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**SYNTHESIS AND PROPERTIES OF POLYMERS  
AND COPOLYMERS CONTAINING  
POLYBENZIMIDAZOBENZOPHENANTHROLINE  
AND POLYIMIDE STRUCTURES**

*JOHN F. COLEMAN*

*R. L. VAN DEUSEN*

TECHNICAL REPORT AFML-TR-70-232

FEBRUARY 1971

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FOREWORD

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

This report includes work conducted in this Laboratory from April 1967 to March 1968. The manuscript was released in October 1970 for publication.

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This technical report has been reviewed and approved.



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

## ABSTRACT

A high molecular weight benzimidazobenzophenanthroline (BB) polymer containing both the "Bis-BB" (BBB) and the "BB-Ladder" (BBL) polymer structures has been prepared. This BBB/BBL polymer was synthesized from 1,4,5,8-naphthalene tetracarboxylic acid (NTCA) and a stoichiometric mixture of 3,3'-diaminobenzidine (DAB) and 1,2,4,5-tetraaminobenzene tetrahydrochloride (TAB.4HCl) by polycondensation in polyphosphoric acid. The polymer was black and amorphous with an intrinsic viscosity of 2.80 dl/gm at 30°C in sulfuric acid and 3.25 dl/gm at 30°C in methane sulfonic acid and found to be stable to 500°C in air and 600°C in nitrogen by thermogravimetric analyses. Films of this polymer were prepared using both casting and precipitation techniques. This polymer also appeared to have fiber-forming properties.

Using a conventional synthetic route for polyimide formation a series of polyimides containing five, six and seven-membered rings were prepared. Then a series of polymers containing a mixture of five- and six-, five- and seven-, and six- and seven-membered imide rings were prepared by reacting aromatic diamines with stoichiometric amounts of pyromellitic dianhydride (PMDA) and/or 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) and/or 2,2',6,6'-biphenyl tetracarboxylic dianhydride (BPTCDA) in N,N'-dimethylacetamide to give film-forming polyamic acids. These were subsequently converted to aromatic polyimides which possessed thermal properties approaching conventional polyimides.

Another series of polymers containing both the "BB" structure and the imide structure were prepared by the condensation of NTCA with stoichiometric amounts of DAB (or TAB.4HCl) and either 4,4'-diaminobiphenylether (oxydianiline), m-phenylene diamine or 4,4'-diaminobiphenyl. These polycondensations were carried out 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 viscosities ranging from 0.08 to 0.29 dl/gm at 30°C in sulfuric acid, and to exhibit stability in air to over 500°C by thermal gravimetric analyses. Isothermal aging studies were performed and the polymers with mixed structures were found to be less resistant to a thermooxidative environment than the most stable parent homopolymers.

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## SECTION I

### INTRODUCTION

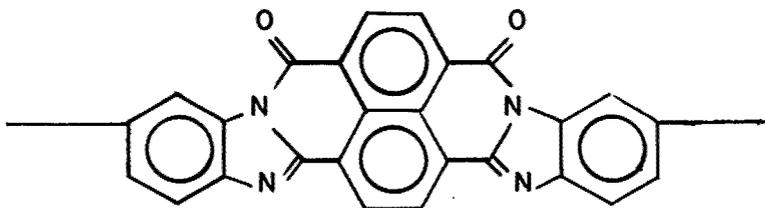
The experimental work described in this report is related and is a follow-on to previous work performed in the Materials Laboratory on BB type polymers (References 1, and 2). The BBB polymer has already been shown to have great promise as a high temperature fiber (References 3 and 4) and the potential of the BBL polymer seems to be greater as a result of recent accomplishments in improving the quality of this polymer system (Reference 5).

In light of the fact that complex aromatic-heterocyclic polymers such as BBB and BBL present problems with regard to processing and fabrication it is important to gain information on the effects of structure-property relationships when BBB, BBL and other cyclic structures are incorporated into the same polymer backbones. The synthesis and preliminary evaluation of the mixed backbone polymers are necessary if one is to consider the possibilities of being able to alter molecular structures as a means to enhance aspects of polymer processability without losing essential thermomechanical properties.

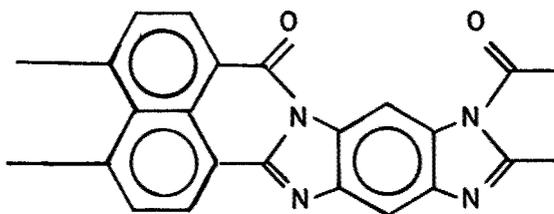
The first steps to acquire such information needed for this polymer system have already been taken. We have synthesized mixed BBB/BBL polymers as reported earlier (Reference 1). In the work described in this report the quality (molecular weight, purity, thermal stability) of BBB/BBL has been improved. In addition the synthesis of some BB polymers containing polyimide structures are reported. The synthesis of various mixed polyimides are also described to add to variations of cyclic structures which can be considered. Work to further vary the structural characteristics of ring systems and also to introduce non-cyclic linking structures is still underway. The completion of this overall synthetic effort coupled with the preliminary evaluation of properties should then provide the basic information necessary to develop approaches toward solving important processability problems associated with the BB polymer systems.

The following symbols have been used to designate the types of backbone ring structures synthesized in this investigation:

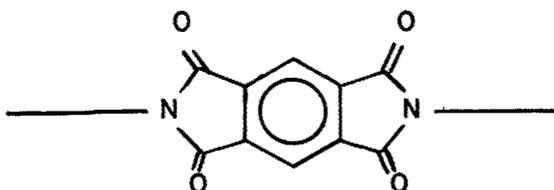
BBB



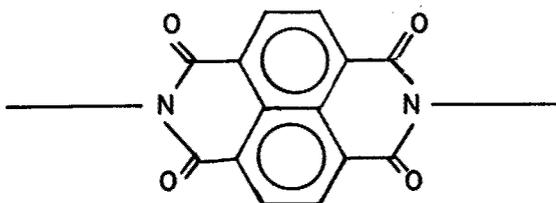
BBL



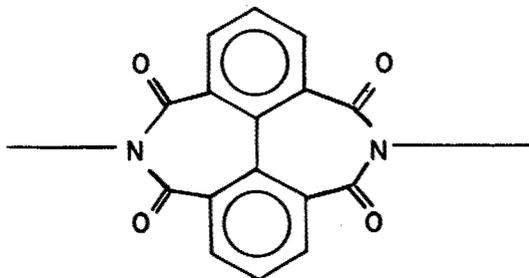
PI-5



PI-6



PI-7



SECTION II  
EXPERIMENTAL

Monomers and Solvents

1,4,5,8-Naphthalene tetracarboxylic acid (NTCA) was purified by the method previously reported (Reference 1).

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·4HCl) was purified by the method previously reported.

4,4'-Diaminodiphenylether (Oxydianiline, ODA) was obtained from Dow Chemical Company and was recrystallized from methanol/water (m.p. 190-191°C, uncorrected).

m-Phenylene Diamine (M-PDA) was obtained from Matheson, Coleman and Bell Company and was purified by sublimation under reduced pressure before use (m.p. 63-65°C).

4,4'-Diaminobiphenyl (benzidine) was obtained from Hartman-Leddon Company and was recrystallized from ethanol before use.

2,2',6,6'-Biphenyltetracarboxylic Acid (BPTDA) was obtained from Monsanto Research Corporation and used as received (References 6 and 8).

2,2',6,6'-Biphenyl Tetracarboxylic Dianhydride (BPTCDA) was prepared by the method of Goins and Van Deusen (Reference 7). The calculated yield based on the tetra acid was 77.8%. The white, crystalline dianhydride had m.p. 257-259°C (uncorrected).

1, 4, 5, 8-Naphthalenetetracarboxylic Dianhydride (NTCDA) was prepared from the tetra acid by treatment with acetic anhydride. The dianhydride was then dried before use

Anal Calcd. for $C_{14}H_4O_6$	C-62.70; H-1.80; O-35.80
Found	C-62.86; H-1.57; O-35.21

1, 2, 4, 5-Benzenetetracarboxylic Dianhydride (PMDA) was obtained from Hexagon Chemical Company and sublimated at 215-218°C (0.05 mm Hg) to give a pure white monomer.

