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**HETEROCYCLIC POLYMERS DERIVED FROM  
1,2,4,5-NAPHTHALENETETRACARBOXYLIC  
ACID DIANHYDRIDE**

*G. A. LOUGHRAN*

*F. E. ARNOLD*

TECHNICAL REPORT AFML-TR-73-221

NOVEMBER 1973

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AIR FORCE MATERIALS LABORATORY  
AIR FORCE SYSTEMS COMMAND (AFSC)  
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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004 "Synthesis of Novel Polymer Materials for High Temperature Resin Applications." It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as Project Scientist.

This report covers work conducted from January 1972 to July 1972. The manuscript was released by the author in August 1973 for publication as a technical report.

This technical report has been reviewed and is approved.



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## ABSTRACT

Polycondensation of 3,3'-diaminobenzidine and 1,2,4,5-naphthalenetetracarboxylic acid dianhydride in aprotic solvents at 80°C to 120°C gave soluble low molecular weight polymers. Increasing the reaction temperature to 160°C led to further condensation and gave increasing amounts of undesirable insoluble cross-linked material. Some higher molecular weight soluble polymer was obtained when m-cresol was used as a solvent. The low molecular weight polymers could be further condensed and chain extended with about a twofold increase in molecular weight by heating at 250°C/0.1 mm. However, linear polymers which had been prepared in aprotic solvents up to 80°C on "second-staging" gave 33% to 39% of insoluble cross-linked material. This is believed to be due to a branching reaction taking place between 80°C and 120°C at the ortho anhydride linkage.

TABLE OF CONTENTS

SECTION	PAGE
I INTRODUCTION	1
II DISCUSSION OF RESULTS	5
III CONCLUSIONS	15
IV EXPERIMENTAL	17
V REFERENCES	29

## LIST OF ILLUSTRATIONS

FIGURE	PAGE
1. Preparation of Pyrrole Polymers	2
2. Polycondensation of 1,4,5,8-Naphthalenetetracarboxylic Acid Dianhydride With Diaminobenzidine (DAB)	3
3. Preparation of 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride, IV	5
4. Model Reaction Between 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride and o-Phenylenediamine (OPD)	6
5. Polycondensation of 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride With Diaminobenzidine (DAB)	8
6. Branching Reaction in the Polycondensation of 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride With Diaminobenzidine (DAB)	9
7. TGA Curves of the Heat Treated Polymer Samples	22
8. Infrared Spectrum of 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride, IV	23
9. Infrared Spectrum of the Model Compound N-(o-Aminophenyl)-7-oxo-7H-Benzimidazo [2,1-a]Benz[de]Isoquinoline-4,5-Dicarboximide, V	24
10. Infrared Spectrum of the Model Compound 6,10-Dihydro-6,10-Dioxobenzimidazo[2,1-a] Benzimidazo[1,2':1,5]Pyrrolo [3,4-g]Benz[de]Isoquinoline, VI	25
11. Infrared Spectrum of the Unidentified Compound $C_{24}H_{20}O_3N_4$ , [M] <sup>+</sup> = 412	26
12. Infrared Spectrum of the Soluble Polymer, $C_{26}H_{14}O_4N_4$ , IX	27
13. Infrared Spectrum of the Soluble Heat Treated Polymers, X	28

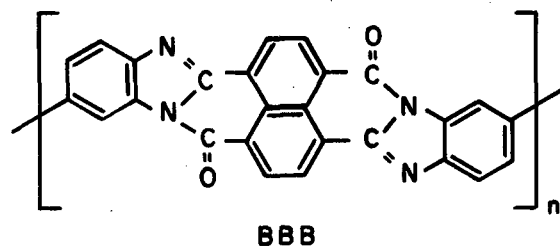
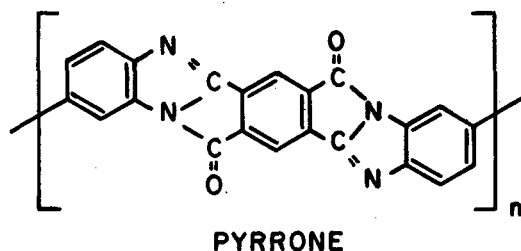
## LIST OF TABLES

TABLE		PAGE
1.	Polycondensation of Equimolar Quantities of 3,3'-Diaminobenzidine and 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride With Initial Mixing of the Monomers	11
2.	Polycondensation of Equimolar Quantities of 3,3'-Diaminobenzidine and 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride With Slow Addition of the Dianhydride to the Tetraamine in Solution	12
3.	Comparison of Properties of Polymers After Heat Treatment at 250°C/0.01 mm	13

## SECTION I

## INTRODUCTION

The polycondensation of aromatic tetraacids or dianhydrides with aromatic tetraamines has been studied extensively and is well documented in the literature (References 1 and 3). A variety of highly fused aromatic heterocyclic polymer systems have been synthesized through the polycondensation reactions. The most prominent and attractive thermally stable systems of all those investigated are the polybenzoylbenzimidazoles (pyrrones) and polybisbenzimidazo benzophenanthrolines (BBB). Although both polymer systems are prepared with the same type of tetra-functional monomers, the chemistry of the polymerizations are quite different which results in entirely different end use applications.



The pyrrone polymer is prepared by a two-stage polymerization process as indicated in Figure 1 (References 4 and 5). A room temperature polycondensation of pyromellitic dianhydride (PMDA) with 3,3'-diaminobenzidine (DAB) in an aprotic solvent leads to a poly (amide-acid-amine) I which is converted to the poly(imidazole-imide) structure II by the solid phase second staging at temperatures up to 400°C. The purity of structures I and II along the polymer backbone has been the subject of many studies in the last five years (References 6 to 8). A substantial amount of branching occurs during the preparation of prepolymer I, which in most cases produces an insoluble cross-linked product II from the second-stage process. The fact that one can obtain a soluble prepolymer in aprotic solvents has allowed the pyrrone system III to be processed into moldings (Reference 9), foams (Reference 10), and structural composites (Reference 11).

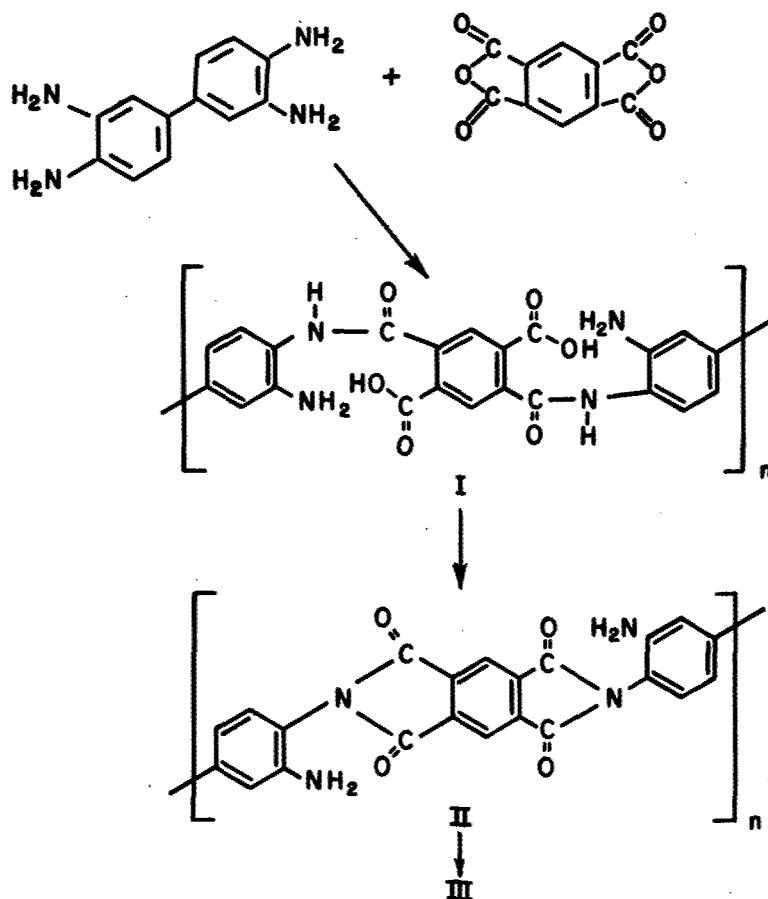


Figure 1. Preparation of Pyrrone Polymers

The BBB polymer is prepared from the solution polycondensation of 1,4,5,8-naphthalenetetracarboxylic acid or its dianhydride with DAB in polyphosphoric acid as depicted in Figure 2 (Reference 12). High molecular weight polymers of high quality are obtained in the synthesis which exhibit excellent thermal and thermal oxidative stabilities (References 13 and 14). The BBB polymer is soluble only in strong acidic solvents, thereby limiting it as a material for structural composites; however, the polymer has been developed (References 15 and 16) into a fibrous material showing excellent properties for deployable aerodynamic decelerators.

