AFWAL-TR-82-4038

SYNTHESIS AND PROPERTIES OF MODEL AROMATIC POLYIMIDE SYSTEMS

B.A. Reinhardt
F.E. Arnold

Polymer Branch
Nonmetallic Materials Division

August 1982

Final Report for Period January 1980 to October 1980

MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

NOTICE

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

F. E. Arnold

F. E. ARNOLD
Project Scientist

R. L. Van De

R. L. VAN DEUSEN
Chief, Polymer Branch

FOR THE COMMANDER

F. D. Cherry

F. D. CHERRY, Chief
Nonmetallic Materials Division

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
AFWAL-TR-82-4038

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (*and Subtitle*)
SYNTHESIS AND PROPERTIES OF MODEL AROMATIC POLYIMIDE SYSTEMS

5. TYPE OF REPORT & PERIOD COVERED
Final Report
January 1980 to October 1980

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(*s*)
B.A. Reinhardt
F.E. Arnold

8. CONTRACT OR GRANT NUMBER(*s*)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Materials Laboratory (AFWAL/MLBP)
Air Force Wright Aeronautical Laboratories
Wright-Patterson Air Force Base, Ohio 45433

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
62102F/2419/04
24190415

11. CONTROLLING OFFICE NAME AND ADDRESS
Materials Laboratory (AFWAL/MLB)
Air Force Wright Aeronautical Laboratories
Wright-Patterson Air Force Base, Ohio 45433

12. REPORT DATE
August 1982

13. NUMBER OF PAGES
26

14. MONITORING AGENCY NAME & ADDRESS(*if different from Controlling Office*)

15. SECURITY CLASS. (*of this report*)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (*of this Report*)

Approved for public release, distribution unlimited.

17. DISTRIBUTION STATEMENT (*of the abstract entered in Block 20, if different from Report*)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (*Continue on reverse side if necessary and identify by block number*)
Oligomers
Polymers
Polymides

20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

In an effort to investigate the hydrolytic stability of completely aromatic polymides a series of model polymeric imide structures have been synthesized. The materials consist of oligomeric thermoset systems and high molecular polymers. Equivalent backbone structures were synthesized differing only in respect to the size of the imide ring. It is anticipated that the utilization of the model systems prepared will establish the hydrolytic stability of aromatic polyimides.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*)

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419 "Aerospace Structural Materials," Task No. 241904 Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F.E. Arnold as the AFWAL Project Scientist. Co-authors were Mr. B.A. Reinhardt and Dr. F.E. Arnold, Materials Laboratory, (AFWAL/MLBP).

This report covers research conducted from January 1980 to October 1980.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

SECTION I

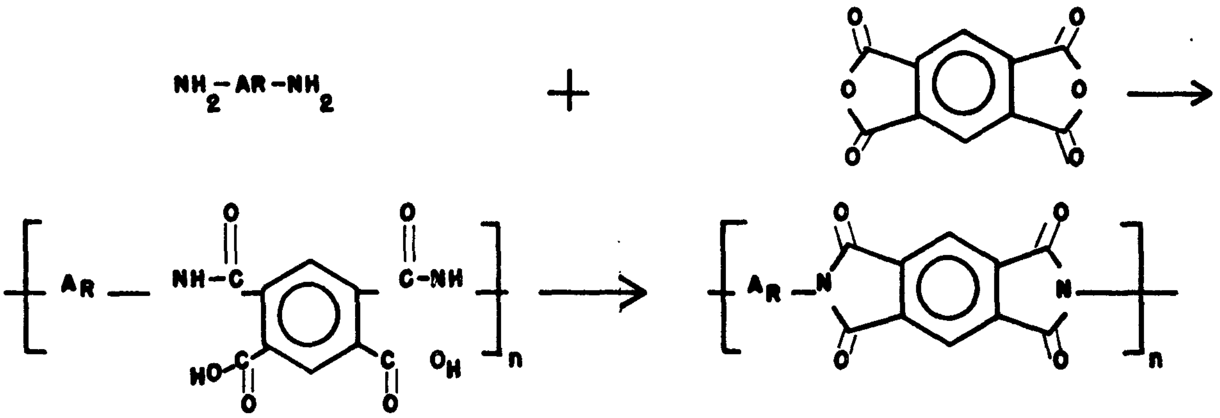
INTRODUCTION

Environmental resistance of matrix and adhesive resins has become increasingly important as such materials are being used to a greater extent in applications for lighter weight Air Force and Aerospace systems. The environment differs quite drastically depending on the mission requirements of a new space system in contrast to a land based system.

The primary element pertinent to land based systems is the effect of moisture in the environment. Resin matrix materials absorb moisture under ambient exposure conditions which cause degradation of resin properties at elevated temperatures. The effect of moisture pickup by composite materials can result in a loss of matrix controlled mechanical properties, reduction in interface properties, controlled properties, sustained dimensional changes and increased rates of stress relaxation and creep.

Mechanisms by which matrix resins are effected by moisture involve either a plasticization by water or longer term, hydrolytic cleavage of the polymer chains. Plasticization is evident in the current state-of-the-art epoxide matrix materials. The cured epoxides absorb moisture at ambient temperatures which reduces their mechanical properties quite severely at elevated temperatures due to a plasticization effect of the water molecules (Reference 1). Epoxide systems are limited to 200-250°F use temperature, although thermal and thermal mechanically they have the potential of a 350°F use temperature in a dry atmosphere.

Longer term effects such as hydrolytic stability is more difficult to investigate. The aromatic polyimide resins which are the next generation of high temperature matrix materials are suspect from their hydrolytic stability. Aromatic polyimide polymers are synthesized by the condensation of an aromatic diamine and an aromatic dianhydride to first form a polyamic acid which is then dehydrated to form the cyclic imide structure.



Any determination of the hydrolytic stability of aromatic polyimides is complicated by the presence of residual polyamic acid due to incomplete dehydration in the imide forming step of the reaction. Although the concentration of amic acid groups is usually very low, any amic acid groups incorporated in the polymer backbone present a two-fold problem in a study of hydrolytic stability. The amic acid groups not only are sites for hydrolysis to easily take place but the acid groups themselves may catalyze any reaction of water with the more prevalent imide linkages.

The objective of this work is to synthesize model polyimide systems, which are free of any amic acid and could be studied both for the short and long term stabilities toward absorbed moisture. The approach chosen to circumvent the above problems involved the synthesis of acetylene terminated imide (Reference 2) monomers and polymers via a method not involving amic acid intermediates. The imide monomers could then be thermally polymerized to form a thermoset model system for investigation. As a comparison, six-membered imides of identical structure could also be synthesized. The six-membered imide ring system has been shown (Reference 3) to be very hydrolytically stable and would provide an ideal comparative material.

