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BENZIMIDAZOBENZOPHENANTHROLINE POLYMERS DERIVED FROM PHENYLATED QUINOXALINE TETRAAMINES

R. KOVAR
F. E. ARNOLD

TECHNICAL REPORT AFML-TR-72-266

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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, "New Organic and Inorganic Polymers." 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, Project Scientist.

This report covers work conducted in this Laboratory from July 1971 to July 1972.

The work was supported, in part, by Air Force Materials Laboratory Director's Discretionary Funds.

This technical report has been reviewed and is approved.

R L Van Deusen
R. L. Van Deusen
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

New phenylated quinoxaline tetraamines have been prepared and polymerized with 1,4,5,8-naphthalene tetracarboxylic acid. The resulting BB-type polymers with pendant phenyl groups along the polymer backbone are soluble in m-cresol. The polymers with inherent viscosities ranging from 0.3 to 0.6 dl/gm in sulfuric acid exhibited thermal stabilities near 500°C under nitrogen and near 400°C in air.

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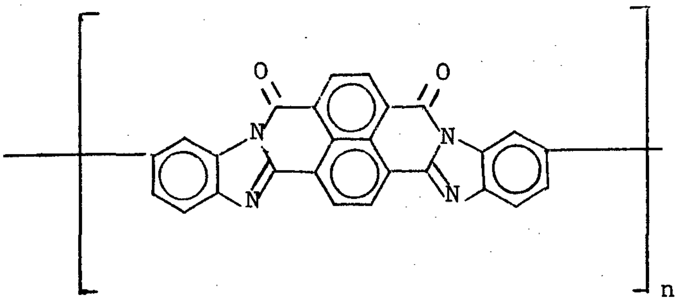
SECTION PAGE

ILLUSTRATIONS

INTRODUCTION

Poly (6,9-dihydro-6,9-dioxobisbenzimidazo [2,1-*b*: 1',2'-*j*]benzo [*lmn*] [3,8] phenanthroline-3,12-diyl), referred to as BBB, is one of the most thermally stable aromatic heterocyclic polymers now known. First prepared in our laboratory (References 1 and 2), BBB has been developed (References 3 and 4) into a fibrous material showing excellent properties for deployable aerodynamic decelerators.



BBB

The polymer has been studied extensively with respect to its synthesis (Reference 5), thermal degradation (Reference 6), thermal oxidative degradation (Reference 7), molecular weight (Reference 8), glass transitions (Reference 9), and solution properties (Reference 10). The BBB polymer represents the state of art material in the field of aromatic heterocyclic polymer chemistry.

Although BBB is under development as a fibrous material, it has not as yet been successfully evaluated as a high temperature coating, adhesive and composite material. A difficulty encountered with BBB and other highly fused aromatic heterocyclic polymers is that they are not soluble in conventional organic solvents by which they can be fabricated. BBB exhibits solubility in only highly corrosive solvents such as sulfuric, chlorosulfonic, and methane sulfonic acids.

In contrast to the BBB type polymers, the aromatic heterocyclic polyphenylquinoxalines (II) (References 11 and 12) exhibit very desirable solubility behavior. This class of materials is prepared by the polycondensation of aromatic debenziels with aromatic tetraamines. High molecular weight materials have been prepared which are soluble in solvents such as tetrachloroethane, chloroform, and m-cresol. Pendant phenyl groups greatly improve the solubility of the heterocyclic quinoxalines (Reference 13) and also have been shown to solubilize aromatic polyphenylenes (References 14 and 15).

