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THERMALLY STABLE LAMINATING RESINS

by

E. A. Burns, R. J. Jones, R. W. Vaughan and W. P. Kendrick

TRW
SYSTEMS GROUP
ONE SPACE PARK • REDONDO BEACH • CALIFORNIA

prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center

Contract NAS3-12412

Tito T. Serafini, Project Manager

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FINAL REPORT

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17 January, 1970

Contract NAS3-12412

NASA Lewis Research Center
Cleveland, Ohio

Tito T. Serafini, Project Manager
Materials Sciences Branch

FOREWORD

This document constitutes the final report for the work accomplished between 17 September 1968 and 17 November 1969 by TRW Systems for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-12412 on Thermally Stable Laminating Resins.

This work was conducted under the technical direction of Dr. Tito Serafini of the Lewis Research Center, Cleveland, Ohio.

The Chemical Research and Services and Chemical Technology Departments of the Chemistry and Chemical Engineering Laboratory, Science and Technology Division was responsible for the work performed on this program. Mr. B. Dubrow, Manager, Chemistry and Chemical Engineering Laboratory provided overall program supervision and Dr. E. A. Burns, Manager, Chemical Research and Services Department was Program Manager. The Principal Investigator responsibilities for the program were shared: Dr. R. J. Jones during the major portion of the program and Mr. H. R. Lubowitz during the initial phases. Major technical contributions throughout the program were provided by Mr. R. W. Vaughan and Mr. W. P. Kendrick. Acknowledgment is made of the technical assistance provided during the program by the following TRW Systems personnel.

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ABSTRACT

The TRW A-type polyimide resin and resin reinforced composites were investigated. Detailed synthesis and characterization studies were conducted which defined a realistic mechanism of pyrolytic polymerization employing model compounds and identified a superior A-type polyimide formulation from six candidate prepolymers and polymers. E-glass laminate processing and characterization studies employing the identified polyimide formulation, were conducted together with studies of high performance, high modulus graphite reinforced composites.

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SUMMARY

This report is the final program report describing the work performed by TRW Systems for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-7949. The principal objective of this program was to develop thermally stable laminating resins (minimum 450°F) that possess improved processability over that of currently available polymers. This objective was accomplished with a) support of detailed studies which determined a postulated pyrolytic polymerization mechanism through synthesis and characterization of model compounds and their pyrolyzed products, b) polymer synthesis and characterization studies, c) preliminary glass reinforced prepreg and laminate fabrication studies, and d) evaluation of graphite fiber reinforced composite properties.

The first phase of the work involved the synthesis and characterization of model compounds. In this study two model imides which simulate the TRW A-type polyimide prepolymers were synthesized, characterized and subsequently subjected to detailed pyrolysis studies in the temperature range of 250°C - 350°C. The linear polymers prepared by the pyrolysis studies were characterized in detail and the results permitted interpretation of the pyrolytic polymerization mechanism. From these studies it was postulated that the A-type polyimide model compound, N-phenyl nadimide was polymerized by an addition-type reaction encompassing first a partial reverse Diels-Alder reaction to give free cyclopentadiene and N-phenyl maleimide followed by the <u>in situ</u> co- and terpolymerization of the fragments and unreacted model compound. It was established that a temperature of >275°C is required to convert the model compound to polymeric structures. From these studies the nadimide end group was selected as an efficient reactive species for the pyrolytic polymerization.

The second phase consisted of investigations involving candidate prepolymers. Screening and characterization studies of six A-type polyimide prepolymers derived from a combination of aromatic dianhydrides and aromatic diamines were conducted to select specific ingredients providing the most promising candidate material based on thermo-oxidative and hydrolytic stability as well as processing considerations. Several prepolymers of different formulated molecular weights were prepared and the polymerized products were characterized to determine the effect of prepolymer molecular weight on polymer properties.

From these screening studies the selection of an A-type polyimide formulation having 1000 molecular weight consisting of nadic anhydride end groups, methylene dianiline and pyromellitic dianhydride (NA/MDA/PMDA) was selected as the most promising prepolymer. This selection was based on the results of processability, thermo-oxidative stability and hydrolytic stability determinations.

In the third phase of this project preliminary fabrication studies were conducted 1) to determine processing conditions which resulted in acceptable prepregs suitable for preparation of glass reinforced laminates, and 2) to establish molding conditions which gave the best combination of glass reinforced laminates properties. Prepreg processing conditions of four minutes drying at 325°F and two minutes imidization at 475°F were selected based on a previously determined volatile matter/resin content ratio, flow properties and general appearance. Process molding conditions which showed the best combination of flexural properties at room temperature and 550°F, room temperature shear strength and minimum void contents by statistical evaluation were 600°F molding temperature, 1000 psig applied mechanical pressure, 30 minutes processing duration and no post cure.

Because of the significant progress achieved in identifying a material having superior high temperature properties with glass reinforced laminates, the original scope of the fourth phase of the program was modified to permit acquisition of detailed property data from laminates prepared using Thornel 50S high modulus graphite fiber and the 1000 formulated molecular weight NA/MDA/PMDA resin. Graphite fiber reinforced prepreg was prepared using a drum winding, spray gun application procedure (previously developed for boron reinforced prepregs). The unidirectional prepreg prepared by this technique had excellent collimation and showed no apparent yarn fraying.

After some cursory examinations of imidization processes, it was decided not to use a distinct separate imidization procedure but rather imidize the prepreg in situ during the molding cycle. In a brief screening study of the cure temperature, cure pressure and dwell time variables, the best combination of molding conditions were determined to be 600°F temperature, 500 psig pressure, and 50 seconds dwell time. Techniques were developed involving control of cool-down rate and utilization of an oversize mold to compensate for expansion of the graphite fiber on cooling; this methodology permitted preparation of crack-free Thornel 50S graphite fiber reinforced composites.

Room temperature properties of these composites had flexural strength and modulus values of 105 Ksi and 23 Msi, respectively, and 5 Ksi shear strength. Aging the specimens at 400°F for over 1000 hours showed negligible affect on properties. At 600°F the flexural strength retention was ∿80%, flexural modulus retention was ∿85% and the shear strength retention was ∿74%. Aging the specimens at 600°F caused significant degradation of mechanical properties. This finding was contrary to the observation of the stability of the neat resin. A detailed analysis of this observation showed that the properties of specimens aged at elevated temperature in air are highly dependent on the surface area to volume ratio and the rate of air flow by the sample.

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ILLUSTRATIONS (CONTINUED)

1. INTRODUCTION

This final report presents the work accomplished by TRW Systems for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-12412 during the period 17 September 1968 through 17 December 1969. This program consisted of experimental studies aimed towards the development of thermally stable laminating resins (minimum 450°F) that possessed processability improved over currently available polymers. The underlying motivation for conducting this program is development of high performance resin-fiber composites for use in air breathing engine systems which would permit significant system advantages (high strength-to-density ratios, high modulus-to-density ratios, excellent damping characteristics and low costs).

Over the past few years, several new aromatic and heterocyclic polymer systems were developed which offer thermal stability in the 500°F - 600°F temperature range. These systems offer potential as resin matrices for the advanced composite materials needed for the high performance air breathing engine system use. In a previous NASA contract (NAS3-7949) addressed towards improved ablative resin systems (Reference 1), TRW developed a new polyimide resin system which offered distinct advantages in processing over the then currently available polymers based on a condensation cure. This new polymer system was designed to:

- Cure with the evolution of minimal volatile matter
- Form from precursors that are oxidatively, thermally and hydrolytically stable both in solution and solid state form
- Require no post cure

The new resin system, termed A-type polyimide, is formed by a curing mechanism which is believed to be unique in polymer art, namely, pyrolytic polymerization. Specifically, the technique involves the preparation of soluble low molecular weight polyimide prepolymers having alicyclic rings at the terminal positions. It was found that pyrolysis of polymers caused the formation of macro molecules *in situ*. The polymerization of these prepolymers was found to meet the properties delineated above and fiber-reinforced laminates were processed with relative ease.

The A-type polyimide system has been carried to a further degree of advancement by TRW Systems through extensive development studies with the aim of determining its commercial potential. The past TRW studies provided a sound foundation to build upon for improving the processability and enhancing thermal stability of this new polymer system.

In the program reported here the pyrolytic polymerization reaction was investigated through polyimide model compounds. The mode of reaction was investigated together with the hydrolytic, thermo-oxidative stabilities of the pyrolyzed product. The information obtained from the model compound studies was utilized to guide the synthesis of prepolymers and polymers. The ease of conversion of the polyimide precursor (amic-acid) to form the fully cured imide was studied together with the conditions necessary for the subsequent conversion to cured polyimide polymer.

Key process variables were investigated to determine the degree of improvement afforded by the chemical backbone used in the preparation of the new polyimide polymers. Glass reinforced composites were prepared using prepolymers which offered the highest promise for further improvement in processing and thermo-oxidative stability. Mechanical properties of glass fabric and graphite fiber reinforced composites were determined at room and elevated temperatures and the results of these studies were assessed in terms of operational properties and processing conditions. From this key experimental program recommendations for future processing and further product improvements investigations have been generated.

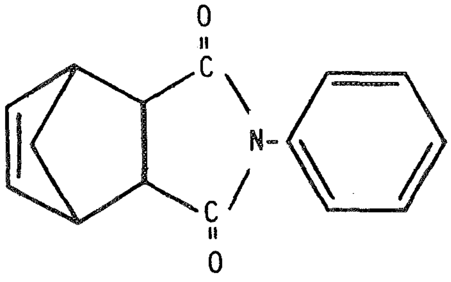
This report is divided into four principal sections covering consecutive program tasks: 1) synthesis and characterization of model compounds, 2) polymer synthesis and characterization studies, 3) preliminary fabrication studies, and 4) evaluation of composite properties.

The significant conclusions reached from evaluation and assessment of the results are listed together with the recommendations for activities that warrant further investigation. This report identifies in a separate section the new technology originating from the program. The information presented in the main body of this report is supplemented by appendices covering detailed descriptions of procedures, equipment, and statistical evaluation of test data.

2. SYNTHESIS AND CHARACTERIZATION OF MODEL COMPOUNDS

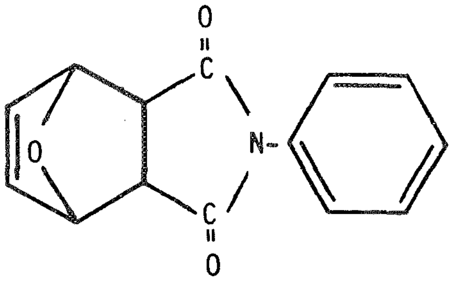
2.1 MODEL COMPOUND SYNTHESIS

The synthetic methods used to prepare the model compounds employed in Task I pyrolyses studies are detailed in Appendix A. The two model compounds, N-phenyl nadimide (I) and N-phenyl oxynadimide (II), used extensively throughout the Task I studies are shown below.



I

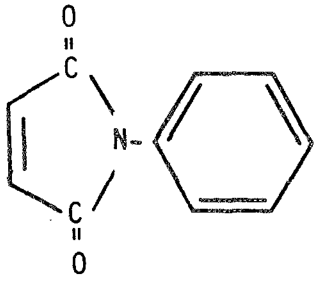
N-phenyl Nadimide



II

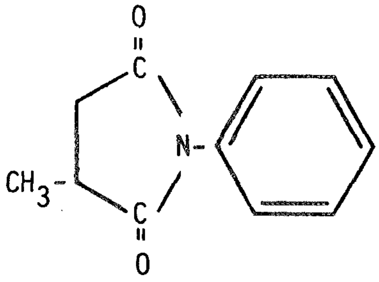
N-phenyl Oxynadimide

One pyrolysis experiment was performed with N-phenyl maleimide (III) for product comparative purposes. This material was purchased commercially and recrystallized prior to use. Another model compound used only for comparative spectral purposes as described in Appendix C, Page 110, was N-phenyl 2-methylsuccinimide (IV), prepared by the synthetic method described on Page 71 from 2-methylsuccinic anhydride and aniline. The structure for (III) and (IV) are presented below.



III

N-phenyl Maleimide



IV

N-phenyl 2-Methylsuccinimide

2.1.1 Model Compound Characterization

The two model compounds, N-phenyl nadimide (I) and N-phenyl oxynadimide (II), synthesized for use in the pyrolyses studies, were characterized prior to pyrolysis. Characterization included melting point (differential scan calorimetry), ultraviolet, infrared, nuclear magnetic resonance, and elemental analyses, thermo-oxidative stabilities (thermogravimetric analyses in nitrogen and air) and hydrolytic stability (two-hour water boil). The results of these characterization studies are given in detail in Appendix A.

2.2 PYROLYSIS OF MODEL COMPOUNDS

2.2.1 Pyrolysis Methodology

The experimental set-up used for the model imide pyrolysis studies is shown in Figure 1. The operation of the apparatus and pyrolysis methodology are described below. In this description, sections of the apparatus are identified by reference to Figure 1 by letter designation.

A weighed sample of model imide is placed in the sample tube (A) and the entire system is purged with nitrogen. After purging, the system is evacuated to ∿1 torr with an efficient vacuum pump (B-vacuum line) and the system is closed. A crucible furnace (C) is preheated to test temperature and is then put into place so it completely envelops the sample tube containing the sample to initiate the pyrolysis experiment. The temperature inside the sample tube is monitored by a thermometer (D). The sample temperature and the time from reaction initiation are recorded at frequent intervals during the experiment along with the system pressure (measured by manometer E). At the end of a predetermined time period, the stopcocks to the gas collection bulbs (F) are closed, the tube furnace is removed, and the system is allowed to slowly cool. When the temperature has reached 25-30°C in the sample tube, the pressure in the system is adjusted to atmospheric pressure with a nitrogen purge. The solid pyrolysis residue and any sublimed material are then isolated separately as well as any liquid material trapped in a cold trap (G) and all samples are numbered for characterization. The equation employed for calculation of gas quantities is given in Appendix B.

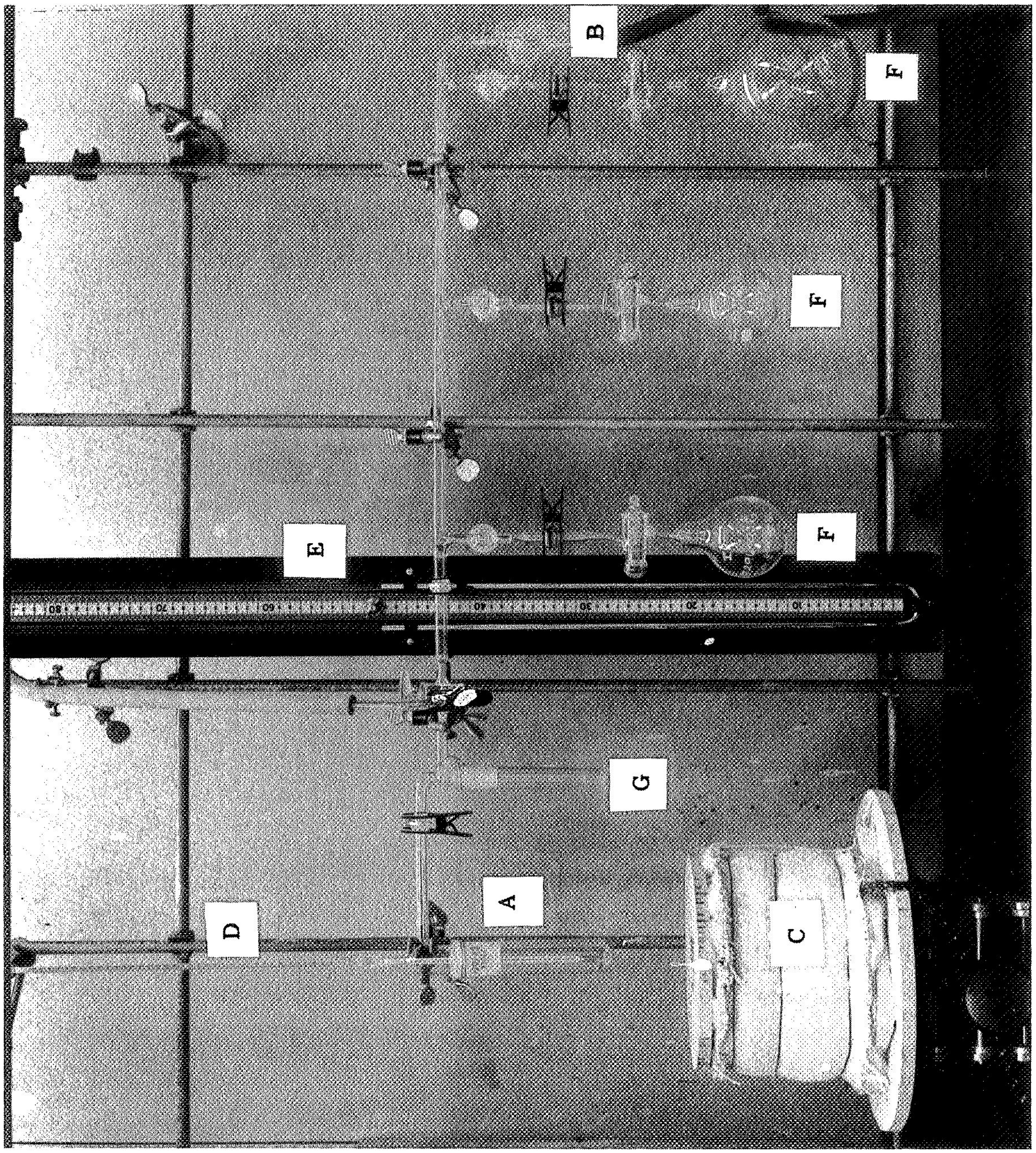


Figure 1. Apparatus Employed for Model Compound Pyrolysis Studies
(See Page 4 for description of lettered components)

For convenience and clarity in subsequent discussions of the pyrolysis experiments and the conditions employed, a code was devised which in four sequential characters provide the key information regarding model compound and pyrolysis conditions. The first character is a Roman numeral and identifies the model compound: I=N-phenyl nadimide, II=N-phenyl oxynadimide, and III=N-phenyl maleimide. The second character is a three-digit number relating to the pyrolysis temperature in degrees Centigrade. The third character gives the pyrolysis duration in hours, and the fourth character identifies the atmospheric environment on onset of pyrolysis, i.e., vacuum (V) or 760 torr nitrogen (N). For example, pyrolysis of N-phenyl nadimide (I) at 300°C for three hours that had vacuum as the environment at onset to pyrolysis is termed I-300-3-V.

2.2.2 Pyrolysis of N-phenyl Nadimide

Initial experiments on the pyrolysis of N-phenyl nadimide (I), Runs 20 and 21 (I-350-2-V and I-350-3-V), in which pyrolysis products were not recovered showed that polymeric matter was obtained and permitted checking out the general operation of the pyrolysis chamber. Subsequently, seven additional pyrolysis experiments were conducted. Their results are tabulated in Table I and show that essentially quantitative recovery of products was achieved. The small deviation from quantitative recovery might be attributed to one or more of the following, 1) condensation of liquid on surface other than in the cold trap or section where the sublimed matter was collected, 2) deposition of small quantities of sublimated matter at locations other than were isolated and weighed, and/or 3) deviation from the ideal gas law. Table I provides information concerning the pyrolysis conditions, and the weight distribution of the original quantity, W_o, through the system after pyrolysis in either the pyrolysis tube residue weight (W_r), sublimed weight on the neck of the pyrolysis chamber (W_s), collected in the cold trap (W_t) or that located in the gas phase (W_g).

From the data listed in Table I it is seen that at a constant temperature, a greater residue weight, W_r is observed when the initial atmospheric environment is nitrogen (Samples 32 and 42). Comparison of the 300°C

TABLE I

SUMMARY OF N-PHENYL NADIMIDE PYROLYSIS EXPERIMENTS

Sample No.	Pyrolysis Conditions[a]	Initial Weight, (g) W_o	Weight Distribution of Matter After Pyrolysis				Total Recovered Weight (g)	Percent Recovery
			Residue W_r(g)	Sublimed W_s(g)	Cold Trap W_t(g)	Gas Phase W_g(g)		
67	I - 350 - 2 - V	20.00	16.76	1.51	c	0.47	18.74	94
42	I - 350 - 2 - N	20.00	17.17	1.39	0.74	b	19.30	97
43	I - 300 - 3 - V	20.00	16.86	1.16	1.62	0.18	19.72	99
59	I - 300 - 2 - V	10.00	8.58	0.71	0.43	0.11	9.83	98
66	I - 300 - 2 - V	20.00	17.47	1.67	0.48	0.21	19.93	100
32	I - 300 - 2 - N	20.00	19.20	0.20	0.21	b	19.61	98
44	I - 275 - 2 - V	20.00	12.71	6.83	0.02	0.13	19.69	98

[a] Characters identify in sequence: model compound, pyrolysis temperature (°C), pyrolysis duration (hours), and atmospheric environment at onset of pyrolysis, i.e., vacuum (V) or 760 torr nitrogen (N)

[b] Not measured

[c] Cold trap not in system

pyrolysis conditions (Samples 59 and 66) shows that a greater amount of material is evolved from the pyrolysis tube the longer the pyrolysis is continued. Finally, it may be concluded that for Sample 44 (I-275-2-V) considerable amount of sublimation (W_s) occurred indicating that pyrolytic polymerization of the reactive alicyclic groups occurs to a greater extent at 300°C than at 275°C. The findings that polymeric matter was formed in the vacuum (or reduced pressure environment during pyrolysis) is highly significant in the interpretation of the mechanism of the pyrolytic polymerization discussed in Section 2.4.

2.2.3 Pyrolysis of N-phenyl Oxynadimide

The result of the pyrolysis investigations of N-phenyl oxynadimide (II) are tabulated in Table II. It was extremely difficult to account for the total gaseous products in the initial experiments (Samples 22-30) because of the volatility of furane (VI). However, in later experiments(47 and 68), the recovery of the pyrolytic products was nearly quantitative. These samples gave evidence for ∿95% loss of (VI) during pyrolysis and no evidence of furane in the polymeric product (see Appendix C). Because it appeared that for the pyrolysis of (II) that the reverse Diels-Alder reaction to form (VI) and N-phenyl maleimide (III) occurs at a lower temperature than that of the pyrolytic polymerization reaction, an experiment on the direct pyrolysis of (III) was conducted under similar conditions to permit comparison of the products. The results of the pyrolysis of (III) are also included in Table II.

2.3 PYROLYSIS PRODUCT CHARACTERIZATION

The residue, sublimed matter, trapped material and gaseous pyrolytic products have been characterized by a variety of means. Primary emphasis has been placed on the characterization of the pyrolytic residue because of its relationship to the polymeric matter produced on curing the A-polyimide prepolymers. Because the model compound is mono functional, the degree of polymerization is considerably less than that which occurs on

TABLE II

SUMMARY OF N-PHENYL OXYNADIMIDE AND N-PHENYL MALEIMIDE PYROLYSIS EXPERIMENTS

Sample No.	Pyrolysis Conditions[a]	Initial Weight, (g) W_o	Weight Distribution of Matter After Pyrolysis				Total Recovered Weight (g)	Percent Recovery
			Residue W_r(g)	Sublimed W_s(g)	Cold Trap W_t(g)	Gas Phase W_g(g)		
29	II - 250 - 1 - V	20.00	13.52	b	b	b	13.52	68
28	II - 250 - 2 - V	20.00	13.37	0.41	b	b	13.37	67
65	II - 250 - 2 - V	15.00	9.64	1.72	c	0.47	11.83	78
30	II - 250 - 2 - N	20.00	13.22	b	b	b	13.22	66
68	II - 350 - 2 - V	20.00	12.50	1.43	5.11	0.87	19.91	99
47	II - 350 - 3 - V	20.00	12.93	0.78	5.03	0.68	19.42	97
64	III - 350 - 2 - V	15.00	13.05	1.64	0.00	0.00	14.69	98

[a] Characters identify in sequence: model compound, pyrolysis temperature (°C), pyrolysis duration (hours), and atmospheric environment at onset of pyrolysis, i.e., vacuum (V) or 760 torr nitrogen (N)

[b] Not measured

[c] Cold trap not in system

curing the A-type polyimide prepolymers thereby forming a linear, tractable low molecular weight polymer which permits detailed characterization. Characterization of the sublimed matter, trapped material and gaseous products consisted principally only of quantitative analysis to permit material balance calculations.

The pyrolyses residues obtained from the experiments conducted on N-phenyl nadimide (I) and N-phenyl oxynadimide (II) listed in Table I and II, respectively, were subjected to detailed characterization. Methods included elemental analysis, molecular weight determinations by vapor phase osmometry and gel permeation chromatography, unsaturation content by bromine absorption, structure determination by infrared and nuclear magnetic resonance analysis, thermo-oxidative stability by thermogravimetric analysis and stability to bases by saponification. The data are presented and discussed in detail in Appendix C.

Representative gas samples of cyclopentadiene (V) and furane (VI) were analyzed qualitatively by mass spectrometric analysis. Semiquantitative gas mass balances were derived and tabulated. The data are recorded and discussed in Appendix D.

The most significant results arising from the characterization of N-phenyl nadimide (I) pyrolysis residues are given below.

- Unsaturation is present in all products as indicated by 1630 cm^{-1} (C=C stretch) band in the infrared spectra.
- Unsaturation content as one alkene group per $\geq$600g of polymer is present as indicated by bromine titration.
- Unsaturation as a double bond containing olefinic protons is not discernible by nuclear magnetic resonance analysis but may be present at a concentration below the sensitivity of the spectrometer.
- Carbon linkages containing methylene and methinyl hydrogen present in N-phenyl 2-methylsuccinimide (IV), cyclopentene (VII), and norbornane (IX) are indicated by nuclear magnetic resonance analysis and are present in all samples to a higher number than phenyl hydrogens.

- Cyclopentadiene (V) is retained in some form in the polymeric residue as indicated by elemental analysis and cyclopentadiene mass balance.
- Molecular weights by vapor phase osmometry indicate products occur reproducibly as $\overline{M}_n$'s of approximately 700-750 and 1150-1250.
- Thermogravimetric analysis shows chain thermal stability to approximately 300°C.
- Gel permeation chromatography analysis shows polymeric products to have relatively narrow molecular weight distribution with little lower or higher molecular weight contaminants ($\sim$10%).
- No stable polymer forms below 275°C, the temperature at which the reverse Diels-Alder reaction is known to occur for the model imide.

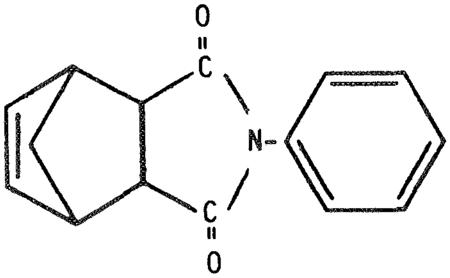
These findings were utilized to postulate a pyrolytic polymerization mechanism for (I) as discussed in Section 2.4.

Characterization data associated with a mechanistic interpretation for the pyrolytic polymerization of N-phenyl oxynadimide (II) are discussed in Section 2.4.2 on Page 20.

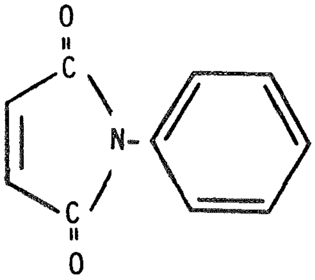
2.4 MECHANISTIC INTERPRETATION OF TASK I PYROLYSES AND CHARACTERIZATION DATA

2.4.1 N-phenyl Nadimide (I)

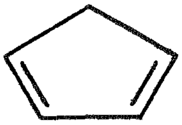
The pyrolyses and characterization data discussed in the previous sections are employed here to present the most satisfactory explanation for the structure of the polymeric products arising from pyrolysis of N-phenyl nadimide (I). One can speculate on the formulation of a number of different structures arising from the pyrolysis of (I) at temperatures above that necessary for reverse Diels-Alder unzipping of the molecule. However, all Task I pyrolyses and characterization data support one general type of polymer backbone configuration. To facilitate the discussion of the polymerization mechanism the following code is used for the three species as shown below:



N-phenyl Nadimide (I) = N



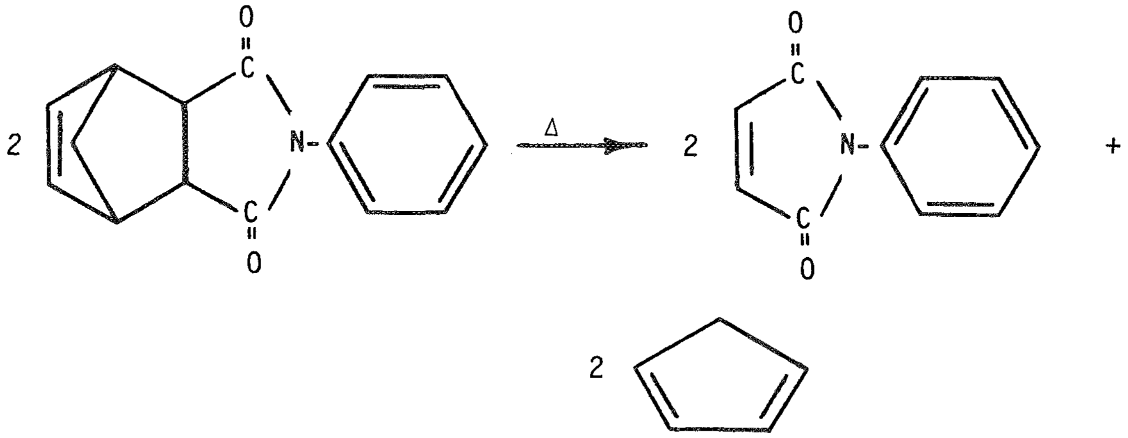
N-phenyl Maleimide (III) = M



Cyclopentadiene (V) = C

Upon inserting the sample tube (A-Figure 1) containing the model imide (I) into the furnace (C-Figure 1), a spontaneous reaction is observed to occur at approximately 275°C, accompanied by the evolution of a gas (pressure buildup as measured by the manometer (E-Figure 1) identified by mass spectrometric analysis to be cyclopentadiene and accumulation of liquid in the cold trap (G-Figure 1). When the residue reaches a temperature of 300°C or greater the pressure buildup levels off and the product appears to slowly build up viscosity as indicated by visual inspection.

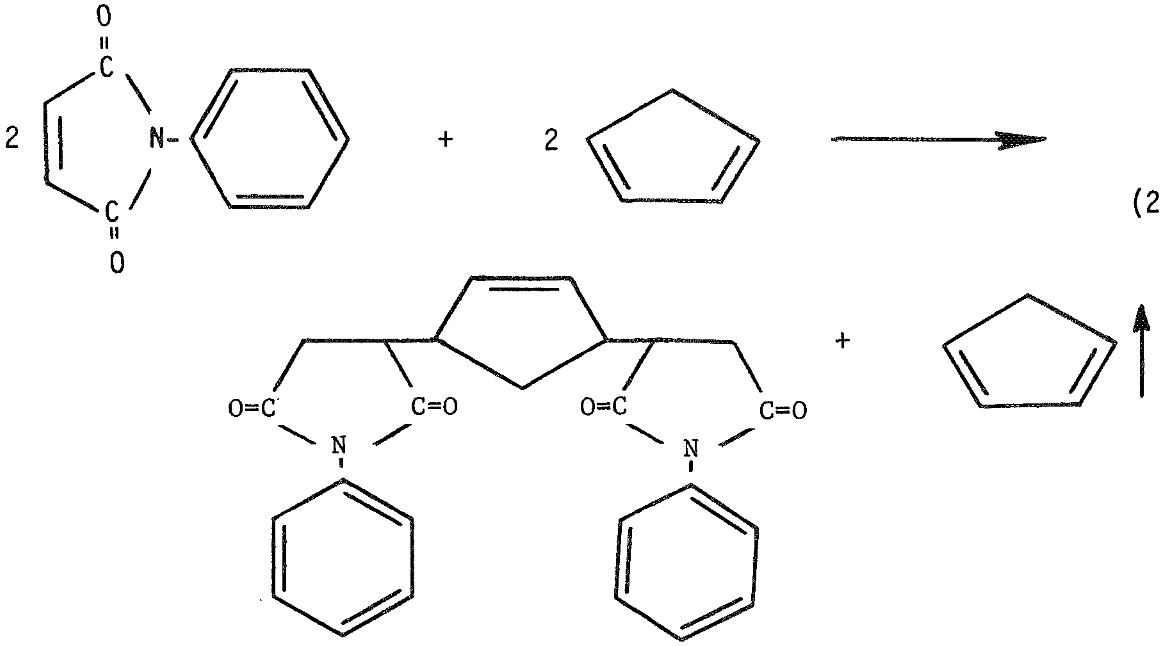
These observations indicate that the first step in the reaction sequence resulting in polymerization is in fact reverse Diels-Alder which gives thermally activated molecules of both N-phenyl maleimide (III) and cyclopentadiene (V) and during this period some (V) volatilization from the polymerization tube as explained above. In the simplest case this can be envisioned as follows in Equation 1.



(1)

$$2N \xrightarrow{\Delta} 2M + 2C$$

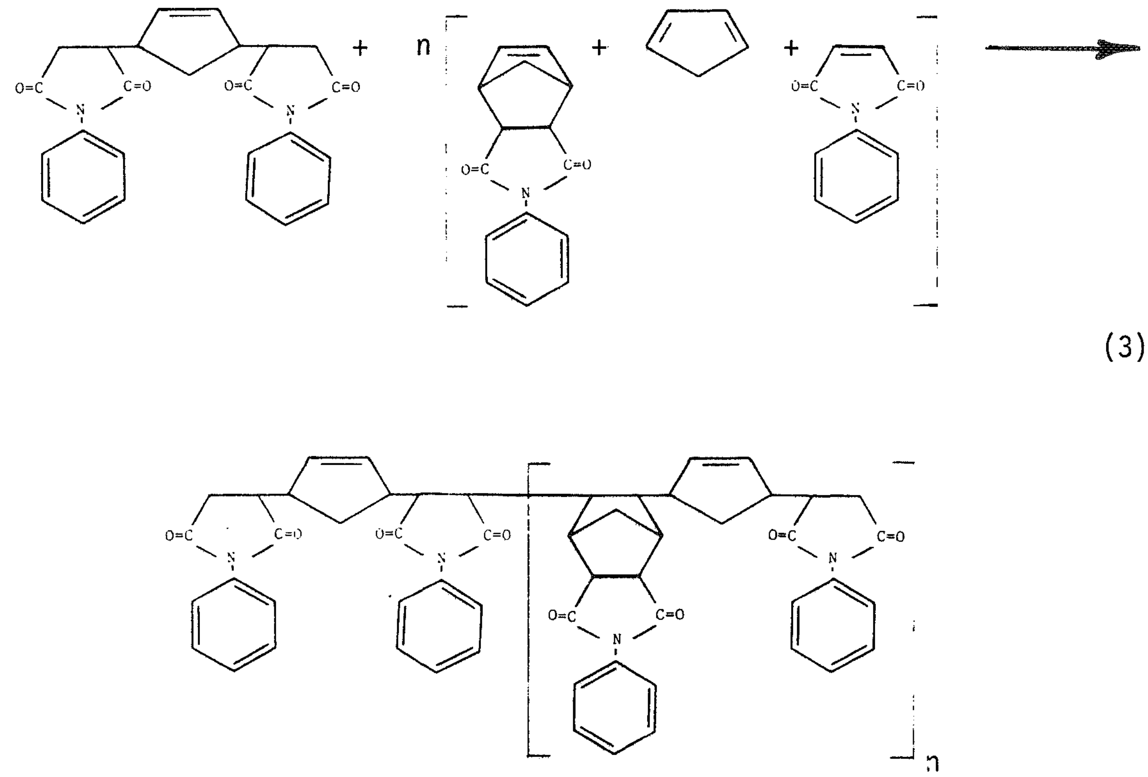
It is postulated that the (III) linearly consumes (V) initially in a 2:1 ratio according to Equation 2. This reaction gives an activated species



(2)

$$2M + 2C \longrightarrow M—C—M + C\uparrow$$

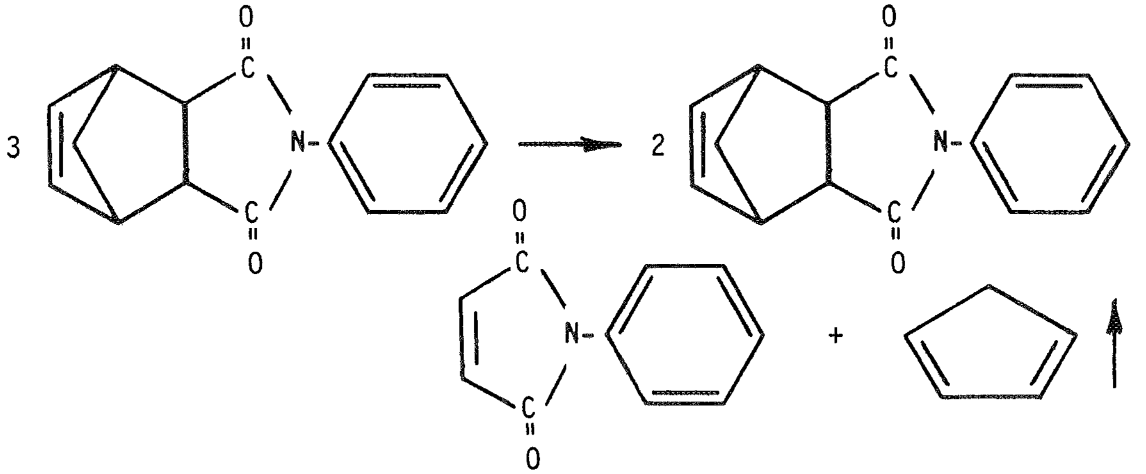
which is presumed to initiate further polymerization via co- or terpolymerization involving all three unsaturated species, namely, N-phenyl nadimide (I), N-phenyl maleimide (III), and cyclopentadiene (V). The species from Equation 1 reacts with N, C, and M, the latter two evolving from continual reverse Diels-Alder reaction to give the following possible backbone structures:



(3)

$$\text{M-C-M} + n\,(\text{N} + \text{C} + \text{M}) \longrightarrow \text{M-C-M-(N-C-M)}_n$$

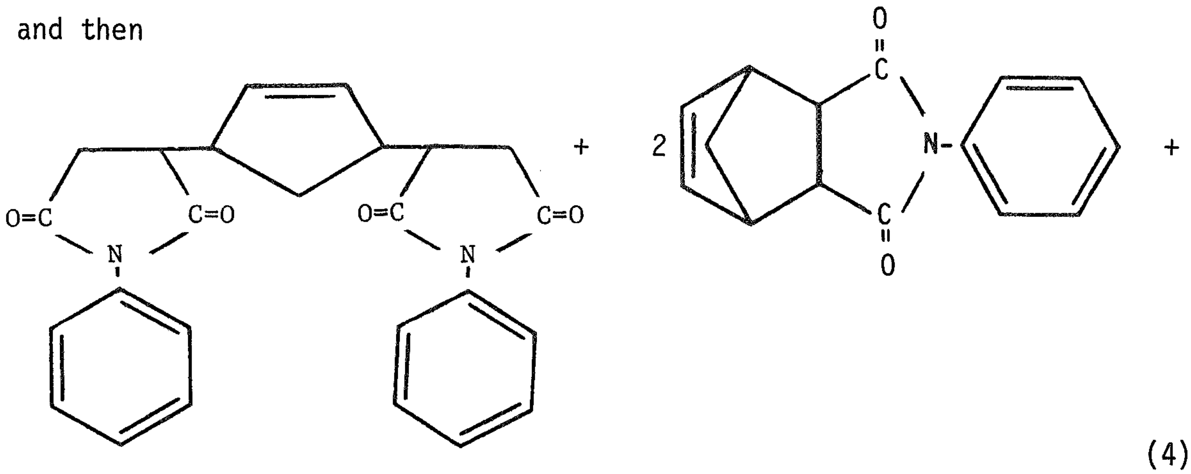
or during continual reverse Diels-Alder reaction the following can occur:



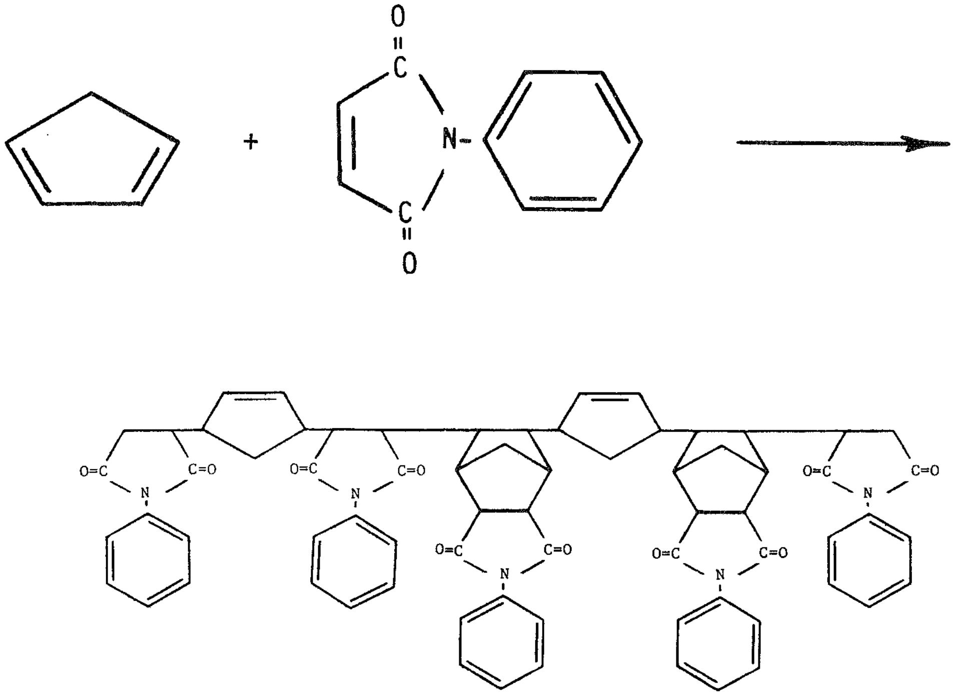
(3a)

$$3\text{N} \longrightarrow 2\text{N} + \text{M} + \text{C}\uparrow$$

and then



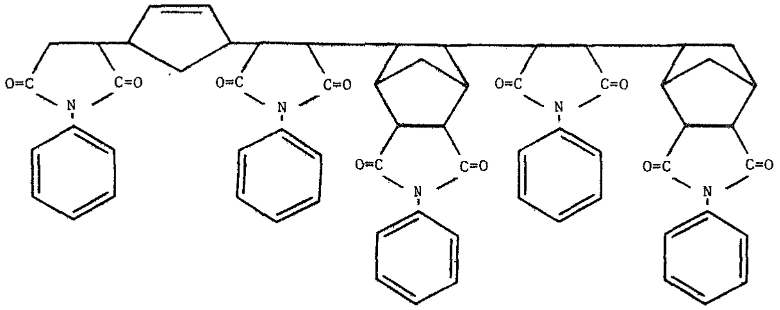
(4)



M-C-M + 2N + C + M ⟶ M-C-M-N-C-N-M

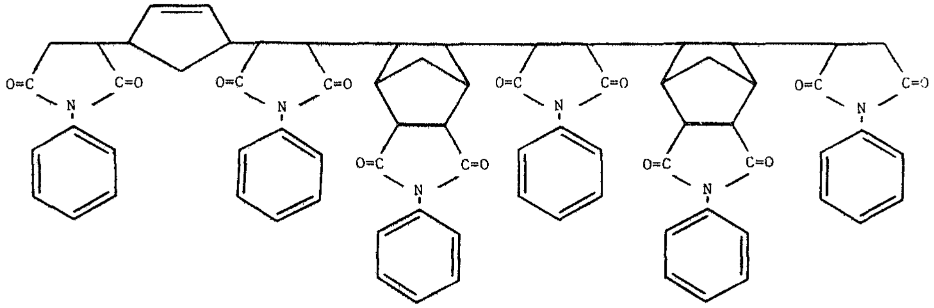
This combination of M-C-M-N-C-N-M gives $\overline{M}_n$ equal to 1129 and a ratio of protons equal to 25 phenyl to 36 non-phenyl or 1/1.44

If more cyclopentadiene (C) is lost during the reverse Diels-Alder/ polymerization reaction the following structures can be formed:



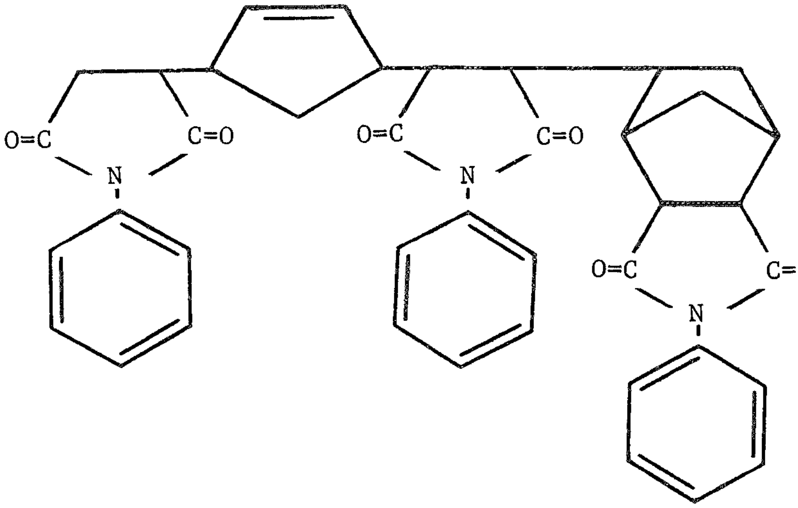
M-C-M-N-M-N
($\overline{M}_n$ = 1063)
Non-phenyl/phenyl
proton ratio = 1.16

or

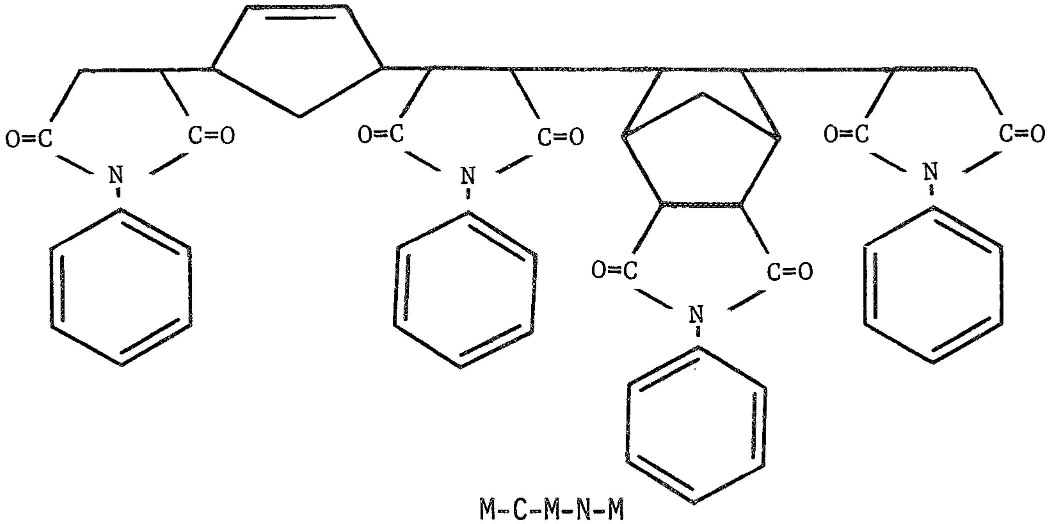


M-C-M-N-M-N-M
($\overline{M}_n$ = 1236)
Non-phenyl/phenyl
proton ratio = 1.07

These three cases average 1150 $\overline{M}_n$ and non-phenyl/phenyl proton average equal to 1.23. Also plausible in this same scheme is the combination of M-C-M with only one molecule of N-phenyl nadimide (N) or N and N-phenyl maleimide (M) to give lower $\overline{M}_n$ species as follows:



M-C-M-N
($\overline{M}_n$ = 651)
Non-phenyl/phenyl
proton ratio = 1.27
or



M-C-M-N-M
($\overline{M}_n$ = 824)
Non-phenyl/phenyl
proton ratio = 1.20

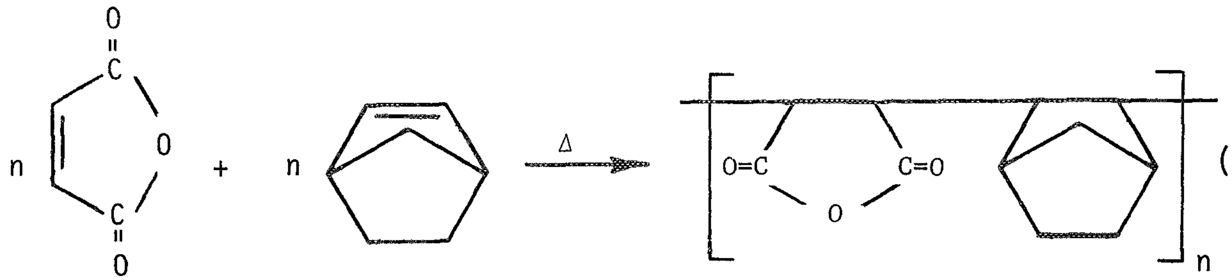
for an average of $\overline{M}_n$ equal to 738 and a non-phenyl/phenyl protons = 1.24.

