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SYNTHESIS AND PROPERTIES OF SOME BENZIMIDAZOBENZOPHENANTHROLINE POLYMERS POSSESSING BOTH NON-LADDER AND LADDER STRUCTURES

JOHN F. COLEMAN
R. L. VAN DEUSEN

TECHNICAL REPORT AFML-TR-69-289

MARCH 1970

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. R. L. Van Deusen, Project Scientist.

This report covers work conducted in this Laboratory from April 1967 to March 1968. The manuscript was released in October 1969 for publication as an AFML Technical Report.

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

This technical report has been reviewed and approved.

W E Gibbs
W. E. GIBBS
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

A series of benzimidazobenzophenanthroline (BB) polymers containing both the "Bis-BB" (BBB) and the "BB-Ladder" (BBL) polymer structure have been prepared from NTCA and stoichiometric mixtures of DAB and TAB by polycondensations in polyphosphoric acid. The polymer structures were verified by elemental and infrared absorption analyses. The polymers were found to be black and amorphous, to have inherent viscosities ranging from 0.25 to 1.7 dl/gm at 30° C in sulfuric acid, and to exhibit stability in air to over 500° C by thermal gravimetric analysis. Isothermal aging studies were performed and showed the polymers with mixed structures to be less resistant to a thermooxidative environment than the parent homopolymers.

This abstract is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Air Force Materials Laboratory (MANP), Wright-Patterson AFB, Ohio 45433.

TABLE OF CONTENTS

ILLUSTRATIONS

ILLUSTRATIONS (Cont'd)

TABLES

SECTION I

INTRODUCTION AND OBJECTIVES

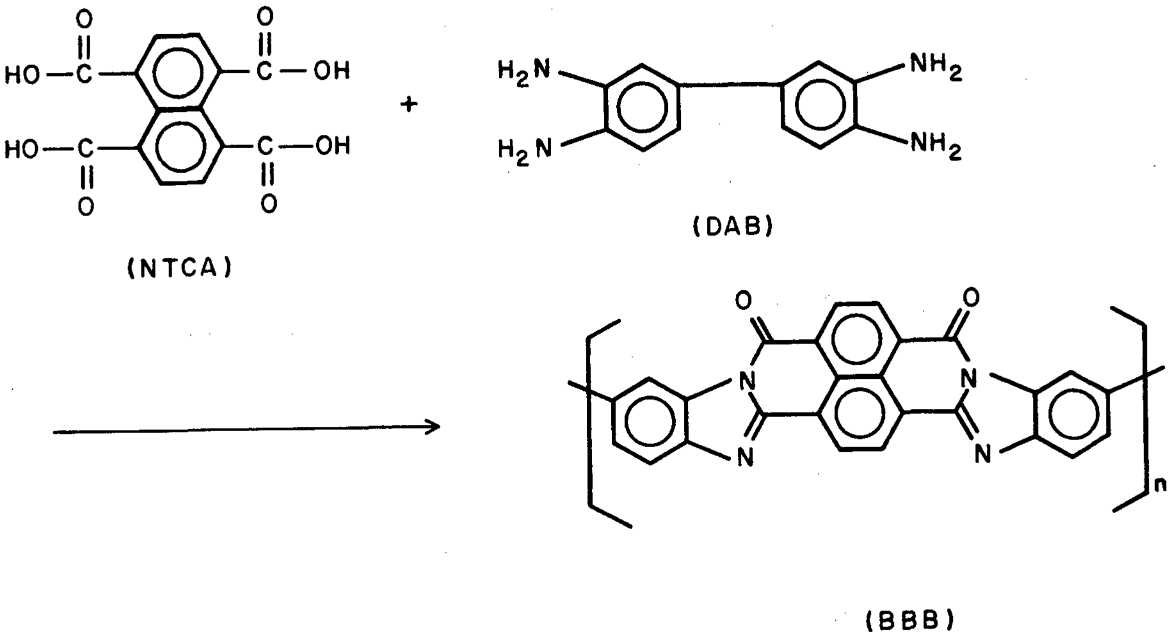
During the past few years research efforts to synthesize polymers which resist thermal degradation above 400° C have for the most part dealt with investigations of complex aromatic-heterocyclic systems. This emphasis is largely based upon earlier achievements stemming from the discoveries and developments of the thermally stable polybenzimidazoles (References 1, 2) and polyimides (References 3 - 5). There are many other examples of polymer systems which offer proof of the high temperature stability attainable from aromatic-heterocyclic backbone structures (Reference 6), a notable example being the polyquinoxalines (Reference 7). Several relatively recent investigations have lead to the discoveries of remarkably stable polymers prepared by condensing a variety of aromatic tetraacids or dianhydrides with aromatic tetraamines. Although these have sometimes been collectively referred to as types of pyrrones (Reference 8) or polyarylimidazole-imides (Reference 9) these complex polymers have been named more specifically as polybenzimidazolimides (Reference 10), polybenzoylenebenzimidazoles (Reference 11), polybenzimidazobenzopyrrols (Reference 8), polybenzimidazobenzophenanthrolines (Reference 12), polyisoindolopyrimidoperimidines (Reference 10), polynaphthoylenebisbenzimidazoles (Reference 13), and polyperimidoperimidines (Reference 14).

In addition to the many approaches which have been pursued to synthesize high temperature polymers comprised of novel aromatic-heterocyclic backbone structures, very worthwhile approaches to obtaining variations in physical properties have been taken by copolymer synthesis. To maintain desirable thermal stabilities two or more parent backbone systems, each known to be thermally stable, have been coincorporated in polymer chains. The mixed aromatic-heterocyclic polymers which result can be expected to be thermally stable and possess some compromise of properties which differ from either parent system. Due to the great degree of flexibility in tailoring polymers to meet specific needs a variety of thermomechanical properties have been produced by this approach. For example, copolymers composed of various types of unit structures found in polybenzimidazoles, polybenzoxazoles, polyimides, polyoxadiazoles and others have been reported (References 15 - 17).

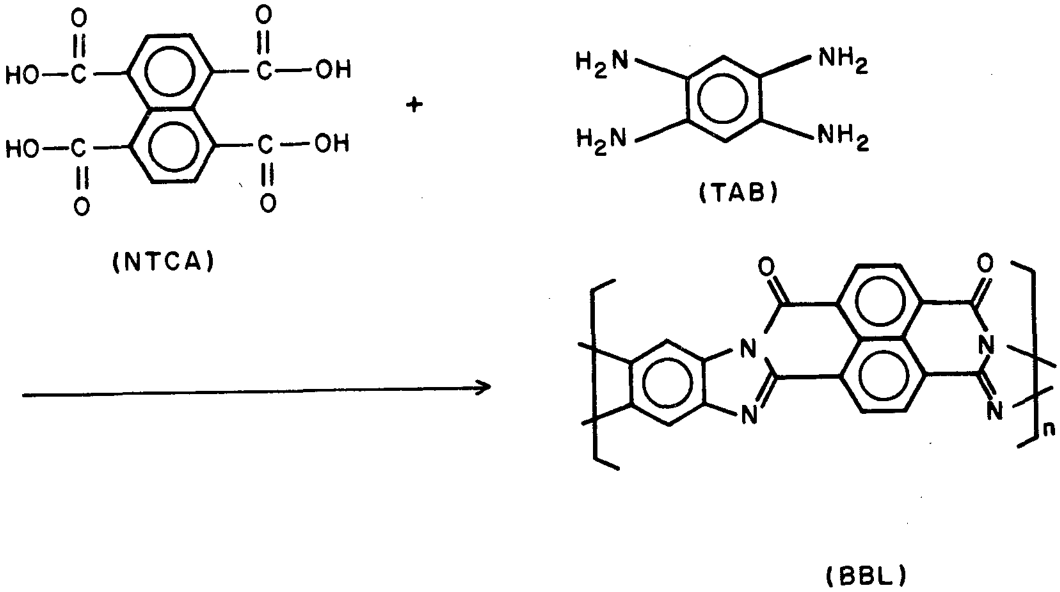
In this laboratory, considerable effort has been spent on the synthesis, characterization, and development of benzimidazobenzophenanthroline (BB) polymers (References 12, 18-20). Equations 1 and 2 shown below summarize the synthetic routes for synthesizing both the "Bis-BB" polymer (BBB) and the "BB-Ladder" polymer (BBL) of this class. These polymers have exceptionally good thermal and chemical stabilities and thus have high potential for aerospace applications. In particular, BBB is a very attractive candidate material for use as a high temperature fiber (Reference 21).

It has been found in our laboratory, as well as in other laboratories dealing with complex polycondensation polymers (References 10, 12), that aromaticheterocyclic ladder structured polymers tend to be less tractable than non-ladder analogs. In our work BBL was found to have poorer solubility characteristics than BBB (Reference 12). This is generally considered to be a disadvantage, but conversely, the more highly fused ladder polymers can be expected to exhibit some improvement in thermal properties over analogously structured polymers which are not completely double stranded (References 22). Although this has not been clearly demonstrated by experimental findings, the difficulties encountered in attempting to devise suitable techniques for synthesizing high quality ladder polymers may be a responsible factor. Research in this laboratory has been devoted to improving the synthesis of ladder polymer BBL but a significant improvement over BBB stability has not yet been observed.

In view of the high potential for the BBB polymers it is realized that valuable information on structure-property relationships will be gained if the effects of some BBL structure incorporated into BBB polymer backbone can be determined. This report describes work having to do with this aspect. One of the objectives of this work is to learn whether or not mixed BBB/BBL copolymers can be synthesized by conventional techniques or whether novel synthetic approaches will be required to obtain such copolymers. Further, indications of the effects of mixed BBB/BBL structures upon thermal stabilities are considered important to learn prior to any attempts to determine whether or not advantages in mechanical properties may be gained from copolymer compositions. Thus, synthetic approaches known to produce BBB and BBL polymer structures have been taken to synthesize mixed polymer structures by using mixtures of the tetraamines shown in Equations 1 and 2 as the base monomer. The reaction is represented by Equation 3 where a 1:1 or 50-50 charge of DAB/TAB monomer mixture can be expected to produce a BBB/BBL-50/50 copolymer.

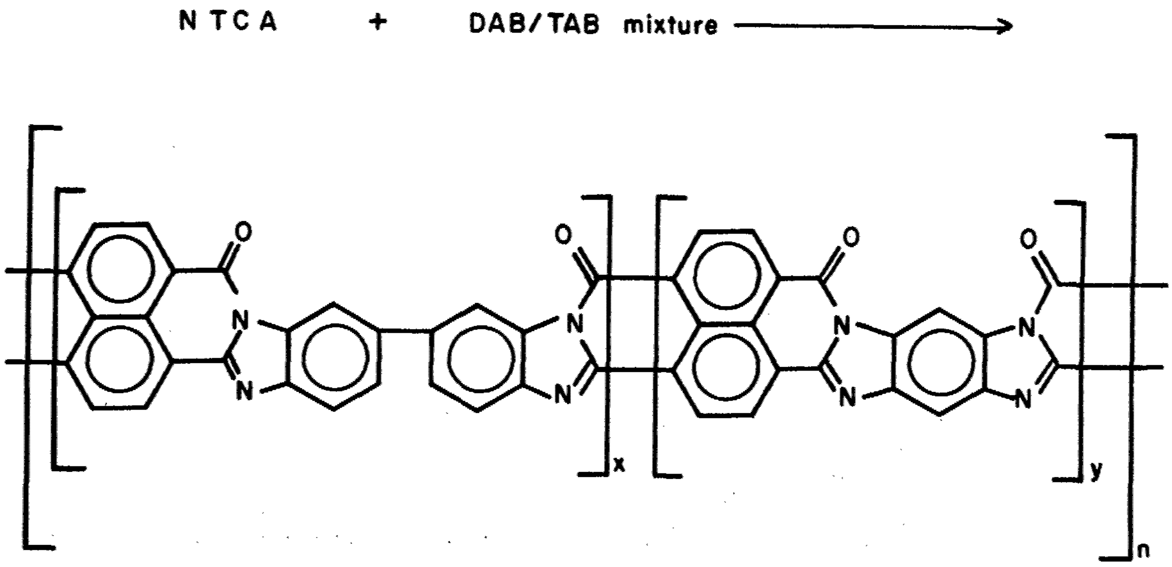

HO—C
C—OH
HO—C
C—OH
O
O
O
O
(NTCA)
+
H2N
H2N
NH2
NH2
(DAB)
O
O
N
N
N
N
n
(BBB)

(1)


HO—C
C—OH
HO—C
C—OH
O
O
O
O
(NTCA)
+
H2N
H2N
NH2
NH2
(TAB)
O
O
N
N
N
N
n
(BBL)

(2)

As implied, the current work may be considered to be a preliminary investigation of BBB copolymers to aid in determining whether or not potential exists for these mixed polymer systems in extreme environment applications of interest to the Air Force.



(3)

(BBB/BBL Copolymer)

SECTION II

EXPERIMENTAL

MONOMERS AND SOLVENT

1, 4, 5, 8-Napthalene tetracarboxylic acid (NTCA) (Aldrich Chemical Company) was purified by the Dayton Laboratory of Monsanto Research Corporation by a permanganate oxidation procedure (Reference 23). This monomer was dried over concentrated sulfuric acid at 30 mm Hg for at least 72 hours before use.

3, 3'-Diaminobenzidine (DAB) was obtained as polymer grade monomer from Celanese Research Company and used as received.

1, 2, 4, 5-Tetraaminobenzene tetrahydrochloride (TAB•4HC1) was purchased from Burdick and Jackson and purified by reprecipitation according to the method previously used by the Dayton Laboratory of Monsanto Research Corporation (Reference 23).

1, 2, 4, 5-Tetraaminobenzene (TAB) was prepared by the method of Vogel and Marvel (Reference 1), and dried before use (m. p., 272-275° C).

4, 5-Dinitronaphthalene-1, 8-dicarboxylic anhydride was obtained from the Dayton Laboratory of Monsanto Research Corporation (Reference 23) and recrystallized from p-dioxane (m. p., 328-330° C uncorr.) before use.

Polyphosphoric acid (82-84% P_2O_5) (PPA) (Matheson Coleman and Bell) was deoxygenated before using by heating the stirred solvent under continuous nitrogen flow at 100-110° C for 16 hours to displace any air. Without exposure to the atmosphere the PPA was cooled and stored under nitrogen prior to use as a reaction solvent.

REFERENCE POLYMERS

Samples of previously synthesized BBB and BBL polymers were used for comparisons with the BBB/BBL copolymers prepared in this investigation. With regard to BBB Reference Polymers, samples B, D, E, and F were previously synthesized in this laboratory according to Equation 1 (Reference 12). By a similar procedure BBB Reference Polymer samples A and C were synthesized by Monsanto Research Corporation (Reference 24) and sample G by Celanese Research Company. Of the BBL Reference Polymer samples utilized, samples A, B, and D were previously synthesized in this Laboratory (Reference 19) according to Equation 2. More recently BBL Reference Polymer sample C was also synthesized in this Laboratory (Reference 20).

Pertinent properties of these Reference Polymer samples are listed in Table I.

MODEL COMPOUNDS

Bis(3,3-dihydro-6,7-dinitronaphthalimido) [3,2-b:2',3'-g] benzo [1,2,4,5] -bisimidazole (Figure 1) was prepared as follows. A solution of 0.8292g (0.006 moles) of TAB dissolved in 30 ml of 99.7% acetic acid was added to a solution of 3.4580g (0.012 moles) of 4,5-dinitronaphthalene-1,8-dicarboxylic anhydride dissolved in 250 ml of 99.7% acetic acid. The resulting solution was heated at 100° C for four hours, and the precipitate which formed was collected on a medium porosity glass frit by hot filtration. The product was extracted with dioxane at 100° C for four hours and then collected and dried for 20 hours at 175° C, 15 mm Hg. The yield was 1.797g (46.6%), m.p., 400° C. The product was identified by comparing its infrared spectrum with that of the non-nitrated parent compound.

Bis(3,3-dihydro-6,7-dinitronaphthalimido) 3,2-b:2', 3'-b' 5,5'-bibenzimidazole (Figure 2) was previously prepared in this Laboratory from the condensation of 4,5-dinitronaphthalene-1,8-dicarboxylic anhydride with DAB by a similar method (Reference 26).

POLYCONDENSATIONS

General

Polycondensations were carried out under nitrogen in deoxygenated PPA. Tetraacid and tetraamine monomers were charged in equimolar quantities each at a concentration of 0.05 m/l in the solvent. In cases where tetraamine monomer mixtures were used, the total mole concentration of the amines was equivalent (i.e., 0.05 m/l), although the mixtures varied in composition. The total amine stoichiometries were made up of various quantities of TAB•4HCl, TAB, and DAB, depending upon the method of polycondensation employed and the copolymer composition desired.

Method A

Under a slightly positive nitrogen atmosphere pressure reaction mixtures of PPA (200 ml), NTCA (0.01 mole) and tetraamine(s) (0.01 mole) were heated with stirring to approximately 60° C until solution appeared complete. In cases where TAB•4HCl was present as a monomer, the reaction temperature was held between 60 and 80° C until HCl evolution had ceased (about two hours) so that the free tetraamine was dissolved. The reaction temperature was then increased to about 180° C over a four-hour period, and held between 180 and 200° C for a total of 18 hours.

