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Some Recent Results on the Synthesis of Certain Aromatic Heterocyclic Polymers

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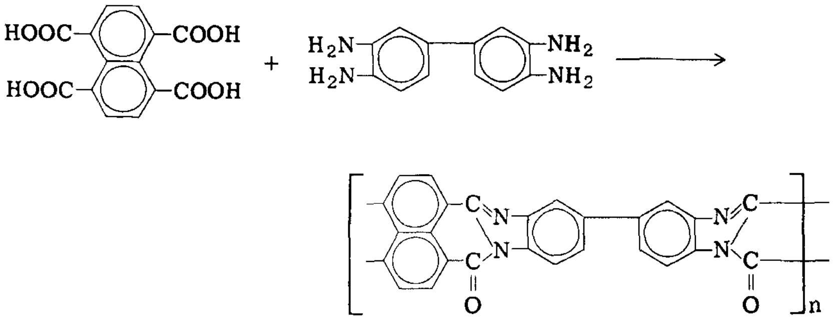
SUMMARY

Continued research on poly(bisbenzimidazobenzophenanthrolines) from one-step condensation of 1, 4, 5, 8-naphthalene tetracarboxylic (NTA) acid and 3, 3′-diaminobenzidene in polyphosphoric acid (PPA) has led to good-quality fibers with outstanding resistance to high temperatures and Fade-O-Meter aging. The condensation of 4, 5-diamino-1, 8-naphthalene dicarboxylic acid derivatives produces low molecular weight polyperimidines which have good stability. The polyimide from condensation of 1, 1′, 5, 5′-diphenyldianhydride is insoluble in all solvents tried and shows moderate thermal stability. The completely soluble ladder polymer from condensation of 1, 4, 5, 8-naphthalene tetracarboxylic acid with 1, 2, 4, 5-tetraamino benzene in polyphosphoric acid has been obtained in high molecular weight (intrinsic viscosities in methane sulfonic acid at 30°C of over 5 dl/g).

Since the early 1960s, the Air Force Materials Laboratory has been actively involved in the synthesis of a variety of aromatic heterocyclic polymers. As an outgrowth of part of this effort, in 1966, Van Deusen et al. [1] reported the synthesis of a high molecular weight poly(bisbenzimidazobenzophenanthroline) (BBB polymer) by the condensation of 1, 4, 5, 8-naphthalane tetracarboxylic acid (TCN) with 3, 3′-diaminobenzidine (DAB) in polyphosphoric acid (PPA).

