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BISBENZIMIDAZOBENZOPHENANTHROLINE-DIONE POLYMERS

R. L. VAN DEUSEN

TECHNICAL REPORT AFML-TR-65-295

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AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
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BISBENZIMIDAZOBENZOPHENANTHROLINE-DIONE POLYMERS

R. L. Van Deusen

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, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. R. L. Van Deusen, Project Engineer.

This report covers work conducted from July 1964 to June 1965. The manuscript was released by the author in July 1965 for publication as an RTD technical report.

The author gratefully acknowledges the laboratory contributions of Mr. A. J. Sicree and Lt. O. K. Goins which were extremely valuable in establishing polymer structure. Appreciation is also extended to Drs. W. E. Gibbs and T. E. Helminiak for their excellent cooperation in discussing technical aspects of the work.

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This technical report has been reviewed and is approved.

WILLIAM E. GIBBS
Chief, Polymer Branch
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ABSTRACT

Bisbenzimidazobenzophenanthroline-dione (BBB) polymers have been prepared from 1,4,5,8-naphthalene tetracarboxylic acid and 3,3'-diaminobenzidine by polycondensations in polyphosphoric acid. Polymer structure was verified by elemental and infrared analysis. BBB polymers were found to be black and amorphous, to have high softening points and to exhibit 600°C stability in N_2 by TGA. Intrinsic viscosities ranging from 0.1 to 1.2 dl/gm in sulfuric acid were obtained, the highest viscosity polymers having been produced by reactions near 200°C. Polymers were soluble in strong acid and base and could be wet spun from acid solution.

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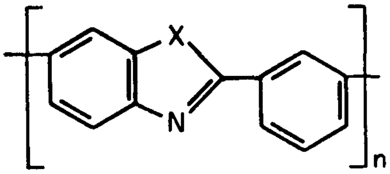
I. INTRODUCTION AND OBJECTIVES

Needs for thermally stable organic materials have existed for some time, and to fulfill these needs much attention has been given to the synthesis of high temperature polymers. As a result, research efforts over the past few years have led to the synthesis of new polymers which possess superior thermal stabilities. Noteworthy examples of such materials are the polyaromatic-benzoxazoles (Reference 1), -benzimidazoles (Reference 2), -imides (Reference 3), -triazoles (Reference 4), -benzothiazoles (Reference 5), -oxadiazoles (Reference 6), and -quinoxalines (Reference 7). Methods to prepare completely aromatic hydrocarbon polymers, the polyphenylenes (Reference 8), have also been developed. All these polymers have conjugated unsaturation and some are stable to temperatures exceeding 500°C when examined by thermal gravimetric analysis in an inert atmosphere.

Despite these accomplishments, the attainment of better polymer properties has not kept pace with the continually increasing properties requirements being placed on materials for high temperature applications. Some cause for this is the fact that many attempts to synthesize thermally stable polymers have resulted in the production of "brick dust-like" materials, extremely stable but infusible, and intractable. Conjugated aromatic hydrocarbons, particularly fused-ring types, tend to have these properties. Thus, the synthesis of high temperature polymers poses an unusual problem--structural features which contribute the most toward thermal stability are also features which are responsible for intractability.

The important property of aromaticity is undoubtedly responsible for the well-known stability of heterocyclic compounds containing conjugated unsaturation through nitrogen. Unlike the completely aromatic hydrocarbon polymers (Reference 8), some high molecular weight nitrogen containing polymers have been found to be soluble and fusable, and in addition they can be formed into fibers and laminates. The polybenzimidazoles mentioned above have these useful properties, and they represent one of the most promising classes of high temperature polymers. Useful properties have been realized from fused-ring polymers which contain heterocyclic rings. For example, aromatic-heterocyclic polymers of the type:



where X is NH (benzimidazole), O (benzoxazole), and S (benzothiazole), have very good thermal stability and are soluble in strong acid (References 1, 2, and 5).

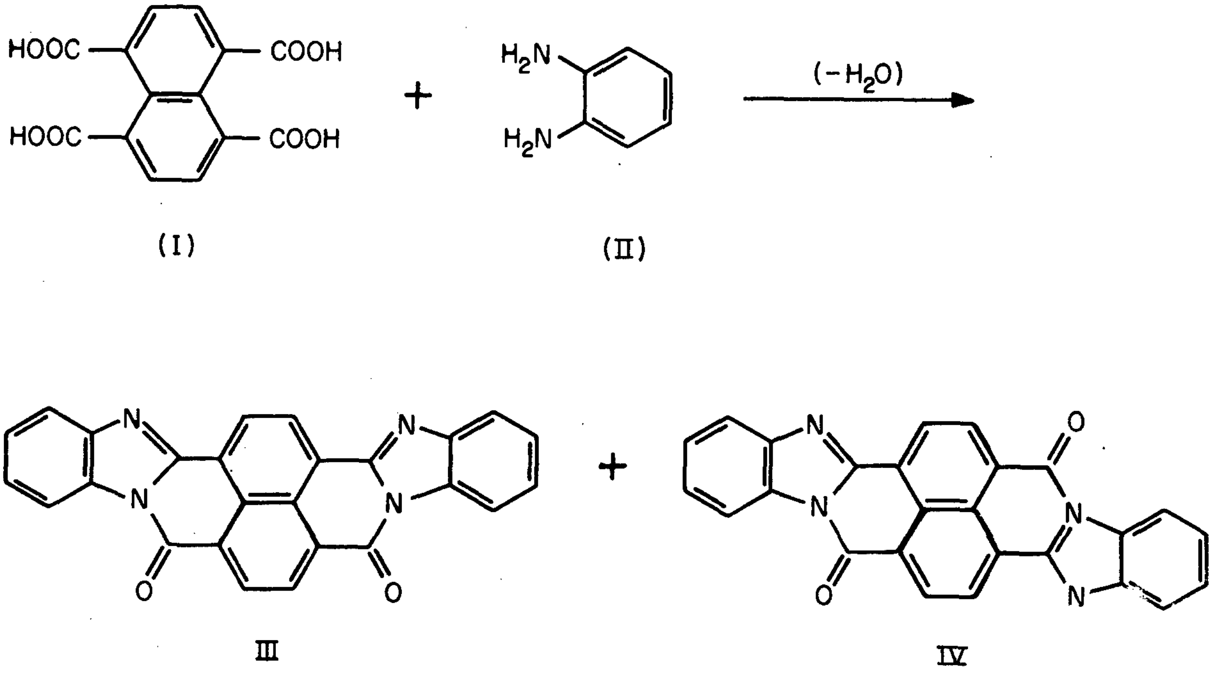
A logical approach to obtaining tractable polymers with higher thermal stabilities seems to center around synthesizing aromatic polymers which contain heterocyclic structures more highly fused than those discussed above. Proper tailoring of structure may permit the synthesis of completely fused ring, ladder polymers (References 9, 10, 11, 12, and 13) which will still possess tractability.

It is the objective of this and related work to synthesize highly fused aromatic-heterocyclic polymers as possible candidate materials for high temperature use. This report describes a phase of the current effort directed toward attaining this objective.

II. GENERAL DISCUSSION AND SUMMARY OF RESULTS

A. BASIC CHEMISTRY OF THE SYSTEM

The research reported here is based primarily upon the synthesis of certain indanthrene dyes (Reference 14) involving reactions between 1,4,5,8-naphthalene tetracarboxylic acid (I) and o-phenylene diamine (II) (See Page 3). Isomers III and IV are also products from the reaction of the corresponding acid dianhydride. They can be separated as a result of their differences in solubility in alcoholic KOH. The currently recommended nomenclature (Reference 15) for the <u>cis</u>-isomer (III) is bisbenzimidazo(2,1-<u>b</u>:1',2'-<u>j</u>)benzo(lmn)(3,8)phenanthroline-6,9-dione, whereas the <u>trans</u>-compound (IV) would necessarily differ in substituent numbering. Structures of this type can also be referred to as derivatives of 4,9-diazopyrene rather than the 3,8-benzophenanthroline.



