated MW_n	GPC MW_n	GPC MW_w	η
1	APA	4K	7140	12332	0.24
2	APA	8K	14339	25710	0.35
3	PA	15K	21471	37413	0.44
4	PA	25K	24292	42881	0.47

APA - Aminophenylacetylene Endcapped
PA - Phthalic Anhydride Endcapped
GPC relative to polystyrene standard

Intrinsic viscosity measured at 30°C, 0.5g./ml in NMP

The melt/flow characteristics of the initial 3F polymer batches were not acceptable for composite processing. It was apparent that the acetylene endcapped polymers were undergoing polymerization (cure) prior to melting, and thus the ethynyl terminated 3F polyimides were not suitable for processing into composite laminates. The Program emphasis was shifted to SIPN blends of phenylethynyl terminated polyimides, and a SIPN blend of a phenylethynyl terminated 3F polyimide thermoset component IX with the previously prepared phthalic anhydride terminated 3F polyimide thermoplastic component VIII was selected. Both the thermoset and thermoplastic components have the same 3FDA/BPDA backbone, but the thermoset component is endcapped with 3-(phenylethynyl)aniline. The synthetic procedure used for the preparation of 3-(phenylethynyl) aniline is shown in Figure 2. Small amounts of these phenylethynyl terminated (PET) polymers were prepared. These materials showed promise of more superior melt behaviour and a more favorable processing window due to their higher cure temperatures. Rheometrics and differential scanning calorimetry (DSC) of sample blends indicated good processability characteristics. Rheometrics of 1:1 and 3:1 blends of thermoset:thermoplastic components are shown in Figure 3, and the DSC of the phenylethynyl terminated 3F polyimide SIPN component is shown in Figure 4. Examination of the DSC and rheometrics data shows a reasonable processing window between the polyimide melt phase and the dissipation of the polymerization exotherm. A 1:1 blend of the two SIPN components was selected, and this blend was scaled up to a quantity of about 3.5 kilograms. Solvent prepregging of this blend on Hercules IM7 graphite fibers using cyclopentanone as solvent provided about 200 ft. of 12" prepreg tape having a resin content of 35+/-3%.



IX. PHENYLETHYNYL TERMINATED 3F OLIGOMER

Making use of dielectric cure monitoring techniques, a number of laminates were laid up and cured to fabricated flat panels. The size, ply thickness and ply orientation of these panels are shown in Table 1. The use of dielectric cure monitoring provided a "window" by which key events in the cure cycle could be followed in real time. A typical dielectric monitoring trace is shown in Figure 5. By use of appropriate sensors for resistance and capacitance monitoring, events such as solvent egress, viscosity changes, minimum viscosity, cure exotherm, gelation, and crosslinking, with suitable interpretation, can be followed during the cure.

