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TRW

Improved High Temperature Resistant Matrix Resins

Contract NAS3-23274

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16. Abstract

This final report document describes the work performed by the TRW Electronics and Defense Sector for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-23274. The technical work was performed during the period of January through December, 1982.

The objective of this program was to develop organic matrix resins suitable for service at temperatures up to 644°K (700°F) and at air pressures up to 0.4 MPa (60 psia) for time durations of a minimum of one hundred hours. Matrix resins capable of withstanding these extreme oxidative environmental conditions would lead to increased use of polymer matrix composites in aircraft engines and provide significant weight and cost savings.

In this program, six linear condensation, aromatic/heterocyclic polymers containing fluorinated and/or diphenyl linkages were synthesized. The thermo-oxidative stability of the resins was determined at 644°K and compressed air pressures up to 0.4 MPa. Two formulations, both containing perfluoroisopropylidene linkages in the polymer backbone structure, exhibited potential for 644°K service to meet the program objectives. Two other formulations could not be fabricated into compression molded zero defect specimens.

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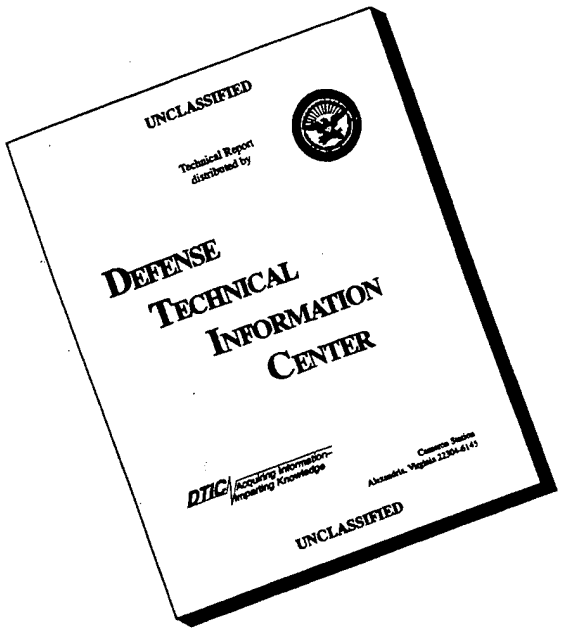

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FOREWORD

This report was prepared by TRW Electronics and Defense Sector under Contract NAS3-23274, "Improved High Temperature Resistant Matrix Resins". The technical effort was conducted during 1982 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. Robert J. Jones, program manager, Dr. Glenn E. C. Chang, principal investigator and Mr. Steven H. Powell, who was responsible for polymer fabrication studies. Ms. Christine P. Brown assisted in polymer processing studies. Monomer and polymer characterization work was conducted under the direction of Mr. Michael K. O'Rell. Participants in the characterization work included Mrs. Judy W. Scott, Mr. John F. Clausen and Mr. Thomas W. May.

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SUMMARY

This final report document describes the work performed by the TRW Electronics and Defense Sector for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-23274. The technical work was performed during the period of January through December, 1982.

The objective of this program was to develop organic matrix resins suitable for service at temperatures up to 644°K (700°F) and at air pressures up to 0.4 MPa (60 psia) for time durations of a minimum of one hundred hours. Matrix resins capable of withstanding these extreme oxidative environmental conditions would lead to increased use of polymer matrix composites in aircraft engines and provide significant weight and cost savings.

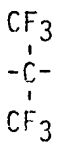
In this program, six linear condensation, aromatic/heterocyclic polymers containing fluorinated and/or biphenyl linkages were synthesized. The thermo-oxidative stability of the resins was determined at 644°K and compressed air pressures up to 0.4 MPa. Two formulations, both containing perfluoroisopropylidene linkages in the polymer backbone structure, exhibited potential for 644°K service to meet the program objectives. Two other formulations could not be fabricated into compression molded zero defect specimens.

1.0 INTRODUCTION

This final report documents the work performed by TRW Electronics and Defense Sector for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-23274. The effort was conducted during 1982. The objective of the program was to develop new organic matrix resin candidates suitable for service as advanced jet engine compressor components which operate in extreme oxidative environments consisting of temperatures up to 644°K (700°F) and pressures up to 0.4 MPa (60 psia or four atmospheres).

Designs and performance requirements for advanced jet engine hardware offering significant improvements in fuel efficiency, coupled with increased maneuverability performance, demand the increased use of advanced composite, particularly polymer matrix composites. This program addressed the feasibility for synthesizing organic matrix resins capable of surviving the extreme oxidative conditions projected to be encountered during exposure in the compressor section of advanced engines.

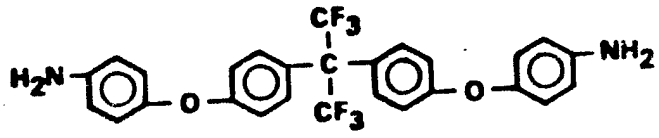
Preliminary studies performed by the General Electric Aircraft Engine Group, Evendale facility showed that linear condensation polyimides containing a perfluoroisopropylidene linkage, shown below, may be suitable for 644°K (700°F) service in highly oxidative environments (Reference 1).



The General Electric experimental work on thermo-oxidative stability at 644°K in compressed air environments was conducted on the Du Pont polyimide, NR-150B (Reference 2), which is no longer available as a general item of commerce. Although this polyimide possesses a glass transition temperature of less than 644°K, it demonstrated capability for resisting oxidative degradation at this temperature. Thus, a polyimide matrix resin containing a minimum of one perfluoroisopropylidene linkage in the polymer backbone repeat unit, plus glass transition

temperature greater than 644°K appeared to be a model baseline polymer which had the potential to meet the objectives of this program.

Under NASA Lewis Research Center sponsorship on Contract NAS3-17824 (Reference 3), TRW synthesized and screened a new family of linear condensation polyimides containing a perfluoroisopropylidene backbone linkage. These polymers, subsequently designated partially fluorinated polyimides, were prepared from a new diamine monomer containing the perfluoroisopropylidene linkage. Specifically, it was discovered that a new aromatic diamine monomer, 2, 2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (shown below and designated 4-BDAF) could be used to prepare linear condensation polyimides possessing initial thermo-oxidative



4-BDAF

stabilities determined by thermalgravimetric analysis approaching 773°K (932°F). Subsequent investigations at TRW and General Electric showed that Tg of the polyimide prepared from 4-BDAF diamine and pyromellitic dianhydride (PMDA) could be as high as 663°K (737°F) (Reference 1). Thus, the 4-BDAF/PMDA polyimide was selected as the baseline resin structure for this program.

Experimental work conducted on this program identified that the baseline 4-BDAF/PMDA polyimide formulation and a new candidate, synthesized from 4-BDAF diamine and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (designated 6-FDA), have potential for 644°K service. Two other new resin candidates, based upon a halogen substituted 4-BDAF derivation combined with both PMDA and 6-FDA demonstrated promising thermo-oxidative stability at 644°K. However, these two candidates could not be compression molded into zero defect neat resin test specimens. The latter, however, could be solution cast into tough films and, thus, may be

suitable for applications other than matrix resins (e.g., protective coatings).

This final report is divided into the additional sections as follows:

2.0 SELECTION OF CANDIDATE MATRIX RESINS

3.0 POLYMER SYNTHESIS AND CHARACTERIZATION

4.0 PROCESSING STUDIES

5.0 NEAT RESIN THERMO-OXIDATIVE STABILITY

6.0 CONCLUSIONS AND RECOMMENDATIONS

7.0 REFERENCES

8.0 APPENDICES

2.0 SELECTION OF CANDIDATE MATRIX RESINS

The initial effort conducted on the program involved selection of candidate generic matrix resins for investigation. An integral subsequent portion of this activity emphasized monomer ingredient and specific polymer structure selection. The selection process is described below.

2.1 SELECTION OF CANDIDATE GENERIC MATRIX RESINS

The initial work conducted on the program involved selection of a generic aromatic/heterocyclic matrix resin system having given preliminary evidence for oxidative stability and thermo-mechanical integrity at 644°K (700°F). A key factor in the selection process was also evidence for isothermal oxidative stability in air environments up to 0.4 MPa (60 psia).

The selection process was conducted by assessment of published information and contacts made with government and industrial organizations known to have participated in development of high temperature matrix resins. The selection criteria employed in this effort are as follows in descending importance:

- Resistance to initial weight loss by thermalgravimetric analysis (TGA) in air > 616°K (842°F)
- High weight retention (90% or greater) on isothermal aging for a minimum of 100 hours in air pressure at temperatures of 616°K (650°F) or greater
- High initial glass transition temperature of 616°K or greater
- High weight retention (90% or greater) on isothermal aging for a minimum of 100 hours in 0.4 MPa (60 psia) air pressure at temperatures of 616°K or greater

Other criteria such as processability, future availability, costs, and monomer toxicity were considered, but not to the extent of the thermo-oxidative and glass transition temperature factors.

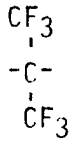
During the literature assessment and trade contact effort, it was discovered that only minimal high temperature (i.e., 616°K or greater) data existed on high performance polymer systems that may have been viable candidates for this program. The most comprehensive source of

useful polymer characterization data at temperatures of 616°K or greater was found to exist at the General Electric, Aircraft Engine Group, Evendale facility (Reference 1). It was found that data existed on oxidative stability of neat (i.e., non-reinforced) polymer candidates at temperatures up to 630°K (675°F) under compressed air pressures up to 0.4 MPa (60 psia) for time durations of up to several hundred hours. Also, glass transition temperature information existed for many of the polymers tested.

At the time that the polymer selection was performed, discussions with General Electric representatives indicated that several linear condensation and thermosetting polyimides exhibited potential for engine applications at 533°K to 589°K (500°F to 600°F) in compressed air environments up to 0.4 MPa. However, very few polymers had given promising characterization results on oxidative aging at 630°K (675°F) at 0.4 MPa.

The two polymers assessed by General Electric to have potential for service at 630°K (675°F) in compressed air environments were both linear condensation polyimides. One candidate was DuPont's NR-150B polyimide (Reference 2) and the other was a partially fluorinated polyimide (Reference 4) being developed by TRW.

The two polyimides have a similarity in the polymer backbone structure which is thought to be an important factor in contributing to their very high thermo-oxidative stability. Each resin has a perfluoroisopropylidene linkage, shown below, incorporated into the structure.



PERFLUOROISOPROPYLIDENE LINKAGE

A comparison of the oxidative stabilities and the glass transition temperatures of the DuPont and TRW polyimides is provided in Table 1. As can be seen from the screening results presented in Table 1, both of the polyimides demonstrate an acceptable, low neat resin weight loss of less

TABLE 1

COMPARISON OF THE OXIDATIVE STABILITY AND GLASS TRANSITION TEMPERATURE OF PROMISING DU PONT AND TRW POLYIMIDES

Polyimide	Key Properties: Glass Transition Temperature[a]	Key Properties: Oxidative Stability at 630°K (675°F)[b]
Du Pont NR-150B	633°K (680°F)	95% Weight Retention
TRW Partially Fluorinated Polyimide	665°K (738°F)	91% Weight Retention

a) Determined on a DuPont Model 990 thermalmechanical analysis attachment operating in a penetration mode.

b) Determined on neat resin discs employing aging conditions of a 630°K (675°F) temperature for 100 hours employing 0.4 MPa compressed air flow.

than ten percent in the oxidative test at 630°K (675°F) under 0.4 MPa pressure for one hundred hours. However, only the TRW polyimide possesses a glass transition temperature greater than the minimum goal of 644°K.

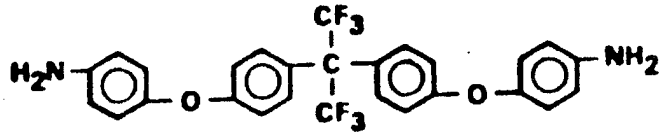
The unavailability of NR-150B necessitated the elimination of this resin as a candidate for investigation on this program.

On the basis of the literature and trade assessment, particularly the General Electric test results presented in Table 1, TRW recommended that modifications of the partially fluorinated polyimides be synthesized to meet the objectives of the program for 644°K service. This recommendation was approved by the NASA Lewis Research Center program manager.

2.2 SELECTION OF POLYIMIDE CANDIDATES

This section discusses the partially fluorinated polyimides which were selected for study on this program.

In 1975, on NASA Lewis Research Center Contract NAS3-17824 (Reference 3), TRW discovered a new partially fluorinated aromatic diamine. This new compound, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (designated 4-BDAF) is shown in the structure below. This diamine was reacted with several aromatic dianhydrides on this prior program. It was determined that the linear condensation polyimide prepared from 4-BDAF diamine and

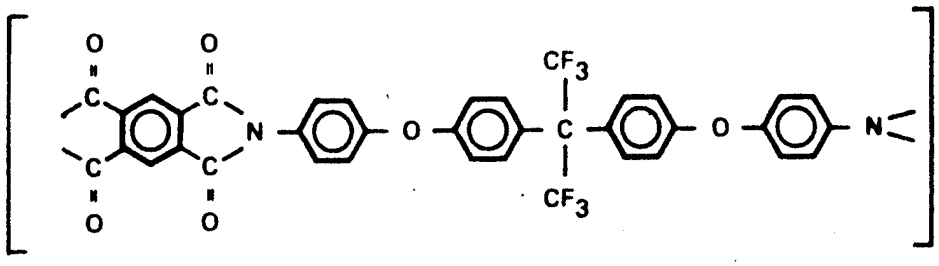


4-BDAF

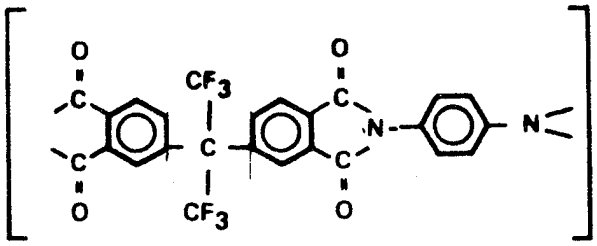
pyromellitic dianhydride (PMDA) possessed a very high resistance to initial weight loss in air by thermalgravimetric analysis. No weight loss was observed up to 763°K (914°F) in this screening analysis.

In 1980, in response to urging by the jet engine primes and government agencies, TRW initiated studies to determine whether the partially fluorinated polyimides produced from 4-BDAF diamine had promise for matrix applications. A secondary objective was to assess their potential as a substitute for the very high performance NR-150B polyimides.

As was mentioned in Section 2.1, both the TRW partially fluorinated and the NR-150B polyimides each contain a perfluoroisopropylidene linkage in the backbone structure. Representative polyimide structures are shown below for each resin family. The 1980 study determined that the 4-BDAF/PMDA formulation possessed a glass transition temperature of 665°K (738°F) and that the polyimide prepared from 4-BDAF and 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) possessed a glass transition temperature of only 583°K (590°F). This low glass transition temperature rendered the



4-BDAF/PMDA PARTIALLY FLUORINATED POLYIMIDE



REPRESENTATIVE NR-150B POLYIMIDE

4-BDAF/BTDA polyimide unsuitable for investigation in this program.

At the time the experimental work on this program was planned in detail, Morton Chemical Division of Morton Thiokol became a source for commercial production of the 4-BDAF diamine. The 4-BDAF diamine, produced by Morton Chemical at a minimum of 95% purity, was used throughout this NASA sponsored program. Additional data on the 4-BDAF diamine produced by Morton Chemical are provided in Section 3.

Based upon data existing at the time this investigation was initiated, a total of six monomeric ingredients were selected for investigation to prepare polyimides to be screened for 644°K (700°F) service. The monomers selected for study and the rationale for selection are as follows (see Table 2 for chemical structures):

- Aromatic Anhydrides

Compound	Rationale for Selection
- Pyromellitic Dianhydride (PMDA)	Showed promise in preliminary evaluation at General Electric and TRW as a co-ingredient in combination with 4-BDAF diamine

- 2,2-Bis(3,4-dicarboxyphenyl) hexafluoropropane Dianhydride (6-FDA)	Showed promise as the dianhydride ingredient in the Du Pont NR-150B polyimides
• Aromatic Diamines	
- 2,2-Bis[4-aminophenoxy)-phenyl]hexafluoropropane (4-BDAF)	Showed promise as the diamine ingredient in combination with PMDA in prior work
- 2,2-Bis[4-(3-halo-4-amino-phenoxy)phenyl]hexafluoro-propane (3-H-4-BDAF)	A 3-halo substituent may inductively or sterically stabilize the imide linkage in polymers prepared from this compound
- 2,2-Bis[4-(2-halo-4-amino-phenoxy)phenyl]hexafluoropro-pane (2-H-4-BDAF)	A 2-halo substituent may inductively or sterically stabilize the ether linkage in polymers prepared from this compound.
- 4,4'-Bis(4-aminophenoxy) biphenyl (4-BPDA)	A biphenyl linkage replacing the perfluoroisopropylidene linkage in a diamine containing four aromatic rings may offer thermo-oxidative stability, process-ability and/or lower cost advantages over the other three diamine candidates.

It was decided to investigate introduction of a chlorine atom as the halogen substituent in 3-H-4-BDAF and 2-H-4-BDAF (see Section 3).

