UNCLASSIFIED

AD NUMBER

AD871648

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; May 1970. Other requests shall be referred to Air Force Materials Laboratory, Nonmetallic Materials Division, Polymer Branch, Attn: MANP, Wright-Patterson AFB, OH 45433.

AUTHORITY

AFML ltr, 7 Dec 1972

THIS PAGE IS UNCLASSIFIED

AFML-TR-70-98
AD0871648

PREPARATION AND CHARACTERIZATION OF A BISBENZIMIDAZOPYRAZINE POLYMER

ROBERT C. EVERS

TECHNICAL REPORT AFML-TR-70-98

MAY 1970

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Polymer Branch, MANP, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433.

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

20040302221

NOTICE

100 - June 1970 - CO455 - 121-2652

PREPARATION AND CHARACTERIZATION OF A BISBENZIMIDAZOPYRAZINE POLYMER

ROBERT C. EVERS

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Polymer Branch, MANP, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project Nr. 7340, "Nonmetallic and Composite Materials", Task Nr. 734004, "New Organic and Inorganic Polymers". It was administered under the direction of the Air Force Materials Laboratory, Aeronautical Systems Division, for which Dr. R. C. Evers was project engineer. This report was submitted by the author in March 1970.

This report covers work from November 1968 to October 1969.

The author wishes to thank the Analytical Branch, Air Force Materials Laboratory for performing the elemental analysis, mass spectroscopy, and x-ray diffraction determinations. Dr. G. F. L. Ehlers performed the softening point determinations and Mr. K. R. Fisch contributed the differential thermal analysis data.

This technical report has been reviewed and is approved.

William E. Gibbs

WILLIAM E. GIBBS
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

A bisbenzimidazopyrazine polymer was prepared by the melt and solution homopolymerization of 2, 2'-bis(carbophenoxy)-5, 5'-bibenzimidazole. A maximum inherent viscosity of 0.62 in methane sulfonic acid was obtained. Polymer structure was verified by elemental and infrared analysis. The polymer was an orange-brown amorphous powder which did not soften up to 450°C. Onset of breakdown during thermogravimetric analysis in a nitrogen atmosphere occurred at 475 - 500°C.

CONTENTS

ILLUSTRATIONS

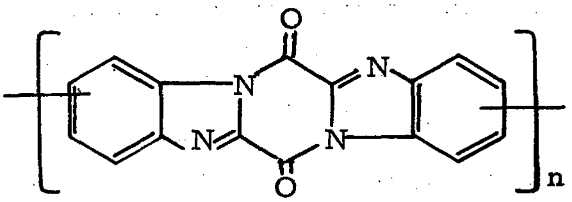
TABLES

INTRODUCTION

Considerable research effort has been directed over the past decade to the preparation of aromatic - heterocyclic polymers which possess superior thermal stability. A variety of aromatic - heterocyclic polymers of varying chemical and thermal stability have consequently been reported. The thermal stability of some of the systems is remarkable. Several noteworthy examples are the BBB and BBL polymers (Reference 1) which have been prepared at the Air Force Materials Laboratory. These polymer systems are stable in an inert atmosphere in the range of 500-650°C and are of interest to the Air Force as candidate materials for fibers, composites, etc.

In a search for other potentially useful polymers, additional research is being performed on novel aromatic - heterocyclic polymer systems. Of interest are thermally stable systems which possess higher degrees of solubility and fusibility or which can be prepared in a manner which lends itself more readily to conventional processing and fabrication techniques.

This report describes a recent effort directed toward the preparation and characterization of a polymer of the general structure:



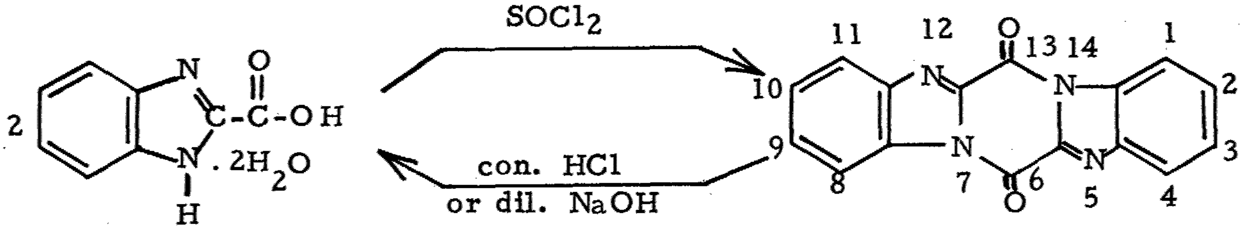
This system contains a 6H, 13H-bisbenzimidazo[1, 2-a:1', 2'-d] pyrazine-6, 13-dione ring system as the repeating unit in the polymer backbone. Since the exact nomenclature of this polymer is cumbersome, it will be referred to in this report as a polybisbenzimidazopyrazine. It was initially felt that this polymer could be prepared in the form of a low-molecular weight, soluble prepolymer by the homopolymerization under appropriate conditions of 2, 2'-(carbophenoxy)-5, 5'-bibenzimidazole. Thermal treatment of the prepolymer would then yield a high molecular weight, relatively insoluble polymer of high thermal stability.

In an attempt to achieve this objective, the basic chemistry of the 6H, 13H-bisbenzimidazo[1, 2-a:1', 2'-d] pyrazine-6, 13-dione system was studied and appropriate monomers were prepared. The subsequent preparation and characterization of the polybisbenzimidazopyrazine was performed and is discussed below.

DISCUSSION

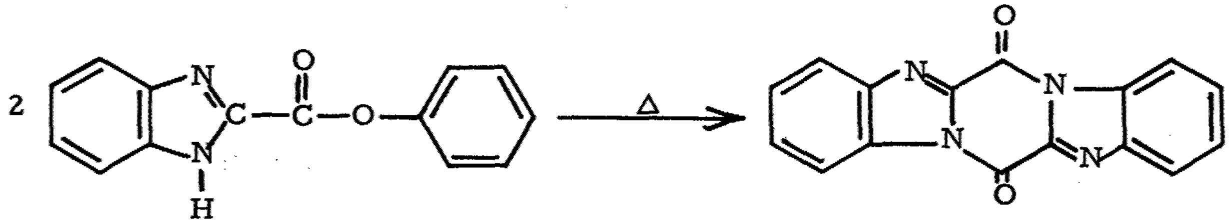
1. Basic Chemistry of the System

The only bisbenzimidazopyrazine-dione reported in the literature is the parent compound, 6H, 13H-bisbenzimidazo-[1, 2-a:1', 2'-d] pyrazine-6, 13-dione, which was prepared in 87% yield by the condensation of 2-carboxybenzimidazole dihydrate in thionyl chloride (Reference 2).



It is stable to cold concentrated sulfuric acid and prolonged refluxing with dilute hydrochloric acid has little effect on this compound. However, concentrated hydrochloric acid and dilute sodium hydroxide dissolve this compound upon heating with the formation of 2-carboxybenzimidazole and the corresponding sodium salt, respectively (Reference 2). This would be indicative of a limited hydrolytic stability for the corresponding polymer.

