AFML-TR-70-306
A D0726545

PREPARATION AND CHARACTERIZATION OF A BENZOBISTRIAZOLOPHENANTHROLINE POLYMER

ROBERT C. EVERS

TECHNICAL REPORT AFML-TR-70-306

FEBRUARY 1971

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FOREWORD

This effort was accomplished by the Polymer Branch, Nonmetallic Materials Division of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734004, "New Organic and Inorganic Polymers". It was administered under the direction of Dr. R. C. Evers (AFML/LNP), project scientist.

This report covers work from May 1969 to April 1970.

The author wishes to thank the Analytical Branch, Air Force Materials Laboratory for performing the elemental analysis and mass spectroscopy determinations. Dr. G. F. L. Ehlers performed the softening point determinations and Mr. K. R. Fisch contributed the differential thermal analysis and differential scanning calorimetry data. The assistance of Dr. K. L. Loening of Chemical Abstracts Services in naming the model compounds and polymers is appreciated.

This report was submitted by the author November 1970.

This technical report has been reviewed and is approved.

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ABSTRACT

A benzobistriazolophenanthroline polymer was prepared by the polycondensation of 2,6-pyridinediyldihydrazidine with 1,4,5,8-naphthalene tetracarboxylic acid or 1,4,5,8-naphthalene tetracarboxylic dianhydride in polyphosphoric acid. Inherent viscosities in the range of 0.25-0.87 dl./g. were recorded. Polymer structure was established by elemental and infrared analysis. The polymer was a reddish-brown powder soluble in sulfuric-or methane sulfonic-acid. Onset of breakdown during thermogravimetric analysis in a nitrogen atmosphere occurred at 475°C.

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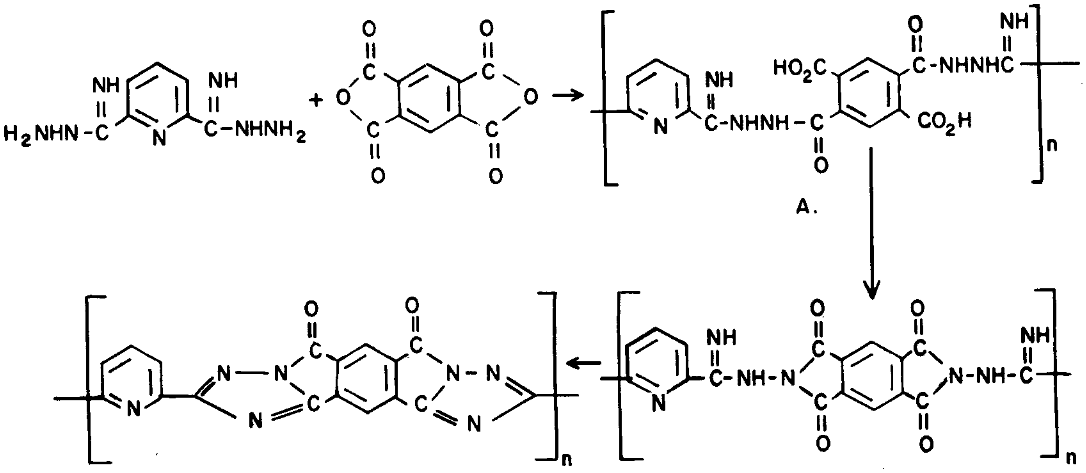
SECTION I

INTRODUCTION

Aromatic-heterocyclic polymers of superior thermal and chemical stability have been of interest to the Air Force for some time as potential candidate materials for high temperature applications. Some of these polymers are stable to temperatures exceeding 500°C. when examined by thermogravimetric analysis in an inert atmosphere. Several noteworthy examples are the BBB and BBL polymer systems which have been prepared at the Air Force Materials Laboratory and are currently being developed for specific Air Force applications (Reference 1).

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 high degrees of solubility and fusibility or which can be prepared in a manner which lends itself readily to conventional processing and fabrication techniques.

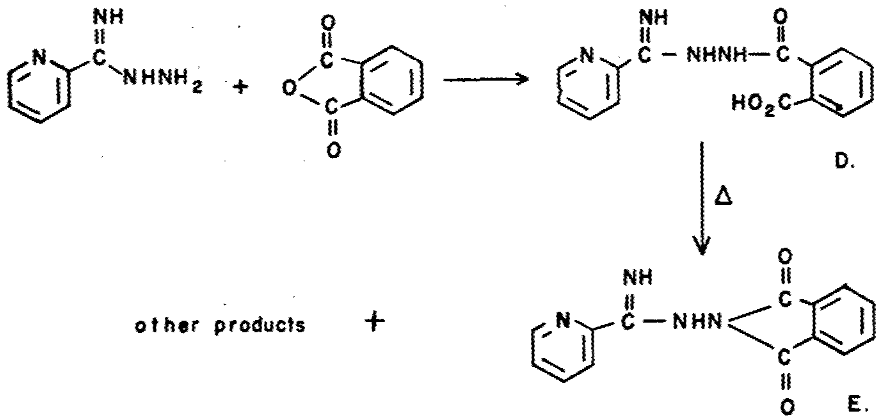
A proposed approach to a high molecular weight, thermally stable polymer via a soluble intermediate prepolymer is pictured in the reaction scheme below. It was initially felt that the low temperature solution polycondensation of 2,6-pyridinediyldihydrazidine and pyromellitic dianhydride would lead to a high-molecular weight, soluble prepolymer A. Cyclodehydration by thermal means would then proceed through the intermediate structure B to a fully cyclized relatively insoluble polymer C of high thermal stability.



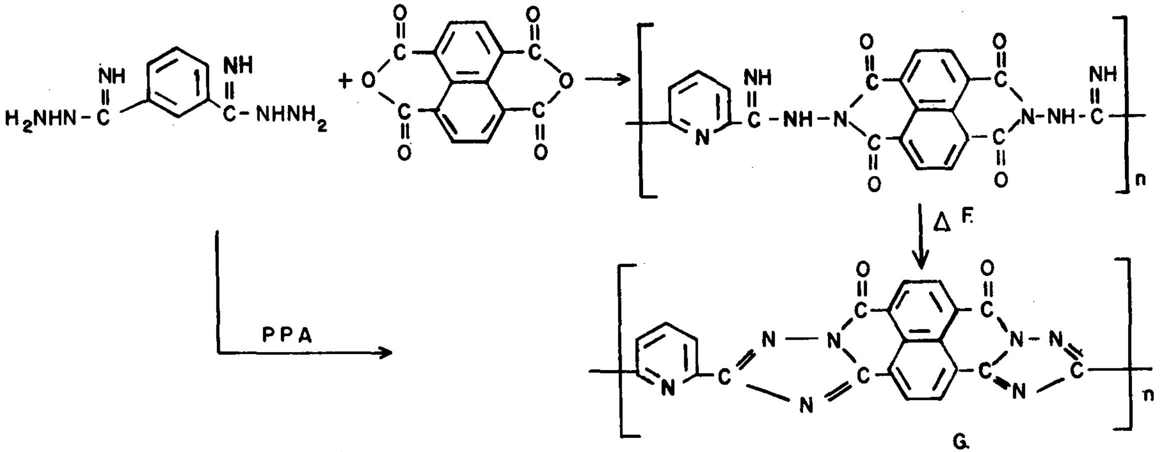
Soon after in-house work was initiated in this area, Korshak and co-workers reported the low temperature polycondensation of pyromellitic dianhydride with aromatic dihydrazidines (Reference 2). The soluble prepolymer obtained was subjected to stepwise temperature elevation to 350°C. to give an insoluble polymer corresponding to structure C. No supporting data (elemental analysis, viscosity measurements, etc.) were given.

Subsequent work within this laboratory indicated that the low temperature polycondensation of pyromellitic dianhydride and 2,6-pyridinediyldihydrazidine did lead to soluble, moderate molecular weight polymers from which weak films could be cast. Thermal treatment of these polymers under a variety of conditions led to dark, insoluble products of rather poor thermal stability. The elemental analysis and infrared spectra of the thermally treated polymers were completely inconsistent with structure C.

Model compound studies using phthalic anhydride and 2-pyridylhydrazidine as reactants demonstrated that thermal treatment of the intermediate amic acid D at 250°C. did not proceed exclusively to the phthalamide structure E but produced instead a complex mixture of compounds whose infrared spectrum indicated the presence of oxadiazole, triazole, cyclohydrazide, etc. type structures. Further heating at 350°C. to complete cyclization resulted in a mixture of ill-defined, partially decomposed reaction products. Thus, it is not surprising that the reaction of pyromellitic dianhydride with 2,6-pyridinediyldihydrazidine produced a complex, intractable material.



As an alternate approach, the polycondensation of 2,6-pyridinediyldihydrazidine with 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) was considered. From a consideration of the stereochemical requirements of the condensation reaction, one would expect that the use of NTCDA should lead to less complex reaction products since the peri position of the carboxyl groups greatly favors the formation of a naphthalimide structure over the various other partially cyclized structures which are possible. Thermal cyclization of this naphthalimide structure F would then lead to the fully condensed polymer system G. An alternative route would be the one-step polycondensation of the monomers in polyphosphoric acid (PPA). This polymer, as shown, contains a



G.

2,11-di-2-pyridylbenzo[lmn]bis-s-triazolo[5,1-b:1',5'-j][3,8]phenanthroline-5,8-dione ring system in the polymer backbone. The trans carbonyl structure is also possible. The exact name of the polymer according to structure base nomenclature would be poly(5,8-dihydro-5,8-dioxobenzo[lmn]bis-s-triazolo[5,1-b:1',5'-j][3,8]phenanthroline-2,11-diyl)-2,6-pyridinediyl]. Since this nomenclature is cumbersome, the polymer will be referred to in this report simply as a benzobistriazolophenanthroline polymer.