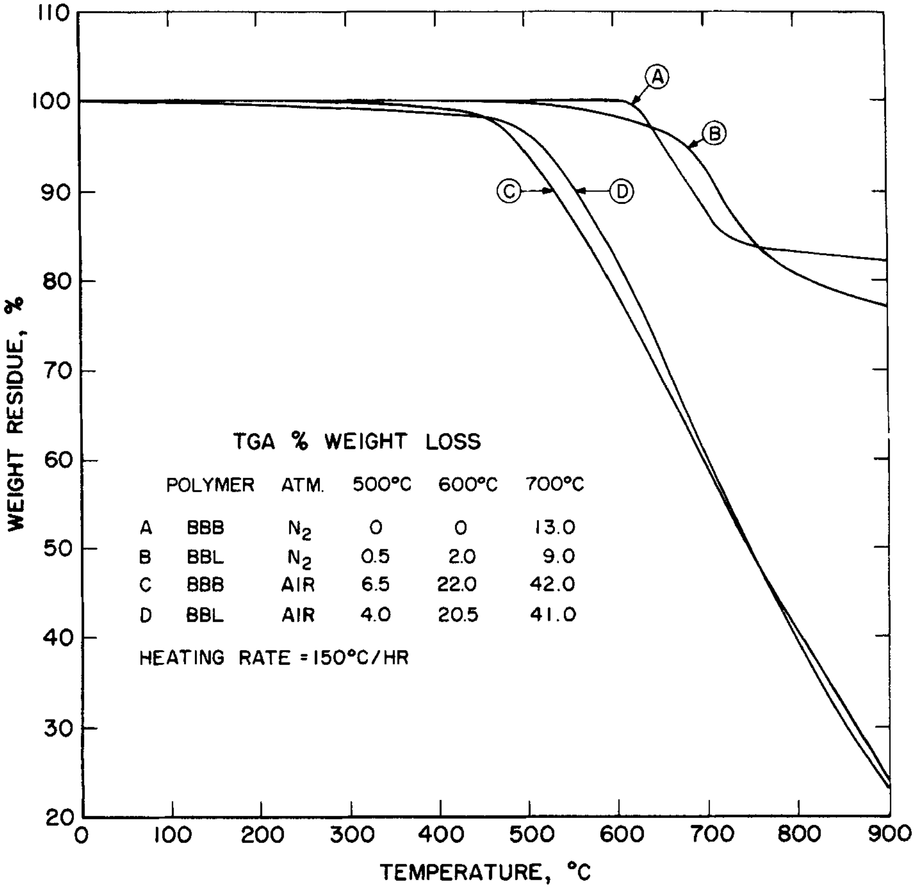


This polycondensation proceeded smoothly at temperatures near 200°C to yield a completely soluble polymer with intrinsic viscosities in concentrated H_2SO_4 up to about 1 dl/g. As shown in Fig. 1, this polymer showed very good stabilities by TGA measurements in nitrogen and air. Multifilament yarns were successfully spun by Gloor [2] from concentrated H_2SO_4 solutions. Tensile measurements on the undrawn, nonoptimized fibers showed tenacities in the range of 1 g/denier.

Since these reports a few years ago, further developments and refinements have been made in this system. In this paper I shall review these results and discuss some work conducted in closely related areas. My concluding remarks will concern the preparation of high molecular weight ladder polymers from TCN and 1, 2, 4, 5-tetraaminobenzene, which are closely related to the BBB polymer.

The work I shall describe in AFML was conducted by R. L. Van Deusen, F. E. Arnold, A. J. Sicree, O. K. Goins, and W. A. Gloor. The further work on BBB fibers was conducted at Celanese Research Corporation under AF contract, and involved contributions from A. J. Rosenthal, E. C. Chenevey, J. Steinberg, and others. The data on evolved products from the thermal degradation of BBB polymers were obtained by H. L. Friedman and H. W. Goldstein of the General Electric Company, also under AF contract.

The fact that the condensation of TCN with DAB in PPA proceeds to yield a soluble, high molecular weight polymer with no evidence of insoluble, cross-linked material was regarded as an extremely fortunate event. It had been anticipated that it would be necessary to impose some steric hindrance in the monomer structure to suppress the cross linking that would be expected from the classical condensation of pairs of tetrafunctional monomers. Indeed, the formation of insoluble products from the condensation of similar