N, N'-Dimethylacetamide (DMAC) was distilled from calcium hydride onto molecular sieves and maintained under a nitrogen atmosphere prior to its use.

Polyphosphoric Acid (82-84%  $P_2O_5$ ) (PPA) was obtained from Matheson, Coleman and Bell Company, and deoxygenated before use as reported elsewhere (Reference 1).

### Reference Polymers

BBB (Reference Polymer A) was synthesized by Monsanto Research Corporation (Reference 8) and is reported elsewhere (Reference 1).

PI-6 (Reference Polymer A) was synthesized by Monsanto Research Corporation (Reference 9).

### Polymerizations

In PPA-Polycondensations of NTCA with amines were carried out at 180-200°C for approximately 18 hours by Method A as previously described (Reference 1). When polyimides were prepared in PPA, the diamines were reacted with the corresponding tetraacids by this same method.

In DMAC-Under nitrogen, the amine was dissolved in freshly distilled, deoxygenated DMAC (50-75 ml). With stirring at room temperature, an equimolar

quantity of the dianhydride was added along with 15-25 ml of deoxygenated DMAC as wash liquid. The exothermic reaction caused a temperature increase of from 2 to 7°C, but externally cooling was not used. After dissolution of the anhydride, the temperature of the resulting solution decreased to room temperature and maintained at room temperature for 4 to 5 hours. Whenever NTCDA was used as the (or one of the) anhydride monomer(s), the temperature of the reaction mixture was slowly increased to 100°C for one hour after anhydride addition was complete.

At the end of the reaction period, the solvent was removed under reduced pressure. The remaining polyamic acid was isolated. About 100 mg of this polyamic acid film was then dried at 50°C/1 mm Hg/20 hrs for infrared analyses. The remainder of the prepolymer was mixed with acetic anhydride and this was refluxed for 20-24 hours. The product was collected by filtration and washed with diethyl ether. The yield was calculated after drying the polyimide at 180°C for 18-20 hours at 1 mm Hg.

### Polymer Characterizations

Solution viscosities of all BBB/PI copolymers and most polyimides were run in a modified Ubbelöhde dilution viscometer in concentrated sulfuric acid. The BBB/BBL copolymers were also run in methane sulfonic acid at 30°C at a concentration of 0.5 g/dl. Inherent and intrinsic viscosities of the polymers are listed in Tables I, II and III. Viscosities of the polyamic acid prepolymers were run in freshly distilled, deoxygenated DMAC at a concentration of 0.5 g/dl. See Tables I and II.

Infrared Spectra were obtained on a Perkin-Elmer Model 137 Infracord spectrophotometer (Figures 5-14, 16-21). The analytical spectrum (Figure 1) was provided by W. Crawford and Lt. H. Wells of the Analytical Branch, Materials Physics Division, AFML, on a Perkin-Elmer Grating Spectrophotometer, Model 521.

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 studies were performed in static air at 700°F by the method previously reported (Reference 1). All aging runs were made using BBB (Reference Polymer A) as an internal standard.

### SECTION III

#### DISCUSSION AND RESULTS

##### BBB/BBL Polymers

Based upon our earlier report (Reference 1), a set of reaction conditions known to produce polymer products varying in composition from either BBB or BBL homopolymers to various mixed BBB/BBL backbone compositions was selected in an attempt to prepare high molecular weight BBB/BBL copolymers. Polymerization mixtures were prepared according to the previously described method referred to as Method A (Reference 1) in which 1,4,5,8-naphthalene tetracarboxylic acid (NTCA) was reacted with equivalent mole quantities of 3,3'-diaminobenzidine (DAB)/1,2,4,5-tetraaminobenzene (TAB) mixtures. Three polymers were prepared using DAB/TAB mole ratios of 80/20, 65/35 and 50/50, respectively, in polyphosphoric acid (PPA). The TAB was actually charged as the tetrahydrochloride salt (TAB·4HCl) in these polymerization mixtures. The polycondensations were carried out under an inert atmosphere at 180-200°C for about 18 hours. After cooling to room temperature, the polymers were isolated by mixing the PPA reaction mixtures with large excesses of methanol in a blender. These were filtered from the liquid and washed several times in the blender with additional methanol. The crude polymers were then dried at 180°C for 20 hours at 1 mm Hg and subsequently dissolved in methane sulfonic acid for reprecipitation in methanol. After repeated washings in methanol they were finally washed in diethyl ether and dried at 190°C for 20-24 hours at 1 mm Hg.

Physical properties of these three different BBB/BBL polymers were obtained from samples of the purified products. All three polymer compositions were completely soluble in both concentrated sulfuric and methane sulfonic acids. Chemical analyses were obtained on these samples and one, the BBB/BBL 65/35 (Table I, Appendix), was in very good agreement with the theoretical calculation for the expected composition (Table IV, Appendix). The analyses of the 80/20 and 50/50 lacked conclusiveness (Table IV, Appendix), although their empirical compositions were not grossly inconsistent. Solution viscosities of these polymers were obtained at 30°C in purified methane sulfonic acid (100%) or in

concentrated sulfuric acid. The relatively high intrinsic viscosity of the 65/35 polymer compared to the other two (e.g., 3.25 compared to 0.45 and 0.47) may offer explanation for the much better analysis just referred to. The former appears to be a high quality, high molecular weight copolymer composition comparable in these respects to the parent homopolymers.

As previously reported (Reference 1), behavior possibly attributable to polyelectrolyte effects have been noted with methane sulfonic acid solutions of these polymers where solution concentrations are less than 0.35 gm/dl. Therefore, the intrinsic viscosities given in Table I in methane sulfonic acid are taken from determinations made in solutions varying in concentrations between 0.35 and 0.50 gm dl.

Infrared absorption spectra of these polymers were obtained from cast film samples rather than KBr pellet samples (Figure 1). The absorptions of these samples are in agreement with previously reported data (Reference 1) for BBB/BBL polymers.

The unusually high intrinsic viscosity of the BBB/BBL-65/35 copolymer (2.80 dl/gm in sulfuric acid and 3.25 dl/gm in methanesulfonic acid) and the good agreement of elemental analysis with theoretical calculations led to further work with this polymer. It was found that dark gold colored films could be prepared by the precipitation techniques of Arnold (Reference 16) and by casting techniques. Isothermal aging at 700°F for up to 240 hours and thermogravimetric analyses in both nitrogen and air (Figure 22) were performed. These showed a higher degree of thermal stability for this 65/35 copolymer than for the other two copolymers (Tables I and V). The isothermal aging curves of BBB (See Polymer A in Reference 1) and BBB/BBL-65/35 are compared in Figure 2 and show that the copolymer has very good thermal stability which approaches that of BBB.

### Imide Polymers

Using established methods for the preparation of conventional (five membered ring) aromatic polyimides (3,5,6,7,8,9), a series of polymers were prepared in this work containing five-, six- or seven-membered imide rings. These

polyimides are referred to symbolically as PI-5, PI-6 and PI-7 types, respectively. When either pyromellitic dianhydride (PMDA) or 2,2',6,6'-biphenyltetracarboxylic acid (BPTCDA) was used to prepare a polyimide, i. e., either a PI-5 or PI-7 polymer, respectively, the anhydride monomer was slowly added to a stirred solution of the aromatic diamine used as comonomer. The diamine comonomers were previously dissolved in 50-75 ml of freshly distilled and deoxygenated DMAC. These reactions were exothermic, a greater exotherm being noted on PMDA addition than on BPTCDA addition. After stirring the reaction solutions 4-5 hours at room temperature, the polymerizations were terminated by removal of the solvent under reduced pressure. This procedure lent itself to producing polyamic acid films which could be converted to polyimides by cyclodehydration in refluxing acetic anhydride. The resulting PI-5 and PI-7 type polyimides were washed in ether and dried at 180°C for 20 hours at 1 mm Hg.

