

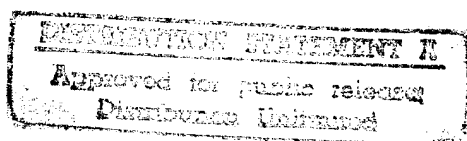
Improved High-Temperature Resistant Matrix Resins

Contract NAS3-23933

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Prepared by:

**H.E. Green, G.E. Chang, W.F. Wright,
K. Ueda and M.K. O'Rell**



April 1989

Prepared for:

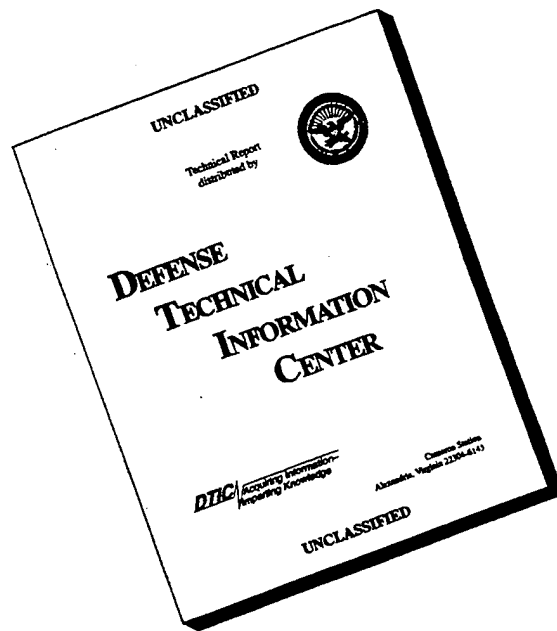
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16. Abstract A study was performed with the objective of developing matrix resins that exhibit improved thermo-oxidative stability over state-of-the-art high temperature resins for use at temperatures up to 644K (700°F) and air pressures up to 0.7 MPa (100 psia). The work was based upon a TRW discovered family of polyimides currently licensed to and marketed by Ethyl Corporation as EYMYD ^R resins. The approach investigated to provide improved thermo-oxidative properties was to use halogenated derivatives of the diamine, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (4-BDAF). Polyimide neat resins and Celion ^R 12,000 composites prepared from fluorine substituted 4-BDAF demonstrated unexpectedly lower glass transition temperatures (T _g) and thermo-oxidative stabilities than the baseline 4-BDAF/PMDA polymer.			
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FOREWORD

This report was prepared by TRW Electronics and Defense Sector under Contract NAS3-23933, "Improved High Temperature Resistant Matrix Resins." The technical effort was conducted from late 1983 to early 1985 under sponsorship of NASA Lewis Research Center. Dr. Tito T. Serafini served as the NASA Program Monitor.

The project team at TRW consisted of Dr. Howard E. Green, program manager and Dr. Glenn E. C. Chang, principal investigator. Mr. Ward F. Wright and Mr. Ken Ueda performed the composite evaluation under the direction of Mr. Michael K. O'Rell.

SUMMARY

A study was performed with the objective of developing matrix resins that exhibit improved thermo-oxidative stability over state-of-the-art high temperature resins for use at temperatures up to 644K (700°F) and air pressures up to 0.7 MPa (7 atm). The work was based upon prior work at TRW which had identified a family of polyimides termed Partially Fluorinated Polyimide (PFPI). The approach selected to provide improved thermo-oxidative properties was to use halogenated derivatives of the base diamine, 2,2-bis[(4-aminophenoxy)phenyl]hexafluoropropane (4-BDAF).

Fluoro and chloro derivatives of 4-BDAF were prepared and used to make polyimides from pyromellitic dianhydride (PMDA) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6-FDA). Isothermal aging studies were performed on molded samples of the new polymers and two control samples prepared from 4-BDAF and phenylenediamines. All samples performed fairly well at 589K (600°F), even at 0.7 MPa (7 atm) pressure. Differences in thermo-oxidative stability were very noticeable at 644K, especially at elevated pressures. The best thermo-oxidative stability, as measured by weight retention, was displayed by the PDAs/6-FDA (NR-150 formulation) followed by 4-BDAF/PMDA. The fluorinated 4-BDAF polymers were next best and the polymers with the lowest thermo-oxidative stabilities were the chloro derivatives of 4-BDAF.

Four polymers were used to fabricate unidirectional laminates from Celion 12000 which had been sized with 4-BDAF/PMDA. In addition to the two controls, 4-BDAF/PMDA and PDAs/6-FDA, two other polymer systems, 2-F-4-BDAF/PMDA and 2-F-4-BDAF/6-FDA, were selected for study based on the thermo-oxidative aging results. Problems were encountered with prepreg preparation at the prepreg vendor resulting in limited amounts of prepreg for each system. Accordingly, only unaged laminate properties were obtained at 297K and 644K for three of the four systems. The laminates prepared from 6-FDA containing polymers showed the highest room temperature mechanical properties but significant loss of properties was noted at 644K. Samples of the 4-BDAF/PMDA laminates were aged at 644K at

0.1 MPa (1 atm) and 0.4 MPa (4 atm) for 50 and 100 hours. The samples showed good property retention at 0.1 MPa; however, severe degradation was noted in 0.4 MPa aged samples after 100 hours. It was evident from the 4-BDAF/PMDA laminate mechanical properties and aging results that additional refinements are needed in the laminate process cycle to obtain the full potential of this polymer.

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1.0 INTRODUCTION

This final report documents the work performed by TRW Space and Defense Sector for the National Aeronautics and Space Administration, Lewis Research Center, under contract NAS3-23933. The effort was conducted from October 1983 through March 1985. The objective of the program was to develop matrix resins that exhibit improved oxidative stability, compared to state-of-the-art high temperature resistant resins, during exposure to temperatures of up to 644K (700⁰F) and air pressures of up to 0.7 MPa (102 psia). The work built upon the foundation established under NASA/LeRC contract NAS3-23274 (Reference 1) and centered on polyimides based on modifications of TRW's Partially Fluorinated Polyimide (PFPI) technology. This technology has since been licensed to Ethyl Corporation by TRW.

The technical effort was divided into three sequential tasks. The first task was devoted to monomer and polymer synthesis. A total of six polymers were to be produced. Two were synthesized from 2,2-bis[(4-aminophenoxy)-phenyl]hexafluoropropane (4-BDAF) and pyromellitic dianhydride (PMDA), Polymer I, and from 95:5 by mol para:meta-phenylenediamine (PPDA and MPDA, respectively) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6-FDA), Polymer II. The other four polymers were based on halogenated modifications of the 4-BDAF diamine in conjunction with PMDA and 6-FDA dianhydrides. The synthesis and characterization of the monomers and polymers is described in Section 2.0.

During the second task, "Polymer Thermo-oxidative Stability," described in Section 3, neat resin disks of the six (6) polymers were compression molded. After postcure, the glass transition (T_g) temperature of each polymer was determined. The weight loss characteristics of the molded resins were determined after prolonged exposure in air at 589K (600⁰F) and 644K (700⁰F) and at 0.1 MPa (15 psia), 0.4 MPa (60 psia) and 0.7 MPa (102 psia). On the basis of the T_g and weight loss data, two of the four new polymers and polymers I and II were selected for the Task III effort.

Task III, "Composite Fabrication and Evaluation," was concerned with the preparation of prepreg and fabrication of composites of the four selected polymers. Ferro Corporation prepared the prepreg using Celion[®] 12000 carbon fiber sized with 4-BDAF/PMDA and supplied by Celanese. The composites fabricated from the prepreg were tested for interlaminar shear and flexural strength at room temperature and 644K. The flex and shear properties of 4-BDAF/PMDA were also tested after aging in air at 644K under 0.1 MPa and 0.4 MPa pressure. The Task III effort is treated in detail in Section 4. Conclusions and Recommendations are to be found in Section 5; References in Section 6.

2.0 POLYMER SYNTHESIS

During this task the monomers for the candidate polymers were procured or synthesized and the polymers were prepared for use in Task II, "Polymer Thermo-oxidative Stability." The synthesis of a total of six (6) polymers was required for this task. Two of the polymers were selected as controls based on their known excellent thermo-oxidative performance. One of the control polymers, designated Polymer I, is a version of TRW's Partially Fluorinated Polyimide (PFPI) technology (References 2, 3 and 4) and is formed from 2,2-bis[(4-aminophenoxy)phenyl]hexafluoropropane(4-BDAF) and pyromellitic dianhydride (PMDA) (see Table I for structures) and currently marketed by Ethyl Corporation as EYMYD^R L-30N. The second control polymer (designated Polymer II) is based on DuPont's NR-150B technology (Reference 5), and is formed from 95:5 by mol para:-meta-phenylenediamine (PPDA and MPDA, respectively) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6-FDA). Three additional diamines and one dianhydride were selected as monomers for study in candidate polymeric compositions. The monomer synthesis efforts are described in Section 2.1 and the Polymer Synthesis in Section 2.2.

2.1 MONOMER SYNTHESIS STUDY

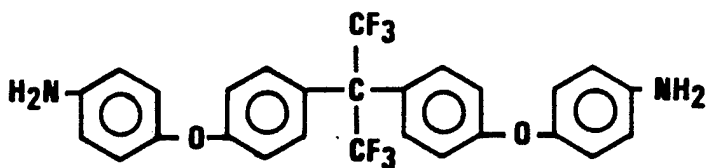
The monomers selected for study are shown in Table I. The 2-F and 3-F-4-BDAF monomers were selected on the basis of the high promise shown by 3-Cl-4-BDAF under contract NAS3-23274 (Reference 1) and to determine if fluorine substitution in the 3- or 4- position afford additional thermo-oxidative stability over the unsubstituted 4-BDAF or with chlorine in those positions. The pyrazine dianhydride (PYDA) was selected to determine if the absence of labile hydrogens will result in improved thermo-oxidative performance.

2.1.1 4-BDAF

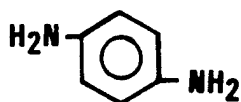
The 4-BDAF used in this work was purchased from Morton Chemical which at that time produced the material under license from TRW. Morton's FADII grade was used without further purification. The infrared spectrum, DSC scan and nuclear magnetic resonance spectrum of the material are to be found in Figures 1, 2 and 3, respectively.

Table I. Monomers Selected for Study

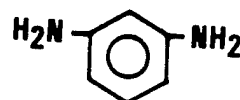
Diamines



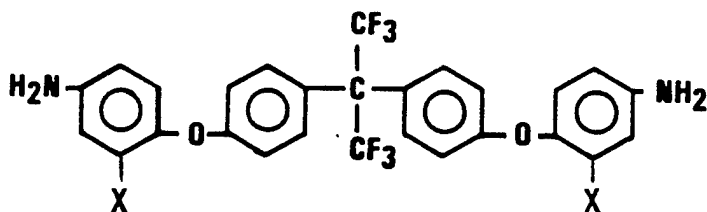
4-BDAF



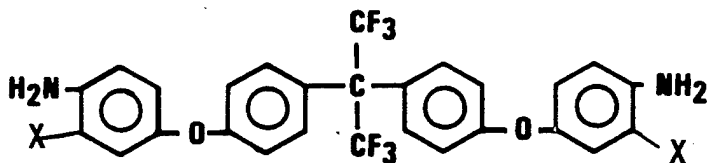
Para-phenylenediamine (PPDA)



Meta-phenylenediamine (MPDA)



2-F-4-BDAF or 2-Cl-4-BDAF
where x = Fluorine or Chlorine

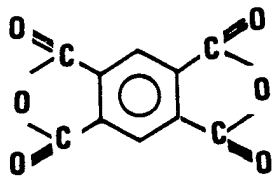


3-F-4-BDAF

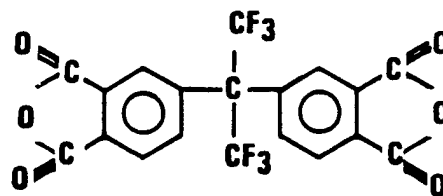
where x = Fluorine

Table I. Proposed Monomers (cont.)

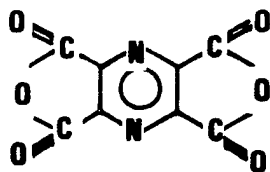
Dianhydrides



PMDA



6-FDA



PYDA

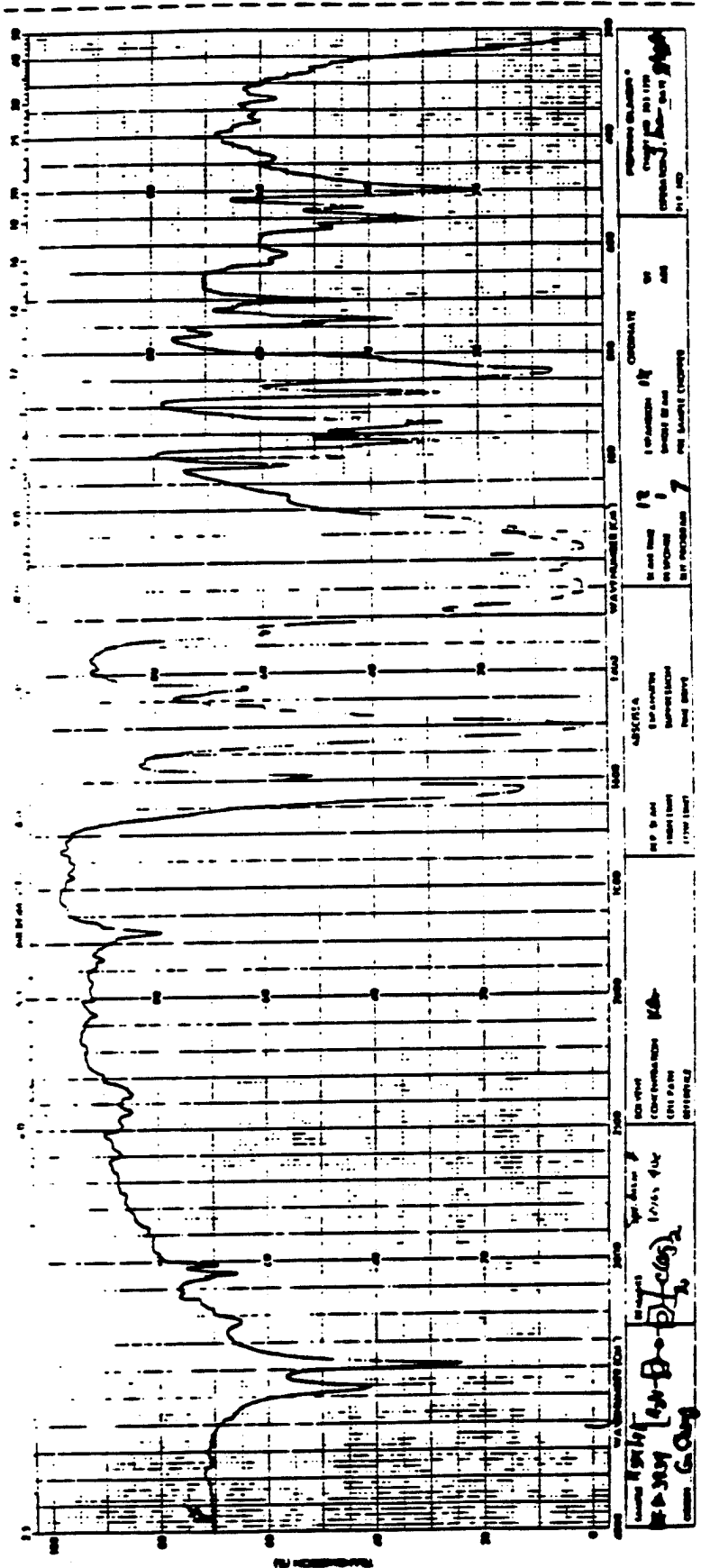


Figure 1. Infrared spectrum of 4-BDAF.

Sample: FAD2 #1641-88 2/1/83
Size: 4.7MG
Rate: 10C/MIN
Program: Interactive DSC V2.0
Date: 28-Mar-83 Time: 16:18:36
File: 1641-88.03 T.A.#3
Operator: TM
Plotted: 28-Mar-83 17:06:57

DSC

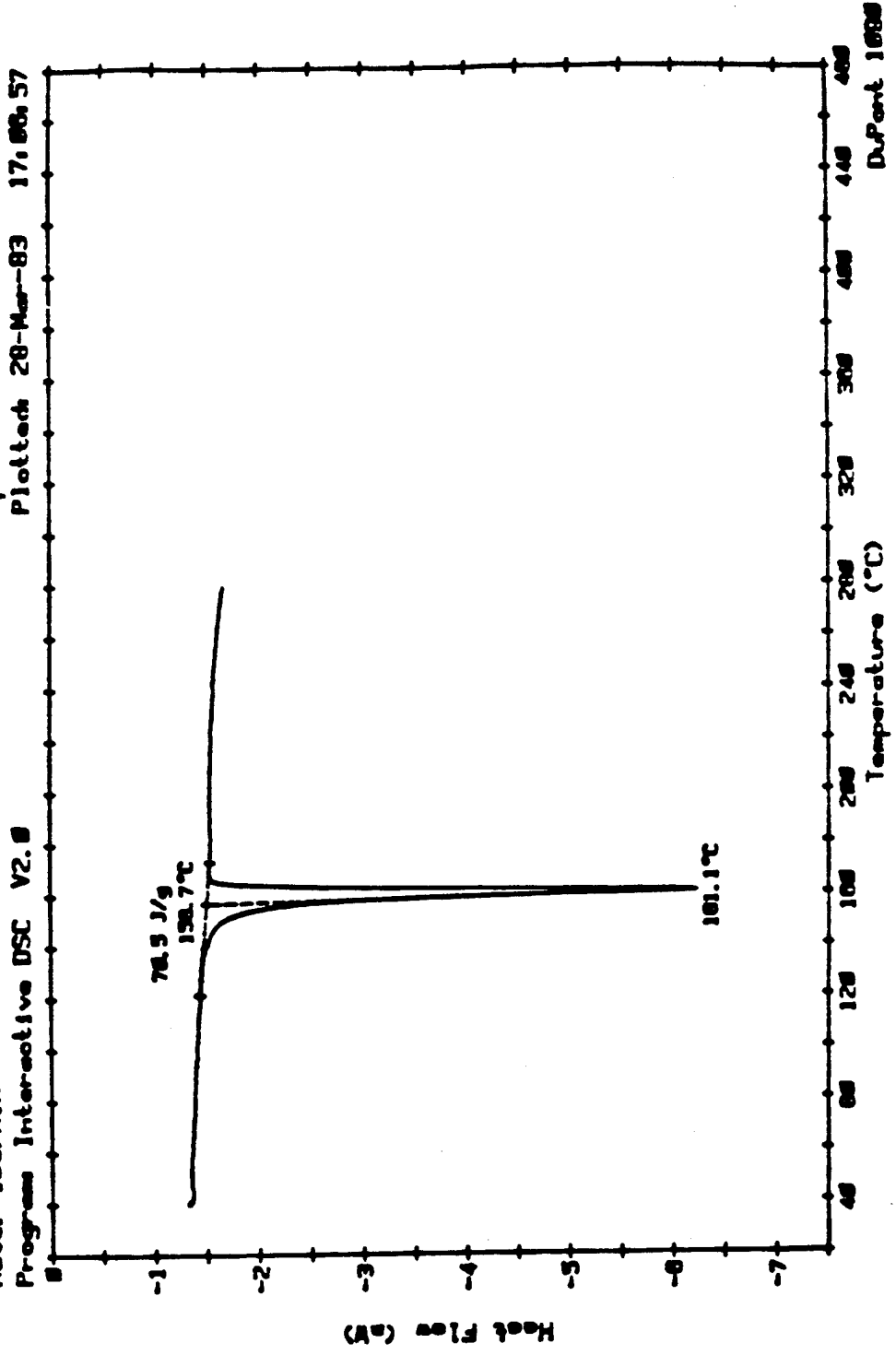


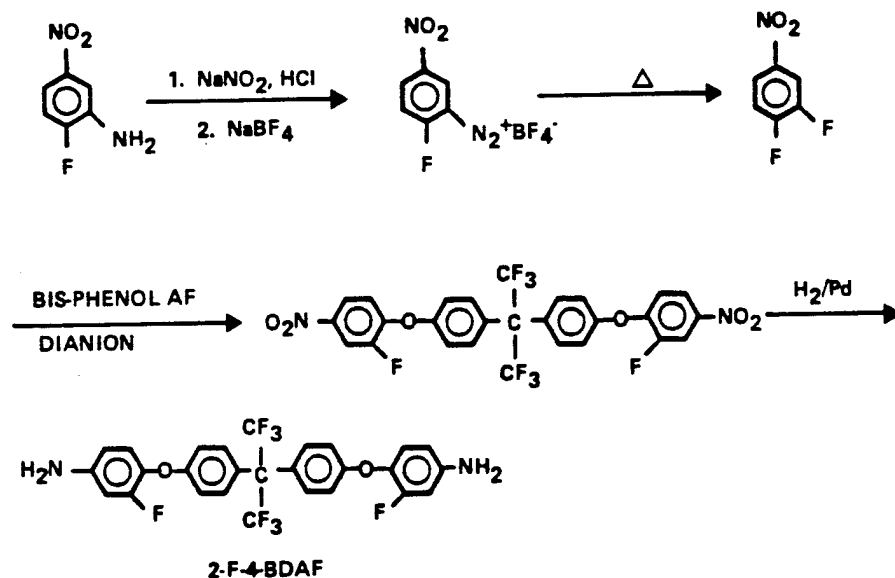
Figure 2. DSC scan of 4-BDAF.

2.1.2 Phenylene Diamines

Commercially available (Aldrich) p- and m-phenylene diamine were obtained and recrystallized from ethanol. The infrared spectrum and DSC scan of p-phenylene diamine are shown in Figures 4 and 5; those for m-phenylene diamine are in Figures 6 and 7, respectively. The apparent post melting point decomposition behavior displayed in the DSC scans is typical of free aromatic diamines.

2.1.3 2-F-4-BDAF

The synthesis of 2,2-bis[(2-fluoro-4-aminophenoxy)phenyl]hexafluoropropane (2-F-4-BDAF, see Table I for structure) initially was based on the reaction scheme shown below. Beginning with 2-fluoro-5-nitroaniline, it was planned to prepare 3,4-difluoronitrobenzene via decomposition of the diazonium fluoroborate salt. This key intermediate would then be allowed to react with Bisphenol AF dianion to give the four-ring dinitro precursor to the desired diamine, similar to preparation of 4-BDAF and 2-C1-4-BDAF.



Conversion of 2-fluoro-5-nitroaniline (commercially available from Aldrich Chemical Company) to the diazonium fluoroborate salt proceeded without incident. A suspension of starting material in aqueous acid was treated at 273-278K with an aqueous solution of sodium nitrite. The yellow diazonium chloride was then treated with an aqueous solution of sodium tetrafluoroborate and allowed to stir for 2 hours, filtered and washed with water and ice-cold ethanol. The solid diazonium fluoroborate was dried in air overnight.