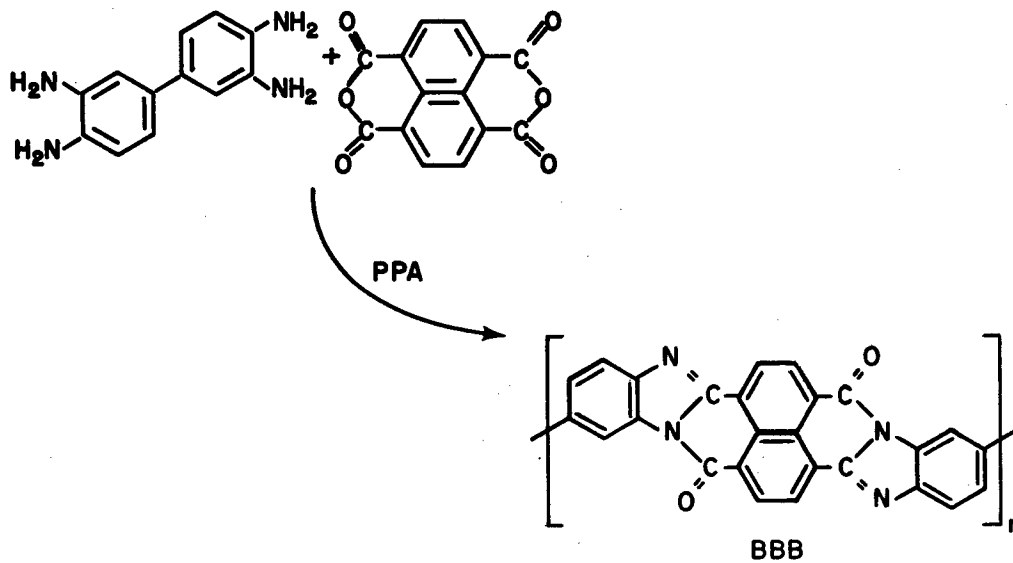


Figure 2. Polycondensation of 1,4,5,8-Naphthalenetetracarboxylic Acid Dianhydride With Diaminobenzidine (DAB)

The use of both heterocyclic systems as a material in applications is solely dependent on the difference in reactivity of an ortho and peri anhydride. Ortho anhydrides, such as PMDA, are very easily opened to an amide-acid-amine by DAB and are therefore very difficult to close to the imide-amine or completely fused "pyronne." The system as a prepolymer (amide-acid-amine) is soluble in aprotic solvents. "Peri" anhydrides, on the other hand, are more thermodynamically stable dianhydrides and when opened to the amide-acid-amine immediately close to an imide-amine III, which is insoluble in the aprotic polymerization medium. Polymerization of NTCA-DA and DAB in aprotic solvents results in a low molecular weight insoluble and infusible imide-amine oligomer (III) which is of little use as a candidate composite material.

The objective of this work is to combine both the "ortho" and "peri" anhydride groups into one monomer, and study its polymerization in aprotic solvents.

## SECTION II

## DISCUSSION OF RESULTS

## 1. Monomer Preparation

The monomer chosen for this study was 1,2,4,5-naphthalenetetracarboxylic dianhydride, IV. It was prepared by a two-step oxidation of 1'-methyl-3'-keto-2,3-cyclopentenoacenaphthene, which on treatment with sodium dichromate in glacial acetic acid gave the intermediary 2-acetonaphthene-1,4,5-tricarboxylic acid (Reference 17). Subsequent oxidation with sodium hypochlorite followed by refluxing with acetic anhydride gave the desired monomer IV. Low yields were consistently obtained because of poor conversion in the dichromate oxidation. However, some increase in the quantity of 2-acetonaphthene-1,4,5-tricarboxylic acid was realized when the dichromate oxidizing mixture was reduced in volume to a thick paste and boiled with concentrated hydrochloric acid. The reaction scheme is depicted in Figure 3.

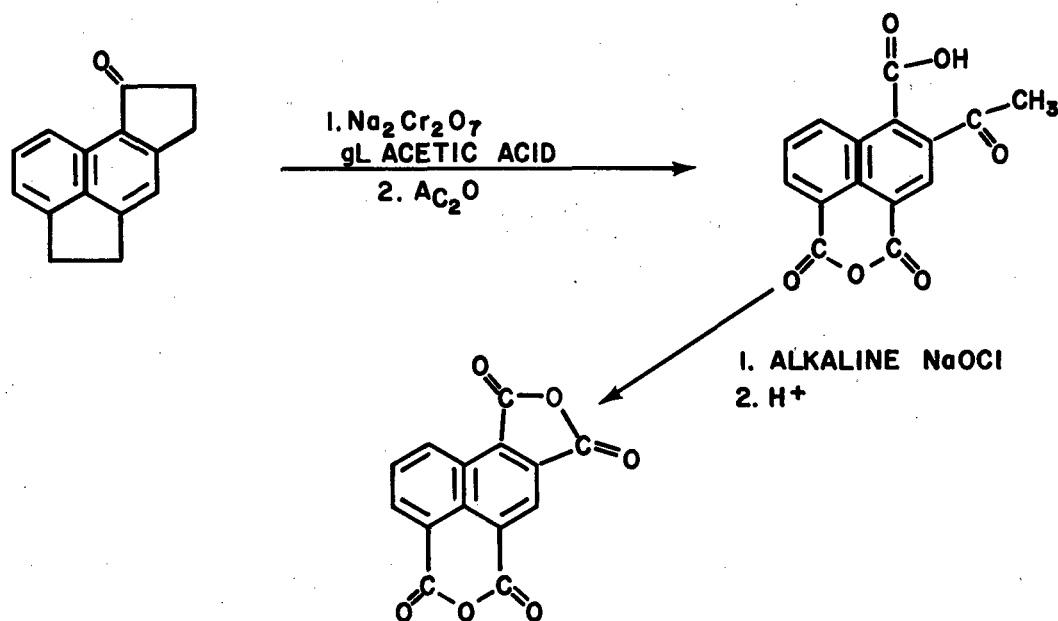


Figure 3. Preparation of 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride, IV

## 2. Model Reaction

To aid in characterization of the polymers, a model reaction was run in dimethylacetamide between two moles of *o*-phenylenediamine and one mole of 1,2,4,5-naphthalenetetracarboxylic acid dianhydride, IV, at 80°C. The chief product, obtained in pure state by crystallization from benzene and followed by recrystallization from tetrahydrofuran, was identified as *N*-(*o*-Aminophenyl)-7-oxo-7H-benzimidazo[2,1-*a*]benz[*de*]isoquinoline-4,5-dicarboximide, V. The molecular ion peak at  $[M]^+ = 430$  and its fragmentation pattern are consistent with this structure. This is confirmed by the presence of the medium imide carbonyl band in its infrared spectrum at  $1770\text{ cm}^{-1}$  (Figure 9). The reaction scheme is depicted in Figure 4.

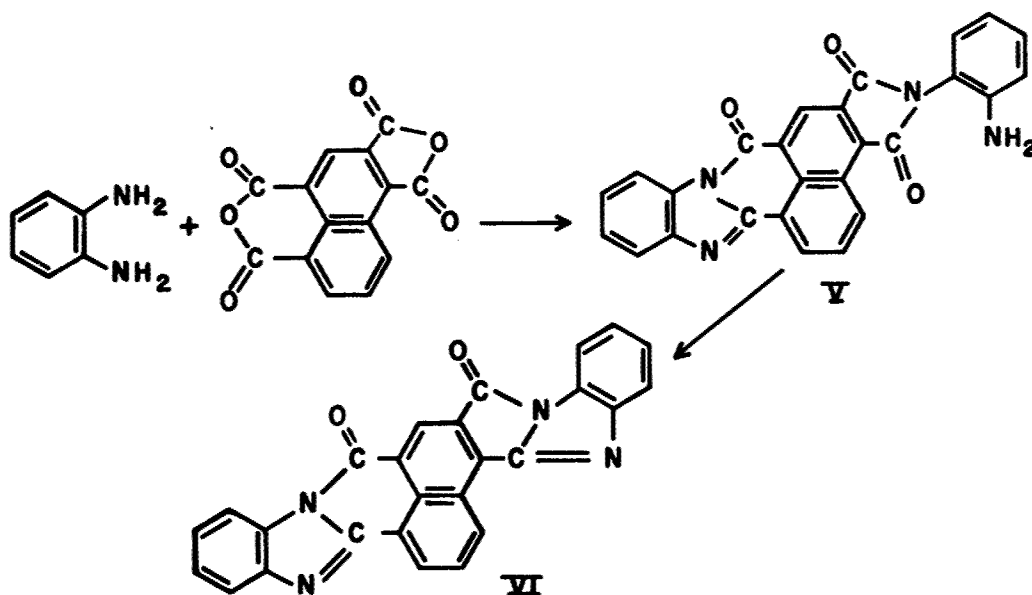


Figure 4. Model Reaction Between 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride and *o*-Phenylenediamine (OPD)