The two averaged cases for the higher molecular weight and lower molecular weight polymer species meet all or most of the observed polymerization and characterization experimental results, summarized on Pages 10 and 11.

These postulated structures meet the analytical data criteria as follows:

- The cyclopentene ring as M-C-M fulfills the observed C=C stretch band at 1630 cm^{-1} in the infrared.
- The cyclopentene double bond fulfills observed bromine pickup indicating one double bond per approximately $\overline{M}_n$ $\sim$600 or greater.
- The inclusion of all three possible species as M, C, and N explain the presence of N-phenyl maleimide, cyclopentene, and norbornane methylene and methinyl protons in the n.m.r. spectra.
- The low (<7%) presence of olefinic hydrogens in relation to other protons explains why these hydrogens in the cyclopentene ring do not give discernible peaks in the n.m.r.
- Cyclopentadiene retained in the polymer structure is explained by presence of C or N.
- The $\overline{M}_n$'s of the two postulated molecular weight species fall within the range indicated by VPO experiments.
- The thermal weight loss above 300°C is concurrent with thermal degradation of cyclopentene and N in the backbone.
- The onset of polymerization at 275°C, the temperature at which reverse Diels-Alder occurs, is consistent with the proposed mechanism as supported by cyclopentadiene mass balance data and observed experimental results and product characterization data.

The pyrolytic polymer structures as postulated are in agreement with the work performed by Potter and Zutty (Reference 2) who describe a copolymer which almost identically simulates the backbone postulated in this report. Specifically, maleic anhydride and bicyclo (2.2.1) hept-2-ene(norbornene) were reacted to form an alternating copolymer by reaction in a sealed tube at 90°C for five and one-half hours. This reaction is shown as follows:



(5)

These authors also claim that a third unsaturated monomer can be reacted to form a terpolymer from the above species.

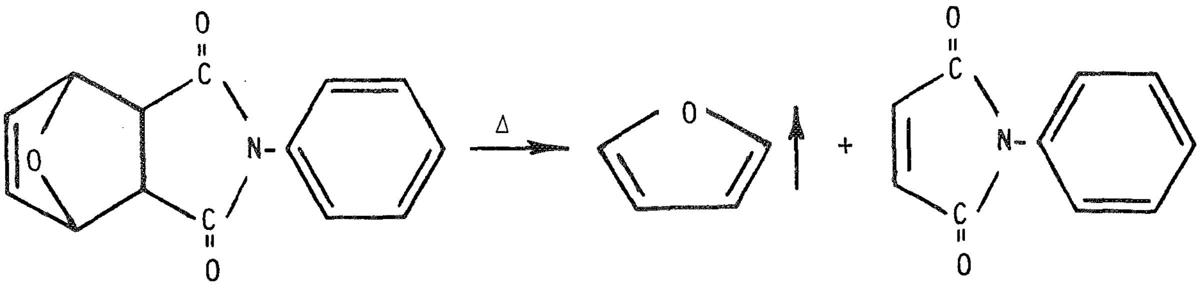
These results, from monomers very similar to N-phenyl nadimide (I) and N-phenyl maleimide (III) (as norbornene and maleic anhydride, respectively), give strong argument for the postulated pyrolytic polymer backbone from (I) described here. The statement that a third unsaturated monomer can be employed strengthens the case for some cyclopentadiene (V) in the polymer backbone as a cyclopentene (VII) structure.

Another patent by Zutty (Reference 3) describes a similar addition polymer from nadic anhydride and ethylene.

It is felt that all model compound pyrolyses data obtained in Task I studies are best described by the polymer backbone linkages appearing on Pages 16 and 17 of this report for the N-phenyl nadimide (I) species. Direct comparison of the pyrolytic polymers arising from (I) with A-type polyimide polymers prepared in Task II polymer synthesis studies is very difficult due to the intractable nature of the latter. However, an infrared structural analysis comparison of these products (Appendix E, Page 131ff) gives evidence that the structures are similar. Therefore, TRW Systems feels that the pyrolytic polymerization mechanism derived for the model compound, N-phenyl nadimide (I), is a workable model for the reaction scheme that gives the thermosetting A-type polyimide cured product.

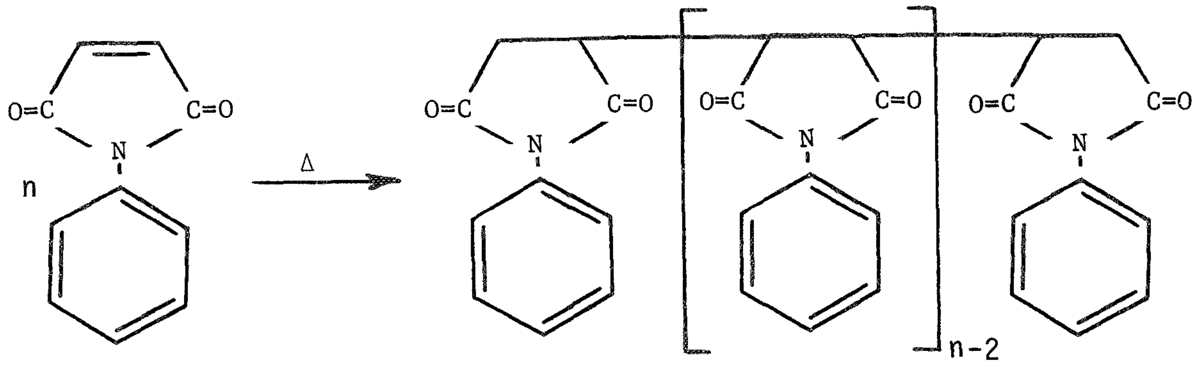
2.4.2 N-phenyl Oxynadimide (II)

The polymeric species arising from the pyrolyses experiments employing N-phenyl oxynadimide (II) as the model compound all gave partially intractable polymeric products very similar to the product obtained from the pyrolytic polymerization of N-phenyl maleimide (III). The evolution of an almost quantitative amount of furane (VI) during these studies with (II), coupled with the structural characterization data that gives no indication of (VI) in the pyrolytic polymer backbone, suggests that the pyrolysis product is indeed a poly-(N-phenyl maleimide) which arises according to Equation 6.



(6)

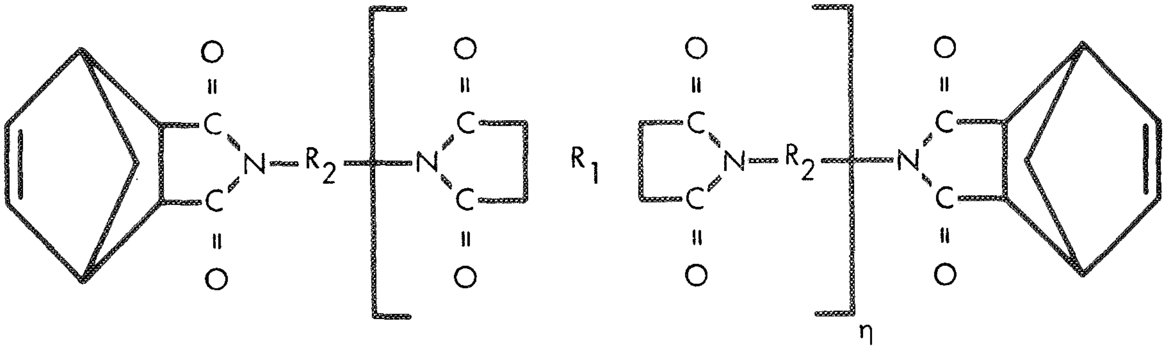
then



Data to substantiate this postulation (n.m.r. and IR) are discussed in detail in Appendix C and D. An in-depth study of the polymerization of N-phenyl maleimide (III) was not intended to be carried out in this project. Complete characterization of the pyrolysis products from (III) for comparison with products from N-phenyl oxynadimide (II) was beyond the scope of Task I studies. It is believed the rapid evolution of furane (VI), which occurs during reverse Diels-Alder reaction of II, would also occur in prepolymers capped with oxynadimide groups thereby resulting in a composite structure of high void content. Previous studies have shown that composites having a high void content possess low initial mechanical properties and poor stability after long duration to isothermal exposure in air at elevated temperatures. Consequently, nadic anhydride was selected as the A-type prepolymer end cap for all Tasks II - IV efforts.

3. POLYMER SYNTHESIS AND CHARACTERIZATION STUDIES

The experimental data arising from Task I model compound studies were interpreted that a nadic endocyclic species would give a more processable and stable polymer product when employed as a prepolymer end cap than an oxynadic configuration (as discussed in Section 2). The nadic end cap is shown in the general A-type polyimide structure below:



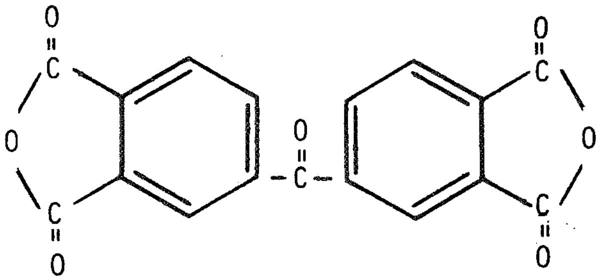
The general A-type polyimide prepolymer structure given above was the direct result of experimental studies conducted by TRW Systems in Contracts NAS3-4188 and NAS3-7949. In these prior studies, aromatic dianhydrides (R_1) and aromatic diamines (R_2) in combination with nadic anhydride were shown to give A-type polyimide polymers demonstrating excellent thermo-mechanical properties. The objective of the current polymer work described below was to conduct an in-depth investigation of six aromatic monomer candidates possessing excellent individual attributes for inclusion in A-type polyimide polymers. One specific combination of monomers was to be chosen from the polymer screening studies based upon the best combination of polymer thermo-oxidative stability, hydrolytic stability and processability. Task I studies demonstrated that a nadic species was the best prepolymer reactive end cap group of the two investigated. Consequently, the polymer screening studies were concentrated on defining the best combination of dianhydride and diamine components for combination with a nadic endocyclic end capping group.

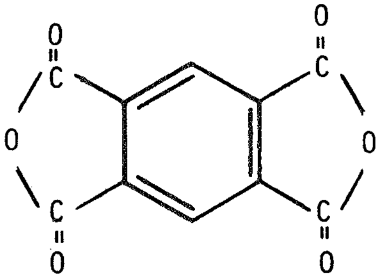
Accordingly, nadic anhydride (NA) was chosen for Task II polymer studies. This endocyclic compound was combined with combinations of two aromatic dianhydrides (R_1) and three aromatic diamines (R_2) to give candidate backbone configurations for the polymer and prepolymer screening studies described below.

3.1 POLYMER SCREENING STUDIES

3.1.1 Varnish Synthesis Studies

Nadic anhydride (NA) was used as a prepolymer end capping monomer and combined separately in each instance with one different aromatic dianhydride and one aromatic diamine, where the aromatic dianhydrides employed were:





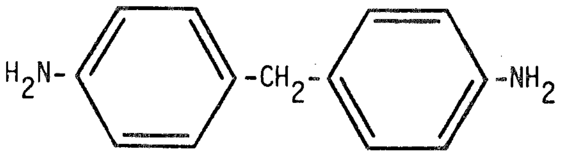
and

Benzophenone Tetracarboxylic Acid Dianhydride (BTDA)

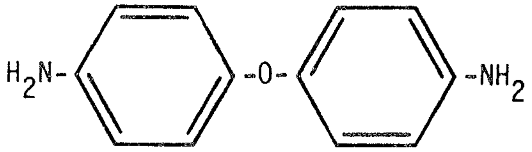
Pyromellitic Dianhydride (PMDA)

These monomers were chosen because of commercial availability, favorable economics, and previously demonstrated feasibility (Reference 1) for producing thermally stable A-type polyimide products. The carbonyl linkage in BTDA allows an additional parameter, namely, flexibility, to be investigated. The effect of this linkage on polymer properties could be directly compared with those obtained for the "stiffer" PMDA.

And the aromatic diamines utilized were:

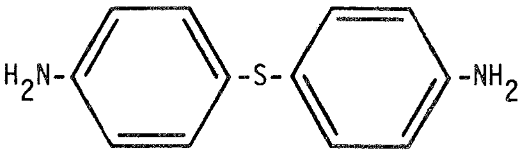


Methylene Dianiline (MDA),



Oxydianiline (ODA)

and



Sulfodianiline (SDA)

These three diamines were selected because of commercial availability, favorable economics, and thermo-oxidatively stable aromatic structure. In addition, each diamine contains a flexible linkage between the aromatic rings so that a direct comparison of the linkage effect on polymer thermo-oxidative stability, hydrolytic stability and processability could be made.

In addition to selection of appropriate monomers, the A-type polyimide prepolymer formulated molecular weight (FMW) for polymer screening was considered a very important variable. Previous studies in Contract NAS3-7949 had identified suitable polymer processing and properties occurred at a FMW $\geq$1000. It was decided to employ a FMW equal to 1300 for preliminary polymer screening studies. It was felt that 1300 gave an intermediate value that could be optimized in subsequent prepolymer studies once the proper ingredients had been selected.

The possible different combinations in one reaction arising from NA, one aromatic dianhydride, and one aromatic diamine gave six individual A-type polyimide candidates for synthesis and characterization studies. Specifically, the ingredients given above were allowed to react in dimethyl formamide in quantities necessary to yield amic-acid (A-A) resins as a 40% w/w solids loaded varnish at a 1300 prepolymer formulated molecular weight (FMW). The experimental details are given in Appendix E, Page 123ff.

3.1.2 Preparation of Molding Powders

The A-type A-A prepolymer solutions in DMF prepared as described above were converted to imidized molding powders by vacuum evaporation and drying according to the procedure given in Appendix E, Page 123ff. The resulting six A-type polyimide prepolymer molding powders were cured into neat resin plugs under pressure as described below.

3.1.3 Preparation of Cured Polyimide Resin Plugs

All prepolymer molding powders prepared as described above were subjected to a processing variable study to convert the prepolymer to final cured polymer plugs. The objective of this study was to assess processing variables that furnished neat material giving the highest Barcol hardness readings at the lowest processing conditions possible. The variables chosen for this study were pressures of 325, 500 and 1000 psi at temperatures of 540°F and 590°F, employing a fixed dwell time of three minutes and a fixed cure time of 30 minutes. In these screening tests, the lowest pressure examined was 325 psi, however, lower pressures in the autoclave molding range (e.g., 200 psi) were investigated in the Task III laminate processing studies described on Page 43ff.

The results of the molding experiments are summarized in Table III.

TABLE III

RESIN BARCOL HARDNESS AS A FUNCTION OF PRESSURE AND TEMPERATURE

Formulation	Pressure (psi)	Temperature (°F)	Barcol Hardness
NA/MDA/BTDA	500	540	53/53
	1000	540	47/48
	325	590	49/49
	500	590	46/46
	1000	590	48/49
NA/ODA/BTDA	325	540	48/47
	500	540	48/48
	1000	540	52/52
	325	590	47/44
	500	590	50/50
NA/MDA/PMDA	500	540	30/30
	1000	540	35/20
	500	590	40/42
	1000	590	35/15

These initial data gave insight into processing variables required which were confirmed in later composite fabrication studies. The first two formulations show that 540°F (13° above the 527°F minimum defined for nadic cure in Task I) press temperature is sufficient to prepare neat resin plugs of good Barcol hardness from BTDA containing materials under relatively mild processing pressures, e.g., 325 psi.

The results given in Table III also show that 1300 FMW prepolymer containing PMDA does not form as well compacted products as BTDA-containing prepolymers (as indicated by Barcol hardness) even when processed at 1000 psi at 590°F. The processing condition limits were investigated in further experimentation at other prepolymer FMW's as described in Section 3.2.

The NA/ODA/PMDA prepolymer powder was molded under identical conditions given in Table III for fabrication of the NA/MDA/PMDA material. The ODA prepolymer could be molded into specimens giving an outward appearance of consolidation. However, all samples crumbled on attempts to determine Barcol hardness. Since initial processability was not to be the single most important criterion for rejecting a candidate formulation, provided a neat, cured plug specimen could be molded, the NA/ODA/PMDA polymer was characterized along with the resins listed in Table III.

However, the NA/SDA/BTDA and NA/SDA/PMDA formulations gave almost 100% flow (out of the mold) at all processing conditions screened (540°F and 325 psi up to 590°F and 1000 psi). In no instance was a consolidated specimen attained that approached apparent cure of the NA/ODA/PMDA formulation described above. Because of the consistent negative results obtained in these molding experiments the SDA containing formulations were eliminated from the polymer characterization studies described below.

3.1.4 Characterization of Molded (Cured) A-Type Polyimides

The four formulations that yielded reasonably consolidated products in polymer molding studies were characterized for structure by instrumental methods, for hydrolytic stability by water boil resistance and thermo-oxidative stability by TGA screening and isothermal aging in air at 400°F and 600°F. The results of these studies are discussed below. Experimental details are described in Appendix E.

3.1.4.1 Structure Analysis - Infrared spectra were obtained for the NA/MDA/BTDA, NA/ODA/BTDA, NA/MDA/PMDA, and NA/ODA/PMDA formulations which moleded into consolidated specimens. Analysis of the spectra showed that the cured A-type polyimide resins all contained the desired imide backbone configuration and differed only in fine structure. These data and gross comparisons of cured polymer with model compounds are discussed in Appendix E, Page 127ff.

After it had been established that the four modifications had the desired A-type polyimide structure, they were further characterized for thermo-oxidative stability as described below.

3.1.4.2 Determination of Thermo-oxidative Stability - The four resin candidates were screened for thermo-oxidative stability employing TGA analysis. In each case, the thermal stability (TGA in N_2) approached 400°C before weight loss began, whereas for oxidative stability (TGA in air) weight loss set in about 325°C and amounted to ∿10% weight loss at 400°C. Because all A-type polyimides screened for thermo-oxidative stability by TGA analysis appeared to be of equal thermal and oxidative resistance, it was necessary to choose the most stable formulation from isothermal aging results discussed below. The TGA data obtained for the resins are given in Appendix E.

One thousand-hour aging studies employing neat resin plugs of NA/-MDA/BTDA, NA/ODA/BTDA, NA/MDA/PMDA and NA/ODA/PMDA in air (100 ml/min flow) at 400°F and 600°F were determined. In each case the specimens aged at 400°F showed $<2\%$ weight loss after 1000 hours. The results of the 600°F aging study for the above formulations are displayed graphically in Figure 2. The NA/ODA/PMDA formulation was aged only 650 hours due to the apparent instability. All of the formulations aged for 1000 hours demonstrated excellent thermo-oxidative stability at 600°F with the least stable specimen (NA/ODA/BTDA) displaying a weight loss of $>30\%$. The NA/MDA/PMDA formulation displayed excellent weight retention (85%) at the end of the aging period.

A graphic representation of the NA/MDA/PMDA neat resin molded plug after the 1000 hour aging period in air at 600°F is shown in Figure 3. The photo is representative of the physical configuration of A-type polyimides after exposure to an oxidizing environment at 600°F. The other formulations aged demonstrated considerable warping in addition to the surface cracks shown for the NA/MDA/PMDA.

As discussed in Section 5, it is believed that the surface cracking phenomenon arises from both stress relief of the molded plug as well as continuous surface oxidation. Because similar behavior was observed in the Thornel 50S high modulus graphite composites prepared from this resin, TRW

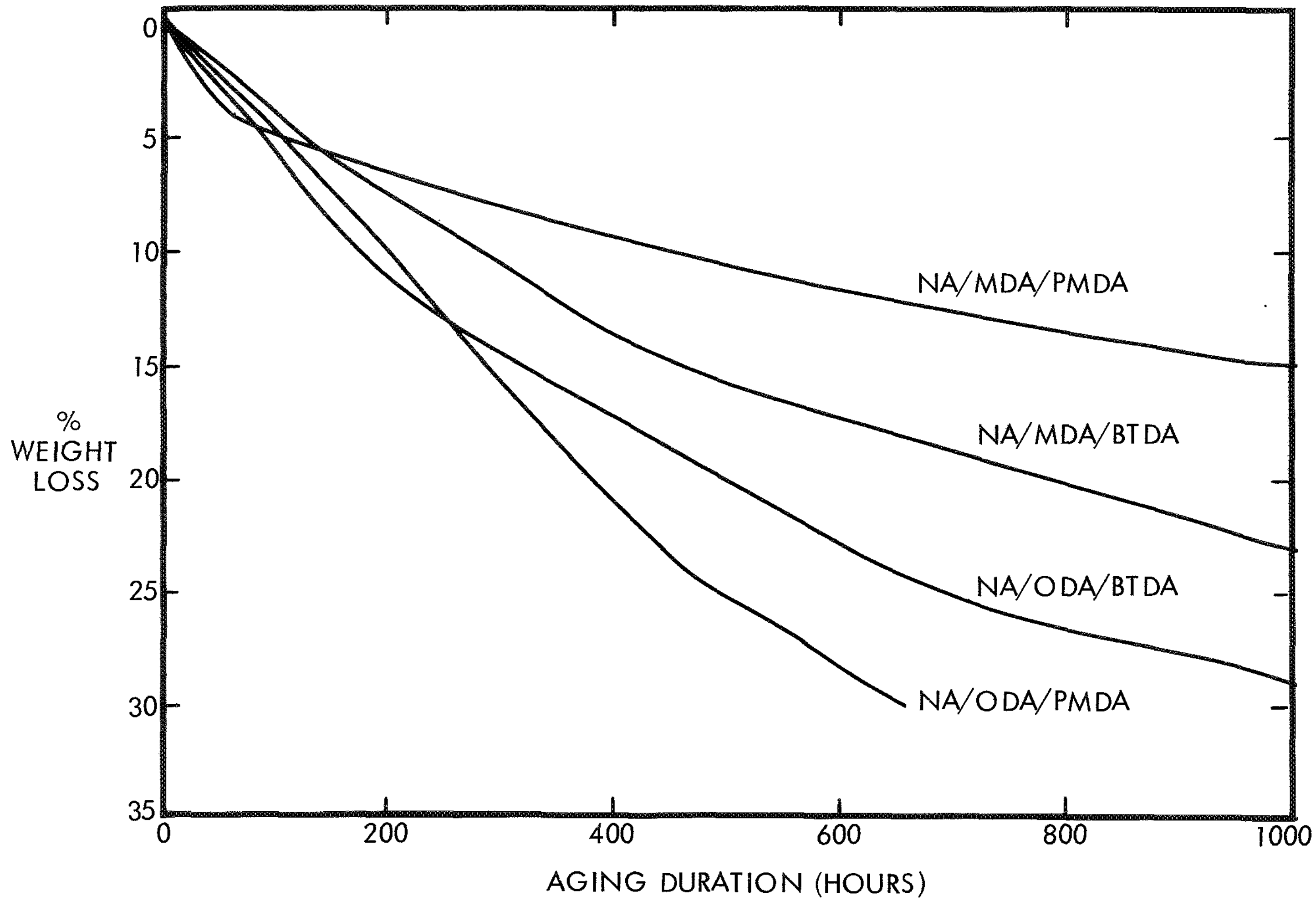


Figure 2. Neat Resin Weight Loss as a Function of Duration of Isothermal Aging in Air (Flow = 100 ml/min) at 600°F

Figure 3. NA/MDA/PMDA Specimen After Aging for 1000 Hours at 600°F

Systems believes neat resin plug aging at 600°F in air can be employed in future work for approximating resin behavior in graphite composites.

3.1.4.3 Hydrolytic Stability - The hydrolytic stability of all prepolymers and cured resins prepared in Task II polymer screening studies was determined. This screening of hydrolytic stability consisted of a two-hour water boil on powdered samples followed by weight loss measurements The results of the experiments are summarized in Table IV and are detailed in Appendix E on Pages 134-5.

The data obtained definitely showed that formulations containing PMDA as the dianhydride portion of the resin are less susceptible to hydrolytic degradation than those containing BTDA, both in prepolymers and cured resin.

TABLE IV

HYDROLYTIC STABILITY OF PREPOLYMERS AND CURED RESINS

Prepolymer and Cured Polymer Specimens	Hydrolytic Stability as Weight Loss (%)
NA/MDA/BTDA Prepol	9.2
NA/MDA/BTDA Cured Polymer	7.3
NA/ODA/BTDA Prepol	7.7
NA/ODA/BTDA Cured Polymer	5.0
NA/MDA/PMDA Prepol	1.3
NA/MDA/PMDA Cured Polymer	2.3
NA/ODA/PMDA Prepol	2.3
NA/ODA/PMDA Cured Polymer	0.0

3.1.5 Selection of a Specific A-Type Formulation for Use in Remainder Of Program

The processing and characterization data described previously in this Section were utilized to select a specific A-type polyimide formulation for use in all subsequent program activities. The key selection criteria employed consisted of the following:

- Thermo-oxidative stability,
- Hydrolytic stability, and
- Processability.

Each of the four candidate formulations were ranked from one to four, one being defined as best and four as the worst on the basis of relative position in the criteria given above. The results of the ranking are presented below in Table V in which equal consideration was given to each of the four categories.

TABLE V

RANKING CRITERIA FOR SELECTION OF BEST CANDIDATE FORMULATION

Formulation	Thermo-Oxidative Stability	Hydrolytic Stability		Processing Ease[a]	Sum of Digits
		Prepolymer	Cured		
NA/MDA/PMDA	1	1	2	3	7
NA/MDA/BTDA	2	4	4	1	11
NA/ODA/PMDA	4	2	1	4	11
NA/ODA/BTDA	3	3	3	2	11

[a] Based on ease of consolidation of molded plug as indicated by Barcol hardness at comparable processing temperatures and pressures.

Hydrolytic stability of both prepolymer and polymer was considered, because instability in prepolymer form strongly indicates poor storage and handleability characteristics of the resin in prepreg form prior to use in composite fabrication.

The NA/MDA/PMDA candidate gave a sum of digits in relative ranking equal to seven (the lowest sum being indicative of the best candidate) which gave this material a clearly superior ranking to the other three candidate formulations. Neither NA/MDA/BTDA, NA/ODA/PMDA, or NA/ODA/BTDA could be assigned a second best status since all gave a sum of relative ranking digits equal to eleven. Because all other candidate resins ranked considerably (and equally) lower, the NA/MDA/PMDA formulation was chosen for all subsequent program activities. The prepolymer study conducted on this specific combination of monomers is described in Section 3.2 as follows.

3.2 PREPOLYMER SCREENING STUDIES

The excellent properties of the NA/MDA/PMDA A-type polyimide formulation were sufficient to allow choice of this material for all subsequent studies as discussed above in Section 3.1. The next technical effort was directed toward investigations to optimize the prepolymer formulated molecular weight (FMW) for resin and prepregging properties prior to undertaking laminate studies in Tasks III and IV. The polymer screening studies described in Section 3.1 utilized 1300 as an arbitrary FMW in order to fix this variable to permit selection of the proper monomer ingredients. Because 1300 FMW represented only a non-optimized arbitrary prepolymer molecular weight, the investigation of several other FMW's was necessary to define a near optimum product for preparation and evaluation of composites. The NA/MDA/PMDA formulations were investigated at FMW's of 1000, 1500, and 2000. Two FMW's (c.a., 1500 and 2000) were chosen above 1300, since it was felt that the degree of resin thermo-oxidative stability and hydrolytic stability should increase with increasing FMW. Conversely, the 1000 prepolymer FMW was chosen for investigation because the key variable of processability should improve at a lower FMW. The ultimate selection criteria for the best candidate FMW was again to be a trade-off in thermo-oxidative stability, hydrolytic stability, and processability which allowed selection of the NA/MDA/PMDA formulation.

The experimental investigations conducted on 1000, 1500, and 2000 FMW NA/MDA/PMDA resins are described below. The results are related to the original 1300 FMW material, when applicable, so that the selection of an optimum material could be made from four candidates.

3.2.1 Prepolymer Varnish Synthesis Studies

Three NA/MDA/PMDA amic-acid varnish solutions formulated for 1000, 1500, and 2000 molecular weights were prepared at 40% w/w solids loading in DMF according to the synthesis scheme detailed in Appendix E, Page 123. The solution viscosities of the three varnishes were determined at 25°C employing a Brookfield viscometer. The results are summarized in Table VI. All of the samples were in a viscosity range acceptable for prepreg operations, because they compared favorable with that of TRW commercial A-type polyimide P13N (viscosity ∿200 cps at 25°C).

TABLE VI

NA/MDA/PMDA VARNISH SOLUTION VISCOSITIES

Formulated Prepolymer Molecular Weight	Viscosity (Centipoises)
1000	93
1500	171
2000	278

3.2.2 Prepolymer Drying and Imidization Studies

The three A-A prepolymers in DMF prepared above were used to prepreg Style 181 E-glass cloth coated with A-1100 amino-silane soft finish by the method described in Appendix F , Page 137. The prepregged cloth was subjected to a DMF drying cycle at 325°F in a forced air oven, followed by a subsequent prepolymer imidization cycle at 475°F in a forced air oven. A time-temperature matrix study was undertaken for the 1500 formulated molecular weight prepreg species during which the progress of drying and/or imidization was monitored by infrared analysis of resin isolated from the prepreg. The results of this study are summarized in Appendix F. The degree of imidization was followed by the disappearance of the resin amic-acid (A-A) amide band. It was observed that a temperature of 325°F for up to four minutes is not sufficient to afford complete imidization of the A-A resin. However, a temperature of 325°F for two minutes followed by drying at 475°F for two minutes or more is sufficient to imidize the A-A material completely as evidenced by the disappearance of the amide band. For further detailed information see Appendix F and Section 4.

3.2.3 Prepolymer Molding Powder Studies

Portions of the three NA/MDA/PMDA prepolymer varnishes prepared as described above were converted to fully imidized resin samples by the method outlined in Appendix E, Page 123ff. The structure of the prepolymer molding powders was confirmed to be identical to the material obtained in the imidization studies by comparing the respective infrared spectra.

3.2.4 Prepolymer Molding Studies

The three NA/MDA/PMDA prepolymer molding powders, prepared as described above, were subjected to a processing study to convert the material to final cured polymer plugs. The data generated in prior polymer screening studies and discussed on Page 28 that demonstrated 590°F to be the minimum temperature for reasonable consolidation of the 1300 FMW NA/MDA/-PMDA system were fully utilized in this study. In this study, only the 1000 molecular weight species could be fabricated into consolidated, neat resin plug specimens.

The 1000 FMW prepolymer powder readily processed into neat plugs employing a 30-second dwell time, followed by a 30-minute cure cycle at 590°F under 325 psi applied pressure. The Barcol hardness of the cured species averaged 49. These data reflect a significant improvement of Barcol hardness and processing conditions over those displayed by the 1300 FMW NA/MDA/PMDA species reported on Page 27. The 1300 FMW prepolymer material under identical dwell and cure times at 590°F required applied pressure of 1000 psi to produce a consolidated, cured plug demonstrating a Barcol hardness reading in the range of 40-42.

The 1500 and 2000 FMW prepolymers could not be fabricated into consolidated, neat plugs over a wide range of processing conditions. The fabrication study employed cure temperatures of 590-600°F and applied pressures of 325-3250 psi and dwell and cure times of 0-3 minutes and 5-30 minutes, respectively. In each experiment, the neat resin product either was obtained from the press as a non-consolidated mass or gave a very brittle specimen that crumbled on attempts to determine a Barcol hardness reading.

3.2.5 Characterization of Molded Plugs

The neat resin cured samples prepared above were characterized as discussed below.

3.2.5.1 Infrared Analysis - The similarity in structure of the three formulated molecular weight (FMW) NA/MDA/PMDA cured samples was confirmed by infrared analysis. Figures F-8, F-9, and F-10 in Appendix F show the spectra obtained for the 1000, 1500, and 2000 FMW cured species, respectively. The only variation in the spectra which appears to be significant is the intensity of the absorption band in the 2750-3000 cm^{-1} region. This absorption is primarily due to $-CH_2-$ stretching in cyclopentene or nadic species (see Page 99). As expected, absorption intensity in this region decreases as the FMW increases, because less nadic anhydride (NA) monomer is introduced into the material.

3.2.5.2 Thermo-Oxidative Stability - The thermo-oxidative stability of the cured polymers was screened by thermogravimetric analysis (TGA) in air. The results of the screening showed that the 1000, 1300, 1500, and 2000 cured FMW species increase in stability with increase FMW (Page 150). The 1000 FMW resin appeared to be consistently ∿50°C less stable than the three higher molecular weight materials which all demonstrated higher resistance to air oxidation by TGA characterization. The concern for this indication of lessened thermo-oxidative stability of the 1000 FMW cured polymer as opposed to cured NA/MDA/PMDA materials derived from higher FMW prepolymers (c.a., 1300-2000) was alleviated by isothermal aging in air at 600°F. These isothermal aging data are discussed below.

The thermo-oxidative stability of the readily processed 1000 FMW material was investigated by subjecting a sample to the identical isothermal aging conditions employed for the 1300 FMW species, (see Appendix E for details). A comparison of the resin weight loss data for the 1000 and 1300 FMW materials is given in Table VII.

TABLE VII

COMPARISON OF RESIN WEIGHT LOSS DATA FOR 1000 AND 1300
FORMULATED MOLECULAR WEIGHT NA/MDA/PMDA CURED POLYMER PLUGS AT 600°F

Duration of Aging at 600°F in Air (Hrs)	Resin Weight Loss (%)	
	1000 M.W.	1300 M.W.
80	1.5	5.0
160	2.5	7.0
240	3.5	7.5
300	4.5	8.5

As can be seen from these data, the cured resin prepared from 1000 FMW prepolymer demonstrated thermo-oxidative stability in air at 600°F after 300 hours at a level almost double that of the cured 1300 molecular weight material. Cured specimens prepared from 1500 and 2000 FMW prepolymers demonstrated greater resin weight losses than the 1000 and 1300 materials under identical aging conditions. These findings showed a trend in a direction opposite to that one would predict from the TGA results. It appears that this trend is directly related to the degree of consolidation that is achieved under identical processing conditions. It is felt that further optimization of the FMW prepolymer in the range of 1000 to 1300 may offer a still further improved product, however, this second order study was beyond the scope of this project.

3.2.5.3 Hydrolytic Stability - The hydrolytic stability of the cured resins prepared from 1000, 1500 and 2000 FMW prepolymers was assessed by measurement of weight loss after a two-hour immersion in boiling water. The resistance to aqueous hydrolysis was excellent for each of the NA/MDA/PMDA cured samples. The data obtained are summarized in Appendix F along with the weight loss numbers previously determined for the 1300 FMW materials. The maximum weight loss observed was only 4%.

3.2.6 Selection of a Specific NA/MDA/PMDA Prepolymer Formulated Molecular Weight for Composite Fabrication Studies

The processing and characterization data completed on NA/MDA/PMDA resins prepared at 1000, 1300, 1500, and 2000 prepolymer formulated molecular weights (FMW's) were interpreted to select a specific FMW for utilization in Task III and IV composite fabrication and evaluation studies.

The three key criteria employed for this selection process were again

- Thermo-oxidative stability,
- Hydrolytic stability, and
- Processability.

Each of the four candidate prepolymer FMW's were ranked from one to four using the method described on Page 31 for selection of the NA/MDA/PMDA monomer combination. The results of the ranking process are given in Table VIII. In this particular ranking procedure, one specific FMW was not clearly better than the other alternate candidates. As can be seen from the sum of the digits in Table VIII, the four candidates all involved varying degrees of trade-off in the selection criteria.

TABLE VIII

RANKING CRITERIA FOR SELECTION OF BEST NA/MDA/PMDA FORMULATED MOLECULAR WEIGHT (FMW)

FMW	Thermo-Oxidative Stability	Hydrolytic Stability		Processing Ease[a]	Sum of Digits
		Prepolymer	Cured		
1000	1	4	4	1	10
1300	2	1	3	2	8
1500	3	3	2	3	11
2000	4	2	1	4	11

[a] Based on ease of consolidation of molded plugs indicated by Barcol hardness at comparable processing temperatures and pressures

At this point in the program it became necessary to decide which selection criteria were the most important. The ultimate end use products of this program were to be composites demonstrating high thermo-mechanical properties. Therefore, it was deemed logical that high thermo-oxidative stability in conjunction with processing ease should be given more consideration than hydrolytic stability for two reasons as follows: 1) the hydrolytic stability of all four FMW's in the severe water boil test (see Appendix F, Page 152 was excellent, and 2) the ultimate end use of composite products such as jet engine fan blades configurations demand ease of processing for facile fabrication and high thermo-oxidative stability for high performance at all times regardless of high or low humidity environments.

Consequently, the 1500 and 2000 FMW candidates were eliminated because of low thermo-oxidative stability and difficulty in processing. The combination of highest thermo-oxidative stability and ease of processing allowed the 1000 FMW candidate to be selected instead of the 1300 FMW material. This distinction in the latter case was not clearly defined as for the 1500 and 2000 resins and represents a strong case for further optimization of FMW in the range of 1000 to 1300. However, further prepolymer work was beyond the scope of this program.

The 1000 FMW NA/MDA/PMDA A-type polyimide resin was utilized for the preparation and evaluation of Style 181 E-glass and high modulus graphite reinforced composites as is discussed in Sections 4 and 5, respectively.

4. TASK III - PRELIMINARY FABRICATION STUDIES

The higher degree of processability and thermo-oxidative stability of the cured resin prepared from 1000 FMW NA/MDA/PMDA prepolymer as described in the preceding studies resulted in its selection for preliminary fabrication studies. The objectives of these studies were 1) determine processing conditions which resulted in acceptable prepregs suitable for preparation of glass reinforced laminates, and 2) establish molding conditions which gave the best combination of laminate properties. In addition, the prepregs prepared would be characterized for the properties which could be used to ensure reproducible preparation of prepregs. The molding processing study was conducted to determine the cure temperature, time, pressure and post cure parameters required to make specimens suitable for mechanical property testing and evaluation. The results of these studies were analyzed by statistical means to determine whether variations in the conditions caused significant effects on resultant mechanical properties of flexural strength and modulus at room and 550°F, shear strength and void content.

4.1 PREPREG FABRICATION STUDIES

The 1000 FMW NA/MDA/PMDA prepolymer was employed as an amic-acid varnish at 40% w/w resin solids in dimethyl formamide to prepare prepregs from fabric Style 181 E-type glass, A1100 soft amino silane finish. This fabric was impregnated by immersing it in the amic-acid varnish until it was fully saturated after which it was slowly pulled through half-inch diameter steel wiper bars set at a constant gap of 0.018-inch.

Drying and imidizing conditions were investigated for the impregnated materials after which the resultant prepregs were characterized for resin solids content, volatile matter content, and resin flow. Specific conditions investigated and prepreg characteristics are listed in Table IX. The test procedures used to characterize resin solids content, volatile matter content and resin flow were generally in compliance with the methods defined by the Society of the Plastics Industry, Inc. (SPI), Reinforced Plastics Committee (References 4 and 5) and are detailed in Appendix H. The only variations to these procedures were in the processing temperatures employed.

TABLE IX

THE EFFECT OF PREPREG AND LAMINATE PROPERTIES AS A FUNCTION OF PREPREG PROCESSING CONDITIONS

Prepreg Processing Conditions				Prepreg Results		Laminate Molding Pressure psi	Laminate Results	
Drying Cycle		Imidizing Cycle						
Time Min	Temp °F	Time Min	Temp °F	Volatile Matter % w/w	Resin Content % w/w		Resin Flow % w/w	Appearance
4	325	15	375	3.72	34.0	1000	18.1	*
						200	9.9	*
		60	375	5.20	25.1	1000	13.3	Good
						200	6.6	*
		2	475	4.26	27.6	1000	15.0	Good
						200	7.9	Good
		4	475	3.64	30.0	1000	13.2	*
						200	4.8	*
30	325	15	375	4.12	30.6	1000	14.5	Good
						200	12.2	*
		60	375	3.30	25.5	1000	15.0	Good
						200	5.4	*
		2	475	**	**	1000	8.1	*
						200	3.0	*
		4	475	**	**	1000	5.72	*
						200	1.9	*
20	250	15	375	3.30	36.0	1000	15.5	*
						200	12.0	*
		60	375	2.50	33.1	1000	9.6	*
						200	1.1	*
		2	475	3.20	28.0	1000	13.0	*
						200	8.4	*
		4	475	2.51	29.4	1000	12.8	*
						200	6.1	*
60	250	15	375	3.28	26.1	1000	12.4	*
						200	9.8	*
		60	375	3.50	28.8	1000	16.0	*
						200	7.5	Good
		2	475	3.48	25.6	1000	16.8	*
						200	7.5	Good
		4	475	1.74	26.2	1000	14.4	*
						200	3.3	*

* Poor Quality

** Sample lost during equipment malfunction

Interpretation of the data in Table IX resulted in the selection of four minutes "drying" at 325°F and two minutes "imidizing" at 475°F based upon the following analyses:

- The volatile matter content of the prepreg at 4.26% w/w with a resin solids content of 27.6% w/w provided a volatile/resin content ratio of 0.15. (In previous Task II studies it was found that prepregs with an acceptable degree of resin imidization were obtained when the volatile/resin content ratio was at this level),
- The resin flows at both 200 psi and 1000 psi employing this prepreg were good, and
- The general appearance of laminates fabricated was very good (particularly the translucent property).

Only these particular prepreg processing parameters provided acceptable looking laminates at both molding pressures.

4.2 LAMINATE FABRICATION STUDIES

The 1000 FMW NA/MDA/PMDA A-A prepolymer at a 40% w/w solids loading in DMF was employed to prepare sufficient prepreg for fabrication into thirty-two 1/8-inch x 6-inch x 12-inch laminate specimens. The Style 181 E-glass cloth prepregs were prepared employing the experimental conditions defined above. The reproducibility of prepreg samples was monitored by determination of resin and volatile matter contents. The minimal variation of these parameters in three prepreg samples prepared are shown in Table X.

TABLE X

PREPREG PROPERTIES FOR LAMINATE FABRICATION STUDIES

Sample[a] No.	Resin Content % w/w	Volatiles Content % w/w
1	28.5	4.10
2	27.0	3.78
3	26.4	3.88

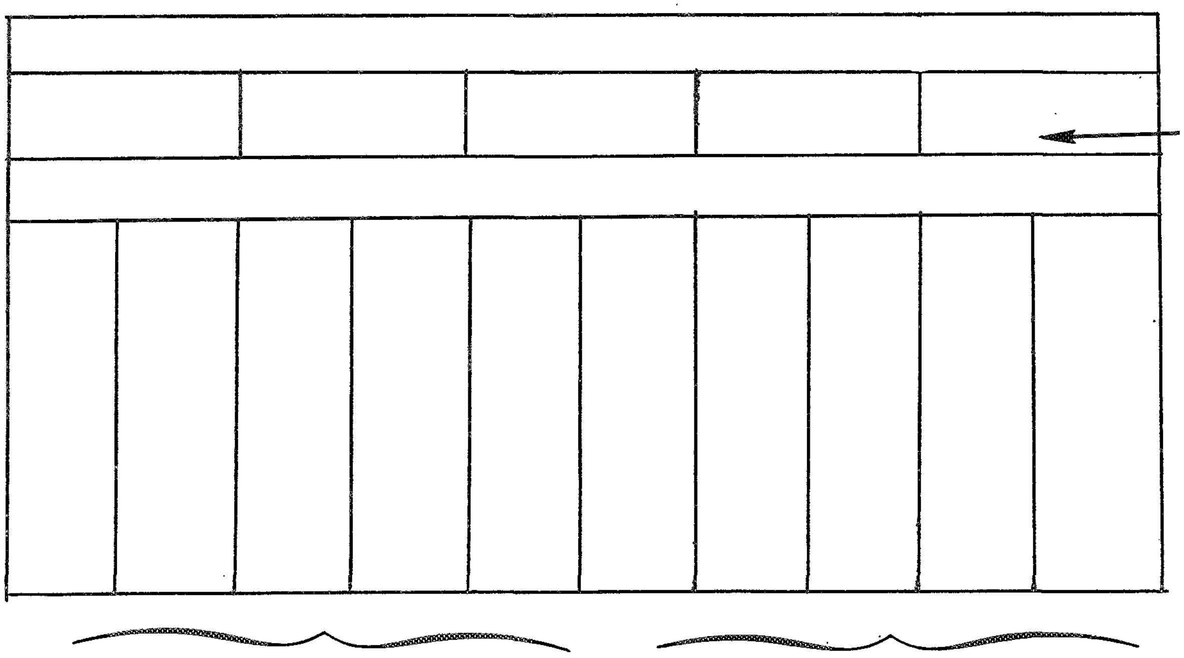
[a] Random selections from 75 yards of 12-inch wide prepreg.

A molding processing parametric study was undertaken to determine the effect of processing temperature, pressure, duration and post cure on laminate properties. To permit assessment of the significance of interactions among the parameters it was decided to perform the experimentation in duplicate. The processing conditions of interest were durations of 30 and 60 minutes, applied pressures of 200 and 1000 psi and post cure of none and eight hours at 600°F. The prepreg was molded at several exploratory cure temperatures in an effort to select a second molding temperature to the established 600°F molding temperature. During these studies it was established that at temperatures between 500°F and 590°F, good resin flow and laminate consolidation can be obtained. However, laminates molded at temperatures below 590°F for extended cures of up to eight hours remained thermoplastic thus indicating that chain extension and/or crosslinking proceeds at very slow rates at the lower temperature ranges. Laminates molded at temperatures of 650°F and higher were generally delaminated and blistered. A molding temperature of 640°F was evaluated and it was demonstrated that good laminates could be molded at this temperature reproducibly. This temperature, therefore, was selected as the second molding temperature.

All of the panels prepared in this four-factor, two-level factorial experiment with replication were molded in an automatic pressure and temperature-controlled press using a 30-second closing rate. A separator film of aluminum foil coated with Frekote 33 release agent was used on the top and bottom of each laminate. Two panels were molded for each processing condition; all panels were 13-plies thick, 6-inch long and 12-inch wide.

Test specimens were cut from the panels in accordance with Figure 4 and evaluated for the properties compiled in Table XI. Determinations of flexural strength and modulus were performed in accordance with ASTM D790; the elevated tests at 550°F were performed after a 30-minute soak at 550°F in the air circulating test chamber. Shear strengths were determined using the short beam flexural test procedure with a span-to-depth ratio of four. Standard deviations of these data were obtained from a minimum of five determinations on a single panel.

In order to calculate the void contents of the laminates, it was necessary to establish the density of the 1000 FMW NA/MDA/PMDA cured polyimide



(5) Short Beam Shear Specimens 1-0 inch wide 2-0 inch long

(5) Specimens 1-0 inch wide by 4-0 inch long for room temperature flexural properties determinations.

(5) Specimens 1-0 inch wide by 4-0 inch long for 550°F flexural properties determinations.

Panel Size - 12 inch by 6 inch less 0.5 inch per side for rough trim. Sawcuts are approximately 0.1 inch wide.