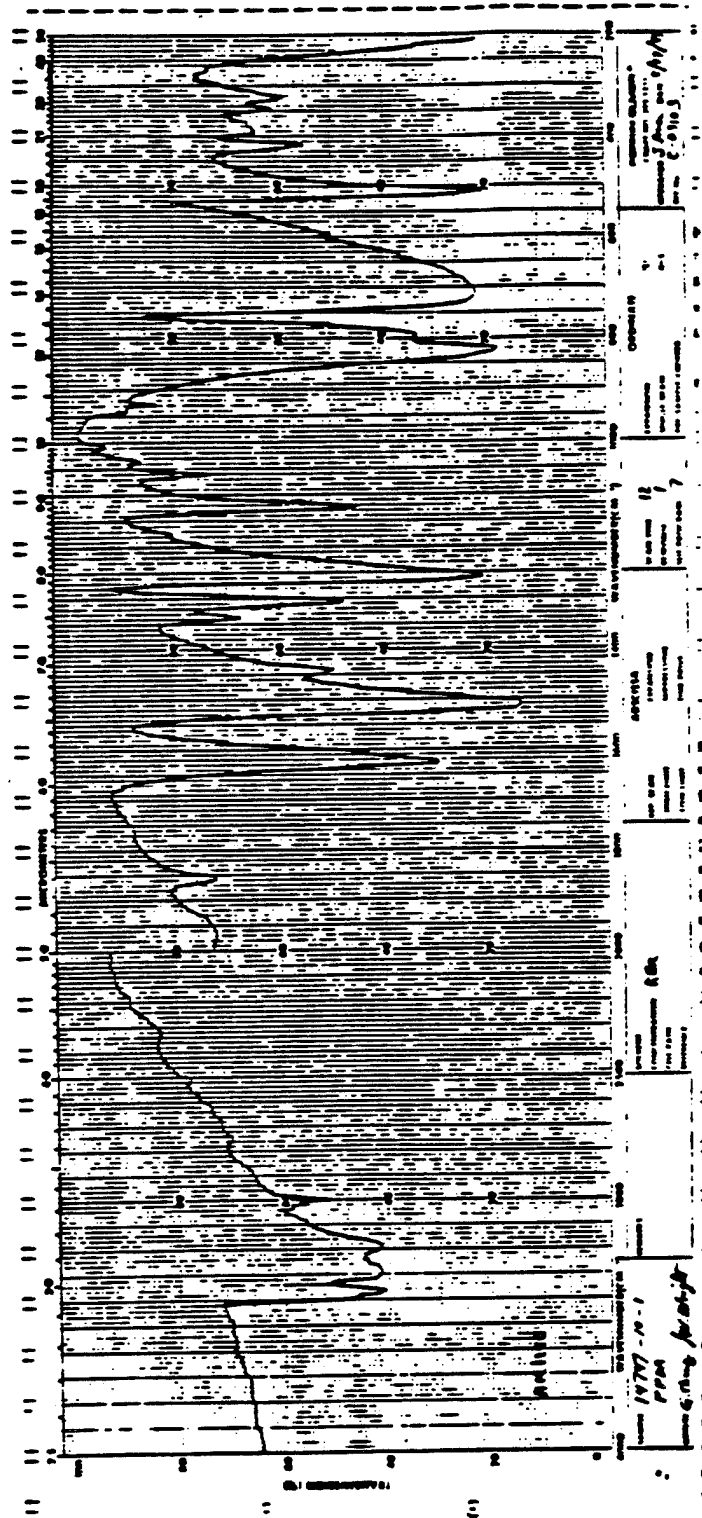


Figure 4. Infrared spectrum of para-phenylenediamine.

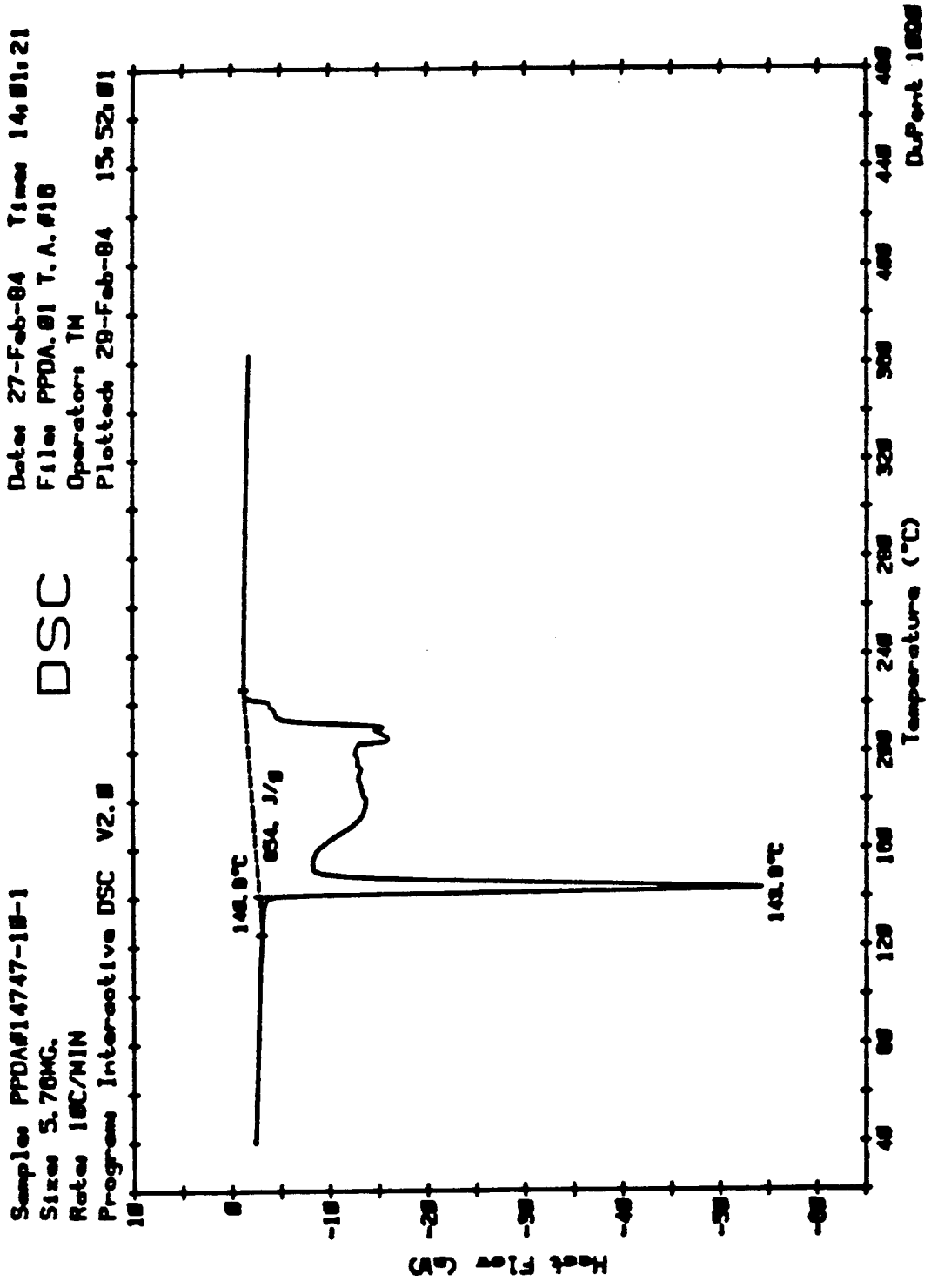


Figure 5. DSC scan of para-phenylenediamine.

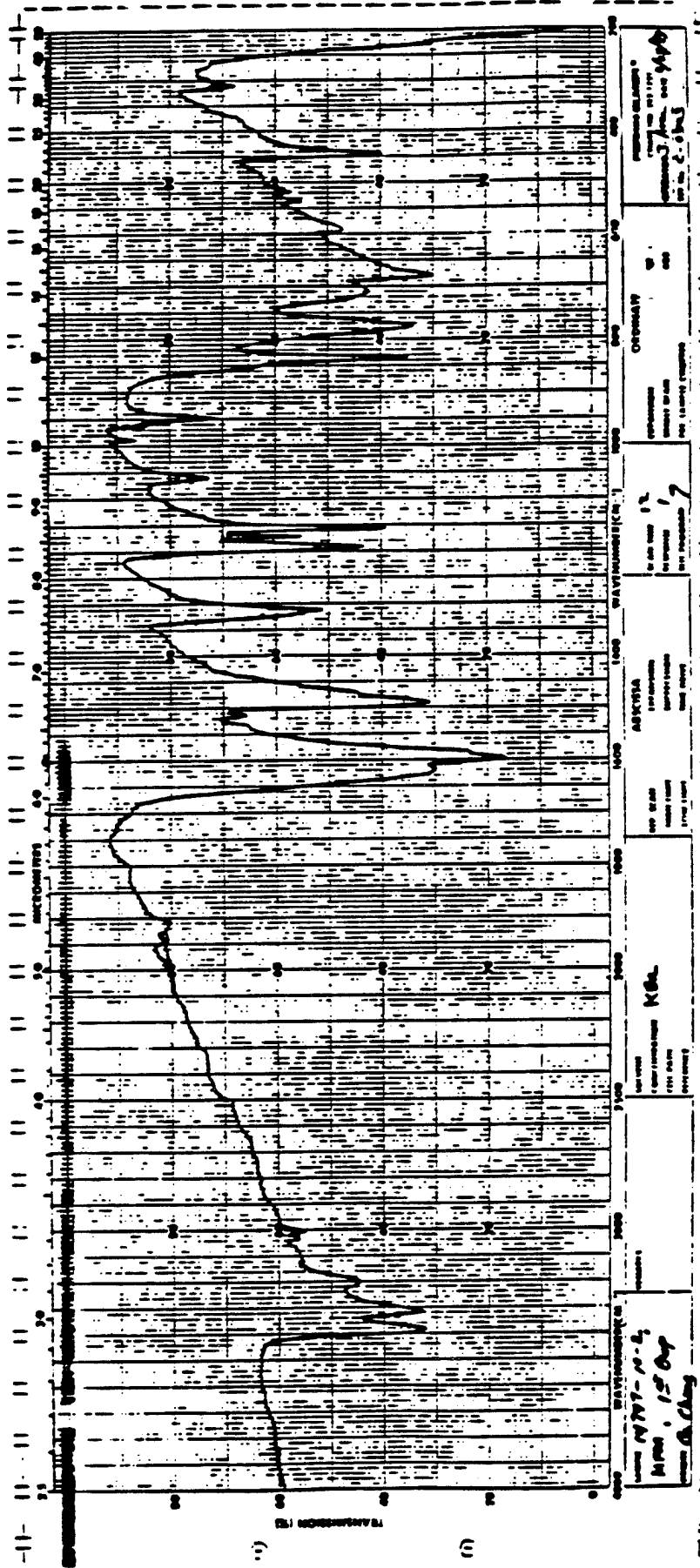


Figure 6. Infrared spectrum of meta-phenylenediamine.

Sample: MPDA#14747-10-3
Size: 5.44MG. 2ND. CROP
Rate: 10C/MIN
Program: Interactive DSC V2.0
Date: 27-Feb-84 Time: 15:41:48
File: MPDA.02 T.A.#17
Operator: TM
Plotted: 28-Feb-84 10:12:15

DSC

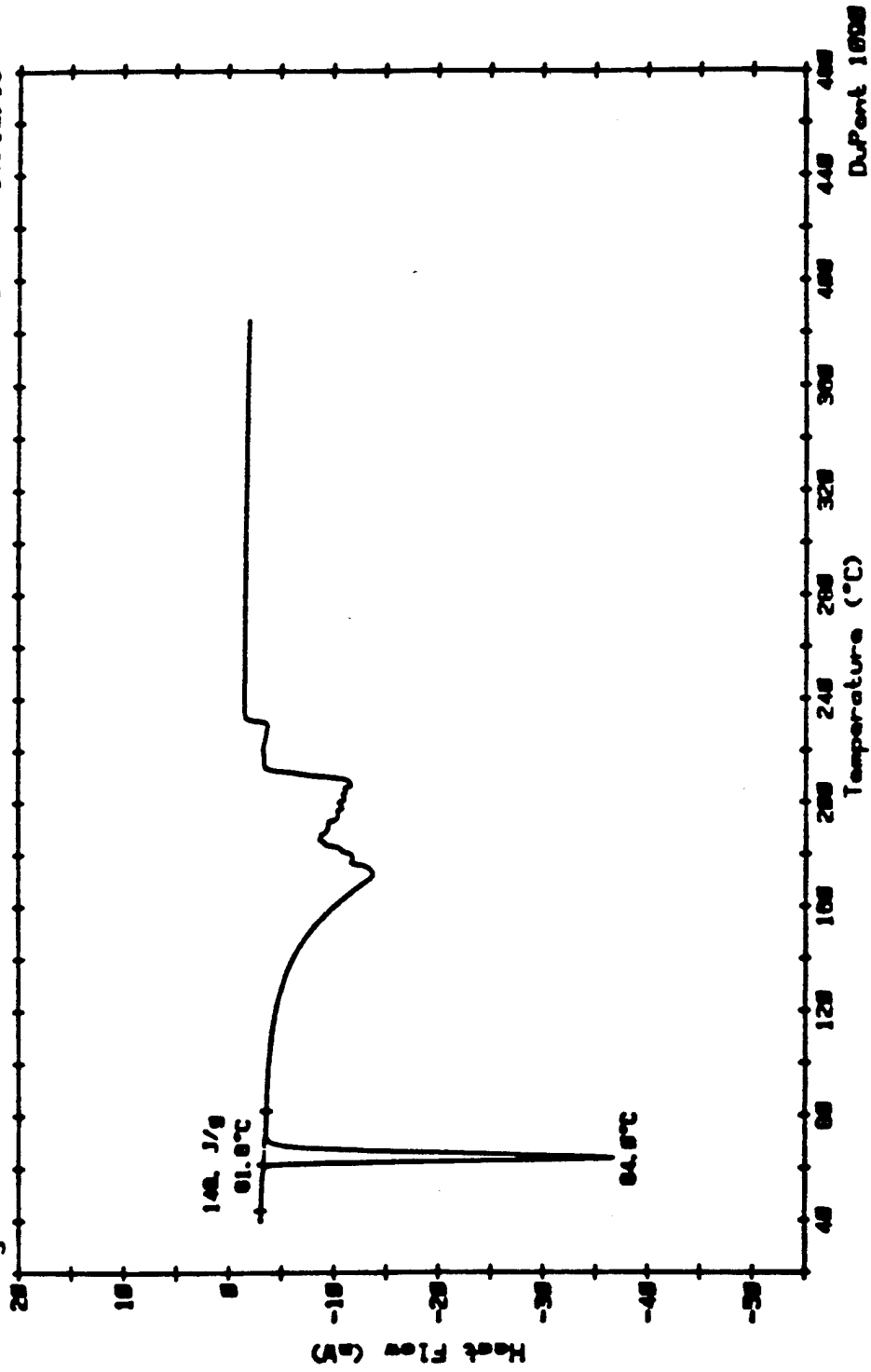
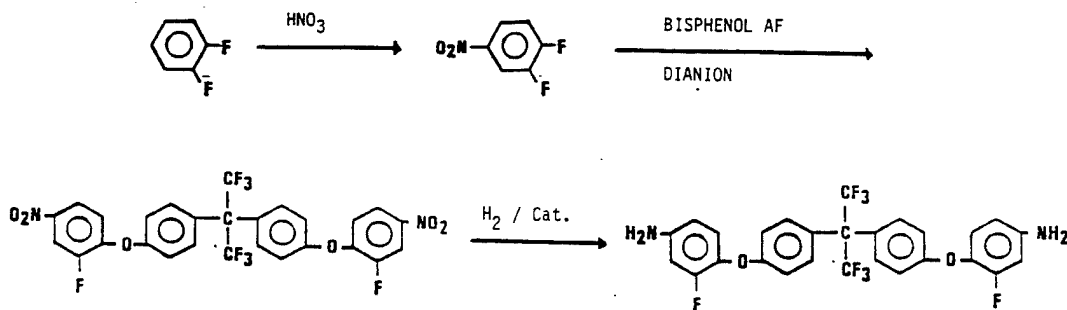


Figure 7. DSC scan of meta-phenylenediamine.

Following the procedure outlined in Reference 6, the diazonium fluoroborate salt was placed in a flask under an argon blanket and gently heated for several seconds with a Bunsen flame. Shortly after removal of the flame a rapid decomposition occurred without warning, exploding the flask. The cause of the rapid decomposition is not known at this time. A literature review completed prior to performing the reaction did not uncover a report of explosive decomposition of these materials.

The incident involving the decomposition of the diazonium salts prompted a search for an alternative synthesis for 2-F-4-BDAF. This search and the temporary disability suffered by the principal investigator as a result of the incident caused a significant delay in the program schedule.

A detailed literature search revealed an alternative synthesis for 2-F-4-BDAF based on a reaction scheme which involves aromatic nitration of 1,2-difluorobenzene to give 3,4-difluoronitrobenzene. Nucleophilic coupling with Bisphenol AF dianion and subsequent hydrogenation should give us desired product (see below).



Nitration of 1,2-difluorobenzene at 273-281K gave the key intermediate in 69% yield (b.p. 367K/15-17 mm; Reference 7, 353-354K/14-mm); the infrared spectrum (Figure 8) and the nmr spectrum (Figure 9) are consistent with the structure. This material was then reacted with a

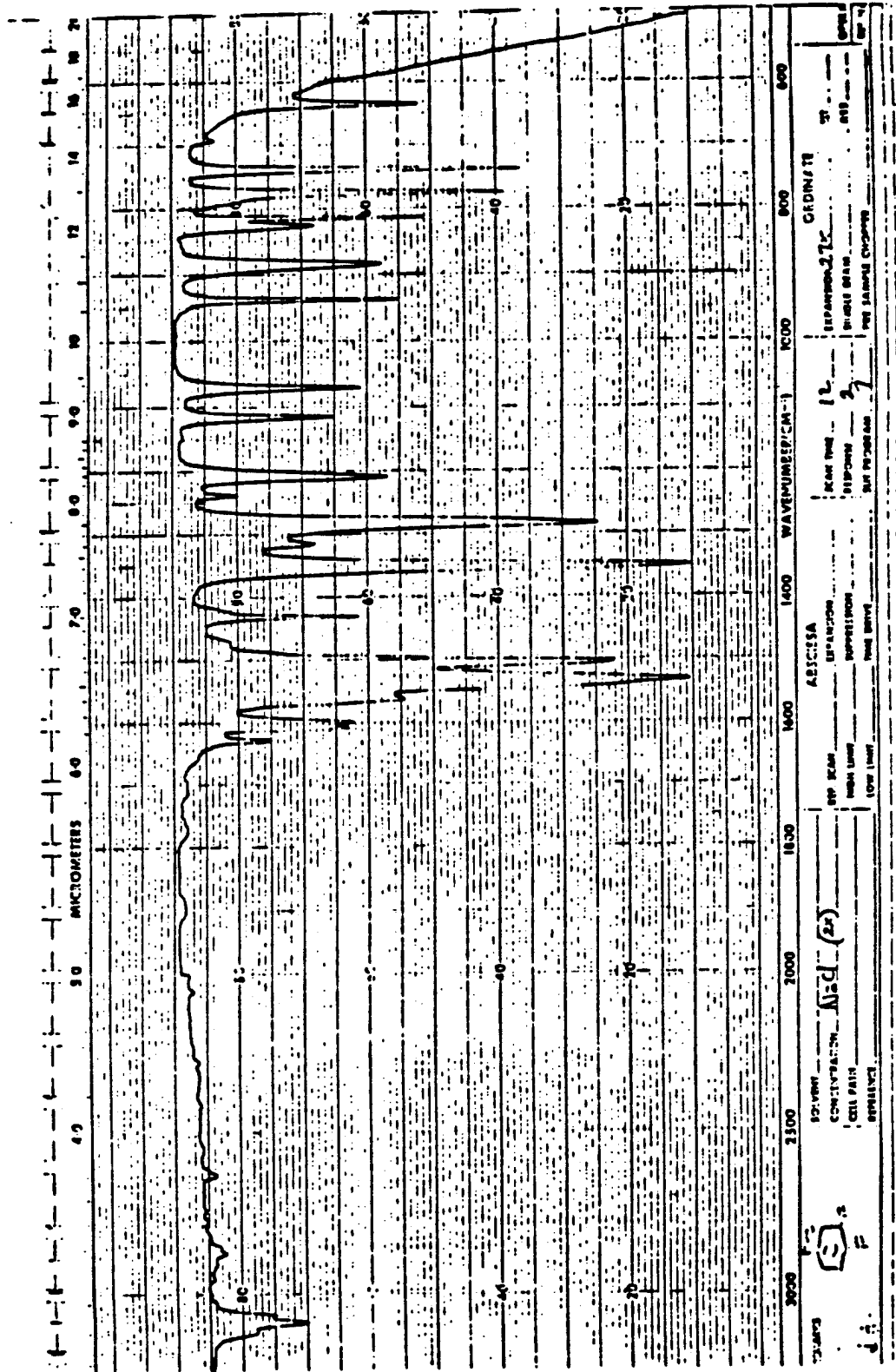


Figure 8. Infrared Spectrum of 3,4-difluoronitrobenzene.

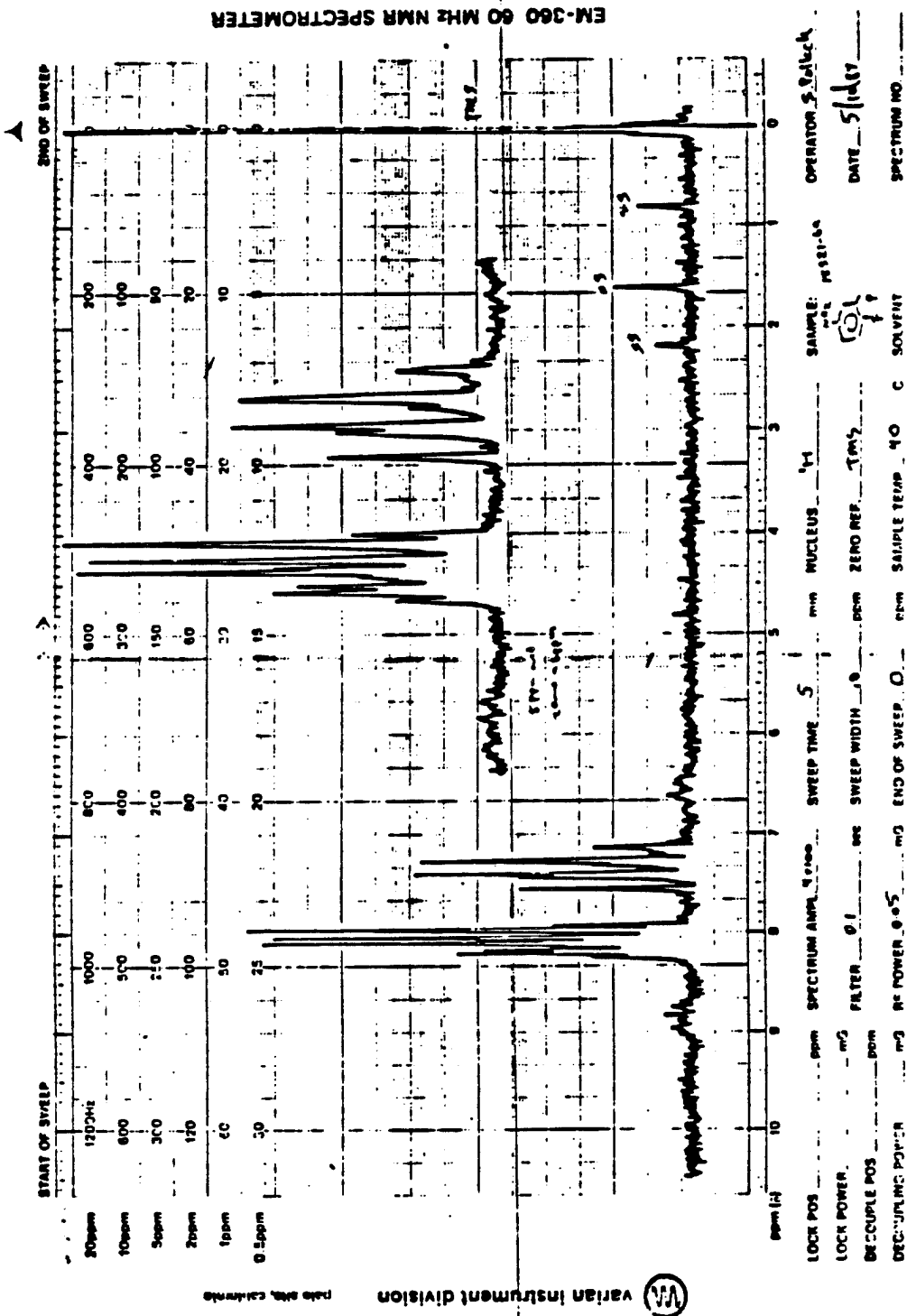


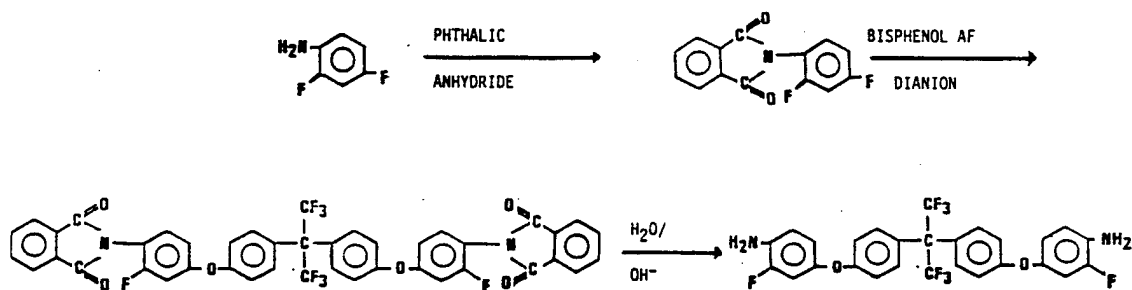
Figure 9. Nmr (60 MHz) spectrum of 3,4-difluoronitrobenzene.
(Insert is expansion of aromatic region.)

stoichiometric amount of Bisphenol AF dianion (formed from Bisphenol AF and sodium hydroxide in DMAC) at elevated temperature (ca. 423K). The reaction product was isolated by adding the reaction mixture to water. The crude product was recrystallized (ethyl acetate/ethanol/hexanes) to give 2,2-bis[(2-fluoro-4-nitrophenoxy)phenyl]hexafluoropropane (2-F-4-BDNF) as a yellow solid in 67% yield. Differential scanning calorimetry (DSC) showed a melting point of 425K (see Figure 10); the infrared spectrum (Figure 11) is consistent with the proposed structure (absorptions for -NO_2 at 1340 and 1530 cm^{-1}) as is the nmr spectrum, Figure 12.