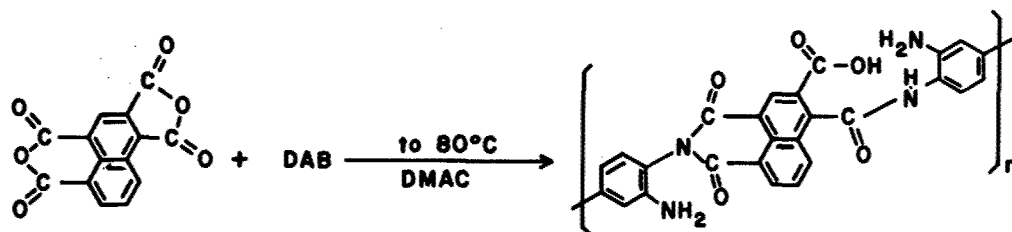
Two other products were isolated from the mother liquors, from crystallization of V by employing column chromatography. One was the fully ring closed dehydrated product, 6,10-dihydro-6, 10-dioxobenzimidazo-[2,1-a]benzimidazo-[1',2':1,5]pyrrolo[3,4-g]benz[de]isoquinoline VI. Its infrared spectrum is shown in Figure 10. The other compound, as yet unidentified  $C_{24}H_{20}O_3N_4$ , VII, was obtained in very low yield. The molecular ion appears in its mass spectrum at  $[M]^+ = 412$ , and strong aliphatic -CH absorption was observed in its infrared spectrum (Figure 11).

### 3. Polymerization Reactions

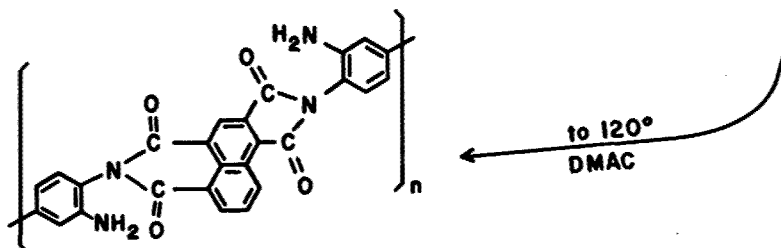
The solvents chosen for use in the polymerization studies were dimethylacetamide, and m-cresol. Both solvents were highly purified by drying and subsequent fractional distillation under reduced pressure. The polymerizations were run under anhydrous conditions in a nitrogen atmosphere using equimolar quantities of diaminobenzidine and 1,2,4,5-naphthalenetetracarboxylic acid dianhydride, IV. In the first method the monomers were dissolved together in the solvent at room temperature and stirred for 24 hours. This was followed by subsequent heating at 80°C (and up to 120°C or 160°C in some cases) to increase molecular weight and induce further ring closure. In order to minimize chances of branching, a second method was employed which involved dropwise addition of a solution of the dianhydride to a solution of the tetraamine at 80°C. The polycondensation reaction is shown in Figure 5 and the branching reaction is shown in Figure 6.

Soluble low molecular weight polymers were obtained when polycondensations were carried out after premixing the monomers in dimethylacetamide and heating up to 80°C. Analytical and infrared spectral data indicate that the products consist of a mixture of structures: VIII and IX containing the "peri" imide-amine moiety along with some of each of the "ortho"-amide-amino-acid, and the "ortho"-imide-amine moieties. This is aptly demonstrated by the presence of a sharp band typical of ortho-imide carbonyl absorption in its infrared spectrum (Figure 12) at  $1760\text{ cm}^{-1}$  (References 6,7,9, and 10).

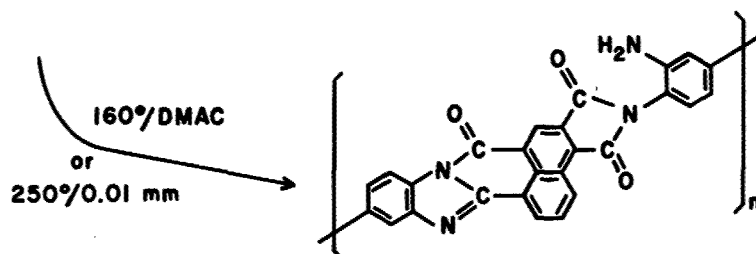
Figure 5. Polycondensation of 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride With Diaminobenzidine (DAB)



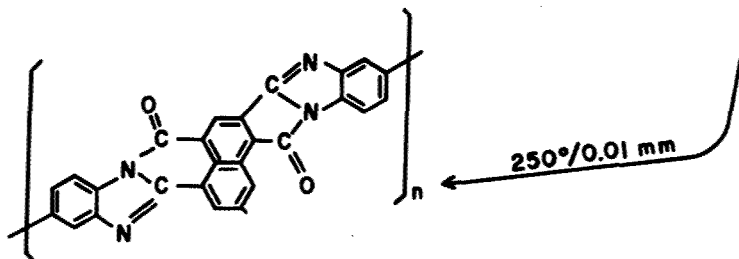
Poly[(5-carboxy-1,3-dioxo-1H-benz[de]isoquinoline 2,6(3H)-diyl)carbonylimino(3,3'-diamino-4,4'-biphenylene)], VIII



Poly(8,10-dihydro-4,6,8,10-tetraoxobenz[de]pyrrolo[3,4-g]-isoquinoline-5,9(4H,6H)-diyl)(3,3'-diamino-4,4'-biphenylene)], IX



Poly[4,8-dihydro-4,6,8-trioxobenzimidazo[1,2-b]-benzo[de]pyrrolo[3,4,-o]isoquinoline-5,12(6H)-diyl)(3-amino-p-phenylene)], X



Poly(6,10-dihydro-6,10-dioxobenzimidazo[2,1-a]benzimidazo-[1',2':1,5]pyrrolo[3,4-g]benz[de]isoquinoline-3,13-diyl), XI

Figure 6. Branching Reaction in the Polycondensation of 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride With Diaminobenzidine (DAB)

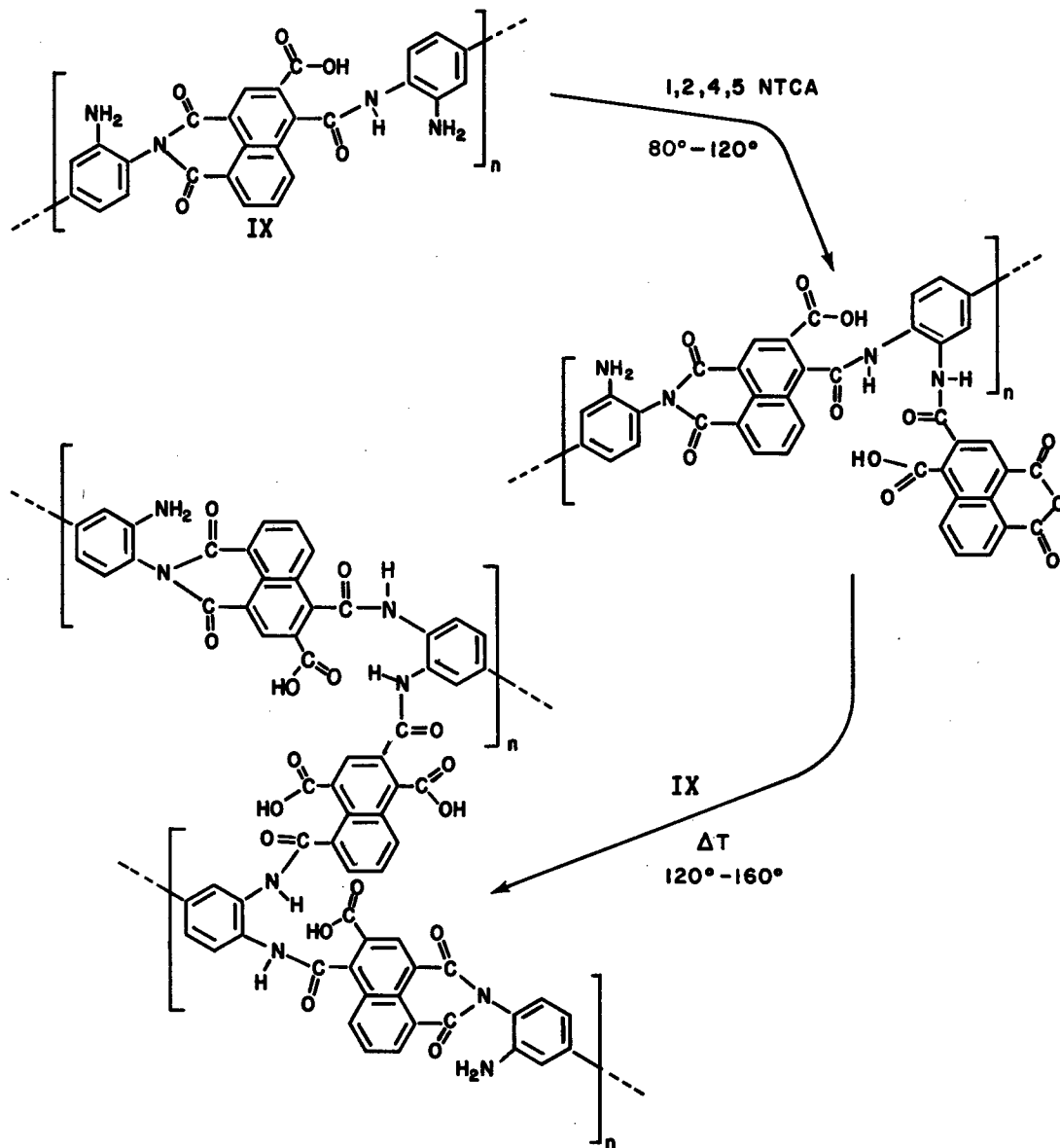


Figure 6. Branching Reaction in the Polycondensation of 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride With Diaminobenzidine (DAB)