A third dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) was used to produce PI-6 type polymers. When NTCDA addition was made to a room temperature solution of diamine no exotherm was detected unlike the above cases for either PMDA or BPTCDA. Polymer formation from NTCDA occurred only upon heating to near 100°C as previously reported (Reference 9). This is not consistent with the results of Plonka and Albrecht who reported significant reactions at 15-30°C (Reference 14).

Although we found the reaction of NTCDA with an amine in DMAC to be very sluggish at room temperature, the analogous DMAC reactions of an amine with a stoichiometric mixture of either NTCDA and PMDA or of NTCDA and BPTCDA appeared to be much faster reactions. These co-acid polymerizations seemed to approach the reactivities of BPTCDA reactions with amines under the same conditions. However, in these cases it is apparent that both PI-6 and -5 imide structures, as well as both PI-6 and -7 type imide structures are obtained in the mixed backbone polymers from the respective types of copolymerizations. To insure high conversion, polyimide reaction mixtures containing, by charge, equimolar amounts of the five- and six-membered ring anhydrides and six- and seven-membered ring anhydrides were run for one hour at 100°C in DMAC before the solvent was removed and ring closure

effected chemically. In the polymerization reactions to derive still a third type of polymer with mixed structure equimolar charges of five- and seven-membered ring anhydrides were reacted with an amine. This reaction temperature was maintained at room temperature for four to five hours.

Without considering any variations in polymer structures resulting from the use of different diamines, the varied use of the three above types of anhydrides gives rise to six different types of polyimide structures: PI-5, PI-6, PI-7, PI-5/6, PI-5/7 and PI-6/7.

In a number of the above reactions, an aliquot of about 5 ml of the DMAC-prepolymer dope was withdrawn from the reaction mixture and precipitated into diethyl ether. After drying at 70-80°C for 20 hours at 1-2 mm Hg., these samples were used to determine prepolymer viscosities in DMAC (Tables I, II and III). Viscosities of the polyimides were obtained in concentrated sulfuric acid by stirring an 0.5000 g/dl mixture for a maximum of 1/2 hour. The resulting solutions were filtered and the inherent viscosities were immediately obtained. Due to the questionable stability of polyimides in strong acids, these viscosities must be considered in a relative sense only.

In addition to the more conventional methods used above, attempts were also made to prepare polyimides by polycondensation in polyphosphoric acid (PPA). Conditions known to give good "BB" polymers (Reference 1) were used. A polyimide from NTCA and oxydianiline (ODA) designated PI-6 (0-2) and a polyimide from BTCA and oxydianiline designated as PI-7 (0-3) were prepared in this manner. As can be seen from the data in Table II, polyimides prepared by the conventional two-step process have better properties than these prepared in PPA.

As the imide ring size was increased from five to six to seven in the polymer backbone structures, the thermal stability of the polyimides we prepared was decreased. This is evidenced in Table II where the thermogravimetric analyses (TGA) of a PI-5, PI-6 and PI-7, each prepared in DMAC with oxydianiline (ODA) as the diamine, are compared. Isothermal aging data at 700°F for over 200 hours also indicated this (Table VI and Figure 3). Extending this it might be expected that copolyimides containing five-membered imide ring structure would be more

stable than those containing only six- and seven-membered imide rings. Again the TGA and isothermal aging data tend to bear this out and show that PI-5/6 is more thermooxidatively stable than either the PI-5/7 or PI-6/7 (Table VI and Figure 4). In this case the PI-5/6 polymer exhibits higher thermal stability than does its PI-6 polyimide analog.

Although some of the physical properties of the seven-membered polyimides from oxydianiline and m-phenylene diamine were previously reported (Reference 3), Table VII lists properties for seven-membered polyimides prepared from oxydianiline or benzidine with BPTCDA. As can be seen from Table VII, the analytical results of benzidine-containing polymers are not good, showing high oxygen and low carbon and nitrogen, which is indicative of poor ring closures.

Infrared absorption spectra of representative polymers including PI-5, PI-6, PI-7 and PI-5/7 and PI-6/7 are found in the Appendix (Figures 6 to 15). Figure 12 shows the IR of the ether-isolated prepolymer of PI-5/7 (0-2). After chemical ring closure, the spectrum becomes typical of Figure 13. Similar changes were noted for all polyamic acid/polyimide pairs.

### BB/Imide Polymers

Much has been published on the synthesis of polyimides by an initial, low or room temperature reaction of diamine and dianhydride in an aprotic solvent followed by a second step cyclodehydration. The second step has been carried out thermally or in the presence of acetic anhydride or other dehydrating agent. As reported here and elsewhere (Reference 11) polyimides can also be prepared by condensation in polyphosphoric acid, even though it is not the preferred route. Furthermore, previous work (Reference 11) indicates that BB polymers can be prepared by the two-step route using DMAC or DMSO as the aprotic solvent, however, with these types of polymers polycondensation in PPA is the preferred route. In this current investigation a series of polymers containing both the BB and PI ring systems were prepared by both of the above methods.

Polycondensations in polyphosphoric acid were carried out by the previously reported method referred to above as Method A (Reference 1). Polymers were obtained by heating stoichiometric mixtures of the tetraacids and tetraamines in PPA near 200°C. In the two-step process, the initial reaction was carried out at room temperature in an aprotic solvent as described earlier for polyimide prepolymer formation, and subsequent ring closures were effected in refluxing acetic anhydride. Isolated products were washed in ether and dried at 180-190°C and 1-2 mm Hg. for 20-24 hours. Purification was accomplished by precipitation from concentrated sulfuric acid solutions. Physical properties, including viscosities, infrared and elemental analyses, TGA's, and isothermal agings were obtained from purified samples.

Copolymers of BBB/PI-6 were prepared from NTCA with equimolar quantities (50/50) of DAB and either m-phenylene diamine, oxydianiline, or benzidine in polyphosphoric acid. One BBL/PI-6 was prepared in like manner from NTCA and equimolar quantities (50/50) of TAB as the tetrahydrochloride and m-phenylene diamine. As a basic for comparison, the BBB/PI-6 polymers of 50/50 compositions were also prepared from the dianhydride NTCDA with DAB and the three different diamines used above. The physical properties of these seven polymers are given in Table I, Appendix. From the data of Table I, it is difficult to decide which approach gives the better polymer since polycondensation in PPA gives better polymers where the diamine is m-PDA or ODA, but the two-step method yields a more thermally stable polymer where benzidine is the diamine. Figure 16 shows the isothermal aging curves for several of the BB/PI copolymers compared with the curves for BBB (see Polymer A) (Reference 1) and PI-6 (see Polymer A) (Reference 1). Although these aging curves for the BBB/PI-6 polymers are fairly good, they do not equal those of the homopolymers. This lower degree of thermal stability is at least partly due to the lower inherent viscosities of the BB/PI polymers of the BBB reference polymer (2.01 in sulfuric acid at 30°C). No viscosity is reported for PI-6 (see Polymer A) due to insolubility in sulfuric acid (Reference 9). Good thermal properties seem to appear when solution viscosities are 0.2 dl/gm or greater in sulfuric acid. Infrared spectra of these polymers are found in Figure 17-21, Appendix and TGA curves in Figure 23.

## SECTION IV

### CONCLUSIONS

From the results presented in this report, it is concluded that high molecular weight thermally stable BBB/BBL polymers can be prepared by condensing stoichiometric mixtures of diaminobenzidine and tetraaminobenzene with naphthalenetetracarboxylic acid in PPA. From thermogravimetric analyses and isothermal aging data, it appears that these copolymers approach the expected thermal stability properties exhibited by the parent homopolymers when high molecular weights are achieved.

It is further concluded that polyimides containing a seven-membered ring, and a mixture (50/50) of five- and six-; five- and seven-; and six- and seven-membered imide rings can be prepared by the conventional two-step process for preparing polyimides. When a six-membered ring is present, increased reaction temperature is required to effect prepolymer formation in DMAC. Copolyimides of the following structures -- PI-5/6, PI-5/7 and PI-6/7 -- possess thermal properties approaching, but not exceeding those of the more thermally stable homopolyimides. Of the polyimides synthesized in this investigation those containing five-membered imide rings are more stable than those containing six-membered imide rings, which in turn, are more stable than those containing seven-membered rings. All the polyimides and copolyimides have the tendency to form prepolymer films when DMAC is carefully removed from the prepolymer dope. The prepolymers from BPTCDA give a clear, colorless film while those from PMDA give tougher yellow films. The prepolymers of mixed anhydride copolymers give films displaying properties of both components.