The reaction was terminated by externally cooling to 90° C. The dark viscous liquid was poured into 3.5 liters of cold water with stirring to cause precipitation of the product. The mixture was allowed to settle and the supernatant liquid was siphoned off. The volume was replenished with distilled (pH 4.5-5.0) water, and the mixture stirred for several hours. The polymer was again allowed to settle and the washing process was repeated until the pH of the supernatant liquid was 4.0 to 4.5. On the final water wash, the mixture was heated to about 90° C with stirring for two hours and then allowed to settle. The polymer was separated by filtration through a medium porosity glass frit, and transferred wet to methanol (1.5 liters). The methanol mixture was slurried for two hours with heating and then refiltered. The filtrate was washed on the frit with additional methanol and then thoroughly washed with ether. The air dried product was vacuum dried at 175° C/10 mm Hg for 40 hours. The product was then reprecipitated from concentrated sulfuric acid using similar wash procedures.

The following polymers were prepared by this method: BBB, BBL, BBB/BBL-80/20, BBB/BBL-50/50, and BBB/BBL- 20/80 (see Table II).

Modification A-I

Method A given above was followed except that the monomer concentrations in the reaction solvent were doubled. In 200 ml of deoxygenated PPA, 0.02 moles of NTCA, 0.01 moles of DAB and 0.01 moles of TAB•4HCl were reacted to produce a BBB/BBL-50/50 polymer (see Table II).

Modification A-II

The monomer concentrations of Modification A-I were used, but the procedure for combining monomers was varied. A mixture of 0.01 moles of TAB•4HCl and deoxygenated

PPA (200 ml) was heated under nitrogen, as above, between 60 and 80° C until HCl evolution had ceased. The resulting pink solution was cooled to room temperature under the inert atmosphere, and NTCA (0.02 moles) and DAB (0.01 moles) were added. In this case the polycondensation was carried out at 180-188° C for 18 hours and then isolated as above. During reprecipitation of the isolated polymer, it was found that only 78% of the product appeared to be soluble in concentrated sulfuric acid at concentrations as low as 0.25%. The soluble fraction was reprecipitated and used for property determinations (See Table II).

Method B

This method was similar to Method A except that TAB-free base was used rather than the tetrahydrochloride salt. The volume of deoxygenated PPA was increased to 225 ml but the monomers were charged at 0.01 mole of NTCA and a stoichiometric quantity of TAB or a stoichiometric mixture of DAB and TAB. Polymers prepared by this method are listed in Table II, Appendix.

Modification B-I

The monomer concentrations of Method B were used but the addition of the TAB was delayed until the NTCA and DAB had reacted together in deoxygenated PPA at 70-80° C for four hours under the inert atmosphere. After the delayed TAB addition, the polycondensation was carried out at 180-190° C for 18 hours. The standard work-up was used for isolation and purification of the resulting BBB/BBL-50/50 copolymer (see Table II).

Modification B-II

The concentrations of Modification B-I given above were used but the DAB addition was delayed until the NTCA and TAB had reacted together in deoxygenated PPA for four hours under the inert atmosphere. After the delayed DAB addition, the polycondensation was carried out at 180-188° C for 18 hours. The standard work-up was used for isolation and purification of the resulting BBB/BBL-50/50 copolymer (see Table II).

Method C

This method was identical to that of Method B except that a new shipment of PPA and a new batch of NTCA was used. Latter investigations showed that the PPA was substandard and that the NTCA contained about 2-4% of the corresponding mono- and/or dianhydride(s) of NTCA. Polymers prepared by this method are listed in Table II.

Method D

The monomer concentrations of Method B were used with freshly obtained PPA, but with the same NTCA as used in Method C. The polycondensation was carried out at 180-190° C for 18 hours. The polymer-PPA mixture was then cooled to room temperature and the polymer isolated by pouring into methanol as described elsewhere (Reference 20). The physical properties of the polymer prepared by this method was obtained on an isolated sample rather than on a sample precipitated from acid as in the other methods (see Table II).

POLYMER CHARACTERIZATIONS

Viscosities were run in a modified Ubbelohde dilution viscometer in either concentrated sulfuric acid or methane sulfonic acid at 30° C at a concentration of 0.5g/dl. Inherent and intrinsic viscosities are listed in Tables I and II.

Elemental analyses were performed by Huffman Laboratories, Inc., and the results are tabulated in Tables I and II.

Infrared spectra were obtained on a Perkin-Elmer Model 137 Infracord spectrophotometer (Figures 1, 2, 14-16). Analytical spectra were provided by W. Crawford of the Analytical Branch, Materials Physics Division, AFML, on a Perkin-Elmer Corporation Grating Spectrophotometer, Model 521 (Figures 5-13).

Thermogravimetric analyses were run on either an Aminco or Chevenard Thermobalance and were obtained through Dr. G. F. L. Ehlers, Polymer Branch, Nonmetallic Materials Division, AFML.

Isothermal aging was performed by a reproducible method. Polymer samples were ground for five minutes in a metal Wig-L-Bug apparatus, dried at 175° C for 66 hours at 10 mm Hg and allowed to cool in a vacuum dessicator over Drierite. Sample weights were determined in small crucibles which had previously been conditioned at 700° F for 66 hours and allowed to cool in a dessicator. Care was taken to use identical weighing procedures. Seven samples, contained in loosely covered crucibles supported by a seven-place dessicator plate, were prepared for each aging experiment.

The sample plate containing the samples was removed from the dessicator and placed in a static air, constant temperature oven at 700° F, for additional drying. After a three-hour period, the sample plate was removed from the oven, replaced in the vacuum dessicator and allowed to cool for 1 1/2 hours. Sample weights were then determined in sequence. These weights were then used as initial polymer weight. This procedure was duplicated for given time periods until heating periods totaled at least 200 hours for each run. For each sample the percent weight loss was plotted vs. total time at temperature to obtain aging curves. For duplicate (or triplicate, etc.) runs the data was averaged. For example, weight losses taken from three BBB aging curves at selected times (Figure 3) were tabulated (Table IV). Average values were calculated (Table IV) and were replotted to obtain a single average aging curve (Figure 4) for BBB. Data for all polymers were averaged in a similar manner and compiled in Tables V and VI. The BBL (Reference Polymer A) and BBL (Reference Polymer B) data were taken from single runs since available quantities of samples were insufficient for duplicate runs.

SECTION III

DISCUSSION OF RESULTS

POLYMER SYNTHESIS AND ISOLATION

Based upon prior works (References 12, 18, 19) a set of BBB reaction conditions was selected to prepare polymers for this investigation. This procedure involving a solution polycondensation in PPA was known to give good results for synthesizing BBB homopolymers. It was employed here, with only minor modifications in specific instances to determine whether or not it could provide a feasible approach to the preparation of BBB copolymers. No attempt was made in this preliminary investigation to optimize or seek new reaction conditions for each individual type of polycondensation.

Thus without significantly changing reaction conditions, polymer products varying in compositions from BBB/BBL-100/0 through BBB/BBL-0/100 were obtained by using either stoichiometric quantities of the required tetraamines (see Equations 1 and 2), or stoichiometric mixtures of these tetraamine monomers. For example, polymerization mixtures which were charged to produce 80/20, 50/50, and 20/80 BBB/BBL compositions were prepared (Method A) by reacting NTCA with equivalent mole quantities of DAB/TAB mixtures in mole ratios of 80/20, 50/50, and 20/80, respectively. The TAB was actually charged as TAB•4HCl in these polymerization mixtures.

In a variation of Method A, Modification A-II, the free amine of TAB•4HCl was generated in situ before DAB addition at a low temperature. This was done to avoid any reaction of free base DAB prior to the liberation of free base TAB for reaction, as would be possible in Method A. In this instance, the mole ratio of bases was 50-50 and the TAB was freed by first heating the salt in deoxygenated PPA in an inert atmosphere. The resulting monomer solution was then cooled before the addition of DAB comonomer and tetraacid. Examination of this polymer product designated BBB/BBL-50/50 (Method A-II) gave no indication that this modification had been beneficial. Compared with the BBB/BBL-50/50 sample prepared by Method A, the BBB /BBL-50/50 sample prepared by Method A-II had some insolubles. The reprecipitated sample from A-II had a slightly lower inherent viscosity (Table II), and its isothermal aging properties were inferior (Table VI, Figure 25) compared to the sample from Method A.

The monomer concentrations in Modification A-II, above, had been increased from that of Method A from 0.05 mole/liter in acid and base in Method A up to 0.10 mole/liter in A-II. Therefore, another BBB/BBL-50/50 polymer was prepared by Modification A-I which followed the methods of A but used the higher monomer concentrations of Modification A-II. Compared with the BBB/BBL-50/50 samples prepared by Method A and Method A-II, the BBB/BBL-50/50 sample prepared by Method A-I had a much lower inherent viscosity (Table II), but its aging properties were almost identical to the BBB/BBL-50/50 sample prepared by Method A-II.

Although the relative reactivities of the DAB, TAB, and TAB•4HCl comonomers in PPA have not been determined, it was recognized that the copolymer compositions would be dependent upon any existing differences in them. A detailed kinetic study which would be required to determined relative reaction rates (as well as possible rate changes due to the presence of HCl) was considered to be beyond the scope of this preliminary investigation, but the variations just described for Method A did not point up any one significantly best method.

A second series of polycondensations (Method B) was then initiated to increase the number of different copolymers of BBB and BBL available for comparisons. A change in the method of polymerization was also incorporated in this series. Polymer products which were 80/20, 65/35, 50/50, 35/65, 20/80, and 10/90 in BBB/BBL composition were prepared (Method B) by reacting an amount of NTCA which was an equivalent mole quantity to 80/20, 65/35, 50/50, 35/65, 20/80, and 10/90 ratios of DAB/TAB mixtures, respectively, with the TAB charged as the previously isolated free base. For these experiments a quantity of TAB•4HCl was treated with aqueous sodium hydroxide to liberate the free TAB, and it was then collected and dried before use. The physical properties of these polymer products are given in Table II.

As in Method A, two modifications of Method B were used to study the effect of varied amine concentrations upon the polymerizations. In Method B-I, a nonstoichiometric mixture of 0.01 mole of NTCA was reacted with 0.005 mole of DAB for four hours at 70-80° C before the addition of 0.005 mole of TAB was made to provide a total balance in stoichiometry in the reaction mixture. The inherent viscosity of the BBB/BBL-50/50 (Method B-I) polymer product was lower than that of the BBB/BBL-50/50 polymer prepared by Method B (Table II). Also the isothermal aging properties of the Method B-I polymer were inferior to those of the BBB/BBL-50/50 polymer prepared by Method B.

In another modification of Method B (Method B-II), a nonstoichiometric mixture of 0.01 moles of NTCA was reacted with 0.005 moles of TAB for four hours at 70-80° C in an inert atmosphere before the addition of 0.005 moles of DAB was made to give total stoichiometry to the reaction mixture. The inherent viscosity of this BBB/BBL-50/50 (Method B-II) polymer product was the same as that of the BBB/BBL-50/50 (Method B-I) polymer and less than that of the BBB/BBL-50/50 polymer prepared by Method B. The isothermal aging properties of the BBB/BBL-50/50 polymer prepared by Method B-II were also inferior to those of the BBB/BBL-50/50 polymer prepared by Method B, and equal to those of the BBB/BBL-50/50 polymer prepared by Method B-I.

As in the case of polymer products derived from Method A polymerizations, the variations described for these Method B types of polymerizations did not indicate a clearly superior approach which seems to be based upon the relative reactivities of the tetraamines.

A third series of BBB/BBL copolymers referred to under Method C in Table II were prepared like those in Method B, but using newly purchased PPA and a new batch of polymerization grade NTCA being used for fiber formation (Reference 25). The hope was to obtain polymers of higher molecular weight, although the BBB/BBL polymer products having DAB/TAB charge ratios of 100/0, 65/35, 50/50, and 0/100 were inferior with regard to both solution viscosities and thermal stabilities. These poor results led to the discovery of some impurity in the new batch of NTCA. By comparison of the infrared spectrum of the new batch of NTCA with the spectrum of NTCA known to give higher viscosity polymer, it was found that a small portion of the new NTCA appeared to exist as either the mono- or di-anhydride. An absorption band at 5.6 μ for anhydride carbonyl was found to be present. This anhydride could be sufficient to cause a lowering of the solution viscosities of the polymer due to the stoichiometry imbalance it would impose. (See Table II).

Since the NTCA was obtained from Celanese Research Co. as a small portion of a large batch of the acid which had been used to synthesize fiber grade BBB polymer some months earlier (Reference 25), another synthesis of BBB was performed by Method C in an attempt to gain more information to explain the poor results. However, in this case a different but also newly purchased PPA solvent was used and the polymerization is differentiated by listing it as Method D in Table II. The change of PPA solvent led to a significant improvement in the solution viscosity of the resutling BBB, although it was still not as high as that previously obtained with the original NTCA by Method A (Table II).

It now appears reasonable to suppose that gradual anhydride formation during storage of the monomer contributed to some stoichiometric imbalance resulting in a molecular weight lowering, and further, that the PPA used in Method C had some sort of inhibiting effect upon chain growth which was not evidenced in Method D. The possible nature of a PPA contaminant is not known. Attempts to eliminate what is believed to be the anhydride contamination of the NTCA by usual reprecipitation techniques have thus far been unsuccessful.

The physical properties of the polymers prepared by Methods A and B listed in Table II, Appendix, were obtained on polymer samples which had been precipitated from either concentrated sulfuric acid or methanesulfonic acid. Properties of polymer samples prepared by Method C and Method D were obtained on isolated samples. All BBB polymers and most BBB/BBL copolymers were easily soluble in concentrated sulfuric acid. The difficulties that have been encountered in handling the BB polymers have been described (References 12, 18-20) and are largely related to their poor solubility characteristics. For comparison, we noted that BBL in sulfuric acid solution gave an intense but lighter red solution than the very dark red characteristic of BBB solutions. The BBB/BBL copolymers in solution gave more the appearance of BBB. It should also be noted that BBL polymers with solution viscosities greater than ~ 0.5 dl/g in sulfuric acid are more difficultly soluble than the non-ladder BBB and may require heating to complete dissolution. Since the start of this work other investigations in this Laboratory (Reference 20) indicate that concentrated methanesulfonic acid is a better solvent for BBL polymers. We found that BBB, BBL and BBB/BBL copolymers are all conveniently soluble in methanesulfonic acid. One exception was encountered when the BBB/BBL-50/50 copolymer prepared by Method A-II was found to be only 78% soluble in concentrated sulfuric acid. That insoluble portion of the polymer was not found to be soluble in concentrated methanesulfonic acid either. This gave good indication that a significant portion of this copolymer product was cross-linked. Otherwise the copolymers exhibited enhanced solubilities compared to that of homopolymers. This was particularly evident in concentrated sulfuric acid, the poorer of the two polymer solvents.

POLYMER CHARACTERIZATION

Elemental analyses were obtained on purified samples of all polymers prepared by Method A and Method B using previously established procedures for these thermally stable polymers. Table III, Appendix, gives the theoretical elemental compositions expected for the various ratios of BBB/BBL structure based upon monomer charge. Experimental elemental analyses for carbon, hydrogen, ash, nitrogen, and oxygen (when reported) are given in Table II. Although not shown in Table II, all polymer samples prepared in PPA contained from 0.01 to 0.05% phosphorous. In addition, trace amounts of sulfur were also present from sulfuric acid reprecipitations.

All BB polymers tested have been found to possess metallic impurities. These are present in polymers prepared in PPA and reprecipitated in sulfuric acid. A typical emission spectra was obtained on the residue left after microanalysis of a finely ground (74 micron or less) sample of BBB (Reference Polymer A) dried at 250° C for 18 hours at 5 mm Hg. The results based on ash weight, indicated impurity levels of copper 30 ppm, aluminum 10 ppm, iron 60 ppm, silicon 30 ppm, magnesium 10 ppm, and potassium 40 ppm.

The use of elemental analyses in determining the actual copolymer ratio in the copolymer products was not found to be feasible, since this analytical technique is not accurate enough when dealing with the very thermally stable polymer. Nevertheless, when theoretical elemental composition calculations for BBB were compared with corresponding experimental composition results, good correlations were obtained (Tables II and III). On the other hand, correlations obtained between theoretical and experimental elemental compositions for BBL homopolymer were rather poor since carbon percentage values generally differed from theoretical by ±1.5 and nitrogen was about 1 lower than theoretical. The percentage of hydrogen is very low in these polymers, so these determinations cannot be considered to be very accurate. Because of the relatively small differences in theoretical elemental composition between BBB and BBL, and the relatively large variations from theoretical composition, no valid determination of exact copolymer composition could be made from the data.

Solution viscosities of the polymers were obtained at 30° C in a Cannon Ubbelöhde viscometer in either concentrated sulfuric acid (97-98%) or in purified methanesulfonic acid (100%). Inherent viscosities were obtained at a concentration of 0.5 g/dl. Intrinsic viscosity determinations in concentrated sulfuric acid on both BBB homopolymers and

BBB/BBL, as well as those for BBL homopolymers in methanesulfonic acid were straight forward. However, data obtained for BBB homopolymers and BBB/BBL copolymers in in methanesulfonic could not be well fitted for extrapolations to zero concentrations. This behavior may well be indicative of a polyelectrolyte effect. Graphic deviations from linearity were found to occur between concentrations of 0.35 to 0.25 g/dl in these cases so intrinsic viscosities reported in Table II for BBB homopolymers or BBB/BBL copolymers in methanesulfonic acid are the results of extrapolations of the data between concentrations of 0.35 and 0.50 g/dl.

