R78-912941-15 NASA CR-159510

SYNTHESIS OF IMPROVED MOISTURE RESISTANT POLYMERS

Final Report

Under Contract NAS3-21010

(NASA-CR-159510) SYNTHESIS OF IMPROVED MOISTURE RESISTANT POLYMERS Final Report (United Technologies Research Center) 105 p HC A06/MF A01 CSCL 07C
N79-23218
Unclas
G3/27 25204

Prepared for

NASA-Lewis Research Center
Cleveland, Ohio 44135

by

D.A. Scola

R.H. Pater

December 20, 1978

UNITED TECHNOLOGIES RESEARCH CENTER
UNITED TECHNOLOGIES

EAST HARTFORD, CONNECTICUT 06108

1. Report No.
NASA CR-159510

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle

SYNTHESIS OF IMPROVED MOISTURE RESISTANT POLYMERS

5. Report Date
December 20, 1978

6. Performing Organization Code

7. Author(s)
D. A. Scola and R. H. Pater

8. Performing Organization Report No
R78-912941-15

9. Performing Organization Name and Address
United Technologies Research Center
Silver Lane
East Hartford, Connecticut 06108

10. Work Unit No.

11. Contract or Grant No
NAS3-21010

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546

13. Type of Report and Period Covered
Contractor Report

14. Sponsoring Agency Code

15 Supplementary Notes
Project Manager, P. Delvigs, Materials and Structures Division
NASA Lewis Research Center, Cleveland, Ohio, 44135

16. Abstract The synthesis and characterization of novel moisture resistant aliphatic polyimides are described in this report. Several novel aliphatic imides of diversified functionalities were synthesized, purified, and characterized. They include N-(12-aminododecyl)-5-norbornene-2,3-dicarboximide (1), N,N'-[[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis[(1,3-dioxo-5,2-isoindolinediyl)dodecamethylene]]di-5-norbornene-2,3-dicarboximide (2), N,N'-dodecamethylenedi-5-norbornene-2,3-dicarboximide (3), N,N'-dodecamethylenebis[5,6-epoxy-2,3-norbornanedicarboximide] (4), and N,N'-Bis[12-(5-norbornene-2,3-dicarboximidido)dodecyl]-1,2,3,4-butanetetracarboxylic 1,2:3,4-diimide (5). The structures of those compounds were established by elemental analysis, IR, NMR, and mass spectra. Mass spectrometry showed that the principal fragmentation of the nadimide system proceeded through the reverse Diels-Alder reaction to produce cyclopentadiene and bismaleimide fragments. The synthesis of compounds 1 and 2 was accomplished via several different methods and a comparison of synthetic advantages among these routes was made. In addition, the syntheses of the monomer precursors, 4-vinylphthalic anhydride and 1,3-butadiene-2,3-dicarboxylic anhydride, were attempted. Thermal and catalytic polymerization and copolymerization of monomers 2 through 5 were investigated. Thirty polymer discs were fabricated in two steps. First, the monomer (or comonomer mixture) was polymerized to give tough and flexible "B-stage" resins showing adequate flow for the final molding. This process was accomplished in one hour at 290°C in air or nitrogen atmosphere and did not seem to be affected by the presence of various organic peroxides for either reverse Diels-Alder or addition polymerization. Next, the "B-staged" resins were molded at 300°C for 1 to 4 hours under pressure varying from 100 to 200 psi (6.90 to 1.38 Mpa). This afforded, in most cases, tough, intractable, and void free polymer discs. The polymers were characterized by infrared and nuclear magnetic resonance spectroscopy, elemental analysis, and differential scanning calorimetry. Their physical properties including moisture absorption, glass transition temperatures (Tg), and isothermal weight loss were also determined. Some of the polymers exhibited a significant improvement in moisture resistance

17. Key Words (Suggested by Author(s))
Synthesis, Moisture Resistant Polymers,
Polymers, Bisnadimides, PMR Polyimides,
Alphatic-aromatic Polyimides,
Alphatic-aromatic bisnadimides
Alphatic bisnadimides, alphatic nadimide,
(Continued)

18. Distribution Statement
Unclassified-Unlimited

19 Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of Pages
97

22 Price*

* For sale by the National Technical Information Service, Springfield, Virginia 22161

16. Abstract (Continued)

over conventional epoxy resins and aromatic polyimides, i.e., PMR -15 and -11. Polymer disc - from monomer 2, for example, absorbed 0 percent moisture after 72 hours exposure to distilled water at room temperature, compared to 1.0 percent absorption by a conventional epoxy resin after the same treatment. The glass transtion temperature (Tg) of the polymers ranged from 10 to 200°C (212 to 392°F), substantially lower than the Tg of aromatic polyimides but comparable to the Tg of epoxy polymers. Several of the polymer discs exhibited less than 5 percent weigh loss after aging 500 hours at 260°C (500°F) in air. Most of these discs remained intact and showed no appreciable changes in moisture resistance and Tg after this treatment.

17. Key Words (Continued)

imide-epoxy
copolyimides
imide amines

R78-912941-15

Synthesis of Improved Moisture Resistant Polymers

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Cont'd)

LIST OF FIGURES (Cont'd)

Synthesis of Improved Moisture Resistant Polymers

SUMMARY

The synthesis and characterization of novel moisture resistant aliphatic polyimides are described in this report. Several novel aliphatic imides of diversified functionalities were synthesized, purified, and characterized. They include N-(12-aminododecyl)-5-norbornene-2,3-dicarboximide (1), N,N'-[[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis[1,3-dioxo-5,2-isoindolinediyl)dodecamethylene]]di-5-norbornene-2,3-dicarboximide (2), N,N'-dodecamethylenedi-5-norbornene-2,3-dicarboximide (3), N,N'-dodecamethylenebis[5,6-epoxy-2,3-norbornanedicarboximide] (4), and N,N'-Bis[12-(5-norbornene-2,3-dicarboximido)dodecyl]-1,2,3,4-butanetetracarboxylic 1,2:3,4-diimide (5). The structures of those compounds were established by elemental analysis, IR, NMR, and mass spectra. Mass spectrometry showed that the principal fragmentation of the nadimide system proceeded through the reverse Diels-Alder reaction to produce cyclopentadiene and maleimide fragments.

The synthesis of compounds 1 and 2 was accomplished via several different methods and a comparison of synthetic advantages among these routes was thus made.

In addition, the syntheses of the monomer precursors, 4-vinylphthalic anhydride and 1,3-butadiene-2,3-dicarboxylic anhydride, were attempted.

Thermal and catalytic polymerization and copolymerization of monomers 2 through 5 were investigated. Thirty polymer discs were fabricated in two steps. First, the monomer (or comonomer mixture) was polymerized to give tough and flexible "B-stage" resins showing adequate flow for the final molding. This process was accomplished in one hour at 290°C in air or nitrogen atmosphere and did not seem to be affected by the presence of various organic peroxides for either reverse Diels-Alder or addition polymerization. Next, the "B-staged" resins were molded at 300°C for 1 to 4 hours under pressure varying from 100 to 200 psi (6.90 to 1.38 Mpa). This afforded, in most cases, tough, intractable, and void free polymer discs.

The polymers were characterized by infrared - and nuclear magnetic resonance - spectroscopy, elemental analysis, and differential scanning calorimetry. Their physical properties including moisture absorption, glass transition temperatures (Tg), and isothermal weight loss were also determined. Some of the polymers exhibited a significant improvement in moisture resistance over conventional epoxy resins and aromatic polyimides, i.e., PMR -15 and -11. Polymer disc -4 from monomer 2, for example, absorbed 0 percent moisture after 72 hours exposure to distilled water at room temperature, compared to 1.0 percent absorption by a

conventional epoxy resin after the same treatment. The glass transition temperature (Tg) of the polymers ranged from 100 to 200°C (212 to 392°F), substantially lower than the Tg of aromatic polyimides but comparable to the Tg of epoxy polymers. Several of the polymer discs exhibited less than 5 percent weight loss after aging 500 hours at 260°C (500°F) in air. Most of these discs remained intact and showed no appreciable changes in moisture resistance and Tg after this treatment.

I. INTRODUCTION

Advanced fiber reinforced epoxy resin composite materials are being seriously considered for application in aerospace, military and more recently in commercial primary and secondary structural materials where replacement of heavy structures will reduce fuel consumption. However, advanced structural composites lose a substantial fraction of their unaged room and elevated temperature mechanical properties on long term exposure to atmospheric moisture at ambient conditions. This presents a serious problem for these materials intended for use in the aforementioned applications, and one which must be understood, defined and solved in order to take complete advantage of these advanced composites.

There are several approaches toward trying to solve the problem of environmental degradation of the thermomechanical properties of composites. For the epoxy matrix used as the binder in these systems, a more careful quality control in materials and processing is one approach that is being taken. More basic approaches are to study the interaction of moisture with the epoxy matrix and the interaction of moisture in the interface or interphase region of composites. Studies in the combined effects of stress and moisture on the strength degradation process are also important approaches toward understanding the mechanism of the degradation process.

The kinds of resin matrices which are useful in advanced composites are epoxies and polyimides. The former for moderate temperature applications (∿177°C, 350°F); the latter for more elevated temperature applications (∿317°C, 600°F). A common feature inherent in these two resin systems is the presence of polar functionality, such as $\geqslant$C-OH, -NH, -O-, in the case of epoxides, and $>$N- and $>$C=O in the case of polyimides. The presence and the high concentration of polar functionality are responsible for the excellent bonding characteristics present in composite systems containing epoxy or polyimide resin matrices.

It follows that the poor adhesive properties of polymer materials such as polytetrafluoroethylene (teflon) or polyethylene, are related to the absence of polar groups in the molecule. However, polar functional groups which are responsible for adhesion, are also responsible for the strong attraction to polar materials such as water, ketones or alcohols. These materials can interact with the polymer either physically and/or chemically thereby causing a lowering of the glass transition temperature (Tg) and a subsequent lowering of the thermomechanical capability of the composite system. The polar resins also provide a path by which moisture can diffuse to the interface. The presence of moisture at the interface weakens the fiber resin interaction causing a lowering of the shear and flexural strengths of the composite.

There is evidence which shows that composites containing polyimide resins are not affected by moisture to the same extent as composites containing epoxy matrices. Therefore, it is conceivable that a polymer molecule incorporating moisture resistant nonpolar portions, such as alicyclic or methylene units, and polar portions, such as imide functionality could exhibit both moisture resistance and adhesive properties. This is supported by studies carried out recently by Stevens and Scola (Ref. 1) who demonstrated a correlation between moisture resistance and aliphatic carbon chain length in poly(bis-aliphatic nadimides).

Therefore, this research program was based on two correlations:

(1) The demonstration of moisture resistance improvement with increasing aliphatic content ($-CH_2-$groups) in the bisnadimide polymers (Ref. 1), and

(2) the fact that polar groups of polyimides appear to be responsible for the good adhesive properties (shear strengths) exhibited by graphite fiber reinforced polyimide composites.

II. OBJECTIVE

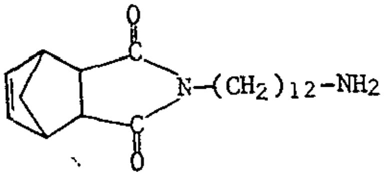
The objective of this program is to develop moisture-resistant polymers with good adhesive properties and to derive these polymers from monomers that can be cured at temperatures below 260°C (500°F). The tasks of this investigation can be summarized as follows:

1. Synthesis and characterization of several aliphatic bisnadimides.
2. Determination of reaction parameters for preparation of resin discs.
3. Fabrication of polymer discs.
4. Determination of the moisture absorption characteristics and other physical properties.
5. Determination of optimum polymerization conditions and feasibility of copolymerizing bisnadimides with other available comonomers.

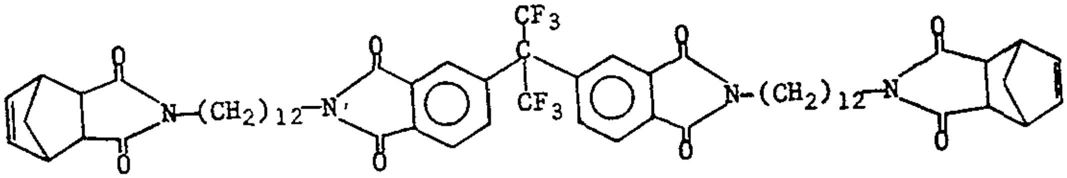
III. RESULTS AND DISCUSSION

A. Synthesis and Characterization of Aliphatic Bisnadimides

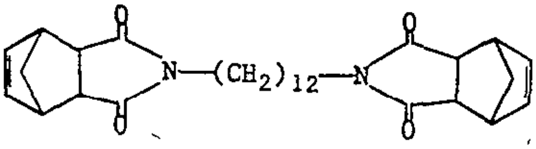
The synthesis, purification, and characterization of five aliphatic imides whose structures are represented by formulas 1 through 5 are described in this section. Those compounds have not been reported in the literature, according to our recent literature review. In addition, the attempted synthesis of 4-vinylphthalic anhydride (6) and 1,3-butadiene-2, 3 dicarboxylic anhydride (7) are also discussed. The IR spectra of compounds 1, 1a, 2, 3, 4 and 5 are shown in Figs. 2 through 7, the NMR spectra of 1, 2, 3, 4, and 5 are given in Figs. 8 through 12, and the DSC thermograms of 2 through 5 are shown in Figs. 13 through 16. All of the physical properties, spectral data, and elemental analyses for the compounds synthesized in this study are given in the Experimental Section.



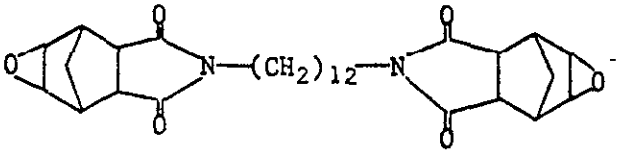
N-(12-aminododecyl)-5-norbornene-2,3-dicarboximide (1)



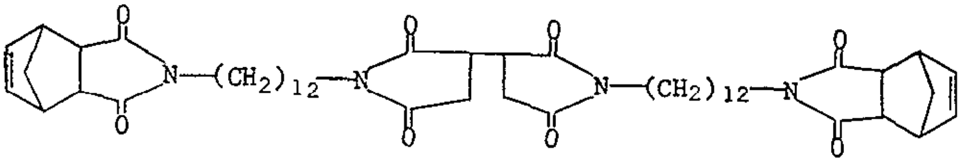
N,N'-[[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis[(1,3-dioxo-5,2-isoindolinediyl)dodecamethylene]]di-5-norbornene-2,3-dicarboximide (2)



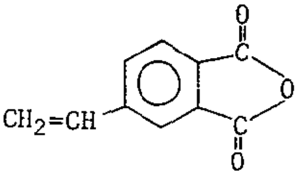
N,N'-dodecamethylenedi-5-norbornene-2,3-dicarboximide (3)



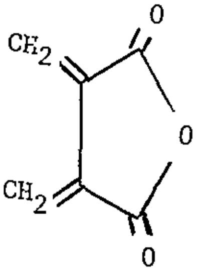
N,N'-dodecamethylenebis[5,6-epoxy-2,3-norbornanedicarboximide] (4)



N,N'-Bis[12-(5-norbornene-2,3-dicarboximido)dodecyl]-1,2,3,4-butanetetracarboxylic 1,2:3,4-diimide (5)

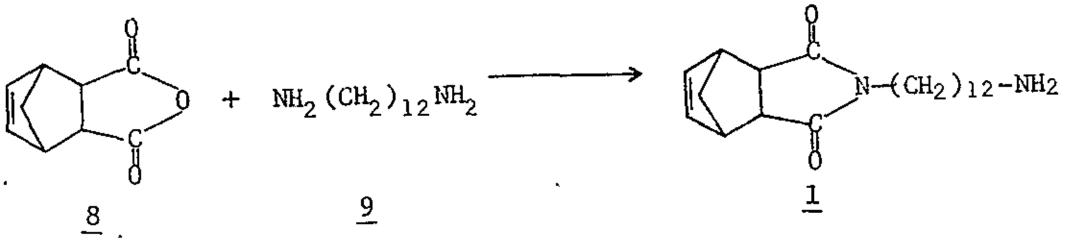


6



7

1. N-(12-aminododecyl)-5-norbornene-2,3-dicarboximide (1)



(1)

As a common precursor of bisnadimides 2 and 5, this compound was prepared by the following four synthetic methods:

(1) The reaction of the commercially available nadic anhydride (8) and 1,12-diaminododecane (9) in refluxing DMF (Route A).

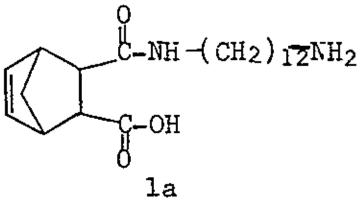
(2) The fusion of 8 and 9 in the absence of a solvent (Route B).

(3) The reaction of 8 with monohydrochloride salt of 9 in refluxing DMF (Route C), and finally,

(4) The reaction of 8 and 9 in the presence of phosphorus pentoxide (P_2O_5), acting as a dehydrating agent for the imidization, in refluxing THF (Route D).

Specific details on each synthesis are discussed below.

Route A - Anhydride 8 was treated with 1 equivalent of 9 in refluxing DMF for 96 hours. Evaporation of the volatile solvents led to crude 1 as a dark brown oil in 98 percent yield. The IR spectrum showed imide absorptions at 1765, 1680, and 720 cm^{-1}; amine N-H stretching at 3300 cm^{-1}. The NMR spectrum was also consistent with this compound. The gel permeation chromatogram (Fig. 1) exhibited one major peak corresponding to the desired product and three minor peaks identified as bisnadimide 3, amide acid intermediate 1a, and the solvent DMF as indicated in Table 1. Chromatography of the mixture on silica gel afforded an analytical sample of 1 whose IR (Fig. 2), NMR (Fig. 8) and mass spectra, plus elemental analysis were determined and provided evidence for the assigned structure.

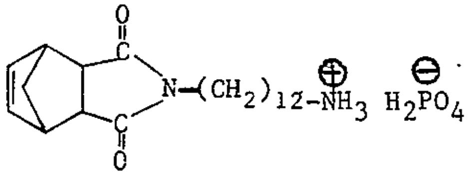


1a

Route B - An intimate mixture of 8 and 9 in equal molar ratio was rapidly heated to 220°C and maintained at that temperature for 1/2 to 1 hour. Upon cooling to room temperature, a yellow oil material was afforded. The IR spectrum revealed that the desired compound was formed along with considerable amounts of amide acid 1a. This was confirmed by the results of elemental analysis. When the reaction mixture was heated at 220°C for an additional two hours, imidization of the amide acid seemed to occur. But, complete transformation of the intermediate to 1 was not observed. Purification of the mixture by solvent extraction failed to remove all impurities.

Route C - This procedure involved a two-stage synthesis. First, the monohydrochloride salt of diamine 9 was prepared from treating 9 with 1 equivalent of HCl in THF. This led to a white solid, m.p. 243-260°C. Both the elemental analysis and IR spectrum were consistent with the named salt. Next, this salt was allowed to react with 8 in equal molar ratio in refluxing DMF for 3 hours. Three products were isolated. On the basis of the elemental and IR data, they were characterized as the dihydrochloride salt of 9, 3 and maleimide probably derived from a reverse Diels-Alder reaction of 1. The desired compound 1 could not be detected among the products isolated, however.

Route D - In the presence of a catalytic amount of P_2O_5, 8 was treated overnight in refluxing THF with 1 equivalent of 9. A white chloroform soluble solid was afforded. The IR spectrum indicated that salt of 1, rather than free amine 1, was formed. Since phosphoric acid is formed during the imidization, a logical form of this amine salt is phosphoric acid salt of 1.

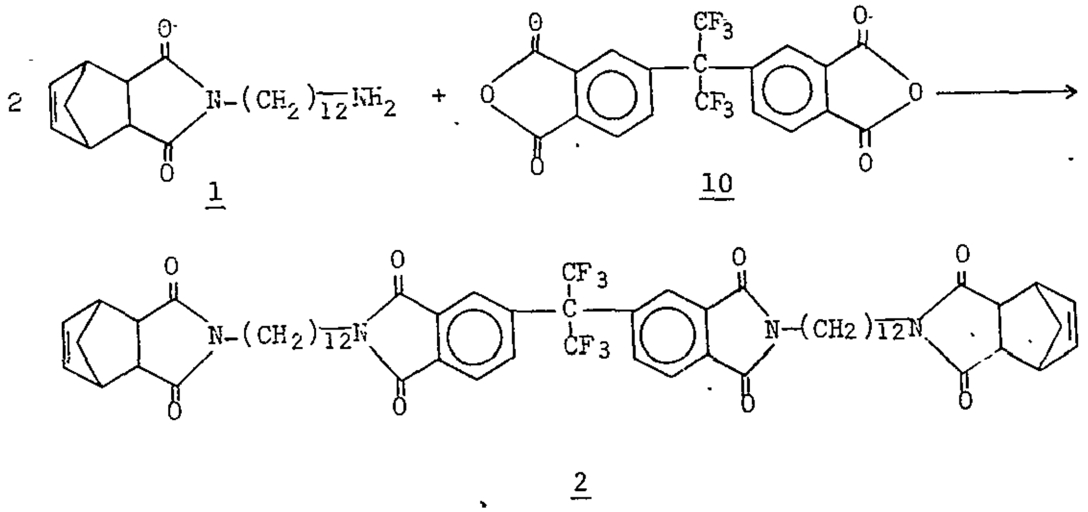


This is supported by the IR spectrum that showed a doublet at 1140 cm^{-1} and a broad band at 1070 cm^{-1} due to a PO_2 group.

Of the four synthetic routes discussed above, Route A is considered the method of choice because of the purity (90 percent) and high yield (98 percent) of crude 1 obtained.

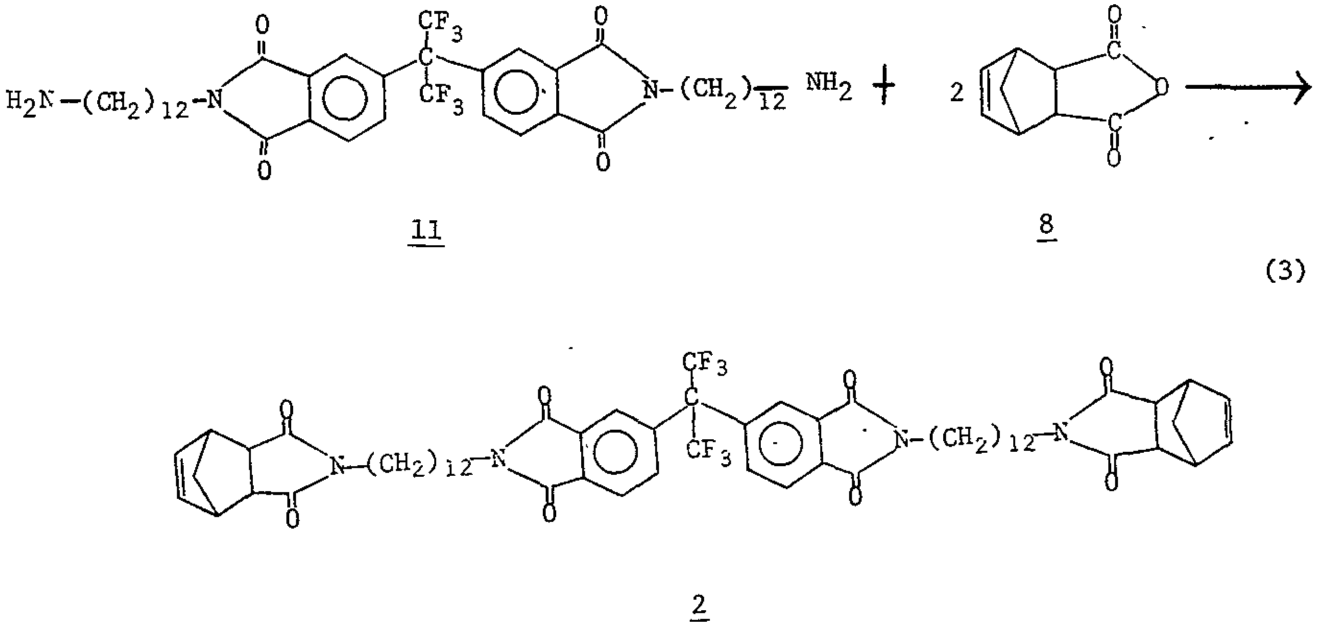
2. N,N'-[[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis[1,3-dioxo-5,2-isoindolinediyl)dodecamethylene]]di-5-norbornene-2,3-dicarboximide (2)

The preparation of this compound was attempted by two methods. Method A involved the reaction of 1 with 10,



(2)

and Method B, the reaction of <u>11</u> with <u>8</u>



(3)

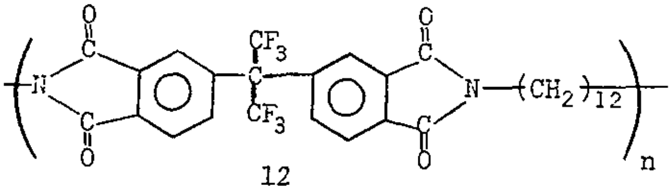
Method A - Anhydride 10 was not directly available from a commercial source. It was prepared from the dehydration of the corresponding tetracarboxylic acid isolated from a Dupont resin solution NR-150-B2. Crude compound 1 was treated with 10 in a 2 to 1 molar ratio in refluxing DMF for 42 hours. Concentration of the solution gave crude product 2 as a dark brown oil. The IR spectrum (Fig. 4) exhibited imide bands at 1775, 1710, 725 cm^{-1}, aromatic absorptions at 1600, 1440, 1400 and 850 cm^{-1}, aliphatic C-F vibrations at 1370, 1260, 1210, and 1140 cm^{-1}.

Confirming the structure assigned, the NMR spectrum (Fig. 9) showed aromatic proton signals at δ 7.35, 7.80 and 7.85, olefinic proton signal at δ 6.08, and signals due to aliphatic protons in the region of δ 3.5 to 1.27. The gel permeation chromatogram indicated one major peak (80 percent calculated from the peak area) correlated with 2, along with unreacted starting materials, DMF, and the amide acid precursor of 2. The desired product was purified by chromatography of the mixture on silica gel. Aside from the consistent IR, NMR, and elemental analysis, the mass spectrum showed a base peak at m/e 66 attributable to a cyclopentadiene fragment (from a reverse Diels-Alder reaction of 2) and a peak at m/e 69 due to a CF_3 cation.

Method B - Since the required precursor 11 was not commercially available, this synthesis began with the preparation of 11. Exposure of 10 with an equivalent of 9 in refluxing DMF for 2 hours gave two products - white and green solids.

The white solid as minor product melted around 96.5 - 99.5°C. The IR spectrum was consistent with this compound as 11, for it exhibited the expected bands at 3250 cm^{-1} (amine), 1770, 1700 and 780 cm^{-1} (imide) 1630, 1520, 1455, and 840 cm^{-1} (aromatic) and a series of absorptions between 1100 to 1350 cm^{-1} due to the CF_3 group. The NMR spectrum (Fig. 17) also supported this structure. However, the elemental analysis did not confirm this.

The major product, a green solid, had a melting range of 125 - 130°C. Its IR spectrum showed identical imide bands as those that appeared in the IR spectrum of the elemental analysis was more consistent with an imide polymer 12 than compound 11.

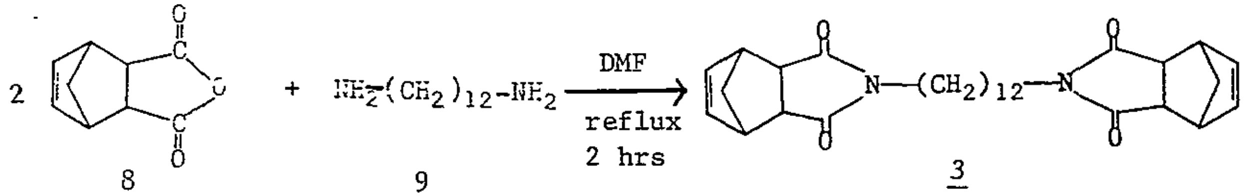


12

Additional evidence is that the yield of the green solid increased as the molar ratio of reactants 9 to 10 was changed from 2:1 to 1:1, a condition which favors the formation of the imide polymer.

Due to the difficulty in obtaining the required precursor 11 in sufficient quantity, this approach toward obtaining the reaction product 2 was discontinued.

3. N,N'-dodecamethylenedi-5-norbornene-2,3-dicarboximide (3)

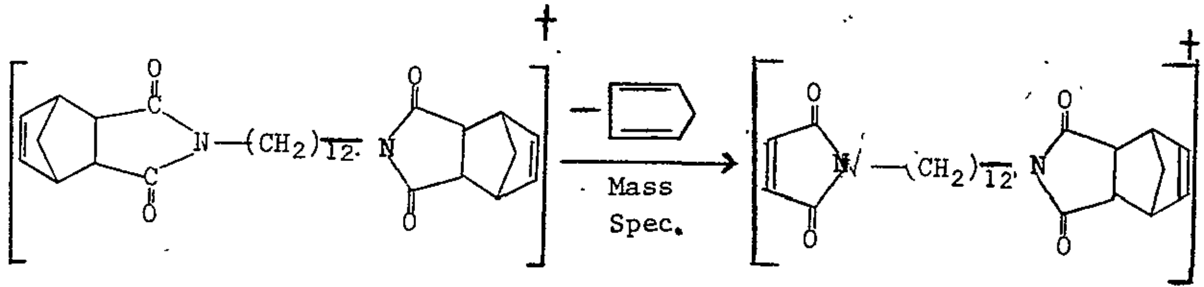


8 9 3 (4)

The synthesis of this compound was straightforward. This was accomplished by treating 9 with 2 equivalents of 8 in refluxing DMF for 2 hours. The yield of crude 3 was moderate (57 percent). This procedure also offered a simple purification: recrystallization of the crude product from ethanol was sufficient to obtain an analytical sample.

In addition to the IR (Fig. 5), NMR (Fig. 10), and elemental analysis which are fully consistent with the structure of 3, the mass spectrum of this compound merits some discussion. The fragmentation pattern of this compound represents a typical cleavage observed for all the bisnadimides synthesized in this study. The molecular ion peak appeared at m/e 493. The fairly high intensity of this peak (23 percent) reflects the stability of this compound. The base peak appeared at m/e 66, in addition to peaks at m/e 427 and 361. These peaks suggest that a stepwise loss of cyclopentadiene from the molecule of 3 occurred in the mass spectrometer. This is shown in the following scheme:

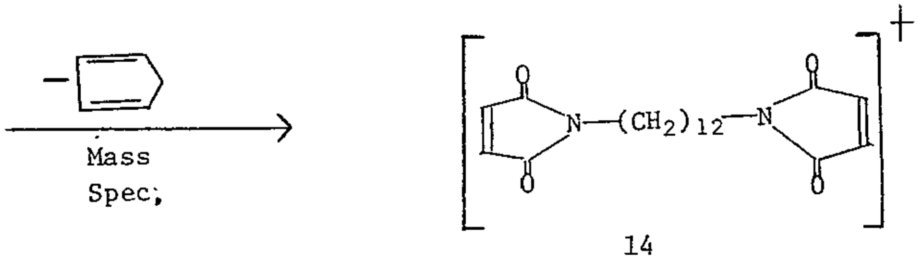
SCHEME I



(5)

3
m/e 493

13
m/e 427

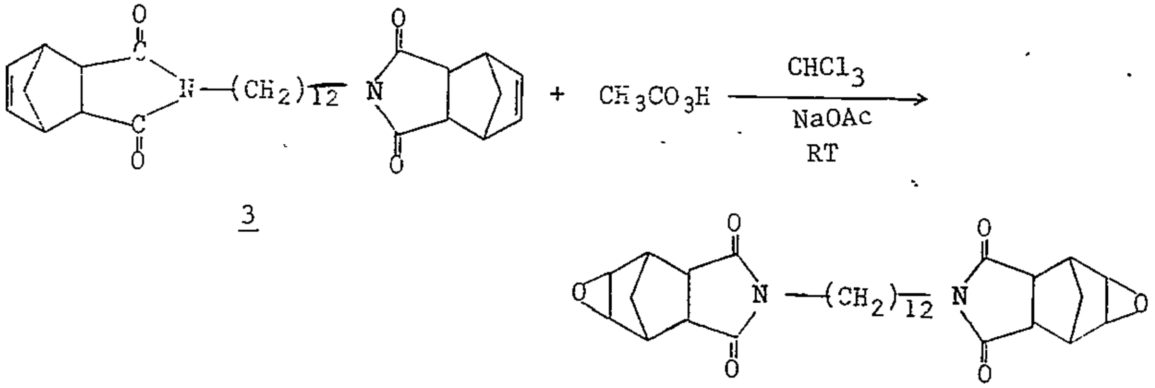


14

m/e 361

(6)

4. N,N'-dodecamethylenebis[5,6-epoxy-2,3-norbornanedicarboximide] (4)



3

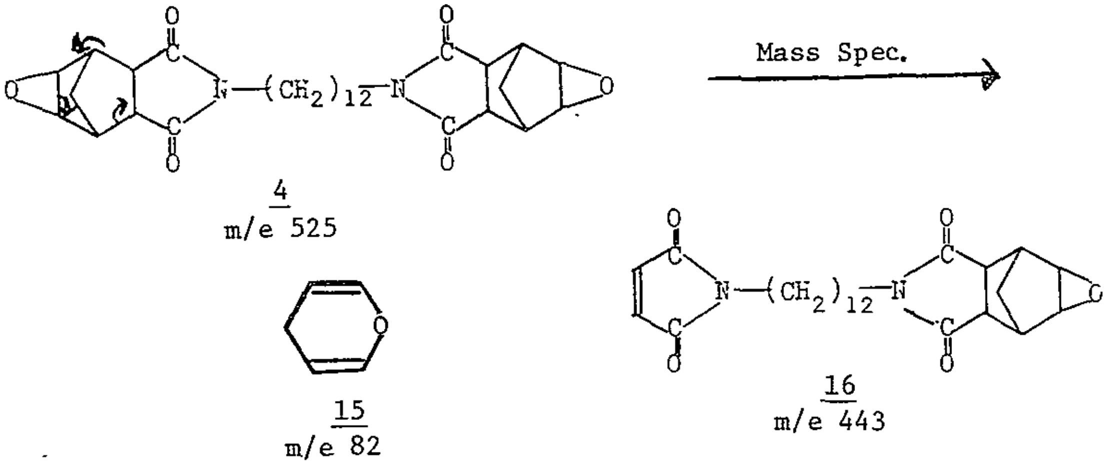
4

(7)

The preparation of this compound proceeded via the epoxidation of bisnadimide 3 with an excess of peracetic acid, according to eq. (7).