It is also concluded that polymers possessing both "BB" and imide structures in the polymer backbone can be prepared either by polycondensations in polyphosphoric acid or by the conventional polyimide processes. The thermooxidative stability of the resulting BB/PI-6 copolymers is good but less than that of the parent polymers, however, these copolymers do appear to have enhanced stability to strong acids.

## REFERENCES

1. John F. Coleman and R. L. Van Deusen, AFML-TR-69-289 (1969).
2. R. L. Van Deusen, AFML-TR-65-295 (1965).
3. W. H. Gloor, AFML-TR-66-79 (1966).
4. A. J. Rosenthal, et. al., AFML-TR-67-172 (Parts I-III, 1967-1969).
5. F. E. Arnold and R. L. Van Deusen, *Macromolecules*, 2, 497 (1969).
6. E. S. Blake, R. E. Debrunner and J. A. Webster, AFML Tech. Report 65-187, Part II (1967).
7. O. K. Goins and R. L. Van Deusen, AFML-TR-68-104 (1968).
8. J. A. Webster and E. S. Blake, AFML-Interim Tech. Report Under Contract AF 33(615)-2648 (1966).
9. J. K. Fincke, et. al., AFML-TR-67-136 (1967).
10. G. M. Bower and L. W. Frost, *J. Poly. Sci.*, A-1, 3135 (1963).
11. C. E. Scroog, et. al., *J. Poly. Sci.* A-3, 1373 (1965).
12. J. Preston, *J. Poly. Sci.*, A-1, 529 (1966).
13. M. M. Koton, et. al. *Zhurnaz Prikladnoi Khimii*, 38, 2728 (1965).
14. Z. Yu Plonica and V. M. Albrekht, *Vysokomol. soyed.* 7: No 12, 2177 (1965).
15. A. A. Berlin, G. V. Belover, B. I. Logon'hii and C. M. Shamraev, *Vysokomol. Soedin.*, 9, 1936 (1967).
16. F. E. Arnold and R. L. Van Deusen, "Approaches to the Preparation of Films from BBL and Other Ladder Polymers," AFML-TR-71-17 (1970). (In preparation.)

APPENDIX

TABLE I  
PHYSICAL PROPERTIES OF BB-CONTAINING POLYMERS

Polymer Designation	Reaction Solvent	Solution Viscosities		Elemental Analysis				TGA Temp(°C)		Iso(%) <sup>f</sup> Air	
		H <sub>2</sub> SO <sub>4</sub> <sup>a</sup>	Other	%C	%H	%Ash	%N	%O	Air		Inert
BBB/BBL-80/20-H	PPA		0.47	70.21	3.02	1.0	12.00	12.70	410	380	96.5
BBB/BBL-65/35-H	PPA	2.41	2.80 <sup>c</sup> 3.25 <sup>b</sup>	74.62	2.40	0.80	14.44	9.22	600	750	17.6
BBB/BBL-50/50	PPA		0.45 <sup>b</sup>	69.08	2.96	1.2	12.67	12.90	400	400	96.5
BBB/PI-6 (P-1)	PPA	0.29		73.66	2.35	0.55	10.95	11.35	510	585	31.6
BBB/PI-6 (P-2)	DMAC	0.11		71.45	2.80	0.65	10.67	-----	515	575	51.1
BBB/PI-6 (O-2)	PPA	0.18		73.95	2.64	1.00	11.46	12.64	560	630	30.8
BBB/PI-6 (O-4)	DMAC	0.15	0.09 <sup>d</sup>	70.98	2.95	-----	9.27	17.46	455	525	93.7
BBB/PI-6 (B-1)	DMAC	0.20		74.04	3.14	0.75	9.31	12.90	570	620	17.9
BBB/PI-6 (B-2)	PPA	0.10		67.43	3.13	69	8.96	19.13	490	---	66.0
BBL/PI-6 (P-1)	PPA	0.16		70.58	2.58	0.70	12.31	11.34	550	640	6.41

a Inherent viscosity in conc. H<sub>2</sub>SO<sub>4</sub> solution (polymer conc. = 0.5 g/dl)

b Intrinsic viscosity in methane sulfonic acid

c Intrinsic viscosity in conc. H<sub>2</sub>SO<sub>4</sub>

d Inherent viscosity of prepolymer in DMAC (prepolymer conc. = 0.5 g/dl)

e Temperature of 10% weight loss ( $\Delta T = 30^{\circ}\text{C}/\text{min}$ )

f Percent weight loss after 200 hrs. at 700°F in static air oven

TABLE II  
PHYSICAL PROPERTIES OF IMIDE POLYMERS

Polymer Designation	Polymerization Inherent	Solution Viscosities <sup>a</sup>		Elemental Analyses						TGA Temp (°C) <sup>b</sup>		% Loss 200 Hrs at 700°F
		H <sub>2</sub> SO <sub>4</sub>	DMAC	%C	%H	%Ash	%N	%O	Air	Inert		
PI-5 (0-2)	DMAC	0.38	----	69.86	2.51	----	7.17	20.69	555°	590°	32.8	
PI-6 (0-2)	PPA	INS	----	72.75	2.71	----	5.96	18.36	465°	----	81.5	
PI-6 (0-3)	DMAC	0.15	0.09	72.07	2.82	1.95	6.34	18.28	520°	570°	82.6	
PI-7 (0-1)	DMAC	0.08	0.27	72.11	3.24	0.0	6.14	18.42	420°	435°	97.9	
PI-7 (0-3)	PPA	0.07	----	76.14	3.55	----	5.07	17.03	410°	----	87.0	
PI-5/6 (0-1)	DMAC	0.46	70.27-0.13	71.02	2.63	2.0	6.74	19.52	550°	580°	35.4	
PI-5/6 (0-2)	DMAC	0.25	0.13	70.82	2.54	----	7.00	20.21	545°	580°	31.1	
PI-6/7 (0-1)	DMAC	0.15	0.10	71.45	2.97	0.65	6.26	18.57	490°	535°	96.1	
PI-6/7 (0-2)	DMAC	0.15	0.10	72.18	2.97	----	6.45	18.39	480°	500°	99.7	
PI-5/7 (0-1)	DMAC	0.13	----	70.86	3.05	0.85	6.83	20.71	470°	500°	70.0	
PI-5/7 (0-2)	DMAC	0.18	0.28	69.98	2.79	----	6.98	20.36	485°	525°	77.5	

a DMAC soluble prepolymer at 0.5 g/dl

b Temperature of 10% weight loss ( $\Delta T = 3^\circ\text{C}/\text{min}$ )

TABLE III  
PHYSICAL PROPERTIES OF REFERENCE POLYMERS

Polymer Designation	a H <sub>2</sub> SO <sub>4</sub>	b H <sub>2</sub> SO <sub>4</sub>	c MSA	Elemental Analyses					TGA Temp(°C) <sup>d</sup>		% Loss 200 Hrs. at 700°F
				%C	%H	%Ash	%N	%O	Air	Inert	
BBB (Ref. Poly. A)	-----	2.01	2.51	76.37	2.64	0.6	13.38	7.88	525°	660°	53%
PI-6 (Ref. Poly. A)	INS	INS	-----	67.93	2.81	0.0	7.99	-----	540°	-----	10.5%

a Inherent viscosity in H<sub>2</sub>SO<sub>4</sub> at 0.5 g/dl

b Intrinsic viscosity in H<sub>2</sub>SO<sub>4</sub>

c Intrinsic viscosity in methane sulfonic acid

d Temperature of 10% weight loss ( $\Delta T = 3^\circ \text{C}/\text{min}$ )