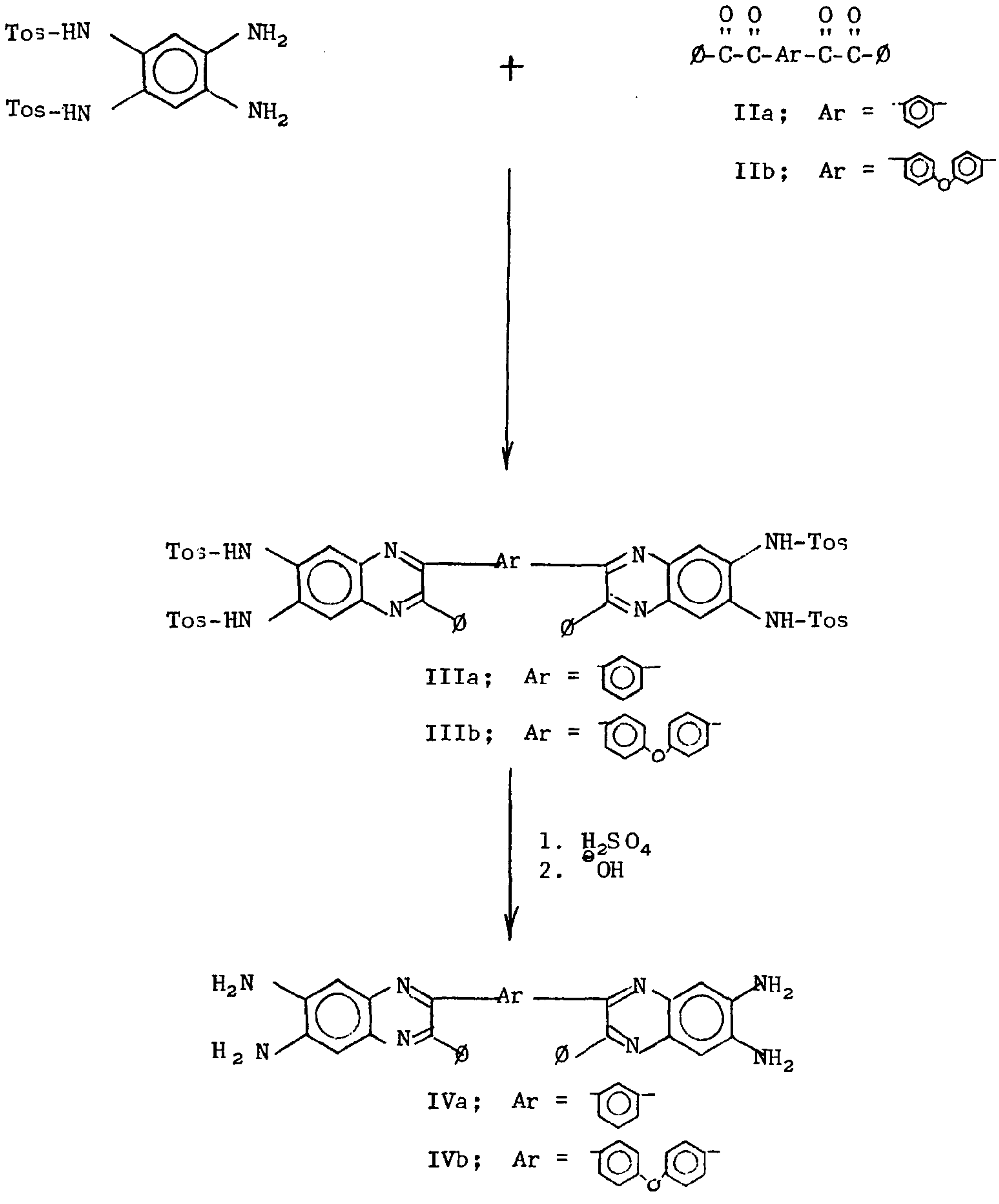
The objective of this work is to synthesize BBB type polymers which contain pendant phenyl groups along the polymer backbone. The purpose of the work is to determine if the pendant phenyl groups would render the polymer soluble in solvents other than strong acids. This report describes a phase of the current effort directed toward attaining the objective.

