

AFML-TR-72-71

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**NOVEL BENZOBISTRIAZOLOPHENANTHROLINE
POLYMERS**

ROBERT C. EVERS

TECHNICAL REPORT AFML-TR-72-71

JUNE 1972

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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 January 1971 to March 1971.

The author wishes to thank the Analytical Branch, Air Force Materials Laboratory for the performing the elemental analysis determinations. Dr. G. F. L. Ehlers contributed the thermogravimetric analysis data. The assistance of Mr. J. L. Burkett in many of the laboratory operations is gratefully acknowledged.

This report was submitted by the author in March 1972.

This technical report has been reviewed and is approved.

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ABSTRACT

Novel, high molecular weight benzobistriazolophenanthroline polymers were prepared by the polycondensation of 1,4,5,8-naphthalene tetracarboxylic acid with iso- or tere-phthaldihydrazidine dihydrochloride in polyphosphoric acid. Inherent viscosities in the range of 1.33 to 2.51 were recorded. Tough, transparent films of these polymers could be cast from methane sulfonic acid. Onset of polymer breakdown during thermogravimetric analysis in an air atmosphere occurred at 450°C.

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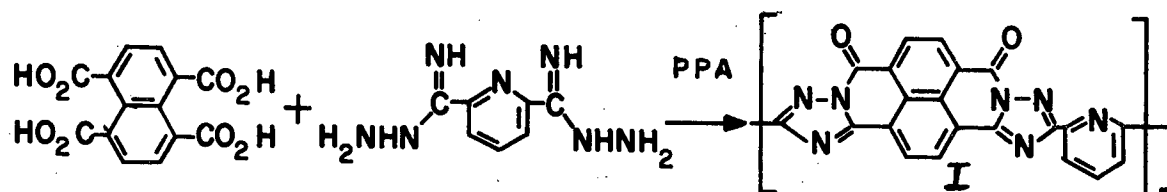
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SECTION I

INTRODUCTION

The preparation of a benzobistriazolophenanthroline polymer I by the polycondensation of 1,4,5,8-naphthalene-tetracarboxylic acid (NTCA) with 2,6-pyridinediylldihydrazidine in polyphosphoric acid (PPA) has been previously reported (Reference 1). The polymer exhibited good although not outstanding thermal stability but was of insufficient molecular



weight to exhibit useful film or fiber forming properties.

The preparation of novel, high molecular weight benzobistriazolo-phenanthroline polymers has recently been achieved by polycondensation reactions analogous to the reaction described above. Polymer properties were very similar to those recorded for polymer I (Reference 1). However, a sufficiently high degree of polymerization was achieved for these polymers to be readily cast into tough, flexible films. The preparation and characterization of these polymers is described in this report.

SECTION II

DISCUSSION

The use of 2,6-pyridinediylldihydrazidine as a monomer for the synthesis of high molecular weight, thermally stable polymers has been reported by Hergenrother and coworkers (Reference 2). Since this compound is quite stable and can be readily purified by recrystallization, it was the monomer of choice in the preparation of a benzobistriazolophenanthroline polymer. Although other aromatic dihydrazidines have been used in polymer synthesis, the resultant polymers have generally been ill-defined and either insoluble or of low molecular weight (Reference 3). The lack of attainment of soluble, high molecular weight polymers may be attributed, in part, to impurities resulting from decomposition of the dihydrazidine monomers. It has been observed at this Laboratory and elsewhere (Reference 4) that aromatic dihydrazidines typically tend to decompose slowly above room temperature and, unlike the uniquely stable 2,6-pyridinediylldihydrazidine, cannot be readily obtained in monomer grade purity. However, purification can reportedly be effected through the formation of stable tetrahydrochloride salts (Reference 4). Dissolution in PPA of purified tetrahydrochloride salt of an aromatic dihydrazidine would be expected to result in the release of hydrogen chloride to give a solution of stabilized aromatic dihydrazidine monomer. Addition of NTCA monomer and subsequent polycondensation would lead to benzobisotriazolophenanthroline polymer.