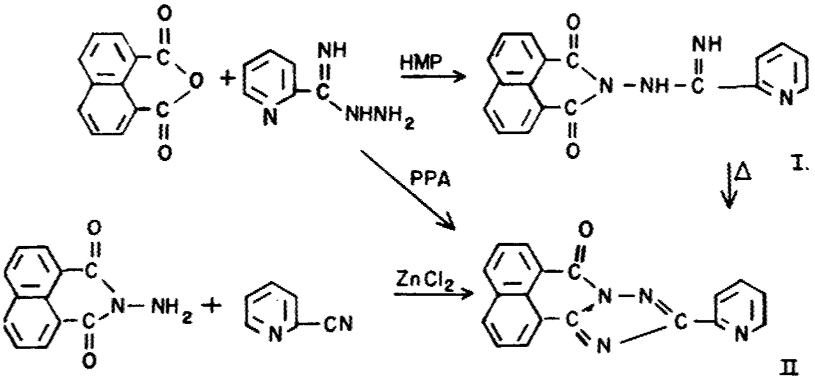
The preparation of the proposed polymer system has not been reported in the open literature. In fact, the preparation of simple model compounds by reactions analogous to those proposed above have not been reported. In order to prove the feasibility of the above reaction scheme, a number of appropriate model compounds were prepared by these methods. The preparation of these model compounds along with the subsequent preparation of the benzobistriazolophenanthroline polymer is described below.

SECTION II

DISCUSSION

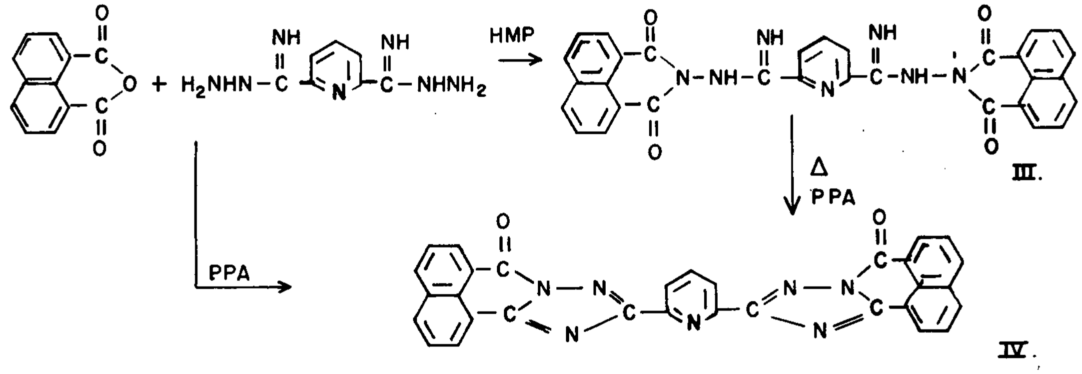
1. PREPARATION OF MODEL COMPOUNDS

Initial efforts were directed toward the condensation of 2-pyridylhydrazidine and 1,8-naphthalic anhydride. Reaction at moderate conditions in hexamethylphosphoramide (HMP) led to a nearly quantitative yield of N-[(amino-2-pyridylmethylene)amino] naphthalimide (I). A 77% conversion to 10-(2 pyridyl)-7H benzo[de]-s-triazolo[5,1-a] isoquinolin-7-one (II) occurred upon heating at 300-325°C for several hours. This crystalline compound could also be prepared in 82% yield by the condensation of 1,8-naphthalic anhydride and 2-pyridylhydrazidine in polyphosphoric acid.



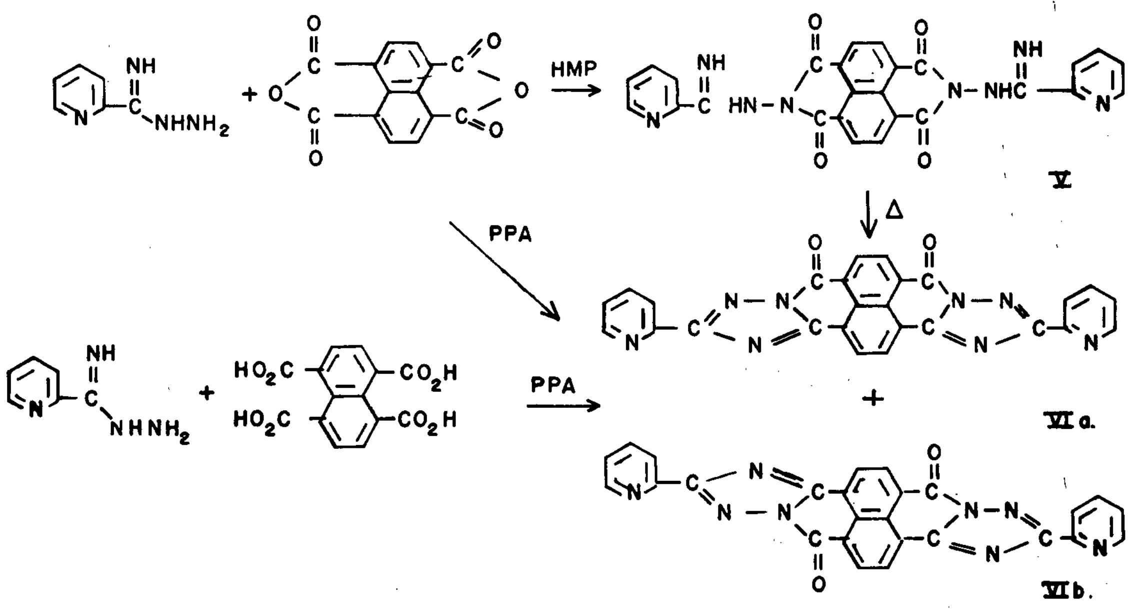
Compounds I and II were characterized by elemental analysis, infrared spectroscopy, and mass spectroscopy. Their nuclear magnetic resonance spectra were consistant with the proposed structures but were not clearly enough defined to warrant definite confirmation of structure. As a further proof of structure, compound II was prepared by a modification of a procedure used to prepare the analogous 10-benzyl-7H-benzo[de]-s-triazolo-[5,1-a] isoquinolin-7-one (Reference 3). The zinc chloride-catalyzed condensation of 2-cyanopyridine and N-amino-1,8-naphthalimide gave an 80% yield of product whose melting point and infrared spectrum were identical to those of compound II.

1,8-Naphthalic anhydride was then reacted with 2,6-pyridinediyldihydrazidine according to the following reaction scheme.



Reaction under moderate temperatures in HMP led to a 95% yield of *N*,*N*',-[2,6-pyridinediylbis[(aminomethylidyne)nitrilo]]dinaphthalimide (III). Further condensation of III by thermal and chemical means (PPA) proceeded in 78% and 70% yields, respectively, to give a reddish-brown powder which was slightly soluble in aprotic solvents and could not be readily recrystallized. This compound could also be prepared in 87% yield by the reaction of 1,8-naphthalic anhydride and 2,6-pyridinediyldihydrazidine in PPA. It was identified from its infrared spectrum and elemental analysis as 10,10'-(2,6-pyridinediyl) bis[7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*] isoquinolin-7-one] (IV).

N,*N*'-Bis[(amino-2-pyridylmethylene)amino] -1,4,5,8-naphthalenetetracarboxylic-1,8:4,5-diimide (V) was prepared in 89% yield by the reaction of 2-pyridylhydrazidine and NTCDA in HMP as shown below:



Thermal treatment of the pale yellow naphthalimide derivative resulted in a high yield of a dark orange solid which was insoluble in organic solvents and did not melt below 450°C. An identical product could be obtained in 81% and 83% yields by the reactions of 2-pyridylhydrazidine with NTCDA and 1,4,5,8-naphthalene tetracarboxylic acid (NTCA) in PPA. Characterization data from elemental analyses and infrared spectroscopy were consistent with the structure of 2,11-di-2-pyridyl benzo[lmn]-s-triazolo[5,1-b:1',5',-j][3,8] phenanthraline-5,8-dione or that of its isomer, 2,9-di-2-pyridylbenzo[lmn]bis-s-triazolo[1,5-c:1,5'-j][3,8] phenanthroline-6, 13-dione (VI b). A mixture of both would probably be considered most likely. No further effort was spent in attempting to separate and identify the cis carbonyl (VI a) and trans carbonyl (VI b) isomers.

The results of the model reactions along with the elemental analyses and physical constants of the model compounds are given in Tables I and II. The infrared spectra of the model compounds can be seen in Figures 1 through 6. From the foregoing model reactions it would appear that the preparation of a high molecular weight benzobistriazolophenanthroline might be achieved by the reaction of NTCDA or NTCA with 2,6-pyridinediyldihydrazidine under appropriate conditions. The various polymerization reactions are discussed below.

2. PREPARATION OF POLYMERS

a. Polymerization in aprotic solvents

2,6-Pyridinediyldihydrazidine was reacted with NTCDA in HMP at 25-30°C. A clear, deep red solution was initially formed but precipitation of polymer occurred after several hours. The polymer was only sparingly soluble in aprotic solvents and had an inherent viscosity of less than 0.10 in methane sulfonic acid. The infrared spectrum exhibited a fairly strong absorption at 5.63 μ, indicative of anhydride end groups (Reference 4). Precipitation of polymer had apparently occurred before any substantial degree of polymerization could be achieved. Attempts to prevent precipitation of polymer by the use of other aprotic solvents (dimethyl sulfoxide, 5% solution of lithium chloride in HMP) were unsuccessful. Higher polymerization temperatures (50-70°C) resulted in almost instantaneous precipitation of polymer with no increase in inherent viscosity being noted.