Figure 4. Cutting Diagram for Glass Fabric Reinforced Laminates

TABLE XI

RAW DATA FOR LAMINATE PROCESSING STUDY

PROCESSING CONDITIONS				PHYSICAL CHARACTERISTICS				FLEXURAL PROPERTIES AT ROOM TEMPERATURES (4)				FLEXURAL PROPERTIES AT 550°F (5)					SHEAR PROPERTIES AT ROOM TEMPERATURES	
Cure Temperature °F	Cure Time Minutes	Cure Pressure psi	Post Cure Hours at °F (1)	Density Grams/ml	Cured Resin Content % w/w	Laminate Thickness Inch (11)	Void Content % w/w (3)	Average Strength Ksi (7)	Standard Deviation Ksi	Average Modulus Msi (7)	Standard Deviation Msi	Average Strength Ksi (7)	Standard Deviation Ksi	Strength Retention % (8)	Average Modulus Msi (7)	Standard Deviation Msi	Average Strength Ksi (7)	Standard Deviation Ksi
640	30	1000	None	2.10 2.08	19.2 19.6	0.0886 0.0896	2.2 2.8	95.5 98.1	2.3 2.9	5.14 5.02	0.36 0.25	69.6 69.4	6.7 2.4	73 71	4.04 4.44	0.23 0.13	9.0 7.1	0.3 0.5
			8 Hours at 600	2.06 2.09	19.9 19.5	0.0907 0.0918	3.5 2.4	86.2 91.6	9.6 3.4	4.88 4.62	0.11 0.08	75.0 69.9	9.5 1.9	88 76	4.36 3.92	0.05 0.08	7.3 6.9	0.3 0.2
		200	None	1.96 1.96	27.4 27.6	0.1062 0.1053	2.7 2.5	84.8 86.8	1.7 2.1	4.42 3.96	0.11 0.05	73.2 77.8	4.8 1.2	86 89	3.54 3.50	0.11 0.10	7.8 7.8	0.1 0.3
			8 Hours at 600	1.98 2.00	27.4 25.5	0.1044 0.1011	1.7 2.1	81.6 90.3	2.5 1.7	4.06 4.22	0.15 0.15	75.7 75.2	3.1 2.3	92 83	3.68 3.56	0.18 0.09	8.1 8.1	0.6 0.2
	60	1000	None	2.11 2.11	19.5 18.7	0.0880 0.0875	1.5 2.1	96.1 92.5	2.8 6.2	4.94 4.68	0.22 0.63	67.9 63.5	2.5 2.4	71 69	4.18 4.18	0.08 0.08	7.8 7.5	0.2 0.3
			8 Hours at 600	2.08 2.13	19.3 18.7	0.0883 0.0873	3.0 1.2	94.7 92.3	5.7 6.4	4.82 4.84	0.19 0.21	73.0 67.2	2.8 2.9	77 75	4.38 4.16	0.23 0.09	7.7 6.9	0.6 0.4
		200	None	1.95 1.97	25.5 24.1	0.1044 0.0996	4.6 4.6	88.4 87.7	1.4 3.8	4.12 4.28	0.16 0.33	63.3 70.1	4.8 2.3	72 81	3.52 3.60	0.11 0.00	6.8 7.4	0.2 0.4
			8 Hours at 600	1.95 1.97	25.9 25.3	0.1029 0.1022	4.3 3.7	88.5 89.5	3.2 1.3	4.24 4.16	0.21 0.23	76.4 68.0	9.9 3.1	86 76	3.74 3.62	0.13 0.08	7.4 7.4	0.3 0.6
600	30	1000	None	2.10 2.13	18.7 18.7	0.0868 0.0859	2.6 1.2	92.2 91.2	1.7 4.9	5.34 4.92	0.18 0.15	67.9 67.3	2.8 5.6	74 74	4.86 4.66	0.09 0.42	7.0 6.9	1.2 0.9
			8 Hours at 600	2.14 2.15	19.1 18.3	0.0871 0.0877	0.4 0.6	94.2 90.3	4.5 2.8	5.22 5.42	0.25 0.08	69.2 70.7	1.7 3.3	73 78	4.78 4.74	0.08 0.11	6.7 6.9	0.4 0.3
		200	None	2.02 2.01	22.9 23.0	0.0975 0.0961	3.1 3.5	83.9 90.5	3.6 2.8	4.50 4.88	0.24 0.11	72.1 81.1	3.2 1.1	86 90	4.00 4.48	0.07 0.16	7.1 7.9	0.5 0.5
			8 Hours at 600	2.08 1.99	20.0 24.1	0.0890 0.1013	2.5 3.6	84.2 88.1	5.7 4.5	4.82 4.54	0.4 0.1	68.5 72.7	1.7 2.8	81 83	4.58 4.24	0.11 0.05	6.4 7.5	0.1 0.3
	60	1000	None	2.10 2.16	19.5 17.4	0.0882 0.0868	1.9 0.9	92.7 92.4	8.6 2.4	5.28 5.48	0.53 0.16	69.2 69.9	5.9 4.8	74 76	4.84 4.60	0.05 0.57	6.4 6.8	0.9 0.6
			8 Hours at 600	2.12 2.13	18.5 18.3	0.0881 0.0874	1.8 1.5	90.8 90.0	3.7 4.4	5.60 5.20	0.10 0.29	69.1 72.5	1.5 4.4	76 81	4.88 4.74	0.08 0.05	5.8 5.8	0.3 0.3
		200	None	2.02 (10)	23.1 (10)	0.1058 0.0971	2.3 (10)	94.3 93.3	3.0 1.9	4.80 4.80	0.19 0.14	67.1 70.8	5.5 3.1	71 76	4.22 4.04	0.08 0.09	6.3 7.0	0.9 0.6
			8 Hours at 600	(10) 1.90	(10) 26.1	0.1086 0.1074	(10) 6.6	86.8 85.0	2.3 3.1	4.63 4.38	0.85 0.33	73.3 75.8	3.3 3.8	85 89	3.98 3.98	0.19 0.11	5.9 6.4	0.5 0.3

(1) Post cured in an air circulating oven.
(2) Ref. Table , Test Matrix for Laminate Property Determinations
(3) Calculated using 1.30 as the cured polyimide resin density
(4) Determined in accordance with ASTM D790.
(5) Determined after 30 minutes soak at 550°F.
(6) Determined by the short beam flexural test procedure using a 4:1 span to depth ratio.
(7) Average of five determinations.
(8) Calculated as percentage of average flexural strength at 550°F over average flexural strength at room temperature.
(9) Laminates molded from 1000 FMN NA/MDA/PMDA A-A prepolymer/style 181, "E" glass fabric, A1100 finish, prepreg ref. Table X

(10) Specimens destroyed during equipment malfunction.
(11) All laminates consist of (13) plies of prepreg.

resin. The density was determined to be 1.30 g/ml on a small molded plug using both the method defined in ASTM D790 and also by use of an air pycnometer to determine the specimen volume. Void contents were calculated assuming additive volumes resin density of 1.30 g/ml, the E-glass density of 2.54 g/ml, determined laminate densities and their resin contents as determined by burn-out of five gram laminate samples.

The raw data of Table XI are summarized in Table XII which shows the average values of laminate properties obtained at specific levels of a single parameter confirming the effect of other parameters, average values, the repeatability of the measurement of the property on replicate samples, and the pooled standard deviation of the measurement. The good repeatability and pooled standard deviation of measurement shows uniformity between test specimens and infers that reproducibility in processing conditions was attained.

TABLE XII

SUMMARY OF LAMINATE PROCESSING STUDY RAW DATA[a]

Parameter	Level	Flexural Strength at R.T., Ksi	Flexural Modulus at R.T., Msi	Flexural Strength at 550°F, Ksi	Flexural Modulus at 550°F, Msi	Shear Strength at R.T. Ksi	Void Content, % v/v
Temperature °F	600	90.0	4.99	71.0	4.48	6.7	2.6
	640	90.3	4.52	71.0	3.90	7.6	2.8
Cure Time min	30	89.3	4.75	72.2	4.21	7.4	2.3
	60	90.9	4.77	69.8	4.7	6.8	3.1
Cure Pressure psi	200	87.7	4.43	72.6	3.89	7.2	3.5
	1000	92.5	5.09	69.5	4.49	7.0	1.9
Post Cure	None	91.3	4.78	70.0	4.17	7.3	2.6
	8-hr at 600°F	89.0	4.73	72.0	4.21	7.0	2.8
Average		90.1	4.76	71.0	4.19	7.1	2.7
Repeatability		2.60	0.187	3.31	0.17	0.49	0.61
Pooled Std. Dev. of Measurement		4.15	0.289	4.21	0.167	0.51	----

[a] Data averaged for a single factor level

The statistical significance of the processing conditions were determined by analysis of variance for the laminate properties of flexural strength at room temperature and 550°F, shear strength and void content. Details of these analyses are presented in Appendix H. The results of the statistical analyses are summarized in Table XIII which identify the processing conditions found to affect the laminate properties significantly at a 99% confidence level. In general the statistical study showed that interactions among the parameters were not significant. The only exception to this finding was the void content, which exhibited several significant two-fold and three-fold interactions. Therefore, the recommended processing conditions are 600°F for 30 minutes under an applied pressure of 1000 psi and utilization of no post cure. The average results obtained using the recommended processing conditions are shown in Table XIV.

TABLE XIV
LAMINATE PROPERTIES OBTAINED USING
RECOMMENDED PROCESSING CONDITIONS

Flexural Strength at Room Temperature	91.7 Ksi
Flexural Modulus at Room Temperature	5.13 Msi
Flexural Strength at 550°F	67.6 Ksi
Flexural Modulus at 550°F	4.76 Msi
Shear Strength at Room Temperature	7.0 Ksi
Void Content	1.9% v/v

TABLE XIII

SUMMARY OF THE EFFECT OF SIGNIFICANT[a] PROCESSING PARAMETERS ON GLASS REINFORCED LAMINATE PROPERTIES

Laminate Properties And Direction of Improvement	Processing Parameters			
	Temperature (°F)	Cure Time (Min)	Cure Pressure (Psi)	Post Cure
Increase R.T. Flexural Strength	---	--	1000	None[b]
Increase 550°F Flexural Strength	---	--	200[b]	----
Increase R.T. Flexural Modulus	600	--	1000	----
Increase 550°F Flexural Modulus	600	--	1000	----
Increase R.T. Shear Strength	640	30	----	----
Decrease Void Content	---	30	1000	----
Recommended Conditions	600	30	1000	None

[a] 99% Confidence Level

[b] 95% Confidence Level

5. TASK IV - EVALUATION OF COMPOSITE PROPERTIES

The objective of this task was changed during the course of the program. Originally it was intended to compare glass reinforced laminates employing the processing conditions identified in Task III and obtain detailed property information at 400°F and 600°F before and after aging the specimens in air for one hour at 400°F and 600°F. Because the underlying purpose of this contract was to obtain and identify new and improved resins for ultimate use with graphite fiber reinforcements, it was decided to change the original objective to one of obtaining detailed property data from laminates prepared using a high modulus graphite fiber and the polyimide resin system identified in Task II. The property information to be obtained was flexural strength, flexural modulus, and shear strength prior to and after aging at 400°F and 600°F for durations up to 1000 hours at test temperatures of 77°F, 400°F and 600°F.

Because of the change in scope of this task the processing procedures established during the Task III studies for glass reinforced laminates provided only a starting point in the processing of the graphite fiber reinforced laminates. The nature of the high modulus graphite reinforcement necessitated conducting a few preliminary screening studies for the identification of preferred processing conditions. Significant changes in processing were implemented in both prepreg preparation and composite molding as discussed below:

- Prepreg Preparation - In Task III, fully imidized glass fabric reinforced prepregs were prepared and used in molding the test panels. Previous experience at TRW Systems has established that a fully imidized resin matrix for unidirectional, graphite fiber and boron filament prepregs is not suitable because of the high fragility imparted to the prepregs by the resin in this form. It was decided, therefore, to use tacky, amic-acid prepregs for the Task IV studies.

- Composites Molding - Two basic approaches to composite molding using the tacky, amic-acid prepregs were examined. The first approach is suitable for molding 0.125-inch or less thick panels and utilizes the *in situ* approach to imidizing. In this process, the prestacked prepreg is dropped into a mold which is preheated to the resin's cure temperature and then

> imidization proceeds while the mold is closing. The second approach was studied specifically for molding thicker sections. In this case, the pre-stacked prepreg is imidized in an air circulating oven at temperatures below 300°F for 20 hours and longer. Optimization of either of these processes has not been accomplished, however, the most practical experience has been obtained with the second approach.

Because an important application of resins developed under this contract would be for air breathing engine compressor blades with thick sections, it was decided to explore the slow imidization approach first with the consideration that if adequate properties were not achieved in the first attempts, then the <u>in situ</u> imidization process would be used instead.

Thornel 50S, high modulus graphite fiber surface treated and sized with TRW P13N polyimide resin, was used as the reinforcement for this effort. The procedures used to prepare the prepreg, to mold the composite panels, and to evaluate the materials are detailed below. Properties of the resulting composites are provided together with an analysis of these data.

5.1 DRUM WINDING OF GRAPHITE

Preliminary prepregging efforts were initiated using Thornel 50S yarn pretreated and sized with P13N polyimide resin. Prepreg tapes were prepared using the drum winding equipment shown in Figure 5. These tapes were 3-inch wide and approximately 93-inch long.

Impregnation of the yarn in these preliminary efforts utilized a dip tank and wiper bars to control the resin content of the single strand. A set gap of 0.021-inch for the wiper bars provided a wet resin pick-up of approximately 65% w/w (approximately 45% w/w dry resin solids content). The resultant prepreg had fairly good collimation, but suffered from excessive yarn fraying.

Preparation of the prepreg used in the final test panels employed a spray gun attachment to the drum winding equipment for fiber impregnation and resin content control. (This technique was developed by TRW Systems during company-supported boron filament/P13N composite studies). All of the graphite prepreg produced by this approach had excellent collimation and there was no apparent yarn fraying.

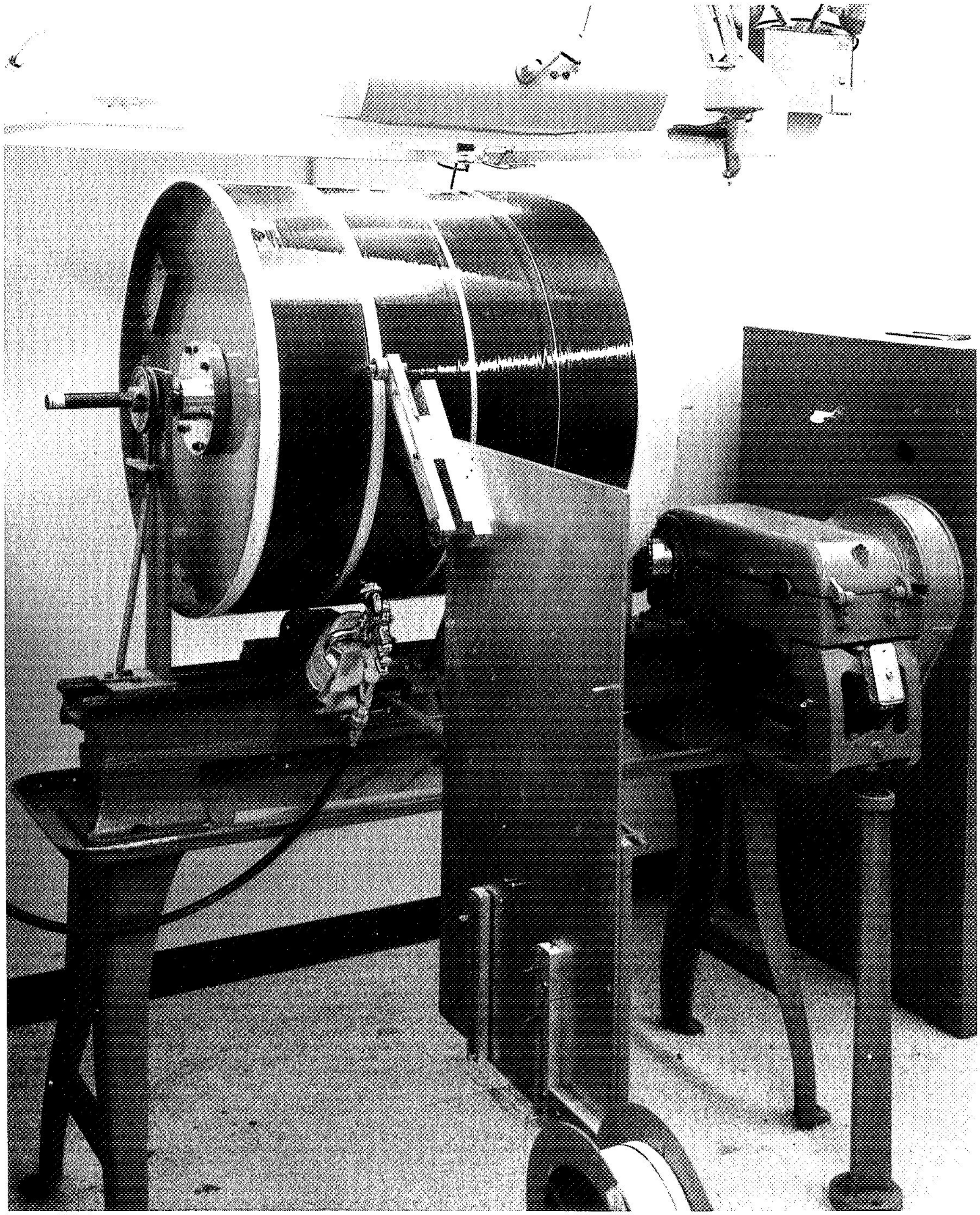


Figure 5. Monofilament Drum Winding Apparatus

5.1.1 Prepreg Processing Details

Mylar film, 0.002-inch thick, was applied to the drum. The Thornel 50S then was wound onto the Mylar backing film at 72 yarns per inch spacing at a winding speed of 72 linear feet per minute. Varnish at 40% w/w resin solids was sprayed onto the yarn as it was collimated. Actual width of the spray "fan" was two inches which provided a one-inch wide post-coating band on the collimated yarn as well as pre-coating a one-inch wide band of the Mylar film as the traversing head progressed along the drum.

5.1.2 Prepreg Control Tests

The resultant prepreg was characterized for volatile matter and resin solids contents. Volatile matter contents were determined by weight loss of prepreg specimens after exposure to 600°F for thirty minutes. Resin solids contents were determined on the retained volatile matter contents specimens after the resin was removed by acid digestion. Properties of the prepregs were:

Resin solids content 43.5% w/w
Volatile matter content 20.2% w/w

5.2 COMPOSITE MOLDING

The few processing screening studies undertaken were directed at molding an acceptable Thornel 50S/polyimide composite panel, however, optimization of the molding processes for this material was not possible within project schedule constraints. The first approach investigated utilized a long, low-temperature, imidization cycle of the stacked prepreg. Good panels were not produced readily by this method; the experimental efforts then were directed toward the rapid in-mold imidization process. It is believed that further investigation of the slow imidization processing method is warranted and when optimized would provide composites exhibiting excellent end properties. Details of the exploratory studies and of the test panel fabrication procedures are presented in the following sections.

5.2.1 Slow Imidization Studies

The tacky prepreg was cut to size, 3-inch wide by 3.75-inch long, and stacked nine-ply thick. The longitudinal axis of the fibers were parallel with the 3.75-inch dimension. This preform then was dried and imidized in an air circulating oven. As a result of escaping volatile matter, considerable fiber movement occurred which resulted in gaps, voids and uneven yarn collimation of the prepreg preform after imidization. In an effort to prevent this, a 0.4-lb weight (0.033 psi) was applied to the prepreg during the drying and/or imidizing cycles.

Specific drying times examined were up to two hours at 150°F followed by up to two additional hours at 200°F. The drying cycles were evaluated with and without the 0.033-psi applied pressure. The dried preforms were imidized with and without the applied 0.033 psi pressure for 30 hours at 300°F in an air circulating oven.

The resultant preforms from these studies suffered from either excessive fiber movement when no pressure was applied during the drying and imidizing cycles, or too low a resin content when pressure was used. Several of the better looking preforms were molded at 640°F under 200 psig pressure for 60 minutes (conditions employed during Task III studies) and were tested. Mechanical properties of the best panel tested were 88.5 Ksi flexural strength, 25.7 Msi flexural modulus and 4.5 Ksi interlaminar shear strength; these properties were considered to be low.

It was concluded at this time that by adjustment of the drying and imidizing temperatures, times and pressures, the process could be optimized to provide better properties. Because this effort was not directed towards process optimization, it was decided to utilize the method of in situ imidization during the molding cycle.

5.2.2 Panel Molding Studies

Panels were molded from non-imidized prepreg using a number of combinations of the conditions as follows:

- Cure temperature, °F: 600 and 640
- Cure pressures, psig: 100, 200 and 500
- Dwell times, sec: 50, 60 and 80

The resultant panels produced in these screening studies indicated that the best combination of molding conditions were 600°F temperature, 500 psig pressure and a 50 second dwell time. These conclusions were drawn from the general appearance of the composites, their resin contents (∿37% w/w), density (∿1.5) and void contents (<0.1%).

In some of the earlier molded panels, a compression failure occurred in the composites during the molding cycle. This failure was evident by the following visual characteristics:

- An elliptical surface discoloration occurred on the top and bottom surfaces of the panels
- Cross-sectioning of this discolored area showed the resin matrix to be powdered and the fibers were crimped or buckled.

The cause of this failure was attributed to the high end stresses during cooling resulting from the large difference in the longitudinal coefficients of thermal expansion of graphite fibers and the steel mold. This problem was solved by cutting the graphite prepreg at least 3% shorter than the mold length.

5.2.3 Test Panel Molding

Panels were molded for evaluation of properties by the following process.

Prepreg prepared in accordance with Section 5.1.1 was cut 6-inch long by 8-inch wide and stacked 8-plies thick. A steel mold with a 9-inch long by 8-inch wide cavity was installed in an electrically heated platen hydraulic press and was preheated to 600°F. All mold surfaces were coated with Frekote 33 release agent.

The stacked prepreg then was dropped into the mold cavity and the mold was closed so that contact was made with the preform but no pressure was applied. Total press closing time was approximately 10 seconds. A total dwell time of 50 seconds was used (from first contact to application of the full molding pressure of 500 psig). This pressure was maintained automatically throughout the cure cycle of 60 minutes. A total of five panels were prepared. The cooling processes for the cured panels varied since the exact technique for obtaining crack-free panels was developed during this effort. Panel 1 was cooled under full molding pressure and was severely cracked upon removal from the mold. Panel 2 was removed from the mold hot and cracked while cooling in the unrestrained condition. A stepwise cooling cycle was used on Panel 3 as follows:

a. Pressure was released completely and then 15 psi pressure was applied.

b. The mold was cooled to 500°F, where it was opened and then 15 psi pressure was reapplied.

c. The above (b) was repeated at 400°F, and 300°F mold temperatures.

d. After the mold had cooled to 200°F the part was removed.

The resultant panel was crack-free. Subsequently, it was decided to cool Panel 4 in the mold under 15 psi pressure directly down to 200°F. Cooling was accomplished using circulating cold water in the press platens. The resultant panel was crack-free, consequently, Panel 5 was molded by the same process. This panel was retained and submitted for evaluation by NASA Lewis Research Center.

In addition to the evolution of a process for molding crack-free panels, there was also a noticeable improvement of the general appearance of panels from Panel 1 to Panel 4. It was apparent that panels molded by the techniques used for Panels 4 and 5 would provide the best end properties. It was necessary to use Panels 1, 2, 3 and 4 to prepare a sufficient number of specimens to permit five-fold replication of the properties of the composites under each of the specified test conditions.

5.3 COMPOSITE TESTING

The four graphite reinforced test panels were machined into flexural and short beam shear test specimens and the following properties were determined:

- Flexural strength, flexural modulus and shear strength at room temperature, 400°F and 600°F.
- Flexural strength, flexural modulus and shear strength at 400°F and 600°F after aging in air circulating ovens maintained at 400°F and 600°F for 100, 500 and 1000 hours.
- Weight-loss after thermally aging at the above conditions.
- Composite physical properties (specific gravity, resin content, void content and 8-ply thickness).

All of the above properties were determined using industry accepted test methods of the American Society for Testing and Materials (ASTM). Details of the test procedures are presented in Appendix G.

5.3.1 Specimen Preparation

Each of the four panels were cut into 19 flexural test coupons and 19 short beam shear test coupons. The flexural test coupons from each of the four panels were numbered consecutively in an identical manner. Shear test coupons were numbered in the same manner. All of the coupons were machined with a diamond impregnated cutting wheel, 0.040-inch thick; water soluble oil was used as a coolant. Flexural specimens had nominal dimensions of 3.0-inch long, 0.50-inch wide; shear specimens were 0.60-inch long by 0.25-inch wide.

During the elevated temperature testing of the unaged short beam shear strength specimens, an equipment malfunction occurred resulting in the loss of the following ten specimens:*

1-7 2-5 2-17 3-13 4-7
1-14 2-12 3-6 3-15 4-8

These specimens were replaced with additional coupons machined from surplus pieces of the same test panels.

5.3.2 Physical Property Results

The physical properties of the four test panels were determined on representative specimens after mechanical property testing and are reported in Table XV. Interpretation of these data in terms of molding conditions permit the following observations:

- The high resin content, low void content and good density of panels 1 and 2 are a result of slightly lower rate of pressure application.
- It appears that the pressure was applied to Panel 3 a little too rapidly resulting in low resin content, thinner specimens, and a marginally high resin content.
- The molding conditions used to prepare Panel 4 appear to produce close to optimum physical properties.

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*Coupon designations refer to panel number followed by coupon number.

TABLE XV
PHYSICAL PROPERTIES OF TEST PANELS

Panel Number	Resin Content % w/w	Void Content % v/v	Density g/ml	Avg[a] Thickness 10^{-3} inch
1	41.5	-2.4	1.51	72.3
2	44.5	-0.5	1.47	76.0
3	38.1	2.4	1.45	66.9
4	36.9	-0.6	1.50	72.4

[a] Avg of specimens prior to testing after 100 hours aging at 400°F; Number of measurements: 7 each for Panels 1 and 3; 8 for Panel 2; and 3 for Panel 4.

5.3.3 Mechanical Property Results

The mechanical property results of both aged and unaged specimens exhibited considerable property variation. In general, it was observed that Panels 1 and 2 had lower property results than those of Panels 3 and 4 under comparable test and aging conditions. The raw data from these studies are reported in Appendix H together with the statistical identification of some "wild" data. A summary of the test results after rejection of the "wild" data is presented in Table XVI together with the averaged values for weight loss after aging. The corrected data has a considerably high degree of variability (pooled standard deviations: flexural strength - 12.9 Ksi; modulus - 1.73 Msi; and shear strength - 0.88 Ksi). Although the general trends were for lower values for Panels 1 and 2, there was no clear-cut statistical reason for rejecting these lower data.

In spite of the high variability, the room temperature flexural strength and modulus of unaged specimens are higher than those reported for Thornel 50/epoxy and Thornel 50S/epoxy composites (Reference 6). Mechanical property data as a function of temperature without aging show that 400°F test temperature had little effect on flexural strength, modulus and shear strength whereas at 600°F test temperature the flexural strength retention is ∿80%, the flexural modulus retention is ∿85% and the shear strength retention is ∿74%.

TABLE XVI
SUMMARY OF REVISED PROPERTY DATA

Test Temperature °F	Aging		Flexural Strength		Flexural Modulus		Shear Strength		Weight Loss on Aging	
	Temperature °F	Duration hrs	Avg Ksi	Std Dev Ksi	Avg Msi	Std Dev Msi	Avg Ksi	Std Dev Ksi	Flexural Specimens Avg, % w/w	Shear Specimens Avg, % w/w
77	---	---	105.3	9.2	23.1	1.8	5.0	0.6	---	---
400	---	---	106.7	14.6	21.8	3.1	4.7	0.8	---	---
600	---	---	84.5	16.4	19.7	2.7	3.7	1.0	---	---
400	400	100	113.2	9.3	23.1	1.6	4.8	0.8	∼0.1	0.62
		500	97.7	14.1	22.7	2.0	4.1	1.2	0.36	0.77
		1000	103.8[a]	13.3[a]	23.0[a]	1.8[a]	4.3	1.0	0.69[a]	1.33
600	400	100	99.3[a]	9.4[a]	21.6[a]	1.5[a]	4.4	0.3	∼0.1[a]	0.64
		500	88.3	13.3	21.5	1.1	3.4	1.0	0.37	0.75
		1000	99.0[a]	13.2[a]	22.3[a]	0.3[a]	4.4[a]	1.0[a]	0.68[a]	1.04[a]
400	600	100	105.5[a]	16.1[a]	23.1[a]	1.2[a]	4.4	0.8	3.1[a]	4.0
		500	60.5	12.6	20.6	2.4	2.7	0.8	17.8	18.3
		1000[c]	---	---	---	---	---	---	30.3[b]	31.4[b]
600	600	100	96.5	11.6	20.5	0.8	3.8	1.1	4.2	5.4
		500	60.8	7.5	19.2	0.4	2.6	0.7	14.1	17.8
		1000[c]	---	---	---	---	---	---	30.3[b]	31.4[b]
Pooled Std Dev				12.9		1.73		0.88	---	---

[a] Value generated after rejection of one statistically significant extreme data point

[b] Average weight loss obtained on measurement of all 10 samples aged at 600°F for 1000 hours

[c] All specimens after this aging treatment were unsuitable for testing.

It is interesting to observe that the properties of specimens aged for 100 hours at 400°F and 600°F were considerably higher than those observed for the unaged specimens at comparable test temperatures. Aging at 400°F for longer periods showed negligible affect on properties. However, aging at 600°F caused a significant degradation of mechanical properties. After 1000 hours aging, over 75% of the resin had been removed from the composites and the specimens were not suitable for testing. This last finding is most interesting in light of the fact that the 1000 FMW NA/MDA/PMDA material was selected because neat resin plugs exhibited excellent resin weight retention as a function of aging in air at 600°F. The property data reported in Section 3.2.5.2 indicated that only a 12% weight loss was observed after 1000 hours at 600°F which appears to be contrary to the findings from the composite specimens. A reasonable explanation for this difference appears to be based in variation in the surface area-to-volume ratios for the two types of samples. Details of the interpretation of this experimental finding is presented in Section 5.3.4.

5.3.4 Parameters Affecting Elevated Temperature Aging Behavior

This section discusses 1) the effect of sample size and shape and velocity of air on the behavior of specimens aged at elevated temperature, and 2) provides recommendations for control of tests to ensure generation of information suitable for comparative evaluation of materials.

It is reasonable to expect that uniform chemical attack (such as air oxidation) would cause a more detrimental effect to specimens having larger surface area-to-volume ratio. The flexural specimens (average dimensions 0.5-inch wide x 3.0-inch long x 0.073-inch high, surface area/volume = 32.1 inch^{-1}) have a surface area-to-volume ratio over 26 times greater than neat resin plugs (dimension 1.0-inch diameter x 0.025-inch high, surface area/volume = 1.2 inch^{-1}).

The extent to which oxidative attack could cause a degrading change in the mechanical properties of the composite has been examined semi-quantitatively. This analysis is based on the fact that the mechanical properties retention is inversely related to resin weight loss. Therefore, it is possible to predict the weight loss of a composite using the weight loss information on the neat resin plug at 600°F and assuming 1) the weight loss of a specimen is directly related to available surface area, and 2) the total surface area of the composite specimens is available for attack and is constant throughout aging. The predicted weight loss for composites from neat resin aging information were calculated as follows:

$$\Delta w_c = \frac{A_c}{A_p} \quad w_p \quad f_\ell \tag{7}$$

where:

Δw_c = the predicted weight loss of the composite

A = the surface area of the specimen noted by the subscript, (c for composite and p for neat resin plug)

w_p = the weight of the neat resin plug

f_ℓ = the fraction of neat resin loss after aging for a specific time.

A comparison of the observed and predicted weight loss using the above formula is shown in Table XVII. The relative good agreement observed tends to substantiate the hypothesis, namely, that the weight loss of a specimen is directly related to the exposed surface area and the inherent ability of the material to withstand thermal oxidation.*

The assumption that all of the surface of the composite is available for oxidative attack is valid at the beginning of aging, however, as the resin is consumed and graphite fiber appears, less lateral surface area remains exposed. As was observed in the neat resin plugs (Page 31) the aging plugs develop a considerable number of small micro cracks, presumably caused by relieving residual stresses in the specimens thereby permitting a larger surface area available for oxidative attack. In addition, the difference between coefficient of expansion between the resin and graphite fiber provides a potential means for oxidative attack of the resin immediately surrounding the fiber.

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*Extrapolation of this approach to standard glass reinforced flexural specimens (4.0 x 1.0 x 0.125-inch surface area/volume ratio of 18.5 inch^{-1}) shows that after 1000 hours aging in air one would predict a weight loss of ∿2.0 g, or only ∿12% w/w weight loss.

TABLE XVII
COMPARISON OF PREDICTED AND OBSERVED 600°F WEIGHT LOSS OF GRAPHITE REINFORCED FLEXURAL SPECIMENS

Aging Duration, hrs	f_{ℓ}[a]	Predicted[b] Weight Loss, g	Observed Weight Loss[c] g
100	0.018	0.12	0.11
500	0.060	0.38	0.44
1000	0.115	0.74	0.82

[a] Fractional weight loss of neat resin plug

[b] Predicted using Equation 7.

[c] Average of weight losses determined on specimens aged for both 400°F and 600°F property testing.

The effect of surface area-to-volume on weight loss is further reinforced by comparing the results of the flexural and shear test specimens. The weight loss of the shear specimens was uniformly higher than that of the flexural specimens. This finding is directly related to a comparison of the surface area-to-volume ratio of the test specimens; 38.7 inch^{-1} for the smaller shear test specimens compared to a 32.1 inch^{-1} value for the flexural specimens.

The differences in air velocity maintained over the specimens during aging may account for further variations in observed weight losses between the neat resin plugs and the composite test specimens. The air velocity controls the diffusion boundary layer thickness in the vicinity of the specimen which in turn affects the rate of oxidation (depending on the oxidation kinetics at the temperature under question). The forced air ovens which were used to age the composite specimens had a velocity of 250 ft/min at an air change rate of 400 ft^3/min (11,812 l/min), which is considerably more than the 0.100 l/min maintained over the neat specimens during the aging studies reported in Task II. The increased velocity in the composite studies would permit more efficient attack of the surface area exposed on formation of micro cracks.

The velocity in the forced air oven was so great that in the 1000-hour aging test the resin had degraded to such an extent that some of the graphite fibers were vibrating in the air stream potentially adding a mechanical agitation effect to the rate of air oxidation. The graphite fibers were so badly entwined it was not possible to measure the weight of the individual specimens and it was necessary to combine all ten specimens aged for 1000 hours at 600°F together to obtain a measure of weight loss.

From the findings it is quite evident that the nature of the isothermal aging test is of significant importance in making comparisons between different reinforced composites. A question one must ask is whether a mechanical property obtained on a 0.073-inch thick composite after aging a certain length of time is representative of what that composite may have when employed in a much thicker part. The only meaningful approach for this kind of testing is to ensure that comparative specimens are tested by identical test methods and even then the extrapolation of these data to larger actual component parts is subject to question unless the surface area-to-volume ratio of the test specimens is taken into account.

The observations clearly point out the need for specifying the size and shape of the specimens and the velocity of air when conducting thermo-oxidative aging testing together with the temperature and duration of test. Additional study into these important parameters appears to be warranted to define their effect on aging of test specimens.

6. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this experimental effort to study improved thermally stable laminating resins. Based on the findings, recommendations are given for further material and process improvement studies.

6.1 CONCLUSIONS

1. Based on the experimental studies of model compounds, a preliminary theory for the mechanism of pyrolytic polymerization has been generated. Simply stated, the mechanism involves two distinct chemical reactions; the first being a partial completion of a reverse Diels-Alder reaction of the reactive end groups followed by a second linear extension and crosslinking reaction of the products and unreacted materials of the first reaction.

2. Model compound studies identified the minimum temperature to ensure effective pyrolytic polymerization to be 550°F.

3. Of the two reacting alicyclic prepolymer end groups studied, the nadic anhydride was identified as the best endocyclic material for preparation of superior polymers by pyrolytic polymerization.

4. A new A-type polyimide prepolymer consisting of nadic anhydride/pyromellitic dianhydride/methylene dianiline having a FMW of 1000 was identified as possessing excellent processing characteristics for conversion to a high molecular weight polyimide polymer having improved thermo-oxidative and hydrolytic stabilities.

5. Laminate processing studies were undertaken for preparation of glass reinforced laminates. Process conditions which showed the best combination of flexural properties at room and 550°F temperatures, room temperature shear strength and minimum void contents were 600°F molding temperature, 1000 psi applied mechanical pressure, 30-minute processing duration and no post cure.

6. Processing methodology was established for preparing crack-free Thornel 50S graphite fiber reinforced composites with the recommended new A-type polyimide formulation. Specific techniques were developed involving control of cooled down rate and utilization of an oversize mold to compensate for expansion of the graphite fiber on cooling.

7. To permit valid comparison of the thermo-oxidative retention of properties of a variety of composites, thermal aging methodology must include identification of sample size and shape for rate of air flow by the sample.

6.2 RECOMMENDATIONS

1. Further study of model compounds is warranted towards achieving still further reduced processing conditions. Specific emphasis should be placed on control of the two distinct curing reactions by modification of chemical composition, utilization of catalysts and regulation of the degree of crosslinking through pressure control.

2. Polymer synthesis and characterization studies should be conducted to confirm that the conclusions reached with model compound studies can be attained.

3. The findings on the oxidative degradation of graphite fiber reinforced composites indicate a study should be conducted to determine the effect of oxygen partial pressure and degree of stress applied to the specimen. These studies would permit simulation of conditions to be encountered when employed in high performance jet engine components.

4. Further processing studies should be undertaken to optimize fabrication procedures and to determine the effect of post curing on graphite fiber reinforced composites.

5. Finally, it is recommended from observations made during this program, that specific formulations amenable to autoclave molding of composites should be investigated to determine the merit of the A-type polyimides for this application.

7. NEW TECHNOLOGY

This section provides discussions of new applications of the resin system recommended in this program together with new approaches for processing graphite. These concepts are believed to be of sufficient novelty that invention disclosures have been submitted to the TRW Patent Office. The subject matter of these disclosures are listed below:

Docket No.	Title
4766	Polyimide Resin Precoating of Graphite or Carbon Filaments
70-176	Thermo-oxidatively Stable Polyimide Composition
5102	Production of A-type Polyimide Reinforced Composites
5112	Bag Molding Technique for Reinforced Plastic Composites
70-192	Production of Crack-Free Graphite Reinforced Plastic Composites

A separate report covering these disclosures has been submitted to the NASA LeRC Technical Utilization Officer. A brief discussion of these inventions, their novelty, features and applications is presented below.

7.1 POLYIMIDE RESIN PRECOATING OF GRAPHITE OR CARBON FILAMENTS

During the processing studies of this program it was observed that A-type polyimide resins are useful in pre-coating graphite fiber strands. The pre-coating with a typical A-type polyimide, such as the commercially available P13N, from a dilute solution (less than 2% w/w) will result in a sized yarn which eliminates the fuzzy surface of these fibrous materials, therefore, permits accurate collimation of fibers. Sizing graphite fibers with an A-type polyimide results in a fiber product similar to that normally obtained with epoxy resins, however, the polyimide permits integrity of the sizing - resin interface at temperatures which normally degrade epoxies (>400°F).

7.2 THERMO-OXIDATIVELY STABLE POLYIMIDE COMPOSITION

During this program a highly promising formulation modification of the A-type polyimide was identified as having enhanced thermo-oxidative stability.

This resin system (1000 FMW NA/MDA/PMDA) demonstrated greater weight retention of in back-to-back comparisons with other candidate formulation modifications on aging in air at 600°F. The utilization of this resin system as a laminating resin was demonstrated by preparation of glass and graphite fiber reinforced composites.

7.3 PRODUCTION OF A-TYPE POLYIMIDE REINFORCED COMPOSITES

Processing procedures have been identified which permits production of thick (up to 1/2-inch) prepreg lay-ups or wrappings yielding composites having low void contents and good structural integrity. These preforms were prepared from unidirectional amic-acid A-type polyimide prepregs by laying up the amic-acid prepreg to the desired thickness and then imidizing the lay-up for relatively long cycles (∿24 hours) at low temperatures (∿300°F) at ambient pressure. These preforms are molded by the same techniques used to prepare laminates from fully imidized glass prepregs.

7.4 BAG MOLDING TECHNIQUE FOR REINFORCED PLASTIC COMPOSITES

Processing studies of the 1000 FMW NA/MDA/PMDA A-type polyimide formulation showed that it possesses excellent flow characteristics and hence, offers promise in bag molding processing methodology. This high resin flow property is important to vacuum bag, autoclave, pressure bag, and hydroclave fabrication because it permits molding at low pressures (50-200 psi) and at relatively low heat-up rates (3-15°F/min).

7.5 PRODUCTION OF CRACK-FREE GRAPHITE REINFORCED PLASTIC COMPOSITES

Molding procedures were developed that produced crack-free, structurally sound composites from the candidate polyimide/graphite prepregs. These procedures circumvented the problems of cracking and compressive failures in the composites during molding in a closed mold. The method consists of 1) cutting the prepregs approximately 3% shorter than the mold cavity, and 2) releasing the molding pressure and restraining the composite against warping during cool-down.

APPENDIX A
MODEL COMPOUND SYNTHESIS AND CHARACTERIZATION STUDIES

The synthesis and characterization of the two model compounds discussed in Section 2.1 was the first experimental work performed in the program. In one case it was necessary to prepare a model compound precursor. Specifically, 3,6-endooxy-1,2,3,6-tetrahydrophthalic anhydride, (oxynadic anhydride) was prepared and subsequently converted to N-phenyl 3,6-endooxy-1,2,3,6-tetrahydrophthalimide, (N-phenyl oxynadimide). N-phenyl 3,6-endomethylene-1,2,3,6-tetrahydrophthalimide (N-phenyl nadimide) was prepared directly from recrystallized nadic anhydride. A detailed description of the synthesis and characterization of these compounds is given below.

A.1 MODEL COMPOUND SYNTHESIS

A.1.1 3,6-Endooxy-1,2,3,6-tetrahydrophthalic Anhydride

A quantity of 980 g (10.0 moles) of maleic anhydride was dissolved with stirring in 817 g (12.0 moles) of furane at 50°C. After the maleic material was completely dissolved, heating and stirring were terminated. The product crystallized from solution and was isolated by vacuum filtration and dried to give 800 g (48%) of white crystals. Recrystallization (twice) from equal volumes of petroleum either (b.p. 60-110°C) and acetone yielded product in white needles; m.p. 107-108°C.

A.1.2 N-phenyl 3,6-Endooxy-1,2,3,6-tetrahydrophthalimide

A quantity of 332 g (2.0 moles) of 3,6-endooxy-1,2,3,6-tetrahydrophthalic anhydride (prepared above) was dissolved in 100 ml of DMF. To this stirred solution at 30°C was added 196 g (2.1 moles) of aniline and the solution was stirred for 90 minutes, followed by addition of 16 g (0.2 mole) of anhydrous sodium acetate and 204 g (2.0 moles) of acetic anhydride. The resulting mixture was stirred for one hour at 50°C, then allowed to cool to 25°C. The product formed was collected by vacuum filtration and dried to give 467 g (93%) of white crystals. Recrystallization from methanol gave white platelets; m.p. 156-157°.

A.1.3 N-phenyl Nadimide

A quantity of 246 g (1.5 moles) of nadic anhydride (recrystallized to a 1°C melting point range) was dissolved in a co-solvent consisting of 450 ml of toluene and 225 ml of DMF. To this solution was added 147 g (1.6 moles) of aniline and the mixture was heated and stirred under reflux for 18 hours, during which time water formed from the imidization was collected in a Dean-Stark trap. One-half of the solvent (∿400 ml) was stripped under vacuum on a rotary-evaporator and the remainder of the solution was allowed to cool to 25°C. After standing overnight, 324 g (89%) of brown crystals was collected by vacuum filtration. Recrystallization from methanol yielded light tan crystals; m.p. 143-144°C.

A.2 CHARACTERIZATION OF MODEL COMPOUNDS

A.2.1 Differential Scanning Calorimetry (DSC)

In both cases below, the slope of the DSC curves are attributed to sample volatility.

A.2.1.1 N-Phenyl Nadimide - The DSC behavior of N-phenyl nadimide (Figure A-1) displays an endotherm (145.5°C) corresponding to the observed capillary melting point.

A.2.1.2 N-phenyl Oxynadimide - The DSC characteristics of this compound (Figure A-2) did not show an endotherm corresponding to an observed capillary melting point of 156 to 157°C. Instead, the curve is characterized by a plateau from 165-170°C, followed by an endotherm at 175°. This endotherm corresponds exactly to the inflection point observed in the TGA tracing of this material. The assignment of this endotherm is onset of pyrolysis temperature and initiation of reverse Diels-Alder reaction of this compound. For further discussion refer to the TGA interpretation on Page 85.

A.2.2 Ultraviolet Analysis

The ultraviolet spectrum of oxynadic anhydride (0.061 w/w in acetonitrile) shows no absorption in the region of 220-340 mμ indicating the double bond in this compound absorbs below 220 mμ.

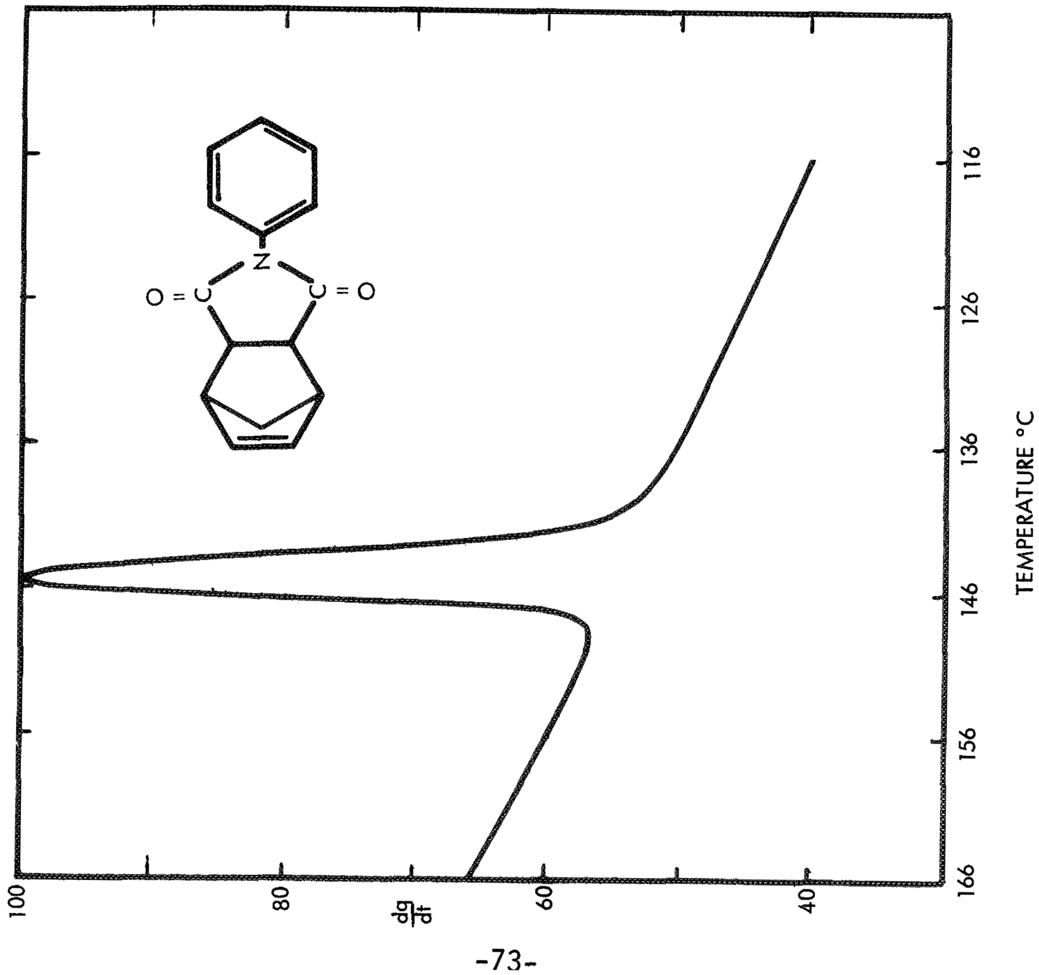

Figure A-1. Differential Scanning Calorimetry Curve for N-phenyl Nadimide

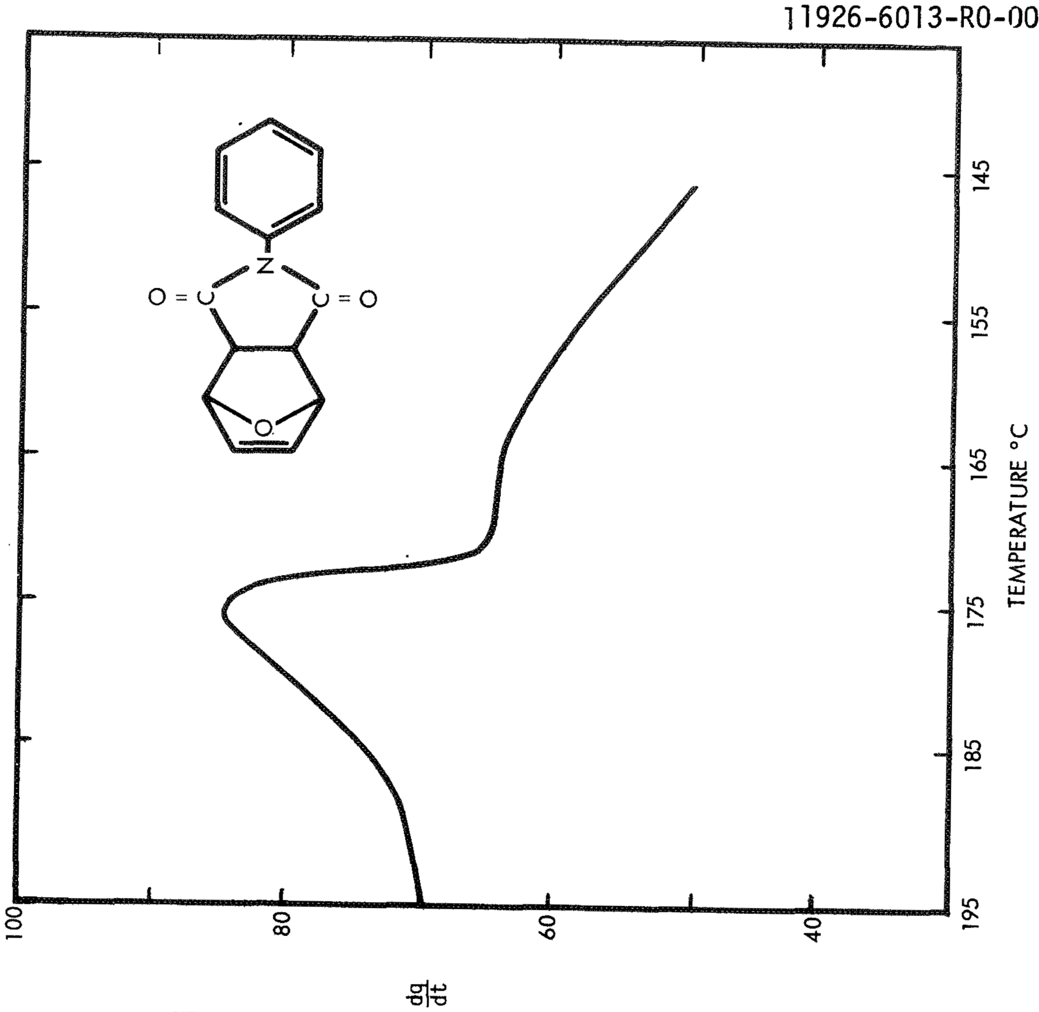

Figure A-2. Differential Scanning Calorimetry Curve for N-phenyl Oxynadimide

Ultraviolet spectra obtained for N-phenyl nadimide and N-phenyl oxynadimide, also determined in acetonitrile, gave absorption in the region of 280 mμ and below, attributable to phenyl as imide N-phenyl.