The initial polyimides selected for investigation included six combinations of the ingredients described above. The six polyimides selected for study are as follows (see Table 2 for monomer structures):

- 4-BDAF/PMDA (selected as the control resin)
- 2-H-4-BDAF/PMDA (new candidate)
- 2-H-4-BDAF/6-FDA (new candidate)
- 3-H-4-BDAF/PMDA (new candidate)
- 4-BPDA/PMDA (new candidate)
- 4-BPDA/6-FDA (new candidate)

TABLE 2

MONOMERS SELECTED FOR STUDY ON CONTRACT NAS3-23274

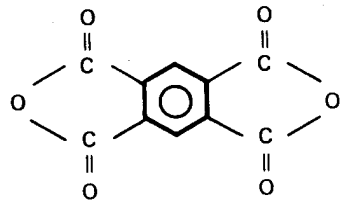
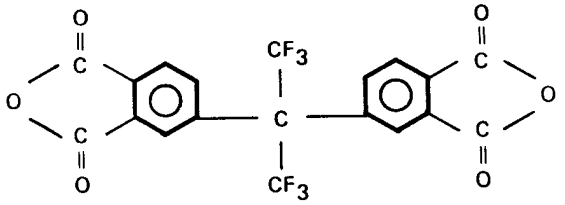
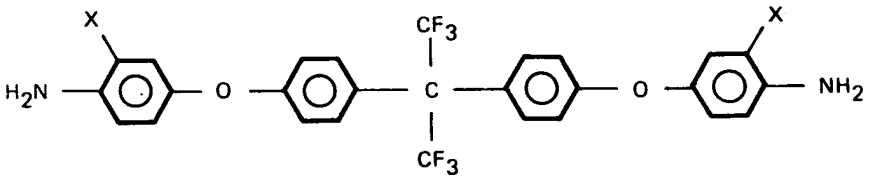
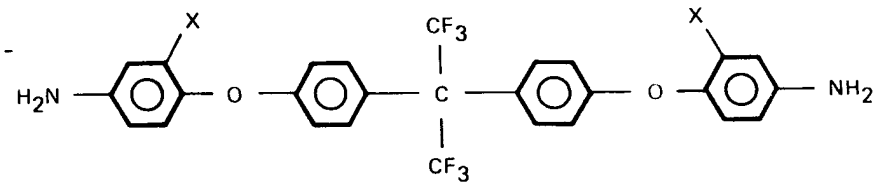
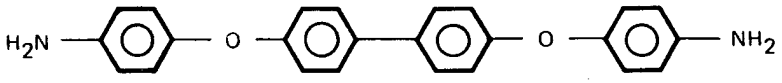
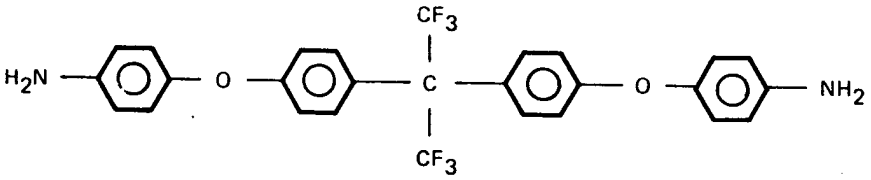
Monomer Name/Abbreviation	Monomer Structure
Pyromellitic Dianhydride (PMDA)	
2,2-Bis(3,4-dicarboxyphenyl)hexafluoro-propane dianhydride (6-FDA)	
2,2-Bis[4-(3-Halo-4-aminophenoxy)-phenyl]hexafluoropropane [a] (3-H-4-BDAF)	

TABLE 2 (CONTINUED)

MONOMERS SELECTED FOR STUDY ON CONTRACT NAS3-23274

Monomer Name/Abbreviation	Monomer Structure
2,2-Bis[4-(2-halo-4-aminophenoxy)phenyl]-hexafluoropropane [a] (2-H-4-BDAF)	
4,4'-Bis(4-aminophenoxy)biphenyl (4-BPDA)	
2,2-Bis[4-(4-aminophenoxy)phenyl]-hexafluoropropane (4-BDAF)	

a) Chlorine was selected as the halogen atom to be introduced.

A reiteration of the polyimides selected for investigation is provided in Table 3.

A discussion of the synthesis and characterization of the monomers and polymers selected for study is provided in Section 3.

TABLE 3

MATRIX OF POLYIMIDES SELECTED
FOR INITIAL STUDY

Aromatic Dianhydrides	Aromatic Diamines 2-H-4-BDAF	3-H-4-BDAF	4-BPDA	4-BDAF
PMDA	X	X	X	X (control)
6-FDA	X		X	

a) See Table 2 for chemical names and structures of the dianhydrides and diamines.

3.0 POLYMER SYNTHESIS AND CHARACTERIZATION

The synthesis and characterization of the polyimide candidates selected for study is presented in this section. The synthesis or procurement and characterization of the monomers employed in this investigation is presented first, followed by a discussion of polyimide preparation and characterization.

3.1 MONOMER SYNTHESIS AND CHARACTERIZATION

Prior to undertaking polyimide studies it was necessary to synthesize or procure the six monomeric ingredients selected as discussed in Section 2. A chlorine substituent was selected as the halogen to be investigated in halogen modified 4-BDAF diamines. A summary of the approach employed to secure each monomeric ingredient is as follows:

- Dianhydrides
  - PMDA: Procure from commercial sources
  - 6-FDA: Recover from NR-150B polyimide samples
- Diamines
  - 4-BDAF: Procure from Morton Chemical
  - 2-Cl-4-BDAF: Synthesize this new compound
  - 3-Cl-4-BDAF: Synthesize this new compound
  - 4-BPDA: Synthesize this new compound

A description of the effort conducted to secure the monomers prior to initiating polyimide studies is described below.

3.1.1 Procurement of Dianhydride Ingredients

The PMDA and 6-FDA aromatic dianhydrides employed in this study were procured from available sources. Each compound was thermally treated at 473°K (392°F) to assure a high degree of ring closure of the carboxylic acid substituents to the desired anhydride derivative. Each dianhydride, after thermal treatment, was characterized for melting point and dianhydride content. A summary of these data is provided in Table 4. Only those dianhydride samples analyzing to contain a > 95% anhydride content were employed to prepare polyimides as discussed in Section 3.2.

TABLE 4

ANALYSIS OF AROMATIC DIANHYDRIDES

Dianhydride	Melting Point (°K/°F)[a] Determined	Literature	Dianhydride Content (meq/g)[b] Determined	Theoretical
PMDA	560/549	559/347	8.82	9.17
6-FDA	519/475	525/486	4.37	4.77

a) Determined on a Du Pont Model 1090 differential scanning calorimeter.

b) Determined by non-aqueous titration in ethyl acetate.

3.1.2 Synthesis and Characterization of Diamine Ingredients

The synthesis of the aromatic diamines selected for study in this investigation was attempted for each by the reaction sequence given in Equation 1. This chemical reaction is that claimed by TRW for preparation of 4-BDAF diamine (Reference 5).

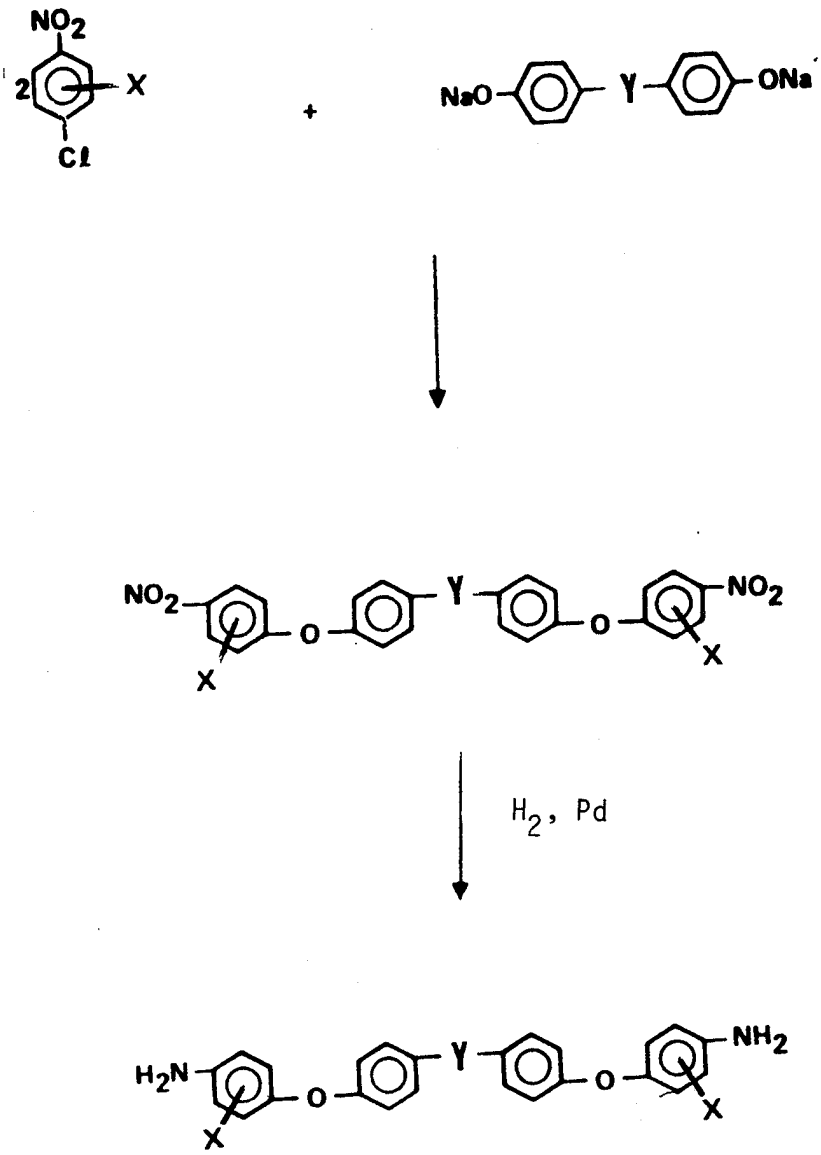
The synthesis of each new diamine, 2-Cl-4-BDAF, 3-Cl-4-BDAF and 4-BPDA, was attempted employing the TRW developed process shown in Equation 1. It was experimentally determined that the new 2-Cl-4-BDAF and 4-BPDA diamines could be prepared in relatively high yield and purity by this reaction. Characterization data obtained on these compounds are summarized in Table 5. The experimental procedures and representative analysis spectra are presented in Appendix A. These new diamines were employed to synthesize new polyimide candidates as discussed in Section 3.2.

It was experimentally determined that the 3-Cl-4-BDAF diamine candidate could not be prepared in an acceptable yield or purity level by the nucleophilic reaction sequence shown in Equation 1. The key starting ingredient, 2,4-dichloronitrobenzene, apparently is susceptible to a high degree of nucleophilic attack by the disodium salt of 2,2-bis-(4-hydroxyphenyl)hexafluoropropane (designated bisphenol A-F) at both the *ortho* and *para* chlorine substitutes. Thin layer chromatographic analysis repeatedly showed a minimum of three major reaction products, which most probably consisted of 2-, 4- and 2,4- nucleophilic substitution of 2,4-dichloronitrobenzene by the dianion of bisphenol A-F. It was recommended by TRW that the 3-Cl-4-BDAF diamine be dropped from further consideration as a diamine candidate on this program. This recommendation was approved by the NASA program manager. An alternative polyimide was approved for investigation to replace the 3-Cl-4-BDAF/PMDA polyimide initially selected for investigation as summarized in Table 3. The alternative polymer selection is presented and discussed in Section 3.2.

The conversion of the PMDA, 6-FDA, 4-BDAF, 2-Cl-4-BDAF and 4-BDAF monomers into 644°K polyimide candidates and their subsequent characterization is described in Section 3.2.

3.2 POLYIMIDE SYNTHESIS AND CHARACTERIZATION

This section provides technical details of the polyimide synthesis and characterization investigation conducted on the program. A total of six polymer candidates were screened, including 4-BDAF/PMDA as the control resin, plus five new polyimides.



WHERE: X = H or Cl; Y = $C(CF_3)_2$ or Direct Bond

Equation 1. Synthetic Sequence Employed for Diamine Synthesis

TABLE 5

AROMATIC DIAMINE PROPERTIES

Aromatic Diamine[a]	Differential Scanning Calorimetry Melting Point, °K (°C)[b]	Key Nuclear Magnetic Resonance Absorption Peaks (In ppm)[c]	Key Infrared Absorption Peaks (cm^{-1})[d]	Amine Group Titration, meg/g (Theoretical)[e]	Elemental Analysis, % Determined (% Calculated) C	H	N	F
4-BPDA	468 (195)	Aromatic C-H (6.7-7.1, 7.5-7.7); N-H (4.65)	3380 (N-H)	5.17 (5.43)	78.1 (78.3)	5.7 (5.4)	7.5 (7.6)	-- --
2-CL-4-BDAF	473 (200)	Aromatic C-H (6.5-7.5) N-H (4.95)	3640 (N-H)	3.24 (3.41)	56.1 (55.2)	3.3 (3.1)	5.9 (4.8)	18.3 (19.4)
4-BDAF	437 (164)	Aromatic C-H (6.7-7.1, 7.3-7.5); N-H (4.7)	3380, 3460 (N-H)	3.78 (3.86)	62.64 (62.54	3.9 (3.9)	5.4 (5.36)	22.16 (21.99)

a. Please see Table 2 for chemical names and structures.

b. Determined employing a Du Pont Model 990 instrument.

c. Determined employing a Bruker Model WP 200 insturment; acetone-d_6 solvent.

d. Determined employing a Perkin Elmer Model 283 spectrophotometer; compound in KBr pellet.

e. Determined employing a non-aqueous titration method; perchloric acid in acetic acid.

3.2.1 Polyimide Synthesis

The following polyimide resins were synthesized on the program as follows (see Table 2 for monomer structures):

- 4-BDAF/PMDA (control),
- 2-Cl-4-BDAF/PMDA,
- 2-Cl-4-BDAF/6-FDA,
- 4-BDAF/6-FDA (substituted for 3-Cl-4-BDAF/6-FDA due to unavailability of 3-Cl-4-BDAF)
- 4-BPDA/PMDA
- 4-BPDA/6-FDA

The process employed to prepare the candidate resins is described below.

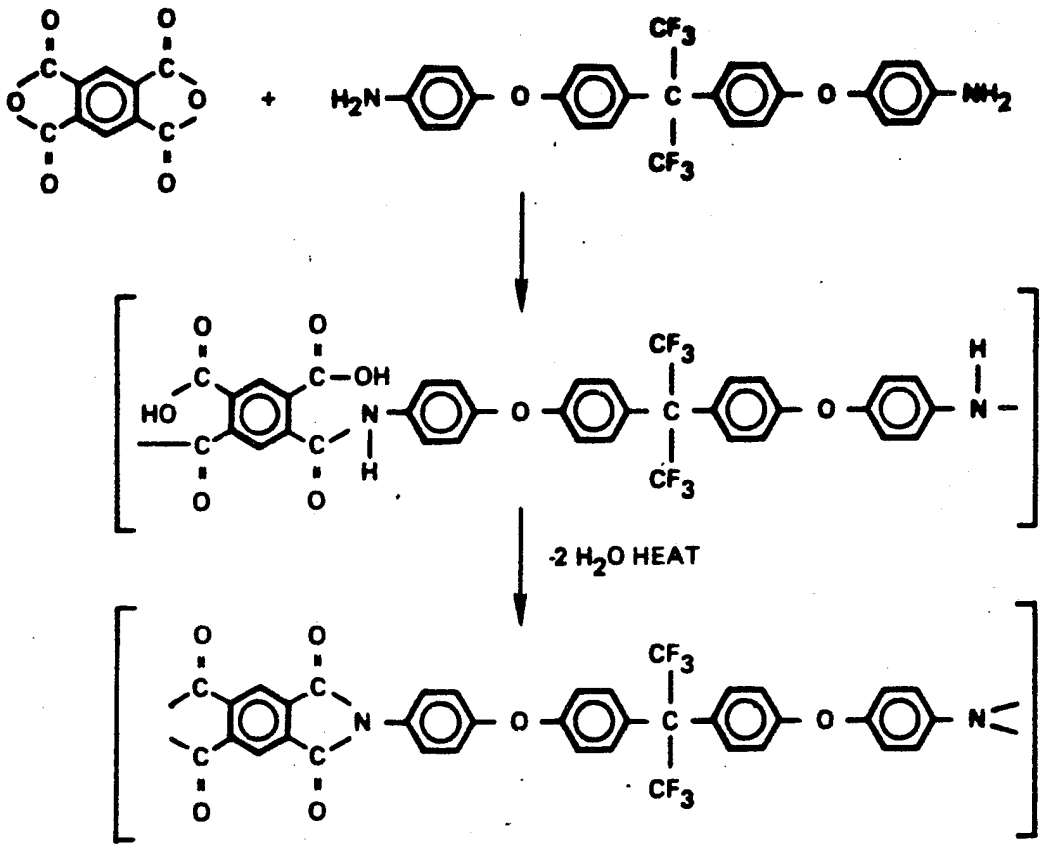
The six polyimides were prepared in solution as their amide-acid precursors, followed by solvent evaporation *in vacuo*, then thermally imidized in air at 473°K (392°F). Dimethylacetamide (DMAC) was employed as the polymerization solvent and the monomers were combined at a twenty-five percent (25%) solids loading in the solvent. This solvent and varnish solids loading were selected because prior work employing this combination yielded the promising initial thermo-mechanical results determined on the 4-BDAF/PMDA as discussed in Section 2.

A representative reaction sequence employed to prepare the linear condensation polyimide candidates is provided in Equation 2. Detailed experimental procedures employed to prepare the amide-acid precursor, then isolate the polyimide candidates are provided in Appendix C.

No problems were encountered during the polymerization and polyimide isolation experimentation. The screening characterization conducted on the six polyimide candidates is discussed below.