With this goal in mind, iso- and tere-phthaldihydrazidine were prepared. Attempts to purify the pale yellow products by recrystallization yielded only deeply colored, partially decomposed products. Although conversion of the aromatic dihydrazidines into their snow-white hydrochloride salts was readily achieved, some difficulty was encountered in isolating exclusively the pure tetrahydrochloride salts. Drying under carefully controlled conditions to eliminate water and excess hydrogen chloride finally yielded the previously unreported dihydrochloride salts, iso- and tere-phthaldihydrazidine dihydrochloride.

The new potential monomers underwent polycondensation reactions with NTCA in PPA (Table I). Use of iso- and tere-phthaldihydrazidine predictably resulted in only moderate molecular weight polymers. However, a high degree of polymerization was achieved in the case of the corresponding dihydrochloride salts. This increase in polymer molecular weight can be readily attributed to differences in monomer purity. However, the failure to achieve high molecular weight polymer I can hardly be explained on this basis (Reference 1). Possibly the electronic effects which may contribute to the rather unique stability of 2,6-pyridinediylldihydrazidine might also be responsible for lowered monomer reactivity during the polycondensation reaction.

Transparent, deep red films could be cast from methane sulfonic acid solutions of the high molecular weight polymers. The films, although quite thin (thickness $\approx$ 0.5 mil), were tough and creasable. Attempts to form precipitated films as can be done with BBL polymers were unsuccessful (Reference 5).

TABLE I PREPARATION OF POLYMERS IN PPA							
Monomers		Time- Hrs.	Temp.- °C.	η_{inh} - dl/g.	(a) C	Analysis H	(d) N
NTCA	Isophthalaldihydrazidine	18	180-185	0.55	66.82	2.30	18.38
"	Terephthalaldihydrazidine	18	180-185	(b) 0.84	67.08	2.22	18.24
"	Isophthalaldihydrazidine Dihydrochloride	20	195-200	2.38	65.80	2.15	(e) 18.03
"	Terephthalaldihydrazidine Dihydrochloride	18	180-185	1.33	66.78	2.43	18.37
"	"	22	185-190	(c) 2.51	67.08	2.39	18.83

(a) 0.2g./dl., 25° C., CH₃SO₃H

(b) η_{inh} = 0.65 (0.2 g./dl., 25° C., H₂SO₄)

(c) $[\eta]$ = 2.62 (0.2 g./dl., 25° C., CH₃SO₃H)

(d) Calculated for fully cyclized benzobistriazolophenanthroline structure (C₂₂H₈N₆O₂)_n: C, 68.04; H, 2.06; N, 21.65

(e) Ash content = 2.10%

Except for film forming properties, the polymers were quite similar in physical properties to polymer I. The fibrous, reddish-black polymers were completely soluble in sulfuric- and methane sulfonic-acid but insoluble in all aprotic solvents tested. They appeared to be somewhat susceptible to base hydrolysis but were quite resistant to attack by strong acid such as warm concentrated sulfuric acid.

Thermogravimetric analysis thermograms (Figure 1) of a high molecular weight benzobistriazolophenanthroline polymer indicate onset of breakdown in air and nitrogen atmospheres at 450 and 475°C, respectively. This polymer exhibited no softening under load up to 450°C, the operating limit of the test apparatus (Reference 6).

Discrepancies in elemental analysis (Table I) were observed and followed the same pattern as reported for polymer I. This may be indicative of side reactions or of incomplete cyclization in the polymer chain but may also be caused, in part, by the presence of tightly bound water in the polymer. The elemental analyses were further complicated by trace amounts of phosphorus and sulfur and ash residues as high as 2.10%.