A.2.3 Infrared Analysis

A.2.3.1 Oxynadic Anhydride - The infrared spectrum of oxynadic anhydride appears in Figure A-3. The assignments of principal absorption bands are given in Table A.I.

TABLE A.I

MODEL COMPOUND INFRARED PRINCIPAL ABSORPTION ASSIGNMENTS

Compound	Absorption, cm^{-1}	Band Assignment
1. Oxynadic Anhydride	1855 and 1790	Endocyclic anhydride
	1020	Ether as oxygen in bridge
	731	*cis*-olefin
2. N-phenyl Nadimide	2880	Endocyclic methylene
	1700 and 1765	Endocyclic imide
	1592	Phenyl stretch
	1495	Phenyl stretch
	740	*cis*-olefin
3. N-phenyl Oxynadimide	1775 and 1710	Endocyclic imide
	1592	Phenyl stretch
	1495	Phenyl stretch
	710	*cis*-olefin

A.2.3.2 N-phenyl Nadimide - The infrared spectrum of N-phenyl nadimide appears in Figure A-4. The assignments of principal absorption bands are given in Table A.I.

A.2.3.3 N-phenyl Oxynadimide - The infrared spectrum of N-phenyl oxynadimide appears in Figure A-5. The assignments of principal absorption bands are given in Table A.I.

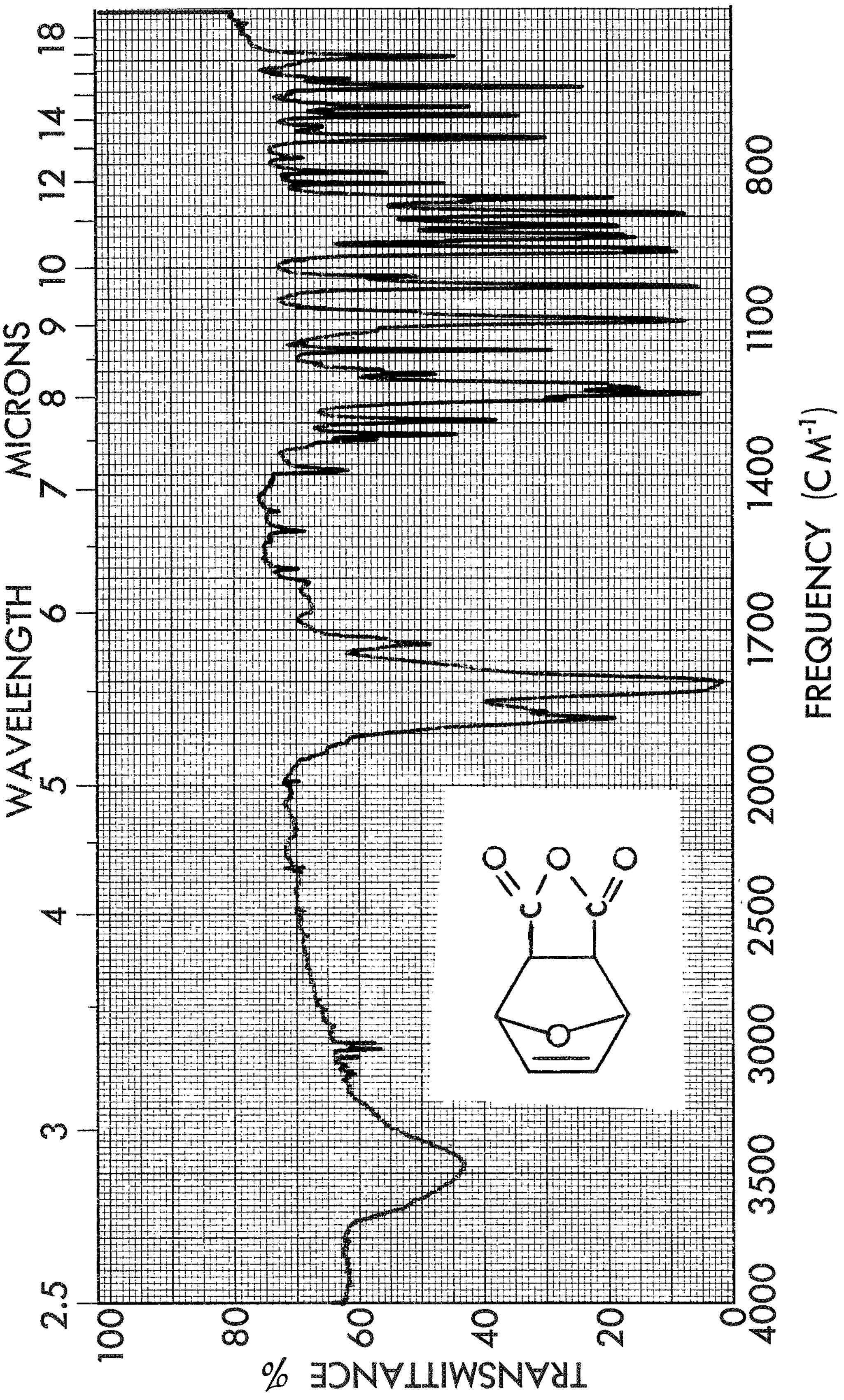

Figure A-3. Infrared Spectrum of Oxynadic Anhydride (KBr)
Concentration: 1.9 mg/g KBr

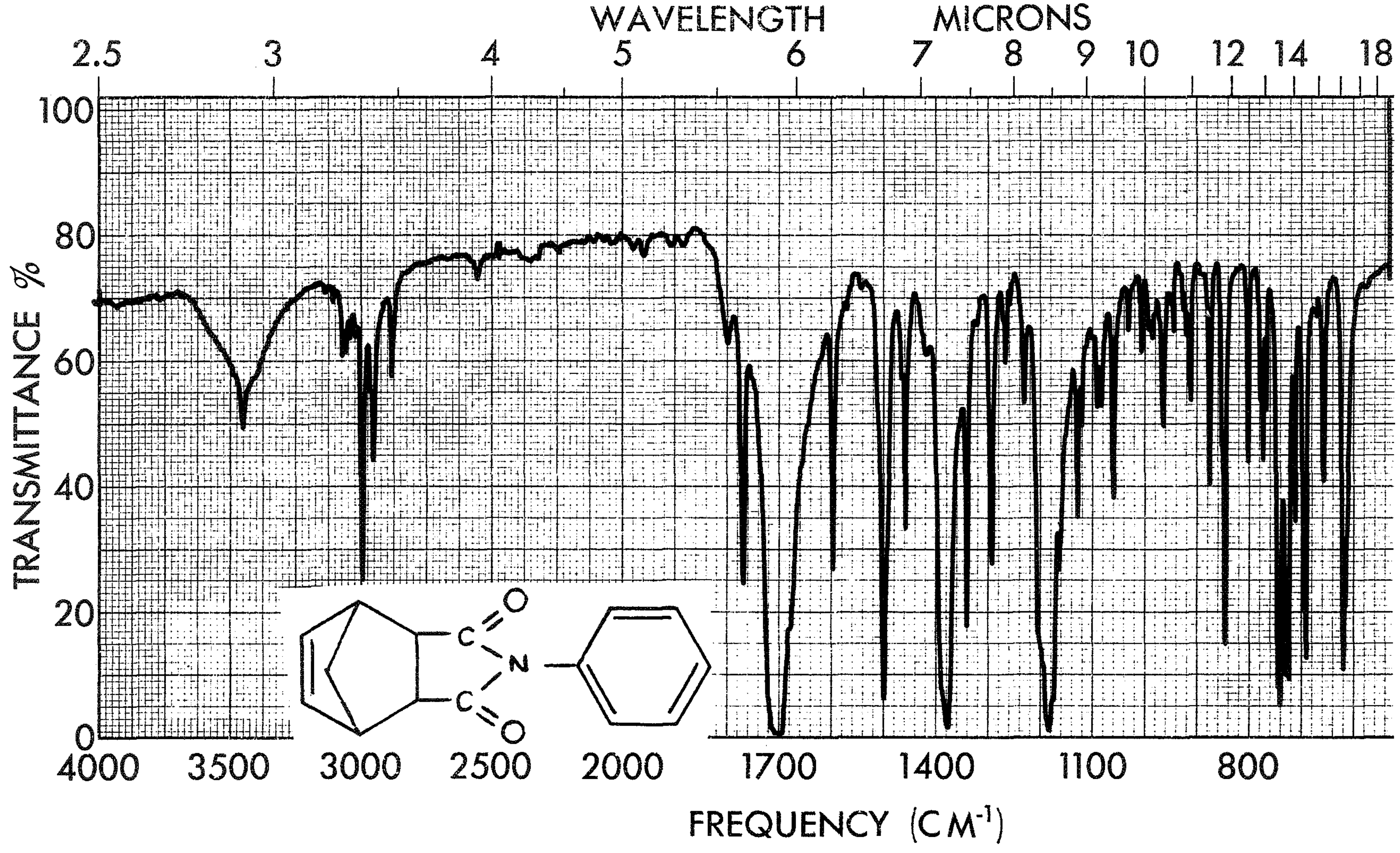

Figure A-4. Infrared Spectrum of N-phenyl Nadimide (KBr)
Concentration: 4.8 mg/g KBr

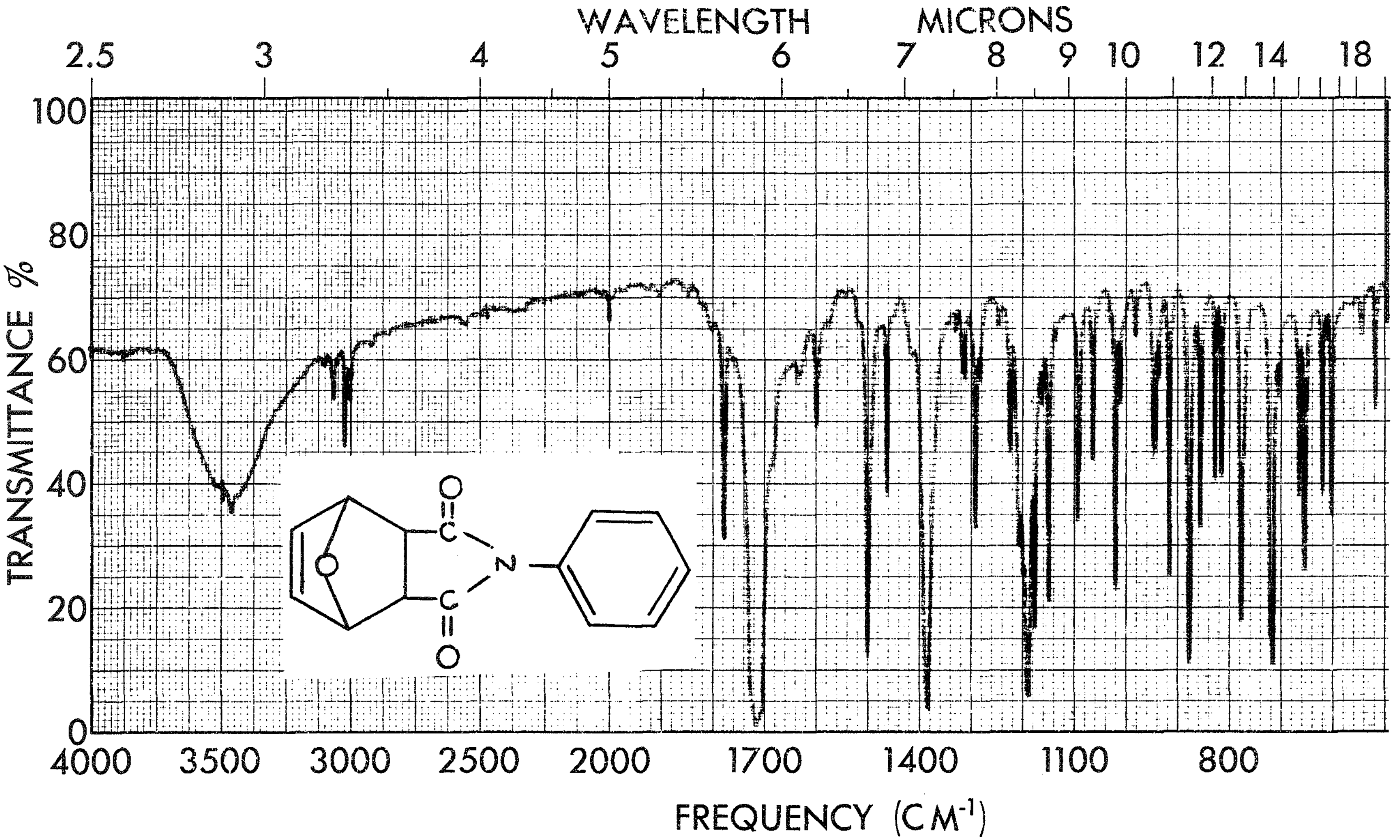

Figure A-5. Infrared Spectrum of N-phenyl Oxynadimide (KBr)
Concentration: 2.5 mg/g KBr

The principal differences between the precursor oxynadic anhydride Figure A-3 and this compound involve the disappearance of anhydride absorption bands in the 1790-1855 cm^{-1} and 600-1000 cm^{-1} regions of Figure A-5, and the appearance of aromatic (as N-phenyl) and imide bands throughout the region from 1800-600 cm^{-1}. Although the spectra of the two N-phenyl model compounds in Figures A-4 and A-5 are quite similar, the absorption band at 2880 cm^{-1} appearing in Figure A-4, but absent in Figure A-5 has been tentatively assigned to nadic endomethylene and conversely, the strong absorption band at 1020-1040 cm^{-1} present in Figures A-3 and A-5, but absent in Figure A-4 has been assigned to endocyclic oxygen.

A.2.4 Elemental Analysis

As a further fix on the purity of the synthesized models, elemental analyses were determined on samples of the monomer oxynadic anhydride as well as the model imides N-phenyl nadimide and N-phenyl oxynadimide Each of the samples gave acceptable data which are given in Table A.II below.

TABLE A.II
ELEMENTAL ANALYSIS DATA

1. Oxynadic Anhydride		
	Calculated for $C_8H_6O_4$:	C, 58.20; H, 3.65
	Found:	C, 58.00; H, 3.70
2. N-phenyl Nadimide		
	Calculated for $C_{15}H_{13}NO_2$:	C, 75.45; H, 5.49; N, 5.86
	Found:	C, 75.44; H, 5.51; N, 6.10
3. N-phenyl Oxynadimide		
	Calculated for $C_{14}H_{11}NO_3$:	C, 69.82; H, 4.60; N, 5.82
	Found:	C, 69.85; H, 4.62; N, 6.20

A.2.5 Nuclear Magnetic Resonance Analysis

The nuclear magnetic resonance (n.m.r.) spectra of the synthesized model compounds substantiated the high purity of these materials. The n.m.r.

spectra, determined in deuterated chloroform, employing tetramethyl silane (TMS) as an internal standard, are discussed individually below.

A.2.5.1 Oxynadic Anhydride - The n.m.r. spectrum of oxynadic anhydride is shown in Figure A-6. In this spectrum proton absorptions in the correct 2:2:2 ratio were observed at 6.82τ, 4.59τ and 3.47τ and have been assigned to anhydride juncture, bridgehead, and olefinic protons, respectively. These data and literature substantiations of assignments appear in Table A.III.

A.2.5.2 N-phenyl Oxynadimide - The n.m.r. spectrum of this model compound is presented in Figure A-7. As expected, this spectrum is quite similar to that of oxynadic anhydride (Figure A-6). In this spectrum, integration has shown a proton ratio of 5:2:2:2 which corresponds to the correct number of protons. The shielding effect of the imide phenyl ring, whose protons absorb as a multiplet centered at 2.70τ, causes the other protons to shift slightly upfield. Absorptions at 7.02τ, 4.60τ and 3.50τ have been assigned to anhydride juncture, bridgehead, and olefinic protons, respectively, based upon assignments established for the oxynadic anhydride precursor. These data are summarized in Table A.III.

A.2.5.3 N-phenyl Nadimide - The n.m.r. spectrum of N-phenyl nadimide is shown in Figure A-8. This model compound gives a proton resonance spectrum quite dissimilar from N-phenyl oxynadimide (Figure A-7). The spectrum integrates for four distinct protons in the ratio of 5:2:4:2, instead of the expected five distinct protons in a ratio of 5:2:2:2:2. The five imide phenyl protons appear again as a multiplet centered at 2.70τ as in Figure A-7, but the influence of shielding by the endocyclic methylene bridge has apparently caused an upfield shift of the remaining proton peaks. These two methylene bridge protons appear as a complex multiplet (double-doublet) centered at 8.40τ. The olefinic protons show resonance absorption at 3.80τ. The only remaining protons (4 by integration) appear as a peak centered at 6.67τ. These protons have been assigned as the two bridgehead protons and the two imide ring juncture protons.

A.2.6 Thermal and Oxidative Stabilities

The TGA curve of N-phenyl nadimide in Figure A-9 (N_2) and Figure A-10 (air) show that the thermal and oxidative stabilities of this model compound

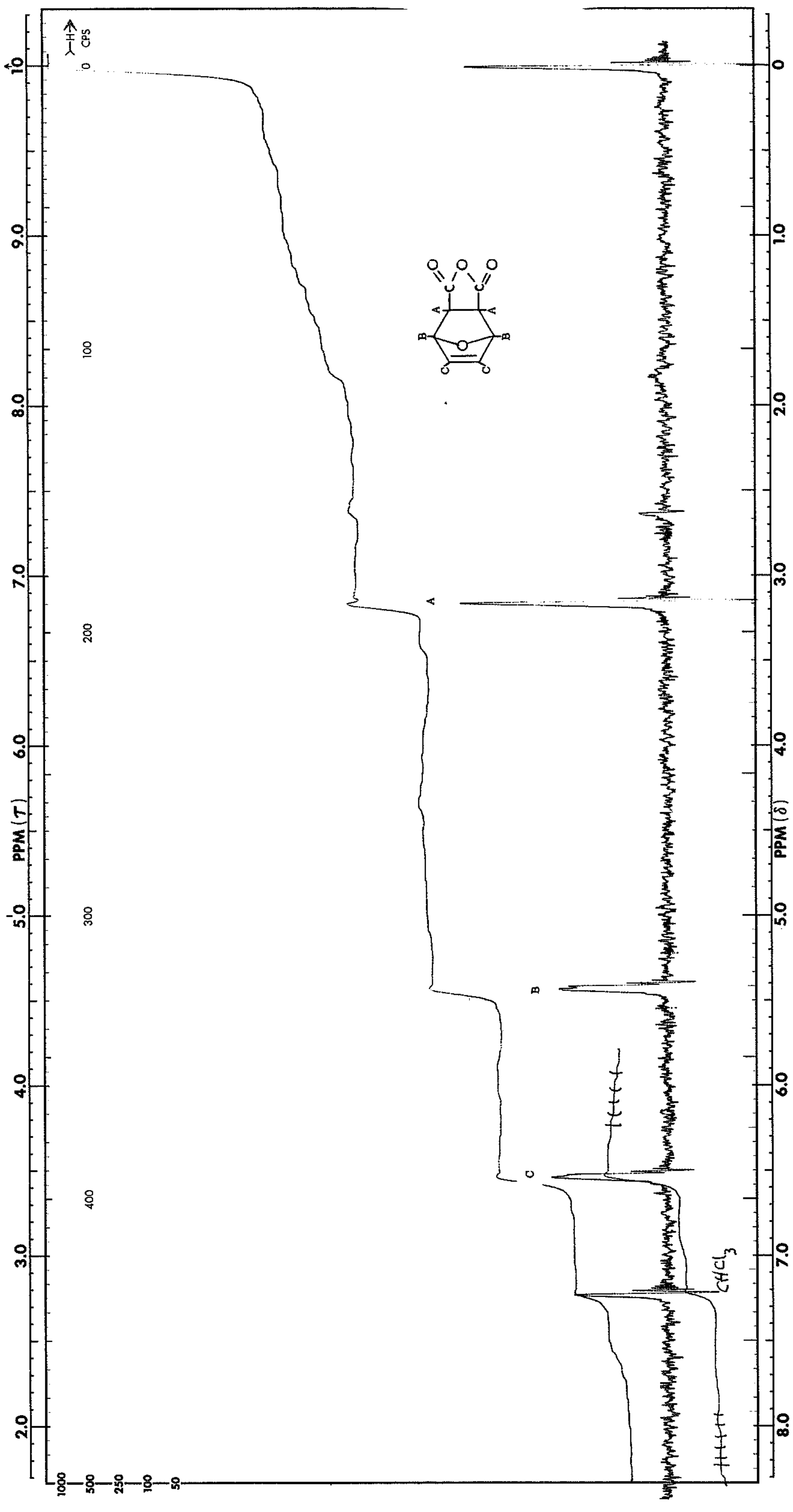

Figure A-6. Nuclear Magnetic Resonance Spectrum of Oxynadic Anhydride
Solvent: $CDCl_3$

TABLE A.III

MODEL COMPOUND NMR DATA[a]

Compound	Proton Ratio	Observed Proton Chemical Shifts (τ)	Literature[b]		Chemical Shift (τ)
			Compound	Solvent	
1. Oxynadic Anhydride	2:2:2	A. 6.82 anhydride juncture B. 4.59 bridgehead C. 3.47 olefin	Same	CH_3CN	A. 6.75 B. 4.66 C. 3.47
2. N-phenyl Oxynadimide	5:2:2:2	A. 7.02 anhydride juncture B. 4.60 bridgehead C. 3.50 olefinic D. 2.70 phenyl			
3. N-phenyl Nadimide	5:2:4:2	A. 8.40 methylene bridge B.} 6.67 anhydride juncture C.} and bridgehead D. 3.80 olefinic E. 2.70 phenyl	Nadic anhydride	CCl_4	A. 8.36 B.} 6.50 C.} D. 3.72

[a] All spectra run on a Varian Model A-60 spectrometer employing deuterated chloroform as a solvent and tetramethyl silane as an internal standard.

[b] See References 10, 11 and 12

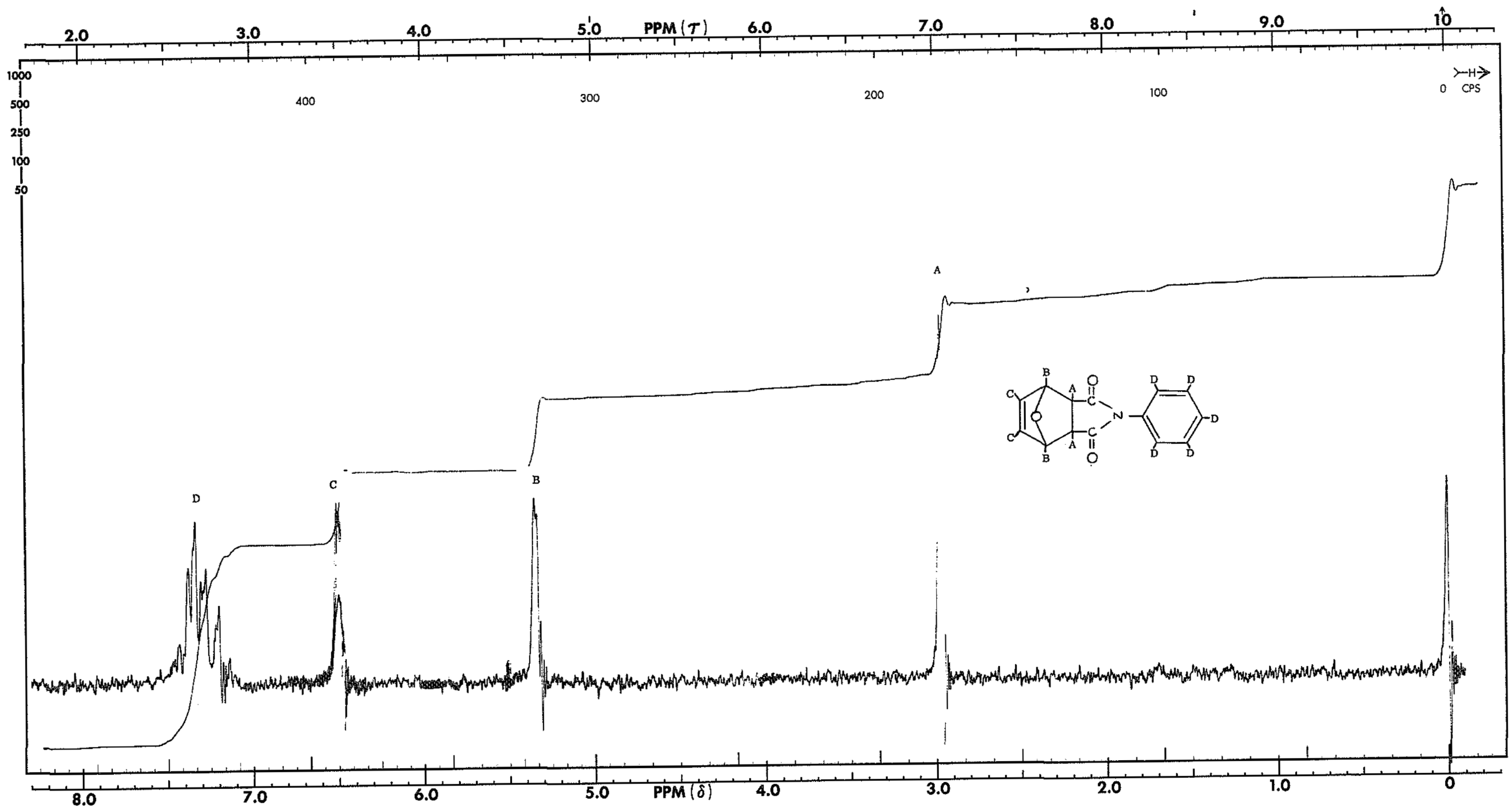

Figure A-7. Nuclear Magnetic Resonance Spectrum of N-phenyl Oxynadimide
Solvent: $CDCl_3$

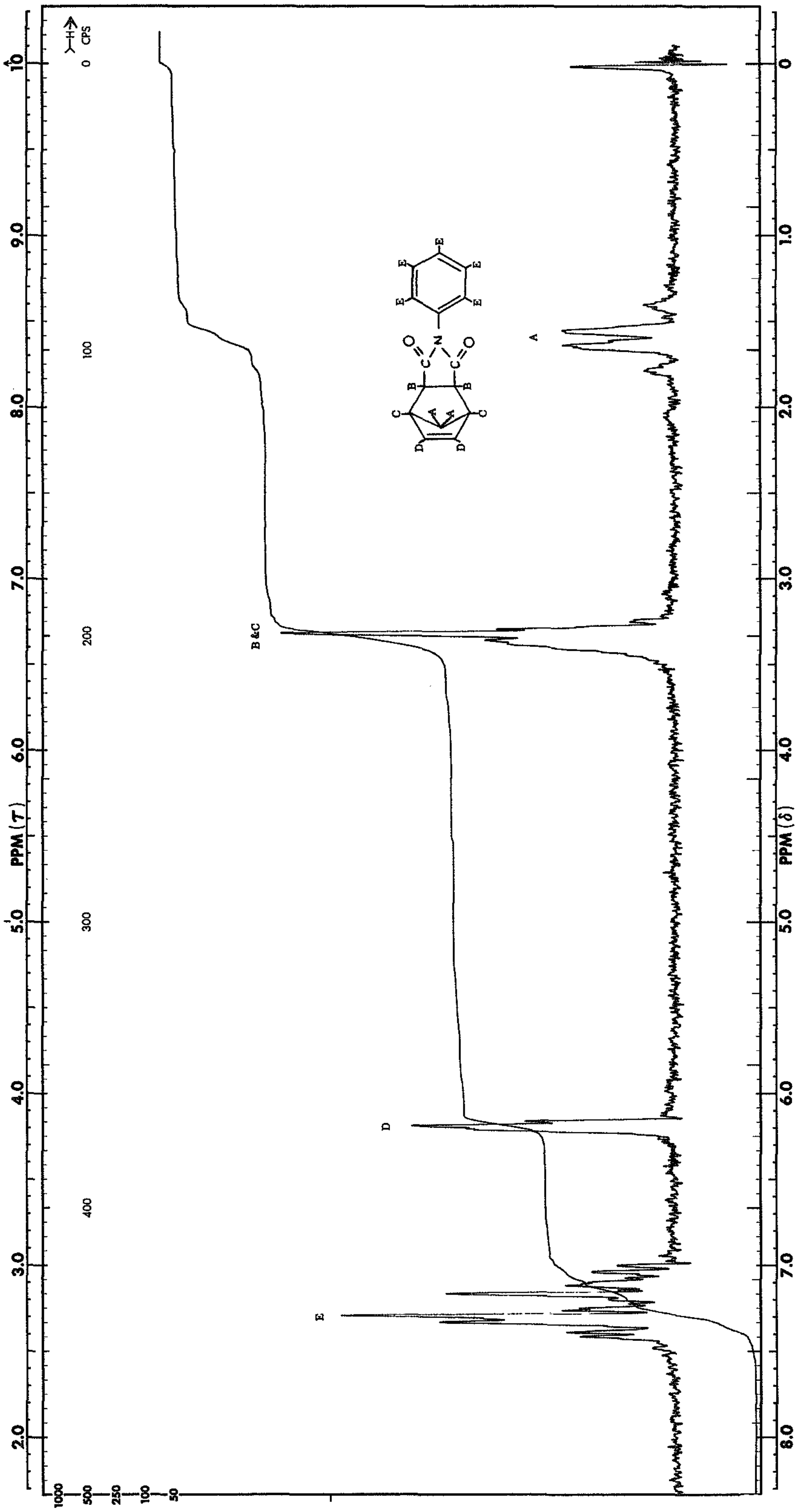

Figure A-8. Nuclear Magnetic Resonance Spectrum of N-phenyl Nadimide
Solvent: $CDCl_3$

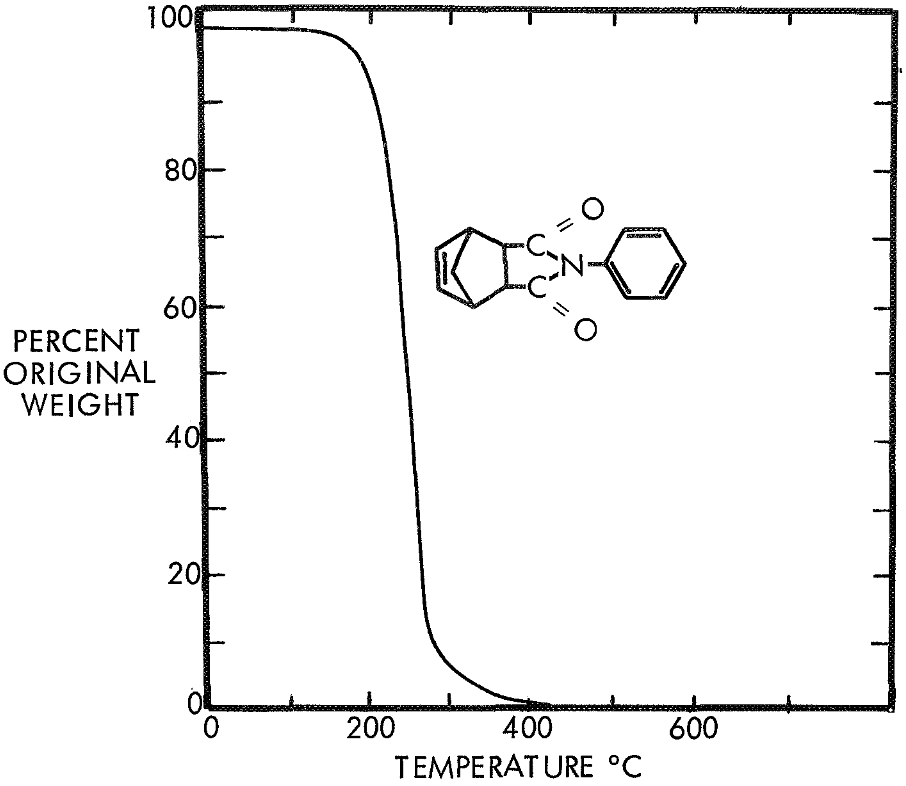

Figure A-9. Thermogram of N-phenyl Nadimide
Environment: Nitrogen; Scan Rate: 3°C/min

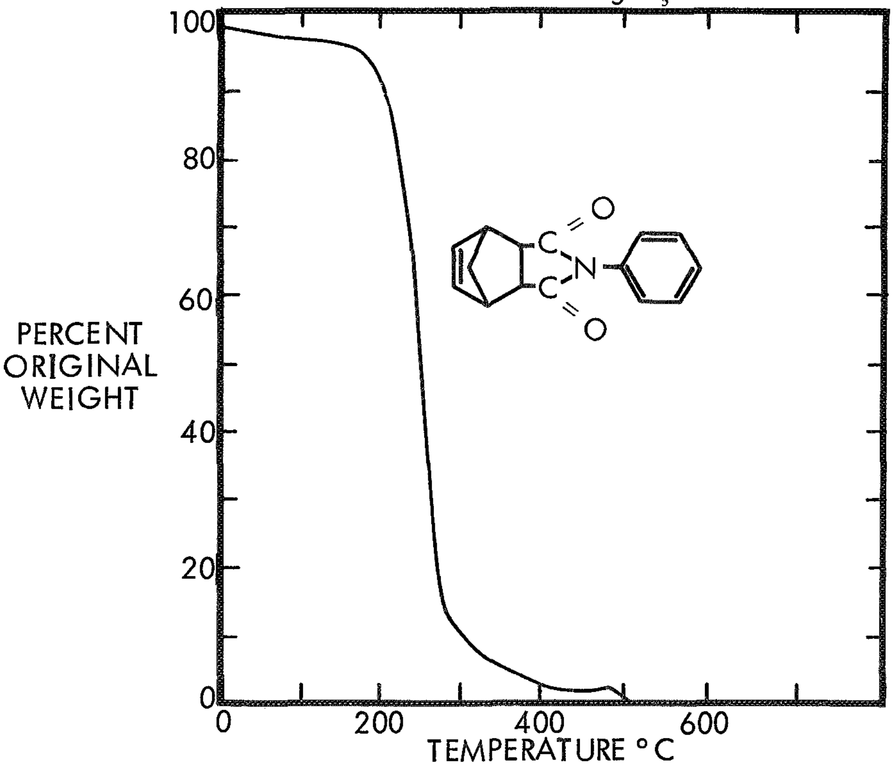

Figure A-10. Thermogram of N-phenyl Nadimide
Environment: Air; Scan Rate: 3°C/min

are essentially identical. Although approximately 90% of the material had volatilized by the time apparent reaction had occurred, sufficient material was present to show that this compound appears to be undergoing the reverse Diels-Alder-addition polymerization in the temperature range of 285-350°C in both inert and oxidizing environments. Prior preliminary pyrolysis of this material at TRW in a closed, constant volume system has shown volatility to be no problem.

It was proposed originally that the oxynadic species appeared to undergo the reverse Diels-Alder-addition polymerization at a temperature considerably below that of the nadic group. Such a species could consequently serve as an imide prepolymer end cap offering potential lower processing conditions than the nadic group, but still yielding a stable polymer after pyrolysis reaction. The TGA curves of N-phenyl oxynadimide, Figure A-11 (N_2) and Figure A-12 (air) strongly supported this concept.

The TGA curves for N-phenyl oxynadimide in both N_2 and air are essentially identical. Considerable volatilizing of the compound (80-85%) had occurred before any apparent polymer was obtained. This proved to be of no hindrance, consequently attention is called to the 175°C area in both Figures A-11 and A-12. It is at this temperature in both N_2 and air that an inflection occurs during apparent compound volatilization. This temperature (175°C) appears to be the point at which reverse Diels-Alder-addition polymerization begins to occur. The 175°C temperature is identical to the temperature of the endotherm observed in the DSC analysis shown previously in Figure A-2. The pyrolysis phenomena evidently are complete and a stable polymeric resin formed at 250-270°C as evidenced by a plateau in both curves out to ∿380-420°C, at which point both curves display a plateau giving evidence of thermal stability to temperatures >500°C.

A.2.7 Hydrolytic Stabilities

As expected, oxynadic anhydride is quite hydrolytically labile. A sample of this material dissolved completely in boiling water in thirty minutes.

However, both N-phenyl nadimide and N-phenyl oxynadimide were quite resistant to distilled water hydrolysis. Approximately 95% of both

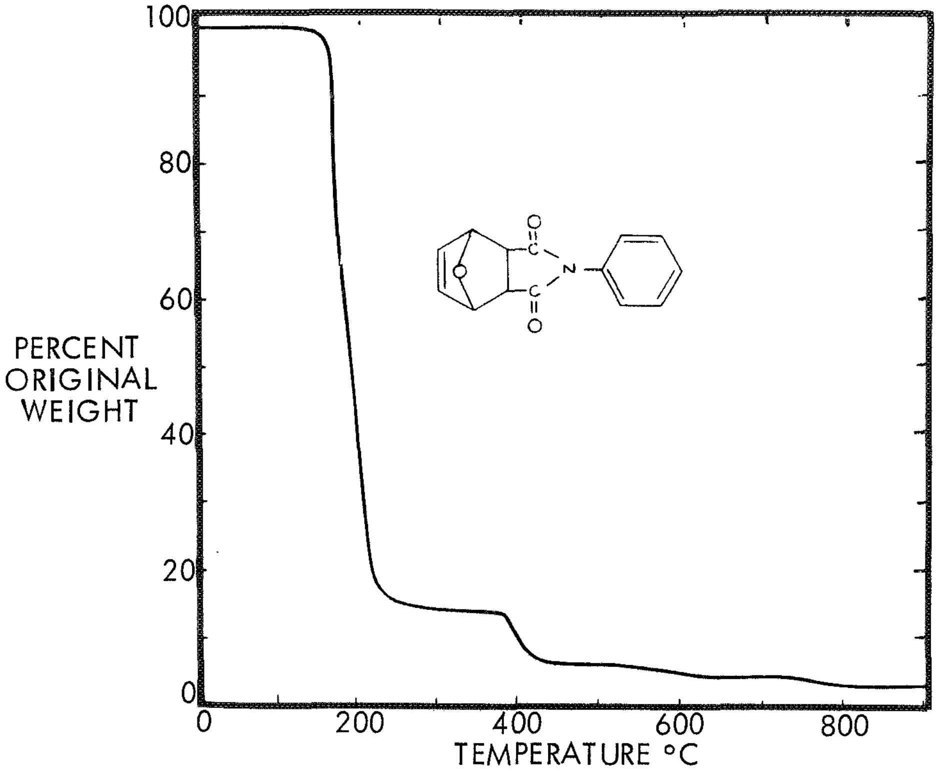

Figure A-11. Thermogram of N-phenyl Oxynadimide
Environment: Nitrogen Scan Rate: 3°C/min

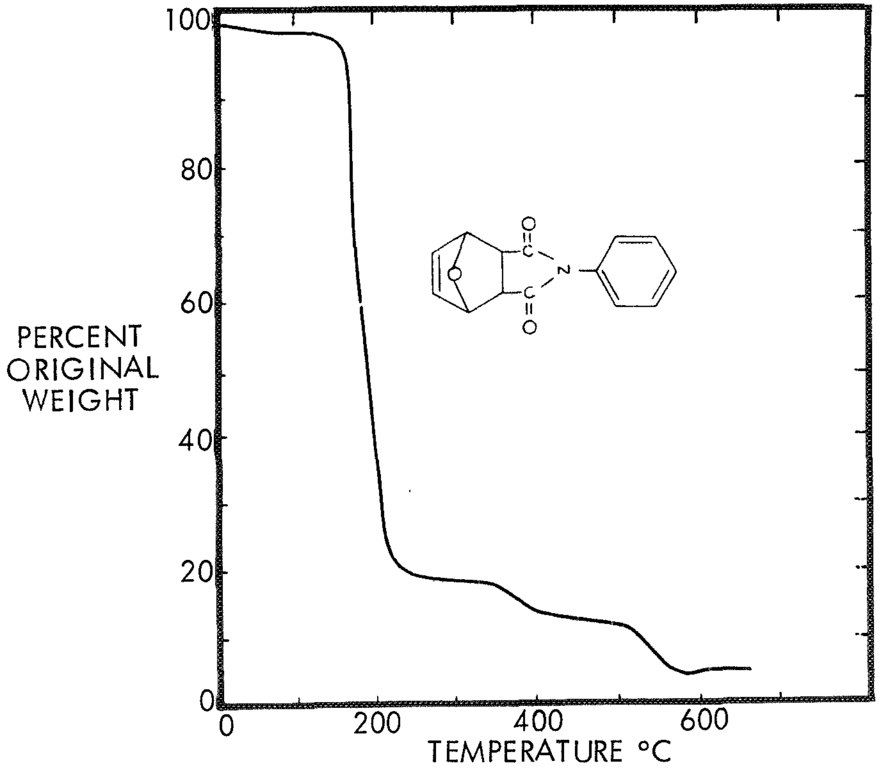

Figure A-12. Thermogram of N-phenyl Oxynadimide
Environment: Air Scan Rate: 3°C/min

model compounds remained insoluble after a two-hour water boil. The insoluble material was identified as unchanged original imide by infrared analysis by comparison of spectra with those previously determined for the original model compounds.

APPENDIX B
MODEL COMPOUND PYROLYSIS GAS CALCULATIONS

The pyrolysis apparatus and pyrolysis runs described in Section 2.2 employed the following theory and equations to calculate masses of gas evolved during experimentation. Two methods were used depending on whether nitrogen or vacuum environments were employed.

In experiments designed to determine the effect of nitrogen pressure on the pyrolysis of the model compounds, the system was filled with dry nitrogen gas to a pressure of 760 torr after prior evacuation to 1 torr as above. The pyrolysis was then conducted following the identical steps as described above for the case of a vacuum as the environment at the onset of pyrolysis.

In the case when a vacuum was used as the initial pyrolysis environment, the gas formed during the pyrolysis was isolated and analyzed. On pyrolysis of N-phenyl nadimide (I) the principal gaseous product was cyclopentadiene (V) and on pyrolysis of N-phenyl oxynadimide (II) the principal gaseous product was essentially all furane (VI). Because of these findings it was possible to compute the mass of the gaseous products assuming the products behaved as ideal gases. Because sections of the pyrolysis system are at different temperatures the total amount of material is calculated from the ideal gas equation as follows:

$$n_t = n_1 + n_2 + n_3 \tag{B-1}$$

where n_t = total moles of gas

n_1 = moles of gas maintained in the pyrolysis section volume (V_1) at the pyrolysis temperature (T_1)

n_2 = moles of gas maintained in the cold trap section volume (V_2) at the its temperature (T_2)

and n_3 = moles of gas in the system volume (V_3) maintained at room temperature (T_3)

therefore
$$n_t = \frac{P}{R}\left(\frac{V_1}{T_1} + \frac{V_2}{T_2} + \frac{V_3}{T_3}\right) \tag{B-2}$$

where P = pressure in the system and
R = the ideal gas constant = 82.01 ml-atm/mole-°K

The analysis of the pyrolysis gas (Appendix D, Page 119) showed that small amounts of methyl alcohol were present. Consequently, using the molecular weight of (V) to calculate its mass from the pressure in the system is not strictly correct, however, these quantities were in general quite small and when calculated rigorously correspond to a methyl alcohol weight of less than 10 mg (or an equivalent amount of less than 0.05% methyl alcohol in the starting model compound). Consequently, its presence in the gas phase is attributed to residual methanol remaining from recrystallization of the model compound.

APPENDIX C
PYROLYSIS RESIDUE CHARACTERIZATION

The solid residues arising from the pyrolysis of N-phenyl nadimide (I) and N-phenyl oxynadimide (II) as described in Section 2.2 were analyzed extensively by several chemical and instrumental methods. The interpretation of these characterization data culminated in the pyrolytic polymerization mechanism described in Section 2.4. All pertinent data obtained from the solid residues are described and tabulated below.

C.1 ELEMENTAL ANALYSIS

The elemental analysis of the residues obtained from the pyrolysis of (I) are listed in Table C.I. The carbon content, and to a lesser extent, the nitrogen content, can be used to estimate the relative ratio of the analytical concentration (amount in all forms) of cyclopentadiene (V) remaining in the residue obtained on pyrolysis of N-phenyl nadimide (I). This analysis assumes that (I) consists of N-phenyl maleimide (III) and (V). The carbon

TABLE C.I

ELEMENTAL ANALYSIS OF RESIDUE OBTAINED ON PYROLYSIS OF N-PHENYL NADIMIDE

Sample No.	Pyrolysis Conditions	Elemental Analysis		n_r^c/n_r^m	
		%C	%N	Carbon Method	Nitrogen Method
20	I-350-2-V	73.71	6.01	0.6_6	0.9_1
21	I-350-3-V	73.95	6.08	0.7_0	0.8_7
42	I-350-2-N	74.54	5.71	0.8_2	1.0_0
43	I-300-3-V	73.05	6.22	0.5_4	0.7_0
59	I-300-2-V	74.65	5.58	0.8_5	1.1_8
32	I-300-2-N	74.59	5.75	0.8_4	1.0_7
44	I-275-2-V	74.46	6.37	0.8_2	0.7_1

and nitrogen contents of (I) are 75.29% and 5.85% and of (III) are 69.34% and 8.09%, respectively. The molar ratio of (V) to (III) maleimide (n_r^c/n_r^m) is calculated from the carbon fractional (C) contents as follows:

$$n_r^c/n_r^m = \frac{2.884\ C-2.000}{1-1.100\ C} \qquad \text{(C-1)}$$

Calculation of this same ratio from the nitrogen fractional content (N) is accomplished with the aid of Equation C-2.

$$n_r^c/n_r^m = \frac{0.212}{N} - 2.62 \qquad \text{(C-2)}$$

As can be seen from Table C.I the (V) content in the pyrolysis products of (I) varies from 0.54 to 0.85 when calculated on the basis of carbon content (Equation C-1) and 0.71 to 1.18 when calculated on the basis of nitrogen content (Equation C-2). These data are consistent with the (V) isolated outside the residue as a liquid or gas (Table I, Page 7). The presence of (V) in the residue as discussed in the sections below is fundamental to the proposed polymerization mechanism given in Section 2.4.

Table C.II lists the elemental analysis of the residues obtained from pyrolysis of N-phenyl oxynadimide (II) and N-phenyl maleimide (III). The analysis data for products 28-30 from (II) strongly suggest that furane (VI) is not present in the pyrolysis residues. Based on the model compound, the theoretical percent (VI) available for reaction is 28.2% and for a 20 g sample this amounts to a quantity of 5.64 g. In the two experiments

TABLE C.II

ELEMENTAL ANALYSIS OF RESIDUE OBTAINED ON PYROLYSIS OF N-PHENYL OXYNADIMIDE AND N-PHENYL MALEIMIDE

Sample No.	Model N-Phenyl Imide Type	C (%)	N (%)
28	II-250-2-V	69.38	7.59
29	II-250-1-V	69.38	7.66
30	II-250-2-N	69.33	7.28
22	II-350-2-V	69.94	8.07
47	II-350-3-V	70.00	7.49
64	III-350-2-V	71.18	7.32

where acceptable recovery was achieved, Samples 47 (II-350-3-V) and 68 (II-350-2-V), the total matter isolated as liquid and gas ($W_t + W_g$) was 5.71 and 5.98 g, respectively, which agrees reasonably well with the theoretical amount of (VI). Subsequent analysis of these products (see Section C.4 and C.5) confirm that the furane volatilized away from the pyrolysis tube and was not available for reaction during pyrolysis. The similarity of N-phenyl oxynadimide (II) polymer to N-phenyl maleimide (III) polymer is discussed in Sections C.4 and C.5.

C.2 MOLECULAR WEIGHT DETERMINATION

C.2.1 Vapor Phase Osmometry (VPO)

The experimental results of number average ($\overline{M}_n$) molecular weight determination for several key pyrolyses runs are summarized in Table C.III. These data were obtained using standard VPO methodology and dimethyl formamide (DMF) solvent and at a sample temperature of 100°C.