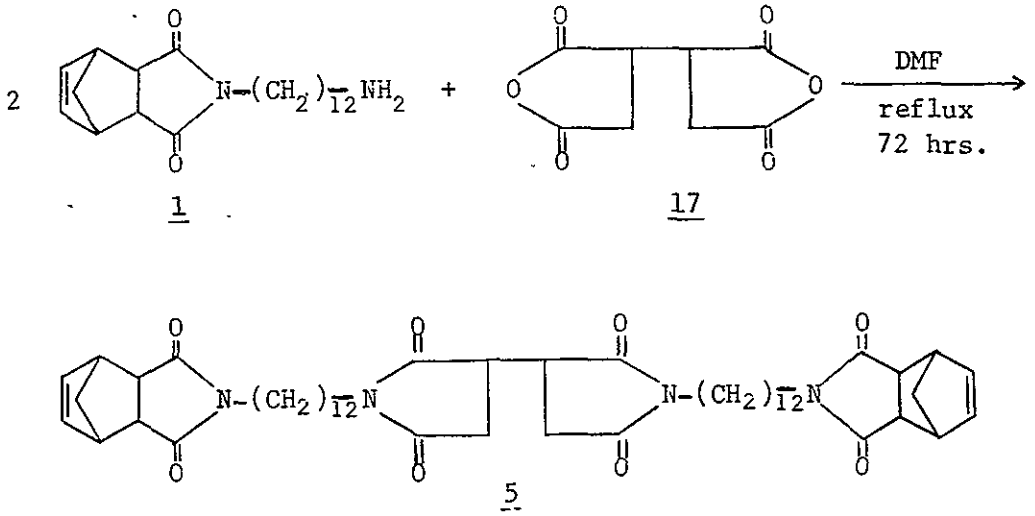
The NMR spectrum (Fig. 11) of this product revealed that the vinyl proton signal at δ 6.07 which appeared in the NMR of 3 (Fig. 10) has now disappeared. Instead, two new signals emerged at δ 3.33 and 3.47 consistent with the epoxy ring protons. The IR spectrum (Fig. 6) also supported the formation of an epoxide. The evidence for this is the appearance of a band at 920 cm^{-1}, which is typical of an epoxy absorption. The elemental analysis and the molecular ion peak at m/e 525 shown in the mass spectrum established the formula $C_{30}H_{40}N_2O_6$. The base peak now appeared at m/e 82, rather than at m/e 66 as in the case of 3. An additional peak at m/e 443 also showed up in the mass spectrum. This indicated that the fragmentation occurred as follows:

SCHEME II



(8)

5. N,N'-Bis[12-(5-norbornene-2,3-dicarboximido)dodecyl]-1,2,3,4-butanetetracarboxylic 1,2:3,4-diimide (5)



(9)

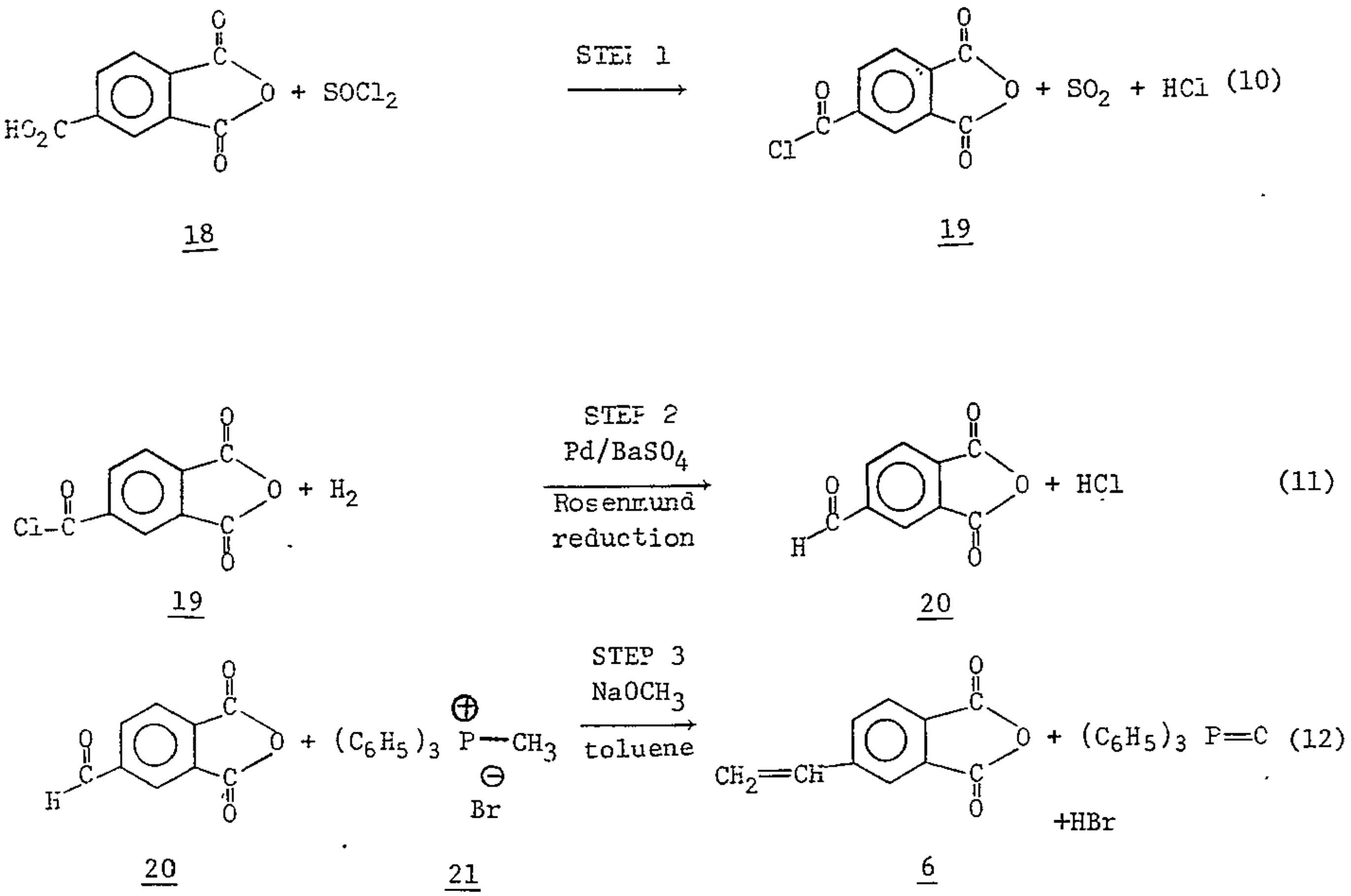
Similar to the synthesis of 2, this compound was prepared from treatment of 1 with butanetetracarboxylic dianhydride (17) in refluxing DMF for 72 hours. The gel permeation chromatogram of the crude product (Fig. 19) exhibited one major peak corresponding to the desired product and two minor peaks which were assigned as unreacted starting materials.

Chromatography of the mixture on silica gel afforded a pure sample of 5 whose gel permeation chromatogram (Fig. 20) showed only one peak.

6. Attempted Synthesis of 4-vinylphthalic Anhydride (6)

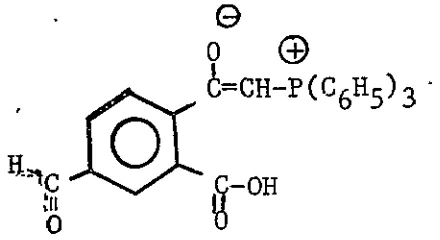
A three-step synthesis of this compound has been attempted. The overall reaction sequence is outlined in Scheme III.

SCHEME III



Step one involved the reaction of the commercially available trimellitic anhydride (18) with thionyl chloride (Ref. 2). This led to the isolation of 4-chloroformylphthalic anhydride (19) as a white solid, m.p. 67-68°C (reported in Ref. 2 m.p. 67-68°C) in 50 percent yield. This was followed by Rosenmund reduction of crude 19 to give 4-formylphthalic anhydride (20), m.p. 108-118°C. Sublimation of the crude product afforded an analytical sample of 20, m.p. 122-123°C (reported in Ref. 2, m.p. 127-129°C). The overall yield of anhydride 20 was 8 percent from 18. The infrared spectrum was consistent with this compound. It exhibited aldehyde C-H stretching at 2735 cm^{-1}, aldehyde C=0 absorption at 1720, anhydride C=0 absorptions at 1860 and 1785 cm^{-1}.

In the final step, the conversion of aldehyde 20 to the desired olefin 6 was attempted via the Wittig reaction. Compound 20 was treated with methylenetriphenylphosphorane, presumably formed from methyltriphenylphosphonium bromide (21) and sodium methoxide, in toluene. This afforded two solid products. The infrared spectrum of the toluene insoluble material showed no absorptions due to the anhydride group, but exhibited aldehyde carbonyl absorption at 1720 cm^{-1}, carboxylic O-H stretching around 3400 cm^{-1} as a broad and strong band with carbonyl stretching at 1690 cm^{-1}, and a series of bands due to an aromatic group. In addition, a strong and broad band appeared at 1570 cm^{-1} attributable to ylide carbonyl (Ref. 3). The IR spectrum seemed to support this compound as the ylide salt (Ref. 4) shown below.

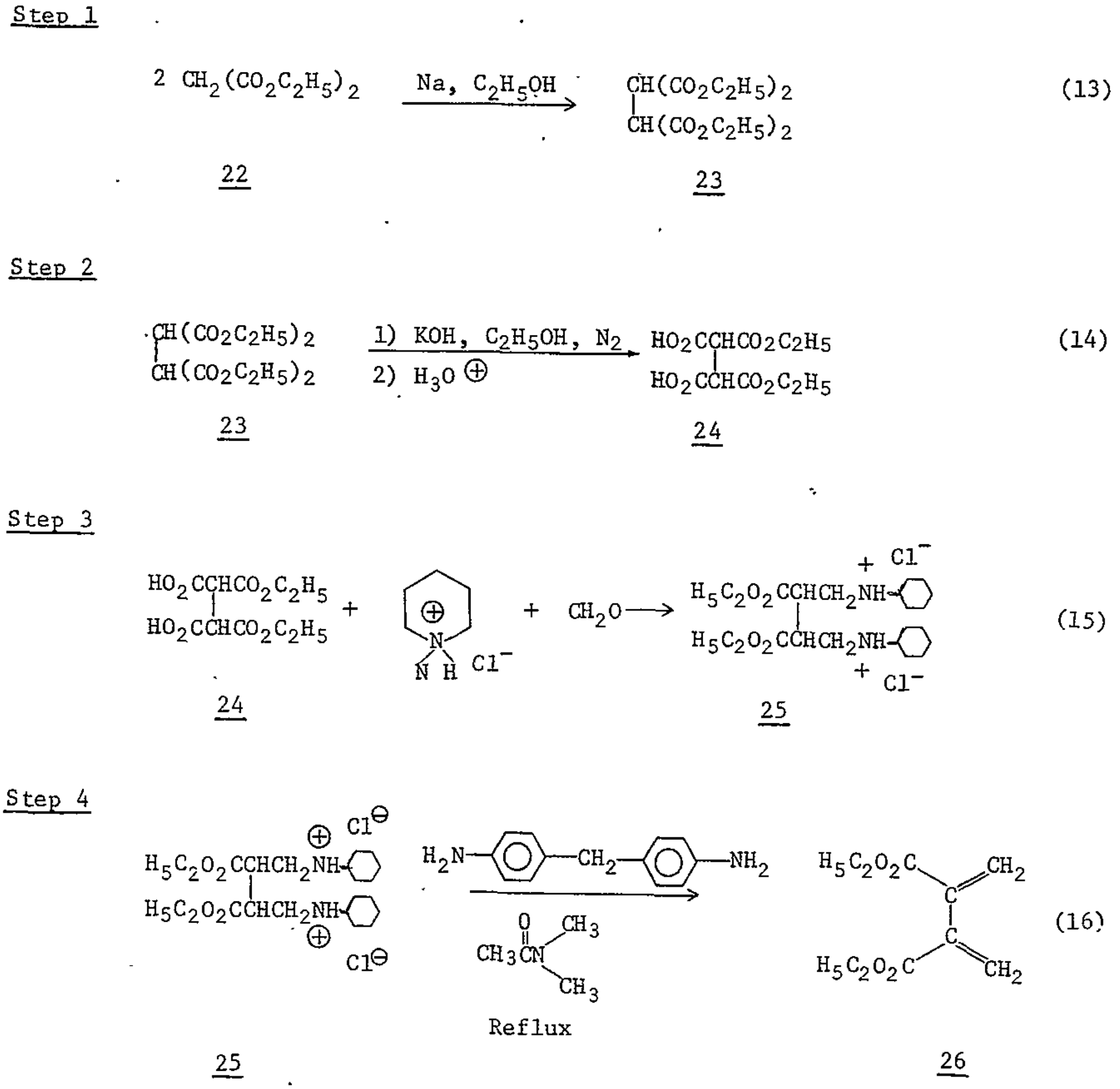


The IR spectrum of the toluene soluble material showed no absorptions due to anhydride or ylide carbonyl, but showed sharp bands at 3040 and 1590 cm^{-1}, attributable to an olefinic or an aromatic functionality. The presence of the aldehyde group was also revealed by the IR spectrum. No further identification of this compound was made. Additional work was not carried out on this compound.

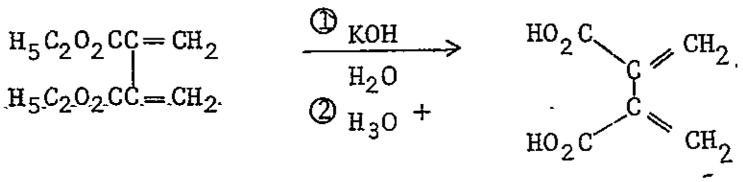
7. Attempted Synthesis of 1,3-Butadiene-2,3-Dicarboxylic Anhydride (7)

The synthesis of this compound (Scheme IV) was attempted in six steps. The first step involved the coupling reaction of the commercially available diethylmalonate (22), following the procedure of Bailey and Sorenson (Ref. 5). Thus, treatment of 22 with a freshly prepared sodium ethoxide in ethanol afforded tetraester 23 as a white solid, m.p. 73-5°C (lit (Ref. 5) m.p. 75-6°C). The yield was 68 percent.

SCHEME IV


Step 1
2 CH2(CO2C2H5)2
Na, C2H5OH
CH(CO2C2H5)2
CH(CO2C2H5)2
22
23
(13)
Step 2
CH(CO2C2H5)2
CH(CO2C2H5)2
1) KOH, C2H5OH, N2
2) H3O ⊕
HO2CCHCO2C2H5
HO2CCHCO2C2H5
23
24
(14)
Step 3
HO2CCHCO2C2H5
HO2CCHCO2C2H5
+
N
H H Cl⁻
+ CH2O
H5C2O2CCHCH2NH
H5C2O2CCHCH2NH
+ Cl⁻
24
25
(15)
Step 4
⊕ Cl⊖
H5C2O2CCHCH2NH
H5C2O2CCHCH2NH
H2N
CH2
NH2
O
CH3CN
CH3
CH3
Reflux
H5C2O2C
CH2
C
C
H5C2O2C
CH2
25
26
(16)

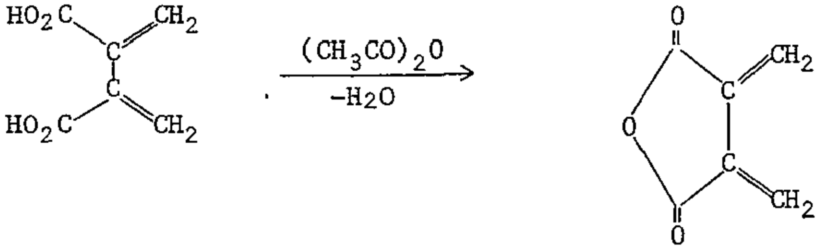
Step 5



26 27

(17)

Step 6



27 7

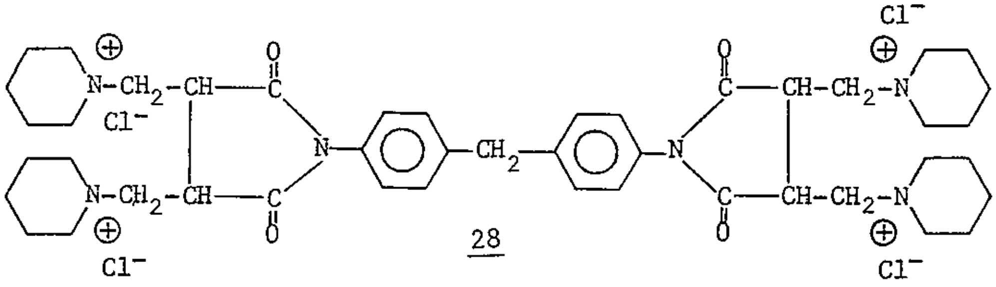
(18)

Next, the partial hydrolysis of tetraester 23 to diester dicarboxylic acid 24 was accomplished in 57 percent yield by treating 23 with slightly over 2 equivalents of potassium hydroxide in absolute ethanol under a dried nitrogen atmosphere (Ref. 6). The product obtained as white crystals was reasonably pure as reflected by the narrow melting range, 133-4°C (lit. (Ref. 6) 133-5°C). Both steps 2 and 3 followed the procedure of Zahorsky and Musso (Ref. 6).

In the third step, the conversion of 24 to quaternary ammonium salt 25 proceeded through treatment of 24 with piperidinium hydrochloride salt and 37 percent aqueous formaldehyde. This led to a white crystalline product in 15 percent yield. The melting range was 163.5-165°C which is close to the reported value 163-4°C for salt 25 (Ref. 6). The infrared spectrum was similar to that reported (Ref. 6) and was consistent with the structure of 25.

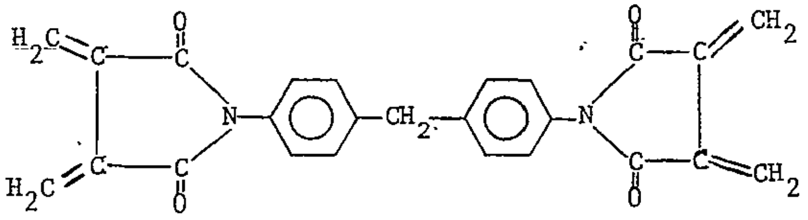
Zahorsky and Musso obtained compound 26 by pyrolyzing 25 at 130-135°C in vacuum for 5 to 6 hours. Here this compound was obtained by treatment of the dipiperidinium salt with 4,4'-methylenedianiline. Compound 25 was treated with 4 4'-methylenedianiline in refluxing N, N-dimethylacetamide (b.p. 164-166°C) for 4 hours. This led to the isolation of a dark oil after vacuum distillation. The IR spectrum showed absorptions at 3100 cm^{-1} due to $C = CH_2$, at 2940 and 2860 cm^{-1} owing to adiphatic CH_3 and CH_2 groups, at 1720 due to ester carbonyl, in addition to a series of absorptions in the region of 1540 to 855 cm^{-1} attributable to unsaturated and saturated hydrocarbon groups. This oil was extracted with ether. Concentration of the ether extract afforded a brownish organic oil. This oil showed a positive bromine test. Its IR spectrum was similar to that of the dark oil discussed above. The DSC showed one sharp endotherm at 145°C. These results are consistent with compound 26.

The original intention of running this reaction was to prepare the desired precursor 28.



28

Monomer 28 was to be converted to 29 as outlined in the original program (Ref. 7).



29

Apparently in the attempt to prepare the bisimide 28, elimination of the quaternary ammonium salt 25 occurred more easily than the imidization reaction.

B. Polymerization of Aliphatic Bisnadimides and Synthesis of Polymer Discs

A variety of polymerization reactions based on monomers 2, 3, 4, and 5 were investigated. The purpose was to determine reaction parameters for preparation of resins and, more importantly, to see if polymers could be processed at temperatures below 260°C (500°F). In addition, a series of press-molded neat polymer discs were fabricated for polymer evaluation. For each polymer disc prepared, a two-stage synthesis was applied. First, a monomer or comonomer mixture, with or without catalyst was consolidated to form a fusible (flow) "B-stage" polymer. Then, the "B-staged" polymer was advanced in a one-inch diameter mold at 300°C, 100 to 200 psi (6.9 to 1.38 MPa) and from 1 to 4 hrs to give an intractable and presumably high molecular weight cross-linked polymer. Listed below are the synthetic reactions investigated.

From Monomer 2

$$\underline{2} \xrightarrow{290^{\circ}\text{C, 1 hr}} \begin{array}{l}\text{orange}\\ \text{Disc-1}\end{array} \qquad (19)$$

$$\underline{2} \xrightarrow[\text{(2) } 300^{\circ}\text{C, 100 psi (6.9 MPa), 1 hr}]{\text{(1) } 290^{\circ}\text{C, 1.5 hrs}} \begin{array}{l}\text{dark brown}\\ \text{Disc-2}\end{array} \qquad (20)$$

$$\underline{2} \xrightarrow[\text{(2) } 300^{\circ}\text{C, 200 psi (1.38 MPa), 1 hr}]{\text{(1) } 290^{\circ}\text{C, 1.25 hrs}} \begin{array}{l}\text{dark brown}\\ \text{Disc-3}\end{array} \qquad (21)$$

$$\underline{2} \xrightarrow[\text{(2) } 300^{\circ}\text{C 200 psi (1.38 MPa), 1.5 hrs}]{\text{(1) CHP, } N_2\text{, } 305^{\circ}\text{, 5 min}} \begin{array}{l}\text{dark brown}\\ \text{Disc-4}\end{array} \qquad (22)$$

From Monomer 2

$$\underline{2} \xrightarrow[\text{(2) } 300^{\circ}\text{C, 200 psi (1.38 MPa), 3 hrs}]{\text{(1) CHP, } N_2\text{, } 305^{\circ}\text{C, 5 min}} \text{dark brown Disc-5} \tag{23}$$

$$\underline{2} \xrightarrow[\substack{\text{(2) } 290^{\circ}\text{C, 1 hr} \\ \text{(3) } 300^{\circ}\text{C, 200 psi (1.38 MPa), 1.75 hrs}}]{\text{(1) DCP, } 135^{\circ}\text{C, 18 hrs}} \text{dark brown Disc-6} \tag{24}$$

From Monomer 3

$$\underline{3} \xrightarrow[\text{(2) } 300^{\circ}\text{C, 200 psi (1.38 MPa), 1 hr}]{\text{(1) } 275^{\circ}\text{C, 0.5 hr, } N_2} \text{yellow Disc-7} \tag{25}$$

$$\underline{3} \xrightarrow[\text{(2) } 300^{\circ}\text{C, 200 psi (1.38 MPa), 1 hr}]{\text{(1) } 275^{\circ}\text{C, 3 hrs}} \text{yellow Disc-8} \tag{26}$$

$$\underline{3} \xrightarrow[\substack{\text{(2) } N_2\text{, } 290^{\circ}\text{C, 1/2 hr} \\ \text{(3) } 300^{\circ}\text{C, 200 psi (1.38 MPa), 2 hrs}}]{\text{(1) BP, } N_2\text{, } 90^{\circ}\text{C, 2 hrs}} \text{yellow Disc-9} \tag{27}$$

$$\underline{3} + \text{DVB} \xrightarrow[\substack{\text{(2) } 290^{\circ}\text{C, 1 hr} \\ \text{(3) } 290^{\circ}\text{C, 100 psi (6.90 MPa), 1 hr}}]{\text{(1) DCP, DMF, } 152^{\circ}\text{C, 72 hrs}} \text{brown Disc-10} \tag{28}$$

From Monomer 4

$$\underline{4} \xrightarrow[\substack{\text{(2) } N_2\text{, } 300^{\circ}\text{C, 1 hr} \\ \text{(3) } 310^{\circ}\text{C, 200 psi (1.38 MPa), 1 hr}}]{\text{(1) } N_2\text{, } 230^{\circ}\text{C, 2 1/2 hrs}} \text{black Disc-11} \tag{29}$$

$$\underline{4} + \text{HFA} \xrightarrow[200^{\circ}\text{C, 4 hrs}]{\text{DBDL}} \text{dark brown Disc-12} \tag{30}$$

$$\underline{4} + \text{HFA} \xrightarrow[\text{(2) } 225^{\circ}\text{C, 75 psi (.517 MPa), 1 hr}]{\text{(1) DBDL, } 200^{\circ}\text{C, 4 hrs}} \text{dark brown Disc-13} \tag{31}$$

From Monomer 4 (Cont'd)

$\underline{4}$ + HFA	$\xrightarrow[\text{(2) 225}^{\circ}\text{C, 75 psi (.517 MPa), 1 hr}]{\text{(1) } BF_3 \cdot Et_2O\text{, 200}^{\circ}\text{, 4 hrs}}$	dark brown Disc-14	(32)
$\underline{4}$ + HFA	$\xrightarrow[\text{(2) 230}^{\circ}\text{C, 300 psi (2.07 MPa), 1.75 hrs}]{\text{(1) } BF_3 \cdot NH_2Et\text{, DBDL, 230}^{\circ}\text{C, 2.5 hrs, } N_2}$	dark brown Disc-15	(33)
$\underline{4}$ + MDA	$\xrightarrow[\text{225}^{\circ}\text{C, 2 hrs}]{\text{DBDL}}$	dark brown Disc-16	(34)
$\underline{4}$ + MDA	$\xrightarrow[\text{(2) 210}^{\circ}\text{C, 75 psi (.517 MPa), 1 hr}]{\text{(1) } N_2\text{, DBDL, 205}^{\circ}\text{C, 64 hrs}}$	dark brown Disc-17	(35)

From Monomer 5

$\underline{5}$	$\xrightarrow[\text{1 hr}]{\text{290}^{\circ}\text{C}}$	dark brown Disc-18	(36)
$\underline{5}$	$\xrightarrow[\text{(2) 300}^{\circ}\text{C, 200 psi (1.38 MPa), 1 hr}]{\text{(1) 290}^{\circ}\text{C, 1 hr}}$	black Disc-19	(37)
$\underline{5}$	$\xrightarrow[\substack{\text{(2) 290}^{\circ}\text{C, 0.5 hr} \\ \text{(3) 290}^{\circ}\text{C, 300 psi (2.07 MPa), 2 hrs}}]{\text{(1) DCP, 135}^{\circ}\text{C, 18 hrs}}$	black Disc-20	(38)
$\underline{5}$	$\xrightarrow[\text{250}^{\circ}\text{C, 2 hrs}]{\text{CHP}}$	dark brown Disc-21	(39)

From Comonomers 2 and 3

$\underline{2} + \underline{3}$	$\xrightarrow[\text{(2) 300}^{\circ}\text{C, 200 psi (1.38 MPa), 2 hrs}]{\text{(1) } N_2\text{, 300}^{\circ}\text{C, 2 hrs}}$	black Disc-22	(40)
$\underline{2} + \underline{3}$	$\xrightarrow[\text{(2) 300}^{\circ}\text{C, 200 psi (1.38 MPa), 3 hrs}]{\text{(1) } N_2\text{, 300}^{\circ}\text{C, 2 hrs}}$	black Disc-23	(41)

From Comonomers 2 and 3 (Cont'd)

$$\underline{2} + \underline{3} \xrightarrow[\text{(2) } 300^{\circ}\text{C, 200 psi (1.38 MPa), 4 hrs}]{\text{(1) } N_2\text{, } 300^{\circ}\text{C, 2 hrs}} \begin{array}{l}\text{black}\\ \text{Disc-24}\end{array} \qquad (42)$$

$$\underline{2} + \underline{3} \xrightarrow[\substack{\text{(2) } 300^{\circ}\text{C, } N_2\text{, 1/2 hr} \\ \text{(3) } 310^{\circ}\text{C, 300 psi (2.07 MPa), 1.3 hrs}}]{\text{(1) CHP, } N_2\text{, } 215^{\circ}\text{C, 21 hrs}} \begin{array}{l}\text{black}\\ \text{Disc-25}\end{array} \qquad (43)$$

From Comonomers 2 and 5

$$\underline{2} + \underline{5} \xrightarrow[\text{(2) } 300^{\circ}\text{C, 200 psi (1.38 MPa), 2 hrs}]{\text{(1) } N_2\text{, } 300^{\circ}\text{C, 2 hrs}} \begin{array}{l}\text{black}\\ \text{Disc-26}\end{array} \qquad (44)$$

$$\underline{2} + \underline{5} \xrightarrow[\text{(2) } 300^{\circ}\text{C, 200 psi (1.38 MPa), 3 hrs}]{\text{(1) } N_2\text{, } 300^{\circ}\text{C, 2 hrs}} \begin{array}{l}\text{black}\\ \text{Disc-27}\end{array} \qquad (45)$$

$$\underline{2} + \underline{5} \xrightarrow[\text{(2) } 300^{\circ}\text{C, 200 psi (1.38 MPa), 4 hrs}]{\text{(1) } N_2\text{, } 300^{\circ}\text{C, 2 hrs}} \begin{array}{l}\text{black}\\ \text{Disc-28}\end{array} \qquad (46)$$

From Commonomers 3 and 5

$$\underline{3} + \underline{5} \xrightarrow[\text{(2) } 300^{\circ}\text{C, 200 psi, (1.38 MPa), 1.5 hrs}]{\text{(1) } 300^{\circ}\text{C, } N_2\text{, 1/2 hr}} \begin{array}{l}\text{black}\\ \text{Disc-29}\end{array} \qquad (47)$$

$$\underline{3} + \underline{5} \xrightarrow[\text{(2) } 280^{\circ}\text{C, 200 psi, (1.38 MPa), 2 hrs}]{\text{(1) } N_2\text{, } 290^{\circ}\text{C, 1 hr}} \begin{array}{l}\text{black porous}\\ \text{Disc-30}\end{array} \qquad (48)$$

The following abbreviations occur in the formula:

CHP = Cumene Hydroperoxide

DCP = Dicumyl Peroxide

DVB = Divinyl Benzene

DMF = Dimethyl Formamide

HFA = Hexafluoroisopropylidene Diphthalic anhydride

DBDL = Dibutyltin Dilaurate

MDA = 4, 4' - Methylenedianiline

BP = Benzoyl Peroxide

1. Thermal Polymerization

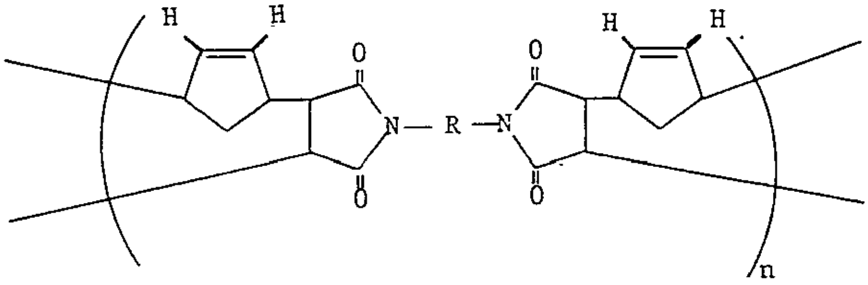
Bisnadimides readily undergo thermal polymerization above 250°C. The optimum conditions for preparation of "B-staged" resins were found to be ∿ 290°C, 1 hr, and in N_2 atmosphere. When reaction was carried out in air, skinning occurred. When the reaction was run at temperatures around 250°C, the gelatin occurred in a considerably longer reaction time (∿ 21 hrs).

Crosslinking of the resins also occurred rapidly at temperatures around 300°C. In all cases, one hour molding time was sufficient to obtain tough, infusible, insoluble polymer discs. Increasing molding time from one hour to four hours did not appreciably improve the properties (e.g., Tg and moisture absorption).

No volatile materials were evolved during polymerization at temperatures above 250°C. This enabled monomers to be molded into void- and blister-free polymer discs as observed in most cases. The easy processability of these monomers may be attributed to the fact that preformed imide monomers were involved in the polymerization reaction. The ability of the nadimide system to undergo thermal addition polymerization so readily is probably due to a combination of ring strain and the formation of two other reactive species, maleimide and cyclopentadiene, upon retrograde Diels-Alder reaction. Unstrained olefins are quite reluctant to polymerize in the absence of initiators, particularly the cationic or coordination type. Bismaleimides, also possessing a strained ring, are the only other type known to react this way. Thus, the bisnadimides and bismaleimides are unique in their ease of processing and are by no means representative of the usual type of addition polymerization monomers.

To clarify the mechanism of the polymerization, the reaction was followed by infrared spectroscopy. No essential changes were observed in the infrared spectrum during polymerization. This is reflected in nearly identical IR spectra that were obtained both for the crosslinked polymer discs and the corresponding monomers. Thus, infrared spectroscopy offers no useful information on the chemical change of the reaction. The retention of cyclopentadiene during the polymerization is confirmed by the results of elemental analysis, given in Table II, which approached closely with those of the corresponding monomers.

NMR spectroscopy offers an important clue to the mechanism of the addition polymerization. Figures 21-22 show the NMR spectra of the "B-staged" polymers thermally cured from monomers 2 and 3. Comparison of these spectra with those of the corresponding monomers revealed that a new signal at δ 6.28 appeared in the NMR spectra of the "B-staged" polymers. This signal is probably due to the vinyl protons of the cyclopentene moiety of the polymers formed.

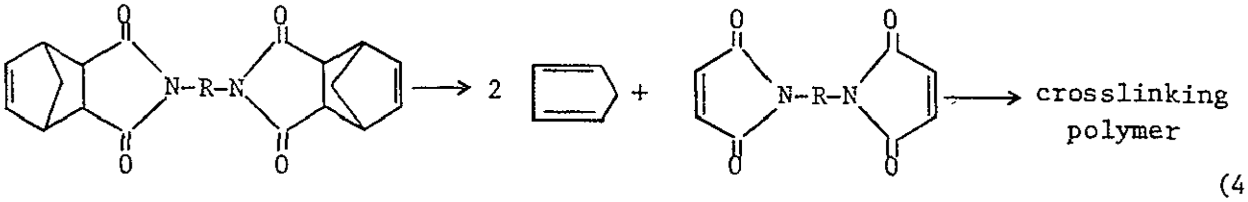


This correlation was corroborated when the resins were thermally advanced from 1/2 hr to 1 hr, for the relative intensity of the signal at δ 6.28 increased while the relative intensity of the signal at δ 6.10 decreased. The latter signal is assigned to the vinyl protons of the monomers. The NMR spectra offer sound evidence for the insertion of the cyclopentene moiety between maleimide groups as the mechanism by which crosslinking occurs in these polymer systems. The NMR spectrum of the "B-staged" polymer from monomer 5 is shown in Fig. 23.

2. Catalytic Polymerization

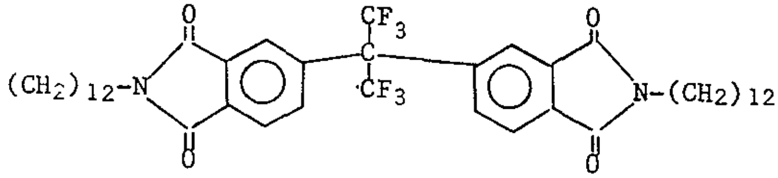
The peroxide catalyzed vinyl polymerization of 2, 3, and 5 was attempted, but, though the polymerization was successful, we failed to achieve our second objective of curing the monomers at a temperature below 260°C (500°F). The peroxides tested include dicumyl peroxide, cumene hydroperoxide, t-butylhydroperoxide, and benzoyl peroxide.

Since the temperatures for the decomposition of the peroxides (as shown in Table III) are substantially lower than the temperatures required for the reverse Diels-Alder reaction (302°C, 575°F), it was felt that vinyl polmerization (crosslinking) could be affected by one of these peroxides in the temperature range (91°C to 200°C) noted, thereby preventing the reverse Diels-Alder reaction. This did not occur. Crosslinking was accomplished at 300°C (575°F) and above via the Diels-Alder route, as shown in Eq. (49).



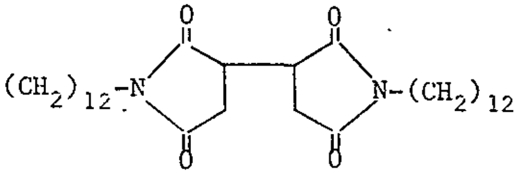
(49)

where 2 , R =



3 , R = $(CH_2)_{12}$

and 5 , R =



3. Copolymerization

Several attempts to achieve copolymerizations of 3 with divinylbenzene, and of 4 with HFA and MDA failed.

A possible explanation in the case of 3 and divinylbenzene is the fact that the latter polymerizes more readily than 3. Divinylbenzene polymerizes at a temperature of approximately 150°C while 3 requires a temperature above 250°C.

In the case of 4 with HFA or MDA, steric hindrance generated during attempted copolymerization might prevent polymerization. In addition, the effectiveness of $BF_3.NH_2Et$ and/or dibutyltin dilaurate as catalysts for the copolymerization raised some questions.

Copolymerization between two bisnadimides, i.e., 2 and 3, 2 and 5, and 3 and 5, has also been studied. The processing of the comonomer mixtures is similar to that of a single monomer.

Visual inspection of the copolymer discs prepared indicated that they were probably homogeneous, and most likely consisted of copolymerized molecular chains.

C. Characterization of Polymer Discs

1. Structure

Polymer discs 3, 6, 7, 11, 20, 25, 27, and 15 were selected for structural identification. Their structures were suggested on the basis of evidence from the IR spectra and elemental analysis of the polymer discs, the NMR spectra of some of the "B-staged" polymers, and in concurrence with the mechanism of the polymerization discussed previously., and are depicted below in 30, 31, 32 and 33 through 37.