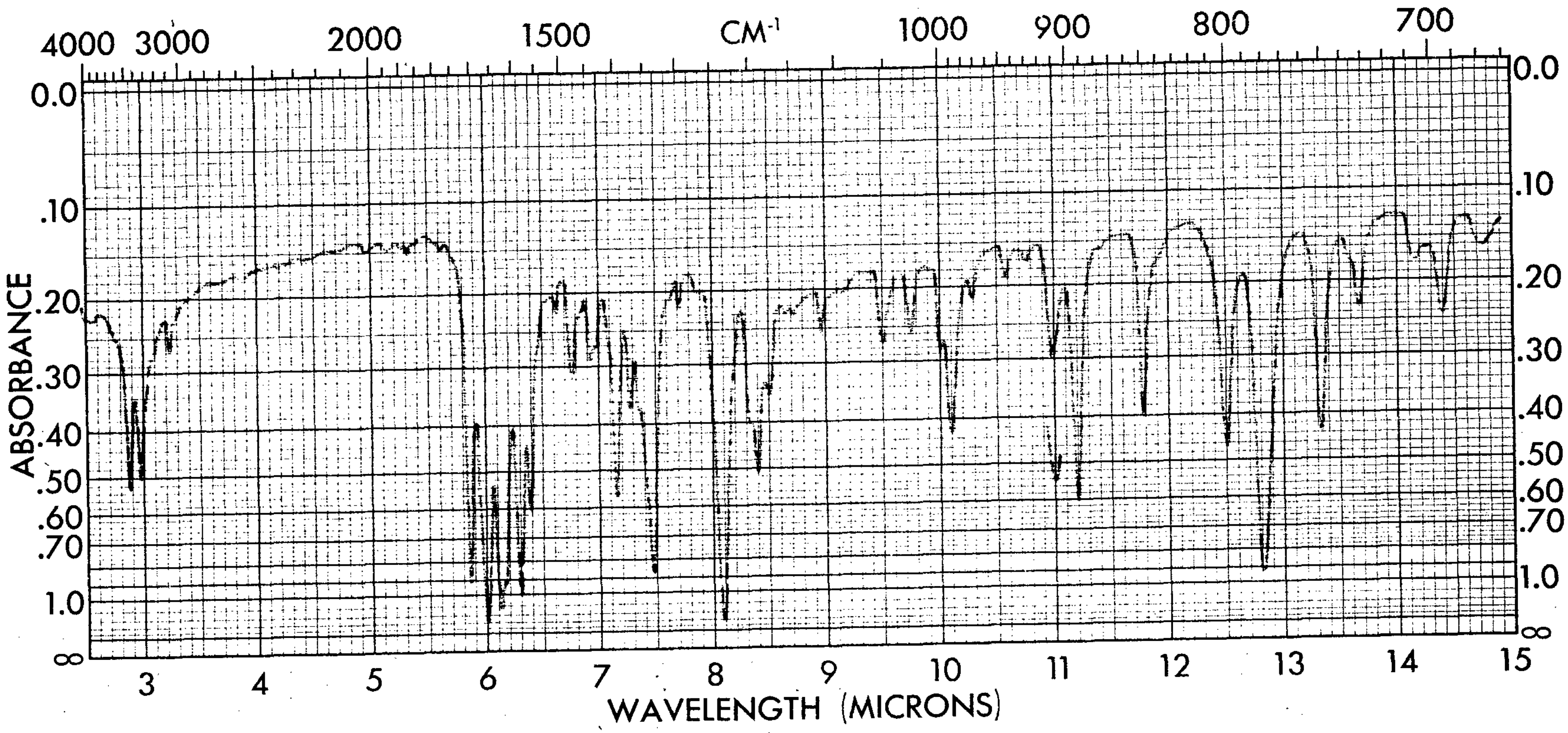


Figure 1. Infrared Spectrum of Model Compound I

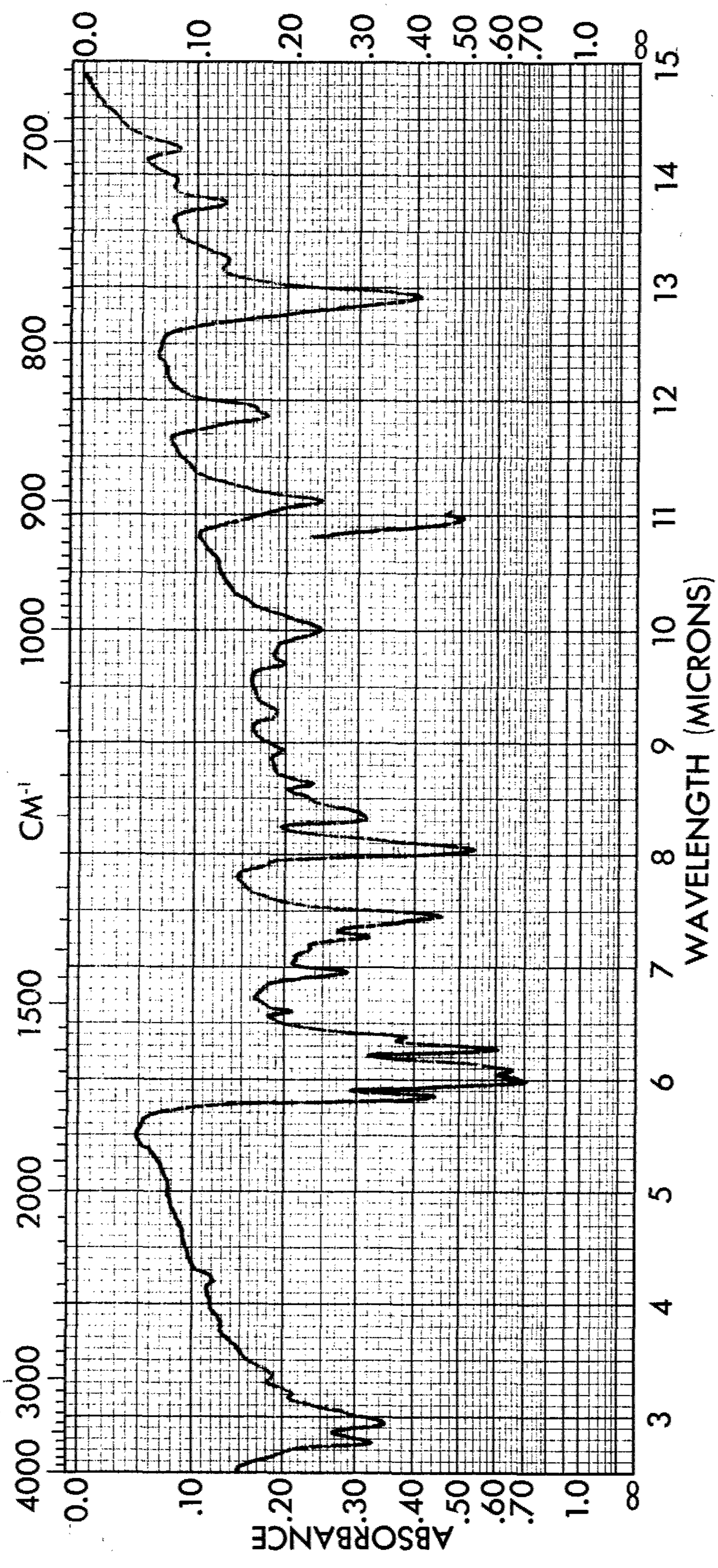


Figure 2. Infrared Spectrum of Model Compound III

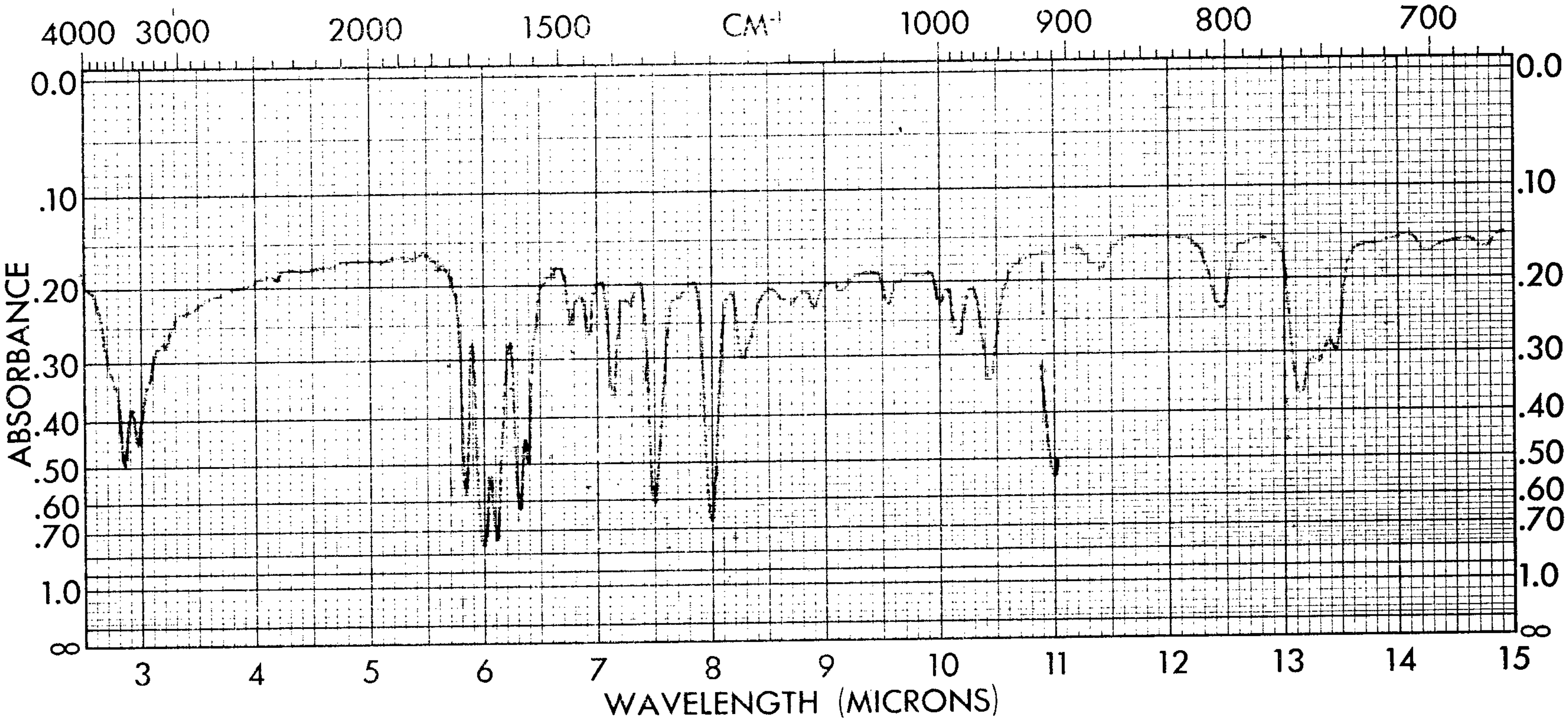


Figure 3. Infrared Spectrum of Model Compound V

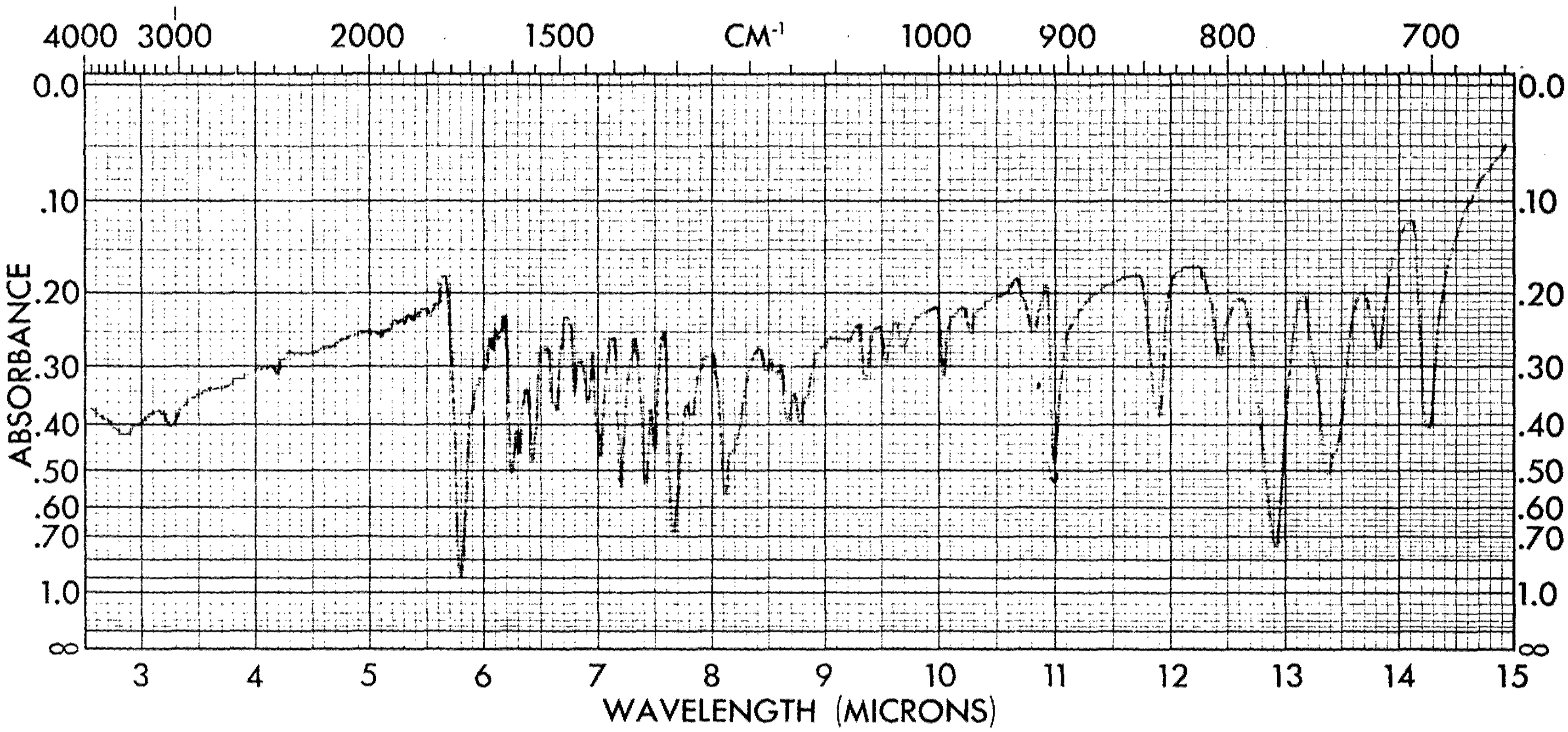