SECTION II

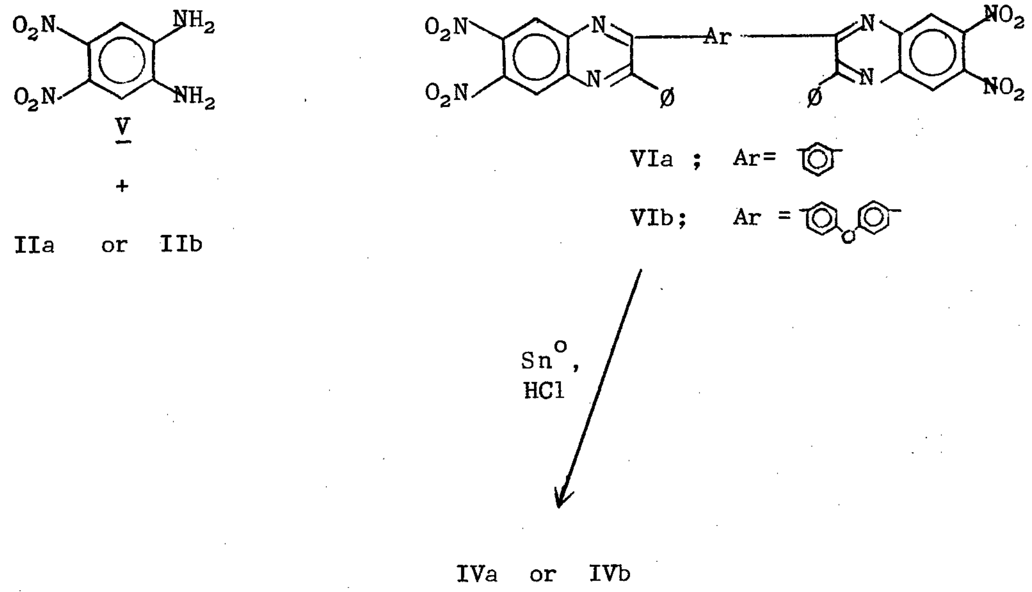
DISCUSSION

The BBB polymer is prepared by the solution polycondensation of 1,4,5,8-naphthalene tetracarboxylic acid and 3,3'-diaminobenzidine in polyphosphoric acid. In an effort to attach pendant phenyl groups along the BBB backbone, phenylated quinoxaline tetraamine monomers were prepared and used in place of 3,3'-diaminobenzidine. Thus, two phenyl groups would be incorporated per repeat unit.

The synthetic approach chosen involved the condensation of 1,2-diamino-4,5(p-toluenesulfonamide)benzene(I) with 1,3-bis(phenylglyoxaloyl) benzene (IIa) and p,p'-bis(phenylglyoxaloyl)diphenyl ether (IIb) which gave rise to tetrafunctional tosylates IIIa and IIIb, containing the phenylated quinoxaline structure. Detosylation of tosylates IIIa and IIIb in concentrated sulfuric acid and subsequent treatment of the resulting amine salts with methanolic potassium hydroxide afforded the free tetraamines, IVa and IVb. The amine monomers were easily obtained in a high state of purity by column chromatography on alumina and recrystallization from methanol/water mixtures.

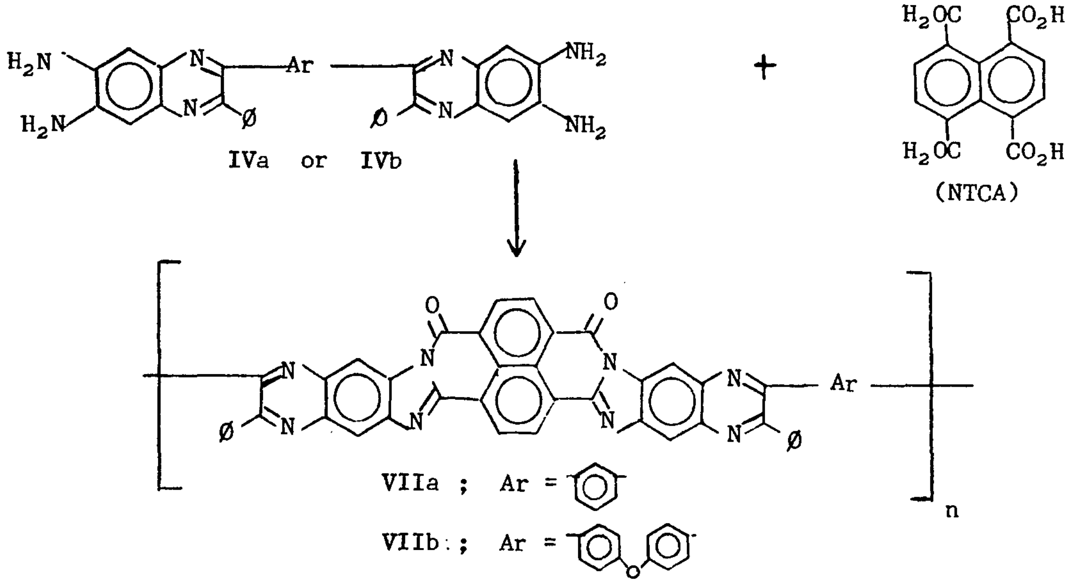


An alternate route to the phenylated quinoxaline tetraamines was provided by the reaction 1,2-diamino-4,5-dinitrobenzene (V) with IIa and IIb, leading to tetranitro intermediates VIa and VIb.



Reduction of VIa and VIb using tin and hydrochloric acid followed by neutralization of the hydrochloride salts provided the free tetraamines IVa and IVb in high yields which were identical in properties with samples isolated via the de-tosylation of IIIa and IIIb.

Tetramine monomers IVa and IVb were polymerized with 1,4,5,8-naphthalene tetracarboxylic acid (NTCA), giving rise to polymers VIIa and VIIb which contained alternating bis-imidazonaphthaldiimide and bis-phenyl-quinoxalino-benzene structures, the latter heterocyclic structure being generated during the polycondensation process.



Polymers VIIa and VIIb were analyzed with respect to their solubility characteristics, inherent viscosities, thermal stability, and glass transition temperature.