The infrared spectra of the polymers are consistent with the proposed benzobistriazolophenanthroline structure. The structure of polymer I was established by elemental analysis and by infrared and ultraviolet comparisons of the polymer with model compounds (References 1 and 7). In the present work, model compounds were not synthesized and consequently polymer-model compounds spectral comparisons were not possible. However, infrared comparisons (Figure 2) of previously characterized polymer I and polymer prepared from isophthaldihydrazidine dihydrochloride provide strong evidence for the proposed benzobistriazolophenanthroline structure. It is to be noted that the polymer infrared spectra (prepared from KBr pellets) are rather poorly resolved and low intensity absorptions may have been obscured. The preparation of thin films from the high molecular weight polymers afforded the opportunity to obtain more highly resolved spectra. Comparison of infrared spectra obtained from a KBr pellet and a film (Figure 3) revealed few additional absorptions. Improved resolution

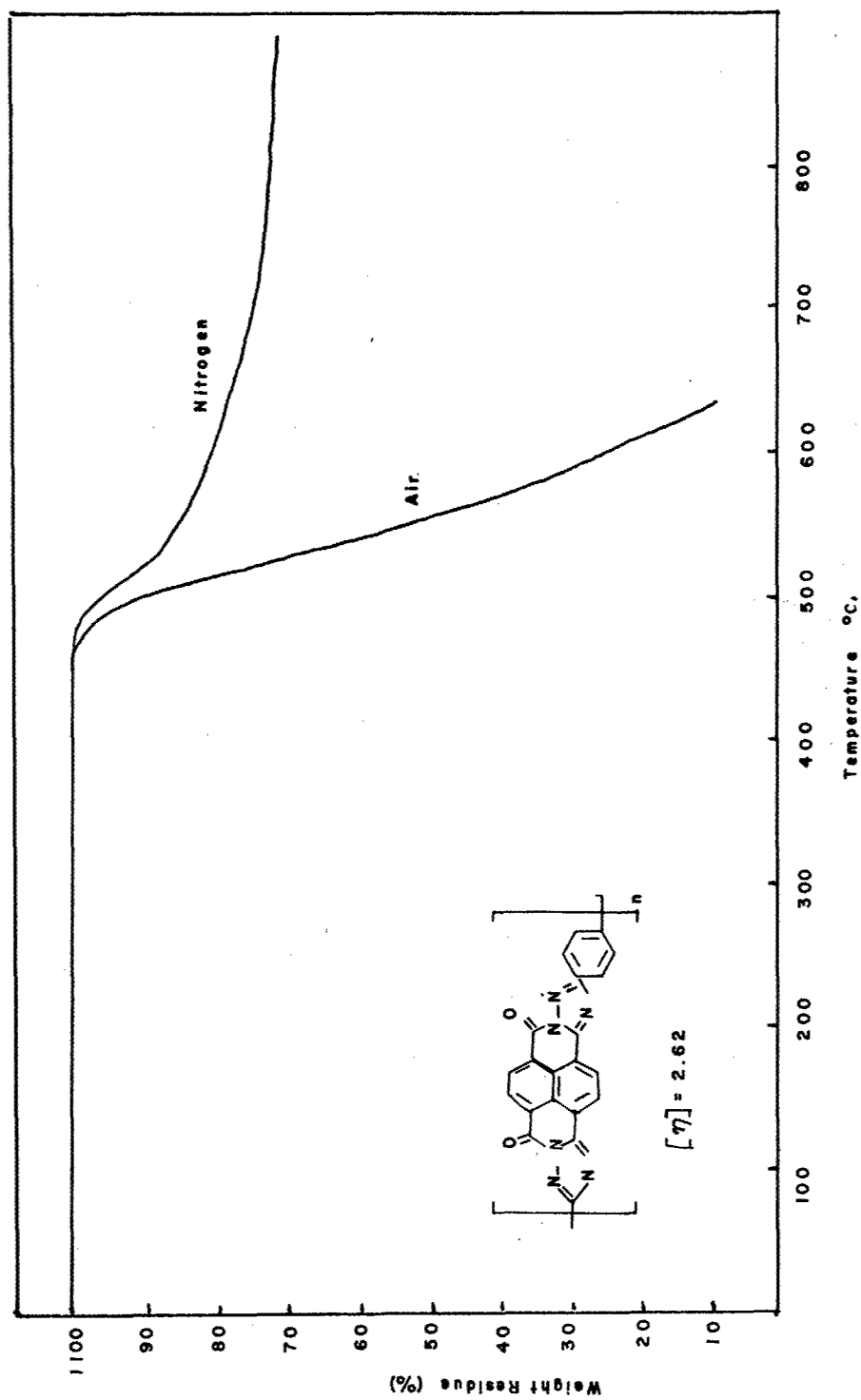


Figure 1. Thermogravimetric Analysis of a Benzobistriazolophenanthroline Polymer in Air and Nitrogen