Reactions of the above acid (I) or anhydride with aromatic compounds containing ortho diamine sites can be readily illustrated by the following Reaction Scheme (Figure 1). Intermediate amide, imide or imadazole derivatives are possible depending upon the nature of reactions between 1,8-naphthalic acid (or anhydride) and o-phenylene diamine (II). The model reactions labeled (A), (B), and (C) (Reference 16) are the most pertinent to this work, as will be pointed out later. For purposes of this discussion the completely fused ring product is referred to as a 6-5 ring compound in designating the fused 6-membered ring formed from beta carboxy groups and the 5-membered ring originating from the alpha amino groups.

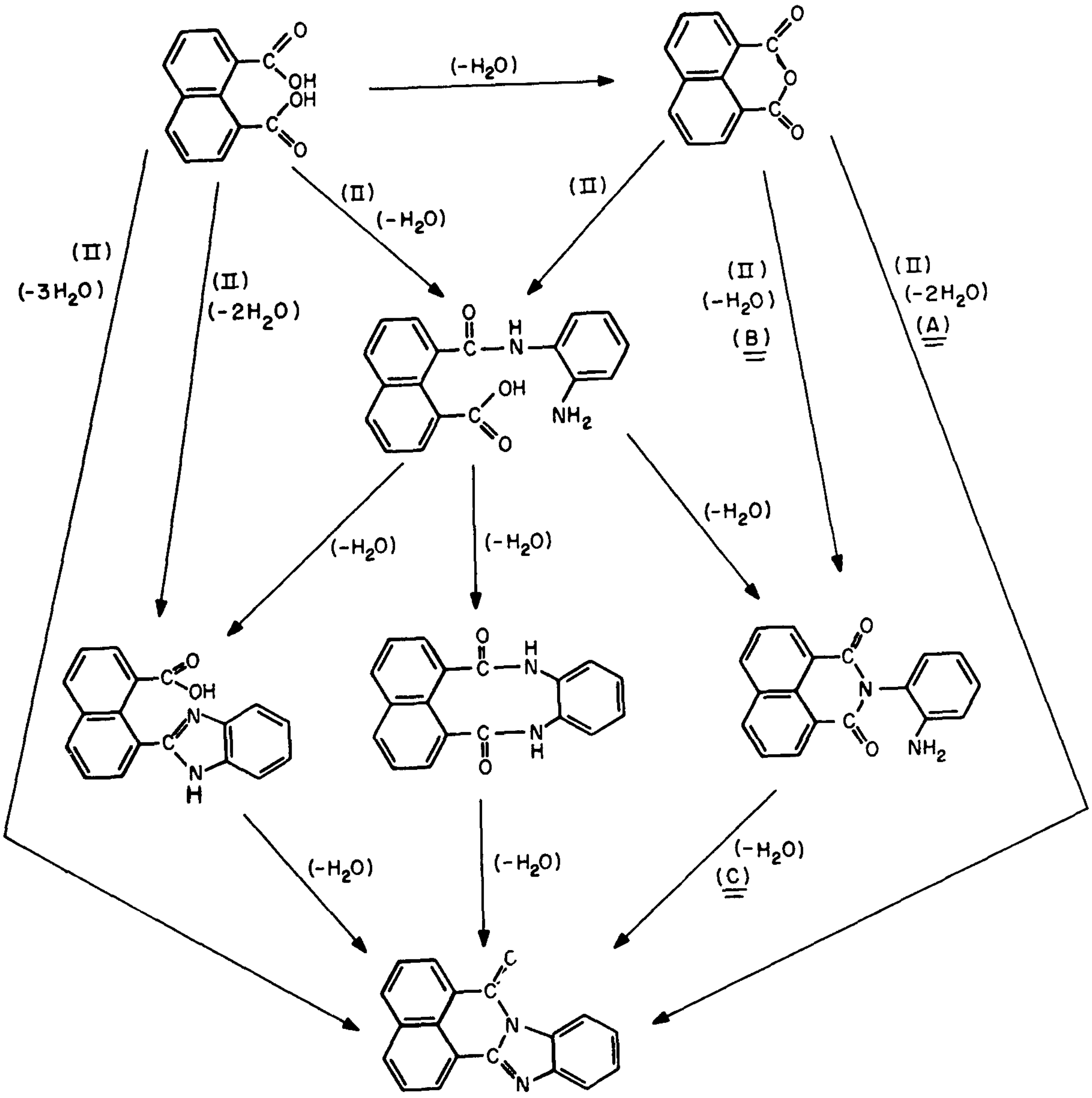


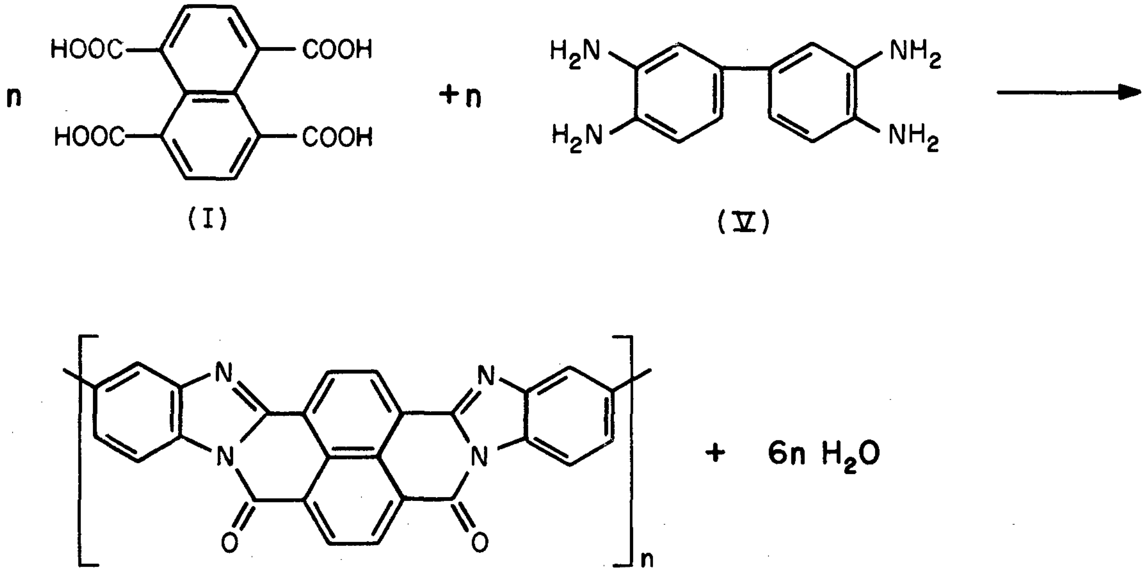
FIGURE 1 Reaction Scheme

Closely related reactions involving pyromelletic acid (or dianhydride) with o-phenylene diamine and 1,8-diaminonaphthalene have also been reported (References 17 and 18). These reactions result in cyclizations to produce 5-5 and 5-6 fused-ring types, respectively, which differ from those in Figure 1.

Recently, Dawans and Marvel (Reference 12) have disclosed extensions of the above 5-5 and 5-6 type reactions to the polymer synthesis. These polymers have stabilities in the 500°C range (thermal gravimetric analysis (TGA) in N_2) and are produced from reactions of pyromelletic acid dianhydride and 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride with aromatic tetraamines: 3,3'-diaminobenzidine, 1,2,4,5-tetraaminobenzene and 1,4,5,8-tetraaminonaphthalene. Also it has been reported in recent news releases (Reference 13) that Pezdirtz and Bell of NASA have prepared highly condensed aromatic-heterocyclic polymers from similar monomers.