Tosylates IIIa and IIIb proved to be useful as monomers themselves, since both underwent virtually quantitative de-tosylation in polyphosphoric acid at elevated temperatures. Stoichiometric amounts of the tosylates with NTCA were polymerized in PPA by slowly heating the reaction mixture to 180°C for 20 hours. Polymerizations were carried out in PPA, since this solvent has been used with repeated success during previous polymerizations involving aromatic tetramines and tetraacids.

The crude polymers obtained from the above reactions were precipitated into methanol, collected, and then reprecipitated from m-cresol or concentrated sulfuric acid, depending upon the solubility characteristics of the polymer. Since the polymers were found to be unstable toward long-term storage in sulfuric acid solutions, the use of this solvent was avoided whenever possible.

Tetramine IVa was polymerized with naphthalene tetracarboxylic acid dianhydride in m-cresol and antimony trichloride solutions in attempts to improve upon the observed viscosities of the isolated polymer, VIIa. The dianhydride offered the advantage of being available in a higher state of purity than NTCA, which always contained residual amounts of anhydride as an impurity.

SECTION III

RESULTS

The results of this study are tabulated in Table I.

Polymer VIIa, derived from reactions of NTCA with IIIa or IVa, exhibited viscosities ranging from 0.32 to 0.65 dl/g in concentrated sulfuric acid (0.30 g/100mℓ/H_2SO_4)and 0.20 to 0.46 dl/g in m-cresol. Inherent viscosities of polymers determined in sulfuric acid were found to decrease substantially with time, an indication that decomposition was occurring. As a result, polymer purification by reprecipitation as well as viscosity measurements on polymer VIIa were run in m-cresol. Unfortunately, polymer VIIb was not sufficiently soluble in m-cresol for determination of inherent viscosities in that solvent.

Polymerization of tetramine IVa with naphthalene tetracarboxylic acid dianhydride in antimony trichloride solution yielded only low molecular weight material. The filtrate obtained upon collection of the precipitated polymer was strongly colored, indicating substantial amounts of oligomeric products. Reaction of IVa with NTCA dianhydride in refluxing m-cresol however, yielded polymer of viscosity comparable to that obtained from reaction in PPA solution.

Polymer VIIb, derived from the reaction of NTCA with monomers IIIb and IVb, exhibited viscosities in the range of 0.60 in concentrated sulfuric acid. The polymers did not possess sufficient solubility in m-cresol to allow viscosity determinations in that solvent.

Attempts to cast films of polymers VIIa and VIIb from m-cresol or methane sulfonic acid resulted in the formation of brittle films which fractured spontaneously into tiny fragments upon removal of the solvent. The films obtained from polymer VIIa were deep red in color, while those cast from solutions of VIIb were brownish-red.

TABLE I

POLYMER PROPERTIES

Monomers	Solvent	Temp.	Polymer	Viscosity H_2SO_4	Viscosity m-cresol	Solubility in m-cresol
IIIa + NTCA	PPA	190	VIIa	0.65	0.45	100%
IVa + NTCA	PPA	190	VIIa	0.61	0.42	100%
IVa + NTCADA	$SbCl_3$	190	VIIa	0.32	0.21	100%
IVa + NTCADA	m-cresol	200	VIIa	0.63	0.46	100%
IIIb + NTCA	PPA	190	VIIb	0.66		80%
IVb + NTCA	PPA	190	VIIb	0.63		80%

Infrared spectra of polymer samples were obtained on fragile films cast from m-cresol solutions onto sodium chloride plates. The weak spectra obtained showed the expected absorption of 1690cm-1 as well as strong absorptions at 1725 and 1765 cm-1, indicative of anhydride end groups in the polymers.

Thermal gravimetric analysis of polymer VIIa showed 10% weight loss at 700°C in nitrogen and 410°C in air. Polymer VIIb lost 10% weight at 610°C in nitrogen and 460°C in air.

Analysis of polymer VIIa by torsion braid techniques indicated that the Tg was above 450°C. Polymer VIIb was not sufficiently soluble in m-cresol to permit determination of Tg.

