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THE FORMATION AND PROPERTIES OF A CLASS OF HIGHLY CONDENSED AROMATIC-HETEROCYCLIC POLYMERS

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TECHNICAL REPORT AFML-TR-66-373

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AIR FORCE SYSTEMS COMMAND
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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, 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 1965 to June 1966. The manuscript was released by the author in November 1966 for publication as an RTD technical report.

The authors gratefully acknowledge the contributions of Drs. W. E. Gibbs and T. E. Helminiak in discussing technical aspects of the work.

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

This technical report has been reviewed and is approved.

William E. Gibbs

WILLIAM E. GIBBS
Chief, Polymer Branch
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ABSTRACT

Thermally stable polymers, the polybenzimidazobenzophenanthrolines, were synthesized from 1,4,5,8-naphthalene tetracarboxylic acid (NTCA) and aromatic tetraamines. Polycondensations of NTCA with both 3,3'-diaminobenzidene (DAB) and 1,2,4,5-tetraaminobenzene tetrahydrochloride (TAB) in polyphosphoric acid gave soluble polymers which exhibited thermal stabilities near 600°C under nitrogen and near 500°C in air. Although these polycondensates were found to possess the highly fused benzimidazobenzophenanthroline structure by infrared and elemental analysis, they are soluble in a few strong acids and bases. Polymers derived from DAB could be prepared which had intrinsic viscosities in the range of 1 to 2 in sulfuric acid, and these were found to be fiber forming. Low viscosity polymer from NTCA and DAB could also be prepared by solid phase polycondensation. The analogously structured ladder type polymer prepared from TAB had poorer solubility characteristics and solution viscosities greater than 1.0 dl/gm were not obtained. Analysis of both type polymers which had viscosities less than 1.0 dl/gm indicated the presence of some incompletely cyclized chain structure. It was possible to cause some advancement in the viscosities of polymers synthesized from DAB by secondary solid phase reactions.

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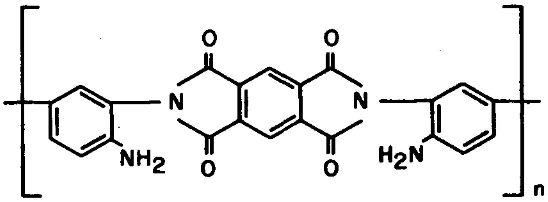
SECTION I

INTRODUCTION

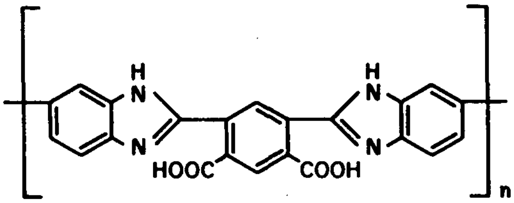
Over the past several years, a substantial number of organic polymers which exhibit excellent thermal stabilities have been discovered (References 1 and 2). Some specific examples of polymers which resist thermal decomposition in inert atmospheres in temperature regions near 500°C are the polybenzimidazoles (References 3 and 4), polyimides (References 5 and 6), polyoxadiazoles (References 7, 8, and 9), polybenzoxazoles (References 10, 11 and 12), polybenzothiazoles (References 12 and 13), polyquinoxalines (References 14, 15, 16, and 17) and polyquinazolinediones (Reference 18). Among the most highly developed of these are the polyimides (PI) and the polybenzimidazoles (PBI).

Two additional types, or classes, of polymers have been reported recently which are structurally related to both PBI and PI (References 19, 20, 21, 22 and 23). These also appear to have outstanding thermal behavior. One of these classes is referred to by three different nomenclatures: the polybenzimidazolimides (Reference 19) reported by the University of Arizona, the polyimidazopyrrolones or "pyrrones" (Reference 20) reported by the NASA Langley Research Center and the polybenzoylenebenzimidazoles (Reference 21) reported by the Buffalo Laboratory of E. I. duPont Company. The second class of polymers was reported by this Laboratory (References 22 and 23) and is referred to as the polybenzimidazobenzophenanthrolines.

Structural relationships of polybenzimidazolimides and polybenzimidazobenzophenanthrolines to PBI and PI are illustrated in Table I. Comparable structures representative of each type are given. The structural similarities become even more apparent if one considers possible intermediate structures. For example, possible prepolymer structures of polybenzimidazolimide (Table I) include:



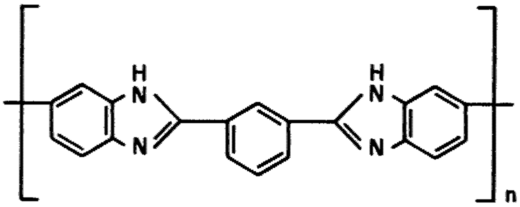
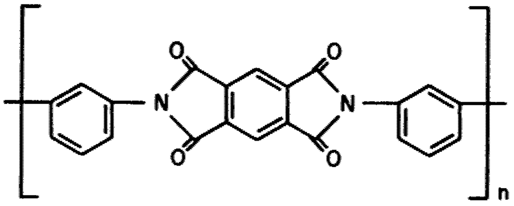
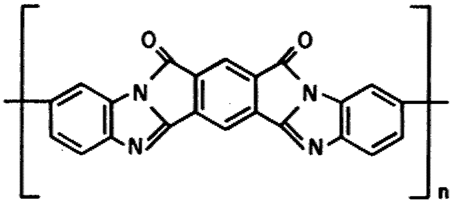
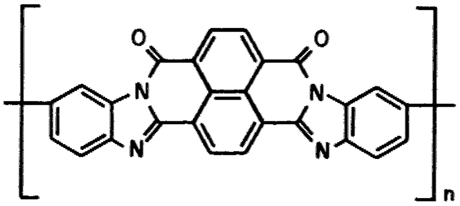
which resembles polyimide and:



which resembles polybenzimidazole. Dehydration of either intermediate could result in the structure depicted for polybenzimidazolimide (Table I). Currently available evidence indicates that the former, the polyimide-amine, is the predominant intermediate obtained experimentally (Reference 21).

TABLE I

SOME REPRESENTATIVE STRUCTURES WHICH DIFFERENTIATE BETWEEN CERTAIN CLASSES OF THERMALLY STABLE POLYMERS

Representative Structure	Type Polymer
	Polybenzimidazole
	Polyimide
	Polybenzimidazolimide
	Polybenzimidazo- benzophenanthroline

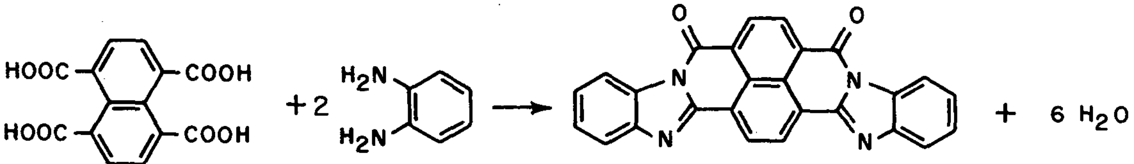
The thermal stability as compared by thermogravimetric analysis (TGA) in inert atmosphere (Figure 14) appears to be slightly better for PBI than for PI. This may reflect a comparison of inherent thermal stability between the tertiary nitrogen structure in aromatic cyclic imide (PI) and the conjugated, heterocyclic nitrogen structure in aromatic imidazole (PBI). Conversely, in an oxidative atmosphere such as air, PI appears to be slightly superior (Figure 14). This reversal in relative stability is probably the result of lower temperature oxidative decomposition processes associated with NH of PBI. Preliminary results from thermal analysis of the other two, more highly fused, types shown in Table I seem to indicate that a higher level of thermal stability may be attainable by further development of these materials. Possible advantages of these two unit structures as compared with PI and PBI are (a) the presence of oxidatively stable =CO, -N= and $-\overset{|}{N}-$ in the absence of NH and (b) the completely fused nature of all heterocyclic moieties. Although TGA comparisons are not considered to be quantitative, currently available data (References 22, 19 and 21) tend to indicate that polybenzimidazobenzophananthrolines are slightly superior to the polybenzimidazolimides. Perhaps the presence of the six membered ring heterocyclic structure found in the benzimidazobenzophenanthrolines (Table I) will prove to be more desirable for achieving thermal stability.

A discussion of the formation and the properties of polybenzimidazobenzophenanthrolines is the topic of this present report. These polymers are gaining importance as candidate materials for high temperature applications and their development for specific Air Force applications is currently underway. Since the exact nomenclature of these materials is cumbersome and not well established, the benzimidazobenzophenanthroline polymers are referred to as "BB" polymers (Reference 22). Two types are discussed: the "bis-BB type" called BBB and the analogous "BB-ladder type" called BBL.

SECTION II

DISCUSSION OF RESULTS

The chemistry of BB polymers is based upon well known chemical systems derived from reactions of various 1,8-dicarboxynaphthalene compounds with amines. Reactions of this type have been reported in the open literature (Reference 24) and are common in patent literature of the dye industry (Reference 25). Compounds such as N-phenylnaphthalimide (Reference 26), N(2-aminophenyl)naphthalimide (Reference 27) and 7H-benzimidazo(2,1-a)benz(de)isoquinolin-7-one (Reference 27) are representative of the types of chemical structures obtained (see Table V, Model Compounds I-III, respectively). Indanthrene dyes can be prepared by condensing 1,4,5,8-naphthalene tetracarboxylic acid with ortho-phenylenediamine and isolated as cis (IV) and trans isomers of bis(benzimidazo)benzophenanthroline-dione (Reference 28). Reactions of this type are analogous to those utilized to synthesize polymers described below.



(IV)

TABLE II

COMPARISONS OF SOME TYPICAL EQUIMOLAR POLYCONDENSATIONS IN PPA

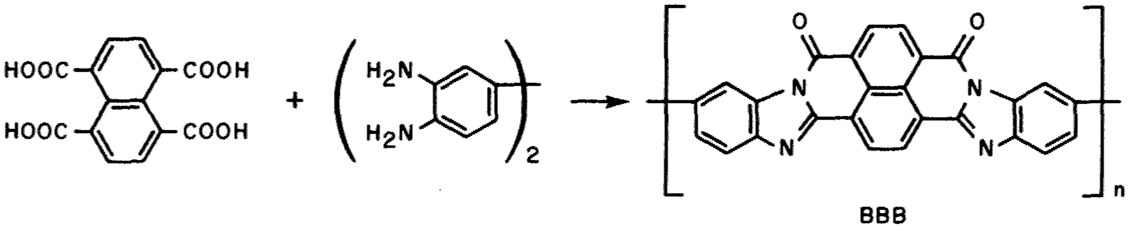
Type Reaction	Conc.[a] (m/l)	Reaction T (°C)	Conditions t (hrs)	Viscosity[b] (H_2SO_4)
BBB	0.40	110-120	18	0.57
BBL	0.20	100-130	18	0.28
BBB	0.22	180-190	20	1.35
BBL	0.18	180-190	20	0.63
BBB	0.40	200-220	3.5	0.75
BBL	0.19	200-220	4.5	0.34
BBL	0.13	190-195	24	0.90

[a] Total conc. of monomers in PPA

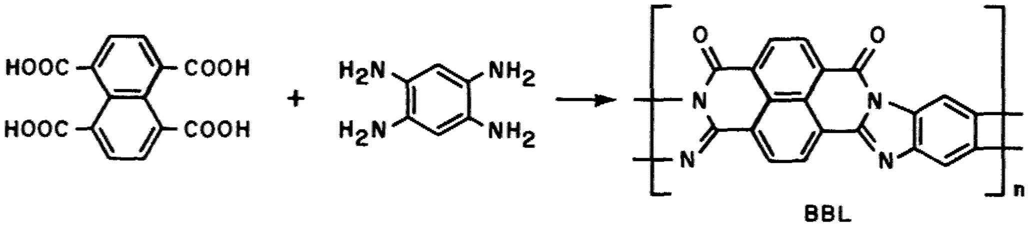
[b] η_{inh} @ 30°C; conc. BBB = 0.5g/dl, conc. BBL = 0.2g/dl.

POLYMER SYNTHESIS AND ISOLATION

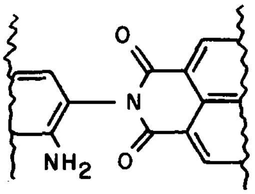
Polybenzimidazobenzophenanthrolines varying in solution viscosities were prepared in polyphosphonic acid (PPA) from reactions of 1,4,5,8-naphthalene tetracarboxylic acid with: (a) 3,3'-diaminobenzidine:



and (b) 1,2,4,5-tetraaminobenzene:

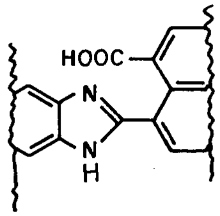


In addition to anhydrides and amides, the multistep polycondensation reactions can be expected to produce intermediate imide-amines and/or imidazole-acids:



IMIDE-AMINE

V



IMIDAZOLE-ACID

VI

The significance of these intermediate structures is discussed below in the section on INFRARED ABSORPTION CHARACTERISTICS.

BBB and BBL were obtained by slowly heating equimolar mixtures of monomers to relatively high reaction temperatures in PPA under nitrogen. For typical dilute solution BBB polycondensations (Table II) more vigorous reaction conditions tended to produce polymers with higher solution viscosities. Similar effects were noted for BBL reactions although significantly lower viscosities (approximately one-half) were found under comparable conditions. The difference in concentration of viscosity solutions (BBLs lower than BBBs due the poorer solubilities of BBLs) should not invalidate the basic relationship which is observed since inherent viscosities are good approximations of intrinsic viscosities. Nevertheless, valid comparisons of viscosities to reflect relative degrees of polymerization between BBB and BBL cannot be made without additional information concerning what effects the different molecular structures have upon the observed solution properties.

Follow-on research sponsored by this Laboratory has demonstrated the feasibility of producing higher viscosity BBB polymers than those shown in Table II by using higher monomer concentrations and more stringent controls of reaction conditions. Intrinsic viscosities approaching 3.0 have been obtained for BBB (Reference 29).

BBB with solution viscosities less than 0.5 dl/g can be prepared in PPA under milder conditions. Reactions of short duration near 100°C were found to produce more readily soluble products with viscosities of 0.1 to 0.2 dl/g. The BBB monomers can be condensed in the solid phase to give low polymer (see EXPERIMENTAL section), and evidence of reactions has been observed in DMAC. In general, however, polymerizations of these types which are not expected to result in extensive reaction have not been thoroughly examined as a part of this research. Approaches to obtaining low polymers or prepolymers are, nevertheless, being investigated elsewhere under Air Force sponsorship (Reference 30). Obtaining suitable prepolymers which can be fabricated into laminated composites for evaluation at elevated temperatures is an objective of this research.