TABLE C.III
MOLECULAR WEIGHT OF PYROLYSIS PRODUCTS

Sample No.	Pyrolysis Conditions	$\overline{M}_n$
20	I-350-2-V	662
67	I-350-2-V	614
42	I-350-2-N	590
43	I-300-3-V	1210
59	I-300-2-V	734
66	I-300-2-V	752
32	I-300-2-N	1160
44	I-275-2-V	565
29	II-250-1-V	650
28	II-250-2-V	1390[a]
30	II-250-2-N	1900[a]
47	II-350-3-V	976[a]
64	III-350-2-V	831[a]

[a] Sample not completely soluble in DMF

These data show certain trends as to the degree of polymerization versus pyrolysis variables employed. The variations of temperature, time, and environment affect the $\overline{M}_n$ of products from (I). For Samples 32 and 43 it appears that conditions of 300°C for two hours under nitrogen (Sample 32) gives polymer of $\overline{M}_n$ approximately equivalent to that obtained under conditions of 300°C for three hours in vacuum. This fact was confirmed by gel permeation chromatographic analysis as discussed below. The effect of time of pyrolysis at 300°C under vacuum on apparent $\overline{M}_n$ of polymeric product is shown by comparing Sample 43, pyrolyzed for three hours, with Samples 59 and 66.

The lower $\overline{M}_n$ for Sample 44 was expected in light of the n.m.r. spectrum of this compound which showed it to contain remnants of both model compound and polymer as described in Section C.5. The $\overline{M}_n$ of Sample 67 showed the product pyrolyzed at 350°C for two hours under vacuum to have a lower degree of polymerization than all samples pyrolyzed at 300°C. This strongly suggests that temperatures >300°C were indeed unnecessary to define a superior polymeric product, such as those described in Section 3.

Samples 28, 29, 30 and 47 are products from the pyrolysis of N-phenyl oxynadimide (II) and 64 is the product obtained from N-phenyl maleimide (III). The conclusions drawn above for the effect of time and temperature on the $\overline{M}_n$ of the pyrolysis residues of (I) are valid for the results observed for pyrolysis of (II). Sample 29 was heated for only one hour at 250°C under vacuum whereas both Samples 28 and 30 were heated for two hours at 250°C under vacuum and nitrogen, respectively. Sample 47 pyrolyzed at 350°C resulted in a lower $\overline{M}_n$. Only Sample 29 of this series was tractable, suggesting onset of crosslinking in Samples 28, 30 and 47. Because of the partial insolubility of Samples 28, 30 and 47, no direct comparison can be made between these materials.

Sample 64, the product isolated from pyrolysis of (III) also was partially intractable. The similarity of this product to those obtained for products from (II) is discussed in Sections C.4 and C.5. Because the pyrolysis of (III) was run under only one set of experimental conditions, no further conclusions can be made.

C.2.2 Gel Permeation Chromatography (GPC)

Several pyrolysis products obtained during this study were analyzed by GPC to provide an indication of the molecular weight distribution formed during the pyrolysis. A typical curve is given in Figure C-1.

The gel permeation chromatographic results can be summarized by the following:

- Pyrolyzing (I) at 300°C for two hours in a nitrogen environment results in a polymer having approximately the same $\overline{M}_n$ and $\overline{M}_w$ as that obtained from pyrolyzing it for three hours under a vacuum environment.
- The average number molecular weight obtained from pyrolysis of (II) is approximately twice that obtained from pyrolysis of (I) and (III).
- The molecular weight distribution is much broader in the pyrolysis products obtained from (II) and (III).
- The close agreement between the ratios of number average molecular weights infers validity to the absolute numbers obtained from VPO.
- The products obtained on pyrolysis of (I) have two distinct molecular weight ranges, a relatively small high molecular weight portion and large low molecular weight portion.
- The products obtained from pyrolysis of (II) (II-350-2-V) give three high molecular weight fractions and one low molecular weight fraction.

C.3 UNSATURATION CONTENT

The unsaturation content of the pyrolysis residues was determined by bromine absorption and semiquantitatively confirmed by infrared analysis. The results of these studies are tabulated in Table C.VI.

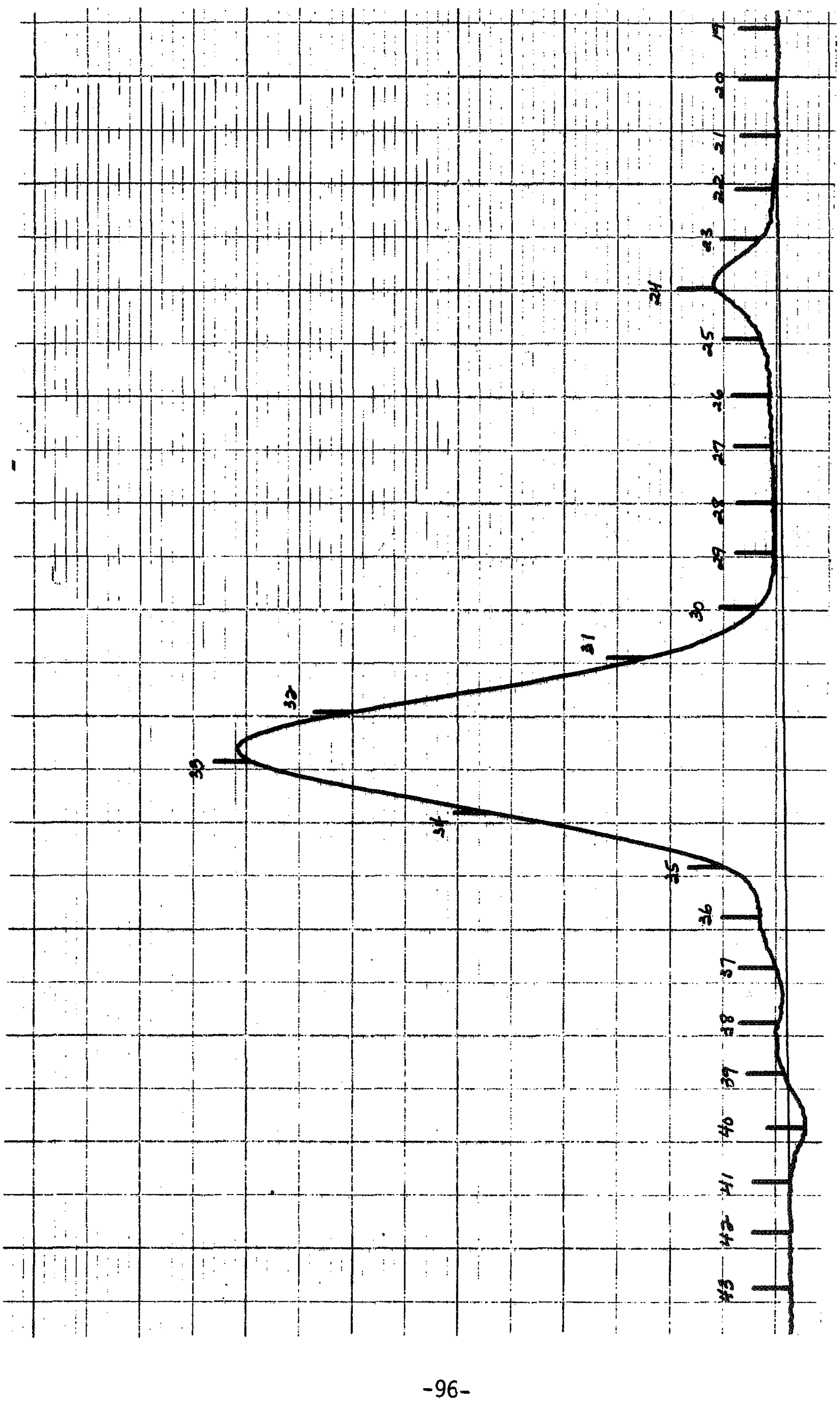

Figure C-1. Gel Permeation Chromatogram of N-phenyl Nadimide Pyrolysis Residue Sample 32

TABLE C.IV
SUMMARY OF UNSATURATION ANALYSIS RESULTS

Sample No.	Pyrolysis Conditions	Bromine Absorption, meq/g	$[\text{Br}][\overline{M}_n]$[a] eq/mol	A/c,[b] mg^{-1}	A/c[Br] 10^2g/meq-mg
21	I-350-3-V	0.39	----	0.042	10.8
67	I-350-2-V	1.60	0.98	0.129	8.0
42	I-350-2-N	0.87	0.51	0.066	7.6
43	I-300-3-V	0.71	0.86	0.066	9.3
59	I-300-2-V	0.99	0.76	0.061	6.2
66	I-300-2-V	1.51	1.14	0.058	3.9
32	I-300-2-N	1.34	1.55	0.108	8.0
44	I-275-4-V	0.56	0.32	0.060	10.7
28	II-250-2-V	0.76	1.06	----	----
30	II-250-2-N	0.19	0.36	----	----
47	II-350-3-V	0.43	0.42	0.047	11.0
64	III-350-2-V	0.57	0.47	0.071	12.5

[a] Bromine content x number average molecular weight

[b] Absorbance at 1630 cm^{-1}/weight of pyrolysis residue in KBr pellet

In each of the samples of pyrolyzed N-phenyl nadimide (I) there was definite appearance of 1630 cm^{-1} olefinic unsaturation band ascribed by Bellamy (Reference 7) to <u>cis</u>-unsaturation in a five-membered ring. It was experimentally established that (I) does not absorb bromine, presumably because of steric interference by the methylene bridge. The 1630 cm^{-1} band present in the spectrum of Sample 32 in Figure C-2 (representative for all pyrolytic residues of (I)) is not present in the spectrum of model compound (I) given in Figure C-3.

Bromine absorption was found to range between 0.39 - 1.60 meq/g for the residues corresponding to one titratable double bond per ∿600-2500 molecular weight. The model compound (I) has an unsaturation content of 4.18 meq/g which means the polymeric product has only 40% titratable double bond character of that potentially available. The presence of no

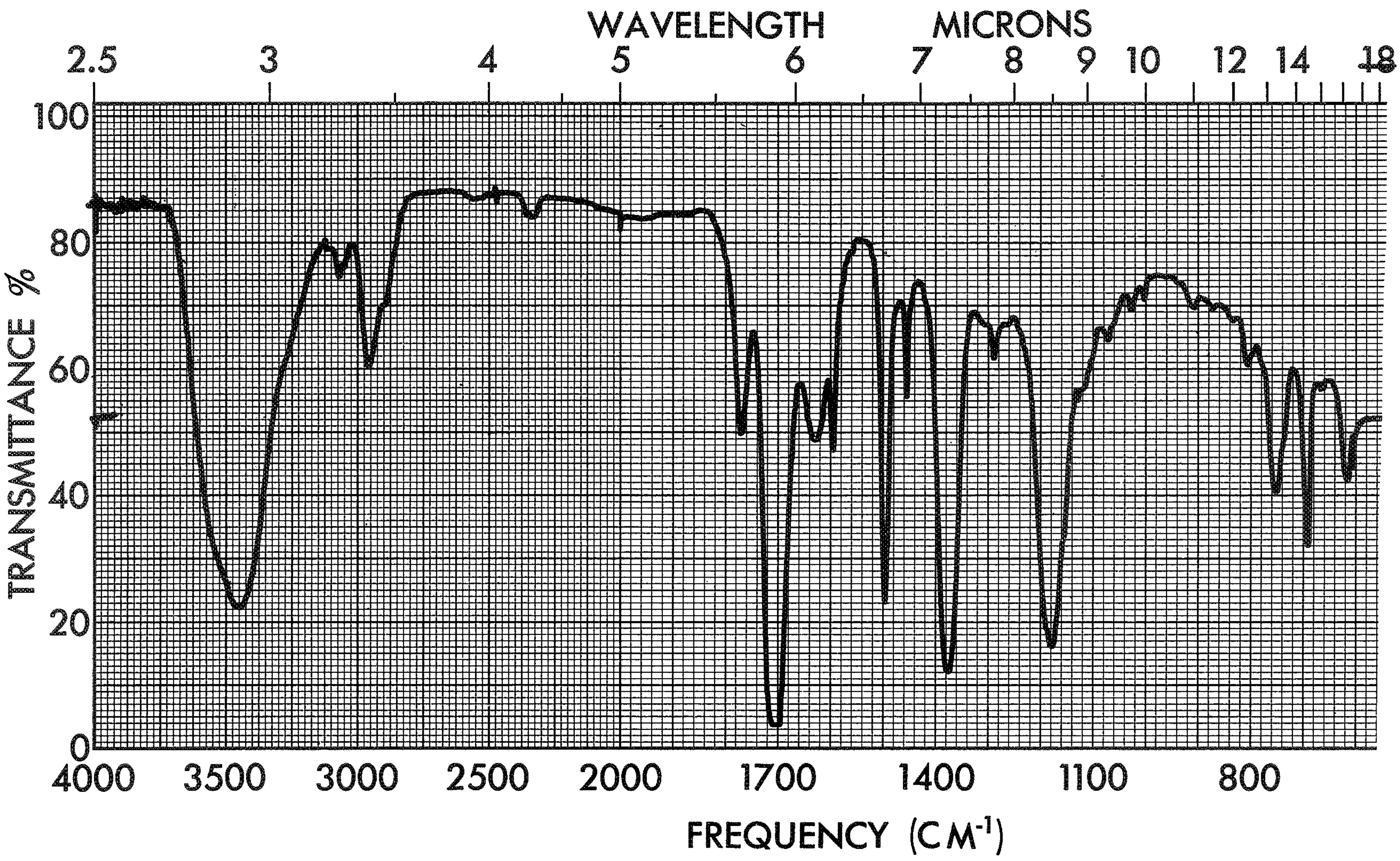

Figure C-2. Infrared Spectrum of N-phenyl Nadimide
Pyrolysis Residue Sample 32 (KBr)
Concentration: 3.7 mg/g KBr

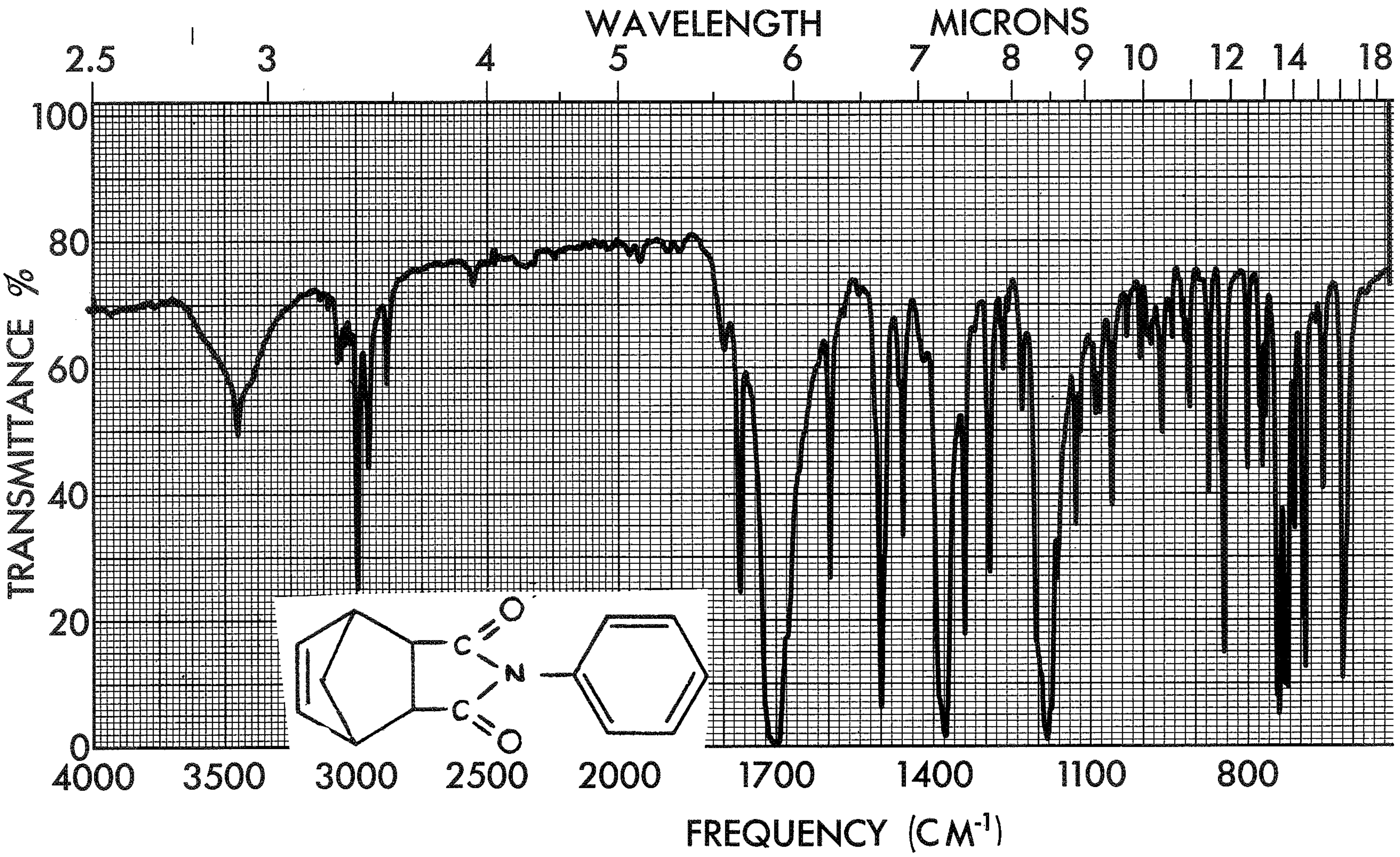

Figure C-3. Infrared Spectrum of N-phenyl Nadimide (KBr)
Concentration: 4.8 mg/g KBr

discernable olefinic protons was established by nuclear magnetic resonance (n.m.r.) analysis as discussed in C.5.

An estimation of the number of alkene groups per molecule was obtained by multiplying the bromine content [Br] by $\overline{M}_n$ (See Table C.III). These data are also listed in Table C.VI and show that the pyrolysis products of (I) have a range of 0.5 to 1.5 eq/mol. The results of Sample 44 are lower but this is explained by the presence of an unreacted starting material. The products from pyrolysis of (II) and (III) generally have fewer alkene groups per mole.

A semiquantitative estimation of the relative double content from the infrared studies was calculated by dividing the absorbance at 1630 cm^{-1} by the weight of the sample in the KBr pellet, A/c (directly related to the concentration in the optical path). These data are also presented in Table C.VI together with the ratio of A/c to bromine absorption content. Although there is some scatter in the data, the A/c[Br] ratio shows good correlation between infrared and bromine absorption studies. The scatter is attributed to errors attendant with obtaining low absorbance values.

C.4 INFRARED SPECTROSCOPIC ANALYSIS

C.4.1 N-phenyl Nadimide

The infrared analysis of all pyrolysis products from N-phenyl nadimide (I) gives strong indication for the presence of a considerable number of non-phenyl protons, namely, methinyl and methylene hydrogens. The presence of these characteristic carbon-hydrogen vibrations can be seen by inspection of the 2800-3000 cm^{-1} region of Figure C-3. Infrared absorption in this region is attributed to carbon-hydrogen stretching of methylene and methinyl linkages (Reference 8). The infrared spectrum of 3,5-dimethyl cyclopentene gives strong absorption in this region as reported by Aso and coworkers (Reference 9).

The strong carbon-hydrogen stretch abosrption bands present in the spectra of pyrolysis products from (I) are greatly diminished in the spectra of polymeric products from N-phenyl oxynadimide (II) as discussed below.

C.4.2 N-phenyl Oxynadimide

Strong physical evidence that N-phenyl oxynadimide (II) pyrolysis residues contained little or no furane as part of the polymer structure prompted investigation of the residue produced from the pyrolysis of N-phenyl maleimide (III). A commercial sample of N-phenyl maleimide (III) was recrystallized and subjected to pyrolysis conditions identical to those employed for the other model imides. The pyrolysis residue (Sample 64) obtained was subjected to a screening characterization for comparison with data obtained for an N-phenyl oxynadimide (II) residue obtained under identical experiment pyrolysis conditions (2 hours at 350°C under vacuum).

The identical structural nature of the two products is vividly shown by referring to the infrared spectrum of the N-phenyl oxynadimide (II) residue in Figure C-4 and comparing it with the spectrum of the N-phenyl nadimide residue in Figure C-5. The two spectra are identical down to the smallest fine structure. All infrared spectra of products from (II) were essentially identical and gave no indication of the presence of furane (VI).

C.5 NUCLEAR MAGNETIC RESONANCE ANALYSIS (n.m.r.)

The n.m.r. spectra of the N-phenyl nadimide (I) pyrolyses products has given insight into the probable structure of the polymer backbone. Data for these products as well as principal proton absorption peaks for N-phenyl oxynadimide (II) products are given in Table C.VII.

Listed in Table C.VII are definitely discernible proton absorption peaks along with tentative peak assignments and the ratio of non-phenyl (cyclopentadiene (V)) and/or maleic to phenyl (as N-phenyl) protons.

The n.m.r. spectra of all polymeric products from (I) contained phenyl proton absorption at approximately 2.60τ and a resolved peak at approximately 7.30τ characteristic of the presence of methinyl protons. Except for Sample 44, (discussed on Page 114), no olefinic protons were present such as those at 3.80τ (D) appearing in the spectrum of model compound (I) in Figure C-6. The best resolution of bands in the region of 6.0-9.0τ was obtained for Sample 21 whose spectrum appears in Figure C-7. The three non-phenyl proton peaks in Figure C-7 at 7.46τ, 7.22τ, and 6.65τ are assigned

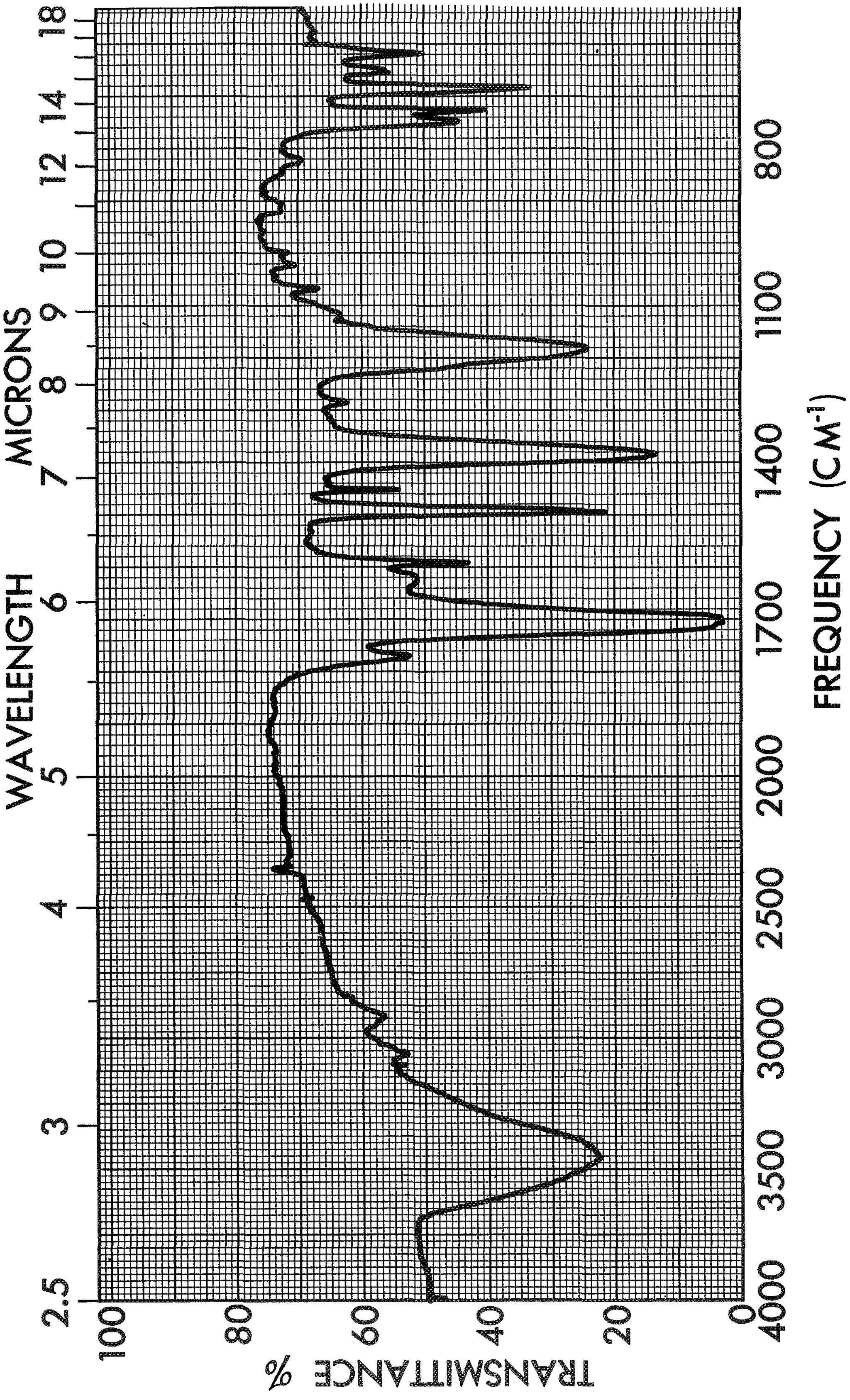

Figure C-4. Infrared Spectrum of N-phenyl Oxynadimide Pyrolysis Residue Sample 22 (KBr)
Concentration: 3.6 mg/g KBr

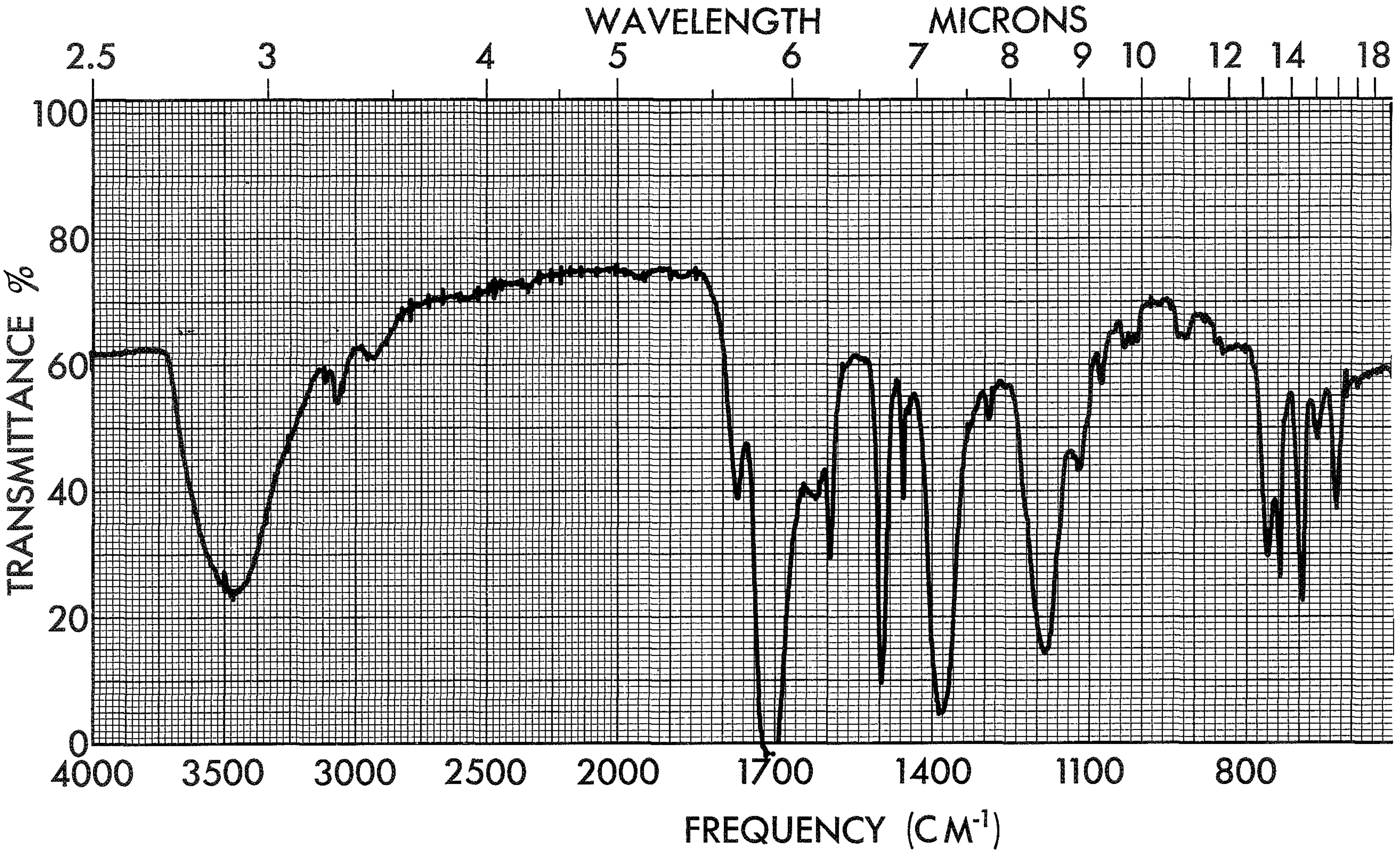

Figure C-5. Infrared Spectrum of N-phenyl Maleimide Pyrolysis Residue Sample 64 (KBr)
Concentration: 2.9 mg/g KBr

TABLE C.V

NUCLEAR MAGNETIC RESONANCE ABSORPTION DATA FOR TASK I PYROLYSIS PRODUCTS

No.	Principle Absorption Peaks (τ)	Tentative Assignment	Ratio Non-Phenyl/ Phenyl Protons
20	2.70	Phenyl	9.9:8.3 = 1.2:1
	7.32	Non-phenyl	
43	2.68	Phenyl	10.7:7.4 = 1.4:1
	7.30	Non-phenyl	
42	2.61	Phenyl	10.1:8.2 = 1.2:1
	7.22	Non-phenyl	
59	2.57	Phenyl	10.5:9.8 = 1.1:1
	7.25	Non-phenyl	
44	2.55	Phenyl	43:37 = 1.2:1
	7.28	Non-phenyl	
	8.50	Bridge	
	6.68	Bridgehead	
	3.68	Olefin	
21	2.61	Phenyl	
	7.22	Methinyl (IV)	12:10 = 1.2:1
	7.46	Methylene (IV)	
	6.65	Bridgehead (I)	
37	2.65	Phenyl	2.5:7 = 1:2.8
	3.30	Olefinic	
28	2.65	Phenyl	3.3:10 = 1:3
	3.26	Olefinic	
29	2.60	Phenyl	3.3:10 = 1:3
	3.02	Olefinic	
30	2.68	Phenyl	2.8:9.2 = 1:3.3
	3.12	Olefinic	
22	2.63	Phenyl	2.6:10.3 = 1:4
	2.77	Phenyl	
	3.20	Olefinic	

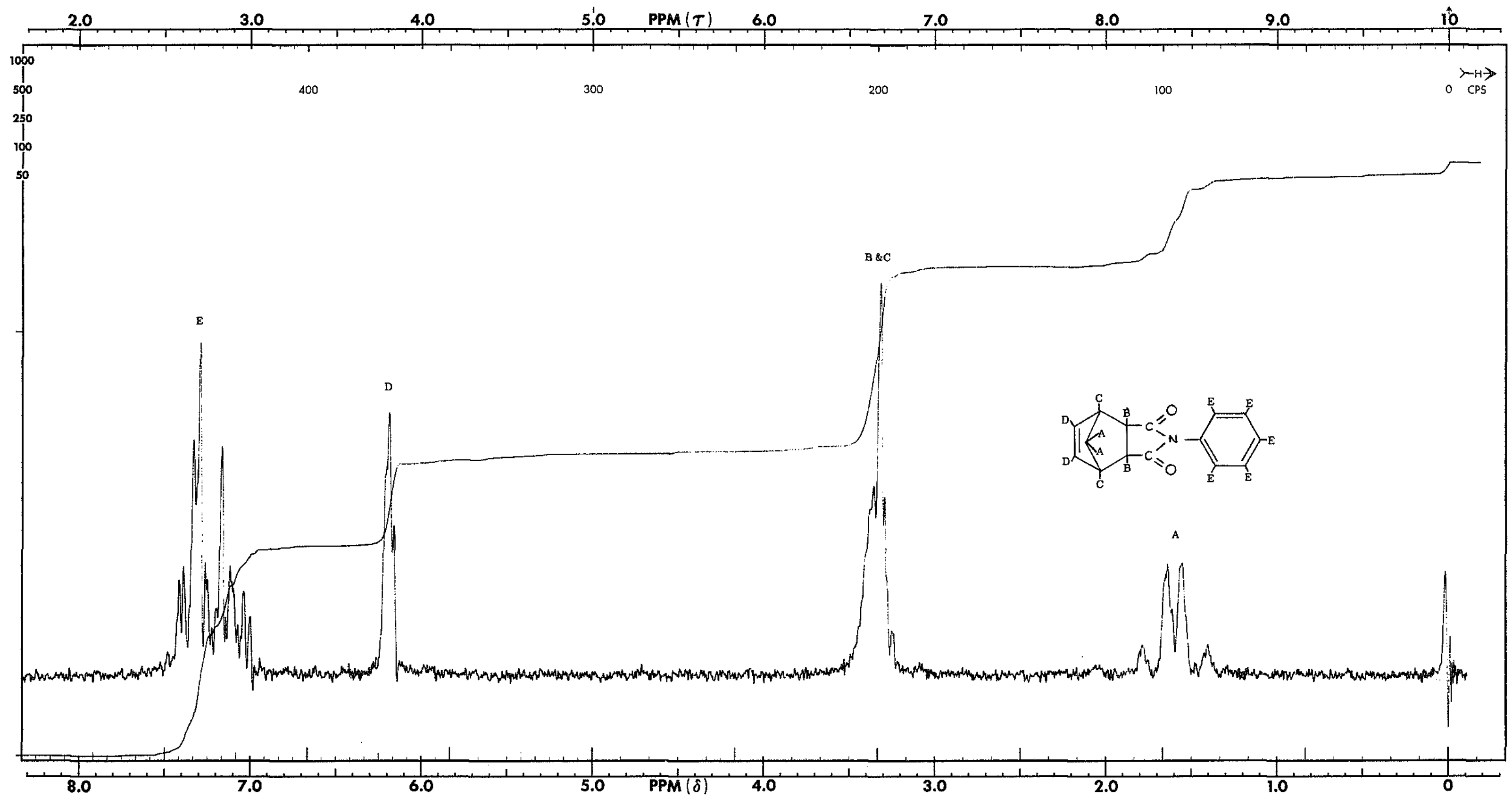

Figure C-6. Nuclear Magnetic Resonance Spectrum of N-phenyl Nadimide
Solvent: $CDCl_3$

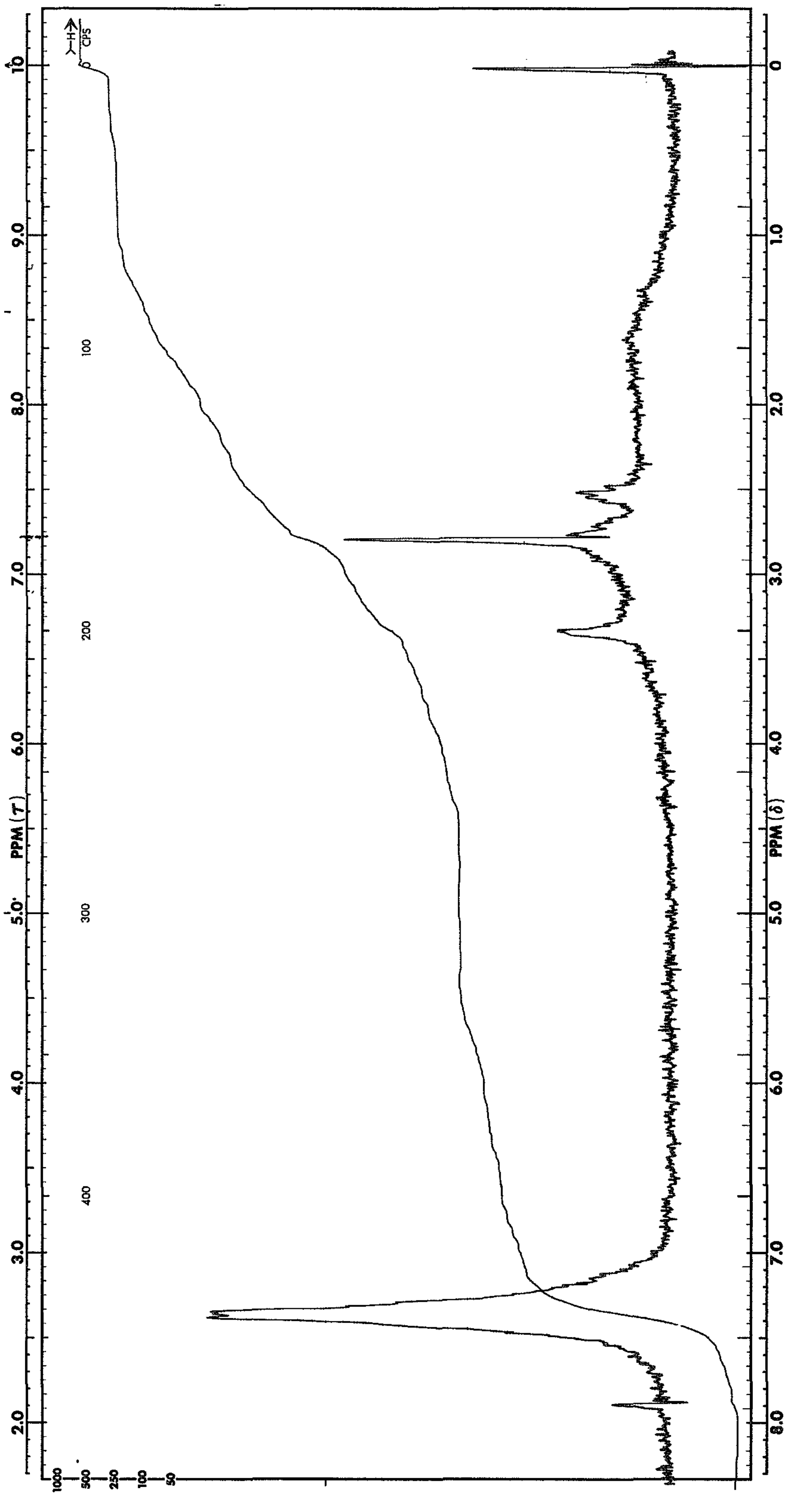

Figure C-7. Nuclear Magnetic Resonance Spectrum of N-phenyl Nadimide Pyrolysis Residue Sample 21 Solvent: $CDCl_3$

to 1) methylene in N-phenyl maleimide, 2) methinyl in N-phenyl maleimide, and 3) bridgehead and ring juncture protons, respectively. These assignments were made with the aid of the model imide (I) spectrum (Figure C-7 shows that bridgehead methinyl and ring juncture protons absorb at 6.65τ). The other assignments were made with the aid of N-phenyl-2-methyl-succinimide (IV) whose spectrum appears in Figure C-8. This compound simulates saturated N-phenyl maleimide groups on the end of a polymer chain, where the methyl group represents a remaining polymer chain. The methinyl proton Y in (IV) appears as a complex multiplet centered at approximately 7.20τ in Figure C-8. The two methylene protons Z appear as a multiplet centered at approximately 7.60τ. These absorptions relate to the 7.22τ and 7.46τ peaks appearing for Sample 21 in Figure C-7. It is believed the broad unresolved areas from 6.3 - 9.0τ include possible combinations of protons listed in the summary in Table C.VIII, including bridge protons as A in Figure C-6.

TABLE C.VI

SUMMARY OF OTHER PROTONS POSSIBLE IN MODEL POLYMERS

Compound	Proton Absorption Peaks (τ)	Source
N-phenyl Nadimide (I)	8.40 (bridge methylene A)	Reference 10
Cyclopentene (VII)	7.72 (methylene 2)	Reference 10
	8.10 (methylene 3)	
Cyclopentane (VIII)	8.49 (methylene)	Reference 11
Norbornane (IX)	7.81 (methylene)	Reference 12

The spectra obtained for all N-phenyl oxynadimide (II) pyrolyses products bear no resemblance to those of (I) and show only one principle absorption band other than phenyl at approximately 3.20τ. A representative spectrum, that of Sample 28, appears in Figure C-9. This spectrum is very similar to that obtained for model N-phenyl maleimide (III) included as Figure C-10. This strongly suggests the polymeric products obtained undergo rapid thermal dehydrogenation to give a partially unsaturated polymer, or partial reversion back to model compound on heating, accounting for the absence of any bands for methylene or methinyl protons present for (IV) in Figure C-8 which should simulate N-phenyl maleimide polymer.

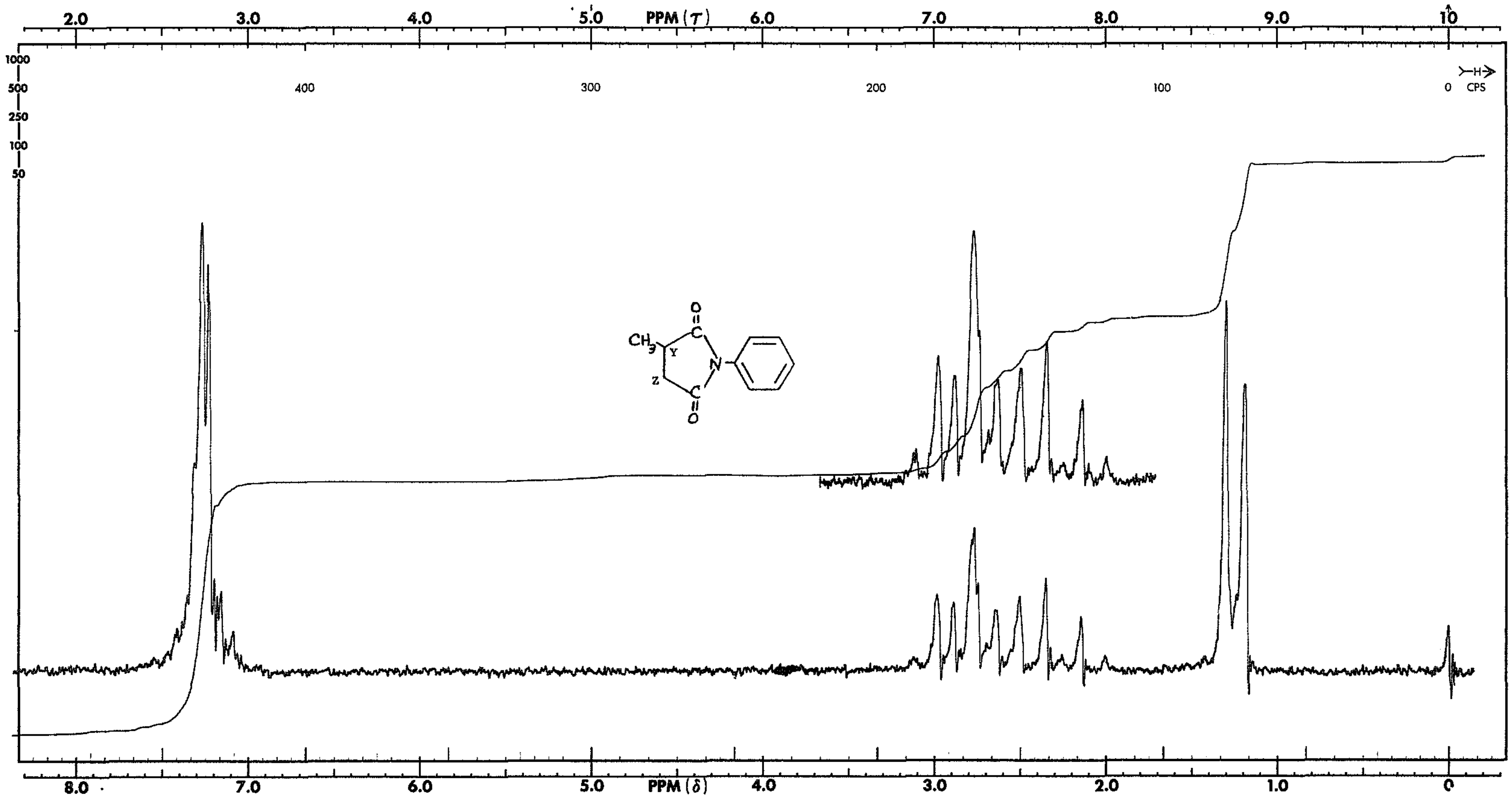

Figure C-8. Nuclear Magnetic Resonance Spectrum of N-phenyl-2-methylsuccinimide Solvent: $CDCl_3$

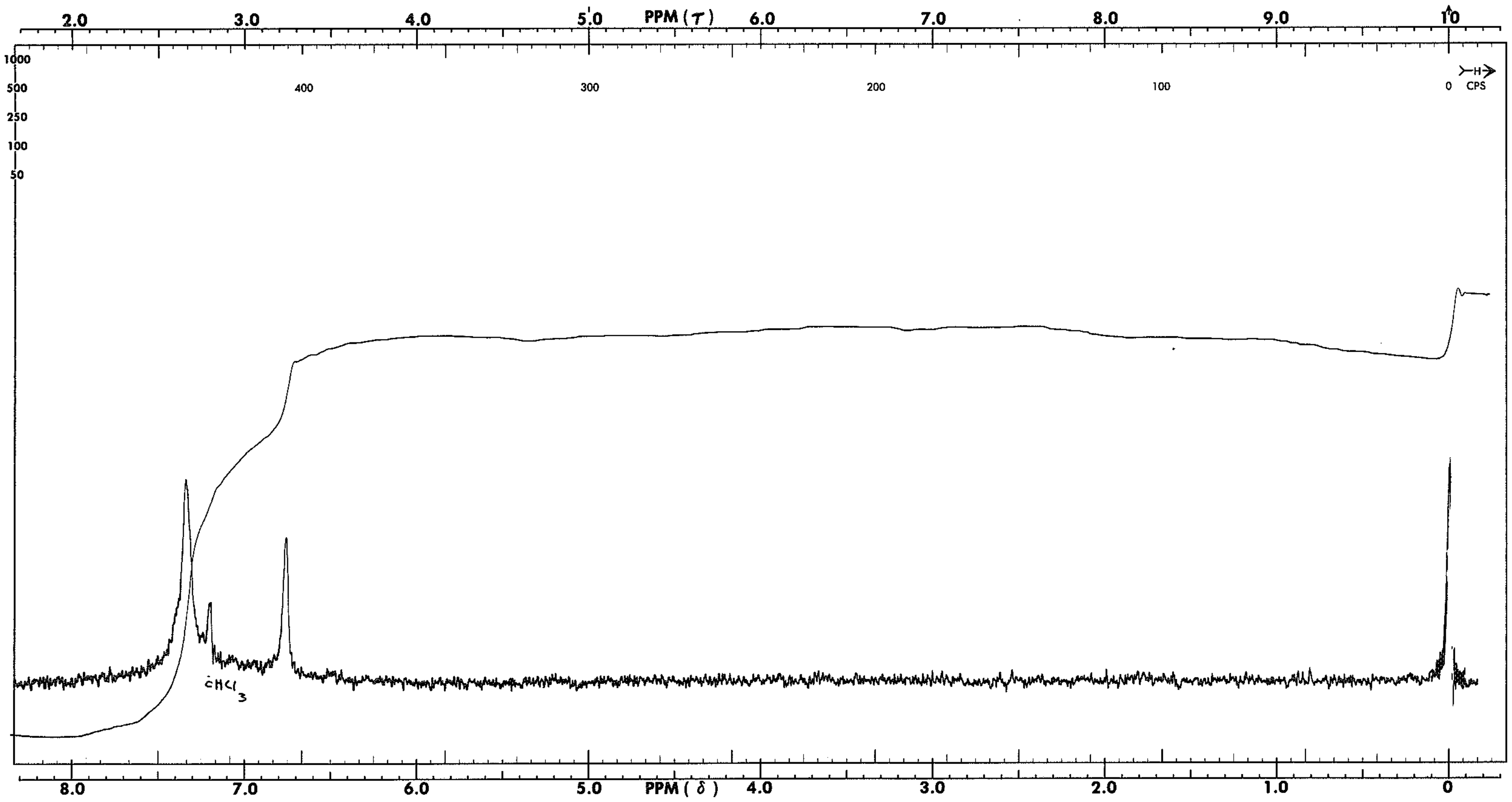

Figure C.9. Nuclear Magnetic Resonance Spectrum of N-phenyl Oxynadimide Pyrolysis Residue Sample 28 Solvent: $CDCl_3$

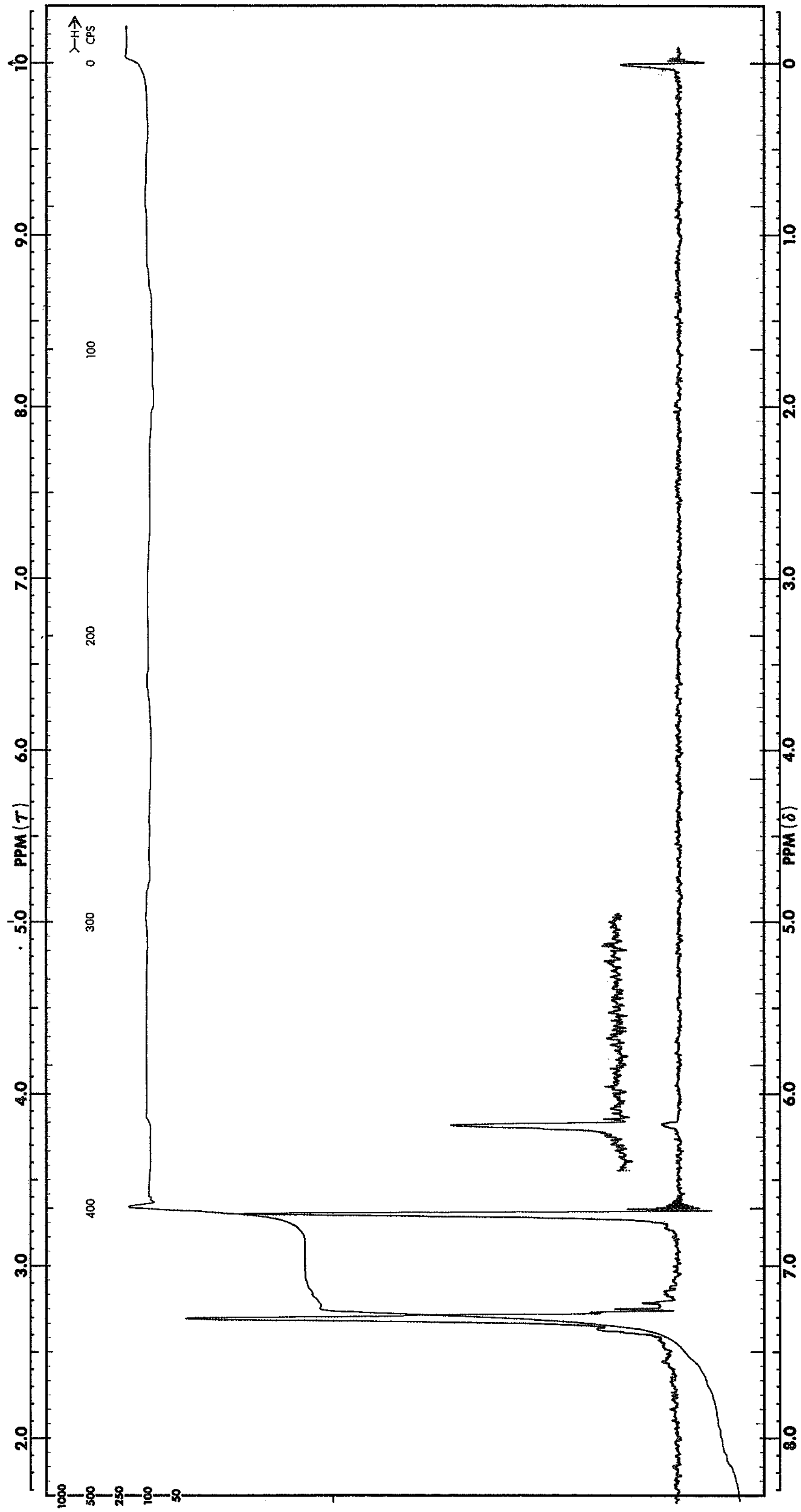

Figure C-10. Nuclear Magnetic Resonance Spectrum of N-phenyl Maleimide Solvent: $CDCl_3$

Nuclear magnetic resonance (n.m.r.) spectra of Sample 44 in Figure C-11 graphically shows the effect of temperature on the nature of the pyrolytic polymerization product. Table A.III summarizes n.m.r. characterization data for the N-phenyl nadimide model compound and that for pyrolysis Sample 44 is given in Table C.VII.