SECTION IV

EXPERIMENTAL

1. MONOMERS

a. 1,2-Diamino-4,5-o-phenylene-bis(p-toluenesulfonamide): (1)

To a solution of 30.4 g (60 mmole) of 1,2-dinitro-4,5-o-phenylene-bis-(p-toluenesulfonamide) in 150 ml of dimethylacetamide at 95°C was added dropwise an aqueous solution containing 62.6 g (360 mmole) of sodium hydrosulfite and 14.4 g (360 mmole) of sodium hydroxide. After the addition was completed, the reaction mixture was added to one liter of water to precipitate the product as a white solid. The solid material was collected, washed with several portions of water, then washed with methanol and air dried yielding 20 g (74%) of 1,2-diamino-4,5-o-phenylene-bis(p-toluenesulfonamide), m p 238-9°C (lit.[16] 238-9°C).

b. 1,3-Bis[2-phenyl-6,7(p-toluenesulfonamido)quinoxaline] -
-3-yl-benzene: IIa

A mixture of 30.8 g (68.8 mmole) of 1,2-diamino-4,5-o-phenylene-bis (p-toluenesulfonamide) and 11.9 g (34.4 mmole) of 1,3-bis(phenylglyoxaloyl) benzene in 100 ml of m-cresol was heated at reflux under nitrogen for three hours. The reaction mixture was then evaporated to dryness in vacuo, and the tarry residue triturated with hexane causing solidification of the product. The pink solid thus obtained was twice recrystallized from methanol/methylene chloride, yielding 37 g (93%) of an orange powder, m p 275°C (DEC).

Anal. Calcd. for $C_{62}H_{50}N_8O_8S_4$: C, 64.01: H, 4.33: N, 9.63

Found: C, 63.54 H, 4.79 N, 9.20

c. 1,3-Bis[2-Phenyl-6,7-Diamino-Quinoxaline]-3-yl-Benzene: IIIa

To 100 ml of de-aerated concentrated sulfuric acid was added under nitrogen 20 g (17.2 mmole) of finely powdered 3-bis[2-phenyl-6,7-bis(p-toluenesulfonamido)quinoxaline]-3-yl-benzene. The stirred mixture was heated at 90°C under nitrogen for one hour, at which time it was cooled to 0°C and poured over ice, precipitating an orange solid. The solid material was then dissolved in 10% methanolic potassium hydroxide, and the filtered solution poured into a large volume of hot water. The resulting yellow suspension was heated on the steam bath until all of the methanol had evaporated, leaving a yellow precipitate of 1,3-bis[2-phenyl-6,7-diamino-quinoxaline]-3-yl-benzene. The product was collected, washed with water and dried. Chromatography of the material on a dry column of alumina afforded pure product, m p 400°C (dec.). The material sublimed with decomposition at 400°C/0.01mmHg.

Anal. Calcd. for, $C_{34}H_{26}N_8$: C, 74.71 H, 4.79 N, 20.50

Found: C, 74.14, H, 4.34 N, 19.82

d. p,p'-Bis[2-Phenyl-6,7-Bis(p-Toluenesulfonamido)Quinoxaline]-3-yl-Diphenylether: (IIb)

A mixture of 10.0 g (11.2 mmole) of 1,2-diamino-4,5-o-phenylene-bis (p-toluenesulfonamide) and 5.0 g (5.6 mmole) of p,p'-bis(phenylglyoxaloyl) diphenylether in 50 ml of m-cresol was heated at reflux under nitrogen for three hours. The reaction mixture was then evaporated to dryness in vacuo, and the tarry residue triturated with hexane until solidification of the product occurred. The pink solid thus obtained was twice recrystallized from methanol/methylene chloride yielding an orange powder, m.p. 183-5°C.

Anal. Calcd. for $C_{68}H_{54}N_8O_9S_4$: C, 65.06; H, 4.34; N, 8.93

Found: C, 64.68 H, 4.52 N, 8.71

e. p,p'-Bis[2-Phenyl-6,7-Diamino-Quinoxaline]-3-yl-Diphenylether: (IIIb)

To 50 ml of de-aerated concentrated sulfuric acid was added under nitrogen 15.0 g (24 mmole) of finely powdered p,p'-bis[2-phenyl-6,7-bis (p-toluenesulfonamido)quinoxaline]-3-yl-diphenylether. The stirred mixture was heated at 90°C under nitrogen for one hour, at which time it was cooled to 0°C and poured over ice, precipitating an orange solid. The solid tetramine salt was collected, washed with water and air dried. The solid material was then dissolved in 10% methanolic potassium hydroxide, and the filtered solution poured into a large volume of hot water. The resulting yellow suspension of tetramine was heated on the steam bath until all of the methanol had evaporated. The product was collected, washed with water and air dried. Chromatography of the material on a dry column of activity grade II alumina afforded pure p,p'-bis[2-phenyl-6,7-diamino-quinoxaline]-3-yl-diphenylether as yellow crystals, m p 180-181°C.