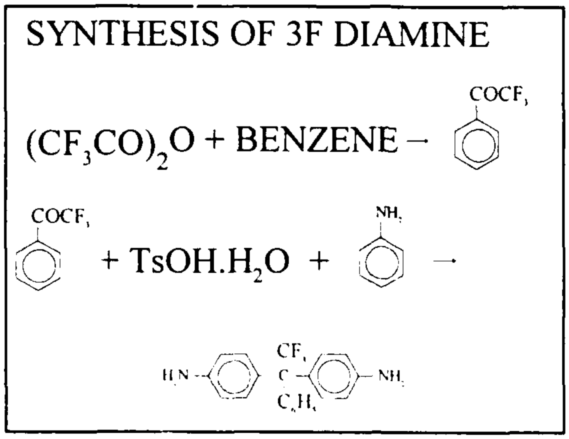


Figure 1. SYNTHESIS OF 3F DIAMINE

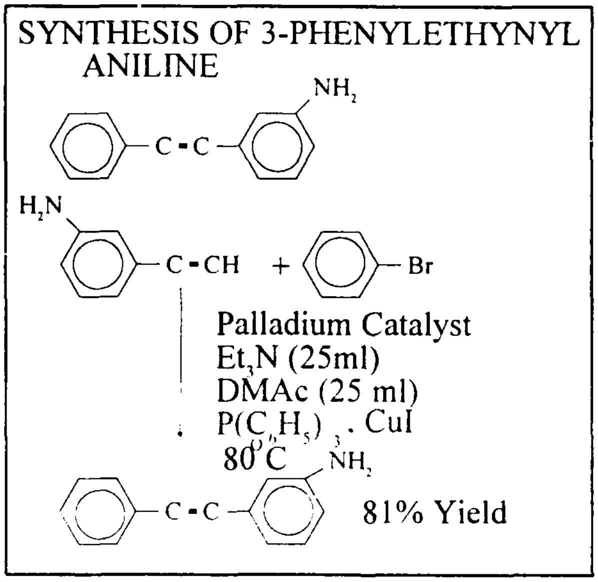


Figure 2. SYNTHESIS OF PHENYLETHYNYLANILINE

DISCUSSION OF EXPERIMENTAL RESULTS

A semi-interpenetrating polymer network, (SIPN) containing a 1:1 blend of a thermoplastic phthalic anhydride endcapped 3F polyimide oligomer VIII and a thermosetting 3F polyimide oligomer IX has been synthesized, scaled up, impregnated on graphite tape, and fabricated into composite panels. Program activities on this SIPN system have included (1) Monomer and Oligomer Synthesis; (2) Resin Scaleup; (3) Differential Scanning Calorimetry (DSC) and Rheometrics; (4) Blending to SIPN; (5) Solution Impregnation on IM7 6K Tow to Yield 12" Wide Prepreg Tape; (6) Fabrication of 8-Ply, 16-Ply and 24-Ply Unidirectional Laminates, and 12-Ply, +/-45° Laminates, with Applcation of Dielectric and Resistance Cure Monitoring; (7) Ultrasonic C-Scan and Tag-end Tests on Panels.

OBSERVATIONS AND RESULTS

Considerable care was necessary during the cure cycle in order to dissipate the large cure exotherm. (See Figure 4, Differential Scanning Calorimetry) Some of the earlier attempts at panel fabrication resulted in burned panels. After development of a suitable cure cycle by dielectric monitoring, fabricated panels up to 24 plies thickness appeared visually to be well consolidated, however ultrasonic C-scan, microscopic analyses, and quantitative void content by acid digestion revealed that the level of porosity was of the order of 2-3%, compared to an acceptable level of porosity of <2%. Resin starved areas on some panels indicated that improved resin dispersion would have alleviated the porosity problem. With minimum resin viscosity prior to cure of about 200 poise, resin flow may not be adequate prior to onset of the cure exotherm.

PROPOSED SOLUTION AND PROGRAM MODIFICATION

Approximately 1 kilogram of SIPN resin powder is remaining after solution prepregging. It is recommended that powder prepreg be fabricated from this resin powder, followed by fabrication of towpreg into tape, and layup and cure of additional laminates. During powder impregnation, dispersion of resin throughout the fiber bundles is considerably more extensive, thus reducing the sensitivity of laminate quality to resin flow.

PROGRAM TASKS TO BE PERFORMED BY VIRGINIA TECH AND LOCKHEED

The tasks shown below are to be performed during the remainder of the technical portion of the Program, from May 1 to June 30, 1994, with available Program funds remaining.

Task 1. Fabrication of powder prepreg tape from residual SIPN resin. This includes drying and micronizing the SIPN blend, powder impregnation and sintering of graphite tow, and consolidation of impregnated graphite tow into tape.

Task 2. Fabrication of test panels from powder towpreg tape. Prepreg tape will be used to fabricate test panels. Small panels (6-8 plies) will be fabricated using dielectric cure monitoring procedures to optimize the process cycles, followed by fabrication of larger panels. The size, thickness and number of test panels will be dependent upon the quantity of prepreg tape produced.

Task 3. Quality assurance of fabricated panels. The quality of the panels from powder prepreg tape will be assessed by use of ultrasonic C-scan, microscopic analyses, resin content by chemical degradation, and grinddown to determine ply integrity.

Task 4. Mechanical testing of fabricated panels. Panels will be tested in tension, compression and shear, depending upon the number, size and thickness of panels available from fabrication.