3.2.2 Polyimide Characterization

The five new polyimide candidates, plus the control, which were synthesized by the method described in Section 3.2.1, were analyzed for key structural, molecular weight and thermo-oxidative stability characteristics. The specific characterization tests conducted on each polyimide are as follows:



Equation 2. Reaction Employed to Form the Linear Condensation Polyimide Candidate 4-BDAF/PMDA

- Molecular weight distribution by gel permeation chromatography
- Structural behavior by infrared analysis
- Initial thermo-oxidative stability by thermalgravimetric analysis in air
- Isothermal thermo-oxidative stability by aging in air at 644°K for 240 hours

No phase changes ascribable to a normal resin melting point or glass transition temperature could be determined by differential scanning calorimetry analysis. Also, no dynamic melt viscosity results could be obtained by Rheometrics instrumentation due to instrumental temperature limitations of 673°K (725°F) maximum operating temperature.

3.2.2.1 Gel Permeation Chromatography

The five new polymer samples and the 4-BDAF/PMDA control were

analyzed for comparison of the relative molecular weight distribution by gel permeation chromatography (GPC). The polymers were tested as the amide-acid precursors of the polyimides.

The samples were analyzed on a Waters Model 150C GPC instrument equipped with 10^5, 10^4 and 10^3 μ-styragel columns connected in series. The column oven, injector compartment and pump temperatures were held at 308°K, 308°K and 300°K, respectively. The samples were injected at a volume of 100 μl at a concentration of 2% by weight in dimethylformamide (DMF) solvent. The run time employed was 45 minutes for each sample. A Spectra Physics Model SP 4000 data system was used to monitor and plot the sample elution as determined by an infrared detector.

The representative GPC tracings for the 4-BDAF/PMDA control and 4-BDAF/6-FDA are shown in Figures 1 and 2, respectively. The elution data and key comments for all the polyimides are summarized in Table 6.

Each sample gave a bimodal peak in the retention time range of 759 to 1159 seconds for higher molecular weight polymer with varying amounts of lower molecular weight material occurring down to a retention time of 1799 seconds.

The presence of a significant amount of lower molecular weight fractions, particularly in the 4-BPDA/PMDA and 4-BPDA/6-FDA polymers, may have been a significant contributor to the high weight loss observed in isothermal aging in air at 644°k (700°F) as discussed in Section 3.2.2.4.

3.2.2.2 Infrared Analysis

The spectra obtained are typical of those normally obtained for linear condensation polyimides. Key absorption band data are summarized in Table 7. Representative infrared tracings are presented in Figures 3 and 4 for 4-BDAF/PMDA and 4 BDAF/6-FDA, respectively.

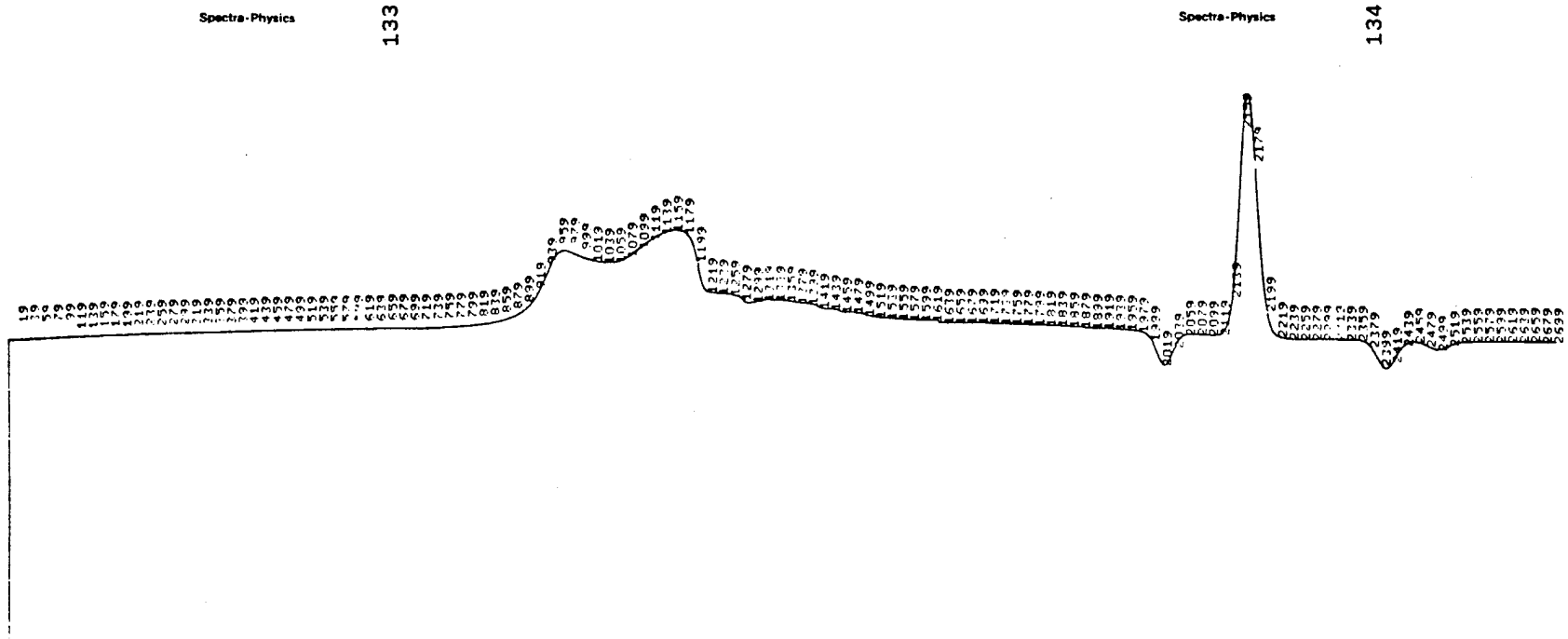


Figure 1. Gel Permeation Chromatograph of 4-BDAF/PMDA (Control).

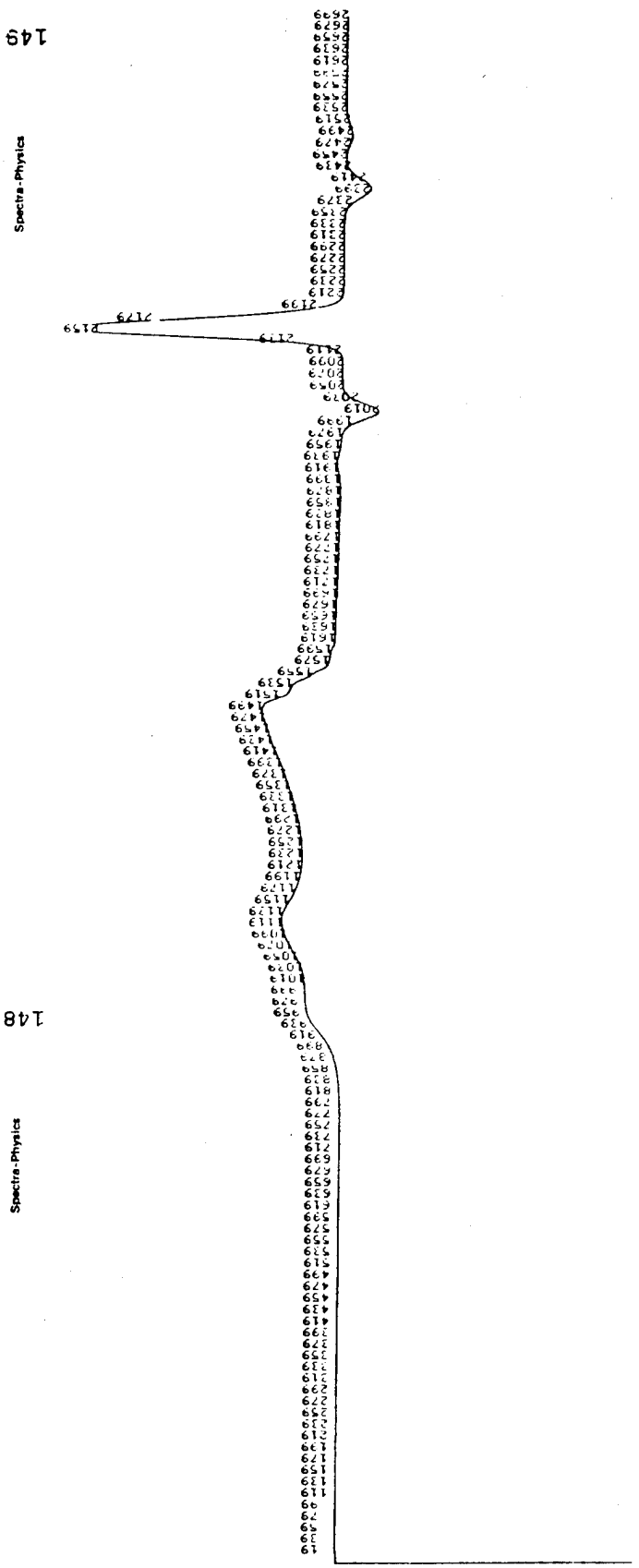


Figure 2. Gel Permeation Chromatograph of 4-BDAF/6-FDA.

TABLE 6

SUMMARY OF GEL PERMEATION CHROMATOGRAPHY ANALYSIS RESULTS[a)]

Polymer Candidate	Retention Time of Higher Molecular Weight Fractions (Seconds)		Retention Time of Bimodal Peaks in Higher Molecular Weight Fractions (Seconds)		Estimated Retention Time of Low Molecular Weight Fractions (Seconds)		Comments
	Onset	Terminus	Higher	Lower	Begin	Complete	
4-BDAF/PMDA CONTROL	799	1219	959	1159	1219	1619	Predominant fractions appear to be higher molecular weight
2-Cl-4-BDAF/PMDA	799	1279	959	1119	1299	1619	Same as for the control; the distributions are similar
2-Cl-4-BDAF/6-FDA	839	1279	979	1159	1279	1599	Same as for control; the distributions are similar to the control and 2-Cl-4-BDAF/PMDA
4-BDAF/6-FDA	879	1219	979	1119	1219	1599	This sample contains an unexpected large amount of low molecular weight polymer
4-BPDA/PMDA	699	999	759	939	1019	1799	Lower molecular weight fractions predominate
4-BPDA/6-FDA	799	1259	979	1159	1259	1679	Lower molecular weight fractions predominate

[a)] See Section 3.2.2.1 for experimental analyses conditions.

TABLE 7

SUMMARY OF INFRARED ANALYSES[a)]

Polyimide Candidate	Key Infrared Absorption Bands (cm^{-1})	
	Imide	$-CF_3$
4-BDAF/PMDA	1650 and 1750	1150 and 1300
4-BDAF/6-FDA	1680 and 1740	1060 and 1300
2-Cl-4-BDAF/PMDA	1680 and 1760	1080 and 1200
2-Cl-4-BDAF/6-FDA	1680 and 1740	1050 and 1300
4-BPDA/PMDA	1650 and 1750	----
4-BPDA/6-FDA	1650 and 1710	1040 and 1340

a) Determined on a Perkin-Elmer Model 283 Spectrometer employing polyimide powder in KBr.

3.2.2.3 Thermalgravimetric Analysis

The five new polyimide candidates, plus the control, were screened for initial thermo-oxidative stability in air by thermal gravimetric analysis (TGA). Prior to testing the polyimides were postcured for four hours at 672°K (750°F). The conditions employed for the TGA analysis were a heating rate of 283°K (10°C) per minute employing an air flow of 60cc per minute. The TGA analyses were performed on a DuPont Model 990 instrument. The TGA results for each polyimide are presented in Table 8. A representative TGA tracing is presented in Figure 5 for 2-Cl-4-BDAF/6-FDA.

The TGA results on each polyimide were interpreted to be promising. Polymers which exhibited a weight loss onset temperature of at least 713°K (826°F) in air were considered to have potential for longer-term oxidative stability performance at 644°K (700°F). Only those polyimides containing a perfluoroisopropylidene linkage showed promise on isothermal aging at 644°K.

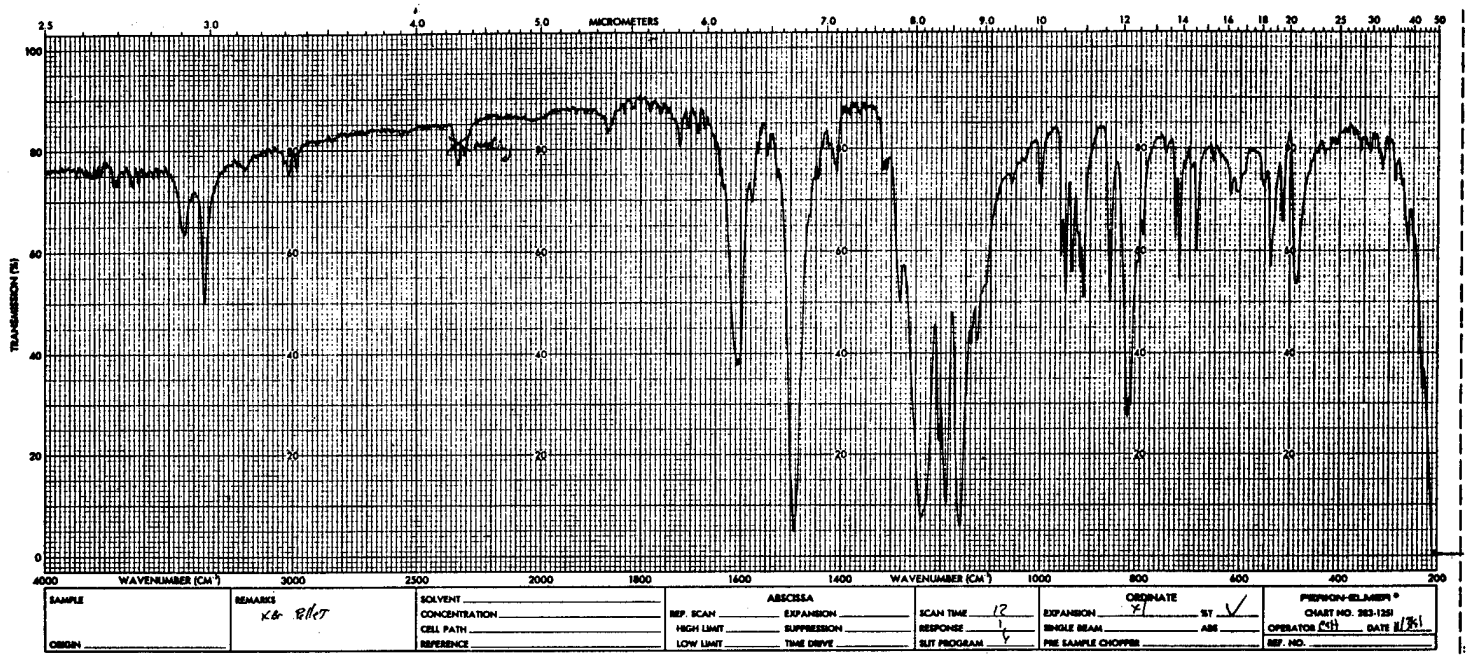


Figure 3. Infrared Spectrum of 4-BDAF/PMDA (KBr)

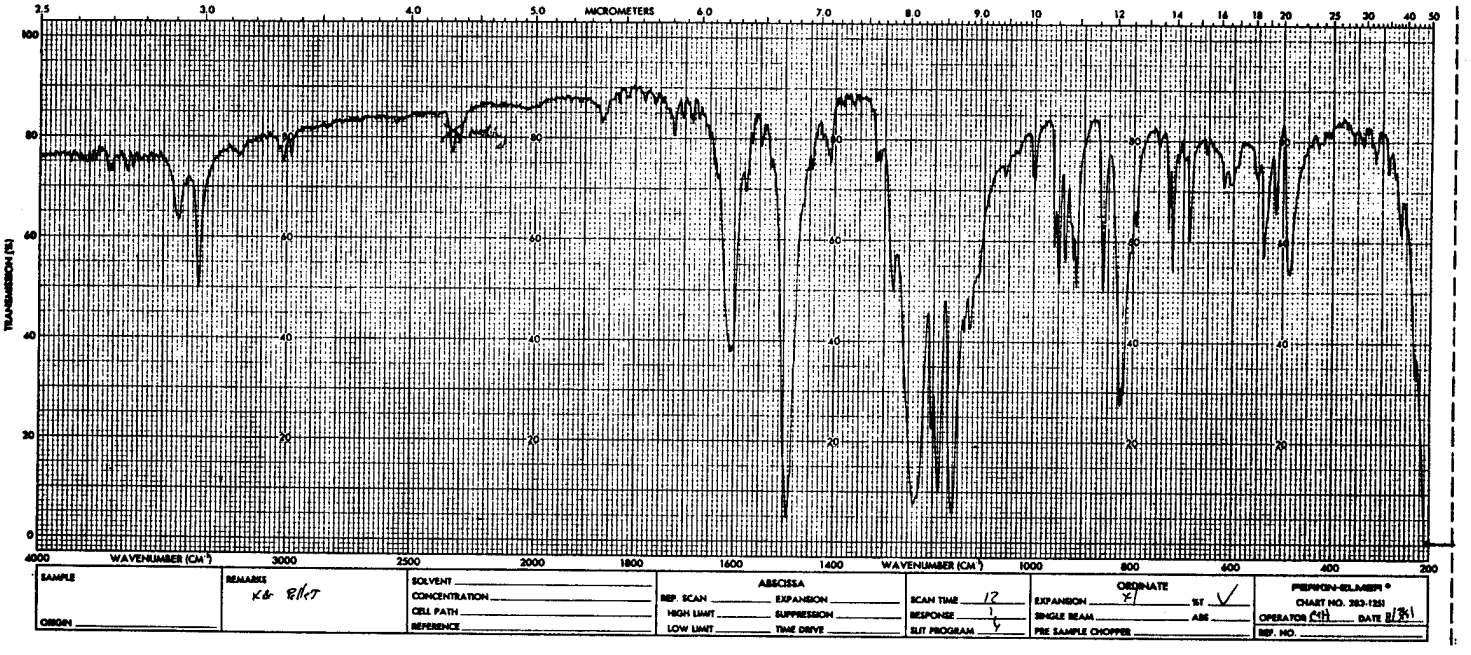


Figure 4. Infrared Spectrum of 4-BDAF/6-FDA (KBr)