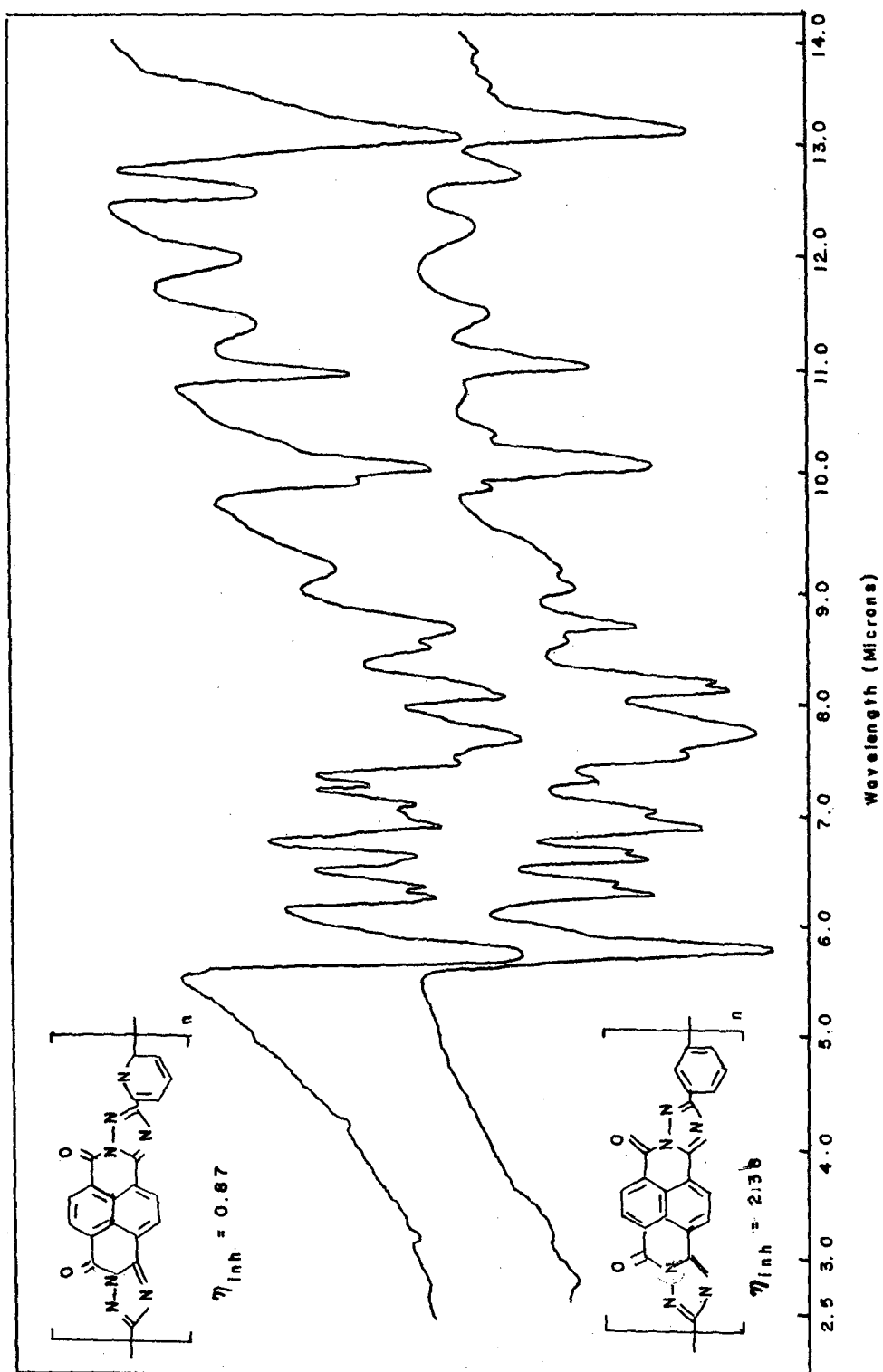


Figure 2. Infrared Spectra of Benzobistriazoloanthroline Polymers

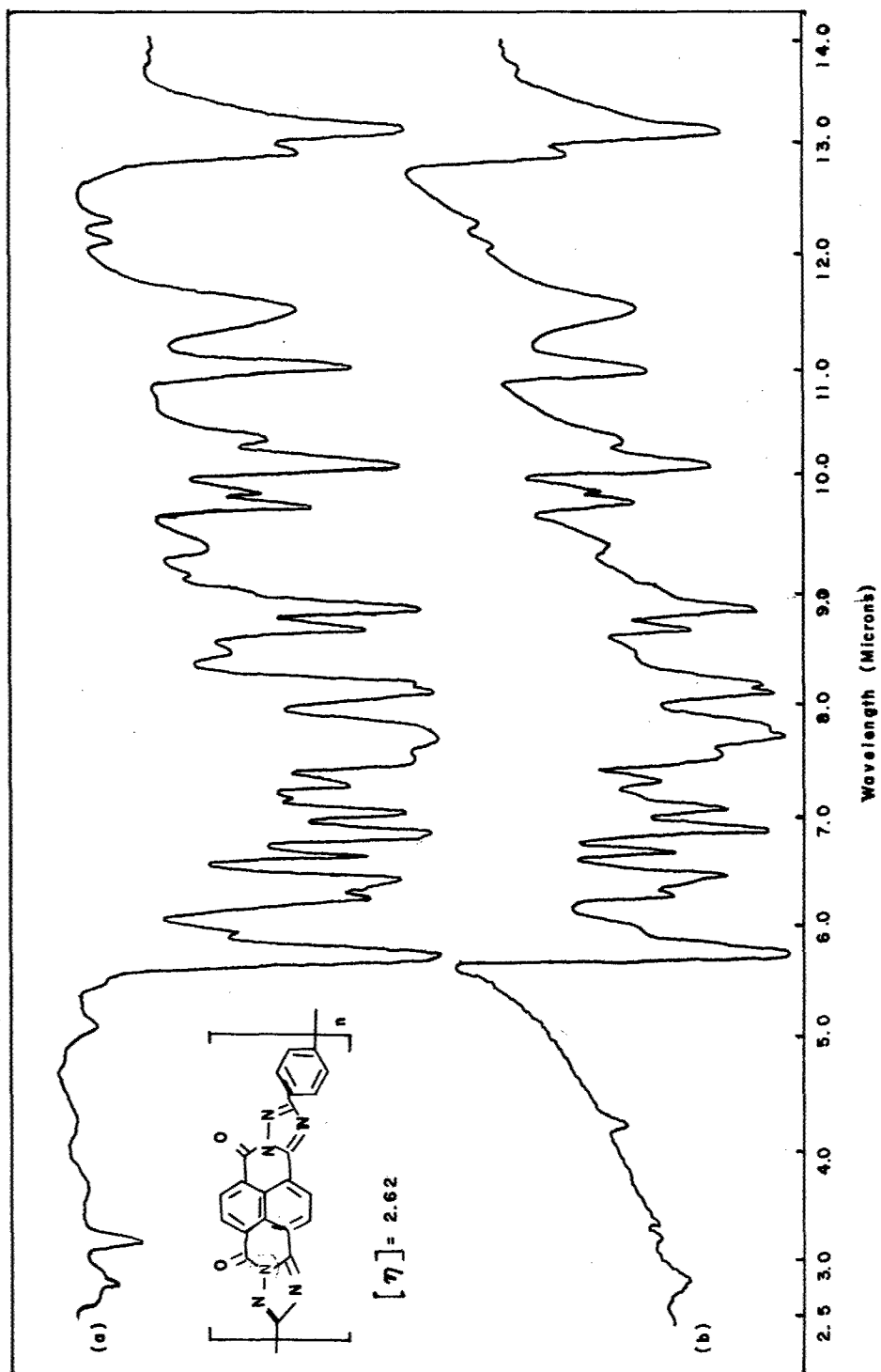


Figure 3. Infrared Spectra From (a) Film and (b) KBr Pellet

of a shoulder on the strong absorption at $5.80\ \mu$ did give rise to a relatively weak absorption at $6.00\ \mu$ which cannot be readily interpreted in terms of the benzobistriazolophenanthroline structure. Little other additional information could be derived from the spectrum.

On the basis of the elemental analysis and infrared spectral data, the presence of structural units in the polymer chain resulting from incomplete cyclization or side reactions cannot be excluded. This same evidence, while not sufficiently unambiguous to rule out such structures, does indicate a predominance of fully cyclized benzobistriazolophenanthroline structure in the polymer chain.

SECTION III EXPERIMENTAL

1. Preparation of Solvent and Monomers

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

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

a. Isophthalaldihydrazidine Dihydrochloride