Infrared absorption spectra of ground polymer samples were not readily obtained since the solids were found to be very difficult to pulverize and grind. Therefore, film samples of a representative number of the homo- and co-polymers were prepared. Studies of the infrared spectra indicated that in going from the BBB homopolymer to the BBL homopolymer to the BBL homopolymer through the 80/20, 65/35, 50/50, 35/65, 20/80, and 10/90 BBB/BBL copolymers (Figure 5-12) there are several changes in absorbance which can be directly correlated with either the BBB or BBL homopolymer spectra. Qualitatively at least, these appear to be in accord with the copolymer compositions to be expected from charge ratios of the monomers. Since quantitative studies are lacking, no differences between copolymer composition and homopolymer mixtures can be distinguished. Nevertheless, the solubility properties give no indications that polymer products could be mixtures of homopolymers.

There are four absorptions in the 6.5 to 9.0 micron region which appear in the BBB and all BBB/BBL copolymer spectra, but which are absent in the BBL spectrum. These absorb at 6.87-6.89 microns, 6.95-7.00 microns, 7.35-7.40 microns, and at 8.70-8.73 microns. The first two absorptions appear to be shifted slightly higher in the copolymers than in the BBB homopolymer. Absorptions which appear in the BBL and in all BBL copolymer spectra but which are absent in the BBB spectrum are located at 7.03-7.06, 7.07-7.09, 7.64-7.70, and 8.52-8.55 microns. In addition, there are definite changes occurring in the 6.1-6.5 micron region which are complicated by the number of absorptions falling within this region. Upon inspection of the 6.1-6.5 micron region of Figures 5-12, these changes can be seen. An analytical film spectrum of a 50/50 physical mixture of BBB and BBL homopolymers (Figure 13) was obtained for further comparisons. The only notable difference (see Figures 8 and 13) is the presence of a 6.28-micron absorption in the copolymer spectrum. This may be indicative of copolymer formation, although confirming this would be very difficult. The 6.1-6.5 micron region is complicated by other polymer bands, in addition to the fact that all three monomers (NTCA, DAB, and TAB) absorb in this same region (Figures 14-16).

It should be noted that homopolymers do not exhibit absorption in the 5.60-5.63 and 5.73-5.76 micron regions if prepared in high molecular weight. However, these absorptions do occur in low viscosity polymers and are quite probably due to anhydride end-groups (Reference 20). The copolymer products derived in this investigation are low viscosity polymers and exhibit these absorptions, as might be expected.

THERMAL GRAVIMETRIC ANALYSIS (TGA)

As expected, the thermal stabilities of the BBB, BBL, and BBB/BBL copolymers appeared to be very good. The temperatures at which 5% weight loss occurred in both air and an inert atmosphere (nitrogen or helium) are given in Tables I and II. In Figure 17, the TGA curves in air are compared for three BBB polymers having different solution viscosities. Figure 18 similarly compares the TGA curves of three BBL polymers in air. From these two figures and from the data on homopolymers collected in Tables I and II, it is seen that a relatively wide variation in the temperature is found at which a 5% weight loss occurs. These variations are seen again in the TGA curves of the five polymers prepared by Method A as shown in Figure 19 (air) and Figure 20 (inert atmosphere). The TGA curves for other polymers prepared by different methods show that these polymers constitute a series or family of high temperature materials which are thermally stable to about 500° C in air and to higher temperatures in an inert atmosphere.

ISOTHERMAL AGING STUDIES

To further characterize the thermal stabilities of these polymers, isothermal aging studies were undertaken. The standardizing method explained in the Experimental section was used to obtain average isothermal aging curves for all the polymers. The reproducibility of this method was adequate for valid comparisons, since the calculated standard deviation after 240 hours aging of six samples of BBB (Reference Polymer A) was a value of 8 ±1.7% weight loss.

The weight losses during isothermal aging at 700° F for 240 hours in a static air oven for the BBB reference Polymers are shown in Figure 21. As expected, better thermal stability was exhibited by polymers with the higher solution viscosities. Similar data for all BBL Reference Polymers are shown in Figure 22, and again the higher viscosity polymers are found to age better, with one exception, the anomalously behaving BBL (Reference Polymer B). In Figure 23, the weight losses for the polymers prepared by Method A are compared, and it is noted that the higher viscosity homopolymers exhibit higher thermal stabilities than the lower viscosity copolymers. A discussion of the quantitative differences in the thermal stabilities of these polymers becomes difficult because of the differences in the molecular weights which are indicated for the polymers. When the weight losses of polymers prepared by Method B are compared (Figure 24), no conclusions on thermal stability versus copolymer change composition can be drawn. However when the weight losses of all the BBB/BBL-50/50 copolymers (prepared by Methods A, A-I, A-II, B, B-I, and B-II) are compared (Figure 25), it can be seen that the polymers prepared by Methods A and B are more thermally stable than those prepared by the modified methods. This is especially so where delayed addition of one monomer was made (B-I, B-II). The data from which Figures 21-25 were drawn is given in Tables V and VI.

In Table VII, the ash content and viscosities of many of the polymers discussed above are compared with the corresponding thermal data. From this table it can be seen that both molecular weight reflected by the solution viscosities and the ash content found in combustion analyses affect the thermal stabilities. This can occur to the extent that a high ash content can cause a polymer of high solution viscosity to have a lower thermal stability than a similar polymer having a lower solution viscosity. Good examples of this are the lower-than-expected weight losses for BBB (Reference Polymer C) (Figure 21) and BBL (Reference Polymer B) (Figure 22). Other examples of this can be seen in the data for the copolymers.

SECTION IV

CONCLUSIONS

From the results presented in this report, it is concluded that thermally stable BBB/BBL polymers can be prepared from NTCA and stoichiometrically prepared mixtures of DAB and TAB by polycondensations in PPA. The polymers thus prepared have enhanced solubility in sulfuric acid compared to the difficultly soluble BBL ladder polymer. Nevertheless, the mixed polymers obtained in this way are inferior to both the nonladder BBB and ladder-type BBL homopolymers in thermal stability. The basis for this is indicated by TGA and isothermal aging studies. The low inherent viscosities of the BBB/BBL polymers suggests that the conventional polycondensation of these monomers in polyphosphoric acid is not the optimum route to obtain the high molecular weight copolymers which would be expected to possess thermal properties more nearly approaching those of the parent polymers.

Since the enhancement of solubility properties does not appear to be especially significant, any potential advantages which might be realized by optimizing polymerization conditions do not now seem worth the additional research effort which would be required. For this reason, further work to optimize the polycondensation is not planned at this time but could be conducted if specific materials problems should arise which would likely be solved by BBB/BBL polymer compositions. This must be considered a real possibility, however, and the investigations reported here form a firm basis for such a research program.

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TABLE I

PHYSICAL PROPERTIES OF BBB AND BBL REFERENCE POLYMERS

Reference Polymer Designation	Solution Viscosity at 30° C			Elemental Analyses					5% Loss By TGA	
	η inh	$[\eta]$	$[\eta]$ MSA	%C	%H	%Ash	%N	%O	Air	Inert
BBB (Ref A)	-	2.01	2.51	76.37	2.64	0.6	13.38	7.88	525°	660° C
BBB (Ref B)	-	0.60	-	71.22	3.20	0.3	13.13	-	-	480° C
BBB (Ref C)	$1.3^{0.50}$	-	-	73.92	2.91	0.0	13.69	9.25	610°	725° C
BBB (Ref D)	-	0.16	-	71.17	3.17	0.75	12.37	-	450°	525°
BBB (Ref E)	-	0.80	-	-	-	-	-	-	-	590°
BBB (Ref F)	-	1.03	-	-	-	-	-	-	-	640°
BBB (Ref G)	-	2.96	4.28	75.26	2.57	0.0	13.32	7.86	595°	720°
BBB (Ref A)	$0.34^{0.20}$	-	-	-	-	-	-	-	490°	560°
BBB (Ref B)	$0.28^{0.24}$	-	-	68.48	3.21	1.01	17.25	-	490°	665°
BBB (Ref C)	-	-	5.2	70.57	2.09	6.0	15.66	10.90	580°	705°
BBB (Ref D)	$0.89^{0.15}$	-	-	71.89	2.38	3.49	15.21	11.12	-	590°

TABLE II

PHYSICAL PROPERTIES OF BBB, BBL, AND BBB/BBL POLYMERS

Polymer Designation	Method of Polymerization	% Yield Purified	Solution Viscosity at 30° C			Elemental Analysis					5% Loss By TGA	
			η_{inh} at 0.5g/dl	$[\eta]$	$[\eta]$MSA	% C	% H	% Ash	% N	% O	Air	Inert
BBB	A	96.8	1.68	-		75.60	2.59	0.8	13.23	-	545°	690°
BBB/BBL-80/20	A	>100	0.36	-		75.00	2.71	1.2	12.27	-	505°	625°
BBB/BBL-50/50	A	99.0	0.50	-		73.56	2.36	2.85	13.15	-	520°	675°
BBB/BBL-50/50	A-I	96.0	0.24	-		73.60	2.56	1.45	12.74	8.23	450°	600°
BBB/BBL-50/50	A-II	78.0	0.41	-		75.40	2.52	0.65	11.49	9.13	630°	625°
BBB/BBL-20/80	A	93.7	0.39	-		72.82	2.20	0.7	13.35	10.25	450°	565°
BBL	A	>100.0	1.05	-	1.74	70.74	2.02	0.9	15.86	-	535° C	660° C
BBB/BBL-80/20	B	>100.0	0.36	0.36	0.59	75.03	2.71	0.5	12.69	-	475°	670°
BBB/BBL-65/35	B	96.9	0.58	0.61	0.86	74.12	2.39	0.25	14.52	-	570°	710°
BBB/BBL-50/50	B	99.1	0.36	0.36	0.50	74.77	2.44	0.65	13.28	-	555°	650°
BBB/BBL-50/50	B-I	>100.0	0.26	0.27	-	75.81	2.70	0.65	12.57	-	480°	550°
BBB/BBL-50/50	B-II	>100.0	0.26	0.25	-	74.61	2.78	0.65	12.75	-	430°	575°
BBB/BBL-35/65	B	94.7	0.27	0.27	0.42	73.42	2.59	0.2	14.65	-	520°	670°
BBB/BBL-20/80	B	93.0	0.33	0.31	0.47	73.55	2.39	0.7	14.89	-	530°	660°
BBB/BBL-10/90	B	85.5	1.17	0.93	0.56	73.33	2.29	0.6	15.68	-	525°	700°
BBL	B	95.7	-	-	0.43	73.33	2.44	0.75	15.52	-	520°	710°
BBB	C	92.0	-	-	0.52	-	-	-	-	-	400°	-
BBB/BBL-65/35	C	98.0	-	-	0.39	-	-	-	-	-	-	-
BBB/BBL-50/50	C	>100.	-	-	-	-	-	-	-	-	-	-
BBL	C	>100	-	-	0.69	-	-	-	-	-	340°	-
BBB	D	>100	0.92	0.90	1.41	-	-	-	-	-	475°	-

TABLE III

THEORETICAL ELEMENTAL COMPOSITIONS OF POLYMERS

POLYMER	CHARGE RATIO	% C	% H	% N	% O
BBB/BBL	100/0	76.09	2.46	13.65	7.80
"	80/20	75.36	2.35	14.18	8.10
"	65/35	74.80	2.26	14.60	8.34
"	50/50	74.19	2.17	15.05	8.60
"	35/65	73.54	2.07	15.52	8.87
"	20/80	72.85	1.96	16.02	9.17
"	10/90	72.37	1.89	16.39	9.36
"	0/100	71.86	1.81	16.76	9.57

TABLE IV

ISOTHERMAL AGING OF BBB AT 700° F

	% WEIGHT LOSS VS. TIME AT 700° F								
Run Number/Time (Hrs)	18	44	66	88	157	175	200	220	240
I-2	0.9	2.3	3.0	4.7	9.6	10.7	16.7	20.0	25.1
III-2	0.3	1.7	3.2	3.5	13.4	15.8	21.6	24.7	32.0
IV-5	0.2	1.0	1.7	2.7	6.0	7.0	8.0	12.6	19.1
Average	0.5	1.7	2.6	3.6	9.8	11.2	15.4	19.1	25.4

TABLE V

ISOTHERMAL AGING OF REFERENCE POLYMERS AT 700° F

	% WEIGHT LOSS VS. TIME AT 700° F								
Reference Polymer/Time (Hrs)	18	44	66	88	157	175	200	220	240
BBB (Ref. A)	0.3	0.9	1.2	1.6	3.4	4.1	5.3	6.4	7.4
BBB (Ref. C)	0.3	0.6	0.7	1.4	4.6	5.5	7.0	9.3	10.8
BBB (Ref. D)	5.2	13.8	24.0	31.5	57.6	69.9	83.4	94.2	100.0
BBB (Ref. E)	1.1	3.0	4.3	6.1	13.2	16.0	22.7	27.5	37.2
BBB (Ref. F)	0.5	2.1	3.1	4.7	12.3	13.7	18.9	22.3	26.3
BBB (Ref. G)	0.4	0.6	0.8	1.1	1.2	1.4	1.6	2.0	2.0
BBL (Ref. A)	2.8	4.8	7.2	8.5	18.6	22.7	25.7	31.3	37.7
BBL (Ref. B)	1.6	2.2	3.3	5.2	11.8	14.2	17.1	20.0	22.6
BBL (Ref. C)	0.2	1.8	2.0	2.5	4.5	5.5	5.5	5.5	5.5
BBL (Ref. D)	0.0	1.2	2.2	4.9	18.7	22.0	28.7	33.0	38.2

TABLE VI

ISOTHERMAL AGING OF BBB, BBL, AND BBB/BBL POLYMERS AT 700° F

	% WEIGHT LOSS VS. TIME AT 700° F								
POLYMER/TIME (Hrs)	18	44	66	88	157	175	200	220	240
			METHOD A						
BBB	0.5	1.7	2.6	3.6	9.8	11.2	15.4	19.1	25.4
BBB/BBL 80/20	2.6	5.5	8.9	11.7	25.2	29.9	38.0	46.6	56.2
BBB/BBL 50/50	2.9	9.6	16.6	23.9	47.7	54.6	63.5	71.5	83.6
BBB/BBL 50/50 (A-I)	6.9	18.0	32.5	47.6	78.8	84.9	90.3	92.7	-
BBB/BBL 50/50 (A-II)	7.1	18.1	32.6	43.7	80.4	87.4	91.9	94.4	-
BBB/BBL 20/80	4.1	8.9	12.6	17.2	40.2	50.1	58.3	64.7	73.8
BBB	0.7	3.6	5.7	7.9	16.1	18.5	21.6	26.3	28.3
			METHOD B						
BBB/BBL 80/20	6.0	16.3	25.6	35.7	60.2	76.9	84.5	85.2	91.8
BBB/BBL 65/35	0.5	1.4	2.4	3.3	9.1	10.6	13.9	15.7	19.4
BBB/BBL 50/50	3.3	5.8	9.3	13.1	27.1	31.6	37.9	44.2	48.8
BBB/BBL 50/50 (B-I)	17.7	37.8	53.6	66.4	85.4	89.7	90.8	92.7	93.7
BBB/BBL 50/50 (B-II)	16.0	36.1	49.2	62.3	87.8	90.5	93.7	95.2	96.2
BBB/BBL 35/65	6.9	11.9	17.6	26.2	48.4	55.0	64.0	72.7	77.6
BBB/BBL 20/80	6.9	13.9	20.5	28.0	47.4	53.7	60.9	68.6	74.1
BBB/BBL 10/90	3.8	9.6	15.9	22.3	43.6	47.8	54.2	59.3	64.4
BBL	6.0	12.7	18.4	25.9	44.0	50.1	58.9	67.3	73.4

TABLE VII

PHYSICAL AND THERMAL PROPERTIES OF POLYMERS

Reference Polymer	% Ash	η (H_2SO_4)	η (MSA)	TGA % loss, Air	Isothermal Aging % loss at 200 Hrs. at 700° F
BBB (Ref. A)	0.6	2.0	2.5	525° C	5.0
BBB (Ref. C)	0.0	1.3	-	610° C	8.5
BBB (Ref. D)	0.75	0.16	-	450° C	83.0
BBB (Ref. G)	0.0	2.96	4.28	595° C	1.6
BBL (Ref. B)	1.01	0.28	-	490° C	22.0
BBL (Ref. C)	-	-	5.2	580° C	5.1
BBL (Ref. D)	3.49	0.89	-	-	27.0
BBB - Method A	0.8	1.7	-	545° C	17.0
BBB/BBL-80/20 Method A	1.05	0.36	-	505° C	37.0
BBB/BBL-50/50 Method A	2.85	0.50	-	520° C	62.0
BBB/BBL-20/80 Method A	0.70	0.39	-	450° C	56.0
BBL - Method A	0.9	1.05	1.74	535° C	22.0
BBB/BBL -80/20 Method B	0.5	0.36	0.59	475° C	84.5
BBB/BBL-65/35 Method B	0.25	0.61	0.86	570° C	13.9
BBB/BBL-50/50 Method B	0.65	0.36	0.50	555° C	37.9
BBB/BBL-35/65 Method B	0.20	0.27	0.42	520° C	64.0
BBB/BBL-20/80 Method B	0.70	0.31	0.47	530° C	60.9
BBB/BBL-10/90 Method B	0.60	0.92	0.54	525° C	54.2
BBL - Method B	0.75	-	0.43	520° C	58.9
BBB/BBL-50/50 Method A-I	1.45	0.24	-	450° C	86.0
BBB/BBL-50/50 Method A-II	0.65	0.41	-	630° C	90.0
BBB/BBL-50/50 Method B-I	0.65	0.27	-	480° C	90.8
BBB/BBL-50/50 Method B-II	0.65	0.25	-	430° C	93.7