TABLE IV  
THEORETICAL ELEMENTAL COMPOSITIONS OF POLYMERS

Polymer	Monomer Charge Ratio	%C	%H	%N	%O
BBB/PI-6 (P)	2NTCA+1DAB+1MPDA	73.59	2.42	11.19	12.39
BBB/PI-6 (B)	2NTCA+1DAB+1 Benzidine	75.54	2.69	10.17	11.61
BBB/PI-6 (O)	2NTCA+1DAB+1 ODA	74.11	2.63	9.47	13.29
BBL/PI-6 (P)	2NTCA+1TAB·4HCl+1M PDA	71.22	2.09	12.46	14.23
BBB/BBL	1NTCA+0.8DAB+0.2TAB·4HCl	75.36	2.35	14.18	8.10
BBB/BBL	1NTCA+0.65DAB+0.35TAB·4HCl	74.80	2.26	14.60	8.34
BBB/BBL	1NTCA+0.5DAB+0.5TAB4HCl	74.19	2.17	15.05	8.60
PI-5 (O)	1PMDA+1ODA	69.11	2.64	7.33	20.93
PI-6 (P)	1INTCDA+1MPDA	70.59	2.37	8.23	18.81
PI-6 (O)	1INTCDA+1ODA	72.22	2.80	6.48	18.50
PI-7 (O)	1BPTCDA+1ODA	73.36	3.08	6.11	17.45
PI-7 (B)	1BPTCDA+1 Benzidine	76.01	3.19	6.33	14.47
PI-5/6 (O)	1PMDA+1INTCDA+2ODA	70.76	2.72	6.88	19.64
PI-5/7 (O)	1PMDA+1BPTCDA+2ODA	71.43	2.88	6.66	19.03
PI-6/7 (O)	1INTCDA+1BPTCDA+2ODA	72.81	2.94	6.29	17.96

TABLE V  
 ISOTHERMAL AGING (PERCENT WEIGHT LOSS) OF BB-CONTAINING  
 POLYMERS AT 700°F

Time, Hours Polymer	18	44	66	88	157	175	200	220	240
	BBB (Ref. Poly. A)	0.3	0.9	1.2	1.6	3.4	4.1	5.3	6.4
BBB/BBL-65/35-H	0.6	1.6	2.4	3.6	8.6	9.8	12.4	14.7	17.6
BBB/PI-6 (P-1)	1.5	2.9	6.7	9.8	18.7	25.7	31.6	36.4	45.0
BBB/PI-6 (P-2)	1.6	3.8	7.1	11.5	31.9	39.6	51.1	58.8	65.4
BBB/PI-6 (0-2)	2.0	3.2	5.5	7.2	17.9	21.0	30.8	35.0	39.0
BBB/PI-6 (0-4)	10.4	22.1	42.3	55.8	82.6	87.9	93.7	95.7	97.2
BBB/PI-6 (B-1)	0.5	2.2	2.7	4.3	11.9	15.5	17.9	22.3	27.0
BBL/PI-6 (P-1)	4.1	9.7	14.3	19.9	47.1	53.8	64.1	69.7	76.4

TABLE VI  
ISOTHERMAL AGING (PERCENT WEIGHT LOSS) OF IMIDE  
POLYMERS AT 700°F

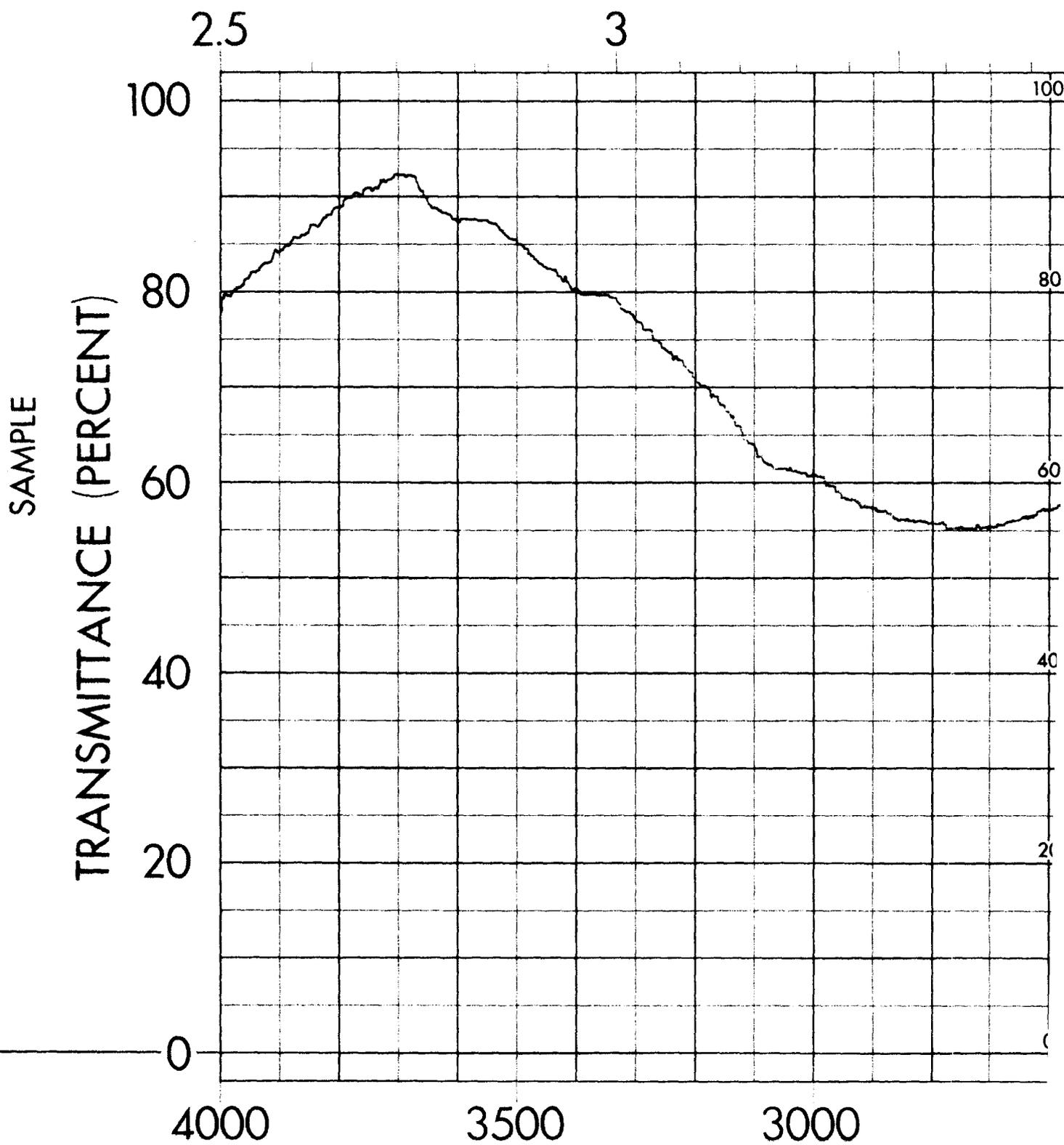
Time, Hours	18	44	66	88	157	175	200	220	240
Polymer									
PI-6 (Ref. Poly. A)	1.0	1.3	3.1	3.3	6.8	8.8	10.5	11.2	12.2
PI-5 (0-2)	1.1	4.0	6.0	7.3	20.7	25.2	32.8	38.0	43.2
PI-6 (0-2)	32.7	61.9	71.6	73.2	79.0	80.5	81.5	83.0	83.0
PI-6 (0-3)	3.5	11.9	18.4	22.2	62.6	75.4	82.6	90.3	94.7
PI-7 (0-1)	8.9	28.6	50.3	70.3	94.5	96.1	97.9	98.3	98.7
PI-7 (0-3)	35.9	67.3	74.9	79.3	85.6	86.1	87.0	87.3	87.6
PI-5/6 (0-1)	1.3	4.3	6.9	10.7	17.7	23.8	35.4	----	55.1
PI-5/6 (0-2)	1.3	4.3	6.9	9.5	18.7	23.2	31.1	----	43.7
PI-6/7 (0-1)	7.5	16.5	18.6	38.3	90.0	92.7	96.1	----	98.4
PI-6/7 (0-2)	9.7	25.5	35.7	63.6	94.4	97.2	99.7	----	99.9
PI-5/7 (0-1)	4.4	10.2	15.4	21.0	56.4	61.3	70.0	----	78.2
PI-5/7 (0-2)	5.0	10.5	15.4	20.9	66.1	70.5	77.5	----	85.0