Diethyl isophthalimidate (11.0 g, 0.05 mole) as prepared by the method of Shono et al (Reference 8) was slurried at room temperature in a solution of anhydrous hydrazine (3.2 g, 0.05 mole) in 200 ml of acetonitrile. The white solid gradually dissolved resulting in a clear yellow solution. The pale yellow precipitate which eventually formed was isolated by filtration after a total reaction time of 48 hours. Drying at room temperature and 0.10 mm Hg gave 8.5 g (88% yield) of crude isophthalaldihydrazidine, m.p. 163-165°C (dec.) (Lit 172°C, dec.) (Reference 9).

Isophthalaldihydrazidine (5.0 g.) was dissolved in 75 ml of methanol. Hydrogen chloride gas was slowly bubbled through the clear solution at -10°C, until a white precipitate formed. The stirred solution was warmed to room temperature and the white solid slowly dissolved. After one hour, additional hydrogen chloride gas was introduced into the reaction mixture at -78°C. The resultant white precipitate was isolated by filtration, washed well with ether, and dried over P_2O_5 and KOH at

140°C, and 0.05 mm Hg for twenty hours to give 3.4 g (51% yield) of isophthaldihydrazidine dihydrochloride, m.p. 240-243° (dec.).

Analysis Calc'd: C, 36.24; H, 5.32; N, 31.70; Cl, 26.74

Found: C, 36.67; H, 5.28; N, 31.88; Cl, 26.58

b. Terephthaldihydrazidine Dihydrochloride

Terephthaldihydrazidine was prepared by the reaction of diethyl terephthalimide (11.0 g, 0.05 mole) as prepared by the method of Zaitseva et al (Reference 10) and anhydrous hydrazine (3.2 g, 0.05 mole) under reaction conditions as described above. The yield of pale yellow product was 8.9 g. (92%), m.p. 223-225°C (dec.) (Lit 220°C, dec.) (Reference 9).

The unpurified terephthaldihydrazidine (2.0 g) was dissolved at room temperature in 30 ml of 4N hydrochloric acid. Hydrogen chloride gas was slowly bubbled through the stirred solution at 0°C. The resultant white precipitate was isolated by filtration and washed well on the filter with cold concentrated hydrochloric acid. The snow white solid was dried over P₂O₅ and KOH at 140°C and 0.1 mm Hg for twenty hours to give 2.0 g (74% yield) of off-white terephthaldihydrazidine dihydrochloride, m.p. 317-320°C (dec.).