The recoveries in both the isolations from PPA reaction mixtures and the purifications by reprecipitations were difficult due to the swollen nature of the polymers. The precipitates were neutralized in aqueous media and usually collected by centrifugation since filtration proved to be extremely slow. As a result significant losses were incurred by decanting supernates between sucessive operations, and in practice polymer yields after one reprecipitation were of the order of 60 to 90 percent. The lowest yields were obtained on BBL where it was not unusual to obtain an estimated 2 to 15 percent of insoluble products from the polymerizations. On the contrary, insolubles from BBB polymerizations were seldom observed.

Final collections of neutralized polymer were generally made by filtration. Subsequent extractions with nonaqueous liquids such as methanol and ether, respectively, caused pronounced shrinking, although DMAC extractions of water wet polymer did not produce this effect. Polymer was found to be noncrystalline and surprisingly dense. Solids sometimes exhibited a metallic luster and BBB yarn spun from sulfuric acid also tended to give this appearance (Reference 31).

POLYMER PROPERTIES IN SOLUTION

Finely ground powders of polymer were black, although acid solutions were intensely colored red with BBL being a lighter shade than BBB. In aqueous alkali polymer solutions appeared dark brown and solubility appeared to be enhanced by the addition of ammonia. Of many solvents examined BB polymers were found to be soluble in conc. H_2SO_4, PPA, methane and benzene sulfonic acids, methylene sulfate dimer, 85% H_3PO_4, conc. HNO_3 and conc. aqueous sodium or potassium hydroxide. Many common organic solvents have been examined and a list of those which do not dissolve the polymers is given in Table III. Thus far, the casting of films and the determination of molecular weights have not been accomplished due to the lack of suitable solvents. The search for solvents is continuing.

BBB polymers were more easily dissolved than BBL, but a matter of days was required to prepare H_2SO_4 solutions of 1 to 2 percent at room temperature. BBB solutions of 5 to 10 percent were obtainable by heating, but were extremely viscous, and unfilterable by ordinary techniques. Concentrations of this magnitude were utilized for wet spinning of the polymer (Reference 31), but filtering under pressure was required.

Polymers have been reprecipitated from all of the solvents found to dissolve them and then examined spectroscopically to detect evidence of possible decomposition or alteration in structure. Thus far changes have not been observed. For example, no infrared absorption changes were noted for: a sample of BBB reprecipitated from conc. HNO_3 at room temperature; a sample of BBL reprecipitated from 15 to 20 M KOH after heating near 100°C for several hours; a sample of BBB reprecipitated from conc. H_2SO_4 after heating to 70 to 80°C for approximately 16 hours. The solution viscosity of this later sample was essentially unaffected (i.e., $[\eta] = 0.80$ before, and 0.79 after the heating in H_2SO_4). The BB polymers were routinely extracted in boiling water for many hours as a means of removing impurities and no evidence of hydrolysis was observed.

Low viscosity BBB polymers were prepared under relatively mild reaction conditions and their inherent viscosities found to be affected to some extent by polymer sample treatment. For example, a reprecipitated BBB polymer sample dried for a few hours near 100°C at reduced pressure had an inherent viscosity (0.5 g/dl in H_2SO_4) of 0.12. Another sample of this polymer heated under reduced pressure for 114 hours at 165 to 175°C gave 0.15. Similarly a polymer sample dried at 135 to 145°C for 65 hours at reduced pressure had an inherent viscosity of 0.18 and this was advanced to 0.24 by more vigorous heating under nitrogen, 18 hours at 275 to 290°C followed by five and one-half hours at 300 to 335°C. These small increases in determined values could have resulted from chain extension, although, the removal of water, either strongly absorbed or generated from some continued intramolecular cyclization, could have been a contributing factor. Subsequently, an unreprecipitated portion of the 0.12 polymer from above was subjected to secondary reaction in PPA for four hours at 210 to 240°C. Approximately one-half of the recovered product was found to be insoluble, probably indicating that further reaction had taken place to produce a network structure. The soluble portion, reprecipitated and dried 24 hours near 200°C, was found to have an inherent viscosity of 0.29. This was a significant increase from the original value of 0.12 and indicative of chain extension.

TABLE III

SOME NON-SOLVENTS FOR BB POLYMERS

dimethylformamide	gl. acetic acid
dimethylacetamide	perfluoroacetic acid
N,N-dimethylaniline	88% formic acid
tetramethylurea	conc. hydrochloric acid
hexamethylphosphoramide	phenol
N-methylpyrrolidone	m-cresol
N-methylformamide	methyl alcohol
N-methylacetamide	glycerine
dimethylsulfoxide	ether
dimethylsulfone	acetone
diphenylsulfone	methylethyl ketone
sulfolane	ethyl acetate
dixylyl sulfone	pyridine
benzene	N,N-dimethylpyridine
toluene	N-methylthiomorpholine-1,1-dioxide
dioxane	tetrahydrofuran

A qualitative comparison of infrared spectra (Figures 4 to 8) indicates that absorptions in the regions of 5.6 to 5.7 tend to disappear in the polymer subjected to solid phase reaction (see Figures 5 and 6). The insoluble polymer (Figure 8), presumably cross-linked as a result of the secondary PPA reaction, also appears to show this tendency (see Figures 4, 7 and 8). The particular absorptions mentioned are believed to be associated with incomplete cyclization as discussed more fully in the following section on INFRARED ABSORPTION CHARACTERISTICS. These results lead to the tentative conclusion that secondary reactions on low polymer cause chain extension to occur with some concurrent cyclization (i.e., in solid phase) or cross-linking (i.e., in PPA) at the incompletely cyclized chain sites.

During the course of these investigations, some increases in viscosities were observed to occur as a result of polymer reprecipitations in concentrated aqueous alkali or extractions of polymer with dilute aqueous alkali. Apparently strong base tended to remove some lower molecular materials which were carried through H_2SO_4 reprecipitations. Extracted substances were not identified since working quantities were small; however, the absence of changes in polymer spectra after this treatment (see Figures 4 and 5) suggests that any extracted substances were of similar structure.

The occurence of linear polycondensation by thermal dehydration in the solid phase was further established by heating an equimolar mixture of monomers under nitrogen. By increasing the temperature of this mixture at a rate of approximately five degrees per minute, water evolution was visually observed above 150°C as a condensate on unheated walls of the reaction apparatus. After continued heating to 290°C and maintaining this temperature for four hours, the reaction mixture was cooled under nitrogen, dissolved in sulfuric acid and reprecipitated in water. After drying near 100°C, the product was finely ground and reheated for 72 hours at approximately 250°C. This was identified as low viscosity (0.22) BBB by IR and found to exhibit only a three percent weight loss at 600°C by TGA under nitrogen. The occurrence of intramolecular cyclization by thermal dehydrolysis was thus established by these results. Since no evidence of melting or fusing was apparent it was assumed that solid phase polymerization had occurred.

In one instance, we obtained low viscosity BBB polymer unexpectedly. An equimolar PPA reaction at 140 to 150°C was allowed to run for an extended period (168 hours) under nitrogen in a pyrex flask. Etching of the flask occurred during the reaction. The reprecipitated polymer had an intrinsic viscosity of only 0.20 and analyzed approximately one percent high for nitrogen. Subsequent solid phase reaction at 310 to 312°C (4 hrs) produced insoluble polymer. These results were inconsistent and possibly due to an unusual chain termination or chain cleavage caused by impurities leached from the reaction vessel. Further, after a secondary reaction in PPA the inherent viscosity was found to be 0.22, essentially unchanged. It seemed reasonable to assume that impurities in the initial polycondensation rendered this polymer incapable of linear chain extension. Nevertheless, the thermal stability for this product was not poor (3% wt. loss in N_2 at 600°C by TGA).

It is evident that follow-on research will be required to explain more fully the nature of low viscosity BBB polymers. Currently Air Force sponsored research directed toward the synthesis of suitable prepolymers for the fabrication of test composites is under way. This program should produce valuable information concerning the synthesis and properties of low viscosity BBB polymers.

High viscosity BBB polymers with intrinsic viscosities near one or above (Table II) appeared to have cyclized structure, as discussed in the following sections on INFRARED ABSORPTION CHARACTERISTICS and POLYMER COMPOSITION. These have also been found to undergo chain extension in the solid phase to give higher intrinsic viscosities as shown in Table IV. The 0.49 viscosity polymer (Table IV) exhibited an overall two fold increase in viscosity which was comparable to the results obtained for lower viscosity polymer discussed above. The higher molecular weight polymers did not appear to be affected to this great an extent. As evidenced in Table IV the intrinsic viscosity of BBB appears to be higher in benzene sulfonic acid than in sulfuric acid.

Polymers listed in Table IV and others with viscosities up to 2.5 (Reference 29) have been spun into multifilament yarn under a separate Air Force investigation primarily oriented toward fibrous materials applications. Currently tenacities above 3 gms/denier have been obtained on these fibers spun from H_2SO_4 solutions and drawn at temperatures exceeding 1000°F. Research on high viscosity BBB is continuing in this and in other applications areas.

BBL polymer viscosities were found to be significantly lower than those found for BBBs prepared under similar conditions (Table II). The limited solubility of more highly fused BBL (less than 0.5 g/dl) has thus far precluded an examination of secondary reaction effects. The inherent viscosities listed in Table II for BBL polymers were measured on solutions of near maximum room temperature concentrations attainable after several days of stirring in sulfuric acid. In fact the BBL polymer prepared at 200 to 220°C (Table II) required special attention in order to obtain a solution of the desired concentration for comparison with other BBL viscosities. This polymer was originally reprecipitated from a large excess of sulfuric acid,

TABLE IV

EFFECTS OF SOLID PHASE HEATING (IN VACUO) UPON INTRINSIC VISCOSITIES OF BBB POLYMERS[a]

100 - 120°C 16 hrs. (or more)	165 - 185°C 114 hrs.	300 - 350°C 4 - 5 hrs.
0.49	0.60	1.01
0.79[c]	-	1.03[b]
-	1.15	1.43

a. Reppt'd from H_2SO_4 prior to $[\eta]$ detn. in H_2SO_4(30°C).

b. 36 hrs. at 200°C (N_2).

c. $[\eta]$ in benzene sulfonic acid = 1.29.

but could not be completely redissolved at a concentration of 0.1 g/dl after stirring for two weeks at room temperature followed by two days at 65°C. A small amount of insoluble material was detected upon filtration. Following the suggestion of a fellow worker (Reference 32), a 0.2 g/dl solution of this BBL was finally obtained by taking advantage of the fact that BB polymers are swollen when reprecipitated in aqueous media. Thus in this instance the swollen polymer was not washed with alcohol and ether to remove water in the usual manner. Instead the wet sample was placed in a freeze drying apparatus and residual water was sublimed off below its freezing point under reduced pressure. Apparently this procedure did not permit shrinkage since the resulting sample appeared to be more finely divided than previously obtained samples which had been pulverized to reduce particle size. It was soluble at a concentration of 0.2 g/dl and the inherent viscosity found to be 0.34 dl/g.

Increasing solvent temperatures (i.e., 80° to 100°C) also appeared to favor the solubilities of BBL polymers. Nevertheless, the difficulties associated with avoiding small amounts of precipitation during slow filtrations and hot transfers of viscous solutions rendered high temperature viscosity determinations unattractive and beyond the scope of this present investigation. Future consideration may be given to high temperature techniques, particularily if better BBL solvents are not discovered.

INFRARED ABSORPTION CHARACTERISTICS

Reasonably good IR spectra of polymers samples were difficult to obtain. The potassium bromide pellet technique gave the best results, but this required mechanical grinding of KBr-polymer mixtures in metal capsules for several minutes to pulverize the dense solids. Long grinding periods resulted in temperature increases which in turn led to moisture condensation and the appearance of large OH bands below 3 μ in spectra. This could not be avoided without sacrificing resolution and even so, the resolution of polymer spectra was less than desired for confidently ruling out the possible presence of low intensity absorptions.

We examined spectra of high viscosity BBB polymers (i.e., intrinsic viscosity greater than 1.0) and made comparisons with spectra of Model Compounds I-III. Our findings were then related to the spectra of lower viscosity BBB and BBL polymers. References to common absorption characteristics were taken from well known works (References 33, 34, and 35).

TABLE V

COMPARISON OF IR ABSORPTION CHARACTERISTICS IN REGIONS BETWEEN 3 AND 8 MICRONS

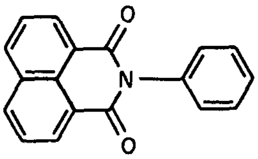
Micron Region	BBB $\eta > 1.0$	Model I	Model II	Model III	Acid Monomer	BBB $\eta < 0.5$
3.0 - 3.1	-	-	XX(X) (X)	-	-	-
3.3 - 3.5	-	-	-	-	XXX	(?)
5.6 - 5.7	-	(X) (X)	(?)	-	-	XX^e
5.8	-	-	-	-	X^e	X^e
5.9	5.88-5.92	X	X	X	X^e	X
6.0 - 6.1	-	M	M	-	-	-
6.2	6.18-6.22	X(X?)	XX	XX	-	X
6.3	6.32-6.35	X(X?)	X(X?)	XX	X	X
6.4 - 6.5	6.45-6.53	-	-	X	X	X
6.6 - 7.0	6.67-6.69 6.87-6.90 6.96-7.00	XXX X(X)	XXX XXX (X)	XXX (X)	X	XXX
7.3	7.25-7.33	X	X	X	X	X
7.4	7.38-7.42	X	X	X	-	X
7.5	-	-	-	X	-	-
7.6	7.59-7.67	-	X	X	X	X
7.7	-	(X?)	X	-	-	-
7.8	-	(X)	-	X	-	(X?)
7.9	-	(X)	X	-	-	-
8.0	-	-	-	X	-	-
8.1	8.08-8.11	X	X	X	-	X

X - Single absorption discernible in the micron range specified for BBB ($\eta > 1.0$)
(X) - Relatively small absorption
(?) - Absorption questionable (very poor resolution)
e - Result of band splitting
M - Multiple peak (see discussion)

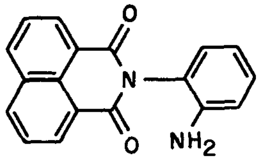
TABLE V (Cont'd)

Model Compounds I — III (References 27, 26, and 22)

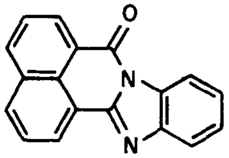
I



II



III



IR spectra of high viscosity BBB polymers (Figure 9) were found to possess absorption peaks of particular interest in the 6 to 8 μ region (Table V). Comparing these with the spectral data obtained for Model Compounds I-III (Figures 1 through 3, Table V) some evidence to substantiate the BBB cyclized structure became apparent.

