



NASA TM-83192

**NASA Technical Memorandum 83192**

NASA-TM-83192 19810023649

CHARACTERIZATION OF INITIAL CURE REACTIONS  
IN PROPARGYL AND NADIC END CAPPED  
MODEL COMPOUNDS

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AUGUST 1981

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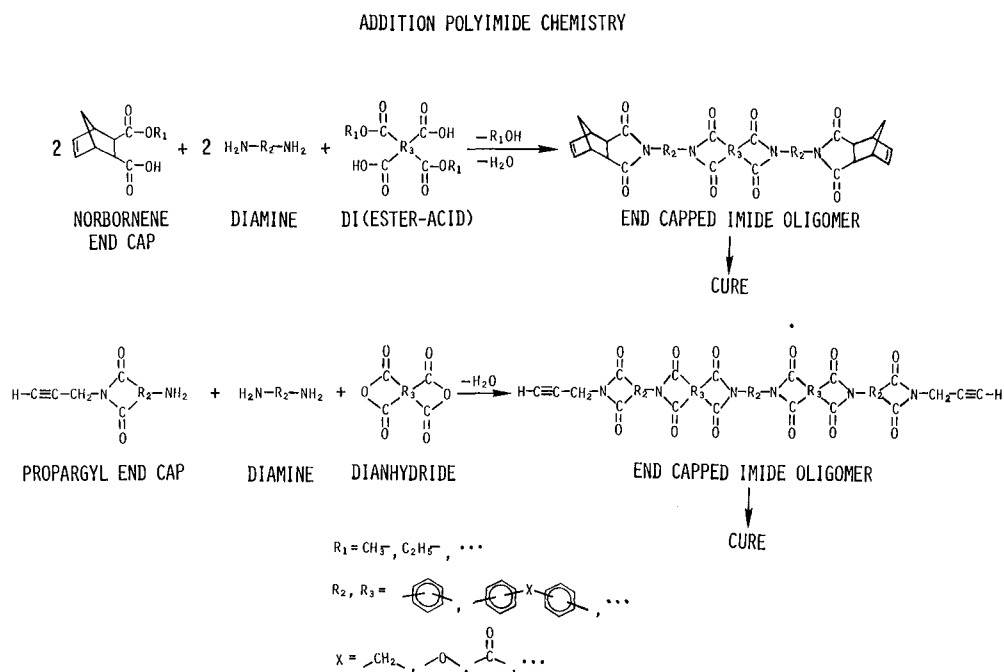
## INTRODUCTION

Aromatic polyimides display considerable promise for extensive use in various aerospace adhesive and composite applications (ref. 1 and references therein). Interest in these materials is focused primarily on the retention of desirable chemical and physical properties at elevated temperatures. Linear polyimides, made by reacting aromatic dianhydrides with aromatic diamines, possess unusual thermal stability (ref. 2). However, these polymers are difficult to process into useful articles due to their inherent high glass transition temperatures (ref. 3) and the evolution of volatiles during cure (ref. 4). Addition polyimides (ref. 5, 6, and 7) represent a compromise between the need for thermal integrity and processability. Addition polyimides are generally used as monomeric mixtures, B-staged to yield imide oligomers, and subsequently cured at elevated temperature through the reactive end groups. Ideally, crosslinking occurs without the evolution of volatiles.

The objective of the present research was to obtain a fundamental understanding of the reaction of propargyl and norbornene end caps on imide oligomers. These are two groups of polymers currently being evaluated in adhesive and matrix resin programs at the NASA-Langley Research Center. To achieve the objective, imide model compounds containing propargyl and norbornene groups were studied. These model compounds, which represent the end segment of the corresponding polymer, are more adaptable to analytical characterization than the more intractable, crosslinked polymers. The initial cure reactions were examined using high pressure liquid chromatography, infrared spectroscopy, thermal analyses, and mass spectroscopy.

## ADDITION POLYIMIDE CHEMISTRY

A general scheme for the synthesis of norbornene and propargyl end capped addition polyimides is given below. Norbornene or nadic oligomers are usually prepared from aromatic diamines and half-esters of the appropriate anhydride. Propargyl terminated oligomers may be prepared from aromatic diamines and dianhydrides. The order of reactant addition, stoichiometry, and temperature are controlled to stop the reaction at the imide oligomeric stage. The imide oligomer is cured at elevated temperature through a crosslinking reaction involving double or triple bonds in the end cap. Examples of  $R_1$ ,  $R_2$ ,  $R_3$ , and the connecting X group are shown.

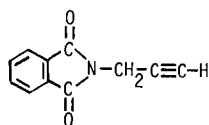


## PROPARGYL TERMINATED STUDY

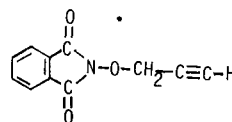
The two propargyl model compounds were prepared by Pratt at Mississippi University for Women on a research grant from the NASA-Langley Research Center (ref. 8). The structure of the compounds, the elemental analysis for the samples used to make this study, and corresponding differential thermal analysis (DTA) thermograms are shown below. Both compounds melted at about the same temperature. The ether model, N-(propargyloxy)phthalimide, exhibited a crystal transition at 112°C. This particular compound cured over a smaller temperature range than the other propargyl model. Both compounds had to be cured under nitrogen pressure to prevent decomposition. In spite of the nitrogen, some weight loss was still observed.

Both compounds became insoluble in common organic solvents as they were heated to temperatures where curing occurred as evidenced by exotherms in the thermograms. Thus, high pressure liquid chromatographic (HPLC) analysis was impossible. The most convenient method for studying these materials was Fourier Transform Infrared (FTIR) spectroscopy. A discussion of the FTIR results follow.

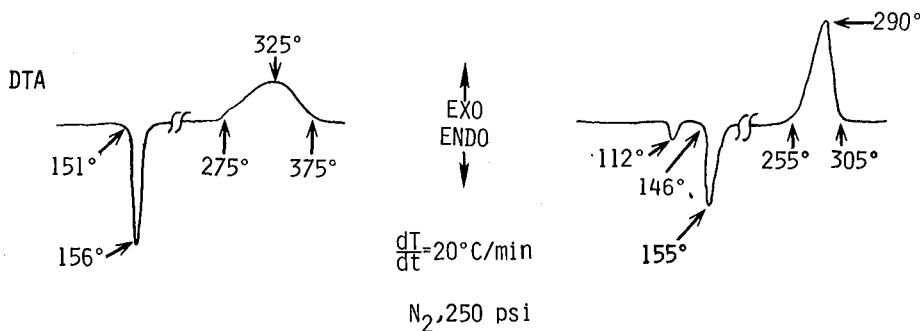
### PROPARGYL TERMINATED STUDY



	% C	% H	% N	% O
CALC	71.35	3.81	7.56	17.28
FOUND	71.39	3.90	7.50 (17.21)	