TASK PERFORMANCE

Tasks 1, 2, and 3 will be conducted by Virginia Tech and Tasks 4 and 5 will be performed by Lockheed. Virginia Tech will also contribute to characterization of panels in Task 5.

TECHNICAL PRESENTATION

"Preparation, Scaleup and Evaluation of 3F Polyimide Matrix Composites", Presented at High Temple Workshop XIV, Cocoa Beach, Florida, February 2, 1994.

TABLE 1. LAMINATES FROM 3F SIPN POLYIMIDE BLEND

LAMINATE #	LAMINATE SIZE	NUMBER OF PLIES	PANEL ORIENTATION
1	18"x18"	8	0°/90°
2	12"x14"	8	unidirectional
3	12"x14"	16	unidirectional
4	12"X14"	24	unidirectional
5	2"x2"	4	unidirectional
6	2"x2"	4	unidirectional
7	12"x14"	16	unidirectional
8	12"x14"	16	unidirectional
9	12"x14"	16	unidirectional

Figure 3

RHEOMETRICS

MELT VISCOSITY PROFILE OF SOLUTION BLENDED 3F POLYIMIDES VIII AND IX

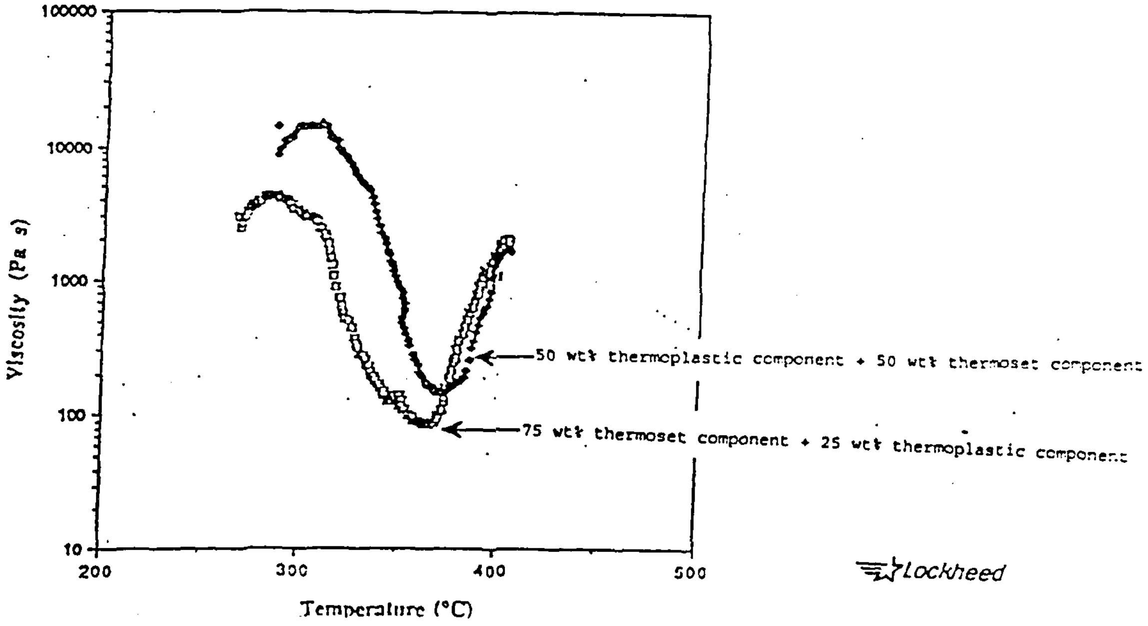
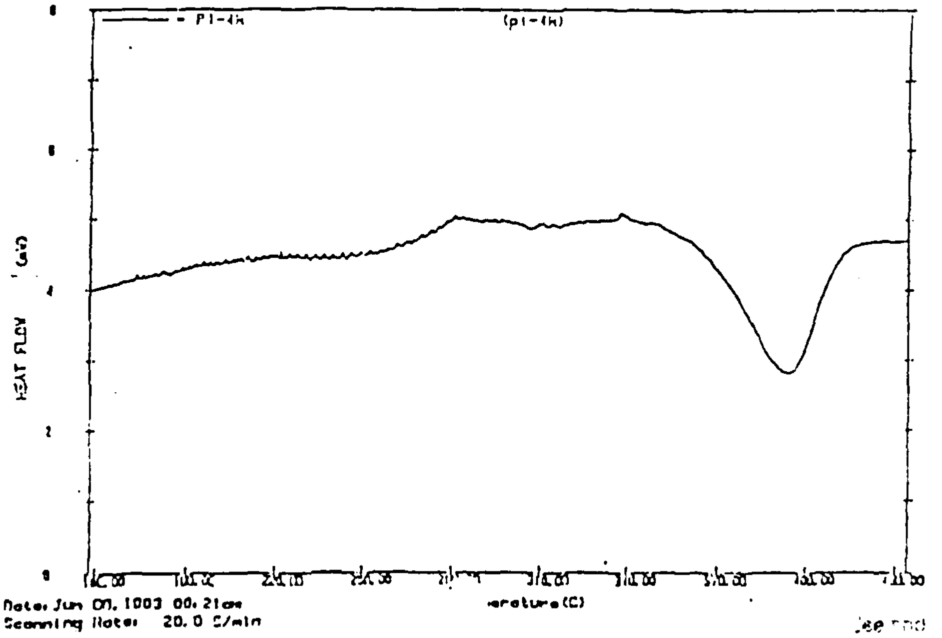