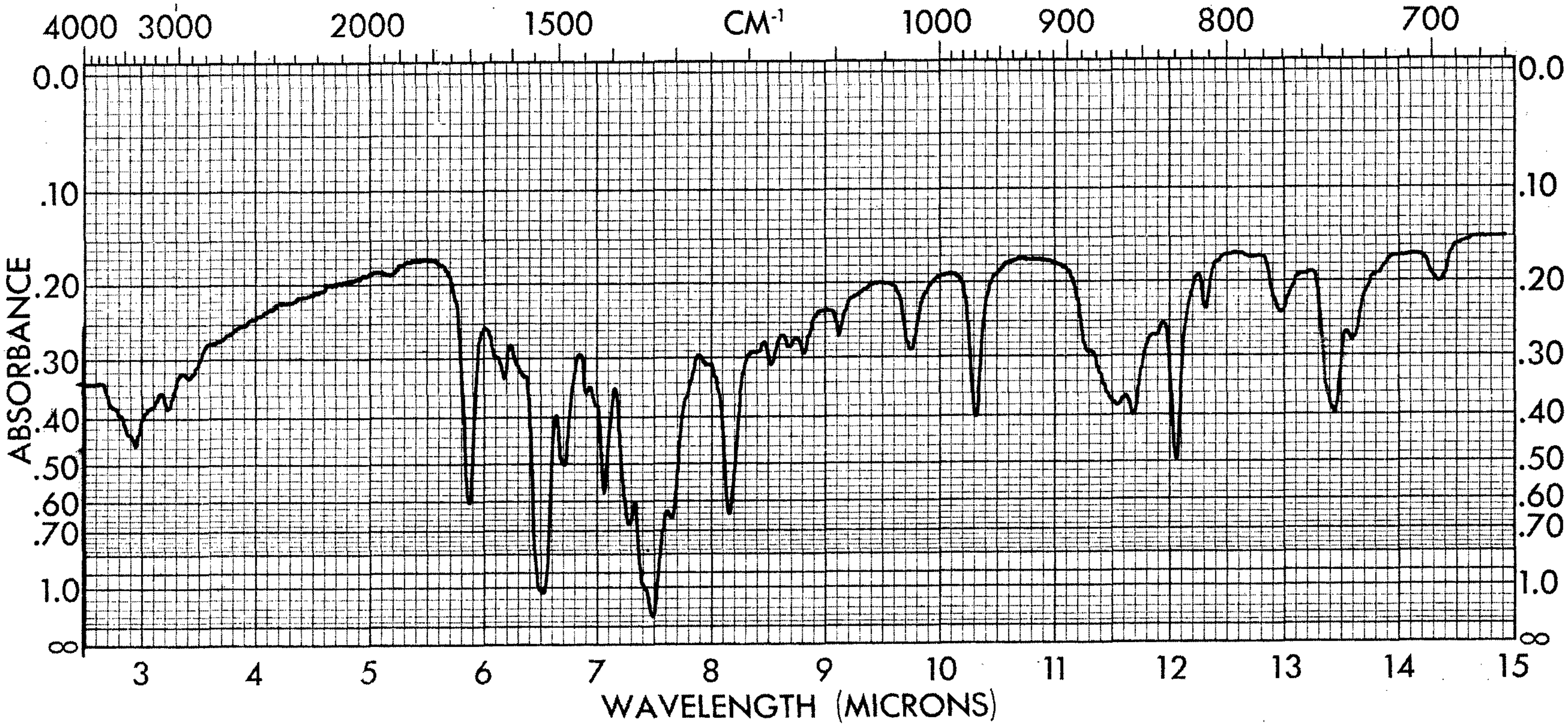

Figure 1. Infrared Spectrum of Bis(3, 3-dihydro-6, 7-dinitronaphthalimido) 3, 2-b:2', 3'-g benzo 1, 2, 4, 5 bisimidazole

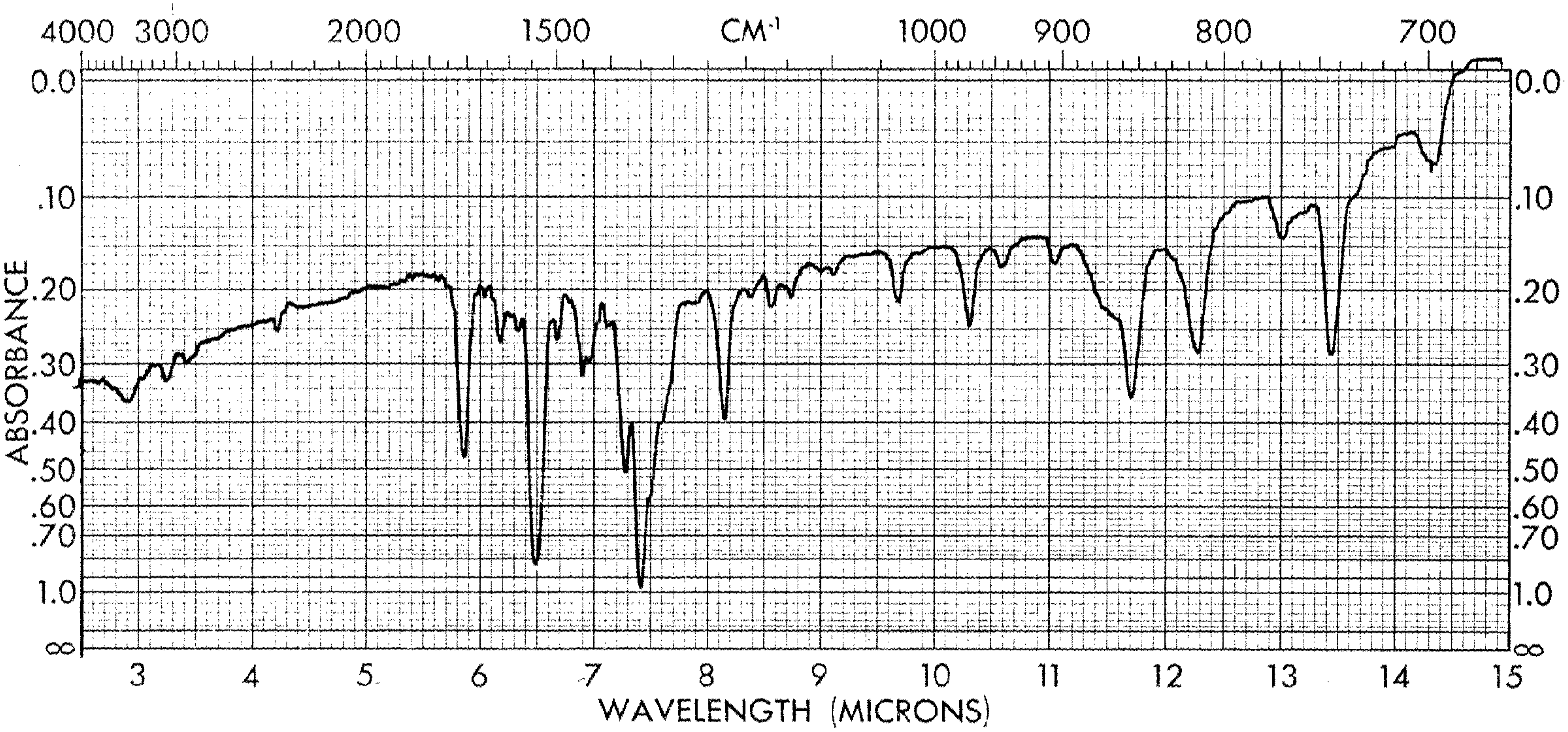

Figure 2. Infrared Spectrum of Bis (3, 3-dihydro- -6, 7-dinitronaphthalimido 3,2-b:2', 3'-b' 5,5'-bibenzimidazole