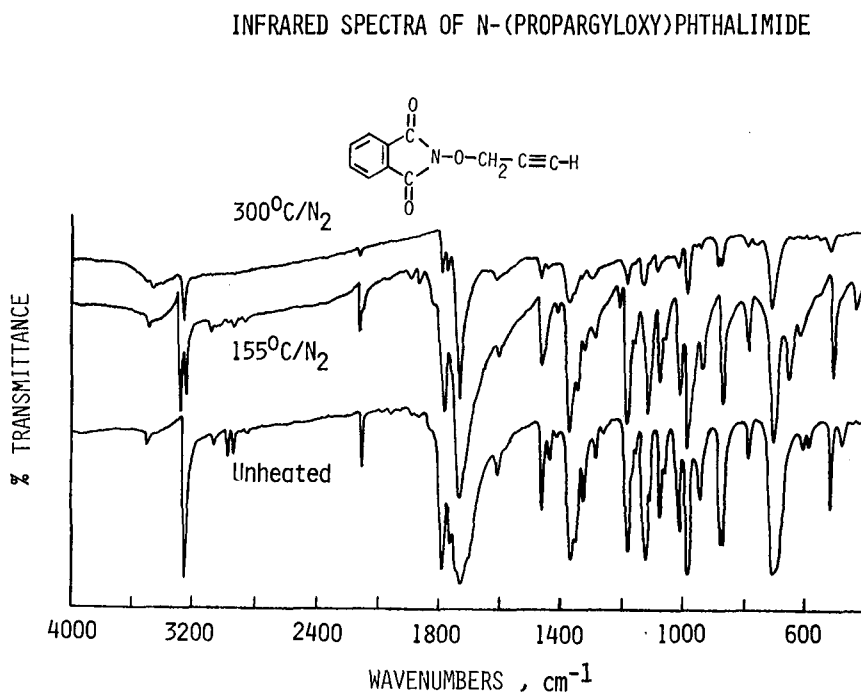


	% C	% H	% N	% O
CALC	65.67	3.51	6.96	23.86
FOUND	65.58	3.60	6.86 (23.96)	



## INFRARED SPECTRA OF N-(PROPARGYLOXY)PHthalIMIDE

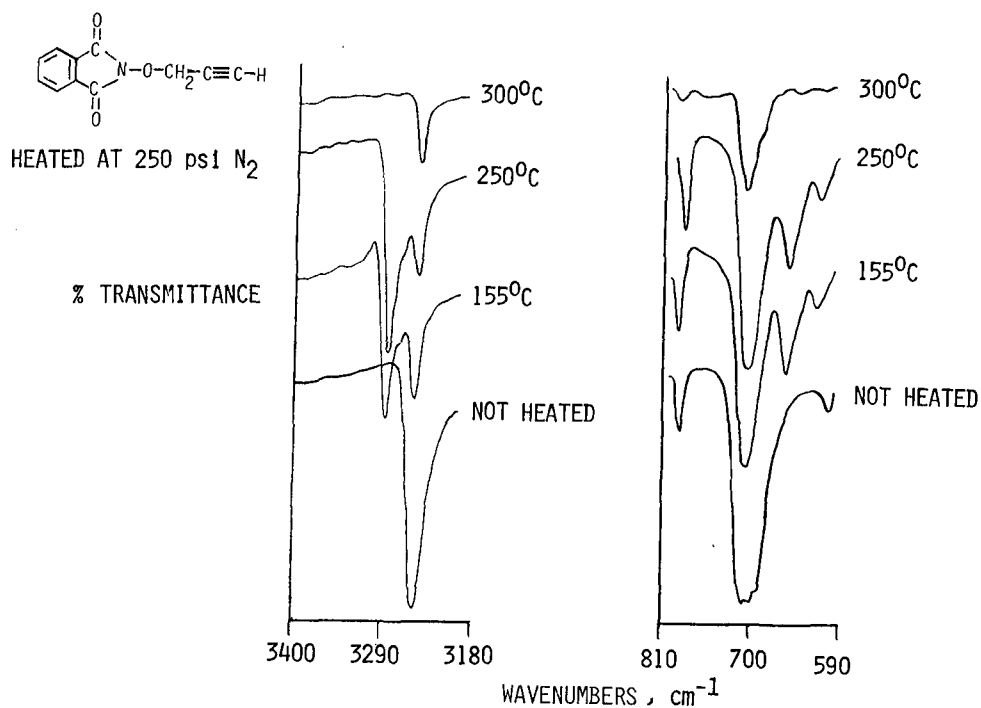
The two model compounds were individually heated in a sample pan on the DTA to various temperatures, cooled, and the infrared spectra were obtained. The figure shows the spectra of one of the model compounds unheated, heated to 155°C, and heated to 300°C. Significant changes were noted near 3200 $\text{cm}^{-1}$  and 700 $\text{cm}^{-1}$ . The acetylenic C-H stretch at approximately 3200 $\text{cm}^{-1}$  split into two bands after heating to 155°C. A new C-H band appeared at about 700 $\text{cm}^{-1}$  and correlated with the new stretching vibration. These new bands then disappeared with further heating. All acetylenic group related bands were gone after heating to 325°C. The other bands in the spectra were apparently unchanged during cure. The second model compound exhibited similar behavior.



## IR SPECTRA DURING CURE OF N-(PROPARGYLOXY)PHTHALIMIDE

The two infrared regions of interest were expanded to illustrate more clearly the changes which occurred during cure. The original acetylenic C-H stretch at  $3252\text{cm}^{-1}$  decreased in intensity with cure. A new band at  $3289\text{cm}^{-1}$  had formed after heating to  $155^\circ$ , intensified after heating to  $250^\circ$ , and disappeared after heating to  $300^\circ$ . No absorption was noted in this region after heating to  $325^\circ$ . The acetylenic C-H bending vibration in the unheated sample was apparently masked by the broad band at about  $700\text{cm}^{-1}$ . However, a new band appeared at  $658\text{cm}^{-1}$  after heating to  $155^\circ$ , corresponding to the new C-H stretching band. This absorption diminished with additional cure.

INFRARED SPECTRA DURING CURE OF N-(PROPARGYLOXY)PHTHALIMIDE

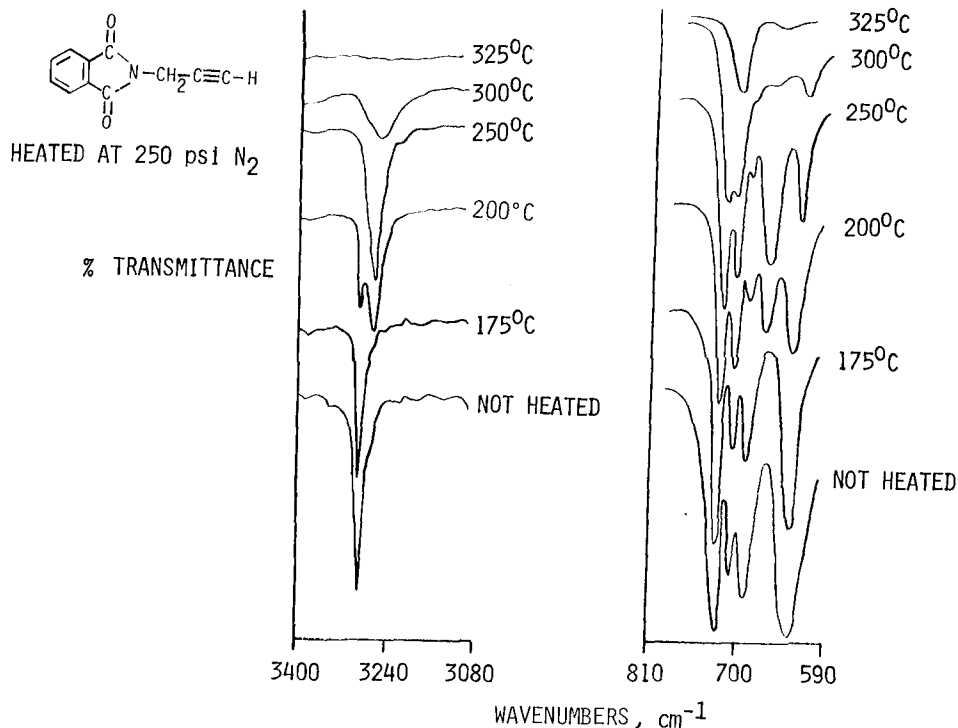


## INFRARED SPECTRA DURING CURE OF N-(PROPARGYL)PHTHALIMIDE

Similar spectra were obtained for N-(propargyl)phthalimide. Once again, the original C-H stretch, this time at  $3292\text{cm}^{-1}$ , decreased in intensity with cure and a new band at  $3268\text{cm}^{-1}$  appeared. This was the only band in the region after heating to  $250^\circ\text{C}$ . No absorption was noted after heating to  $325^\circ\text{C}$ . Corresponding to the C-H stretch, the original C-H bend at  $691\text{cm}^{-1}$  decreased in intensity with cure and a new band appeared at  $670\text{cm}^{-1}$ . This band disappeared with further cure.