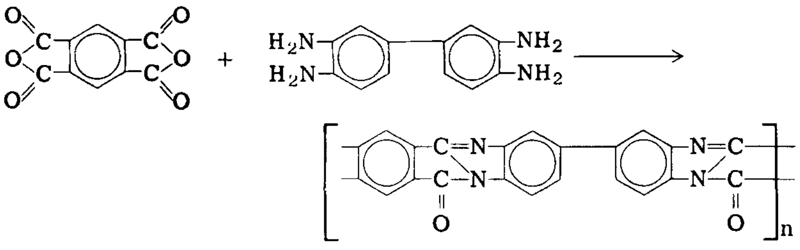
TGA % WEIGHT LOSS

	POLYMER	ATM.	500°C	600°C	700°C
A	BBB	N_2	0	0	13.0
B	BBL	N_2	0.5	2.0	9.0
C	BBB	AIR	6.5	22.0	42.0
D	BBL	AIR	4.0	20.5	41.0

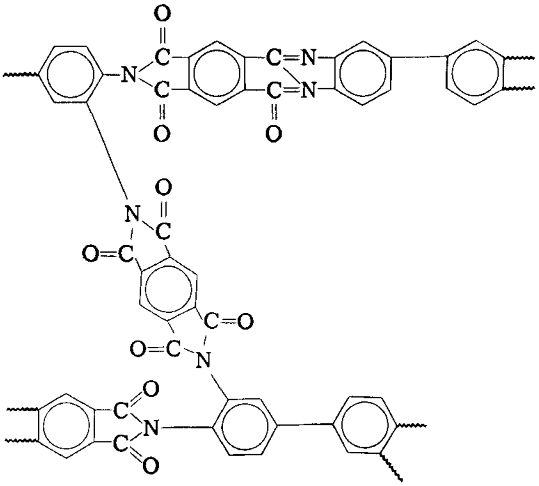
HEATING RATE = 150°C/HR

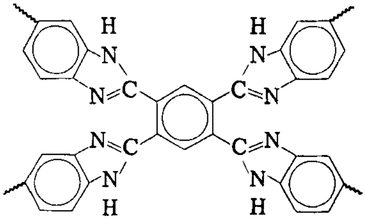
Fig. 1. Typical TGA plots of high molecular weight BBB and lower molecular weight BBL polymers measured in nitrogen and air at 150°C/hr.

monomers, e.g., pyromellitic dianhydride with DAB [3-5], is



generally ascribed to three-dimensional polymerization and cross-linked polymers. Bell and Jewell [6] and Dawans and Marvel [3] have speculated on the nature of the cross-linking process.





Possible reasons for the efficiency of linear condensation and cyclization with such low extents of branching and/or cross-linking in this particular system are:

1. The formation of a favored 6-5 fused heterocyclic ring structure, as compared with the probably less favored 5-5 ring systems in most other cases.
2. The nature of the reaction solvent (PPA), which is well known for promoting cyclization and dehydration reactions.
3. The heterogeneous nature of the reaction system, where the tetraacid is apparently relatively insoluble even at reaction temperatures around 200°C, and may be fed, therefore, at a delicately balanced rate into the reaction zone.

Which, if any, of the above factors are most important is not now known. However, the soluble, apparently linear character of the BBB polymer is a matter of fact.

The results of Van Deusen on synthesis of BBB have been successfully reproduced by several others. Improvements in molecular weight due to availability of better purified monomers and refinements in polymerization have produced polymers with intrinsic viscosities ranging up to 5.0 dl/g in concentrated H_2SO_4. Further work is underway on preparation of fibers from these higher molecular weight systems.

The better combinations of properties obtained currently are from polymers with intrinsic viscosities in the 2.5-3.5 dl/g range. The fiber is spun from concentrated H_2SO_4 solution into a 70% H_2SO_4/H_2O coagulating bath. The fiber is drawn at temperatures near 600°C. Some properties of the partially optimized fibers are shown in Table 1. The zero strength temperature of this fiber is very high, apparently above that of any reported organic fiber. The current properties of the fiber are not regarded as fully optimized and further research on the spinning and drawing of the fiber is underway.

Table 1. Typical Fiber Properties of BBB

Inherent viscosity[a]	Av. precursor tensile properties		Av. after drawing tensile properties	
	E, %	T, g/denier	E, %	T, g/denier
1.98	60	1.25	6	3.5
2.10	68	1.25	7	4.0
2.57	70	1.30	8	4.0
3.20	65	1.40	8	4.2

[a] In concentrated H_2SO_4 at 30°C.

From the utility point of view, the BBB fibers show two particularly interesting properties.

1. Samples of the fiber conditioned 1 min at various temperatures up to 800°C, then tested in tension, show very high strength retention at high temperatures. This is illustrated in Fig. 2. Some discrepancy exists between the two tests, but the best sample retained nearly 50% of its room-temperature strength at 800°C. This in terms of tenacity is about 2 g/denier at 800°C. These results suggest that this fiber may be an outstanding candidate for uses where retention of strength under exposure to very high temperatures for short times is a prime requirement. In addition, the longer term stability of this fiber at lower temperatures, i.e., 600-700°F, is very good relative to any other polymeric fibers.