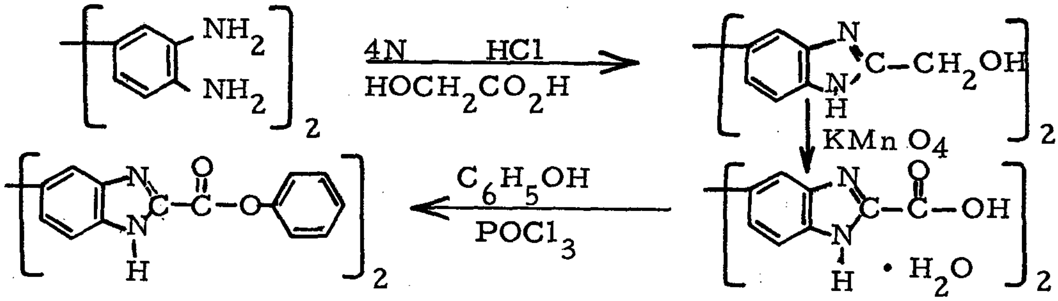
The possibility of preparing this model compound by the thermal condensation of 2-carbophenoxybenzimidazole was investigated. Several attempts were made to prepare the requisite phenyl ester from 2-carboxybenzimidazole. Conventional methods for the synthesis of phenyl esters of amino acids were used. The reaction of 2-carboxybenzimidazole (a) with trifluoroacetic anhydride and phenol (Reference 3) and (b) diphenyl phosphite and pyridine (Reference 4) yielded only starting material while the reaction (c) with diphenyl sulfite in pyridine (Reference 4) gave a low yield of the model compound but no phenyl ester. 2-Carbophenoxybenzimidazole was finally prepared in 32% yield by the reaction of 2-carboxybenzimidazole and phenol in phosphorus oxychloride.



The thermally induced condensation of the phenyl ester proceeded smoothly at 300°C. to give 6H, 13H-bisbenzimidazo[1, 2-a:1', 2'-d] pyrazine-6, 13-dione in 91% yield. This model compound was characterized in respect to its infrared spectrum so as to serve as a basis of comparison for the characterization of the bisbenzimidazopyrazine polymer.

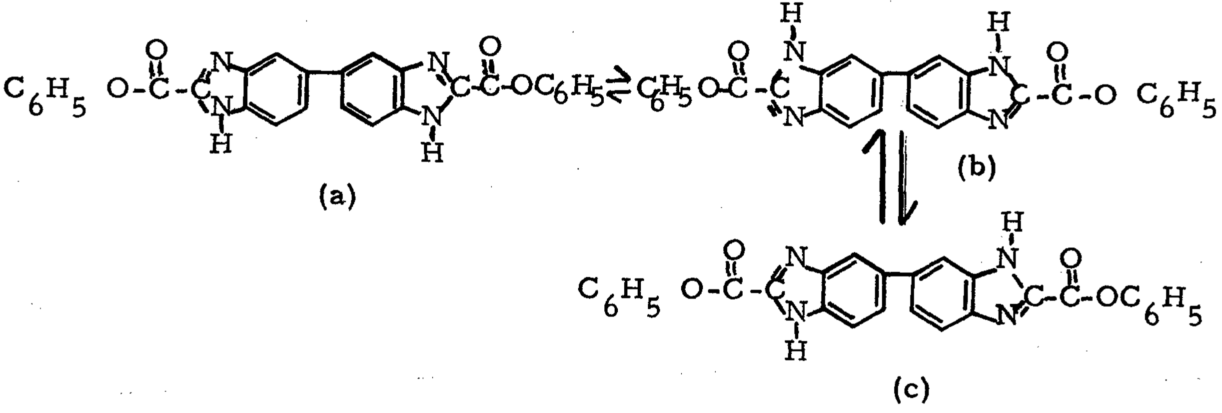
2. Preparation of Monomer

Since the model compound could be readily prepared in high yield by the condensation of 2-carbophenoxybenzimidazole, one would expect the thermal homopolymerization of an appropriate monomer to yield high molecular weight polymer. Initial efforts were, therefore, directed toward the synthesis of 2, 2'-bis(carbophenoxy)-5, 5'-bibenzimidazole, the readily available 3, 3'-diaminobenzidine being used as a starting material.



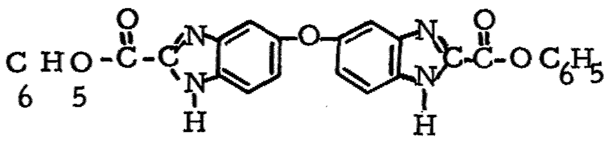
The reaction of the aromatic tetraamine with glycolic acid proceeded readily to give a high yield of pure 2, 2'-bis(α - hydroxymethyl)-5, 5'-bibenzimidazole. Unfortunately, the subsequent oxidation of this compound with potassium permanganate gave a relatively low yield of a white powder which was identified as 2, 2'-bis(carboxy)-5, 5'-bibenzimidazole dihydrate. Reaction of this diacid with phenol in phosphorus oxychloride followed by an extensive purification process gave a low yield of pure monomer.

The monomer is represented and referred to in this report as 2, 2'-bis(carbophenoxy)-5, 5'-bibenzimidazole (a) although it also probably exists in the tautomeric forms, 2, 2'-bis(carbophenoxy)-6, 6'-bibenzimidazole) (b) and 2, 2'-bis(carbophenoxy)-5, 6'-bibenzimidazole (c).

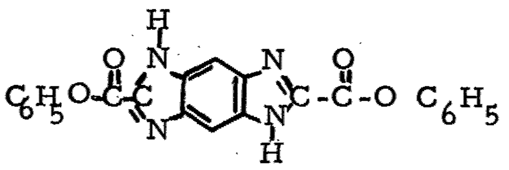


The polymerization of this monomer could thus lead to a polymer with isomeric 2, 9-, 2, 10-, and 3, 10-(6H, 13H-bisbenzimidazole-[1, 2-a:1', 2'-d] pyrazine-6, 13-dione) repeating units in the polymer chain. For this reason, the polymer is represented in this report as a general structure possessing uncertain stereochemistry.

A number of attempts were made to prepare 5, 5'-oxybis(2-carbophenoxy) benzimidazole (A) and 2, 6-bis(carbophenoxy)-imidazo[5, 4-f] benzimidazole (B).



A



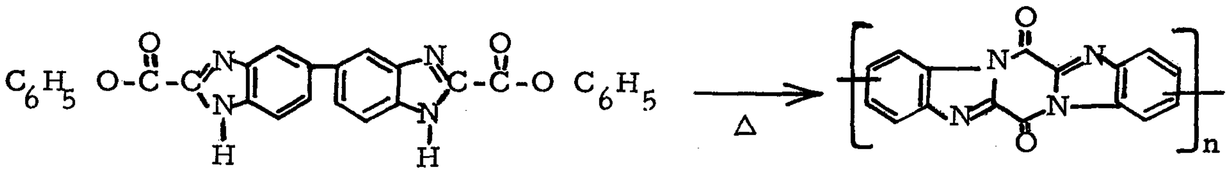
B

The successful homopolymerization of monomer A would result in a polymer containing ether linkages in the polymer backbone. The flexible ether linkage would be expected to increase the fusibility and solubility of the polymer compared to the polymer prepared from 2, 2'-bis(carbophenoxy) bibenzimidazole. Monomer B, on the other hand, might lead to a novel, completely double-strand on "ladder" system with increased thermal stability.

An attempt to prepare the desired monomers by substituting 3, 3', 4, 4'-tetraaminodiphenyl ether and 1, 2, 4, 5-tetraaminobenzene tetrahydrochloride for 3, 3'-diaminobenzidine in the above reaction scheme was unsuccessful. Both tetraamines reacted readily with glycolic acid to form the bis(α-hydroxymethyl) compounds. Repeated attempts to convert these compounds to the corresponding diacids by oxidation, however, yielded only unidentified decomposition products. No further efforts were made to synthesize these monomers.