TABLE VII  
PROPERTIES OF ADDITIONAL IMIDE POLYMERS

Polymer Designation	Acid	Amine Solvent Used	Viscosity <sup>a</sup> H <sub>2</sub> SO <sub>4</sub>	Elemental Analyses					TGA Temp (°C) <sup>b</sup>		% Loss, 200 Hrs at 700° F	
				%C	%H	%Ash	%N	%O	Air	Inert		
PI-5 (B-1)	PMDA	Benzi- dine	DMAC	Ins.	69.41	3.26	0.0	7.29	18.34	580°	---	---
			Theoretical		72.13	2.75	---	7.65	17.47			
PI-6 (B-1)	NTCA	B	PPA	0.03	64.32	2.77	10.0	3.56	27.94	---	---	---
			Theoretical		75.00	2.91	---	6.73	15.34			
PI-7 (0-2)	BPTCDA	ODA	DMAC	0.08	72.11	3.24	0.0	6.14	18.42	420°	435°	97.9%
			Theoretical		73.36	3.08	---	6.11	17.45			
PI-7 (B-1)	BPTCDA	B	DMAC	0.08	70.46	3.98	0.0	5.49	20.28	430°	440°	---
			Theoretical		76.01	3.19	---	6.33	14.47			
PI-5/7 (B-1)	PMDA BPTCDA	B	DMAC	0.11	70.39	3.99	0.0	6.49	18.35	470°	490°	---
			Theoretical		74.25	2.99	---	6.93	15.83			

a Inherent viscosity in H<sub>2</sub>SO<sub>4</sub> at 0.5 g/dl

b Temperature of 10% weight loss ( $\Delta T = 3^\circ \text{C}/\text{min}$ )



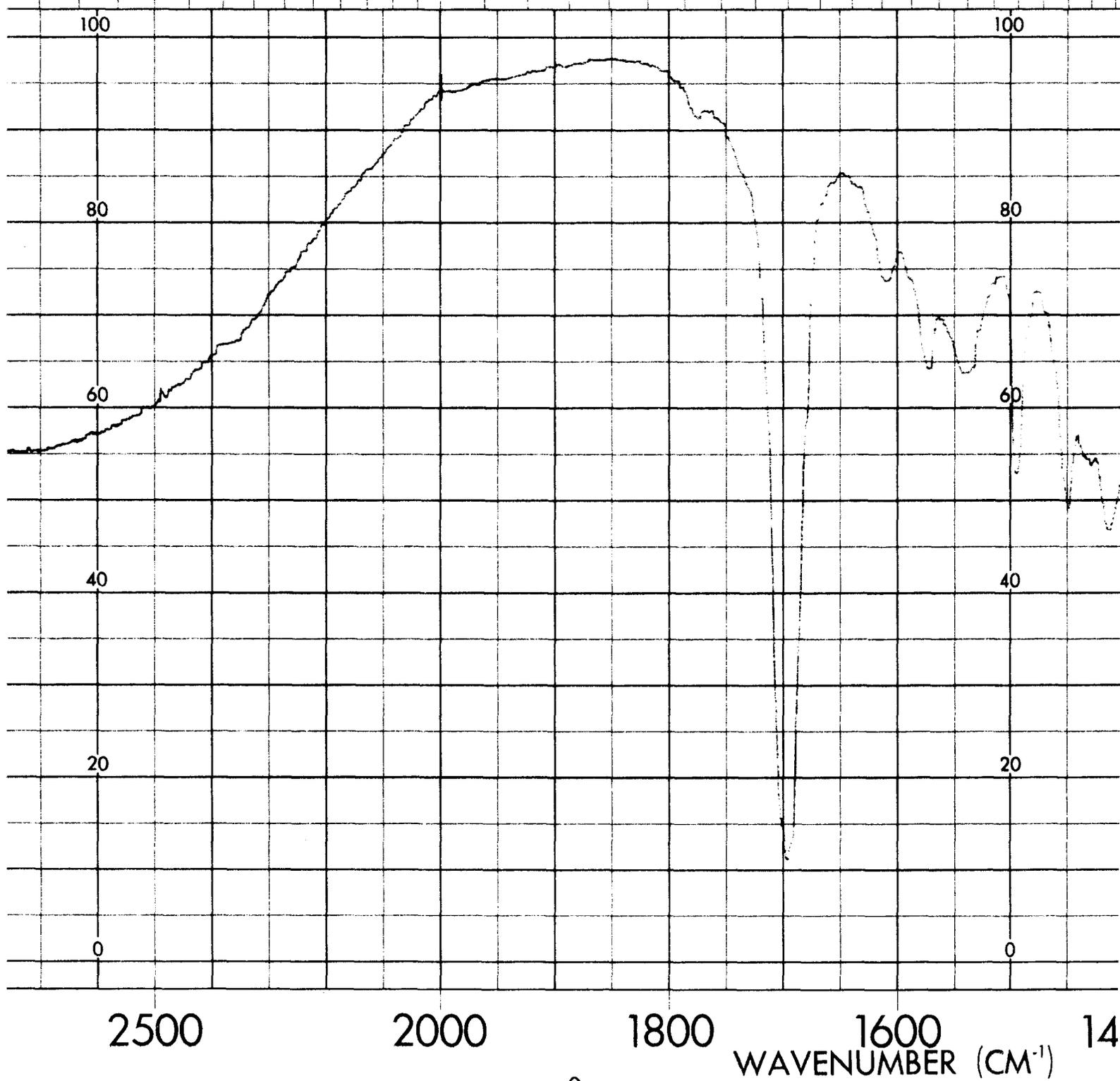
WAVELENGTH (MICRONS)