The conclusion from this preliminary investigation was that the initial step in the cure of these propargyl terminated compounds involves the formation of a new terminal acetylenic group. Evidence for this is the disappearance of stretching and bending vibrations associated with the original terminal acetylenic group, and the appearance of stretching and bending vibrations associated with a new terminal acetylenic group. Two or more molecules must react to form this new group. Details of the reaction to yield the new terminal group have not been resolved. Further cure reactions beyond this initial step were not investigated.

### INFRARED SPECTRA DURING CURE OF N-(PROPARGYL)PHTHALIMIDE





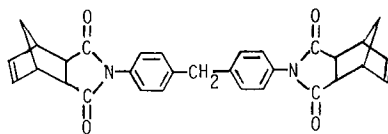
## NADIC MODEL COMPOUND STUDY

Reactions involving nadic model compounds have been extensively studied under pyrolytic conditions (ref. 5). The resulting product is intractable. The use of milder thermal conditions employed in this study rendered most of the sample soluble and allowed some novel observations to be made.

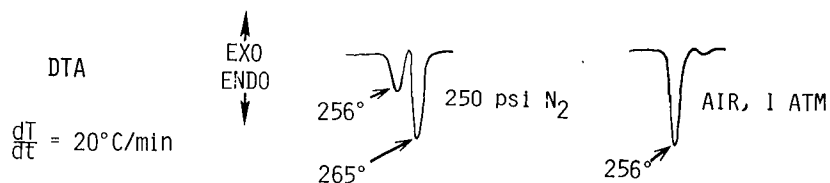
The structure and elemental analysis of the compound used in this study are given below. All nadic models were prepared by Pratt (ref. 8). This particular compound has been identified in aged LARC-160 resin (ref. 9). It is considered to be undesirable in LARC-160 because it upsets the designed resin stoichiometry by producing short, highly crosslinked segments in the cured resin. Higher molecular weight imide oligomers must then form to compensate for the loss of nadic end caps.

Two different DTA thermograms were obtained depending on whether the sample was heated in air or in nitrogen. Only one endotherm was evident in air while two endotherms were present in nitrogen. No visual changes could be correlated with the 256°C endotherm in nitrogen. The behavior was of interest in regard to possible cure mechanisms in LARC-160 resin.

### NADIC MODEL COMPOUND STUDY



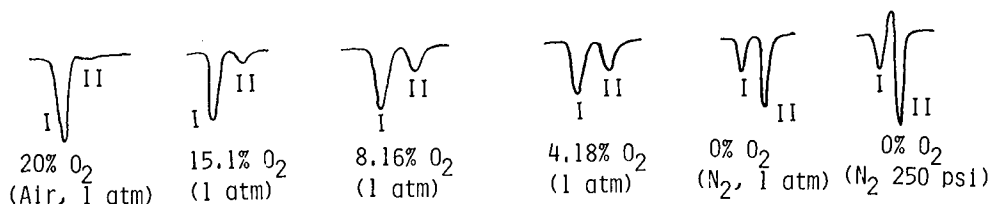
	% C	% H	% N	% O
CALC	75.90	5.34	5.71	13.05
FOUND	76.03	5.18	5.79	12.92



## DSC TRENDS

The nadic model compound was analyzed on a differential scanning calorimeter (DSC) in atmospheres of differing oxygen contents. The thermograms obtained showed the first endotherm decreased in intensity and the second endotherm increased as the amount of oxygen decreased. Calorimetric data supported this observation. The  $\Delta H$  associated with the first transition decreased at the same time the  $\Delta H$  associated with the second transition increased. The total  $\Delta H$  for both endotherms remained fairly constant except for the pure nitrogen atmosphere which was about 6 mcal/mg greater than the others. An exotherm between the two peaks was observed for the 250 psi nitrogen analysis. A quantitative determination for this sample was not attempted. The results suggest that oxygen has an effect on the thermal behavior of this model compound.

### DSC TRENDS



ONSET TEMPERATURE

PEAK I: 250°C

PEAK II: 259°C

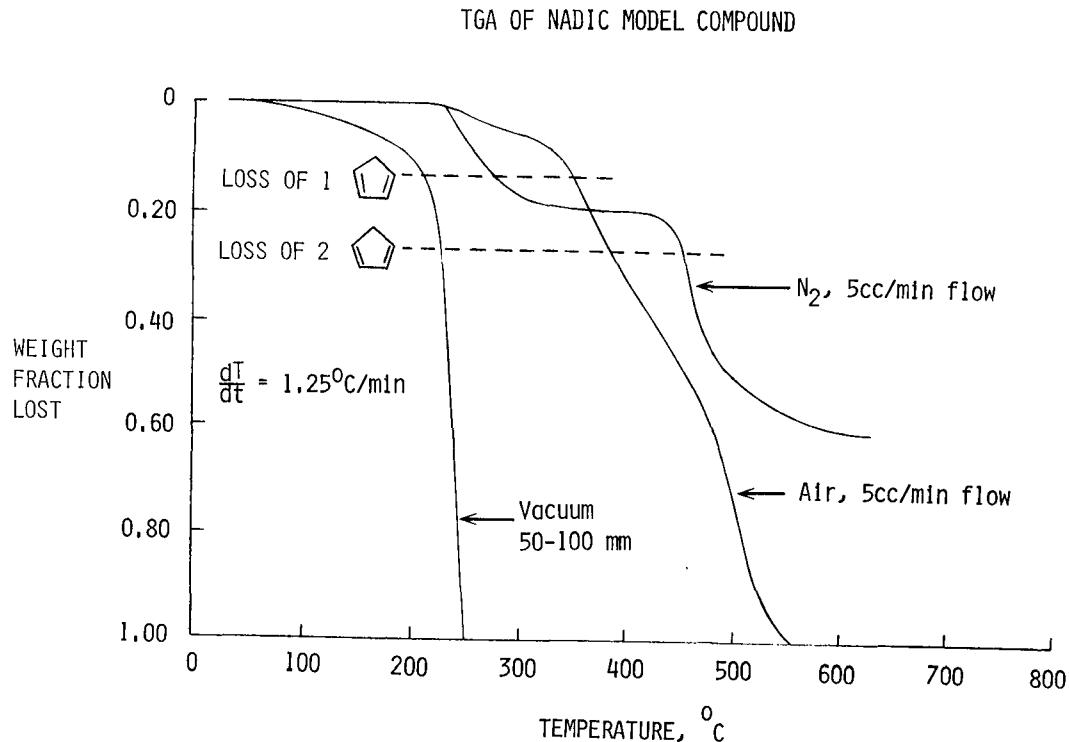
<u>% OXYGEN</u>	<u>*<math>\Delta H</math> (mcal/mg)</u>		
	PEAK I	PEAK II	TOTAL
20 (AIR)	22.7	---	22.7
15.1	20.5	0.6	21.1
8.16	16.6	4.4	21.0
4.18	15.5	6.1	21.6
0 (N <sub>2</sub> )	9.4	17.6	27.0
0 (N <sub>2</sub> , 250 psi)	---	---	---

\*Ave. of Three Values

## TGA OF NADIC MODEL COMPOUND

Thermal gravimetric analysis (TGA) weight loss was determined on the model compound in flowing air and nitrogen and in vacuum at a 1.25°C/min temperature rise rate. Two different weight loss curves were obtained depending on whether the sample was heated in air or in nitrogen. The curves suggest two different curing mechanisms may be occurring. The nitrogen-cured sample appeared to lose the equivalent of about one and one-half moles of cyclopentadiene. No such observation could be made for the air-cured sample, which exhibited better thermal stability between 250° and 375°C. The vacuum sample sublimed before the air and nitrogen samples began to cure.