3. Preparation of Polymer

2, 2'-Bis(carbophenoxy)5, 5'-bibenzimidazole was subjected to melt polymerization. Evolution of phenol began below 250°C. and became quite vigorous at 300°C. with the formation of a red melt which rapidly resolidified to a bright orange solid. Solid phase reactions at 350°C. and 400°C. under reduced pressure yielded orange-brown powders which were over 95% soluble in cold concentrated sulfuric or methane sulfuric acid. Inherent viscosities of greater than 0.20 were not obtained.



Subsequent efforts were directed toward the solution polymerization of the monomer in tetramethylene sulfone. Appreciable reaction did not occur until the reaction temperature reached 270 - 275°C. After 15 to 30 minutes at this temperature, precipitation of polymer occurred. An inherent viscosity of 0.28 was recorded. Several additional runs were made under almost identical conditions. In these cases, the molecular weights of the polymers were further advanced by secondary solid phase reactions at 350°C. Inherent viscosities of 0.51 and 0.62 were realized.

A summary of the above polymerization reactions is given in Table I.

TABLE I

Polymerization of
2,2'-Bis(carbophenoxy)-5,5'-bibenzimidazole

Trial Nr.	Reaction Medium	Total Reaction Time Hrs.	Maximum Reaction Temp. °C.	ηinh-dl/g (Solvent)
1	melt	1.5	400	0.15 (H_2SO_4)
2	melt	3.5	350	0.20 (H_2SO_4)
3	TMS[a.]	1.5	280	0.28 (CH_3SO_3H)
4	TMS[a.]	6.5[b.]	350	0.62 (CH_3SO_3H)
5	TMS[a.]	8.0[c.]	350	0.51 (CH_3SO_3H)

a. Tetramethylene sulfone
b. Includes thermal treatment for 3 hrs,; prepolymer had η_{inh} = 0.27 (CH_3SO_3H, 25°C.)
c. Includes thermal treatment for 4.5 hrs.

4. Physical Properties of the Polymer

The polymer samples from the various reactions were bright orange to orange-brown powders which were insoluble in all organic solvents tested. The low-molecular weight samples ($\eta_{inh} \leq 0.20$) were almost completely soluble in cold concentrated sulfuric or methane sulfonic acid. At higher molecular weights, the samples were appreciably soluble only in methane sulfonic acid with gentle warming (up to 60°C.) being necessary, in some cases, to effect solution. The inherent viscosities of all the polymer samples were determined in concentrated sulfuric or methane sulfonic acid and ranged from 0.15 to 0.62. Since the model compound was somewhat unstable toward warm mineral acid, there was some concern as to any deleterious effect the acidic solvents might have upon the degree of polymerization of the polymer samples. The relationship between the inherent viscosity and the age of a methane sulfonic acid solution of polymer was, therefore, studied. The results are summarized in Table II. The polymer sample (Trial Nr. 4) upon gentle warming in pure methane sulfonic acid (m.p. ~20°C.) was found to be 80 percent soluble with an initial inherent viscosity of 0.60. Aging at 25°C. for three, six and twenty hours resulted in solution viscosities of 0.58, 0.55 and 0.52, respectively. Aging of the solution at 60°C. for three hours resulted in little change in solution viscosity. If a slightly wet solvent sample was used, the polymer was 85 percent soluble and had an inherent viscosity of 0.62. After sixteen hours at 25°C., the inherent viscosity had decreased to 0.29. The use of methane sulfonic acid from a bottle which had been opened for some time and appeared to have a considerable water content resulted in immediate dissolution of the polymer at room temperature. An initial inherent viscosity of 0.10 was recorded. These tests pointed out the necessity of using pure methane sulfonic acid for the viscosity determinations. The relatively slow rate of decrease of the inherent viscosity in pure methane sulfonic acid both at 25°C. and 60°C. would seem to indicate that only limited hydrolysis of the polymer sample had occurred during dissolution. The inherent viscosity values obtained would thus appear to be indicative of the true degree of polymerization of the polymer.

The hydrolytic stability of the polymer in the presence of strong base was also investigated. A finely ground sample (Trial Nr. 4) was slurried in 1N sodium hydroxide at both room temperature and 60°C. Dissolution to a light yellow solution occurred almost immediately at 60°C. and over the course of a few minutes at room temperature. Careful acidification of the solution yielded a white solid which from its infrared spectrum appeared to be fairly pure 2,2'-bis(carboxy)-5,5'-bibenzimidazole dihydrate. Base hydrolysis appeared to have been both rapid and complete.

TABLE II

Effect of Methane Sulfonic Acid on
the Inherent Viscosity of the Polymer

CH_3SO_3H Sample	Percent soluble Polymer	η_{inh} - dl/g				
		initial	3 hr	6 hr	16 hr	20 hr
1[a]	80	0.60	0.58	0.55	--	0.52
2[b]	82	0.62	--	--	0.29	--
3[c]	100	0.10	--	--	--	--

to flow times (sec.) of a, 196.2; b, 206.2; c, 233.4.

The various polymer samples were, in general, characterized by their elemental analyses, infrared spectra, and thermogravimetric analyses (TGA). Most of the polymer characterization, however, centered on the polymer sample from Trial Nr. 4 which was used in the above solution stability studies. Its properties are summarized in Table III. It was a powdery, orange-brown material which was only slightly soluble in sulfuric acid but 82% soluble in methane sulfonic acid. It could be reprecipitated without apparent change if methane sulfonic acid/methanol was used as the solvent/non-solvent system. A finely pulverized sample was found to be completely amorphous by x-ray diffraction techniques and to have a softening point higher than 450°C., the limiting temperature of the test apparatus (Reference 5). No transitions could be detected by differential thermal analyses. TGA under nitrogen indicated that initial breakdown begins at 475 - 500°C. with 32% weight loss at 900°C. In an air atmosphere, TGA indicated catastropic breakdown commencing at 375°C. with essentially no residue at 900°C. The TGA curves are shown in Figure 1. Little difference was noted in comparing these TGA results with those from lower molecular weight samples (η_{inh} = 0.20 and 0.28).

The structure of the bisbenzimidazopyrazine polymer was established by elemental analysis and by comparison of its infrared absorption characteristics with those of the model compound, 6H, 13H-bisbenzimidazo[1,2-*a*:1', 2'-*d*] pyrazine-6,13-dione. The elemental analysis results for the polymer agreed fairly well with the calculated values for the proposed polymer structure. Despite thorough drying of the analytical samples at elevated temperatures and reduced pressures, the hydrogen determination yielded results higher than the theoretical value. Elemental analysis for nitrogen by the Kjeldahl method gave low and unreproducible results. Ordinary Dumas techniques, however, proved to be more satisfactory and gave results which compared fairly well with the theoretical value.