An increase in the reaction temperature to 120°C results in further ring closure and completes imide formation to IX without any measurable increase in molecular weight. Its infrared spectrum is shown in Figure 12. Some insoluble material (about 33%) is produced, presumably as a result of branching. Further ring closure to X and complete precipitation of a cross-linked polymer occurred when the reaction temperature was raised to 160°C. These results seem to suggest that the growth of the polymer to high molecular weight may be prevented by a branching reaction which occurs early in the condensation.

An attempt to minimize the branching effect and increase molecular weight by slow addition of the dianhydride IV to the tetramine solution in dimethyl acetamide, and in m-cresol at 80°C, still gave soluble low molecular weight polymers, IX. Some improvement in molecular weight was observed when the reaction was run at 120°C in a refluxing mixture of m-cresol and benzene (2.5:1) with azeotropic removal of water. Complete conversion to the "ortho" and "peri" imide-amine structure poly[(8,10-dihydro-4,5,8,10-tetraoxobenzo[de]pyrrolo[3,4-g]isoquinoline-5,9(4H,6H)-diyl)(3,3'-diamino-4,4'-biphenylene)], IX, occurred. About one third of the product was insoluble in dimethylacetamide and in m-cresol, but soluble in methanesulfonic acid with an inherent viscosity of 0.94. None of the products of this reaction were cross-linked. This suggested that azeotropic removal water not only favored extension of the polymer chain, but also may have minimized the branching effect. The results are shown in Tables 1 and 2.

TABLE I

Polycondensation of Equimolar Quantities at 3,3'-Diaminobenzidine and 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride With Initial Mixing of the Monomers

Solvent	Conditions Temp °C	Temp hrs.	% Yield	Solubility	$\eta$	Analytical Results %C	%H	%N
DMAC	25 90	13 3	100%	S <sup>a</sup>	0.08 <sup>a</sup>			
DMAC	26 80	24 24	100%	S <sup>a</sup>	0.19a	Calc'd for C <sub>26</sub> H <sub>16</sub> O <sub>5</sub> N <sub>4</sub> Found VIII	3.47 4.63	12.06 12.75
DMAC	26 80 120	24 24 24	5% 30% 65%	i <sup>a</sup> i <sup>a</sup> , b, c S <sup>a</sup>	- - 0.12	Calc'd for C <sub>26</sub> H <sub>16</sub> O <sub>5</sub> N <sub>4</sub> Found VIII	3.47 3.41 3.61	12.06 10.68 <sup>D</sup> 11.46 <sup>D</sup>
DMAC	26 80 120 120	24 24 24 24	95%	i <sup>a</sup> , b, c	-	Calc'd for C <sub>26</sub> H <sub>12</sub> O <sub>3</sub> N <sub>4</sub> Found X	2.82 3.48	13.10 12.16
m-cresol and benzene (2.5:1)	120	5	41% 31% 35%	S <sup>a</sup> , b, c i <sup>a</sup> , b, c i <sup>a</sup> , b, c	0.11 0.18 0.94	Calc'd for C <sub>26</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub> Found IX	2.93 4.03 3.30 3.29	12.60 <sup>D</sup> 12.45 <sup>D</sup> 11.37 <sup>D</sup> 11.76 <sup>D</sup>

a DMAC; b, m-cresol; c MeSO<sub>3</sub>H; D nitrogen by Dumas; K Nitrogen by Kjeldahl

TABLE 2  
 Polycondensation of Equimolar Quantities of 3,3'-Diaminobenzidine and  
 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride With Slow Addition of  
 the Dianhydride to the Tetraamine in Solution

Anhydride g	Solvent	Conditions		Yield	Solubility	Analytical Results %C	%H	%N
		temp °C	time hrs					
0.6706	DMAC	80°	24	100%	S <sup>a,b</sup>	Calc'd for C <sub>26</sub> H <sub>14</sub> C <sub>4</sub> N <sub>4</sub> IX	2.93	12.60
						Found	3.38	12.41 <sup>D</sup>
0.6706	m-cresol	80°	24	100%	S <sup>a,b</sup>	Found	3.53	12.24 <sup>K</sup>

TABLE 3  
Comparison of Properties of Polymers After Heat Treatment At 250°/0.01 mm

INITIAL POLYMER, BEFORE HEATING				FINAL POLYMER, AFTER HEATING						
Method of Preparation	Solubility		$\eta$		Structure	Structure	%C	%H	%N	
	DMAC	MeSO <sub>3</sub> H	DMAC	MeSO <sub>3</sub> H						DMAC
						Calc'd				
							C <sub>26</sub> H <sub>12</sub> O <sub>3</sub> N <sub>4</sub> X <sup>4</sup>	72.95	2.82	13.10
addition method in m-cresol up to 80°	100%	100%	0.10	0.20 ca	IX	obs.	X	71.58	3.37	11.37 <sup>D</sup>
addition method in DMAC up to 80°	100%	100%	0.10	6.20 ca	IX	obs.	X	71.50	3.90	12.30
initial mixing in DMAC up to 120°	--	100%	0.12	0.24 ca	IX	obs.	X	71.89	3.40	13.17
initial mixing in DMAC up to 80°	100%	100%	0.19	0.38 ca	IX	obs.	XI	73.50	3.04	13.30

To try to determine the extent of the branching reaction, samples of some of the soluble low molecular weight polymers, IX, prepared by the two different methods indicated above were "second-staged" by heating at 250°C/0.01 mm for 18 to 24 hours. Analytical results (Table 3) and infrared spectral data indicates that the products consist mainly of structure X. The branching effect is appreciable only when the soluble polymers prepared by either method in dimethylacetamide up to 80°C are second staged. In these cases 33% to 39% of insoluble cross-linked polymers were obtained.

However, when the soluble polymer, IX,  $\eta = 0.12$ , obtained in dimethylacetamide at 120° was second staged, the resulting product, X, was completely soluble. In light of the fact that some insoluble cross-linked material had been obtained in the initial polymerization reaction, i.e., about 30%, it can be concluded that the branching reaction may be taking place in solution between 80°C and 120°C in dimethylacetamide.

### SECTION III

#### CONCLUSIONS

1. Polycondensation of 3,3'-diaminobenzidine and 1,2,4,5-naphthalene-tetracarboxylic acid dianhydride in aprotic solvents gave soluble low molecular weight polymers at 80° to 120°.
2. Increasing the temperature to 160° gave increasing amounts of insoluble material without an appreciable increase in molecular weight of the soluble material.
3. Low molecular weight soluble polymers prepared at 80° in aprotic solvents (DMAC) could be chain extended with about a twofold increase in molecular weight by heating at 250°C/0.01 mm. This was accompanied by the precipitation of about 33% to 39% of insoluble crosslinked material. However, when the soluble polymer prepared in m-cresol at 120°C was second staged, the resulting polymer was 100% soluble. Hence it is believed that the branching takes place at the 1,2 anhydride linkage when dimethyl acetamide is used as solvent. For some reason no branching effect is observed when m-cresol was used as a solvent. In this case a low molecular weight polymer, X,  $\eta = 0.48$ , still completely soluble, was obtained on "second staging."
4. All the soluble "second stage" polymers, X, appear to have been chain extended somewhat with about a twofold increase in molecular weight. A typical infrared spectrum of a soluble heat treated polymer, X, is shown in Figure 13.
5. The heat treated polymers have a very high degree of thermal stability with weight losses in the 16% to 24% range at 900°C. A comparison of TGA curves is given in Figure 7.

As related to the overall objective given in the introduction of this report, the above experimental work constitutes a preliminary investigation. The results indicate that thermally stable materials are obtainable by the polycondensation of DAB and 1,2,4,5-naphthalene-tetracarboxylic acid dianhydride; however, additional effort will be required to define more clearly the possible potential of such systems for Air Force use. In particular, the investigation of reaction conditions which will circumvent undesirable branching and subsequent cross-linking of the polymer is needed. This will provide suitable materials for more extensive and meaningful evaluation.