Figure 4. Infrared Spectrum of Model Compound II

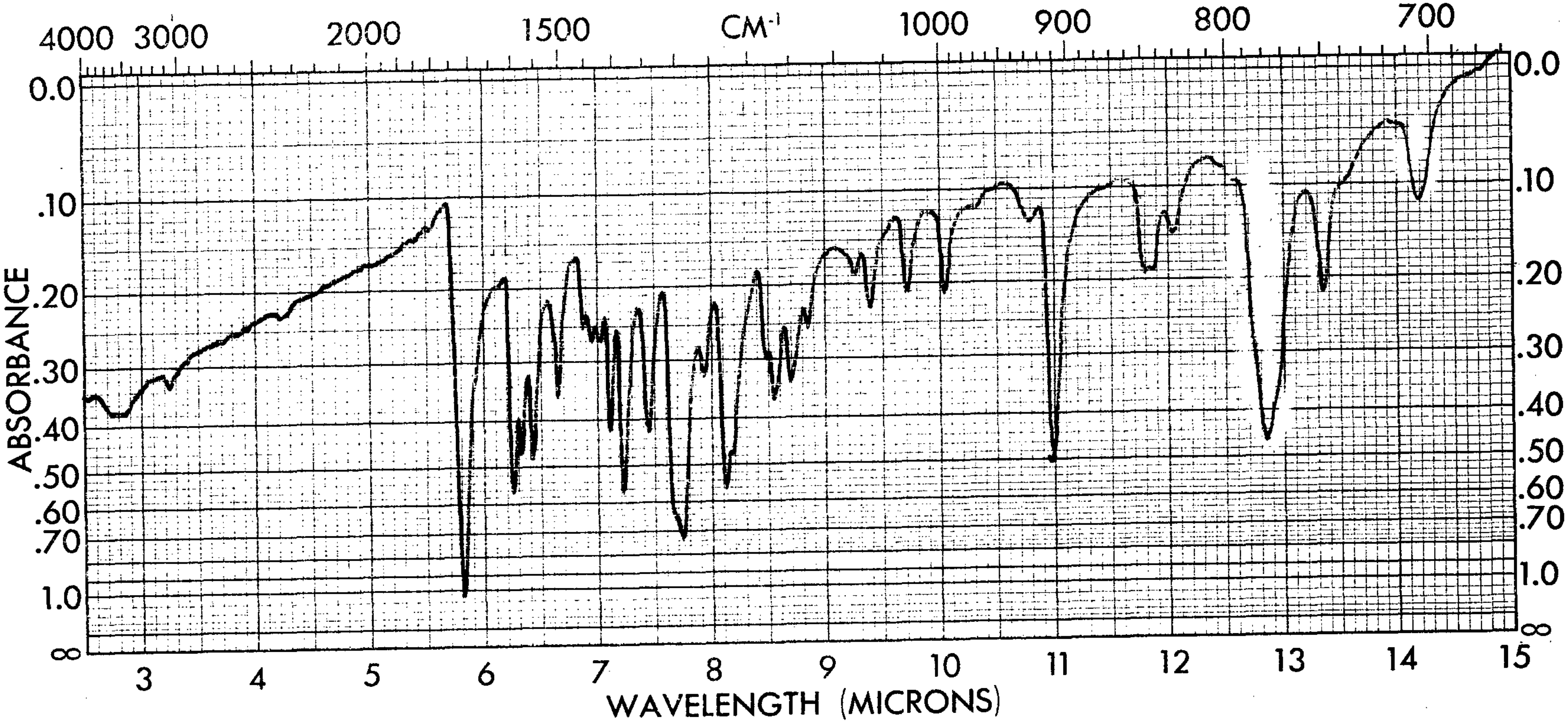


Figure 5. Infrared Spectrum of Model Compound IV

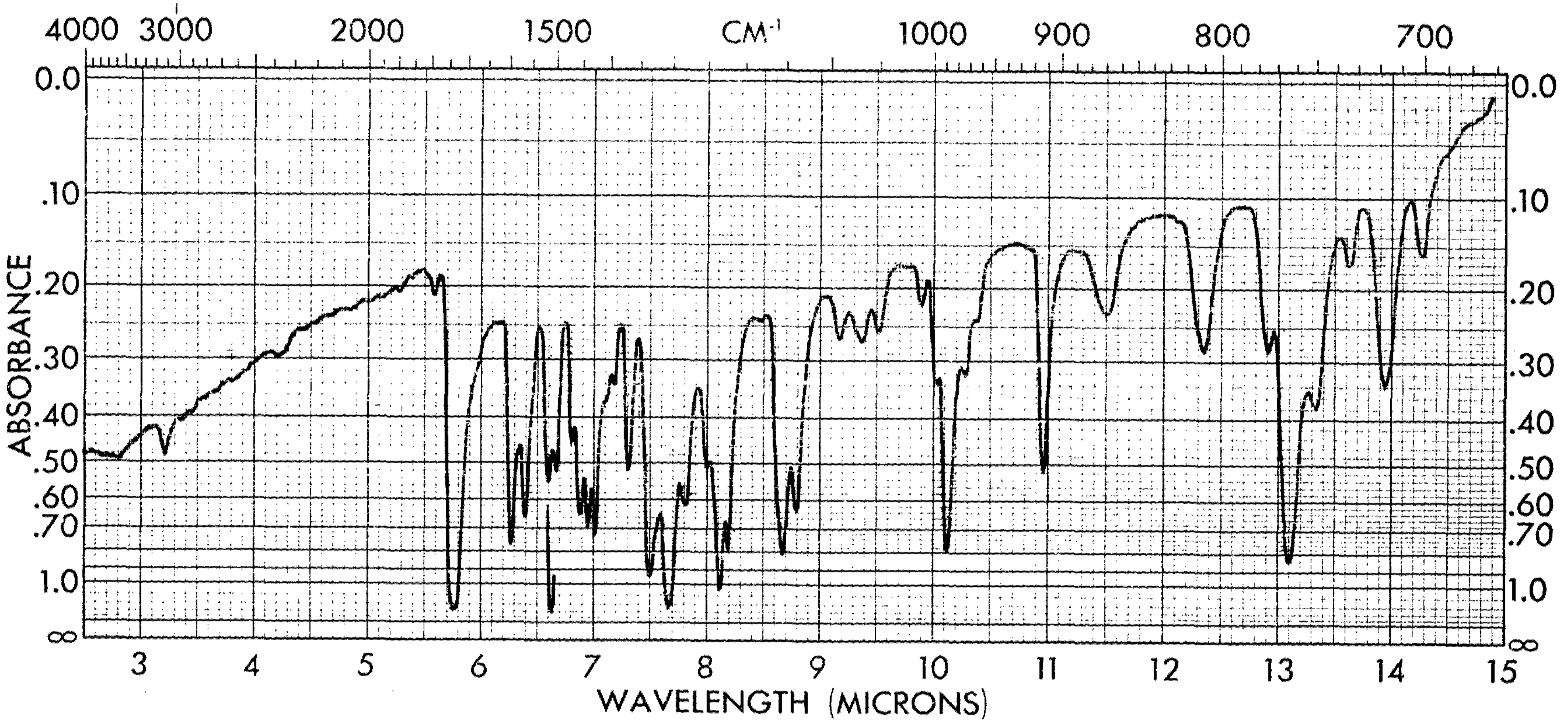
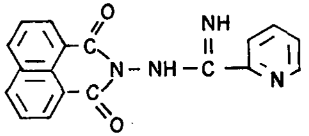
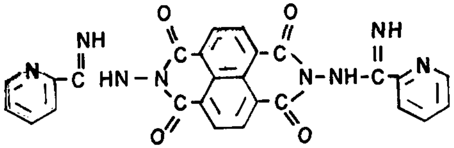
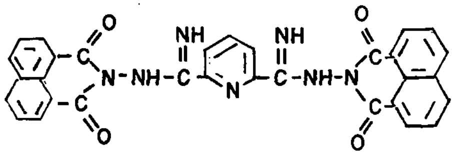