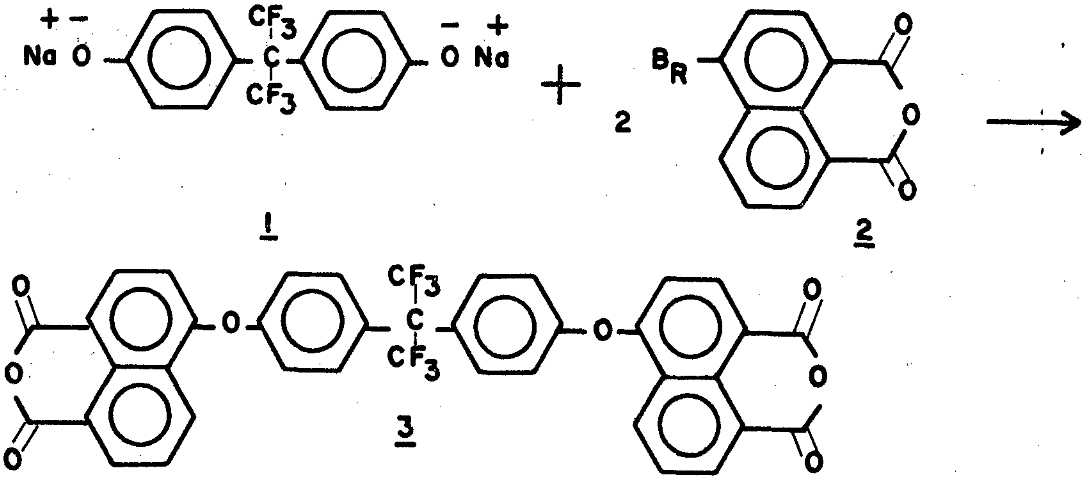
SECTION II

RESULTS AND DISCUSSION

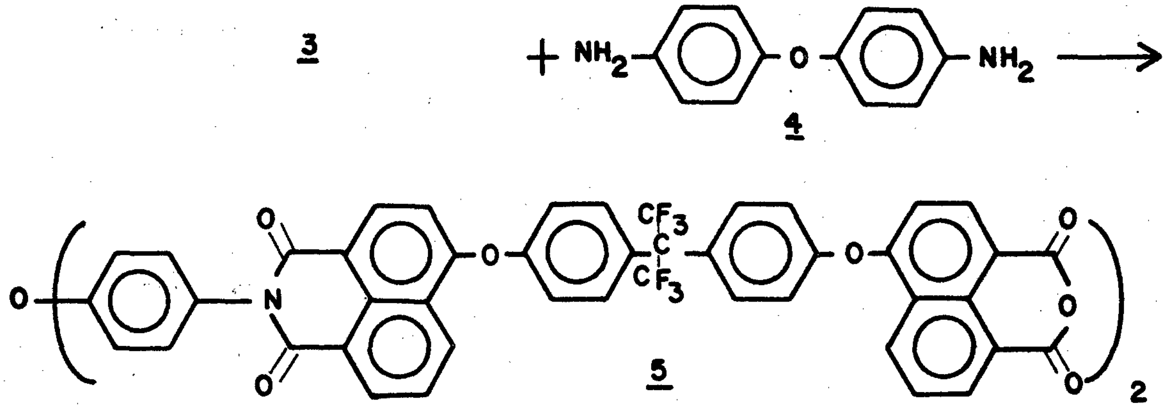
1. SYNTHESIS

It was postulated that in all of the model systems to be synthesized the six-membered analogs would be the most difficult to purify and fabricate into testable specimens. In all cases the six-membered imides were synthesized prior to the five-membered. If they proved to have glass transition temperatures too high to make fabrication feasible, the synthesis of the five-membered of similar structure was not carried out.

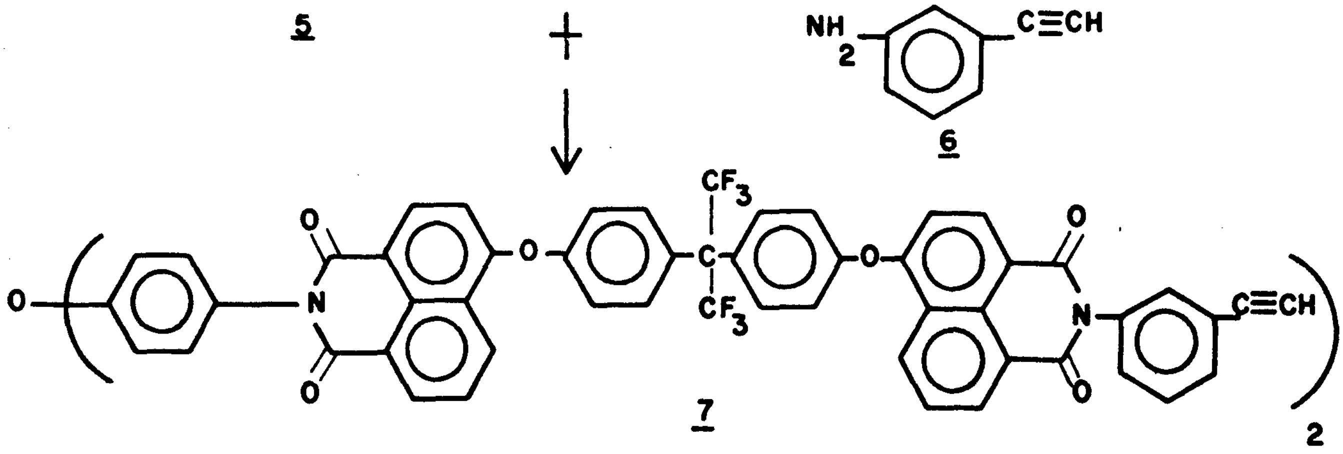
The reaction of the disodium salt of the bis-diol 1 with 2 moles of 4-bromonaphthalic anhydride 2 gave the aromatic dianhydride 3 in 30% yield. Excess 3 was then allowed



to react with 4-,4'-diaminodiphenyl ether I to give the anhydride end-capped imide 5.