TGA of this sample agrees with the previous DSC analysis which indicated that oxygen has an effect on the events associated with cure. These results also suggest that different thermal behavior would be observed for LARC-160 resin depending on whether it was cured in air or in nitrogen.



### ISOTHERMAL WEIGHT LOSS DATA

Isothermal weight loss measurements were made at 285°C and 330°C for the model compound cured in air and in nitrogen. Approximately 100mg samples were cured for 1 hour in the two atmospheres. The results showed samples cured in air exhibited less weight loss than samples cured in nitrogen. At 330°C, a 4.4% weight loss was observed in air compared to a 34.5% loss in nitrogen. This is the same trend shown by TGA under dynamic heating conditions. Once again, oxygen appears to be catalyzing a reaction, perhaps by prohibiting the loss of cyclopentadiene. An attempt was made to determine the solubility of samples after heating in air and nitrogen. Samples heated to 330°C for 1 hour in either atmosphere were insoluble in methylene chloride and N,N-dimethylacetamide. Data at 285°C did not reproduce satisfactorily. However, about 35% of the sample remained soluble in methylene chloride after 1 hour at 285° in either atmosphere.

### ISOTHERMAL WEIGHT LOSS DATA

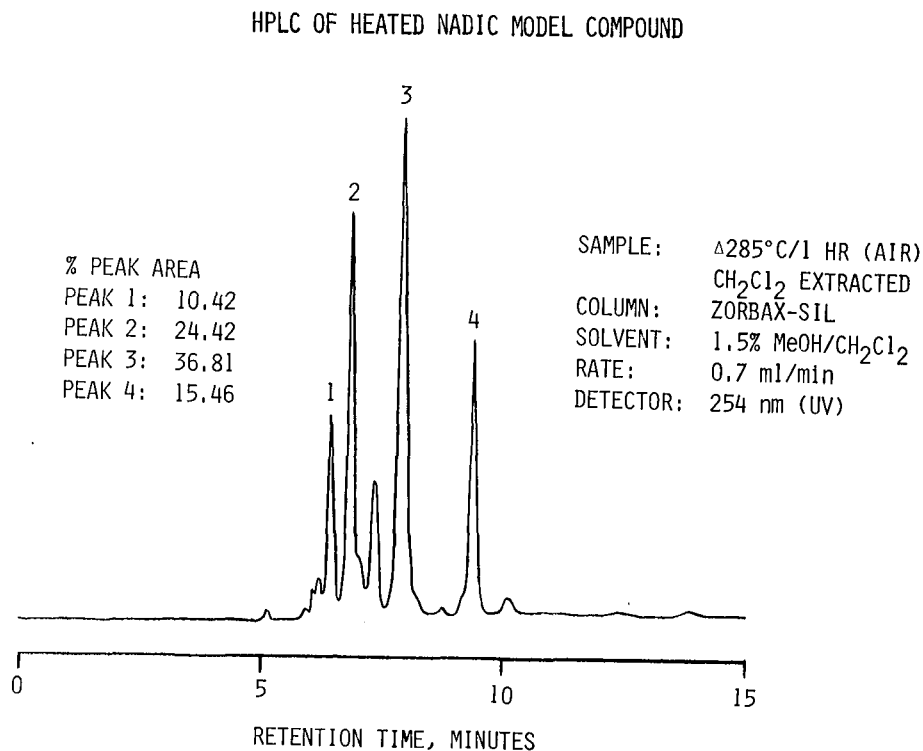
TEMPERATURE*, °C	ATMOSPHERE	WEIGHT LOSS, %
285 <sup>0</sup>	AIR	1.72
285 <sup>0</sup>	N <sub>2</sub>	8.43
330 <sup>0</sup>	AIR	4.40
330 <sup>0</sup>	N <sub>2</sub>	34.50

\*SAMPLES CURED FOR 1 HOUR

## HPLC OF HEATED NADIC MODEL COMPOUND

The chromatogram obtained when the nadic compound was heated is shown below. This particular sample was heated to 285°C for 1 hour in air and extracted with methylene chloride. The general chromatographic conditions used throughout this study are given in the figure and will not be given on subsequent chromatograms.

Several peaks are observed in the chromatogram of the heated sample. Peak 4 is due to starting material and is the only peak obtained for the unheated sample. Peaks 1, 2, 3, and 4 account for about 90% of the total peak area for this sample. Identifying the peaks in this chromatogram was considered to be a major step in elucidating the initial steps involved in the cure of this compound.

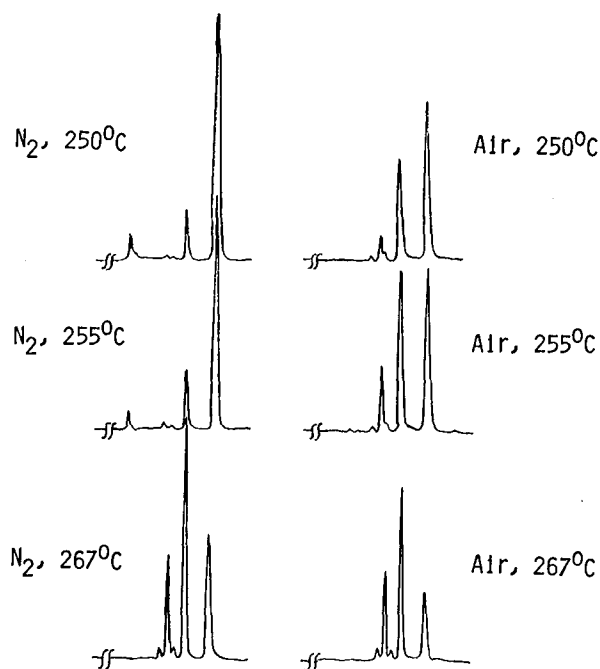


## HPLC OF NADIC MODEL COMPOUND CURED IN AIR AND IN NITROGEN

Liquid chromatographic analysis revealed that samples heated in air react faster than samples heated to the same temperature in nitrogen. Chromatograms are shown for 1mg samples heated to 250°, 255° and 267°C in air and nitrogen and cooled. These temperatures were selected because they encompassed the range where DTA showed different thermal behavior in the two atmospheres. The last peak in each chromatogram is due to starting material.

Starting material accounted for about 85% of the total peak area in the chromatogram of the sample heated to 255°C in nitrogen. It accounted for only 40% of the total peak area for the sample heated to 255°C in air. At 267°C, both chromatograms were quite similar except that less of the sample heated in air was soluble. The total peak area for this sample was about two-thirds the total peak area for the sample heated to 267°C in nitrogen.