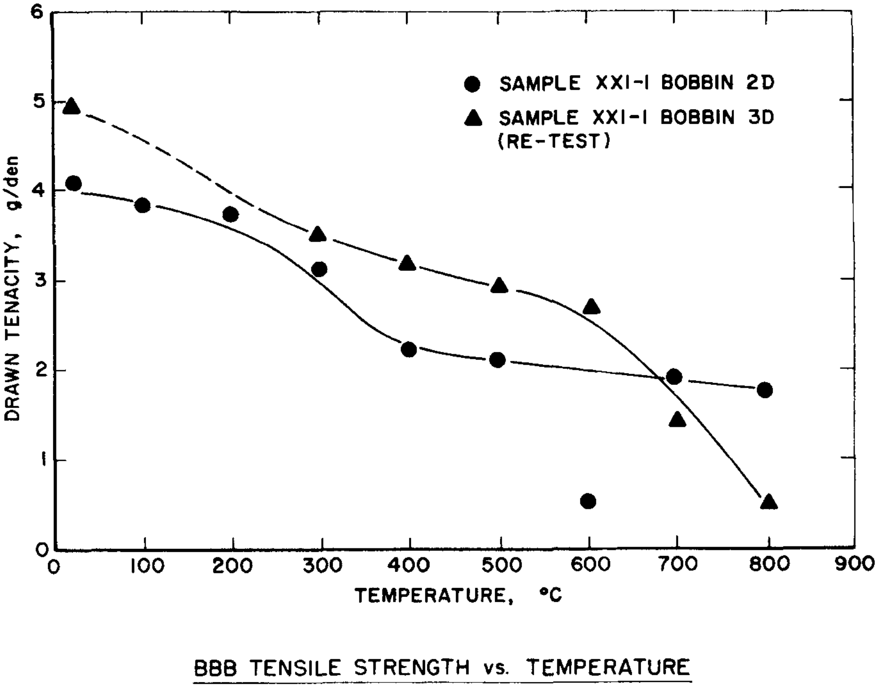


Fig. 2. Variation in tensile strength of BBB fibers after 1-min exposure at several temperatures.

2. Samples of BBB fiber exposed in a standard Atlas Fade-O-Meter test simulating outdoor aging in sunlight (the peak in intensity here occurs, however, more nearly in the 4000-Å region) show no decrease or change in properties (i.e., tenacity, elongation, and modulus) at times to at least 400 hr (the limit of testing thus far). These data are shown in Table 2. This behavior is in distinct contrast to the behavior of most other high-temperature fibers. The poly(m-phenylenebibenzimidazole) fibers are much better than most and they retain only about 62% of their tenacity after 200 hr.

The thermal degradation of BBB polymers does not proceed at a significant rate, in TGA experiments, at temperatures below 600°C. Measurements of the composition of evolved products using time-of-flight mass spectrometry to scan the effluent gases at 1-min intervals indicates a first maximum in evolved products at 720°C. The rate of temperature rise in this particular measurement is much higher than that used for normal TGA experiments, e.g., 600°C/hr versus 150°C/hr.

Table 2. Fade-O-Meter Exposure of BBB Fibers

Exposure, hr	Tenacity, g/denier	Elongation, %	Modulus, g/denier
0	3.9	3.4	163
100	3.8	3.1	166
200	4.3	3.8	157
400	4.0	3.4	170

Quantitative analysis of the products evolved at 720°C yields the data shown in Table 3. The major products are CO (40 mole %), H_2 (31.5 mole %), and H_2O (11.7 mole %). Somewhat smaller quantities of CO_2, NH_3, and HCN are evolved.

At 900°C, a second maximum occurs in evolved products. This composition is shown in Table 4. The two major components are N_2 (46.9 mole %) and H_2 (31.7 mole %).

Table 5 shows the total evolved gases to 900°C as mole % and as moles gas per repeating unit in the polymer chain.

The elimination of CO is a principal over-all reaction and likely results from homolytic cleavage of the fused ring. The H_2 likely results from hydrogen abstractions from the aromatic rings by thermally generated hydrogen atoms. Therefore, both parts of the polymer structure, the fused heterocycle and the aromatic rings,

Table 3. BBB Thermal Degradation at 720°C

Gas	Composition mole %
CO	40
H_2	31.5
H_2O	11.7
CO_2	7.3
NH_3	5.2
HCN	4.5

Table 4. BBB Thermal Degradation at 900°C

Gas	Composition mole %
N_2	46.9
H_2	31.7
HCN	4.9
H_2O	6.0
Acrylonitrile	2.7
Propene	1.9
Acetylene	1.8
Benzene	1.7
Acetonitrile	1.3
Butadiene	1.0