The nitro compound, 2-F-4-BDNF, was treated with hydrogen in the presence of a catalytic amount of palladium on charcoal (5%) as a 10% solution in ethyl acetate. After theoretical uptake of hydrogen was observed, the 2-F-4-BDAF product was recovered (98% of theory) and shown to have the DSC characteristics shown in Figure 13 (m.p. 429K). The infrared and nmr spectra of 2-F-4-BDAF are shown in Figures 14 and 15, respectively.

2.1.4. 3-F-4-BDAF

Two synthetic routes to 2,2-bis[(3-fluoro-4-aminophenoxy)phenyl]hexafluoropropane (3-F-4-BDAF) were investigated. The first involves the conversion of 2,4-difluoroaniline to 2,4-difluorophthalimidobenzene, which would be reacted with Bisphenol AF dianion to produce 2,2-bis[(3-fluoro-4-phthalimidophenoxy)phenyl]hexafluoropropane, which in turn would be hydrolyzed to give 3-F-4-BDAF.



The alternative synthesis involves the reaction of Bisphenol AF dianion with 2,4-difluoronitrobenzene to produce 2,2-bis[(3-fluoro-4-nitrophenoxy)phenyl]hexafluoropropane which can then be reduced to 3-F-4-BDAF.

Sample: 2-F-4-BDNF #15321-2A
Size: 5.62MG.
Rate: 10C/MIN.
Program: Interactive DSC V2.0
Date: 30-Apr-84 Time: 10:50:47
File: NITRO.01 T.A.#19
Operator: TM
Plotted: 30-Apr-84 13:58:45

DSC

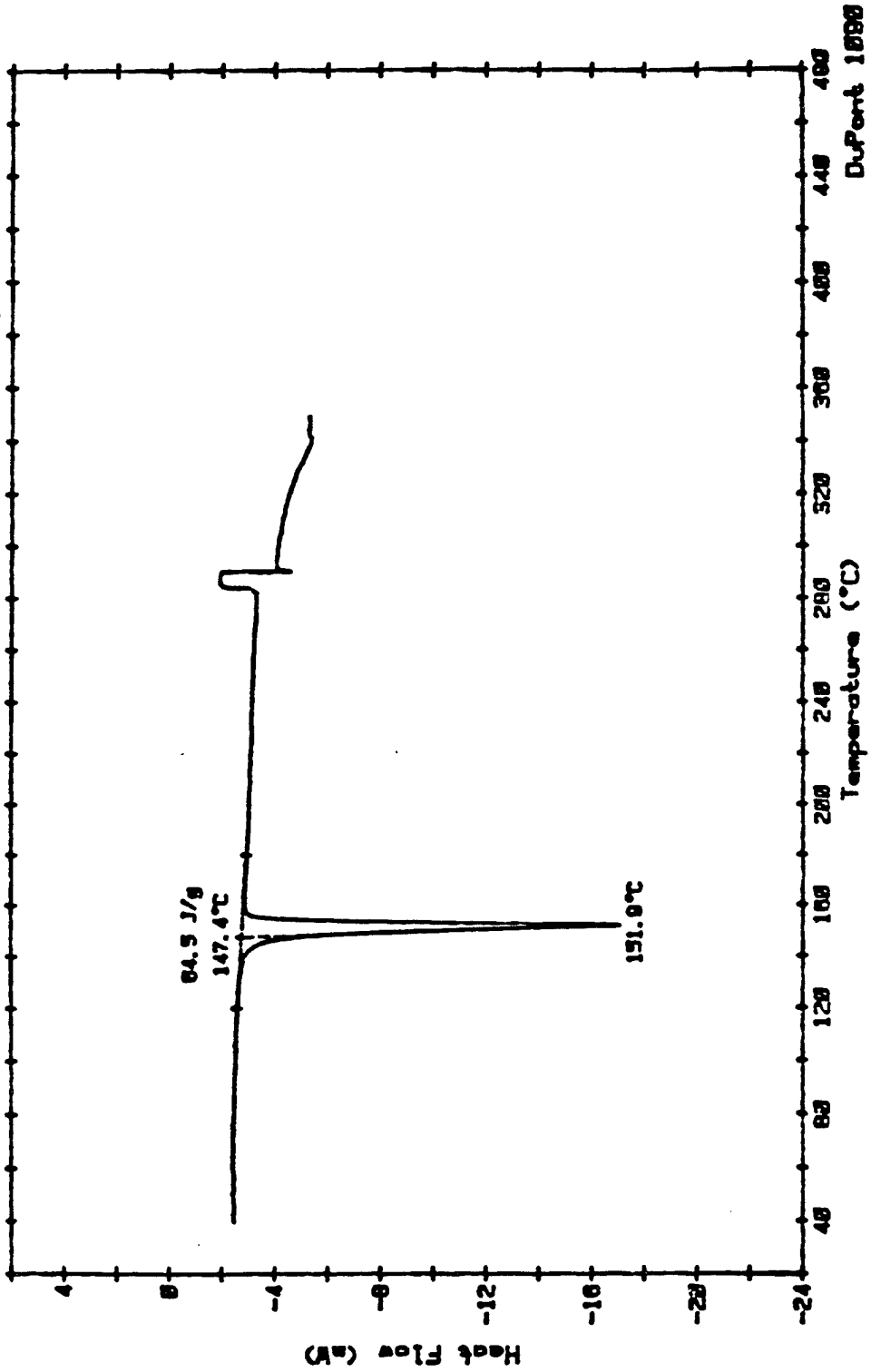


Figure 10. DSC scan of 2-F-4-BDNF.

Sample 2-F-4-BDAF #19321-5A
Size: 3.98MG.
Rate: 10C/MIN.
Program: Interactive DSC V2.0
Dates: 30-Apr-84 Time: 13:41:53
Files: DIAMINE.02 T.A.#19
Operator: TM
Plotted: 30-Apr-84 14:27:19

DSC

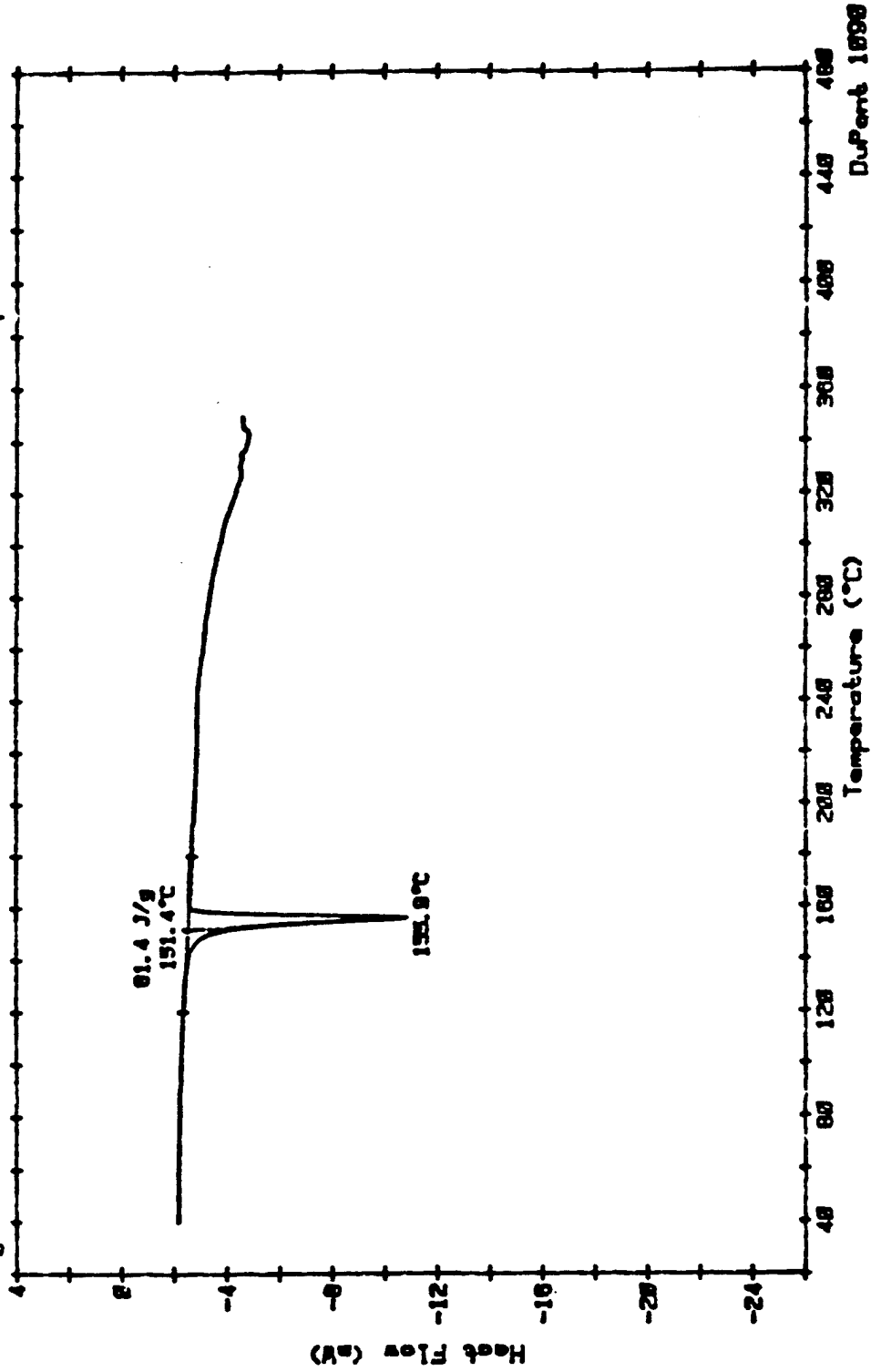


Figure 13. DSC scan of 2-F-4-BDAF.

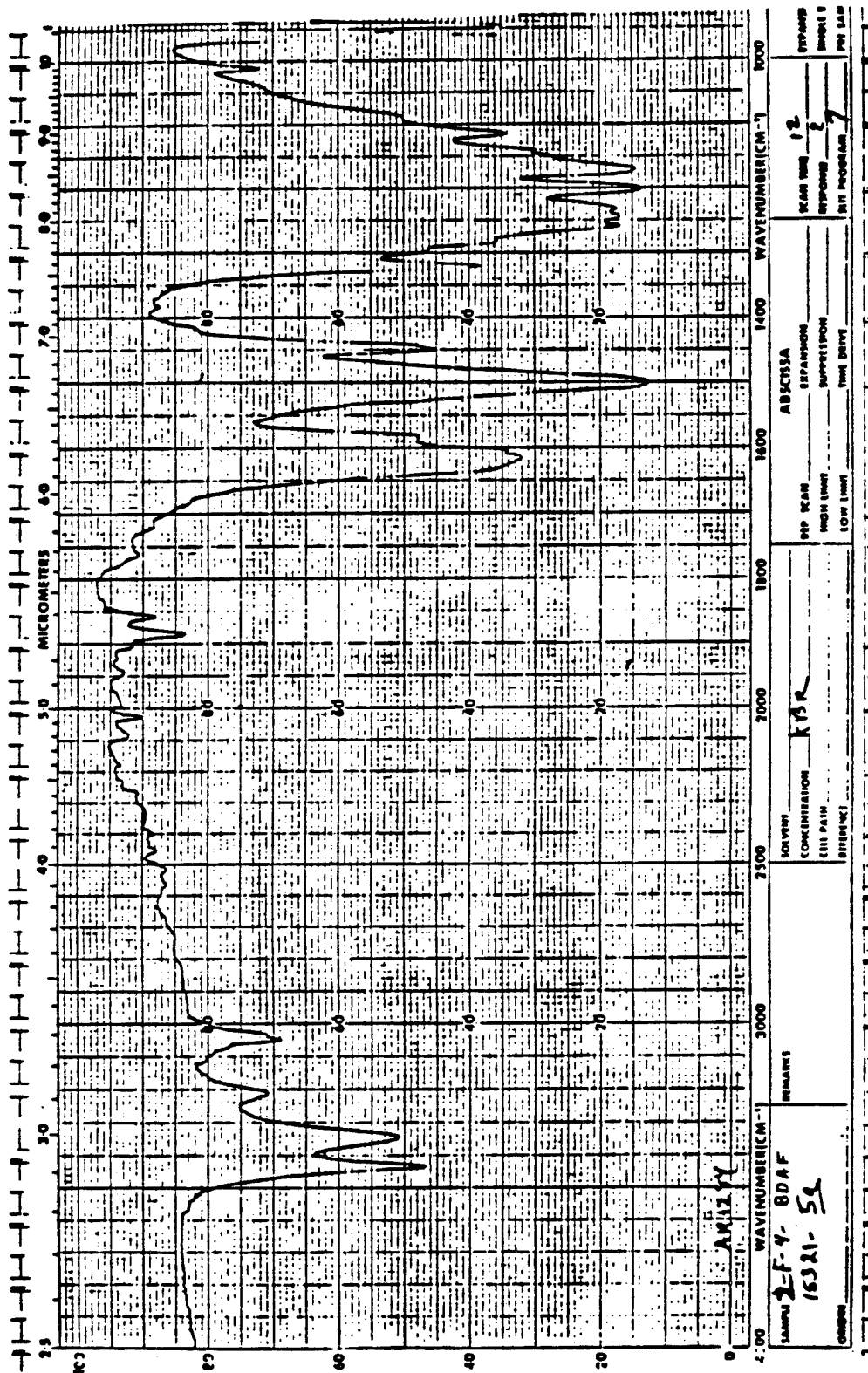


Figure 14. Infrared spectrum of 2-F-4-BDAF.

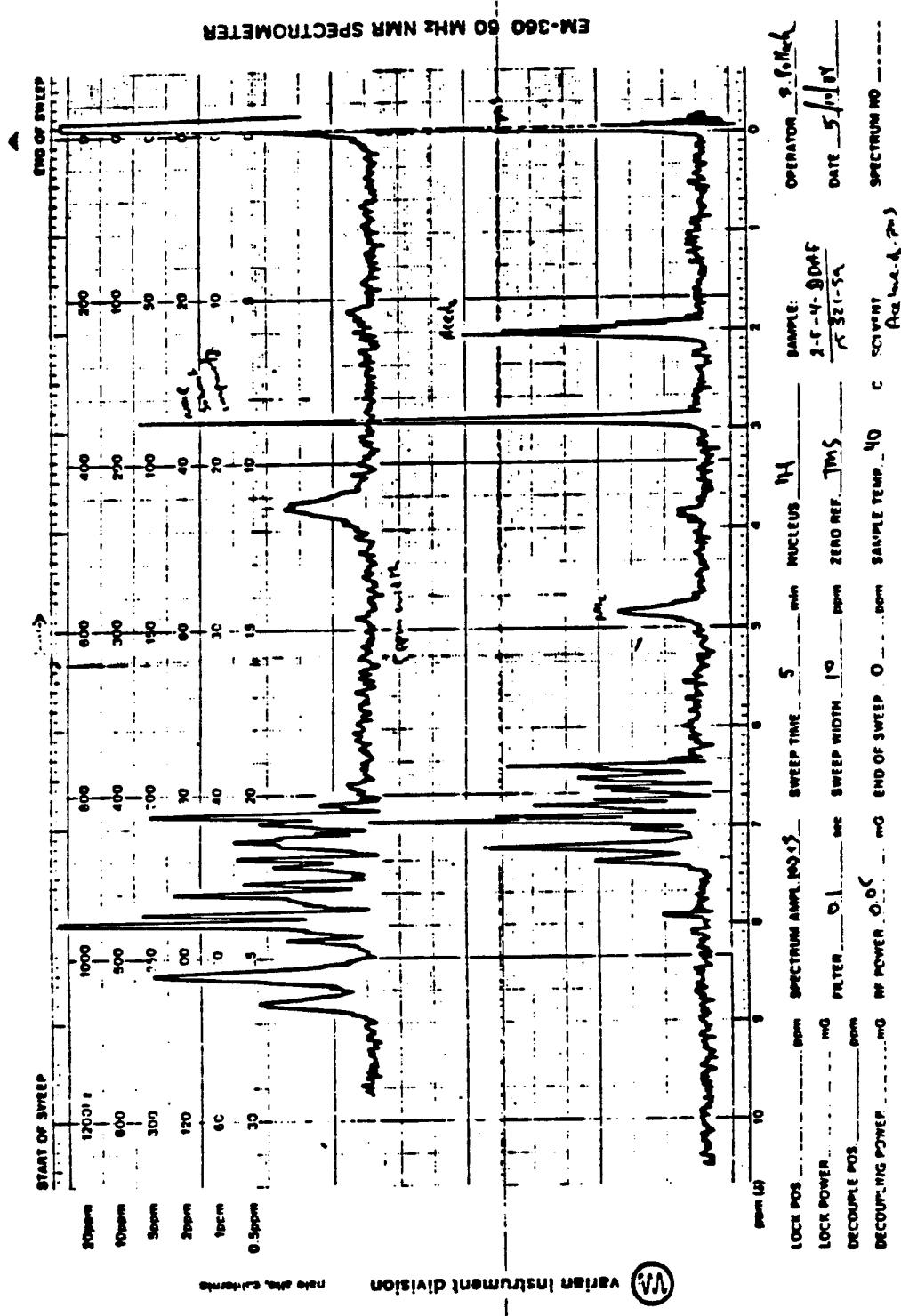
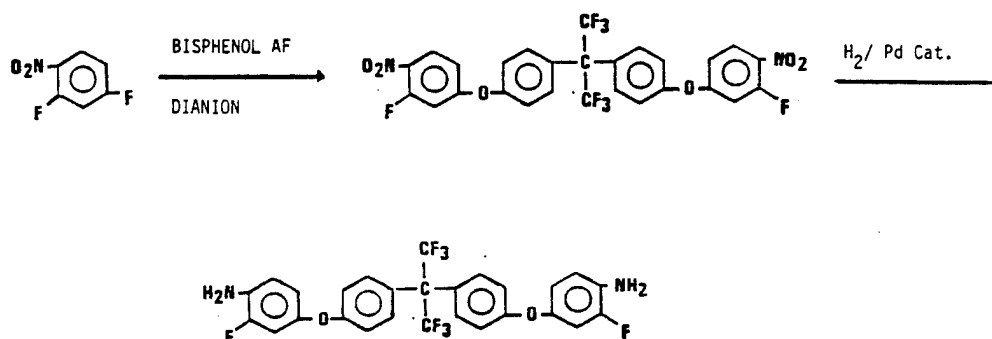


Figure 15. Nmr (60 MHz) spectrum of 2-F-4-BDAF.
(Insert is expansion of aromatic region.)



The first of the two synthesis was initiated by preparing the intermediate 2,4-difluorophthalimidobenzene. Phthalic anhydride in boiling xylene was treated dropwise with an equivalent of 2,4-difluoroaniline with azeotropic removal of water. The mixture was kept at reflux for 4-1/2 hours, then cooled to room temperature. The white precipitate was filtered, washed with xylene and hexane, then air-dried to give an 85% yield of product homogeneous by thin-layer chromatography (silica gel, 1:1 chloroform:hexane eluent, $R_f=0.34$) and containing no trace of phthalic anhydride ($R_f=0$) or 2, 4-difluoroaniline ($R_f=0.46$).

A DMAC solution of Bisphenol AF dianion, prepared by reacting Bisphenol AF with sodium hydroxide in DMAC, was added to two molar equivalents of 2,4-difluorophthalimidobenzene, in dry DMAC, at 373-383K. Aqueous workup of the reaction mixture produced a pasty material which was taken up in diethyl ether. The material was a mixture of isomers and proved to be extremely difficult to separate into pure compounds. The small quantities of pure 3-F-4-BDAF which could have been prepared using this approach or the alternative synthesis route militated against the use of 3-F isomer in the program. Further, the difficulties encountered in the synthesis of 2-F-4-BDAF had resulted in both schedule and financial limitations to pursue preparation of this compound.

2.1.5 2-C1-4-BDAF

With the elimination of 3-F-4-BDAF as a candidate monomer (see Section 2.1.4), it was decided to substitute 2-C1-4-BDAF as an alternative monomer in the test matrix. This approach was low risk because 2-C1-4-BDAF has been prepared during the previous program (Reference 1).

A quantity of 2,2-bis[(2-chloro-4-nitrophenoxy)phenyl]hexafluoropropane (2-C1-4-BDNF) remained from the previous program. The nitro compound was reduced by catalytic hydrogenation according to the procedures in Reference 1 to give the desired 2,2-bis[(2-chloro-4-aminophenoxy)phenyl]hexafluoropropane (2-C1-4-BDAF). Figures 16 and 17 are the nmr spectra of 2-C1-4-BDNF and 2-C1-4-BDAF, respectively.

2.1.6. Pyrazine Dianhydride

The preparation of pyrazine dianhydride (PYDA) has been reported (References 8 and 9). The corresponding tetracarboxylic acid dihydrate (available from PCR, Inc.) was heated with stirring in acetic anhydride to 353K, held there for half an hour, then cooled to room temperature. The solvent was removed under reduced pressure (temperature less than 353K) and the resulting solid was dried overnight at room temperature (pressure ≤ 1 mm). A portion of the very light brown powder was sublimed (T=453K, pressure ca. 1 mm). Yield of whitish-yellow crystals was low (10-20%); most of the material darkened considerably and would not sublime. After the initial attempts to prepare PYDA, it was learned that the precursor, 1,2,4,5-pyrazinetetracarboxylic acid dihydrate, would no longer be commercially available. Therefore, it was agreed to remove PYDA from the test matrix.

2.1.7 Pyromellitic Dianhydride

Pyromellitic dianhydride (PMDA) was obtained from Aldrich Chemical Company and recrystallized from acetic anhydride. The DSC scan and infrared spectrum of the PMDA are to be found in Figures 18 and 19, respectively. The endotherm at 497K (224°C) was present in all PMDA scans but apparently does not represent a polymerization inhibitor.

2.1.8 6-FDA

Initially, 2,2-bis(3,4-dicarboxylphenyl)hexafluoropropane dianhydride (6-FDA) was obtained from Burdick & Jackson or recovered by hydrolysis of NR-150B resins. Later in the program, very high purity 6-FDA was obtained from American Hoechst which produces it on a commercial scale.