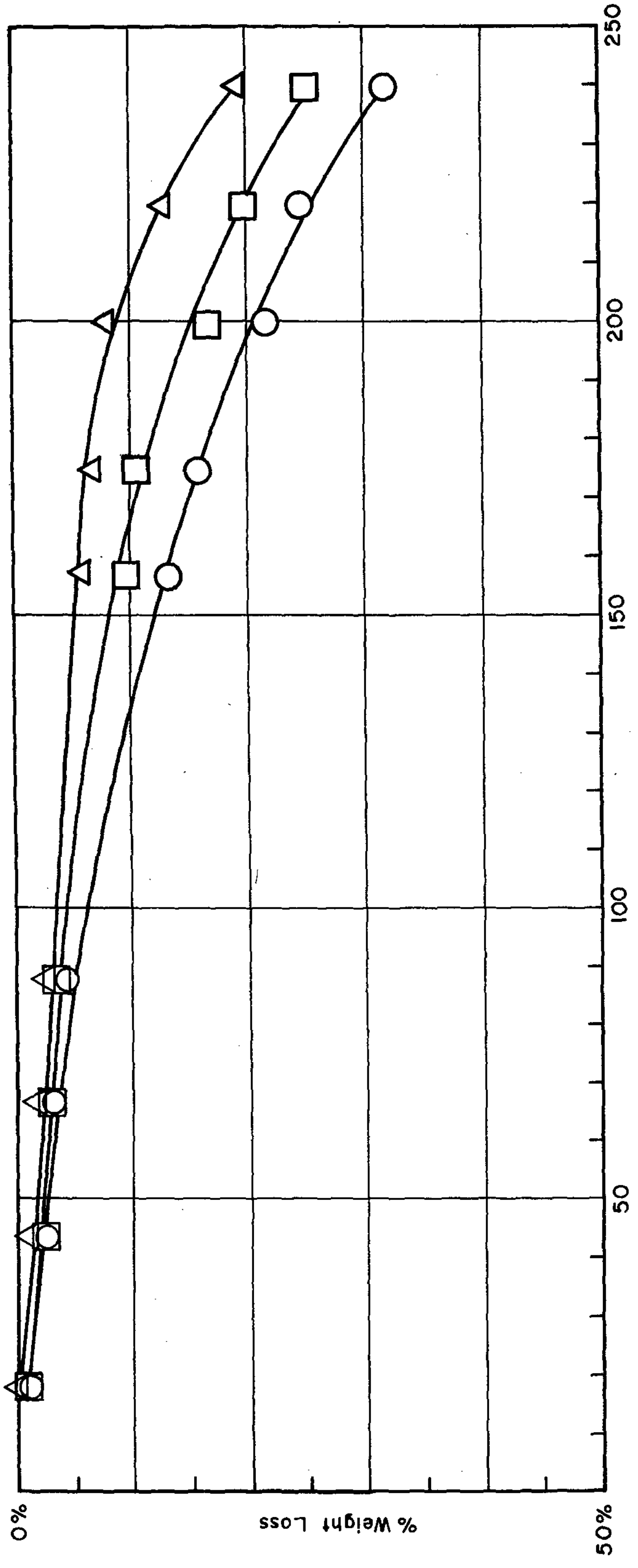

Figure 3. Isothermal Aging Curves of BBB at 700° F

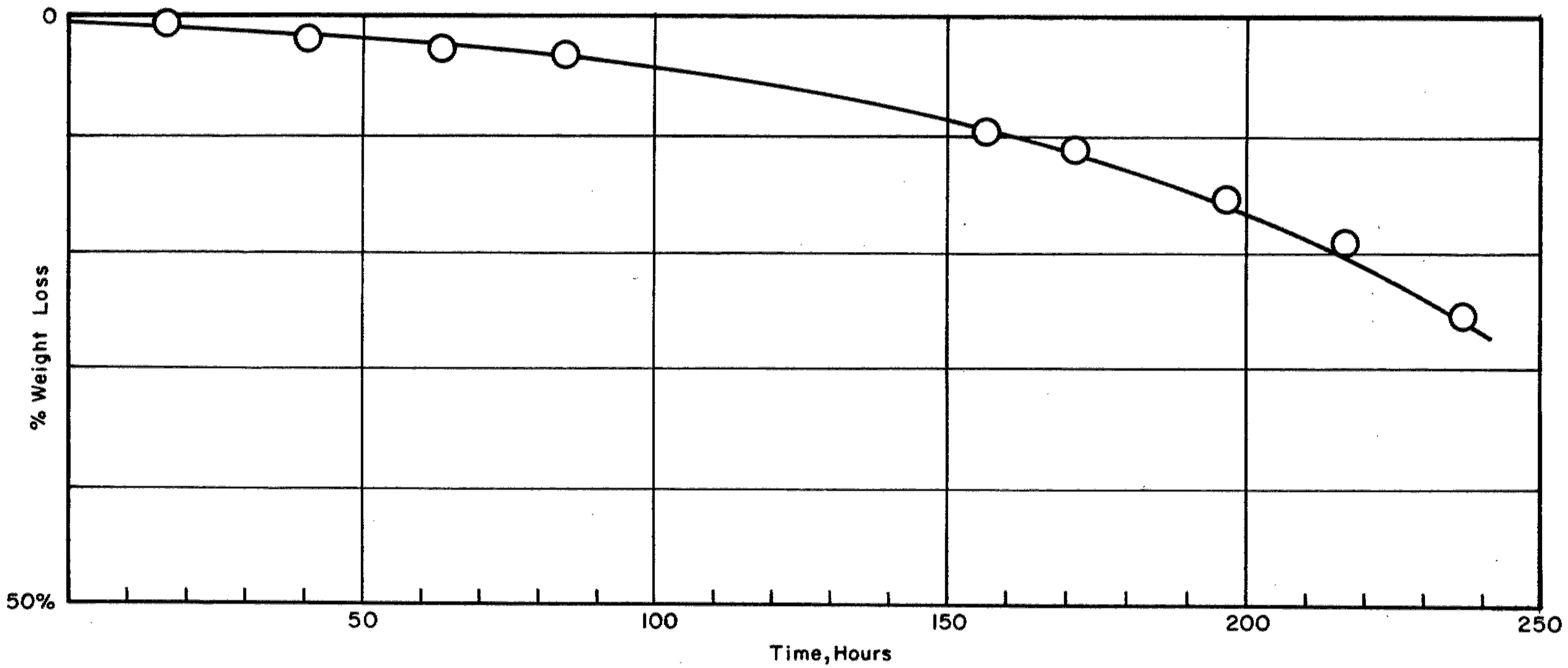

Figure 4. Average Isothermal Aging Curve for BBB at 700° F

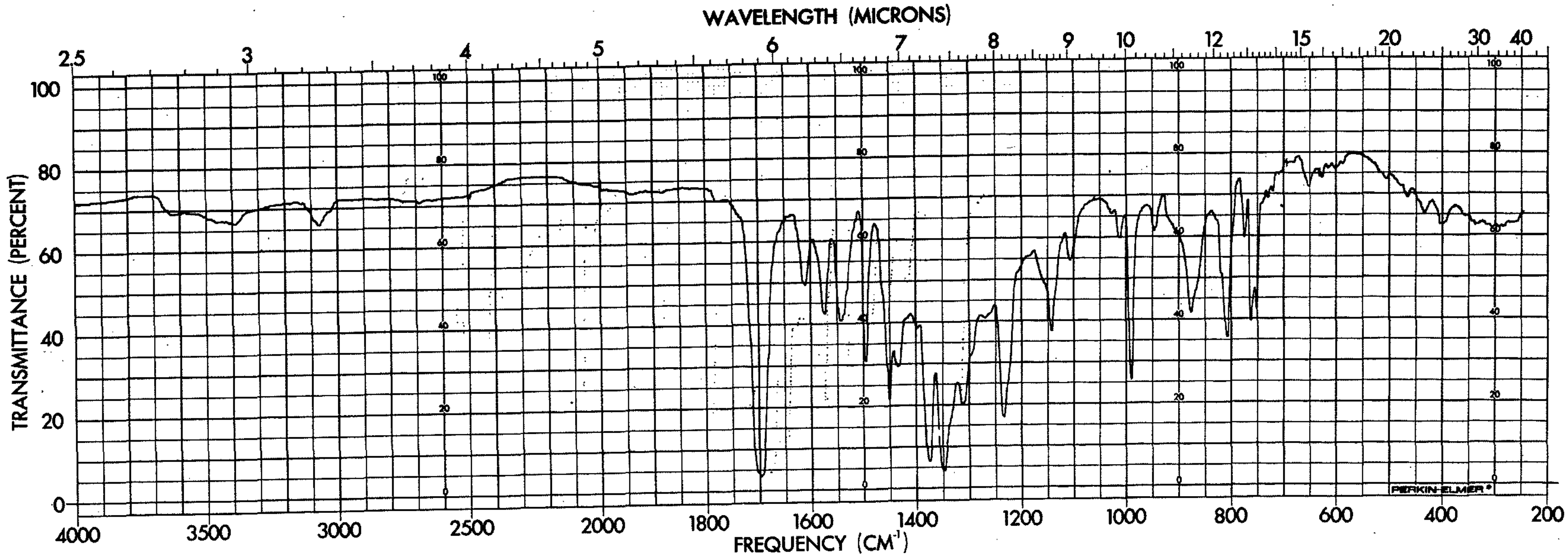

Figure 5. Analytical Infrared Spectrum of BBB

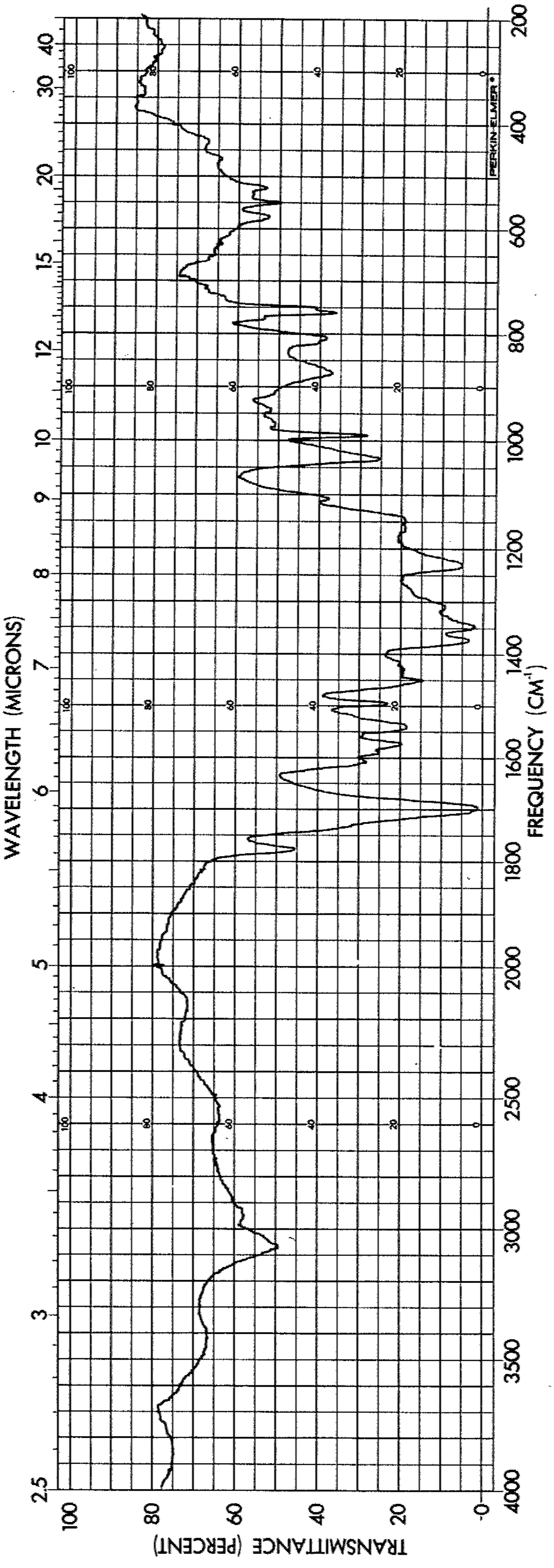

Figure 6. Analytical Infrared Spectrum of BBB/BBL-80/20

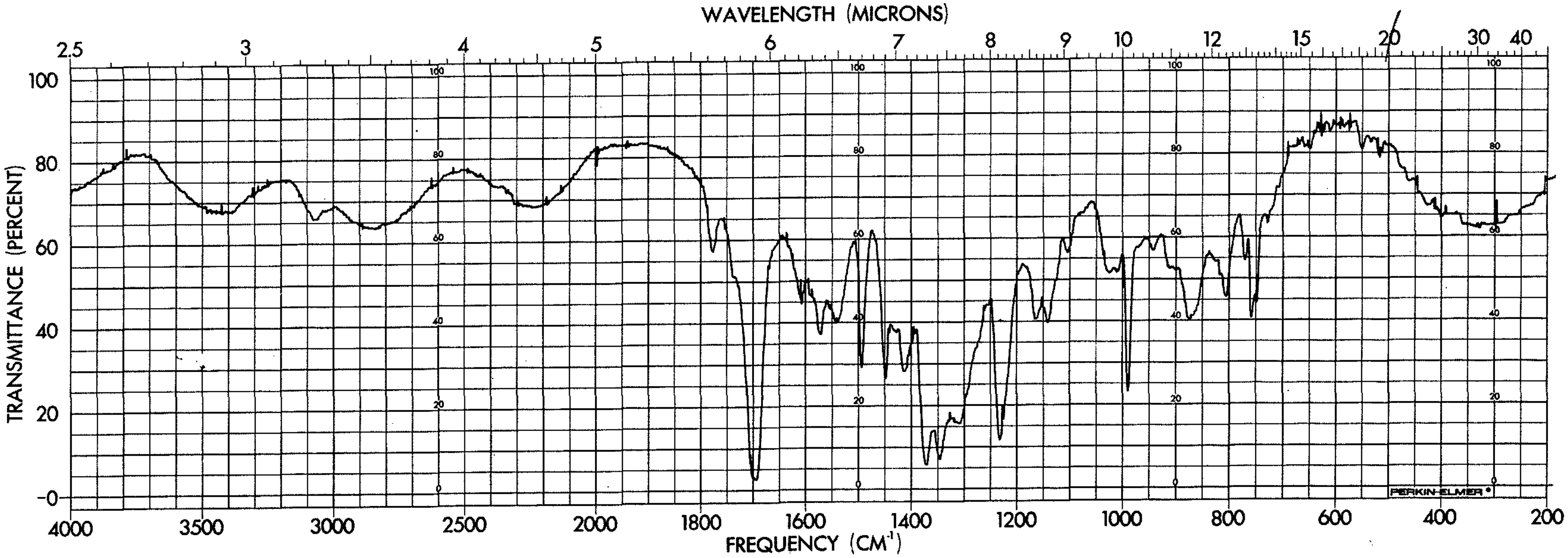

Figure 7. Analytical Infrared Spectrum of BBB/BBL-65/35

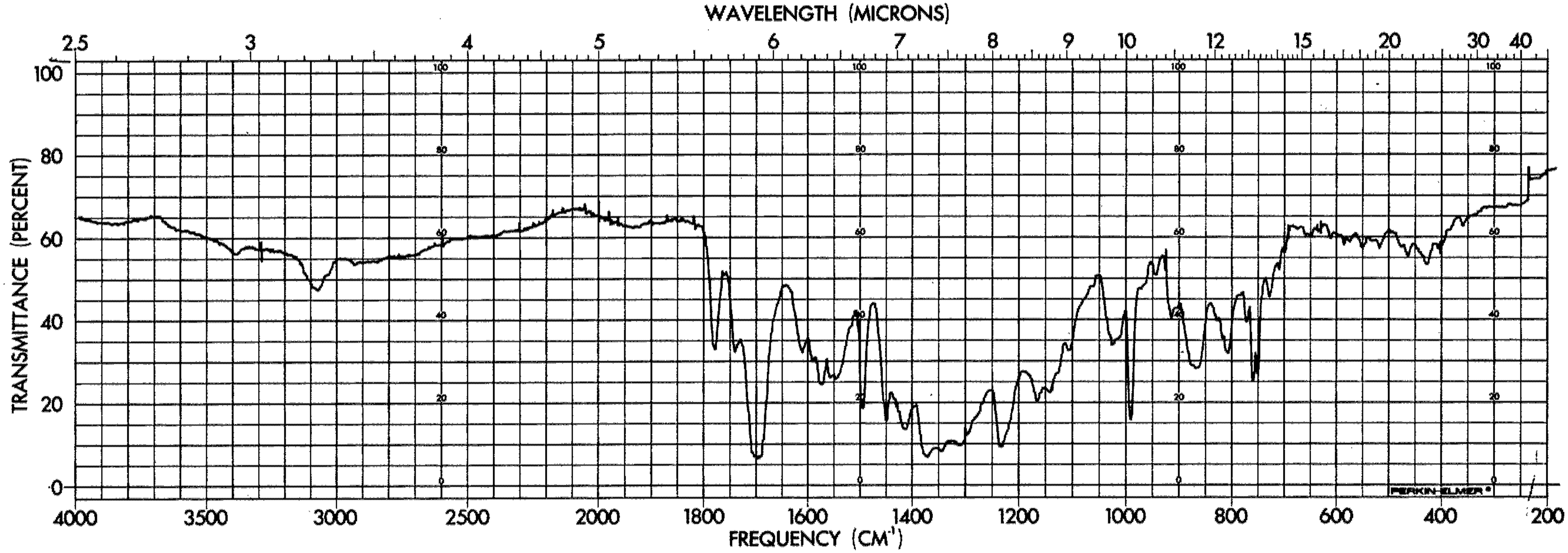