The intense 5.9 μ CO absorption is found to be common; however, Table V strongly points up a significant difference between cyclized (Model III) and uncyclized (Model I and II) structures at 6.0 to 6.1 μ. Model I and II absorb intensely in this region. The BBB polymer spectrum closely resembles that of the completely cyclized Model III which does not exhibit this feature. Close examination of spectra (Figures 1 and 2) suggests that this intense 6.0 to 6.1 μ absorption (near 1655 cm^{-1}) of the uncyclized model compounds is made up of component peaks which differ as shown:

Absorption of Model Compounds I and II in the 6.0 - 6.1 μ Region (cm^{-1})

Model I	—	1658	1652	1648
Model II	1678	1663	1656	1648

This suggests that absorption at 1678 cm^{-1} may be associated with free amine. Others likely result from imide ring structure and are absent or shifted from this region in spectra of the fully fused ring structure typified by Model III.

The 6.4 to 6.5 μ region also affords evidence to indicate the completely cyclized structure for polymer. BBB and III each have a prominent absorption between 6.4 and 6.5 which is not observed in I and II. Further, in the 6.6 to 7.4 μ region polymer exhibits a single peak near 6.7 μ and a pair near 6.9 μ. Model III is similar but Model I and II spectra differ in this respect and appear more complex.

The above observations are qualitative but surely relate BBB closely with III despite the lack of quantitative proof of absorption characteristics in this complex region.

Polymer appears to contain only two absorptions in the 6.2 to 6.3 μ region where conjugated C=N may be expected to absorb. Relationships to model compounds is questionable; however, two sets of overlapping absorptions appear to be present in each model spectrum near 6.2 and 6.3 μ. These four peaks are most readily observed in the spectra of III with maxima at 6.17, 6.22 and 6.27, 6.33 μ. Comparable pairs are detectable in I and II, but it appears that these two pairs absorb simply as two unresolved bands in the polymer spectra. Prominent peaks at 7.4 and 8.1 μ are common, (Table V) but the region between these peaks where absorption characteristics of Ar-NH_2, Ar-NH- and Ar-$\overset{|}{N}$- may be expected to overlap appears to be poorly resolved in polymer. Small 5.6 and 5.7 μ peaks in Model I and possibly Model II may be due to imide carbonyl since polyimides and N,N-diphenyl-1,4,5,8-naphthalene tetracarboxyldiamide absorbs in this region (Reference 36).

Summing the available evidence, very strong support for assuming the bisbenzimidazobenzophenanthroline structure for BBB is available. It is recognized that the resolution of polymer spectra is less than desired; however within the sensitivity limits of few percent, it is tentatively concluded that high viscosity BBB polymers is fully cyclized. Supplementary evidence to support this is also found in the following sections on POLYMER COMPOSITION and THERMAL STABILITIES.

IR spectra of low viscosity BBB polymer differ from those of the high viscosity BBB polymer just discussed since they contain additional bands. Figure 11 shows a representative spectra which was obtained on a solid phase product (η_{inh} = 0.22). The 6.2, 6.3 and 6.5 μ regions of absorption are similar as would be expected, however notable differences appear: possible absorptions at 3.3—3.5 μ, a well defined peak at 5.6 μ and a shoulder absorption on the intense CO band between 5.7 and 5.8 μ. This later absorption is sometimes resolved to show splitting, i.e., 5.73 and 5.76 μ.

Considering these, the questionable absorptions above 3μ are in the region where aromatic CH and broad acid bands occur in the monomer specturm (Figure 10). Also NH absorptions could be shifted to this region if associated. The carbonyl band of monomer acid is rather wide in the 5,8 to 5.9 μ region with evidence of peaks near 5.8, 5.85 and 5.9μ — close to the 5.7 to 5.8 μ absorption found in the low viscosity BBB. Some evidence is available, then, to suggest the presence of incompletely cyclized benzimidazole-acid structure (VI). On the other hand, this evidence does not appear to account for the well defined 5.6 μ absorption which is characteristic of imide carbonyl of the type found in I and II (Reference 36). The small Model I peak (Figure 2) is split (5.60 and 5.65μ) and there is suggestion of a shoulder on the CO absorption at 5.8 μ. Also, although not conclusive, Model II spectrum (Figure 2) gives marginal evidence of weak absorption at 5.6 and 5.7 μ. Model II also has three (possibly four) small bands apparent in the 3.24 to 3.34 μ region.

From these considerations it appears that low viscosity BBB polymers are incompletely cyclized to a degree detectable by infrared. Whether the imide-amine (V), the benzimidazole-acid (VI) or both type structures are responsible for the observed results is not established, although polyimide-amine absorptions of similar type have been reported (Reference 21) for the polybenzoylenebenzimidazoles. Perhaps some consideration should also be given to the possibility that low molecular weight chains possessing anhydride end groups could contribute to detectable absorption at 5.7 and 5.8 μ.

In addition to the examination of analytical spectra it was of interest to note that absorptions in the 5.6 to 5.8 μ region of the 0.12 viscosity polymer discussed earlier (Figure 4) were no longer observable in the insoluble polymer obtained from secondary PPA reaction (Figure 8). However, the secondary reaction product which remained soluble (Figure 7) still exhibited these absorptions. Apparently the functionality responsible for reactions producing insolubility are the same structural features giving rise to 5.6 to 5.8 μ absorptions. This is consistent with the above conclusion that 5.6 and 5.8 μ absorptions are due to incomplete cyclization.

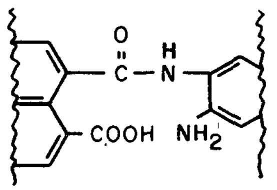
IR spectra of BBL polymers had similarities to the BBB polymers as expected. The 5.9 μ carbonyl absorption is the most striking (Figure 12) and absorptions characteristics in the regions 6.4 to 6.5, 6.6 to 6.7, 8.0 to 8.1, 10.0 to 10.1 and 13.2 to 13.6 μ appear to be essentially the same. The first mentioned is seen as a double peak in BBL but splitting of the 6.4 to 6.5 μ peak of BBB is not apparent. Shifts may be the cause for differences in the 7.0 to 7.5 μ region of BBL. Quite noticeable is the fact that BBL absorptions between 6.0 and 6.4 tend to appear as two poorly resolved peaks with maximum absorptions nearer to 6.1 and 6.4 μ than to the 6.2 and 6.3 μ absorptions found in BBB spectra. In agreement with the findings for low viscosity BBB the BBL polymer has peaks at 5.6, 5.8 and 3.4 μ which are probably attributable to incompletely cyclized chain structure as discussed previously. BBL polymers with viscosities determined to be greater than unity where higher degrees of cyclization might be expected have not been obtained.

In summary, the information gained from infrared spectra tend to show that BB polymers have fused structures similar to compounds III and IV although evidence exists for incompletely cyclized chain sites in low polymer.. High viscosity BBB, however, appears to be cyclized to a very high extent since evidence to suggest the presence of imide-amine or imidazole-acid is not detected in spectra of these materials.

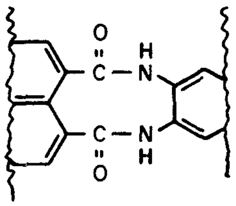
POLYMER COMPOSITION

Some difficulties in obtaining useful results from elemental analysis were encountered, although this cannot be considered to be unusual for highly fused aromatic-hetercyclic polymers. Early results for the BB polymers were inconclusive primarily due to the fact that nitrogen values were irreproducibly low and high phosphorous contaminations were detected. Although less problematic carbon determinations were indicative of only partial cyclization (see Table VI).

Considering the theoretical compositions shown in Table VI amide structures of the following types could be ruled out on the basis of thermal stabilities.



$(C_{26}H_{18}N_4O_6)_n$



$(C_{26}H_{14}N_4O_4)_n$

No evidence that such structures can withstand degradative chain cleavage or intramolecular dehydration at temperatures near 500°C is known. Results of thermogravimetric analysis (TGA) which are discussed in the section on THERMAL STABILITY clearly indicate that a higher degree of stability is present in BB polymers.

During the course of this work it was found (Reference 37) that reduction of polymer samples prior to Kjeldahl determinations gave satisfactory results for nitrogen. Phosphorous contaminations were reduced considerably by treatment of polymers in alkaline media and/or in boiling water for several hours prior to analysis. Heating samples near 300°C in vacuo before combustion analysis improved carbon determinations. The use of these techniques gave good agreement with the theoretical values calculated for fully cyclized structures.

Typically carbon values ranging from 72 to 74 percent for BBB and 69 to 71 percent for BBL were obtained. These results indicated high degrees of cyclization (Table VI), although some discrepancies from theory were expected since impurities such as Si, Pb and numerous

TABLE VI

ELEMENTAL COMPOSITIONS CALCULATED FOR SOME POSSIBLE POLYMER STRUCTURES [a]

Type Structure	Empirical Formula	%C	%H	%N	%O
BBB - Amide	$(C_{26}H_{18}N_4O_6)_n$	64.73	3.76	11.61	19.90
BBB - Partially[b] Cyclized	$(C_{26}H_{14}N_4O_4)_n$	69.95	3.16	12.55	14.34
BBB - Fully Cyclized	$(C_{26}H_{10}N_4O_2)_n$	76.09	2.46	13.65	7.80
BBL - Amide	$(C_{20}H_{14}N_4O_6)_n$	59.11	3.47	13.79	23.63
BBL - Partially[b] Cyclized	$(C_{20}H_{10}N_4O_4)_n$	64.86	2.72	15.13	17.28
BBL - Fully Cyclized	$(C_{20}H_6N_4O_2)_n$	71.86	1.81	16.76	9.57

a. Calculated for homogeneous structures.

b. Imide-amine, imidazole-acid or diamide ladder type structures.

metallic contaminants were discovered when samples were examined by emission spectroscopy (see EXPERIMENTAL section). Apparently BB polymers act as scavengers for trace impurities in solvents or other chemicals in which they come in contact. Nitrogen determinations were of less value in differentiating between possible structures as is evident from inspection of Table VI. Nevertheless, nitrogen determinations agreeing with calculated values for both BBB and BBL have been obtained.

Some inconsistencies prevailing in the large quantity of analytical data collected on BB polymers should be noted. For example, hydrogen and oxygen determinations have normally been found to be approximately one percent high. When carbon values have approached theoretical values for completely cyclized structures nitrogen values have tended to be slightly low. Percentages of contaminants have often varied in duplicate analyses. Numerous explanations can be put forth in an attenpt to explain these discrepancies including absorbed water, incomplete cyclization,, sample inhomogeneity, experimental error in certain techniques and others. The validities of such explanations have not been established in this investigation. Nevertheless the relatively small magnitudes of these anomalies do not detract from the gross findings which indicate that BB polymers are predominantly cyclized to their fullest extent.

THERMAL STABILITY

The thermal stability of BB polymers appeared to be excellent. For example, the 0.75 and 1.03 intrinsic viscosity BBB samples given in Table IV showed no weight loss by TGA in nitrogen to 600°C (Figure 13). Others listed in Table IV showed less than 2 percent weight loss at 600°C. The BBL polymers showed weight losses of 2 to 4 percent in nitrogen below 600°C, although catastrophic decomposition appeared to occur above 600°C. Some typical examples to TGA curves comparing results obtained for BBB and BBL in both nitrogen and air are shown in Figure 15.

In view of the previously discussed conclusions reached by examining BBL viscosities, infrared absorption characteristics and elemental compositions, it does not seem unreasonable to find weight losses occurring earlier than for high viscosity BBB. It is unlikely that complete cyclization is so nearly approached in the BBL polymers. This is further substantiated by the fact that the TGA of low viscosity BBB, which is concluded to be incompletely cyclized as previously discussed, is very similar to the BBL TGA. Uncyclized chain sites likely constitute weak chain links which are responsible for gradual weight losses of up to 5 to 10 percent at 600°C (Figure 16). Improved synthetic techniques will be required to prepare a more perfect BBL structure for valid comparisons of their thermal properties with those of BBB.

In general, TGA weight losses of 5 to 10 percent, usually considered to be catastrophic, were not seen to occur for BB polymers up to ranges to 600 to 650°C in nitrogen and 475 to 525°C in air. These results are very encouraging since they appear to be comparable or superior to those reported for other polymers currently being used or considered for high temperature applications. It is recognized, however, that comparisons by TGA are not quantitative and conclusions drawn can only be considered to be tenative. Results vary with specific samples and varying techniques used by different laboratories. For example, curves B and b of Figure 14 were obtained at a heating rate of 360°C/hr. as compared with 150°C/hr. for the other curves shown. Consequently the samples exhibiting curves B and b were exposed to thermal environment for only half as long as the others and direct comparisons of results cannot be made.

It was of some interest to note that the TGA curve of insoluble polymer resulting from secondary reaction in PPA (assumed to be cross-linked as discussed above) differed significantly from others (Figure 17). It degraded in what appeared to be a stepwise fashion to a weight residue of 70 percent. The first step occurred at a low temperature and appeared to be residual solvent or water, but the discontinuity of weight loss observed between 200 and 400°C was unusual and not observed in any other TGAs of BB polymers. This evidence supports the idea that weaker bonds (such as might be expected for cross-links) are present in the polymer.

Most of our evaluations of thermal properties have been made on the BBB polymer and these are continuing. Some preliminary results on isothermal aging are available (Reference 30) which indicate weight losses to be less than 10 percent at 315°C after 1500 hours in air (Figure 18). The maximum rate of decomposition appears to be in the region of 610 to 620°C when determined by DTA at a heating rate of 10°C/minute in air.

We have not found BBB to soften under a load of 1000 gms/cm^2 after heating to 425°C in air (heated at a rate of 150°C/hr.). Polymers subjected to thermal gravimetric analysis (to 900°C at a rate of 150°C/hr.) were not apparently fused. The recovered powders were examined by infrared analysis and solubility tests which indicated that complete decomposition had occurred. These findings suggest that BB polymers do not melt below their decomposition temperatures.

SUMMARY AND CONCLUSIONS

Both high and low molecular weight, soluble, linear polymers with backbones possessing bis-benzimidazobenzophenanthroline and benzimidazobenzophenanthroline ladder structure have been prepared. These polymers, BBB and BBL respectively, appear black as a result of their highly conjugated structures and are soluble in only a few solvents. The fact that these solvents, in general, are corrosive and difficult to handle has precluded extensive solution properties determinations. However, solution viscosities determined in sulfuric acid are at least indicative of moderately high molecular weights.