Both the Burdick & Jackson and the Hoechst material were used without further purification. The material isolated from the hydrolysis of NR-150B

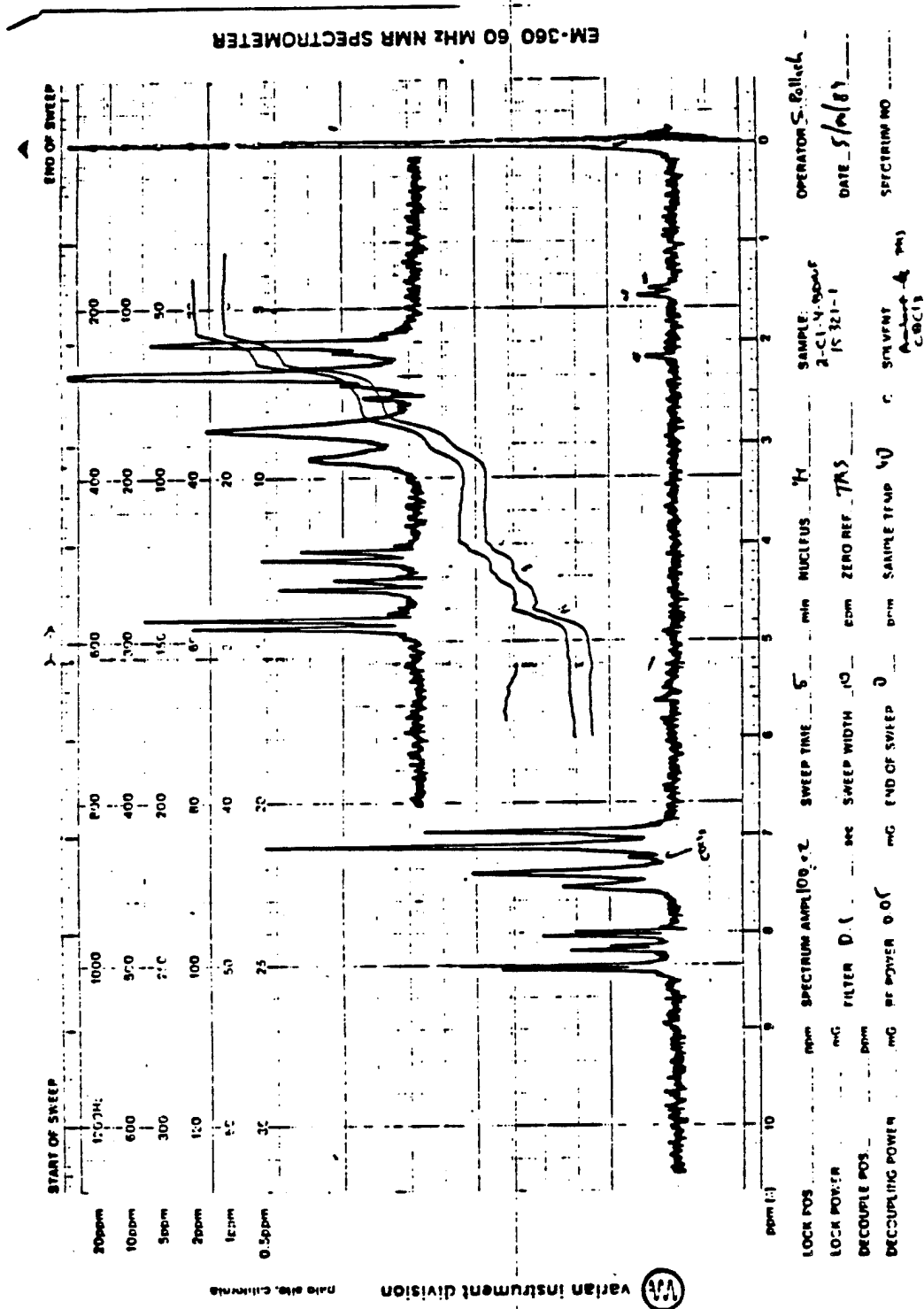


Figure 16. Nmr (60 MHz) spectrum of 2-Cl-4-BDNF.
(Insert is expansion of aromatic region.)

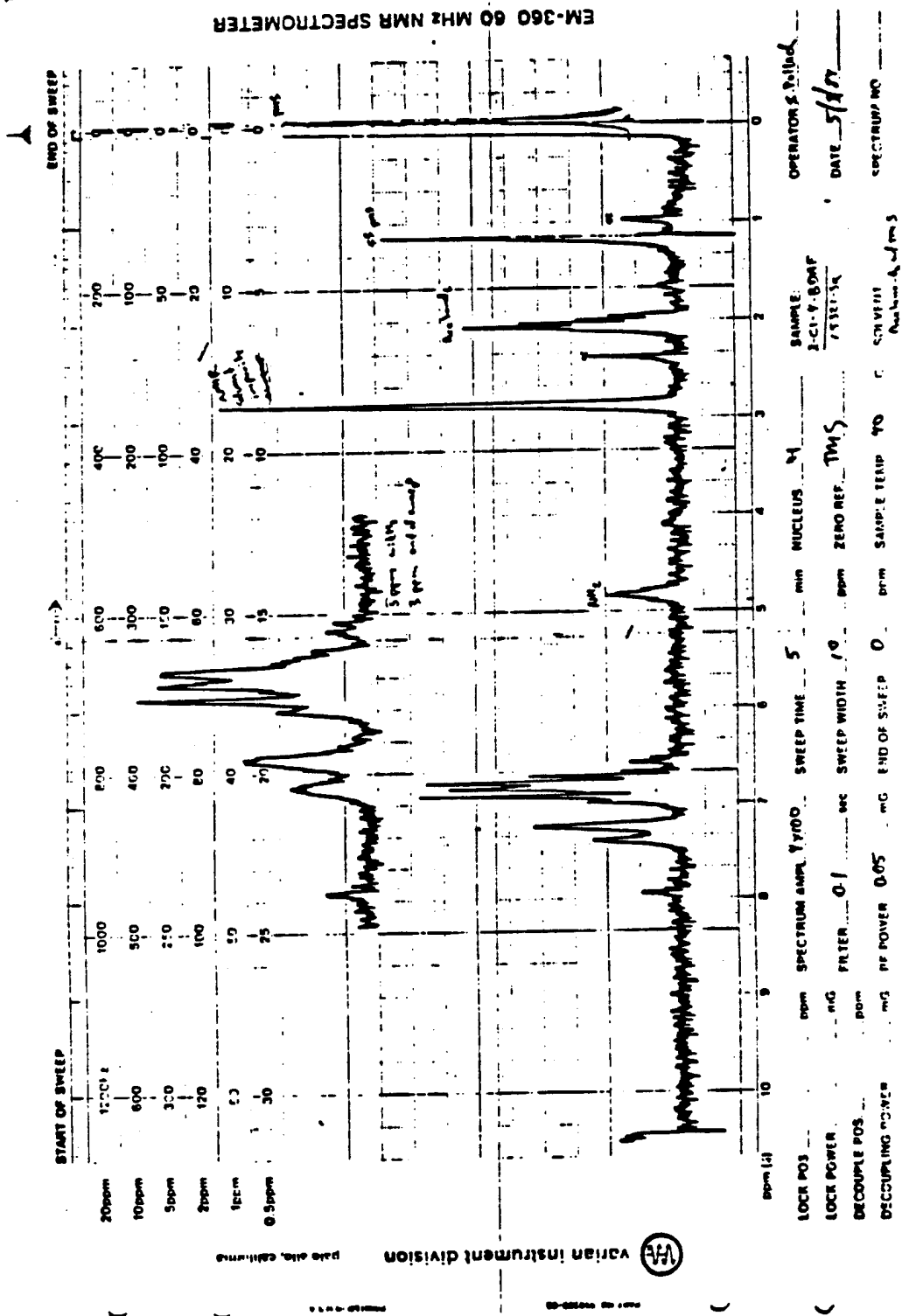


Figure 17. Nmr (60 MHz) spectrum of 2-Cl-4-BDAF.
(Insert is expansion of aromatic region.)

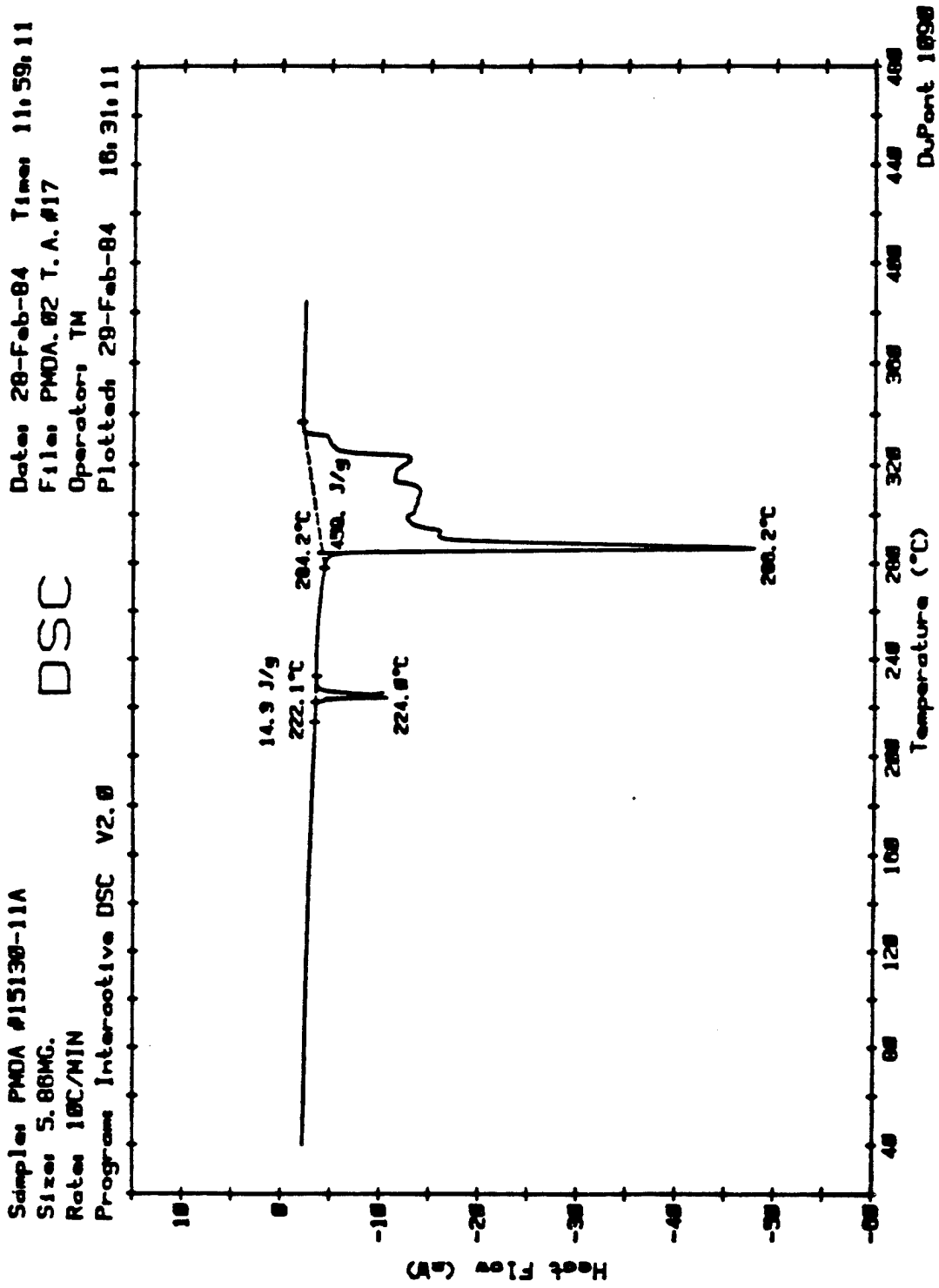


Figure 18. DSC scan of PMDA.

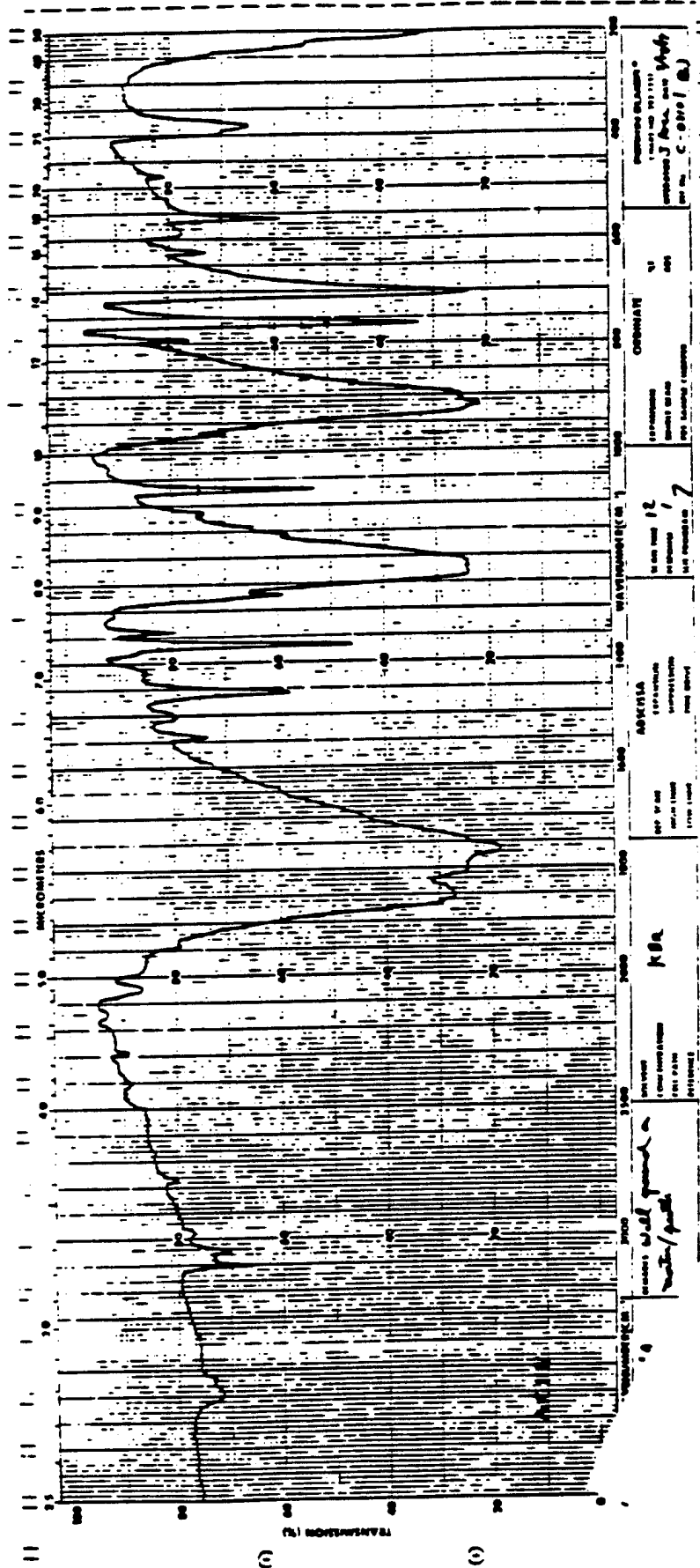


Figure 19. Infrared spectrum of PMDA.

proved to be difficult to purify, perhaps because of the presence of impurities produced in the resin during storage and was not employed to prepare polymers used in neat resin molding or composite fabrication.

The DSC scan, infrared and nmr spectra of Burdick & Jackson 6-FDA are shown in Figures 20, 21 and 22, respectively.

2.2 POLYMER SYNTHESIS

The polymers shown in Table II were selected for study in Task II on the bases of promise of high thermo-oxidative stability, technical interest and monomer availability.

Table II. Candidate Polymers

<u>Polymer</u>	<u>Diamine</u>	<u>Dianhydride</u>
I.	4-BDAF	PMDA
II.	95:5 PPDA:MPDA	6-FDA
III.	2-F-4-BDAF	PMDA
IV.	2-C1-4-BDAF	PMDA
V.	2-C1-4-BDAF	6-FDA
VI.	2-F-4-BDAF	6-FDA

The candidate polymers were prepared by a standard procedure. All materials and equipment were carefully dried before use. The dianhydride was added as a solid to a stirred solution of an equimolar solution of the diamine in DMSO. The reaction solution was maintained at ca. 298K during addition and was stirred for an additional hour after all of the dianhydride had dissolved. A one atmosphere nitrogen blanket maintained in the apparatus throughout the polymerization. The resulting polyamide-acid solutions were generally 25% (w/w) solids.

The polymers were characterized by inherent viscosity (η_{inh}) measurements. Typical values obtained for the polymers are shown in Table III. It should be noted that in these laboratories the 6-FDA-based polymers exhibited uniformly lessor (η_{inh}) values than the corresponding PMDA-based polymers. Since the two classes of polymers are produced by the same methods using monomers of comparable purity, the differences in viscosity may result from differences of solution behavior rather than molecular weight differences.

Sample: 6-FDA BURDICK+JACKSON
Size: 4.02MG.
Rate: 10C/MIN
Program: Interactive DSC V2.0
Date: 28-Feb-84 Time: 13:44:28
File: 6-FDA.03 T.A.#17
Operator: TM
Plotted: 29-Feb-84 16:48:35

DSC

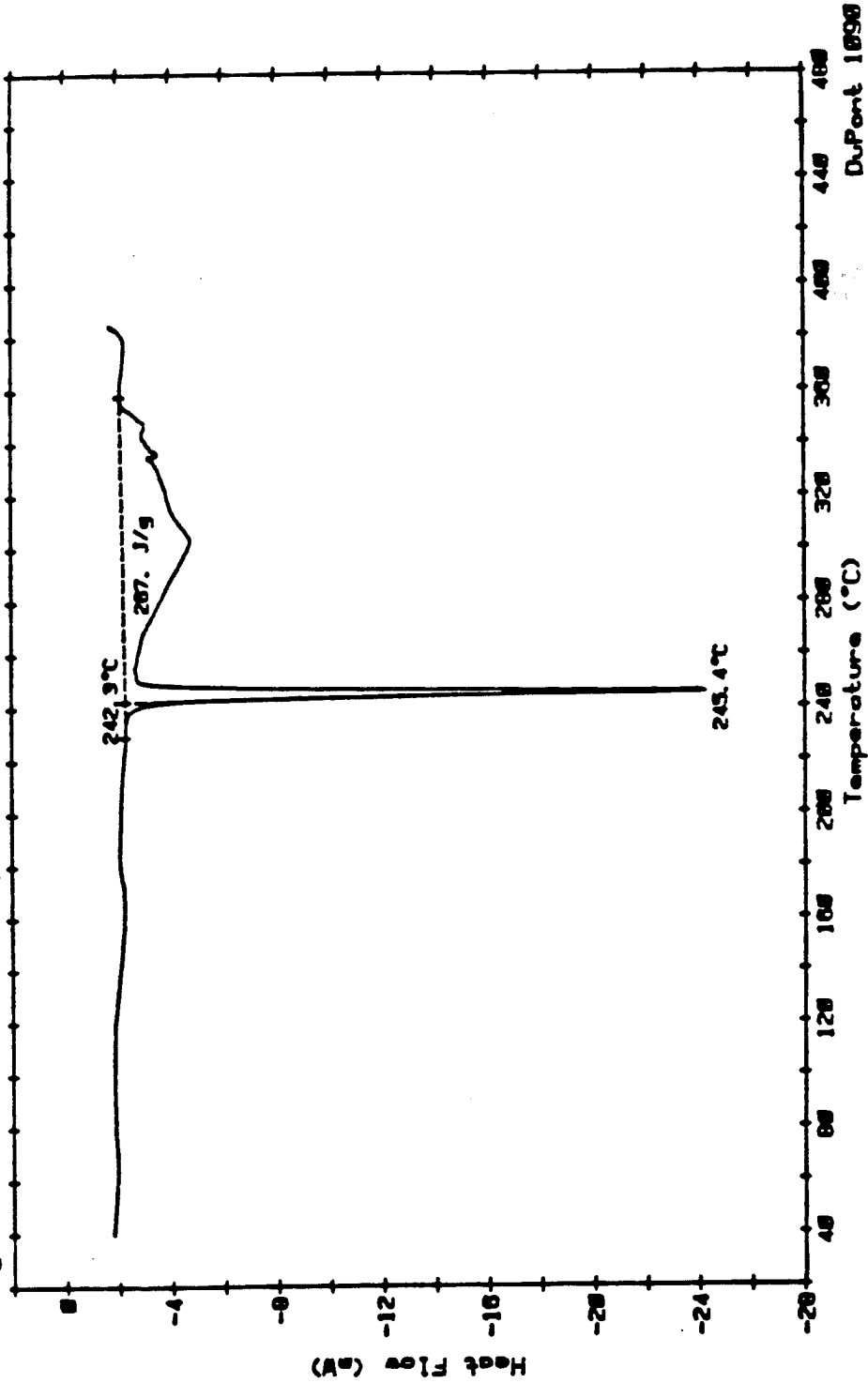


Figure 20. DSC scan of 6-FDA.

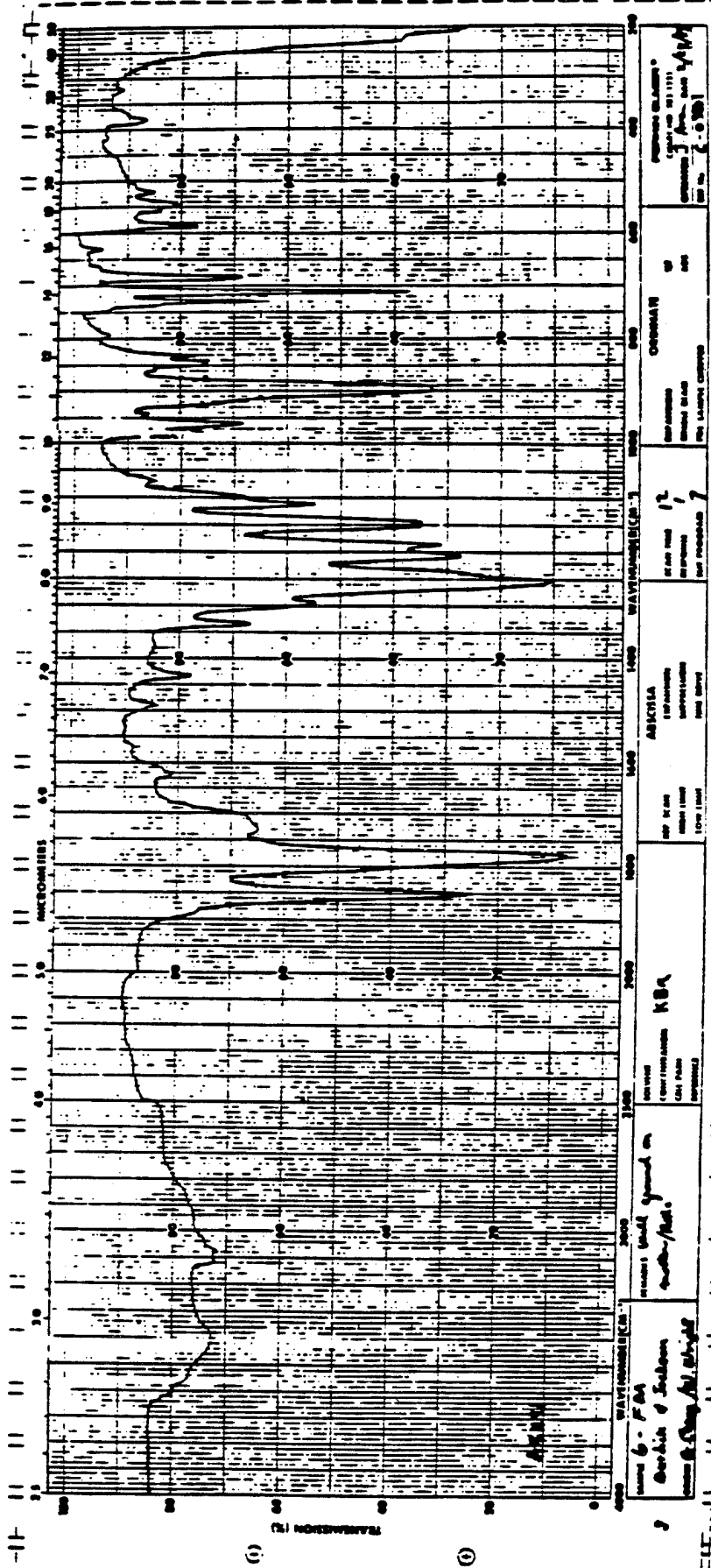


Figure 21. Infrared spectrum of 6-FDA.

Table III. Inherent Viscosities of Prepared Polymers⁽¹⁾

<u>Formulation</u>	<u>Inherent Viscosity (η_{inh}), dL/g</u> ⁽²⁾
I. 4-BDAF/PMDA	1.1
II. 95:5 <u>para:meta</u> -PDA/6-FDA	0.4
III. 2-F-4-BDAF/PMDA	1.0
IV. 2-C1-4-BDAF/PMDA	1.0
V. 2-C1-4-BDAF/6-FDA	0.5
VI. 2-F-4-BDAF/6-FDA	0.5

⁽¹⁾Polymers were prepared as 25% w/w solids in DMSO.

⁽²⁾Measured on 0.5% w/w solids solutions in DMSO at 303K (30°C).

The polyamide-acid solutions were converted to polyimide molding powders by chemical conversion. A typical procedure consisted of dropwise adding the 25% w/w solids varnish into a mixture of 1:1 v:v pyridine:acetic anhydride and stirring well for 1-1 1/2 hours. The suspension was diluted with methanol and then filtered; the resultant filtered solid was vacuum-dried and ground to a fine powder. The fact that the material was converted to a polyimide renders it inert to hydrolysis by methanol under the mild workup conditions. Indeed, infrared analysis material prepared by this method shows essentially complete conversion of polyamide-acide to polyimide.