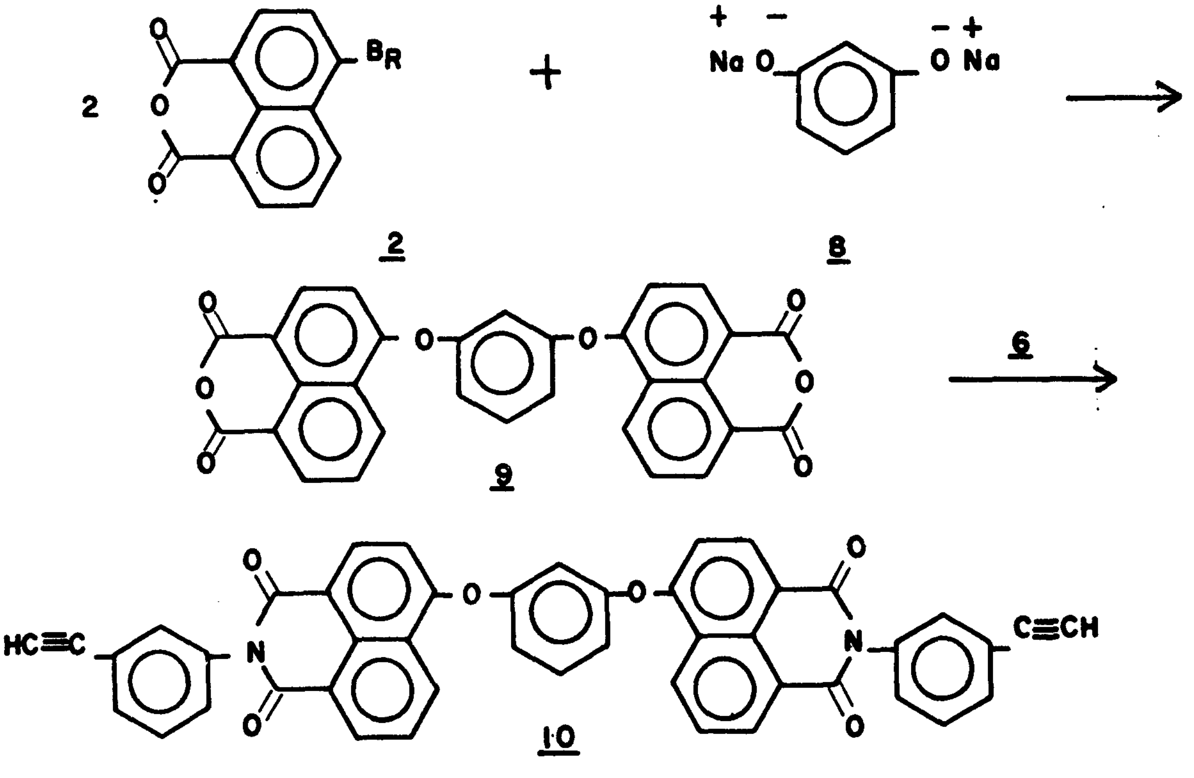


The dianhydride 5 was the end-capped with excess 3-aminophenylacetylene to give the acetylene terminated imide 7.



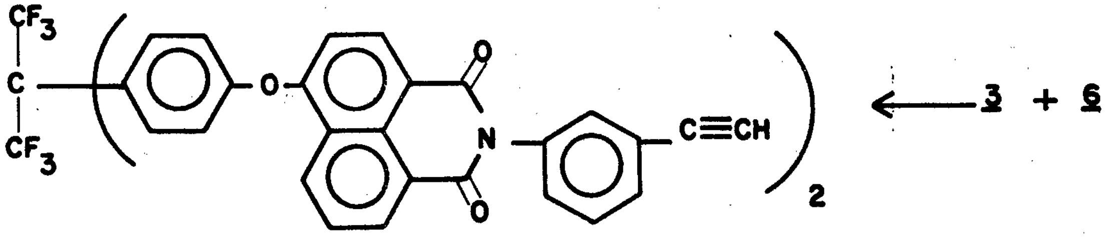
The DSC Thermogram of 7 showed a glass transition temperature of 226° with a polymerization onset temperature of 240°C. The proximity of the two temperatures made fabrication impossible.

In an attempt to synthesize a more processible system, 4-bromonaphthalic anhydride 2 was reacted with the disodium salt of resorcinol 8 to give the anhydride 9. The dianhydride 9 was end-capped with excess 3-aminophenylacetylene 6 to give the acetylene terminated imide 10.



The imide 10 had a lower glass transition temperature (200°C) than 7 but the polymerization exotherm began immediately after the glass transition temperature. This, made 10, like 7, impossible to process.

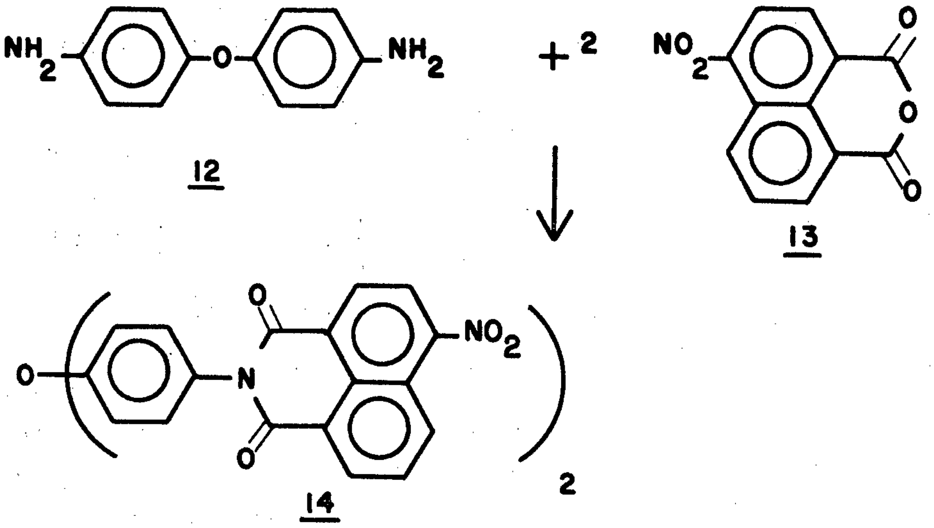
Another system investigated involved the end-capping of the dianhydride 3 with excess 3-aminophenylacetylene 6 to produce 11.



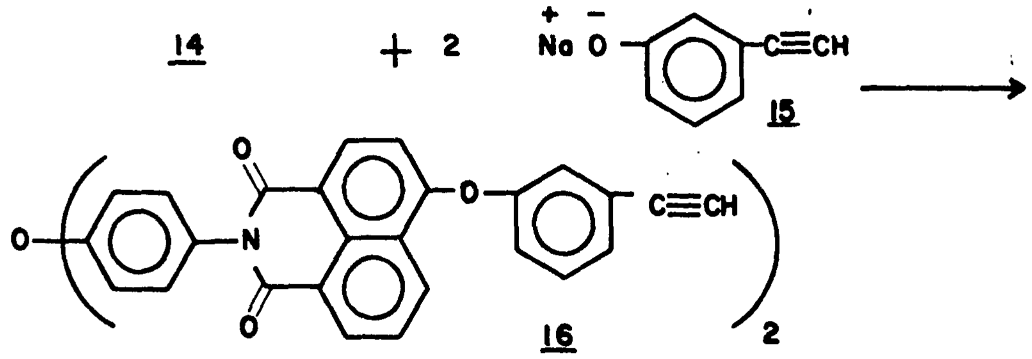
11

The diacetylene 11 could not be purified to a sufficient degree to warrant hydrolysis studies. Preliminary DSC studies on crude material showed the presence of a mixture of compounds. This was confirmed by carbon hydrogen analysis.

A similar diacetylene was synthesized by the reaction of 4-,4'-diaminodiphenyl ether (12) with 2 moles of 4-nitronaphthalic anhydride 13 to give the dinitroimide 14.