Polycondensations in polyphosphoric acid at temperatures near 200°C have readily produced BBB with intrinsic viscosities greater than one, while under similar conditions BBL polymerizations have only produced polymers with significantly lower viscosities. In addition, BBL polymerizations tend to give some insoluble products likely due to the occurrence of some cross-linking. This probably results from the nature of BBL monomer, 1,2,4,5-tetraminobenzene which is unstable and tends to be contaminated with oxidation products. In an effort to improve stability and avoid contamination, the hydrochloride salt of this base was utilized in the polycondensations. Nevertheless, impurities, or possibly the presence of hydrogen chloride, could have resulted in variations of the BBL polymerization mechanisms. Tendencies to branch or cross-link may have been enhanced or unreactive sites could have been introduced which interfered with the desired linear propagation.

Possibly a difference of even greater significance between BBB and BBL reactions is the nature of prepolymers derived from diaminobenzidene and tetraaminobenzene. Tetraaminobenzene which has been incorporated as chain backbone, but has not undergone final cyclization, should be more prone to react further by intermolecular branching or cross-linking reactions. This can be expected since its freedom to orient to the desired site for intramolecular cyclization is expected to be more limited. In comparison, the analogously structured diaminobenzidene prepolymer moiety contains a single bond link and may be expected to be more mobile at elevated temperatures. Any or all of the above factors may have contributed to the production of some insoluble polymer in BBL polymerizations whereas BBB polymerizations seldom produced detectable insolubles.

Readily soluble BBB polymers with low solution viscosities were also prepared and these were obtained from both solution and solid phase polymerizations. The BBL polymers with comparable viscosities had much poorer solubility characteristics which are attributed to the more rigid and highly condensed structure derived from the tetraaminobenzene monomer. Due to this aspect of solubility, secondary reactions on BBL polymers were not investigated as they were for BBB. Secondary reactions on low viscosity BBB in either polyphosphoric acid or in the solid phase were found to advance the viscosity. These were performed on reprecipitated polymer samples so that viscosity increases should reflect chain extension as opposed to continued polymerizations involving unreacted monomers. Some contribution to viscosity increases could have resulted from continued cyclization.

Infrared and elemental analyses of BBB and BBL polymers substantiate the proposed structures. Although the extent of completely cyclized backbone structure is still in some doubt, the evidence for complete cyclization in high viscosity BBB appears to be quite good. In the case of low viscosity polymers, analyses indicate that some low level incomplete cyclization persists.

Probably the most outstanding property of these soluble BB polymers is their inherent stability in extreme environments. In thermal environments these materials exhibit resistance to thermal degradation at 500°C in an oxidative atmosphere, and 600°C stabilities are observed in inert atmosphere. In chemical environments they possess a remarkable resistance to chemical breakdown as evidenced by their excellent stability for long periods in strong acids and alkalis near 100°C. Few soluble organic polymers are known which possess stabilities approaching those found for the BB polymers.

Follow-on research is in progress. The tractability of BB polymer has been demonstrated and it is considered to be a candidate material with considerable potential for high temperature fiber applications. Preliminary results also indicate some degree of promise for its use in structural laminates and possibly protective coatings. Less has been learned about BBL; however it has potential as a high temperature plastic and has merit as a material upon which to base continued research directed toward obtaining a highly desirable "perfect" ladder polymer. Ladder polymers are needed for investigations to determine fundamental relationships between structural characteristics and physical properties of macromolecules.

SECTION III

EXPERIMENTAL

MODEL COMPOUNDS

N-Phenylnaphthalimide (I) was prepared by condensing 1,8-naphthalic anhydride and aniline in ethyl alcohol according to the method Jaubert (Reference 26). Model Compound II, N-(2-aminophenyl)-naphthalimide was synthesized from 1,8-naphthalic anhydride and o-phenylenediamine as previously reported (Reference 27). Two synthetic methods were used to prepare 7H-benzimidazo(2,1-a)benz(de)isoquinolin-7-one (III): (a) the method of Okazaki (Reference 27) involving intramolecular condensation of N(2-aminophenyl)naphthalimide (II) and (b) the direct condensation of 1,8-naphthalic anhydride with o-phenylenediamine in PPA under conditions similar to those used for polycondensations. The product from (a) was found to be identical with that from (b) by mixed melting point determination. Additional details on the synthesis of Model Compounds for this investigation are described in a previous report (Reference 22).

MONOMERS

Monomers utilized in the preparation of BBB polymers (NTCA and DAB) have been described (Reference 22). BBL monomer, 1,2,4,5-tetraaminobenzene tetrahydrochloride (TAB) was prepared by the reduction of 1,3-dinitro-4,6-diaminobenzene and purified as the hydrochloride salt by the Dayton Laboratory of Monsanto Research Corporation. The tetrahydrochloride was used as received.

POLYCONDENSATIONS

Solution polymerizations were carried out in PPA by procedures similar to those described earlier (Reference 22). Most favorable results were obtained when equimolar mixtures of monomers were stirred in warm PPA for a few minutes until the liquids became mobile and the solids appeared to be homogeneously dispersed. These mixtures were then gradually heated to specified reaction temperatures (Table II). After heating at temperature for varying lengths of time the polycondensations were terminated by cooling the reaction solutions to 150°C or below and pouring on to crushed ice or into cold water. Polymer products precipitated and they were washed in aqueous media to remove PPA. These neutralizations were sometimes accomplished by utilizing alkali carbonate solutions. Due to the swollen character of these polymers it was expeditious to collect the solids by centrifugation and decantation as opposed to filtration. The wet solids which were recovered were extracted with DMAC and/or methyl alcohol prior to washing with ether. Unswollen polymers were obtained by this treatment and these were dissolved in an excess of conc. H_2SO_4, reprecipitated and extracted with water to remove acid, and finally washed with absolute methyl alcohol to remove water. Yields were usually determined on the basis of polymer recovered after one such reprecipitation.

Solid phase reactions were carried out in a straightforward manner. Equimolar mixtures of monomers or previously isolated polymers were heated either under nitrogen (after evacuation and flushing with nitrogen) or in vacuo. After specified heating periods the solids were cooled under nitrogen and reprecipitated from conc. H_2SO_4 as above.

Secondary PPA reactions on previously isolated polymers amounted to dissolving the solids in the hot acid and stirring at temperatures near 200°C. The resulting polymers were isolated in the manner described above.

Solution viscosity determinations and the various analytical techniques utilized in this investigation involved conventional methods as discussed for specific polymer samples in the text of this report (see DISCUSSION OF RESULTS). Elemental analyses were performed by the Analytical Branch, Physics Div., AFML, W-PAFB, O. and Huffman Laboratories Inc. Infrared curves were obtained on Perkin Elmer Model 137 Infracord Spectrophotometers and analytical spectra were provided by the Analytical Branch, Physics Div., AFML, W-PAFB, Huffman Laboratories, Inc., and the Dayton Laboratory of Monsanto Research Corp. Results are included in Tables and the associated discussions. Details of some representative experimental procedures are given below.

Polymerization of NTCA and DAB in Solution

A mixture of 11.12g of NTCA, 8.06g of DAB and 350 ml of PPA was stirred at 60°C under nitrogen for 10 minutes. The temperature was gradually increased over a period of 7 hrs. to 180°C and maintained at 180° to 190°C for 20 hrs. The resulting polymer was isolated in water, extracted with DMAC and MeOH, reprecipitated from conc. H_2SO_4, and dried for several hours at 100-130°C in vacuo. The yield was 90 percent of soluble polymer which did not soften at 425°C under a load of 1000 gms/cm^2. Prior to analysis the product was heated for an additional 114 hours at 165-85°C in vacuo. An intrinsic viscosity of 1.15 in conc. H_2SO_4 was determined.

Calcd. for $C_{26}H_{10}N_4O_2$: C, 76.09; H, 2.46; N, 13.65; 0, 7.80.
Found : C, 72.68; 72, 47; H, 3.35, 3.22; Residue, 0.79, 1.03; N, 13.60, 13.33; P, 1,88, 2.10.

Extraction of the sample for several hours with water followed by heating at 310 to 312°C in vacuo caused an increase in intrinsic viscosity to 1.43. The product was dissolved in aq. NaOH and reprecipitated from this solvent:

Found : Pb, 0.5; Si, 0.15; Al, 0.1; Fe, 0.1; Ni, 0.1; Cu, 0.1; Mg, 0.01; Sn, 0.005; Mn, 0.001; P and K, less than 1; Na and Zn, less than 0.1.

Polymerizeration of NTCA and DAB in Solid Phase

A mixture of NTCA (1.57g) and DAB (1.08g) was thoroughly purged with nitrogen and heated at a rate of approximately 5°C/min to 200°C. Evolution of water was observed at 160 to 200°C. Heating was continued at approximately 1°C/min to 285°C and maintained at 285 to 295°C for 4 hours. The reaction mixture was cooled under nitrogen, reprecipitated from conc. H_2SO_4 and found to have an inherent viscosity of 0.22 measured at 0.54 g/dl in conc. sulfuric acid.

Found : C, 73.80, 73.98; H, 3.12, 2.92; Residue, 0.61, 0.69; N, 11.95, 12.21; 0, 10.15, 10.05.

Polymerization of NTCA and TAB in Solution

Under nitrogen 5.90g of NTCA and 5.49g of TAB·$(HC1)_4$ were mixed with 300 ml of PPA and stirred for one hour at 75°C to permit controllable evolution of HC1 to occur. At a rate slightly above 1°/min. the mixture was heated to 180°C and maintained at 180 to 190°C for 20 hours. The resulting polymer was isolated in the usual manner and dried several hours at 160 to 180°C at 1mm Hg (83 % yield). The soluble product was reprecipitated from conc. H_2SO_4 and inherent viscosity of 0.63 was measured at a concentration of 0.15 g/dl in the acid. A sample was heated at 350°C for four hours in vacuo prior to elemental analysis:

Calcd for $C_{20}H_6N_4O_2$: C, 71.86; H, 1.81; N, 16.76; O, 9.57.
Found: C, 70.90, 71.03; H, 2.14, 2.11; Residue 0.0; N, 14.40, 14.53; 0, 12.16, 12.14; P, 0.0.

This sample was heated again for one hour in vacuo at 475°C.

Found: C, 71.43, 71.46; H, 2.19, 2.15; N, 14.66, 14.63; 0, 11.68, 11.40.

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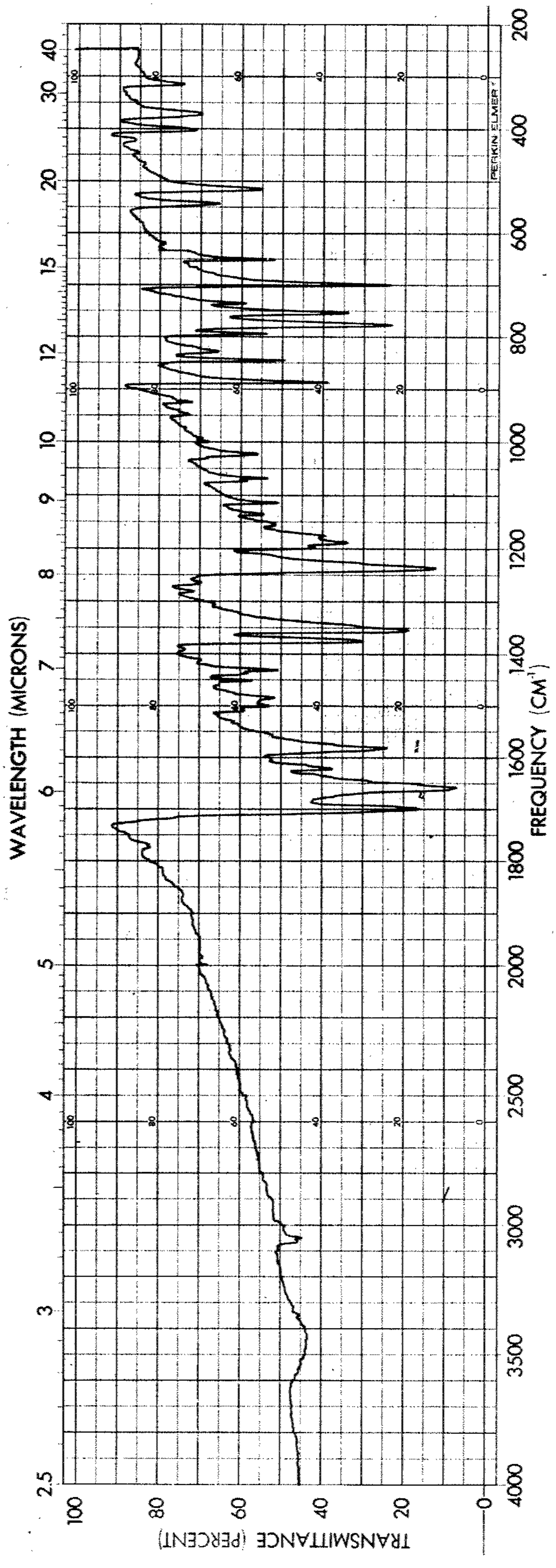

Figure 1. Analytical IR Spectrum of N-Phenylnaphthalimide (Model Compound I)

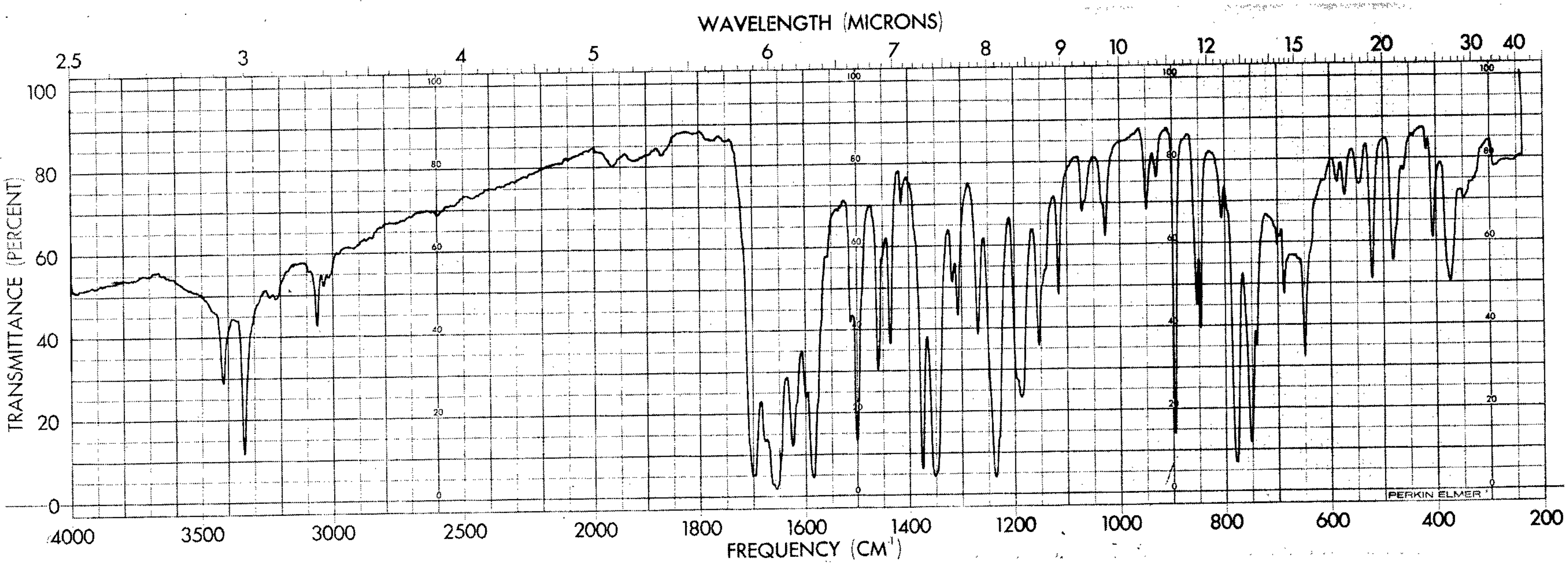

Figure 2. Analytical IR Spectrum of N(2-Aminophenyl)-Naphthalimide (Model Compound II)