3.0 POLYMER THERMO-OXIDATIVE STABILITY

During this task the molding powders of the six (6) selected polymer candidates (Table II) were converted to neat resin molded disks. The disks were subjected to thermo-oxidative aging to aid in the selection of two candidate resins for use in Task III.

3.1 NEAT RESIN MOLDING STUDIES

The neat resin molding methods employed were based on previous experience in these laboratories with chemically imidized 4-BDAF/PMDA molding powder. In the standard procedure, the molding powder is charged into a hot mold (450K) and placed in the press. The mold is heated to 644K without application of pressure. When the temperature of the mold reaches 644K, pressure is applied and the mold is heated to 672K. During the temperature rise to 672K the pressure is relieved periodically to release any volatiles. The molding temperature of 672K and pressure of 31,000 to 41,000 KPa (4500 to 6000 psi) are maintained for one hour. The mold is then allowed to cool to approximately 450K before the pressure is released and the part removed from the mold. The above procedure was modified for 2-C1-4-BDAF/6-FDA and 2-F-4-BDAF/6-FDA, which exhibited excessive flow under those conditions, by using a molding pressure of 20,700 KPa (3,000 psi).

The six candidate resins were molded into disks 7.62 cm (3 in) in diameter and 0.32 cm (0.125 in) thick. The disks were sectioned into 1.27 cm (0.5 in) square pieces for postcure before aging. Non-square pieces which were obtained from the disks were used to determine Tg by thermal mechanical analysis (TMA).

Polymers I, II and III (Table II) were postcured at 644K (700°F) in air for 16 hours. Similar treatment of Polymers IV, V and VI resulted in specimens that were badly cracked and swollen and showed indication of flow. An examination of the TMA traces of these polymers (see below) indicates that 644K is above their respective Tg's. Additional samples of Polymers IV, V and VI were postcured at 616K (650°F) for 16 hours for use in the aging studies.

The as-molded and after postcure TMA curves of the six polymers are shown in Figures 23 to 34. The Tg's derived from the TMA curves are shown in Table IV. Only Polymers I, II and III exhibit Tg's above 644K (700°F) before or after postcure. Polymer V, 2-C1-4-BDAF/6-FDA actually shows a lower Tg after postcure.

Table IV. Neat Resin Glass Transition Temperatures(Tg)

<u>Polymer</u>	<u>As Molded Tg (K/°F)</u>	<u>Postcured Tg (K/°F)</u>
4-BDAF/PMDA	585/594	681/766
PDA _s /6-FDA	604/627	653/716
2-F-4-BDAF/PMDA	556/542	698/797
2-C1-4-BDAF/PMDA	533/500	556/541
2-C1-4-BDAF/6-FDA	566/559	516/470
2-F-4-BDAF/6-FDA	508/455	536/505

3.2 NEAT RESIN ISOTHERMAL AGING

Postcured neat resin specimens of the six polymers were subjected to isothermal aging at 598K (600°F) and 644K (700°F) under 1, 4 and 7 atm compressed air pressure (flow 10 cm³/sec). The weight loss data are shown in Figures 35 through 39 (please note changes in scale among the graphs) and Tables V through VIII. The data show that 6-FDA-containing polymers generally have lesser weight loss than their PMDA-containing counterparts. There is also a trend to reduced thermo-oxidative stability with 2-C1-substitution as compared to 2-F substitution. All but Polymers I and II showed >20% weight loss after only 50 hrs at 644K and 0.7 MPa.

On the basis of the thermo-oxidative aging data and their Tg determinations, 2-F-4-BDAF/PMDA and 2-F-4-BDAF/6-FDA were selected, along with Polymers I and II for test in Task III, Composites Fabrication and Evaluation.

Date: 12-Sep-84 Time: 10:10:41
File: MOLDING.01 T.A.#24
Operator: TOM MAY
Plotted: 13-Sep-84 15:02:27

Sample: POLYIMIDE #15921-51C
Size: 3.27MM
Rate: 10C/MIN.
Program: TMA Analysis V1.0

TMA

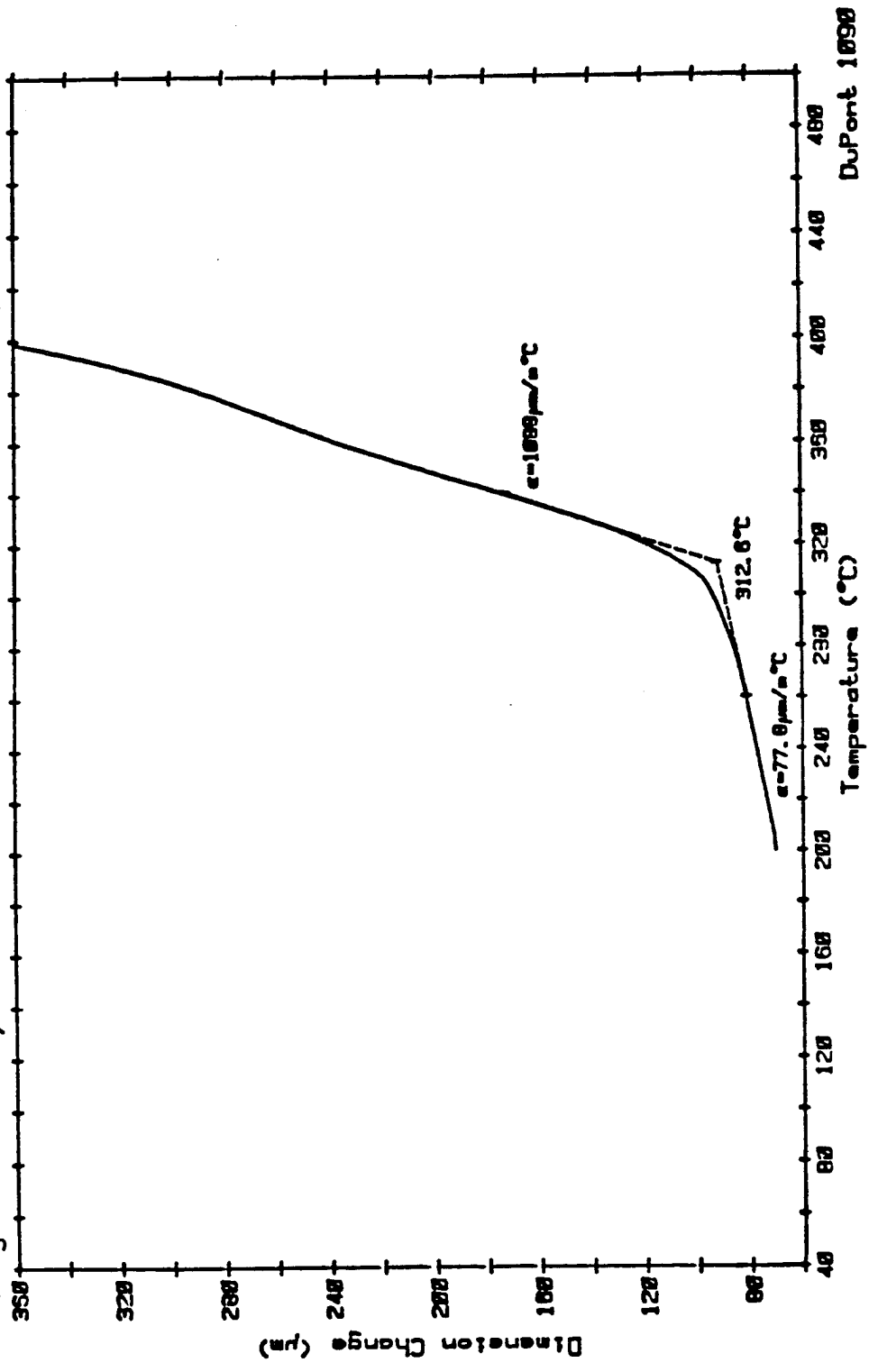


Figure 23. TMA of 4-BDAF/PMDA (as molded).

Sample: POLYIMIDE #15321-51C-PC
Size: 4.37MM
Rate: 10C/MIN.
Program: TMA Analysis V1.0
Date: 11-Sep-84 Time: 12:53:48
File: MOLDING.15 T.A.#23
Operator: TOM MAY
Plotted: 13-Sep-84 13:54:07

TMA

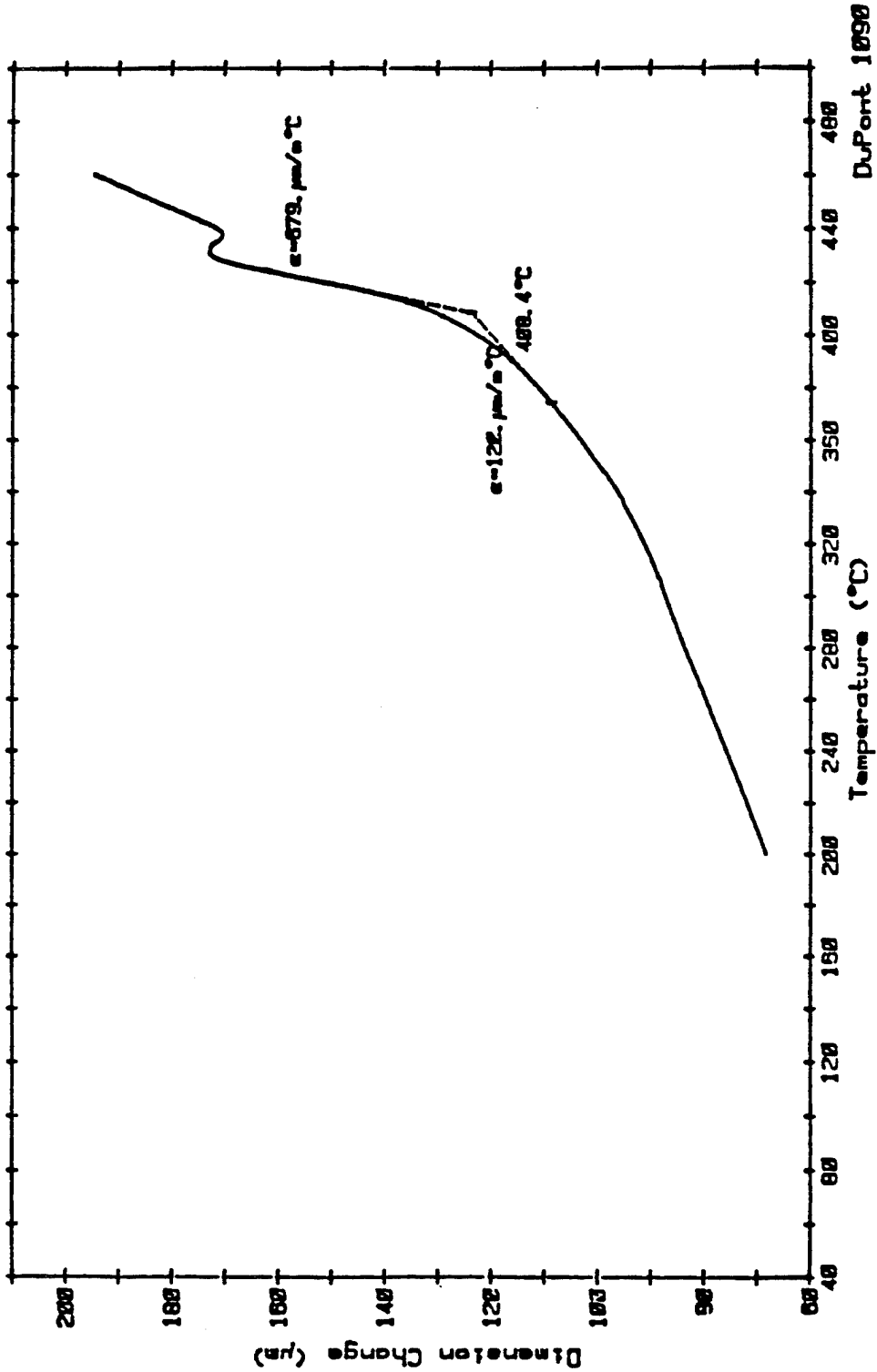


Figure 24. TMA of 4-BDAF/PMDA, postcured at 644K for 16 hours.

Date: 11-Sep-94 Time: 9:23:03
File: MOLDING.13 T.A.#23
Operator: TOM MAY
Plotted: 13-Sep-94 13:16:59

Sample: POLYIMIDE #15321-719
Size: 3.41MM
Rate: 10C/MIN.
Program: TMA Analysis V1.0

TMA

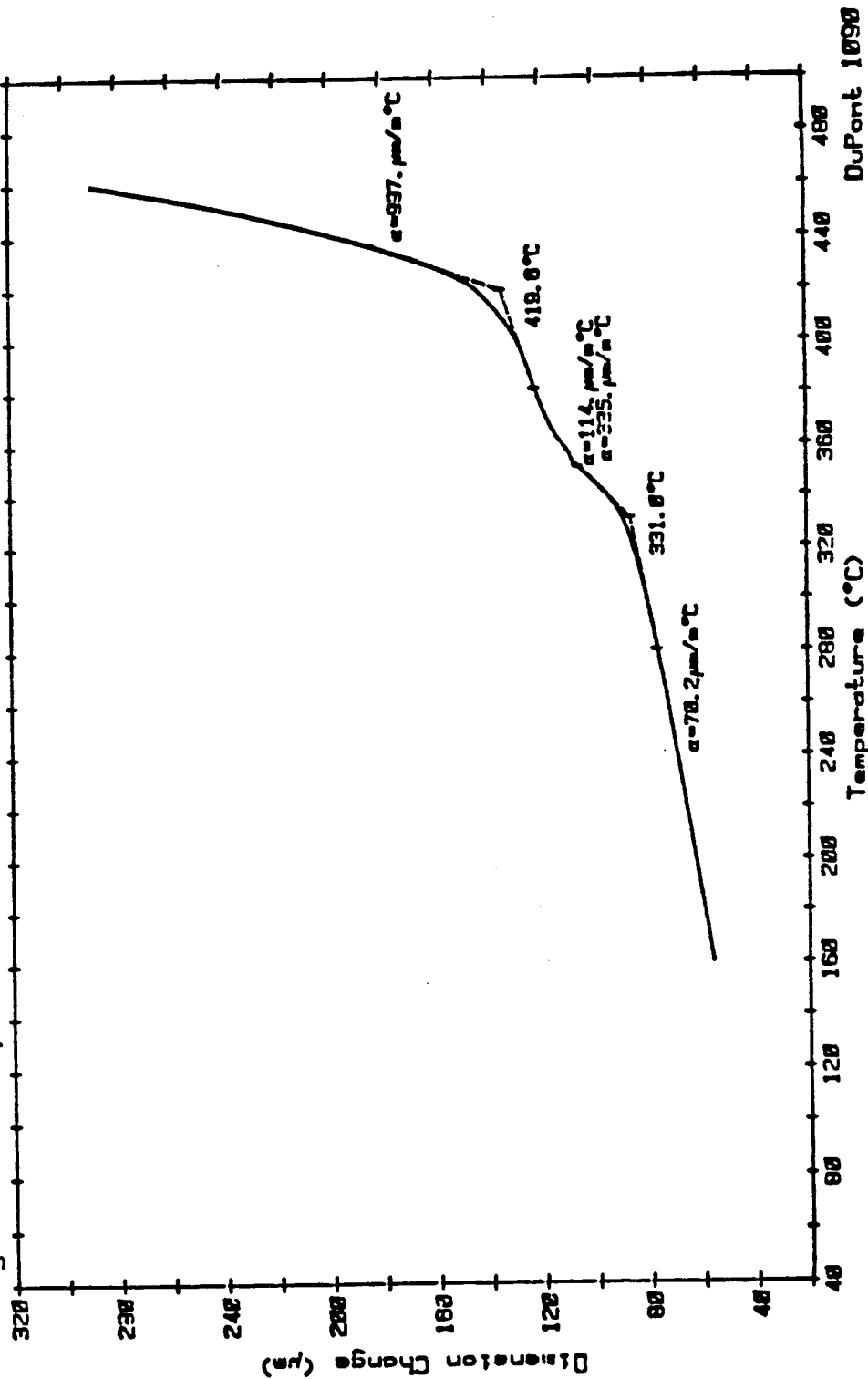


Figure 25. TMA of PDAs/6-FDA (as molded).

Sample: POLYIMIDE #15321-719-FC
Size: 4.05MM
Rate: 10C/MIN.
Program: TMA Analysis V1.0
Date: 12-Sep-64 Time: 12:21:08
File: MCLDING.12 T.A.#23
Operator: TOM MAY
Plotted: 11-Sep-64 9:50:20

TMA

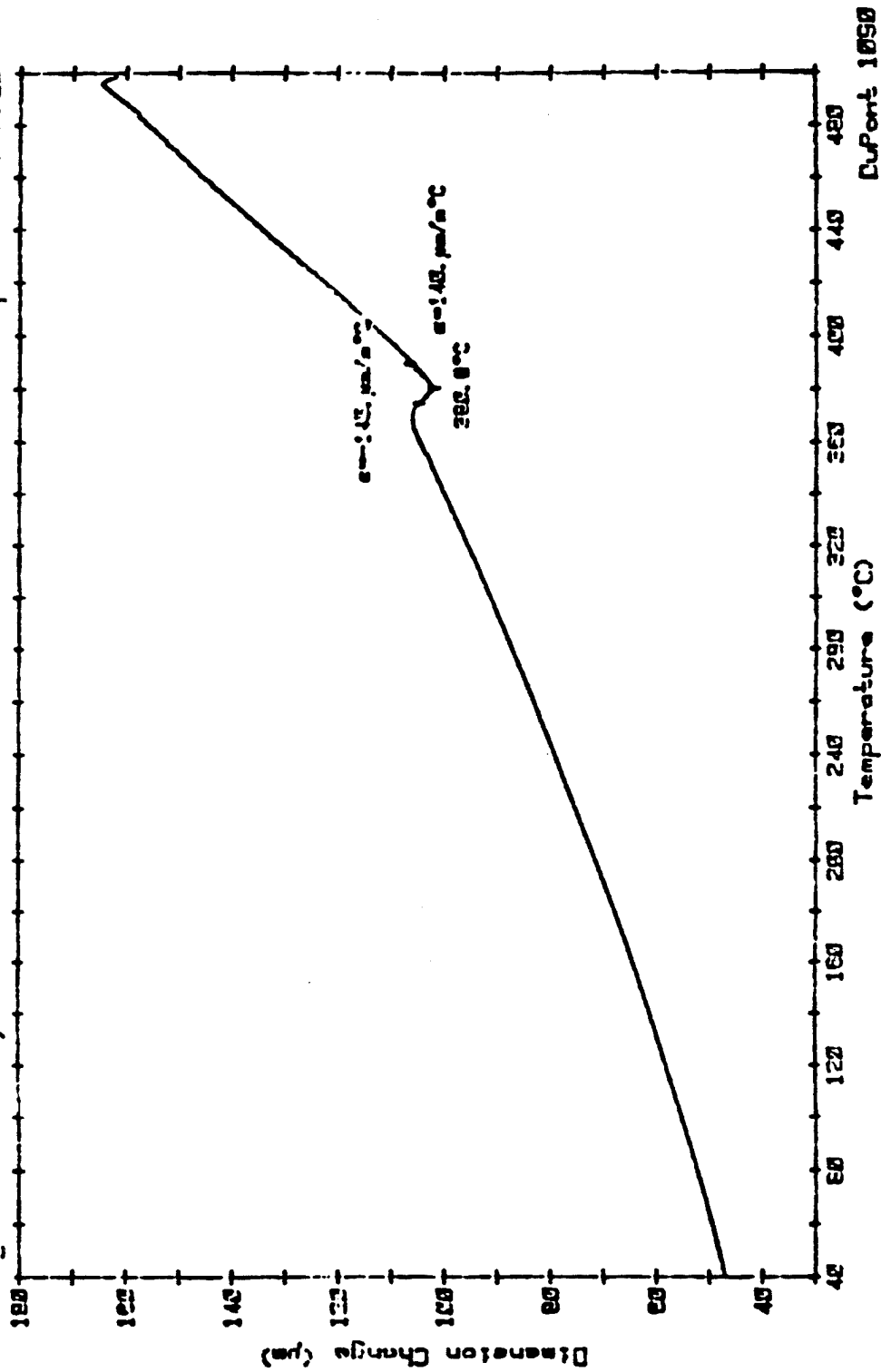


Figure 26. TMA of PDAs/6-FDA, postcured at 644K for 16 hours.

Date: 12-Sep-84 Time: 11:51:33
File: MOLDING.02 T.A.#24
Operator: TOM MAY
Plotted: 13-Sep-84 15:25:12

Sample: POLYIMIDE #15321-59A
Size: 3.13MM
Rate: 10°C/MIN.
Program: TMA Analysis V1.0

TMA

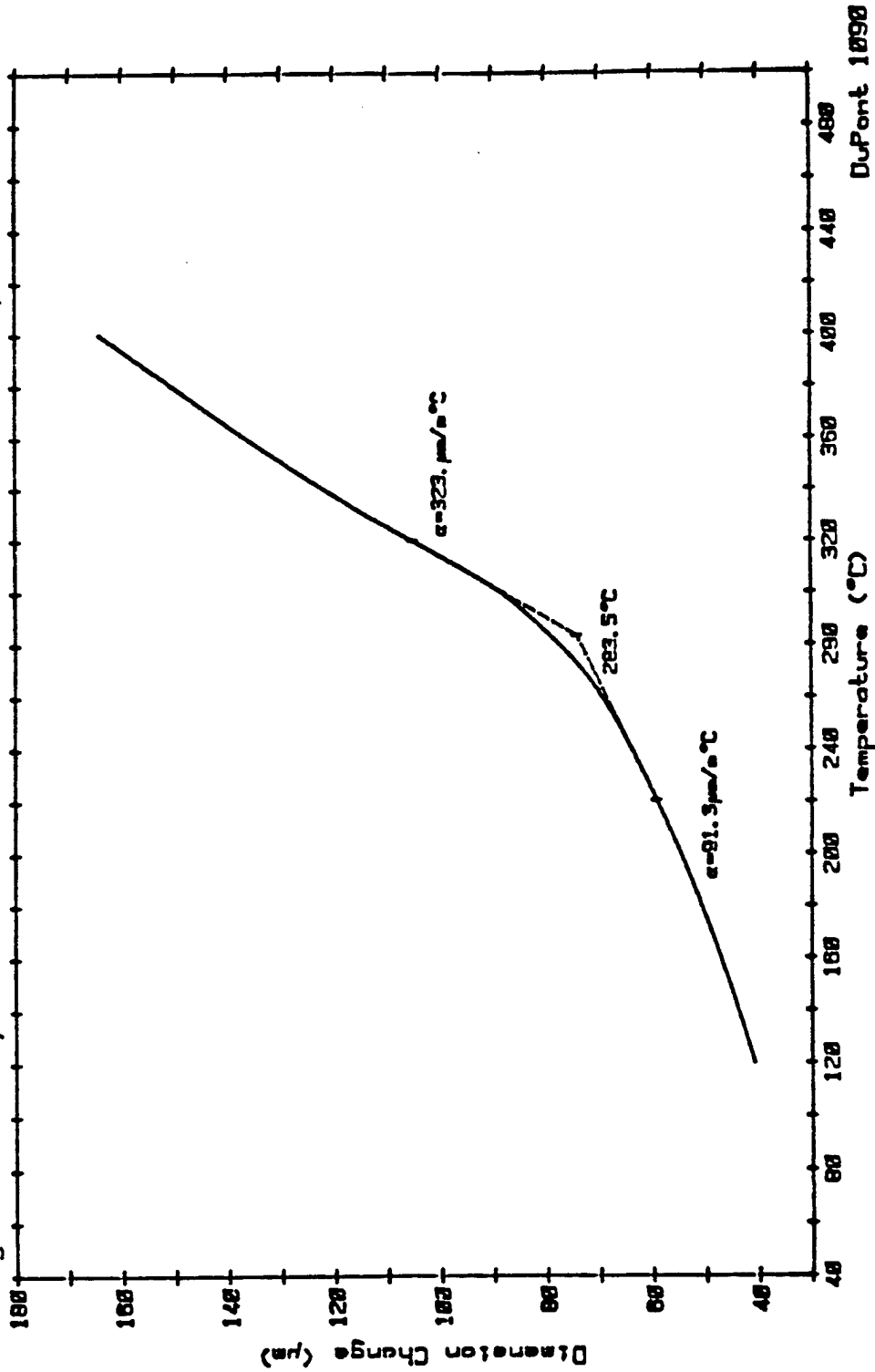


Figure 27. TMA of 2-F-4-BDAF/PMDA (as molded).