Comparison of the polymer infrared spectrum with that of the model compound disclosed a number of correlations. Both spectra exhibited the expected carbonyl bands in the 1740-1745 cm^{-1} region (Reference 6). Also present in both spectra were prominent bands at 1530-1535 cm^{-1}, 1355-1360 cm^{-1}, 1160-1170 cm^{-1} and 1085-1090 cm^{-1}, the nature of which is not fully understood. Absent in both spectra were absorptions at 1200 cm^{-1} and 1775 cm^{-1} which were present in the spectrum of the monomer, 2,2'-bis(carbophenoxy)-5,5'-bibenzimidazole. These absorptions are attributable, respectively, to the C-O and C=O stretching vibrations of the carbophenoxy group (Reference 6). Only the monomer spectrum exhibited a fairly strong band at 3400^{-1}, attributable to the N-H stretching vibration of the benzimidazole ring. It must be noted, however, that mechanical grinding of the polymer samples with potassium bromide led to atmospheric water contamination of the potassium bromide pellets. Absorptions due to water thus appeared in the 3300-3700 cm^{-1} region and may have masked any other absorptions in this region. The infrared spectra of the monomer, model compound, and polymer can be seen in Figures 2-4. A comparison of the infrared spectra in the 4000-1000 cm^{-1} region is shown in Figure 5.

TABLE III

Physical Properties of the Bisbenzimidazopyrazine Polymer

Physical Appearance:	Orange-brown, amorphous powder	
Solubility:	Insoluble in dimethylsulfoxide, N,N'-dimethylacetamide, hexamethylphosphoramide, formic acid, m-cresol. Slightly soluble in concentrated sulfuric acid. Soluble (82%) in methane sulfonic acid.	
Inherent Viscosity:	0.62 dl/g (0.2g/dl at 25°C.)	
Elemental Analysis:	Calc'd: C, 67.12; H, 2.10; N, 19.58; O, 11.19 Found: C, 66.98; H, 3.11; N, 19.07; O, 10.84*	
Thermogravimetric Analysis:	(a) nitrogen:	Initial breakdown at 475°C. Inversion point of curve at 625°C. Weight loss at 900°C. = 32%
	(b) air:	Initial breakdown at 375°C. Inversion point of curve at 525°C. Weight loss at 900° C. = 96%
Softening Behavior:	No softening up to 450°C.	
Differential Thermal Analysis:	No transitions noted.	

* by difference

In general, the infrared spectrum of the polymer compares favorably with that of the model compound. On the basis of the elemental analysis and the infrared spectra correlations, the polybisbenzimidazopyrazine structure can be reasonably assigned to the polymer.

5. Conclusions

From the results published in this report, it is concluded that a soluble bisbenzimidazopyrazine polymer of moderate molecular weight was synthesized. It could be prepared as a low molecular weight prepolymer by the solution polymerization of 2, 2'-bis(carbophenoxy)-5, 5'-bibenzimidazole. The degree of polymerization could then be increased by secondary solid phase reactions at 300-350°C. Although the polymer exhibited a high degree of thermal stability, it was quite susceptible to acid and base hydrolysis. This fact would, in most instances, preclude its use as a candidate material for protective coatings, fibers, etc.

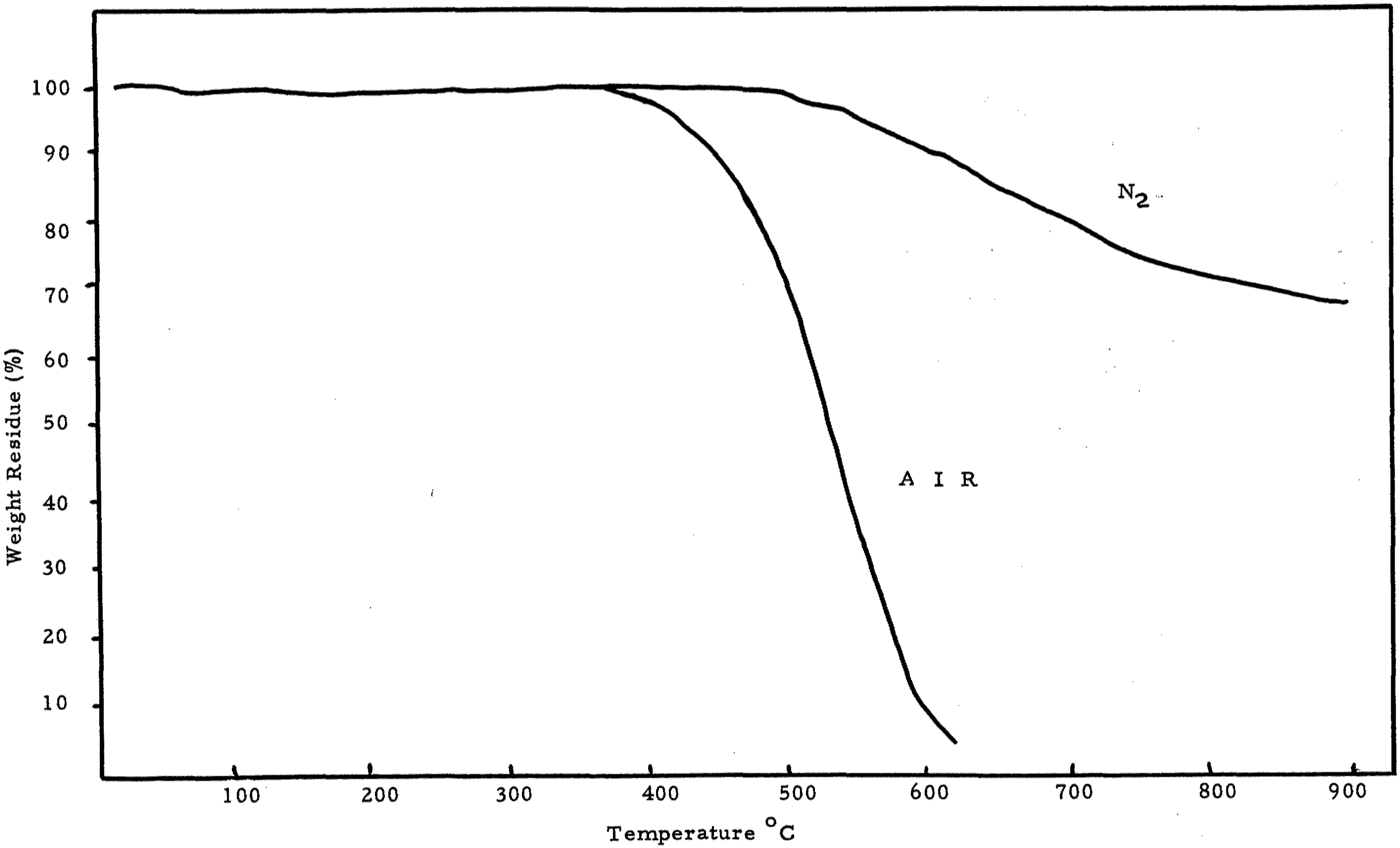


Figure 1. TGA Curves of the Bisbenzimidazopyrazine Polymer in Air and in Nitrogen