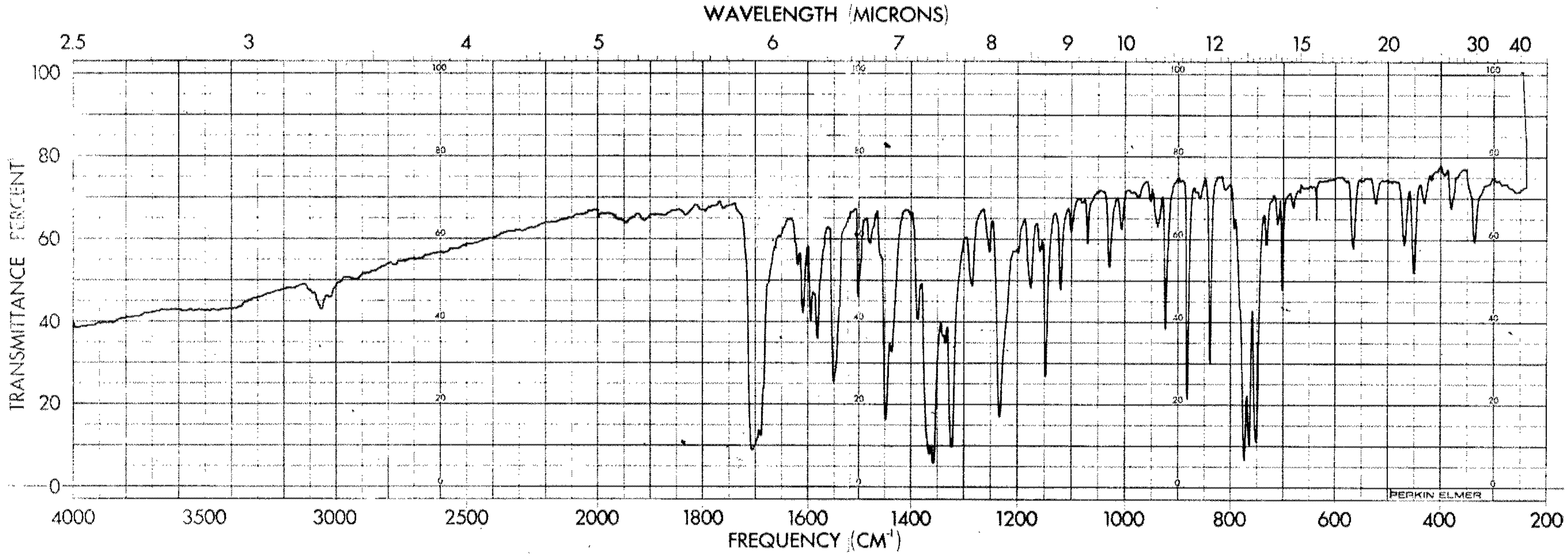

Figure 3. Analytical IR Spectrum of 7H-Benzimidazo (2,1-a)benz(de)-isoquinolin-7-one (Model Compound III)

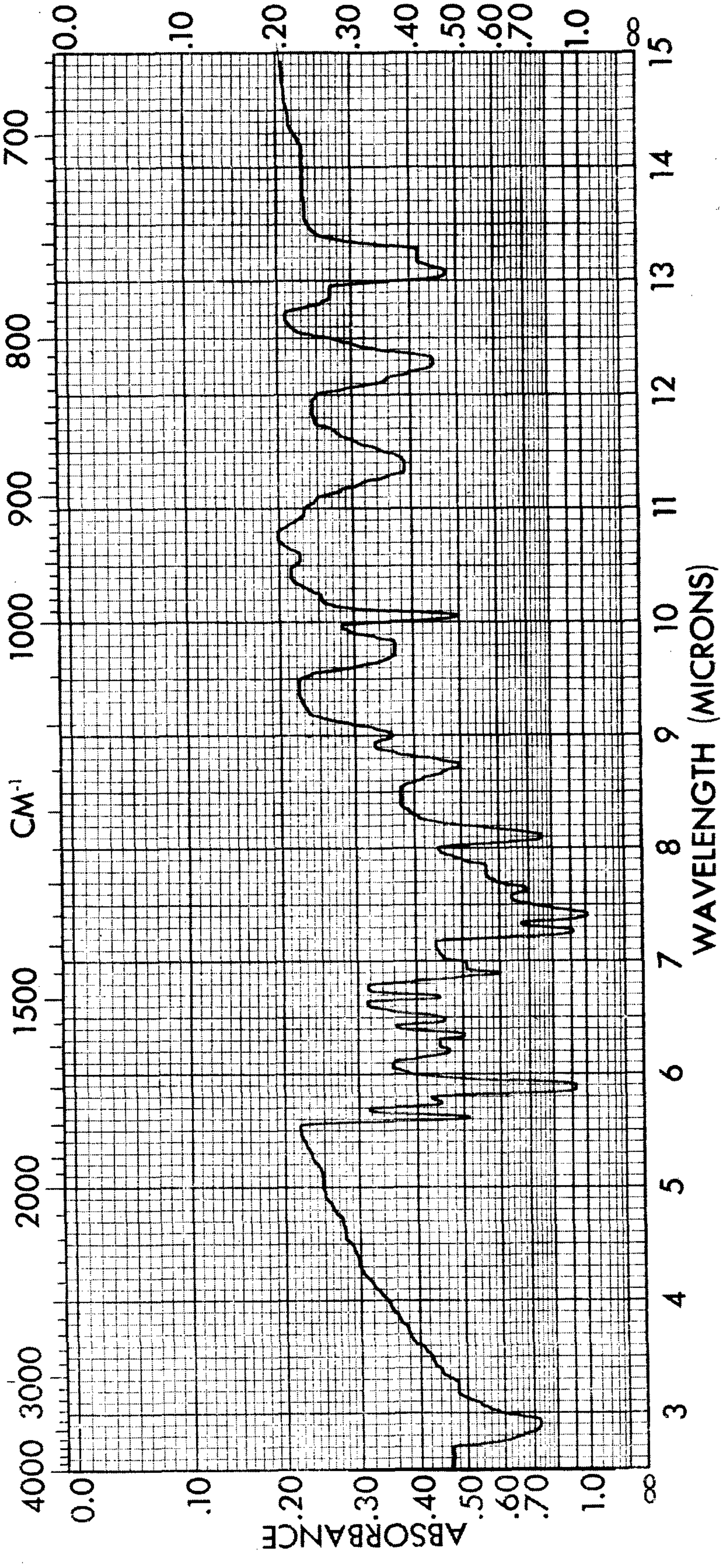

Figure 4. Infrared Spectrum: BBB ($\eta_{inh} = 0.12$) from PPA Reaction

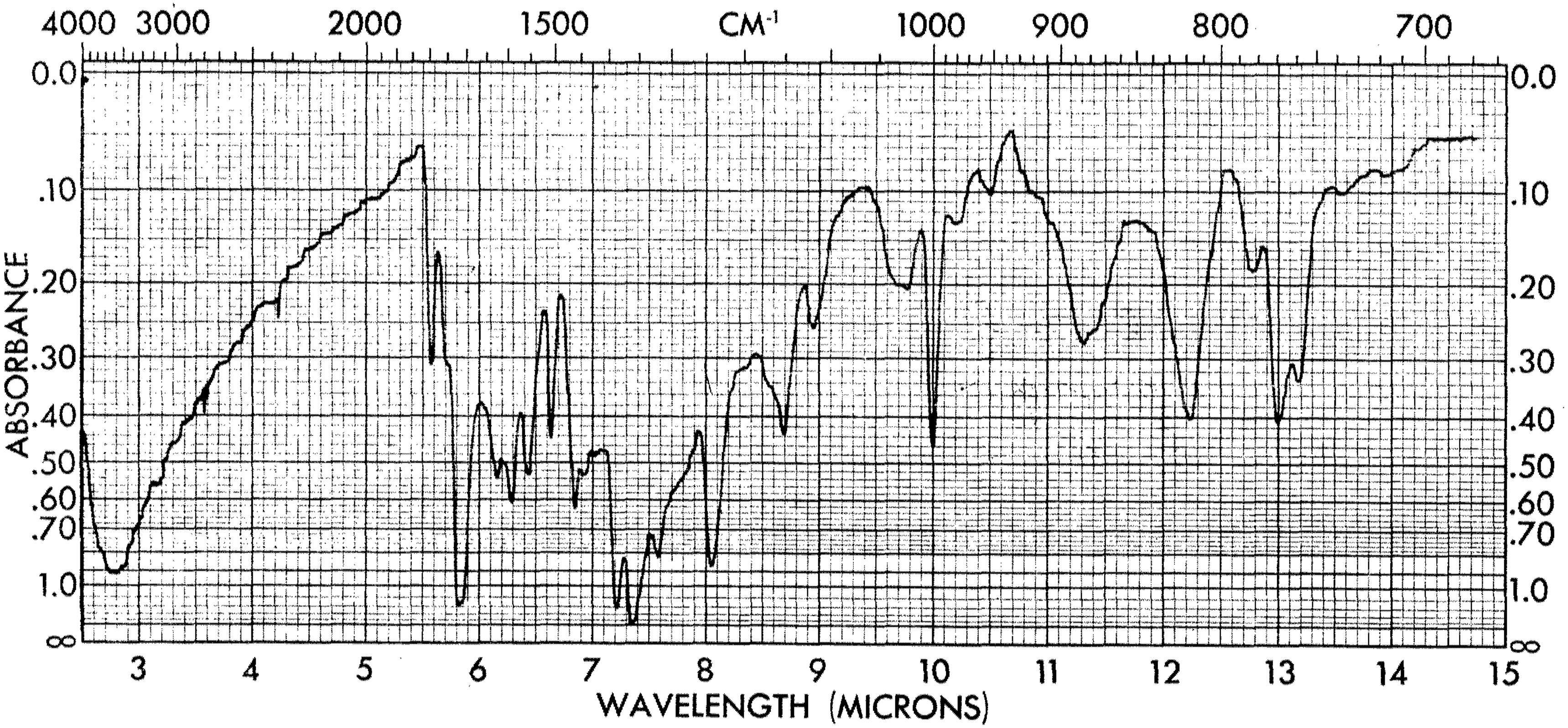

Figure 5. Infrared Spectrum: BBB ($\eta_{inh} = 0.18$) Reprecipitated from both H_2SO_4 and KOH

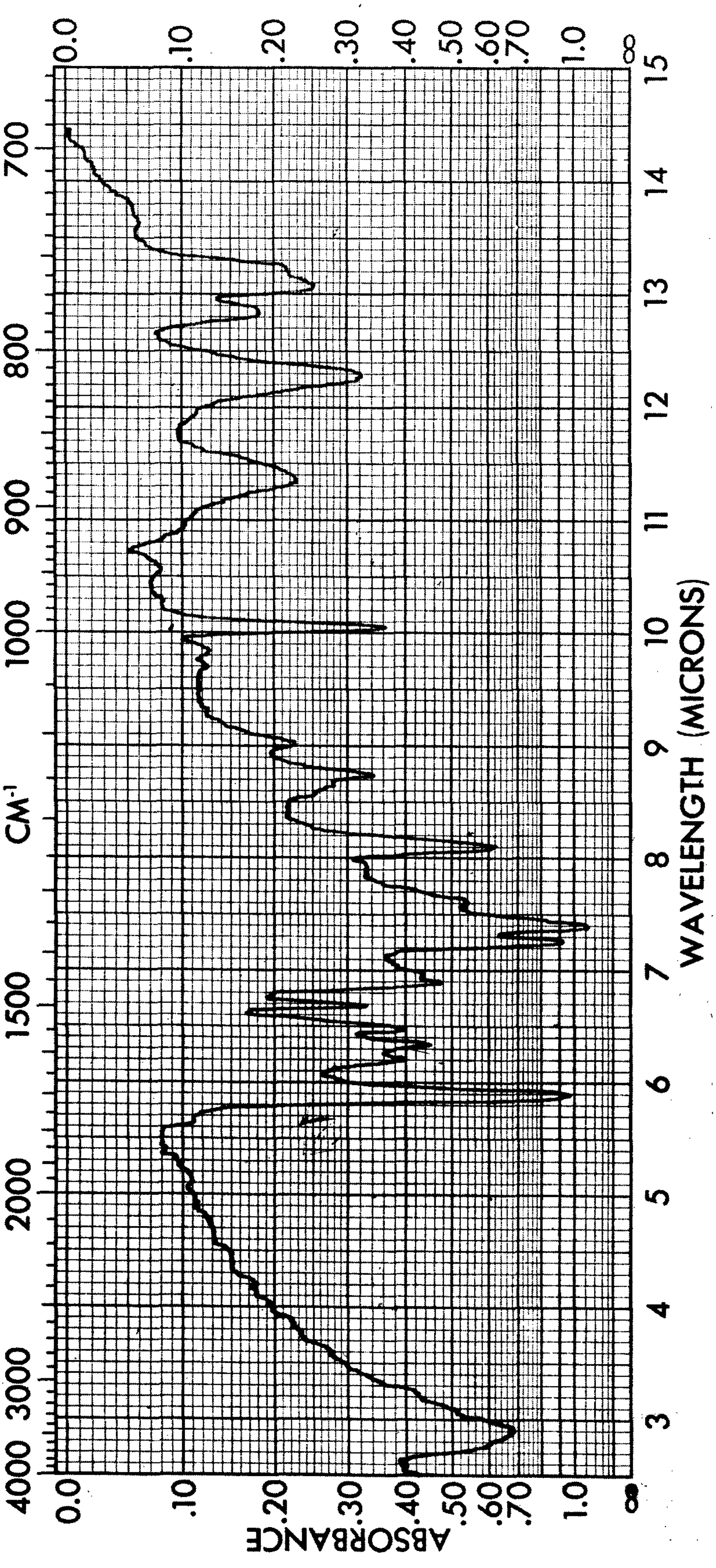

Figure 6. Infrared Spectrum: BBB ($\eta_{inh} = 0.24$) from Solid Phase Reaction of BBB ($\eta_{inh} = 0.18$, Figure 5.)