Date: 11-Sep-84 Times 10:29:57
Files: MOLDING.14 T.A.#23
Operator: TOM MAY
Plotted: 13-Sep-84 13:39:12

Sample: POLYIMIDE #15321-52A-PC
Size: 3.33MM
Rate: 10C/MIN.
Program: TMA Analysis V1.0

TMA

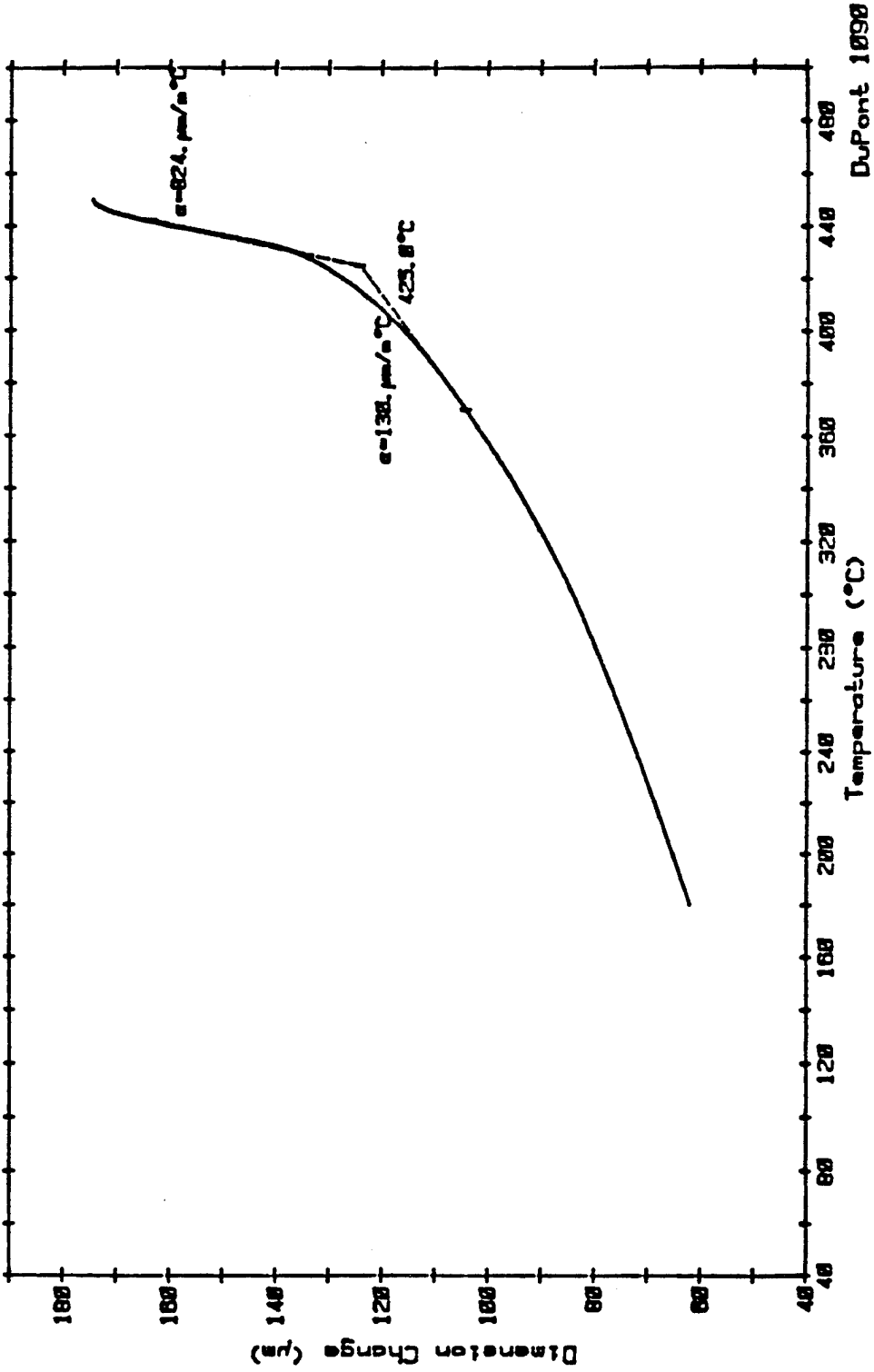


Figure 28. TMA of 2-F-4-BDAF/PMDA, postcured at 644K for 16 hours.

Date: 9-Jul-84 Time: 18:02:53
File: MOLDING.01 T.A.#21
Operator: TOM MAY
Plotted: 4-Sep-84 16:18:31

Sample: MOLDINGS #15321-36M
Size: 1.98MM
Rate: 10C/MIN
Program: TMA Analysis V1.0

TMA

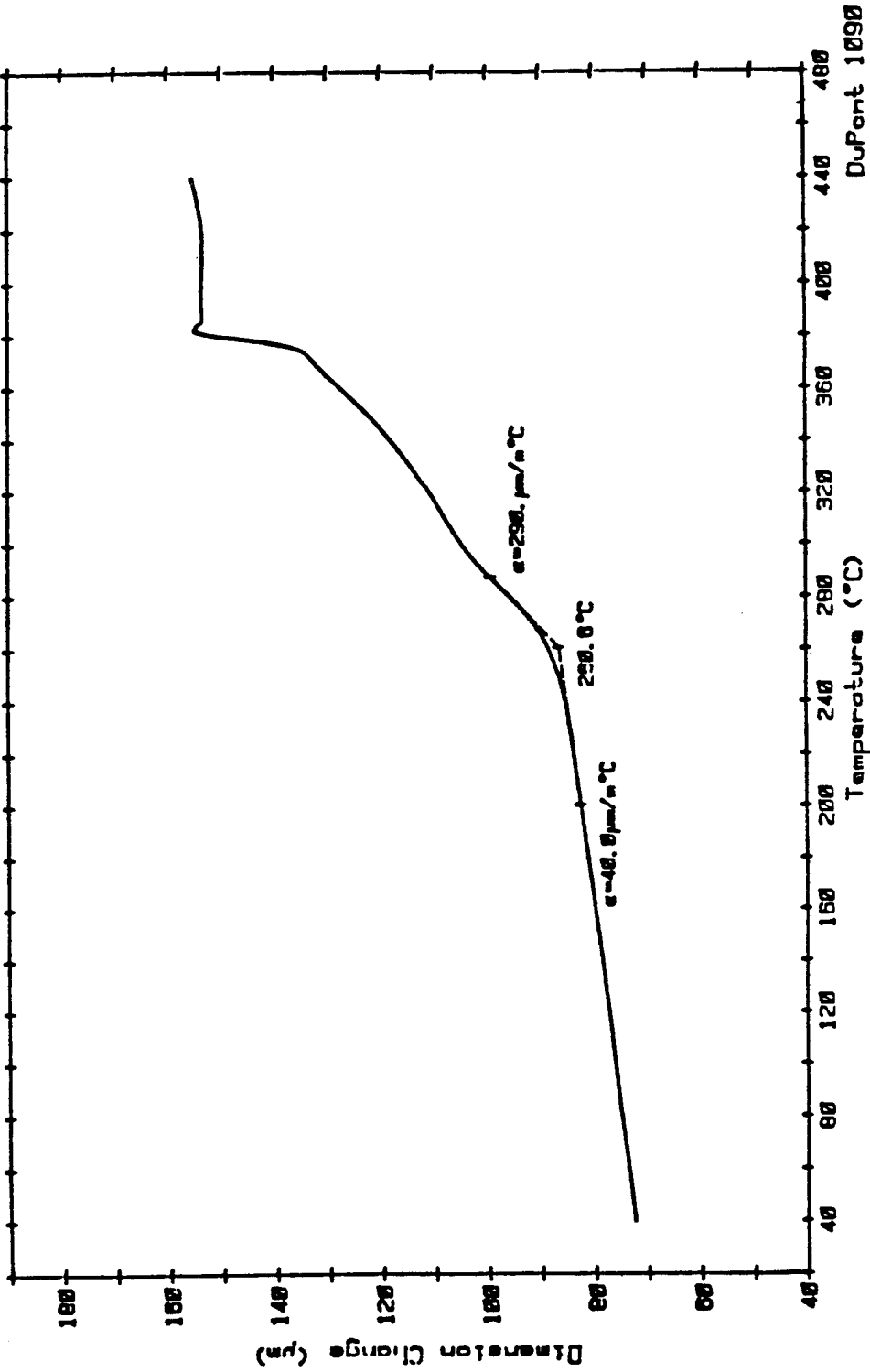


Figure 29. TMA of 2-C1-4-BDAF/PMDA (as molded).

Sample: POLYIMIDE #15321-49M-PC
Size: 3.95MM
Rate: 10C/MIN.
Program: TMA Analysis V1.0

TMA

Date: 21-Aug-84 Time: 12:41:15
File: POLYIMIDE.03 T.A.#23
Operator: TOM MAY
Plotted: 22-Aug-84 11:35:58

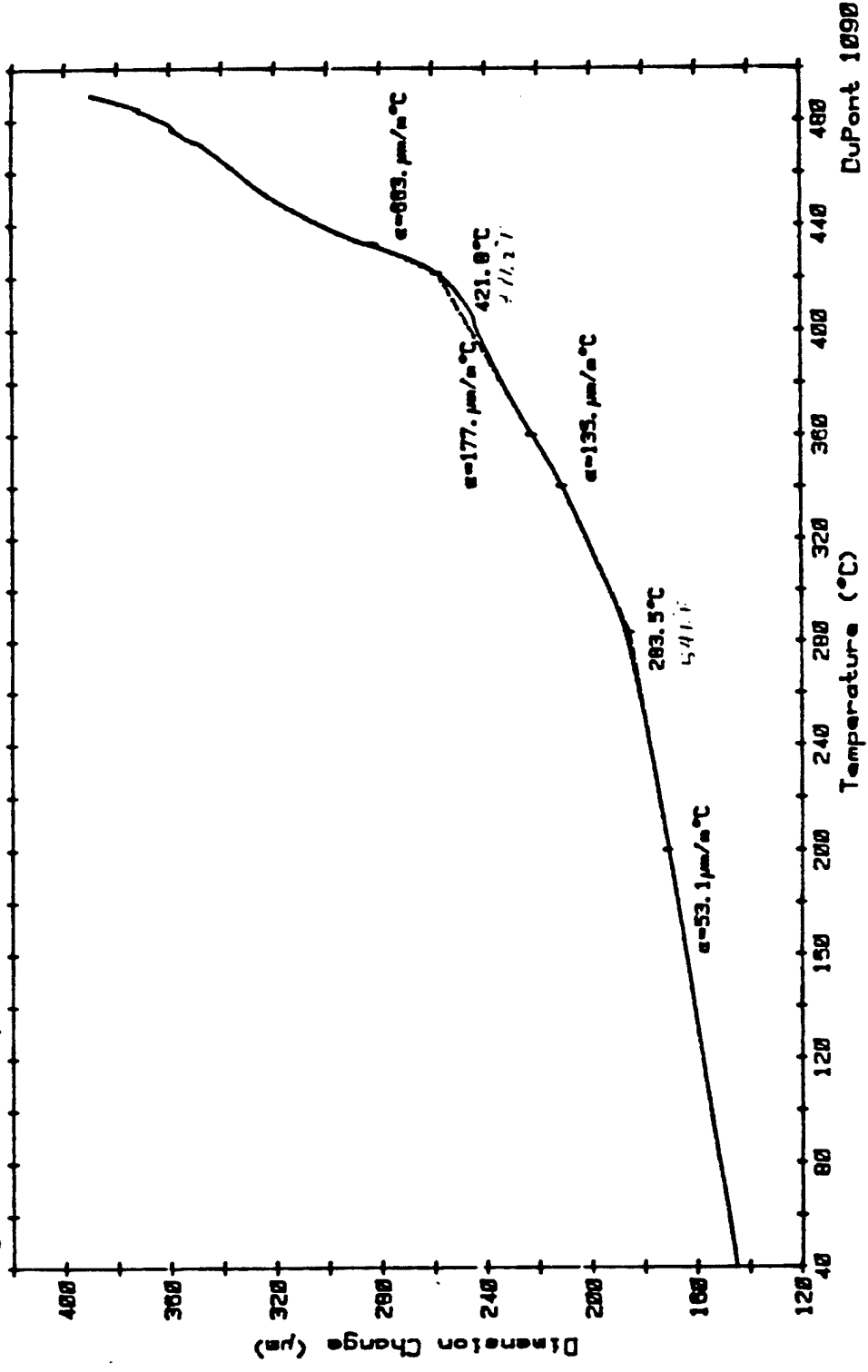


Figure 30. TMA of 2-C1-4-BDAF/PMDA, postcured at 644K for 16 hours.

Date: 21-Aug-84 Time: 14:09:07
File: POLYIMIDE.04 T.A.#23
Operator: TCM MAY
Plotted: 22-Aug-84 11:47:57

Sample: POLYIMIDE #15321-47C
Size: 2.93MM
Rate: 10C/MIN.
Program: TMA Analysis V1.0

TMA

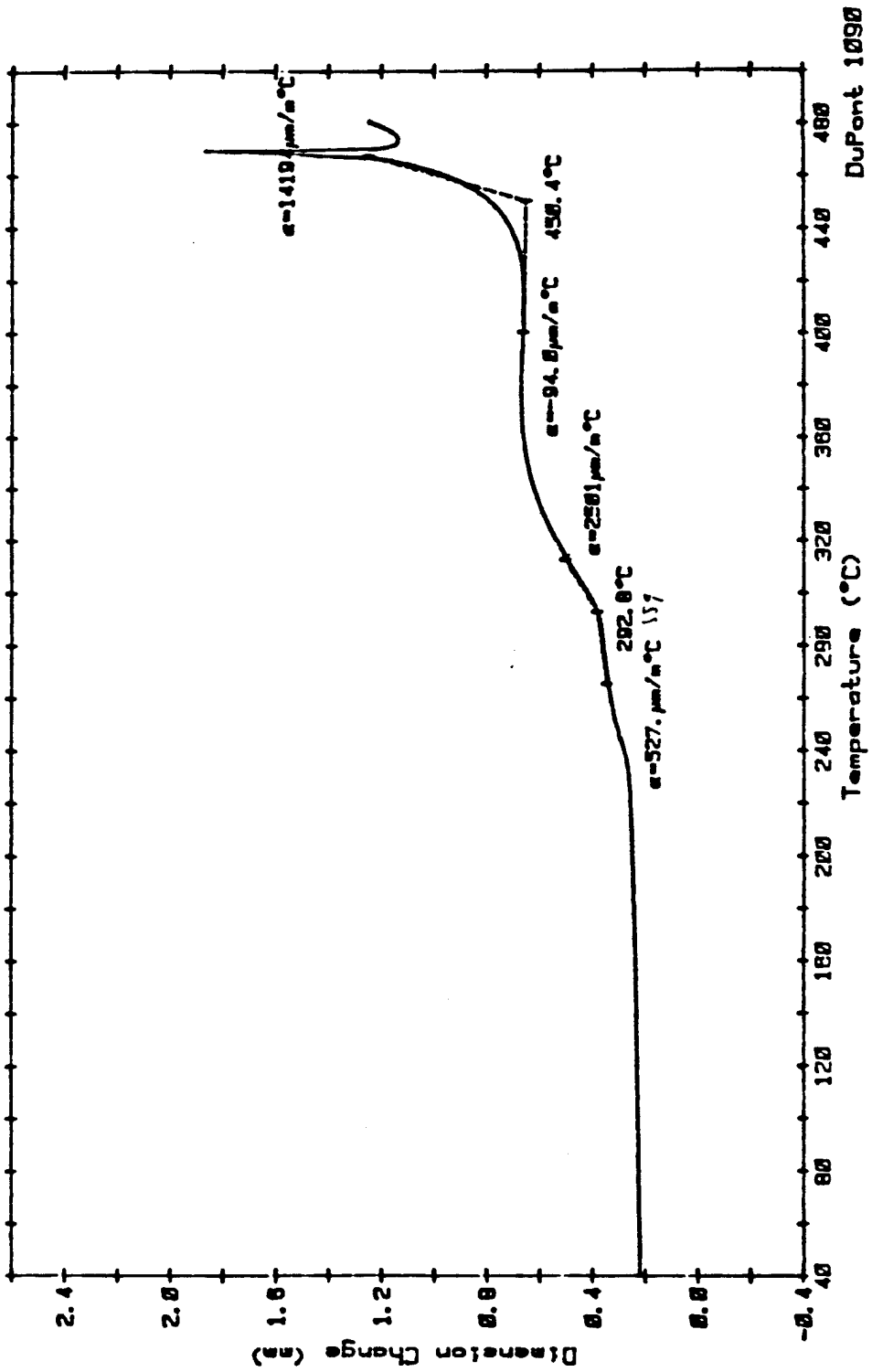


Figure 31. TMA of 2-C1-4-BDAF/6-FDA (as molded).

Sample: POLYIMIDE #15321-47C-PC
Size: 3.29MM
Rate: 10C/MIN.
Program: TMA Analysis V1.0
Date: 22-Aug-84 Time: 10:03:01
File: POLYIMIDE.05 T.A.#23
Operator: TOM MAY
Plotted: 22-Aug-84 13:17:40

TMA

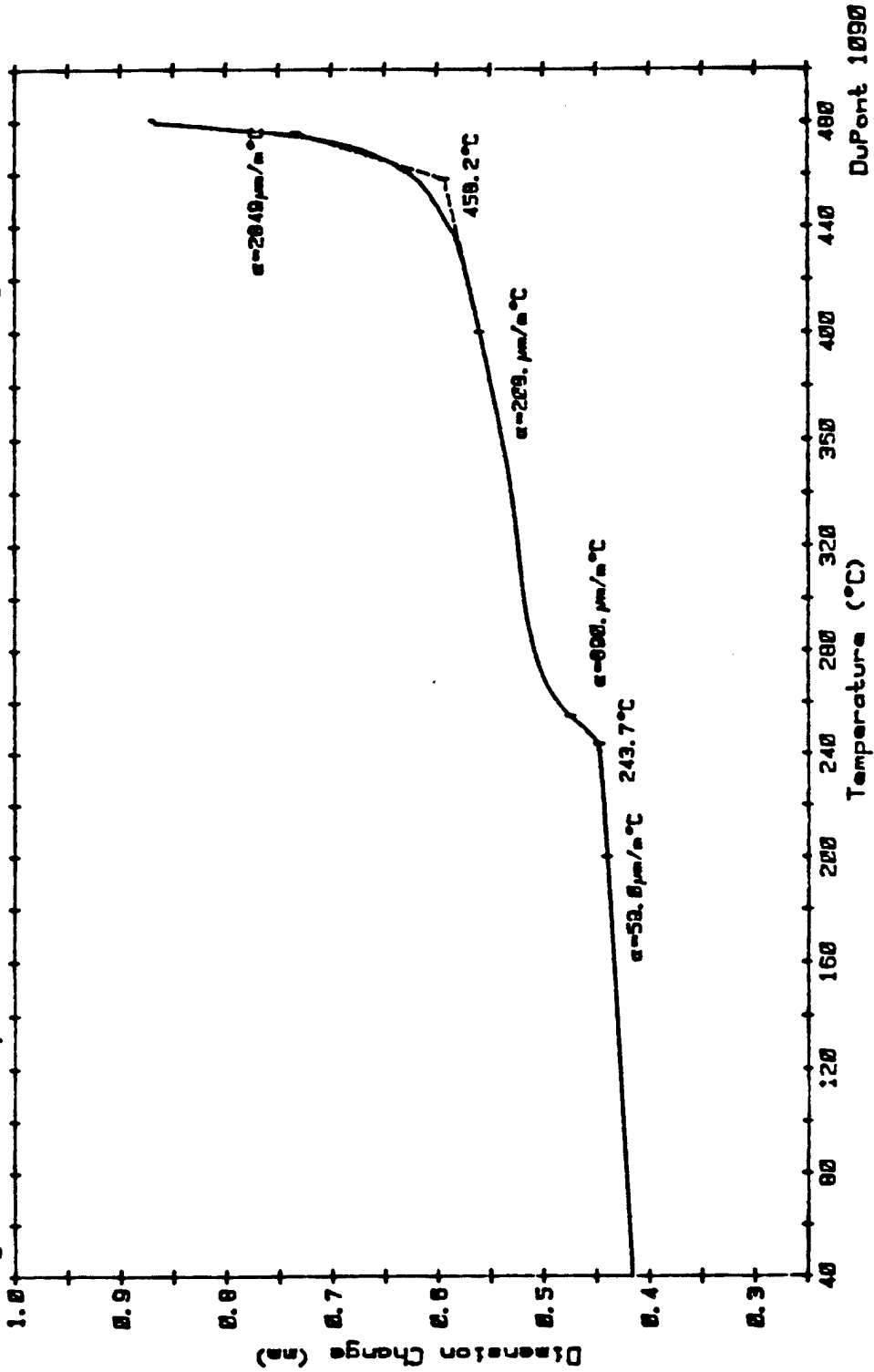


Figure 32. TMA of 2-C1-4-BDAF/6-FDA, postcured at 644K for 16 hours.

Date: 10-Sep-84 Time: 15:38:04
File: MOLDING.12 T.A.#23
Operator: TOM MAY
Plotted: 13-Sep-84 12:16:07

Sample: POLYIMIDE #15321-69A
Size: 4.16MM
Rate: 10C/MIN.
Program: TMA Analysis V1.0

TMA

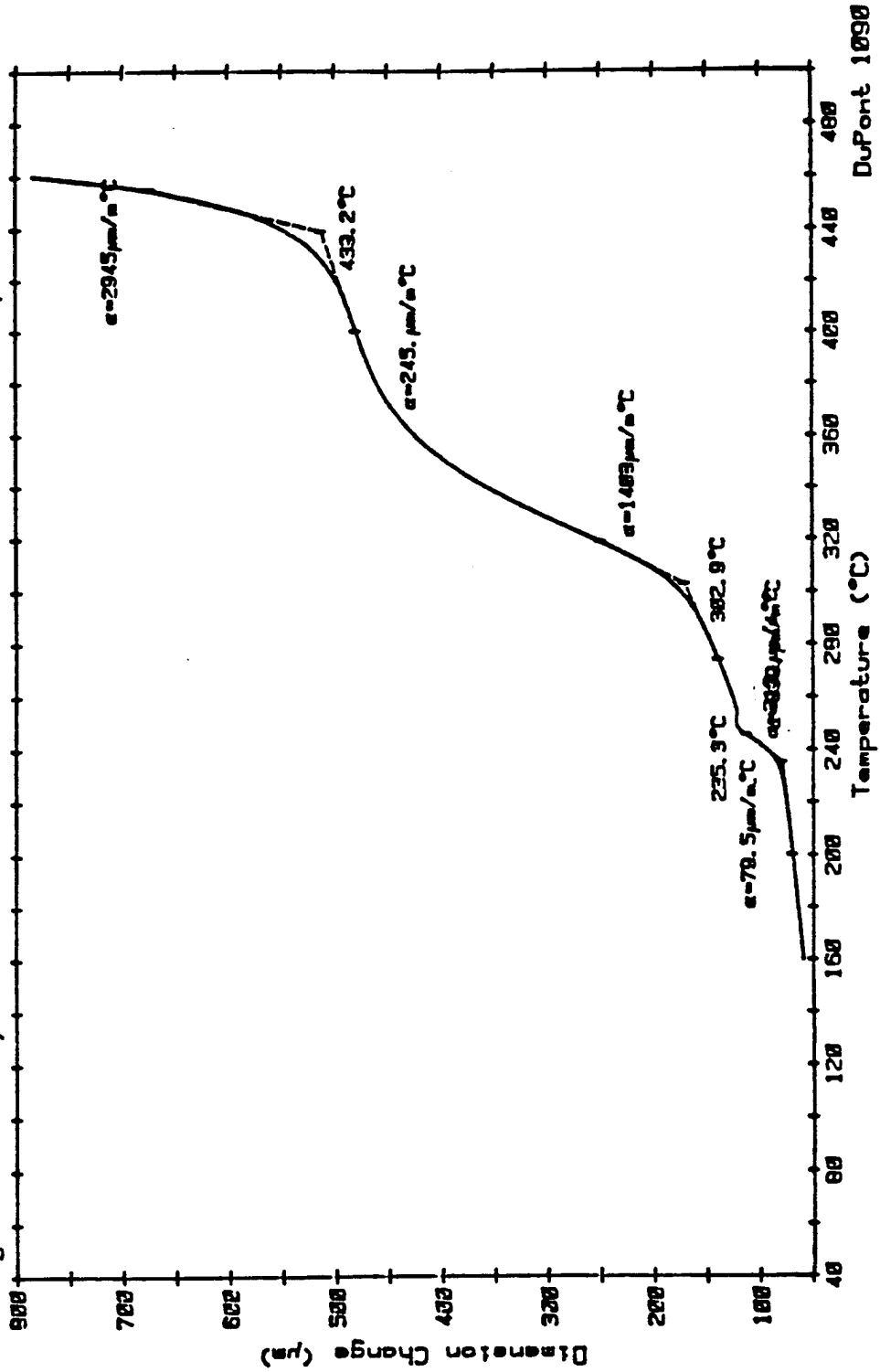


Figure 33. TMA of 2-F-4-BDAF/6-FDA (as molded).