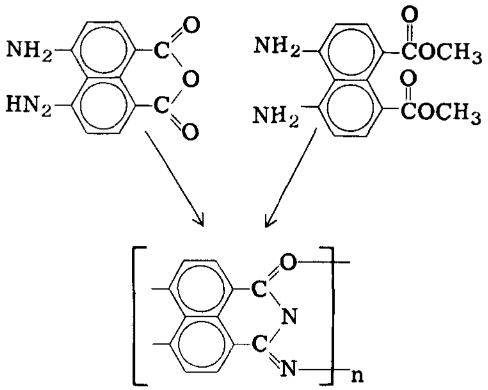
Table 5. BBB Thermal Degradation: Total Gas Evolved

Gas	Mole %	Moles gas/ repeat unit
CO	32.4	1.36
H_2	31.5	1.32
H_2O	10.6	0.45
N_2	8.8	0.37
CO_2	6.0	0.25
HCN	4.5	0.19
NH_3	4.2	0.18

appear to be contributing significantly to the over-all decomposition reaction.

The average polymer repeating unit appears to lose essentially all the oxygen but only about one forth of the nitrogen. This may indicate that some fused nitrogen-containing heterocyclic structure persists at these extreme temperatures.

In work conducted on systems related to the BBB structures, a polyperimidine has been prepared by the PPA condensation of AB monomers [7] based on naphthalene:



The A-A, B-B reaction based on the tetraamino naphthalene and TCN was attempted but with no positive results. This is believed due to the difficulties in preparing and reacting the unstable naphthalene tetraamine. Of the two reactions shown above, the polycondensation of the diester-diamino monomer gives better results than the anhydride-diamine. From the diester-diamine low molecular weight polymers (inherent viscosities 0. 2 to 0. 3 dl/g) were obtained. These gave the correct analysis and spectra for the proposed polymer structure. Despite the low molecular weights, the stability of the polymer was quite reasonable, as indicated by the TGA data in Fig. 3. In nitrogen, the onset of weight loss was ca. 600°C, and in air the values were between 450 and 500°C.

Attempts have been made to prepare the 7-5 fused heterocyclic ring system by the condensation of 2, 2′, 6, 6′-diphenyldianhydride and DAB. However, low molecular weight polymers with evidence of incomplete cyclization were obtained. They demonstrated early weight losses in TGA. It was found that under the reaction conditions, the diphenyldianhydride undergoes decarboxylation to form the fluorenone monoanhydride. This material was isolated and identified [8].

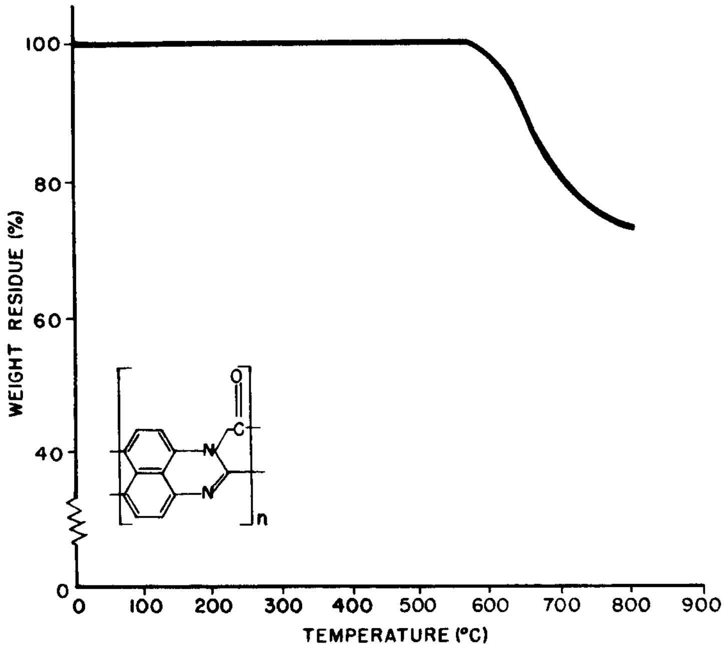
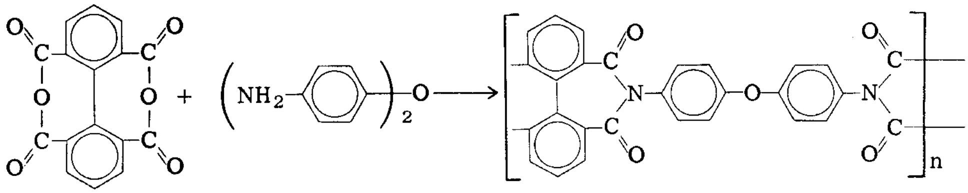