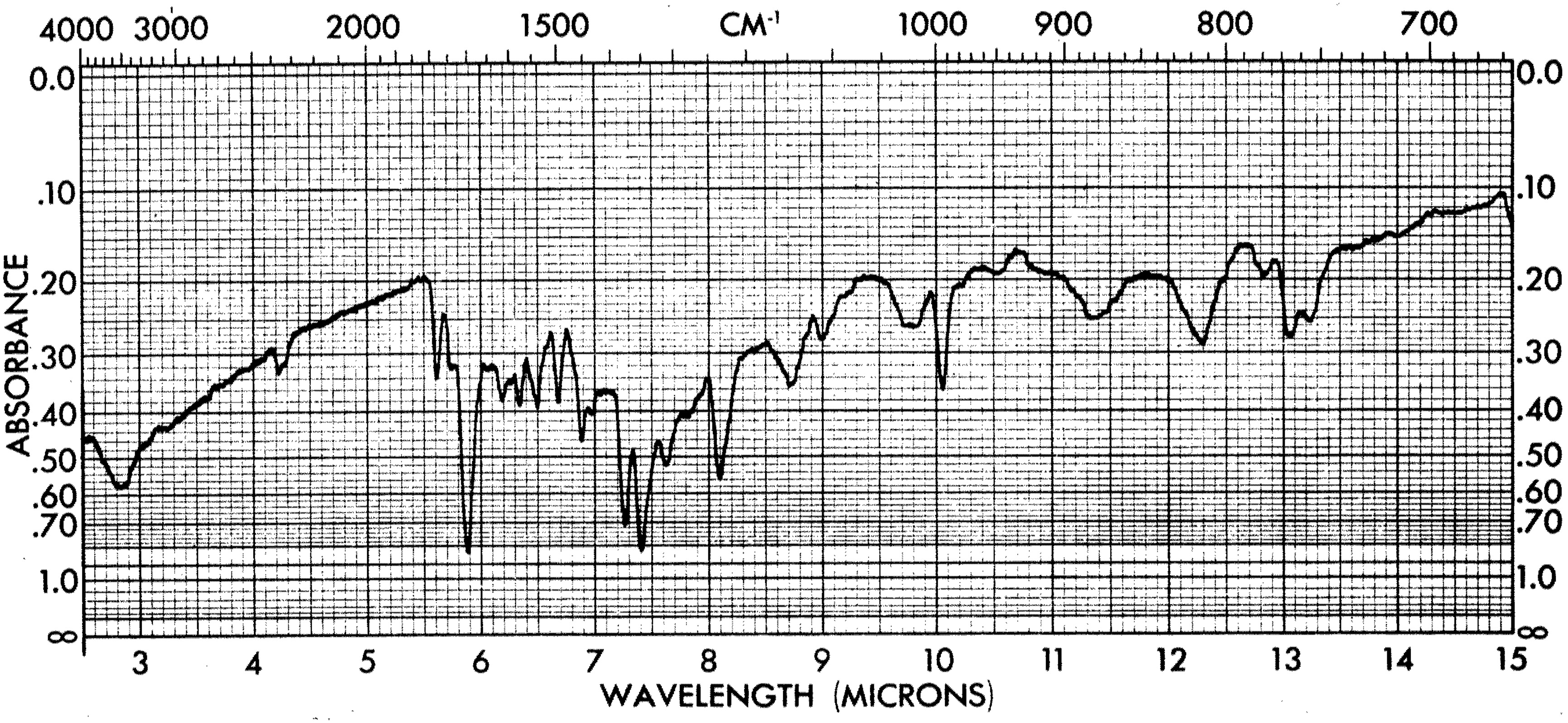

Figure 7. Infrared Spectrum: BBB (η_{inh} = 0.29) from Secondary PPA Reaction of BBB (η_{inh} = 0.12, Figure 4)

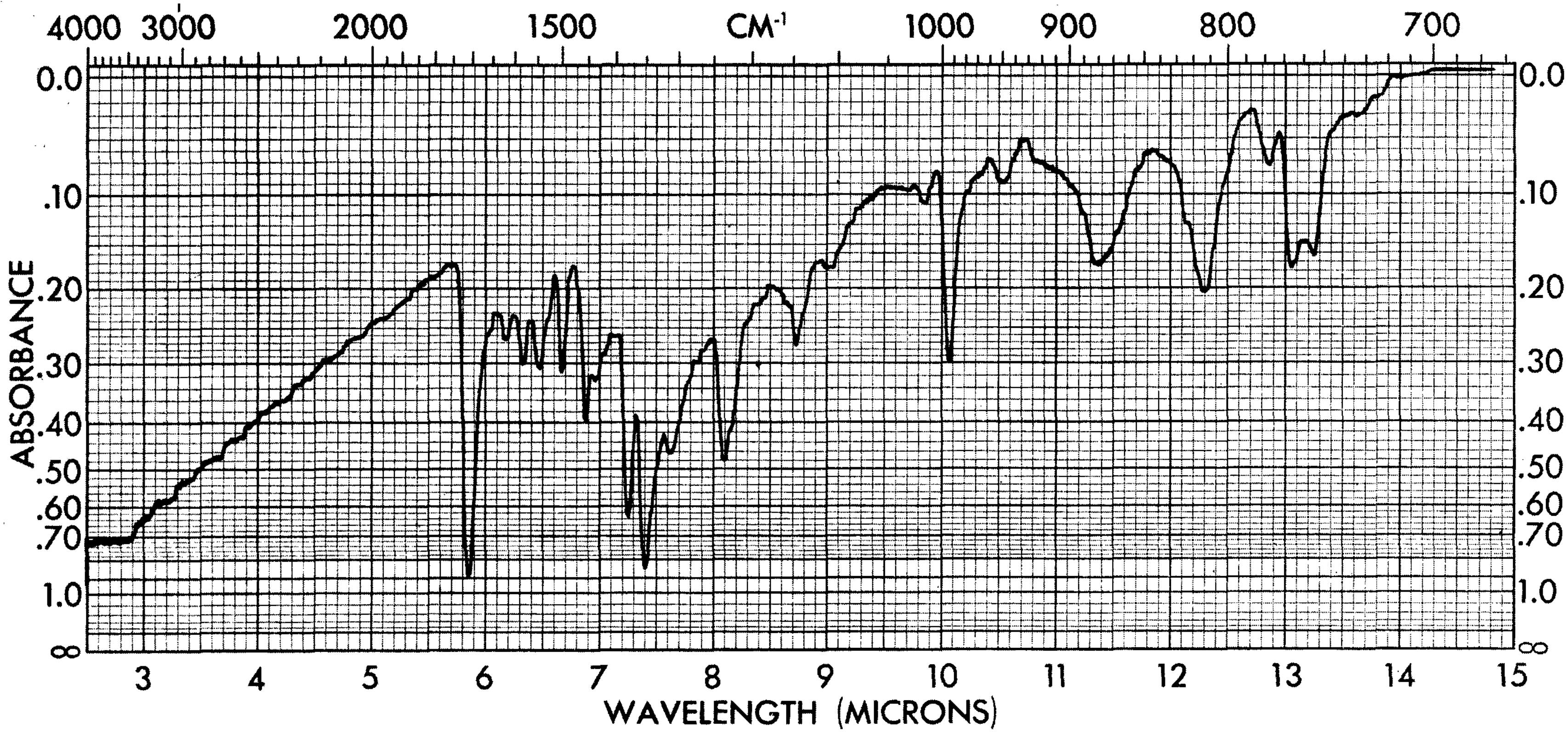

Figure 8. Infrared Spectrum: BBB (Insoluble) from Secondary PPA Reaction of BBB (η_{inh} = 0.12, Figure 4)

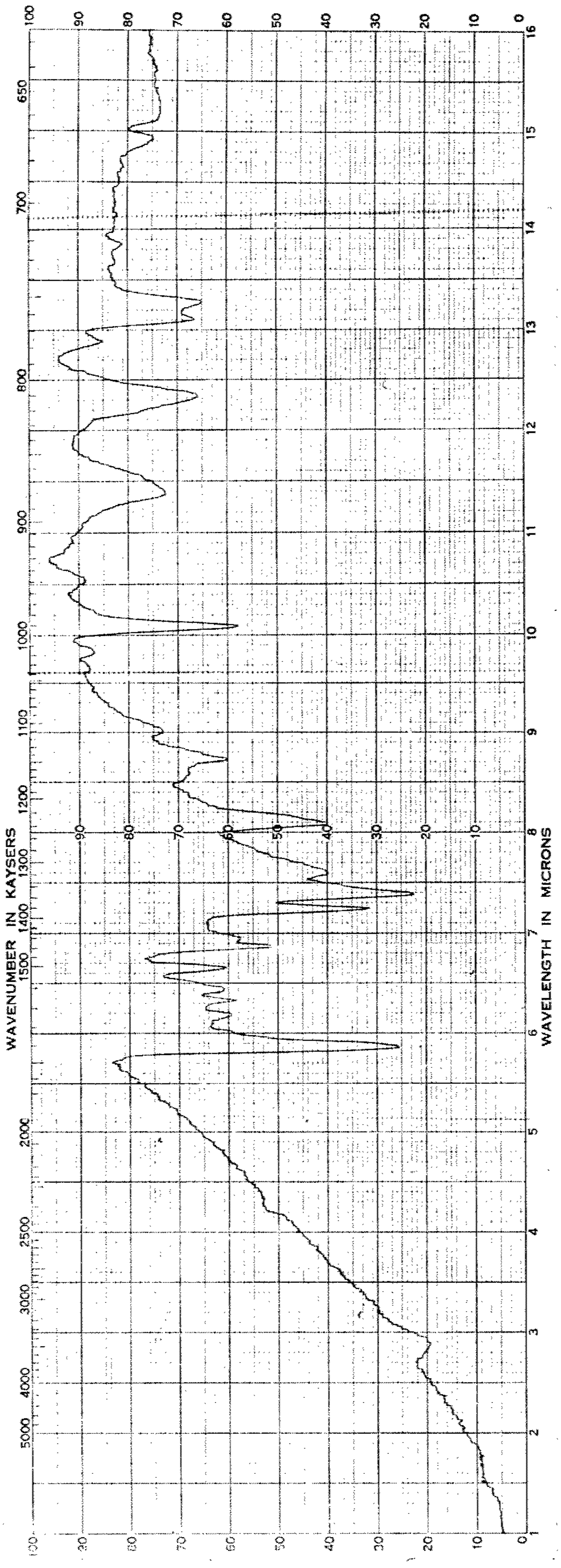

Figure 9. Representative Analytical IR Spectrum of BBB Polymer: Solution Viscosity Greater Than 1.0

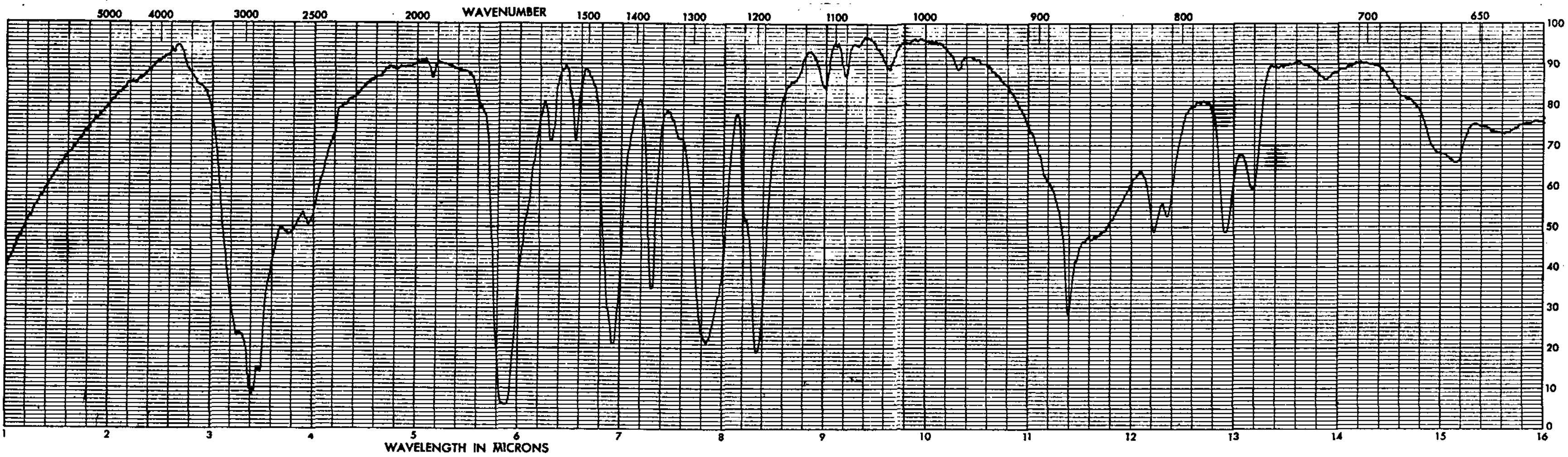

Figure 10. Analytical IR Spectrum of 1,4,5,8-Naphthalene Tetracarboxylic Acid

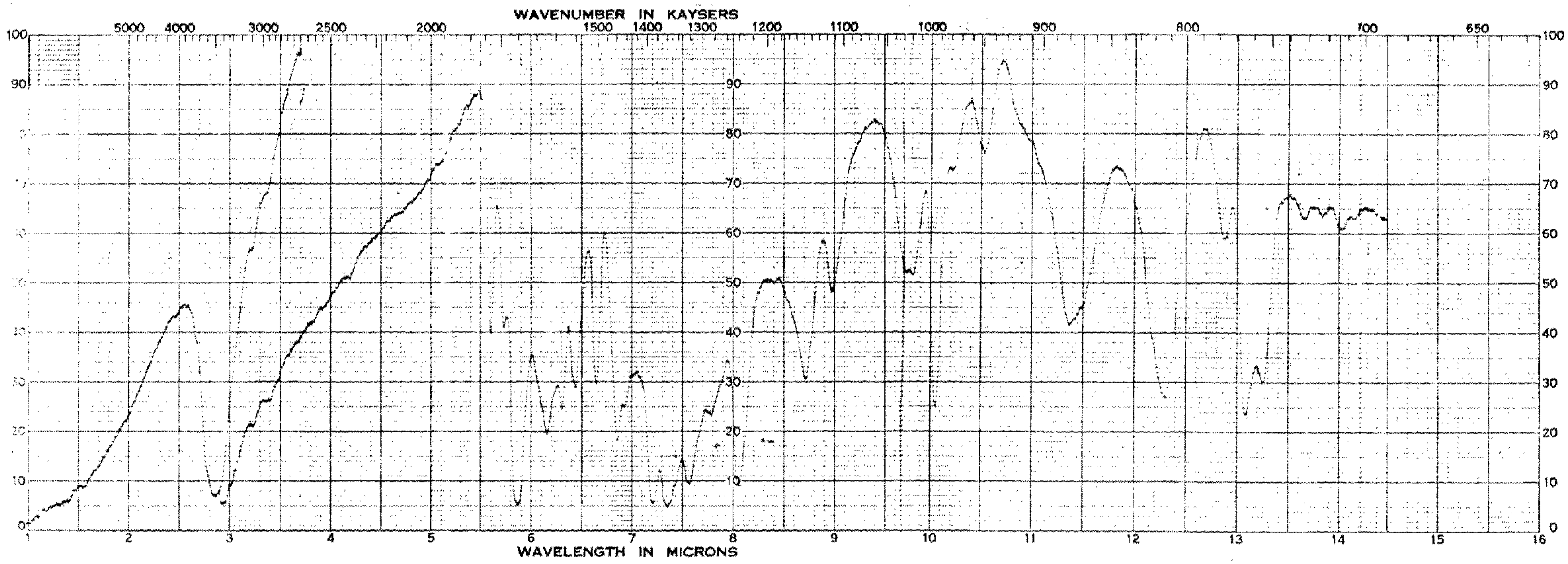

Figure 11. Representative Analytical IR Spectrum of BBB Polymer: Solution Viscosity Less Than 0.5