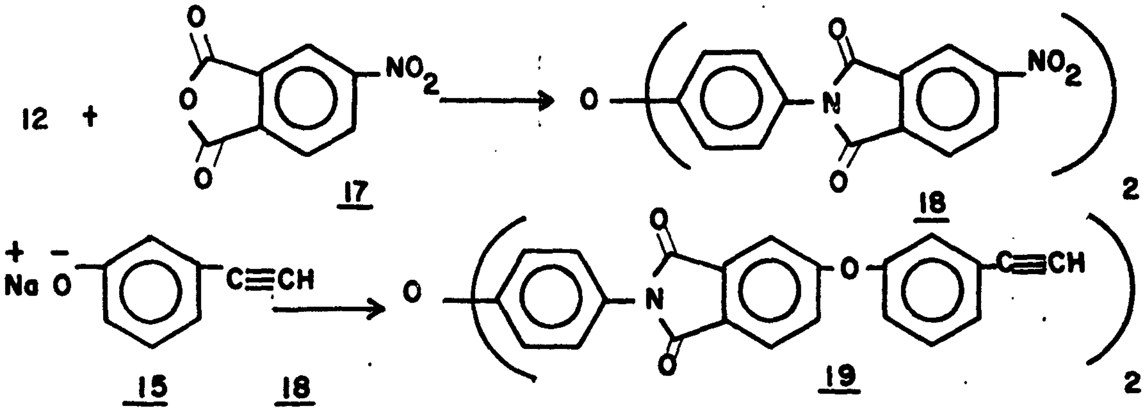


The dinitroimide 14 underwent nitrodisplacement with excess sodium salt of 3-hydroxyphenylacetylene (15) to give the acetylene terminated imide 16.

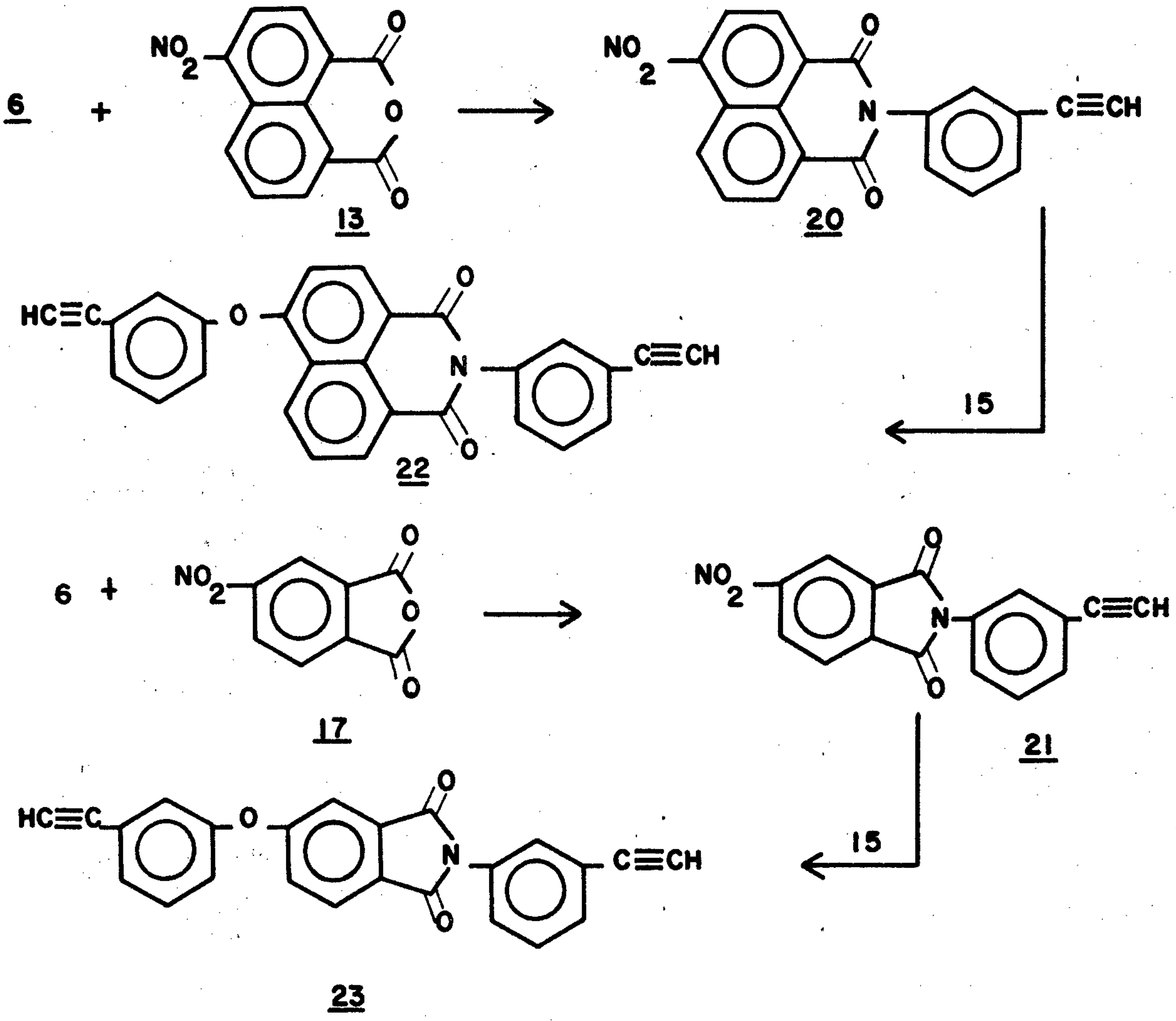


Differential Scanning Calorimetry (DSC) analysis showed 16 to be crystalline and have a doublet melting point at 211° and 216°. These were followed by a doublet exotherms at 249° and 261° corresponding to the onset of polymerization. In addition the diacetylene 16 could be fabricated into films suitable for hydrolysis studies.

The five-membered analog to 16, 19 was synthesized by the condensation of 12 with 3-nitrophthalic anhydride 17 to form the dinitroimide 18 in high yield. The nitrodisplacement of 18 with excess 15 gave a product which appeared to consist mostly of the diacetylene 19. Purification of 19 could not have been carried out to the extent needed to produce material of high enough purity to warrant further study.