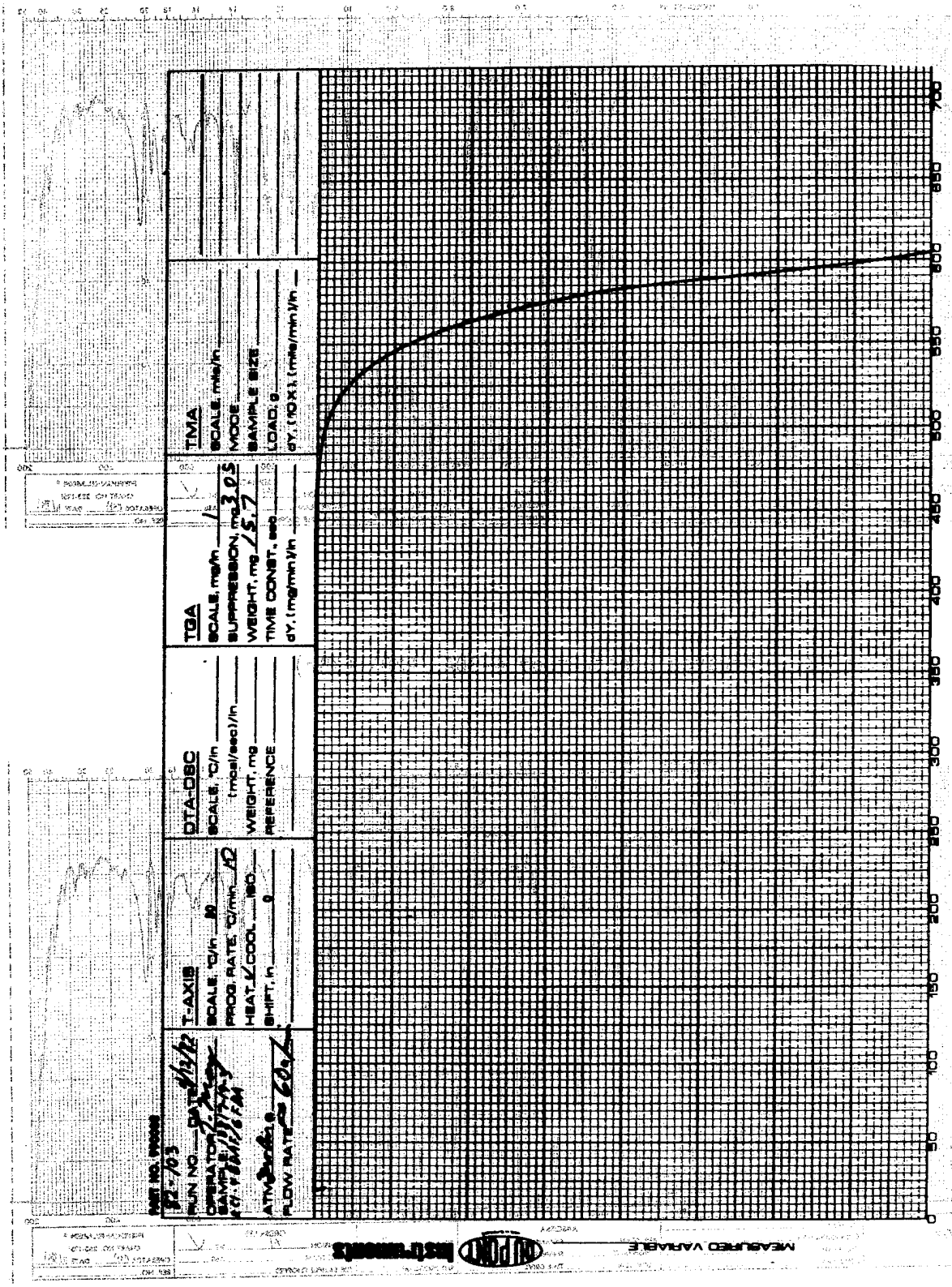


Figure 5. Thermogram of 2-Cl-4-BDAF/6-FDA.

TABLE 8

THERMALGRAVIMETRIC ANALYSIS IN AIR[a)]

Polyimide Candidate	Temperature Yielding Indicated Weight Loss (°K/°F) Onset	50%	10%
4-BDAF/PMDA (Control)	748/887	808/995	823/1022
4-BDAF/6-FDA			
2-Cl-4-BDAF/ PMDA	723/842	810/999	828/1031
2-Cl-4-BDAF/ 6-FDA	748/887	803/986	813/1013
4-BPDA/PMDA	723/842	793/968	810/999
4-BPDA/6-FDA	713/826	783/950	798/977

a) Determined on nominal 25-mesh polyimide powder, postcured for four hours at 672°K (750°F) in air, employing a Du Pont Model 990 TGA using a 283°K (10°C) heating rate/minute at an air flow of 60 cc/ minute.

3.2.2.4 Isothermal Thermo-oxidative Stability Assessment

Each of the five new polymers, 2-Cl-4-BDAF/PMDA, 2-Cl-4-BDAF/6-FDA, 4-BDAF/6-FDA, 4-BPDA/PMDA and 4-BPDA/6-FDA, plus the 4-BDAF/PMDA control, was assessed for thermo-oxidative stability by isothermal aging in air at 644°K for two hundred and forty hours. The polyimides were tested as powders to assure large surface areas for exposure and acceleration of air oxidation to rapidly discern the relative thermo-oxidative stability of the candidates. A molded specimen (one-half of a disc 2.54 cm diam., 0.63 cm thick) of the 4-BDAF/PMDA control was included in the test for comparison with the same material in powder form.

The results of the thermo-oxidative assessment are presented in Table 9. The 644°K aging results are plotted in Figure 6.

The samples were prepared by solvent drying and imidization for 20-24 hours at 493°K (436°F). The polyimide candidates were powdered in a blender, then screened to an average 25-mesh-size particles. The

TABLE 9

SUMMARY OF ISOTHERMAL AGING AT 644°K (700°F) IN AIR

Polyimide Candidate	Weight Loss on Postcure (%)[a]	Weight Loss as a Function of Isothermal Aging in Air at 644°K[b]			
		40 hours	109 hours	166 hours	240 hours
4-BDAF/PMDA Control (Neat Resin Disc)	0.5	1.3	5.4	10.3	19.3
4-BDAF/PMDA Control (Powder)	3.3	4.2	21.5	44.6	69.3
2-Cl-4-BDAF/PMDA (Powder)	4.0	4.6	28.7	62.3	89.7
2-Cl-4-BDAF/6-FDA (Powder)	3.0	4.4	13.0	39.9	58.2
4-BDAF/6-FDA (Powder)	2.9	6.5	24.4	43.1	65.3
4-BPDA/PMDA (Powder)	9.6	53.0	98.1	98.9	99.0
4-BPDA/6-FDA (Powder)	7.3	60.0	92.5	99.5	99.6

[a] The samples were postcured in air at 672°K (750°F) for four hours.

[b] See context for aging test conditions.

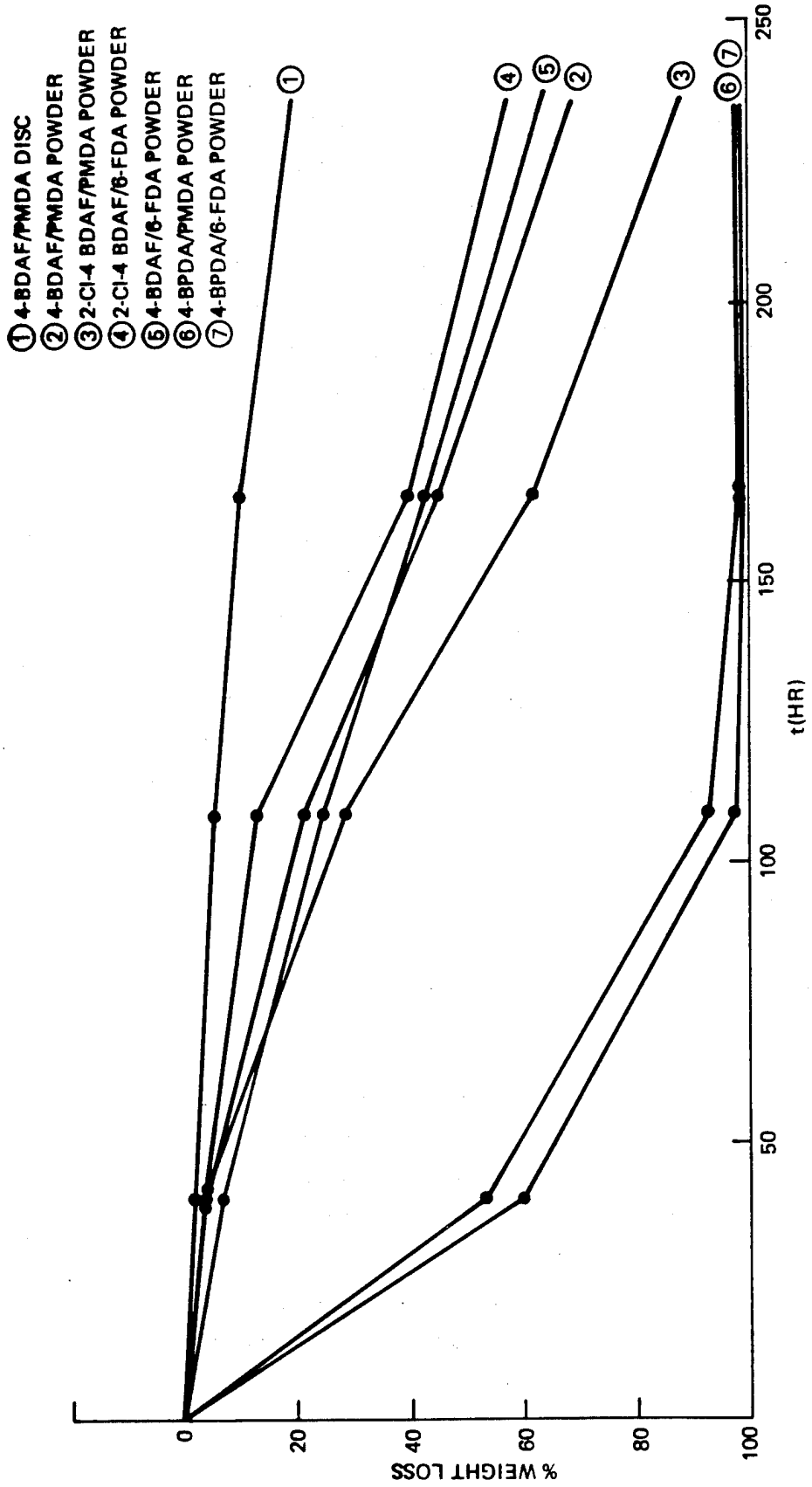


Figure 6. Isothermal Aging Results at 644°K (700°F) in Air

powders were then postcured in a Blue M CFD-10F-4 oven at 672°K (750°F) for four hours in air. The weight loss that occurred for the resin powders and the neat resin slug are given in Table 9.

The samples were placed in number 06 porcelain crucibles and aged in the Blue M Model CFD-10F-4 oven. The samples were aged at 644°K (700°F) for two-hundred and forty hours employing an air flow of 11.8 cc/second. Bottled air was employed as the oxidizing atmosphere.

The weight loss data given in Table 9 show definite trends as to the type of new polyimides thought to be suitable for further evaluation. The polyimide candidates 4-BDAF/6-FDA, 2-Cl-4-BDAF/PMDA and 2-Cl-4-BDAF/6-FDA were judged to be worthy of further study in the program. This conclusion was based on the fact that through 109 hours of aging the disc of the 4-BDAF/PMDA control lost only 5% weight over this aging period versus a fourfold higher weight loss of the powder at 21%. A similar neat resin slug sample of 4-BDAF/PMDA prepared from the same previous resin lot lost only 8% by weight when aged for 100 hours at 357°C (675°F) under 0.4 MPa (60 psi) compressed air flow in prior work conducted at General Electric. The relative weight loss through 109 hours of 24%, 29%, and 13% for 4-BDAF/6-FDA, 2-Cl-4-BDAF/PMDA and 2-Cl-4-BDAF/6-FDA, respectively, could be expected to be reduced (e.g., perhaps up to a four-or fivefold reduction).

Conversely, the two resins prepared from 4-BPDA diamine, 4-BPDA/PMDA and 4-BPDA/6-FDA, clearly are not suitable for consideration for service at 644°K. Although the high weight loss was most probably due to the presence of low molecular weight polymer (see Section 3.2.2.1), the extremely high rate of degradation could have involved rapid thermal and/or oxidative decomposition of the polyimide backbone. This instability was not anticipated, because the candidates did not show an onset of decomposition in air by TGA until a temperature was reached of 713°K (826°F).

3.2.2.5 Selection of Promising Candidates for Further Study

Based upon the polyimide powder aging studies conducted at 644°K as discussed above, resin candidates 4-BDAF/6-FDA, 2-Cl-4-BDAF/PMDA and 2-Cl-4-BDAF/6-FDA, plus the 4-BDAF/PMDA control, were recommended to the NASA program manager by TRW for further study. Approval was obtained to employ these resins to initiate processing studies. Investigation of the processability characteristics of these promising 644°K polyimide candidates is presented in Section 4.

4.0 PROCESSING STUDIES

This section describes the compression molding investigation of the 4-BDAF/6-FDA, 2-Cl-4-BDAF/PMDA and 2-Cl-4-BDAF/6-FDA polyimide candidates, plus the 4-BDAF/PMDA control. Prior to conducting the fabrication study, a method was developed to provide neat resin molding powders that were essentially void of residual solvent and detectable aqueous condensation volatiles.

4.1 PREPARATION OF NEAT POLYIMIDE MOLDING POWDERS

Prior to initiation of this program, no studies had been conducted by TRW to define experimental conditions giving neat resin molding compounds that were essentially free of residual solvent and retained aqueous condensation volatile matter. Volatile matter evolving at temperatures up to 644°K was suspected to be a source of compression molding non-reproducibility in prior studies (References 1 and 6).

In the polyimide synthesis and characterization studies discussed in Section 3.2, neat resin powders were prepared by a thermal solvent drying/imidization cycle at 473°K (395°F) under vacuum, followed by postcure in air for two to four hours at 632°K (750°F). Molding powders prepared by this method could not be compression molded at temperatures up to 755°K (900°F) and pressures up to 68 MPa (10,000 psia) into consolidated neat resin discs. Conversely, molding compounds that were solvent dried and imidized only at 473°K apparently evolved considerable volatile matter giving voidy, micro-cracked discs upon molding at process conditions up to 755°K and 68 MPa. Thus, it was necessary to define conditions that did not overcure the powders as apparently occurred upon postcure at 632°K, yet removed essentially all residual solvent and aqueous condensation volatile matter.

A thermalgravimetric analysis (TGA) study was conducted on the polyimide powders after a three hour imidization cycle at 473°K in vacuo (< 1 Torr). It was determined that the powders consistently lost 3% to 4% of volatile matter when heated up to $\sim$ 773°K (500°C or 932°F). This weight loss occurred in the temperature range of approximately 463°K

(190°F or 374°F) up to 633°K (360°C or 680°F). Loss of weight in this temperature range strongly infers that residual solvent and further imidization was occurring. A representative TGA tracing is presented in Figure 7 for 4-BDAF/PMDA.

An investigation was conducted to determine the minimum postcure conditions required to eliminate evaluation of volatile matter, yet not overcure the polyimide as was observed when the powders were heated at 632°K. Screening of heating or postcure temperatures in the temperature range of 633°K (360°C or 680°F) to 673°K (390°C or 734°F) for different time durations determined that a one hour postcure in air at 644°K (700°F) was sufficient to essentially eliminate volatile matter to the detectability limit of the TGA. A representative TGA tracing for the 4-BDAF/PMDA polyimide powder which was imidized at 473°K (392°F), followed by a one hour postcure at 644°K (700°F), is shown in Figure 8. Most importantly, the 4-BDAF/6-FDA and 4-BDAF/PMDA polyimide powders prepared by this process could be compression molded into essentially defect free neat resin discs. The fabrication investigation is described in Section 4.2.

4.2 COMPRESSION MOLDING STUDIES

Prior to initiation of this program, molding of the 4-BDAF/PMDA control resin had been conducted employing press hardware and tooling that did not possess heat sources that allowed close tolerance control of the compression molding temperatures in the desired range of 672°K (750°F to 900°F). It was necessary to define and employ the close tolerance fabrication equipment in this program. A description of the compression processing equipment and the successful use of this hardware to mold two resin candidates is presented below.