B. SYNTHESIS OF BBB POLYMERS

The synthesis of BBB polymers (VI) from 1,4,5,8-naphthalene tetracarboxylic acid (I) and 3,3'-diaminobenzidene (V) was investigated in this laboratory.



(I)

(V)

(VI)

This polymerization is analogous to reactions shown on the Reaction Scheme (Figure 1) where the 6-5 type ring structure is produced. As shown, the BBB polymer (VI) is a poly[2,13(bisbenzimidazo(2,1-*b*:1',-2'-*j*)benzo(lmn)(3,8)phenanthroline-6,9-dione)]isomer. Other isomers with 3- or 12- linkages, or with *trans*-carbonyl groups can also be expected to occur.

Polymerizations were carried out in polyphosphoric acid (PPA) where reactions of the (A), (B), and (C) types (Figure 1) were expected to occur. Use of this solvent permitted reactions to be carried over a wide range of temperatures, some at temperatures comparable to melt or solid phase reactions without loss of reactant mobility, control of concentration and intimacy of reactants. PPA has often been used for polycondensations since it is a reasonably good solvent for organic compounds, and is well known as a cyclization reagent (Reference 19). The anhydride nature of PPA gives it the ability to remove water as it is formed during reactions of carboxyl compounds with amines to produce amides, benzimidazoles, benzoxazoles, benzothiazoles, etc. (References 20 and 21). The acid used had a P_2O_5 equivalent of 82 to 84 per cent which is a solution of approximately 20 per cent ortho- and pyrophosphoric acids mixed with various polyphosphoric acids, mostly trimers, tetramers, pentamers and hexamers.

BBB polymers were prepared at various temperatures (Table I). Mixtures of monomers (equimolar quantities) and solvent were initially stirred at 50° to 60°C for short times to obtain homogeneity. Color changes were observed and monomers appeared to dissolve as these reaction mixtures were subsequently brought to reaction temperatures for varying lengths of time. Crude polymers obtained from cooled reaction solutions were tacky and unfilterable, and found to be very finely divided and markedly swollen as the acid solvent was removed. Yields were not quantitative since several washes and decantations in aqueous medium were required to circumvent the difficulties of filtration. This was also true for extractions with DMAC and reprecipitations from sulfuric acid. Nevertheless, the swelling disappeared during final washes of polymers with alcohol and ether so that filtrations could be conveniently performed.

Within the ranges used (Table I) concentrations of monomers in the solvent did not appear to change the nature of the reactions, although both reaction temperatures and times significantly affected degrees of polymerization. This was reflected by intrinsic viscosity determinations (Tables I and II). Reaction times ranging from 2 to 18 hours at temperatures a little over 100°C produced polymers with viscosities of 0.1 to 0.5, respectively. Reactions near 200°C resulted in 0.8 to 1.2 intrinsic viscosity polymers at comparable reaction times. These results gave indication that reaction temperatures had the greater influence upon polymer molecular weight. The fact that a reaction of one week's duration at approximately 150°C gave only 0.2 intrinsic viscosity polymer tended to support this conclusion; however this unusually low viscosity could have been due to chain degradation occurring after long exposures to the hot acid.

C. PROPERTIES OF BBB POLYMERS

Polymers prepared in the above manner were black and exhibited metallic luster. They were hard, that is, very difficult to grind. A typical pulverized sample was found to be completely amorphous by X-ray diffraction and to have a softening point higher than 450°C, the limiting temperature of the apparatus used (Reference 22).

Solutions of polymers in conc H_2SO_4, PPA, benzene sulfonic acid and methane sulfonic acid are intensely colored red. Aqueous KOH solutions are brown. No changes are observed in the IR spectra of polymers reprecipitated from any of these solvents. BBB polymers appear to be insoluble in DMF, DMAC, DMSO, cresol, tetramethylene sulfone, N-methylpyrrolidone, N,N-dimethylaniline, tetramethylurea, hexamethylphosphoramide and other more common organic solvents. Low viscosity polymers exhibit some tendencies to dissolve in perfluoroacetic acid and formic acid.

Several polymer samples were heated in the solid phase under various conditions (Table II) to detect possible changes in either IR absorption characteristics or solution viscosities. Spectral changes were not observed and intrinsic viscosities were essentially unchanged except for one case. The intrinsic viscosity of polymer sample B-4 (Table II) was increased from 0.49 to 0.60 (sample B-6) by solid phase heating under reduced pressure at 165-185°C for 114 hours. This was probably attributable to continued polymerization in the solid phase; however this was not a common finding. In one instance (Table II, sample C) the intrinsic viscosity of a room temperature dried sample (C-7) was not significantly changed by vacuum oven heating for 70 hours at 120-125°C in the solid phase and then at 50-80°C for 16 to 18 hours in conc H_2SO_4 solution, C-8. It was of interest to find that the intrinsic viscosity of this later sample was more than one and one-half times greater in benzene sulfonic acid than in H_2SO_4.

The molecular weights of polymers were not determined because of the high color intensity and corrosive nature of known BBB polymer solvents. Nevertheless it is known that useful degrees of polymerization are obtainable. This is evidenced by the fact that 0.8 intrinsic viscosity polymer possesses promising fiber-forming properties. It can be wet spun into ten-filament yarn from the acid solution.

TGA of BBB polymers gave outstanding results. Some polymer samples exhibited no weight loss up to 600°C in nitrogen (Table II). Weight losses of 12-14 per cent at 700°C in nitrogen were common with the exception of room temperature dried samples which probably contained occluded solvent. Significant weight losses began to occur as temperatures were increased above 450°C in air.

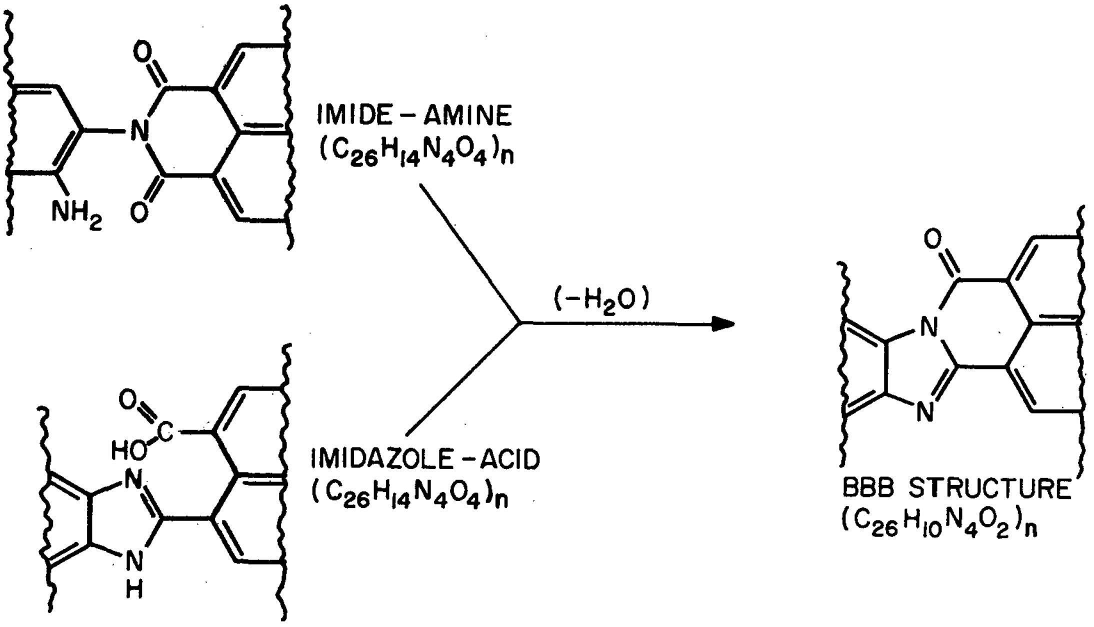
As mentioned in Section I, two of the most promising, soluble, high temperature polymers currently available are the polybenzimidazoles (PBI)(Reference 2) and the polybenzoxazoles (PBO) (Reference 1). To demonstrate the very favorable comparison of BBB polymer stability with that of PBO and PBI the best thermograms obtained in this laboratory for each of these polymers under identical conditions are shown in Figure 2. Based on such a comparison the potential of BBB polymers for high temperature applications is very high.