The pyrolysis product from Sample 44 (Figure C-11) definitely gives evidence of endocyclic methylene (nadic) proton absorption (A) at 8.40τ as well as proton absorptions for bridgehead and ring juncture hydrogens (B and C) at 6.67τ and olefinic protons (D) at 3.80τ when compared with those for the model compound in Figure A-8. Sample 44 also definitely contains polymer proton absorption (F) at 7.25τ which is absent in Figure A-8, but definitely present in all other pyrolysis products from (I). All spectra contain the expected phenyl proton peak (E) at 2.70τ.

These data have proven very valuable for providing direction towards nadic capped polymer synthesis studies discussed in Section 3 and accomplished a major objective of the model compound studies, namely, to approximate minimum processing temperature needed to assure complete polymerization. The identification of allowable processing temperatures to lie above 275°C (527°F) coupled with recent TRW IR&D company supported studies which show that similar polyimide prepolymers can be processed at 550°F (288°C) allowed polymer studies to concentrate on >550°F processing temperatures, which defined sufficient prepolymer to cured polymer conversion.

C.6 THERMOGRAVIMETRIC ANALYSIS

The thermo-oxidative stabilities of all pyrolyses samples as determined in nitrogen and air are given in Table C.IX. These results were obtained by TGA using an Aminco Thermograv on 0.1 g samples, scan rate of 3°C/min and a gas flow rate of 100 ml/min. The resin weight loss is given up to 500°C, although this temperature is certainly above the required use temperature for A-type polyimide polymers under investigation in this program.

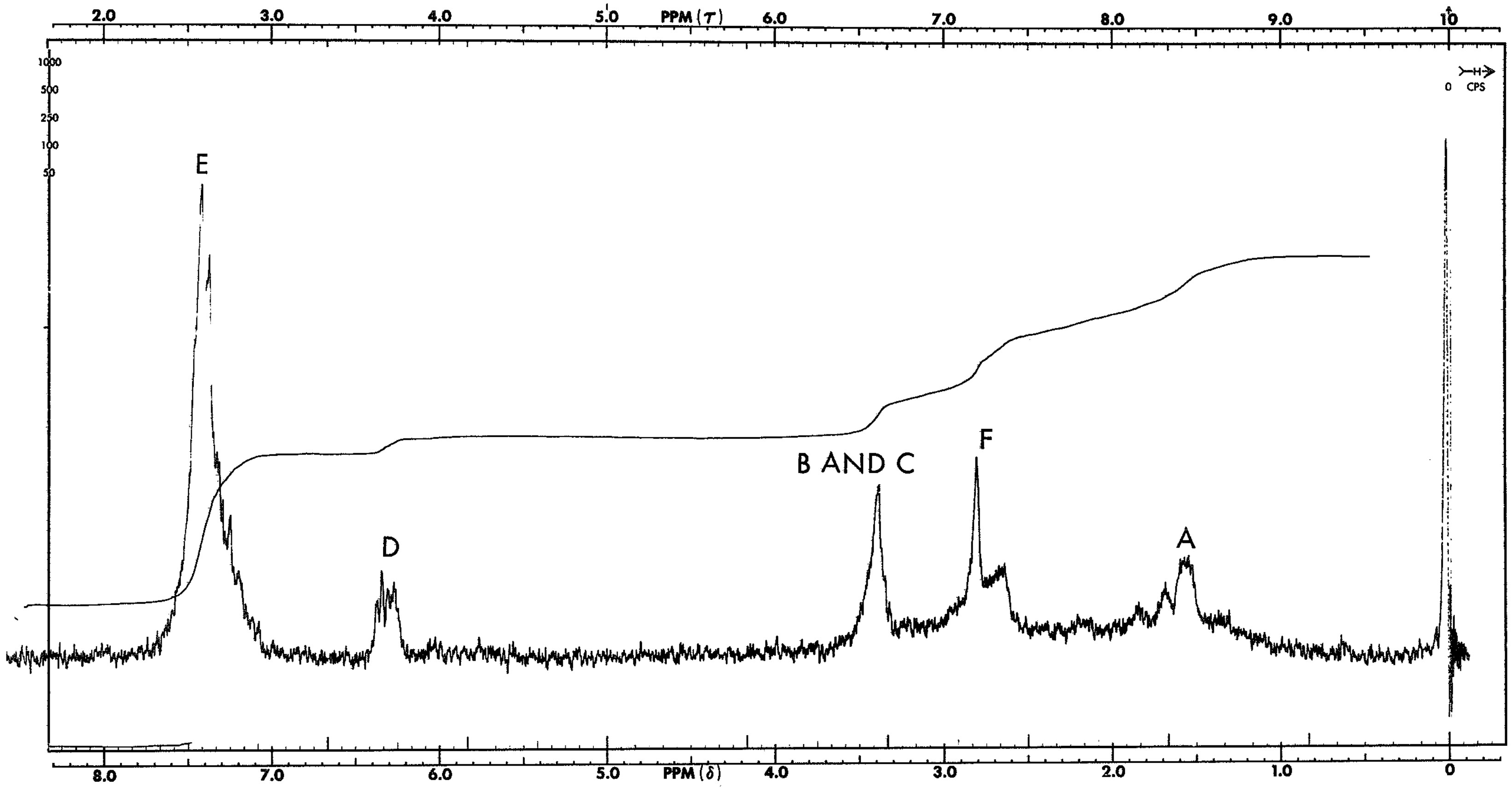

Figure C-11. Nuclear Magnetic Resonance Spectrum of N-phenyl Nadimide Pyrolysis Residue Sample 44 Solvent: $CDCl_3$

TABLE C.VII

THERMAL AND OXIDATIVE STABILITY[a] OF PYROLYSIS PRODUCTS

Sample No.	Pyrolysis Conditions	% Weight Loss in Nitrogen				% Weight Loss in Air			
		200°C	300°C	400°C	500°C	200°C	300°C	400°C	500°C
20	I-350-2-V	4	5	22	73	0	2	26	53
21	I-350-3-V	0	8	30	64	0	8	22	50
67	I-350-2-V	2	10	40	73	3	8	35	68
42	I-350-2-N	10	24	42	100	--	--	--	--
43	I-300-3-V	0	3	4	70	3	7	14	63
59	I-300-2-V	4	4	17	72	1	6	38	70
66	I-300-2-V	6	10	25	85	2	2	20	72
32	I-300-2-N	0	1	32	72	1	3	10	53
44	I-275-2-V	0	14	30	90	---	--	--	--
29	II-250-1-V	30	30	58	75	22	36	57	70
28	II-250-2-V	8	22	35	60	8	28	50	68
65	II-250-2-V	3	7	40	70	4	7	34	45
30	II-250-2-N	2	11	26	55	--	--	--	--
68	II-350-2-V	7	15	40	70	--	--	--	--
22	II-350-2-V	3	7	28	46	3	7	23	40
47	II-350-3-V	7	14	28	57	7	14	32	47
64	III-350-2-V	4	9	27	53	5	14	30	46

[a] Thermogravimetric analysis: scan rate 3°C/min; gas flow rate 100 ml/min

A basic assumption was made that model compounds showing superior weight retention, particularly in air, up to 300°C (572°F) would identify the particular end cap (nadic or oxynadic) for all other program activities, since this temperature range goes far beyond (c.a., 122°F) the minimum composite use temperature of 450°F desired in this program. The polymeric products from N-phenyl nadimide (I) consistently showed better weight retention up to 300°C in both nitrogen and air as shown in Table C.IX, than the products from N-phenyl oxynadimide (II). This fact, along with the almost quantitative evolution of furane during pyrolysis of

(II) which strongly suggested difficult processing problems, led TRW Systems to recommend nadic as the end cap of choice over oxynadic.

The greater resin weight loss in nitrogen than in air for the pyrolytic polymer products during TGA analysis as shown in Table C.IX was a consistent occurrence. An explanation for this phenomenon considers the hydrocarbon unsaturated linkage in the linear polymer as a cyclopentene backbone component as shown in Section 2. It is believed that the carbon-hydrogen bonds in the cyclopentene portion of the linear polymer thermally cleve at temperatures ∿300°C resulting in fragmentation of the polymer and subsequent decomposition. In air, it is believed this thermal carbon-hydrogen clevage is partially alleviated by formation of oxygen adducts such as peroxides which effect in situ addition polymerization through the unsaturation giving a polymer species that is resistant to thermal clevage until a higher temperature (c.a., ≥400°C) is reached. Due to the non-linear (c.a., thermoset) nature of cured polyimide polymers, this phenomenon was not observed in the polymer studies discussed in Section 3.

Indication of a fundamental difference in the polymer backbone structure between products from (I) versus (II) can be seen from the percent weight loss in nitrogen at 500°C. The polymer from (II) consistently showed a higher char yield (∿50%) at this temperature, whereas the products from (I) gave a best char yield of only 36% and averaged ∿20%. This indicates the presence in the polymer backbone of N-phenyl nadimide (I) products, carbon-carbon linkages which degrade or cleave at 500°C, versus formation of more thermally stable crosslinked or highly conjugated species apparently present in products from N-phenyl oxynadimide (II).

C.7 SAPONIFICATION EXPERIMENTS

Saponification of the pyrolyses products from N-phenyl nadimide (I) and N-phenyl oxynadimide (II) were conducted to aid in the structural interpretation of the polymer backbone. This study, however, gave no useful quantitative information on the total number of imide linkages per se, but did yield some important data on the structural make-up of the polymer molecular weight distribution.

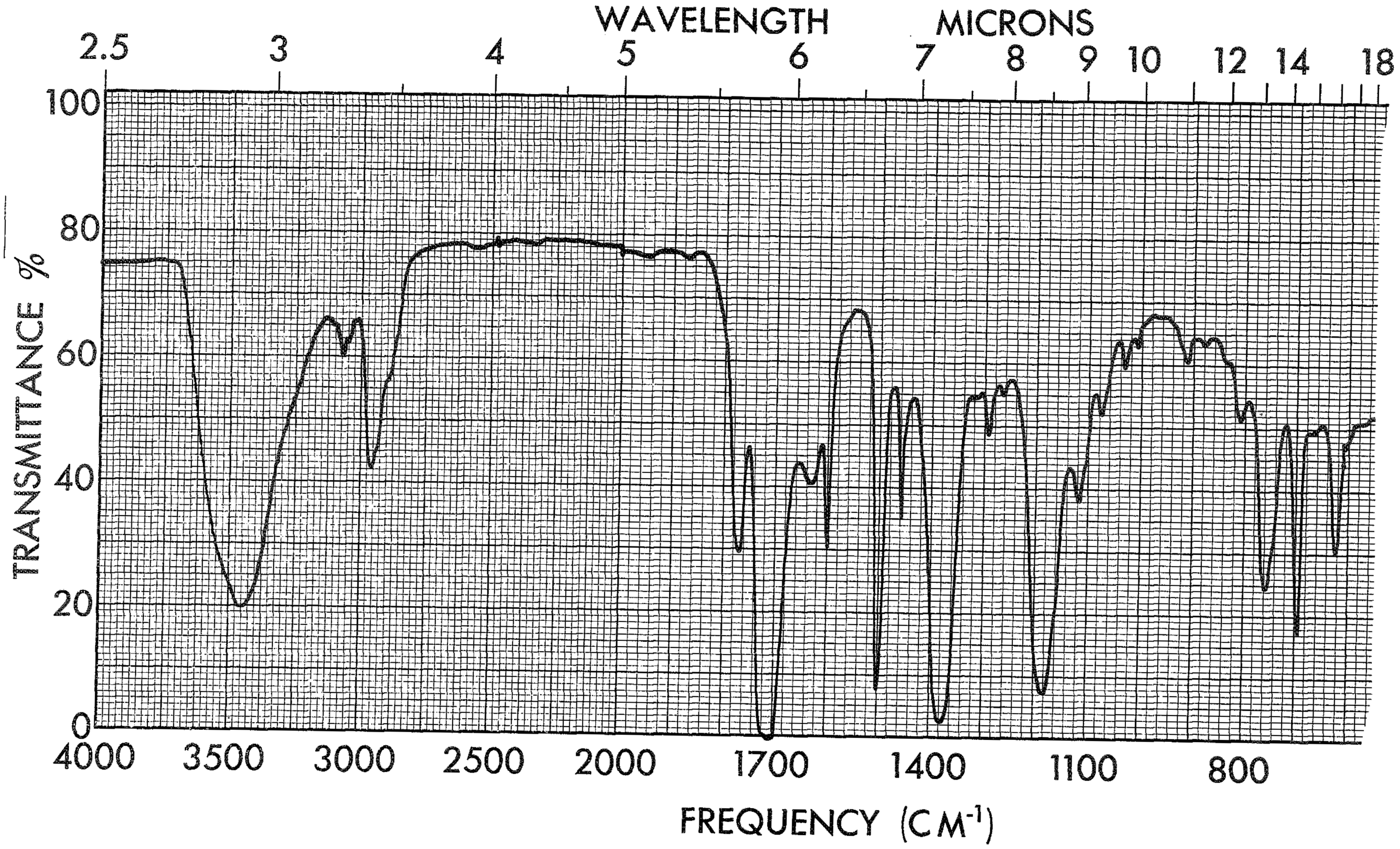

Figure C-12. Infrared Spectrum of N-phenyl Nadimide Pyrolysis Residue Sample 42 (Base insoluble portion) (KBr) Concentration: 4.4 mg/g KBr

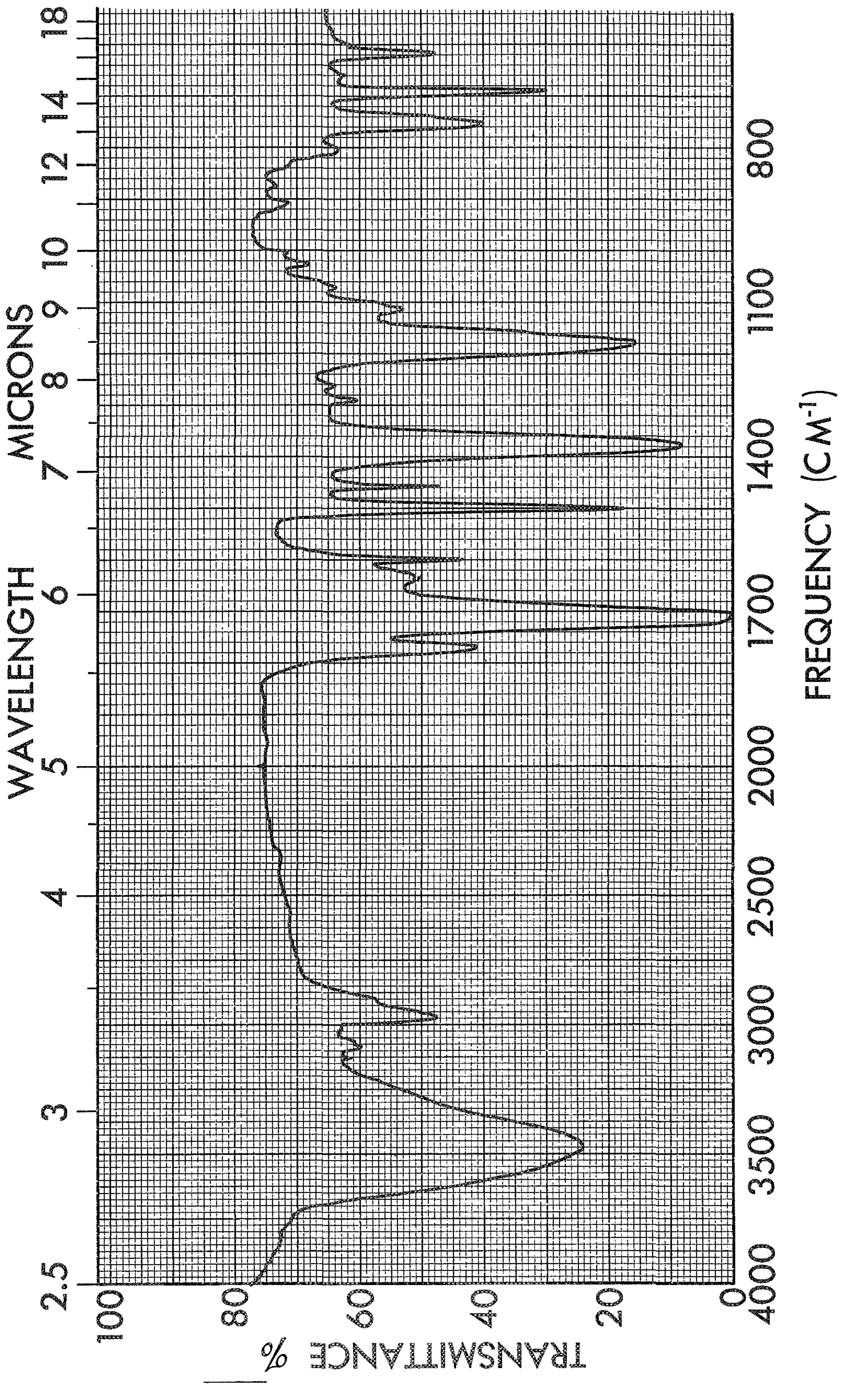

Figure C-13. Infrared Spectrum of N-phenyl Nadimide Pyrolysis Residue Sample 42 (KBr) Concentration: 3 mg/g KBr

Sample 42 was hydrolyzed (saponified) with 0.1N sodium hydroxide for 19 hours at reflux temperatures which resulted in a brown solution containing some insoluble solid material. The alkaline solution separated from the solid residue by filtration. The alkaline material was then titrated with 0.095N hydrochloric acid in the presence of phenolphthalein as an indicator. The equivalent weight of this material was calculated to be 288 g/eq.

The alkaline insoluble portion of the saponification mixture was found to be soluble in acetone and gave the infrared spectrum shown in Figure C-12. This spectrum was identical to that of the original pyrolysis residue shown in Figure C-13. These data strongly suggest that the 0.1N base insoluble portion was a high molecular weight homo-polymer fraction shown to be present in gel permeation chromatography experiments discussed in C.2.2.

The infrared spectrum of the alkaline soluble material appears in Figure C-14. This spectrum shows that both imide and amide carbonyl groups are present in the 1840-1600 cm^{-1} region of the spectrum which in effect means the 288 g/eq titration value could not be ascribed directly to a single structural assignment.

Although this saponification experiment and subsequent ones employing up to 1.0N sodium hydroxide gave equivalent weight results similar to the experiment described, several interesting experimental facts were established as appears below:

- The pyrolysis products from N-phenyl nadimide (I) are highly resistant to complete saponification.
- The saponification experiment (by infrared analysis) indicates the presence of a small amount (∿10%) of high molecular weight homo-polymer in agreement with GPC data.
- Both the original polymer and saponification resistant high molecular weight portion are acetone and DMF soluble supporting presence of only polar linked polymer segments.
- All infrared data (Figures C-12 and C-14) show strong carbon hydrogen stretching bands at 2850-3000 cm^{-1} indicating presence of considerable methinyl and methylene hydrogens as part of a stable polymer backbone.

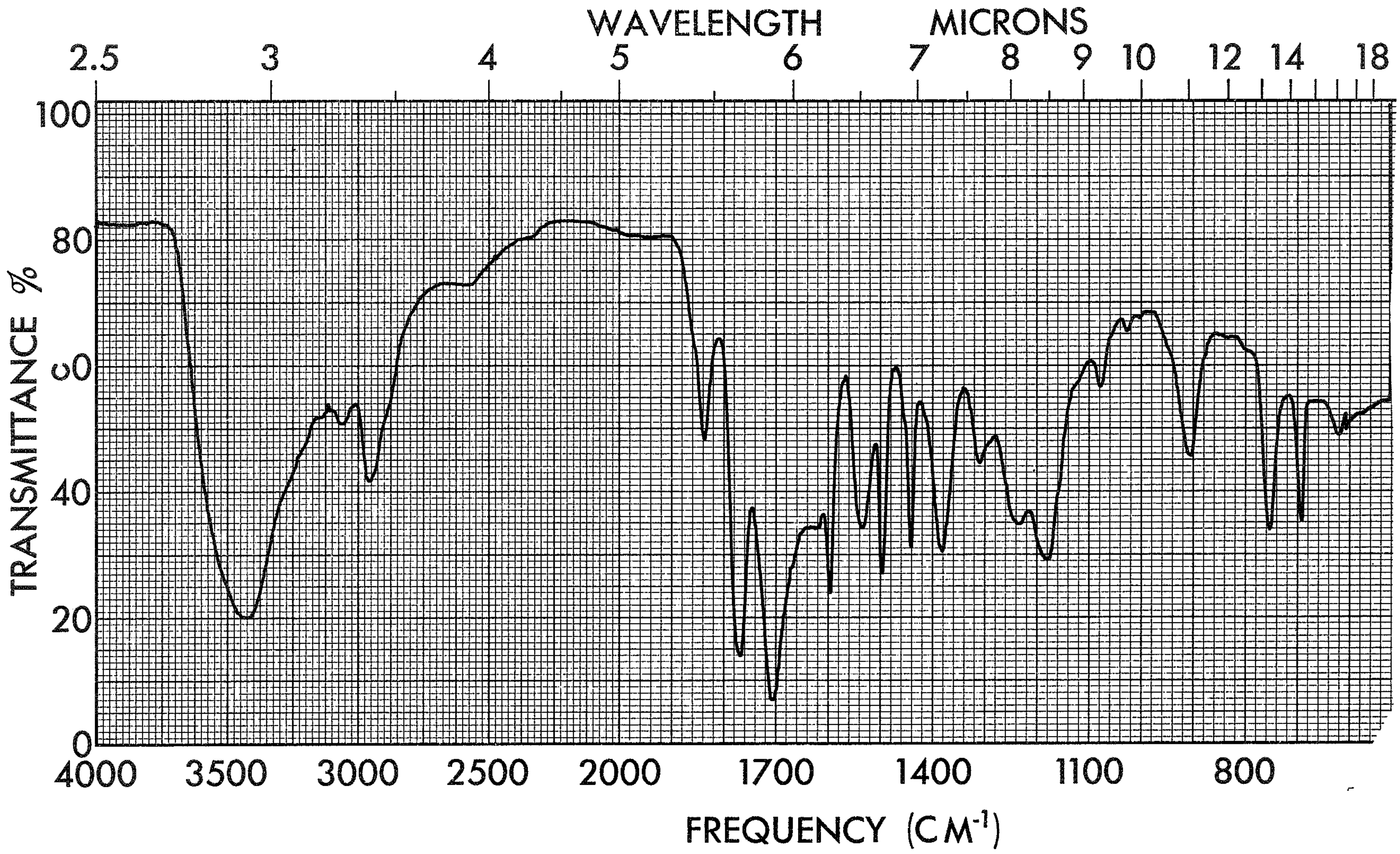

Figure C-14. Infrared Spectrum of N-phenyl Nadimide Pyrolysis Residue Sample 42 (Base soluble portion) (KBr) Concentration: 5.3 mg/g KBr

APPENDIX D

CHARACTERIZATION OF EVOLVED PYROLYSIS PRODUCTS

The gaseous products arising from pyrolysis of N-phenyl nadimide (I) and N-phenyl oxynadimide (II) were characterized by mass spectrometric analysis in several instances. The principle gaseous product from the pyrolysis of (I) was cyclopentadiene (V) and that from (II) was furane (VI). These dienes as gases were expected to evolve due to the postulated reverse Diels-Alder reaction of the model compounds. The data presented here are frequently related back to Sections 2.2 and 2.3 and Appendix B for clarity and continuity, particularly for mass balance calculations.

D.1 CHARACTERIZATION OF THE PYROLYSIS GASES

The gaseous products of several Task I pyrolyses experiments were analyzed by mass spectrometry. The results of the mass spectrometric analyses are delineated in Table D.I.

TABLE D.I
MASS SPECTROMETRY DATA

Sample No.	Pyrolysis Conditions	Product Anticipated	Principle Products Found	(% v/v)
43	I-300-3-V	Cyclopentadiene	Cyclopentadiene	74.1
			Nitrogen	4.5
44	I-275-2-V	Cyclopentadiene	Cyclopentadiene	75.2
			Nitrogen	5.3
59	I-300-2-V	Cyclopentadiene	Cyclopentadiene	12.8
			Methanol	2.9
			Nitrogen	69.1
22	II-350-2-V	Furane	Furane	82.5
			Nitrogen	7.2
28	II-250-2-V	Furane	Furane	98.4
			Nitrogen	1.5
29	II-250-1-V	Furane	Furane	96.4
			Nitrogen	3.2

The results of samples pyrolyzed from N-phenyl nadimide (I) show that the principal product obtained was cyclopentadiene (V). These samples (43, 44 and 59) were calculated (Table I, Page 7; Equation D-4) to give only ∿0.1 g of gas or ∿0.5% total quantity of sample pyrolyzed. The high nitrogen content of Sample 59 suggests that the sample bulb (F-Figure 1, Page 5) was not entirely evacuated after nitrogen purge. The methanol content observed in these gas samples was not anticipated but as mentioned earlier, undoubtedly stems from residual solvent adsorbed on the model compound. The amount of methanol corresponds to less than 0.5% of the starting material.

Similarly, the gaseous product produced from the pyrolysis of (II) is shown in Table D.I to be furane (VI) for Samples 22, 28 and 29, deemed representative for the runs listed in Table I. The only other principal product isolated for each of the samples was a small amount of nitrogen remaining from purging the pyrolysis system (Figure 1).

D.2 CHARACTERIZATION OF VOLATILE SOLID AND LIQUID PYROLYSIS PRODUCTS

Qualitative and semiquantitative characterization of the sublimed matter, W_s, and the condensed liquid matter, W_t, was accomplished by infrared analysis. These studies showed that the principal volatile liquid was cyclopentadiene (V) on pyrolysis of N-phenyl nadimide (I) and furane (VI) on pyrolysis of N-phenyl oxynadimide (II). There was no trace of methanol in these spectra. As a result in the material balance calculations of the pyrolysis of (I) presented below, W_s is considered to be 100% furane (V).

A semiquantitative analysis of the sublimed matter in pyrolysis of (I) resulted in the estimate that it contained 90% N-phenyl nadimide (I) and 10% N-phenyl maleimide (III). A similar analysis of the sublimed matter obtained from pyrolysis of (II) showed to trace of (III) but rather was essentially the starting material.

D.3 MATERIAL BALANCE CALCULATIONS FROM PYROLYSIS OF N-PHENYL NADIMIDE

Using the findings presented in the previous sections, it was possible to perform a material balance of the analytical constituents of N-phenyl nadimide (I), e.g., cyclopentadiene (V) and N-phenyl maleimide (III) in order to determine the ratio of these constituents in the pyrolytic residues. This was accomplished using the gravimetric information provided in Table I.

For simplicity in identifying the various fractions the following code was used:

$W^{\text{superscript}}_{\text{subscript}}$

refers to the weight of material whose identity is given by the superscript e.g., c = (V), m = (III), and the subscript cites the location of the material after pyrolysis. Therefore, W^c_o = the weight of (V) equivalent in the starting material, e.g., 0.276 W_o. In this method the following expressions were used:

$$W^c_r = W^c_o - W^c_t - W^c_g - W^c_s \tag{D-1}$$

$$W^c_s = (0.9)\ (.276)\ W_s \tag{D-2}$$

$$W^c_t = 0.276\ W_t \tag{D-3}$$

$$W^c_g = W_g \tag{D-4}$$

$$W^m_r = W_r - W^c_r \tag{D-5}$$

The results of this analysis are presented in Table D.II. These data show that, in general, the molar ratio is ∿1.0, or slightly less which agrees well with comparable ratios obtained from the elemental analysis results given in Appendix C, Page 92. It is most interesting to note that in spite of the high volatility of (V) at the pyrolysis temperatures, significant quantities remain in the pyrolytic residue, yet as shown in Appendix C, is not homopolymerized (V), but rather is combined with (III) groups in the pyrolytic polymer backbone.

TABLE D.II

CYCLOPENTADIENE BALANCE IN N-PHENYL NADIMIDE PYROLYSES

Sample No.	Pyrolysis Conditions	Cyclopentadiene Available, g	Distribution of Cyclopentadiene, g					
		W_o[a]	W_t^c	W_g^c	W_s^c[a]	W_r^c	W_r^m	n_r^c/n_r^m
67	I-350-2-V	5.52	0.00	0.47	0.38	4.67	12.09	1.0_1
42	I-350-2-N	5.52	0.74	b	0.35	4.43	12.64	0.9_2
43	I-300-3-V	5.52	1.62	0.13	0.29	3.48	13.38	0.6_8
59	I-300-2-V	2.76	0.43	0.11	0.18	2.04	6.54	0.8_2
66	I-300-2-V	5.52	0.48	0.21	0.42	4.41	13.06	0.8_9
32	I-300-2-N	5.52	0.21	b	0.05	5.26	13.94	0.9_9
44	I-275-2-V	5.52	0.02	0.10	1.70	3.70	9.01	1.0_8

[a] Sublimed material typically contains 90% starting material, 10% maleimide (e.g., 24.8% cyclopentadiene analytical concentration)

[b] Not determined

APPENDIX E
POLYMER SCREENING STUDIES

The TRW Systems prior technology in the preparation of A-type polyimide materials was utilized for a detailed screening study of six specific formulation modifications. It was the objective of this study to define a single candidate based on a trade-off of processing ease, long-term exposure ,thermo-oxidative stability, and hydrolytic stability. With this objective in mind nadic anhydride (NA), identified as the best prepolymer end capping group in the model compound studies, was reacted with the six separate two component dianhydride/diamine combinations possible from benzophenone tetracarboxylic acid dianhydride (BTDA), pyromellitic dianhydride (PMDA), methylene dianiline (MDA), oxydianiline (ODA), and sulfodianiline (SDA) according to previously defined technology (Reference 1). The products were characterized to ascertain which specific material met the objectives. A detailed description of this work is presented below.

E.1 VARNISH SYNTHESIS

The amic-acid (A-A) method below was used for the varnish synthesis of 1300 formulated molecular weight prepolymers:

> A quantity of diamine was dissolved in DMF and cooled to 20° with an ice bath. To this solution was added NA in DMF, during which time the temperature was maintained at 30°C by means of an ice bath. This mixture was treated with the addition of a slurry consisting of dianhydride in DMF. The resulting 40% solids loaded solution was stirred at ambient temperature for one hour.

E.2 PREPARATION OF MOLDING POWDERS

The A-type polyimide prepolymer A-A solutions in DMF prepared as described above were converted to imidized molding powders by the following procedure:

> The DMF varnish solution was stripped of solvent by evaporation on a rotary evaporator under vacuum at 150°C for 45 minutes. The moist prepol residue was then heated in a vacuum oven for three hours at 140°C (volatile matter content 7.1%), followed by a 2-1/2 hour drying

> cycle at 125°C, which gave a final imidized molding powder of 5% volatile matter content as measured by weight loss as determined by a 30-minute heating cycle at 600°F (315°C).

E.3 PREPOLYMER MOLDING STUDIES

The six A-type polyimide molding powders prepared as described above were subjected to a temperature-pressure molding (curing) study discussed in 3.1.3 on Page 26. The undesirable products given by NA/SDA/MDA and NA/SDA/PMDA in the processing ranges of 540-590°F and 325-1000 psi eliminated these two candidates at this point from further consideration in the program. The remaining four candidates were characterized as described below.

E.4 POLYMER CHARACTERIZATION

E.4.1 Prepolymers

The imidized prepolymers prepared as described in E.2 were screened for desired structure by the methods described below.

E.4.1.1 Infrared Analysis - All six prepolymer molding powders prepared as described in E.2 were screened for the desired imide linkage. A representative spectrum for NA/SDA/PMDA is given in Figure E-1. The completeness of A-A ring closure to imide is indicated by the strong absorption bands at 1770 and 1710 cm^{-1} as discussed previously for model imides in Section 2 .

E.4.1.2 Nuclear Magnetic Resonance (n.m.r.) Analysis - The n.m.r. spectra of all prepolymers prepared were determined. All of the prepolymer spectra were very similar to that of the NA/MDA/BTDA formulation shown in Figure E-2. In this spectrum the proton absorption peaks 7.4τ, 6.6τ, and 3.8τ arise from the nadic end cap as discussed in Section A.2.5.3. Also, present in this spectrum is a doublet centered at 7.2τ stemming from the methylene protons in methylene dianiline (MDA) and two phenyl proton absorptions from the aromatic portions of MDA and BTDA in the 1.7-3.0τ region. The proton absorption peaks at 7.5τ and 6.0τ arise from impurities in DMSO-d_6 used as a solvent for this prepolymer. The high degree of noise present in the spectrum was caused by the relatively poor solubility of the prepolymer.

Because of the intractibility of the fully cured resin specimens, it was impossible to determine the n.m.r. spectra of these materials.

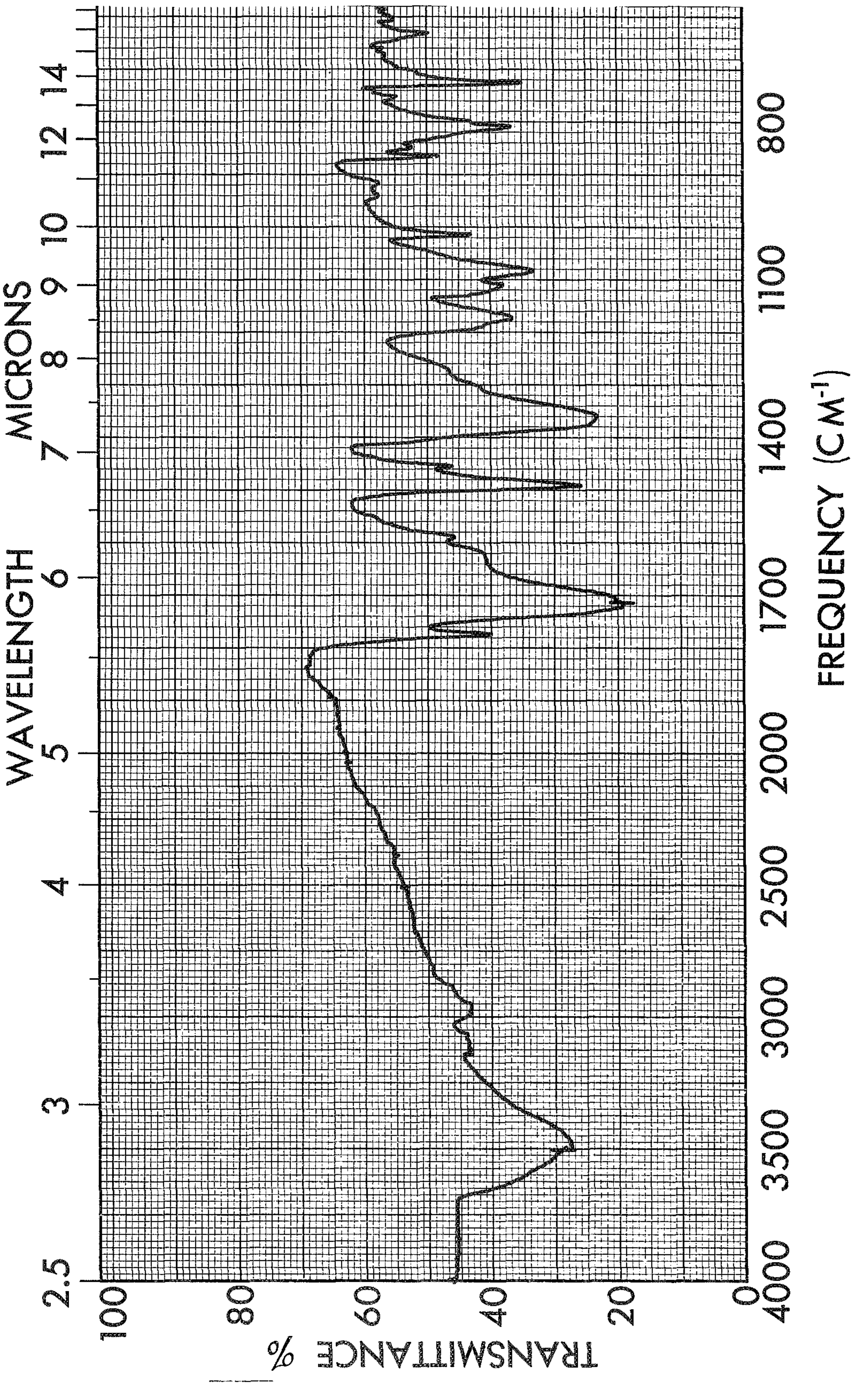

Figure E-1. Infrared Spectrum of NA/SDA/PMDA Imidized Prepolymer (KBr)
Concentration: 4.6 mg/g KBr

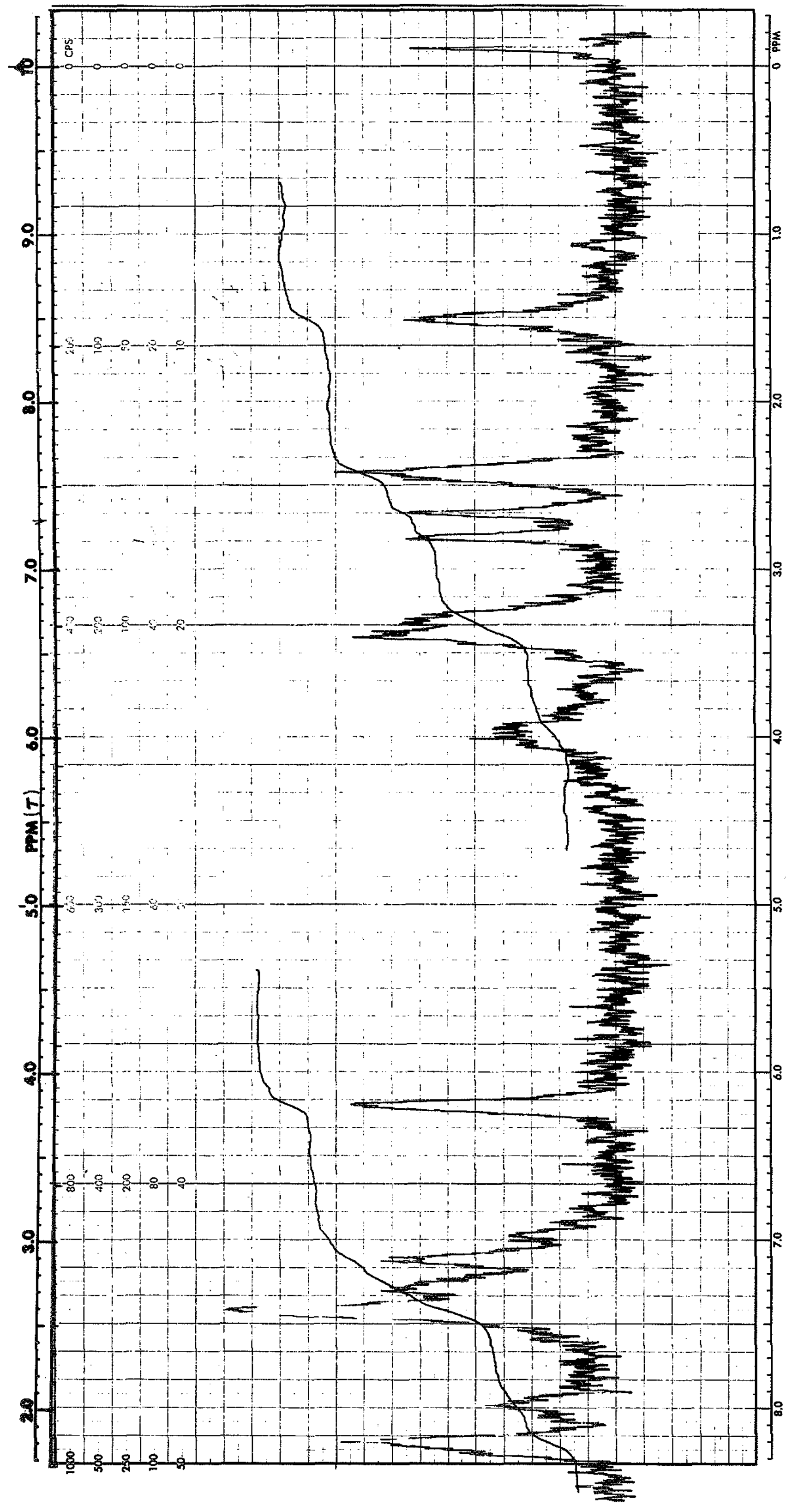

Figure E-2. Nuclear Magnetic Resonance Spectrum of NA/MDA/BTDA Prepolymer
Solvent: DMSO-d_6

E.4.2 Polymers

The NA/MDA/BTDA, NA/ODA/BTDA, NA/MDA/PMDA and NA/ODA/PMDA successfully molded into consolidated, cured specimens as described in E.3 were characterized for structure, thermo-oxidative stability and hydrolytic stability as described below.

E.4.2.1 Infrared Analysis - The infrared spectra of the formulations given above were essentially identical except for some minor shifts in phenyl absorption bands arising from different phenyl species in the dianhydride and diamine formulation modifications. A representative infrared spectrum for the cured NA/MDA/BTDA specimen is shown in Figure E-3. The spectrum displays the expected strong imide linkage absorptions at 1780 and 1710 cm^{-1} as well as strong phenyl absorptions in the 1500-1100 cm^{-1} region. The absorption band at $\sim$2900 cm^{-1} present in model compounds (see Figure C-13, Page 116) and attributed to carbon-hydrogen stretch in cycloaliphatic rings is also present in Figure E-3. The NA/MDA/BTDA spectrum is also very similar to the absorption regions stated above to spectra of NA/ODA/BTDA, NA/MDA/PMDA and NA/ODA/PMDA spectra shown in Figures E-4, E-5, and E-6, respectively.

At this point it is deemed appropriate to make a comparison of the cured A-type polyimide polymer structure with that observed for the model compound N-phenyl nadimide (I). The only technique suitable for comparison of gross structural similarities between the pyrolytic polymer produced from the model compound (I) and the cured A-type polyimide polymers is by infrared analysis. This is due to the intractable nature of the latter polymers.