4.2.1 Process Equipment Definition

The tooling selected to initiate the compression molding studies were three-part Carver molds which are available in inner-diameter sizes of 2.54-cm (1-inch) up to 6.35-cm (2.5-inch) for experimental fabrication work. The disassembled, 2.54-cm Carver mold is shown in Figure 9. It was determined that the tooling must be externally heated to maintain close tolerance temperature control to $\pm$ 2°C ($\pm$ 5°F) over the temperature range of 672°K to 755°K (750°F to 900°F). An Ogden band extruder barrel heater

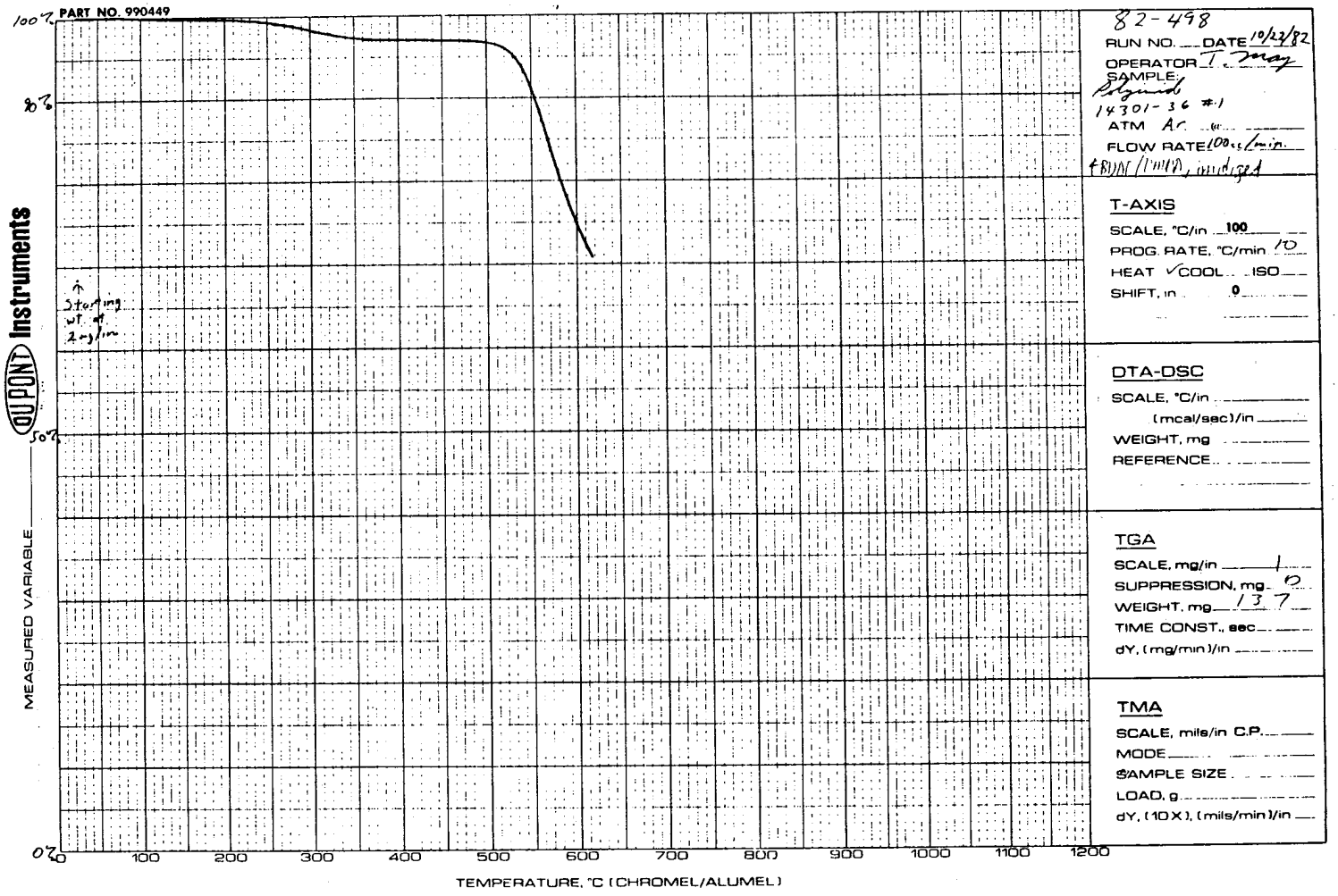


Figure 7. Thermogram of 4-BDAF/PMDA Polyimide Previoulsy Imidized at 473°K.

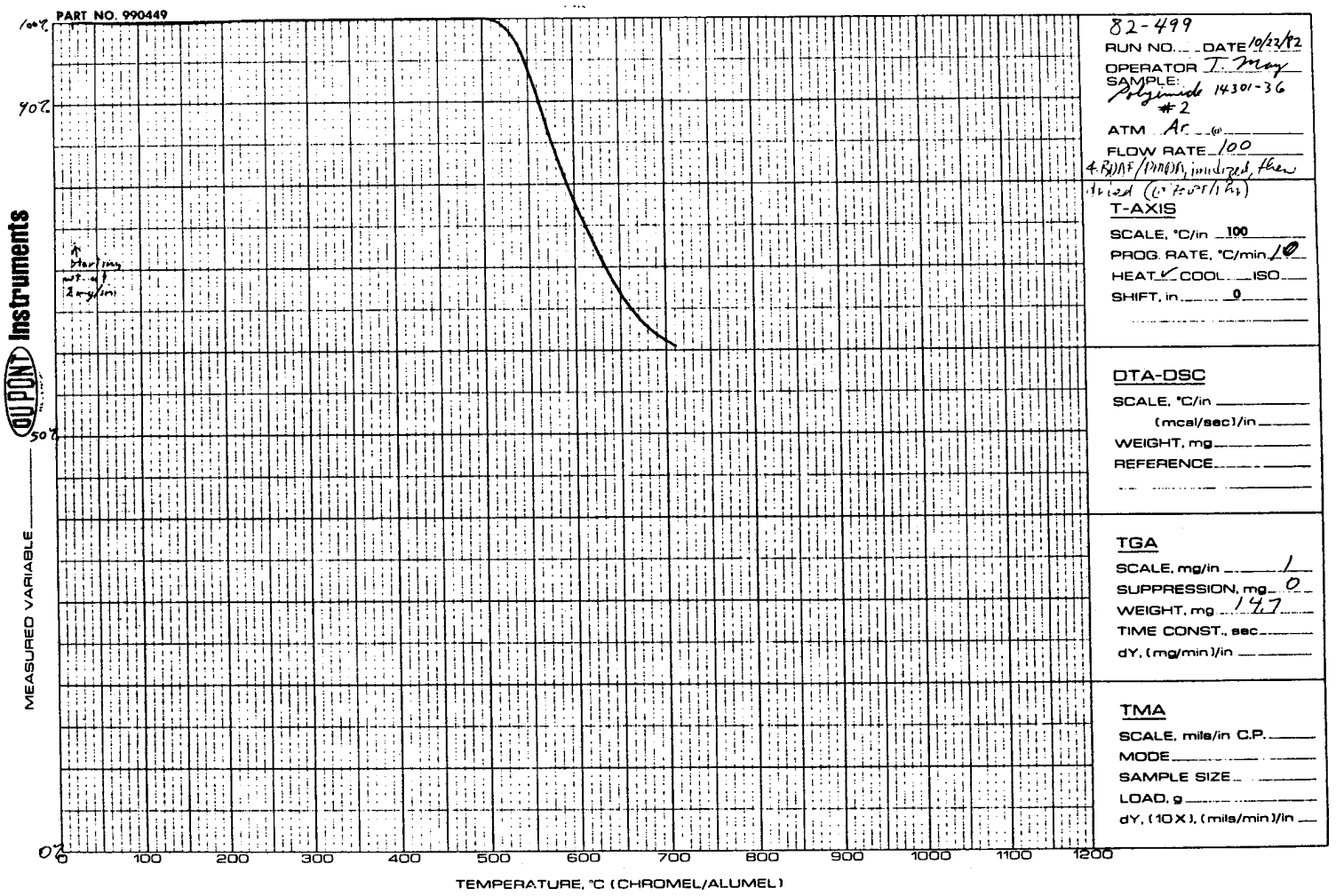


Figure 8. Thermogram of 4-BDAF/PMDA Polyimide Imidized at 473°K and Dried at 644°K

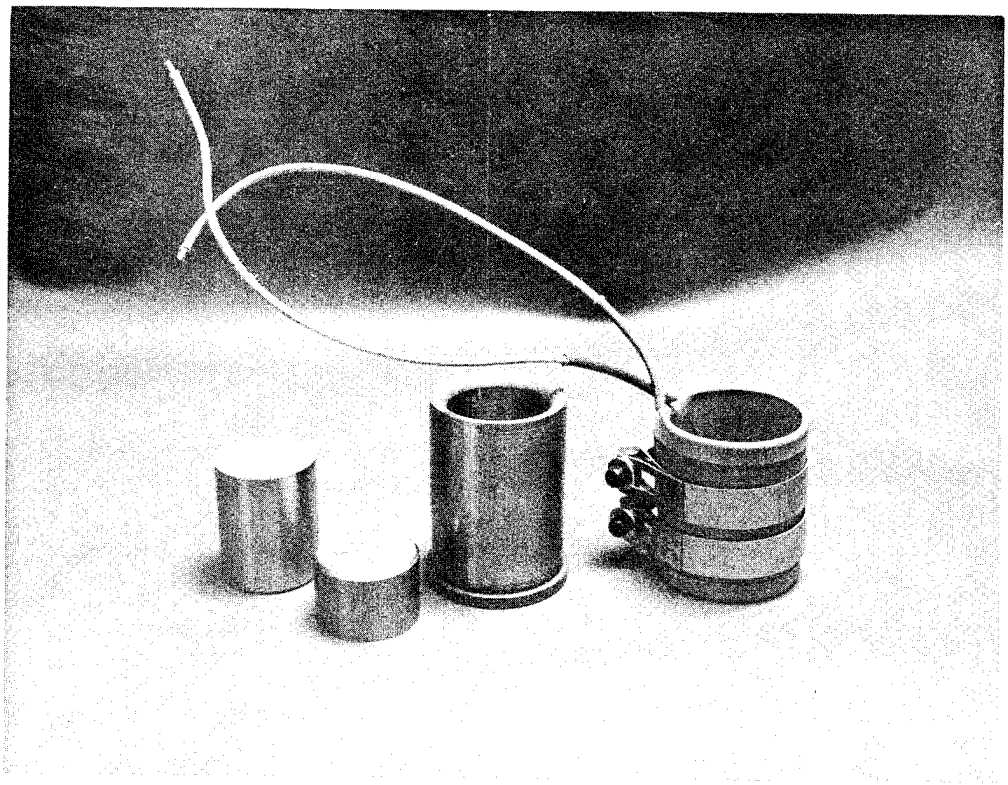


Figure 9. Disassembled Mold and Heater Employed for Polyimide Fabrication.

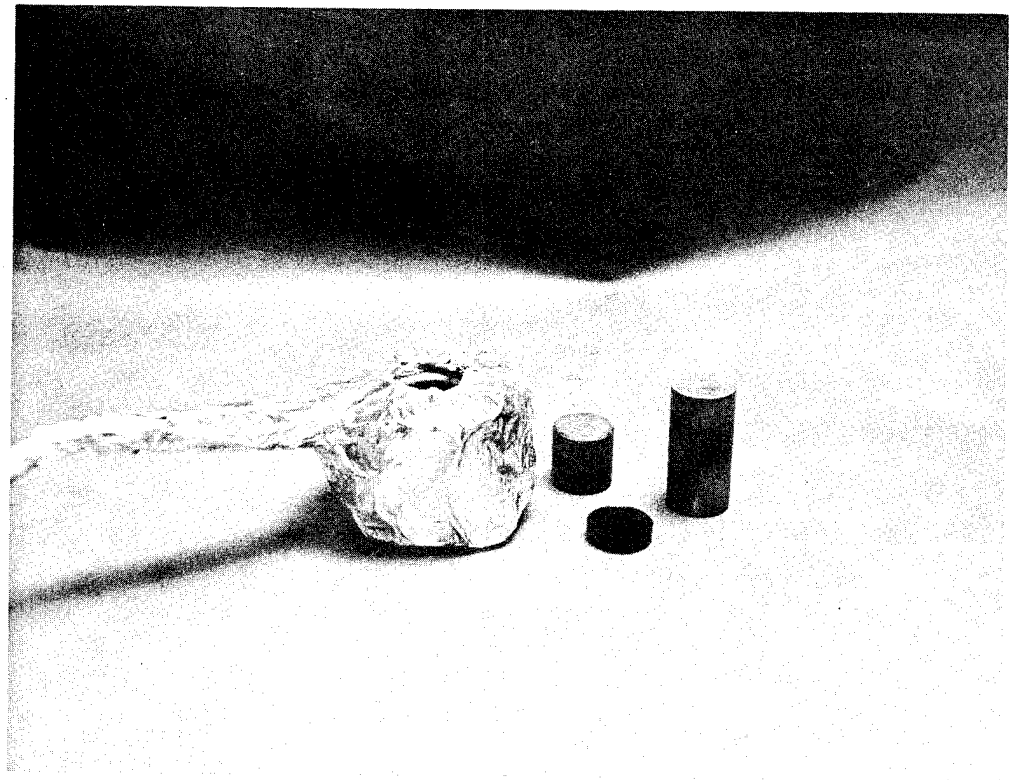


Figure 10. Assembled Mold and Heater Employed for Polyimide Fabrication

The compression molding investigation employing the experimental arrangement described above is discussed in Section 4.2.2.

4.2.2 Compression Molding Process Investigation

An investigation was conducted to determine processing cycles suitable to yield neat resin compression molded discs possessing structure essentially free of defects in terms of voids and microcracks. This study employed polyimide molding powders prepared by the process described in Section 4.1. The fabrication hardware employed was described in the preceding section.

Prior compression molding screening studies conducted at General Electric (Reference 1) and TRW on the 4-BDAF/PMDA, established that very high processing conditions were required to fabricate neat resin samples possessing acceptable consolidation. This prior work, employing temperatures up to 755°K (900°F) and pressures up to 34 MPa (5000 psia), did not consistently yield zero defect specimens. However, the effort did indicate that a minimum polyimide specific gravity of 1.4 was achievable. This prior work provided the baseline information for the effort conducted in this program. In addition to an initial prior processing history, the 4-BDAF/PMDA polyimide was available in significantly larger quantities than the new 4-BDAF/6-FDA, 2-Cl-4-BDAF/PMDA and 2-Cl-4-BDAF/6-FDA candidates. Therefore, this control resin was selected to initiate the compression molding investigation.

Screening of the polyimide candidates to melt or become tacky was performed in the tooling at temperatures up to 783°K (950°F). It was observed that the 4-BDAF/PMDA and 4-BDAF/6-FDA polymers exhibited a tendency to become somewhat tacky in the temperature range of 700°K to 755°K (800°F to 900°F) in the absence of pressure. A charring type of decomposition was observed above 755°K. The 2-Cl-4-BDAF/PMDA and 2-Cl-4-BDAF/6-FDA candidates developed only a slight degree of tack up to 755°K. On heating from 644°K to 755°K, each polyimide candidate was observed to emit volatile matter up to approximately 700°K (850°F), which is a common occurrence with linear condensation polyimides indicative of further polymerization at these extremely high temperatures.

These measurements and observations strongly suggest that the molding process investigation should employ the following conditions:

- "Bump" the molding powder frequently until a temperature of 700°K is attained
- Apply pressure once the resin powder has reached a temperature of 700°K

Subsequent screening of molding cycles determined that frequent bumping up to 700°K is required. Molding cycles which employed little or no bumping consistently yielded highly voided specimens. Application of pressure at temperatures below 700°K likewise yielded voidy molded products.

Screening studies were also conducted to assess the effect of the initial temperature at which the mold was charged with powder. The tooling heat-up rate was held constant at approximately 1.5°C (2°F)/minute up to 689°K to 700°K which was the maximum rate obtainable with the Ogden barrel heater described in Section 4.2.1. It was determined that the temperature at which the mold was charged was not a significant factor in the process. A temperature of 561°K (550°F) was subsequently selected to charge the mold. This temperature minimized personnel safety risk when protective equipment was worn and held the tooling heat-up time required to approximately 60 minutes.

Molding pressures were screened over the range 13.6 MPa (2000 psia) to 68 MPa (10,000 psia), employing temperatures in the range of 700°K (800°F) to 755°K (900°F). It was determined that a pressure of 40.8 MPa (6000 psia) was required to give essentially zero defect molded discs possessing a maximum specific gravity of 1.45.

The results of the compression molding screening study were employed to define a promising and reproducible molding cycle for the 4-BDAF/PMDA polyimide. This molding cycle is summarized in Table 10. These processing conditions were employed to reproducibly produce very low defect content discs with a diameter of 2.54-cm (1-inch) and a thickness of up to 0.64-cm (0.25-inch). The discs consistently possessed a specific gravity in the range of 1.42 to 1.45. Photomicrographs of a representative, sectioned disc are presented in Figures 12 and 13.

Figure 12. 4X Photomicrograph of Sectioned Polyimide Disc.