4

5

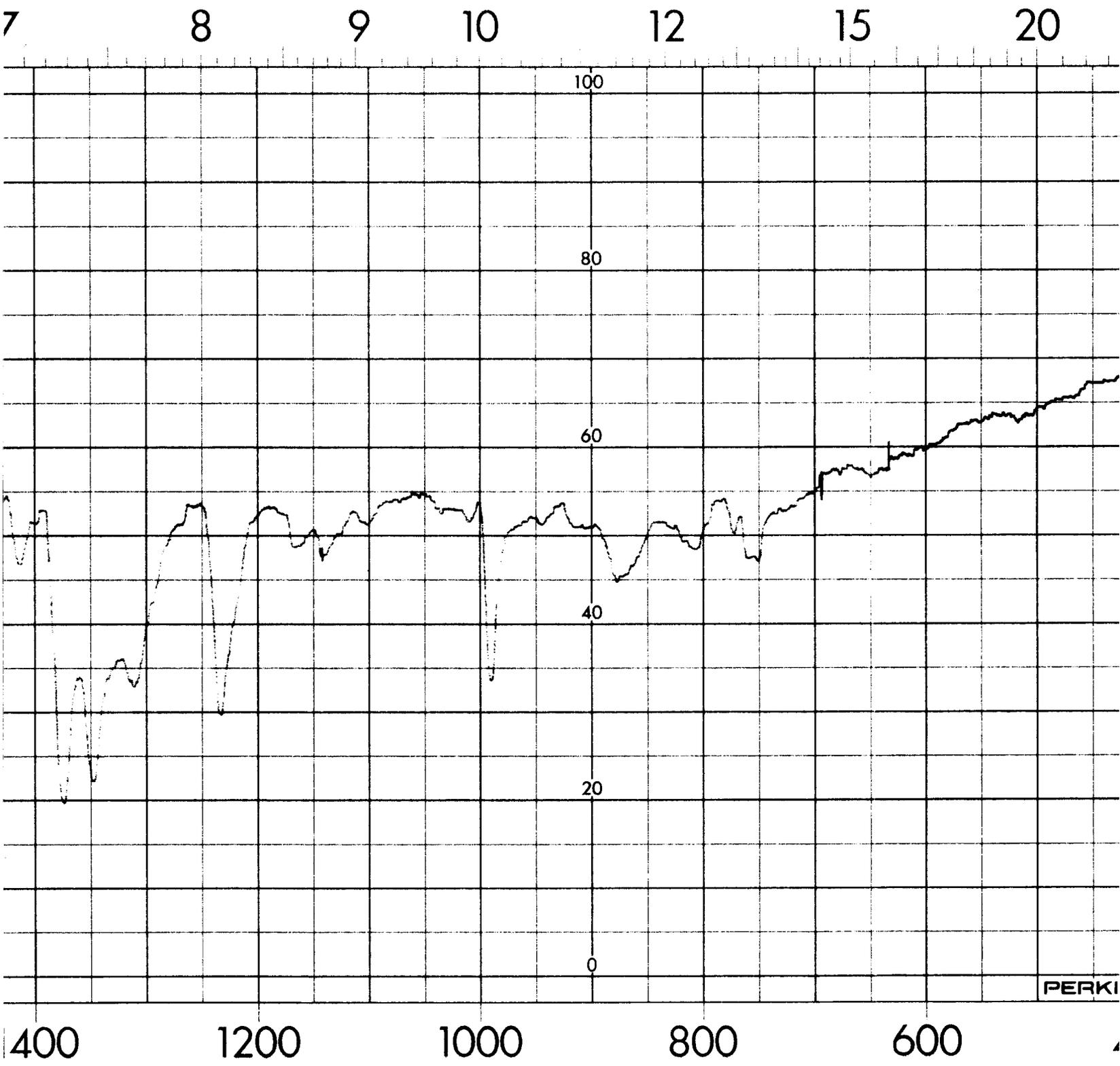
6

7



2

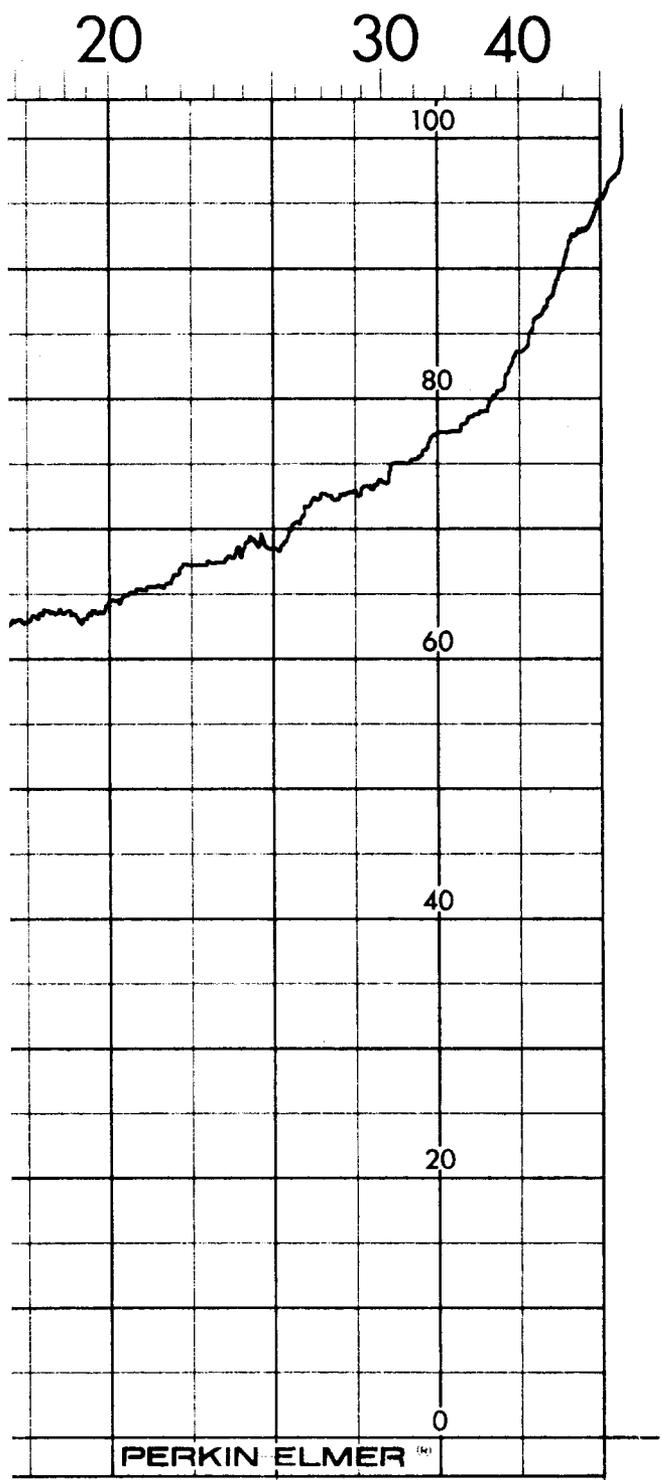
Figure 1. Analytical Infrared Spectrum of BBB/BBL-6



PERKI

L-65/35-H

3



4

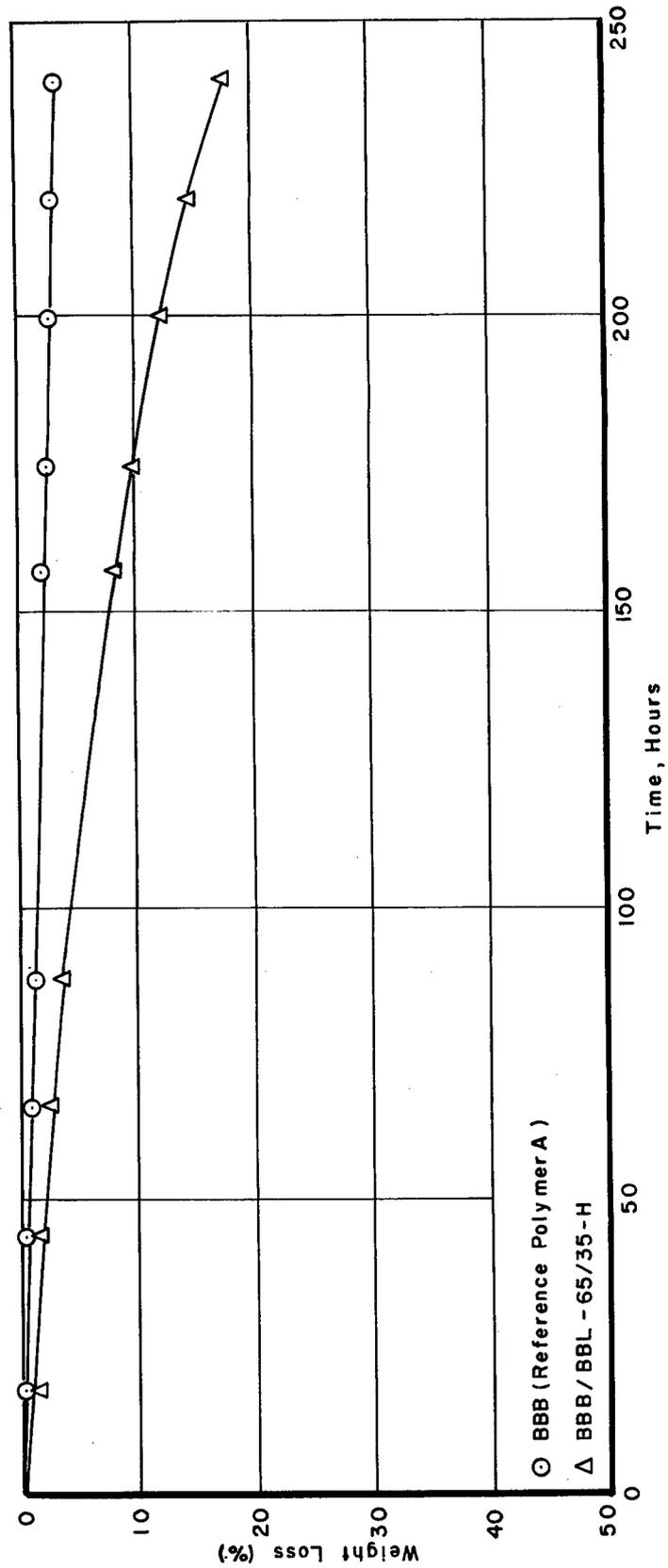


Figure 2. Isothermal Aging Curves for BBB (Reference Polymer A) and BBB/BBL-65/25-H at 700°F