SECTION IV

EXPERIMENTAL

1. General Comments

a. Infrared Spectra

The infrared spectra were obtained in all cases by use of a Beckman IR-33 Infrared Spectrophotometer.

b. Mass Spectrometry

Electron Impact Mass Spectra were run by Mr. Lee Smithson, Analytical Branch, Air Force Materials Laboratory, AFML/TUA, Wright-Patterson Air Force Base, Ohio 45433, and chemical ionization mass spectra were run by Dr. Arun K. Bhattacharva, University of Utah, Salt Lake City, Utah.

c. Thermogravimetric Analyses

The thermogravimetric analyses were performed at the University of Dayton Research Institute, Dayton, Ohio. 50 mg of the sample was heated under  $N_2$  in a Chevenard Balance (Adamel, Paris) to 900°C at a heating rate of 180°C per hour.

d. Monomers

(1) 3,3'-Diaminobenzidine

A polymer grade sample of this material was obtained from the UpJohn Company, Kalamazoo, Michigan 49001.

(2) 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride IV

This compound was prepared from 2-acetonaphthalene-1,4,5-tricarboxylic acid anhydride, by oxidation in aqueous alkaline sodium hypochlorite (Reference 17). The purified product melted at 262.5°C to 263.5°C (corr.). Its infrared spectrum appears in Figure 8. The molecular ion peak appears in its EI mass spectrum at  $[M]^+ = 268$  with other significant peaks at m/e 224, 190, 196, 154, 124, and 98.

Anal. Calc'd. for  $C_{14}H_4O_6$ : %C, 62.70; %H, 1.50; % ash 0.00  
Found: %C, 62.61; %H, 1.63; % ash 0.00

(3) 2-Acetonaphthalene-1,4,5-Tricarboxylic Acid-4,5-Anhydride

This compound was prepared by oxidation of 1'-methyl-3'-keto-2,3-cyclopentenoacenaphthene with sodium dichromate in glacial acetic acid. The compound could only be isolated by reducing the volume of the reaction mixture to a thick paste, and boiling for several hours with a large volume of concentrated hydrochloric acid. After several days of standing the crude product precipitated as a yellow powder. It was purified by boiling with acetic anhydride, and then was crystallized from benzene, m.p. 218°C to 220°C (Reference 17). Its infrared spectrum is shown in Figure 2. A molecular ion peak appears in its EI mass spectrum at  $[M]^+ = 284$ .

Anal. Calc'd. for  $C_{15}H_8O_6$ : %C, 63.39; %H, 2.84  
Found: %C, 62.96; %H, 3.00

## 2. Model Reactions

### a. Condensation of Two Moles of o-Phenylene Diamine with One Mole of 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride, IV

A solution from 0.6490 (0.006 mole) of o-phenylene diamine in 50 ml of dry dimethylacetamide was stirred at 50°C under a dry nitrogen atmosphere. A solution from 0.8048 g (0.003 mole) of 1,2,4,5-naphthalenetetracarboxylic acid dianhydride, IV, in 50 ml of dimethylacetamide was added dropwise over a period of one hour. Then the reaction mixture was stirred at 80°C for 24 hours.

The solvent was stripped off at 30° to 35°/1.0-2.0 mm using a rotary evaporator. The soft clear brown residue was soaked in ether and suction dried at room temperature; yield of crude product, 1.7 g.

It was crystallized from 150 ml of boiling benzene as an orange solid; yield 0.90 g. This product was then crystallized from tetrahydrofuran.

Anal. Calc'd. for  $C_{26}H_{14}O_3N_4$ , V: %C, 72.60; %H, 3.28; %N, 13.05

Found: %C, 72.51; %H, 3.32; %N, 13.22

The molecular ion peak ( $M$ )<sup>+</sup> appears in its CI mass spectrum at m/e 430, with other significant peaks at m/e 412, 369, 257, 255, 219, 161, 143, 119, 111, 97, 85, and 73. Its fragmentation pattern is consistent with structure V. Its infrared spectrum (Figure 9) contains the typical imide carbonyl band of a five-membered ring imide at  $1770\text{ cm}^{-1}$ .

Evaporation of the benzene filtrate to 30 ml followed by filtration gave 0.6 g of crude orange material which when recrystallized from methanol gave 0.26 g of pure product. The material was dried at  $110^\circ/0.1\text{ mm}$  overnight.

Anal. Calc'd. for  $C_{26}H_{12}O_2N_4$ , VI: %C, 75.80; %H, 2.92; %N, 13.60

Found: %C, 74.90; %H, 3.18; %N, 13.44<sup>D</sup>

The molecular ion peak appears in its CI mass spectrum at  $[M]^+=412$  with other significant peaks at m/e 36, 341, 285, 283, 257, 255, 229, 219, 137, 111, 91, and 73. Its fragmentation pattern is consistent with structure VI. The band due to the imide carbonyl at  $1770\text{ cm}^{-1}$  is no longer present in the infrared spectrum (Figure 10) and, instead, a new strong band is observed at  $1730\text{ cm}^{-1}$ .

Evaporation of the benzene filtrate gave an orange-red residue. This was redissolved in 15 ml of warm benzene and stirred with some Fluorisil (fluorescent Silica Gel). The benzene was evaporated and the powder was used to form a yellow band at the top of a large column (24 inches x 1 inch) packed with Fluorisil. The chromatogram was developed with a mixture of dichloromethane and tetrahydrofuran (1:1) into three bands and eluted. From the first band 0.14 g of V was isolated. The second band yielded 0.07 g of its dehydration product, VI. The third band gave 0.07 g of an orange yellow powder which was dried at 110°/0.1 mm.

Anal. Calc'd. for  $C_{24}H_{20}O_3N_4$ : %C, 70.00; %H, 4.89; %N, 13.60  
 Found: %C, 70.20; %H, 4.48; %N, 12.82<sup>D</sup>

Its infrared spectrum (Figure 11) exhibits significant aliphatic absorption bands at  $1830\text{ cm}^{-1}$  and  $1920\text{ cm}^{-1}$ . A molecular ion peak was unidentified in its CI mass spectrum at  $[M]^+ = 412$  with other peaks at m/e 341, 257, 255, 269, 137, 125, 111, 91, 75, 71, 43, and 15. Its structure has not yet been determined.

### 3. Polymerization Reactions

a. Polycondensation of Equimolar Quantities of 3,3'-Diaminobenzidine and 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride in Aprotic Solvents

#### (1) With Initial Mixing of the Monomers

Dimethylacetamide was purified by distilling over calcium hydride under reduced pressure. It was distilled into the reaction flask containing the dry monomers in a dry nitrogen atmosphere. The reaction mixture was stirred under nitrogen under conditions of time and temperature indicated in Table 1. At the conclusion of polymerization, the reaction mixture was filtered through a fritted glass funnel to remove any precipitated material. The solvent was stripped off under reduced pressure in a rotary evaporator. The residue was stirred with ether and the linear polymer was filtered off and dried in a vacuum pistol at 80°C/0.2 mm for 24 hours and sent for analysis. A viscosity determination

was made in the appropriate solvent as indicated in Table 1.

When a mixture of m-cresol and benzene were used as solvents, they were freshly distilled and pipetted into a reaction flask containing the monomers under nitrogen. Water was removed azeotropically through a Dean-Stark Trap.

(2) With Slow Addition of the Dianhydride to a Solution of the Tetramine

The amine monomer was dissolved in the dry solvent (DMAC or m-cresol) and stirred in a closed system under nitrogen at the temperature indicated in Table 2. Then a solution of the dianhydride in the solvent of choice was added dropwise from a dropping funnel over two hours at the temperature indicated. The reaction mixture was stirred for a total of 24 hours at temperature under nitrogen. The solvent was stripped off under reduced pressure using a rotary evaporator. The residual polymer was treated with ether, filtered, and dried at 80° to 100°C/0.1 mm. The inherent viscosities of the products were measured in m-cresol at 25°C.

b. Heat Treatment of the Polymers

A weighed sample of about 100 to 500 mg of the polymer in a small vial was placed in a tube fitted with an adaptor for introduction of a thermocouple wire, and outlet arm with  $\frac{3}{8}$  24/40 ground glass joint, and a vacuum adaptor and trap. The apparatus was heated in an aluminum block by means of a heating mantle. Temperature was controlled by means of a Thermowatch Relay. The apparatus was kept under constant evacuation by means of a vacuum pump at 0.01 mm while the temperature (internal) was maintained at 250°C for 18 to 24 hours. The samples were then cooled and evaluated. A typical infrared spectrum is shown in Figure 13. The results are shown in Table 3.