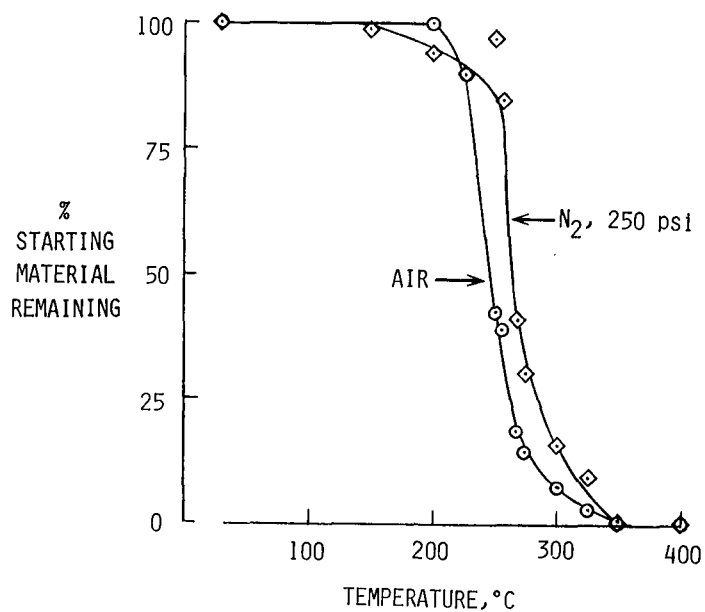
HPLC OF NADIC MODEL COMPOUND CURED IN AIR (1ATM) AND IN NITROGEN (250 PSI)



## REACTION OF NADIC MODEL COMPOUND HEATED IN AIR AND IN NITROGEN

To confirm that this compound reacted at a lower temperature in air than in nitrogen, a quantitative chromatographic study was made for the amount of starting material remaining as a function of temperature in those two atmospheres. This was accomplished by calculating the response factor for pure starting material and using this factor to determine the amount of starting material in heated samples. The results, given below, confirm a lower reaction temperature in air. DSC, TGA, and HPLC all indicate that oxygen plays a role in the initial cure of this compound by causing it to react at a lower temperature and exhibit less weight loss during cure. The results suggest two different cure mechanisms are occurring in air and in nitrogen.

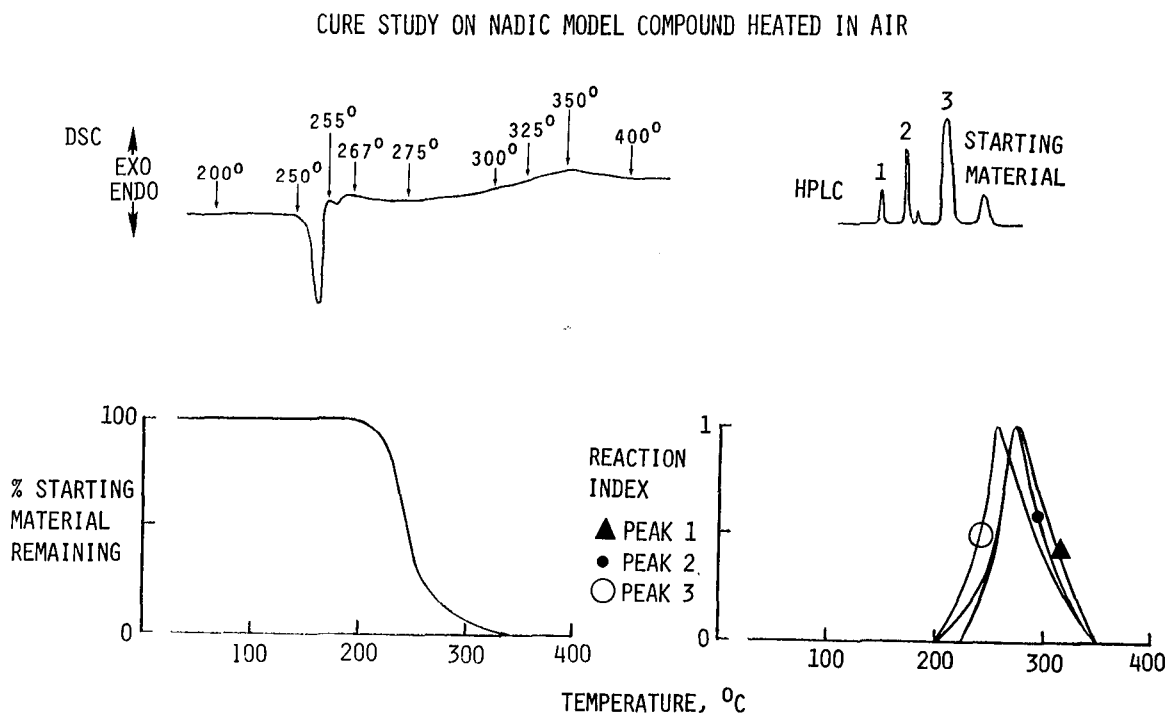
REACTION OF NADIC MODEL COMPOUND HEATED IN AIR AND IN NITROGEN



CURE STUDY ON NADIC MODEL COMPOUND HEATED IN AIR

The results of a cure study on samples heated in air are summarized below. The DSC thermogram shows the temperatures to which samples were heated to prepare them for chromatographic analysis. A typical chromatogram with peaks 1, 2, 3, and the starting material identified is given in the upper right hand corner of the figure. The lower left portion shows the previously discussed curve for the amount of starting material remaining as a function of temperature. The curve on the lower right section illustrates the temperature range where peaks 1, 2, and 3 are present in the chromatogram. These curves were generated from the ratio of the area of a given peak to the largest area for that peak.

This figure illustrates that peaks 1, 2, and 3 were formed as the starting material was being consumed. An undetermined amount of starting material reacted to form compounds which gave peaks 1, 2, and 3. The total peak area for all peaks between 250-300° is fairly constant so the amount of starting material involved in this reaction is large. The exact role of these new compounds in any subsequent cure is unknown, as is the source of the insoluble material observed in this study. Data on samples cured in nitrogen showed similar trends.