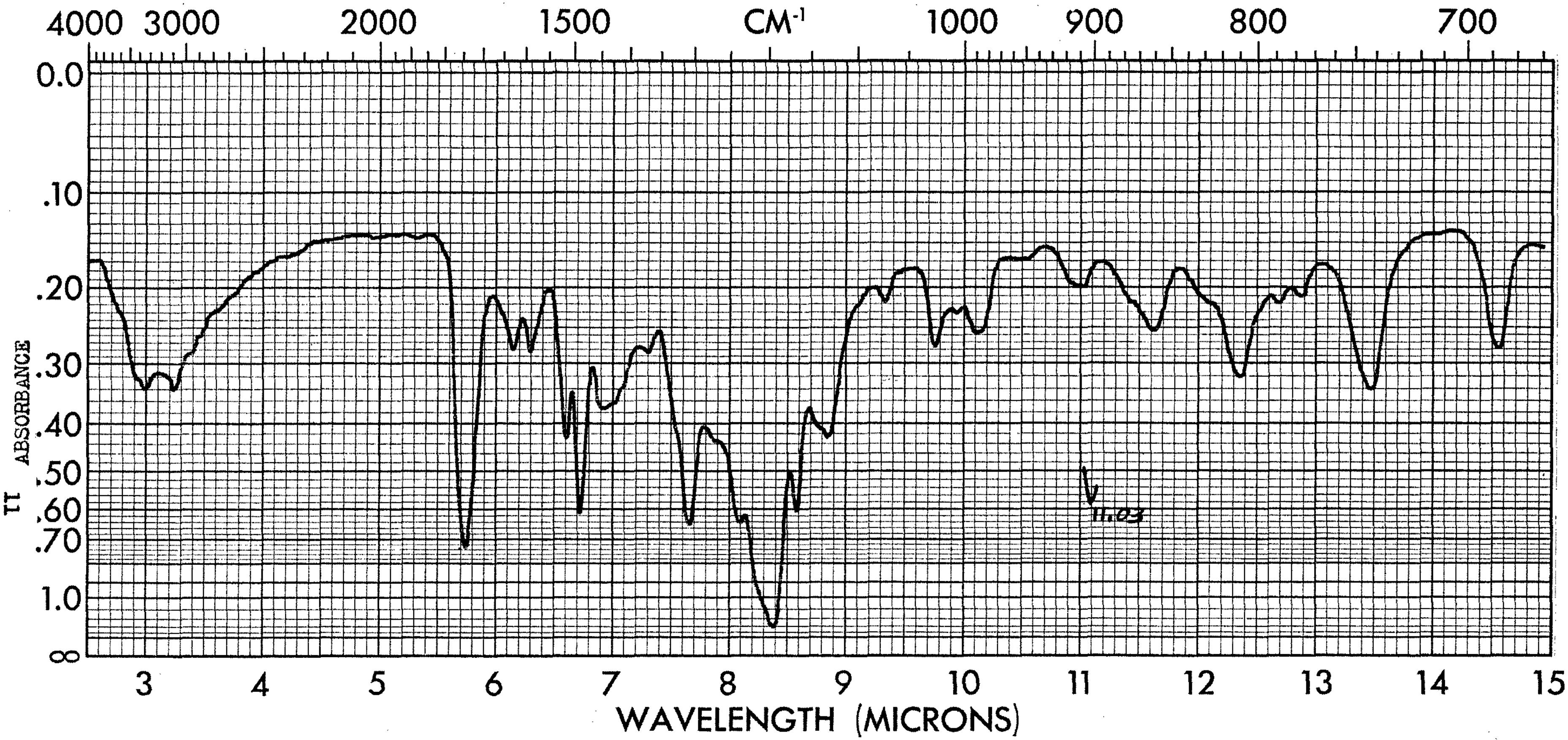


Figure 2. Infrared Spectrum of 2, 2'-Bis(carbophenoxy)-5, 5'-bibenzimidazole

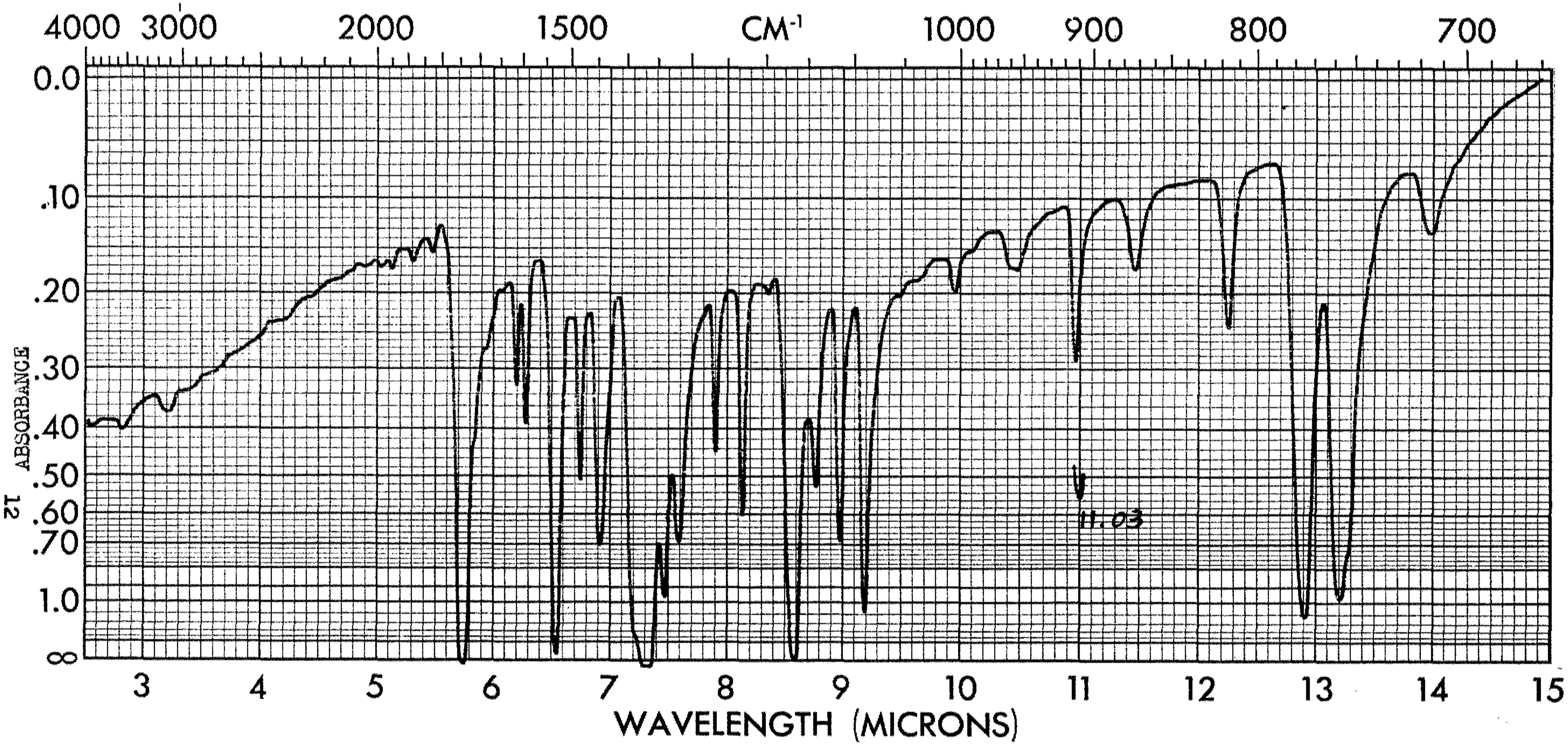


Figure 3. Infrared Spectrum of 6H, 13H-Bisbenzimidazo[1,2-a:1',2'-d] pyrazine-6, 13-dione