Figure 4.

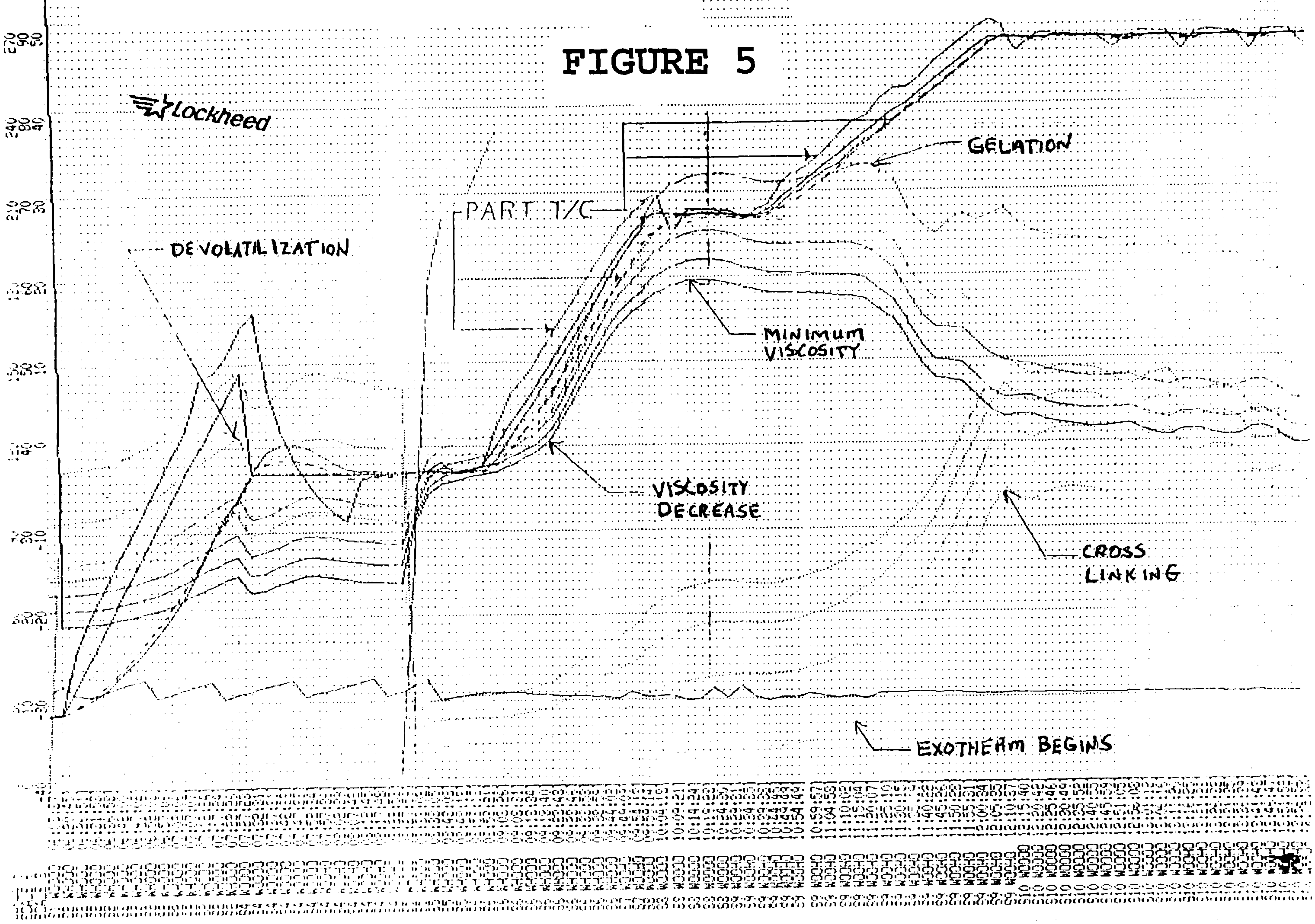
DIFFERENTIAL SCANNING CALORIMETRY

3F THERMOSETTING POLYIMIDE X



DIELECTRIC MONITORING - 3F SIPN POLYIMIDE

FIGURE 5



APPENDIX

SUMMARY OF MONOMER SYNTHESES

<u>Trifluoroacetophenone</u>

Original Procedure

$CF_3COOH \xrightarrow{PCl_5} CF_3COCl + \text{Benzene} \longrightarrow \text{Trifluoroacetophenone}$

1. CF_3COOH/PCl_5/dichloroethane/4 hr.
2. Collect and distill trifluoracetyl chloride
3. Add CF_3COCl to $AlCl_3$/benzene/carbon disulfide -50°C
4. Stir 6 hr at -40°C
5. Add 36% aqueous HCl and ice
6. Separate organic layer and extract aq. layer with ether/benzene
7. Combine organic solutions and wash with bicarbonate
8. Dry
9. Distill to give trifluoroacetophenone in 65% yield

Maxdem Modified Procedure

$(CF_3CO)_2O + \text{Benzene} \longrightarrow \text{Trifluoroacetophenone}$

1. Add $AlCl_3$ to trifluoroacetic anhydride/benzene at RT under N_2
2. Stir 4 hours
3. Add ice water slowly and separate organic layer
4. Dry and distill to give trifluoroacetophenone in 60-73% yield

<u>3F Diamine</u>

Original Procedure

1. Mix aniline/aniline hydrochloride/trifluoroacetophenone
2. Stir 24 hr. at 160°C
3. Cool to 100° and add aqueous bicarbonate. (HPLC yield 65%)