Anal. Calcd. for $C_{40}H_{30}N_8O$: c,77.15; H, 4,86; N, 17.99

Found: C, 76.64 H, 4.78 N, 17.22

f. 1,2-Diamino-4,5-Dinitrobenzene (V)

A slurry containing 50 g of 1,2-dinitro-4,5-bis(p-toluenesulfonamido) benzene suspended in 300 ml of concentrated sulfuric acid was heated to 100°C under nitrogen for one hour. At that time the flask was cooled in an ice bath to 0°C, and the sulfuric acid solution slowly added to one liter of ice-water, giving rise to a voluminous yellow precipitate of amine salt. The sulfate salt was filtered by suction, and then triturated on the buchner funnel with 100 ml of 50% sodium hydroxide solution, forming the brown, dinitro-diaminobenzene. The funnel was sucked dry, and the trituration process repeated with an additional 100 ml of sodium hydroxide solution to insure complete conversion to product. The crude 1,2-diamino-4,5-dinitrobenzene thus obtained was washed with water and air dried. Chromatography on a column of silica gel and subsequent recrystallization from acetone/water afforded 19 g (85%) of pure V.

Calculated for $C_6H_6N_4O_4$: M.W. = 198
Found: (mass spectrum): M.W. = 198

g. 1,3-Bis[2-Phenyl-6,7-Dinitroquinoxaline]-3-yl-Benzene (IVa)

To a solution of 12.0 g (60.6 mmole) of 1,2-dinitro-4,5-diaminobenzene (V) in 100 ml of glacial acetic acid was added 10.2 g (30 mmole) of 1,3-bis(phenylglyoxaloyl)benzene, and the reaction mixture refluxed for one hour under nitrogen. The yellow solution was allowed to cool to room temperature, and the yellow crystals which precipitated were filtered by suction and washed with a small quantity of THF. Recrystallization of the product from DMAC/hexane afforded granular yellow crystals of 1,3-bis[2-phenyl-6,7-dinitroquinoxaline]-3-yl-benzene (VIa), m.p. 340°C (dec.). The infrared spectrum exhibited intense absorptions at 1530 and 1335 cm^{-1}, characteristic of nitro-groups.

Anal. Calcd. for $C_{34}H_{18}N_8O_8$; C, 61.27 H, 2.72 N, 16.81, N.W. = 666.57
Found: C, 60.97 H, 2.61 N, 16.46; M.W. = 666 (Mass spectrum)

h. 1,3-Bis[2-Phenyl-6,7-Diaminoquinoxaline]-3-yl-Benzene (IVa) Via Reduction of the Tetranitro- Intermediate VIa

To a suspension of 50 g of granular tin in 100 ml of concentrated hydrochloric acid was added 15 g (22.5 mmole) of tetranitro- derivative, VI. The resulting mixture was heated on the steam bath with stirring for two hours, at which time a dark purple precipitate had formed. The purple precipitate of tetramine-tetrahydrochloride was carefully decanted from the reaction flask onto a buchner funnel, rinsing the flask with additional HCl. The amine salt was washed with several small portions of concentrated HCl, dried, and then dissolved in a minimum amount of methanol. The methanol extracts were filtered, and then poured into a large volume of 5% aqueous sodium hydroxide solution, forming a bright yellow precipitate of free tetramine IVa. Purification of the tetramine by column chromatography on alumina followed by two successive recrystallizations from methanol/water afforded 9.5 g (79%) of pure IVa as yellow crystals, m p. 400°C (dec.).

The infrared spectrum obtained for compound IVa prepared by this method was identical with that obtained previously for an authentic sample of IVa synthesized via the detosylation of tetratosylate IIIa.

Calculated for $C_{34}H_{26}N_8$: C, 74.71 H, 4.79 N, 20.50, M.W. 546.6

Found: C, 74.22, H, 4.53 N, 19.72 M.W. (mass spectrum) 547.

i. p,p'-Bis[2-Phenyl-6,7-Dinitroquinoxaline]-3-yl-Diphenylether (VIb)

To a solution of 8.0 g (40 mmole) of 1,2-dinitro-4,5-diaminobenzene in 100 ml of glacial acetic acid was added 8.6 g (20 mmole) of p,p'-bis (phenylglyoxaloyl) diphenylether, and the reaction mixture refluxed under nitrogen for one hour. The solution was then allowed to cool, and was added to one liter of water, precipitating a yellow product. The precipitate was collected, washed with water and air dried. The crude tetranitro-product was dissolved in a minimum amount of methylene chloride and the resulting solution filtered through a 1" x 6" dry column of alumina, and the column eluted with methylene chloride. The eluent was slowly added to a beaker containing 200 ml of boiling methanol, and the solution heated until the methylene chloride had been expelled, causing precipitation of granular yellow crystals of tetranitro- compound. The methanol solution was then rapidly cooled in ice to complete the precipitation. The crystals were washed with methanol and dried <u>in vacuo</u>, yielding 13.4 g (89% yield) of p,p'-bis[2-phenyl-6,7-dinitroquinoxaline]-3-yl-diphenylether, m.p. 185°C. The infrared spectrum (KBr pellet exhibited absorptions at, 1585, 1530 (vs), 1495(m), 1400(s), 1335(vs), 1235(vs), 1165(s) cm^{-1}.