D. ANALYSIS OF BBB POLYMERS

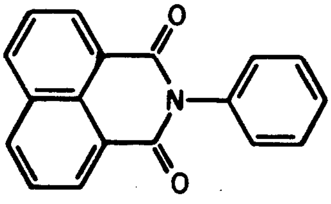
The structure of BBB polymer was established by elemental and infrared analysis of polymers and by comparisons of IR absorption characteristics with model compounds.

Elemental analysis for nitrogen by the Dumas method gave very low and unreproducible results. Ordinary Kjeldahl techniques also gave low results; however reduction of polymers prior to analysis proved to be more satisfactory. This technique has been found to be useful for analyzing heterocyclic compounds where no N-H bonds are present and N is bonded to three carbon atoms. The N values recorded in Table III are those obtained on reduced polymers by Kjeldahl techniques.

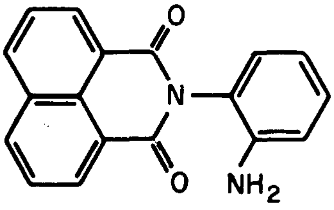
Carbon and hydrogen determinations were complicated by phosphorous contamination (approximately 2%). Assuming the phosphorous to be occluded polyphosphoric acid, or conceivably incorporated phosphate such as in end groups, C and H values found were recalculated taking into account the per cent contamination for each sample (Table III). On this basis the results of elemental analysis are in good agreement with theoretical values for the proposed BBB structure, particularly in light of the fact that all results appear sufficiently high to rule out the incompletely cyclized imide or imidazole structures shown on page 9 (see also Table III).



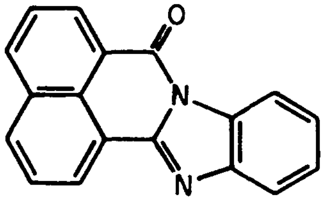
These incompletely cyclized structures were also excluded on the basis of infrared spectra. First of all the imidazole-acid has COOH and NH groups which have well known absorption characteristics near 3500 cm^{-1} and in the region of 3500 to 3300 cm^{-1}, respectively (Reference 23). Characteristic bands for these groups were not present in polymer spectra (Figure 3). Then to compare the absorption characteristics of the imide-amine type structure with the fully cyclized type, the following model compounds were synthesized:



(A)



(B)



(C)

Spectra of these compounds (Figures 4, 5, 6, and 7) all had the expected carbonyl bands prominent near 1700 cm^{-1}, but the spectra were readily distinguishable in the 1700 to 1600 cm^{-1} region. The uncyclized compounds absorbed strongly in the 1680 to 1625 cm^{-1} region characteristically for amide. Bands for amine observable in this region, were also prominent in the 3500-3300 cm^{-1} region for Model Compound (B). The spectra of the fused ring compound (C) differed greatly since they did not exhibit these strong absorption characteristics. Analytical spectra in Figure 7 illustrates this striking difference. Figure 7 also shows that the polymer spectrum resembles that of the cyclized compound (C) and does not contain the prominent peaks between 1680 and 1625 cm^{-1} which are exhibited by the uncyclized free amino compound (B).

The IR absorption characteristics furnish very strong evidence for indicating the BBB type polymer structure as exemplified by structure (C). They fully support the conclusions drawn from elemental analyses given earlier. These complementary findings are considered adequate to assign the fused-ring heterocyclic structure to the polymer.

Grinding of polymer to small particle size was extremely difficult. To obtain spectra with prominent absorption peaks exhaustive pulverization of polymer-KBr mixtures was required. Mechanically vibrated metal capsules containing metal ball pestles were used. This operation caused sample heating, and atmospheric moisture contamination occurring during subsequent pellet preparations became somewhat of a problem. Absorptions due to water tended to mask spectra in the 3500 cm^{-1} region.

III. EXPERIMENTAL

A. POLYMER SYNTHESIS

BBB polymers were prepared by equimolar solution polycondensation reactions. The reaction conditions are summarized in Table I.

TABLE I

POLYMERIZATION CONDITIONS

Reactions	M (moles)	C (moles/l)	Preheating (°C/min)	Reaction T(°C)	Cond t(hrs)	Yield (%)
A	0.02	0.26	3.3	100-20	2.0	--
B	0.02	0.40	2.0	110-30	18	--
C	0.02	0.40	2.1	200-20	3.5	90
D	0.04	0.22	0.3	180-90	20	80
E	0.02	0.08	0.6	140-50	168	60

M (moles): Moles of each monomer
C (moles/l): Combined conc of monomers in PPA
Preheating (°C/min): Approx heating rate to bring the reaction mixture from approx 50°C to reaction temp.
Yield (%): Amount of polymer recovered after DMAC extraction

The preparation of Polymer D (Table I) is given in detail as being representative of the experimental procedures employed.

1,4,5,8-Naphthalene tetracarboxylic acid (NTCA) (Aldrich Chemical Co.) was reprecipitated several times with aq HCl from aq KOH solutions following hot filtrations in the presence of activated carbon.

3,3'-Diaminobenzidene (DAB) (Narmco Research and Development Div., Whitaker Corp.) was analyzed and used as received.

Polyphosphoric acid (82-84% P_2O_5) (PPA) (Matheson Coleman and Bell) was used as received.

Poly[2,13(bisbenzimidazo(2,1-*b*:1',2'-*j*)benzo(lmn)(3,8)phenanthroline-6,9-dione)]. NTCA (11.116 g, 0.038 mole) and DAB (8.056 g, 0.038 mole) were ground under nitrogen and stirred with 350 ml of PPA near 60°C until the mixture was homogeneous (approx 10 min). With continued stirring the pot temperature was gradually (7 hrs) increased to 180°C and then maintained at 180-190°C for 20 hrs. The reaction solution was then cooled below 100°C and poured onto 4 liters of crushed ice-water mixture with stirring. After settling, the supernatant liquid was decanted, the volumn replenished with water, and the procedure repeated several times. A glass fritted siphon was used when the precipitate became finely dispersed. After repeated washings, a supernate pH of 3-4 was attained. The polymer was then filtered on a medium glass frit, transferred wet to DMAC (1 liter), slurried for 2 1/2 hrs. at 100-125°C and refiltered. The DMAC extraction was repeated and the polymer similarly treated with hot MeOH. The product was thoroughly washed with ether and dried at reduced pressure over desiccant. The yield amounted to 16.84 g (88% by weight of reactants). The product was reprecipitated from conc H_2SO_4 (3-4 liters), and 15.82 g (93%) of the polymer was recovered. Calcd for $C_{26}H_{10}N_4O_2$: C, 76.09; H, 2.46; N, 13.65.

Found: C, 72.68, 72.47; H, 3.35, 3.22; N, 13.60, 13.33.

B. POLYMER CHARACTERIZATION

Numerous polymer samples were heated in the solid phase (Table II) prior to determining viscosity, TGA and absorption characteristics. Heating was usually performed in a vacuum oven at 1-2 mm Hg in air. Some exceptions are noted in Table II.