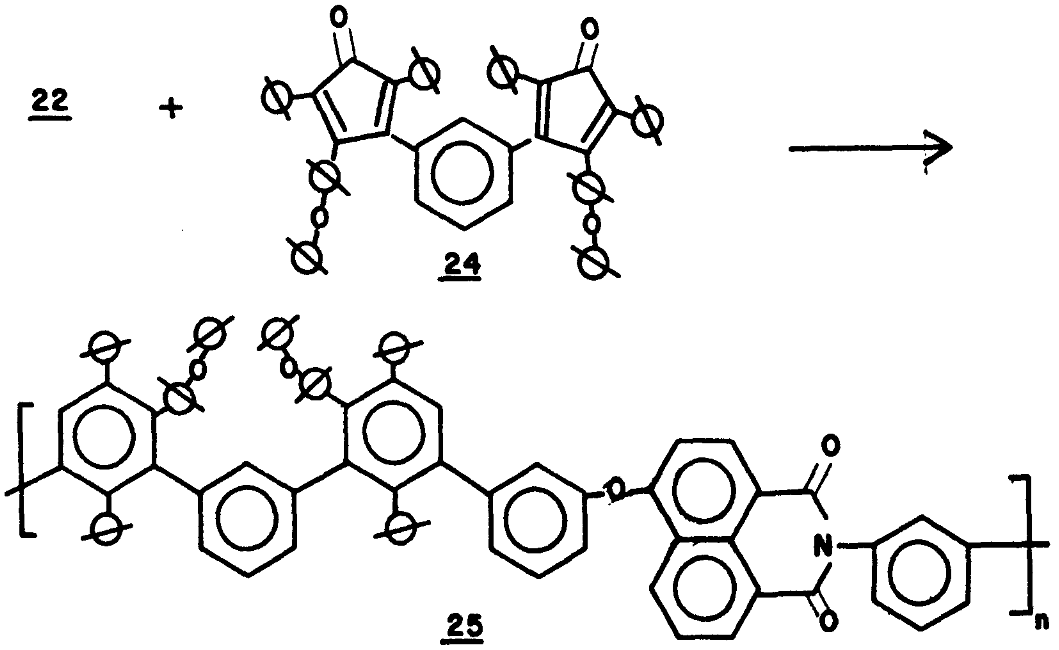


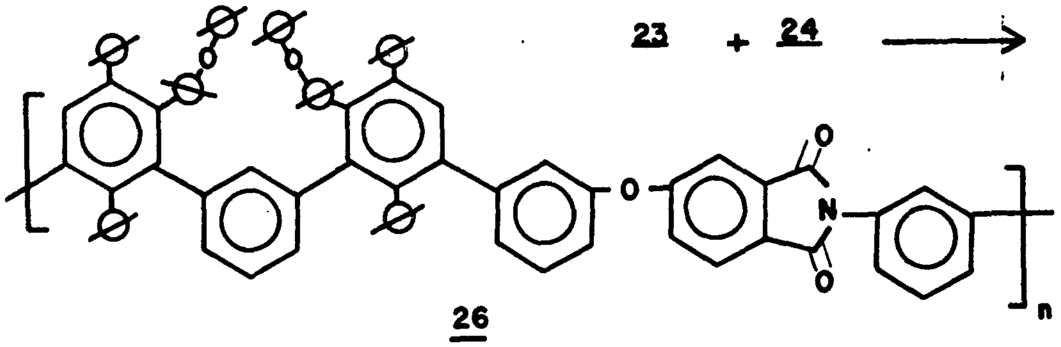
A synthetic approach which did yield pure processible resins involved the reaction of 3-aminophenylacetylene 6, with either the six- or five-membered anhydrides 13 and 17 to produce the corresponding nitro imides 20 or 21. The high nitrodisplacement reaction of these imides with excess gave 22 and 23 in high yields.



The imide 22 by DSC analysis exhibited a melting point of 205°C and 133°C for 23. When the resins were heated through the melting point to the beginning of the polymerization exotherm and then cooled slowly, all crystallinity was lost and a Tg of 78°C for 22 and 3°C for 23 resulted.

In addition to the above thermoset systems, the following high molecular weight thermoplastic systems were synthesized by the Diels-Alder polymerizations of 22 and 23 with the biscyclopentadienone 24. The polymers 25 and 26 were soluble in chloroform and other common organic solvents. Thin flexible films suitable for hydrolysis studies could be cast from chloroform.





The polymer 25 showed a Tg of 273° by DSC analysis while polymer 26 showed a Tg of 238°.

2. FILM FABRICATION

The three thermoset systems which could be fabricated into suitable film specimens included the acetylenes 16, 22 and 23. A representative procedure used in the films fabricated follows:

Two pieces of Teflon film were pressed together at 260° and 71-107 KN. The sheets were cooled under pressure and resin placed between them when they had reached room temperature. The Teflon-resin assembly was then placed between cauls at 221°C and 31 KN of pressure applied immediately. The assembly was heated at 221°C for one-half hour and then allowed to cool slowly under pressure.

SECTION III

EXPERIMENTAL

1. 4,4'-BIS(4-OXY-1,8-NAPHTHALIC ANHYDRIDE)-1,1-PERFLUORODIPHENYL-METHANE-3

A solution of 6.72g (0.02 mole) of 1,1'hexafluoroacetone bisphenol, 2.16g (0.04 mole) of powdered sodium methoxide, 50 ml of absolute methanol and 50 ml of toluene was heated to reflux under nitrogen. The toluene and methanol were removed by distillation. When a white paste had formed, 50 ml of additional toluene were added and distilled to remove the last traces of methanol. When the toluene was completely removed the white disodium salt 1 solidified. To the precipitate under nitrogen was added 200 ml of dry DMAC and 11.04g (0.04 mole) of 4-bromonaphthalic anhydride 2. The reaction mixture was slowly heated to 150° and maintained at that temperature for 6 hours. The reaction mixture was allowed to cool and poured into 1200 ml of ice water. The resulting light yellow solid was filtered, washed with water, and air dried. The crude solid was recrystallized from ethylacetate (charcoal) to give 5.0g (33%) of purified product; mp 165-166°.

Analysis Calcd for $C_{39}H_{18}O_8F_6$: C,64.29; H,2.49

Found: C,64.15; H,2.25

2. 1,3-BIS(4-OXY-1,8-NAPHTHALIC ANHYDRIDE)PHENYLENE 9

To a solution of 2.20g (0.02 mole) of resorcinol in 100 ml of anhydrous benzene under nitrogen was added 2.08g (0.04 mole) of powdered sodium methoxide. The reaction mixture was allowed to stir at room temperature for 1 hour and 11.04g (0.02 mole) of 4-bromonaphthalic anhydride 2 in 200 ml DMAC was added. The reaction mixture was slowly heated to 100° to remove the benzene and any methanol that was formed. The temperature of the dark solution was raised to 150° and maintained there for 6 hours. The reaction mixture was cooled to room temperature and poured onto 600g of ice to aid coagulation of a finely divided precipitate. The result solid was filtered, washed with water, and dried under vacuum at 100° for 18 hours. The product was purified by stirring in boiling acetone. The yield of purified product was 7.6g (75.6%). The melting point determined by DSC was 267°.

Analysis Calcd for $C_{30}H_{14}O_8$: C,71.71; H,2.81

Found: C,71.20; H,2.72

3. SIX-MEMBERED AT-OLIGOMER 10

A solution of 1.3489g (0.0027 mole) of the dianhydride 9 and 0.9434g (0.0081 mole) of 3-aminophenylacetylene 6 in 15 ml of m-cresol was stirred at 90° for 18 hours. The temperature of the reaction mixture was raised to 130° for an additional 18 hours. The reaction mixture was cooled to room temperature and poured into 600 ml of methanol. The resulting precipitate was filtered, air dried, and purified by column chromatography on silica gel using methylene chloride as the eluent. The DSC of the purified compound showed a base line shift at 200° characteristic of a glass transition.