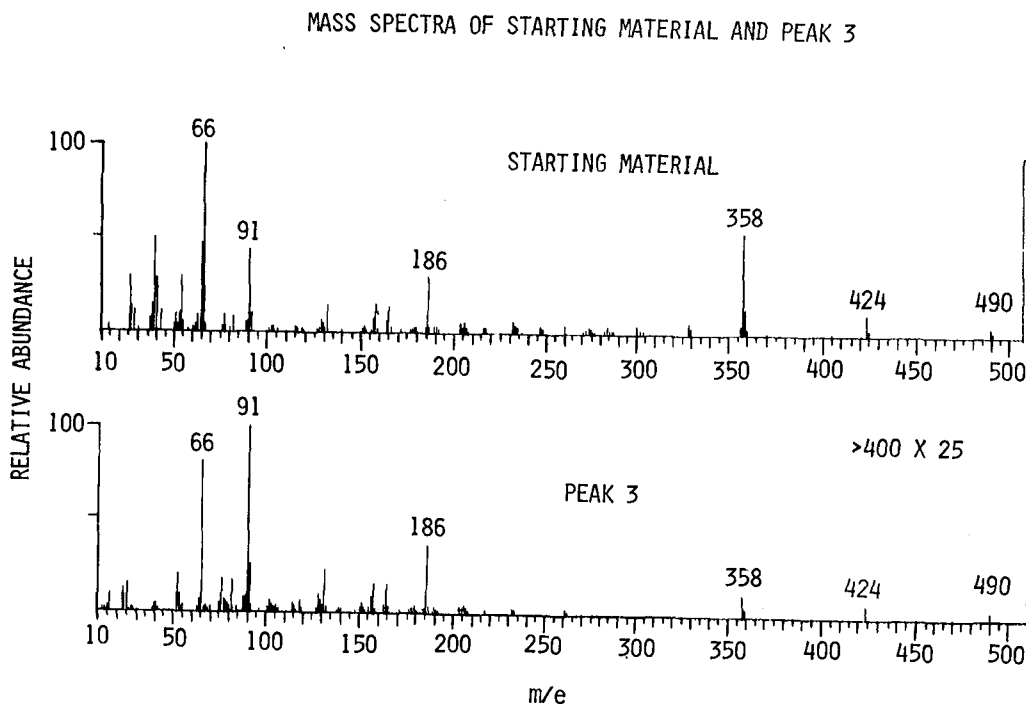




### MASS SPECTRA OF STARTING MATERIAL AND PEAK 3

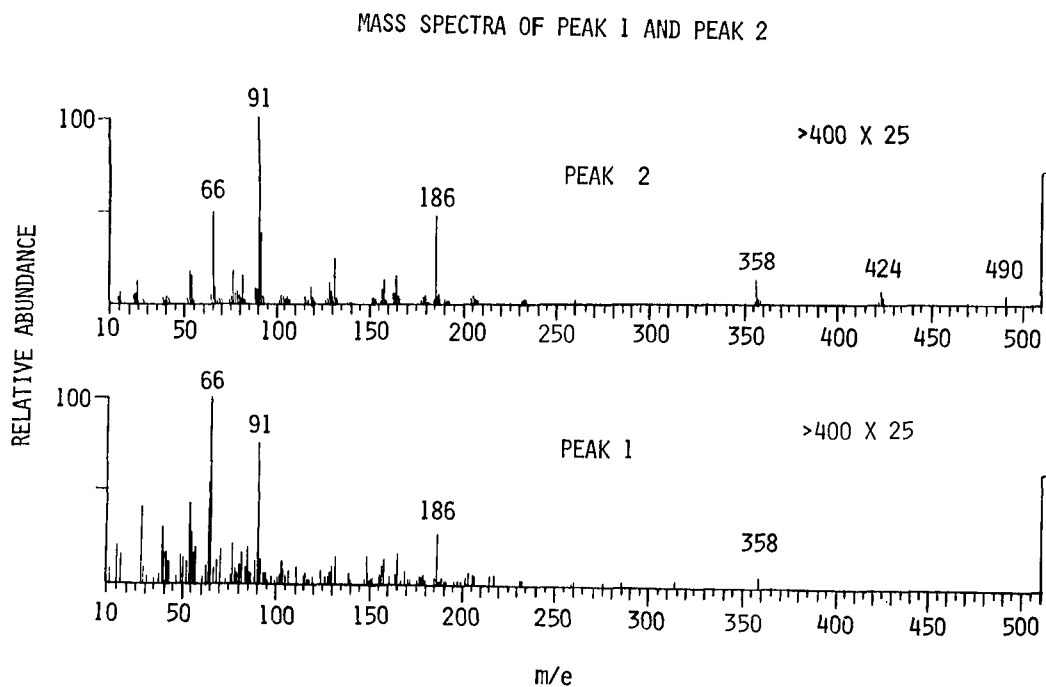
The four major chromatographic peaks were prepped and mass spectra were determined on the recovered residues. The peak at  $m/e=490$  in the spectrum for the starting material is the parent ion. Peaks at  $m/e=424$  and  $358$  are the parent ion minus one and two molecules of cyclopentadiene, respectively. The peak at  $m/e=66$  is due to cyclopentadiene. The peak at  $m/e=186$  may have resulted from fragmentation at the methylene bridge of the diamine and the peak at  $m/e=91$  may be due to tropylium ion.

The spectrum for peak 3 above  $m/e=400$  was multiplied by 25 in order to see the peaks at 490 and 424. The remainder of the spectrum is quite similar to that of the starting material except for differences in relative intensities.



## MASS SPECTRA OF PEAK 1 AND PEAK 2

The mass spectrum of peak 2 was almost superimposable on the mass spectrum of peak 3. The mass spectrum of peak 1 was somewhat different. The  $m/e = 358$  peak suggests that this compound is the bis-maleimide, which resulted from the loss of two molecules of cyclopentadiene from the starting material. However, if this were the case, the peak at  $m/e = 66$  would not appear in the spectrum. Also, the retention time of the authentic bis-maleimide was much less than the retention time for peak 1. The actual sample analyzed was very small. A larger sample would probably have shown a parent ion peak at  $m/e = 424$ . This particular compound is believed to have resulted from the loss of cyclopentadiene from only one end of the starting material.



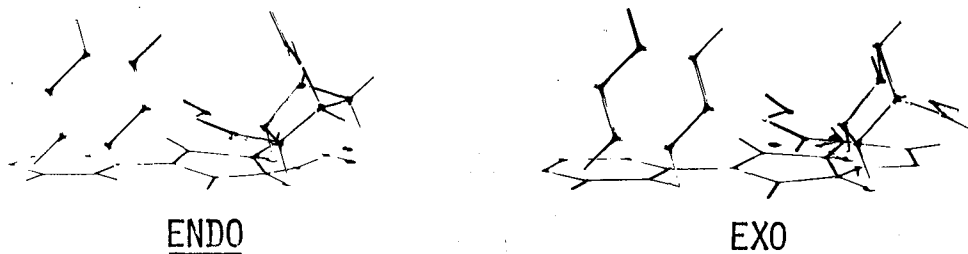
## ENDO AND EXO STRUCTURES FOR NADIC MODEL COMPOUND

The unheated starting material originally gave only one chromatographic peak. Several new peaks appeared after heating above 250°C. Mass spectra of three of these peaks, the starting material, peak 2, and peak 3, were quite similar. An explanation was needed for the type of configurational changes the starting material could undergo which would result in this behavior.

Endo/exo isomerism has been studied for N-phenylnadimide (ref. 10, 11). Structures of these isomers for this compound are shown below. The two methylene bridge protons on the norbornene ring can be cis- and trans- to the two protons on the carbon atoms bonded to the five-membered imide ring, depending on the configuration of those two sp<sup>3</sup>-hybridized carbon atoms.

The model compound in the present study had a possibility for this type of isomerism on both ends of the molecule. Thus, the three peaks in the chromatogram with similar mass spectra are believed to be due to endo/endo, endo/exo, and exo/exo isomerism. An identification for which peak is associated with which isomer has not been made.

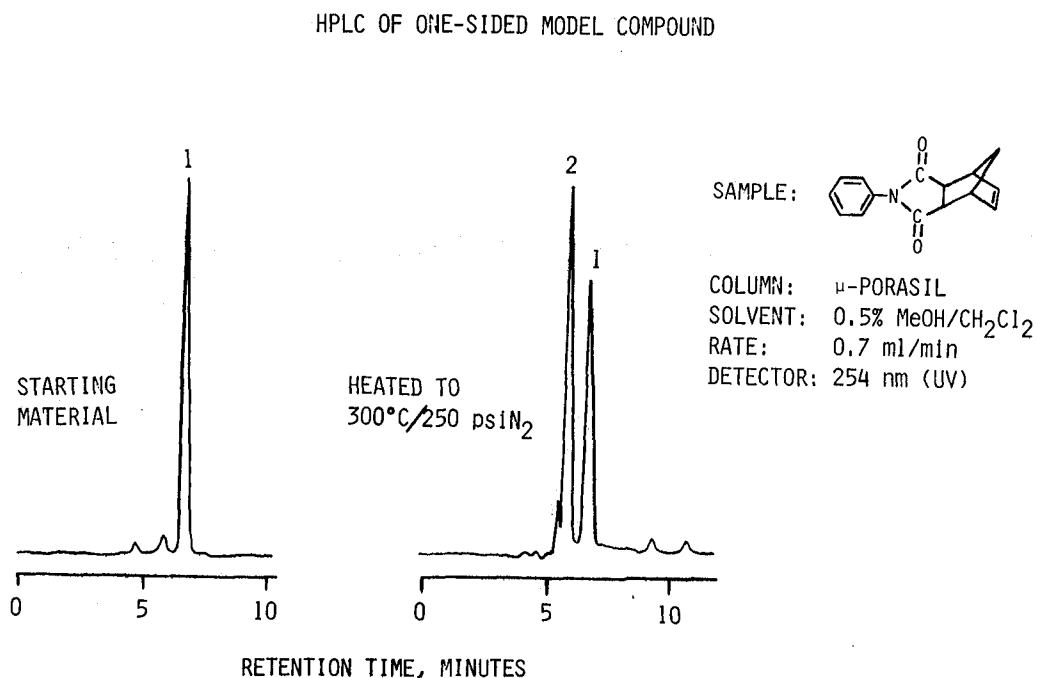
## ENDO AND EXO STRUCTURES FOR NADIC MODEL COMPOUND