Analysis Calc'd: C, 36.24; H, 5.32; N, 31.70; Cl, 26.74

Found: C, 36.14; H, 5.23; N, 31.35; Cl, 26.96

2. Preparation of Polymers

Typical preparative techniques for the polymers are as follows:

a. Polycondensation of Terephthaldihydrazidine and NTCA

PPA (100 g) was deoxygenated by bubbling dry nitrogen through it at 110°C for 14 hours. Terephthalaldihydrazidine (1.728 g, 0.009 mole) and NTCA (2.736 g, 0.009 mole) were ground together and added with stirring to the PPA at 140°C. The temperature was raised to 180-185°C, over the course of an hour and maintained at this level for 18 hours. The reactants gradually dissolved in the vigorously stirred reaction mixture and a viscous, deep-red solution resulted. After being cooled to 100°C, the polymerization mixture was poured into a liter of ice water in a Waring Blender. The resultant suspension was allowed to settle overnight and the clear supernatant liquid was decanted. The polymer was isolated by filtration, and successively washed with 500 ml portions of water (three times) and N,N-dimethylacetamide (two times). Final washings were with hot methanol. The reddish-black product was dried at 180°C, and 0.01 mm Hg over P₂O₅ to give 3.20 g (92% yield) of polymer (inherent viscosity = 0.79 in methane sulfonic acid at 25°C). A portion of polymer (1.0 g) was dissolved in methane sulfonic acid and reprecipitated in methanol. Successive washings with methanol and ether followed by drying as above gave an almost quantitative recovery of polymer (inherent viscosity = 0.84 in methane sulfonic acid at 25°C).

Analysis Calc'd: C, 68.04; H, 2.06; N, 21.65

Found: C, 67.08; H, 2.22; N, 18.24

b. Polycondensation of Terephthalaldihydrazidine Dihydrochloride and NTCA

Terephthalaldihydrazidine dihydrochloride (1.766 g, 0.0067 mole) was mixed with 110 g of deoxygenated PPA and carefully stirred for three hours at 80-90°C to permit controllable evolution of hydrogen chloride to occur. NTCA (2.026 g, 0.0067 mole) was added and the pot temperature

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was raised to 180-185°C, over the course of an hour. After 22 hours at that temperature, an extremely viscous, deep-red solution resulted.

Work-up was as described above and yielded 2.30 g (88% yield) of reprecipitated polymer (inherent viscosity = 2.51 in methane sulfonic acid at 25°C).

Analysis Calc'd: C, 68.04; H, 2.06; N, 21.65

Found: C, 67.08; H, 2.39; N, 18.83

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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 (AFML/LNP) Wright-Patterson Air Force Base, Ohio		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE NOVEL BENZOBISTRIAZOLOPHENANTHROLINE POLYMERS			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Technical Report January 1971 to March 1971			
5. AUTHOR(S) (First name, middle initial, last name) Dr. Robert C. Evers			
6. REPORT DATE June 1972		7a. TOTAL NO. OF PAGES 23	7b. NO. OF REFS 10
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-72-71	
b. PROJECT NO. 7340			
c. Task No. 734004		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Wright-Patterson Air Force Base, Ohio	
13. ABSTRACT Novel, high molecular weight benzobistriazolophenanthroline polymers were prepared by the polycondensation of 1,4,5,8-naphthalene tetracarboxylic acid with iso- or tere-phthalaldihydrazidine dihydrochloride in polyphosphoric acid. Inherent viscosities in the range of 1.33 to 2.51 were recorded. Tough, transparent films of these polymers could be cast from methane sulfonic acid. Onset of polymer breakdown during thermogravimetric analysis in an air atmosphere occurred at 450°C.			

DD FORM 1473
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Security Classification

14.	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	Benzobistriazolophenanthroline Polymer High Temperature Applications Heterocyclic Polymers						

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Security Classification