Sample: POLYIMIDE #15321-69A-PC
Size: 4.55MM
Rate: 10C/MIN.
Program: TMA Analysis V1.0

TMA

Date: 10-Sep-84 Time: 13:51:14
File: MOLDING.11 T.A.#23
Operator: TOM MAY
Plotted: 13-Sep-84 11:33:44

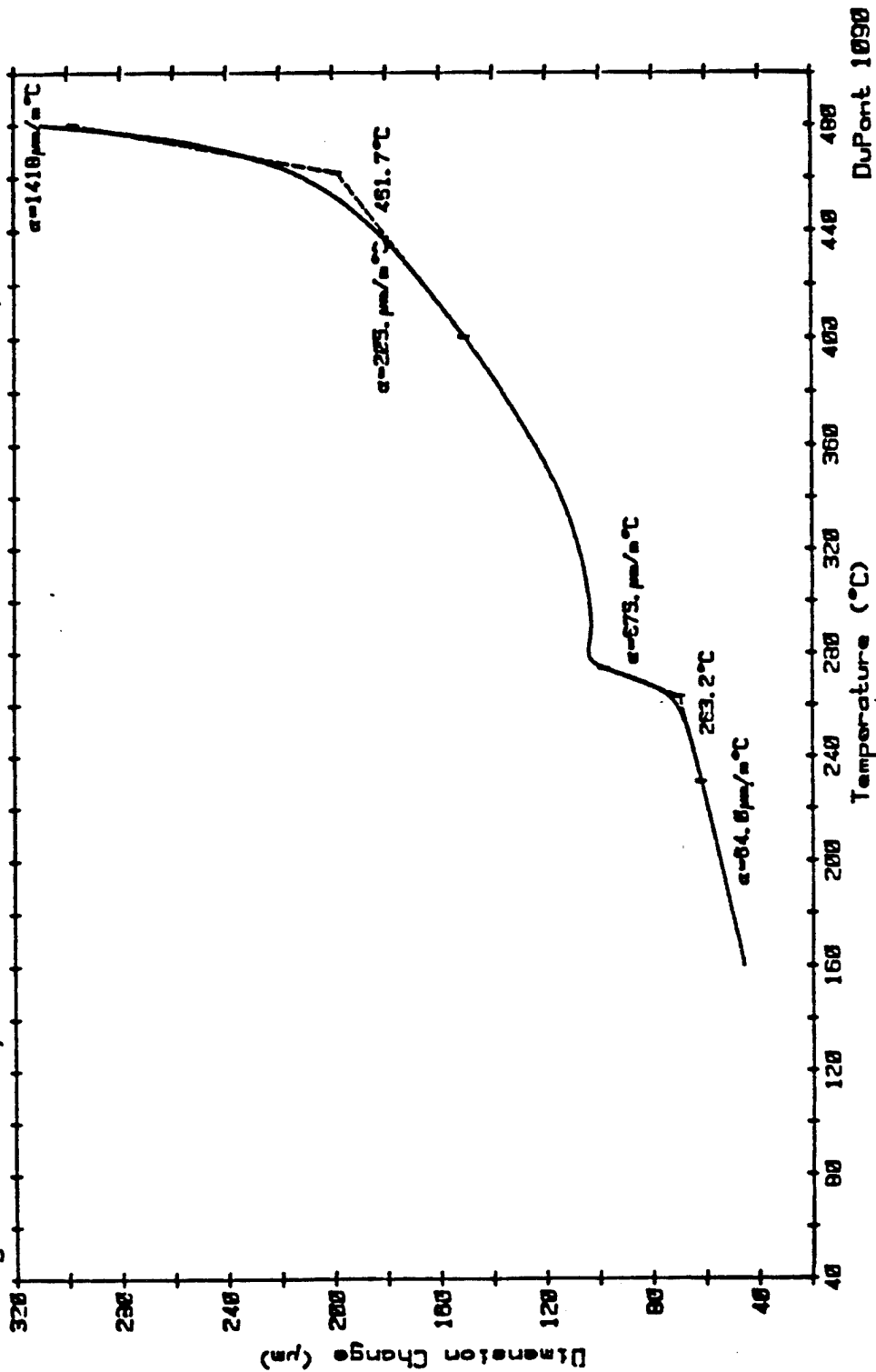


Figure 34. TMA of 2-F-4-BDAF/6-FDA, postcured at 644K for 16 hours.

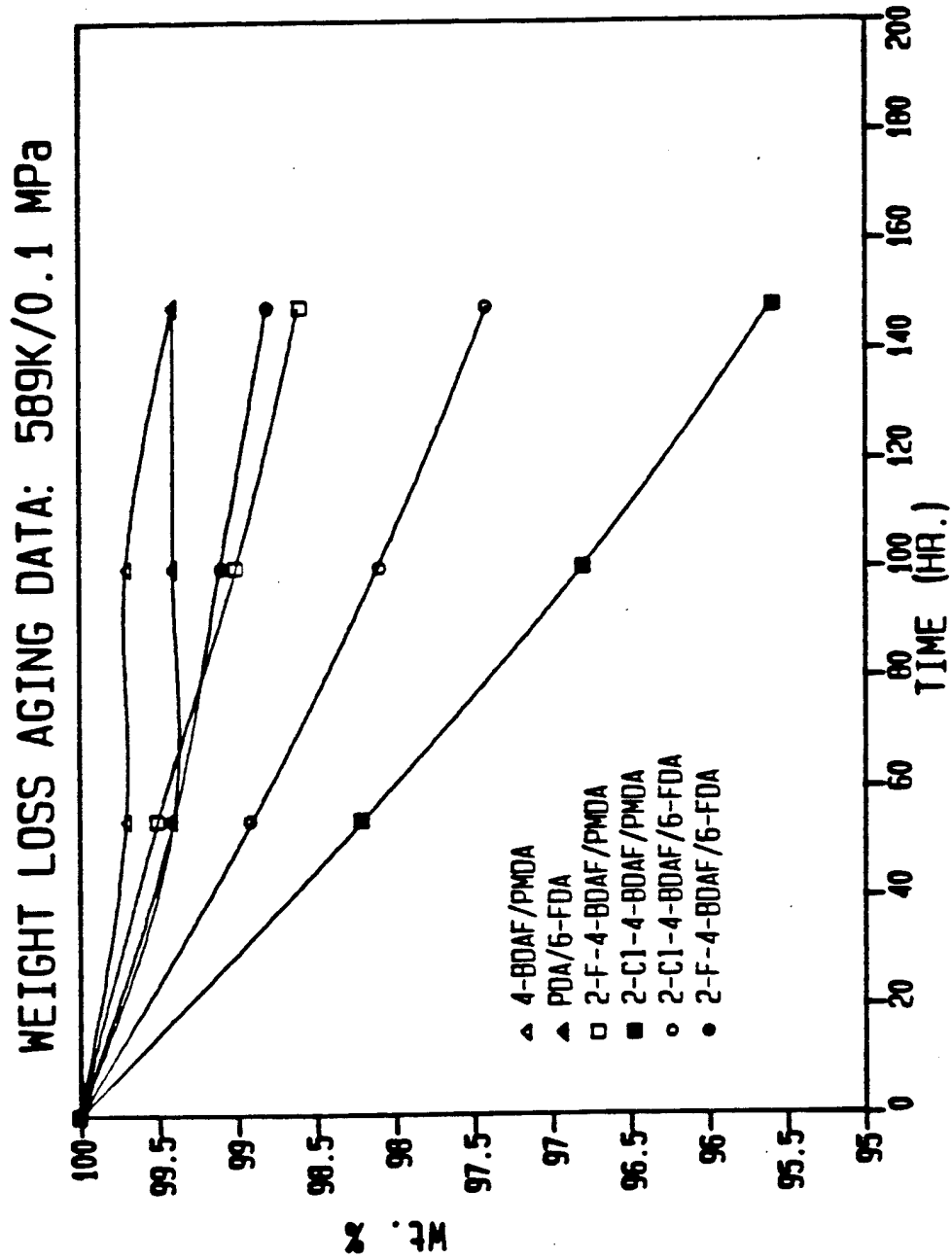


Figure 35. Weight loss aging data at 589K (600°F)/0.1 MPa (ambient pressure).

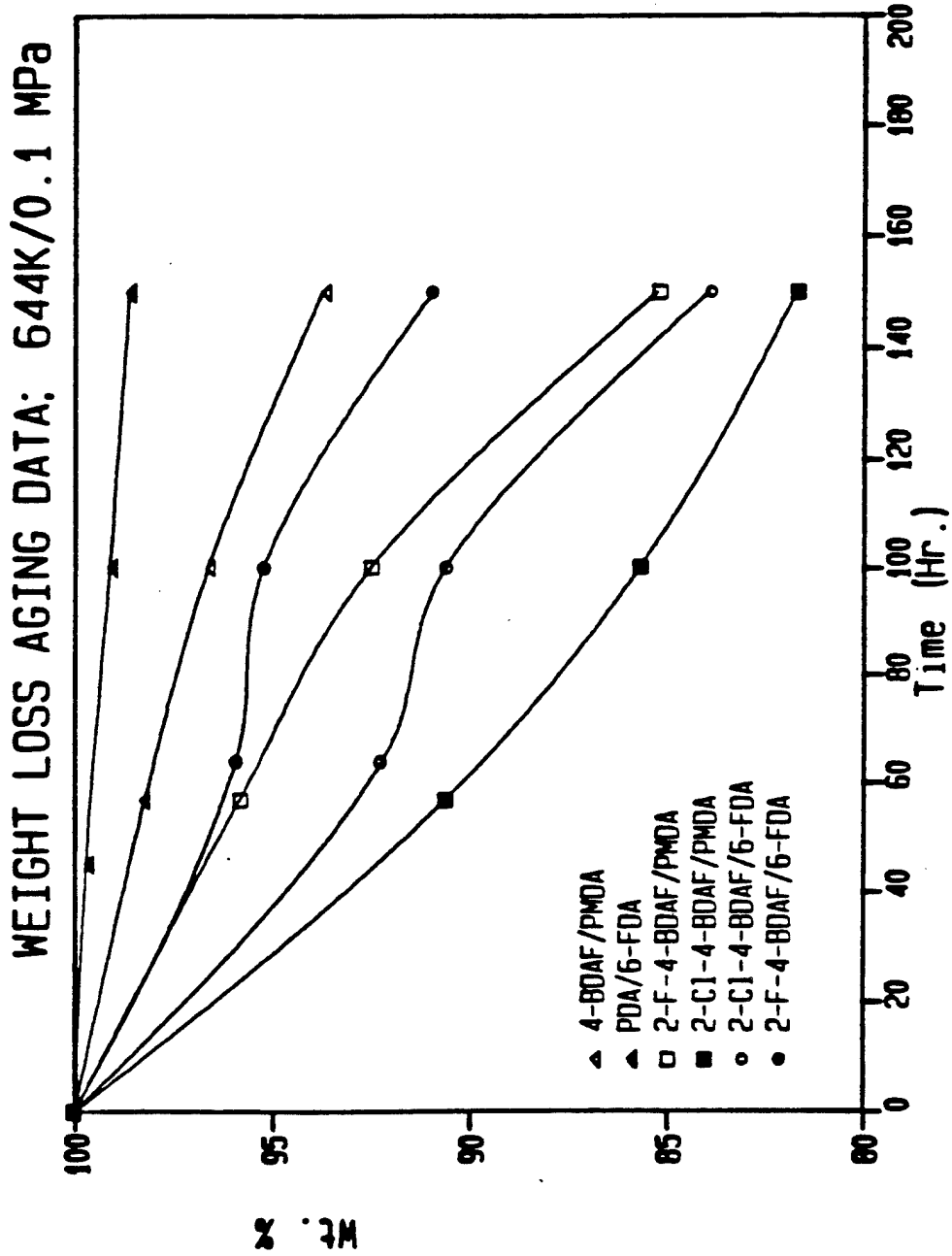


Figure 36. Weight loss aging data at 644K (700°F)/0.1 MPa (ambient pressure).

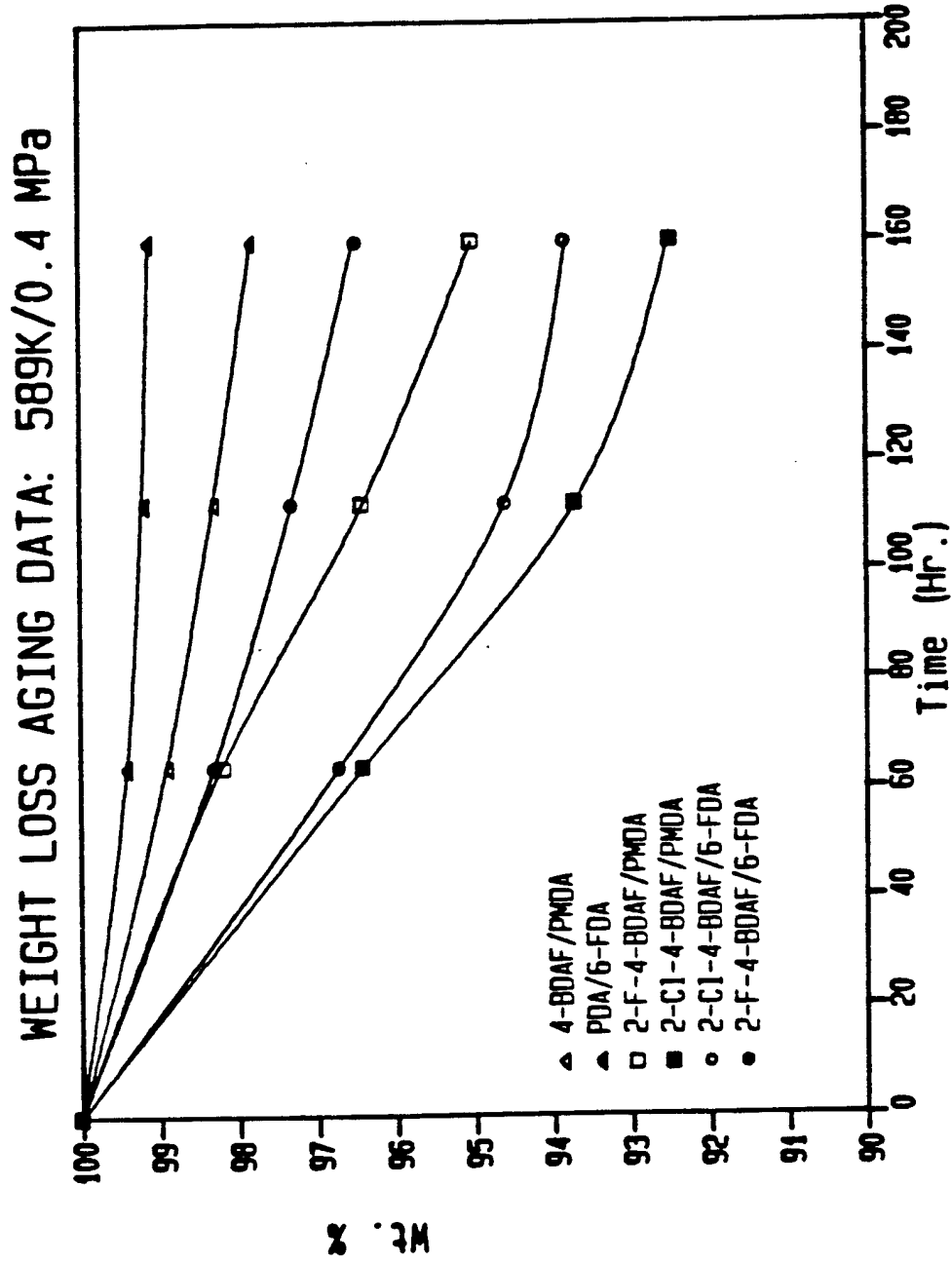


Figure 37. Weight loss aging data at 589K (600°F)/0.4 MPa (4 atmospheres).

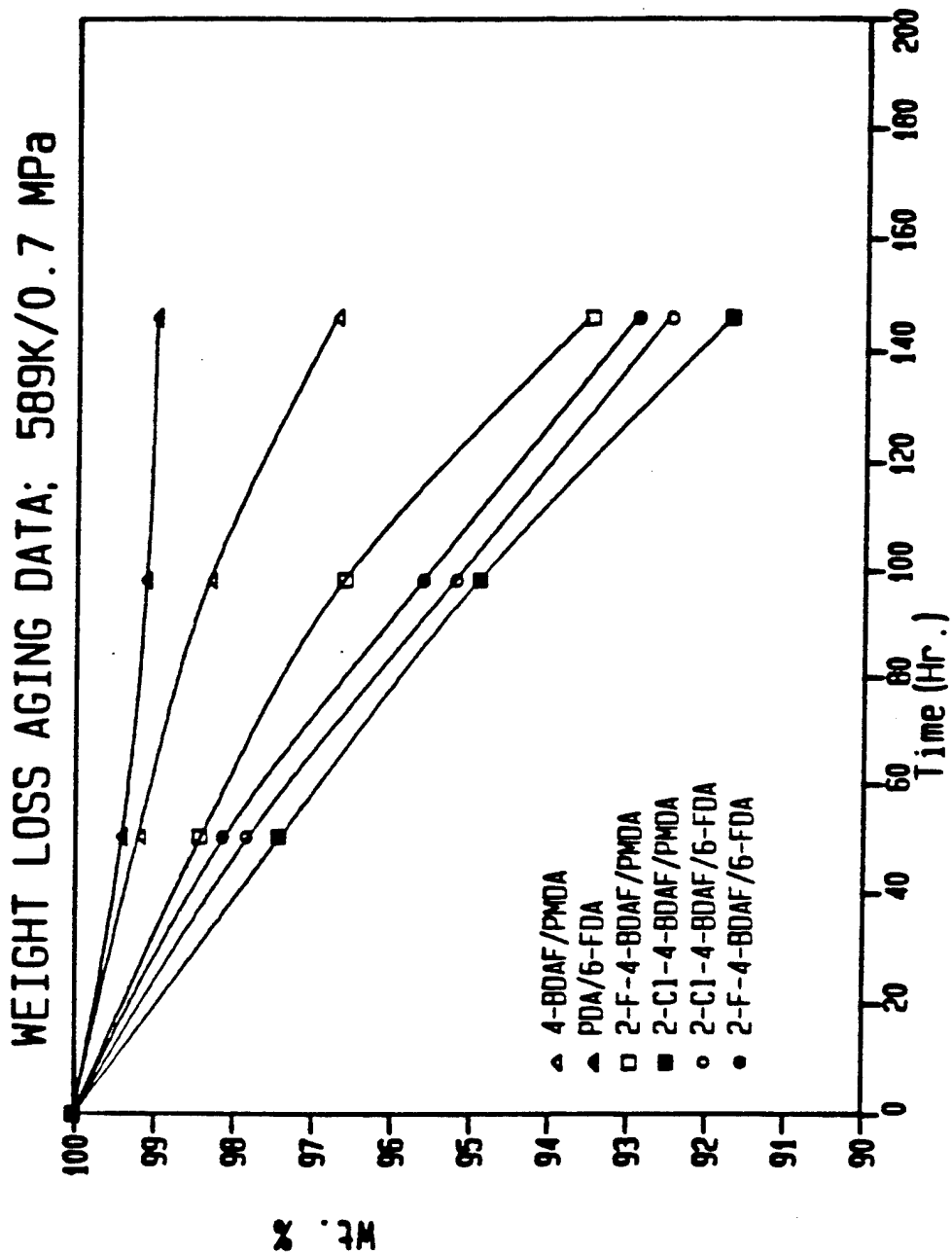


Figure 38. Weight loss aging data at 589K (600°F)/0.7 MPa (7 atmospheres).

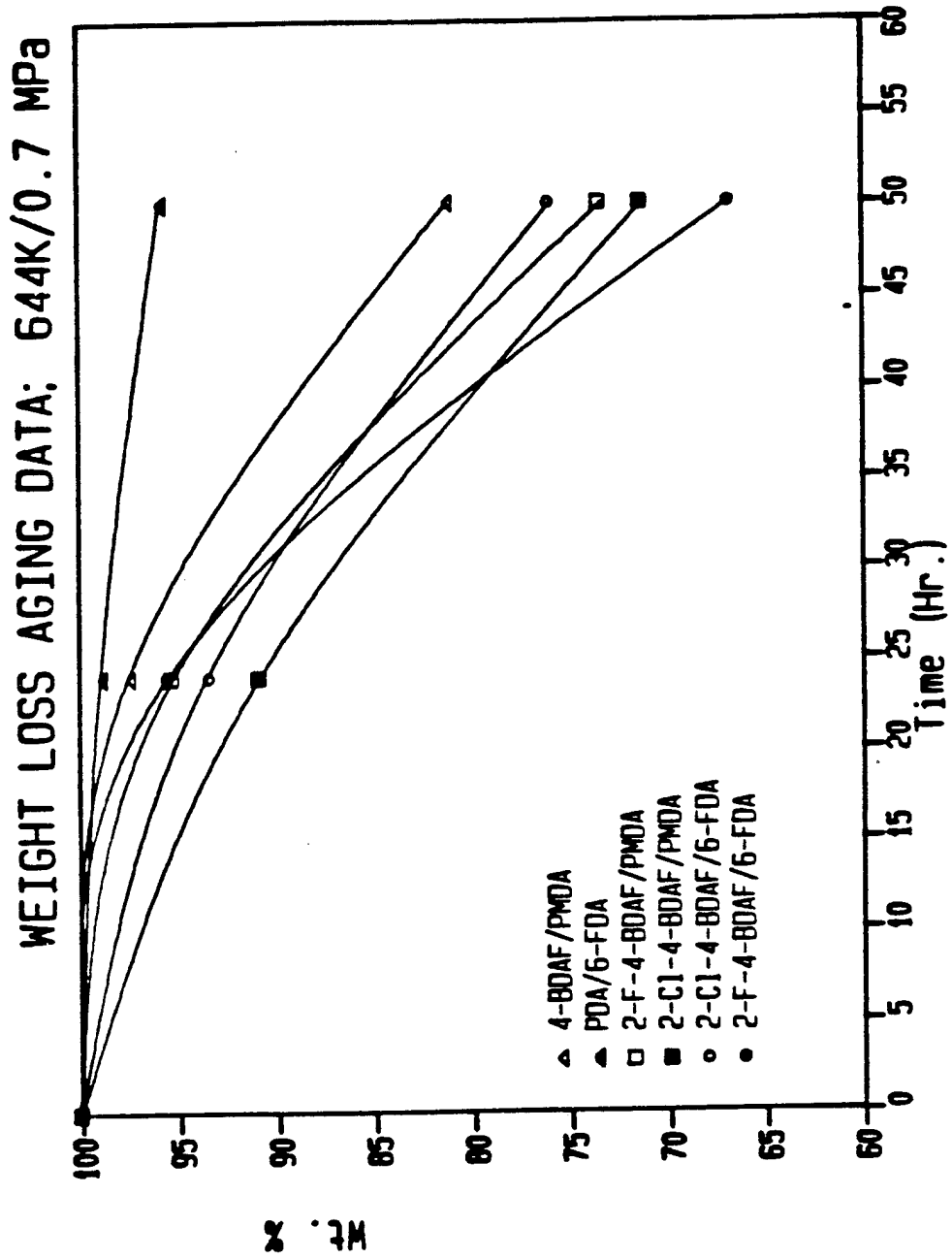


Figure 39. Weight loss aging data at 644K (700°F)/0.7 MPa (7 atmospheres).