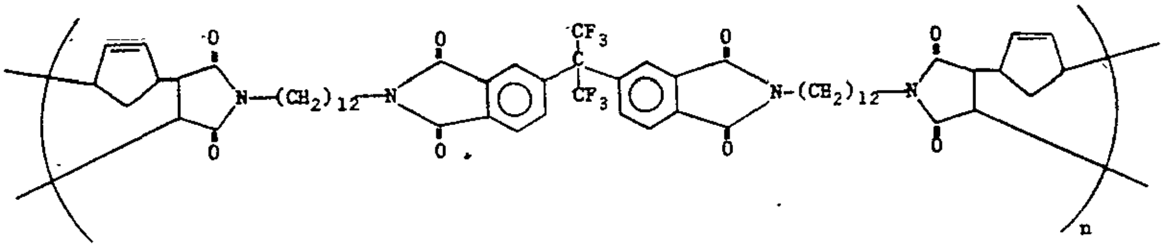
The fourier transform infrared spectra of the polymer discs are shown in Figs. 24-31. The characteristic imide absorption bands at 1770, 1700 and 720 cm^{-1} appear in all of the spectra of the polymers as in those of the monomers 2, 3, 4, and 5. This suggests that the imide group of the monomers remains intact in their polymers. Other noteworthy absorption bands which appeared at 2930, 2840, 1430, and 1380 cm^{-1} in all of the spectra of the polymer discs may be attributable to the presence of aliphatic chain groups. In the spectra of polymer discs 3, 6, and 25 (Figs. 24, 25, and 29) the olefinic absorption bands appear at 3050 and 1620 cm^{-1}. As mentioned previously, the NMR spectra (Figs. 21 and 22) support the presence of a new olefinic function - cyclopentene - in the polymers.

Table II summarizes the results of the elemental analysis. As indicated in Table II, the experimental values for the percentages of carbon, hydrogen, nitrogen, and fluorine fit reasonably well with the corresponding theoretical values that were calculated based on the proposed structures as represented by formulas 30 through 37 shown below. As shown in Table IV, the results of the elemental analysis of the polymers prepared from monomer 2 in the presence of a peroxide consistently gave lower values of carbon percent (e.g., 64.30 percent C for disc-6) than that obtained from the analysis of the polymer prepared from the same monomer in the absence of a peroxide (66.05 percent C for disc-3).

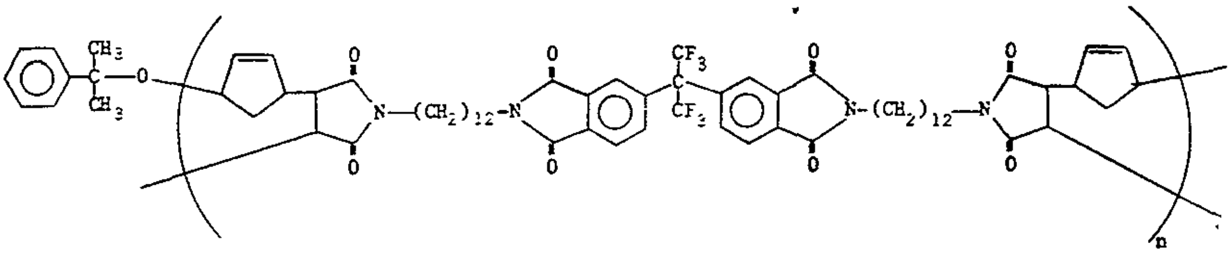
2. Moisture Absorption Studies

The polymer discs prepared were treated with distilled water at room temperature over a period ranging from one to three weeks. In some cases, the discs were also exposed to boiling distilled water. The quantity of water absorbed was determined periodically. The results of the moisture absorption

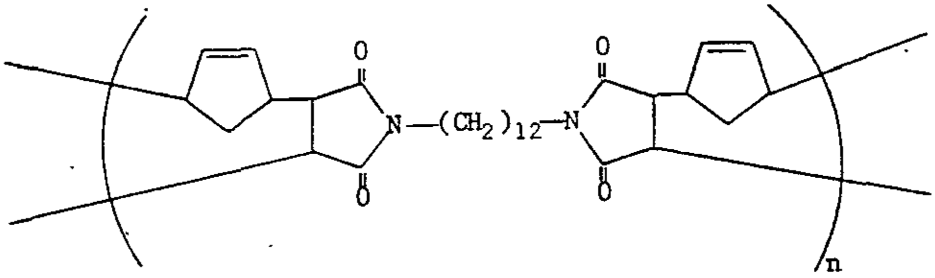
Proposed Structural Formulas



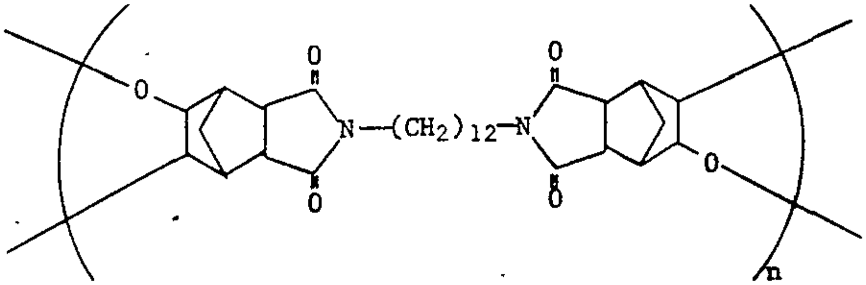
30



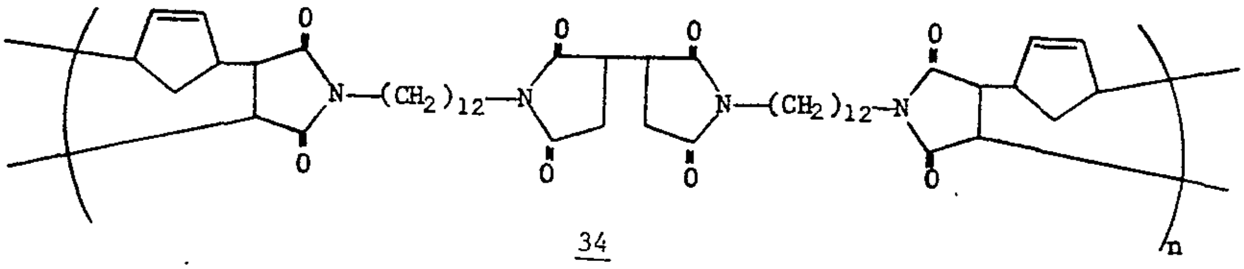
31



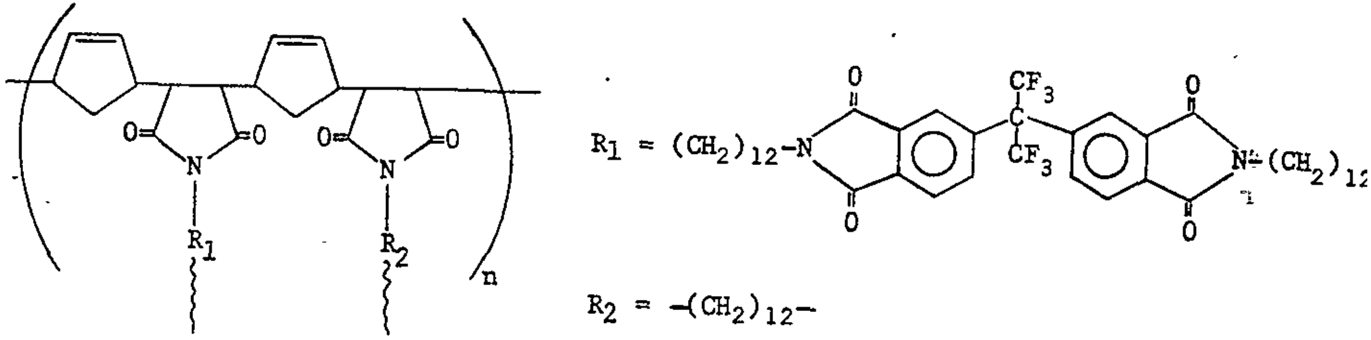
32



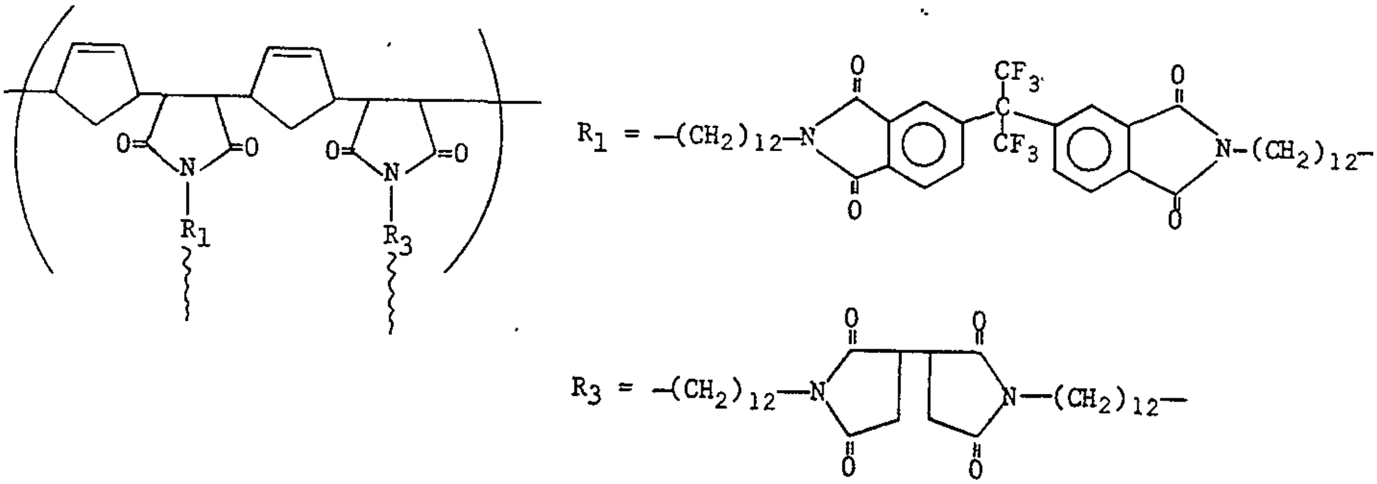
33



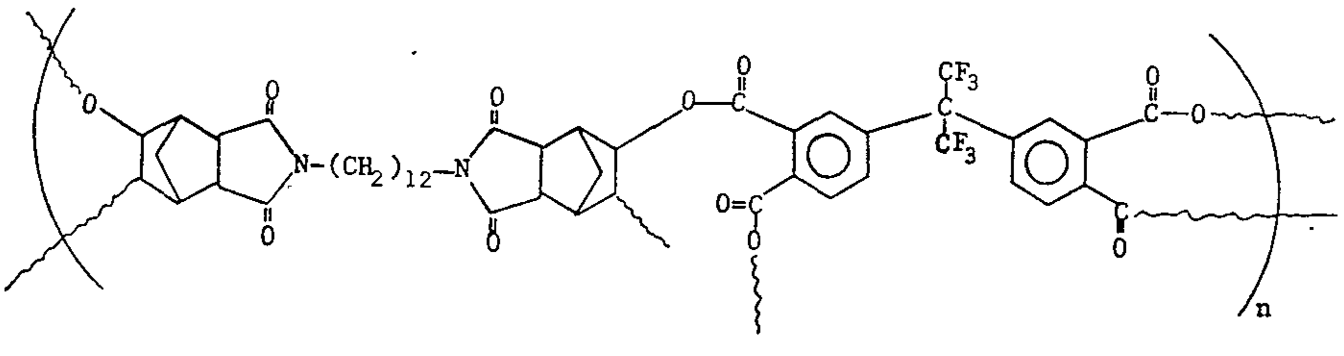
34


R1 = (CH2)12-N
CF3
C
CF3
N-(CH2)12
R2 = —(CH2)12—
n

35


R1 = —(CH2)12—N
CF3
C
CF3
N-(CH2)12—
R3 = —(CH2)12—N
N—(CH2)12—
n

36


N-(CH2)12—N
CF3
C
CF3
n

37

studies are given in tables V-XI. Excellent moisture resistant characteristics of polymers from monomer 2 have been realized. Polymer disc-4, for example, absorbed 0 percent moisture, when it was immersed in distilled water at room temperature for 72 hrs. This experiment was repeated four times and the same results were obtained each time. Thus, the moisture absorption behavior of this disc must be real. Polymer discs from monomer 2 consistently ranked best in moisture resistance among all of the aliphatic polyimide discs prepared. Table XII shows a comparison of moisture resistant characteristics among aliphatic polyimides prepared in this study, and aromatic polyimides (PMR-15, and PMR-11), and conventional epoxy polymer discs (epoxy 934 and epoxy 6350) prepared in the in-house work.

A significant improvement in the moisture resistence of aliphatic polyimide from monomer 2 over conventional epoxy polymers and aromatic polyimides is clearly indicated in the table.

3. Isothermal Weight Loss

Table XIII summarizes the isothermal weight loss of polyimides. Most of the polymer discs suffered less than 5 percent weight loss after aging 500 hrs at 260°C (500°F) in air. Most of these discs remained intact and showed good heat resistance. Few, however, exhibited lines of crack.

4. Glass Transition Temperatures (Tg)

Table XIV shows the glass transition temperatures of the polymer discs. Figure 32 shows a typical thermogram of polymer which indicates a sharp peak at 125°C corresponding to the Tg of the polymer. The values varied from 100 to 200°C. They are substantially lower then the Tg's of aromatic polyimides (300 to 400°C) but are comparable to those of epoxy polymers (150-100°C). Polymers from monomer 3 consistently ranked highest in Tg whereas those from monomer 5 gave loweest values. The correlation between lowering Tg and increasing aliphatic character is therefore established for these aliphatic polyimides. What is also known as demonstrated by Scola and Stevens (Ref. 1) is that increasing aliphatic content of polyimides also increases their moisture resistant characteristics. Thus, increasing aliphastic character of a polymer can exert two effects, namely increasing moisture resistance and decreasing Tg. From this, it follows that only a good balance betwee aliphatic and aromatic contents in the backbone of a polyimide can achieve both high Tg and high moisture resistant properties. Disc-4, which showed excellent moisture resistance, gave 93 percent retention of Tg after isothermal treatment at 260°C (500°F) for 600 hrs, indicating high thermal stability of this polymer. It also showed 90 percent retention of Tg after 7 days exposure to distilled water at room temperature.

5. Differential Scanning Calorimetry

The DSC thermograms of polymer discs 3, 7, 11, and 20 are shown in Figs. 33 through 36. All of the polymers showed exothermic transitions probably due to the decomposition of the polymers at temperatures above 450°C. No transitions occurred at temperatures below 250°C, indicating that the resins were adequately cured.

IV. EXPERIMENTAL

General Method

Infrared spectra of monomers were recorded as thin films on a Perkin-Elmer Model 457 grating spectrophotometer. Infrared spectra of polymers were recorded as potassium bromide pellets containing ∿ 0.25 mg of the substances and 300 mg of KBr on a Nicolet Fourier Transform Spectrometer Model 7199. Proton nuclear magnetic resonance (NMR) spectra were obtained on a Varian A-60A instrument in deuterated chloroform as solvent. Chemical shifts were reported in ppm from tetramethylsilane with the number of protons responsible for the signal added in parentheses. Letters denote the multiplicity: bs, broad singlet, s, singlet, d, doublet, m, multiplet. Mass spectra were recorded on a JEDL Model JMS-D100 spectrometer. Gel permeation chromatograms were run with a Waters Associate High Performance Liquid Chromagraph, equipped with a Differential Refractometer R401 and an Ultraviolet Absorbance Detector Model 440. Glass transition temperatures were determined on a DuPont Thermomechanical Analyzer Model 943. Melting points were determined on a Thomas Hoover melting point apparatus and were left uncorrected. Elemental analyses were performed by Galbraith laboratories.

Materials

5-Norbornene-2,3-dicarboxylic anhydride, m.p. 164-4°C, was purchased from Eastman; 1,12-diaminododecane, m.p. 62-5°C from Aldrich; and 4, 4'-methylene dianiline, m.p. 90-2°C from Matheson Coleman and Bell. These reagents were used as received.

1. N-(12-aminododecyl)-5-norbornene-2,3-dicarboximide (1)

Route A -

In a 500-ml four-necked round-bottom flask equipped with a stirrer, a reflux condenser, a thermometer, a Dean-Stark trap, and a dropping funnel was placed a solution of 1,12-diaminododecane (60.0g, 0.30 mole) in 140 ml of dimethylformamide (DMF). A solution of 5-norbornene-2,3-dicarboxylic anhydride (50.0 g, 0.305 mole) in 100 ml of DMF was added at room temperature. The contents of the flask were protected from moisture by a drying tube. This mixture was stirred and refluxed under N_2 atmosphere for 96 hrs. The water formed during the imidization was condensed and collected in the Dean-Stark trap. Evaporation of the DMF on a rotary evaporator under reduced pressure (1 mm) yielded a brown oil. To remove the trace amount of DMF, the oily materials were placed overnight in an oven at 160°C and 72.2 mm pressure. The IR spectrum (Fig. 2) showed major peaks at 3300, 3040, 2920, 2850, 1760, 1680, 1515, 1425, 1220, and 720 cm^{-1}. The NMR spectrum (Fig. 8) exhibited the following signals: δ 8.00 (bs, 1a CO_2H and DMF CH), 6.00 (bs, 1 C=CH), 3.22 (bs, bridge head H, CCH, and $N-CH_2$), 2.97 (bs, DMF $N-CH_3$), 2.80 (bs, DMF $N-CH_3$), 1.67 (s, bridge H), 1.59 (s, bridge H), and 1.25 (bs, CH_2 and NH_2).

The gel permeation chromatogram (Fig. 1) showed one major peak corresponding to the desired product, in addition to three minor peaks which were identified to be the amic acid intermediate <u>1a</u>, bisnadimide <u>3</u>, and the unremovable DMF. The elemental anaylsis gave the following results:

Calc for $C_{21}H_{34}N_2O_2$: C, 72.8; H, 9.9; N, 8.1

Found: C, 70.5; H, 9.5; N, 7.4

Liquid chromatography of the mixture on silica gel using chloroform as eluting solvent gave <u>3</u> as the first fraction and <u>1</u> as the second fraction. Compound <u>3</u> obtained here had identical retention time in the gel permeation chromatogram and IR spectrum with those determined for the compound prepared by an independent synthesis. Evaporation of the solvent chloroform produced an analytical sample of <u>1</u>: yellow oil; IR: 3450, 3300, 3040, 2920, 1850, 1760, 1690, 1520, and 720 cm^{-1}; mass spectrum (30 eV) m/e (rel. intensity) 345 (6, M^+), 309 (27), 280 (2), 198 (16) 138 (6), 111 (12), 110 (37), 100 (18), 98 (11), 92 (10), 91 (19), 83 (10), 69 (16), 66 (100), 58 (17), 55 (18), and 30 (18); NMR: δ6.05 (2H, s, HC = CH), 3.22 (8H, bs, bridge head H, CH-C=O, and CH_2-N), 1.67 (1H, s, bridge H), 1.59 (1H, s. bridge H), and 1.25 (22H, bs, CH_2 and NH_2).

Calc for $C_{21}H_{34}N_2O_2$: C, 72.8; H, 9.9; N, 8.1

Found: C, 70.50; H, 9.51; N. 7.94

Considerable amounts of brown materials remained in the column and could not be removed by further elution with chloroform. Thus, acetone, a more polar solvent, was used to elute the residue. This led to the isolation of an analytical smaple of amic acid <u>1a</u> as a white solid, m.p. 97-99°C; IR (KBr); 3200, 3030, 2920, 2855, 2740, 1690, 1650, 1630, 1520; mass spectrum (75 eV) m/e (rel. intensity) 18 (10), 28 (15), 29 (18), 30 (100), 41 (48), 42 (11), 43 (22), 44 (21), 46 (54), 55 (52), 58 (93), 59 (63), 66 (4), 69 (34), 72 (40), 73 (23), 83 (20), 91 (1), 97 (110, 100 (45), 101 (12), 114 (34), 115 (13), 128 (19), 142 (15), 158 (14), 170 (18), 184 (16), 198 (25), 227 (6), and 228 (7).

Anal

Calc for $C_{21}H_{36}N_2O_3$: C, 69.2; H, 10.0; N, 7.7

Found: C, 69.25; H, 9.39; N, 7.35

Route B -

In the absence of solvents, equal molar quantities of the reactants were mixed thoroughly and then heated rapidly to obtain a melt phase, and maintained at 160°C to affect amidation and imidization. At 160°C, the reaction foamed indicating that a gas was being evolved. This was continued for 15 minutes until evolution ceased. The reaction mixture was then heated to 220°C to complete imidization. It was cooled to yield a tan-wax-like material, with no definite melting point. The infrared spectrum was identical to the oil isolated in Route A described above. In the second attempt, the reactants were heated at 220°C to a melt for 1/2 hour to yield a light yellow oily mixture. The infrared spectrum of this mixture was similar to the spectrum obtained on product made in the dimethylformamide solvent. Attempts to purify this product by sublimation resulted in removing unreacted 1,12-diaminododecane, leaving an oily residue whose infrared spectrum also showed the presence of the imide and acid amide products. Purification by solution in chloroform, followed by charcoal treatment and then solvent removal, yielded a white solid which gave the following elemental analysis.

Calc for $C_{21}H_{34}N_2O_2$: C, 72.8; H, 9.9; N, 8.1

Found: C, 70.1; H, 9.84; N, 8.03

The infrared again showed impurities which could be attributed to the acid-amide.

A third attempt to prepare a pure material was made by heating the starting materials in an atmosphere of nitrogen, at 220°C for 1 hour. The infrared spectrum of the yellow oily material produced showed strong absorption at 1640 cm^{-1}, in addition to the absorption at 1690 and 1765 cm^{-1} due to imide. Absorption at 1640 cm^{-1} decreased as the sample was heated for an additional 2 hours at 220°C. The infrared spectrum showed absorption due to imide and acid-amide.

A small portion of the oily product from the second run, was treated with 6N HCl. The insoluble material was removed by filtration. The acid solution was concentrated to an off-white solid. The infrared spectrum of this solid indicated that it was the hydrochloride salt of an amino compound. The spectrum showed strong absorption due to an imide group at 1765 and 1695 cm^{-1} and absorption at 1580 cm^{-1}, assigned to NH_3^+.

Route C -

1,12-Diaminododecane monohydrochloride was prepared by adding 0.122 mole (50 ml 1.9N HCl) of hydrochloric acid to a solution of 25g (0.125 mole) of 1,12-diaminododecane in 400 ml of tetrahydrofuran. The solution was concentrated to a white solid. The white solid was triturated in ether three times to remove unreacted diamine. The crude product was recrystallized from absolute ethanol to yield 24.5g (88%) of white crystalline monohydrochloride salt, mp 243-260°C. The infrared spectrum was consistent for the desired product. Elemental analysis gave the following results:

Anal

Calc for $C_{12}H_{29}N_2Cl$: C, 60.8; H, 12.2; N, 11.8; Cl, 15.10

Found: C, 60.5; H, 12.2; N, 11.7; Cl, 15.14

Next, to a solution of 7.5 g (0.046 mole) of nadic anhydride was added 10g (0.042 mole) of 1,12-diaminododecane monohydrochloride. The reaction mixture was refluxed for 3 hours then cooled to RT and then at -5°C. The crystalline off-white material which formed while cooling was removed by filtration. The off-white solid melted at 320-325°C with decomposition. The infrared spectrum of the hydrochloride salt of 1 showed absorptions at 1765 and 1596 cm^{-1} due to imide functionality, and at 1600 cm^{-1} due to NH_3^+ functionality. It was similar to the spectrum of the water soluble hydrochloride salt produced by treatment of the yellow oily material from the second reaction described previously. The elemental analysis gave:

Calc for $C_{21}H_{34}N_2O_2Cl$: C, 65.86; H, 9.21; N, 7.32; Cl, 9.25

Found: C, 53.52; H, 11.31; N, 10.06; Cl, 25.03

The elemental analysis was inconsistent for the monohydrochloride of the desired product. Calculated values for the dihydrochloride salt of 1,12-diaminododecane were compared with the experimental values shown as follows:

Calc for 1,12-diaminododecane dihydrochloride

$C_{12}H_{30}N_2Cl_2$: C, 52.7; H, 10.99; N, 10.26; Cl, 25.98

Found: C, 53.5; H, 11.21; N, 10.06; Cl, 25.03

It is clear that the compound isolated was the dihydrochloride salt of 1,12-diaminododecane.

The filtrate from the reaction mixture was concentrated to an oily solid. This solid was slurried in cold ethanol, filtered, and the white solid which collected was washed with a small amount of water. The white product was air dried to yield 4.7g, mp 76.5-80°C. The infrared spectrum of this solid was not consistent for the desired product. Elemental analysis gave the following results:

Calc for $C_{21}H_{34}N_2O_2$ (1): C, 72.8; H, 9.9; N, 8.1

Found: C, 72.8; H, 8.4; N, 5.8

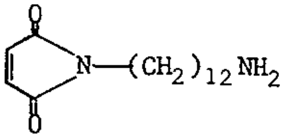
Calc for $C_{30}H_{36}N_2O_4$ (3): C, 73.1; H, 8.2; N. 5.69

The infrared spectrum showed strong imide absorptions at 1700 and 1770 cm^{-1}, but no absorption due to an amino group. The elemental analysis and infrared spectrum are consistent for N,N'-dodecamethylenedi-5-norbornene-2,3-dicarboximide.

The ethanol filtrate was concentrated to an oil, extracted with 10% sodium hydroxide (50 ml). The heavy amber oil which separated out was extracted with ether (3 x 30 ml). The water phase became clear. The combine ether extracts were dried over anhydrous sodium sulfate, decanted and then concentrated to an amber oil (labeled N10182F). The infrared spectrum showed strong amine absorptions at 3450 and 3350 cm^{-1}, and absorptions in the imide and carbonyl regions consistent for imide and amide functionalities. The oil was triturated in ether to a white solid. Elemental analysis gave the following results.

Found: C, 64.7; H, 10.75; N, 9.99

This analysis is inconsistent for the desired compound, but is close for the corresponding maleic anhydride derivative



Calc for $C_{15}H_{28}N_2O_2$: C, 67.1; H, 10.4; N, 10.4

Route D -

To a refluxing and stirred solution of 9 (30.0g, 0.15 mole) in THF (100 ml), a solution of 8 (25.0g, 0.153 mole) and P_2O_5 (21.3g, 0.15 mole) in THF (100 ml), was added. The mixture was refluxed overnight and concentrated to give a white solid. This compound did not melt at a temperature up to 300°C. The IR exhibited prominent bands at 3050, 1070, 2910, 2820, 1760, 1690, 1630, 1550, 1140-20 (doublet), and 720 cm^{-1}.

2. Preparation of 4,4'-hexafluoroisopropylidene bisphthalic anhydride (10) -

This compound was isolated from a DuPont resin solution labeled NR-150B2 in N-methylpyrrolidinone (NMP). Using the procedure of W. Alston (NASA-Lewis private communication), 536g of NR-150B2 (58 w/o solids) yielded 174 g (70%) of white, purple-tinged tetra acid, m.p. 230-234°C. The tetra acid was treated with acetic anhydride to yield white 4,4'-hexafluoroisopropylidene bisphthalic anhydride (150 g, 65% yield), m.p. 244-245°C. IR: 3070, 1840, 1770, 1330, 1180, 1140, 885, and 830 cm^{-1}.

3. N,N'-[[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis[(1,3-dioxo-5,2-isoindolinediyl)dodecamethylene]]di-5-norbornene-2,3-dicarboximide (2)

Method A -

A solution of crude 1 (20.0g, 0.058 mole) prepared by Route A in 100 ml of DMF was added dropwise over a period of 1 hr to a stirred and refluxing solution of 10 (12.9g, 0.029 mole) in 100 ml of DMF. The contents of the flask and dropping funnel were protected from moisture by drying tubes. The water formed during the reaction was removed via the Dean-Stark trap. The mixture was refluxed under N_2 atmosphere for 48 hrs. After cooling to room temperature the reaction flask was refrigerated overnight. Approximately 0.2g of black solid that precipitated from the brown reaction solution was removed by suction filtration. The brown filtrate was concentrated under reduced pressure (1 mm) to give dark brown oil which was placed in a vacuum oven (76.2 mm) at 120°C overnight in order to remove traces of the DMF. This produced 32.77g of crude 2 as a dark brown oil. The gel permeation chromatogram of this brown oil exhibited 5 peaks corresponding to the desired product (80%), the unreacted 1 (7%), the unreacted 10 (6%), amic acid intermediate of 2 (3%), and DMF (4%). The presence of those compounds was confirmed by NMR and IR.

The mixture (2g) was dissolved in chloroform and the solution was washed first with 5% HCl solution and then with saturated NaCl solution. The combined organic layer was dried over $MgSO_4$, filtered, and then concentrated under reduced pressure to give a yellow oil. Chromatography of the oily material on silica gel, first with chloroform and then with acetone as eluting solvents afforded an analytical sample of 2 (0.2g):

yellowish crystals, m.p. 103-4°C. IR (neat) (Fig. 4): 3070 (w, C=CH), 2935 (CH_2 and CH), 2860 (m, CH_2 and CH), 1775 (m, $\overset{O}{\overset{\|}{C}}$-N), 1710 (vs, $\overset{O}{\overset{\|}{C}}$-N), 1640 (m, C=C), 1600, 1440, 1400, 1370, 1260, 1210, 1140, 850, and 725 (m, $\overset{O}{\overset{\|}{C}}$-N) cm^{-1}. NMR ($CDCl_3$) (Fig. 9): δ 1.27 (bs, 40 H, N-C-CH_2), 1.45 (bs, 2 H, bridge H), 1.62 (bs, 2 H, bridge H), 1.68 (bs, 2 H, bridge-head H), 1.90 (bs, 2 H, bridge-head H), 3.17-3.50 (m, 12 H, N-CH_2 and $\overset{O}{\overset{\|}{C}}$-CH), 6.08 (bs, 4 H, C=C-H), 7.35 (s, 2 H, Ar-H), 7.80 (s, 2 H, Ar-H), and 7.85 (s, 2 H, Ar-H). Mass spectrum (75 eV) m/e (rel. intensity 492 (21), 427 (22), 426 (21), 361 (42), 316 (11), 250 (11), 110 (62), 98 (19), 92 (14), 91 (29), 69 (12), 67 (24), 66 (100), 65 (32), 55 (25), 39 (23)

DSC (Fig. 13) endotherms at 80°C, 160°C, 260°C, and exotherms above 300°C.

Anal

Calc for $C_{61}H_{70}F_6N_4O_8$: C, 66.51; H, 6.41; F, 10.36; N, 5.09

Found: C, 65.24; H, 6.45; F, 10.90; N, 5.10

Method B -

To a stirred and refluxing solution of 10 (50g, 0.104 mole) in 50 ml of DMF, a solution of 9 (43.6g, 0.218 mole) in 100 ml of DMF was added in two portions. The reaction mixture was refluxed for 2 hrs. After refrigeration overnight, a white solid precipitated and filtered to give a crude off-white waxy material (18.6g), m.p. 73-86°C, recrystallization of the crude product from ethanol yielded an off-white powder, m.p. 96.5-99.5°C, IR: 3250, 2900, 2820, 1770, 1700, 1630, 1520, 1455, 1360, 1250, 1200, 840, 780, and 650 cm^{-1}; NMR: δ 8.0 (s, 2H), 7.7 (s, 2H), 7.18 (s, 2H), 3.21 (t, 8H), and 1.25 (s, 44H).

The filtrate was concentrated to afford a green and glassy material (66.5g) m.p. 125-130°C, NMR: δ 7.92 (s), 3.7 (t), and 1.27 (s).

Anal

$(C_{29}H_{30}F_6N_2O_4)_n$ as imide polymer Calc: C, 63.7; H, 5.5; F. 13.8; N, 5.1

Found: C, 62.7; H, 6.58; F, 15.25, N. 5.68

4. N,N'-dodecamethylenedi-5-norbornene-2,3-dicarboximide (3)

To a stirred solution of 1,12-diaminododecane (84.0g, 0.42 mole) in 100 ml of DMF, a solution of nadic anhydride (131.2g, 0.80 mole) in 100 ml of DMF was added dropwise over a 1/2 hr period at a temperature of 65°C. The mixture was refluxed for 2 hrs. The solution was concentrated under reduced pressure and cooled in a refrigerator. White crystals which precipitated from the solution were filtered and dried in air to give 118g (57% yield) of crude 3. Two recrystallizations of crude 3 from ethanol yielded an analytical sample:

White crystals, m.p. 79-80°C
IR (neat) (Fig. 5): 3060 (w, C=CH), 3010 (w, C=CH), 2930 (m, CH_2 and CH), 2860 (m, CH_2 and CH), 1770 (doublet, w, $\overset{O}{\overset{\|}{C}}$-N), 1700 (vs, $\overset{O}{\overset{\|}{C}}$-N), and 730 (m, $\overset{O}{\overset{\|}{C}}$-N) cm^{-1}
NMR ($CDCl_3$) (Fig. 8): δ 1.23 (bs, 20 H, N-C-CH_2), 1.43 (bs, 2 H, bridge H), 1.5 bs, 2 H, bridge H), 1.67 (bs, 2 H, bridge-head H), 1.83 (bs, 2 H, bridge-

head H), 3.05-3.50 (m, 8 H, N-CH$_2$ and $\overset{O}{\overset{\|}{C}}$-CH), 6.07 (bs, 4 H, C=CH).
Mass spectrum (75 eV) m/e (rel. intensity) 493 (23, M+), 427 (21), 361 (35), 317 (13), 151 (15), 111 (12), 110 (35), 98 (14), 92 (11), 91 (23), 67 (20), 66 (100), 65 (15), 55 (17), 41 (14).
DSC (Fig. 14) endotherm at 80°C and exotherms above 275°C.

Anal.

Calc for $C_{30}H_{40}N_2O_4$: C, 73.12; H, 8.19; N, 5.69

Found: C, 73.21; H, 8.32; N, 5.57

5. <u>N,N'-dodecamethylenebis[5,6-epoxy-2,3-norbornanedicarboximide]</u> (4)

In a 500-ml four-necked round-bottom flask equipped with a stirrer, a reflux condenser, an addition funnel and a thermometer, was placed a solution of N,N'-dodecylbisnadimide (24.7g, 0.05 mole) in 200 ml of chloroform. Peracetic acid (47.6g, 0.25 mole) and sodium acetate (2.0g) were added dropwise during stirring. The epoxidation proceeded at room temperature for 60 hrs. Concentration of the reaction solution gave white solid. This white solid was washed with 100 ml of 10% potassium bicarbonate, 100 ml of water, filtered and dried in air to give 26.0g (99% yield) of crude 4 m.p. 104-114°C. Two-fold recrystallization of the crude product from ethanol afforded the following analytical sample:

White solid, m.p. 119-120°C

IR (neat) (Fig. 6);2910 (m, CH$_2$ and CH), 2840 (m, CH$_2$ and CH), 1750 (w, $\overset{O}{\overset{\|}{C}}$-N), 1685 (vs, $\overset{O}{\overset{\|}{C}}$-N), 920 (w, $\overset{O}{C-C}$), and 720 (w, $\overset{O}{\overset{\|}{C}}$-N) cm^{-1}. NMR ($CDCl_3$) (Fig. 11): δ 0.98 (bs, 2 H, bridge H), 1.16 (bs, 2 H, bridge H), 1.25 (bs, 20 H, N-C-CH$_2$), 1.60 (bs, 2 H, bridge-head H), 1.77 (bs, 2 H, bridge-head H), 2.93-3.25 (m, 8 H, N-CH$_2$ and $\overset{O}{\overset{\|}{C}}$-CH), 3.33 (bs, 2 H, $\overset{O}{CH-C}$), 3.47 (bs, 2 H, $\overset{O}{C-CH}$).
Mass spectrum (30 eV) m/e (rel. intensity) 525 (18, M+), 497 (16), 496 (13), 471 (12), 469 (18), 461 (22), 444 (30), 443 (12), 333 (14), 235 (11), 221 (11),

193 (14), 192 (15), 180 (49), 110 (12), 109 (12), 108 (16), 107 (13), 91 (14), 83 (16), 82 (100), 81 (99), 79 (62), 77 (14), 66 (20), 55 (16).
DSC (Fig. 15): endotherm at 120°C and exotherms above 275°C.