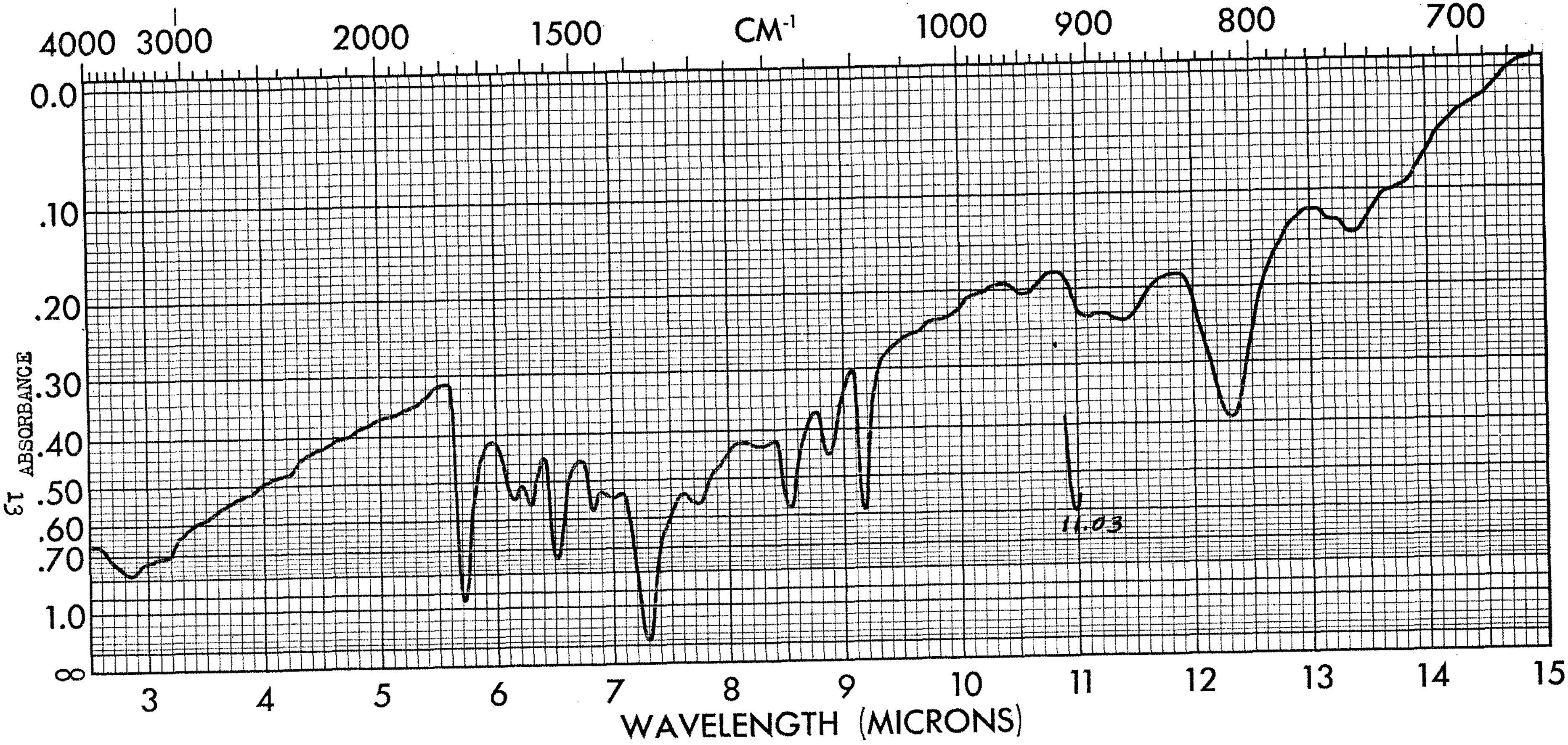


Figure 4. Infrared Spectrum of the Bisbenzimidazopyrazine Polymer

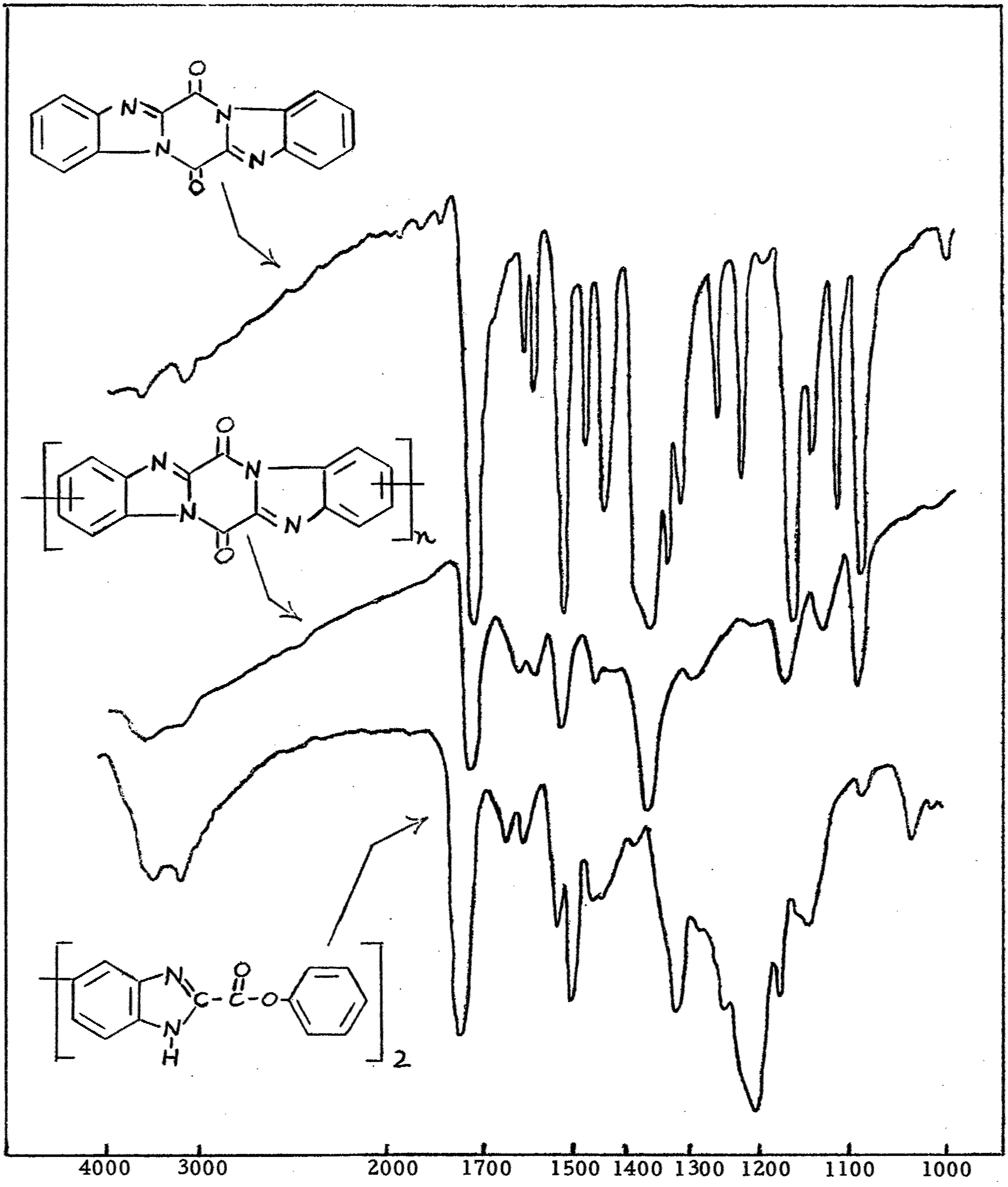


Figure 5. Infrared Spectra in the 4000 to 1000 cm^{-1} Region

EXPERIMENTAL

1. Preparation of Solvents and Intermediates

Tetramethylene sulfone was obtained from standard commercial sources and was purified by vacuum distillation over phosphorus pentoxide. Only the center fraction was retained. The purified material was stored over freshly dried molecular sieves in amber colored bottles.