4. Steam distill and filter solid crude product
5. Wash with water and dry thoroughly to give dark purple crude.
6. Dissolve in ethanol (35 ml/g)
7. Acidify with 17% HCl to pH2
8. Add charcoal (4g. charcoal to 10g crude)
9. Reflux and filter
10. Repeat last two steps twice.
11. Add 50% NaOH to pH8
12. Add toluene (30ml/g)
13. Extract aqueous layer three times with toluene
14. Dry and remove toluene extract under reduced pressure to leave tan solid residue.
15. Suspend solid in water and filter.
16. Wash with water to pH7
17. Dry for 24 hr. at 100°C to give 3F diamine in 50% yield.

APPENDIX (CONT.)

Maxdem Procedure

1. Mix toluenesulfonic acid and aniline and distill water out.
2. Add trifluoroacetophenone
3. Stir 24 hr. at 150°C
4. Add aqueous sodium hydroxide to pH12
5. Cool to RT and add methylene chloride (HPLC yield 85-90%)
6. Separate organic layer and dry with $MgSO_4$
7. Precipitate product by adding hexane.
8. Filter to give pink crude product.
9. Dissolve in toluene (30 ml/g)
10. Filter through silica gel (0.5g silica gel per gram crude)
11. Add charcoal (0.5g charcoal/gram crude)
12. Filter and concentrate toluene solution.
13. Filter the crystals to give purified 3F diamine in 60-70% yield.