## HPLC OF ONE-SIDED MODEL COMPOUND

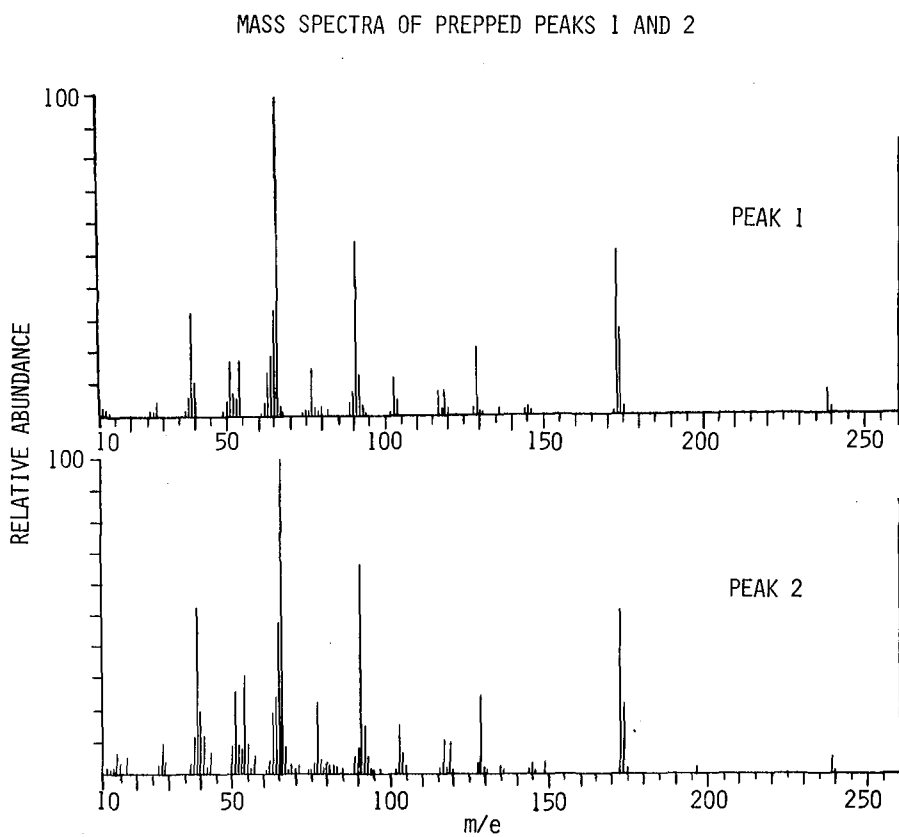
The one-sided model compound, N-phenyladamidide, was also studied. As synthesized, the material yielded only one chromatographic peak. Two chromatographic peaks were obtained after heating the compound to 300°C under 250 psi nitrogen. The two peaks apparently are due to endo/exo isomerism.

Gaylord reported that 30 min. at 260°C yielded a 40/60 endo/exo equilibrium mixture from either pure endo or exo adduct (ref. 11). This chromatographic analysis indicated about a 40/60 mixture. Thus, peak 1 and peak 2 are presumed to be the endo and exo isomers respectively.



## MASS SPECTRA OF PREPPED PEAKS 1 AND 2

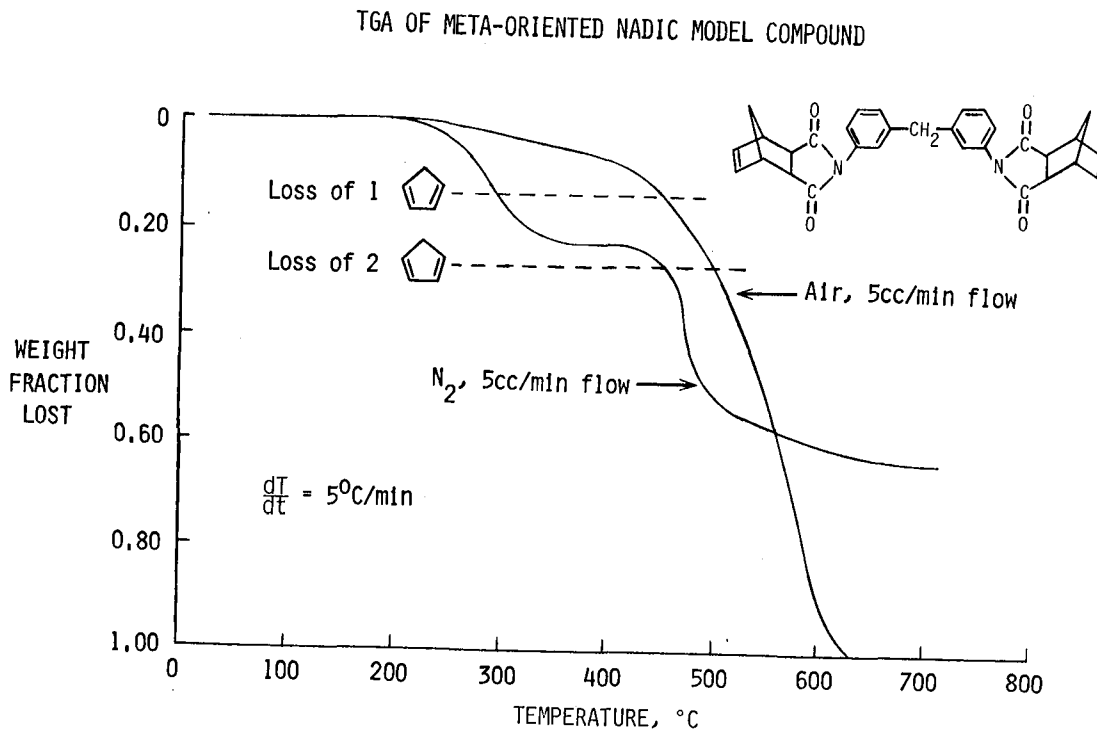
The two chromatographic peaks obtained by heating the one-sided model compound were prepped and their respective mass spectrum determined. The two spectra were virtually identical. Peaks for the molecular ion, a fragment resulting from loss of cyclopentadiene, the presumed tropylium ion, and cyclopentadiene can be readily identified in the two spectra.



## TGA OF META-ORIENTED NADIC MODEL COMPOUND

A third nadic model compound was also examined. The structure of this meta-oriented compound, made by reacting nadic anhydride with m,m'-methylenedianiline, is given in the figure below. This compound serves as a model for LARC-13, a polyimide adhesive developed at the NASA-Langley Research Center (ref. 12).

As with the para-oriented model, TGA on this compound in air and nitrogen suggested that two different cure mechanisms were occurring in the two atmospheres. The material appeared to lose the equivalent of about one and one-half moles of cyclopentadiene in nitrogen. Once again, the material was more thermally stable in air than in nitrogen.