Figure 6. Infrared Spectrum of Model Compound VI

TABLE I

PREPARATION OF NAPHTHALIMIDE MODEL COMPOUNDS

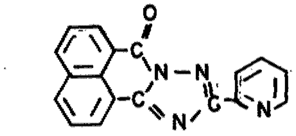
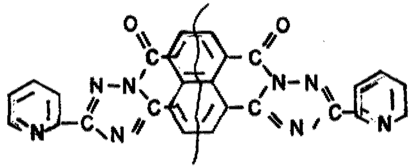
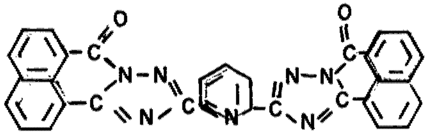
Product	Yield	Appear-ance	(a) m.p. - °C	Recrystal-lization Solvent	Analysis					
					calculated			found		
					C	H	N	C	H	N
	93	pale yellow needles	247-249	ethanol - water	68.35	3.80	17.72	68.09	3.88	17.48
	89	pale yellow powder	320 (sinters & darkens)	DMAC-$^{(b)}$ water	61.90	3.17	22.22	61.73	3.25	22.21
	95	off-white powder	325 (sinters & darkens)	DMAC-$^{(b)}$ water	67.27	3.44	17.72	67.60	3.52	17.97

(a) $\Delta T = 5°C$ /min.

(b) N, N - dimethylacetamide

TABLE II

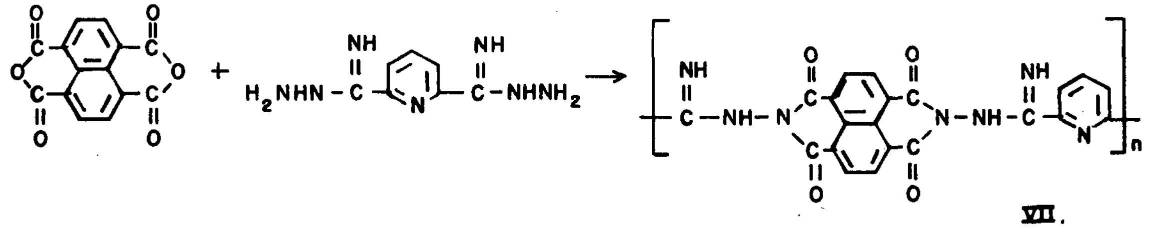
PREPARATION OF FULLY CONDENSED MODEL COMPOUNDS

Compound	Method of Preparation	Yield %	Physical Appearance	(c) m.p. - °C	Analysis					
					calculated			found		
					C	H	N	C	H	N
	A B C	77 82 80	bright yellow needles	269-270.5	72.48	3.36	18.79	72.48	3.51	18.81
	A B	65 81	orange powder	460 (darkens) 500 (dec.)	66.67	2.56	23.93	66.60	2.66	23.56
	A B D	78 89 70	red-brown powder	385 (darkens) 410-415 (melts)	71.95	2.90	18.96	71.60	2.97	19.15

(a) Molecular weight (mass spectroscopy); *calculated*: 298. *found* 298.

(b) A: Thermal cyclization of corresponding naphthalimide derivatives. B: Condensation of appropriate hydrazidine and acid or anhydride in PPA. C: Reaction of N-amino-1, 8-naphthalimide and 2-cyanopyridine in presence of zinc chloride. D: Cyclization of corresponding naphthalimide derivative in PPA.

(c) $\Delta T = 5°$ C./min.

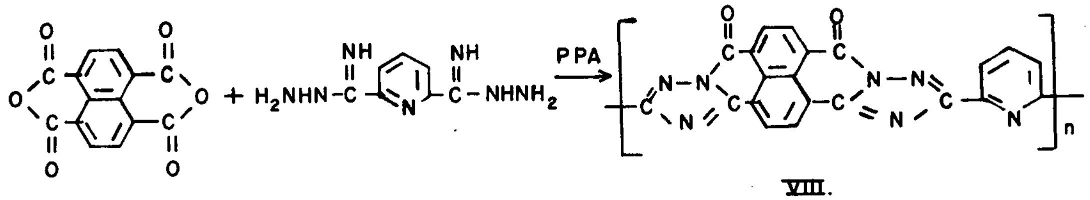


VII.

In an attempt to effect cyclization to the benzobistriazolophenanthroline structure, polymer VII was subjected to thermal treatment under nitrogen at 300-375°C. In each case, the dark-yellow polymer softened and sintered to an infusible, reddish-brown solid soluble only in sulfuric- or methane sulfonic-acid. The formation, however, of a small amount of unidentified white sublimate along with the evolution of ammonia during the thermal treatment indicated the occurrence of undesirable side reactions. It might be mentioned that small amounts of unidentified sublimate had also been formed during the corresponding model reactions. The elemental analyses and infrared spectrum of the very low molecular weight polymer ($\eta_{inh} = 0.09$) were not consistant with the desired benzobistriazolophenanthroline structure.

b. Polymerization in PPA

The polymerization of NTCDA with 2,6-pyridinediyldihydrazidine was initially studied. Polycondensation at 180-190°C. for 20 hrs. led to a high yield of polymer (VIII) with an inherent viscosity of 0.28. An attempt to prepare this polymer in higher molecular weight by the use of more stringent reaction conditions (200-210°C. and 50 hrs.) was unsuccessful. The reaction conditions are summarized in Table III.



VIII.

Attention was then directed toward the polycondensation of NTCA with 2,6-pyridinediyldihydrazidine. The general procedure used in the preceding polymerizations was followed. Equivalent molar quantities of the monomers were

TABLE III

PREPARATION OF POLYMERS IN POLYPHOSPHORIC ACID

Trial No.	Monomers		Reaction Time - Hours	Reaction Temp. - °C	η_{inh} (a) dl/g
1	NTCDA	2,6-Pyridinediyl-dihydrazidine	20	175-185	0.28
2	"	"	50	200-210	0.25
3	NTCA	"	18	170-180	0.41
4	"	"	36	200-210	0.51
5	"	"	20	195-205	0.45
6	"	"	12	185-195	0.87
7	"	"	60	200-210	0.81

(a) 0.2 g/dl, 25°C., CH_3SO_3H

intimately mixed and then added to the rapidly stirred PPA at 140°C. so as to have a reaction mixture concentration of 0.1 mole/ℓ. (total monomer concentration.) The pot temperature was then raised over the course of an hour to the desired reaction temperature and held there for the duration of the polymerization. The initial effort was carried out at 170-180°C. for 18 hrs. with an inherent viscosity of 0.41 being obtained. The use of more stringent reaction conditions (36 hrs. at 200-210°C) resulted in only a slight increase in molecular weight of the polymer (η_{inh} = 0.51).

It was felt that a limiting factor in the attainment of high molecular weight polymer was the purity of the NTCA. This compound had been recently obtained as a polymerization grade monomer through Celanese Research Co. The presence of an indeterminate amount of NTCDA contaminant was indicated by a small absorption in the infrared spectrum at 5.65 μ (Reference 4). Even if the anhydride groups did participate in the propagation reaction their presence would affect the stoichiometry of the reaction and could lead to a lowered degree of polymerization. An attempt was made to compensate for this inbalance in stoichiometry by the stepwise addition of very small quantities of 2,6-pyridinediyldihydrazidine to the reaction mixture after a reaction time of ten hours had elapsed (Trial No. 5). This, hopefully, would lead to coupling of diacid or anhydride end groups and a consequent increase in polymer molecular weight. However, no increase in the inherent viscosity of the polymer compared to earlier runs was observed.

Subsequent work was performed using an earlier NTCA sample which was judged to be of high purity by virtue of its having been used for the preparation of very high molecular weight BBL polymers (Reference 1). Reaction with 2,6-pyridinediyldihydrazidine at 185-195°C. for 12 hrs. led to a polymer with an inherent viscosity of 0.87. The use of higher reaction temperatures and longer reaction times (200-210°C. and 60 hrs.) did not lead to an increase in molecular weight ($\eta_{inh} = 0.81$).

The polymers obtained from the reactions in a PPA medium were completely soluble in concentrated sulfuric- or methane sulfonic-acid. Excluding variations in molecular weights, little difference could be observed between the polymers prepared from NTCDA or NTCA. The infrared spectra of the polymers from NTCDA, however, did show a small absorption at 5.65 μ which was not present in the spectra of the polymers prepared from NTCA. This absorption was attributed to the presence of anhydride end groups (Reference 4).