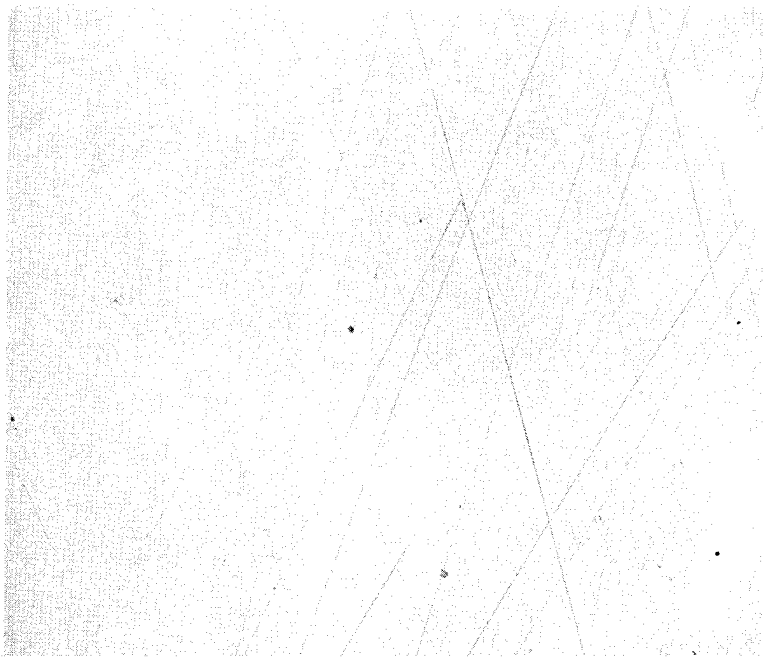


Figure 13. 50X Photomicrograph of Sectioned Polyimide Disc.

TABLE 10

SUMMARY OF THE REPRODUCIBLE MOLDING CYCLE
DEFINED FOR NEAT RESIN FORMULATION 4-BDAF/PMDA

Time at Temperature (minutes)	Bumping Cycles Performed [0 to 40.8 MPa (6000 psi)]	Mold Temperature (°K/°F)[a]
0 to 30	8	557°K/544°F to 607°K/633°F
31 to 60	9	607°K/633°F to 658°K/725°F
61 to 100	8	658°K/725°F to 689°K/780°F
101 to 120	0[b]	689°K/780°F to 725°K/846°F
121 to 150	0[b]	725°K/846°F to 729°K/853°F
151 to 270	0[c]	729°K/853°F to 453°K/356°F

a) Average of three thermocouple measurements.

b) Pressure was applied constantly at 408 MPa.

c) Pressure was released at the end of this cooldown cycle

The same process given in Table 10 was successfully employed to compression mold essentially zero defect 2.54-cm x 0.64-cm neat resin discs from the new 4-BDAF/6-FDA polyimide candidate. The specific gravities measured on this polyimide ranged from 1.41 to 1.47.

Attempts to compression mold the new 2-Cl-4-BDAF/PMDA and 2-Cl-4-BDAF/6-FDA polyimide candidates by the process given in Table 10 were not successful. Varying the temperatures from 662°K (750°F) to 755°K (900°F) and pressures up to 68 MPa (10,000 psia) likewise did not yield consolidated specimens. Examination of the easily breakable discs obtained gave evidence

that very little melt-like consolidation had occurred during the molding attempts. At molding temperatures greater than 755°K, these resins appeared to char in a like manner to the 4-BDAF/PMDA and 4-BDAF/6-FDA candidates. On the basis of this molding process screening, the polyimide candidates prepared from the new 2-Cl-4-BDAF diamine do not appear to be promising matrix resin candidates for 644°K service.

The compression molding process defined for the 4-BDAF/PMDA and 4-BDAF/6-FDA polyimides was successfully employed to prepare larger diameter discs for the oxidative aging studies.

5.0 NEAT RESIN THERMO-OXIDATIVE STABILITY

This section describes the work conducted to compression mold test specimens, determine promising postcure cycles giving high glass transition temperatures and isothermal aging of candidate polyimide moldings at 616°K (650°F) and 644°K (700°F) under compressed air temperatures of up to 0.4 MPa (60 psia) for durations up to 200 hours.

5.1 COMPRESSION MOLDING OF POLYIMIDE TEST SPECIMENS

The neat resin powder preparation process described in Section 4.1 and the compression molding process summarized in Table 10 were employed to fabricate 4-BDAF/6-FDA and 4-BDAF/PMDA polyimide discs in sufficient quantities to perform subsequent postcure, glass transition termperature and oxidative aging experimentation. This fabrication work involved molding of significantly larger neat polyimide discs than those prepared in the processing studies.

A Carver mold suitable for compression molding polyimide discs possessing a diameter of 6.34-cm (2.5-inches) was used. The tool was the same three piece design as that shown in Figure 9 in the previous section. This mold size was selected to accommodate the molding pressure capability of the press shown in Figure 9. As before, an Ogden barrel extrusion band heater, fitted with three thermocouple leads, was employed to heat the Carver mold to a tolerance of ± 2°C (±5°F).

The 6.34-cm diameter polyimide discs were molded into thicknesses from 0.25-cm (0.1-inch) up to 0.63-cm (0.25-inch). The discs were sectioned into four equal parts to assess the quality of each specimen in terms of the presence of microcracks or voids. Essentially zero defect moldings were obtained for each polyimide candidate in an average of 60% of the fabrication attempts. Polyimide specific gravities continued to average 1.42 or greater.

The polyimide discs that were judged to be acceptable were employed for resin postcure/glass transition temperature experimentation and subsequent isothermal oxidation studies.

5.2 POSTCURE STUDIES AND GLASS TRANSITION TEMPERATURE DETERMINATIONS

The 4-BDAF/6-FDA and 4-BDAF/PMDA compression molded polyimide specimens demonstrating very low defects and acceptable specific gravities were subjected to postcure to attempt to obtain a desired glass transition temperature of greater than 644°K (700°F). The postcure studies were structured from prior TRW studies conducted on 4-BDAF/PMDA.

Prior work conducted at TRW showed that a postcure for 4-BDAF/PMDA polyimide of up to twenty-four hours at temperatures in the range of 644°K (700°F) to 672°K (750°F) in air was sufficient to yield neat resin glass transition temperatures (Tg) of greater than 644°K. The Tg measurements were performed by a Du Pont Model 990 thermalmechanical analysis (TMA) instrument operating in an expansion mode. In the prior work, no attempt was made to achieve a Tg greater than 644°K while holding weight loss on postcure to one percent or less.

In this program, minimum postcure conditions in air were investigated for the 4-BDAF/PMDA polyimide that would yield the desired Tg of greater than 644°K and confine weight loss to a maximum of approximately one percent. It was determined that postcure conditions consisting of sixteen hours in air at 644°K gave an acceptable Tg by TMA analysis of 658°K (385°C or 725°F). Neat resin weight loss under these conditions was confined to 0.9%, which is deemed to be an acceptable level. A representative TMA scan for 4-BDAF/PMDA is presented in Figure 12.

Similar postcure conditions were performed on the 4-BDAF/6-FDA polyimide candidate. However, postcure conditions, based upon the 4-BDAF/PMDA work, could not be established that yield a Tg by TMA analysis greater than 577°K (304°C or 580°F). A representative TMA scan for 4-BDAF/6-FDA is presented in Figure 13. Program schedule requirements did not allow an exhaustive matrix of postcure conditions to be investigated for this polyimide candidate. However, it is held to be unlikely that a neat resin Tg approaching the desired 644°K or greater can be achieved for the 4-BDAF/6-FDA polyimide. This speculation is based upon work conducted at General Electric (Reference 1) on DuPont NR-150B polyimides which are based on the 6-FDA dianhydride

(Reference 2). The General Electric investigation showed that a postcure employing conditions of twenty-four hours or less at 630°K (357°C or 625°F) was sufficient to give a Tg of up to 633°K (360°C or 680°F). These General Electric results strongly suggest that linear condensation polyimides prepared from the 6-FDA dianhydride, such as NR-150B resins and the 4-BDAF/6-FDA candidate, attain a high or near-maximum Tg rapidly at high temperatures.

Although the experimental data base is limited, the lower than anticipated Tg obtained for 4-BDAF/6-FDA may infer a basic phenomena is operating in the Tg property to be expected in linear condensation polyimides. This phenomena may be described as an odd-even effect in total aromatic rings in the polymer backbone repeat segment. Evidence now exists that this behavior particularly manifests itself when a four ring diamine, such as 4-BDAF, is employed as a reactant. As stated previously in this report, linear condensation polyimides prepared from 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA-this monomer, like 6-FDA, also contains two aromatic rings) and 4-BDAF diamine also possess an expectedly low Tg of 580°K (307°C or 585°F). Thus, 4-BDAF/6-FDA and 4-BDAF/BTDA, which both contain an even number of six aromatic rings in the polyimide backbone repeat unit, possess a Tg of less than 589°K (316°C or 600°F). In contrast, 4-BDAF/PMDA, which contains an odd number of five aromatic rings in the polyimide repeat segment, repeatedly has been determined to possess a Tg that is significantly higher, such as the 685°K (385°C or 725°F) temperature discussed previously.

The preliminary data suggesting that a significant odd-even aromatic ring effect on expected Tg is operational in polyimides prepared from 4-BDAF is recommended for future study. Polyimides prepared from dianhydrides other than PMDA (or dianhydrides containing three aromatic rings in the backbone) may possess a combination of higher oxidative stability and Tg than those determined for 4-BDAF/PMDA. It is felt that both superior weight retention at 644°K and a Tg greater than 644°K is required for an outstanding structural matrix resin for long-term service in air at 644°K.

Regardless of the relative importance of Tg, both the 4-BDAF/6-FDA and 4-BDAF/PMDA polyimides displayed initial promise for up to 200 hour

service at 644°K in extreme oxidative environments up to compressed air pressures of 0.4 MPa (60 psia).

5.3 THERMO-OXIDATIVE STABILITY INVESTIGATION

The compression molded specimens of polyimide candidates 4-BDAF/6-FDA and 4-BDAF/PMDA were subjected to isothermal aging studies in air at 644°K (700°F) at ambient and 0.4 MPa (60 psia) air pressures for up to 200 hours.

5.3.1 Isothermal Aging at 644°K at Ambient Air Pressure

The two polyimide candidates were isothermally aged in ambient pressure air at 644°K (700°F) for 200 hours. Each polyimide candidate displayed very promising oxidative stability under these severe conditions.

A maximum weight loss average of 9.5% occurred for the 4-BDAF/PMDA after the 200 hour aging period. The 4-BDAF/6-FDA candidate showed a maximum average weight loss of 15.0% after the 200 hour aging point. These data and intermediate duration weight losses are presented in Table 11.

5.3.2 Isothermal Aging at 644°K at 0.4 MPa Air Pressure

The two polyimide candidates were isothermally aged in 0.4 MPa (60 psia) pressure at 644°K (700°F) for one hundred hours. An average weight loss of 27.5% was obtained for the 4-BDAF/PMDA polyimide and 21.1% for the 4-BDAF/6-FDA polyimide. These results are summarized in Table 11.

TABLE 11

SUMMARY OF ISOTHERMAL AGING OF NEAT RESINS AT 644°K (700°F) IN AIR

Polyimide Candidate	Percent Weight Loss on Postcure[a), c)]	Percent Weight Loss on Isothermal Aging in Air at 644°K[b), c)] Determined at 0.1 MPa 24 Hours	48 Hours	108 Hours	160 Hours	208 Hours	Determined at 0.4 MPa[d)] 100 Hours
4-BDAF/PMDA	0.9	0.5	1.0	2.9	5.6	9.5	27.5
4-BDAF/6-FDA	1.0	1.2	2.2	5.6	9.6	15.0	21.1

a) The samples were postcured in air at 644°K for 16 hours.

b) The aging was done in a Blue M CFD-10F-4 oven employing an airflow rate of 10 cc/second.

c) The values are averages of measurements on duplicate samples.

d) The 0.4 MPa tests were conducted at General Electric Aircraft Engine Group employing an airflow rate of 10 cc/second.

6.0 CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations are presented below as derived from this program to investigate improved high temperature resistant matrix resins suitable for service at 644°K (700°F) in extreme oxidative environments of up to 0.4 MPa (60 psia) compressed air pressures.

6.1 CONCLUSIONS

This experimental investigation to identify, synthesize, fabricate and evaluate high temperature matrix resins for 644°K (700°F) service has yielded technical evidence from which the following conclusions are derived:

- Linear condensation polyimides which contain a perfluoroisopropylidene linkage in the polymer backbone have shown promising stability at 644°K (700°F) in extreme oxidative evnironments.
- Linear condensation polyimides prepared from 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (4-BDAF diamine) show promise for application in matrix resins for 644°K service in highly oxidative environments.
- The number of aromatic rings in the dianhydride employed in combination with 4-BDAF diamine appears to have a significant effect on the glass transition temperature obtained on specific ingredient combinations.

6.2 RECOMMENDATIONS

Based upon the experimental work performed on neat polyimide polymers on this program, the following recommendations are offered:

- The effect of fibrous reinforcement on resin dimensional and oxidative stability and thermo-mechanical properties should be investigated.
- The effect of anti-oxidants and resin surface treatments such as ion implanted surface coatings on 644°K (700°F) oxidative stability should be investigated.

- The effect of alternative polyimide polymerization routes and solvents on resin performance at 644°K should be investigated.

- The oxidatively and thermally susceptible linkages in the polymer should be identified and modifications made, where appropriate, to improve polymer performance at 644°K.

- The effect of alternative aromatic dianhydrides to pyromellitic (PMDA) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane (6-FDA) in combination with 4-BDAF diamine should be investigated.

7.0 REFERENCES

1. General Electric, Aircraft Engine Group, Evendale Facility, unpublished results.
2. H. H. Gibbs, 17th National SAMPE Symp., 17 III-B-6 (1972).
3. G. Zakrezewski, M. K. O'Rell, R. W. Vaughan and R. J. Jones, Final Report, Contract NAS3-17824, NASA CR-134900.
4. R. J. Jones, M. K. O'Rell and J. M. Hom, U.S. Patent 4,111,906 (1978).
5. R. J. Jones, M. K. O'Rell and J. M. Hom, U.S. Patent 4,203,922 (1980).

8.0 APPENDICES

This section presents representative experimental procedures employed to synthesize monomers and polymers on this program as discussed in Section 3. Also included are additional characterization spectra which were not shown in Section 3.

8.A. DIAMINE SYNTHESES

The experimental procedures employed to prepare 2-Cl-4-BDAF and 4-BPDA diamines are presented below.

Representative DSC, NMR and IR spectra for 2-Cl-4-BDAF diamine are presented as Figures 8.A.1, 8.A.2 and 8.A.3, respectively.

8.A.1 Preparation of 2,2-Bis[(2-chloro-4-aminophenoxy)phenyl]hexafluoropropane (2-Cl-4-BDAF)

8.A.1.1 Synthesis of 2,2-Bis[2-chloro-4-nitrophenoxy)phenyl]hexafluoropropane (2-Cl-4-BDNF).

In a 1000 mL 3-necked round bottom flask equipped with a magnetic stirring bar, Dean-Stark trap, condensor, heating mantle, and gas inlet adapter, was placed Bis-Phenol AF (112 g, 333 mmol) and sodium hydroxide (26.8 g, 670 mg-at) in dry N, N-dimethylacetamide (DMAc, distilled from calcium hydride, 500 mL) under argon atmosphere. The mixture was stirred and brought to reflux with azeotropic removal of water. After 20 hours, the water and toluene were removed by distillation, and the temperature of the dark burgundy-colored reaction mixture was lowered to 110°C. The solution of Bis-Phenol AF dianion was added hot (ca. 130-140°C) over 20-25 min to a stirred solution of 3,4-dichloronitrobenzene (128.6 g, 670 mmol) in dry DMAC (ca. 400 mL) under argon atmosphere. The temperature of the reaction mixture rose to 105-110°C. After addition was complete, the stirred mixture was heated at 105-120°C for 2 hours, then cooled to ambient temperature and poured onto water (2000 mL). The yellowish-brown solid that precipitated out was filtered, washed with ethanol, dissolved in a minimal amount of ethyl acetate (700 mL), then treated with ethanol (200 mL), and left to recrystallize.

The precipitate from above was filtered, washed once with ice-cold ethanol, pulverized and air-dried to yield glistening beige crystals (148 g, 229 mmol, 69% yield). Mp 160°C (DSC melting point, single peak). Infrared: 1345 cm^{-1} ($-NO_2$). Elemental analysis (% actual, theoretical in parentheses): C, 50.8 (50.1); H, 2.4 (2.2); n, 5.4(4.3); O, 14.8(14.8); Cl, 10.5(11.0); F, 17.7(17.6).

8.A.1.2 Synthesis of 2,2-Bis[(2-chloro-4-aminophenoxy)phenyl]hexafluoropropane(2-Cl-4-BDAF).

The 2-Cl-4-BDNF (23.48 g, 364 mmol) was dissolved in ethyl acetate (350 ml). 5% Palladium on carbon (Alfa, 1.45 g, equivalent of 0.7 mmol Pd, 1.9 mol %) was added, and the mixture treated with hydrogen in a Parr reactor. Theoretical uptake of hydrogen was observed within 4-8 hours. The mixture was filtered, and the supernatant concentrated to yield a beige-colored solid (21.4 g, 100% crude yield), homogeneous by tlc, m.p. 201°C (Fisher-Johns, uncorrected), 200°C (endotherm in differential scanning calorimetry). IR: 3640 cm^{-1} (> N-H), no trace of $-NO_2$ absorption. Elemental analysis (% actual, theoretical in parentheses): C, 56.1 (55.2); H, 3.3 (3.1); N, 5.9 (4.8); O, 7.8 (5.4); Cl, 11.5 (12.1); F, 18.3 (19.4). Amine number (meq/g; theoretical in parentheses): 5.12 (5.43).

8.A.2 Preparation of 4,4'-(4-Aminophenoxy)biphenyl (4-BPDA).

8.A.2.1 Synthesis of 4,4'-(Nitrophenoxy)biphenyl (4-BPDN).