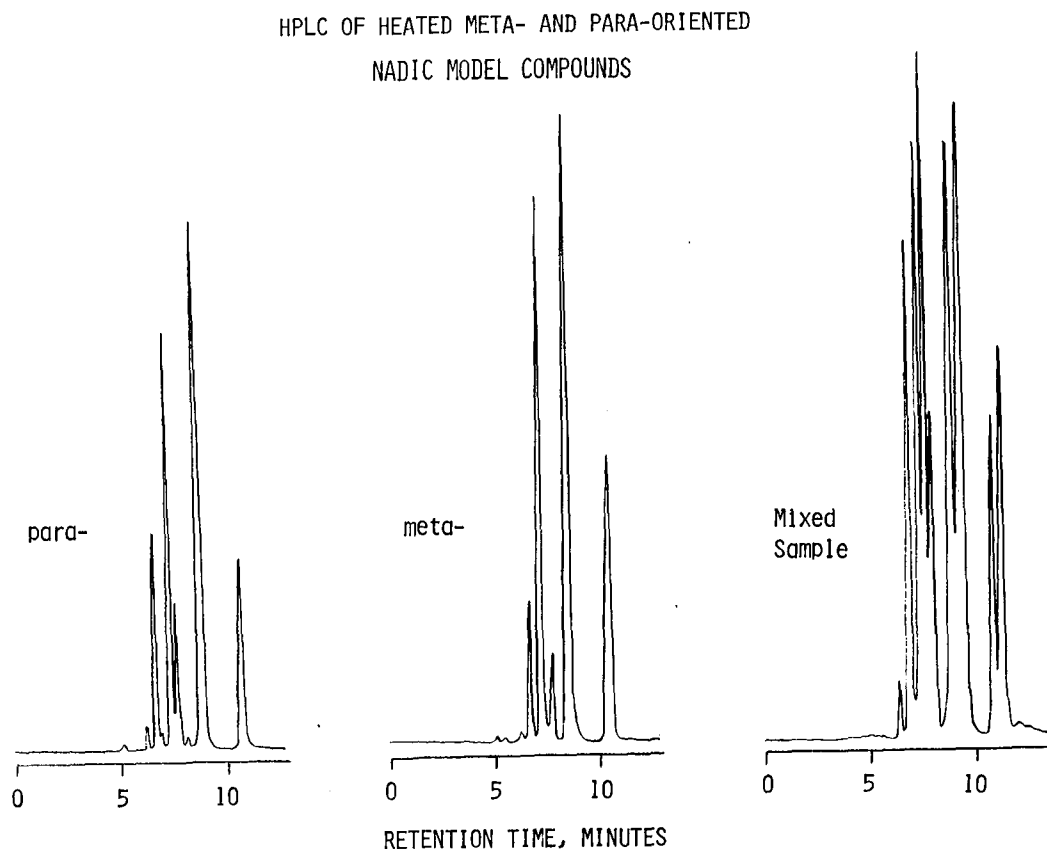


## HPLC OF HEATED META- AND PARA-ORIENTED NADIC MODEL COMPOUNDS

Chromatograms of the meta- and para-oriented compounds after heating to 285°C in nitrogen are given below. The first and third peaks in each chromatogram are believed to be due to endo and exo isomers of the molecule which has lost cyclopentadiene from only one end. The second, fourth, and fifth peaks are due to endo/endo, endo/exo, and exo/exo isomerism. None of the peaks have been assigned to a specific isomer.

The chromatogram of a mixed sample is included in the figure. Meta- and para- derived endo/endo, endo/exo, and exo/exo isomers for both compounds were resolved. The retention times for the first and third peaks were so close the peak areas added.

The meta-oriented model appeared to undergo essentially the same configurational changes as the para-oriented model. The structural isomers in this mixed sample were separated based on the orientation of the amine nitrogens in the original methylenedianiline reactant.

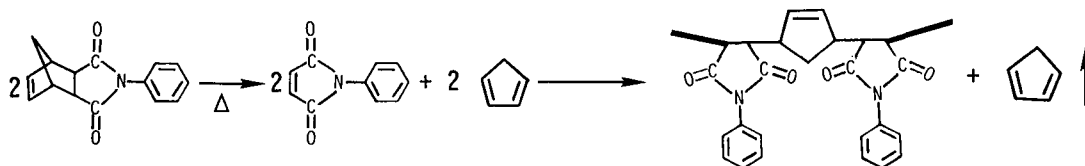


## PROPOSED NADIC CURE MECHANISMS

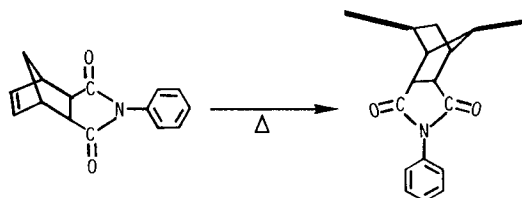
The two most commonly proposed mechanisms for the cure of nadic end capped oligomers are shown below. The first involves a reverse Diels-Alder reaction in the rate determining step followed by chain extension through a recombination with reactants (ref. 5). The second mechanism involves a more direct chain extension (ref. 11). No findings in the present study proves or disproves either mechanism. However, for either to occur, configurational changes involving the breaking and reformation of bonds must take place as an initial step. Only then is the end cap in a conformation favorable for cure.

At least two basic questions remain unresolved. The first involves the exact role of the atmosphere in the cure process. Weight loss and DSC measurements suggest that the first mechanism may be favored in nitrogen and the second mechanism in the presence of oxygen. The second and perhaps more difficult question to answer is how the structure of samples cured in air and nitrogen differ. When the para-oriented model was cured in air and nitrogen for 1 hour at 285°C, about 65% of the sample was insoluble. HPLC analysis showed the soluble portions to be essentially identical. Since all indications are that the bulk samples are different, the difference must be in the insoluble fractions. Unfortunately, this intractable portion is difficult to analyze. No interpretable differences could be found in FTIR spectra of the insoluble portions of samples cured in air and in nitrogen.

## PROPOSED NADIC CURE MECHANISMS



Burns, E. A., Jones, R. J., Vaughan, R. W. and Kendrick, W. P.; TRW-11926-6013-R0-00, NASA CR-72633, January 1970.



Gaylord, N. G. and Martan, M.; ACS Polym. Preprints, 22 (1), 11 (1981).



## SUMMARY

The initial cure reactions in several propargyl and nadimide model compounds were examined by a variety of characterization techniques including HPLC, FTIR, mass spectroscopy, and thermal analyses. Cure reactions in these compounds were found to be complex.

The initial step in the cure of propargyl end capped model compounds probably involved the formation of a new terminal acetylenic group. Configurational changes involving endo/exo isomerism was found in the nadimide model compounds. Although the exact role of oxygen on the cure of these compounds was not determined, model compounds heated in air and in nitrogen appeared to cure by different mechanisms.

## REFERENCES

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1. Report No. NASA TM-83192		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Characterization of Initial Cure Reactions in Propargyl and Nadic End Capped Model Compounds				5. Report Date August 1981	
				6. Performing Organization Code 505-33-33-02	
7. Author(s) Philip R. Young				8. Performing Organization Report No.	
9. Performing Organization Name and Address NASA-Langley Research Center Hampton, VA 23665				10. Work Unit No.	
				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546				13. Type of Report and Period Covered Technical Memorandum	
				14. Sponsoring Agency Code	
15. Supplementary Notes Use of commercial products or names of manufacturers in this report does not constitute official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.					
16. Abstract Imide model compounds containing propargyl and nadic groups were studied to obtain a fundamental understanding of the reaction of these groups attached to imide oligomers. The initial cure reactions were examined by a variety of characterization techniques including high pressure liquid chromatography, infrared spectroscopy, thermal analyses, and mass spectroscopy. The initial step in the cure of propargyl end capped model compounds probably involved the formation of a new terminal acetylenic group. Configurational changes involving <u>endo/exo</u> isomerism was found in the nadimide model compounds. Nadimide compounds heated in air and in nitrogen appeared to cure by different mechanisms.					
17. Key Words (Suggested by Author(s)) imide model compounds propargyl end cap nadid end cap addition polyimide			18. Distribution Statement Unclassified-unlimited Subject Category 23		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 25	22. Price A02