Unfortunately, when one tries to make a comparison of the spectra of the cured polymers (Figures E-3 to E-6), with the spectra of the polymerized model compound (Figure C-2), the fine structure in most cases is marked by non-resolution and/or the absorptions due to several different types of phenyl rings and functional linkages. However, definite similarities do exist and attention is called to three principal areas. Both the pyrolyzed polymer from (I) and the cured polymers exhibit: 1) definite imide backbone linkages as indicated by the absorption bands in the 1700-

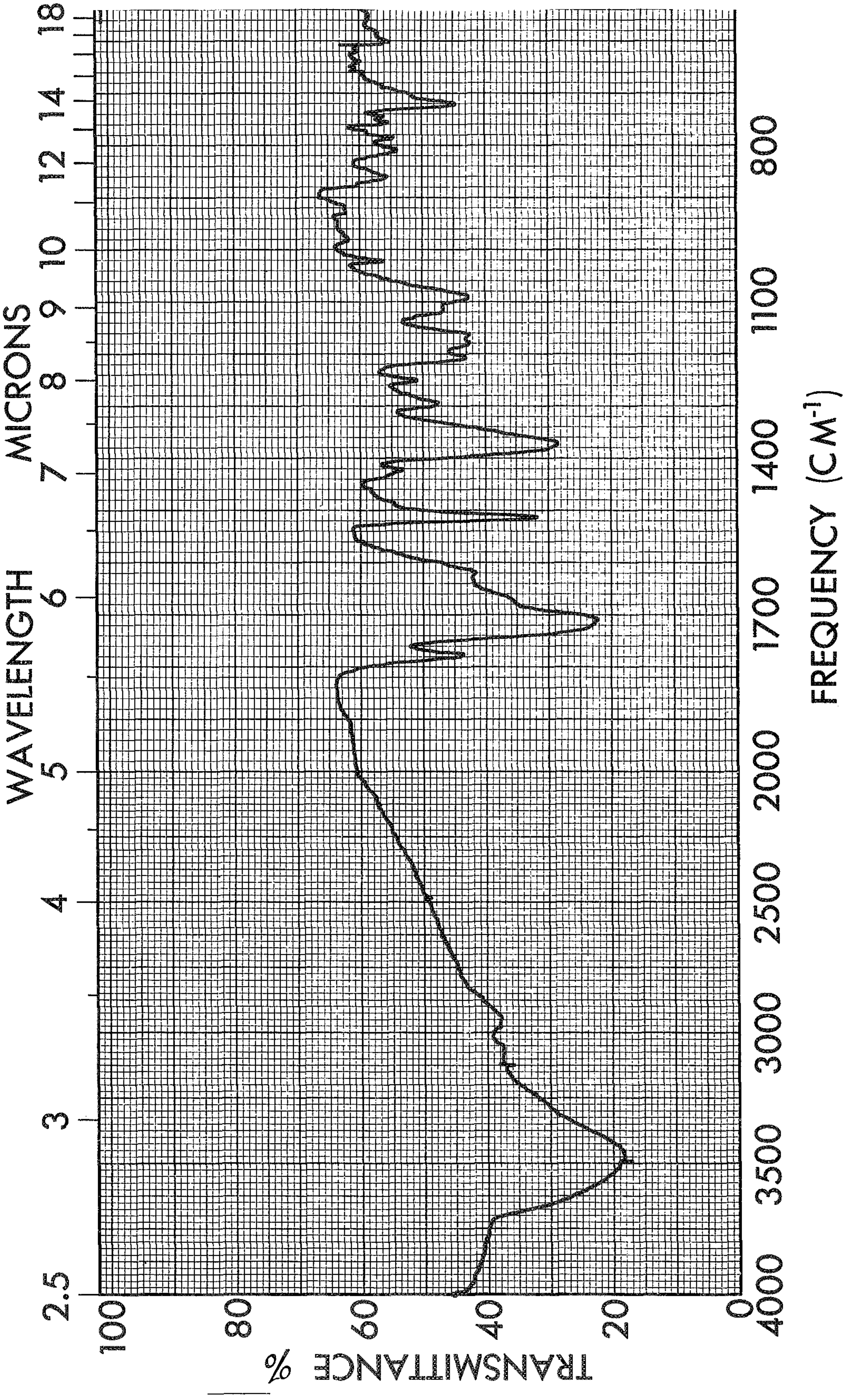

Figure E-3. Infrared Spectrum of NA/MDA/BTDA Cured Polymer (KBr) Concentration: 3.9 mg/g KBr

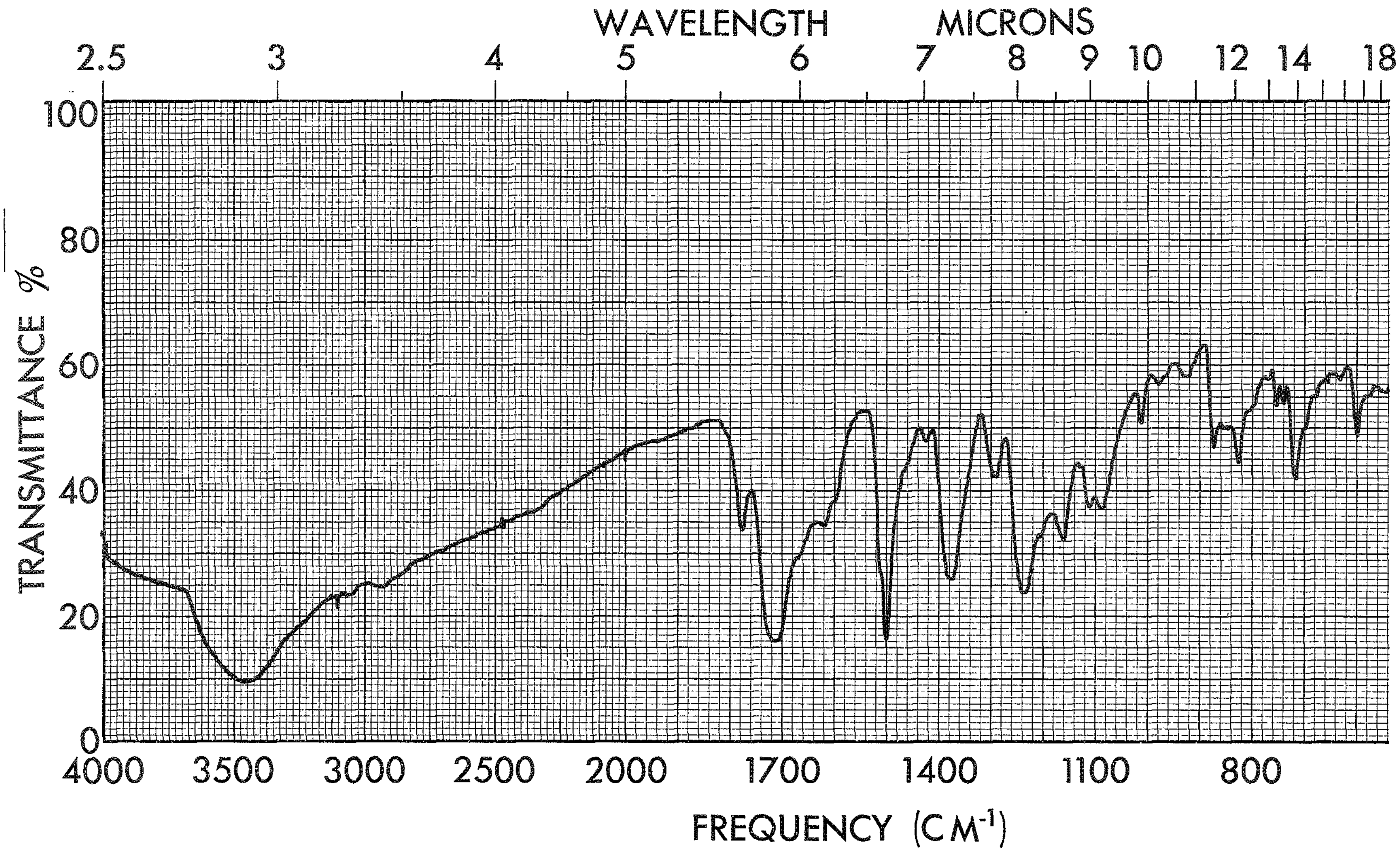

Figure E-4. Infrared Spectrum of NA/ODA/BTDA Cured Polymer (KBr)
Concentration: 3.1 mg/g KBr

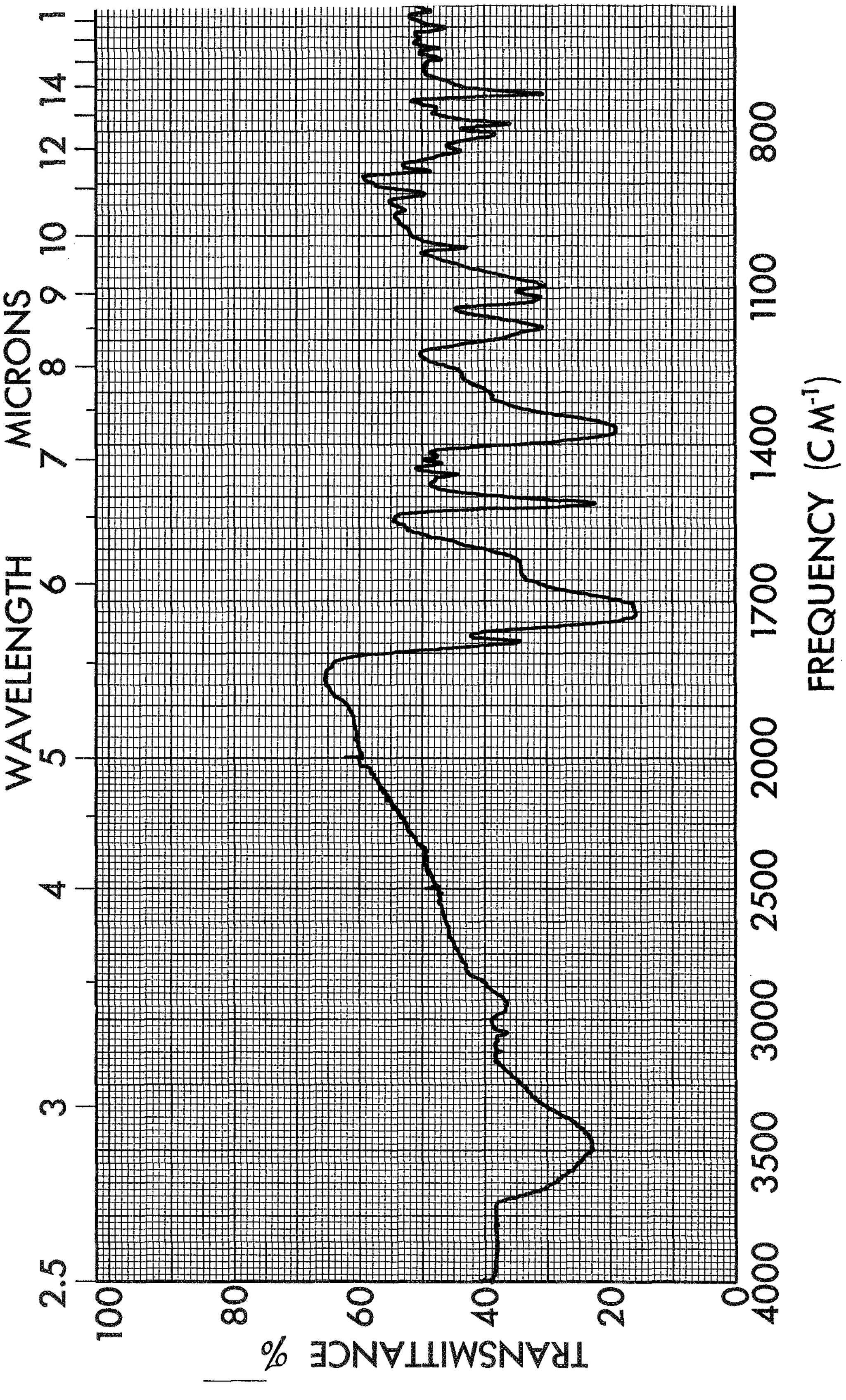

Figure E-5. Infrared Spectrum of NA/MDA/PMDA Cured Polymer (KBr)
Concentration: 5.5 mg/g KBr

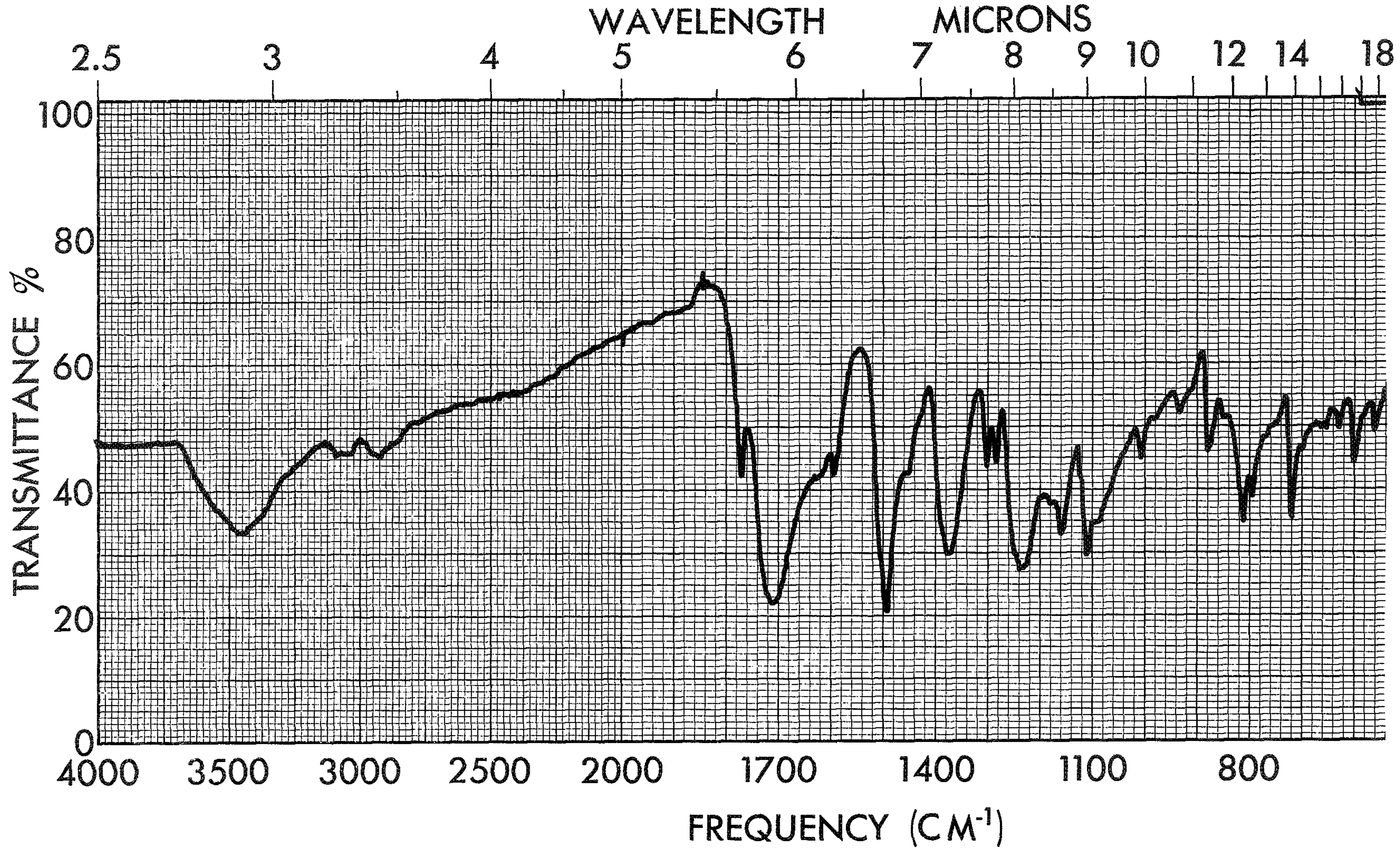

Figure E-6. Infrared Spectrum of NA/ODA/PMDA Cured Polymer (KBr)
Concentration: 5.3 mg/g KBr

1780 cm^{-1} region, 2) definite hydrocarbon C-H stretching mode absorption in the 2850-3000 cm^{-1} region, and 3) evidence for C=C stretch in the 1620-1630 cm^{-1} region. The presence of 2) and 3) in both classes of polymers strongly suggests that the same types of five-membered ring olefin and endocyclic hydrocarbon are present in each. Consequently, TRW Systems feels that the pyrolytic polymerization mechanism postulated and described in Section 2.3 holds to a large degree in cured A-type polyimides as well as for the simpler model, N-phenyl nadimide (I).

E.4.2.2 Thermogravimetric (TGA) Analysis - The NA/MDA/BTDA, NA/ODA/BTDA, NA/MDA/PMDA and NA/ODA/PMDA cured polymers were screened for thermo-oxidative stability in nitrogen and air. The data obtained from the screening determinations in air are summarized below in Table E.I.

TABLE E.I
TGA DETERMINATION OF PERCENT RESIN WEIGHT LOSS
IN AIR AS A FUNCTION OF TEMPERATURE[a]

Formulation	Temperature (°C) at which the Given Percent Resin Weight Loss was Observed			
	10%	20%	30%	40%
NA/MDA/BTDA	375	430	460	470
NA/ODA/BTDA	380	450	465	475
NA/MDA/PMDA	420	480	505	520
NA/ODA/PMDA	410	475	500	515

[a] Determined on powder samples (<5μ diameter) employing an Aminco Thermoanalyzer using a 3°C/min scan rate and 100 ml/min air flow.

These data showed preliminary evidence that PMDA containing materials were more thermo-oxidatively stable in air, which was later confirmed as described below in E.4.2.3. The TGA curves determined in nitrogen showed a trend in the same direction as air data, but were not employed to postulate on stability, because the most important criteria for selecting a candidate resin was stability in air. Figure E-7 displays the thermogram recorded for NA/ODA/BTDA in nitrogen and air, which displays typical resin weight loss curves observed for each of the four resins.

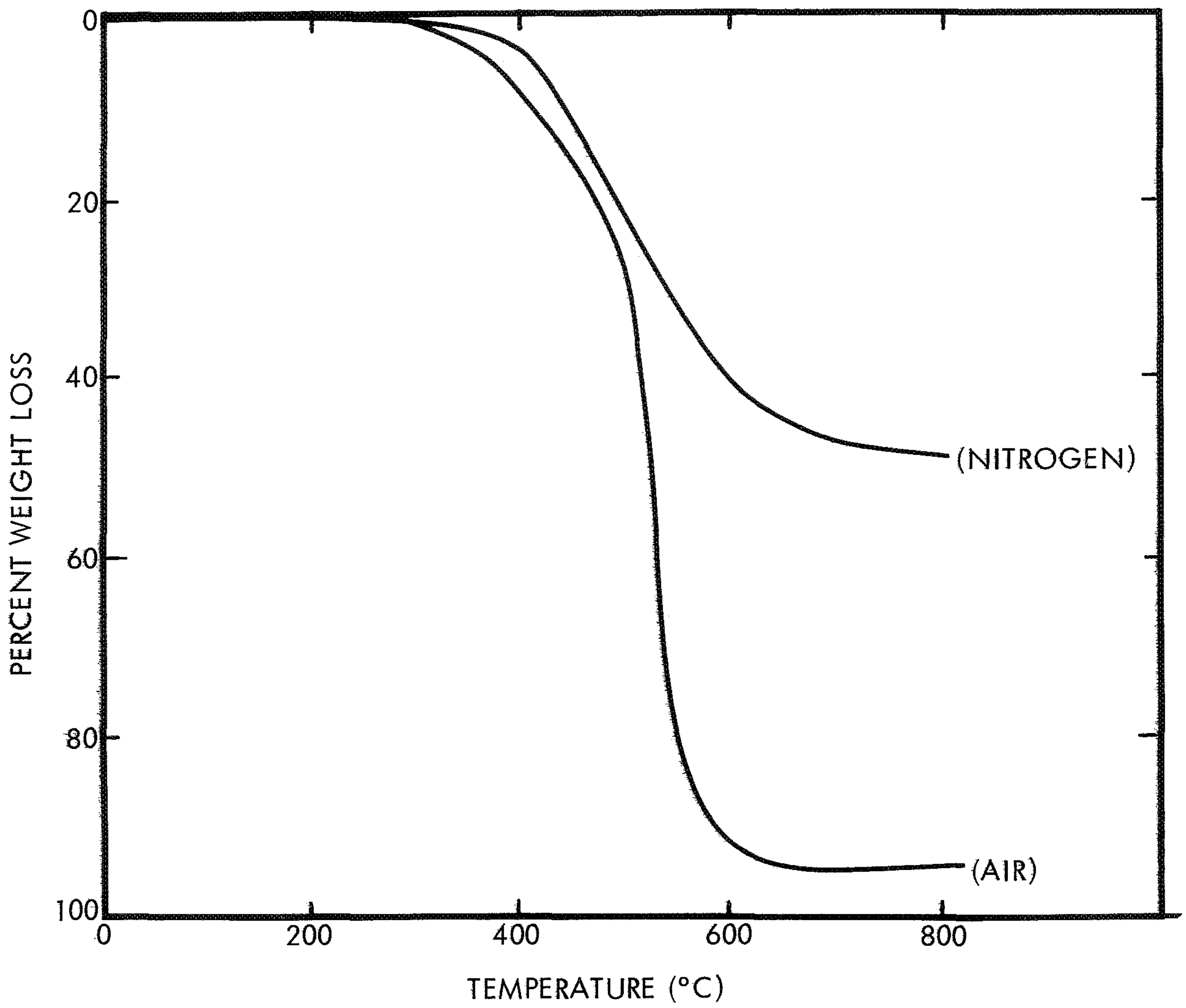

Figure E-7. Thermogram of Cured NA/ODA/BTDA Resin in Nitrogen and Air
Scan Rate: 3°C/min Flow: 100 ml/min

E.4.2.3 Isothermal Aging Experiments - Each of the four cured A-type resins screened for thermo-oxidative stability by TGA analysis described above was isothermally aged for 1000 hours in air at 400°F and 600°F as discussed in Section 3.1.4.2 . The aging experiments were conducted employing a Linberg Heavy Duty crucible furnace, Model 56311, connected to a temperature controller manufactured by the same company. The samples were aged in a half-circle form of approximately 1/8-inch thickness and 1/2-inch diameter after accurately weighing the specimens to the nearest tenth of a milligram. The samples were arranged on a tree-type set-up and placed in the furnace. Air at a 100 ml/min flow (monitored by a bubble-type indicator) was introduced through a capillary tube into the bottom of the furnace and allowed to flow upward through the furnace, exiting through the top. The temperature was monitored by a thermometer calibrated against an NBS standard. The thermometer bulb was inserted into the furnace to a point approximating the center of the sample array. During the aging experiments, the resin weight loss was monitored by removing the samples every 72-96 hours, allowing them to reach 25°C, then weighing them to the nearest tenth of a milligram. After each weighing the samples were rotated from bottom to top on the tree to ensure that each was adequately exposed to the air current at the desired temperature.

After the 1000 hour isothermal aging at 400°F, the samples showed little physical appearance change. However, the samples aged at 600°F displayed many micro-cracks in all surface edges and had warped slightly towards the center. The data arising from this 1000-hour isothermal aging study in air identified the 1300 FMW NA/MDA/PMDA formulation as most thermo-oxidatively stable resin candidate based upon the weight retention procedure measurements described above.

E.4.2.4 Hydrolytic Stability Determinations - All imidized prepolymer and polymer samples prepared as described previously in this Appendix were subjected to hydrolytic stability studies. The results of these stability studies were reported and discussed in Section 3.1.4.3 and recorded in Table IV on Page 32.

The data were obtained by the general procedure as follows:

> The samples were pulverized and passed through a 150 mesh screen. The material was dried above 140°C in a vacuum oven, then weighed to the nearest tenth of a milligram. A quantity of water was heated to boiling, then the sample was added in one portion at approximately a 4% w/w sample/water ratio. The sample was boiled for two hours, then filtered hot. The sample was dried overnight under vacuum at 80°C, then weighed to the nearest tenth of a milligram. The percent resin weight loss reported in Table IV is a ratio of weight loss divided by initial weight x 100.

All formulations containing PMDA investigated by this procedure demonstrated hydrolytic stabilities superior to that demonstrated by the resins prepared from BTDA.

E.5 SELECTION OF THE BEST A-TYPE POLYIMIDE FORMULATION

All data reported previously in this Appendix and in Section 3.1 were evaluated and a logical choice of the best candidate for further consideration in the program was established. The 1300 FMW NA/MDA/PMDA formulation demonstrated reasonable processability and excellent thermo-oxidative and hydrolytic stabilities. Consequently, this specific ingredient combination was chosen for prepolymer studies.

APPENDIX F
PREPOLYMER STUDIES

The NA/MDA/PMDA A-type polyimide formulation evaluated to be the best candidate resin for investigation in the remainder of the program as described in Appendix E was subjected to a prepolymer synthesis and characterization study. Three other prepolymer formulated molecular weights (FMW's) in addition to the 1300 FMW were evaluated. The three FMW's chosen were 1000, 1500, and 2000 which were deemed realistic prepolymers for investigation of processability, thermo-oxidative stability, and hydrolytic stability at FMW's above and below the original 1300 FMW resin. The insight gained from the polymer screening and characterization studies as described in 3.1 and Appendix E as well as prior TRW Systems technology generated on P13N were utilized to investigate the 1000, 1500, and 2000 FMW prepolymers of NA/MDA/PMDA as described below.

F.1 VARNISH PREPARATION

The experimental procedure detailed in E.1 was utilized to prepare NA/MDA/PMDA prepolymers at a 40% w/w solids loading in DMF at FMW's of 1000, 1500 and 2000. The varnish viscosities were determined with a Brookfield viscometer and are reported in 3.2.1 on Page 34.

F.2 PREPREG DRYING AND IMIDIZATION STUDIES

The experimental varnishes prepared as described above were utilized to prepreg Style 181 E-glass cloth containing A-1100 soft amino-silane finish for prepolymer/prepreg drying and imidization studies.

The E-glass cloth was prepregged employing a simple one-step hand dip procedure, followed by a drying cycle at 325°F in a forced air to remove DMF. The dried prepreg was then imidized at 475°F to give prepreg material suitable for laminate processing. Each A-A prepolymer varnish (c.a., 1000, 1500, and 2000 FMW) of NA/MDA/PMDA was investigated for time necessary to ensure removal of DMF at 325°F and imidize the A-A linkages at 475°F. Table F.I summarizes imidization data obtained at these temperatures for the 1500 FMW material. DMF removal was monitored by the disappearance of

TABLE F.I

1500 FORMULATED MOLECULAR WEIGHT PREPOLYMER IMIDIZATION STUDY

Time/Temperature Variables	Imidization by Infrared Analysis	Infrared Spectrum
2 min @ 325°F	Incomplete	Figure F-1
4 min. @ 325°F	Incomplete	Figure F-2
2 min. @ 325°F and 2 min. @ 475°F	Complete	Figure F-3
4 min. @ 325°F and 4 min. @ 475°F	Complete	Figure F-4

a DMF absorption band at 1260 cm^{-1}. As can be seen in Figure F-3 versus Figure F-4, a cycle of four minutes at 475°F was necessary to reduce this 1260 cm^{-1} DMF absorption to a mere shoulder. Identical behavior was observed for 1000 and 2000 formulated molecular weight materials as can be seen by referring to Figures F-5 and F-6, respectively. The four-minute heating cycle at 325°F, followed by a four-minute cycle at 475°F gave a remaining total prepreg volatile matter content of approximately 2-3% (as determined by heating at 600°F for 30 minutes) for each formulated molecular weight prepolymer investigated. This volatile matter content range was judged as suitable for initial laminate studies. Therefore, the imidization study experimental data were directly applicable to Task III preliminary fabrication studies as described in Section 4.

F.3 POLYMER CHARACTERIZATION STUDIES

The NA/MDA/PMDA formulation at 1000, 1500, and 2000 FMW's was evaluated in neat prepolymer and cured polymer configurations for comparison of data with the 1300 FMW resin prepared and characterized as described in Appendix E.

F.3.1 Prepolymer Preparation

Portions of the 1000, 1500 and 2000 FMW NA/MDA/PMDA varnishes prepared as described in E.1 were converted to imidized powders by the method described in E.2 . Characterization is described in F.3.3.

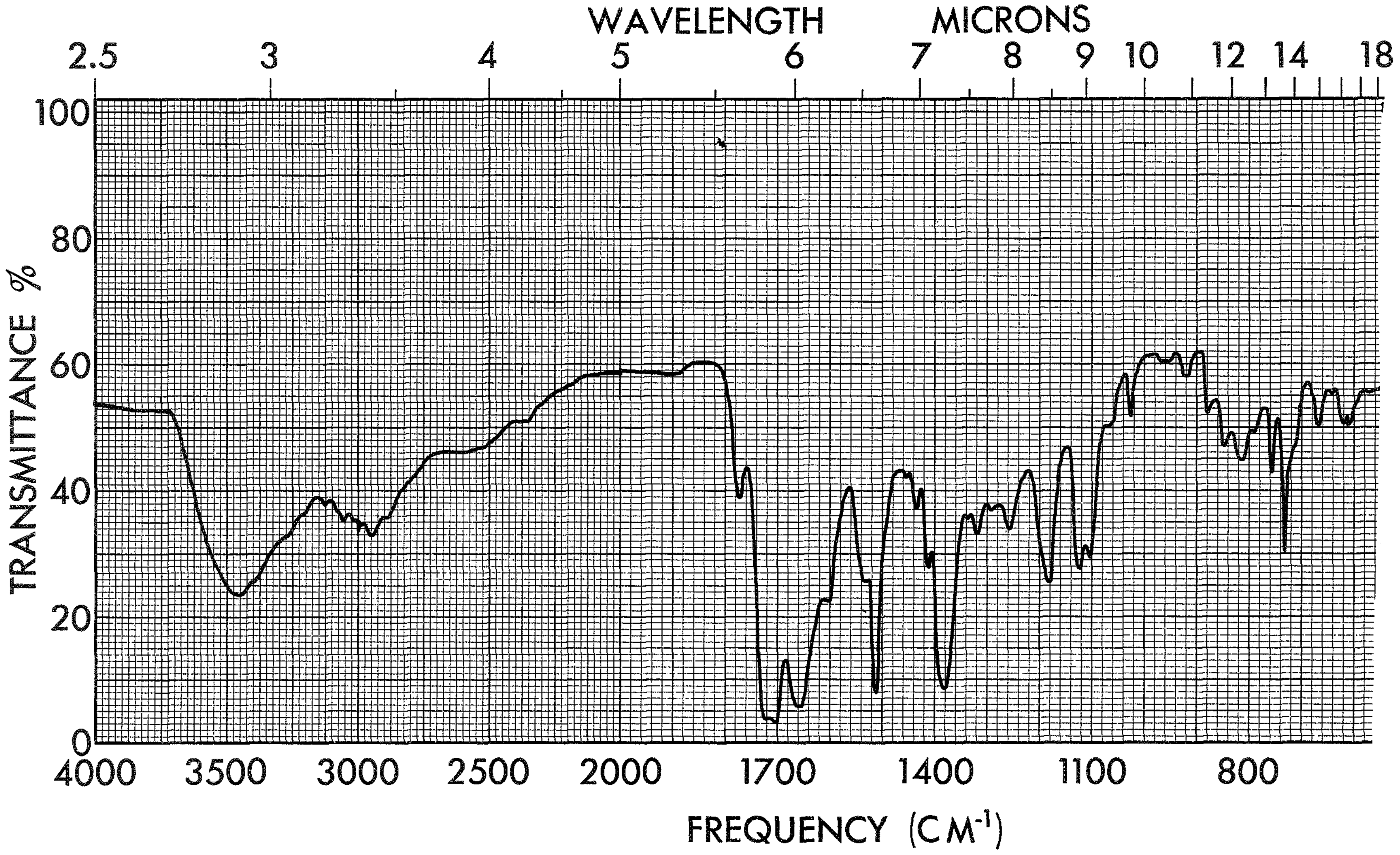

Figure F-1. Infrared Spectrum of NA/MDA/PMDA 1500 Formulated Molecular Weight Prepolymer Heated for Two Minutes at 325°F in Air (KBr) Concentration: 3.5 mg/g KBr

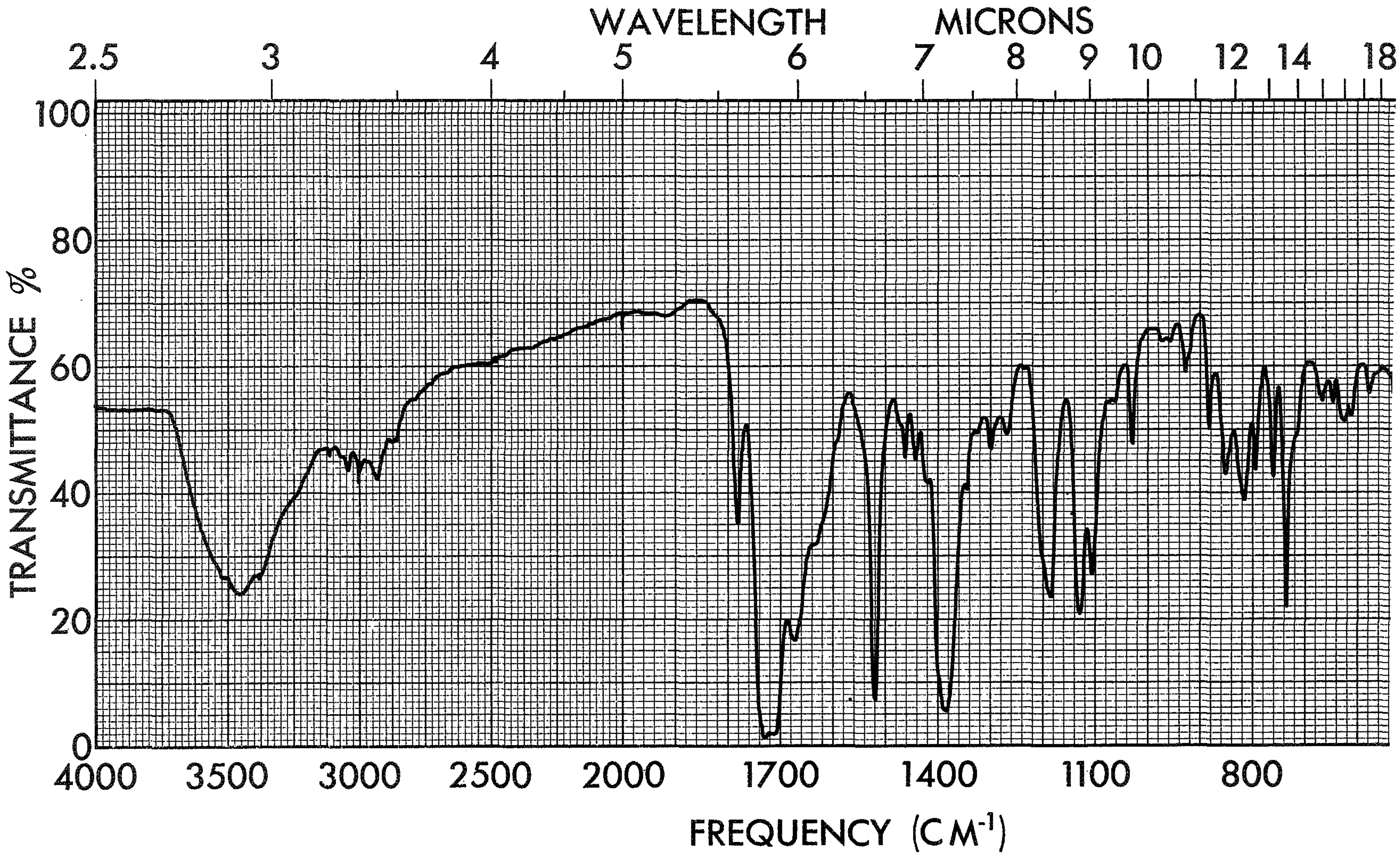

Figure F-2. Infrared Spectrum of NA/MDA/PMDA 1500 Formulated Molecular Weight Prepolymer Heated for Four Minutes at 325°F in Air (KBr) Concentration: 3.9 mg/g KBr

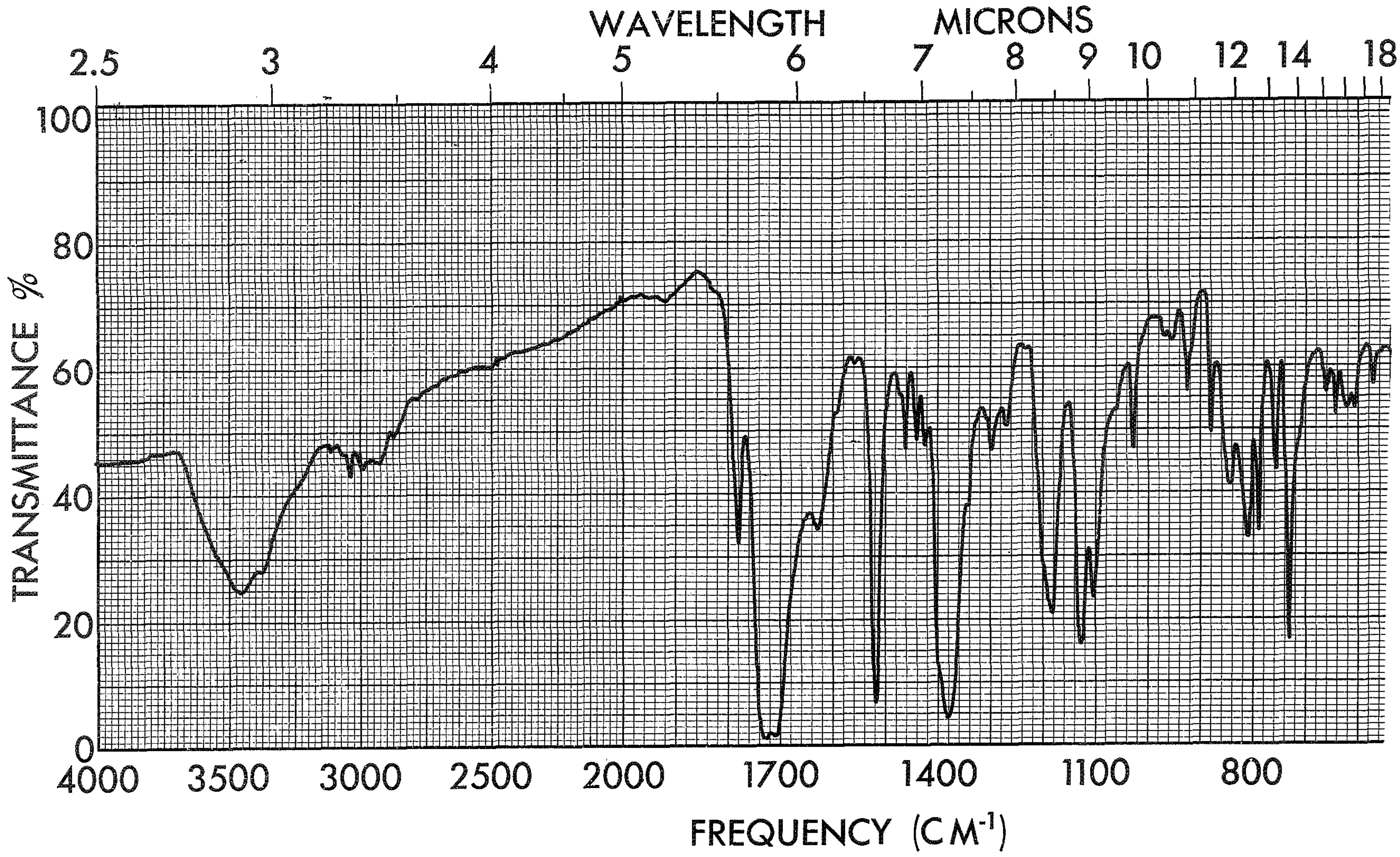

Figure F-3. Infrared Spectrum of NA/MDA/PMDA 1500 Formulated Molecular Weight Prepolymer Heated for Two Minutes at 325°F and Two Minutes at 475°F in Air (KBr)
Concentration: 4.3 mg/g KBr

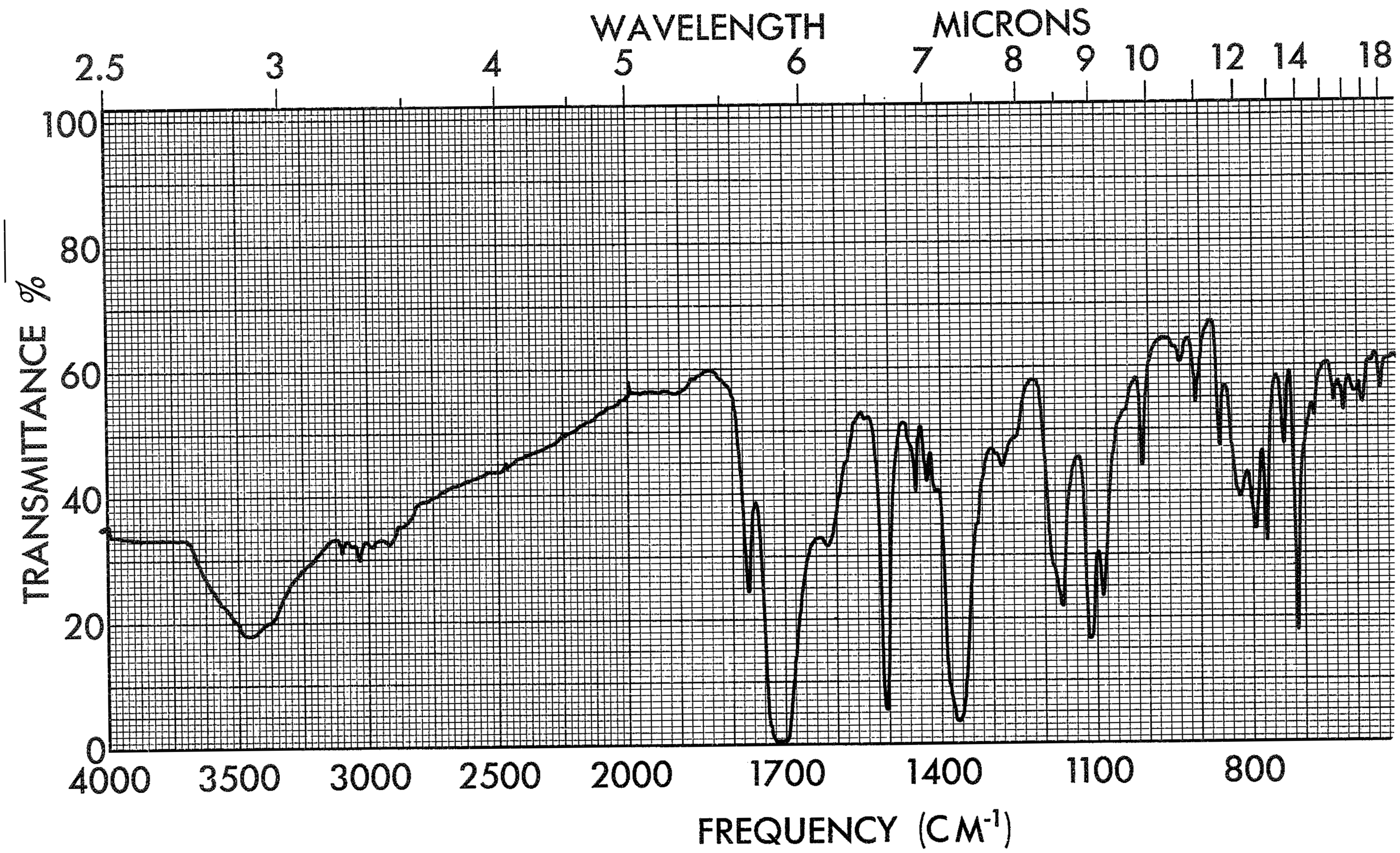

Figure F-4. Infrared Spectrum of NA/MDA/PMDA 1500 Formulated Molecular Weight Prepolymer Heated for Four Minutes at 325°F and Four Minutes at 475°F in Air (KBr)
Concentration: 3.9 mg/g KBr

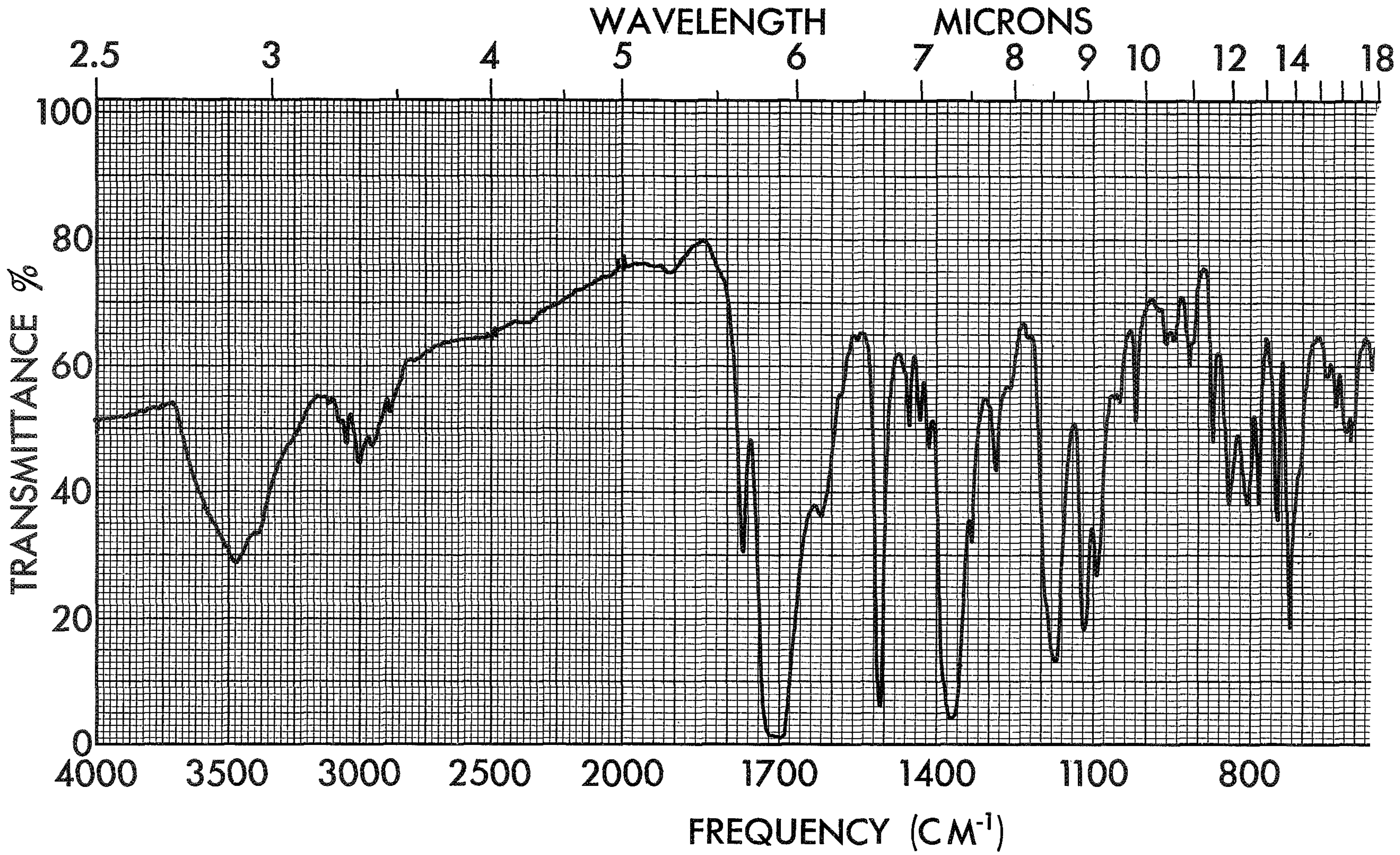

Figure F-5. Infrared Spectrum of NA/MDA/PMDA 1000 Formulated Molecular Weight Prepolymer Heated for Four Minutes at 325°F and Four Minutes at 475°F in Air (KBr)
Concentration: 4.6 mg/g KBr

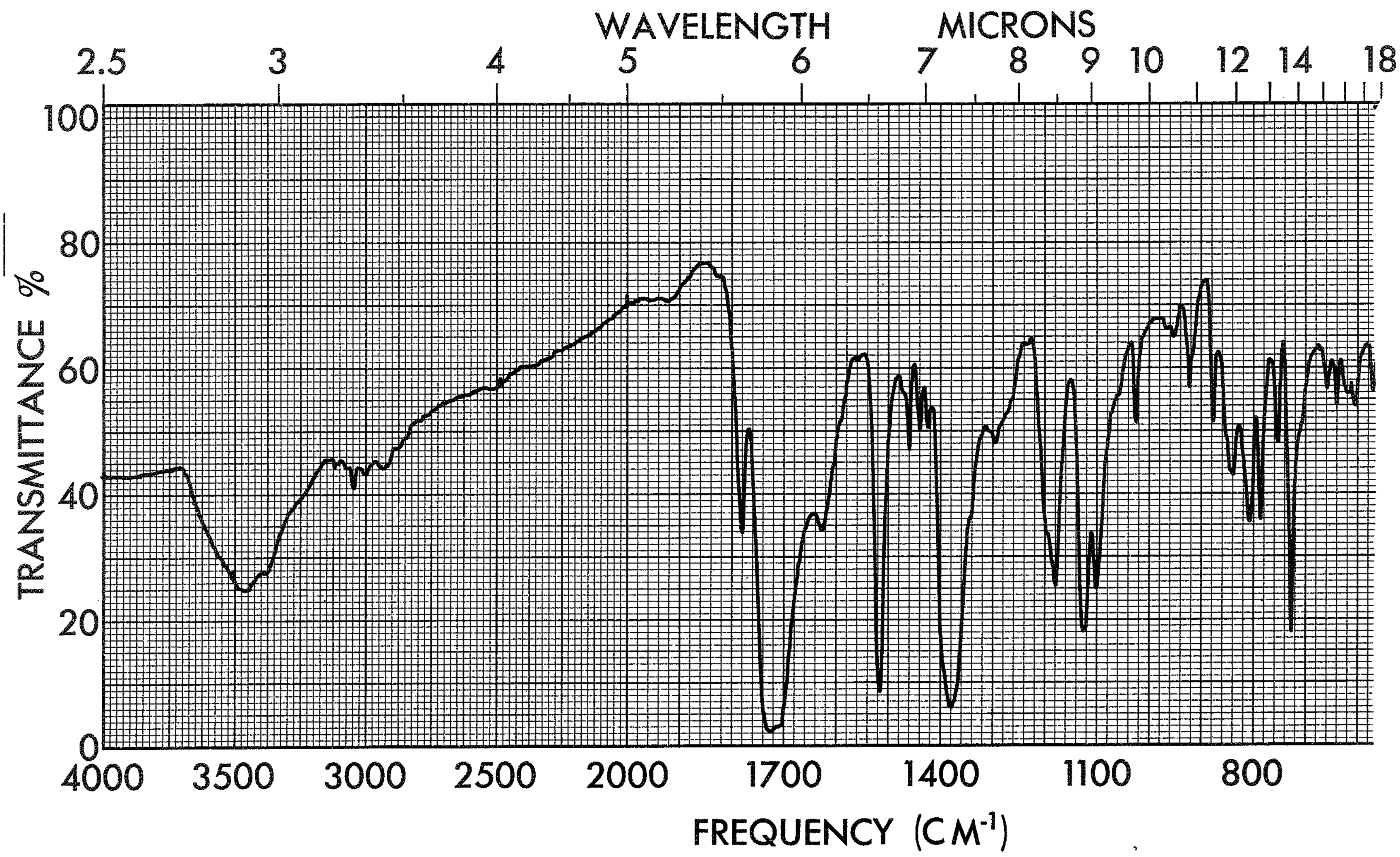

Figure F-6. Infrared Spectrum of NA/MDA/PMDA 2000 Formulated Molecular Weight Prepolymer Heated for Four Minutes at 325°F and Four Minutes at 475°F in Air (KBr)
Concentration: 4.3 mg/g KBr

F.3.2 Cured Polymer Molding Studies

The three imidized prepolymer powders were subjected to a molding study employing molding variables defined for the 1300 FMW species as described in E.3. Employing molding temperatures of 590-600°F and pressures of 325-1000 psi for a curing cycle of 30 minutes, only the 1000 FMW could be processed into a consolidated specimen. However, this particular material easily molded into a plug of Barcol hardness equal to 48-50. The implications of the molding study is discussed in Section 3.2.