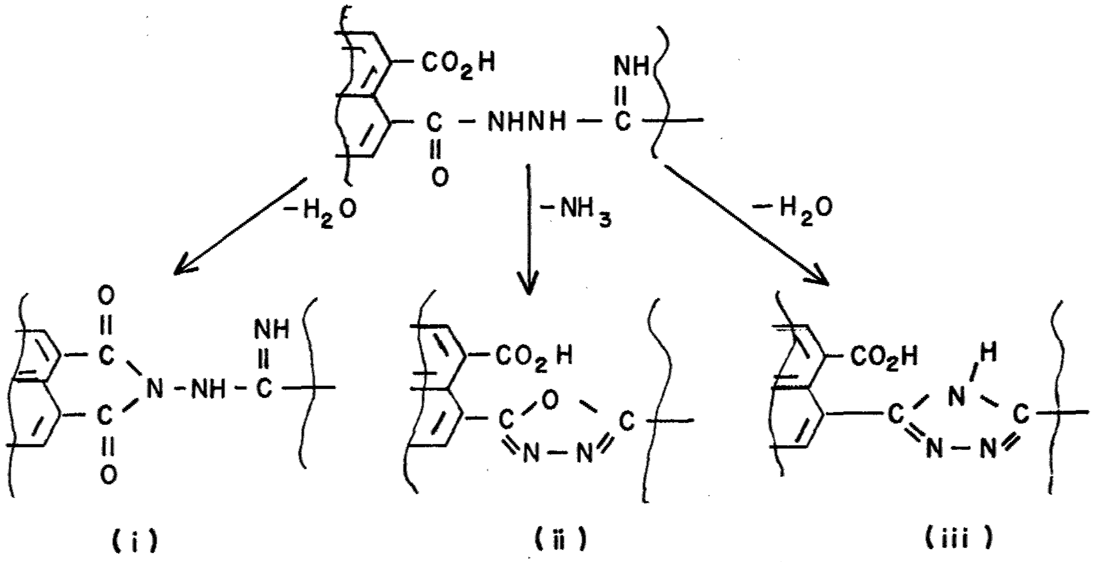
Yields of isolated polymer were in the range of 80-90% and were not quantitative probably due to loss of polymer during the various decantations, filtrations, etc. used in the work-up procedure.

3. CHARACTERIZATION OF POLYMERS

Due to their low molecular weights and generally ill-defined structures, little effort was expended in characterizing the polymers prepared by the room temperature polycondensation in HMP. Attention, instead, was directed toward the characterization of the benzobistriazolophenanthroline polymer VIII prepared in PPA. These polymer samples were generally isolated as reddish black particles which were rather hard and difficult to grind. They dissolved readily in methane sulfonic acid and with some difficulty in sulfuric acid. The solutions were deep red. The polymers were completely insoluble in all organic solvents tested. They appeared to be somewhat susceptible to base hydrolysis but were quite resistant to attack by warm concentrated sulfuric acid. A sample of polymer (η_{inh} = 0.41), for example, dissolved in concentrated sulfuric acid and heated at 70-80°C. for several hours showed no decrease in inherent viscosity upon its isolation by reprecipitation.

The thermal properties of the polymer were studied by thermogravimetric analysis, differential thermal analysis, and softening under load (Reference 5). The thermogravimetric analysis curves can be seen in Figure 7. Onset of breakdown in a nitrogen atmosphere began at 475°C. with a 35% weight loss being recorded at 900°C. In an air atmosphere the polymer exhibited initial breakdown at 425°C. with no weight residue being present at 900°C. Differential thermal analysis of the polymer revealed several very weak transitions in the 300-400°C. range and strong decomposition exotherms in the 430-440°C. range. Differential scanning calorimetry showed only an increasing baseline drift above 460°C. The polymer exhibited no softening under load up to 450°C., the operating limit of the test apparatus.

Considerable effort was spent in establishing the polymer structure. Based on the results of the model compound studies the proposed structure VIII would appear to be quite reasonable. It is possible, however, that other incompletely cyclized structures could conceivably result from the polymerization reaction in PPA. Several of the more likely to be formed from an amic acid type structure are shown below.



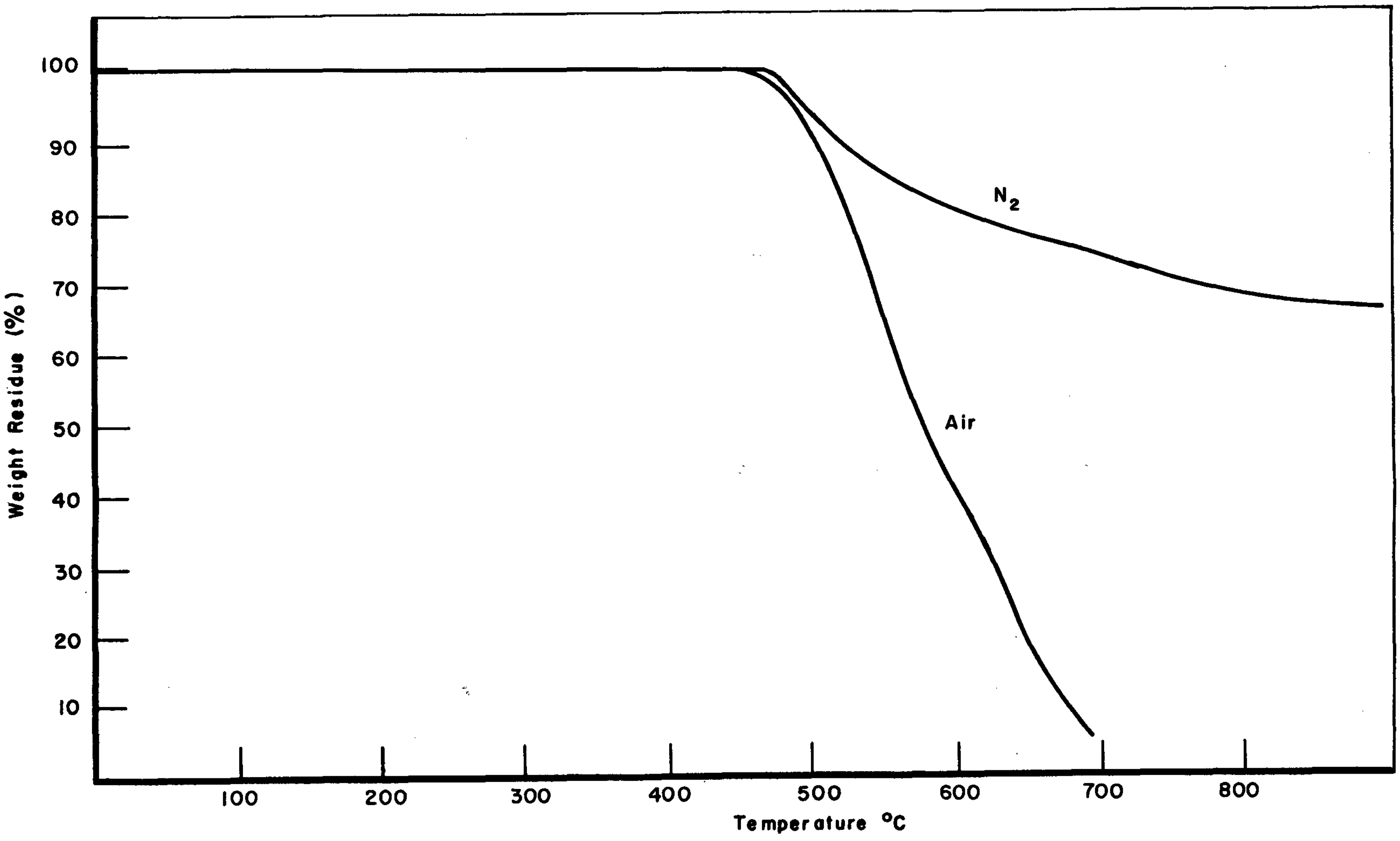


Figure 7. TGA Curves of the Benzobistriazolophenanthroline Polymer in Air and in Nitrogen

The mechanism of the polymerization reaction in PPA is not fully understood but one would expect the peri position of the carboxy groups in NTCA to greatly favor formation of the naphthalimide structure (i) over the oxadiazole (ii) and triazole (iii) structures. It is known from the model compound studies that this structure can be further condensed in PPA to a fully cyclized structure. If, on the other hand, formation of a five-membered azole did occur the oxadiazole structure ii would be the expected product. Other investigators have shown that cyclodehydration of poly-N-acylhydrazidines in PPA leads exclusively to the polyoxadiazole (Reference 6). Structure iii can probably be excluded on this basis. It should be noted that the oxadiazole structure (ii), unlike the naphthalimide structure (i) would not undergo further dehydration and could not possibly lead to the desired benzobistriazolophenanthroline structure.

The predominance of benzobistriazolophenanthroline units in the polymer chain was established by elemental analysis and by comparison of the polymer infrared spectra with those of the model compounds. The elemental analysis values for the various polymer samples are listed in Table IV along with the calculated values for the benzobistriazolophenanthroline structure and structures i and ii. The nitrogen determinations were obtained by modified Dumas techniques and tended to give values lower than calculated for the completely cyclized benzobistriazolophenanthroline structure. While the carbon values also tended to be low the hydrogen values proved to be slightly higher than the calculated values. Although this might be indicative of incomplete cyclization in the polymer chain, it can also be partially attributed to the presence of tightly bound water in the polymer. The determinations were further complicated by trace amounts of phosphorus and sulfur and ash residues of 0.5-1.0%. Although the presence of incompletely cyclized units cannot be excluded on the basis of elemental analysis, the values obtained do indicate a substantial conversion to the desired polymer structure.

The infrared spectra of the polymer samples are consistent with the benzobistriazolophenanthroline structure. A representative polymer spectrum

TABLE IV

ELEMENTAL ANALYSES OF POLYMERS

Trial No.	η_{inh} (a)	Analysis (b-d) C	H	N
1	0.28	-----	-----	-----
2	0.25	63.97	2.03	22.34
3	0.41	64.35	2.16	23.61
4	0.51	64.05	2.02	22.39
5	0.45	63.44	2.11	23.89
6	0.87	63.19	2.06	23.37
7	0.81	63.26	2.21	23.27

(a) 0.2g./dl., 25°C., CH_3SO_3H

(b) Calculated for fully cyclized benzobistriazolophenanthroline structure VIII $(C_{21}H_7N_7O_2)_n$: C, 64.78; H, 1.80; N, 25.19.

(c) Calculated for naphthalimide structure (i) $(C_{21}H_{11}N_7O_4)_n$: C, 59.29; H, 2.59; N, 23.06.