3, 3'-Diaminobenzidine, 3, 3', 4, 4'-tetraaminodiphenyl ether, and 1, 2, 4, -5-tetraaminobenzene tetrahydrochloride were obtained from Burdick and Jackson Laboratories, Inc. They were used without further purification.

Diphenyl sulfite was prepared by the reaction of thionyl chloride and phenol in the presence of pyridine (courtesy of G. A. Loughran). Redistillation yielded a pale yellow liquid, b.p. 181-183°C/15mm (lit. 185°C/15mm) (Reference 4).

2-(α-Hydroxymethyl)benzimidazole

This compound was prepared by the method of Phillips (Reference 7). o-Phenylenediamine (21.6g., 0.20 moles) and glycolic acid (22.8g., 0.30 mole) were refluxed in 175 ml. of 4N hydrochloric acid for three hours. The clear, light-red solution was treated with charcoal and then filtered. The cooled filtrate was neutralized with dilute ammonium hydroxide to give about 28g. of light-tan product. This was recrystallized from 300 ml. of water to give 24g. (81% yield) of fine white needles, m.p. 168-170°C. (lit. 171-172°C) (Reference 8).

2-Carboxy-benzimidazole dihydrate

The method of Bistrzycki and Przeworski was used to prepare this compound. (Reference 8). A solution of 2-(α-hydroxymethyl)benzimidazole (24g., 0.162 mole) in 600 ml. of boiling water was made slightly alkaline by the addition of several ml. of concentrated sodium carbonate solution. Then a slurry of potassium permanganate (37.6g., 0.238 mole) in a liter of warm water was added portion wise so as to avoid excessive foaming. After addition was complete, the reaction mixture was refluxed for an additional hour and then treated with charcoal. The reaction mixture was filtered and the residue treated with 500 ml. of hot water to remove any product adhering to the manganese dioxide. The filtrate and washings were combined and cooled. Neutralization with 50% acetic acid yielded 20.1g. (63% yield) of 2-carboxy-benzimidazole dihydrate, m.p. 156-159°C, rate of heating = 5°C/min. (lit. 168°C., fast heating) (Reference 8).

2-Carbophenoxybenzimidazole

Phenol (16g.) and phosphorus oxychloride (200 ml.) were stirred together at room temperature to form a clear solution. 2-Carboxy-benzimidazole dihydrate (8g.) was added and the resultant yellow slurry was warmed to reflux with stirring being maintained. The reaction mixture gradually cleared and a clear reddish solution resulted. After 90 minutes, the excess phosphorus oxychloride was drawn off under reduced pressure and the residue dissolved in 75ml. of acetone. The insolubles (1g.) were filtered off and the acetone solution added to 300ml. of ice water which was kept slightly alkaline by the addition of saturated sodium carbonate solution. The precipitate was isolated by filtration. The tan solid was recrystallized once from an ethanol-water solution and twice from a dioxane-water solution. Three grams (32% yield) of white platelets were obtained, m.p. 205-206°C.

Analysis: Calc'd: C, 70.59, H, 4.20; N, 11.76.
Found: C, 70.35, 70.67; H, 4.62, 4.66;
N, 11.78, 11.99

2. Preparation of 6H, 13H-Bisbenzimidazo[1, 2-*a*:1', 2'-*d*] pyrazine-6, 13-dione

From 2-carboxybenzimidazole dihydrate and thionyl chloride

The procedure of Copeland and Day was followed (Reference 2). 2-Carboxybenzimidazole dihydrate (10g.) was powdered and added slowly with stirring to thionyl chloride (60ml.). The yellow mixture was refluxed with stirring for three hours and the excess thionyl chloride drawn off under reduced pressure. The yellow, powdery residue was slurried in cold water and then filtered. It was washed on the filter with dilute sodium carbonate solutions , dried, and then extracted in a Soxlett with methanol until the extract was colorless. About 6.4g. (87% yield) of a yellow powder was obtained. It started to discolor at ∼370°C and finally melted with decomposition at 430-440°C. (lit. >300°C.) (Reference 2).

From 2-carbophenoxybenzimidazole

2-Carbophenoxybenzimidazole (1.5g.) was heated under nitrogen in a polymer tube at 300°C. for 30 minutes. A vigorous evolution of phenol resulted. This phenol was drawn off by further heating at 300°C. and 0.01mm. for 15 minutes. The crude product (0.85g., 91% yield) was recrystallized from N, N-dimethylacetamide, a few ml. of water being added to induce crystallization. It was isolated by filtration and washed on the filter with hot water and methanol. The dense yellow crystals started to discolor at ∼370°C. and finally melted with decomposition at ∼440°C. This product had an infrared spectrum identical to that of the product obtained from 2-carboxybenzimidazole dihydrate and thionyl chloride.

Analysis Calc'd: C, 66.66; H, 2.78; N, 19.44
Found: C, 66.74, 66.46; H, 2.99, 2.85; N, 19.20, 18.88
Molecular Weight
Calc'd: 288
Found: 288 (Mass Spectroscopy)

3. Preparation of Monomer

2,2'-Bis(α-hydroxymethyl)-5,5'-bibenzimidazole

3,3'-Diaminobenzidine (10.70g., 0.05 mole) and glycolic acid (11.40g., 0.15 mole) were dissolved with stirring in 200 ml. of hot 4N hydrochloric acid. The resultant clear red solution was refluxed for three hours at which time it was treated with charcoal and filtered. The warm filtrate was treated with 50% ammonium hydroxide solution until basic to litmus. The suspension was stirred for an hour, cooled, and filtered. About 12g. (82% yield) of pale orange material resulted. An analytical sample was recrystallized from a 60-40 dimethylsulfoxide-water solution. The fine, pale orange crystals melted at 335-337°C. to form a red liquid which resolidified almost immediately to a reddish-brown solid.

Analysis Calc'd: C, 65.30; H, 4.76; N, 19.05
Found: C, 65.38, 65.48; H, 4.86, 4.93; N, 19.01, 19.09

2,2'-Bis-(carboxy)-5,5'-bibenzimidazole dihydrate

2,2'-Bis(α-hydroxymethyl)-5,5'-bibenzimidazole (26.46g., 0.09 mole) was placed in 450 ml. of hot water which was made basic by the addition of several ml. of concentrated sodium carbonate solution. Powdered potassium permanganate (41.72g., 0.26 mole) (10% excess) was added portionwise with stirring so as to avoid excessive boiling and foaming. The resultant brown suspension was refluxed with stirring for an additional 45 minutes and then filtered hot. The residue was dried, finely powdered, and boiled with 500 ml. of hot water to remove any product adhering to the manganese dioxide. This suspension was filtered and the extract added to the original filtrate. The combined solutions were cooled and neutralized with 50% acetic acid. The creamy white precipitate was isolated by filtration, redissolved in warm sodium carbonate, and again precipitated by the addition of acetic acid. The product was isolated by filtration, washed with methanol and ether, and dried for several hours at 70°C. in a vacuum oven. About 15g. (46% yield) of product with a m.p. of 188-191°C. was isolated.