Calcd. for $C_{40}H_{22}N_8O_9$: C, 63.33 H, 2.92 N, 14.77 O, 18.98

Found: C, 62.97 H, 2.88 N, 15.06

j. p,p'-Bis[2-Phenyl-6,7-Diainoquinoxaline]-3-yl-Diphenylether (VIb) Via the Tetranitro- Intermediate (VIb)

To a suspension of 25 g of granular tin in 50 ml of concentrated hydrochloric acid was added 5 g (6.4 mmole) of tetranitro-derivative VIb. The resulting mixture was heated on the steam bath with stirring for two hours, at which time a dark precipitate had formed. The precipitate of tetramine-tetrahydrochloride was carefully decanted from the reaction flask onto a buchner funnel, and the flask rinsed with additional HCl.

The amine salt was washed with several small portions of concentrated HCl, air dried, and then dissolved in a minimum amount of methanol. The methanol extracts were filtered, and then poured into a large volume of 5% aqueous sodium hydroxide solution, forming a bright yellow precipitate of free tetramine, IVb. Purification of the tetramine by column chromatography on silica gel followed by two successive recrystallizations from methanol/water afforded 2.1 g (50%) of pure IVb as yellow crystals, m.p. 180°C. The infrared spectrum obtained for compound IVb prepared by this method was identical with that obtained previously for an authentic sample of IVb synthesized via the detosylation of tetratosylate IIIb.

2. POLYMERS

a. Polymerization of Tetramine IVa in Polyphosphoric Acid: (VIIa)

To 20 g of deoxygenated polyphosphoric acid was added, under a nitrogen atmosphere, 0.1667 g (0.548 mmole) of 1,4,5,8-naphthalene tetracarboxylic acid and 0.3000 g (0.548 mmole) of 1,3-bis[2-phenyl-6,7-diamino-quinoxaline]-3-yl-benzene. The reaction flask was slowly heated to 180°C, and was maintained at that temperature for ten hours. At that time, the contents of the flask were cooled to 100°, and poured into one liter of anhydrous methanol, precipitating a dark-red polymer. The product after reprecipitation from m-cresol solution into methanol, and subsequent drying in vacuo, exhibited an inherent viscosity of 0.42 dl/gm in m-cresol, and 0.61 dl/gm in concentrated sulfuric acid.

Anal. Calcd. for $C_{48}H_{22}N_8O_2$; C, 77.62 H, 2.99 N, 15.09
Found: C, 76.82 H, 3.01 N, 14.21

b. Polymerization of Tetramine IVa with NTCADA in Antimony Trichloride:

To 20 g of deoxygenated antimony trichloride was added, under a nitrogen atmosphere 0.1470 g (0.548 mmole) of 1,4,5,8-naphthalene tetracarboxylic acid dianhydride (NTCADA), and 0.3000 g (0.548 mmole) of 1,3-bis[2-phenyl-6,7-diamino-quinoxaline]-3-yl-benzene. The reaction mixture was slowly heated to 180°C, and was maintained at that temperature for ten hours. At that time, the contents of the flask were cooled to 100°C, and poured into one liter of DMAC, precipitating a red polymer. The product, after reprecipitation from m-cresol into methanol, and subsequent drying in vacuo, exhibited an inherent viscosity of 0.21 dl/gm in m-cresol.

Anal Calcd. for $C_{48}H_{22}N_8O_2$: C, 77.62 N, 2.99 N, 15.09
Found: C, 74.73 H, 3.23 N, 13.64

c. Polymerization of Tetratosylated IIIa with NTCA in Polyphosphoric Acid: VIIa

To 60 g of deoxygenated polyphosphoric acid was added, under a nitrogen atmosphere, 0.3445 g (1.1325 mmole) of 1,4,5,9-naphthalene tetracarboxylic acid and 1.3176 g (1.1325 mmole) of 1,3-bis[2-phenyl-6,7-bis(p-toluenesulfonamido)quinoxaline]-3-yl-benzene. The reaction flask was slowly heated to 180°C and was maintained at that temperature for 20 hours. At that time, the contents of the flask were cooled to 100°, and poured into one liter of anhydrous methanol, precipitating a dark, red polymer. The product was collected, washed with several portions of methanol then water, and air dried. The crude polymer was dissolved in 50 ml of m-cresol, and the filtered solution slowly added to one liter of anhydrous methanol. The precipitate that formed was collected, washed with several portions of methanol, and dried in vacuo. The purified polymer thus obtained exhibited an inherent viscosity of 0.45 dl/gm in m-cresol, and 0.65 dl/gm in concentrated sulfuric acid.