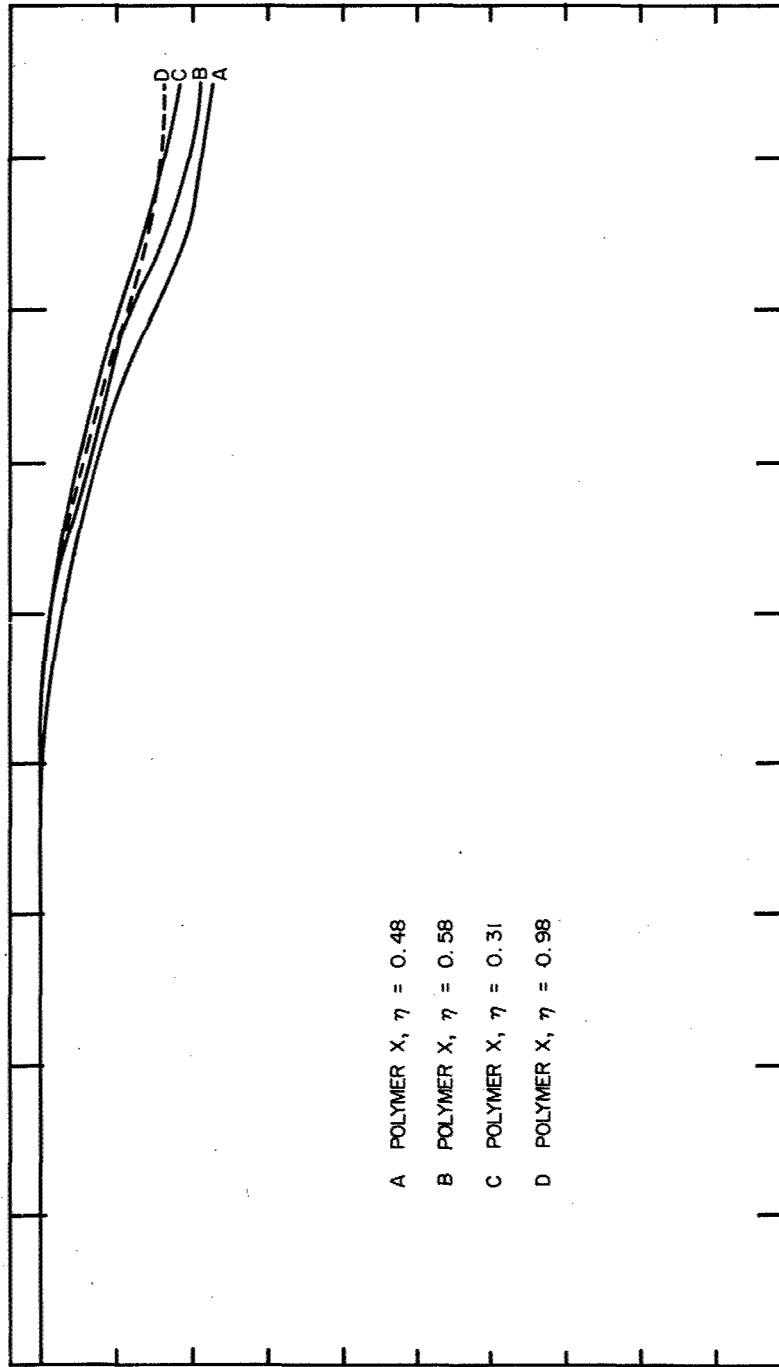


Figure 7. TGA Curves of the Heat Treated Polymer Samples, X

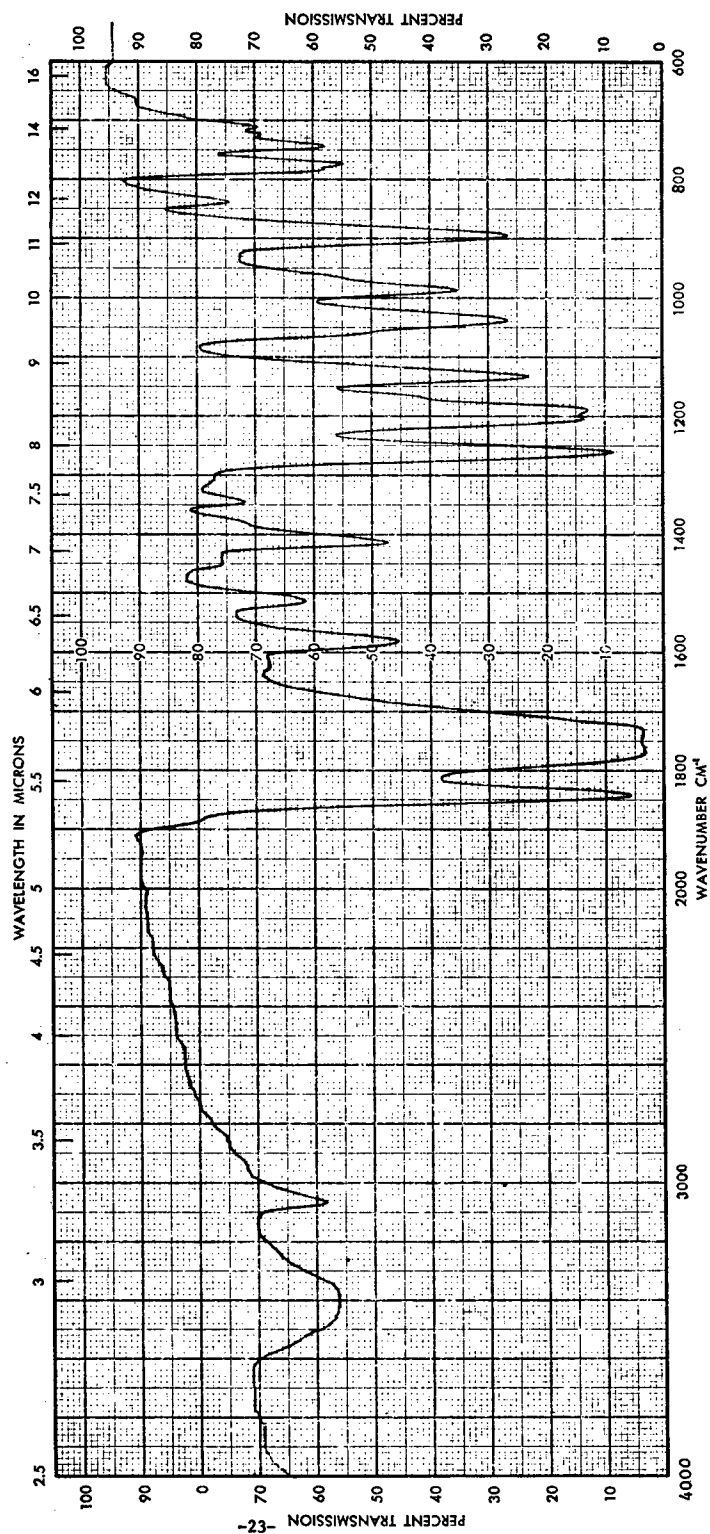


Figure 8. Infrared Spectrum of 1,2,4,5-Naphthalenetetracarboxylic Acid Dianhydride, IV