Anal.

Calc for $C_{30}H_{40}N_2O_6$: C, 68.67; H, 7.77; N, 5.34

Found: C, 68.69; H, 7.95; N, 5.24

6. Preparation of Butanetetracarboxylic dianhydride (17) -

To a solution of 60.0g (0.26 mole) of 1,2,3,4-butanetetracarboxylic acid (supplied by Essex Group) in 225 ml THF, 112.5 ml of acetic anhydride (supplied by Matheson Coleman and Bell) was added. The mixture was refluxed for 2-1/2 hrs. After cooling to room temperature, white crystals were formed and removed by suction filtration to give 50.4g (99.3% yield) of crude 17, m.p. 247-250°C. Recrystallization of the crude product from acetone gave pure 17; m.p. 248-249°C (Lit. (Ref. 8) m.p. 248°C); IR; 2990, 2930, 1750, 1400, 1360, 1300, 1220, 1060, 920 and 660 cm^{-1}; NMR ($CDCl_3$): δ 3.30 (m, 2H) and 2.60 (d, 4H, J = 4 Hz).

7. N,N'-Bis[12-(5-norbornene-2,3-dicarboximido)dodecyl]-1,2,3,4-butanetetracarboxylic 1,2:3,4-diimide (5)

To a stirred refluxing solution of 17 (11.06g, 0.05 mole) in 100 ml of DMF, a solution of crude N-(12-aminododecyl)-5-norbornene-2,3-dicarboximide (1) (40 g, 0.115 mole) in 200 ml of DMF was added dropwise over a period of 1/2 hr. The reaction mixture was protected from moisture by drying tubes and refluxed for 76 hrs under N_2 atmosphere. After cooling to room temperature, a trace of black solid precipitated from the dark brown reaction solution and was removed by filtration. Concentration of the filtrate under reduced pressure (1 mm) followed by placing the brown oil in a vacuum (76.2 mm) oven at 100°C overnight yielded 46 g of dark brown oil. The gel permeation chromatogram of the brown oil as shown in Fig. 19 indicated one major peak correlated to the desired product plus two minor peaks identified to be the unreacted starting materials. The presence of these compounds in the mixture was confirmed by both the NMR and IR spectra. This mixture was used for polymerzation studies and for the preparation of neat polymer discs. An analytical sample of 5 was obtained via the purification procedure described for 2 in Method A:

White crystals, m.p. 75-6°C
IR (neat) (Fig. 7): 3060 (w, C=CH), 3010 (w, C=CH), 2935 (m, CH_2 and CH), 2860 (m, CH_2 and CH), 1770 (doublet, w, $\overset{O}{\overset{\|}{C}}$-N), 1704 (vs, $\overset{O}{\overset{\|}{C}}$-N), and 730 (s, $\overset{O}{\overset{\|}{C}}$-N) cm^{-1}
NMR ($CDCl_3$) (Fig. 12): δ 1.25 (bs, 40 H, N-C-CH_2), 1.43 (bs, 2 H, bridge H), 1.60 (bs, 2 H, bridge H), 1.70 (bs, 2 H, bridge-head H), 1.87 (bs, 2 H, bridge-head H), 3.08-3.50 (m, 18 H, N-CH_2, $\overset{O}{\overset{\|}{C}}$-CH, and $\overset{O}{\overset{\|}{C}}$-$CH_2$-CH-$\overset{O}{\overset{\|}{C}}$), 6.10 (bs, 4 H, C=CH).
Mass spectrum (75 eV) m/e (rel. intensity) 493 (26), 427 (21), 361 (34), 316 (12), 110 (42), 92 (11), 91 (23), 66 (100), 55 (16), and 41 (12).
DSC (Fig. 16) endotherm at 76°C and exotherms above 275°C.

Anal.

Calc for $C_{50}H_{70}N_4O_8$: C, 70.21; H, 8.26; N, 6.56

Found: C, 70.06; H, 8.54; N, 6.57

8. Formylphthalic Anhydride –

To a three-liter neck round bottom flask equipped with a stirrer, condenser, drying tube (calcium chloride), addition funnel, thermometer and nitrogen inlet was added 900 ml of sodium dried toluene and 315g (1.65 mole) of trimellitic anhydride. This was heated to 80°C while 300 g (2.52 mole) of thionyl chloride was added dropwise over a 2 hour period. A clear orange solution resulted. Excess thionyl chloride was removed by distillation. This was continued until a negative test for silver nitrate was obtained. Xylene was then added to maintain the same volume as before distillation. To this was added 36g of freshly prepared palladium on barium sulfate catalyst. While stirring vigorously, hydrogen was bubbled through the solution and allowed to vent into distilled water. This was continued until no more hydrogen chloride evolved, as determined by a negative reaction with blue litmus paper. The reaction mixture was cooled to 50°C, 10g of activated charcoal was added, the material was heated and stirred. Finally it was filtered, using Celite to remove the charcoal. The filtrate was cooled and an equal volume of petroleum ether was added. This solution was cooled. The yellow solid which precipitated was filtered, and dried at 45°C in the vacuum oven, 92.9g (32% yield) m.p. 108-119°C. The filtrate was diluted with an equal volume of petroleum ether and cooled in the freezer. An additional quantity of solid (13.1g) was recovered, m.p. 88-105°C. A sublimed sample melted at 122-123°C (reported (Ref. 2) sublimed sample, m.p. 127-129°C). The infrared spectrum is consistent for the desired product.

9. Attempted Synthesis of 4-vinylphthalic anhydride (6)-

To a 250 ml flask equipped with stirrer, thermometer, and reflux condenser was added a slurry of 3.57g (0.0085 mole) of triphenylmethyl phosphonium bromide in 50 ml of sodium dried toluene. To this was added 2.8g of sodium methoxide while stirring. After stirring for 1 hour, 5.0g of 4-formylphthalic anhydride was added while stirring for 3 hours. Vacuum filtered the solid, and allowed filtrate to concentrate to an oil and solid. The solid melted at 115-126°C, and appeared to be unreacted 4-formylphthalic anhydride. The solid and filtrate were recombined, placed in the reaction flask, diluted with 50 ml of toluene. To this was added 6.52g of triphenyl methylphosphonium bromide and 1.0g of sodium methoxide, and the reaction mixture was stirred for 2 hours at room temperature, then filtered, to remove solid. The toluene filtrate was concentrated to a solid. The infrared spectrum of both solids was taken. The infrared spectrum of the toluene insoluble material showed no absorption due to the anhydride group and very weak absorption at 3040 cm^{-1} due to =C-H stretching. This was not considered to be 4-vinylphthalic anhydride, but contained absorption due to the aromatic ring. It was not further identified. The infrared spectrum of the toluene soluble material also showed no absorption due to anhydride, but showed absorption at 3045 cm^{-1} due to =C-H stretching, absorption at 1700-1725 probably due to carboxyl group or aldehyde group, absorption due to aromatic at 1590 and 1480 cm^{-1}, and aromatic substitution patterns at 885 cm^{-1} (lone H on aromatic ring), and at 700 and 740 cm^{-1} also due to aromatic substitution.

10. Attempted preparation of 1,3-Butadiene-2,3-dicarboxylic anhydride (7)-

(1) Synthesis of tetraethyl-1,1',2,2'-ethanetetracarboxylic acid (23) - According to the procedure of Bailey and Sorenson (Ref. 5), this compound was prepared on a 2 mole scale yielding 216g (68% yield) of tetraester 23, m.p. 73.5°C (Ref. 5).

(2) Synthesis of diethylester of 1,1',2,2'-ethanetetracarboxylic acid (24)-

Into a 2000 ml r.b. flast equipped with N_2 inlet, a stirrer, a reflux condenser, an additional funnel and a thermometer was placed a solution of tetraester 23 (62.8g), 0.20 mole) in 700 ml of absolute ethanol. To this was dropwise added over a period of 8-10 hrs at room temperature a solution of potassium hydroxide (31.8g, 0.48 mole) in 100 ml absolute ethanol. After the addition, the mixture was stirred for an addition 24 hrs under dry nitrogen atmosphere. The solid precipitated from the reaction solution was filtered to give a white crystalline produce (54.5g). This white solid was dissolved in a minimum quantity of water and acidified to pH = 1. On standing at room temperature overnight, a crystalline product formed. This was fileted, washed with cold distilled water to yield 25g (47.7%) of white product 24, m.p. 133-134° (Ref. 6). An additional quantity (5.0g) was obtained by extraction of the aqueous solution with ether, concentration of the ether to a solid.

(3) Synthesis of Piperidinium Hydrochloride -

Into a solution of 500g (5.88 mole) of piperidine in 200 ml ether, was slowly stirred 500 ml (6.0 mole) of concentrated hydrochloric acid. A white crystalline solid formed immediately. The solution was then concentrated to give a crystalline material. This solid was washed with anhydrous ether to yield 450g of crude product, piperidinium hydrochloride m.p. 234-240°C. A half portion was recrystallized from absolute ethanol to yield 175g white solid, m.p. 243-245°C (Ref. 6).

(4) Synthesis of 1,1'-[2,3-bis(ethoxycarbonyl)tetramethylene]dipiperidinium dichloride (25)-

A mixture of 24 (20.0g, 0.084 mole), piperidinium hydrochloride (20.4g, 0.168 mole), and a 37% aqueous formaldehyde (17.0 ml) was stirred at 60°C for 10 hrs. With a rotary evaporator, the reaction mixture was concentrated at 50°C to yield a green oily material, which was partially crysallized to yield a white solid. Further crystallization was induced by the addition of methanol-acetone. The white solid was fitered, air dried and further purified by dissolving it in methanol to which acetone was added. A white solid (5.4g, 15% yield) m.p. 163.5-165°C (Ref. 6) was obtained. The IR spectrum was consistent with a compound 25. An additional product, m.p. 156-8°C, 1.9g was recovered from the filtrate.

A solution of 25 (1.0g, 0.00227 mole) and 4,4'-methylenedianiline (0.2257g, 0.0013 mole) in 25 ml of dimethylacetamide was refluxed for 4 hrs. The solvent was removed by vacuum distillation, bp 63.5°C/10 mm Hg. A dark brown residue was afforded. The IR spectrum exhibited absorption at 3110, 2940, 2860, 1720 cm^{-1} and a series of bands in the region of 1540 to 855 cm^{-1}. The dark oil was treated with ether. A portion of the dark brown material persisted. The ether extract was concentrated to a brownish-orange oil. A DSC of the brownish-orange oil showed one sharp endotherm at 145°C. The IR spectrum of this oil was similar to the spectrum of the dark brown oil.

11. Synthesis of Polymers

Polymers were prepared in two stages. Step one involved thermal or thermal/catalytic cure of monomers to form "B-staged" polymers which were then fabricated into neat polymer discs during the second process. The following procedure used for the preparation of polymer disc-1 is representative.

A one inch by ten inch test tube, equipped with an N_2 gas inlet, an N_2 gas outlet, and a thermometer, received about 4.0g of crude monomer 2. Using an oil bath, the contents of the test tube was heated at a rate of 5°C per minute under N_2 atmosphere. The temperature was maintained at 200°C for 1/2 hr in order to evolve the DMF solvent, after which it was raised slowly to 290°C. Having been heated at 290°C the sample, which showed some flow, was removed immediately from the oil bath. Upon cooling to room temperature, the consolidated prepolymer was ground in a mortar to a fine powder.

The fine powder was placed in a mold having 1 inch diameter. After applying 200 psi (1.38 Mpa) press pressure, the mold was heated at a rate of 2 to 3°C per minute to a maximum temperature of 300°C. Following heating at 300°C under 200 psi (1.38 Mpa) pressure for 1 hr, the disc was cooled slowly under pressure and then extruded from the mold.

V. SUMMARY OF RESULTS AND CONCLUSIONS

On the basis of the preceding results we conclude as follows:

(1) The synthesis, purification, and characterization of five novel aliphatic imides have been firmly established. The evidence for the assigned structures was obtained by IR, NMR, and mass spectrometry. The nadimide system readily undergoes the reverse Diels-Alder reaction above 290°C to form cyclopentadiene and maleimides.

(2) Thirty new aliphatic polyimides have been fabricated using a two step procedure. The final cure was carried out at 300°C and 6.9-1.38 MPa (100-200 psi) for 1-4 hours. Most of the polymers were void-free indicating that no volatile materials were evolved during final cure.

(3) Organic peroxides exerted no appreciable catalytic effect on the rate of bisnadimide polymerization. Peroxides investigated include benzoyl peroxide, dicumyl peroxide, cumene hydroperoxide, and t-butylhydroperoxide. Thus, attempts to lower the processing temperature below 260°C (500°F) by using a peroxide catalyst were unsuccessful.

(4) Several polymers prepared from N,N'-[[2,2,2-trifluoro-1-(trifluoromethyl)-ethylidene]bis[1,3-dioxo-5,2-isoindolinediyl)dodecamethylene]]di-5-norbornene-2, 3-dicarboximide (compound 2) exhibited a significantly improved moisture resistance compared to conventional epoxy resins, as well as excellent thermooxidative stability.

VI. RECOMMENDATIONS

Two polymers derived from monomers 2 and 3, respectively, are recommended for composite fabrication and evaluation. This selection is based on their excellent moisture resistance, relatively easy processability, and high thermal stability.

VII. REFERENCES

1. Scola, D. A., and Stevens, M. P.: Studies to Synthesize Alicyclic - Aliphatic Polyimide Resins From Aliphatic Bisnadimides, Internal Corporate Report UTRC76-152, October 20, 1976.

2. Winslow, E. C., and Laferriere, A.: J. Poly. Sci., 60, 65 (1962).

3. Johnson, A. W.: Ylid Chemistry, Academic Press, New York, N. Y., p. 68, 1968.

4. Henrick, C. A., Böhme, E., Edwards, J. A., Field, J. H.: Amer. Chem. Soc., 90, 5926 (1968).

5. Bailey, W. J., and Sorenson, W. R.: J. Amer. Chem. Soc., 78, 2287-2290 (1956).

6. Zahorsky, U. I., and Musso, H.: Amer. Chem. Soc., 11, 1777-1788 (1973).

7. Scola, D.: Proposed Program to Synthesize Improved Moisture Resistant Polymers. Report P77-37, United Technologies Research Center, pp. 4-10, March 1977.

8. Alder, K., and Schumacher, M.: Ann, 564, 96 (1949).

9. Materials Engineering, Vol. 82, No. 4 (1975).

10. General Catalog of Perioxides and Specialty Chemicals', Lucidol Division, Pennwalt Corporation, Buffalo, N. Y.

Table 1

The Gel Permeation Chromatogram of Crude Product 1 From Route A

Peak No.	Retention Time (min.)	Area (%)	Compound	Method of Identification
1	17.5	5	3	Isolation and comparison of retention time and IR with authentic sample.
2	20.5	3	8	Isolation and identification by IR, Mass spec., and elemental analysis
3	25.0	90	1	Isolation and identification by IR, NMR, Mass spec., and elemental analysis.
4	34.5	2	DMF	Detection by NMR and comparison of retention time with authentic sample.

Table II

Results of Elemental Analysis of Polymer Discs

Monomer	Polymer Disc	Polyimide Structure	Molecular Formula	Elemental Analysis,%							
				Calculated				Found			
				C	H	N	F	C	H	N	F
2	3	30	$(C_{61}H_{70}F_6N_4O_8)_n$	66.51	6.41	5.09	10.36	66.05	6.72	5.16	10.43
2	6	31	$(C_{61}H_{70}F_6N_4O_8)_n$	66.51	6.41	5.09	10.36	64.30	6.60	5.01	10.29
3	7	32	$(C_{30}H_{40}N_2O_4)_n$	73.12	8.19	5.60	-	69.14	8.36	5.78	-
4	11	33	$(C_{30}H_{40}N_2O_6)_n$	68.67	7.77	5.34	-	72.02	8.24	5.13	-
5	20	34	$(C_{50}H_{70}N_4O_8)_n$	70.21	8.26	6.56	-	69.57	8.49	6.88	-
2+3	25	35	$(C_{91}H_{110}F_6N_6O_{12})_n$	68.56	6.90	5.27	7.15	66.32	6.58	5.60	7.98
2+5	27	36	$(C_{111}H_{140}F_6N_8O_{16})_n$	68.12	7.16	5.73	5.83	64.56	6.93	5.46	6.12
4+HFA	15	37	$(C_{49}H_{46}F_6N_2O_{12})_n$	60.74	4.75	2.89	11.78	58.74	5.30	3.48	11.09

Table III

Half-Life of Organic Peroxides (Ref. 10)

Peroxide	Temperature at Which Half-Life Equals 1 Hr, °C
Benzoyl Peroxide	91
Dicumyl Peroxide	135
Cumene Hydroperoxide	190
t-Butyl Hydroperoxide	200

Table IV

Results of Elemental Analysis of Polymer Discs Prepared from Monomer 2 in the Presence of a Peroxide[a,b]

Polymer Disc	%C	%H	%N	%F
6	64.30	6.60	5.01	10.29
4	64.30	6.24	5.21	10.11
5	64.23	6.23	5.36	10.96

[a] 1 mole % peroxide was used

[b] peroxides used include dicumyl peroxide, cumylhydroperoxide

Table V

Moisture Absorption Characteristics of Polymer Discs From Monomer 2

Time, Days	Wt % Moisture Absorbed								
	Exposure to Room Temp. Distilled Water					Exposure to Boiling Distilled Water			
	Disc-2	Disc-3	Disc-4	Disc-5	Disc-6	Disc-3	Disc-4	Disc-5	Disc-6
1	0.26	0	0	0	0.23		0.78	1.48	
2	0.07	0.80	0	0	0.23	3.07	1.45	1.40	1.46
3	0.37	----	0	0	0.43	----	1.01	1.48	1.48
4	----	----	0.03	0.02	----	----	1.50	1.95	----
5	----	1.23	0.05	0.01	----	3.44	----	----	----
6	----	1.35	0.05	0.03	----	3.48	----	----	----
7	0.59	1.41	0.08	0.03	0.53	3.59	1.80	----	1.80
8	0.83	1.41	0.10	0.05	0.53	3.82	2.00	2.00	1.80
9	0.19	----	0.10	0.07	0.58	----	----	----	1.81
10	0.19	----	0.10	0.10	0.56	----	2.00	2.01	1.88
11	0.26	1.56	----	----	0.60	3.84	----	2.09	1.88
12	----	1.56	----	----	----	3.94	----	2.09	----
13	----	1.57	----	----	----	4.60	2.05	2.23	----
14	0.37	1.60	0.15	0.12	0.68	4.74	----	2.24	----
15	0.22	1.60	0.15	0.15	0.68	4.75	----	2.33	2.02
16	0.07	----	0.18	----	0.68	----	2.20	2.34	2.02
17	0.07	----	0.20	----	0.68	----	2.50	2.45	2.02
18	----	1.60	0.20	0.20	0.68	4.75	2.50	2.58	----
19	----	1.63	----	0.20	----	4.75	----	2.58	----
20	----	1.66	0.21	0.21	----	4.74	2.20	2.64	----
21	----	1.66	0.21	0.21	----	4.75	2.50	2.67	----

Table VI

Moisture Absorption Characteristics of Polymer Discs From Monomer 3

Time, Days	Wt % Moisture Absorbed					
	Exposure to Room Temp. Distilled Water				Exposure to Boiling Distilled Water	
	Disc-7	Disc-8	Disc-9	Disc-10	Disc-7	Disc-9
1	0.22	0.24	0.29	0.32	1.64	1.55
2	0.29	0.36	0.54	0.47	1.92	2.35
3	0.52	0.53	0.78	0.99	----	2.42
4	----	----	1.03	----	----	2.47
5	----	----	1.72	----	----	----
6	----	----	----	----	1.92	----
7	0.60	0.73	1.45	0.97	1.92	----
8	0.77	0.79	1.52	0.98	1.92	2.47
9	0.77	0.82	----	1.02	1.92	2.48
10	0.84	0.82	----	1.10	1.92	----
11	0.88	0.83	----	1.10	1.92	----
12	----	----	----	----	----	2.52
13	----	----	----	----	----	2.54
14	1.06	0.95	1.65	1.19	1.92	2.58
15	1.06	0.97	1.76	1.20	1.92	2.61
16	1.09	0.99	1.74	1.21	1.92	----
17	1.10	0.99	1.81	1.24	1.92	----

Table VII

Moisture Absorption Characteristics of Polymer Disc-15[a]

	Wt % Moisture Absorbed	
Time, Days	Exposure to Room Temp. Distilled Water	Exposure to Boiling Distilled Water
4	-	-0.98
5	-	-2.12
6	-	-3.68
7	3.31	-4.55
8	3.53	-5.63
11	4.35	-7.75
12	4.65	-8.26
13	4.83	-8.66
14	5.02	-9.02

[a] Density = 1.2715 g/cc; fine cracks

Table VIII

Moisture Absorption Characteristics of Polymer Discs[a] From Monomer 5

	Wt % Moisture Absorbed		
	Exposure to Room Temp. Distilled Water		Exposure to Boiling Distilled Water
Time, Days	Disc 19	Disc 20	Disc 20
1	0.48	0.39	2.14
2	0.89	----	3.46
3	1.08	----	----
5	----	0.86	----
6	----	0.88	5.46
7	1.51	0.94	----
8	1.63	1.00	5.57
9	1.67	1.07	5.70
10	1.73	----	5.82
11	1.77	----	----
12	----	1.25	----
13	----	1.27	6.03
14	1.96	1.27	6.46
15	1.96	1.28	6.55
16	1.96	----	6.61
17	1.96	----	

---

[a] Density = 1.1172 g/cc; no voids

Table IX

Moisture Absorption Characteristics of Copolymer Discs From Monomers 2 and 3

Time, Days	Wt % Moisture Absorbed							
	Exposure to Room Temp. Distilled Water				Exposure to Boiling Distilled Water			
	Disc 22[a]	Disc 23[b]	Disc 24[c]	Disc 25	Disc 22	Disc 23	Disc 24	Disc 25
1	0.16	0.22	0.37	0.46	1.10	1.33	1.13	1.89
2	0.22	0.43	0.30	----	1.26	1.47	1.15	----
4	----	----	----	0.91	----	----	----	2.19
5	----	----	----	0.99	----	----	----	2.11
6	----	----	----	0.99	----	----	----	2.19
7	0.34	0.50	0.42	1.06	1.38	1.47	1.21	2.24
8	0.35	5.52	0.42	1.08	1.38	1.47	1.21	2.24
9	0.38	0.52	0.42	----	1.38	1.47	1.21	2.24
10	0.40	0.52	0.42	----	1.39	1.47	1.21	----
13	----	----	----	1.09	----	----	----	----
14	----	----	----	1.11	----	----	----	2.24
18	----	----	----	1.14	----	----	----	2.28
19	----	----	----	1.16	----	----	----	2.33
23	----	----	----	----	----	----	----	2.45
24	----	----	----	----	----	----	----	2.58
25	----	----	----	----	----	----	----	2.67
								2.67

[a] Density = 1.20 g/cc; line of cracks

[b] Density = 1.20 g/cc; no voids and no cracks

[c] Density = 1.20 g/cc; no voids and no cracks

Table X

Moisture Absorption Characteristics of Copolymer Discs From Monomers 2 and 5

	Wt % Moisture Absorbed					
	Exposure to Room Temp. Distilled Water			Exposure to Boiling Distilled Water		
Time, Days	Disc-26	Disc-27	Disc-28	Disc-26	Disc-27	Disc-28
3	0.41	0.84	0	1.97	2.79	0.85
4	0.45	0.93	0.20	1.97	2.96	1.96
5	0.53	1.03	0.39	2.00	3.09	2.70
6	0.57	1.04	0.44	2.01	3.10	2.70
10	0.59	1.11	0.46	2.08	3.20	2.87
11	0.63	1.11	0.51	2.24	3.20	2.95
12	0.63	1.13	----	2.26	3.20	----
13	0.63	1.14	----	2.30	3.20	----
14	----	----	----	2.34	3.20	----

Table XI

Moisture Absorption Characteristics of Polymer Disc-29

	Wt % Moisture Absorbed	
Time, Days	Exposure to Room Temp. Distilled Water	Exposure to Boiling Distilled Water
1	0.20	1.65
2	0.39	3.05
6	0.79	3.54
7	0.89	3.45
8	0.91	3.41
9	0.96	3.47

Table XII

Moisture Absorption Characteristics of Aliphatic Polyimides, Aromatic Polyimides, and Epoxy Polymers

	Wt % Moisture Absorbed					
Polymer Disc	Exposure to Room Temp. Distilled Water			Exposure to Boiling Distilled Water		
	24 hrs	168 hrs	336 hrs	24 hrs	168 hrs	336 hrs
Aliphatic Polyimide From Monomer 2	0	0.08	0.15	0.78	1.80	2.05
Aliphatic Polyimide From Monomer 3	0.24	0.73	0.95	1.64	1.92	1.92
Aliphatic Polyimide From Monomer 4	----	3.31	5.02	----	----	----
Aliphatic Polyimide From Monomer 5	0.39	0.94	1.27	2.14	5.50	6.46
Aromatic Polyimide PMR-15[a]	0.58	1.45	1.69	1.24	2.04	2.13
Aromatic Polyimide PMR-11[a]	0.60	1.75	2.16	1.71	2.37	2.43
Epoxy 6350[a]	0.25	0.69	1.03	1.38	2.99	7.18
Epoxy 934[a]	0.19	0.45	0.69	2.68	5.31	5.55

[a] Prepared in the in-house work.

Table XIII

Isothermal Weight Loss of Polyimides at 260°C (500°F) for 100, 200, 300, and 500 hrs in Air

		% Wt Loss			
Polymer Disc	Monomer(s) Used	100 hrs	200 hrs	300 hrs	500 hrs
6	2	1.28	1.84	2.63	2.64
3	2	2.81	4.63	4.61	4.60
2	2	4.82	7.46	7.89	7.94
4	2	0.97	0.97	0.97	1.02
5	2	2.17	2.93	2.93	2.94
7	3	1.13	1.13	1.13	1.13
8	3	1.51	2.77	2.77	2.94
9	3	1.14	1.99	1.99	2.01
11	4	8.87	13.58	13.58	13.59
20	5	1.83	2.81	2.81	2.80
19	5	2.82	3.99	3.89	3.98
26	2 + 5	2.03	3.13	3.15	3.15
27	2 + 5	3.06	4.37	4.52	4.52
25	2 + 3	3.18	5.05	5.18	5.59
29	3 + 5	6.02	10.03	10.05	10.94
15	4 + HFA	6.82	10.22	10.22	9.99
10	3 + divinylbenzene	1.95	3.33	3.34	4.35

Table XIV

Glass Transition Temperatures of Polymer Discs

Disc	Monomer(s) Used	Tg, °C[a]	Tg, °C[b]	Tg, °C[c]	Tg, °C[d]
6	2	125	120		
7	3	200	215		210
8	3	165			
10	3 + DVB	170			
15	4 + 10	130			
19	5	100			
20	5	100	120		
25	2 + 3	140	135	125	
4	2	123	115	110	
26	2 + 5	110			
27	2 + 5	110			
28	2 + 5	110			
22	2 + 3	140			135
23	2 + 3	140			
24	2 + 3	135			

[a] As fabricated

[b] After 500 hrs at 260°C (500°F)

[c] After 168 hrs exposure to room temperature distilled water

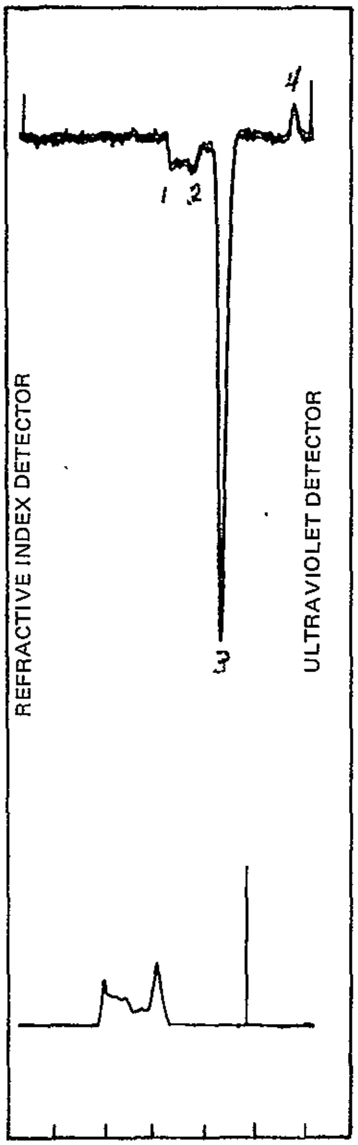
[d] After 168 hrs exposure to boiling distilled water

FIG. 1

GEL PERMEATION CHROMATOGRAM OF CRUDE N– (12–AMINODODECYL) –5–NORBORNENE–2,3–DICARBOXIMIDE

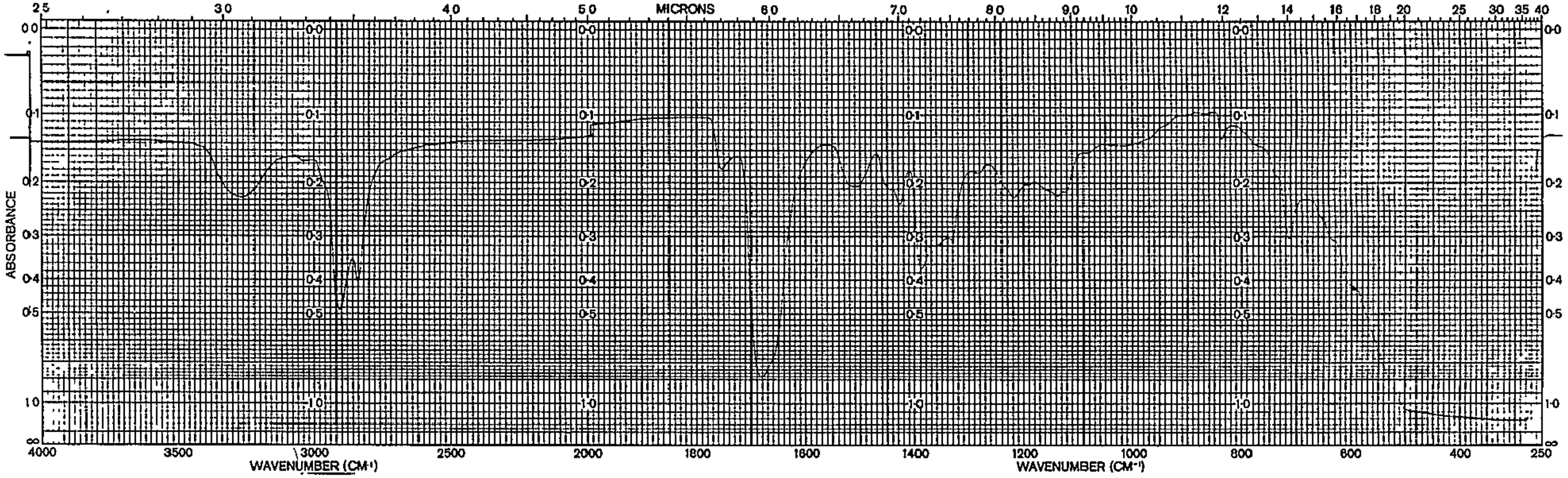
CONDITIONS

2–100 Å MICROSTYRAGEL COLUMNS
2.0 mℓ/MIN FLOW RATE
0.5 CM/MIN CHART SPEED
8XRI
2.0 UV } ATTENUATION
15.0 μℓ INJECTION
THF AS SOLVENT



R78-91294I-15.