Intrinsic Viscosities were determined on polymer samples reprecipitated from conc H_2SO_4. The data was obtained from solutions in conc H_2SO_4 or benzene sulfonic acid at 30°C using Ubbelohde dilution viscometers. Solutions were prepared and dilutions performed quantitatively. Solids determinations on solutions were not performed due to the high boiling points of the solvents. Extrapolations of the data to zero concentrations were straightforward with no polyelectrolyte effects being observed. Intrinsic viscosities are tabulated in Table II.

TGA measurements were obtained by G. F. L. Ehlers of our laboratory using a Chevenard thermobalance with 0.2 g samples. A heating rate of 150°C/hr to 900°C was employed. Determinations were made in dry nitrogen and air atmospheres. The percent weight losses at various temperatures are summarized in Table II and in Figure 2. TGA curves of PBO and PBI, also given in Figure 2, represent the best curves obtained by this laboratory for these materials using procedures identical to the above.

TABLE II

EFFECTS OF HEATING POLYMERS IN SOLID PHASE

Polymer Sample [a]	(Solid Phase)[b] T(°C)	(Solid Phase)[b] t(hrs)	[η] H_2SO_4	TGA - % Wt Loss in N_2 and Air 500°C(air)	600°C(air)	600°C(N_2)	700°C(N_2)
A - 1	-	-	0.1	-	-	-	-
A - 2	200-35	1[c]	0.1	-	-	-	-
A - 3	165-85	114	0.15	12	33	7	17
B - 4	-	-	0.49	-	-	9	21
B - 5	330-35	4[d]	-	-	-	0	14
B - 6	165-185	114	0.60	5	22	3	12
C - 7	-	-	0.80	-	-	10	25
C - 8	120-25	70	0.79[e]	-	-	0	14
D - 9	100-20	108	1.15	5	21	3	12
D - 10	165-85	114	1.15	6	22	1	12
E - 11	165-85	114	0.20	9	27	3	12

a - See Table I for polymer preparation
b - At reduced pressure (1-2 mm Hg in air) unless otherwise indicated
c - Under nitrogen
d - Under high vacuum
e - [η] = 1.29 in benzene sulfonic acid

Elemental Analyses were performed on four polymer samples. The histories of these samples are tabulated in Tables I and II and the analytical results are tabulated in Table III. The methods of analysis are discussed in Section II of the text. Model compound analyses were performed by the Analytical Branch of our laboratory and are given in Part C of this Section.

TABLE III

ELEMENTAL ANALYSIS[a,b,c]

Sample	P^d	C^e	H^e	N^f
A - 3	2.09	75.79	3.35	12.37
B - 6	1.34	73.79	3.33	13.13
D - 10	1.92	76.39	3.46	13.47
E - 11	2.27	76.71	3.34	14.73

a - Calcd for $(C_{26}H_{10}N_4O_2)_n$: C, 76.09; H, 2.46; N, 13.65
b - Calcd for $(C_{26}H_{14}N_4O_4)_n$: C, 69.95; H, 3.16; N, 12.55 (incompletely cyclized; see Section II for discussion)
c - Performed by Huffman Laboratories, Inc., Wheatridge, Colorado (see discussion Section II)
d - Residual P from PPA
e - Recalculated assuming phosphorous contamination to be due to polyphosphoric acid occlusion or incorporated phosphate
f - Kjeldahl method performed on reduced polymer (see discussion Section II)

X-ray Diffraction was performed by W. Baun of our Analytical Branch on a Philips Electronics Inc., diffraction unit by powder techniques.

Analytical Infrared Absorption Spectra were obtained by W. Crawford of the Analytical Branch of our laboratory using KBr pellet techniques on a Perkin-Elmer Corporation Grating Spectrophotometer, Model 521 for comparing spectra. Polymer samples required grinding with mechanically vibrated metal ball pestles in metal containers. Qualitative polymer spectra were obtained on a Perkin-Elmer Infrared Spectrophotometer, Model 137.

Softening Point determination was performed on an automatic Vicat-type heat-distortion and softening-range apparatus (Reference 22) in this laboratory.

Fiber-Forming Properties of polymer were determined by W. Gloor of the Fibrous Materials Division of our laboratory on laboratory scale equipment employing wet spinning techniques from a ten-filament spinnerette. Yarn spun from sulfuric acid solution into water is being evaluated by that Division.

C. SYNTHESIS OF MODEL COMPOUNDS

N-Phenylnaphthalimide was prepared from 1,8-naphthalic anhydride and aniline in ethyl alcohol according to the method of Jaubert (Reference 24). The crude product was precipitated in aq HCl and washed with hot aq Na_2CO_3 and water. Recrystallization from ethyl alcohol gave colorless needles, mp 204-205°C (Lit. mp, 202°C). (IR Spectra Figure 6).

Calcd for $C_{18}H_{11}NO_2$: C, 79.11; H, 4.06; N, 5.13.
Found: C, 78.64; H, 4.15; N, 5.10.

N(2-Aminophenyl)naphthalimide was synthesized from 1,8-naphthalic anhydride and o-phenylenediamine as reported previously (Reference 16). The product was successively extracted with ethanol and acetone. Recrystallizations from anhydrous acetone gave crystals, mp 308-311°C (dec) (Lit. mp, d. 300°C). (IR Spectra Figure 5).

Calcd for $C_{18}H_{12}N_2O_2$: C, 74.99; H, 4.20; N, 9.72.
Found: C, 74.88; H, 4.15; N, 9.67.

7H-Benzimidazo(2,1-a)benz(de)isoquinolin-7-one was prepared (a) by the method of Okazaki (Reference 16) involving intramolecular condensation of N(2-aminophenyl)naphthalimide obtained from above and (b) by direct condensation of 1,8-naphthalic anhydride with o-phenylenediamine under conditions similar to those used for polymerizations (Reference 20).

(a) N(2-aminophenyl)naphthalimide was refluxed in gl acetic acid for 16 hrs. The product was isolated and recrystallized from ethyl alcohol, mp 211-212°C (Lit. mp, 203-204°C). (IR Spectra Figure 4).

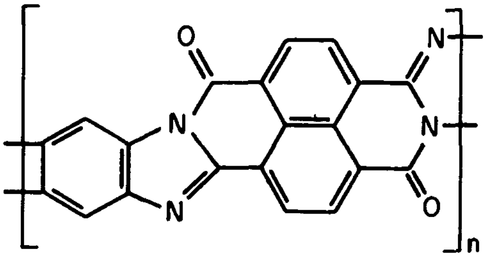
Calcd for $C_{18}H_{10}N_2O$: C, 79.99; H, 3.73; N, 10.36.
Found: C, 80.10; H, 3.85; N, 10.12.

(b) Equimolar quantities of 1,8-naphthalic anhydride and o-phenylenediamine were reacted in PPA (0.02 mole/100 ml PPA) at 160°C for 16 hrs under nitrogen. Precipitation of product in water and washing several times with water gave crude product yields of approx 70%. The product was purified by successive extractions with aq Na_2CO_3, water and ethanol followed by recrystallizations from ethanol, mp 209-211°C. Mixed melting point determinations with the product from (a) above and IR spectra confirmed the identity of these compounds.

IV. CONCLUSIONS

From the results presented in this report it is concluded that uncrosslinked, bisbenzimidazobenzophenanthroline-dione (BBB) polymers of varying D.P. can be prepared in PPA solution polycondensations by varying the time and temperature of reactions. Suitable monomers are 1,4,5,8-naphthalene tetracarboxylic acid (NTCA) and 3,3'-diaminobenzidine.