Figure 8. Analytical Infrared Spectrum of BBB/BBL-50/50

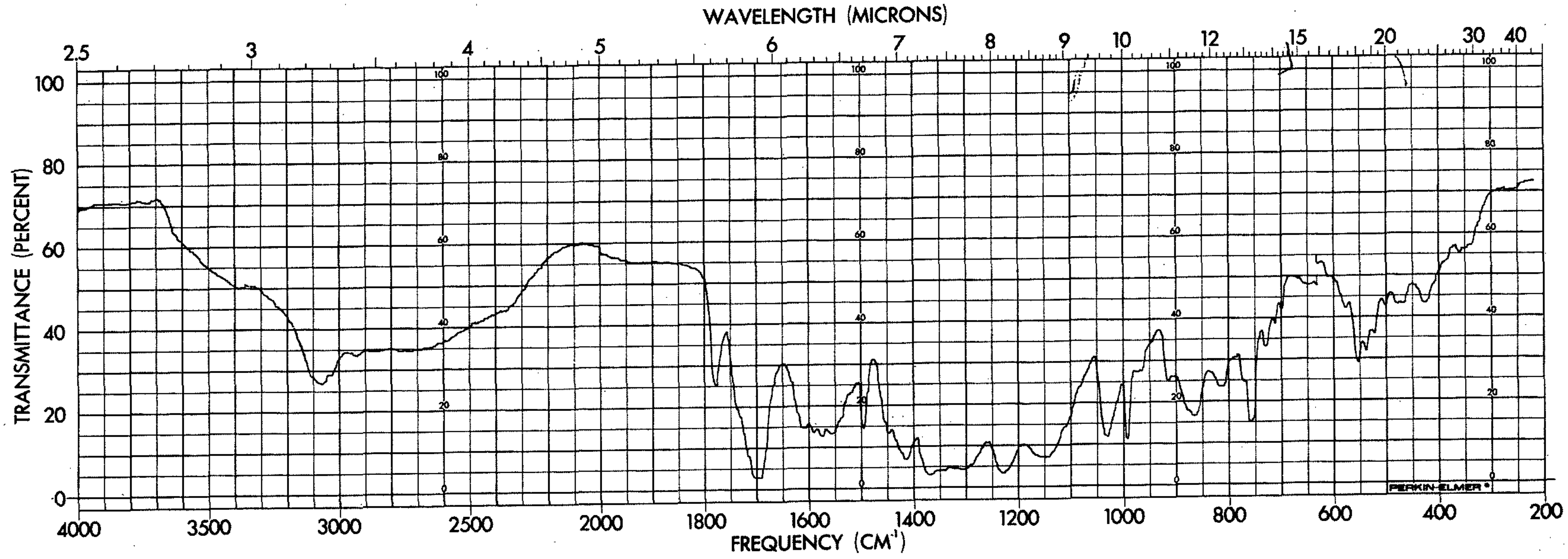

Figure 9. Analytical Infrared Spectrum of BBB/BBL-35/65

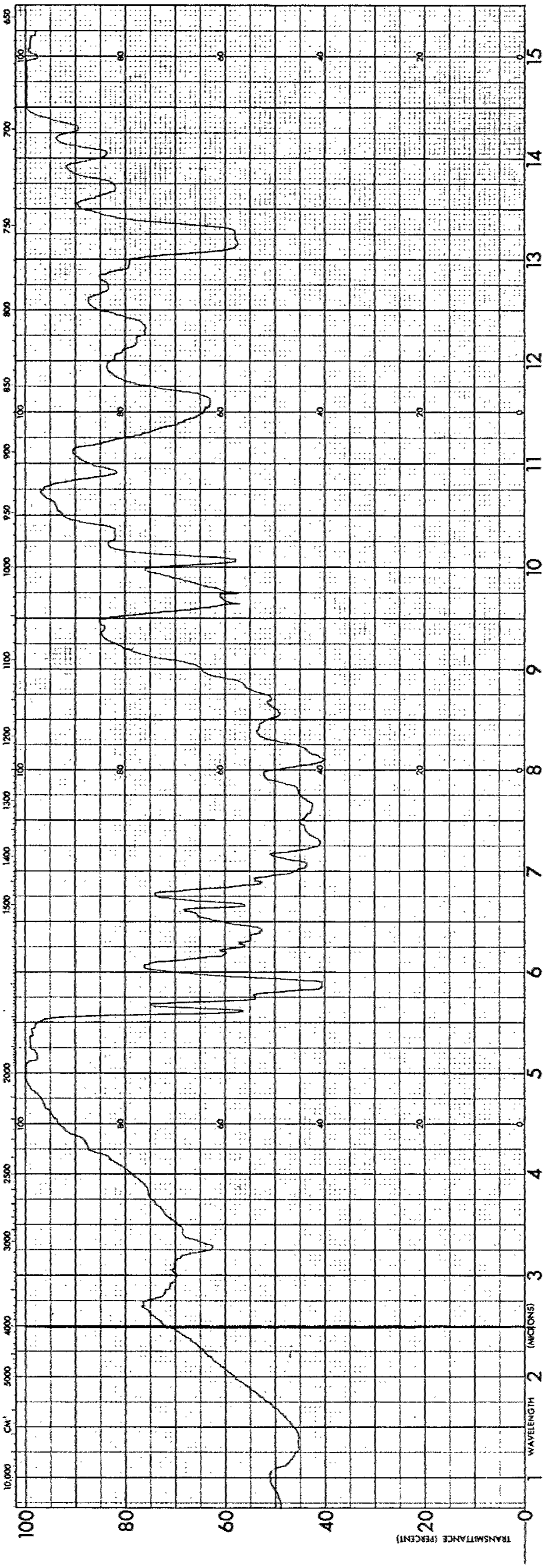

Figure 10. Analytical Infrared Spectrum of BBB/BBL-20/80

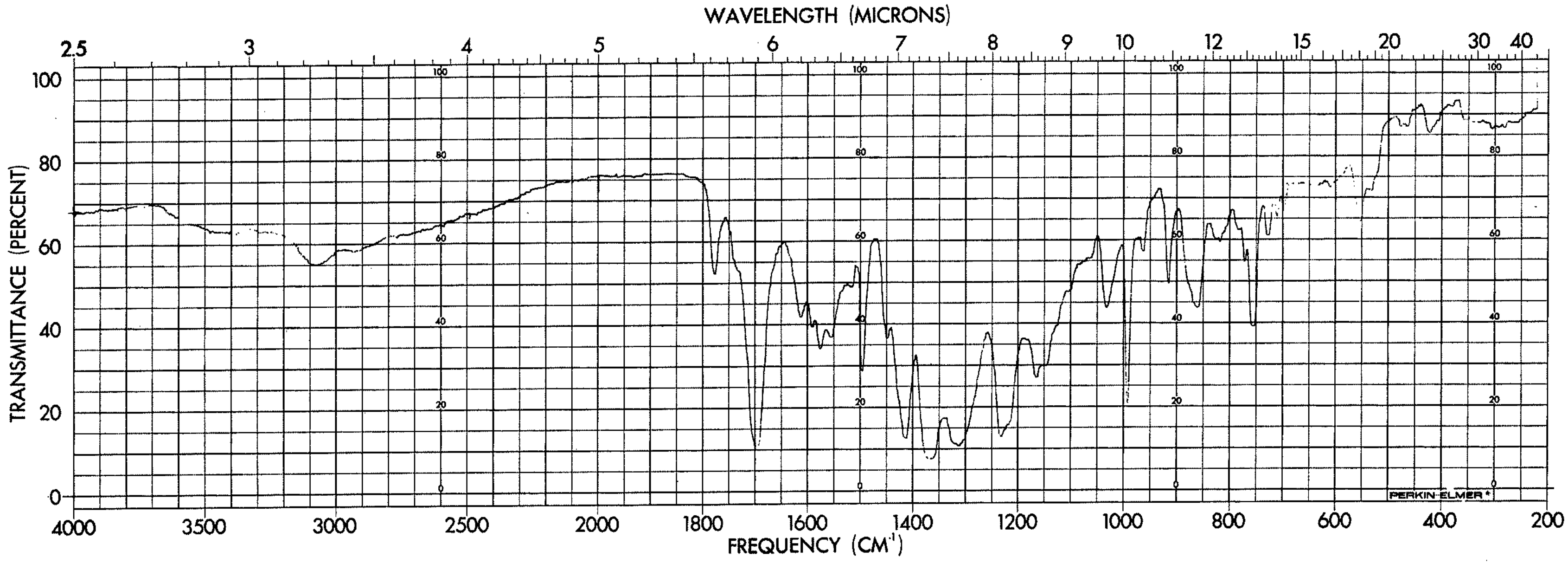

Figure 11. Analytical Infrared Spectrum of BBB/BBL-10/90

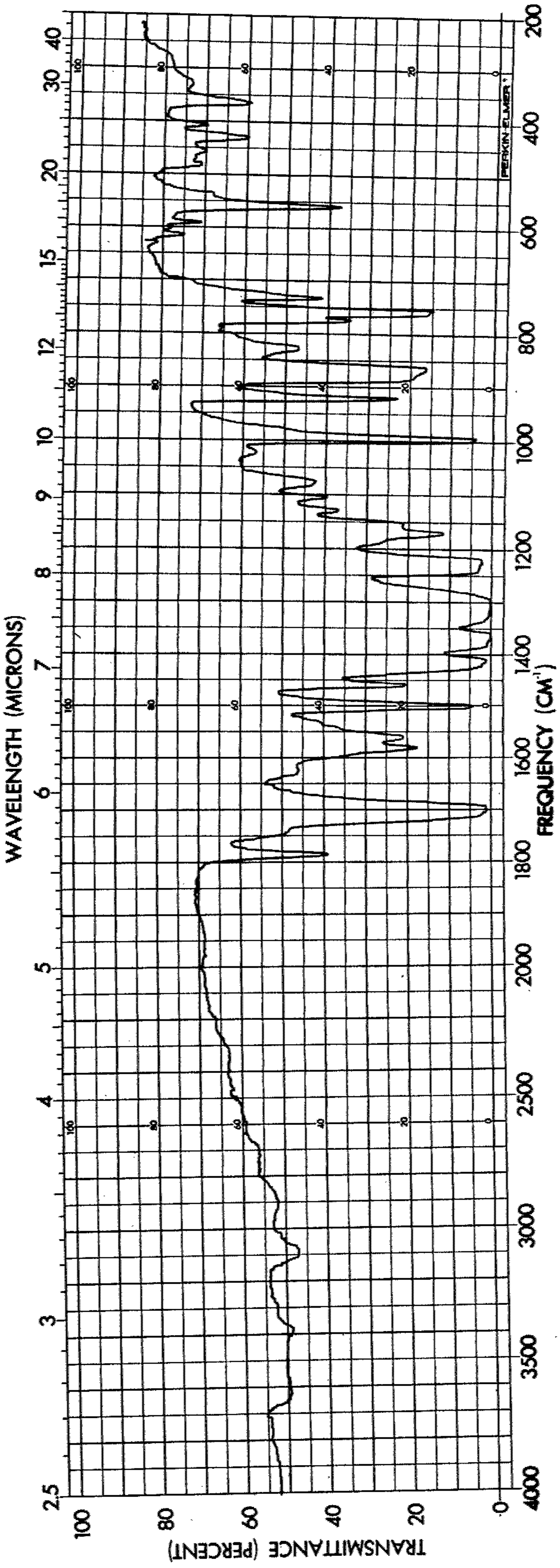

Figure 12. Analytical Infrared Spectrum of BBL

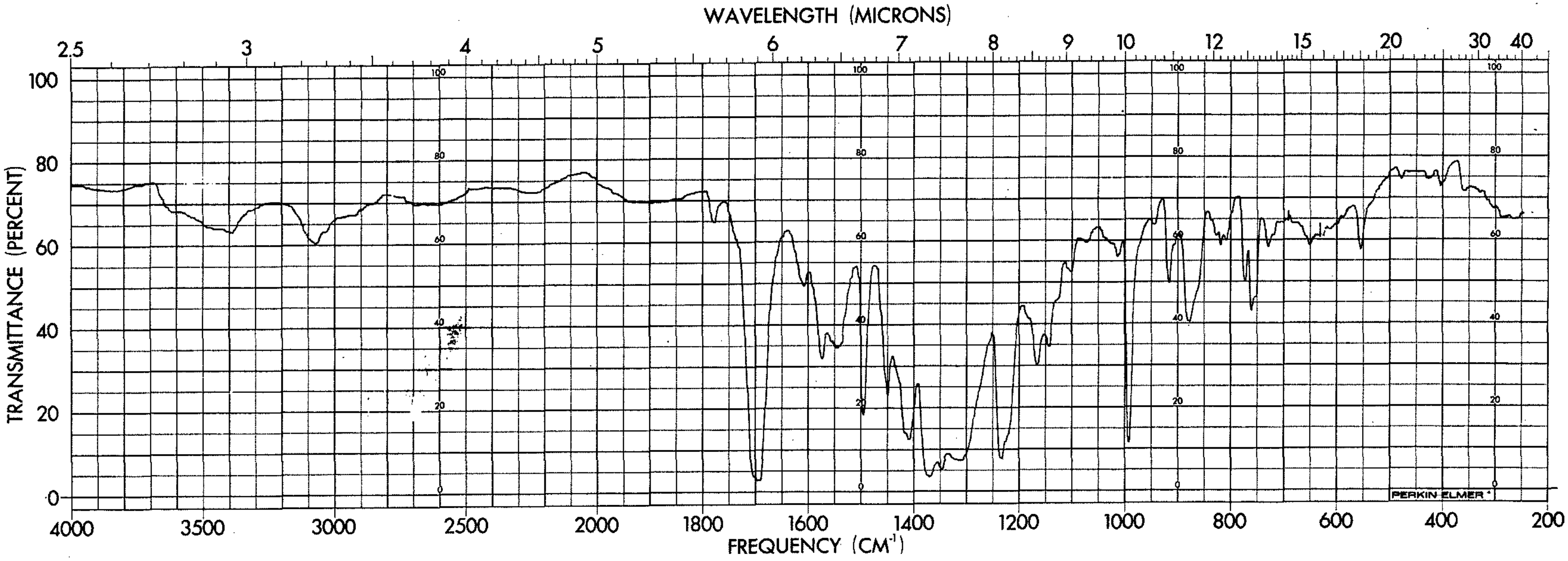

Figure 13. Analytical Infrared Spectrum of a Physical Mixture of 50% BBB and 50% BBL