Analysis Calcd for $C_{46}H_{24}O_6N_2$: C,78.85; H,3.45; N,4.00

Found: C,75.83; H,2.99; N,3.59

4. SIX-MEMBERED AT-OLIGOMER 11

A solution of 1.9561g (0.0027 mole) of the dianhydride 3 and 0.9434g (0.0081 mole) in 15 ml of m-cresol under nitrogen was heated at 130° for 24 hours. The reaction mixture was cooled to room temperature and precipitated into 1000 ml of methanol. The off-white solid was filtered, air dried, and purified by column chromatography using 4:1 methylene chloride-ethylacetate. Carbon hydrogen analysis showed the chromatographed material to be a mixture of compounds. The mixture could not be purified further.

5. SIX-MEMBERED AT-OLIGOMER 16

To a solution of 4.37g (0.018 mole) of 4-nitronaphthalic anhydride 13 and 1.802g (0.009 mole) of 4,4'-oxydianiline 12 in 20 ml acetic acid was heated to reflux for 18 hours. The reaction mixture was cooled to room temperature and the solid which precipitated was filtered, washed repeatedly with water and dried under vacuum at 110°. The crude solid

5.0g (89%) could not be purified further and was used in the crude state for the next synthesis.

A solution of 1.54g (0.013 mole) of 3-ethynylphenol, 0.70g (0.017 mole) of powdered sodium hydroxide, 15 ml of benzene and 50 ml of absolute methanol were heated to reflux under nitrogen. The benzene and methanol were removed by distillation to give the dry sodium salt 15. To the dry salt, under nitrogen was added 4.0g (0.0064 mole) of the bis-nitroimide 14 in 65 ml of dry DMAC. The reaction mixture was heated to 75° for 1 hour, cooled to room temperature and poured into 1500 ml of methanol. The resulting solid was purified by column chromatography on neutral alumina using 5:1 chloroform-hexane as the eluent. The light yellow product had a doublet mp (DSC), at 211° and 216°.

Analysis Calcd for $C_{52}H_{28}O_7N_2$: C,78.78; H,3.56; N,3.53

Found: C,78.57; H,3.23; N,3.36

6. FIVE-MEMBERED AT-OLIGOMER 19

A solution of 3.87g (0.02 mole) of nitrophthalic anhydride and 2.0g (0.01 mole) of oxydianiline in 20 ml of m-cresol containing 2 drops of isoquinoline was heated slowly to 180° under nitrogen for 4 hours. The reaction mixture was cooled and poured into 1l of absolute ethanol. The resulting solid was filtered, air dried, and extracted with ethanol for 24 hours to remove any remaining m-cresol. The yield of bis-nitroimide 18 after extraction was 4.95 (90%), mp 115-116°.

Analysis Calcd for $C_{28}H_{14}N_4O_9$: C,61.10; H,2.56; N,10.17

Found: C,60.85; H,2.24; N,9.94

A mixture of 1.28g (0.018 mole) of 3-ethynylphenol, 0.72g (0.018 mole) of powdered sodium methoxide, 70 ml of dry benzene and 25 ml of absolute methanol was heated to reflux under nitrogen. The benzene and methanol were removed by distillation to give the sodium salt 15. To the dry salt was added 50 ml of dry DMAC and 3.0g (0.0054 mole) of the bis-nitroimide 18 and the reaction mixture heated to 65° for 3 hours. The solution was cooled to room temperature and poured into 1ℓ of methanol. The crude solid which resulted was purified by chromatography on silica gel using methylene chloride as the eluent.

Analysis Calcd for $C_{44}H_{24}O_7N_2$: C,76.29; H,3.49; N,2.04

Found: C,76.68; H,3.15; N,3.59

7. N-3-ETHYNYLPHENYL-4-NITRONAPHTHALIMIDE 20

A mixture of 24.3g (0.10 mole) of 4-nitronaphthalic anhydride and 11.7g (0.10 mole) of 3-aminophenylacetylene in 300 ml of glacial acetic acid under nitrogen was refluxed for 1 hr cooled, and filtered. The precipitate was washed with methanol and air dried. Recrystallization from toluene (charcoal) gave 20.0g (58%) of product, m.p. 265-267 dec.

Analysis Calcd for $C_{20}H_{10}N_2O_4$: C,70.17; H,2.94; N,8.18

Found: C,69.85; H,2.73; N,8.41

8. N-3-ETHYNYLPHENYL-4-(3-ETHYNYLPHENOXY)NAPHTHALIMIDE 22

To the sodium salt of 3-ethynylphenol 15, prepared from 5.95g (0.05 mole) of 3-ethynylphenol and 2.7g (0.05 mole) of sodium methoxide in methanol and benzene and dried by distillation with additional benzene, under nitrogen was added 200 ml of dry N, N-dimethylacetamide. The mixture was heated to 70° and 17.1g (0.05 mole) of N-3-ethynylphenyl-4-nitronaphthalimide was added. The dark solution was heated at 70° for 1 hour, cooled, and poured into 2.5l of ice water. The precipitate was collected by filtration and air dried. Chromatography of the solid on dry silica gel using methylene chloride as the eluent gave 7.5g (36%) of product, mp 200-202.

Analysis Calcd for $C_{28}H_{15}NO_3$: C,81.34; H,3.65; N,3.38

Found: C,81.45; H,3.67; N,3.42

9. 4-NITRO-N-(3-ETHYNYLPHENYL)PHTHALIMIDE 21

To a solution of 19.7g (0.10 mole) of 4-nitrophthalic anhydride in 150 ml of glacial acetic acid was added 12.9g (0.11 mole) of 3-aminophenylacetylene and a white precipitate formed immediately. The mixture was heated to reflux for 1 hr, then cooled and filtered. The precipitate was washed with water and methanol. Recrystallization from toluene gave

25.7g (87%) of product melting at 257-259°.

Analysis Calcd for $C_{16}H_8N_2O_4$: C,65.75; H,2.75; N,9.58

Found: C,65.35; H,2.45; N,9.84

10. 4-(3-ETHYNYLPHENOXY)-N-(3-ETHYNYLPHENYL)PHTHALIMIDE 23

To the sodium salt of 3-ethynylphenol 15, prepared from 4.3g (0.036 mole) of 3-ethynylphenol and 2.0g (0.037 mole) of sodium methoxide in methanol and benzene and dried by distillation with additional benzene, under nitrogen was added 50 ml of dry N,N-dimethylacetamide. The mixture was heated to 70° and 12.0g (0.041 mole) of 4-nitro-N-(3-ethynylphenyl) phthalimide was added. The dark mixture was stirred at 70° for 3 hrs then poured into 1,500 ml of cold distilled water containing some ice. A precipitate formed when about 100 ml of 1N sulfuric acid was added. The precipitate was collected by filtration, air dried, and dissolved in 100 ml of methylene chloride. Any insoluble material was removed by filtration. Chromatography of the filtrate on silica gel using 1:1 hexane-methylene chloride as the eluent gave 5.8g (44%) of product melting at 150-160°. A slight yellow color was removed by washing with methanol.