The synthesis of this soluble polymer which has sufficient molecular weight to exhibit fiber-forming properties and has adequate thermal stability to compare favorably with current high temperature polymers is significant. In somewhat broader scope, the knowledge gained has some additional importance since it describes a direct and rather well defined approach to the synthesis of more highly fused, and potentially more stable, aromatic-heterocyclic polymers. In fact the results available from investigations now in progress indicate that polymer containing ladder structure (VII) has been prepared using the techniques of BBB polymer synthesis. Although somewhat less soluble, these materials appear to be at least as stable as the BBB polymer.



(VII)

In accordance with the objective stated earlier it appears likely that suitable molecular weight BBB polymers can be prepared which will have potential as candidate materials for applications in high temperature plastics and fibrous materials areas.

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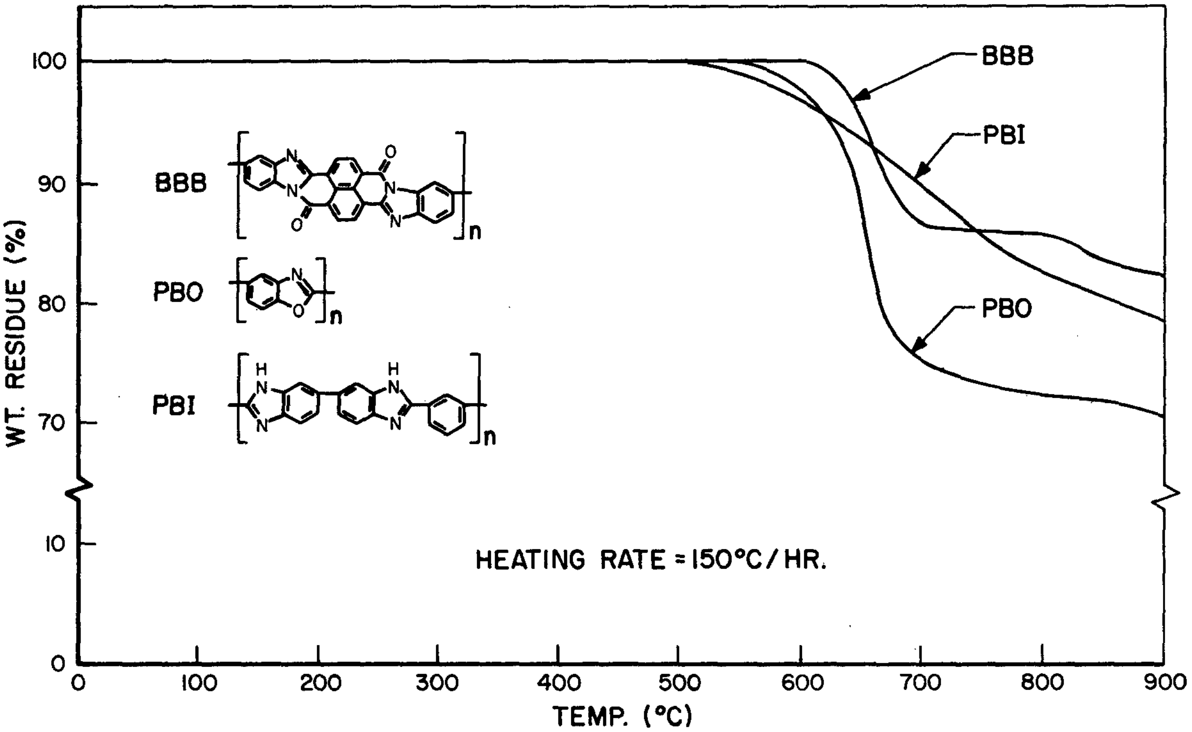