Analysis Calc'd for $C_{16}H_{10}N_4O_4$: C, 59.63; H, 3.11; N, 17.39
Calc'd for $C_{16}H_{10}N_4O_4 \cdot 2H_2O$: C, 53.63; H, 3.91; N, 15.64
Found: C, 53.01, 53.80; H, 4.40, 4.00; N, 15.42, 15.10

Alternatively, reduction in volume of the original filtrate by boiling off water until crystallization was imminent resulted in isolation of the dipotassium salt of 2, 2'-bis(carboxy)-5, 5'-bibenzimidazole as long, white needles, m. p. >300°C. (dec.).

Analysis Calc'd. for $C_{16}H_8N_4O_4K_2$: C, 48.24; H, 2.01; N, 14.07
Found: C, 48.02, 48.02; H, 2.26, 2.38; N, 13.88, 13.92

2, 2'-(Carbophenoxy)-5, 5'-bibenzimidazole

2, 2'-Bis(carboxy)-5, 5'-bibenzimidazole as isolated by the above procedure (8g.) was slurried in a cooled solution of phenol (16g.) in phosphorus oxychloride (200 ml.). The reaction mixture was saturated with dry hydrogen chloride gas and the temperature then slowly raised to reflux. After several hours, a clear, light red solution was formed. The excess phosphorus oxychloride was stripped off under reduced pressure and the gummy residue treated with cold sodium carbonate solution. The crude product was isolated by filtration and then refluxed in benzene. Any occluded water was removed in the benzene-water azeotrope. The residue was isolated by filtration. It was recrystallized twice from water-ethanol and three times from dioxane-water (charcoal) to give about 1g. (10% yield) of snow-white product, m. p. >165°C. (dec.).

Analysis Calc'd: C, 70.89; H, 3.80; N, 11.81
Found: C, 70.59, 70.71; H, 3.80, 3.99; N, 11.76, 11.58

4. Preparation of Polymer

The following examples are typical procedures for the polymerization of 2, 2'-bis(carbophenoxy)-5, 5'-bibenzimidazole.

Melt Polymerization

The monomer (1.0g.) was heated at 300°C. under nitrogen in a polymer tube. Evolution of phenol occurred with subsequent solidification of the polymerization mixture after about 30 minutes. After one hour, the polymer tube was allowed to cool and the bright orange solid finely crushed. The polymer was placed in a rotating 30 ml. flask containing several small ball bearings to facilitate mixing. Heating was resumed at 350°C. and 0.1 mm. pressure for one hour. The final product was an orange-brown powder which was >95% soluble in cold sulfuric acid and had an inherent viscosity of 0.20 in that solvent at 25°C.

Analysis Calc'd: C, 67.13; H, 2.10; N, 19.58
Found: C, 68.34; H, 2.98; N, 20.68

Solution Polymerization

The monomer (1.65g.) was dissolved under nitrogen at 80°C. in tetramethylene sulfone(70ml.). The temperature of the resultant water-white solution was gradually increased. At 180° C., a slight yellow color developed which deepened as the temperature was increased further. After 30 minutes at 260°C., the solution had taken on a deep orange color but no precipitation of polymer had occurred. Precipitation of an orange solid occurred, however, after 15 minutes of heating at 270-275°C. After being heated at 280°C. for an additional three hours, the polymerization mixture was cooled and added to a ten-fold excess of methanol. The bright orange product (0.76g., 76% yield) was isolated by filtration, washed well with methanol, and dried at 150°C. under reduced pressure. It was only partially soluble in cold methane sulfonic acid. An inherent viscosity of 0.27 in methane sulfonic acid at 25°C. was recorded. The finely powdered polymer was heated in a rotating flask at 350°C. for three hours to give an orange-brown powder which was 82% soluble in methane sulfonic acid. It had an inherent viscosity in that solvent of 0.62 at 25°C.

Analysis Calc'd: C, 67.13; H, 2.10; N, 19.58
Found*: C, 66.98; H, 3.11; N, 19.07

* Values found for the combined soluble and insoluble portions.

5. Characterization of Polymer

Viscosity

The inherent viscosities of the soluble portions of the polymers were determined at 25°C. using solution concentrations of approximately 0.2g/dl. Concentrated sulfuric acid and methane sulfonic acid were used as solvents.

Infrared Spectra

Infrared spectra were obtained on the polymers by use of a Perkin-Elmer Infrared recording Spectrophotometer. In all cases, potassium bromide pellets of the samples were used.

X-Ray Diffraction

A sample was evaluated on a Phillips X-ray generator by exposure to a CuK source at 30 kv.

Softening Range Determinations

The softening characteristics of the polymer was obtained by means of a modified Vicat apparatus (Reference 5). Heating was performed at a constant rate of 2.5°C./min. Any evidence of softening could be determined from a plot of temperature versus penetration.

Thermogravimetric Analysis

Determinations were carried out in either a dry air or nitrogen atmosphere on a Chevernard Thermobalance (Adamel, Paris, France) using a constant heating rate of 3.0°C./min. A plot of percent weight residue versus temperature was made for each run.

Differential Thermal Analysis

A Dupont 900 Differential Thermal Analyzer (Standard Cell) with a constant heating rate of 20°C./min. was used. Duplicate runs were made on each sample.

REFERENCES

1. R. L. Van Deusen, J. Polymer Sci., (Part B), 4, 211 (1966). R. L. Van Deusen, O. K. Goins and A. J. Sicree, J. Polymer Sci., 6, 1777 (1968). F. E. Arnold and R. L. Van Deusen, Macromolecules, 2, 497 (1969).

2. R. A. B. Copeland and A. R. Day, J. Amer. Chem. Soc., 65, 1073 (1943).

3. R. C. Parish and L. M. Stock, J. Org. Chem., 30, 927 (1965).

4. B. Iselin, W. Rittel, P. Sieber, B. Schwyger, Helv. Chem. Acta, 40, 373 (1957).

5. G. F. L. Ehlers and W. M. Powers, Materials Res. Stds., 4, 298 (1964).

6. L. J. Bellamy, The Infrared Spectra of Complex Molecules, 2nd Edition, Methuen and Co., Ltd., London (1958).

7. M. A. Phillips, J. Chem. Soc., 2393 (1928).

8. A. Bistrzycki and G. Przeworki, Ber., 45, 3483 (1912).

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Air Force Materials Laboratory Wright-Patterson AFB, Ohio 45433	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

PREPARATION AND CHARACTERIZATION OF A BISBENZIMIDAZOPYRAZINE POLYMER

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

November 1968 - October 1969

5. AUTHOR(S) *(First name, middle initial, last name)*

Robert C. Evers

6. REPORT DATE May 1970	7a. TOTAL NO. OF PAGES 28	7b. NO. OF REFS 8
8a. CONTRACT OR GRANT NO. b. PROJECT NO. 7340 c. Task No. 734004 d.	9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-70-98 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*	

10. DISTRIBUTION STATEMENT This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Polymer Branch, MANP, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Wright-Patterson AFB, Ohio 45433

13. ABSTRACT

A bisbenzimidazopyrazine polymer was prepared by the melt and solution of 2,2'-bis(carbophenoxy)-5,5'-bibenzimidazole. A maximum inherent viscosity of 0.62 in methane sulfonic acid was obtained. Polymer structure was verified by elemental and infrared analysis. The polymer was an orange-brown amorphous powder which did not soften up to 450°C. Onset of breakdown during thermogravimetric analysis in a nitrogen atmosphere occurred at 475-500°C.

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Polymer Branch, MANP, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Polymer						
Aromatic-Heterocyclic Polymer						
Bisbenzimidazopyrazine Polymer						
Pyrazinobisbenzimidazole Polymer						
Thermal Properties						