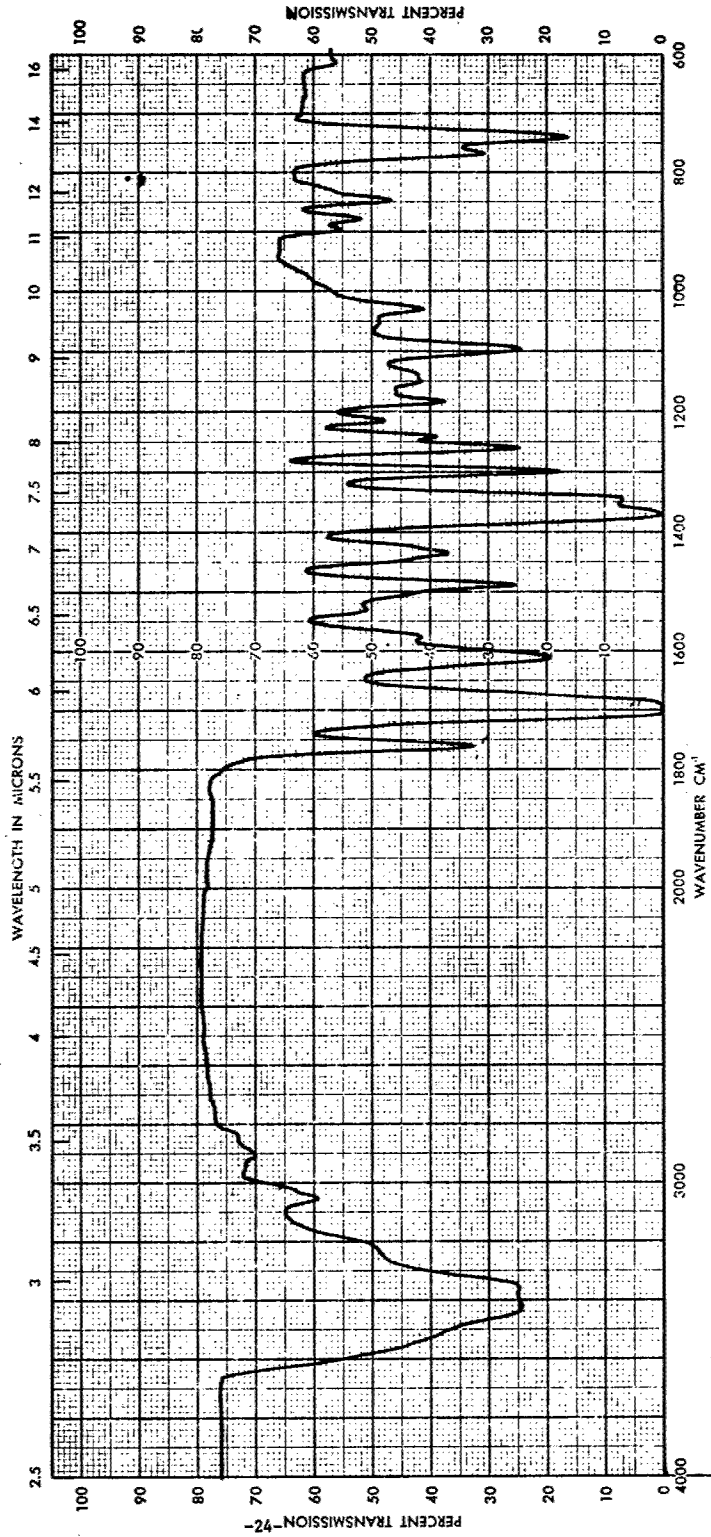


Figure 9. Infrared Spectrum of the Model Compound N-(o-Aminophenyl)-7-oxo-7H-Benzimidazo [2,1-a]Benz[de]Isoquinoline-4,5-Dicarboximide, V

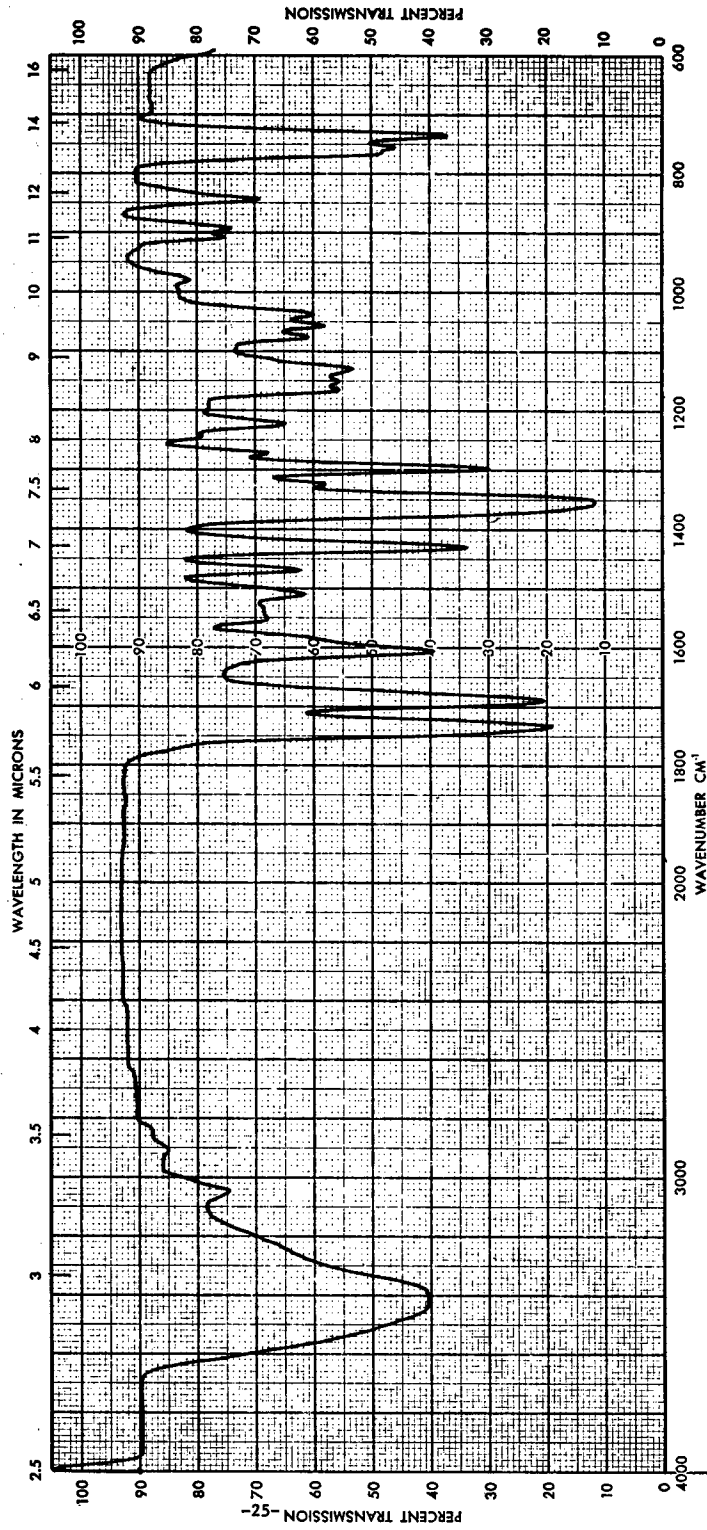


Figure 10. Infrared Spectrum of the Model Compound 6,10-Dihydro-6,10-Dioxobenzimidazo[2,1g]Benzimidazo[1,2':1,5]Pyrrrolo [3,4-g]Benz[de]Isoquinoline, VI

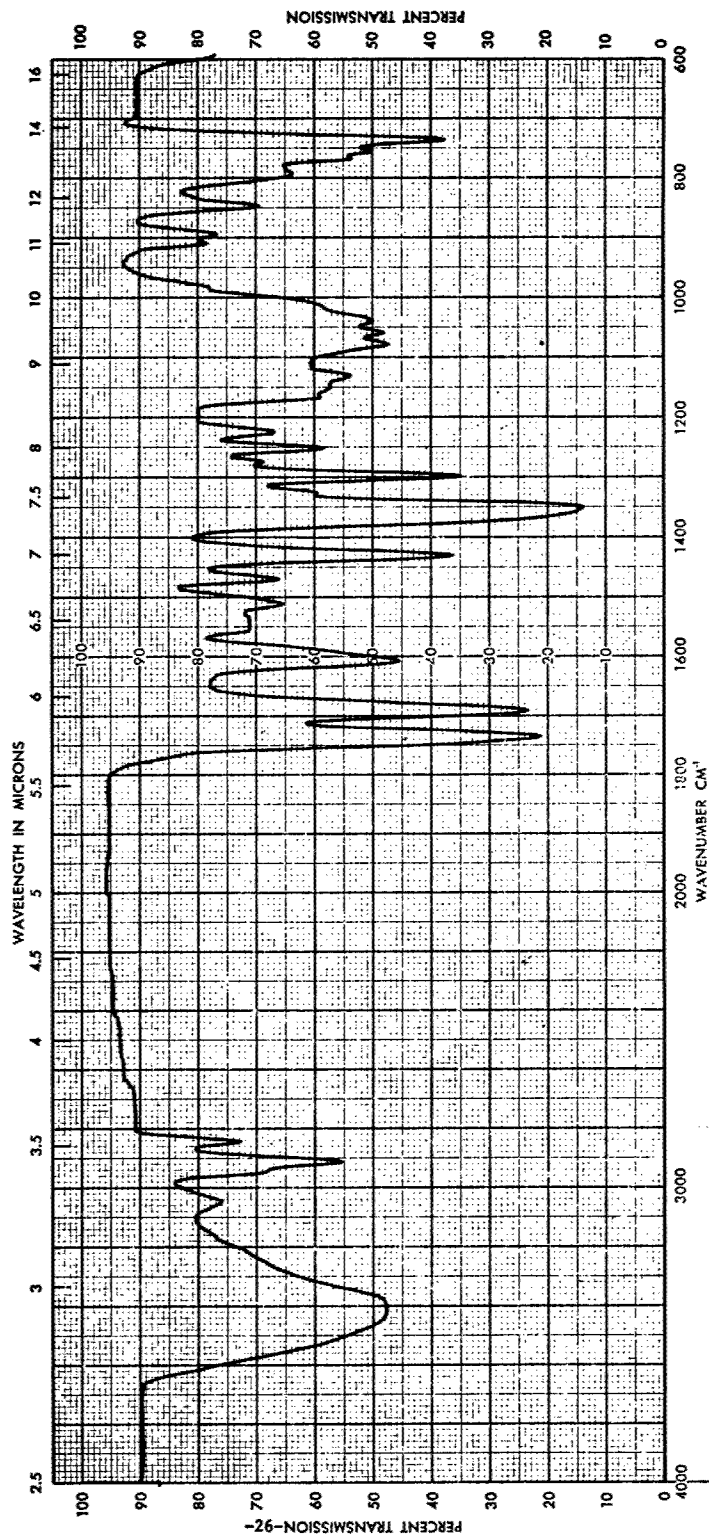


Figure 11. Infrared Spectrum of the Unidentified Compound  
 $C_{24}H_{20}O_3N_4, [M]^+ = 412$