(d) Calculated for oxadiazole structure (ii) $(C_{21}H_9N_5O_6)_n$: C, 59.02; H, 2.11; N, 16.39.

can be seen in Figure 8. The similarity between the polymer spectrum and the spectra of the fully cyclized model compounds can be seen in Figure 9. Absent in the polymer spectrum are absorptions in the 2.80-3.00μ and 6.02-6.18μ region which were present in the spectra of the naphthalimide model compounds. This would seem to indicate the absence of any appreciable amount of naphthalimide structures (i) in the polymer backbone. No evidence of the oxadiazole structure (ii) could be found in the polymer spectrum. Although absorption due to the carboxylic acid group would probably be overlapped in the 5.80-5.90μ region by absorption due to the carbonyl group of the fully condensed structure, one would still expect to see absorption in the 3.3 to 3.9μ region attributable to the stretching vibration of the -OH group. It is to be noted, however, that the polymer infrared spectrum is rather diffuse in this region and low intensity absorptions may have been obscured. In general, however, little if any evidence of incomplete cyclization can be found in the infrared spectrum of the polymer. From the infrared spectral evidence along

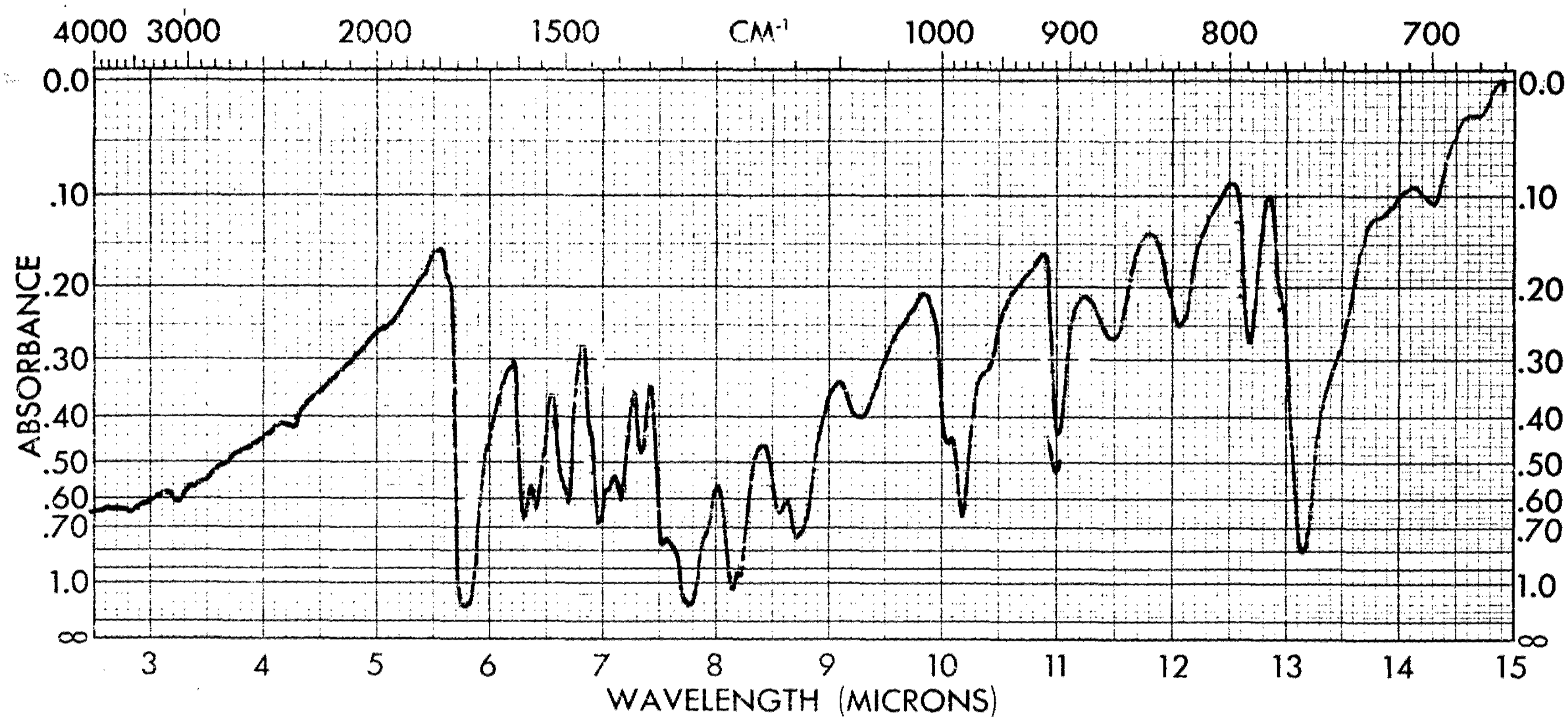


Figure 8. Infrared Spectrum of Benzobistriazolophenanthroline Polymer (η_{inh} = 0.87)

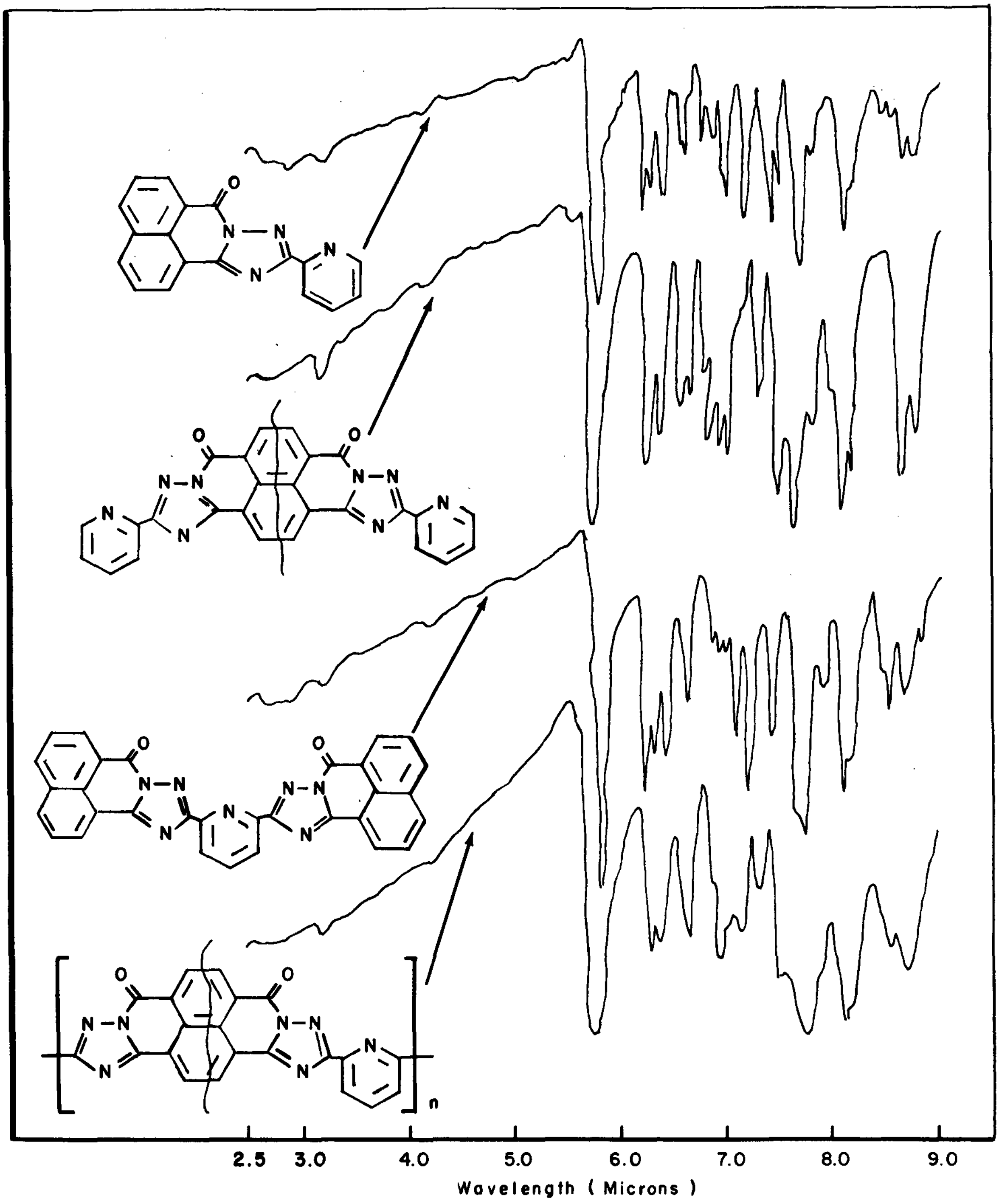


Figure 9. Infrared Spectra in the 2.5 to 9.0 μ Region

with the elemental analysis data it is concluded that a high degree of cyclization to the benzobistriazolophenanthroline structure has been obtained in the polycondensation reactions.

4. CONCLUSIONS

It has been shown that low to moderate molecular weight benzobistriazolophenanthroline polymers can be prepared by the polycondensation of 2,6-pyridinediyldihydrazidine with NTCDA or NTCA in PPA. Infrared and elemental analyses substantiate the proposed structure and are indicative of a high degree of cyclization in the polymer backbone. Attempts to prepare the polymer in a two-step sequence involving the initial formation of a readily soluble prepolymer were unsuccessful.

Since the polymer does not offer outstanding thermal stability or any apparent aid to processibility over present state of the art materials, further work on this system would not be justified.

SECTION III

EXPERIMENTAL

1. PREPARATION OF SOLVENTS, INTERMEDIATES, AND MONOMERS

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

Polyphosphoric acid (82-84% P_2O_5) was obtained from Matheson, Coleman and Bell. It was used as received.