IR OF N-(12-AMINODODECYL)-5-NORBORNENE-2,3-DICARBOXIMIDE



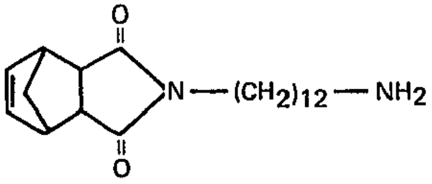
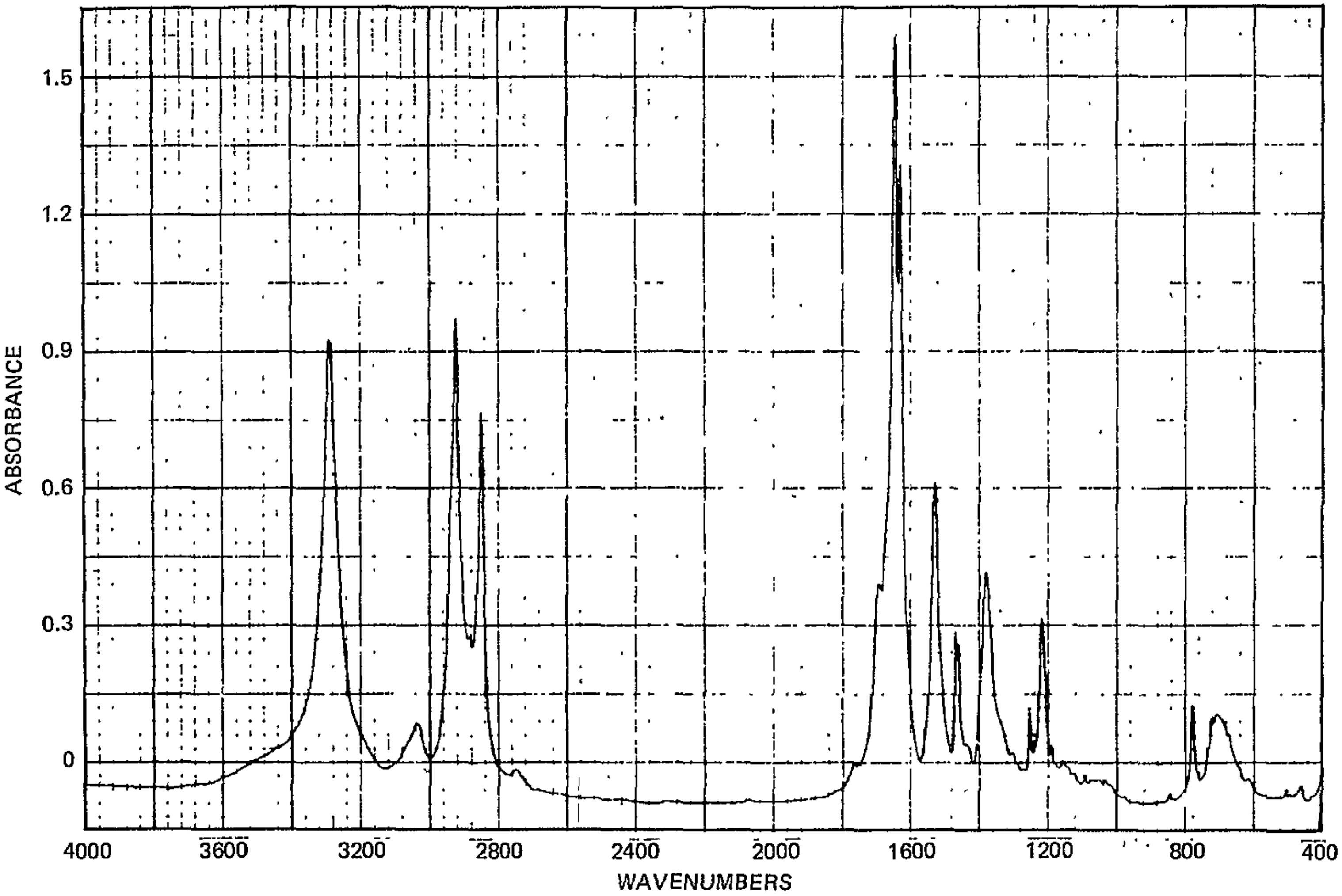


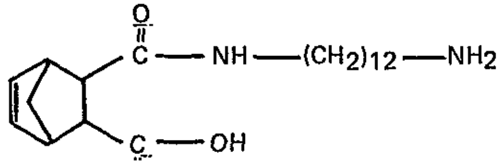
FIG. 2

78-12-11-1

R78–912941–15

FT–IR OF N–(12–AMINODODECYL)–5–NORBORNENE–2,3–DICARBOXIMIDE



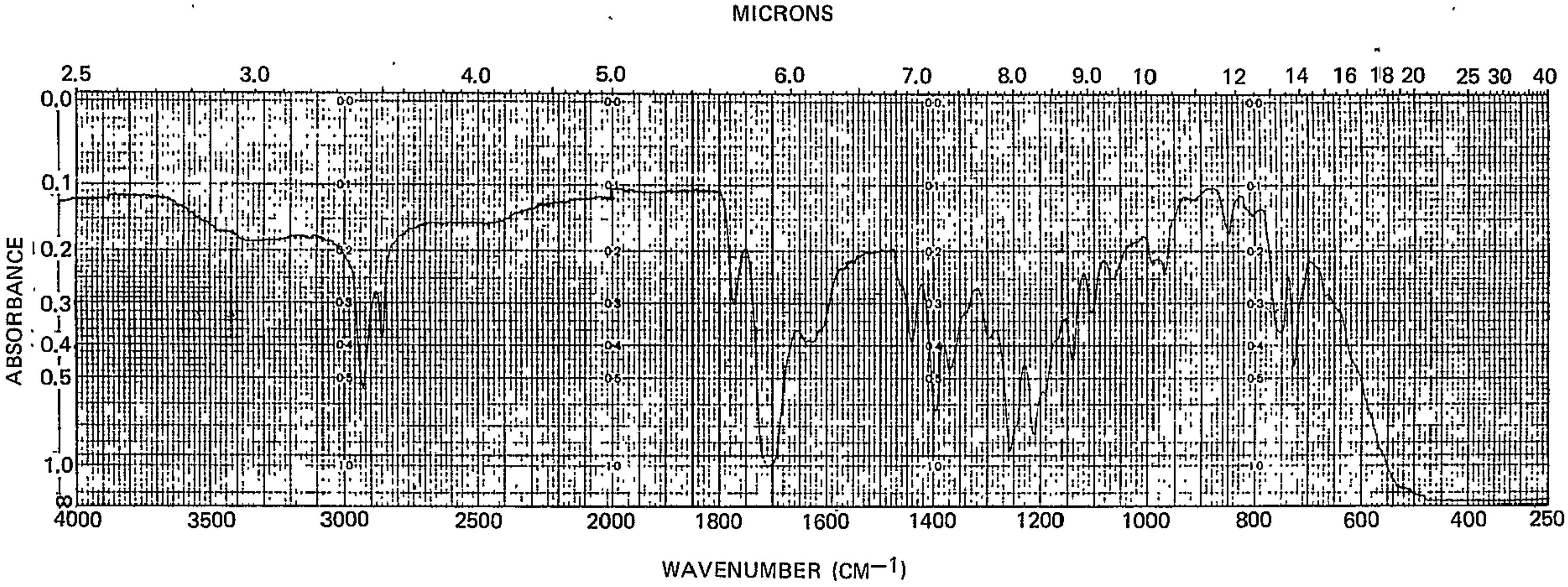


78–12–11

FIG

R78-912941-15

IR OF N,N'–[[2,2,2–TRIFLUORO–1–(TRIFLUOROMETHYL) ETHYLIDENE] BIS [(1,3–DIOXO–5,2– ISOINDOLINEDIYL)–DODECAMETHYLENE]] DI–5–NORBORNENE–2,3–DICARBOXIMIDE



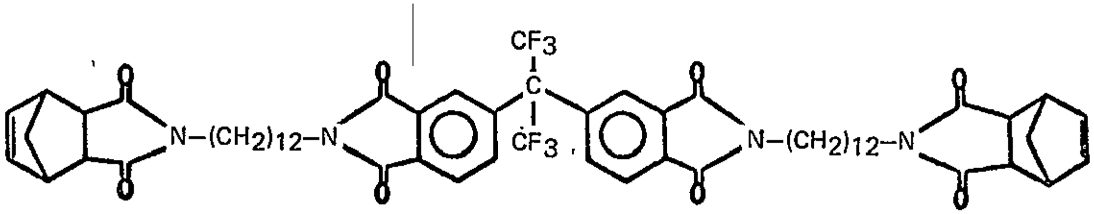
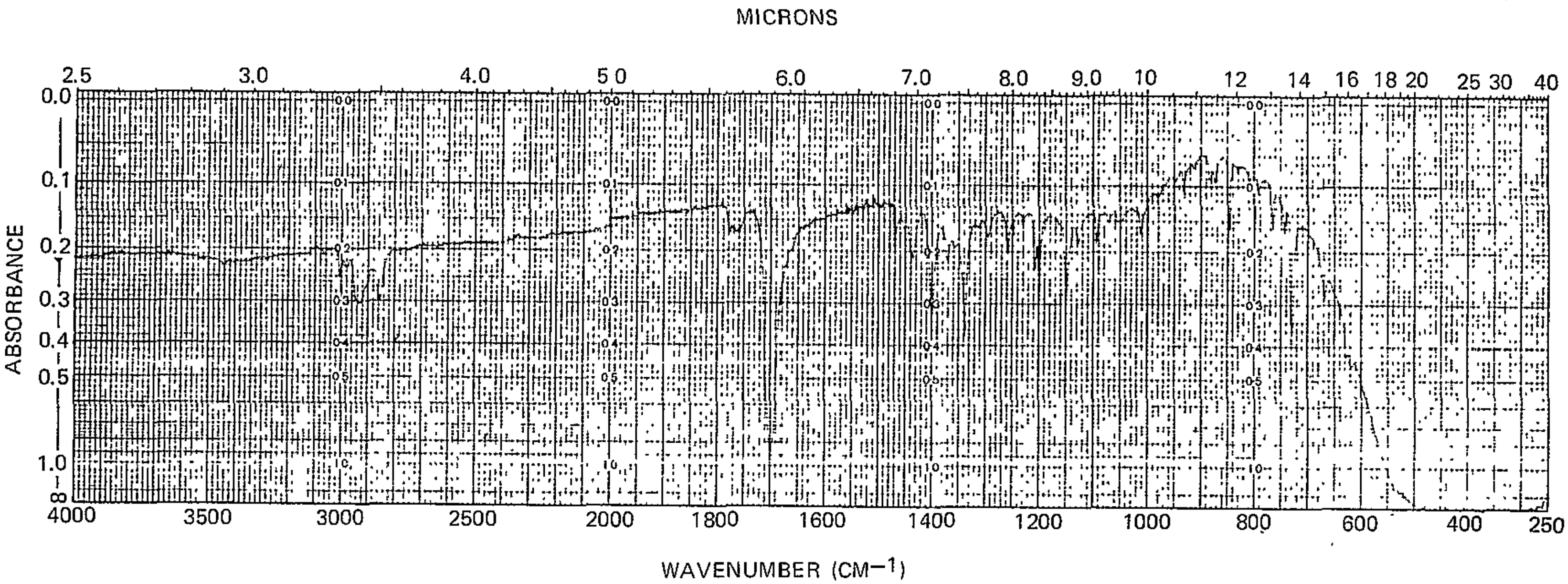


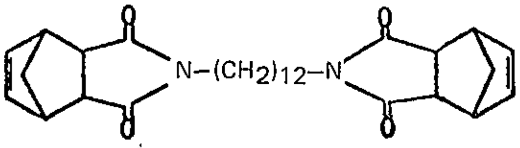
FIG. 4

78–09–11–6

R78-912941-15

IR OF N,N'–DODECAMETHYLENEDI–5–NORBORNENE–2,3–DICARBOXIMIDE



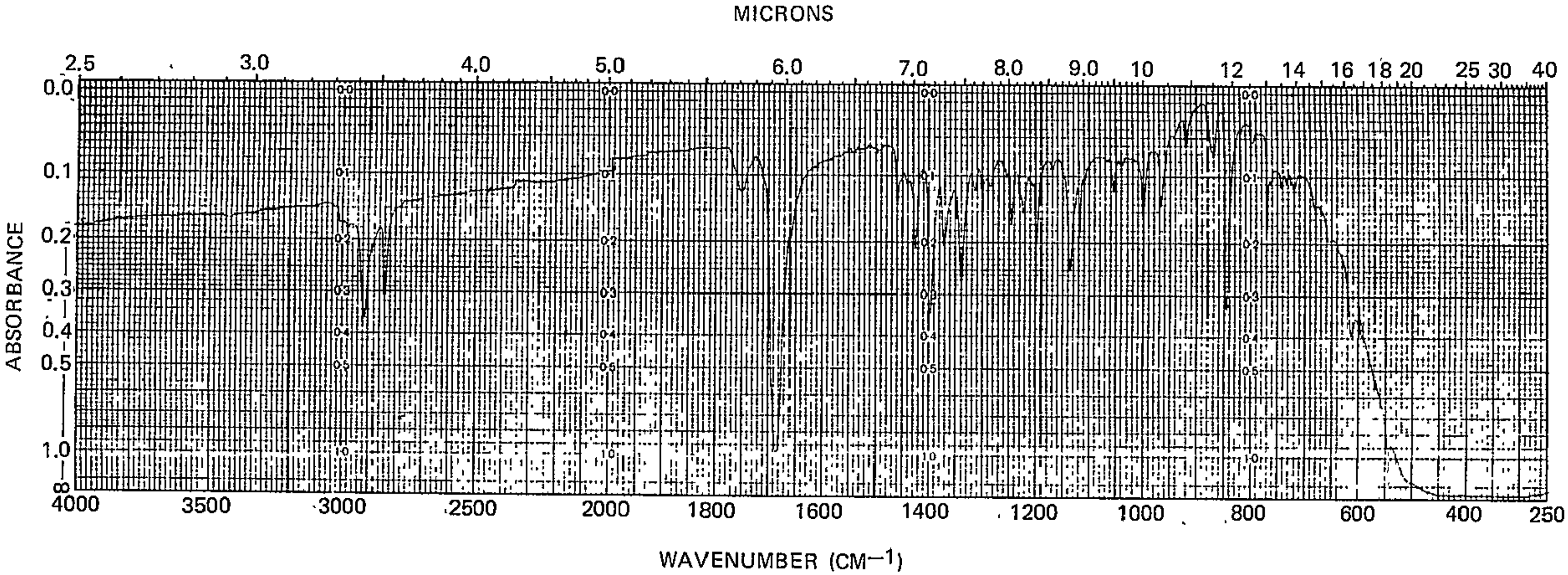


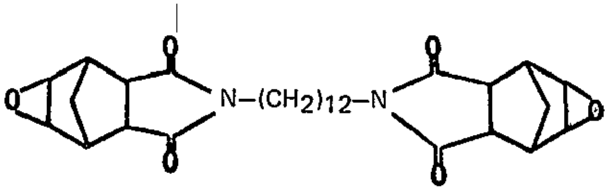
78–09–11–5

FIG. 5

R78–912941–15

IR OF N,N'–DODECAMETHYLENEBIS[5,6–EPOXY–2,3–NORBORNANEDICARBOXIMIDE]



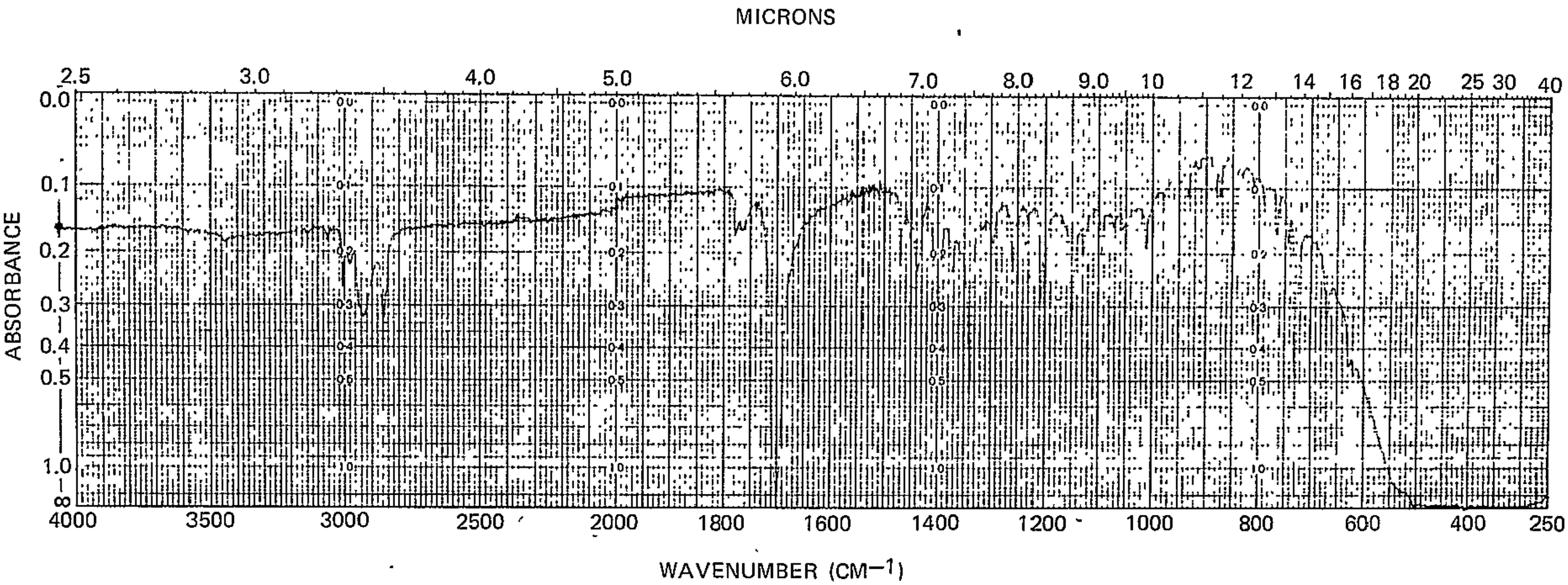


78–09–11–7

FIG. 6

R78–912941–15

IR OF N, N'-Bis[12-(5- NORBORNENE-2, 3-DICARBOXIMIDO)DODECYL]-1, 2, 3, 4-BUTANETETRACARBOXYLIC 1, 2:3, 4-DIIMIDE



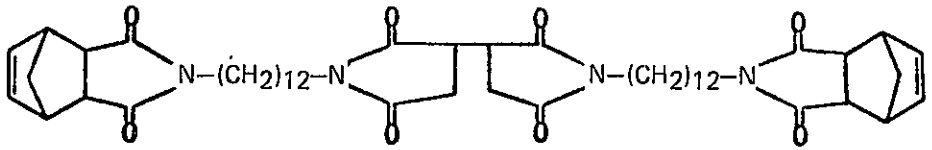


FIG. 7

78–09–11–8

NMR OF N–(12–AMINODODECYL)–5–NORBORNENE–2,3–DICARBOXIMIDE

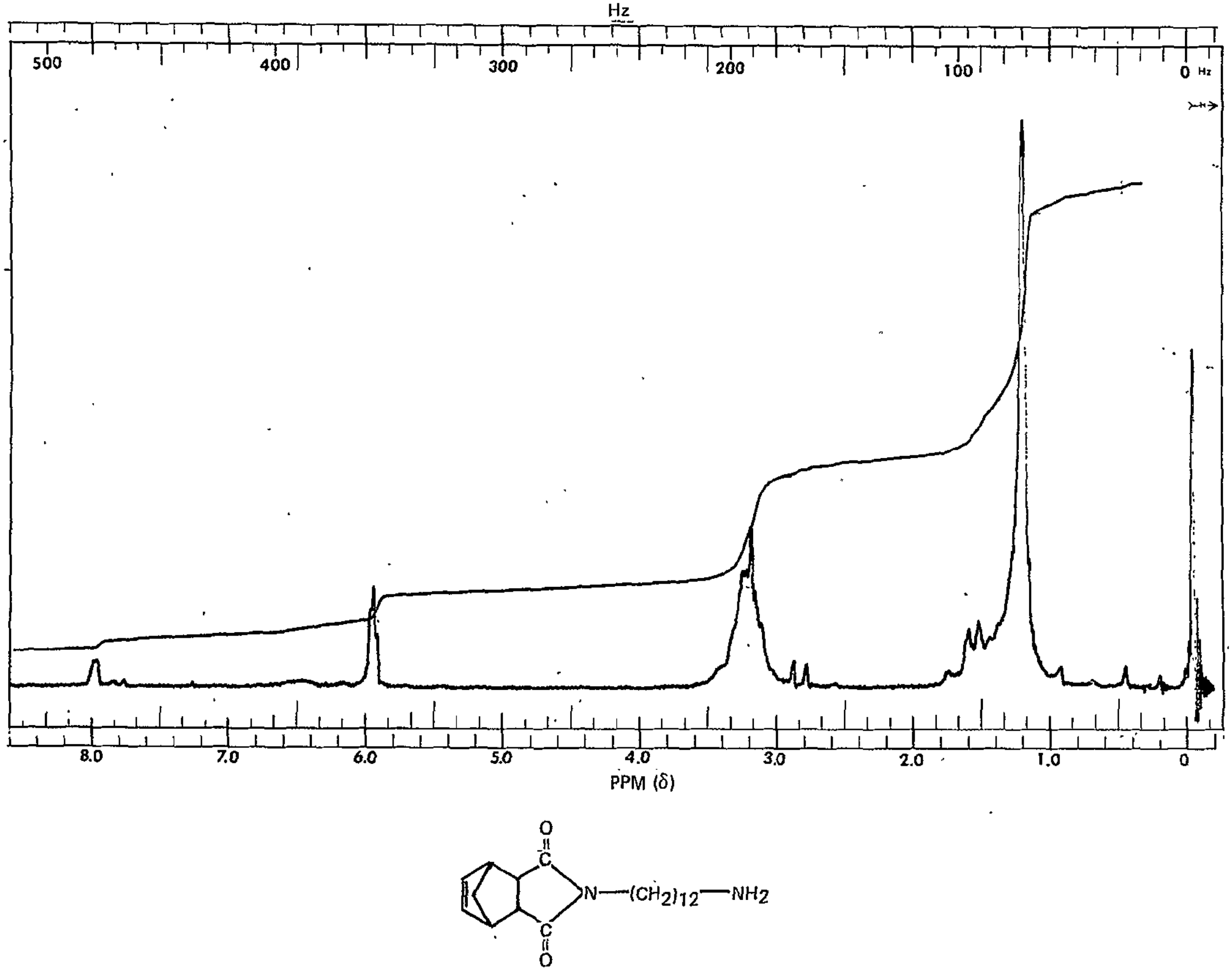
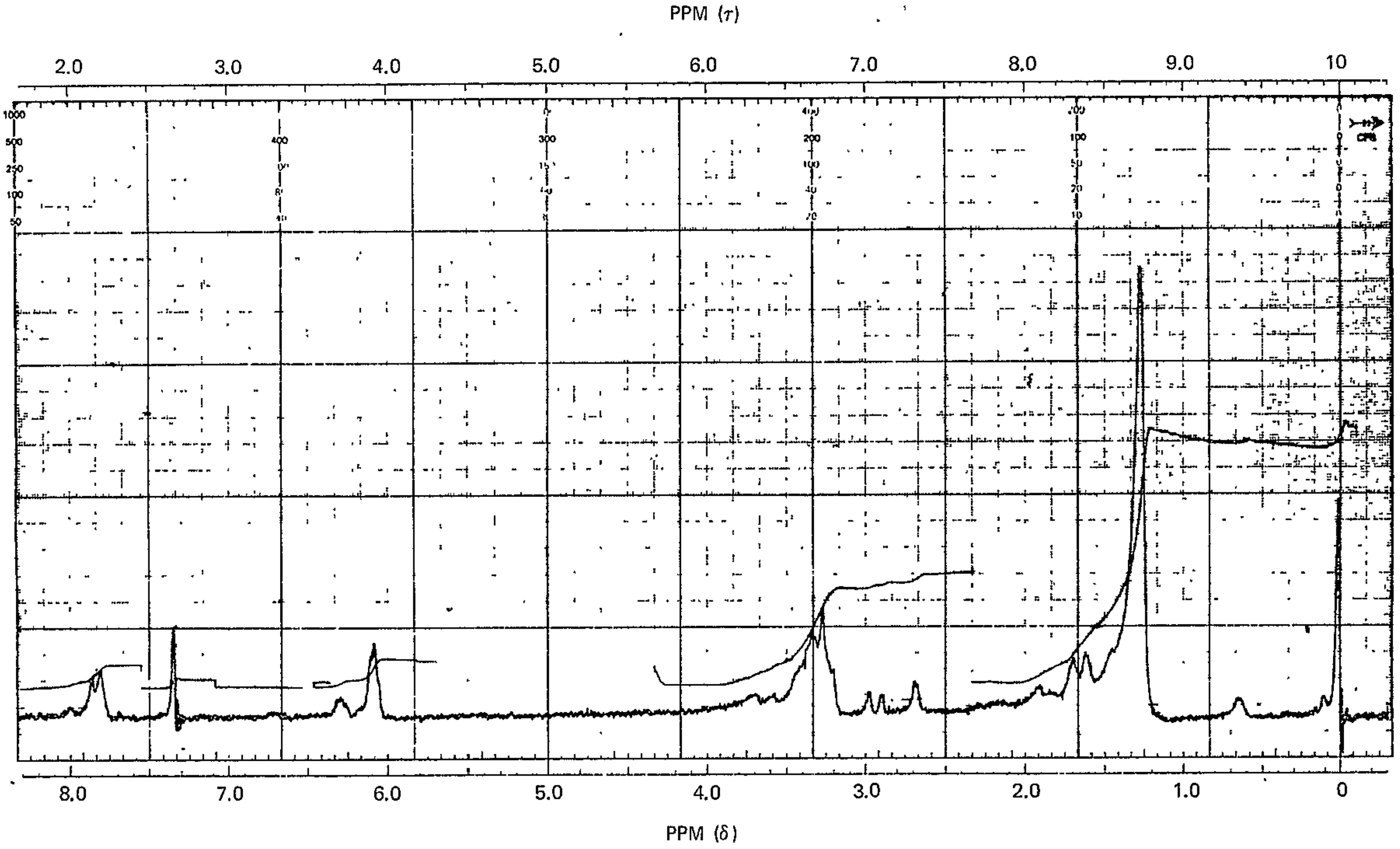
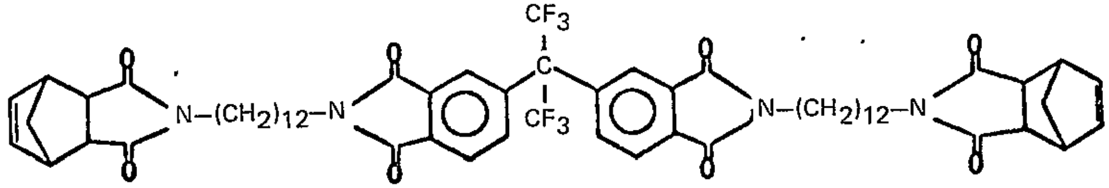


FIG. 8

R78–912941–15

NMR OF N,N′–[[2,2,2–TRIFLUORO–1–(TRIFLUOROMETHYL) ETHYLIDENE] BIS [(1,3–DIOXO–5,2– ISOINDOLINEDIYL)– DODECAMETHYLENE]] DI–5–NORBORNENE–2,3–DICARBOXIMIDE





78–09–11–1

FIG. 9

NMR OF N,N'–DODECAMETHYLENEDI–5–NORBORNENE–2,3–DICARBOXIMIDE

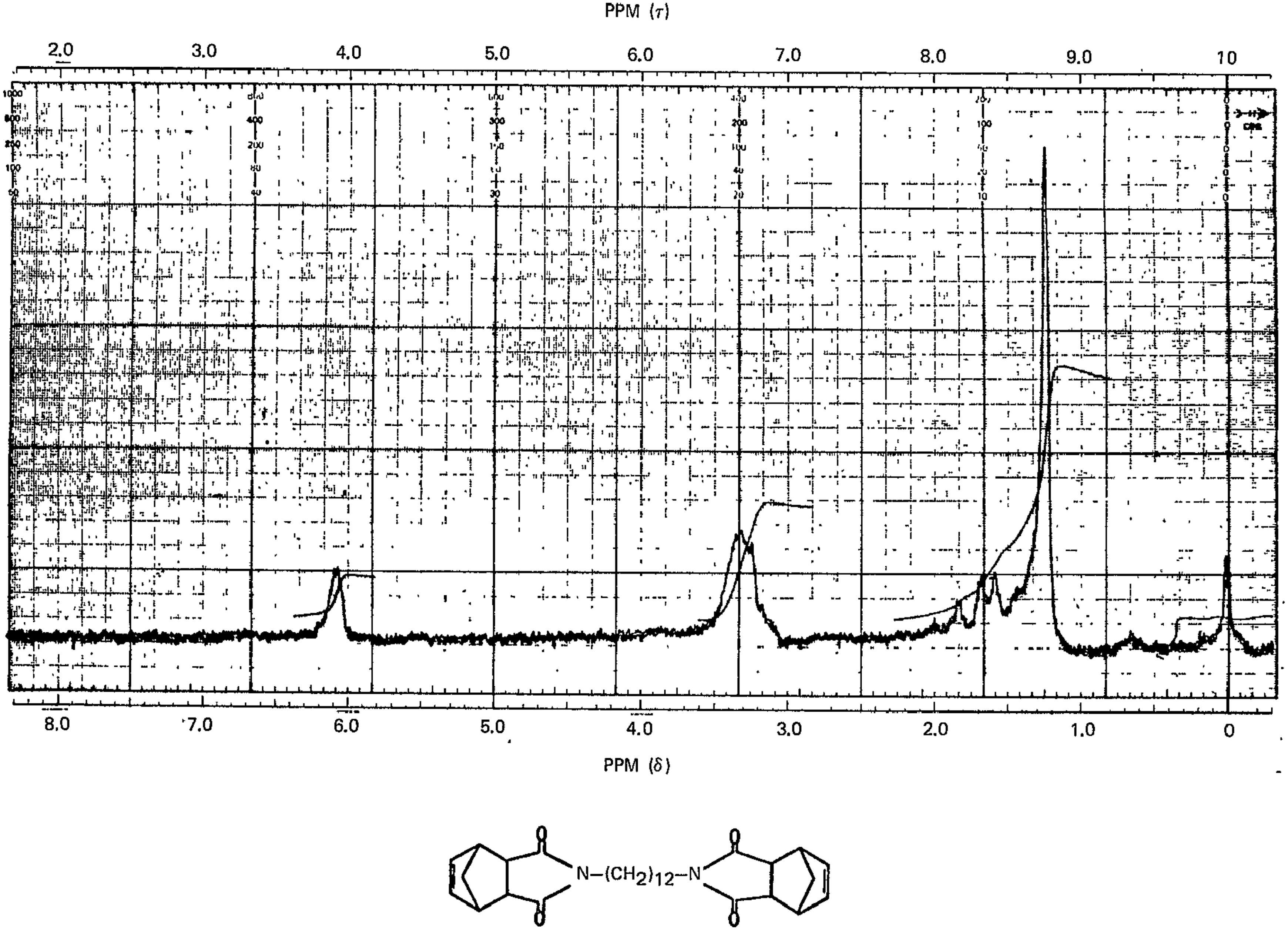
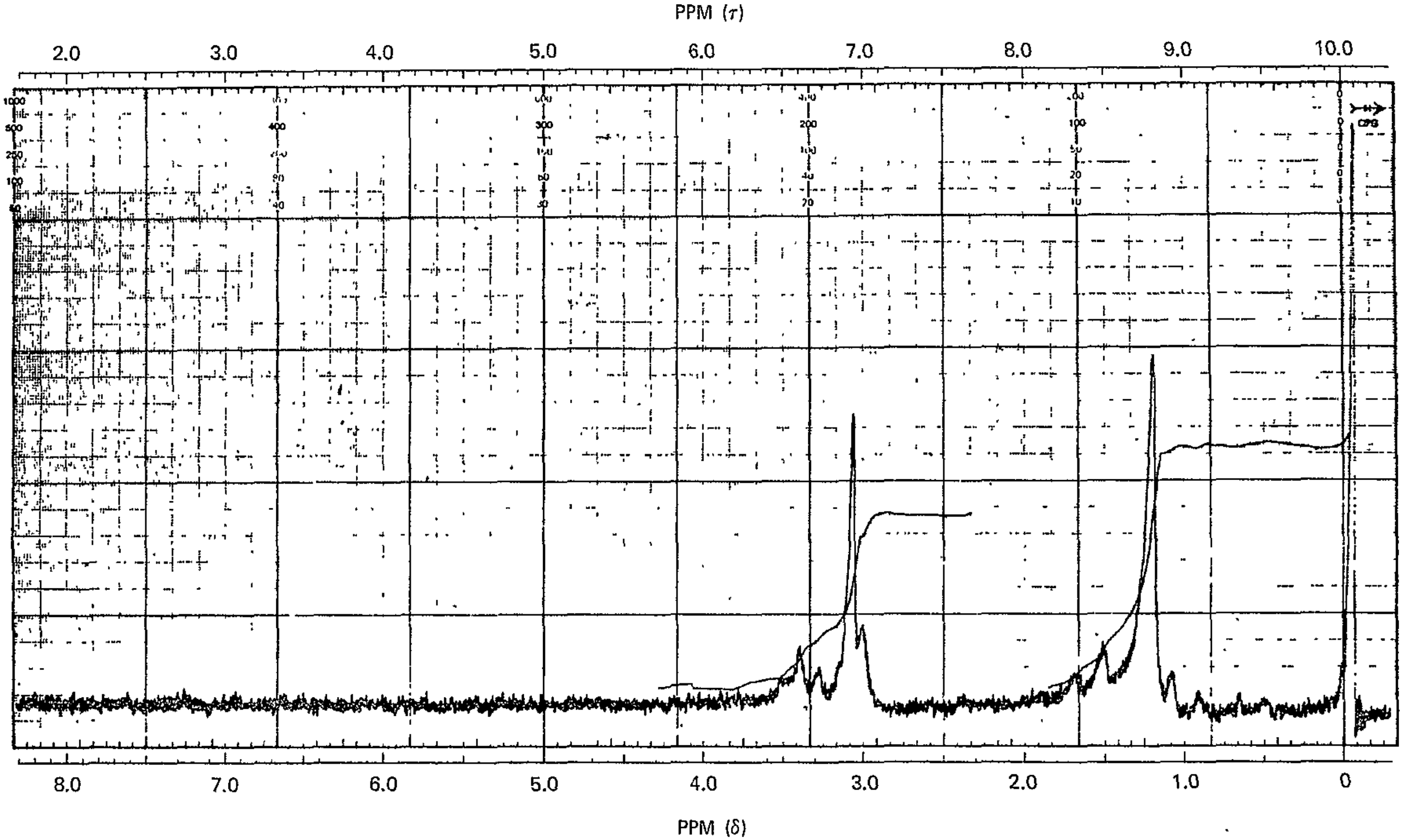


FIG. 10

NMR OF N,N'–DODECAMETHYLENEBIS[5,6–EPOXY–2,3–NORBORNANEDICARBOXIMIDE]



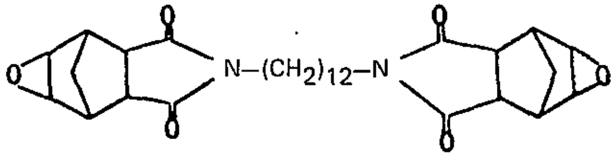


FIG. 11

R78-912941-15

NMR OF N, N'-Bis[12-(5- NORBORNENE-2, 3-DICARBOXIMIDO)DODECYL]-1, 2, 3, 4-BUTANETETRACARBOXYLIC 1, 2,:3, 4-DIIMIDE

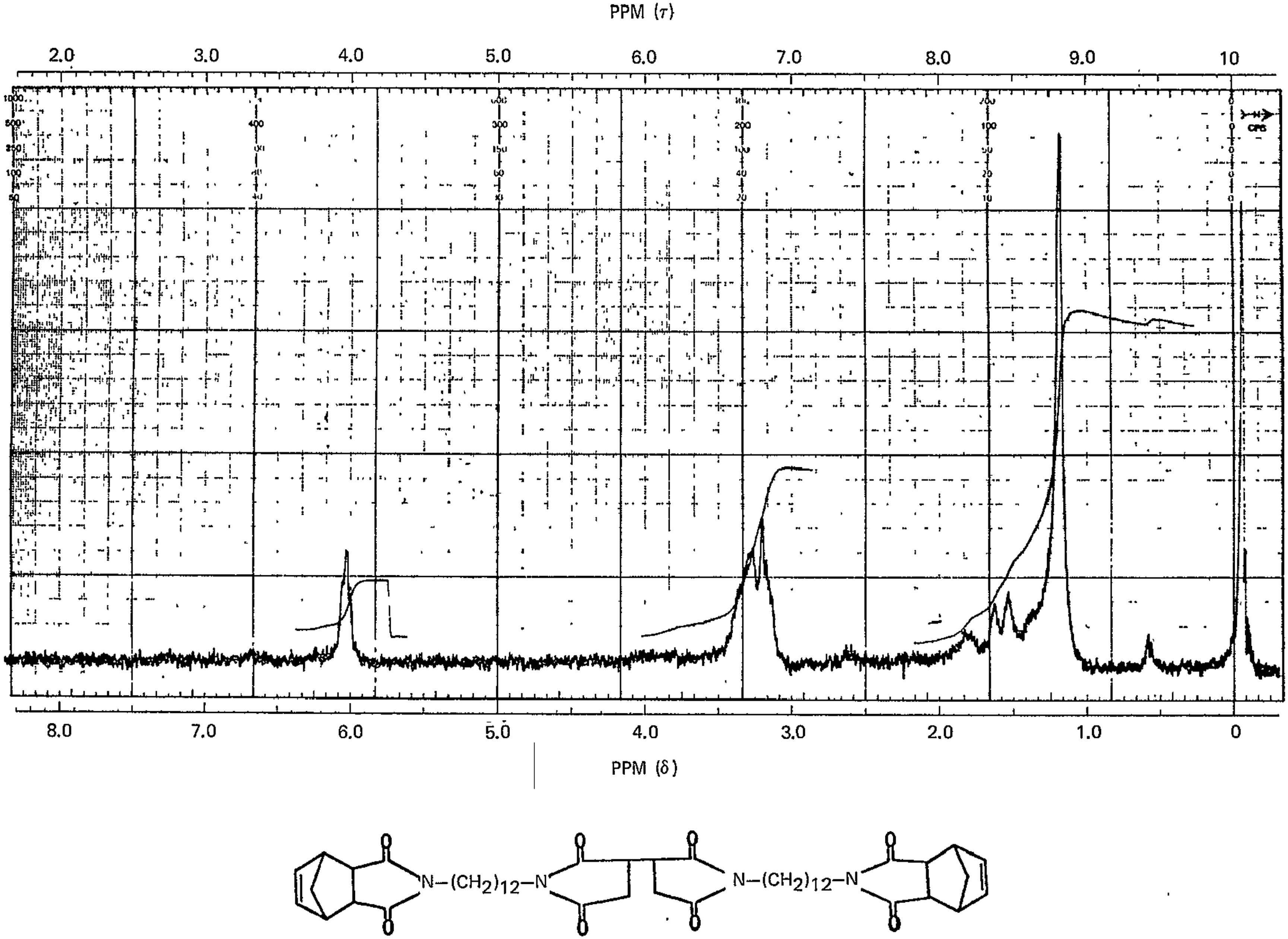


FIG. 12

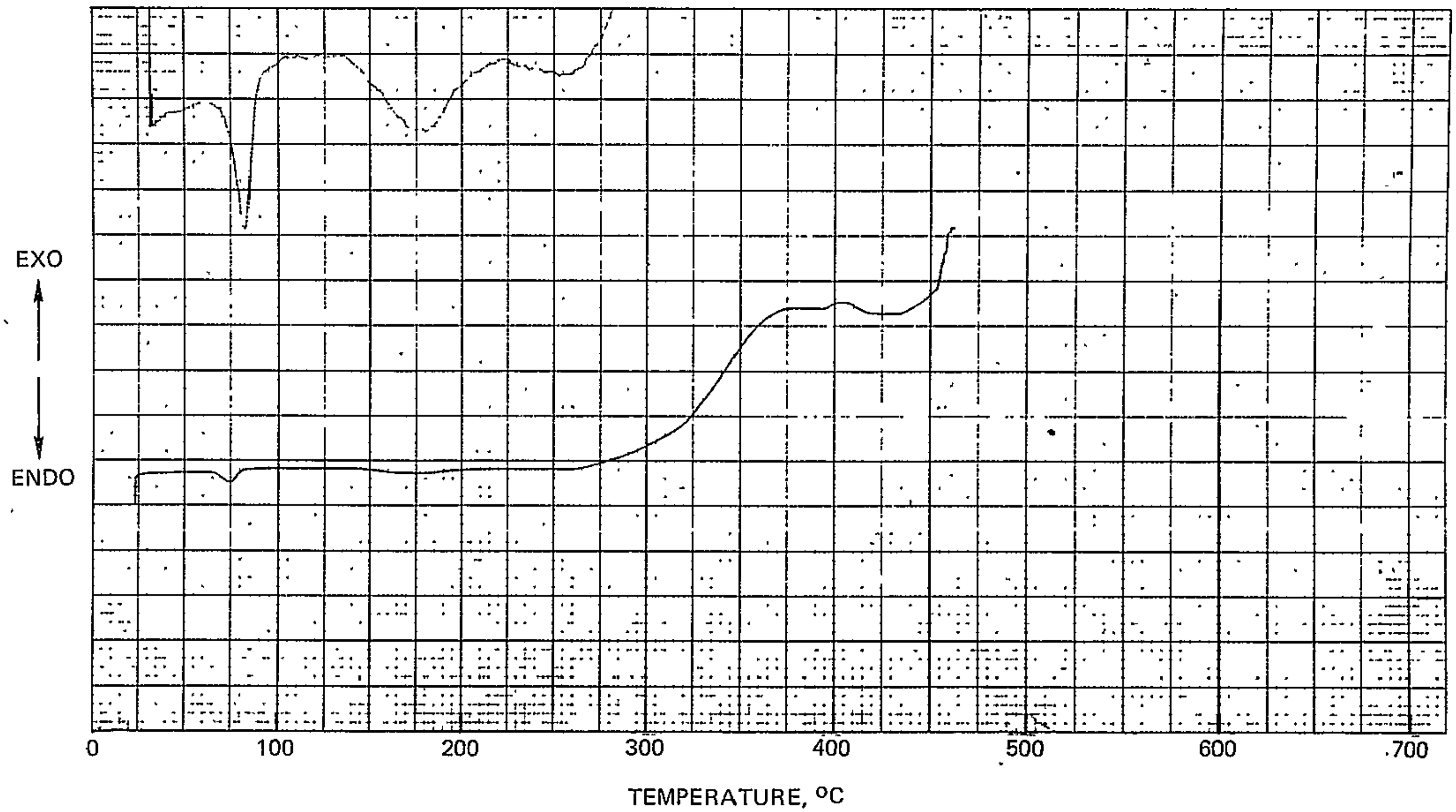
78-09-11-2

R78–912941–15

DSC OF N,N′–[[2,2,2–TRIFLUORO–1–(TRIFLUOROMETHYL) ETHYLIDENE] BIS [(1,3–DIOXO–5,2– ISOINDOLINEDIYL)–DODECAMETHYLENE]] DI–5–NORBORNENE–2,3–DICARBOXIMIDE