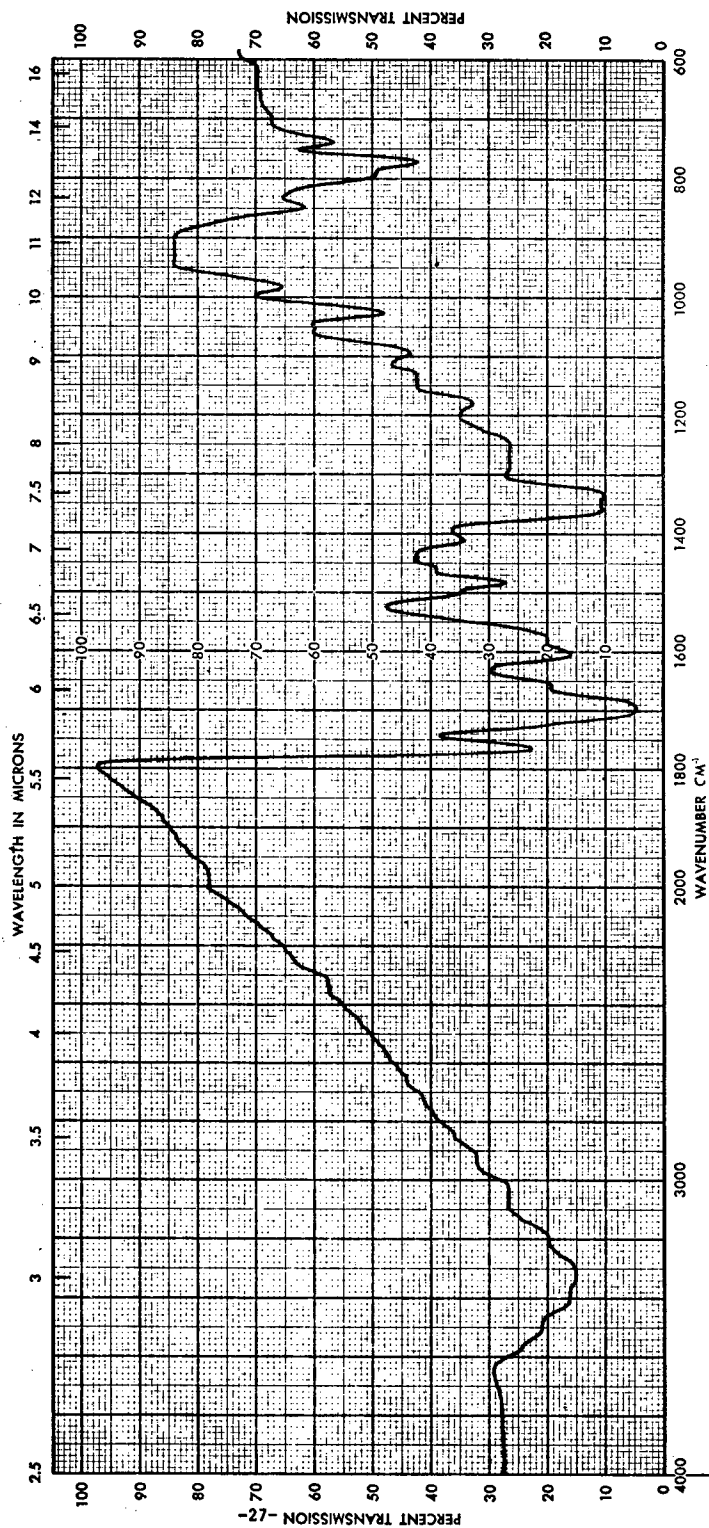


Figure 12. Infrared Spectrum of the Soluble Polymer,  $C_{26}H_{14}O_4N_4$ , IX

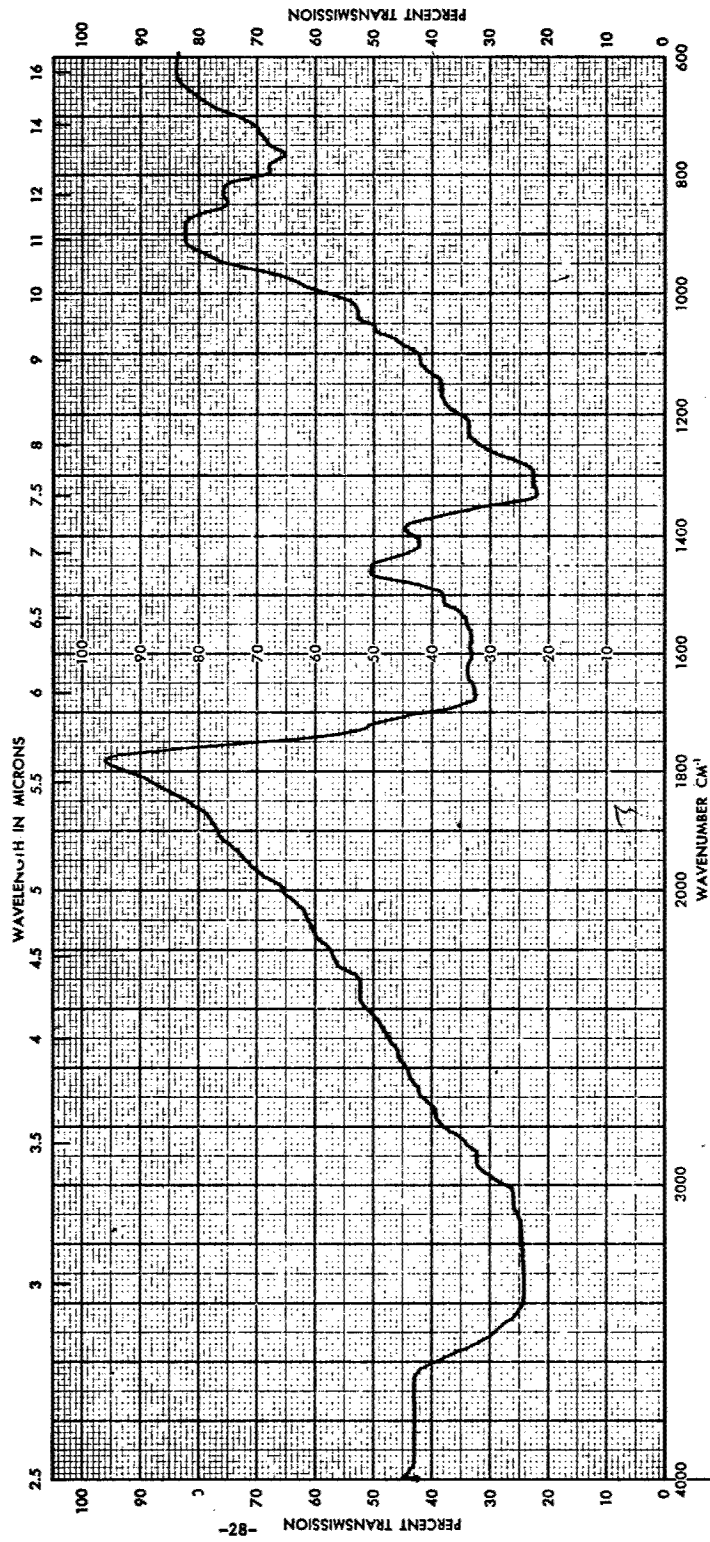


Figure 13. Infrared Spectrum of the Soluble Heat Treated Polymers, X

## SECTION V

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13. ABSTRACT Polycondensation of 3,3'-diaminobenzidine and 1,2,4,5-naphthalenetetracarboxylic acid dianhydride in aprotic solvents at 80°C to 120°C gave soluble low molecular weight polymers, Increasing the reaction temperature to 160° led to further condensation and gave increasing amounts of insoluble cross-linked material. Some higher molecular weight solid polymer was obtained when m-cresol was used as solvent. The low molecular weight polymers could be further condensed and chain extended with about a twofold increase in molecular weight by heating at 250°C/0.1 mm. However, linear polymers which had been prepared in aprotic solvents up to 80°C, on "second staging" gave 33% to 39% of insoluble cross-linked material. This is believed to be due to a branching reaction taking place between 80°C and 120°C at the ortho anhydride linkage.			

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ladder polymers polyaromatics poly[(4,8-dihydro-4,6,8-trioxobenzimidazo [1,2-b]-benzo[de]pyrrolo[3,4-g]isoquinoline-5,12 (6H)-diyl) (3-amino-p-phenylene)] poly(8,10-dihydro-4,6,8,10-tetraoxobenzo[de] pyrrolo[3,4-g]-isoquinoline-5,9(4H,6H)-diyl) (3,3'-diamino-4,4'-biphenylene)]						