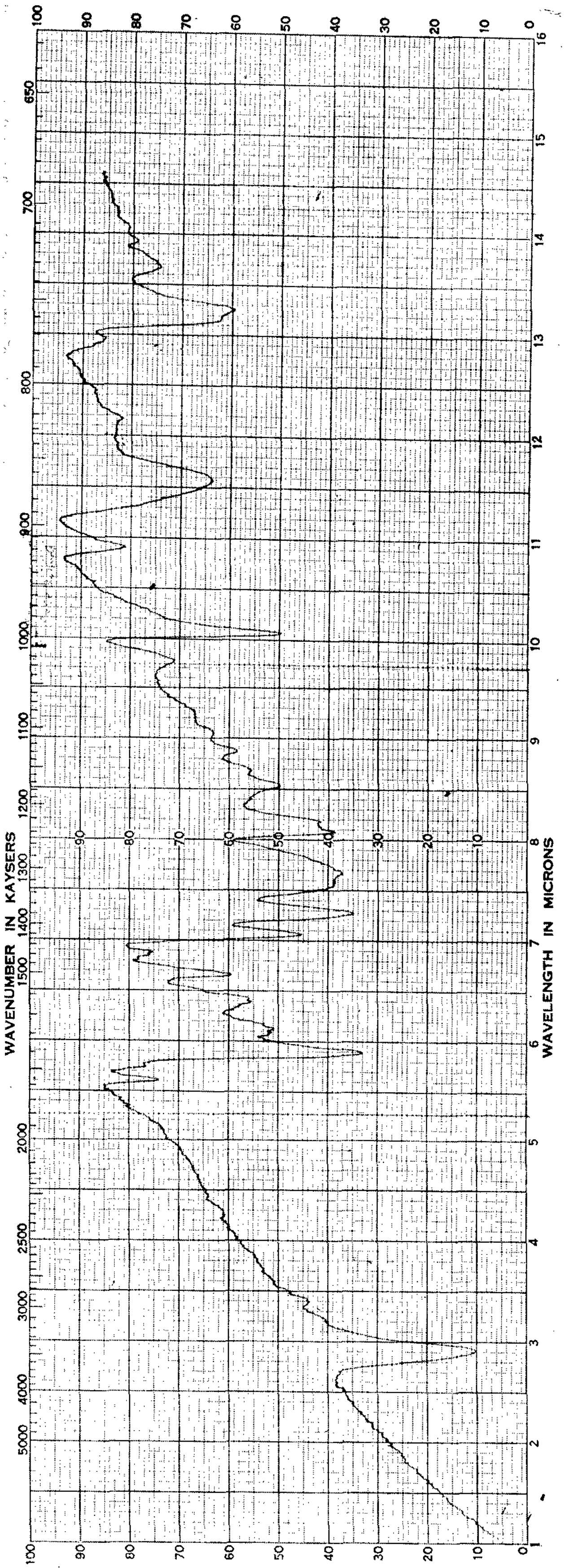

Figure 12. Representative Analytical IR Spectrum of BBL Polymer: Solution Viscosity Less Than 1.0

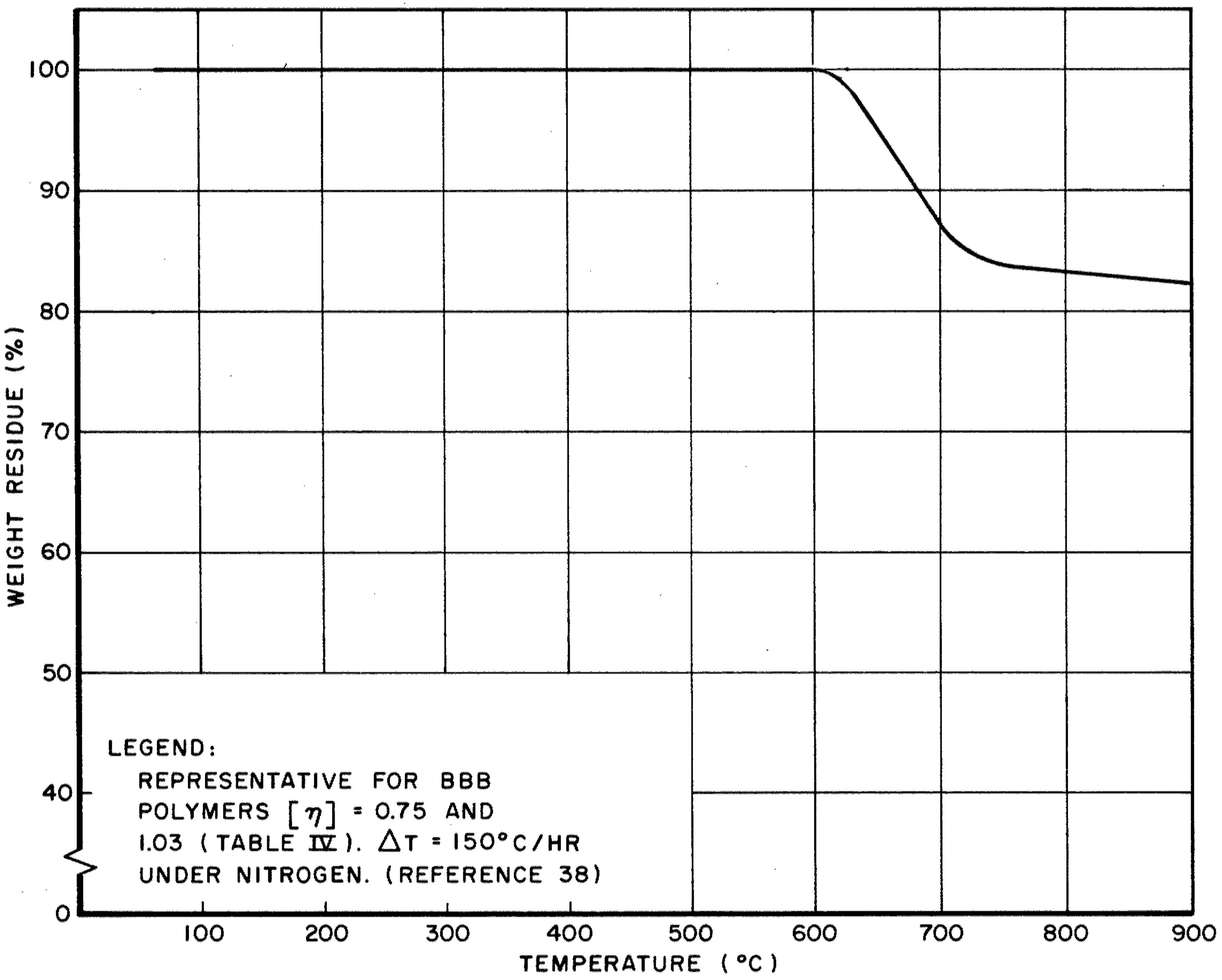

Figure 13. Thermal Gravimetric Analysis of BBB Polymers in Inert Atmosphere

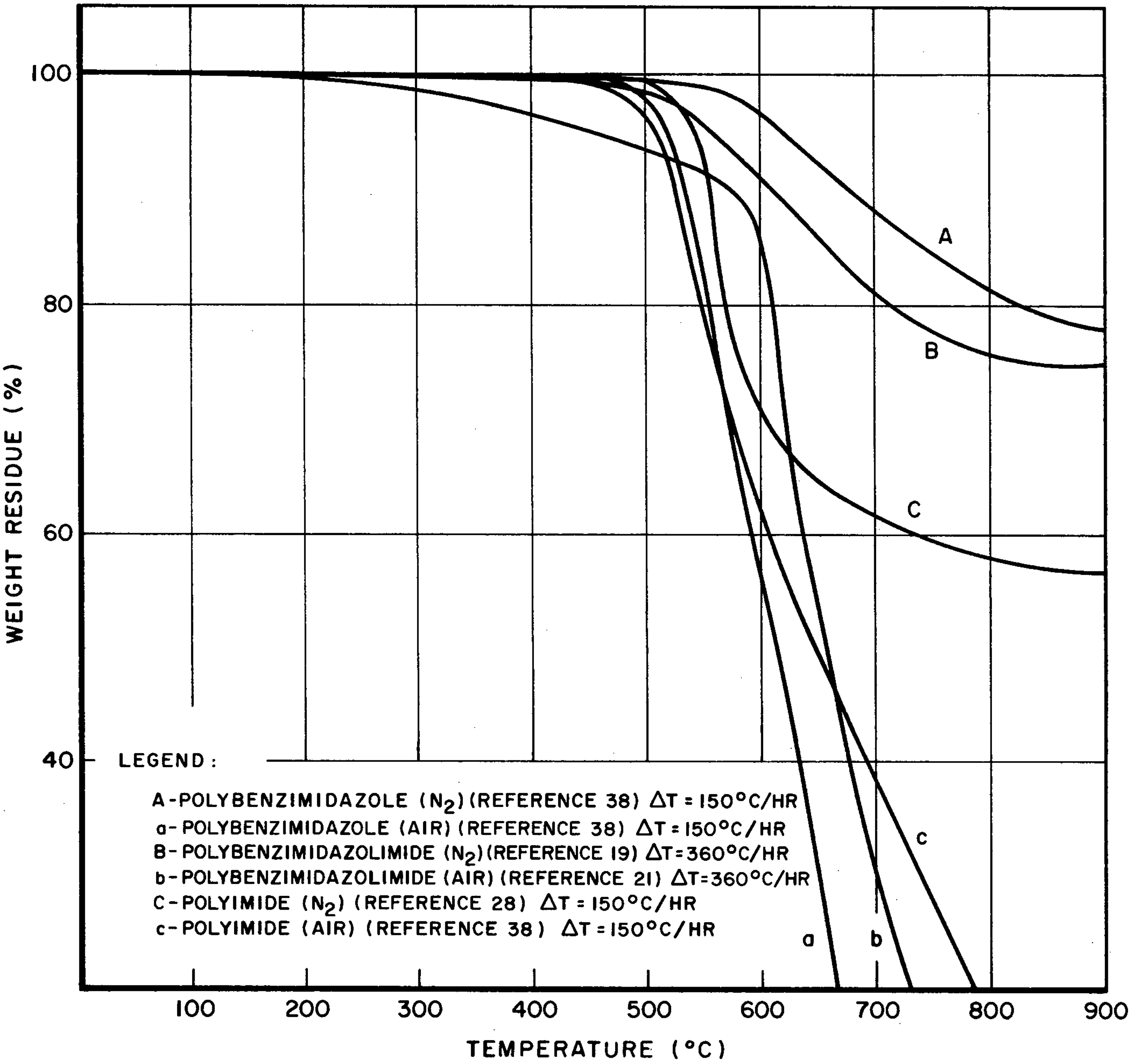

Figure 14. Some Examples of TGA Curves Obtained on Polyimides, Polybenzimidazoles and Polybenzimidazolimides