F.3.3 Characterization of Prepolymers and Polymers

The prepolymers and polymers prepared in this study were analyzed as described below.

F.3.3.1 Infrared Analysis - The prepolymer molding powders were screened by infrared analysis to establish whether complete imidization of the A-A linkages had occurred. The spectrum obtained for the 1500 FMW prepolymer is representative for the group and is given in Figure F-7. The spectrum is essentially identical to that obtained for the same FMW in the imidization studies (Figure F-4) and confirmed complete formation of imide linkages.

The three cured polymers obtained in the molding studies were also screened for structure by infrared analysis. Figures F-8, F-9, and F-10 represent the spectra obtained for the 1000, 1500 and 2000 FMW formulations, respectively. Each is almost identical to that determined on the 1300 FMW (Figure E-5 , Page 130). The only variation in the spectra which appears to be significant is the intensity of the absorption band in the 2750-3000 cm^{-1} region. This absorption is primarily due to $-CH_2-$ stretching in cyclopentene or nadic species. As expected, absorption intensity in this region decreases as the FMW increases, because less nadic anhydride (NA) monomer is introduced into the material.

F.3.3.2 Thermo-Oxidative Stability - The thermo-oxidative stability of the cured polymers was screened by thermogravimetric analysis (TGA) in air. The results of the screening are displayed in Figure F-11 to allow comparison of the 1000, 1500, and 2000 cured FMW species with the previously

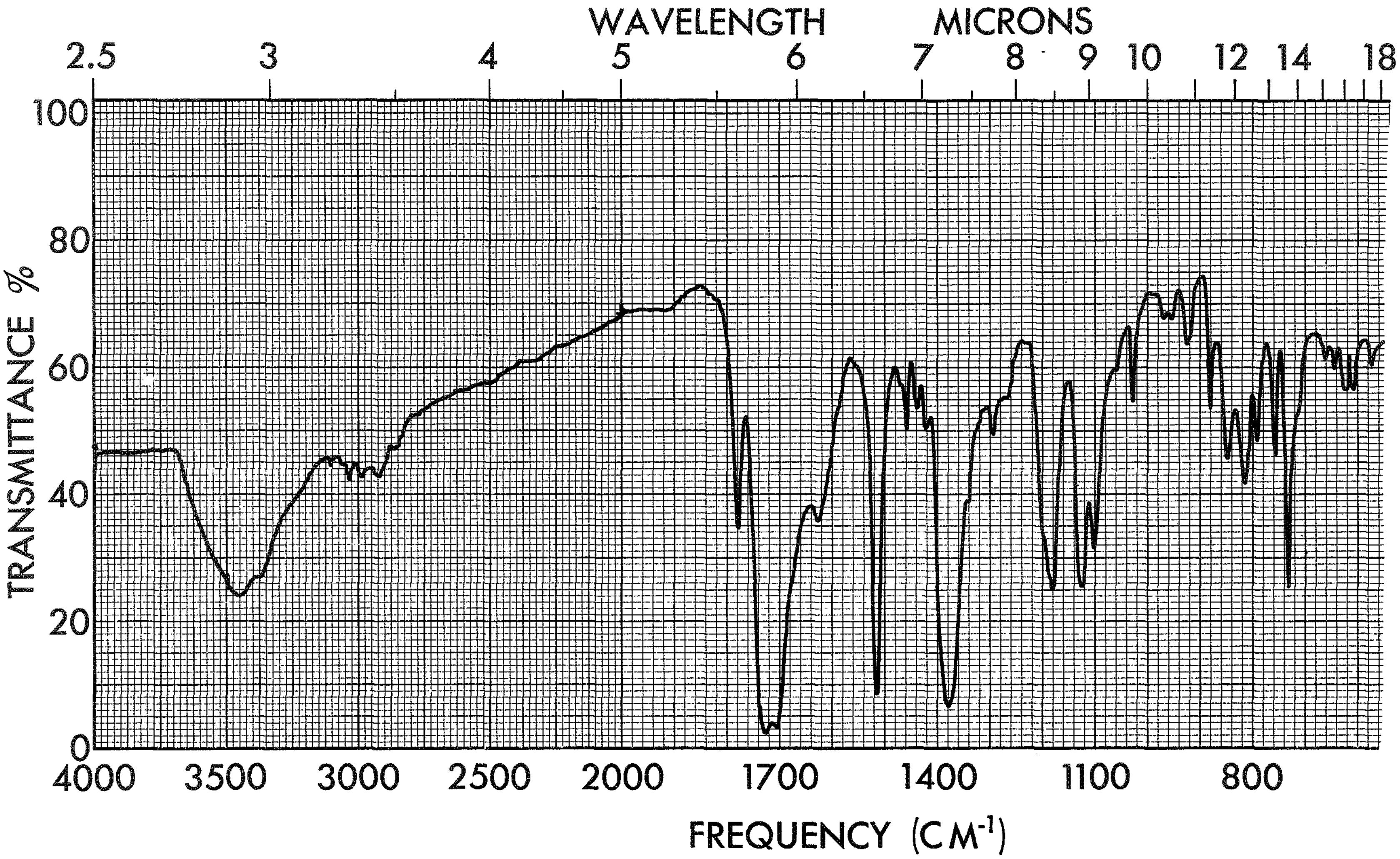

Figure F-7. Infrared Spectrum of NA/MDA/PMDA 1500 Formulated Molecular Weight Prepolymer Prepared as a Molding Powder (KBr) Concentration: 3.6 mg/g KBr

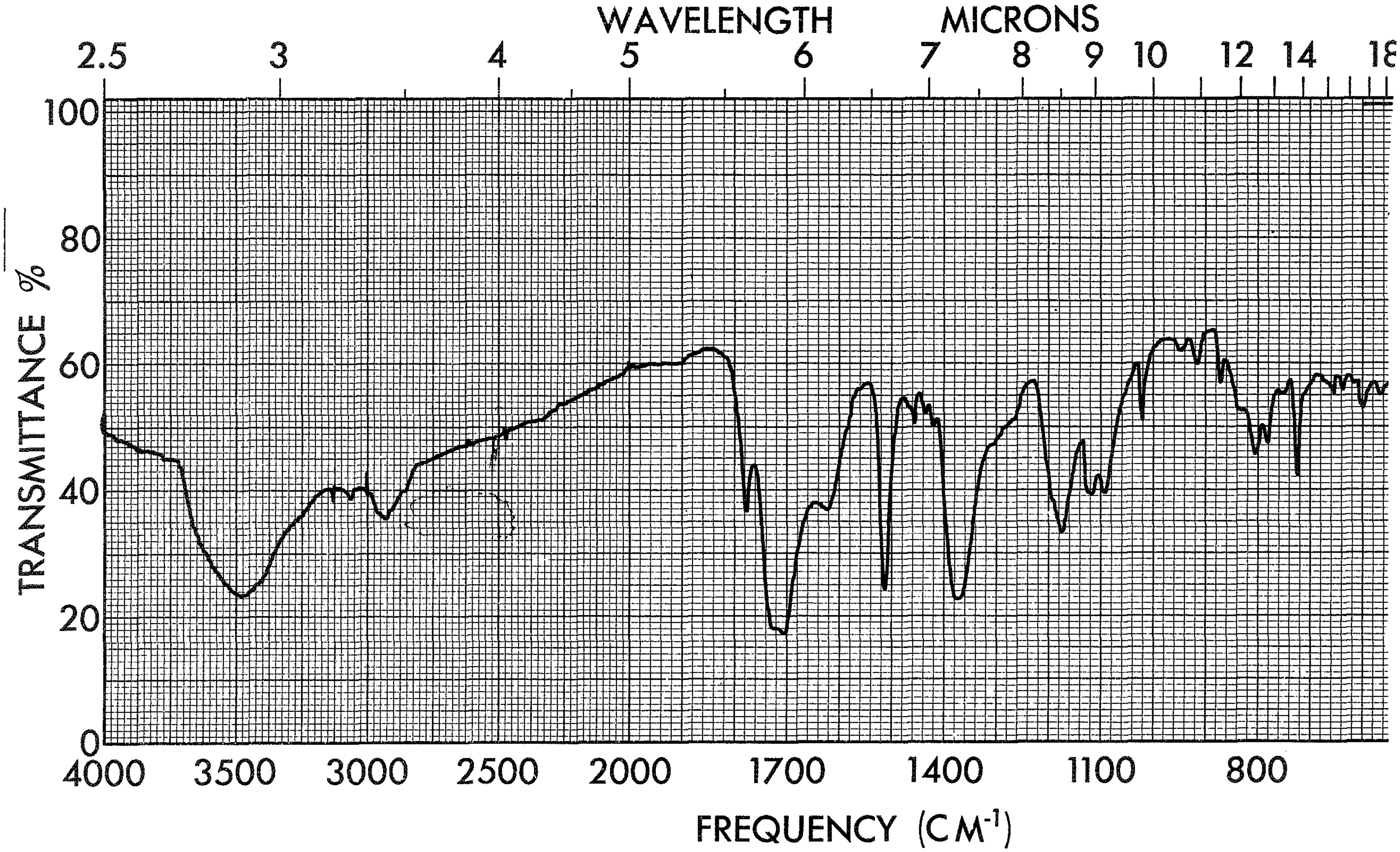

Figure F-8. Infrared Spectrum of NA/MDA/PMDA 1000 FMW
Cured Polymer (KBr)
Concentration: 3.8 mg/g KBr

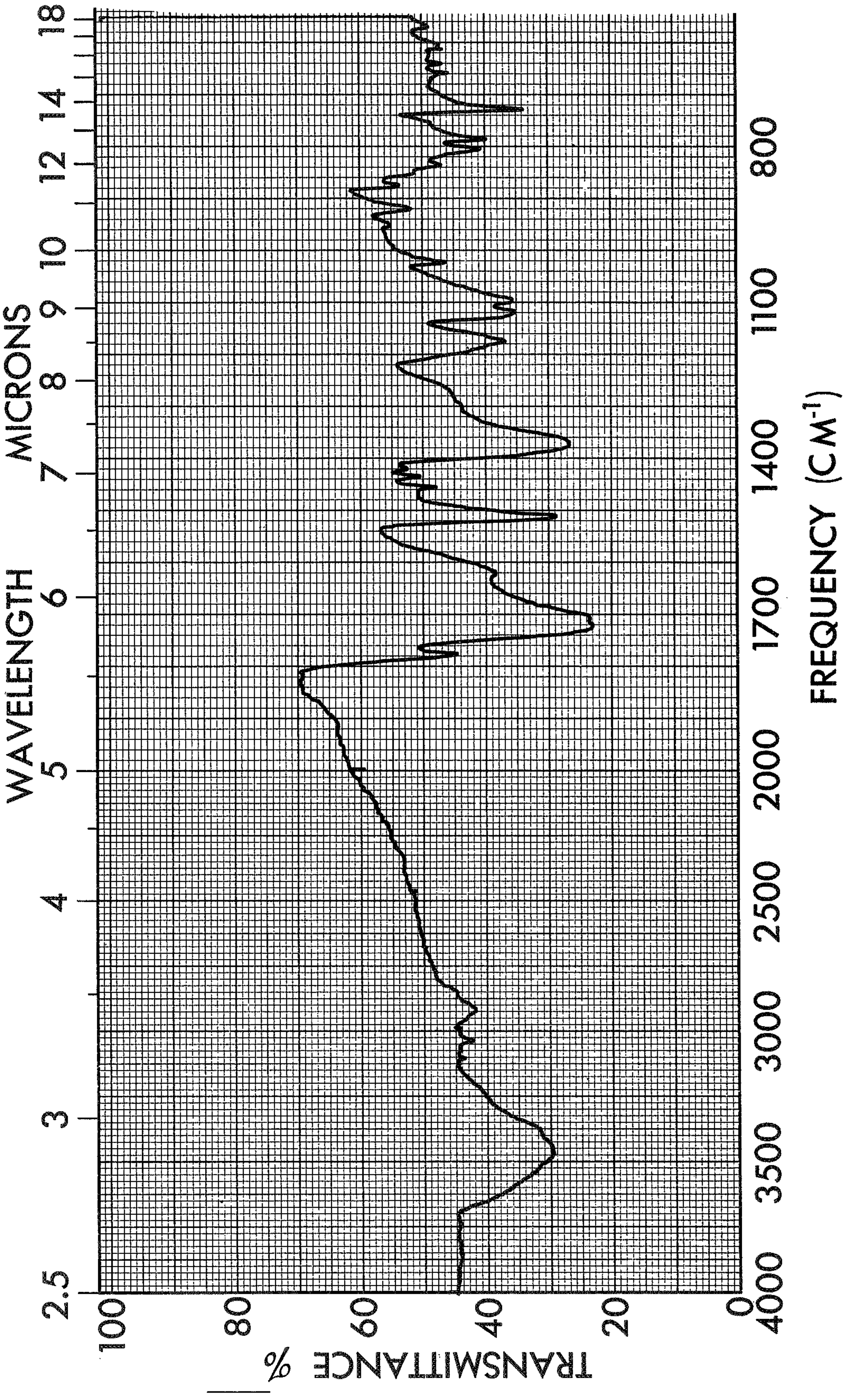

Figure F-9. Infrared Spectrum of NA/MDA/PMDA 1500 FMW Cured Polymer (KBr) Concentration: 5.5 mg/g KBr

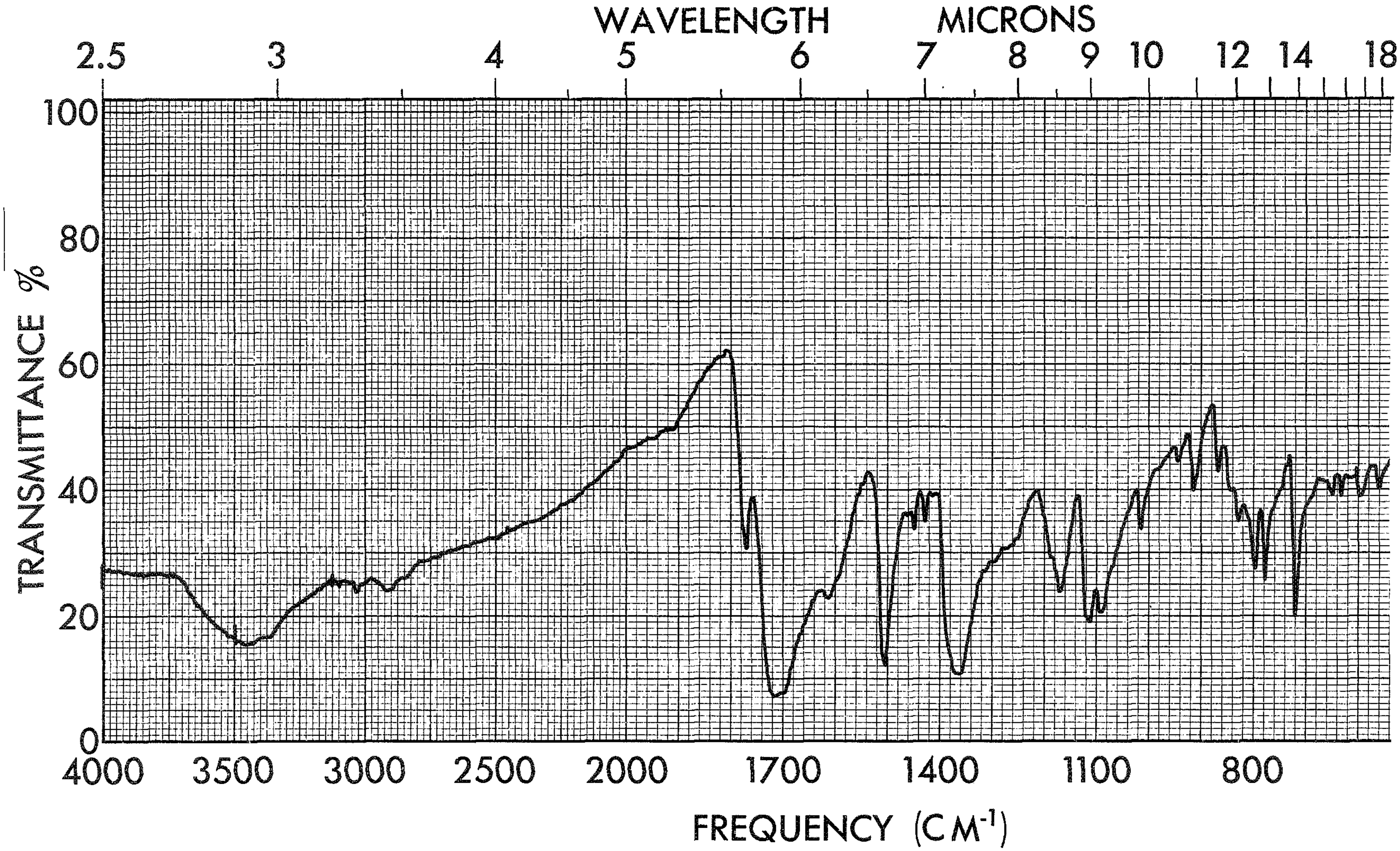

Figure F-10. Infrared Spectrum of NA/MDA/PMDA
2000 FMW Cured Polymer (KBr)
Concentration: 6.6 mg/g KBr

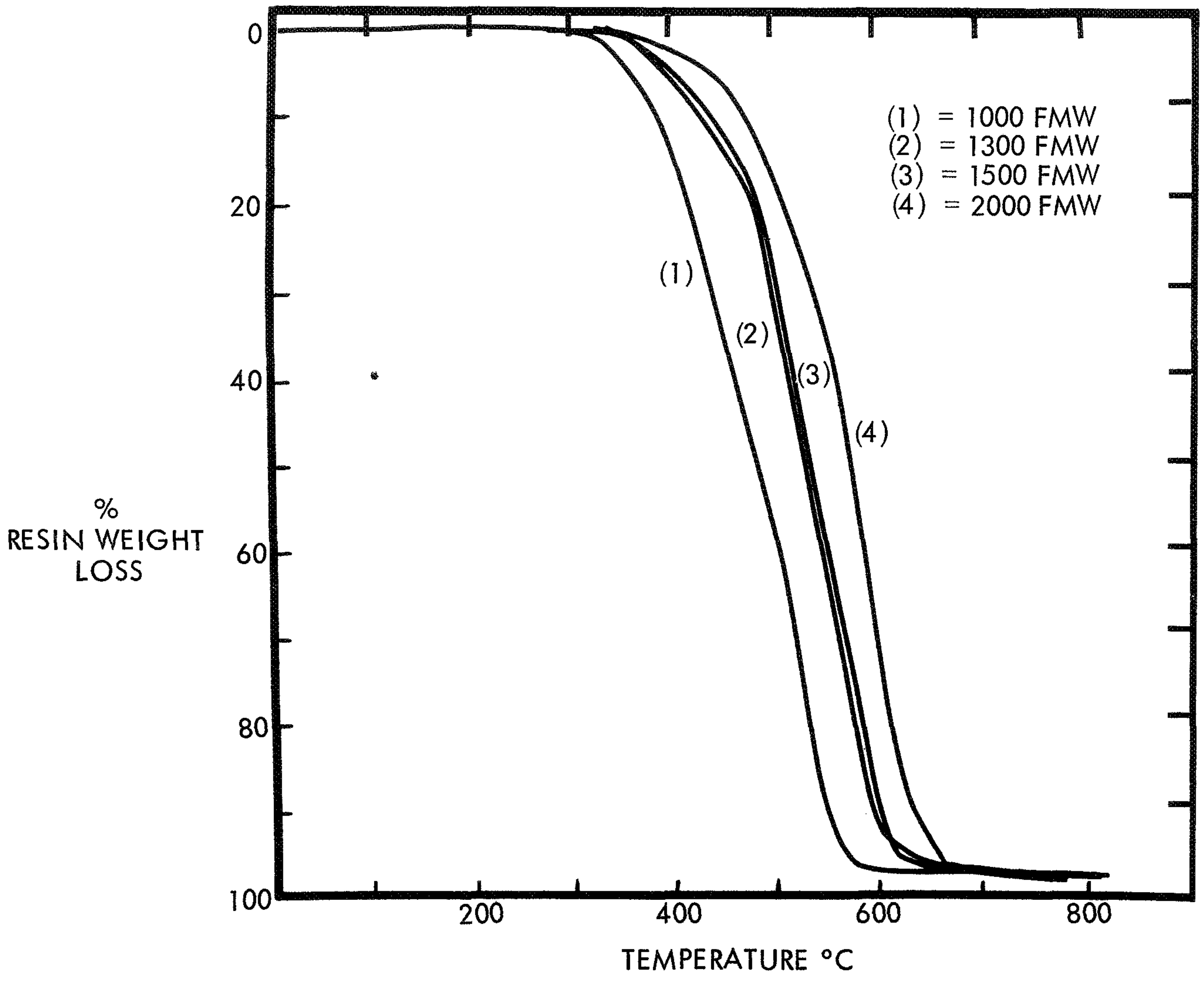

Figure F-11. Thermograms of NA/MDA/PMDA 1000, 1300, 1500, and 2000 FMW Cured Polymer Powders in Air
Scan Rate: 3°C/min Flow: 100 ml/min

prepared 1300 cured FMW material. As can be seen, the 1000 FMW resin appeared to be consistently ∿50°C less stable than the three higher molecular weight materials which all demonstrated higher resistance to air oxidation by TGA characterization. The concern for this indication of lessened thermo-oxidative stability of the 1000 FMW cured polymer as opposed to cured NA/MDA/PMDA materials derived from higher FMW prepolymers (c.a., 1300-2000) was alleviated by isothermal aging in air at 600°F. These isothermal aging data are discussed below.

The results of the TGA screening of NA/MDA/PMDA cured resin materials prepared indicated that the cured polymer prepared from 1000 FMW prepolymer might not demonstrate comparable long-term thermo-oxidative stability at 600°F to that shown by the 1300 molecular weight cured resin. This potential deficiency of the readily processed 1000 FMW material was investigated by subjecting a sample to the identical isothermal aging conditions employed for the 1300 FMW species (c.a., aging at 600°F in an air flow of 100 ml/min). A comparison of the resin weight loss data for the 1000 and 1300 FMW materials is given in Table F.II.

TABLE F.II

COMPARISON OF RESIN WEIGHT LOSS DATA FOR 1000 AND 1300 FORMULATED MOLECULAR WEIGHT NA/MDA/PMDA CURED POLYMER PLUGS

Duration of Aging at 600°F in Air[a] (Hrs)	Resin Weight Loss (%)	
	1000 M.W.	1300 M.W.
80	1.5	5.0
160	2.5	7.0
240	3.5	7.5
300	4.5	8.5

[a] Utilizing air flow of 100 ml/min.

As can be seen from these data, the cured resin prepared from 1000 FMW prepolymer demonstrated thermo-oxidative stability in air at 600°F after 300 hours at a level almost double that of the cured 1300 molecular weight material. Cured specimens prepared from 1500 and 2000 FMW prepolymers demonstrated greater resin weight losses than the 1000 and 1300 materials under identical aging conditions.

F.3.3.3 Hydrolytic Stability - The hydrolytic stability of the cured resins prepared from 1000, 1500 and 2000 FMW prepolymers was assessed by measurement of weight loss after a two-hour immersion in boiling water by the method described in E.4.2.4. The resistance to aqueous hydrolysis was excellent for each of the NA/MDA/PMDA cured samples. The data obtained are summarized in Table F.III along with the weight loss numbers previously determined for their respective prepolymers and those for the 1300 FMW materials.

TABLE F.III
HYDROLYTIC STABILITY OF NA/MDA/PMDA
PREPOLYMERS AND CURED RESINS

Formulated Molecular Weight	Hydrolytic Stability as Weight Loss (%)
1000 Prepolymer	3.9
Cured Resin	3.6
1300 Prepolymer	1.3
Cured Resin	2.3
1500 Prepolymer	2.5
Cured Resin	0.8
2000 Prepolymer	1.7
Cured Resin	0.7

F.4 SELECTION OF ONE PREPOLYMER FORMULATED MOLECULAR WEIGHT

The data included in this Appendix were evaluated and the 1000 FMW NA/MDA/PMDA resin was selected for all remaining program tasks. The discussion of the choice of this resin is described in Section 3.2.6, Page 38.

APPENDIX G
PREPREG AND LAMINATE CHARACTERIZATION METHODS

This appendix provides details of the test methods used to characterize prepregs and composites prepared during this project. These methods have wide use in the laminate and composite processing industry.

G.1 METHODS USED FOR CHARACTERIZATION OF PREPREGS

G.1.1 Volatile Matter Content

Volatile matter content was obtained by weight loss determinations on 4-inch square pieces of prepreg after 30 minutes exposure in an air circulating oven maintained at 600°F.

G.1.2 Resin Solids Content

Resin solid content was obtained from weight loss determinations of the specimens after testing for volatile matter content by heating in air at 1150°F.

G.1.3 Resin Flow

Prepreg was cut 4-inch square with fiber orientation at 45° and stacked 6-ply thick. These plies were molded at 600°F under pressures of 200 and 1000 psig. After molding, the resin flash was removed and the resin flow was calculated as follows:

$$F = \left(\frac{W_1 - W_2}{W_1}\right) \times 100$$

Where:

F = resin flow, % w/w
W_1 = weight of prepreg sample, g
W_2 = weight of molded sample after removal of resin flash, g

G.2 CHARACTERIZATION OF PREPARED FABRICATED COMPOSITES

G.2.1 Flexural Test Procedures

All flexural tests were performed in accordance with ASTM D790 using a 32-to-1 span-to-depth ratio. Specimen deflections were determined from the cross-head motion. Elevated temperature tests were performed in an air circulating temperature chamber mounted on the crosshead. Specimens were preconditioned to the test temperature by heating in the test chamber for 30 minutes prior to test.

G.2.2 Short Beam Shear Test Procedures

All short beam shear strength tests were performed generally as described in ASTM D2344 except that flat specimens were used. Elevated tests were performed in the same manner as described in Section 5.3.2 for flexural tests.

G.2.3 Weight Loss Determinations

Flexural and shear test coupons were weighed before and after thermal aging. The percent weight loss was calculated as follows:

$$\text{Weight Loss} = \frac{W_1 - W_2}{W_1} \times 100$$

Where:

W_1 = original weight of composite specimen
W_2 = weight of composite specimen after thermal aging.

G.2.4 Specific Gravity and Density

Specific gravity of the composites was determined in water in accordance with ASTM D792. The density (g/ml) was calculated as follows:

$$d = (0.997)\ (\text{specific gravity})$$

G.2.5 Resin Content

The resin content of composite specimens was determined by acid digestion. The specimens were boiled in concentrated sulfuric acid for 30 minutes and then washed in distilled water after decanting the sulfuric acid. This was repeated three times after which the fibers were finally washed in acetone and dried for one hour at 300°F. Resin content (% w/w) was calculated as follows:

$$\text{Resin Content} = \frac{W_1 - W_2}{W_1} \times 100$$

Where:

W_1 = original composite specimen weight
W_2 = weight of fibers after acid digestion of the resin matrix.

Previous experiments show that no correction is necessary for loss of graphite weight during this treatment.

G.2.6 Void Content

Void contents of the composites were calculated using additive volumes of resin and graphite fiber as follows:

$$\text{Void Content, \%} = (1 - d_m/d_c)\ 100$$

Where:

d_m = measured density
d_c = composite density calculated assuming zero void content, i.e.,

$$\frac{1}{d_c} = \frac{f_r}{d_r} + \frac{f_r}{d_g}$$

Where:

f is the fraction of resin or graphite indicated by the subscript r or g, respectively,
d_r = density of neat resin, 1.30 g/ml
d_g = density of Thornel 50S reinforcement, 1.63 g/ml.

APPENDIX H

STATISTICAL TREATMENT OF LAMINATE MECHANICAL PROPERTIES

This appendix describes the statistical treatment used to analyze the data generated in Task III and IV. Specifically, it discusses the analysis of variance employed to determine the processing conditions which caused a significant effect on the mechanical properties for the Task III preliminary fabrication studies and evaluation of the effect of aging on graphite fiber reinforced laminates prepared using the candidate polyimide system recommended in this program.

H.1 ANALYSIS OF PROCESSING INFORMATION

The raw data generated during the investigation of the processes parameters in the preliminary fabrication studies was in the form of a four-factor, two-level with replication experimental design. This design is easily treated by the analysis of variance (Reference 11) to determine statistically significant changes. The analysis of variance of effect of processing parameters on the flexural strength and modulus at room temperature and 550°F, shear strength at room temperature and void content are given in Tables H.I through H.VI. It is interesting to note that with the exception of the void content only the single parameters of temperature, cure time, cure pressure, and post cure were significant at the 99% confidence level and a large number of interactions were significant in the void content analysis of variance.

To facilitate the analysis of variance, 1) the pooled standard deviation of a single measurement (as obtained on quintuplicate determinations on the same panel) was not utilized in the analysis of variance and 2) the replication identified in Tables H.I through H.VI was obtained using the separate fabricated panels. Consequently, the replicate variance is that obtainable in preparing identical panels. A test of the differences in the repeatability (e.g.,, the variance associated with preparation of identical panels) as compared to the repeatability of measurements on a single panel was conducted and found that there were no significant statistical differences (by analysis of variance).

TABLE H.I
ANALYSIS OF VARIANCE FOR EFFECT OF PROCESSING PARAMETERS ON FLEXURAL STRENGTH AT ROOM TEMPERATURE

Source	Sum of Squares	Degrees of Freedom	Variance	F
Between Temperatures (t)	0.690	1	0.69	0.10
Between Cure Times (d)	20.320	1	20.32	3.01
Between Cure Pressures (p)	185.763	1	185.76	27.54**
Between Post Cures (c)	41.178	1	41.18	6.10*
2-Fold Interactions: td	0.525	1	0.53	0.07
tp	14.715	1	14.72	2.18
tc	1.088	1	1.09	0.16
dp	13.913	1	13.91	2.06
dc	0.340	1	0.34	0.05
pc	0.750	1	0.75	0.11
3-Fold Interactions: tdp	2.153	1	2.15	0.32
tdc	38.063	1	38.06	5.04*
tpc	36.765	1	36.77	5.45*
dpc	13.650	1	13.65	2.08
4-Fold Interaction: tdpc	0.579	1	0.58	0.86
Replicates	107.885	16	6.743	
Totals	478.377	31		

*Significant at the 95% confidence level

**Significant at the 99% confidence level

TABLE H.II

ANALYSIS OF VARIANCE FOR THE EFFECT OF PROCESSING PARAMETERS ON FLEXURAL STRENGTH AT 550°F

Source	Sum of Squares	Degrees of Freedom	Variance	F
Between Temperatures (t)	0.125	1	0.13	0.01
Between Cure Times (d)	45.601	1	45.60	4.16
Between Cure Pressures (p)	77.501	1	77.50	7.07*
Between Post Cures (c)	32.000	1	32.00	2.92
2-Fold Interactions: td	37.411	1	37.41	3.41
tp	0.061	1	0.06	0.01
tc	11.520	1	11.52	1.05
dp	19.220	1	19.22	1.75
dc	38.281	1	38.28	3.50
pc	4.351	1	4.35	0.40
3-Fold Interactions: tdp	0.045	1	0.05	----
tdc	1.531	1	1.53	0.13
tpc	0.551	1	0.55	0.05
dpc	35.280	1	35.28	3.22
4-Fold Interaction: tdpc	9.247	1	9.25	0.84
Replicates	175.250	16	10.95	
Totals	487.975	31		

*Significant at 95% confidence level

TABLE H.III
ANALYSIS OF VARIANCE FOR EFFECT OF PROCESSING PARAMETERS ON FLEXURAL MODULUS AT ROOM TEMPERATURE

Source	Sum of Squares x 10^2	Degrees of Freedom	Variance x 10^2	F
Between Temperatures (t)	171.588	1	171.59	48.98**
Between Cure Times (d)	0.263	1	0.26	0.07
Between Cure Pressures (p)	350.463	1	350.46	100.00**
Between Post Cures (c)	2.588	1	2.59	0.74
2-Fold Interactions: td	1.853	1	1.85	0.53
tp	0.428	1	0.43	0.12
tc	0.878	1	0.88	0.25
dp	0.228	1	0.23	0.06
dc	0.038	1	0.04	0.01
pc	0.813	1	0.81	0.23
3-Fold Interactions: tdp	5.363	1	5.36	1.53
tdc	9.138	1	9.14	2.61
tpc	7.508	1	7.51	2.14
dpc	2.153	1	2.15	0.61
4-Fold Interaction: tdpc	0.425	1	0.43	0.12
Replicates	56.045	16	3.503	
Totals	609.772			

** Significant at the 99% confidence level

TABLE H.IV
ANALYSIS OF VARIANCE FOR EFFECT OF PROCESSING PARAMETERS ON FLEXURAL MODULUS AT 550°F

Source	Sum of Squares x 10^2	Degrees of Freedom	Variance x 10^2	F
Between Temperatures (t)	263.351	1	263.35	90.9**
Between Cure Times (d)	1.531	1	1.53	0.52
Between Cure Pressures (p)	282.031	1	282.03	97.3**
Between Post Cures (c)	1.361	1	1.36	0.46
2-Fold Interactions: td	6.301	1	6.30	2.17
tp	0.361	1	0.36	0.12
tc	0.151	1	0.15	0.05
dp	3.511	1	3.51	1.21
dc	0.001	1	0.00	0.00
pc	0.281	1	0.28	0.09
3-Fold Interactions: tdp	4.061	1	4.06	1.40
tdc	2.531	1	2.53	0.87
tpc	1.051	1	1.05	0.36
dpc	4.351	1	4.35	1.50
4-Fold Interaction: tdpc	0.665	1	0.67	0.22
Replicates	46.380	16	2.899	
Totals	617.919	31		

**Significant at the 99% confidence level

TABLE H.V
ANALYSIS OF VARIANCE FOR THE EFFECT OF PROCESSING PARAMETERS ON SHEAR STRENGTH

Source	Sum of Squares	Degrees of Freedom	Variance	F
Between Temperatures (t)	6.301	1	6.30	26.33**
Between Cure Times (d)	2.645	1	2.65	11.05**
Between Cure Pressures (p)	0.245	1	0.25	1.02
Between Post Cures (c)	0.911	1	0.91	3.80
2-Fold Interactions: td	0.245	1	0.25	1.02
tp	0.080	1	0.08	0.33
tc	0.211	1	0.21	0.88
dp	0.281	1	0.28	1.17
dc	0.000	1	0.00	0.00
pc	0.405	1	0.41	1.69
3-Fold Interactions: tdp	0.101	1	0.10	0.42
tdc	0.180	1	0.18	0.75
tpc	0.510	1	0.51	2.13
dpc	0.001	1	0.00	0.00
4-Fold Interaction: tdpc	0.203	1	0.20	0.84
Replicates	3.830	16	0.239	
Totals	16.149	31		

**Significant at the 99% confidence level

TABLE H.VI
ANALYSIS OF VARIANCE FOR EFFECT OF PROCESSING PARAMETERS ON VOID CONTENT

Source		Sum of Squares	Degrees of Freedom	Variance	F
Between temperatures (t)		0.383	1	0.38	1.03
Between Cure Times (d)		4.133	1	4.13	11.18**
Between Cure Pressures (p)		22.950	1	22.95	62.1**
Between Post Cures (c)		0.690	1	0.69	1.86
2-Fold Interactions:	td	0.053	1	0.05	0.14
	tp	4.565	1	4.57	12.35**
	tc	1.488	1	1.49	4.02
	dp	7.125	1	7.13	19.27**
	dc	4.728	1	4.73	12.79**
	pc	1.240	1	1.24	3.35
3-Fold Interactions:	tdp	1.768	1	1.77	4.78*
	tdc	4.883	1	4.88	13.21**
	tpc	6.580	1	6.58	17.80**
	dpc	1.240	1	1.24	3.35
4-Fold Interaction:	tdpc	0.869	1	0.87	2.34
Replicates		5.915	16	0.3697	
Totals		68.610			

*Significant at the 95% confidence level

**Significant at the 99% confidence level

A summary of the pooled average of the individual processing parameters for the individual property is given in Table XII (Page 49) together with the repeatability and pool standard deviation of a single measurement. A summary of the statistically significant processing conditions and their effect on the property under consideration is presented in Table XIII (Page 51) together with an indication of the processing conditions to be employed for providing improved properties.

H.2 STATISTICAL TREATMENT OF GRAPHITE FIBER REINFORCED COMPOSITE PROPERTY DATA

The results of mechanical property determinations on the Thornel 50S - 1000 FMW NA/PMDA/MDA composites prepared from Task IV are presented in Tables H.VII through H.XI. Unaged specimen properties obtained at 77°F and after heat soaking for 30 minutes at 400°F and 600°F are presented in Table H.VII. The results of mechanical property testing of specimens aged at 400°F and 600°F for periods up to 1000 hours and tested at 400°F and 600°F are presented in Tables H.VIII through H.XI.

A considerable degree of variability were observed in the properties of replicate specimens. In general, the results from Panels 1 and 2 are lower than those from Panels 3 and 4. A summary of mechanical property data is presented in Table H.XII and identifies the variability of the measurement together with a test of extreme values for a specific group of determinations. The extreme data was evaluated by the u-test in accordance with the equation

$$u = \frac{\Delta_{max}}{\sigma}$$

where:

Δ_{max} = the difference between the extreme value and the average value, and

σ = the pooled standard deviation of the measurement.

The individual extreme data which resulted in an absolute value of u larger than 1.8 (<8% of the population of a normal error curve) were considered to be "wild" and rejected from the population. Specific specimen results

TABLE H.VII

MECHANICAL PROPERTIES OF COMPOSITES PRIOR TO AGING

Test Temperature °F	Specimen	Flexural Strength Ksi	Flexural Modulus Msi	Specimen	Shear Strength Ksi
77	1 - 13	94.3	22.1	1 - 4	3.6
	2 - 3	98.1	21.9	3 - 2	5.0
	2 - 18	107.4	22.5	3 - 4	5.5
	3 - 7	109.6	23.9	3 - 5	5.4
	4 - 15	117.3	25.3	3 - 7	5.5
400	1 - 1	88.3	18.9	1 - 20	3.6
	2 - 8	101.9	22.8	2 - 20	4.3
	2 - 14	117.9	23.7	3 - 20	5.3
	3 - 14	100.7	18.4	4 - 20	5.4
	4 - 16	124.7	25.5	4 - 21	5.1
600	1 - 6	65.4	16.8	1 - 21	2.2
	1 - 9	73.7	17.3	2 - 21	3.2
	2 - 11	101.5	21.2	3 - 21	4.6
	3 - 4	101.4	22.0	3 - 22	4.2
	3 - 12	80.4	21.5	4 - 22	4.4

rejected were flexural specimens 1-15, 1-18, 3-8 and 3-15 and shear specimens 1-13. The flexural specimen 4-16 had an absolute value of >1.8 but was not rejected because the direction of the extreme value was positive, physically a more likely valid number. In general, there are more possible processing variations that will result in a lower value than in a higher value. The revised data are presented in Table XVI (Page 50).

TABLE H.VIII

MECHANICAL PROPERTIES OF COMPOSITES AGED AT 400°F AND TESTED AT 400°F

Aging Time Hrs	Specimen	Flexural Strength Ksi	Flexural Modulus Msi	Weight Loss %	Specimen	Shear Strength Ksi	Weight Loss %
100	1 - 2	102.9	20.9	a	1 - 1	3.9	0.30
	1 - 12	102.3	21.5	a	2 - 3	4.3	0.30
	2 - 12	126.3	25.4	0.20	3 - 14	5.3	0.56
	3 - 18	115.8	23.4	a	3 - 18	5.5	0.60
	4 - 14	118.7	24.3	0.20	3 - 19	5.2	0.71
500	1 - 11	83.2	19.9	0.30	1 - 17	2.6	0.89
	2 - 1	94.5	21.5	0.40	2 - 2	3.8	0.65
	3 - 5	112.7	24.7	0.40	2 - 8	4.2	0.66
	4 - 1	83.8	22.7	0.40	4 - 1	5.2	0.69
	4 - 7	114.7	24.8	0.30	4 - 10	5.1	0.95
1000	1 - 15	89.3	19.0	1.16	2 - 16	3.4	1.76
	2 - 9	104.1	24.7	0.41	2 - 18	3.3	1.54
	3 - 1	114.0	23.5	0.60	4 - 6	5.4	0.96
	3 - 17	84.9	21.2	0.99	4 - 16	5.2	1.08
	4 - 9	112.2	22.7	0.58	4 - 18	4.6	1.11

[a] Less than 0.1% weight loss

TABLE H.IX

MECHANICAL PROPERTIES OF COMPOSITES AGED AT 400°F AND TESTED AT 600°F

Aging Time Hrs	Specimen	Flexural Strength Ksi	Flexural Modulus Msi	Weight Loss %	Specimen	Shear Strength Ksi	Weight Loss %
100	1 - 16	86.0	19.6	a	1 - 8	3.8	0.54
	2 - 6	103.6	22.5	0.20	3 - 1	4.4	0.69
	2 - 16	107.7	23.1	0.20	3 - 8	4.6	0.73
	3 - 9	99.8	21.4	a	3 - 9	4.5	0.62
	3 - 15	68.0	21.5	a	3 - 16	4.7	0.64
500	1 - 19	74.7	19.5	0.30	1 - 6	3.0	0.63
	2 - 7	96.0	22.7	0.30	1 - 9	2.8	0.50
	2 - 13	101.7	22.4	0.40	1 - 16	2.5	1.18
	4 - 4	70.1	20.8	0.57	4 - 9	4.4	0.77
	4 - 5	99.1	22.1	0.30	4 - 17	4.6	0.69
1000	1 - 18	53.5	14.8	0.61	1 - 13	2.0	3.30
	2 - 17	107.9	22.2	0.40	1 - 19	2.8	1.33
	3 - 11	80.9	21.2	1.15	2 - 1	4.8	1.03
	4 - 6	98.4	23.5	0.60	4 - 3	5.1	0.95
	4 - 18	109.6	22.2	0.58	4 - 14	4.9	0.84

[a] Less than 0.1% weight loss

TABLE H.X

MECHANICAL PROPERTIES OF COMPOSITES AGED AT 600°F AND TESTED AT 400°F

Aging Time Hrs	Specimen	Flexural Strength Ksi	Flexural Modulus Msi	Weight Loss %	Specimen	Shear Strength Ksi	Weight Loss %
100	1 - 4	83.2	21.6	5.8	1 - 11	3.2	6.3
	3 - 6	116.3	23.9	2.2	2 - 11	4.5	4.0
	3 - 8	75.1	23.2	8.2	2 - 14	4.1	3.6
	4 - 10	115.6	24.1	2.1	3 - 10	5.0	3.0
	4 - 17	106.9	23.0	2.4	3 - 11	5.3	3.0
500	1 - 3	53.0	22.0	22.3	1 - 3	2.0	23.8
	1 - 17	59.0	20.4	22.3	1 - 18	2.0	22.6
	2 - 15	74.9	22.3	10.3	2 - 10	3.1	15.5
	4 - 8	41.7	17.6	21.8	2 - 15	3.0	15.4
	4 - 12	73.9	21.1	12.2	4 - 19	3.7	14.0
1000	1 - 7	a	a	30.3[b]	1 - 10	a	31.4[b]
	1 - 10	a	a		2 - 4	a	
	2 - 19	a	a		2 - 19	a	
	3 - 10	a	a		3 - 3	a	
	4 - 7	a	a		4 - 13	a	

[a] Not suitable for test

[b] Weight loss established on all ten specimens (Tables H.X and H.XI) simultaneously because the fibers of the individual coupons were intermingled

TABLE H. XI

MECHANICAL PROPERTIES OF COMPOSITES AGED AT 600°F AND TESTED AT 600°F

Aging Time Hrs	Specimen	Flexural Strength Ksi	Flexural Modulus Msi	Weight Loss %	Specimen	Shear Strength Ksi	Weight Loss %
100	1 - 5	78.2	19.8	6.6	1 - 2	2.9	9.4
	2 - 2	91.6	20.5	1.7	1 - 15	2.6	8.5
	3 - 3	110.4	19.2	2.2	4 - 2	4.8	2.9
	3 - 13	99.9	21.6	5.3	4 - 5	4.5	3.0
	3 - 16	103.3	21.4	5.1	4 - 12	4.6	3.0
500	1 - 14	52.5	19.8	20.4	1 - 5	1.9	23.1
	2 - 5	62.5	18.6	9.3	1 - 12	1.4	23.1
	2 - 10	64.3	19.7	11.7	2 - 9	3.0	15.3
	4 - 3	53.2	18.9	18.3	4 - 4	3.3	13.2
	4 - 13	71.7	19.0	10.6	4 - 11	3.4	13.4
1000	1 - 8	a	a	30.3[b]	2 - 6	a	31.4[b]
	2 - 4	a	a		2 - 13	a	
	3 - 2	a	a		3 - 12	a	
	3 - 19	a	a		3 - 17	a	
	4 - 11	a	a		4 - 15	a	

[a] Not suitable for test

[b] Weight loss established on all ten specimens (Tables H.X and H.XI) simultaneously because the fibers of the individual coupons were intermingled

TABLE H.XII

SUMMARY OF RAW PROPERTY DATA AND APPLICATION OF THE U-TEST FOR REJECTION OF EXTREME VALUES

Test Temperatures °F	Aging		Flexural Strength				Flexural Modulus				Shear Strength			
	Temperature °F	Duration hrs	Avg. Ksi	Std. Dev. Ksi	Δ Max. Ksi	u	Avg. Msi	Std. Dev. Msi	Δ Max. Msi	u	Avg. Ksi	Std. Dev. Ksi	Δ Max. Ksi	u
77	---	---	105.3	9.2	±12.0	±0.9	23.1	1.8	+2.2	+1.1	5.0	0.6	-1.4	-1.5
400	---	---	106.7	14.6	-18.4	-1.3	21.8	3.1	+3.7	+1.8	4.7	0.8	-1.1	-1.2
600	---	---	84.5	16.4	-19.1	-1.4	19.7	2.7	-2.9	-1.4	3.7	1.0	-1.5	-1.6
400	400	100	113.2	9.3	+13.1	+1.0	23.1	1.6	-2.3	-1.1	4.8	0.8	-0.9	-1.0
		500	97.7	14.1	+17.0	+1.2	22.7	2.0	-2.8	-1.3	4.1	1.2	-1.5	-1.6
		1000	100.9	11.8	-16.0	-1.2	22.2	2.1	-3.2	-1.5	4.3	1.0	+1.2	+1.3
600	400	100	93.0	14.6	-25.0	-1.8	21.6	1.5	-2.0	-1.0	4.4	0.3	-0.6	-0.7
		500	88.3	13.3	-18.2	-1.3	21.5	1.1	-2.0	-1.0	3.4	1.0	+1.1	+1.2
		1000	90.0	21.1	-36.5	-2.7	20.7	3.5	-5.9	-2.8	3.9	1.3	-1.9	-2.1
400	600	100	99.4	17.1	-24.3	-1.8	23.1	1.0	-1.5	-0.7	4.4	0.8	-1.2	-1.3
		500	60.5	12.6	-18.8	-1.4	20.6	2.4	-3.0	-1.4	2.7	0.8	+1.0	+1.1
600	600	100	96.5	11.6	-18.3	-1.3	20.5	0.8	-1.3	-0.6	3.8	1.1	+1.0	+1.1
		500	60.8	7.5	+10.9	+0.8	19.2	0.4	+0.6	±0.3	2.6	0.7	-1.2	-1.3
Pooled Std. Dev. σ =				13.74				2.05				0.91		

REFERENCES

1. E. A. Burns, H. R. Lubowitz and J. F. Jones, Investigation of Resin Systems for Improved Ablative Materials, Contract NAS3-7949, NASA Report No. CR-72460, Lewis Research Center, Cleveland, Ohio, 10 October 1968.
2. G. H. Potter and N. L. Zutty, U.S. Patent 3,280,080
3. C. J. Whitworth and N. L. Zutty, U.S. Patent 3,277,036
4. Society of the Plastics Industry Inc., SPI - Prepreg - 1 Test Method - Resin and Volatile Content of Preimpregnated Inorganic Reinforcements
5. Society of Plastics Industry, Inc., SPI - Prepreg - 2 Test Method - Flow of Preimpregnated Products
6. Report No. AFML-TR-68-241, Design, Fabrication and Evaluation of Graphite Fiber Reinforced Composite Structural Elements
7. L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., Suffolk, England, 1962, p. 34
8. Ibid., p. 13
9. C. Aso, T. Kunitake, and Y. Ishimoto, J. Polymer Sci., Pt. A, 6, 1163-1174 (1968)
10. F. A. Bovey, "NMR Data Tables for Organic Compounds," Interscience Publishers, 1967, p. 96
11. Ibid., p. 104
12. Ibid., p. 183
13. D. S. Villars, "Statistical Design and Analysis of Experiments for Development Research," William C. Brown Co., Dubuque, Iowa, 1950

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