Fig. 3. TGA plot of a polyperimidine from condensation of the dimethyl ester of 4, 5-diaminonaphthalene-1, 8-dicarboxylic acid in nitrogen at 150°C/hr.

Polyimides were prepared by the DMAC low-temperature condensation of the diphenyldianhydride with oxydianiline or m-phenylenediamine [8]:



The polyamic acid was cast as a film and heated to effect cyclization to the imide. The imides were insoluble in the usual solvents. The stability of the oxydianiline system in nitrogen is illustrated in Fig. 4. The rather slow weight loss beginning around 300°C could indicate that residual solvent is present or perhaps that cyclization was not complete. The loss in weight is relatively small at temperatures of 400°C, where the total weight loss was less than 5%.

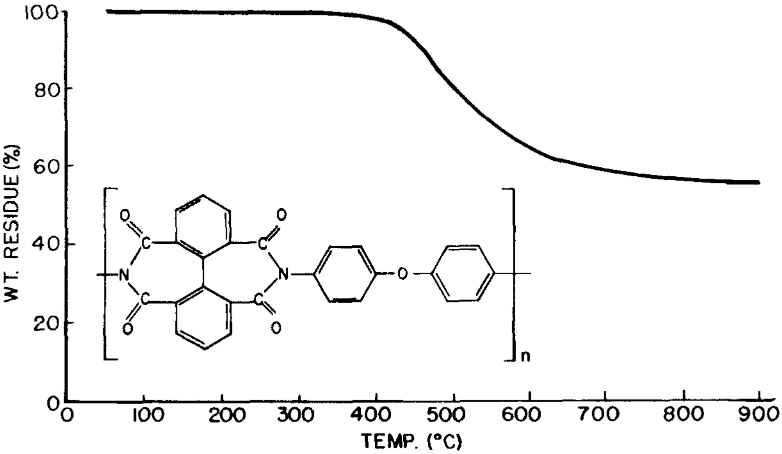


Fig. 4. TGA plot of a polyimide from the condensation of 1, 1′, 5, 5′-diphenyldianhydride with 4, 4′-diaminodiphenylether in nitrogen at 150°C/hr.

The final portion of work I wish to discuss concerns recent attempts to prepare high molecular weight ladder polymers based on the condensation of TCN with 1, 2, 4, 5-tetraaminobenzene (TAB).

This ladder polymer is termed BBL, because of its close analogy to BBB. Earlier attempts with this system had been with TCN and the tetrahydrochloride salt of TAB. Typical results obtained from this were polymers ranging in inherent viscosity to about 1 dl/g. Infrared indicated some proportion of uncyclized units.

More recently using the free tetramine rather than the hydrochloride salt it has been possible to prepare apparently very highly cyclized, high molecular weight BBL. Intrinsic viscosities of these polymers range up to 5.0 dl/g in methane sulfonic acid.

The preliminary information on structure, i.e., elemental analysis and infrared, are quite consistent with the fully cyclized BBL structure; however, further investigation will be required to adequately confirm this preliminary observation. This work is now in progress.

Preliminary examination of the solubility characteristics of this BBL indicate that compared with BBB, it is less soluble; i.e., the polymer will dissolve in good solvents such as methane sulfonic acid in concentrations generally less than about 5%. This is a characteristic of the poor solubility of the polymer, however, and not an indication of cross-linked material, since at these and lower concentrations whole samples are completely soluble.

Even at these low concentrations, the viscosity of the solutions is extremely high.

Recently, some first attempts were made at spinning fibers of this BBL. Fiber forming was possible and gave results similar to the first results on unoptimized, undrawn BBB. Detailed examinations are now underway.

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