Table V. Aging Test Results at 589K at Ambient Pressure

Polymer	<u>Weight Loss (%) After:</u>			<u>Volume Loss (%) After:</u>		
	<u>54 Hr</u>	<u>100 Hr</u>	<u>148 Hr</u>	<u>54 Hr</u>	<u>100 Hr</u>	<u>148 Hr</u>
I. 4-BDAF/ PMDA	0.3	0.3	0.6	0	0	0
II. PDAs/6-FDA	0.6	0.6	0.6	0	0	0
III. 2-F-4-BDAF/ PMDA	0.5	1.0	1.4	0	0	0.6
IV. 2-C1-4-BDAF/ PMDA	1.8	3.2	4.4	0	1.5	3.8
V. 2-C1-4-BDAF/ 6-FDA	1.1	1.9	2.6	1.5	1.5	3.2
VI. 2-F-4-BDAF/ 6-FDA	0.6	0.9	1.2	0	0	1.4

Table VI. Aging Test Results at 644K and Ambient Pressure

Polymer	<u>Weight Loss (%) After:</u>				<u>Volume Loss (%) After:</u>			
	<u>57 Hr</u>	<u>64 Hr</u>	<u>100 Hr</u>	<u>150 Hr</u>	<u>57 Hr</u>	<u>64 Hr</u>	<u>100 Hr</u>	<u>150 Hr</u>
I.	1.8	--	3.4	6.3	0.7	--	1.6	1.2
II.	0.3 ¹⁾	--	0.9	1.4	0 ¹⁾	--	0	2.2
III.	4.2	--	7.5	14.8	2.5	--	4.6	33
IV.	9.4	--	14.3	18.3	6	--	9.2	28.9
V.	--	7.8	9.4	16.1	--	4.7	1.9	(6) ²⁾
VI.	--	4.1	4.8	9.1	--	(1.5) ²⁾	4.8	2.9

1) After 45 Hr. at 589K/ambient pressure.

2) Volume gain.

Table VII. Aging Test Results at 644K and
0.7 MPa Absolute Pressure

<u>Polymer</u>	<u>Wt Loss After:</u>		<u>Volume Loss (%) After:</u>	
	<u>24 Hr</u>	<u>50 Hr¹⁾</u>	<u>24 Hr</u>	<u>50 Hr¹⁾</u>
I.	2.5	18.8	0.7	14.0
II.	1.1	4.2	0.5	1.6
III.	4.8	27.7	2.0	17.8
IV.	9.2	28.8	3.0	13.0
V.	6.5	24.1	2.3	9.6
VI.	4.5	33.1	13	33.5

¹⁾Test terminated; all samples except of Polymer II
were cracked and peeling.

Table VIII. Aging Test Results at 644K and
0.4 MPa Absolute Pressure

<u>Polymer</u>	<u>Wt Loss (%) After 72 Hr</u>	<u>Volume Loss (%) After 72 Hr</u>
I.	6.4	4.5
II.	3.2	2.0
III.	13.4	16.0
IV.	22.0	31.0
V.	16.5	3.1
VI.	9.0	22.2

4.0 COMPOSITES FABRICATION AND EVALUATION

In this task Polymers I and II and the two new polymers, 2-F-4-BDAF/PMDA and 2-F-4-BDAF/6-FDA, selected in Task II, were used to prepare unidirectional prepreg and composites. The composites were employed in thermo-oxidative and mechanical testing.

4.1 PREPREG

The prepreg samples used in this work were prepared by the Composites Division of Ferro Corporation from polyamide acid solutions prepared by TRW. The fiber selected for use in prepreg preparation was Celion 12000 sized by Celanese Corporation with 4-BDAF/PMDA and provided by them to the program. Previous work at TRW had shown that 4-BDAF/PMDA is an excellent size for carbon fibers and can enhance fiber wetting by PFPI resins. However, in retrospect, Celion 6000 fiber may have been a better choice for the base fiber because the 12000 proved difficult to spread and penetrate with the somewhat viscous, DMSO-based polymer solutions.

Ferro's initial attempts to produce prepreg using a modified, proprietary "hot-melt" procedure proved unsuccessful because of resin precipitation and hydrolysis. The use of DMSO as a diluent improved the prepreg to some extent, but was still inconsistent and poorly collimated. Methyl ethyl ketone (MEK) proved to be a superior diluent and better prepreg was prepared using MEK-diluted resin solutions.

4.2 COMPOSITE FABRICATION

Although prepreg quality remained marginal, time and cost constraints mitigated against further developmental efforts and the prepreg was employed as received to make composites.

The composites were fabricated in a 20.3 cm (8 in) x 7.6 cm (3 in) mold to produce unidirectional laminates with a nominal 0.25 cm (0.10 in) thickness. Seven to eleven plies were required to attain the desired thickness, depending on the particular prepreg batch.

A standard composites fabrication procedure was established using the neat resin molding conditions as a starting point. The procedure included the following steps:

1. B-stage at 477K (400°F), contact pressure, 1 hour
2. Increase pressure to 6.9 MPa (1000 psi) and raise temperature
3. At 665K (730°F) raise pressure to 20.7 MPa (3000 psi)
4. Hold at 700K (800°F)/20.7 MPa (3000 psi) for 2 hours
5. Cool to 477K under pressure, then de-mold.

The unidirectional composites prepared by this procedure were postcured under conditions previously employed for the neat resin moldings. The TMA scans of as-molded and postcured 4-BDAF/PMMA/Celion 12000 laminates are shown in Figures 40 and 41, respectively. The postcured Tg of the 4-BDAF/PMMA composite is greater than that for neat resins, i.e., 728K (850°F) vs. 681K (766°F), a surprisingly high number.

The postcured laminates were submitted to Sonic Testing and Engineering Laboratories for non-destructive evaluation by ultrasonic C-scan. Typical C-scans are shown in Figures 42 through 44. The C-scans indicate that the laminates have a significant void content. The best areas of the respective laminates were selected for sectioning into shear and flex specimens. The mechanical properties for the unaged samples are shown in Table IX.

It is clearly evident that the laminates prepared from the polymers which use 6-FDA as the dianhydride provide the best room temperature properties. This result is attributed to the improved melt-flow characteristics of these resins. In contrast, the 4-BDAF/PMMA laminates had very little flow during the molding operation. The elevated temperature properties confirm the earlier findings obtained on the neat resin study: the 2-F-4-BDAF/6-FDA system has very poor strength retention at 644K because this temperature is above the polymer's glass transition temperature. The results for polymers I and III suggest that the addition of the fluorine group helps processability resulting in improved room temperature properties.

Sample: POLYIMIDE COMPOSITE
Size: 2.80MM #15498-8C
Rate: 10C/MIN.
Program TMA Analyze V1.0
Plotted 10-Dec-84 17:20:19

TMA

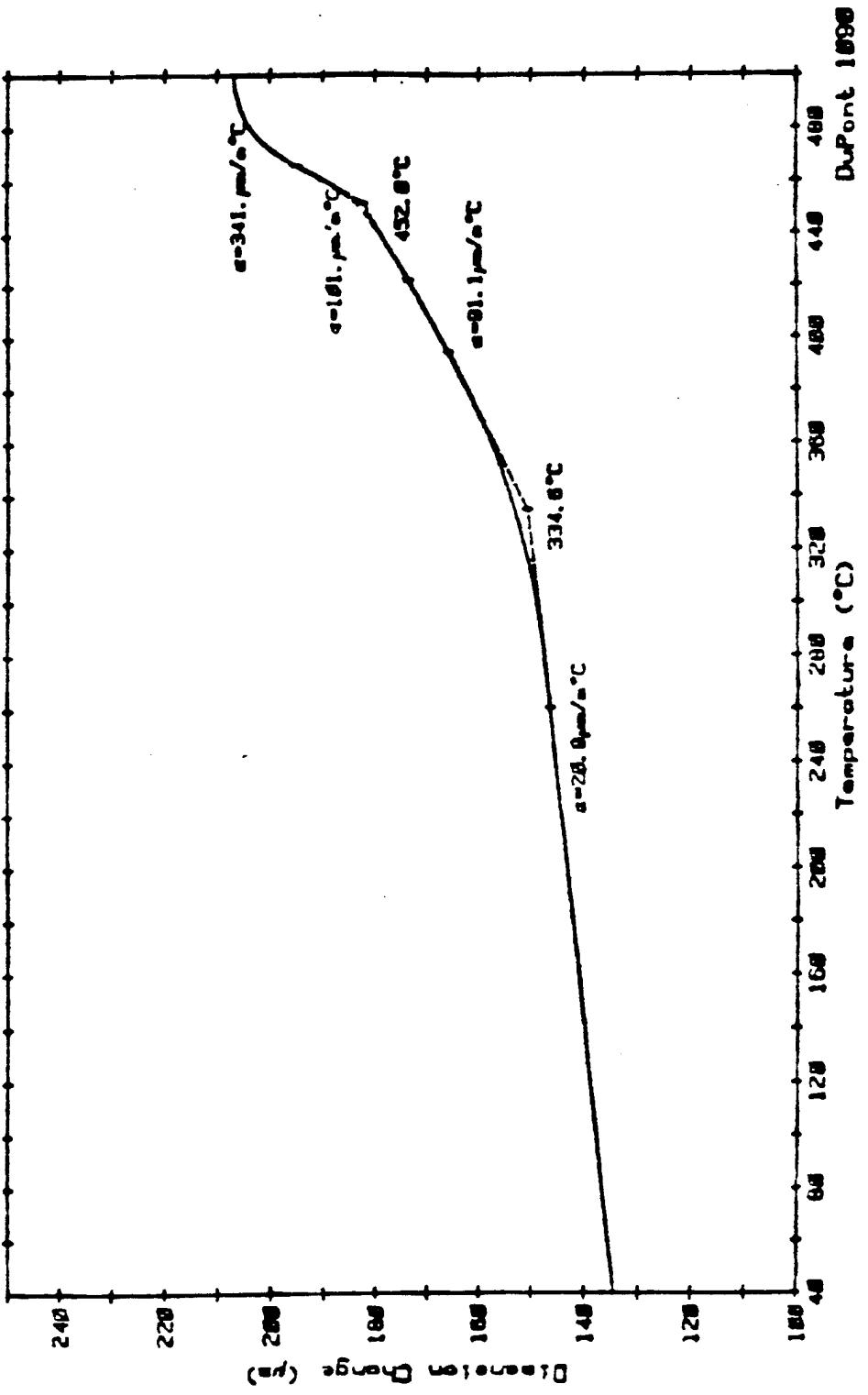


Figure 40. Thermalmechanical analysis of 4-BDAF/PMDA on Celion 12000.

Date: 10-Dec-84 Times 10:20:46
File: POLYIMIDE #2 T.A.#26
Operator: TOM MAY
Plotted: 11-Dec-84 9:01:04

Sample: POLYIMIDE COMPOSITE PC
Size: 2.7MM #15498-8C
Rate: 10C/MIN.
Program: TMA Analysis V1.0

TMA

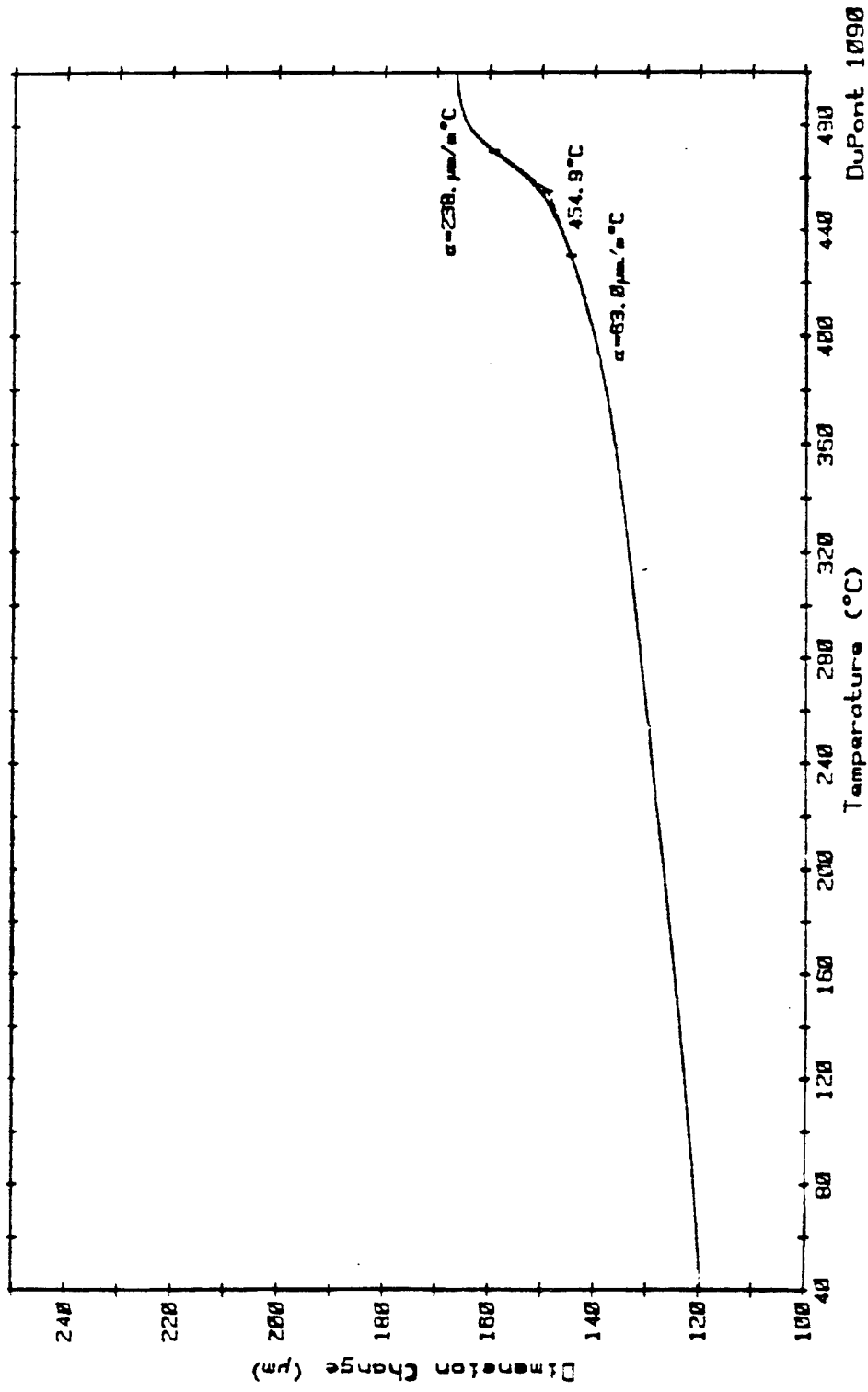


Figure 41. Thermalmechanical analysis of 4-BDAF/PMDA on Celion 12000, postcured at 700°F/16 hr.

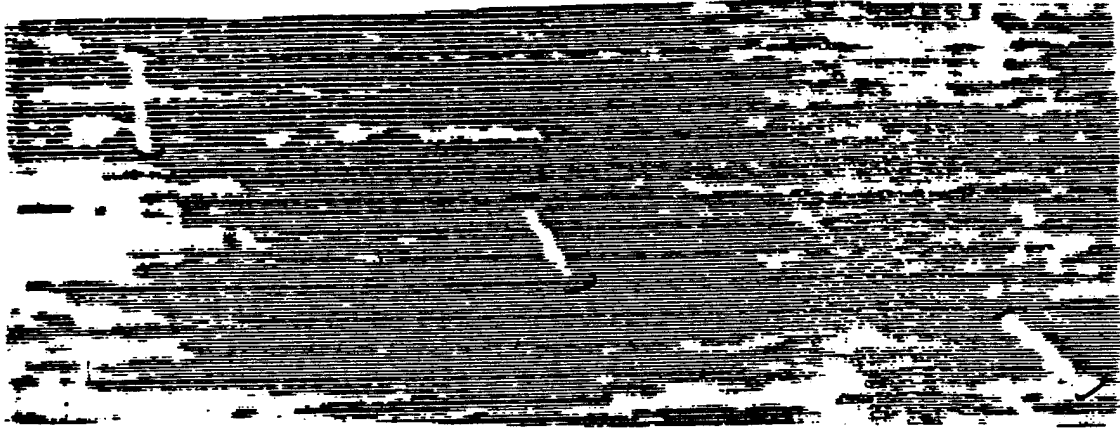


Figure 42. C-scan of 4-BDAF/PMDA/Celion 12000 laminate.

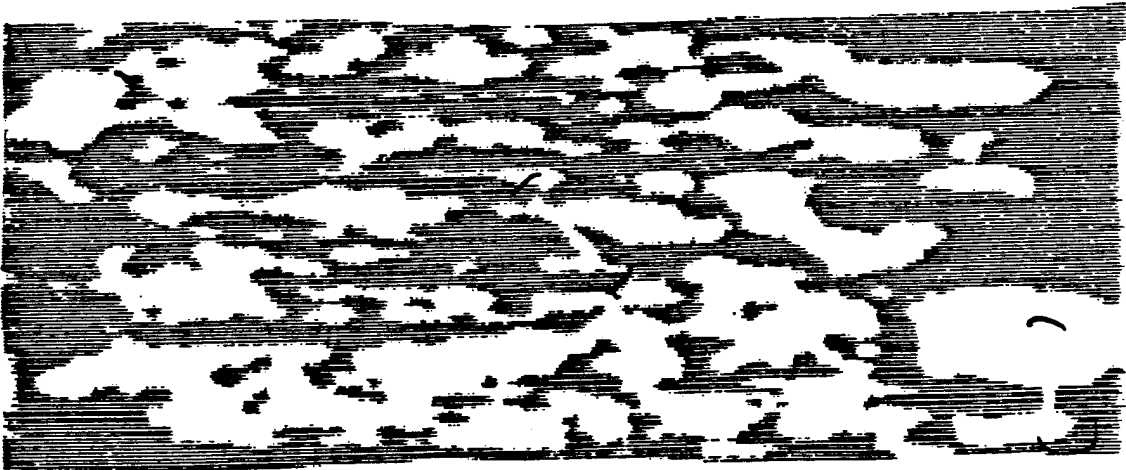


Figure 43. C-scan of 2-F-4-BDAF/PMDA/Celion 12000 laminate.

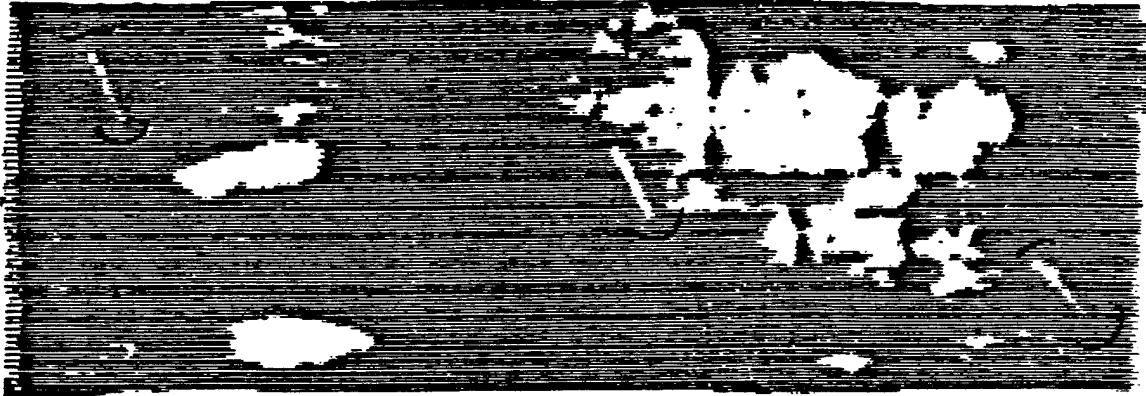


Figure 44. C-scan of PDA/6-FDA/Celion 12000 laminate.

Table IX. Mechanical Properties of Celion 12000 Laminates

Polymer	Test Temp. K	Test Temp. (°F)	Flexural Strength ^{a,b} MPa	Flexural Strength ^{a,b} (Ksi)	Flexural Modulus GPa	Flexural Modulus (Msi)	Shear Strength ^a MPa	Shear Strength ^a (Ksi)
I. 4-BDAF/PMDA	297	(75)	600	(87.1)	47.4	(6.88)	39.2	(5.68)
	644	(700)	293	(42.7)	54.4	(7.87)	19.7	(2.86)
II. PDAs/6-FDA	297	(75)	1076	(156)	29.7	(4.31)	85.5	(12.4)
	644	(700)	445	(64.5)	32.5	(4.72)	36.1	(5.23)
III. 2-F-4-BDAF/PMDA	297	(75)	986	(143)	50.4	(7.31)	69.6	(10.1)
	644	(700)	290	(42.0)	38.9	(5.64)	34.8	(5.05)
IV. 2-F-4-BDAF/6-FDA	297	(75)	1289	(187)	47.4	(6.88)	96.5	(14.0)
	644	(700)	255	(37.0)	23.2	(3.36)	24.1	(3.49)

^a Average of three tests.

^b Span ratio 16:1

4.3 THERMO-OXIDATIVE AGING

The generally poor quality of the composites limited the number of appropriate samples for aging and mechanical test. In view of the schedule and cost constraints it was decided to subject only 4-BDAF/PMDA specimens to thermo-oxidative aging. Triplicate flex and shear specimens were aged at 644K (700°F) under 0.1 MPa (1 atm) and 0.4 MPa (4 atm) of compressed air for 50 and 100 hrs. Mechanical property testing was then performed at 644K (700°F), the aging temperature. The results are shown in Table X. The samples performed fairly well at 0.1 MPa (1 atm), although the weight loss after 100 hours is surprising based on the neat resin aging properties. This may be attributed to how the samples were prepared. The neat resin samples were prepared from chemically imidized molding powder whereas the laminates were prepared from the amide-acid precursor and thermally imidized during the molding process. Both the flexural and shear strengths are in good agreement with the results shown in Table IX. The elevated pressure (0.4 MPa) condition resulted in samples unsuitable for testing after 100 hours. As noted in the weight loss data, very little resin remained after 100 hours. Therefore, these samples were not tested. The mechanical properties after 50 hours of aging at 0.4 MPa are comparable to those obtained at ambient pressure after 100 hours.

Table X. Aging Test Results for 4-BDAF/PMDA/Celion 12000 Laminates

Aging Conditions Pressure, MPa (atm)	Time, Hr	Wt Loss, %		Flexural ^a		Flexural Modulus, at 644K GPa (MSi)	Shear Strength ^a at 744K MPa (Ksi)
		Flex Samples	Shear Samples	Strength, 644K MPa (Ksi)	Strength, 644K MPa (Ksi)		
0.1 (1)	50	2.48	2.69	381 (55.3)	381 (55.3)	58.3 (8.45)	25.4 (3.69)
0.1 (1)	100	8.33	11.9	353 (51.2)	353 (51.2)	56.9 (8.26)	21.4 (3.10)
0.4 (4)	50	8.85	6.65	388 (56.3)	388 (56.3)	58.3 (8.46)	92.5 (3.42)
0.4 (4)	100	41.8	32.1	NT ^{b)}	NT ^{b)}	NT	NT

a Average of three tests.

b Not tested.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The results of the work on this program lead to the general conclusions stated below. More specific conclusions on such items as synthesis routes, processing characteristics and properties are found in the body of the report.

- o A new fluoro derivative of 4-BDAF was successfully prepared, characterized and used to prepare polymer samples and graphite reinforced laminates.
- o The halogenated derivatives of 4-BDAF display a lower degree of thermo-oxidative stability as compared to 4-BDAF.
- o Processability of 6-FDA containing polymers is superior to that of the PMDA containing polymers; however, strength retention is lower at 644K for the 6-FDA polymer containing laminates.
- o Additional processing studies are needed to improve the quality of prepregs and final laminates.
- o 4-BDAF/PMDA/Celion 12000 laminates show good property retention after isothermal aging at 644K for 100 Hours at 0.1 MPa (1 atm) and after 50 hours at 0.4 MPa (4 atm).

Specific recommendations arising from the technical activities on this program are as follows:

- o Perform additional processing studies to provide an improved quality of prepreg and laminates from 4-BDAF/PMDA.
- o Assess further performance of 4-BDAF/PMDA system at elevated pressures between 598K (600^oF) and 644K (700^oF).
- o Evaluate approaches to improve processability of 4-BDAF/PMDA resins.

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