ATMOSPHERE = AIR

HEATING RATE = 10°C/MIN



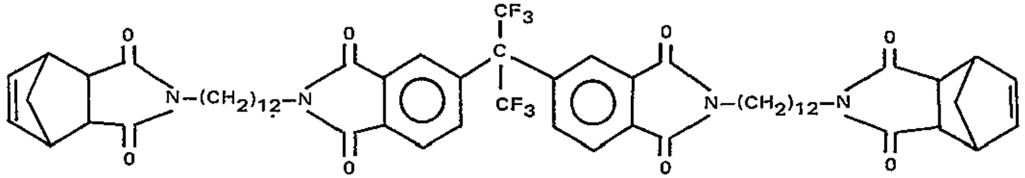
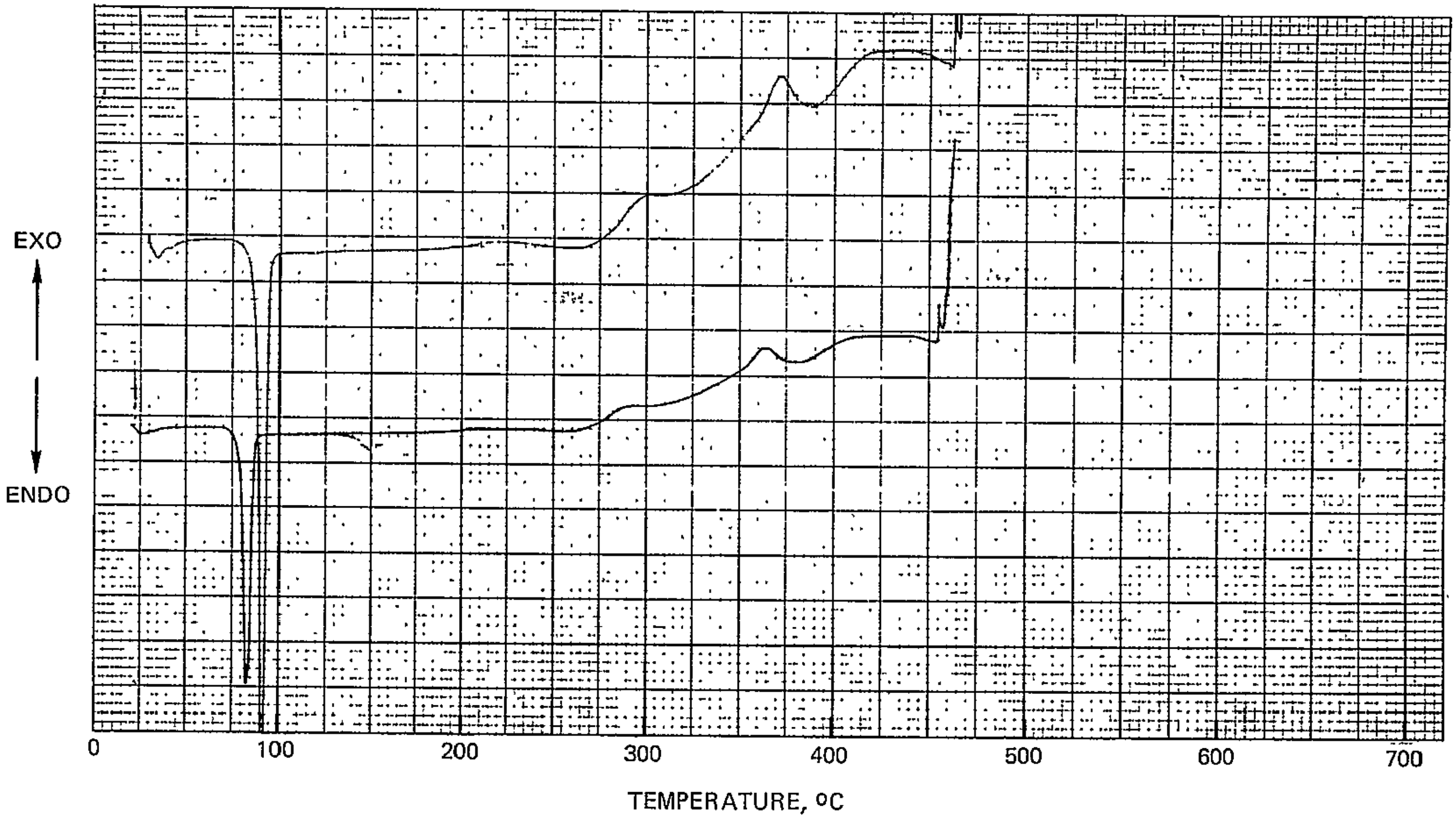


FIG. 13

78–12–38–2

DSC OF N,N'–DODECAMETHYLENEDI–5–NORBORNENE–2,3–DICARBOXIMIDE

ATMOSPHERE = AIR
HEATING RATE = 10°C/MIN
SAMPLE WEIGHT = 5.3 MG



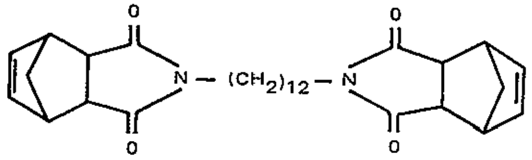


FIG. 14

78–12–38–10

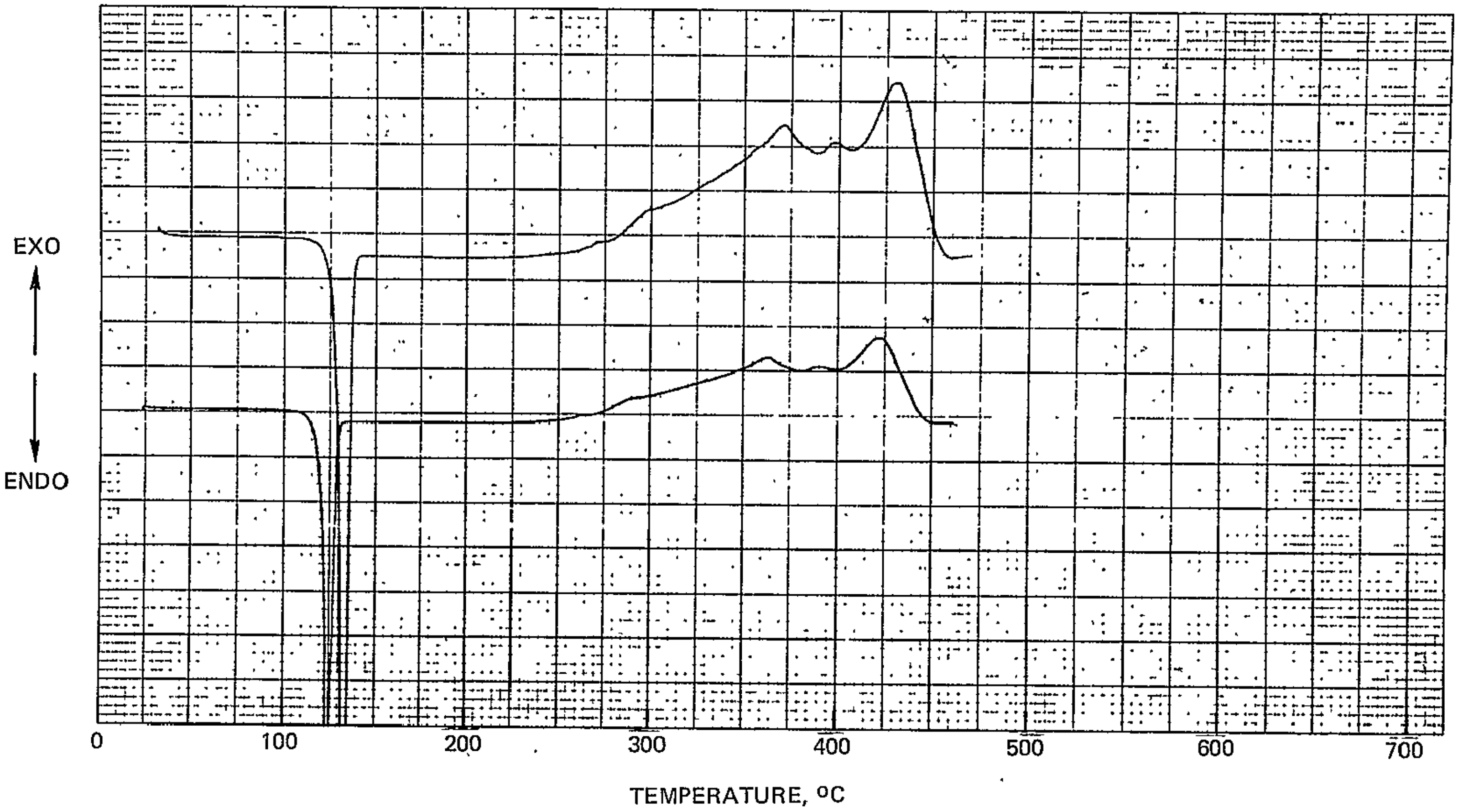
R78–912941–15

DSC OF N,N'–DODECAMETHYLENEBIS[5,6–EPOXY–2,3–NORBORNANEDICARBOXIMIDE]

ATMOSPHERE = AIR

HEATING RATE = 10°C/MIN

SAMPLE WEIGHT = 3.4 MG



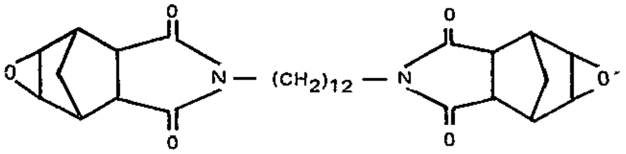


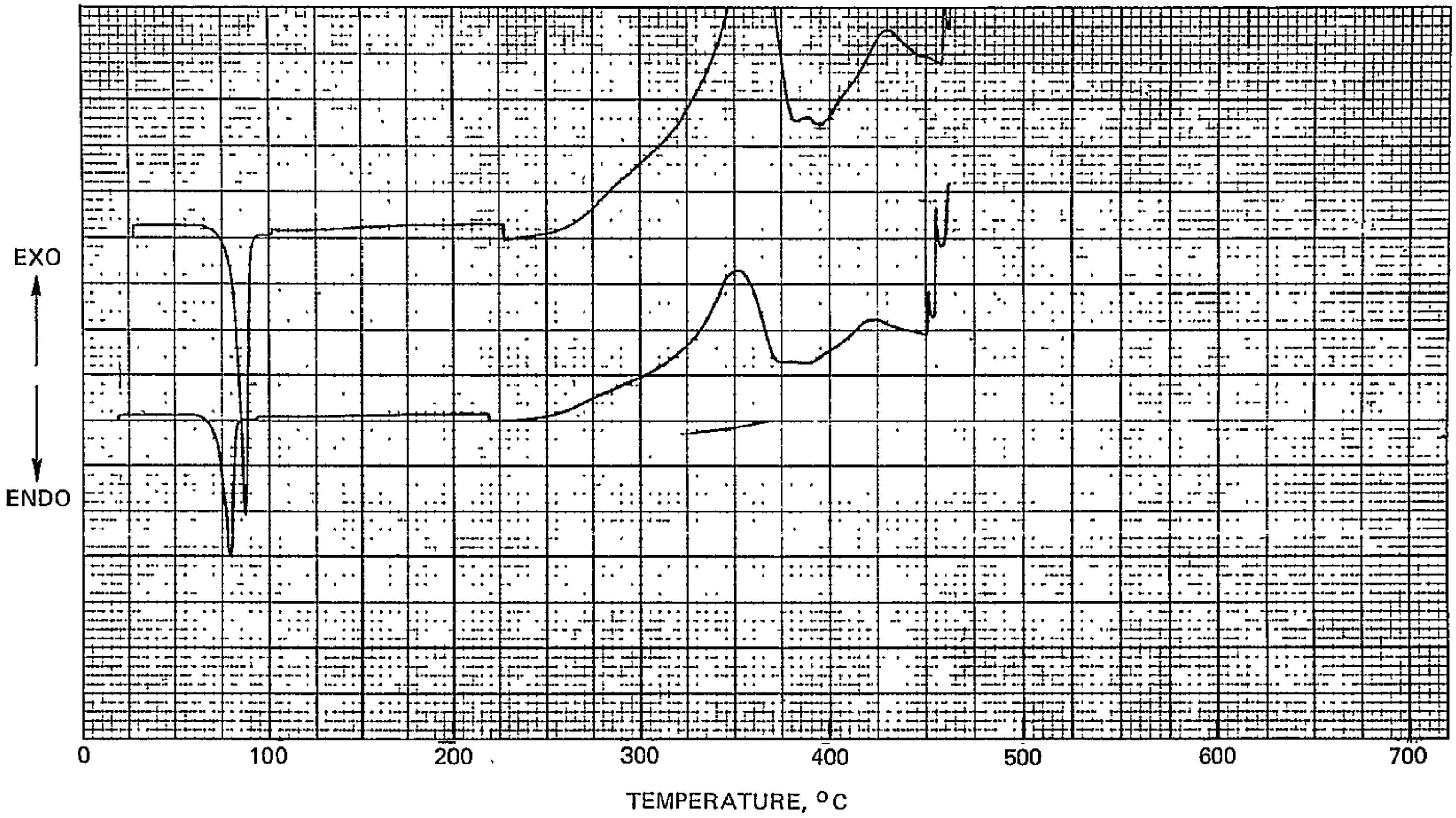
FIG. 15

78–12–38–11

R78–912941–15

DSC OF N, N'-Bis[12-(5- NORBORNENE-2, 3-DICARBOXIMIDO)DODECYL]-1, 2, 3, 4-BUTANETETRACARBOXYLIC 1, 2:3, 4-DIIMIDE

ATMOSPHERE = AIR
HEATING RATE = 10°/C/MIN
SAMPLE WEIGHT = 3.1MG



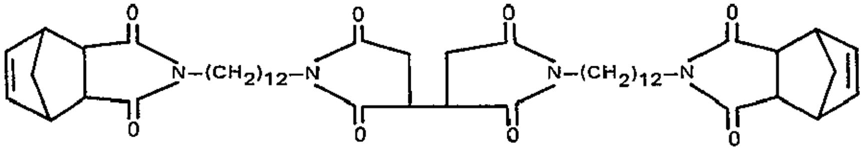
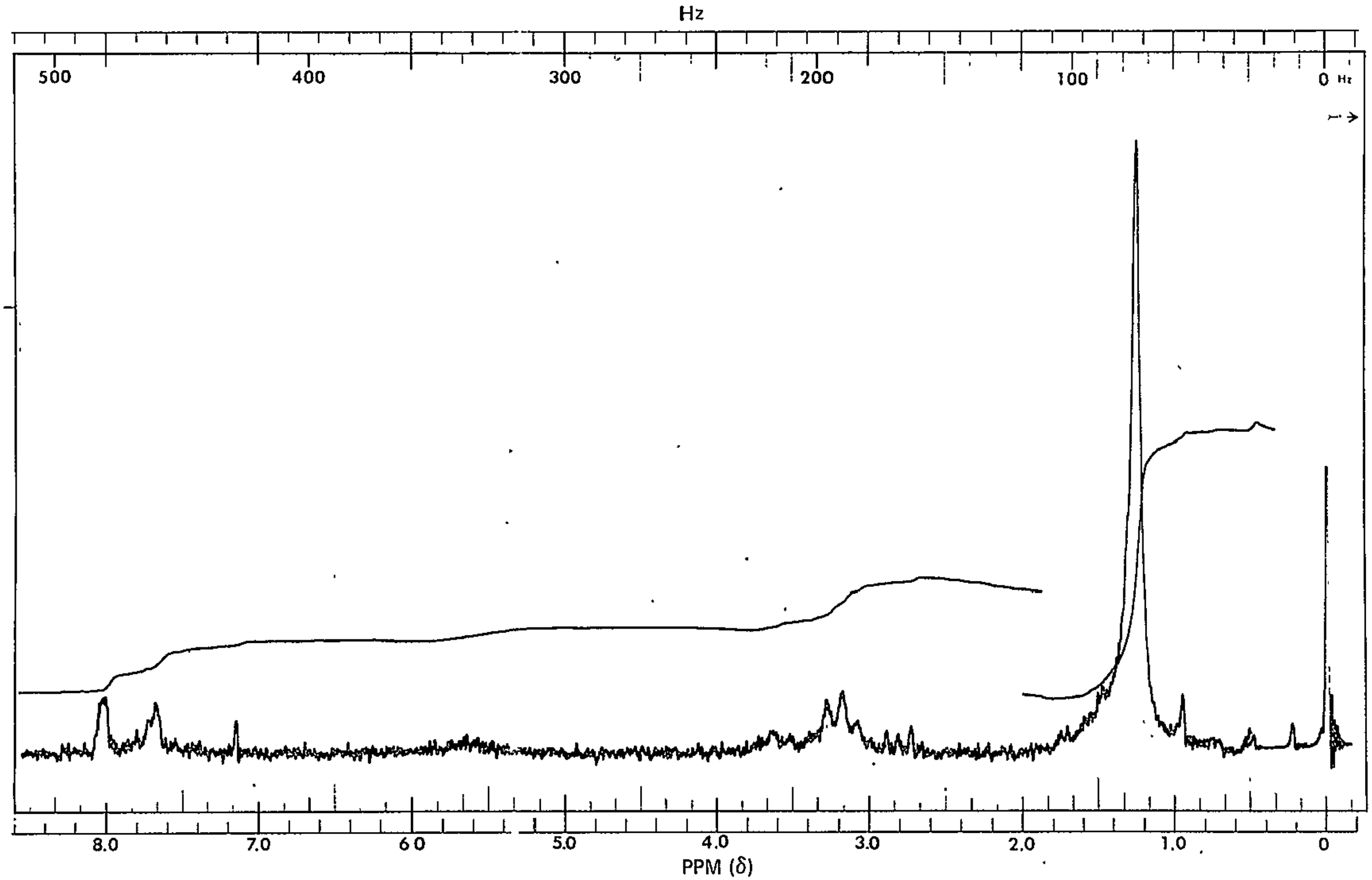


FIG. 16

78–12–38–4

R78–912941–15

NMR OF N,N′–BIS(12–AMINODODECYL)–4,4′–HEXAFLUOROISOPROPYLIDENE BIPHTHALIMIDE



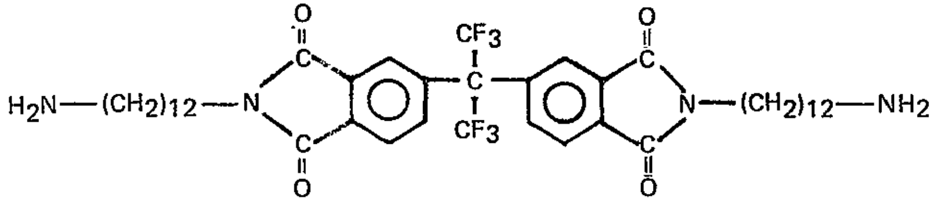


FIG. 17

78–12–11–3

R78–912941–15

NMR OF POLYIMIDE

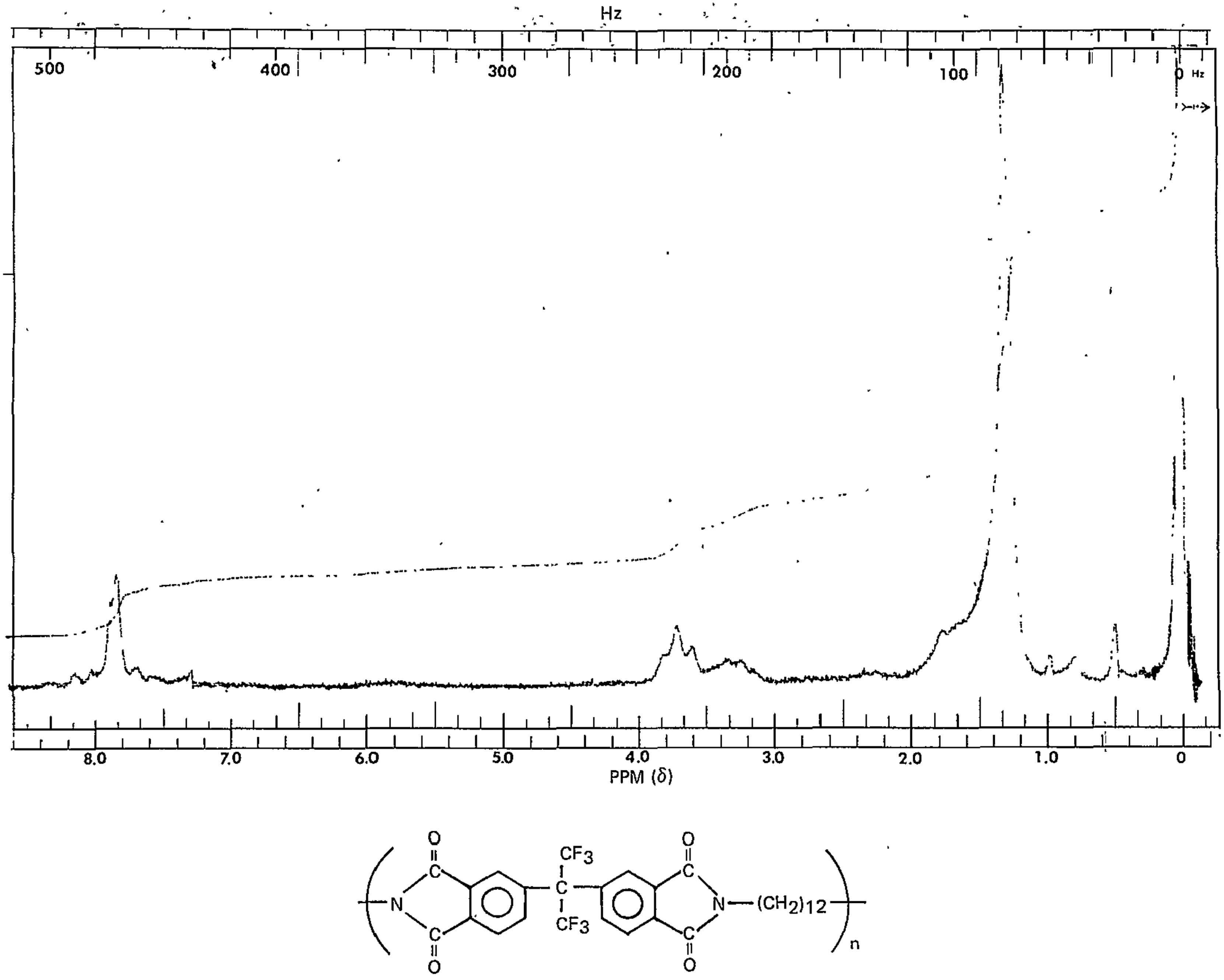


FIG. 18

78–12–11–2

FIG. 19

GEL PERMEATION CHROMATOGRAM OF MONOMER 5 BEFORE PURIFICATION

CONDITIONS

2–100 Å MICROSTYRAGEL COLUMNS
2.0 mℓ/MIN FLOW RATE
0.5 CM/MIN CHART SPEED
8XRI } ATTENUATION
2.0 UV } ATTENUATION
15.0 μℓ INJECTION
THF AS SOLVENT

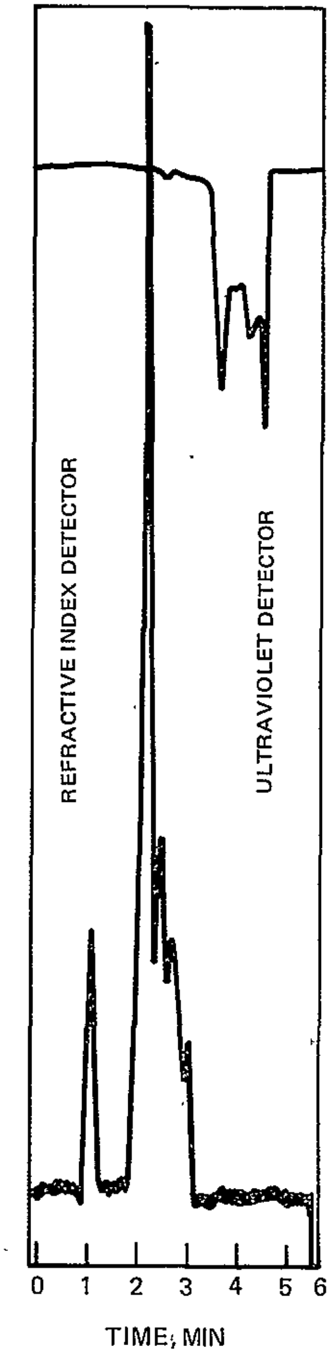
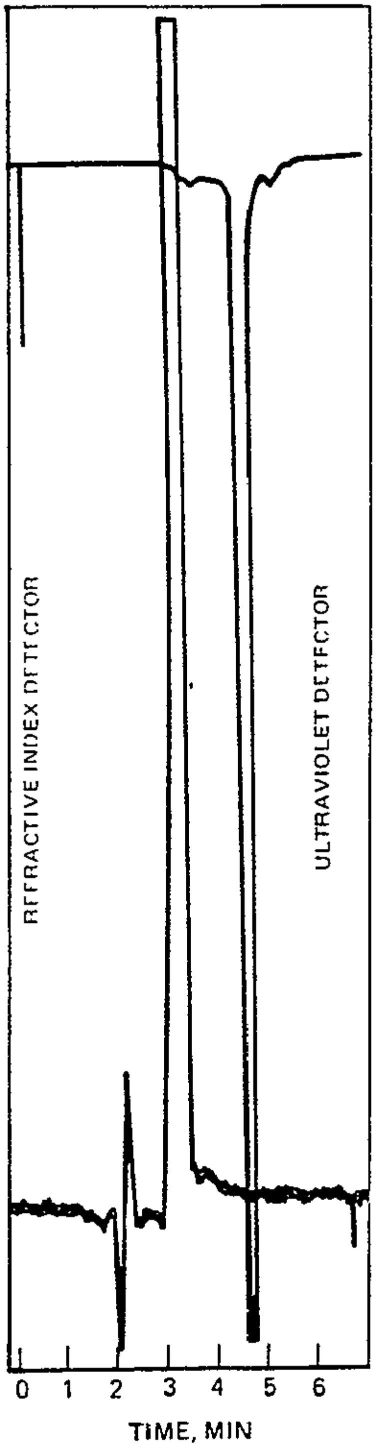


FIG. 20

GEL PERMEATION CHROMATOGRAM OF MONOMER <u>5</u>, AFTER PURIFICATION

CONDITIONS

2–100 Å MICROSTYRAGEL COLUMNS
2.0 mℓ/MIN FLOW RATE
0.5 CM/MIN CHART SPEED
8XRI } ATTENUATION
2.0 UV }
15.0 μℓ INJECTION
THF AS SOLVENT