FIGURE 2 TGA Comparison Between BBB, PBO, and PBI in N_2

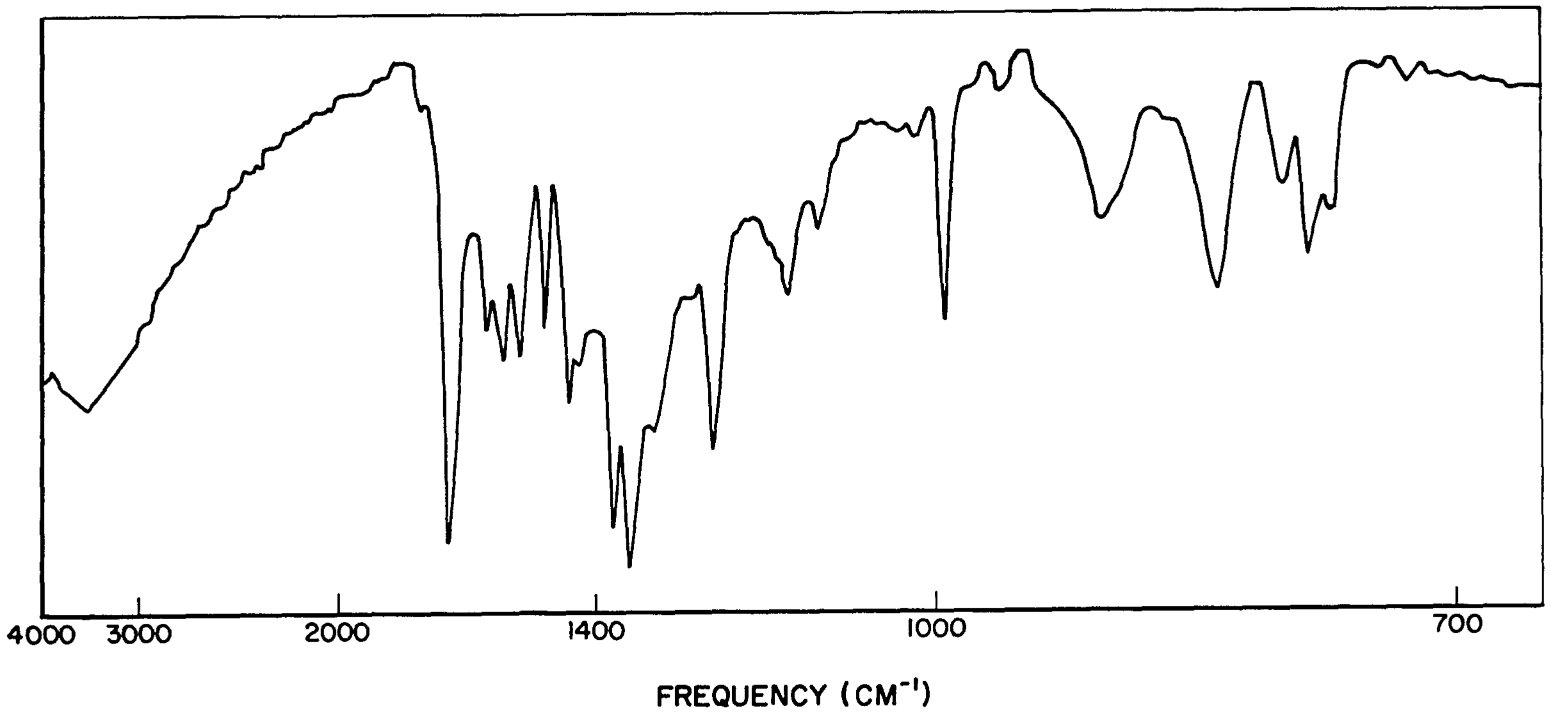

FIGURE 3 IR Spectrum of BBB Polymer

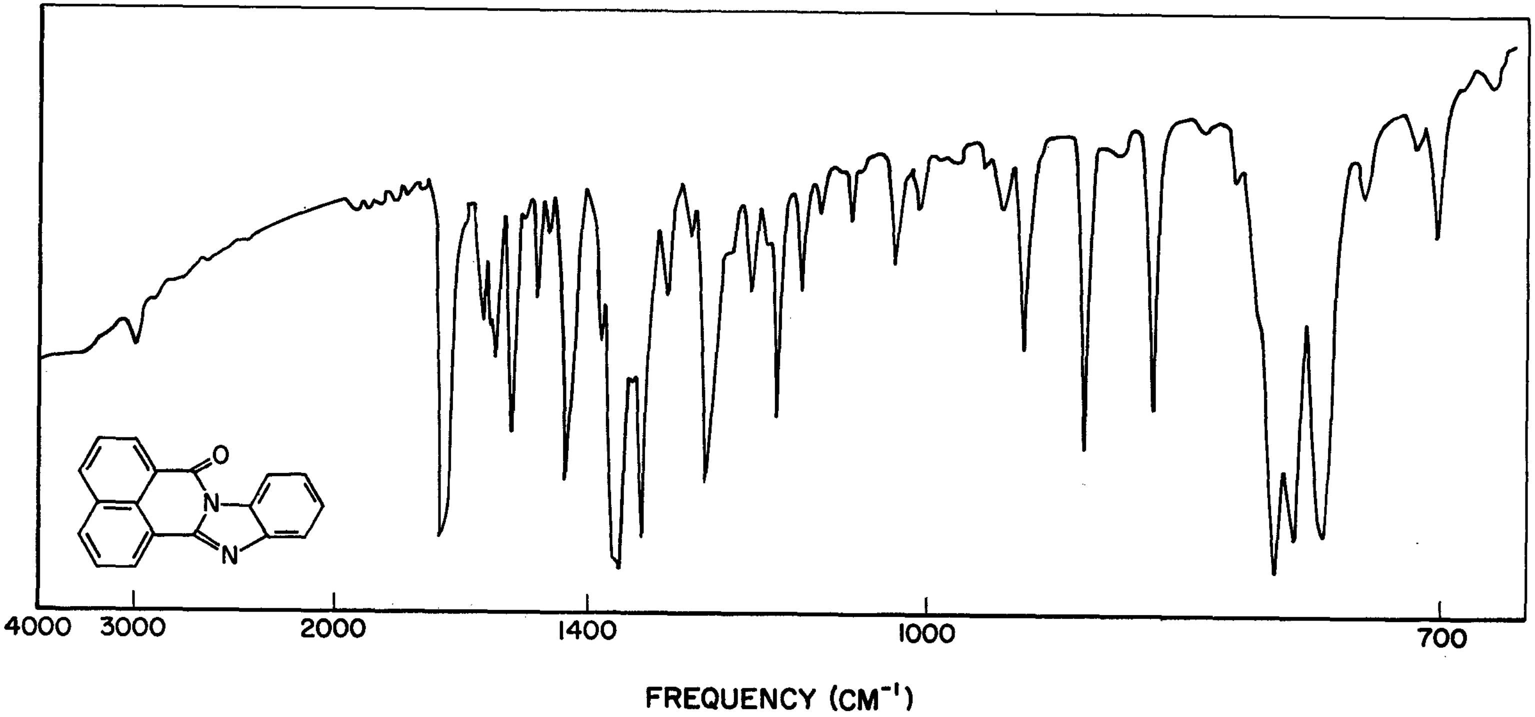

FIGURE 4 IR Spectrum of 7 H-Benzimidazo(2,1-a)benz(de)isoquinoline-7-one

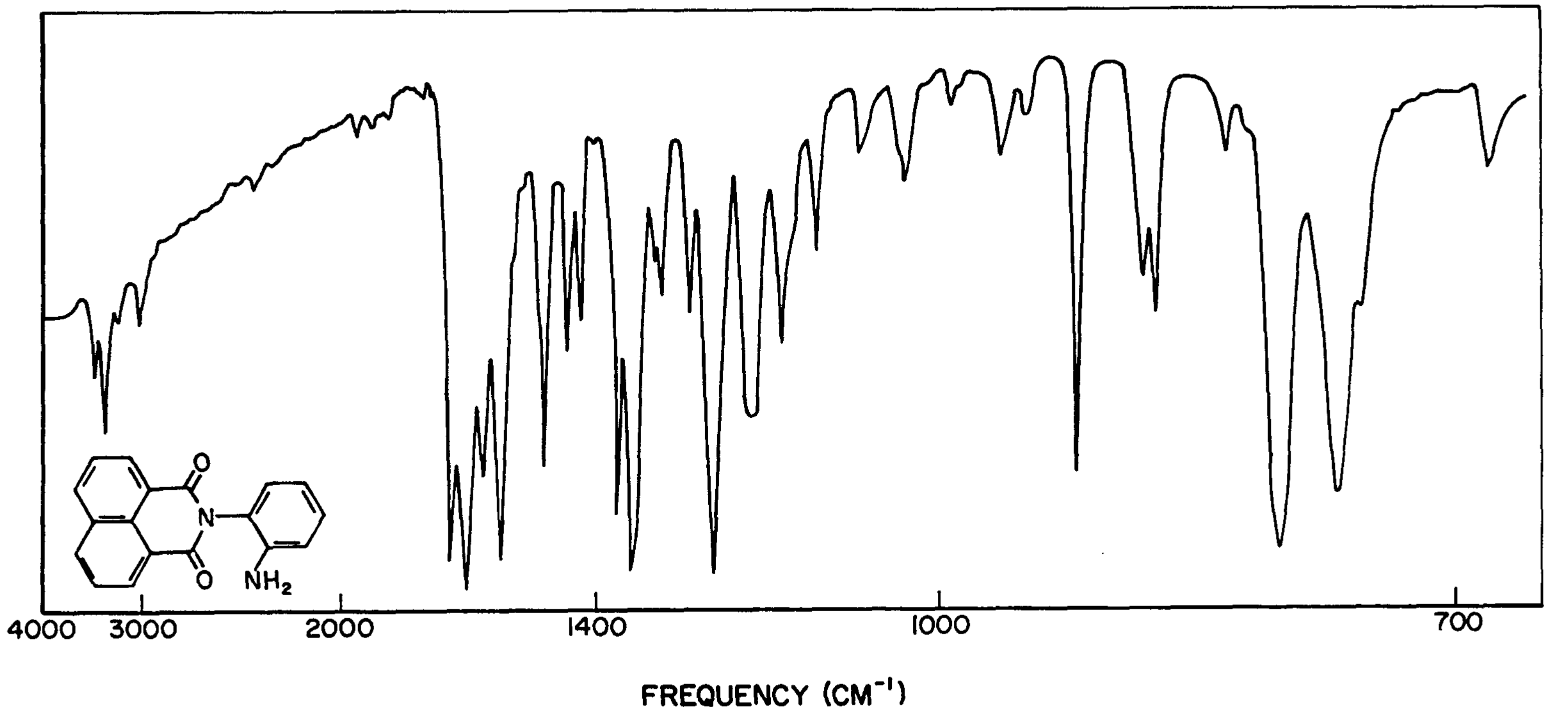

FIGURE 5 IR Spectrum of N(2-Aminophenyl)phthalimide

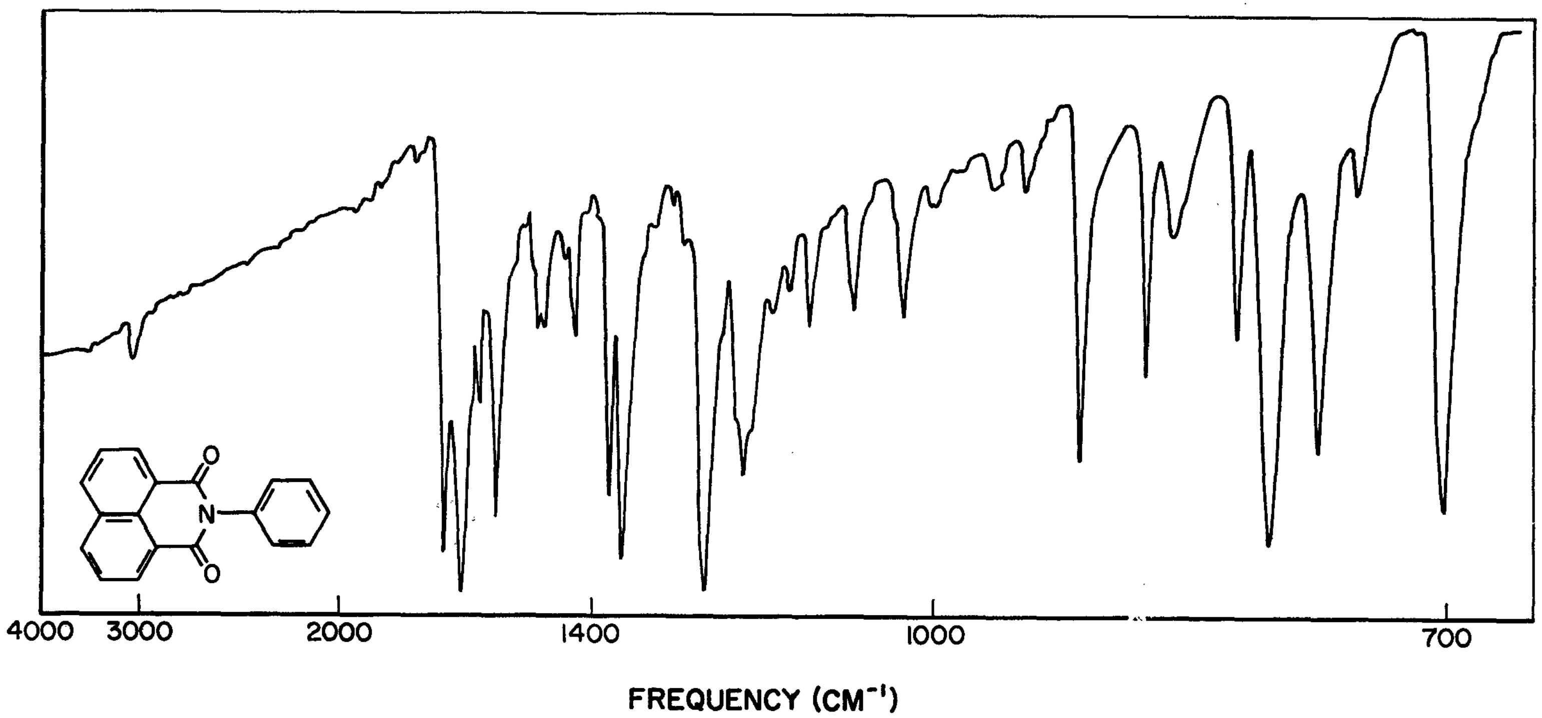

FIGURE 6 IR Spectrum of N-Phenylphthalimide

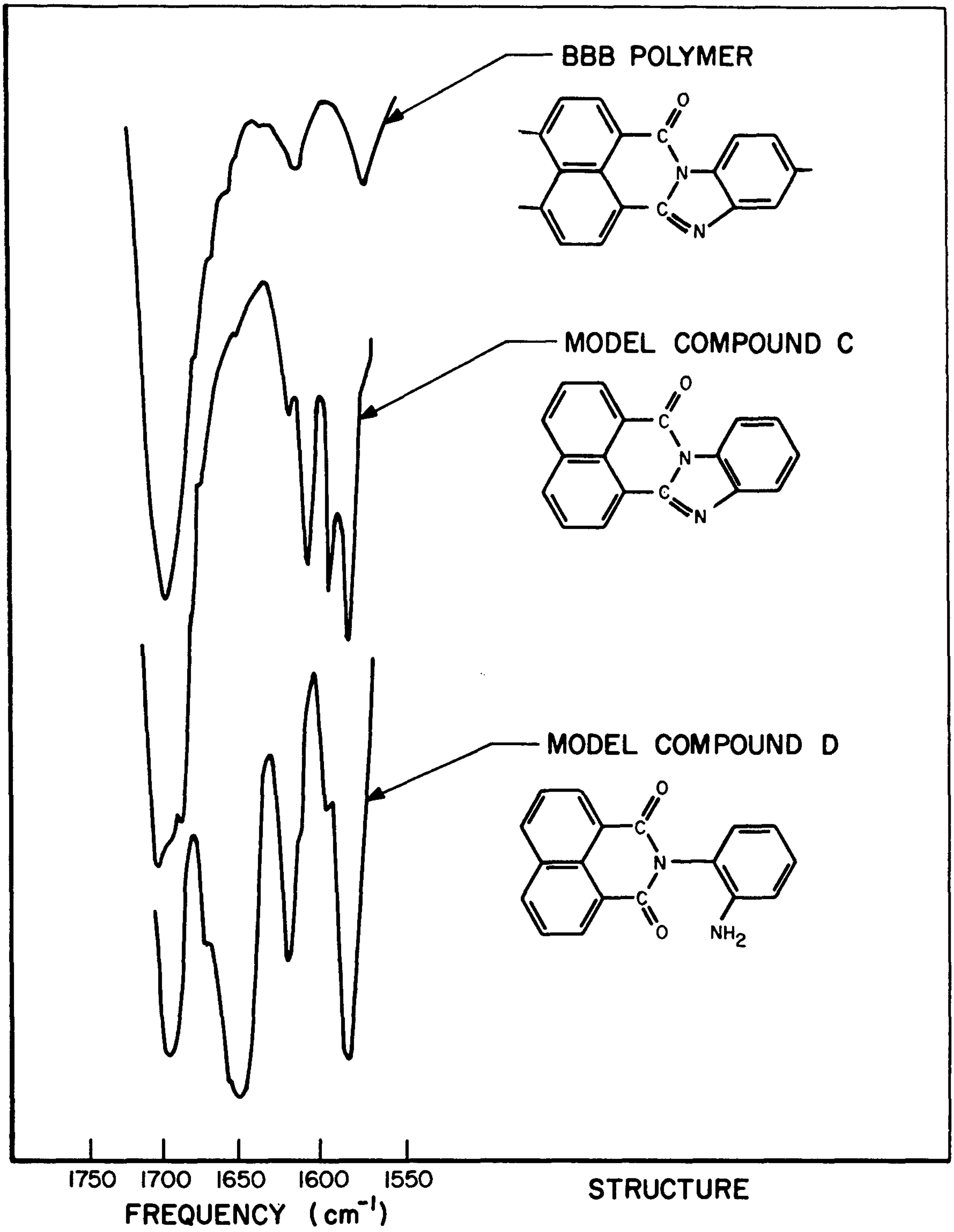

FIGURE 7 Analytical IR Spectra in the 1700 to 1600 cm $^{-1}$ Region

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13. ABSTRACT

Bisbenzimidazobenzophenanthroline-dione (BBB) Polymers have been prepared from 1,4,5,8-naphthalene tetracarboxylic acid and 3,3'-diaminobenzidine by polycondensations in polyphosphoric acid. (Polymer structure was verified by elemental and infrared analysis.) BBB polymers were found to be black and amorphous, to have high softening points and to exhibit 600°C stability in N_2 by TGA. Intrinsic viscosities ranging from 0.1 to 1.2 dl/gm in sulfuric acid were obtained, the highest viscosity polymers having been produced by reactions near 200°C. Polymers were soluble in strong acid and base and could be wet spun from acid solution.

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