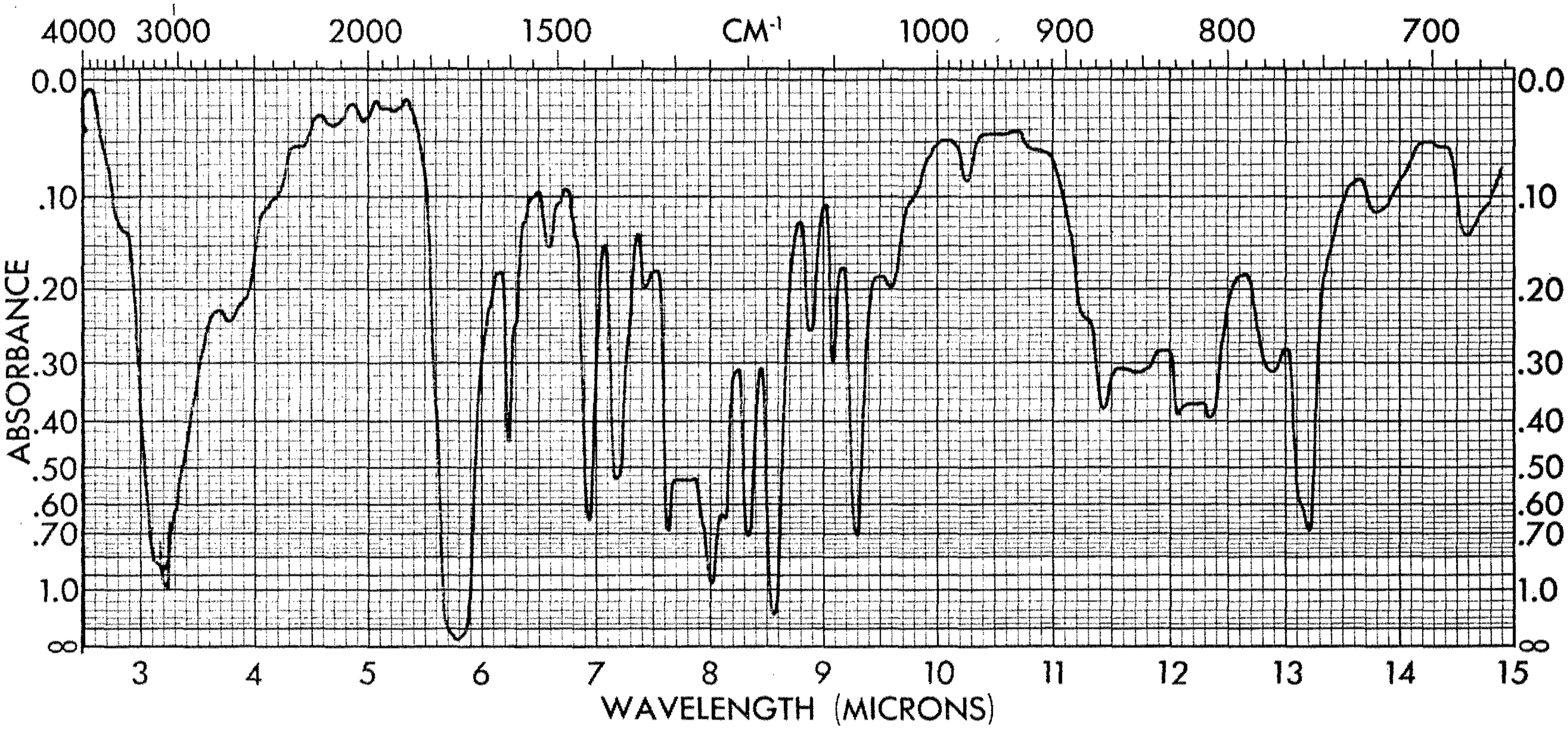

Figure 14. Infrared Spectrum of 1, 4, 5, 8-Naphthalenetetracarboxylic Acid

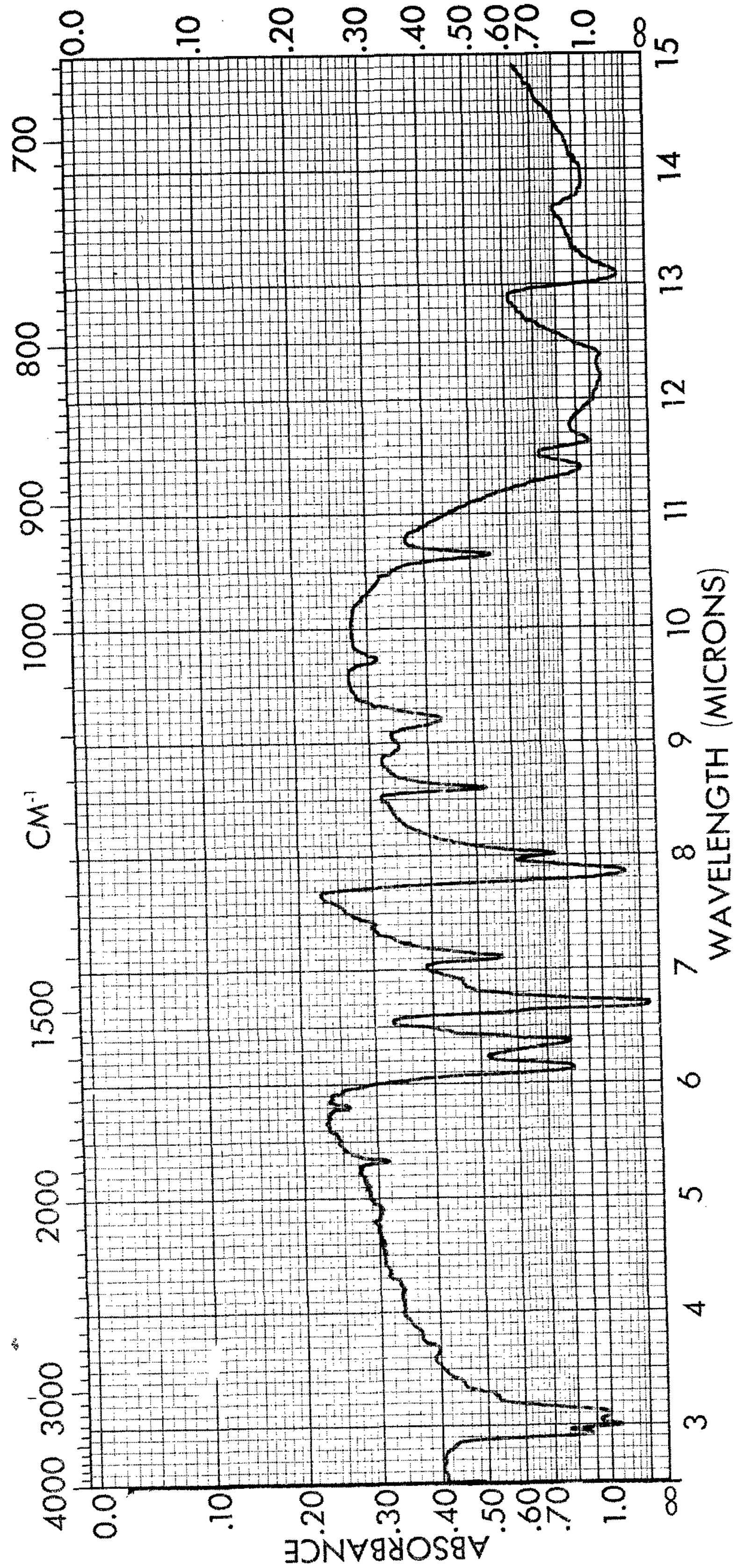

Figure 15. Infrared Spectrum of 3,3'-Diaminobenzidine

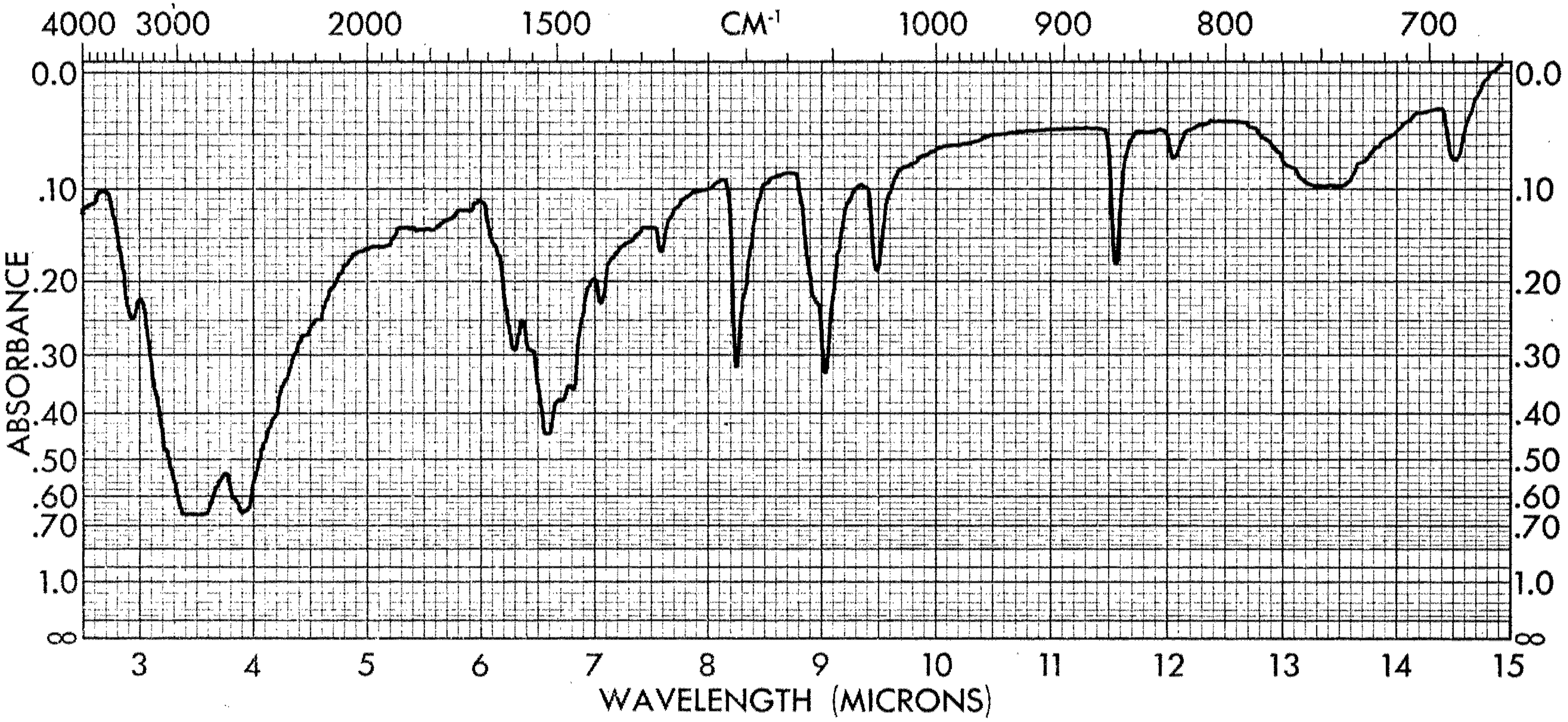

Figure 16. Infrared Spectrum of 1, 2, 4, 5-Tetraaminobenzene Tetrahydrochloride

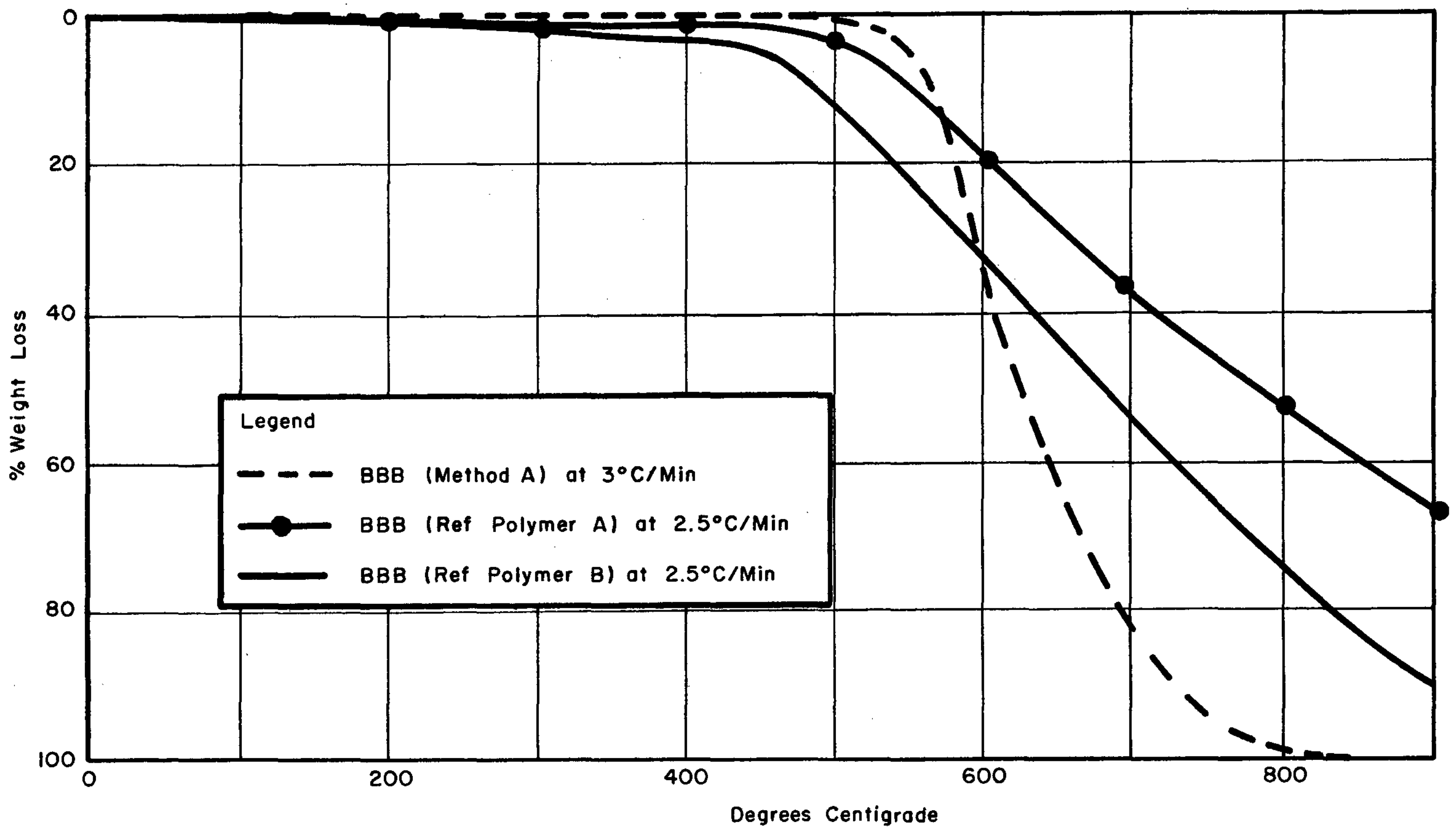

Figure 17. TGA Curves For Three BBB Polymers in Air

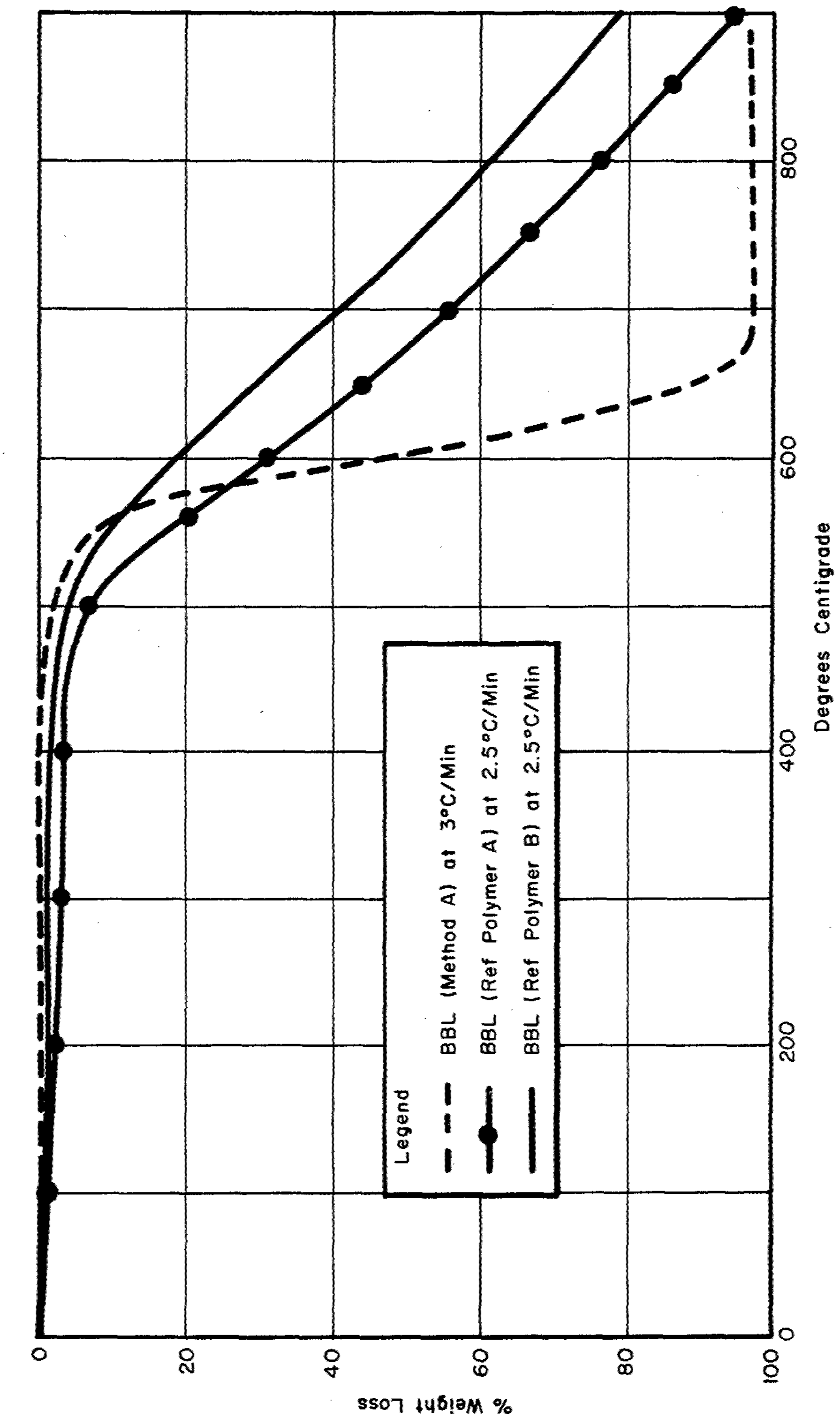

Figure 18. TGA Curves For Three BBL Polymers in Air

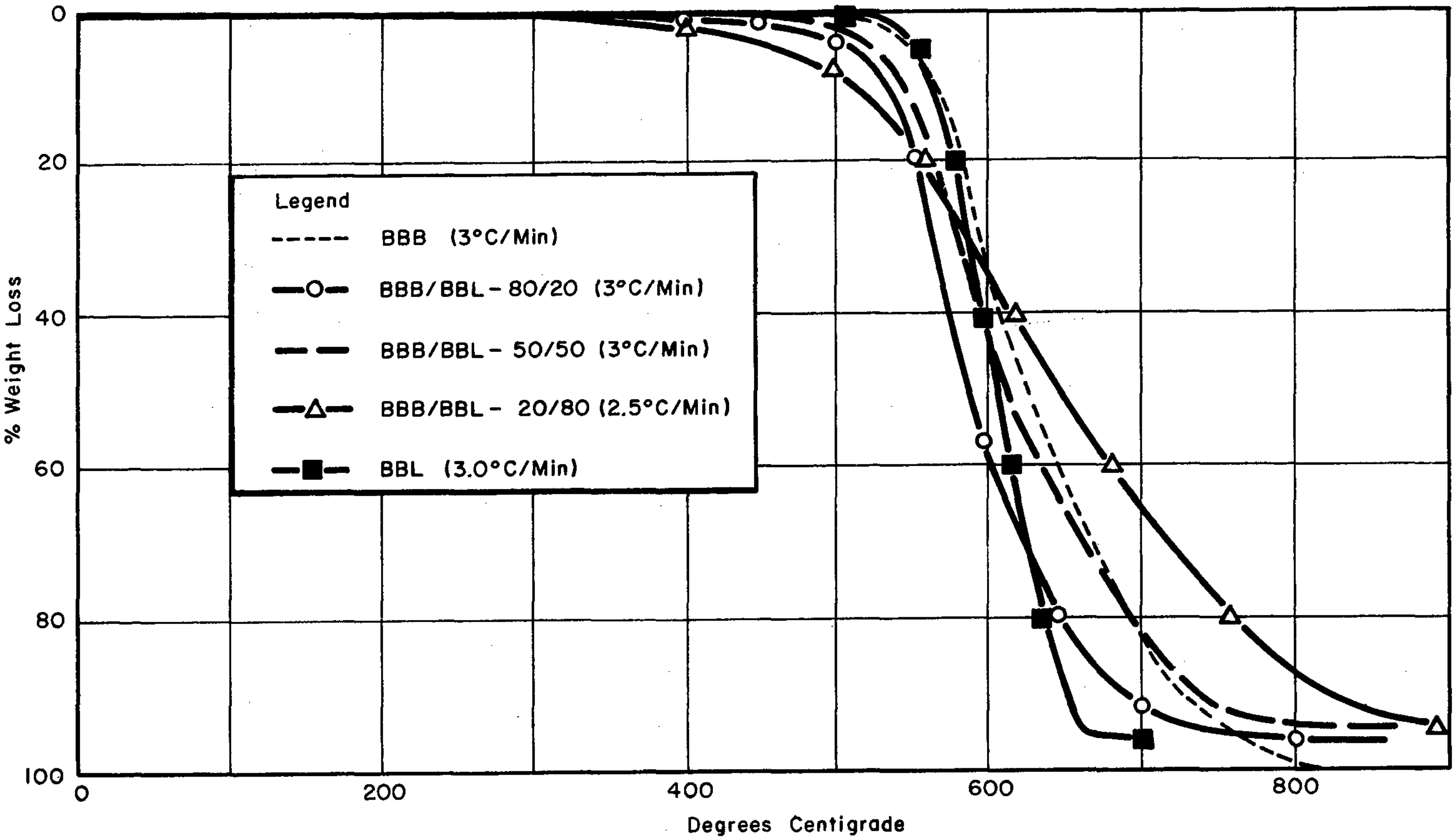

Figure 19. TGA Curves For Method A Polymers (Air)

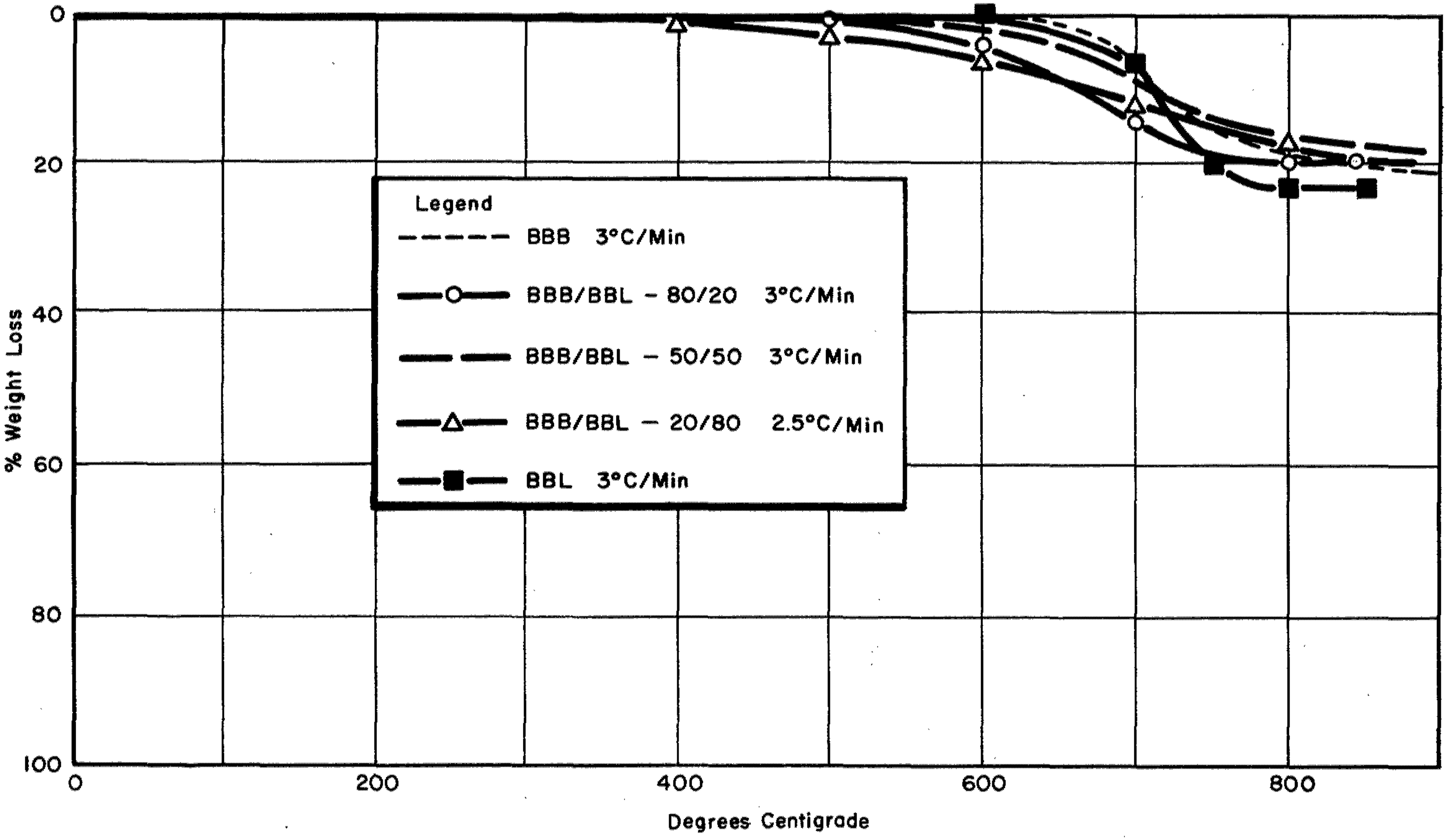

Figure 20. TGA Curves For Method A Polymers (Nitrogen)