In a 1-liter 3-necked round-bottom flask equipped with magnetic stirring bar, condensor, Dean-Stark trap, thermometer, and gas inlet adapter was placed p,p-biphenol (Buffalo Color Corporation, 37.2 g, 200 mmol) and sodium hydroxide (16 g, 400 mmol) in dry N,N-dimethylacetamide (DMAc, distilled from barium oxide, 250 mL) under argon atmosphere. The stirred mixture was brought to reflux with azeotropic removal of water. After 21 hours, the water and solvent were removed by distillation, and the white suspension of the salt was kept at 135-14°C. Then, under vigorous stir, 4-chloronitrobenzene (63.4 g, 400 mmol) was added portionwise rather quickly (5-7 min). The mixture became reddish, foamy, and exothermic during addition. Temperature was maintained at 155°C by rate of addition. After the addition was complete and the exotherm had subsided, the stirred

mixture was maintained at 150°C for 3 days, then cooled to room temperature and poured onto water (1200 mL). The precipitated yellow solid was filtered off, washed well with ice-cold ethanol, and air-dried (80.8 g, 94.4% crude yield). It was homogeneous by analytical thin-layer chromatography (silica gel, 60:40 hexanes: benzene, R_f = 0.092). M.p. 193-195°C (Fisher-Johns, uncorrected); 195°C (somewhat broad endotherm, differential scanning calorimetry). IR: 1330, 1340 cm^{-1} ($-NO_2$). Elemental analysis (%, actual; theoretical in parentheses): C, 68.8 (67.3); H, 4.2 (3.7); N, 6.4 (6.6); O, 22.2 (22.4).

8.A.2.2 Synthesis of 4,4'-(4-Aminophenoxy)biphenyl (4-BPDA).

The crude 4-BPDN (21.5 g, 50 mmol) was suspended in dimethylformamide (200 mL) along with 5% palladium on carbon (Alfa, 1.0 g, 1 mol % Pd). The suspension was treated with hydrogen in the Parr reactor. Theoretical uptake of hydrogen was observed in 3 hours. The mixture was filtered, and the supernatant was concentrated *in vacuo* at elevated temperature to yield a gray solid. The solid was pulverized, washed well with ice cold ethanol, and air dried to yield 17.4 g of material (47.3 mmol, 94.2% yield). M.p. 200-201°C (Fisher-Johns, uncorrected), IR: 3380 cm^{-1} (> N-H; no $-NO_2$ band present). Elemental analysis (% actual, theoretical in parentheses): C, 78.1(78.3); H,5.7(5.4); N, 7.5(7.6); O. 9.8(8.7). Amine number (meq/g, theoretical in parentheses): 3.32(3.41).

8.B POLYIMIDE SYNTHESIS

A representative synthesis procedure employed to prepare 2-Cl-4-BDAF/PMDA is given below.

8.B.1 Synthesis of 2-Cl-4-BDAF/PMDA Resin:

In a flame-dried 100-ml 4-necked resin kettle equipped with overhead stirrer and gas inlet adapter was dissolved 2-Cl-4-BDAF (10.0g, 17 mmol) in distilled dimethylacetamide (41 g) under argon atmosphere. Then PMDA (3.71 g, 17 mmol) was added portionwise over ca. 7 minutes (25% w/w solids content). After all the PMDA was added, themixture became somewhat warm and viscous. The mild exotherm subsided after ca. 30 minutes, and the viscous amber-colored solution was stirred for 2 more hours, then decanted into a container.

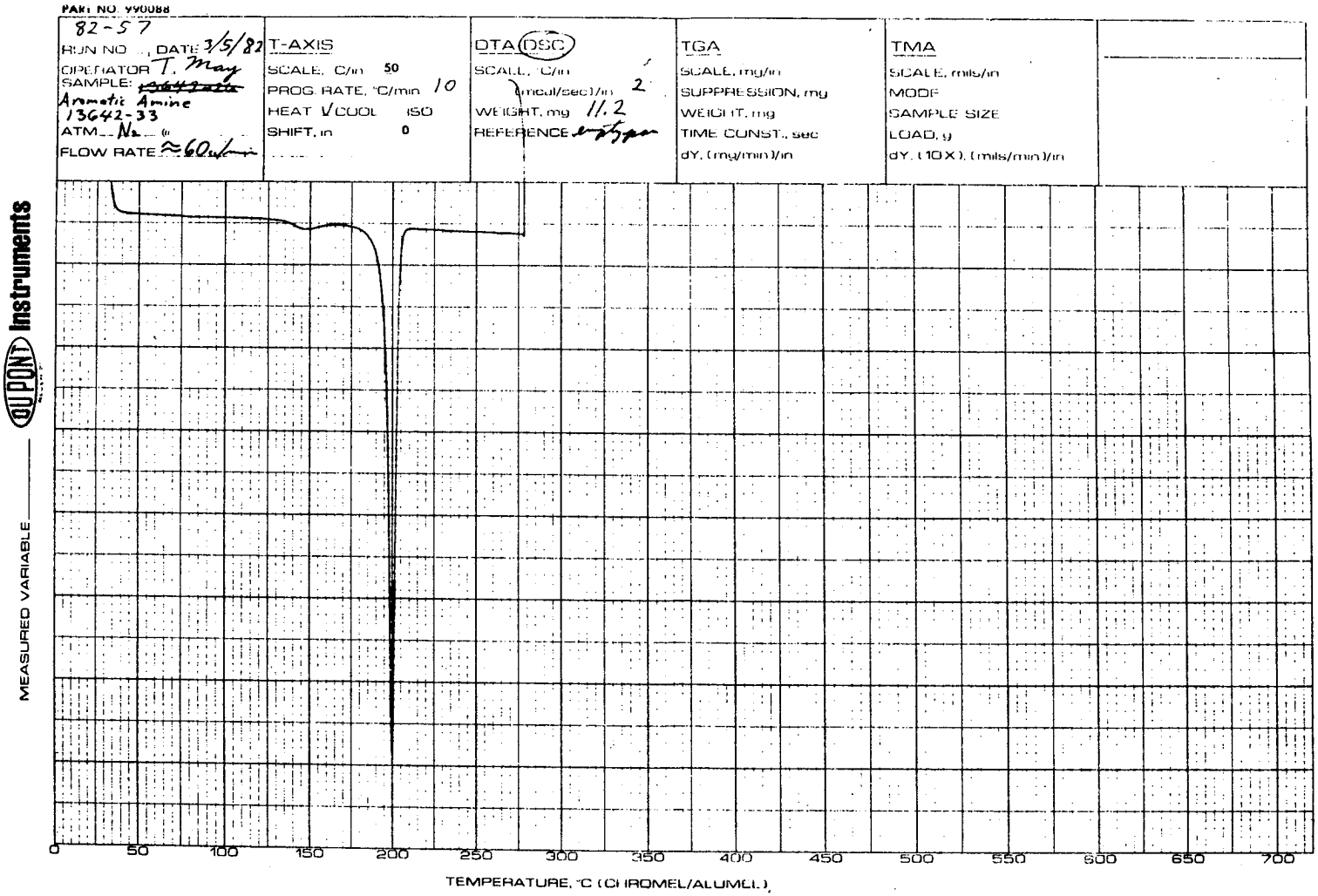


Figure 8.A.1. Differential Scanning Calorimeter Tracing Obtained for 2-Cl-4-BDAF Diamine.

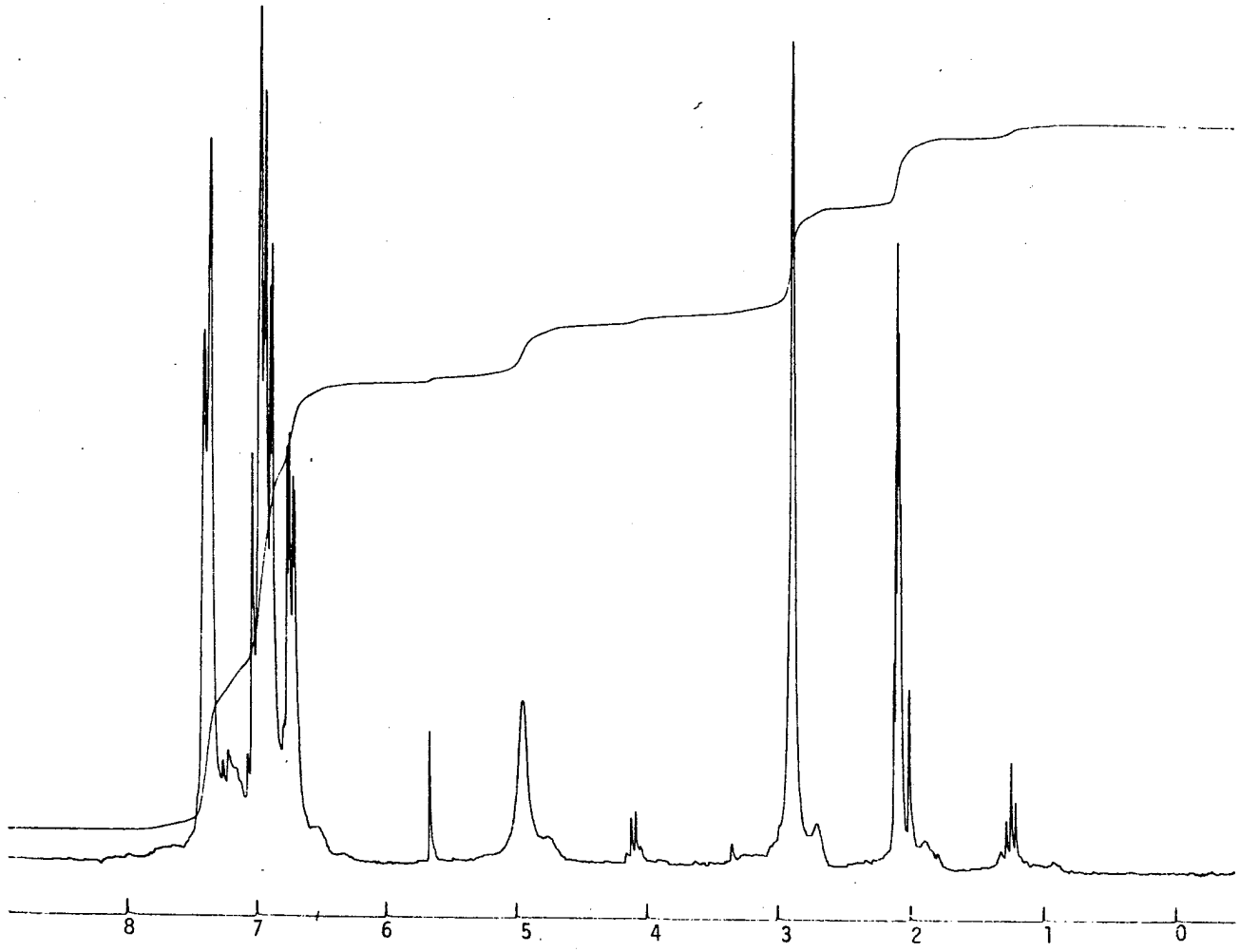


Figure 8.A.2. Nuclear Magnetic Resonance Spectrum Obtained for 2-Cl-4-BDAF Diamine.

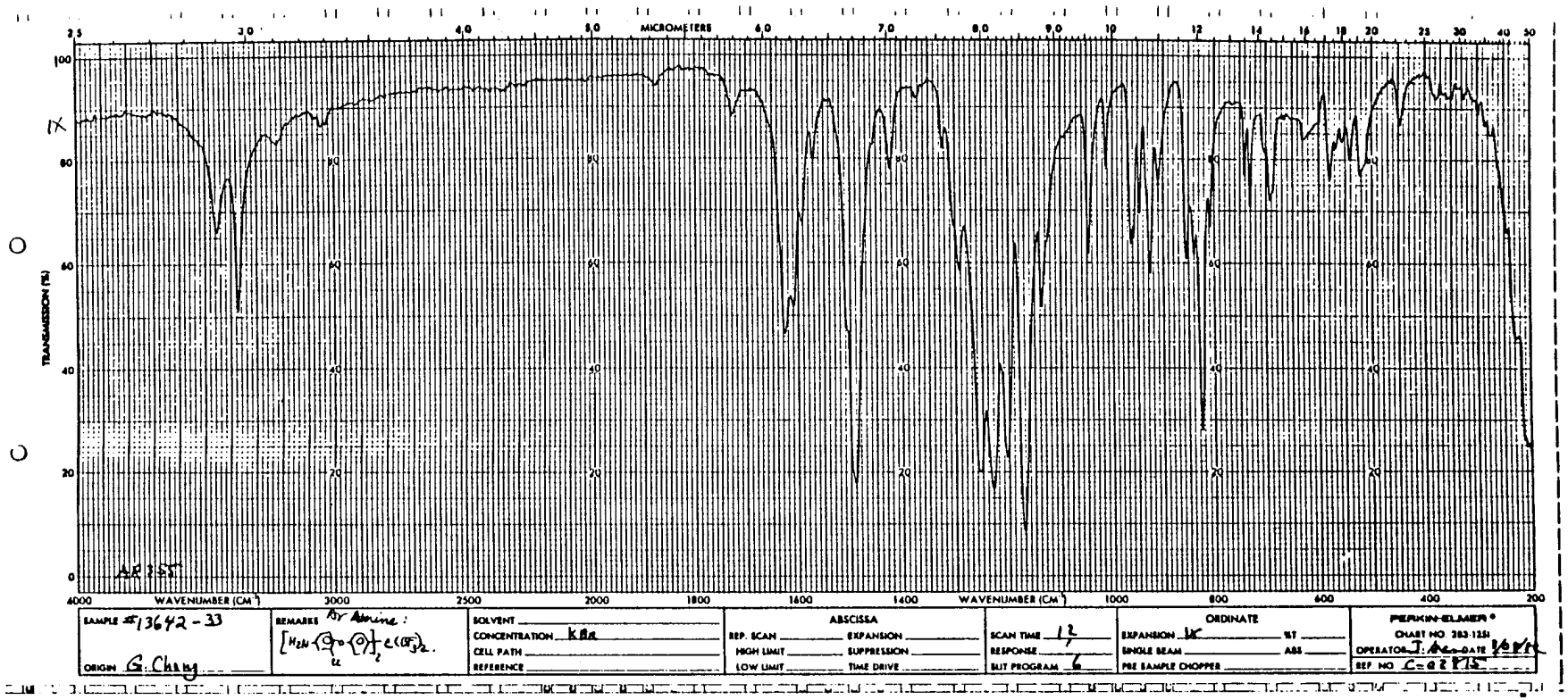


Figure 8.A.3. Infrared Spectrum Obtained for 2-Cl-4-BDAF Diamine.

8.B.2 Imidization and Postcure of 2-Cl-4-BDAF/PMDA:

A several-gram sample of the 25% w/w solution of 2-Cl-4-BDAF/PMDA in DMAC was placed in an aluminum dish (6 cm diameter x 2.6 cm height) and put in a vacuum oven. Heating and partial vacuum was applied to remove solvent, then increased to 200°C and $\leq$ 1 mm Hg for 3 hours to effect imidization.

The imidized resin sample was then postcured in an air-circulating oven at 400°C for 4 hours to yield a reddish-brown, tough, flexible film.

Representative GPC tracings for the polyimide candidates investigated in this program are presented in Figures 8.B.1 through 8.B.6.

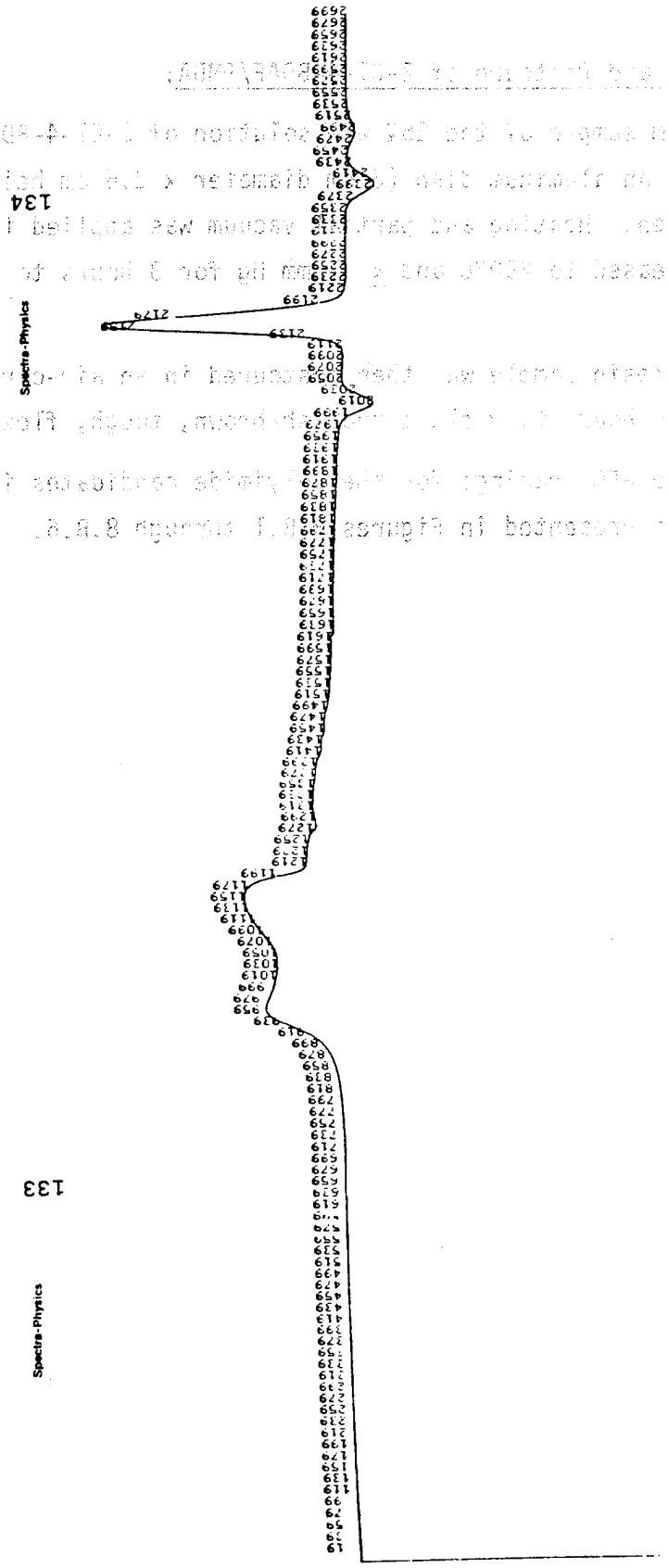


Figure 8.B.1. Gel Permeation Chromatograph of 4-BDAF/PMDA (Control).