78–10–211–2

NMR OF B–STAGED POLYIMIDE

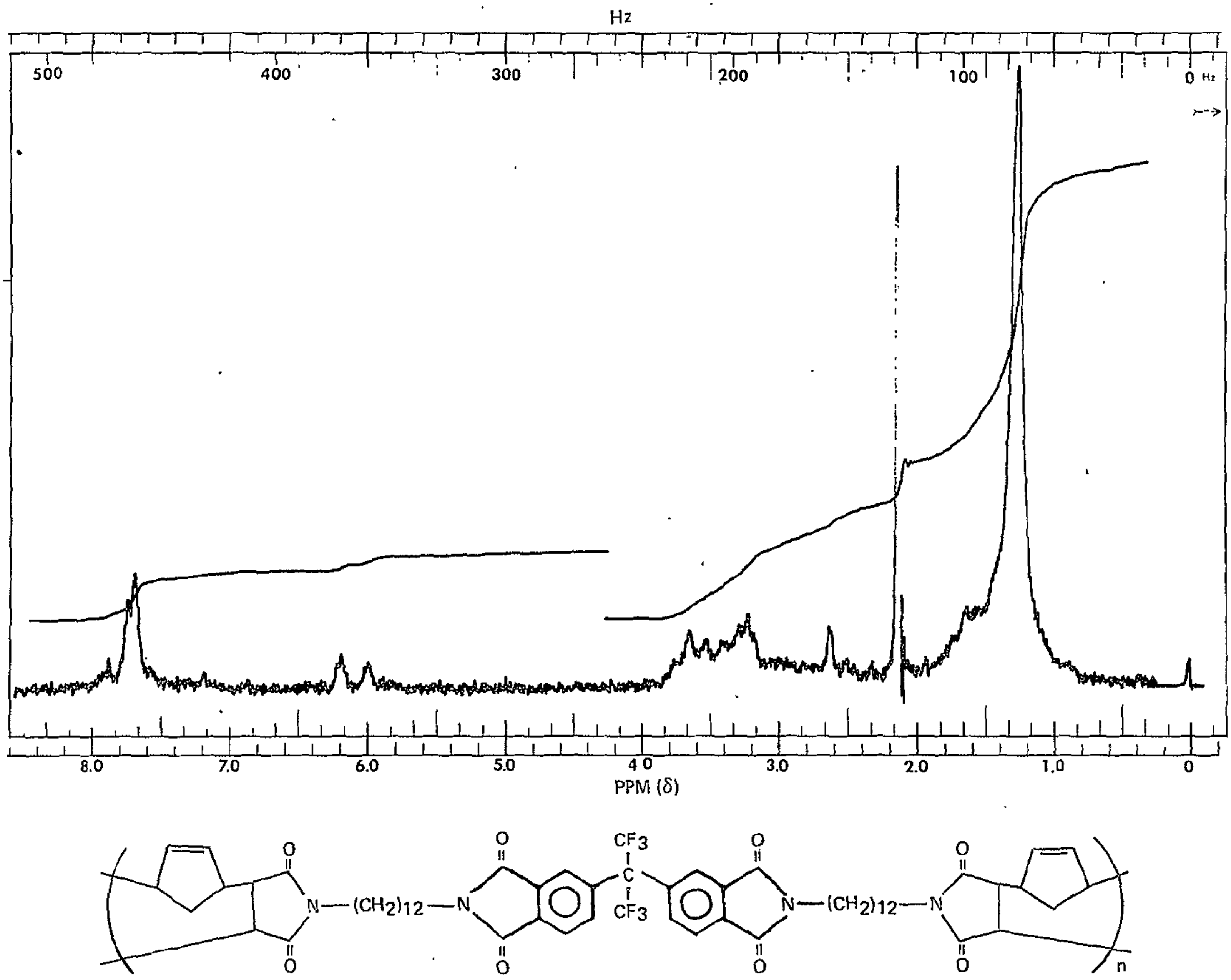


FIG. 21

R78–912941–15,

NMR OF B–STAGED POLYIMIDE

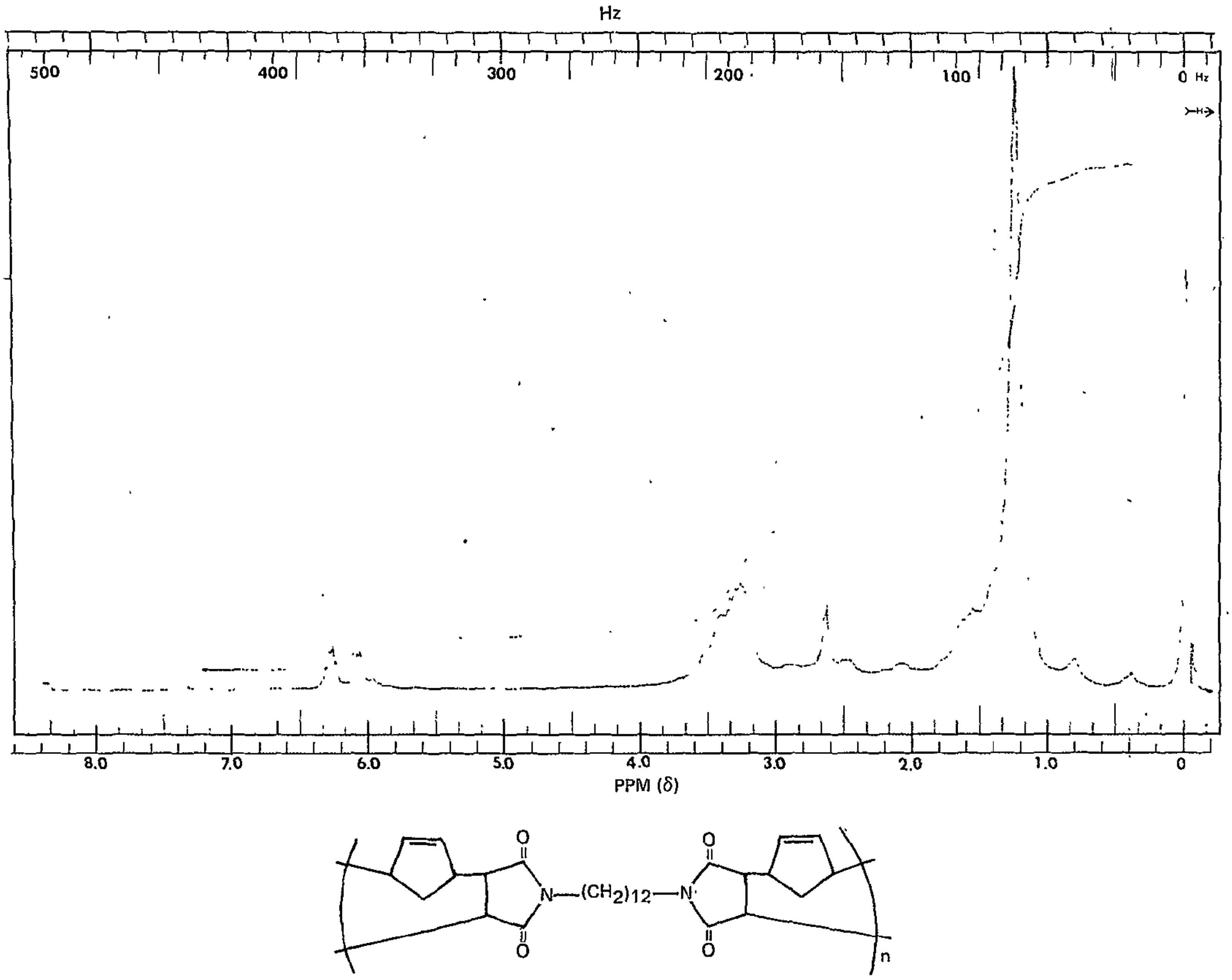


FIG. 22

78–12–11–7

R78-912941-15

NMR OF B–STAGED POLYIMIDE

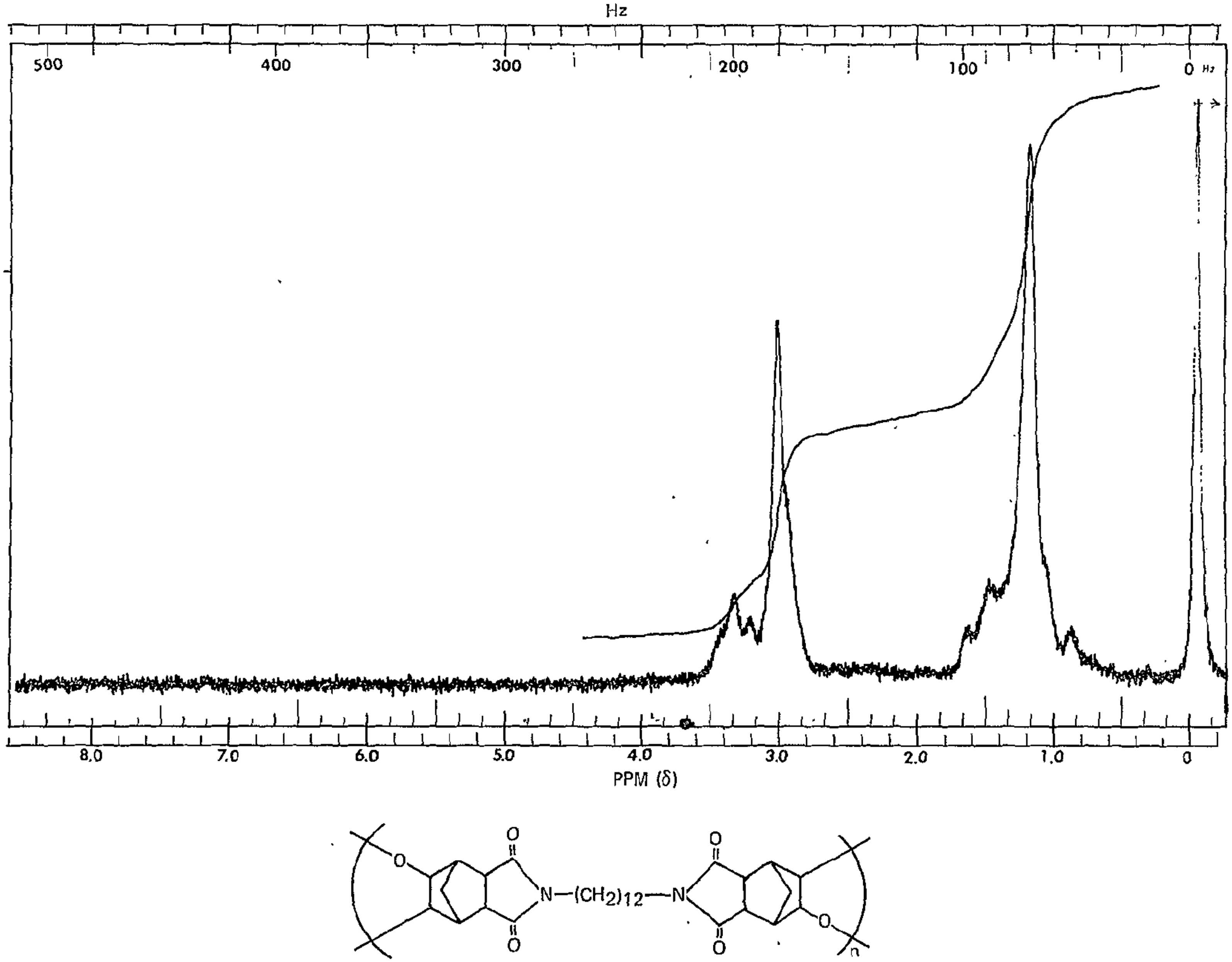
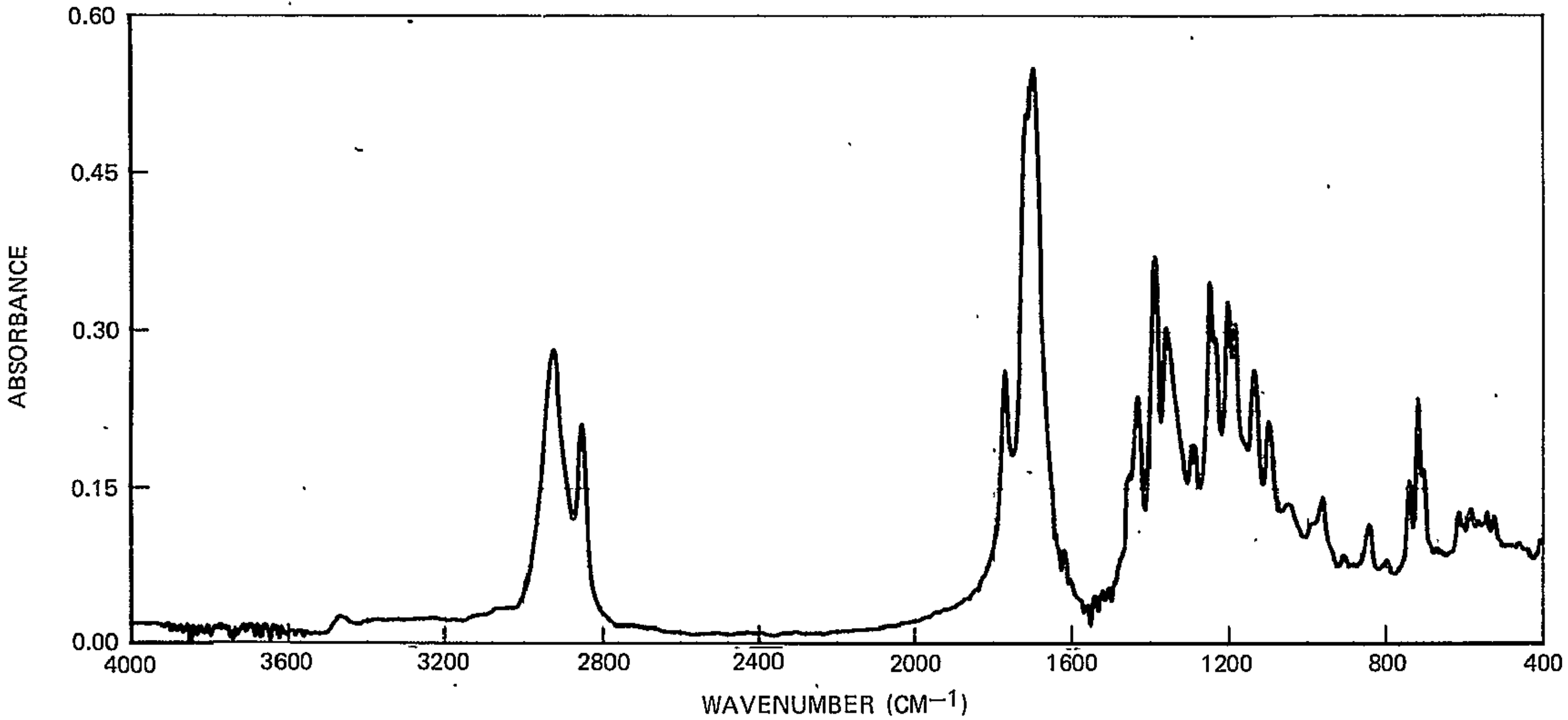


FIG. 23

78-12-11-5

FT–IR OF POLYIMIDE — 30



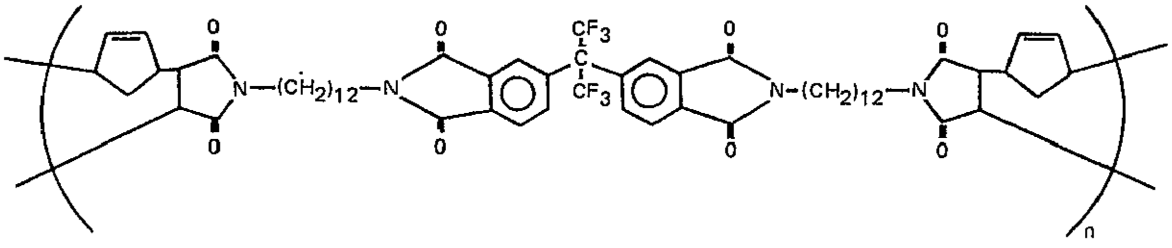


FIG. 24

FT–IR OF POLYIMIDE – 31

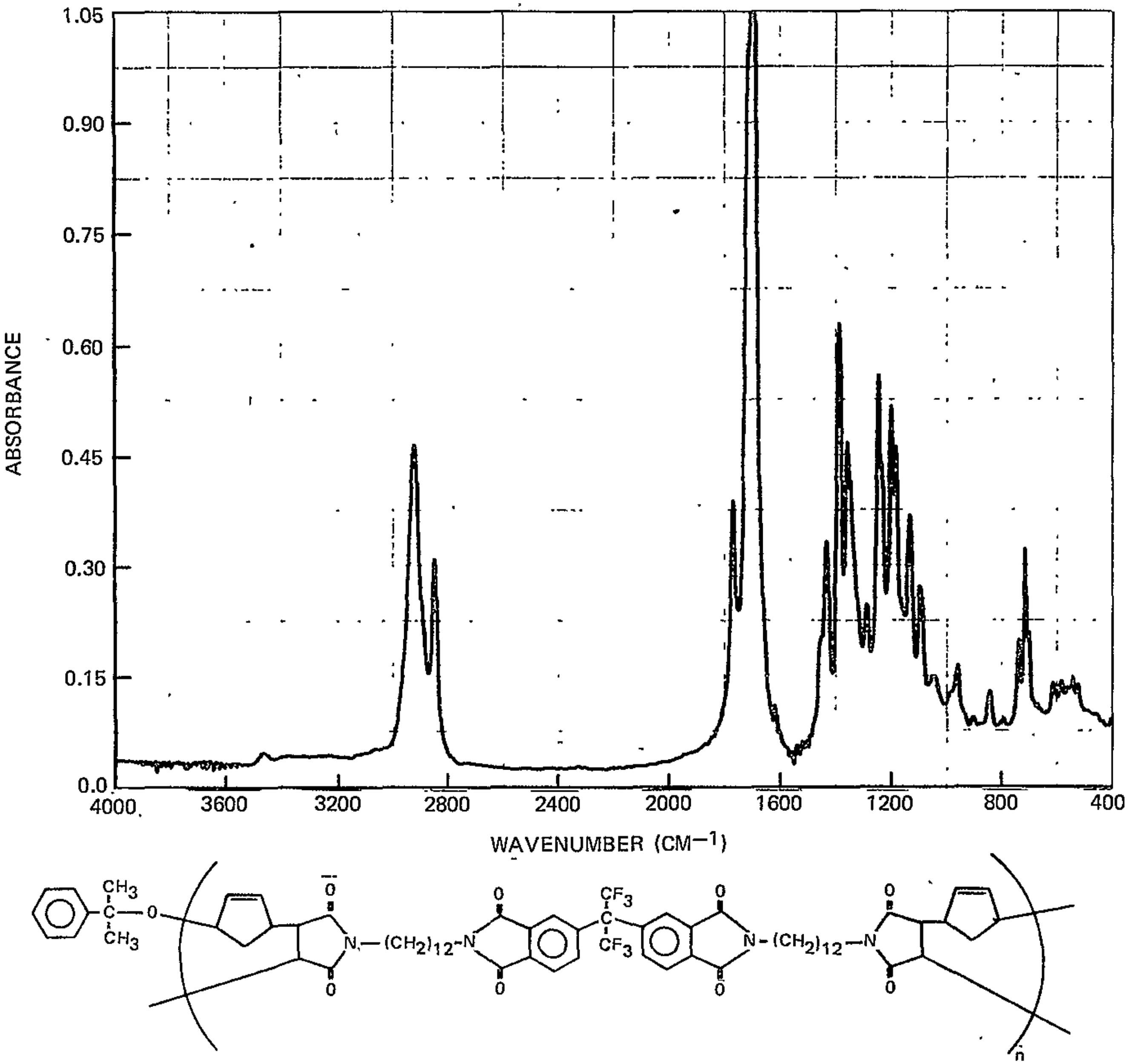


FIG. 25

78–12–17–2

FT–IR OF POLYIMIDE – 32

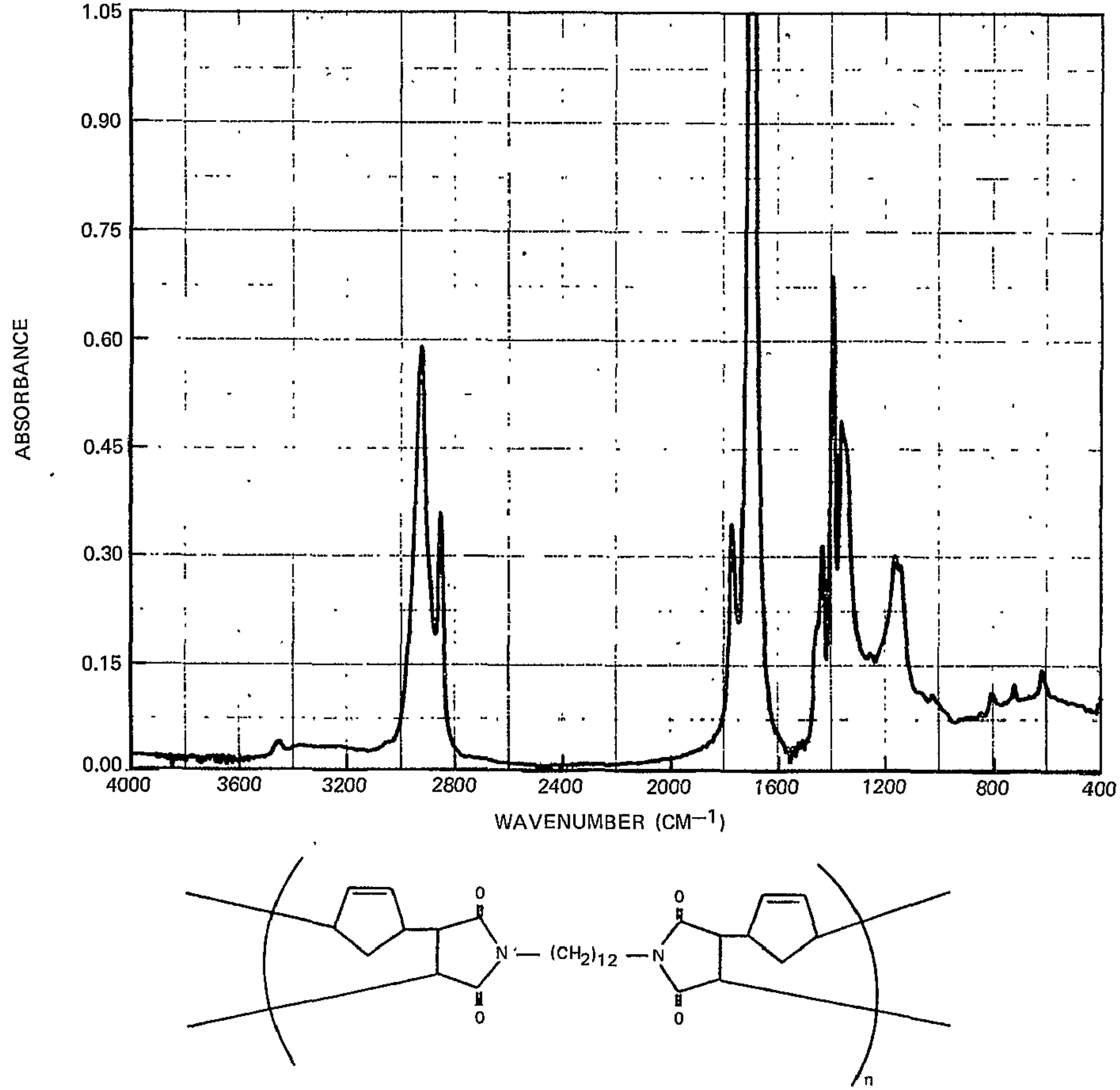
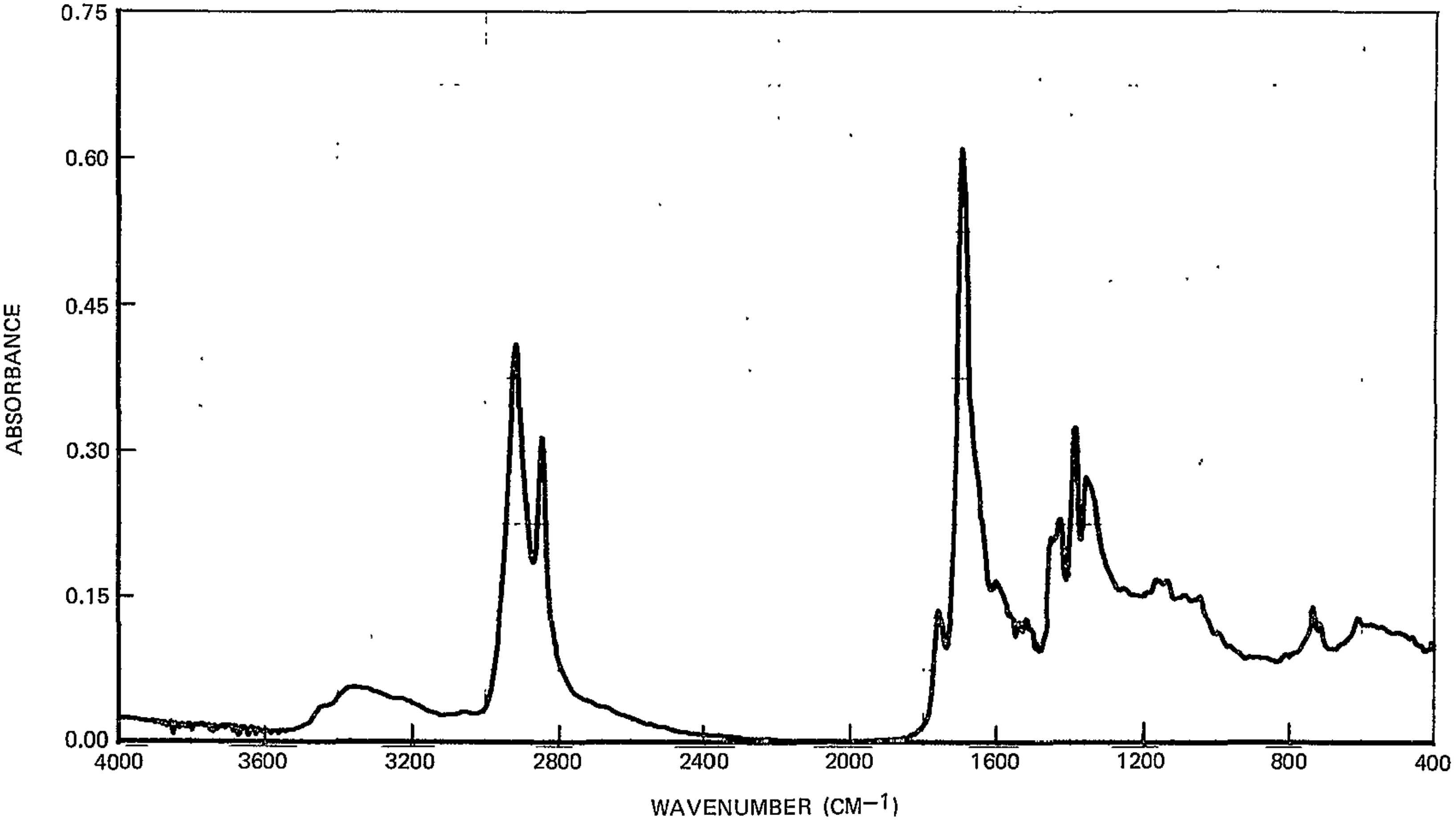


FIG. 26

78–12–17–3

FT–IR OF POLYIMIDE – 33



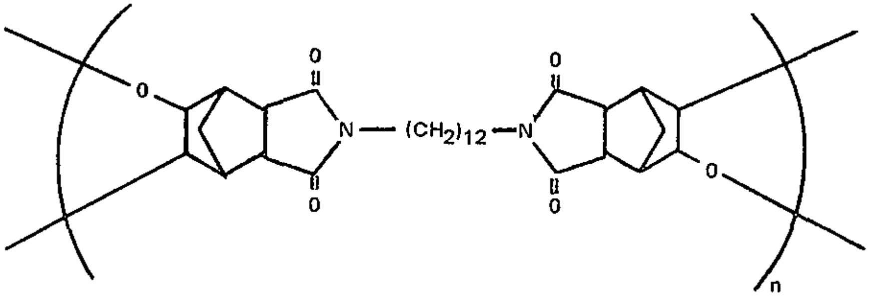


FIG. 27

78–12–17–4

FT–IR OF POLYIMIDE–34

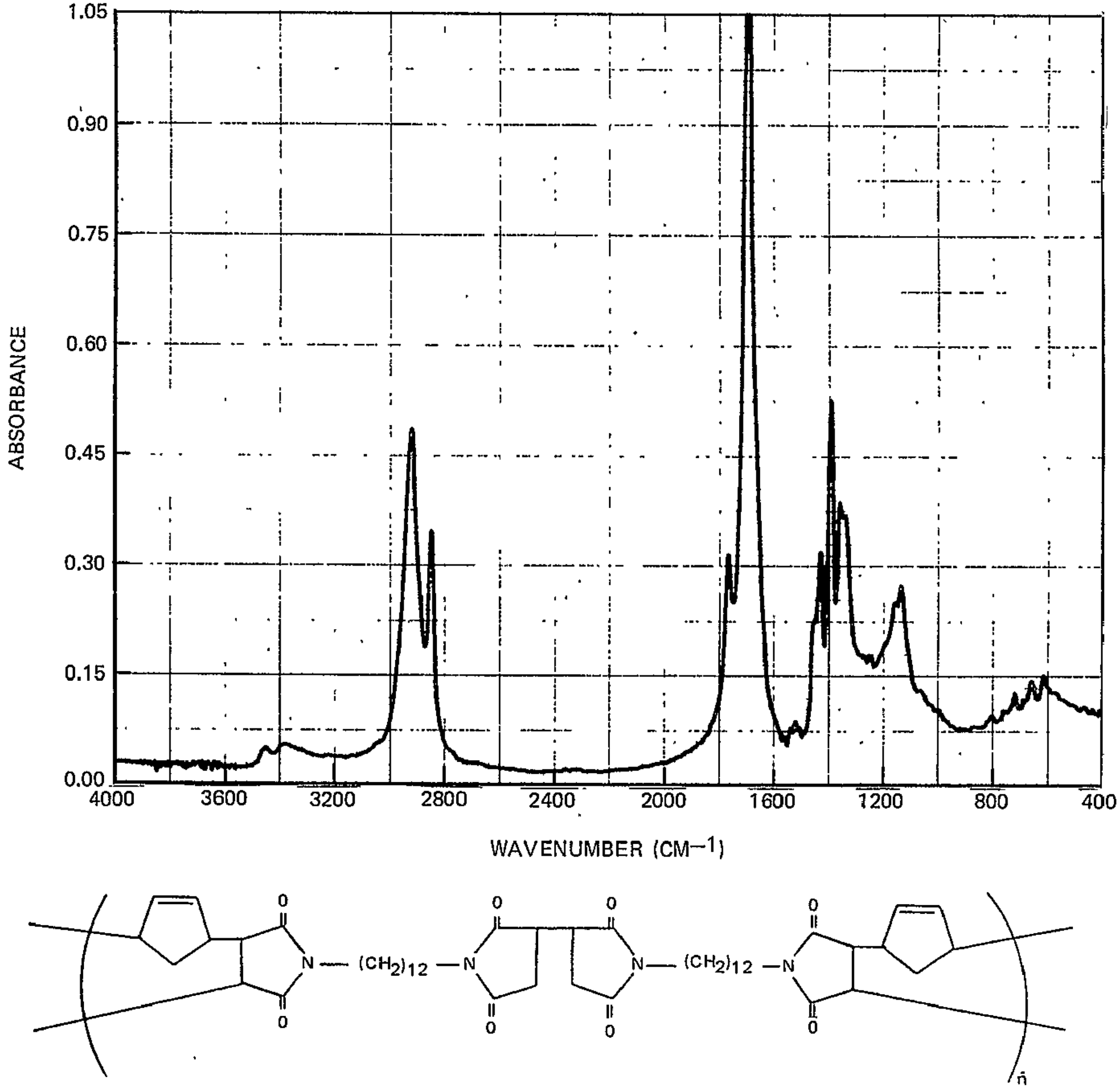
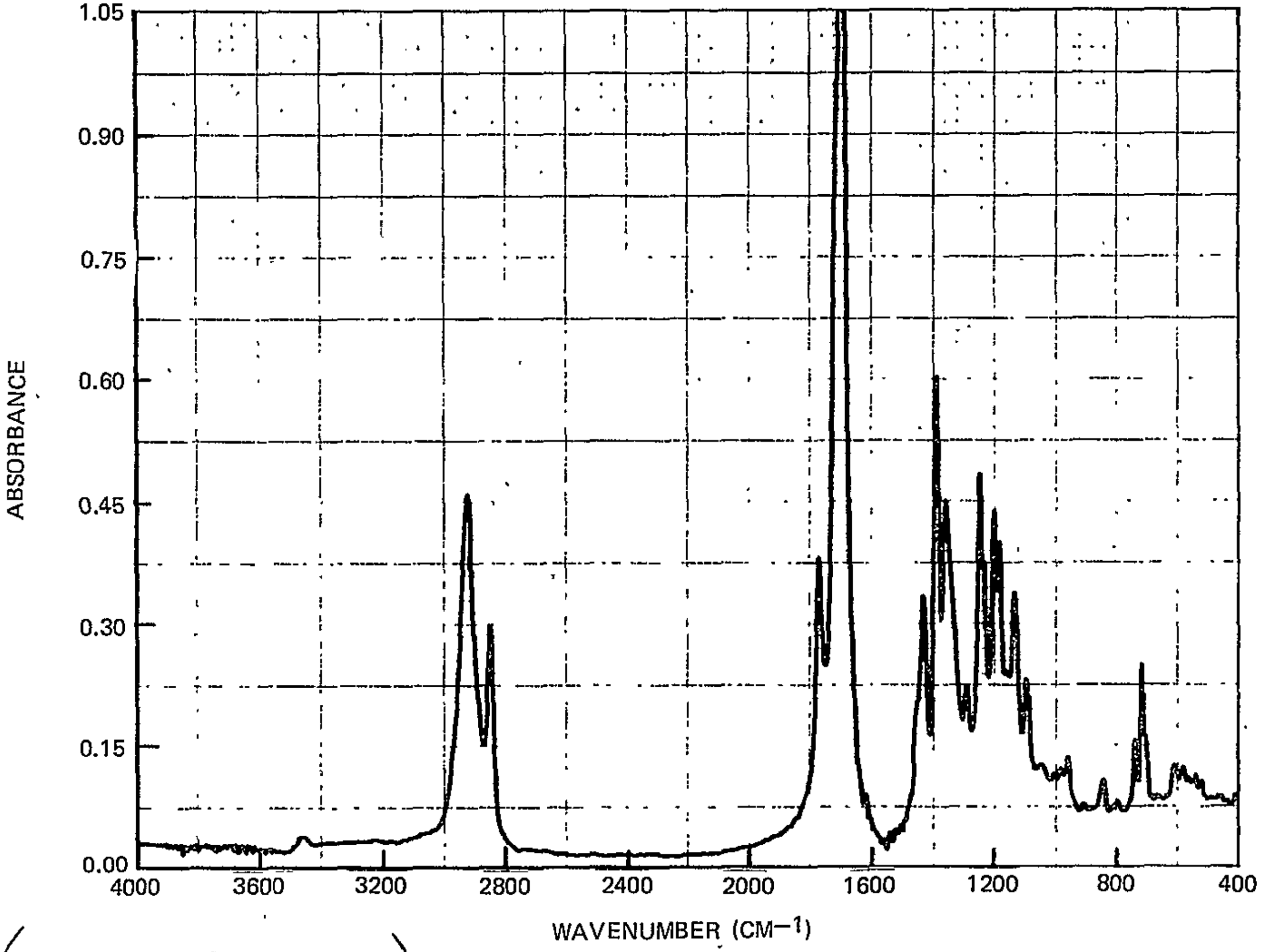
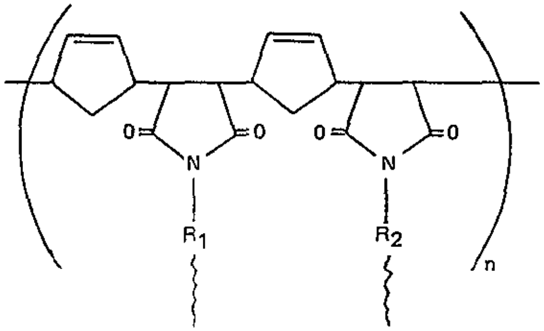