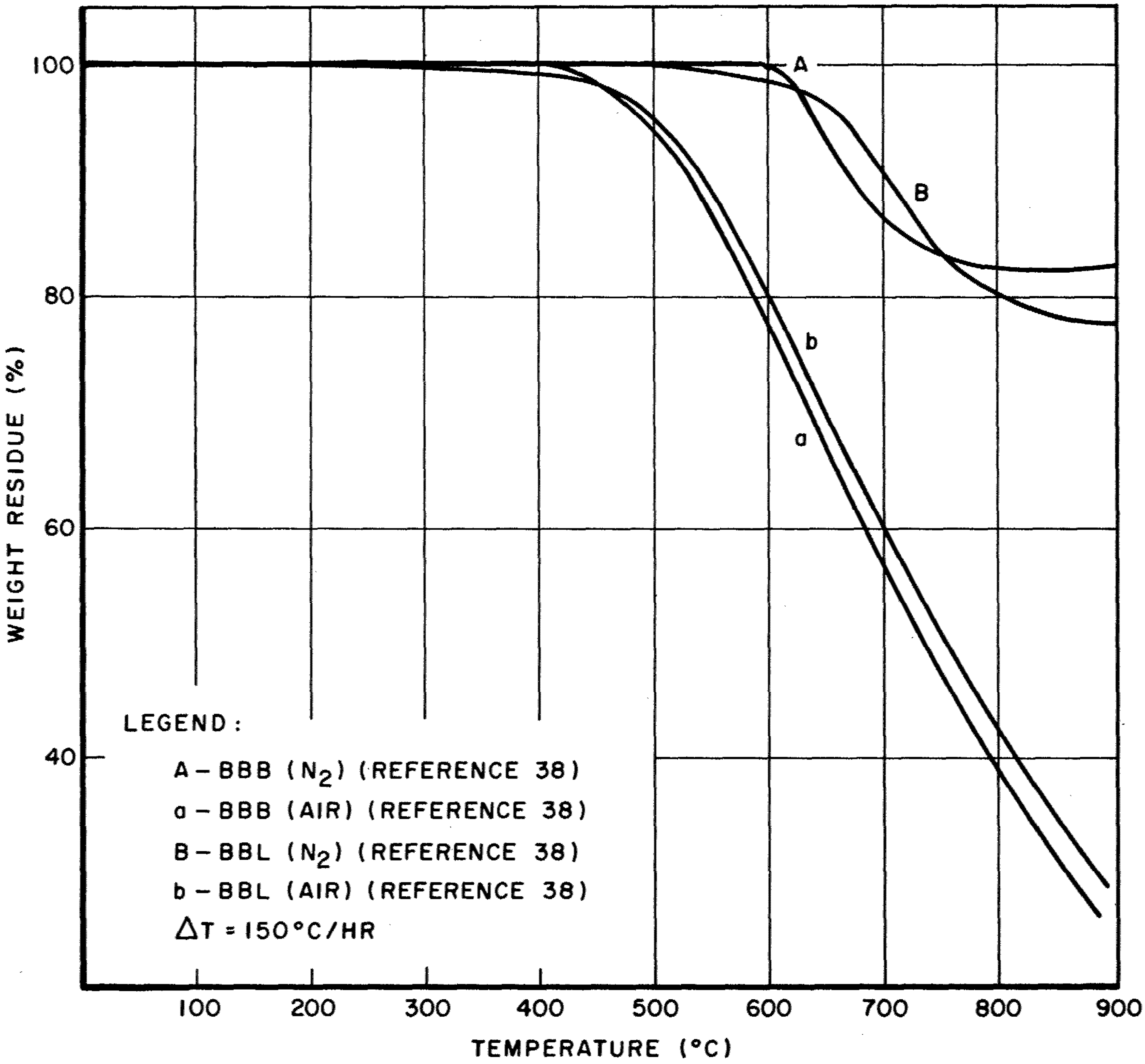

Figure 15. TGA Comparison of BBB and BBL Polymers in Nitrogen and Air

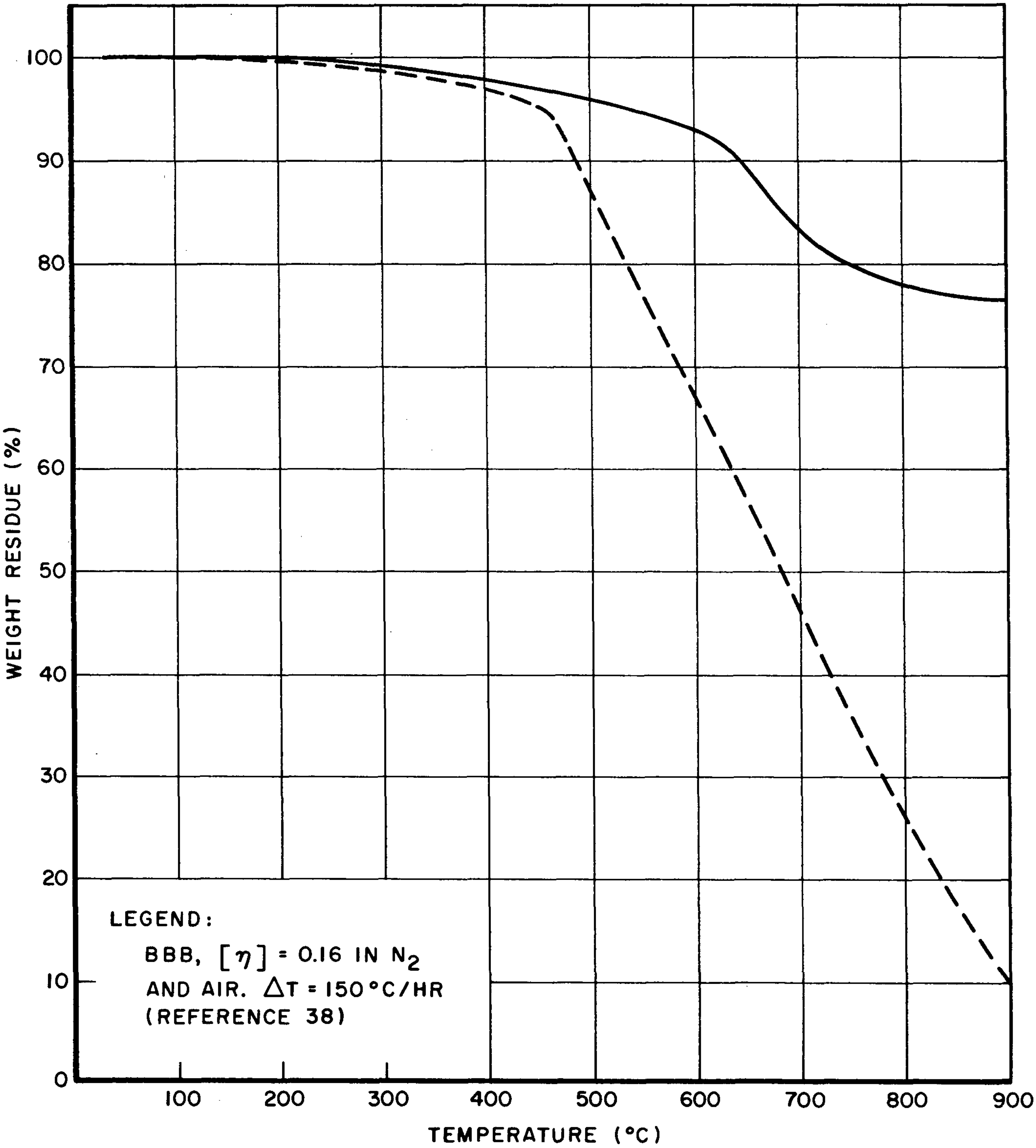

Figure 16. Illustration of Early TGA Weight Losses Found for Incompletely Cyclized BBB Polymers

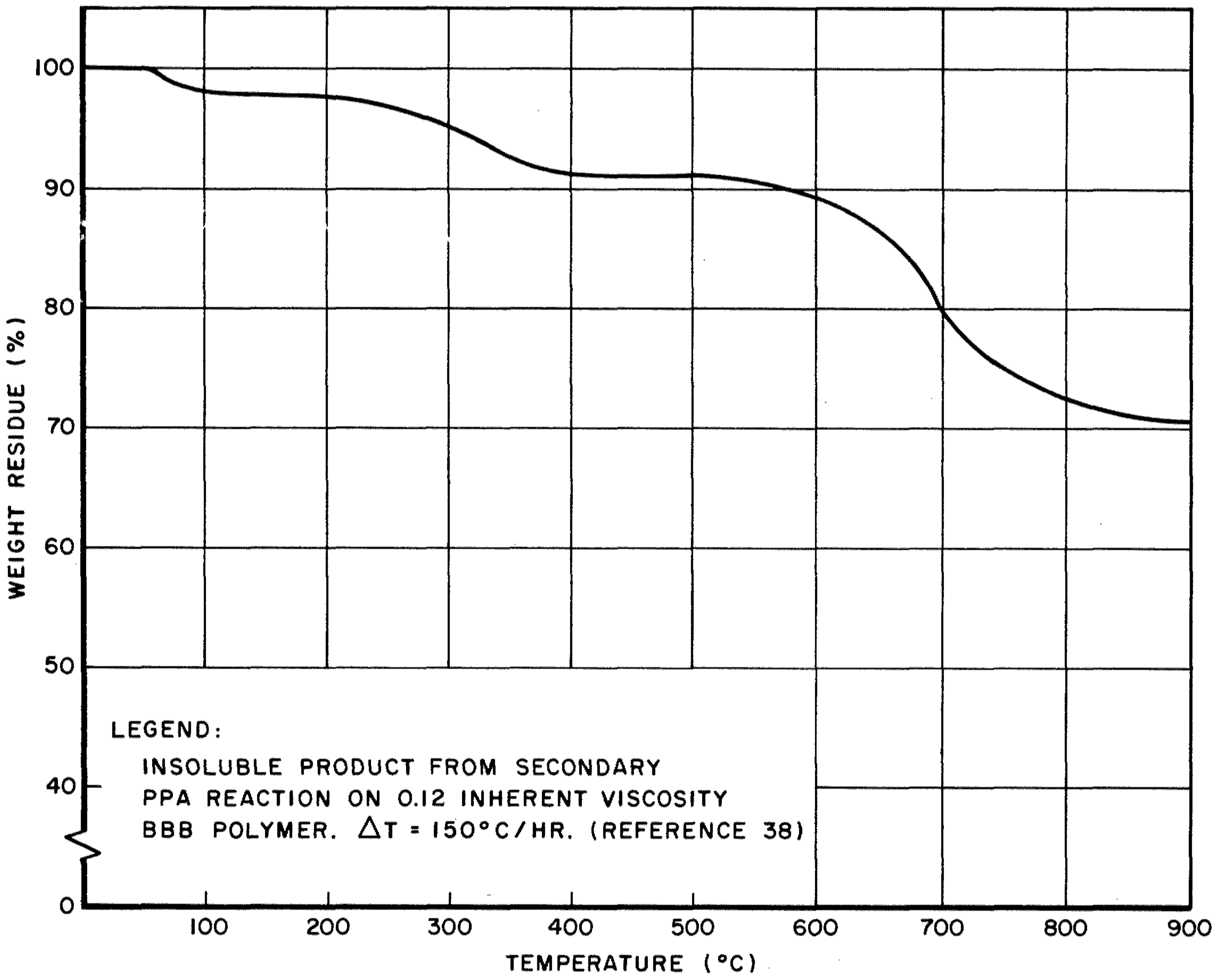

Figure 17. TGA of Insoluble BBB Polymer Assumed to be Cross-linked

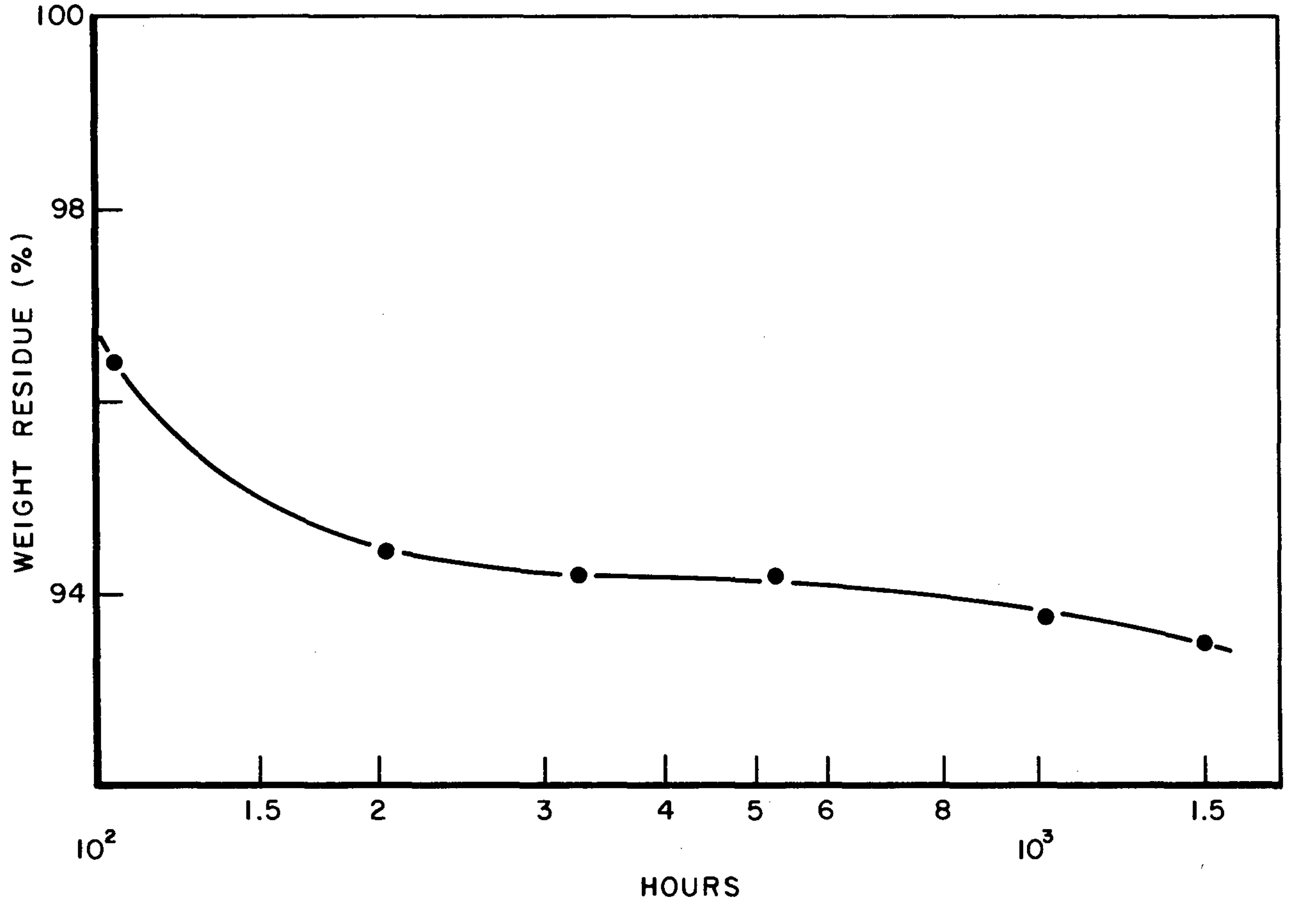

Figure 18. Isothermal Aging of BBB Polymer at 600°F in Air

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13. ABSTRACT

Thermally stable polymers, the polybenzimidazobenzophenanthrolines, were synthesized from 1,4,5,8-naphthalene tetracarboxylic acid (NTCA) and aromatic tetraamines. Polycondensations of NTCA with both 3,3'-diaminobenzidene (DAB) and 1,2,4,5-tetraaminobenzene tetrahydrochloride (TAB) in polyphosphoric acid gave soluble polymers which exhibited thermal stabilities near 600°C under nitrogen and near 500°C in air. Although these polycondensates were found to possess the highly fused benzimidazobenzophenanthroline structure by infrared and elemental analysis, they are soluble in a few strong acids and bases. Polymers derived from DAB could be prepared which had intrinsic viscosities in the range of 1 to 2 in sulfuric acid, and these were found to be fiber forming. Low viscosity polymer from NTCA and DAB could also be prepared by solid phase polycondensation. The analogously structured ladder type polymer prepared from TAB had poorer solubility characteristics and solution viscosities greater than 1.0 dl/gm were not obtained. Analysis of both type polymers which had viscosities less than 1.0 dl/gm indicated the presence of some incompletely cyclized chain structure. It was possible to cause some advancement in the viscosities of polymers synthesized from DAB by secondary solid phase reactions.

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