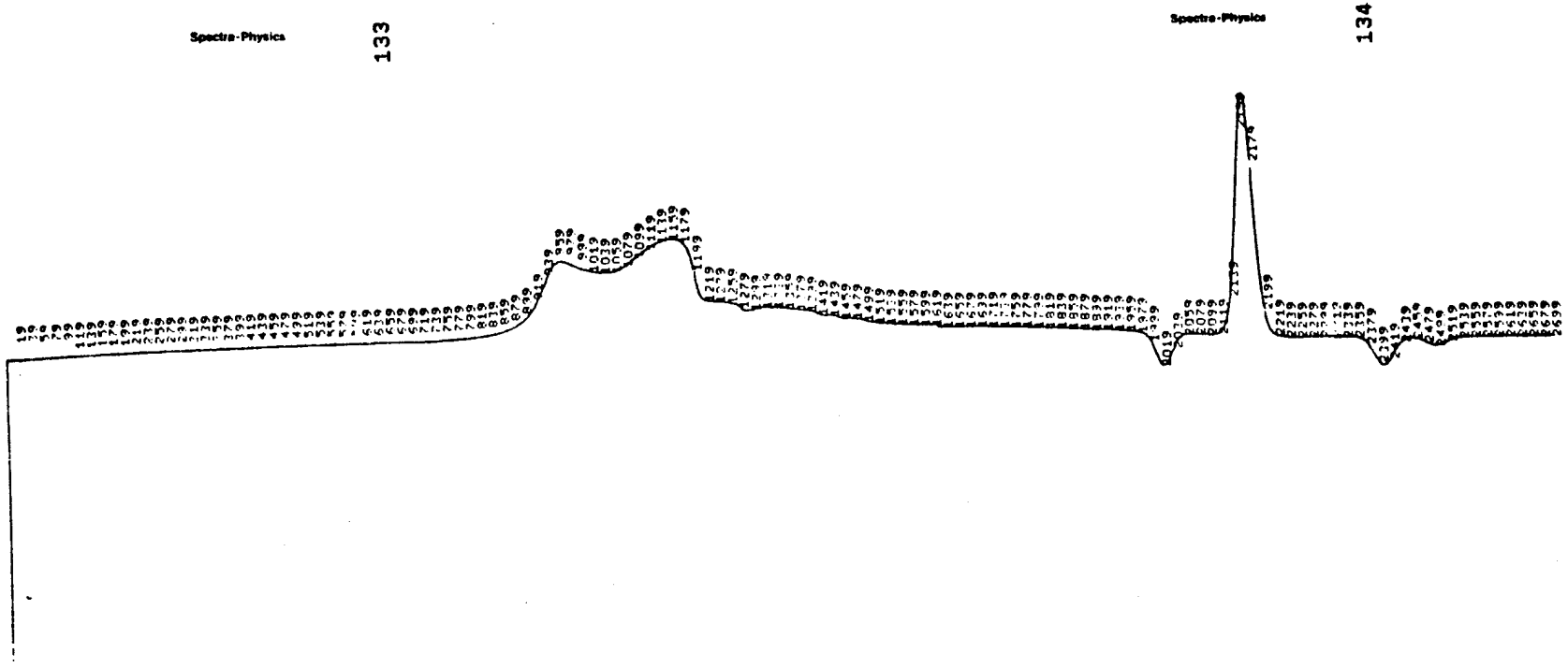


Figure 8.B.2. Gel Permeation Chromatograph of 2-Cl-4-BDAF/PMDA.

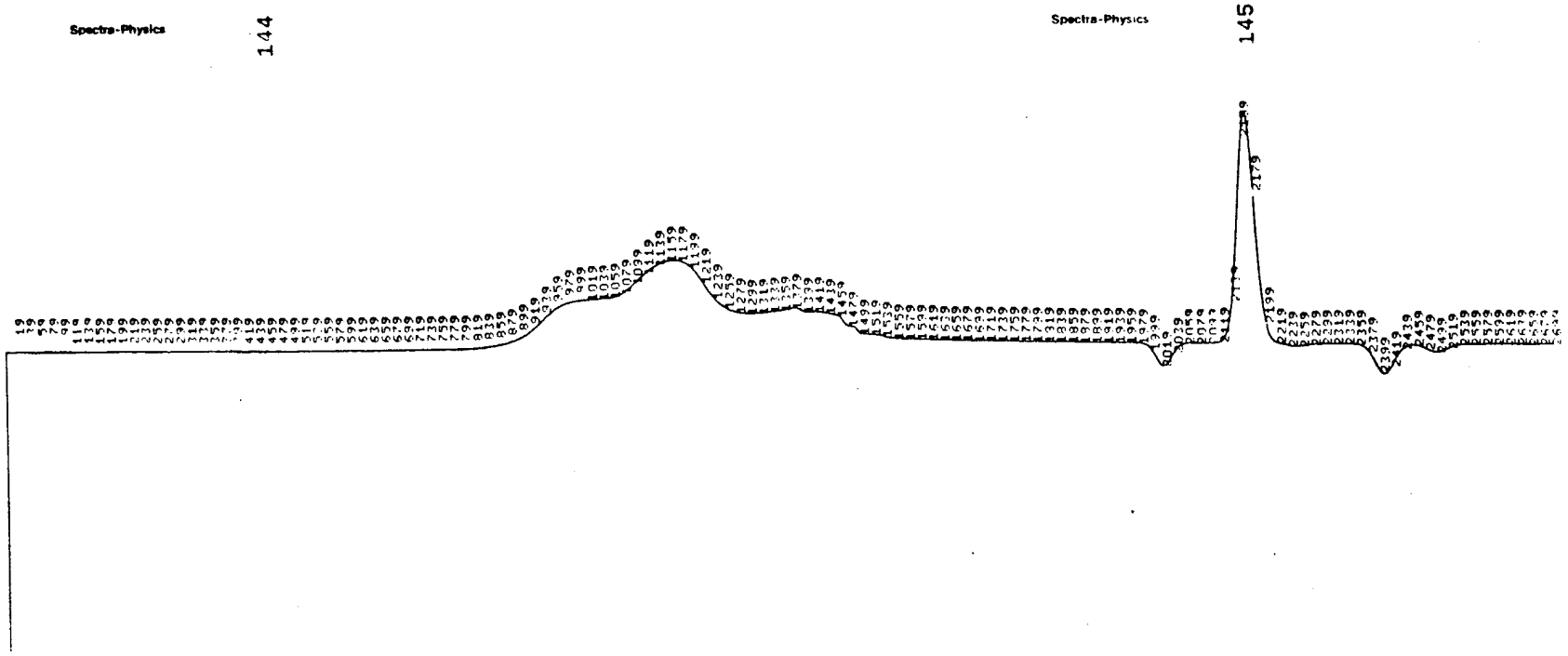


Figure 8.B.3. Gel Permeation Chromatograph of 2-Cl-4-BDAF/6-FDA.

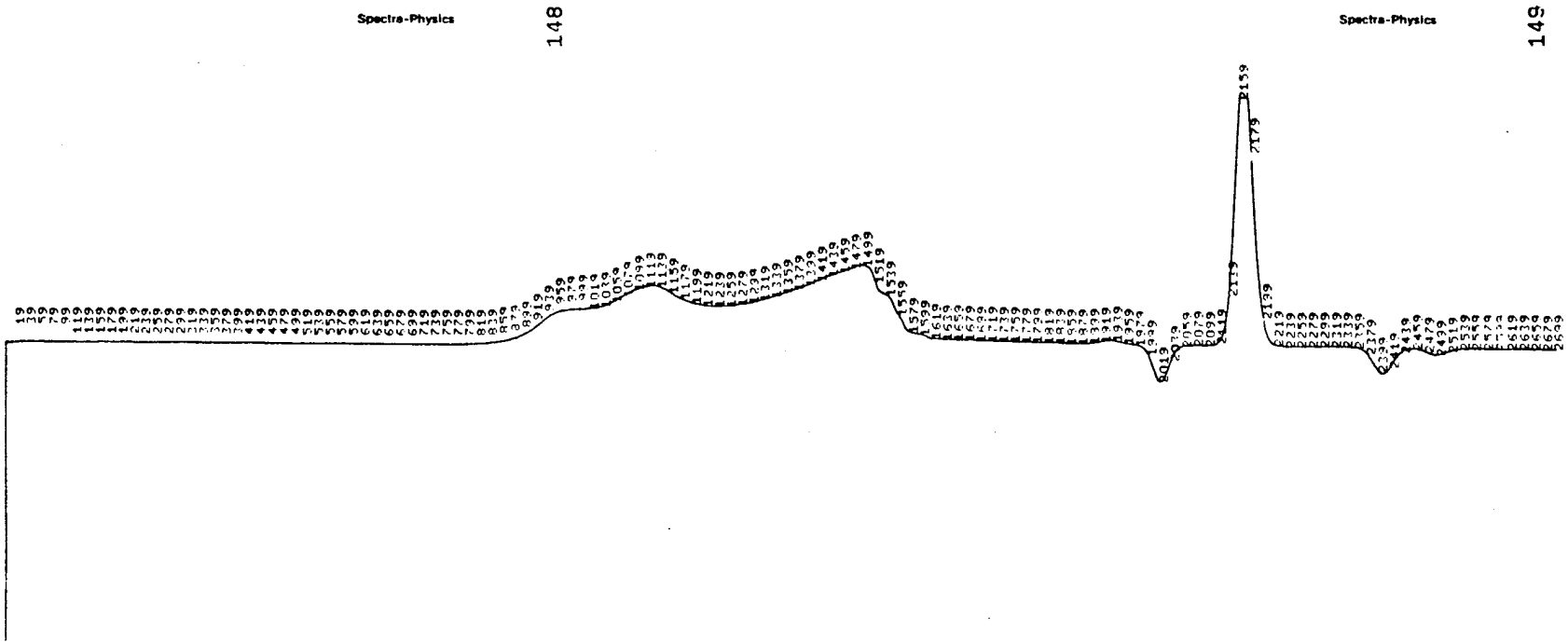


Figure 8.B.4. Gel Permeation Chromatograph of 4-BDAF/6-FDA.

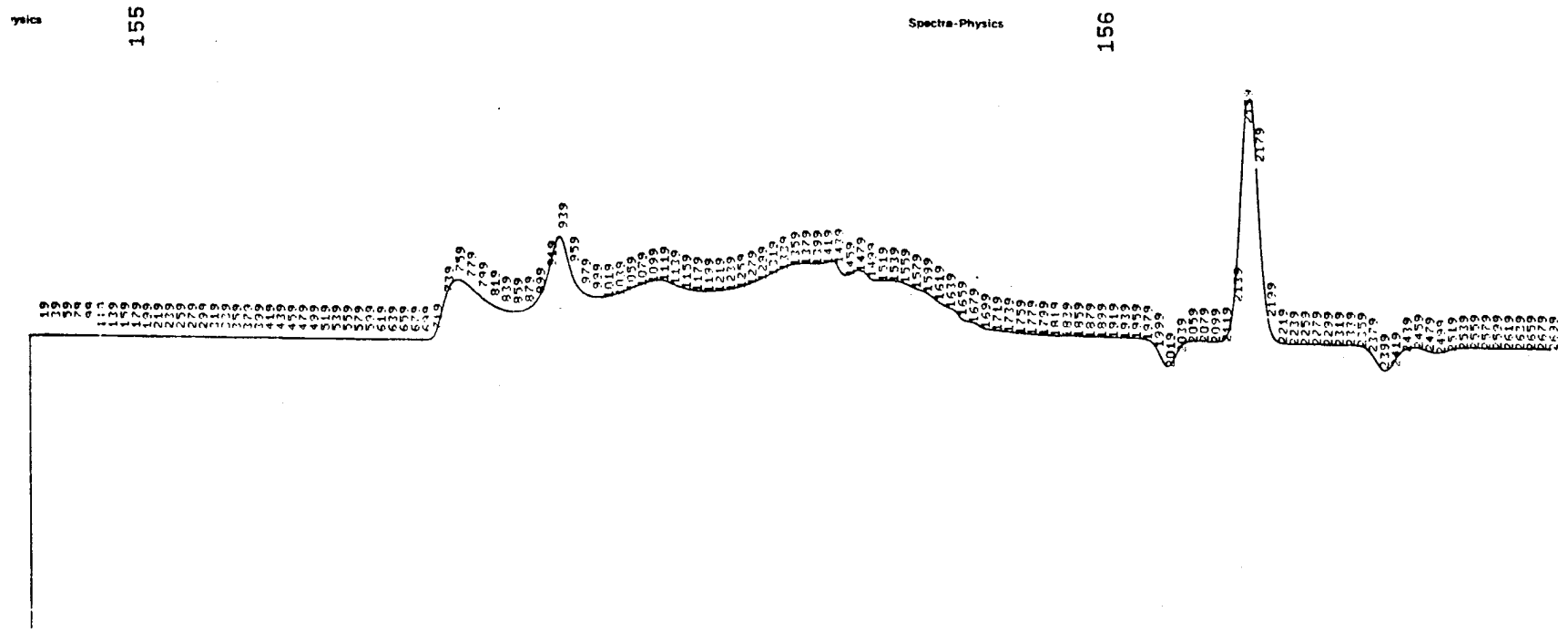


Figure 8.B.5. Gel Permeation Chromatograph of 4-BPDA/PMDA.

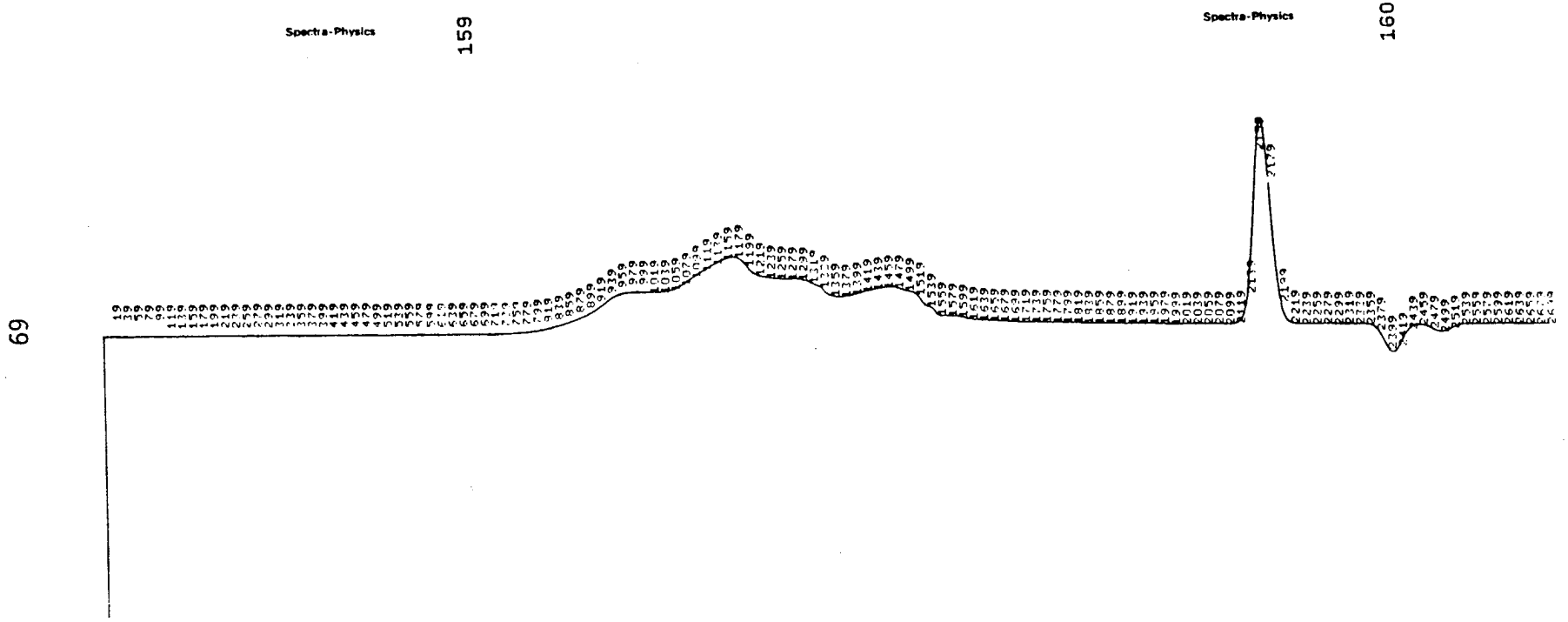


Figure 8.B.6. Gel Permeation Chromatograph of 4-BPDA/6-FDA.

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