FIG. 28

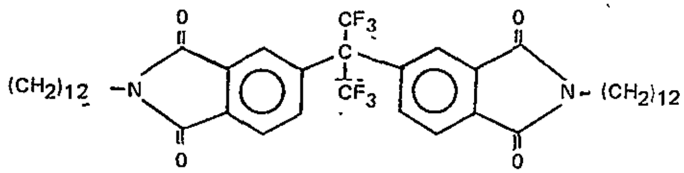
78–12–17–5

FT-IR OF POLYIMIDE-35





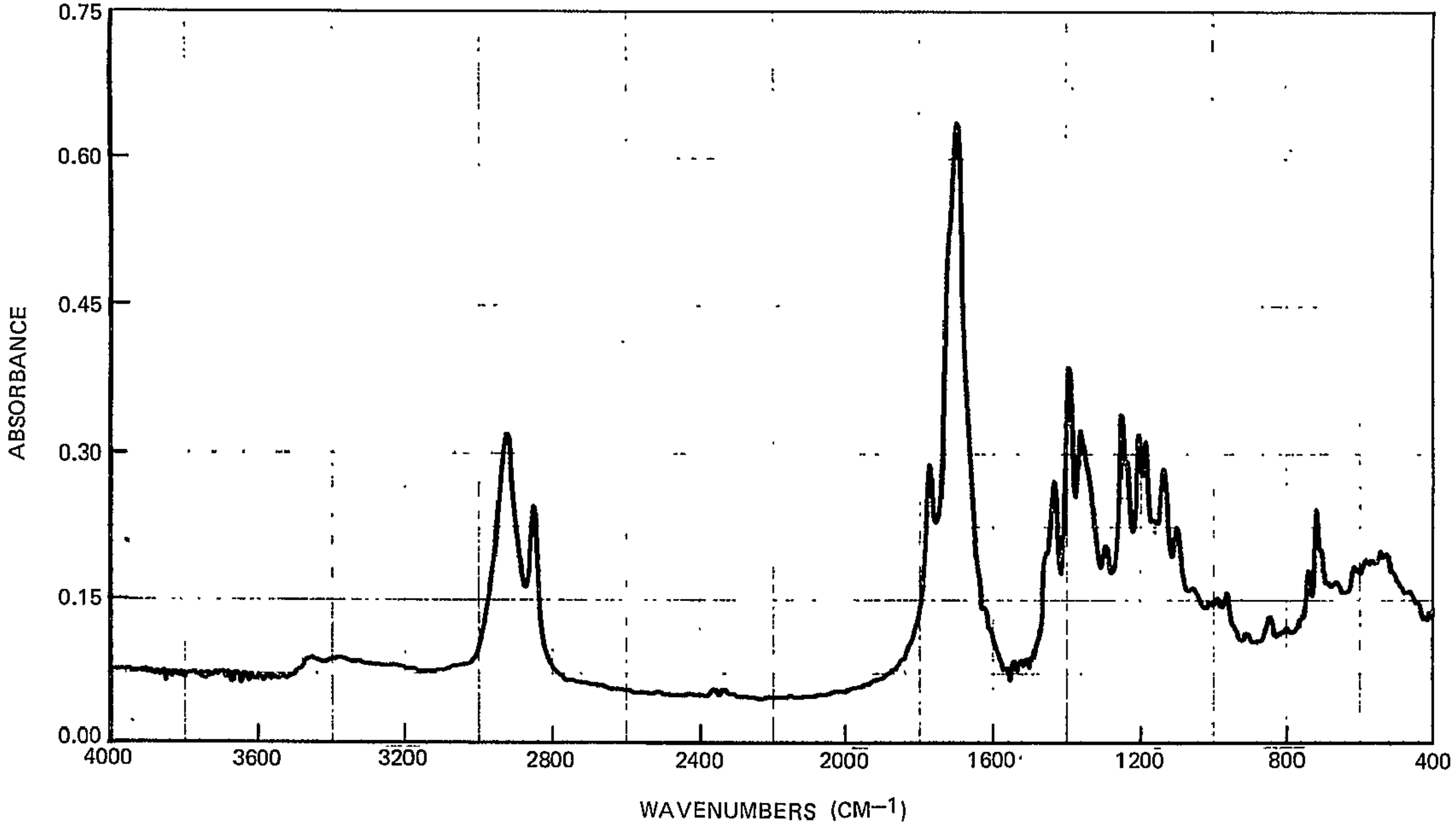
R_1 =



R_2 = $-(CH_2)_{12}-$

FIG. 29

FT-IR OF POLYIMIDE-36



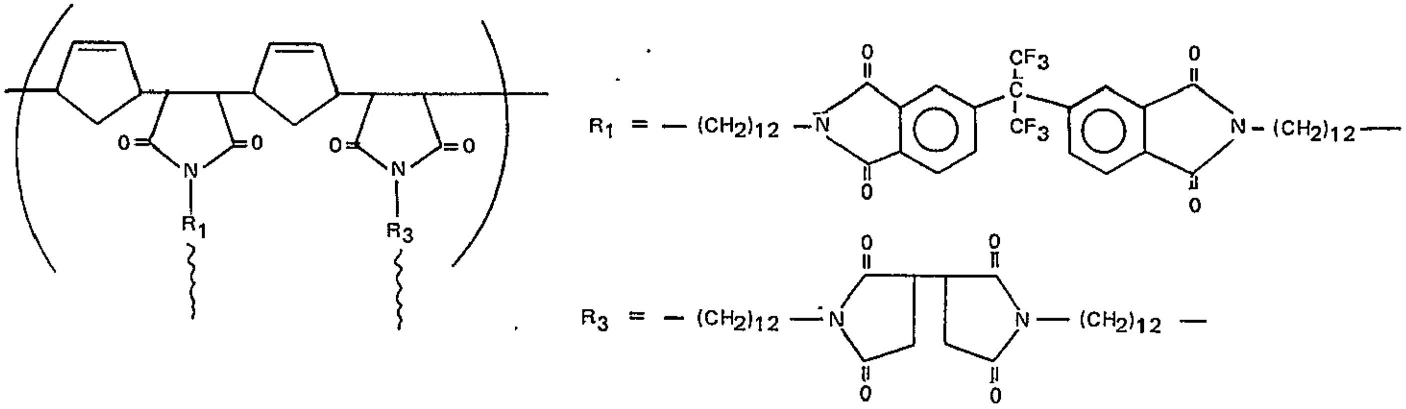


FIG. 30

78-12-17-7

C-2

FT–IR OF POLYIMIDE – 37

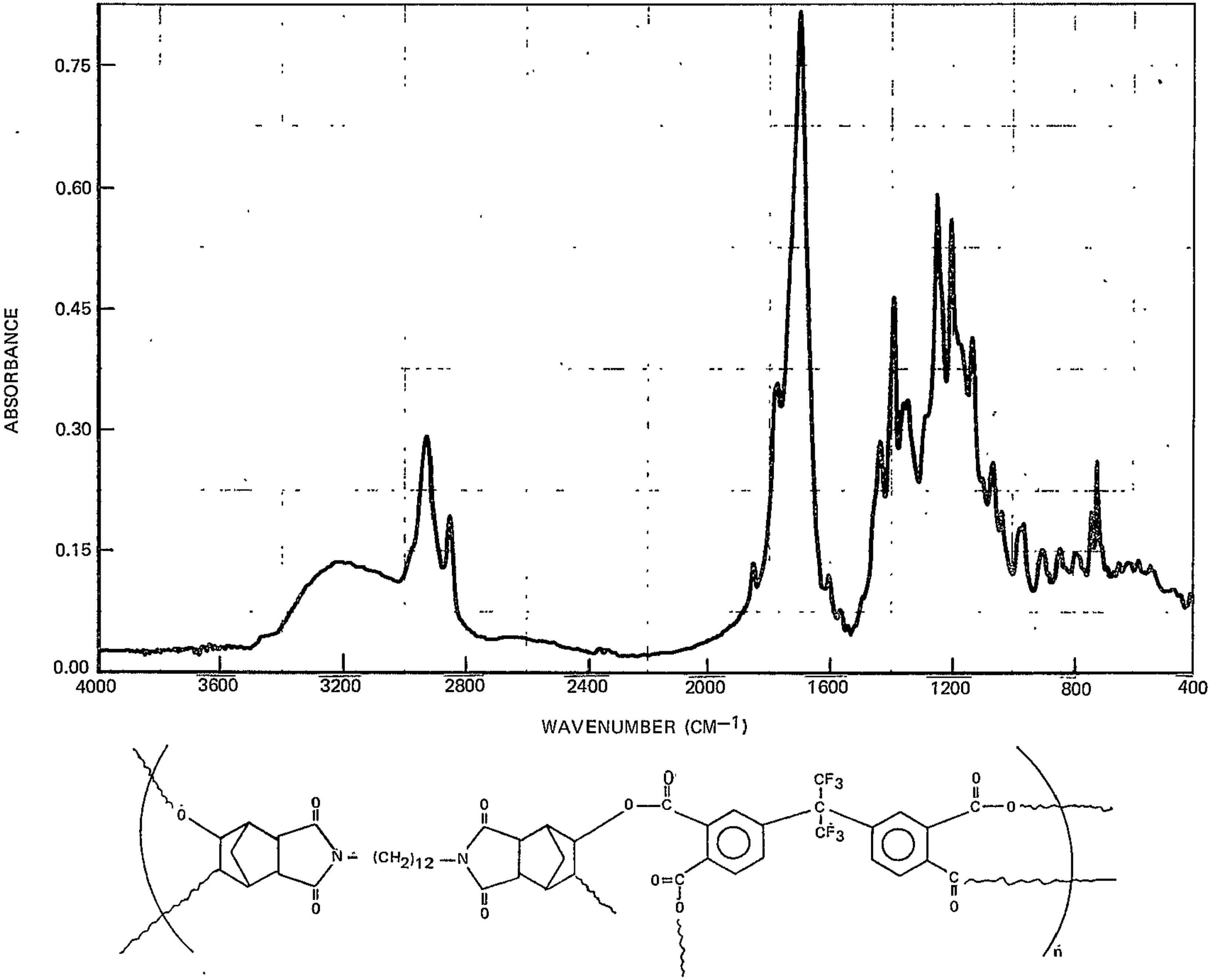


FIG. 31

R78–912941–15

78–12–17–8

GLASS TRANSITION TEMPERATURE OF POLYMER DISC – 22

ATMOSPHERE = N_2

HEATING RATE = 10°C/MIN

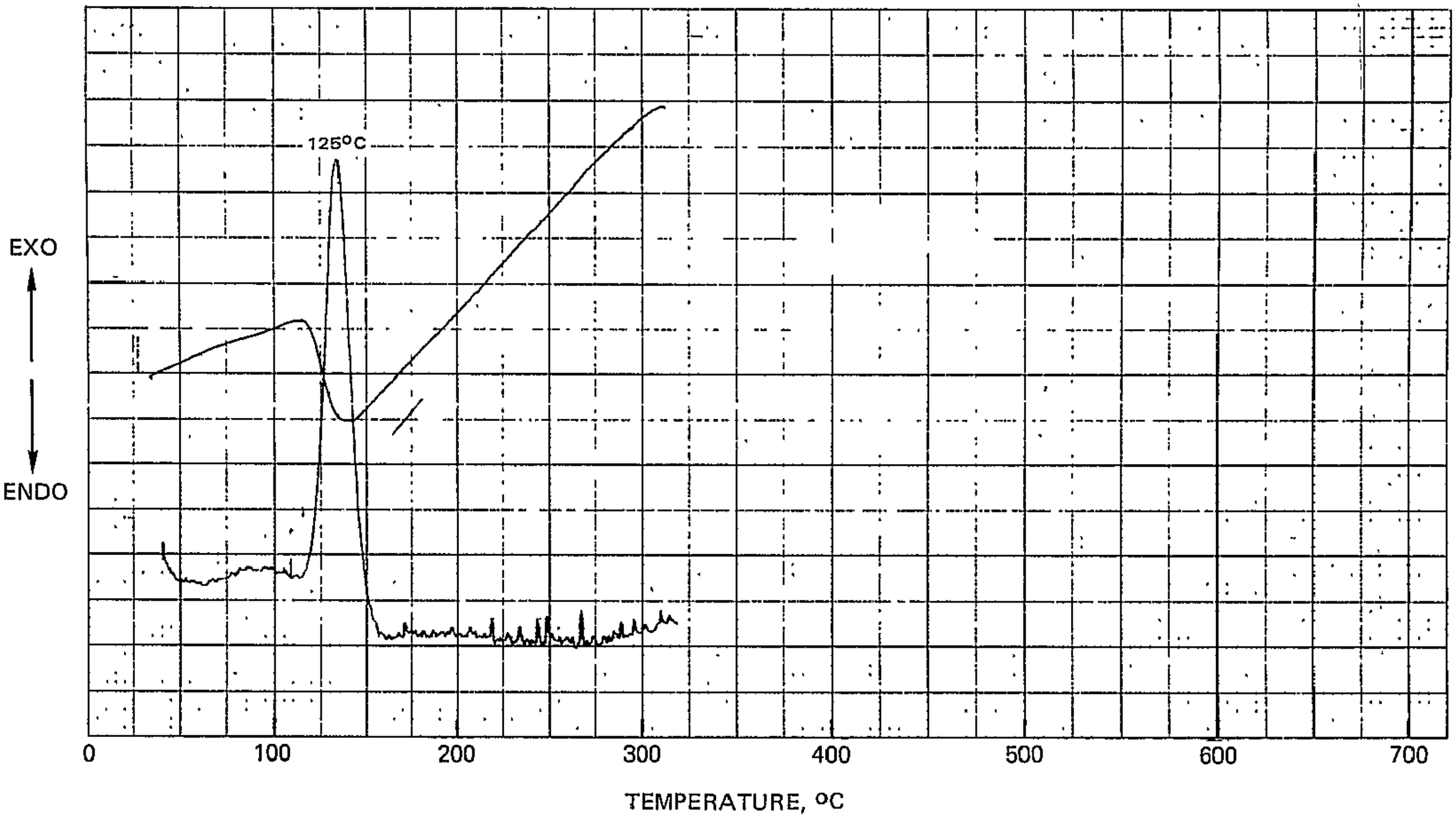
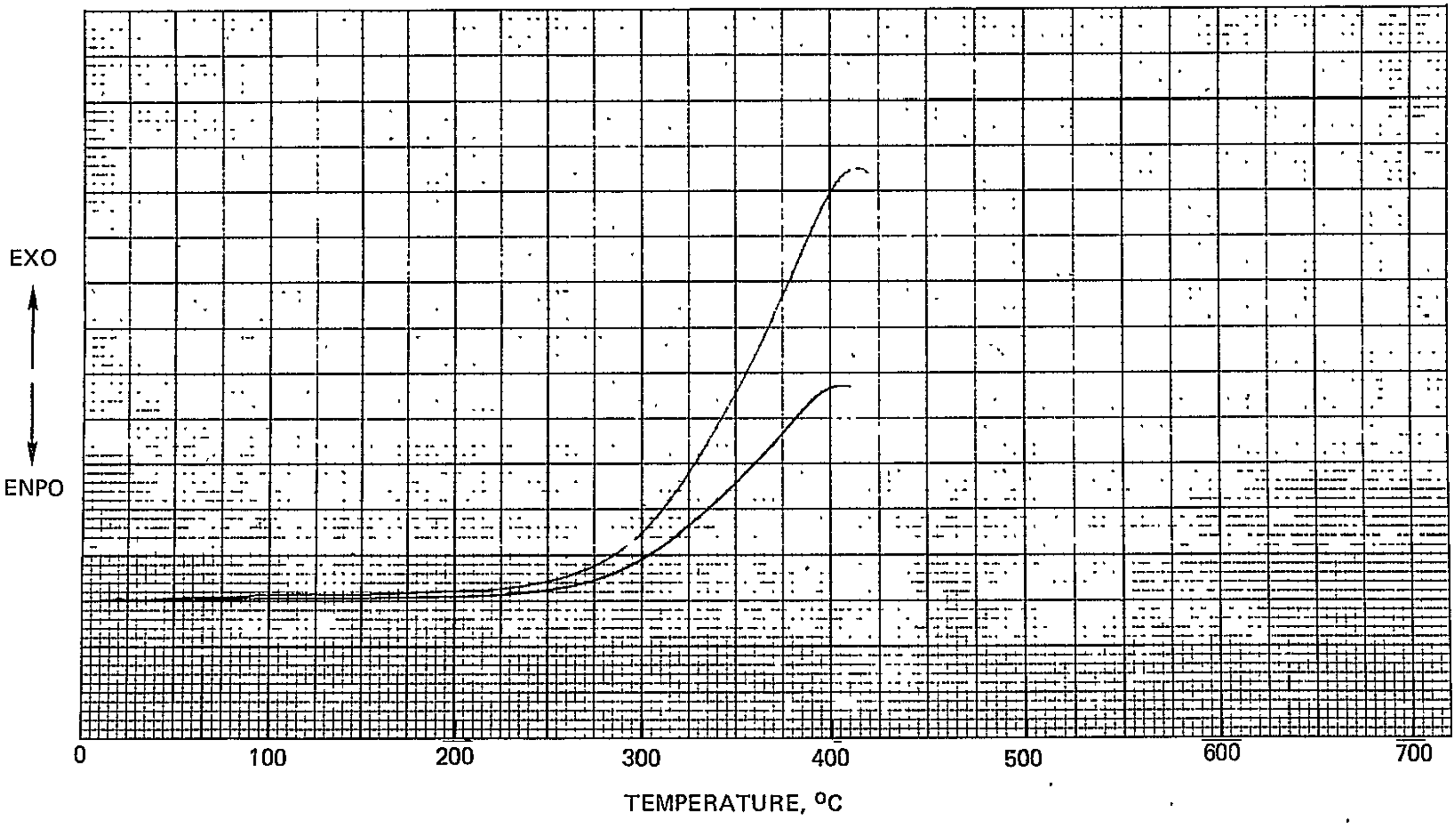


FIG. 32

78–12–38–9

DSC OF POLYMER DISC–3

ATMOSPHERE: AIR
HEATING RATE: 10°C/MIN
SAMPLE WEIGHT: 6.8 MG



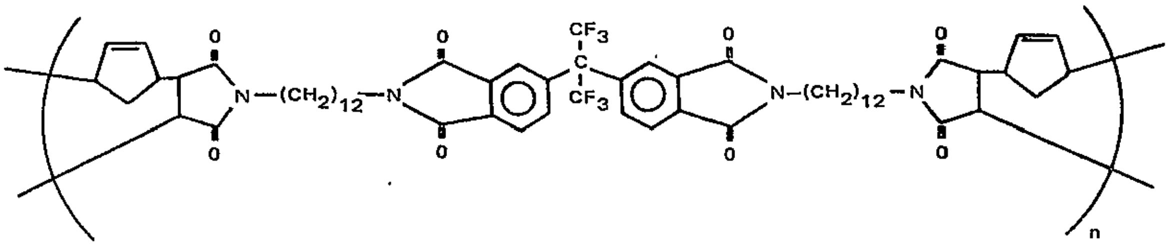
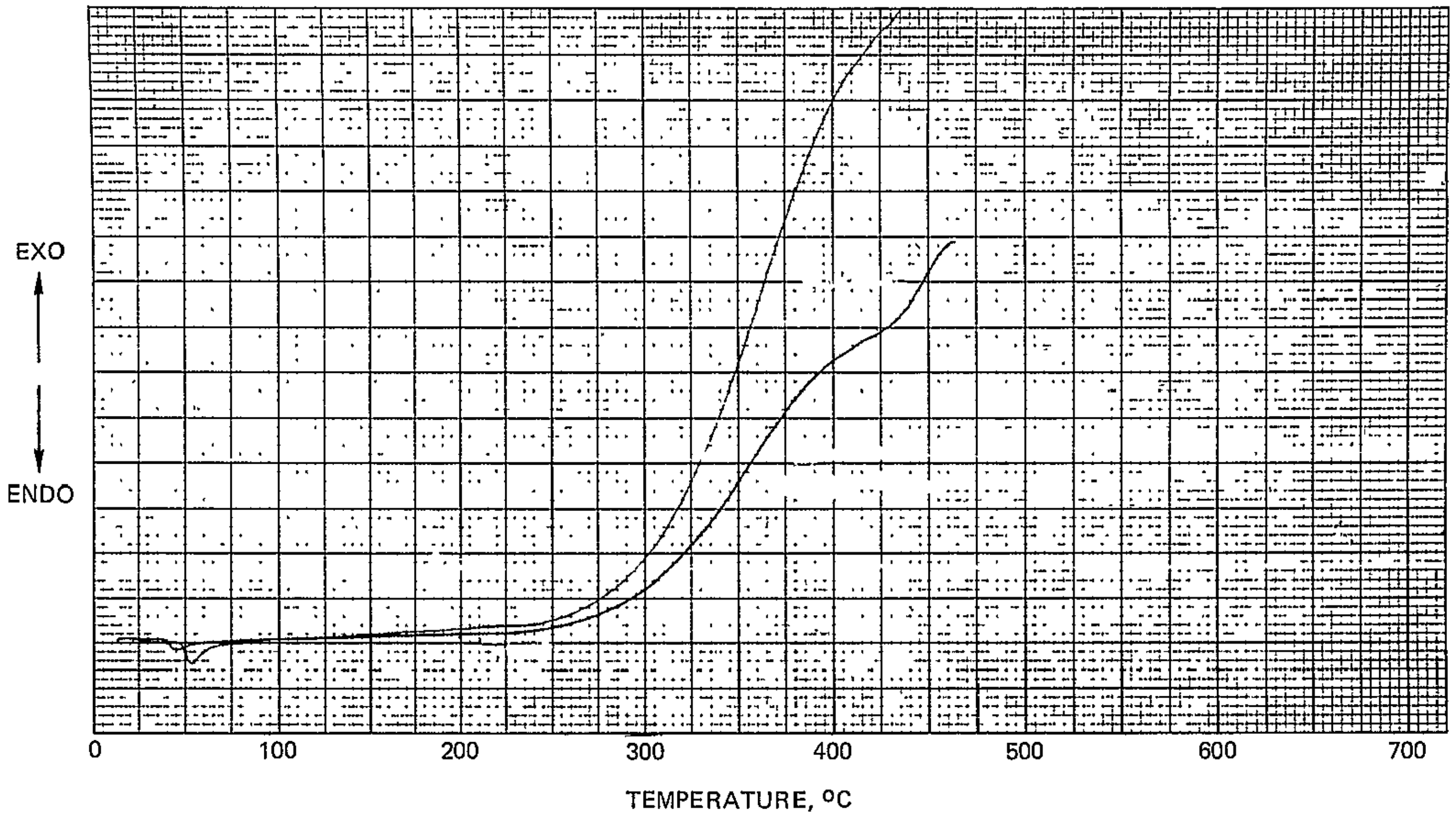


FIG. 33

78–12–38–3

DSC OF POLYMER DISC – 7

ATMOSPHERE = AIR
HEATING RATE = 10°C/MIN
SAMPLE WEIGHT = 4.3 MG



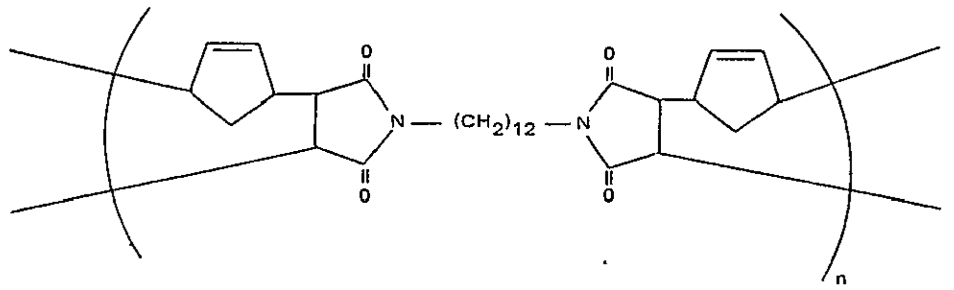
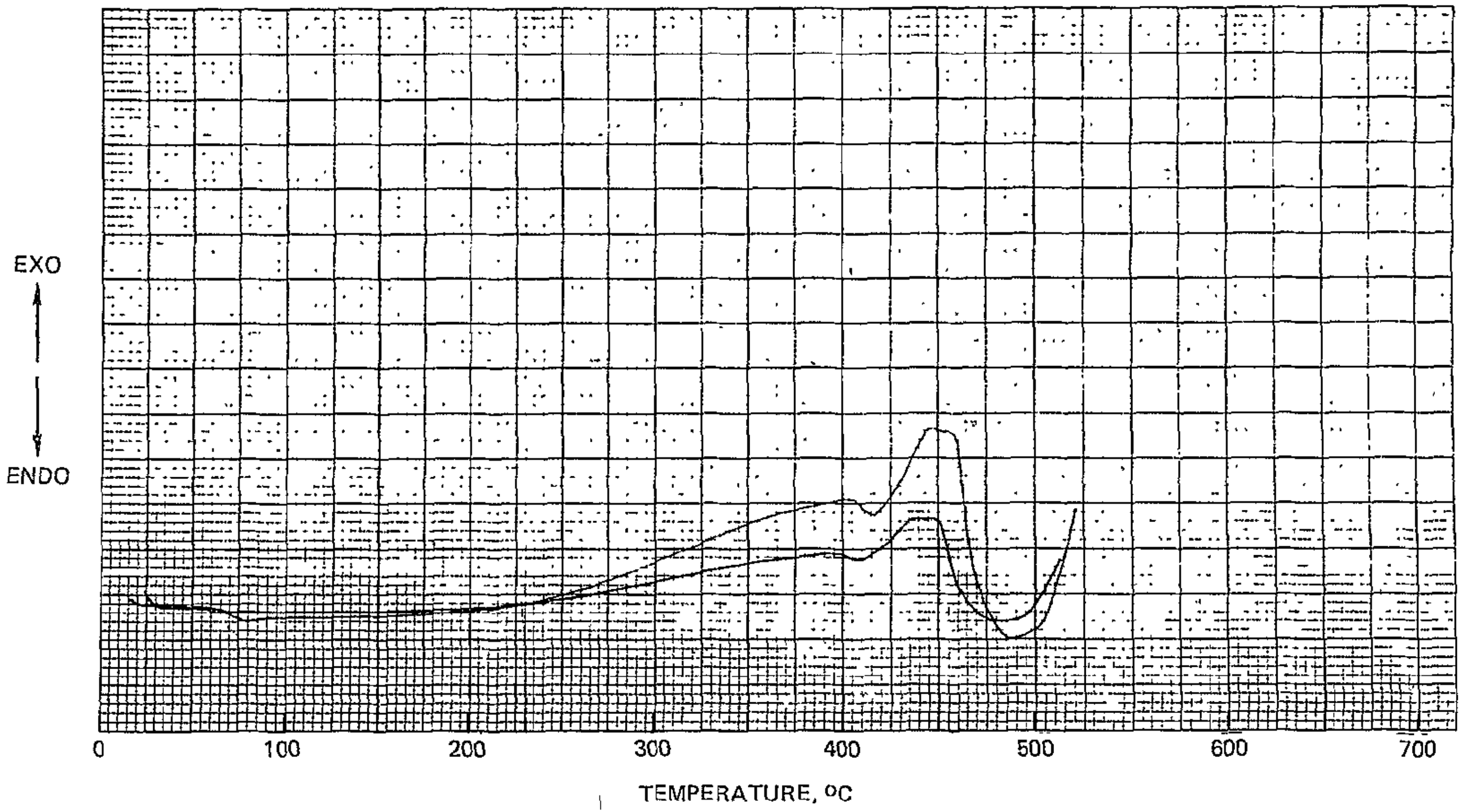


FIG. 34

DSC OF POLYMER DISC – 11

ATMOSPHERE = AIR
HEATING RATE = 10°C/MIN
SAMPLE WEIGHT = 8.2 MG



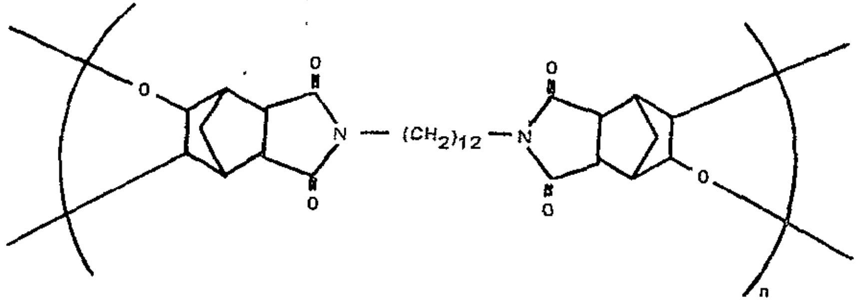


FIG. 35

DSC OF POLYMER DISC – 20

ATMOSPHERE = AIR
HEATING RATE = 10°C/MIN

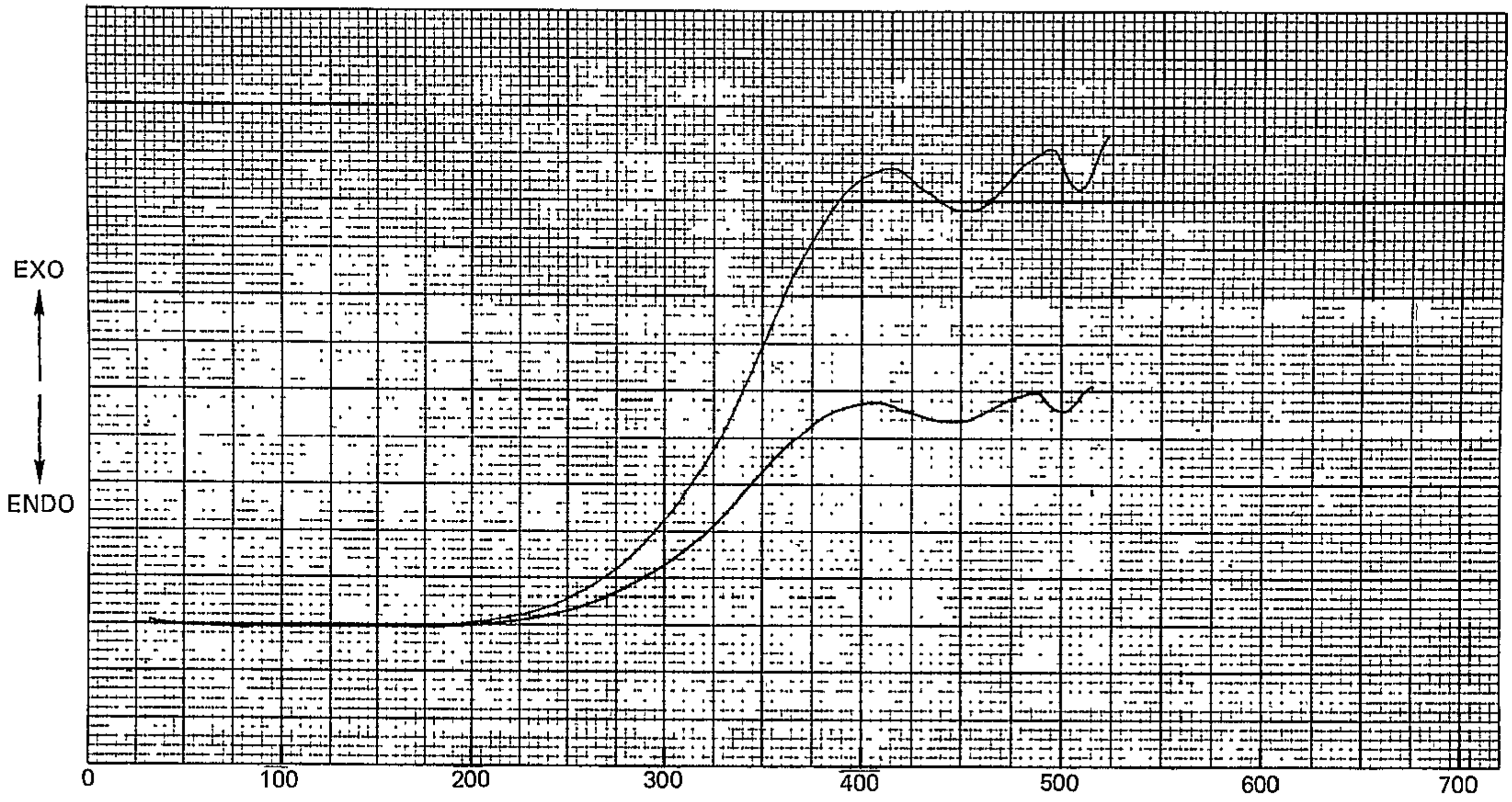


FIG. 36

78–12–38–5

DISTRIBUTION LIST

	Copies
National Aeronautics and Space Administration Lewis Research Center 21000 Brookpark Road Cleveland, OH 44135	
Attn: Contracting Officer, J. E. Bolander, M.S. 500-312	1
Technical Report Control Office, M.S. 5-5	1
Technology Utilization Office, M.S. 3-16	1
AFSC Liaison Office, M.S. 4-1	2
Library, M.S. 60-3	2
Office of Reliability & Quality Assurance, M.S. 500-211	1
M&S Division Contract File, M.S. 49-1	1
P. Delvigs, M.S. 49-1	Balance
N. T. Musial, M.S. 500-311	1
National Aeronautics and Space Administration Washington, DC 20546	
Attn: J. J. Gangler/Code RWM-3	1
NASA Scientific and Technical Information Facility Attn: Acquisitions Branch P.O. Box 8757 Baltimore/Washington International Airport, MD 21240	20
National Aeronautics and Space Administration Ames Research Center Moffett Field, CA 94035	
Attn: John Parker, M.S. 223-6	1
National Aeronautics and Space Administration Flight Research Center P.O. Box 273 Edwards, CA 93523	
Attn: Library	1
National Aeronautics and Space Administration Goddard Space Flight Center Greenbelt, MD 20771	
Attn: Library	1
National Aeronautics and Space Administration John F. Kennedy Space Center Kennedy Space Center, FL 32899	
Attn: Library	1

Distribution List (Cont'd)	Copies
National Aeronautics and Space Administration Langley Research Center Hampton, VA 23665	
Attn: V. L. Bell, M.S. 226	1
N. Johnston, M.S. 226	1
National Aeronautics and Space Administration Manned Spacecraft Center Houston, TX 77001	
Attn: Library	1
Code EP	1
National Aeronautics and Space Administration George C. Marshall Space Flight Center Huntsville, AL 35812	
Attn: J. Curry, EH31	1
J. Stuckey, EH33	1
Jet Propulsion Laboratory 4800 Oak Grove Drive Pasadena, CA 91103	
Attn: Library	1
Office of the Director of Defense Research and Engineering Washington, DC 20301	
Attn: Dr. H. W. Schulz, Office of Assistant Director (Chem.Technology)	1
Defense Documentation Center Cameron Station Alexandria, VA 22314	1
Research and Technology Division Bolling Air Force Base Washington, DC 20332	
Attn: Code RTNP	1
Bureau of Naval Weapons Department of the Navy Washington, DC 20360	
Attn: Code DLI-3	1

Distribution List (Cont'd) Copies

Director (Code 6180)
U.S. Naval Research Laboratory
Washington, DC 20390

Attn: H. W. Carhart 1

SARPA-FR-MD
Plastics Technical Evaluation Center
Picatinny Arsenal
Dover, NJ 07801

Attn: A. M. Anzalone, Bldg. 176 1

Acurex Corporation
Aerospace Systems Division
485 Clyde Avenue
Mountain View, CA 94042

Attn: C. Delano 1

Aeronautic Division of Philco Corporation
Ford Road
Newport Beach, CA 92600

Attn: Dr. L. H. Linder, Manager
Technical Information Department 1

Aerospace Corporation
P.O. Box 95085
Los Angeles, CA 90045

Attn: Library Documents 1

Aerotherm Corporation
800 Welch Road
Palo Alto, CA 94304

Attn: Mr. R. Rindal 1

Air Force Material Laboratory
Wright-Patterson Air Force Base, OH 45433

Attn: AFML/MBC, T. J. Reinhart, Jr. 1

Office of Aerospace Research (RROSP)
1400 Wilson Boulevard
Arlington, VA 22209

Attn: Major Thomas Tomaskovic 1

Composites Horizons
2303 W. Valley Boulevard
Pomona, CA 91768

Attn: Ira Petker 1

Distribution List (Cont'd)

Copies

Air Force Office of Scientific Research
Washington, DC 20333

Attn: SREP, Dr. J. F. Masi 1

American Cyanamid Company
1937 West Main Street
Stamford, CT 06902

Attn: Security Officer 1

AVCO Corporation
Space Systems Division
Lowell Industrial Park
Lowell, MA 01851

Attn: Library 1

Battelle Memorial Institute
505 King Avenue
Columbus, OH 43201

Attn: Report Library, Room 6A 1

Bell Aerosystems, Inc.
P.O. Box 1
Buffalo, NY 14205

Attn: T. Reinhardt 1

The Boeing Company
Aerospace Division
P.O. Box 3999
Seattle, WA 98124

Attn: J. T. Hoggatt 1

Celanese Research Company
Morris Court
Summit, NJ

Attn: Dr. J. R. Leal 1

University of Denver
Denver Research Institute
P.O. Box 10127
Denver, CO 80210

Attn: Security Office 1

Dow Chemical Company
Security Section
P.O. Box 31
Midland, MI 48641

Attn: Dr. R. S. Karpiuk, 1710 Building 1

Distribution List (Cont'd)

	Copies
E. I. DuPont De Nemours & Co. Research and Development Division Wilmington, DE 19898 Attn: Dr. H. H. Gibbs	1
Ultrasystems, Inc. 2400 Michelson Drive Irvine, CA 92664 Attn: Dr. R. Kratzer	1
General Dynamics/Convair Dept. 643-10 Kerny Mesa Plant San Diego, CA 92112 Attn: J. Hertz	1
Ferro Corporation 3512-20 Helms Avenue Culver City, CA 90230 Attn: T. Spooner	1
General Electric Company Technical Information Center N-32, Building 700 Cincinnati, OH 45215 Attn: C. A. Steinhagen	1
Fiberite Corporation 501-559, West 3rd Street Winona, MN 55987 Attn: J. Allen	1
Grumman Aerospace Corporation Advanced Materials & Processes Bethpage, NY Attn: A. London	1
Hexcel 11711 Dublin Blvd. Dublin, CA 94566 Attn: John D. Neuner	1
Hughes Aircraft Company Culver City, CA Attn: N. Bilow	1

Distribution List (Cont'd)

Copies

ITT Research Institute
Technology Center
Chicago, IL 60616

Attn: C. K. Hersh, Chemistry Division 1

Lockheed Missiles & Space Company
Propulsion Engineering Division (D.55-11)
111 Lockheed Way
Sunnyvale, CA 94087 1

McDonnell Douglas Corporation
Douglas Aircraft Company
3855 Lakewood Blvd.
Long Beach, CA 90846

Attn: N. Byrd 1

Monsanto Research Corporation
Dayton Laboratory
Station B, Box 8
Dayton, OH 45407

Attn: Library 1

North American Rockwell Corporation
Space & Information Systems Division
12214 Lakewood Blvd.
Downey, CA 90242

Attn: Technical Information Center, D/096-722 (AJ01) 1

Northrop Corporate Laboratories
Hawthorne, CA 90250

Attn: Library 1

Stanford Research Institute
Menlo Park, CA 94025

Attn: M. Maximovich 1

Union Carbide Corporation
12900 Snow Road
Parma, OH 44130

Attn: Library 1

United Technologies Corporation
Pratt & Whitney Aircraft
East Hartford, CT 06108

Attn: G. Wood 1

Distribution List (Cont'd) Copies

United Technologies Corporation
United Technology Center
P.O. Box 358
Sunnyvale, CA 94088
Attn: Library 1

Westinghouse Electric Corporation
Westinghouse R&D Center
1310 Beulah Road
Pittsburgh, PA 15235
Attn: Dr. J. H. Freeman 1

TRW Equipment
23555 Euclid Avenue
Cleveland, OH 44117
Attn: W. E. Winters 1

TRW Systems
One Space Park
Redondo Beach, CA 90278
Attn: Dr. R. J. Jones, Bldg. 01, Room 2020 1

General Dynamics
Convair Aerospace Division
P.O. Box 748
Fort Worth, TX 76101
Attn: Tech. Library, 6212 1

Material Science Corporation
1777 Walton Road
Blue Bell. PA 19422
Attn: Ms. N. Sabia 1

U.S. Polymeric
700 E. Dyer Blvd.
Santa Ana, CA 92707
Attn: D. Beckley 1

U.S. Army Air Mobility R&D Lab
Fort Eustis, VA 23604
Attn: Mr. H. L. Morrow, SAVDL-EU-TAP 1

U.S. Army Aviation Systems Command
P.O. Box 209, Main Office
St. Louis, MO 63166
Attn: Mr. Ronald Evers 1

Distribution List (Cont'd)	Copies
Air Force Materials Laboratory Wright-Patterson Air Force Base, OH 45433 Attn: Mr. Paul Pirrung, AFML/LTN	1