Analysis Calcd for $C_{24}H_{13}NO_3$: C,79.33; H,3.60; N,3.85

Found: C,79.12; H,3.45; N,3.98

11. HIGH MOLECULAR WEIGHT PHENOXYPHENYLATED NAPHTHALIMIDE POLYMER 25

A solution of 0.8399g (0.00096 mole) of phenoxyphenylated biscyclopentadienone 24 and 0.3968g (0.00096 mole) of 4-(3-ethynylphenoxy)-N-(3-ethynylphenyl) naphthalimide 22 in 7 ml of 1,2,4-trichloro benzene was degassed under vacuum by several freeze thaw cycles and sealed in a tube. The tube-containing the reaction mixture was heated at 220° for 18 hrs and the temperature then raised to 240° for 24 additional hrs. The tube was cooled to room temperature, frozen in liquid nitrogen, and opened. When the contents had warmed to room temperature the solution was diluted with 30 ml of chloroform, and precipitated into 1l of methanol. The off-white polymer was reprecipitated from chloroform-methanol to give an almost quantitative yield of polymer with an intrinsic viscosity in DMAC of 0.54.

Analysis Calcd for $(C_{90}H_{57}NO_5)n$: C,87.71; H,4.66; N,1.19

Found: C,87.64; H,4.43; N, .94

12. HIGH MOLECULAR WEIGHT PHENOXYPHENYLATED PHTHALIMIDE POLYMER 26

A solution of 0.083998g (0.00096 mole) of phenoxyphenylated bis-cyclopentadienone and 0.34881g (0.00096 mole) of 4-(3-ethynylphenoxy)-N-(3-ethynylphenyl)phthalimide 23 in 7 ml 1,2,4-trichlorobenzene was polymerized by the procedure described above the yield a quantitative yield of white polymer. The polymer had an intrinsic viscosity of 0.61 in DMAC.

Analysis Calcd for $(C_{86}H_{55}NO_5)n$: C,87.36; H,4.69; N,1.18

Found: C,87.16; H,4.49; N,1.31

SECTION IV

CONCLUSIONS

This work was performed to provide model aromatic imide polymers which can be utilized in a detailed investigation on the moisture susceptibility of fully aromatic polyimide systems. The materials prepared include both thermoset and thermoplastic systems which can be readily processed into neat film specimens. The model polymers consist of both six-membered and five-membered imide rings which will allow a variance of molecular structure versus short term, thermomechanical effects and longer term hydrolytic stability.

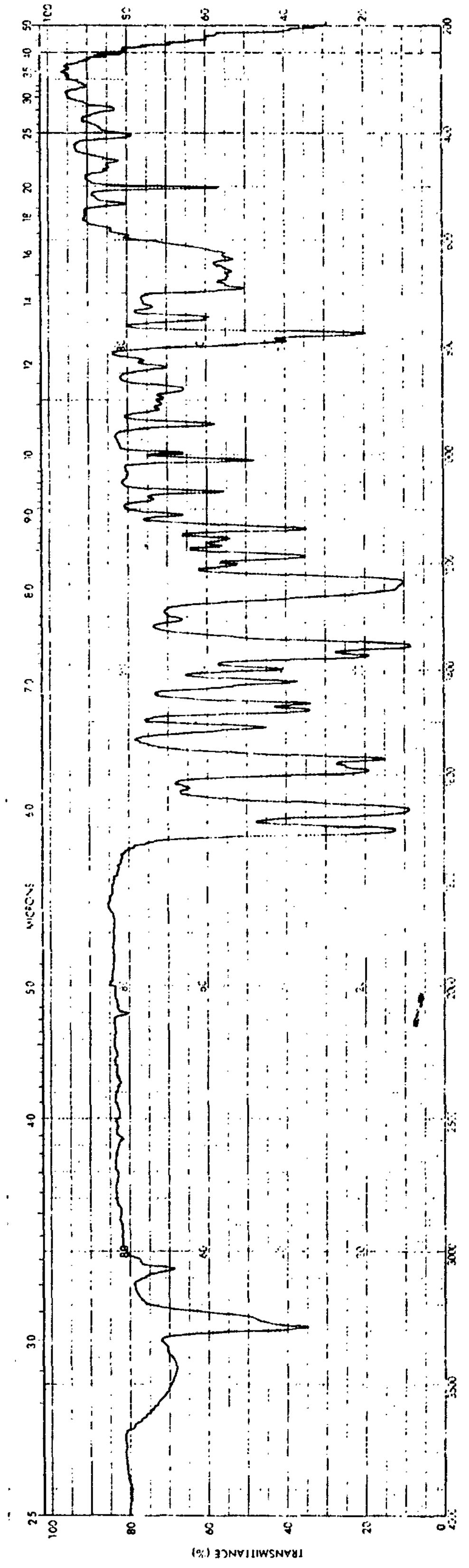


Figure 1. Infrared spectrum of N-3-Ethynyl-4-(3-ethynylphenoxy)naphthalimide. (22)

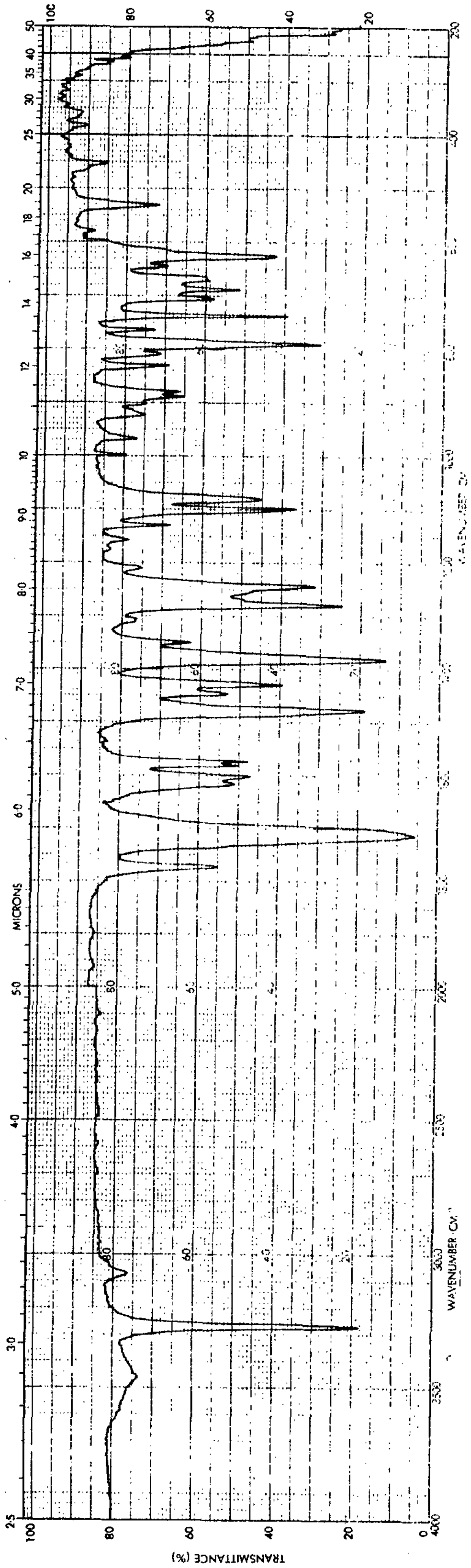


Figure 2. Infrared spectrum of 4-(3-ethynylphenoxy)-N-(3-ethynylphenyl) phthalimide. (23)