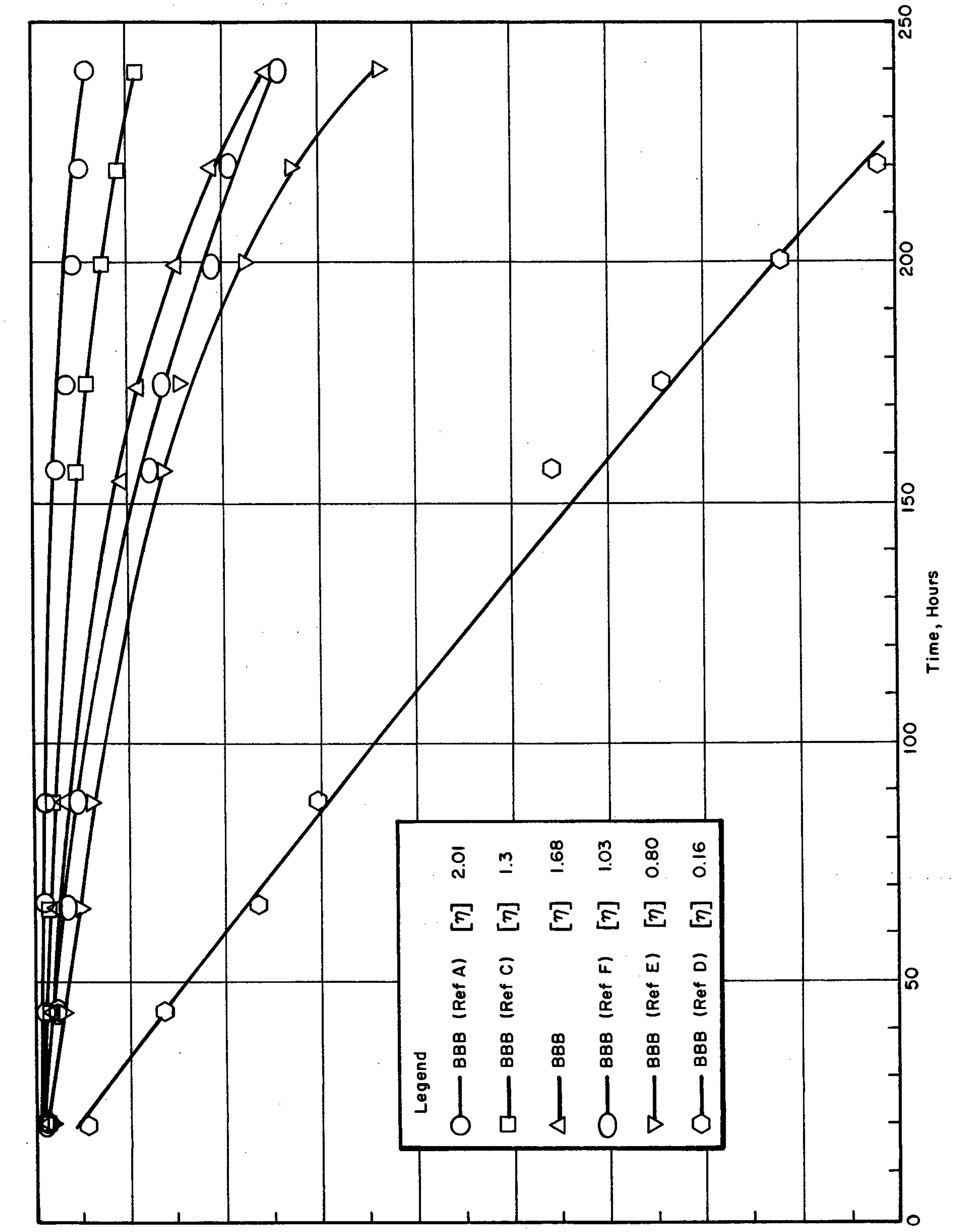

Figure 21. Isothermal Aging Curves for Various BBB Polymers at 700° F

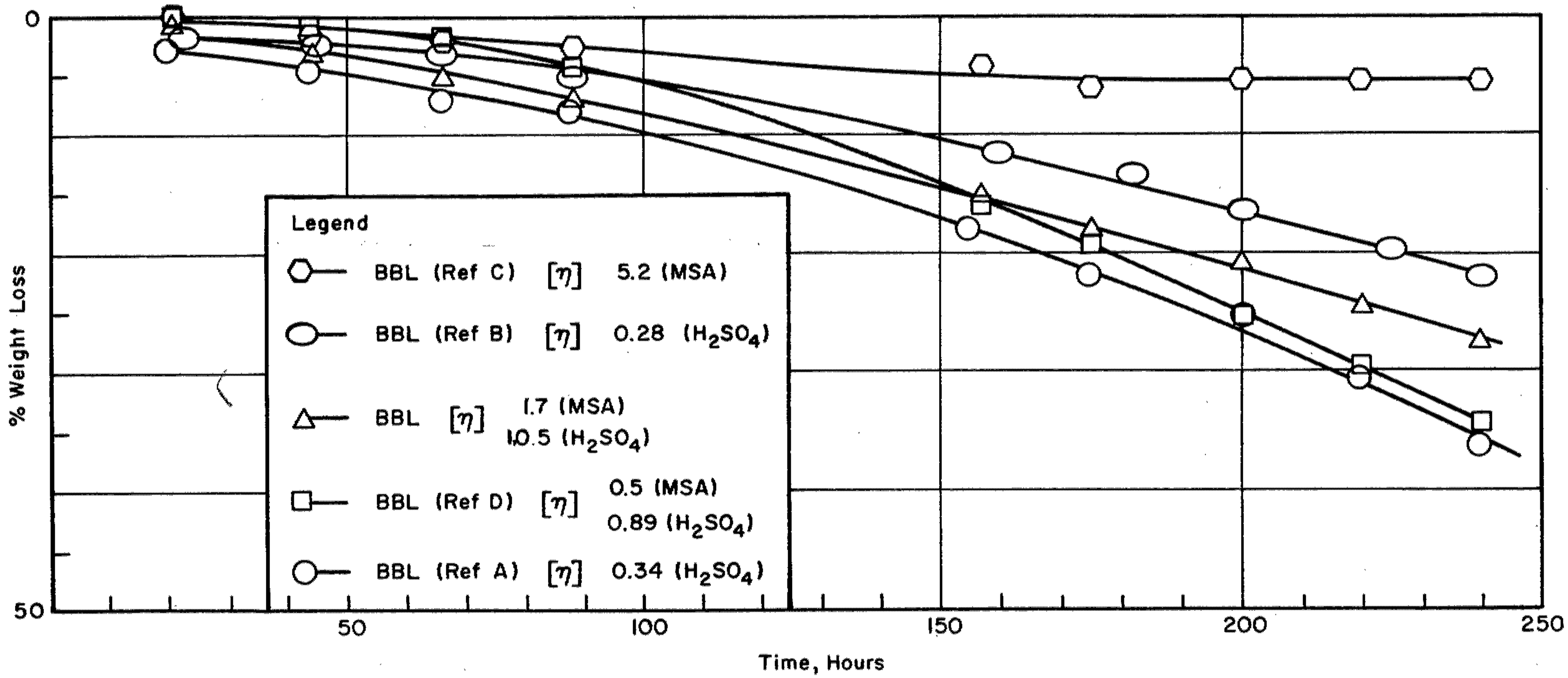

Figure 22. Isothermal Aging Curves for Various BBL Polymers at 700° F

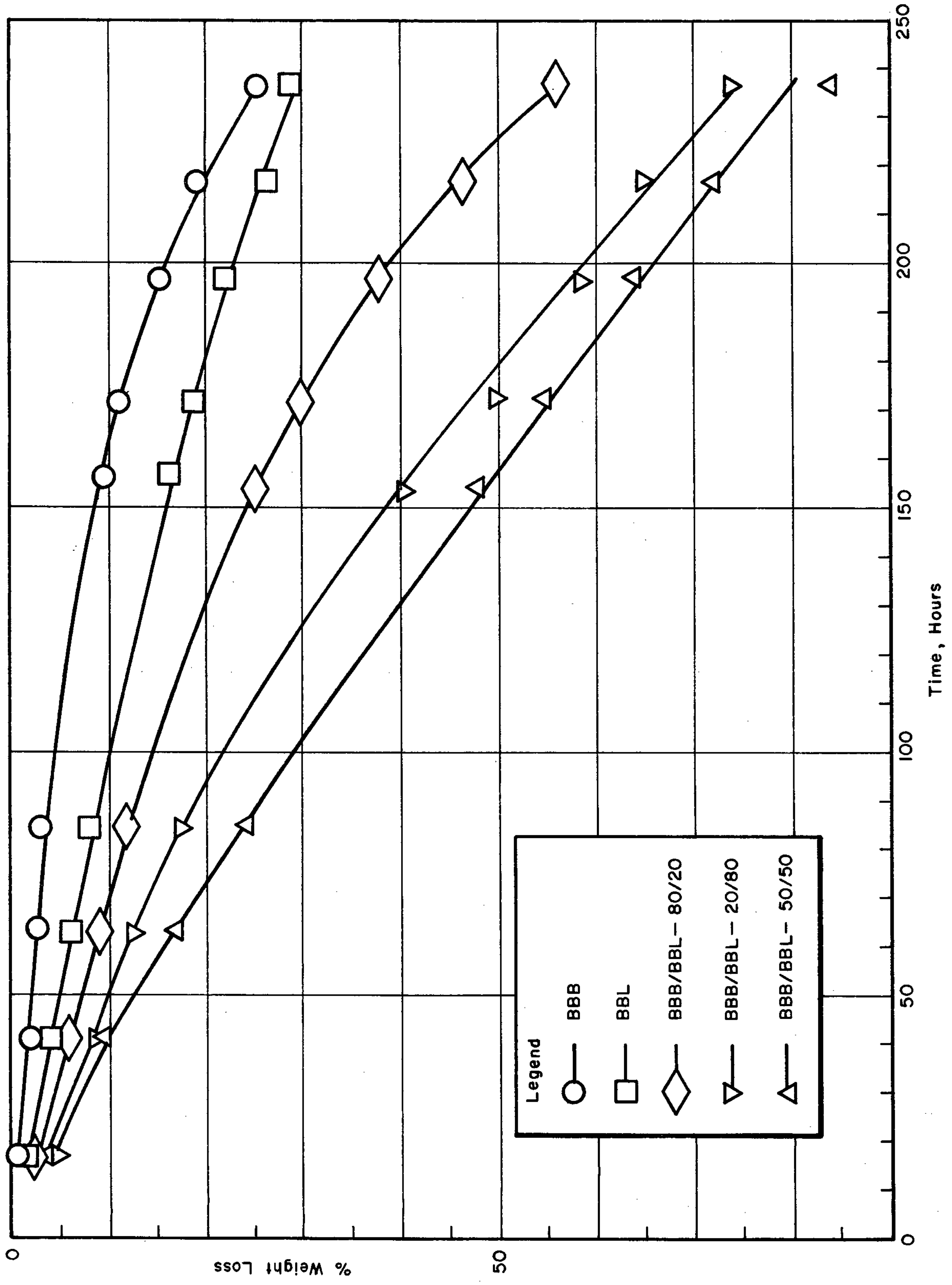

Figure 23. Isothermal Aging Curves for Method A Polymers at 700° F

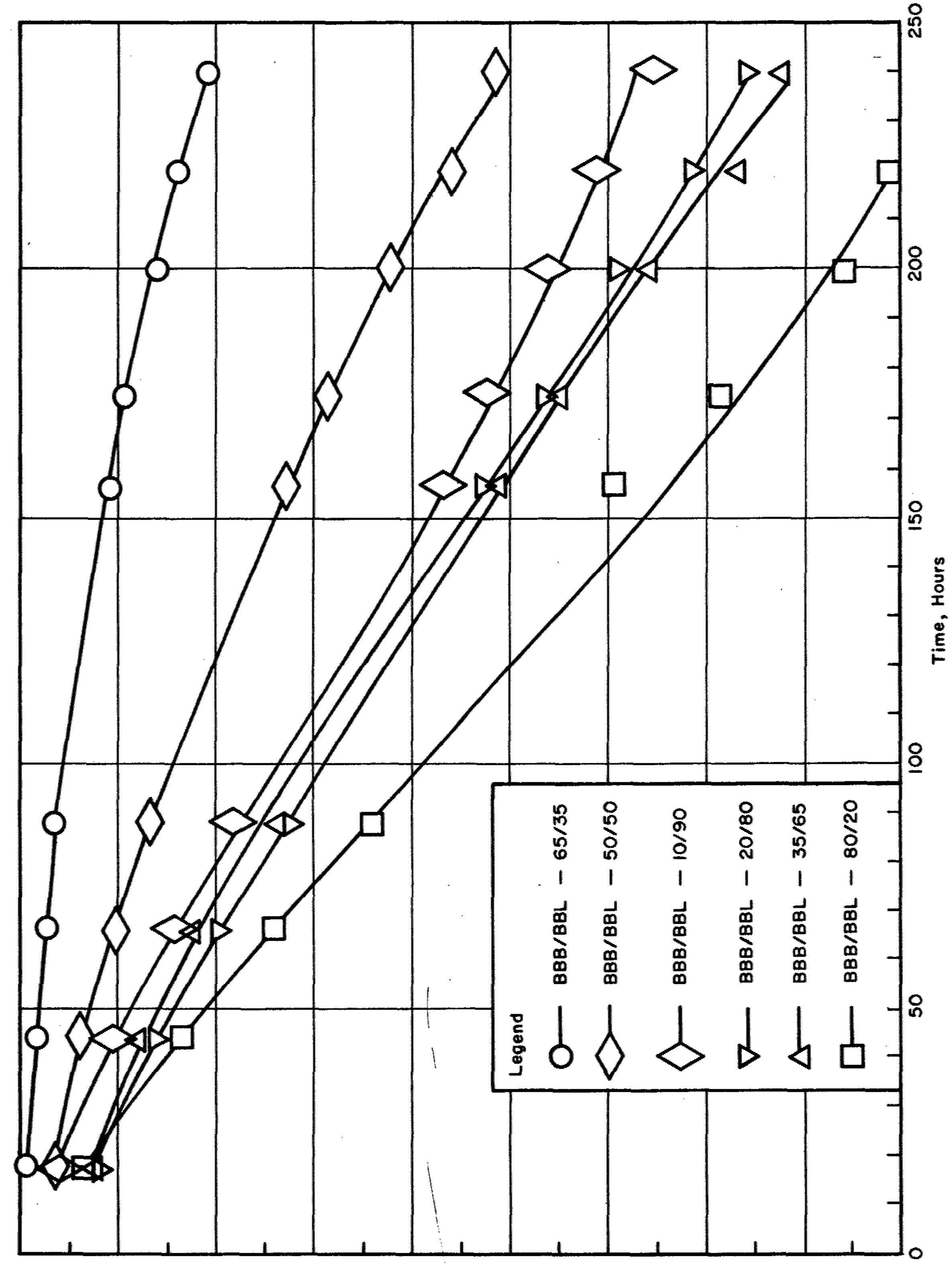

Figure 24. Isothermal Aging Curves for Method B Polymers at 700° F

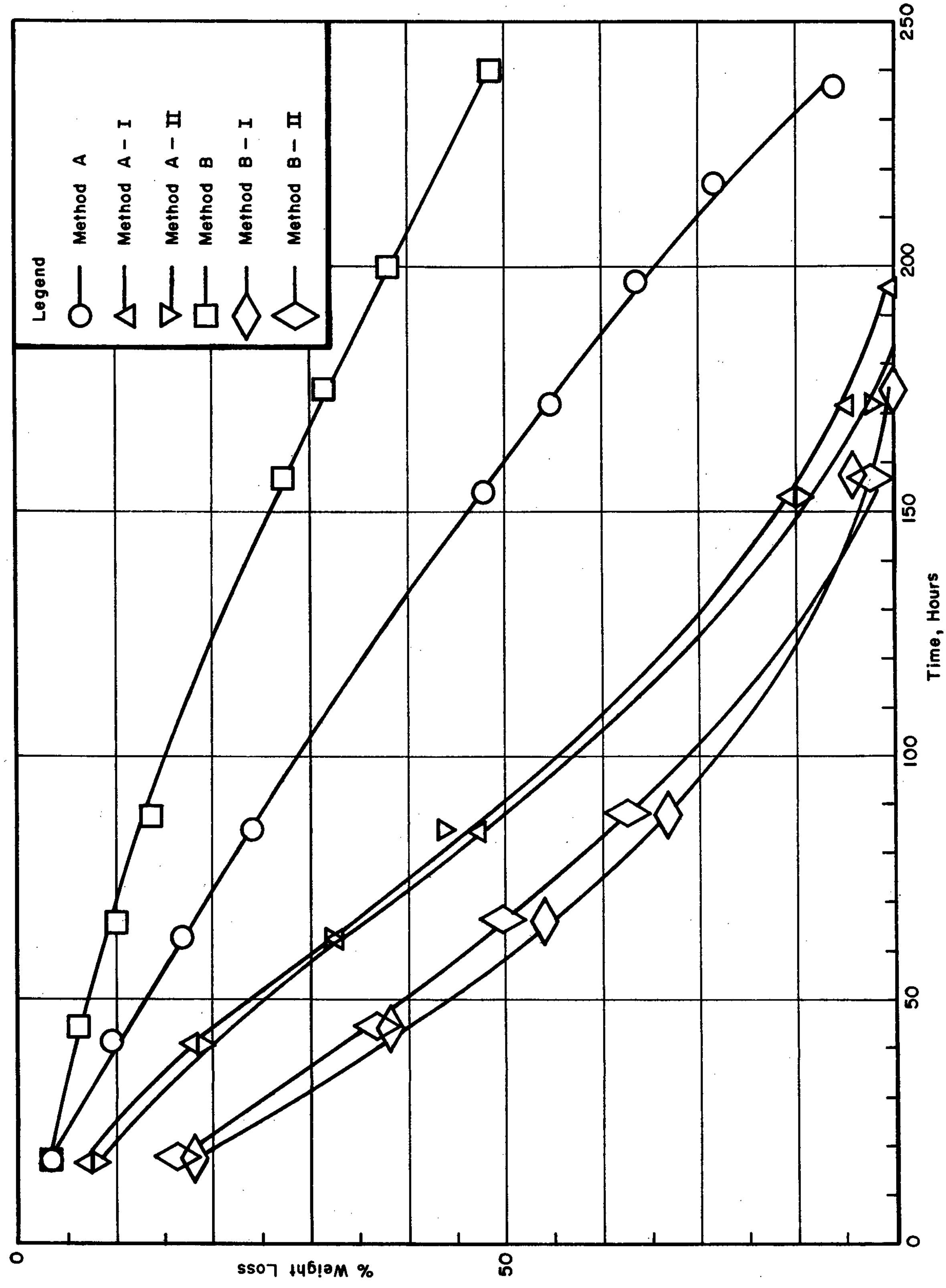

Figure 25. Isothermal Aging Curves for Various BBB/BBL-50/50 Polymers at 700° F

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13. ABSTRACT

A series of benzimidazobenzophenanthroline (BB) polymers containing both the "Bis-BB" (BBB) and the "BB-Ladder" (BBL) polymer structures have been prepared from NTCA and stoichiometric mixtures of DAB and TAB by polycondensations in polyphosphoric acid. The polymer structures were verified by elemental and infrared absorption analyses. The polymers were found to be black and amorphous, to have inherent viscosities ranging from 0.25 to 1.7 dl/gm at 30° C in sulfuric acid, and to exhibit stability in air to over 500° C by thermal gravimetric analysis. Isothermal aging studies were performed and showed the polymers with mixed structures to be less resistant to a thermo-oxidative environment than the parent homopolymers.

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