Anal. Calcd. for $C_{48}H_{22}N_8O_2$; C, 77.62 H, 2.99 N, 15.09
Found: C, 76.79 H, 2.87 N, 14.53

d. Polymerization of Tetramine II with NTCADA in m-cresol:

To 20 g of deoxygenated m-cresol was added, under a nitrogen atmosphere, 0.1470 g (0.548 mmole) of 1,4,5,8-naphthalene tetracarboxylic acid dianhydride, and 0.3000 g (0.548 mmole) of 1,3-bis-[2-phenyl-6,7-diamino-quinoxaline]-3-yl-benzene. The reaction flask was slowly heated to reflux temperature (190°C), and was maintained at that temperature forten hours. At that time, the contents of the flask were cooled to 100°C and added dropwise to one liter of methanol, precipitating a red polymer. The product, after reprecipitation from m-cresol into methanol, and subsequent drying in vacuo, exhibited an inherent viscosity of 0.46 dl/gm in m-cresol (0.3 g/dl).

Anal Calcd. for $C_{48}H_{22}N_8O_2$ C, 77.62 : H, 2.99 : N, 15.09

Found: C, 76.88 H, 2.67 N, 14.54

e. Polymerization of Tetratosylate III b with NTCA in PPA:

A mixture of 0.3146 g (1.034 mmole) of 1,4,5,8-naphthalene tetracarboxylic acid and 1.300 g (1.034 mmole) of p,p'-bis[2-phenyl-6,7-bis(p-toluenesulfonamido]-quinoxaline]-3-yl-diphenylether were polymerized in polyphosphoric acid solution according to the procedure described previously for tetratosylate I. Workup of the reaction mixture in the usual manner afforded 0.81 g of purified polymer. The polymer exhibited an inherent viscosity of 0.66 dl/g in concentrated sulfuric acid (0.3 g/100 ml H_2SO_4).

Anal. Calcd. for $C_{54}H_{26}N_8O_3$: C, 77.69: H, 3.14: N, 13.42

Found: C, 75.96 H, 3.52, N, 14.62

f. Polymerization of Tetramine IVb with NTCA in PPA:

A mixture of 0.2931 g (0.9634 mmole) of 1,4,5,8-naphthalene tetracarboxylic acid and 0.6000 g (0.9634 mmole) of p,p'-bis[2-phenyl-6,7-diamino-quinoxaline]-3-yl-diphenylether were polymerized in polyphosphoric acid solution (5%) according to the procedure described previously for tetramine II. Workup of the reaction mixture in the usual manner afforded 0.7 g of purified polymer. The polymer, which was only partially soluble in m-cresol, exhibited an inherent viscosity of 0.63 dl/g in concentrated sulfuric acid (0.3 g/100 ml/H_2SO_4).

SECTION V

CONCLUSIONS

From the results presented in this report, it is concluded that benzimimidazobenzophenanthroline polymers containing 2-phenylquinoxaline moieties in the unit structure have been synthesized. The polymer system can be prepared from the solution polycondensation of novel phenylated quinoxaline tetraamines with 1,4,5,8-naphthalene tetracarboxylic acid or the acid dianhydride. The tetratosylate precursors to the quinoxaline tetraamines have also been shown to be useful monomers when polyphosphoric acid is used as the polymerization solvent.

It has also been shown that the pendant phenyl groups along the polymer backbone render the BB-type structures soluble in m-cresol. Although the structural modifications on the BBB polymer greatly improved solubility in a solvent that is not highly corrosive, the thermal stabilities of the new polymers are not as good.

As related to the overall objective given in the introduction the above experimental work constitutes a preliminary investigation. The results are positive and encouraging, although it is recognized that future work will be required to define more clearly the possible potential of such systems for Air Force use. For example, continued investigation of reaction conditions to increase the molecular weight and quality of polymers is needed. This will provide suitable materials for more extensive and meaningful evaluation.

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13. ABSTRACT

New phenylated quinoxaline tetraamines have been prepared and polymerized with 1,4,5,8-naphthalene tetracarboxylic acid. The resulting BB-type polymers with pendant phenyl groups along the polymer backbone are soluble in m-cresol. The polymers with inherent viscosities ranging from 0.3 to 0.6 dl/gm in sulfuric acid exhibited thermal stabilities near 500°C under nitrogen and near 400°C in air.

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