1,4,5,8-Naphthalenetetracarboxylic acid was obtained as a polymerization grade monomer through Celanese Research Co.

a. 1,4,5,8-Naphthalenetetracarboxylic Dianhydride

The method of Arnold and Van Deusen was used (Reference 7). To 200 ml. of 75-25% acetic acid - acetic anhydride was added 15g. of 1,4,5,8-naphthalenetetracarboxylic acid. The mixture was refluxed for three hours with stirring and then allowed to cool to room temperature. The light yellow solid was filtered and washed with methanol and ether. The yield of anhydride was 14g. (93%), m.p. 445°C. (Lit. 440°C.) (Reference 7).

b. N-Amino-1,8-Naphthalimide

Naphthalene-1,8-dicarboxylic anhydride (3.96g., 0.02 mole) was dissolved in pyridine (60 ml.) at 80°C. and excess 95% hydrazine (1.5g.) was added slowly. The resultant amber solution was stirred at 100°C. for several hours. Cooling of the solution gave a mass of yellow crystals which were isolated by filtration. Several recrystallizations from glacial acetic acid led to 2.2g. (51% yield) of fine yellow crystals, m.p. 265-267°C. (Lit. 267-268°C.) (Reference 8).

c. 2-Pyridylhydrazidine

2-Cyanopyridine (5.2g., 0.05 mole) and 95% hydrazine (15 ml.) were stirred in ethanol (10 ml.) at room temperature for three hours. The solution was diluted with 30 ml. of water and the product extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate, filtered and reduced to dryness. Recrystallization of the residue from benzene gave 5.2g. (66% yield) of fine, pale yellow needles, m.p. 95-96°C. (Lit. 95-96°C.) (Reference 9).

d. 2,6-Pyridinediyldihydrazidine

2,6-Dicyanopyridine (2.8g., 0.21 mole), as prepared by the method of Lukes and Pergal (Reference 10) was dissolved in 150 ml. of ethanol. An excess of 95% hydrazine (20 ml.) was slowly added and the resultant yellow solution was stirred at 55°C. for two hours. The white precipitate which formed was isolated by filtration and recrystallized twice from water to give 2.0g. (52% yield) of pale yellow needles, m.p. 230-233°C. with dec.) (Lit. 230-231°C. with dec.) (Reference 11).

2. PREPARATION OF MODEL COMPOUNDS

The following are representative examples of the various procedures used in the preparation of the model compounds.

a. Preparation of N,N' -Pyridinediylbis [(aminomethylidyne)nitrilo]] dinaphthalimide (III)

2,6-Pyridinediyldihydrazidine (0.386g., 0.002 mole) was dissolved in HMP (20 ml.) by gentle heating. The clear yellow solution was cooled to room temperature and 1,8-naphthalic anhydride (0.792g., 0.004 mole) was added to the solution with gentle stirring being maintained. After 15 minutes, the tan suspension was heated to 60°C. and a clear, red solution resulted. After one hour, the product was precipitated by the addition of water and isolated by filtration. Thorough washing of the product with methanol followed by drying at 100°C. yielded 1.05g. (95% yield) of crude material. Recrystallization from N,N-dimethylacetamide-water gave the product as an off-white powder which darkens and sinters at 330-335°C.

Analysis Calc'd: C, 67.27; H, 3.44; N, 17.72
Found: C, 67.60; H, 3.52; N, 17.97

b. Preparation of 10,10'-(2,6-Pyridinediyl)bis[7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (IV)

(1) by thermal treatment of III.

III (0.55g., 0.001 mole) was heated under nitrogen at 330-350°C. for thirty minutes. The resultant reddish-brown solid was finely crushed and heating was then continued for an hour. Successive washings of the crude product with cold N,N-dimethylacetamide, hot ethanol, and ether yielded 0.35g. (67% yield) of a reddish-brown solid which could not be sublimed at 350°C. and 0.01 mm Hg pressure. It darkened at about 385°C. and melted at 410-415°C.

Analysis Calc'd: C, 71.95; H, 2.90; N, 18.96
Found: C, 71.60; H, 2.92; N, 19.15

(2) from 2,6-pyridinediyldihydrazidine and 1,8-naphthalic anhydride.

2,6-Pyridinediyldihydrazidine (0.38g., 0.002 mole) and 1,8-naphthalic anhydride (0.792g., 0.004 mole) were crushed together and added to deoxygenated polyphosphoric acid (20 ml.) at 110°C. The stirred reaction mixture was heated under nitrogen to 190°C. at a heating rate of 5°C./min. The resultant red solution was held at 190°C. for 15 hours, cooled to 100°C. and added to 200 ml. of vigorously stirred distilled water. The product was isolated by filtration and washed several times with hot water. Successive washing with cold N,N-dimethylacetamide, hot ethanol, and ether gave 0.90g. (89% yield) of reddish-brown product, m.p. 410-415°C.

c. Preparation of 10-(2-Pyridyl)-7-*H*-benzo[*de*]-*s*-triazolo-[5,1,*a*]isoquinolin-7-one (II)

2-Cyanopyridine (0.52g., 0.005 mole), N-amino-1,8-naphthalimide (1.06g., 0.005 mole), and zinc chloride (1.02g., 0.0075 mole) were intimately mixed in a polymer tube and heated under nitrogen at 150°C. The temperature was gradually raised to 230°C. over the course of three hours with the fused reaction mixture occasionally being finely crushed. The final crude product was washed well with hot water and recrystallized from ethanol/water to give 1.2g. (80% yield) of pale yellow needles, m.p. 269-270.5°C.

Analysis Calc'd:	C, 72.48; H, 3.36; N, 18.79
Found:	C, 72.48; H, 3.51; N, 18.81

3. PREPARATION OF POLYMERS

Typical preparative techniques for the polymers are as follows:

a. Polymerization of 2,6-Pyridinediyldihydrazidine and NTCDA in HMP

2,6-Pyridinediyldihydrazidine (0.386g., 0.002 moles) was dissolved in HMP (20 ml.) by stirring and gentle heating to 60°C. under nitrogen. The clear yellow solution was cooled to 20°C. and NTCDA (0.536g., 0.002 moles) was added as a solid in portions so as to keep the temperature below 30°C. The reddish suspension was stirred at 25°C. for one hour and gradually became a clear red solution. The polymerization mixture over the course of the next hour darkened and became somewhat cloudy. After 2.5 hours, the polymer precipitated out of solution as a gell-like reddish solid. The polymerization mixture was added to methanol and the polymer was isolated by filtration. It was washed with warm N,N-dimethylacetamide and successively extracted in a Soxlett with dioxane and methanol. Drying at 110°C. and 0.1 mm for three hours yielded 0.70g. of yellow polymer with an inherent viscosity of 0.10 in methane sulfonic acid at 25°C.

Analysis Calc'd:	C, 59.29; H, 2.59; N, 23.06
Found:	C, 58.17; H, 2.67; N, 20.65

The above polymer (0.35g.) was heated under nitrogen in a polymer tube at 320-350°C. for one hour. A slight evolution of ammonia was noted along with the formation of a small amount of white sublimate. The fused, reddish-brown polymer was finely crushed and 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 Hg. for one hour. About 0.2g. of the reddish polymer was obtained. It was soluble in both sulfuric and methane sulfonic acid and had an inherent viscosity of 0.09 in methane sulfonic acid at 25°C.

Analysis Calc'd:	C, 64.78; H, 1.80; N, 25.19
Found:	C, 62.34; H, 1.85; N, 19.29

b. Polymerization of 2,6-Pyridinediyldihydrazidine and NTCA in PPA

The PPA (40 ml. was deoxygenated by passing dry nitrogen through it at 110°C for 14 hours. Then 2,6-pyridinediyldihydrazidine (0.306g., 0.002 mole) and NTCA (0.608g., 0.002 mole) were ground together and added with stirring to the PPA at 140°C. The temperature was raised to 185-190°C over the course of an hour and maintained at this level for 12 hours. The reaction mixture gradually changed from a yellow suspension to a very viscous, deep-red solution. This solution was then cooled to 100°C and poured into 500 ml. of ice water in a Waring Blender. The mixture was vigorously stirred for 5 minutes. The suspension was allowed to settle overnight and the clear supernatant liquid was then decanted. The polymer was isolated by filtration, stirred vigorously in several hundred ml. of water, and again isolated by filtration. This washing procedure was repeated twice with water, and similarily with N,N-dimethylacetamide. Final washings were with hot methanol. The polymer was reprecipitated using methane sulfonic acid/methanol as the solvent/non-solvent system. The reddish-brown product was thoroughly washed with ether and dried at 180°C. and 0.01 mm Hg over phosphorus pentoxide to give 0.55g. of polymer. It had an inherent viscosity of 0.87 in methane sulfonic acid at 25°C.

Analysis Calc'd:	C, 64.78; H, 1.80; N, 25.19
Found:	C, 63.19; H, 2.21; N, 23.37

4. CHARACTERIZATION OF POLYMERS

a. Viscosity

The inherent viscosities of the polymers were determined in methane sulfonic acid at 25°C. using solution concentrations of approximately 0.2g./dl.

b. Infrared Spectra

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

c. Softening Range Determinations

The softening characteristics of the polymers were obtained by means of a modified Vicat apparatus (Reference 5). Heating was performed at a constant rate of 2.5°C./min.

d. 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°C./min. A plot of percent weight residue versus temperature was made for each run.

e. 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.

f. Differential Scanning Calorimetry

A Perkin-Elmer Model DSC-1B with a constant heating rate of 20°C./min. was used. Triplicate runs were made on the sample.

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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 (AFML/LNP) Wright-Patterson Air Force Base, Ohio	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

PREPARATION AND CHARACTERIZATION OF A BENZOBISTRIAZOLOPHENANTHROLINE POLYMER

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

Final Technical Report May 1969 to April 1970

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

Dr. Robert C. Evers

6. REPORT DATE February 1971	7a. TOTAL NO. OF PAGES 39	7b. NO. OF REFS 11

8a. CONTRACT OR GRANT NO. b. PROJECT NO. 7340 c. Task No. 734004 d.	9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-70-306 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited

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

13. ABSTRACT

A benzobistriazolophenanthroline polymer was prepared by the polycondensation of 2,6-pyridinediyldihydrazidine with 1,4,5,8-naphthalene tetracarboxylic acid or 1,4,5,8-naphthalene tetracarboxylic dianhydride in polyphosphoric acid. Inherent viscosities in the range of 0.25-0.87 dl./g. were recorded. Polymer structure was established by elemental and infrared analysis. The polymer was a reddish-brown powder soluble in sulfuric-or methane sulfonic-acid. Onset of breakdown during thermogravimetric analysis in a nitrogen atmosphere occurred at 475°C.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Benzobistriazolophenanthroline polymer						
High temperature applications						
Heterocyclic Polymers						