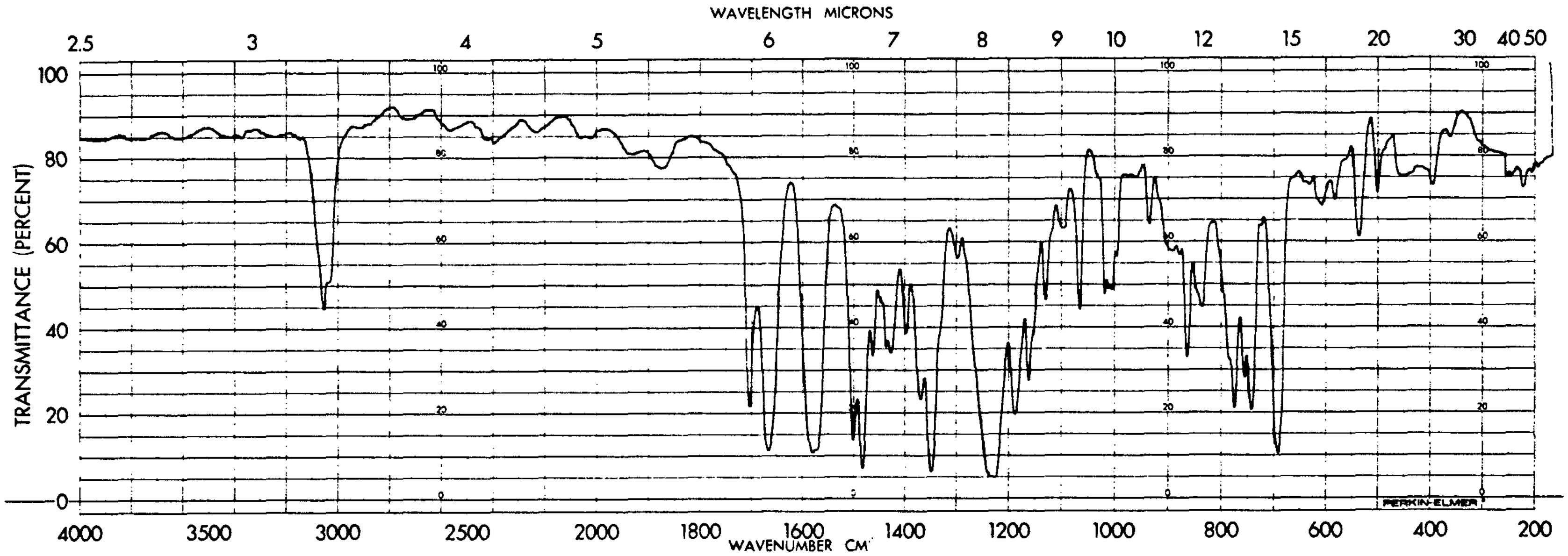


Figure 3. Infrared spectrum of high molecular weight phenoxyphenylated naphthalimide polymer. (25)

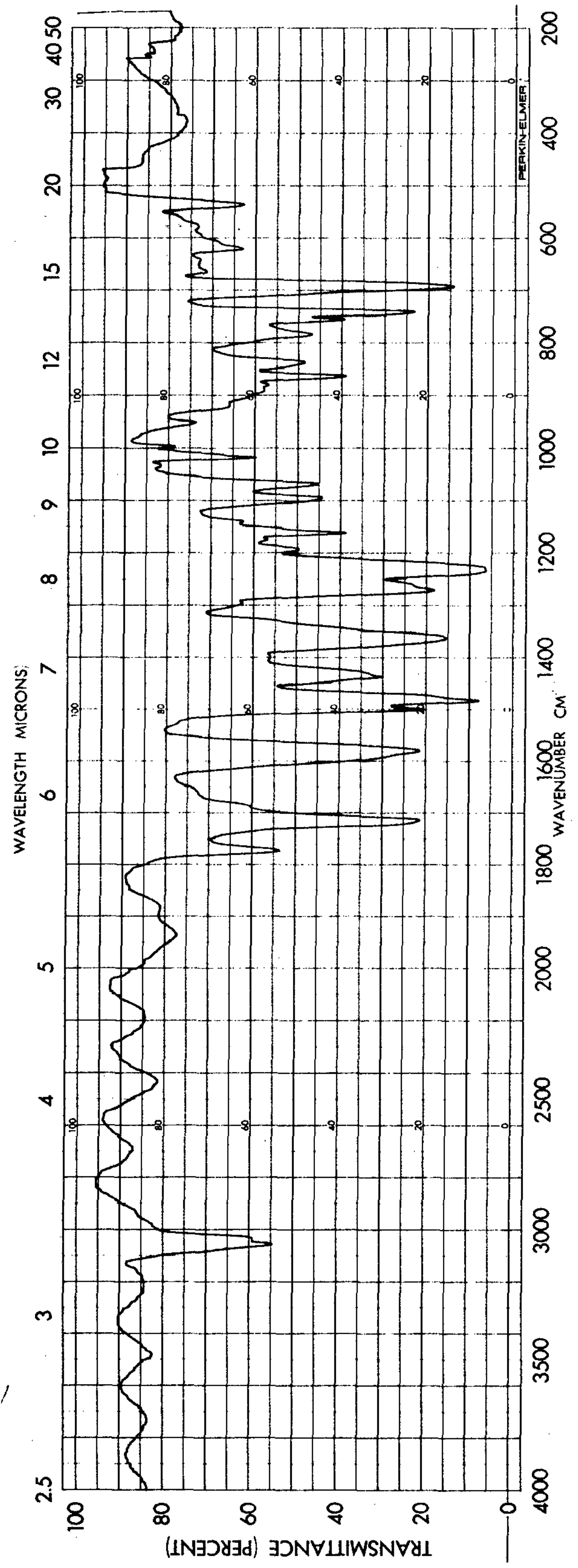


Figure 4. Infrared spectrum of high molecular weight phenoxyphenylated phthalimide polymer. (26)

REFERENCES

1. C.E. Browning, Soc. Adv. Mat'r and Process Eng. Vol 21, 75 (1976).

2. A.L. Landis, N. Bilow, R.H. Boschan, R.E. Lawrence and T.J. Aponyi, Am. Chem. Soc. Div. Poly. Chem. Prepe. 15 (2), 533, 537 (1974).

3. F.E. Arnold and R.L. Van Deusen, AFML-TR-69-52 (1969).