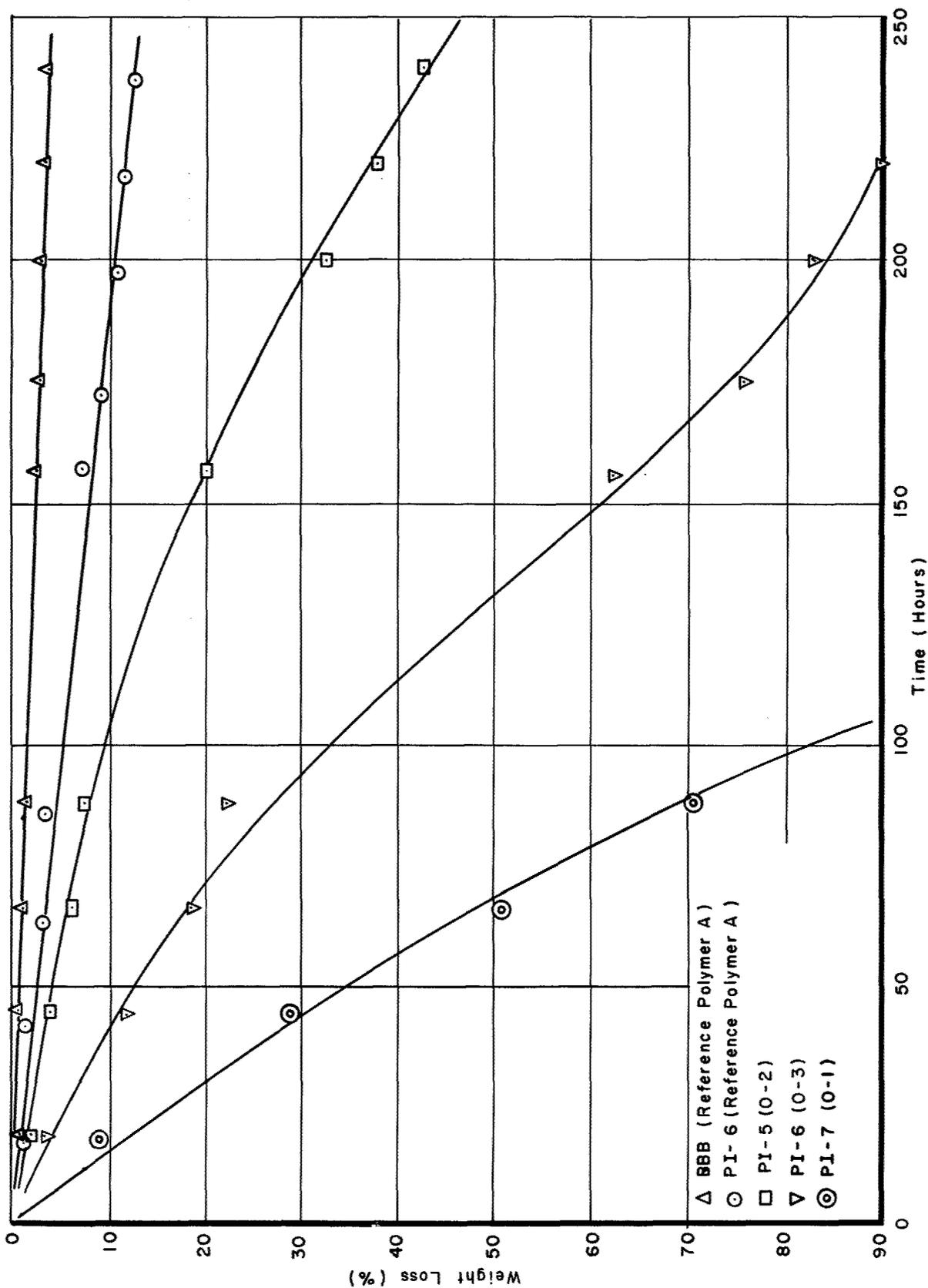


Figure 3. Isothermal Aging Curves for Various Ring-Sized Polyimides at 700°F

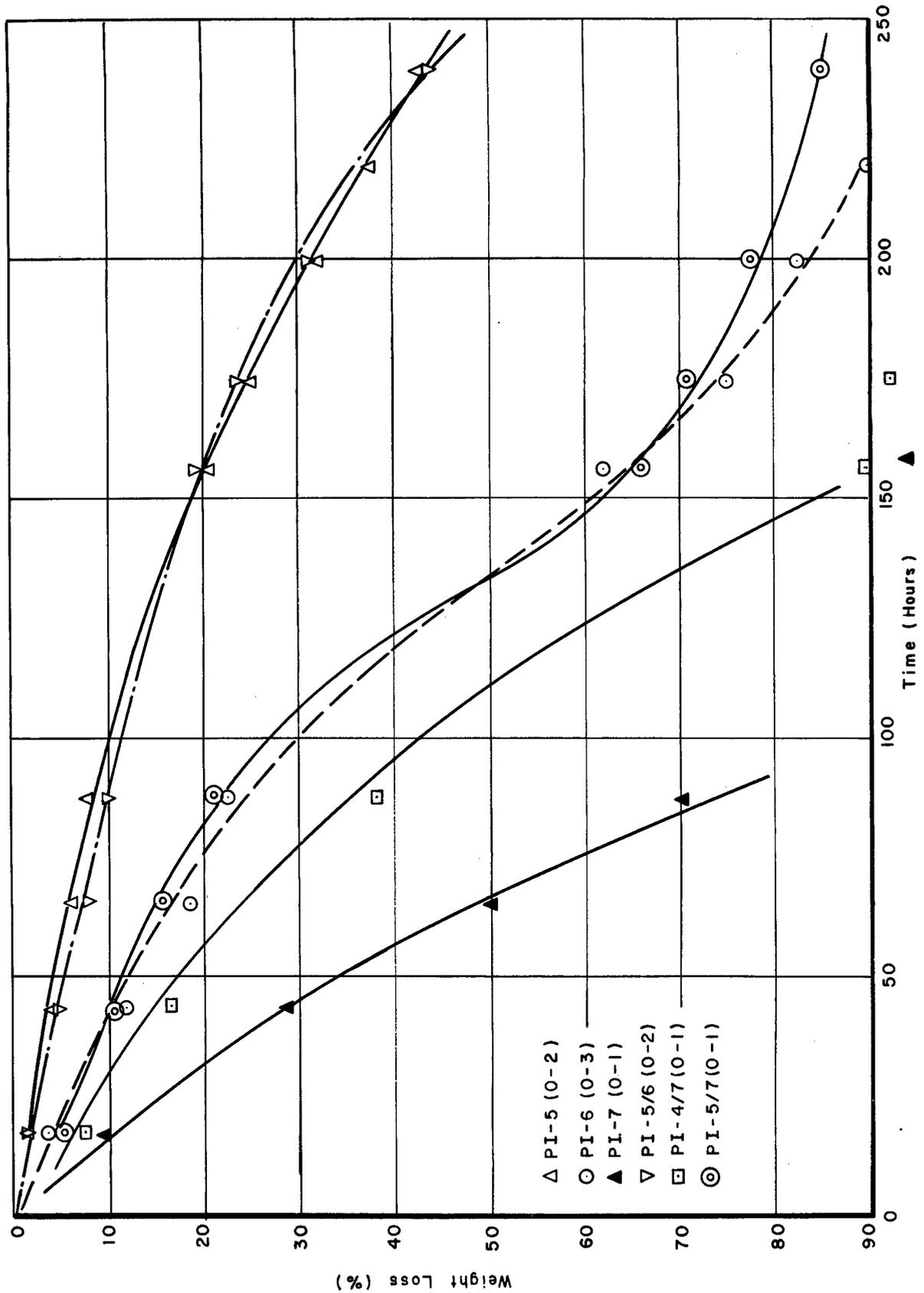


Figure 4. Isothermal Aging Curves of Polyimides and Corresponding Copolyimides at 700°F

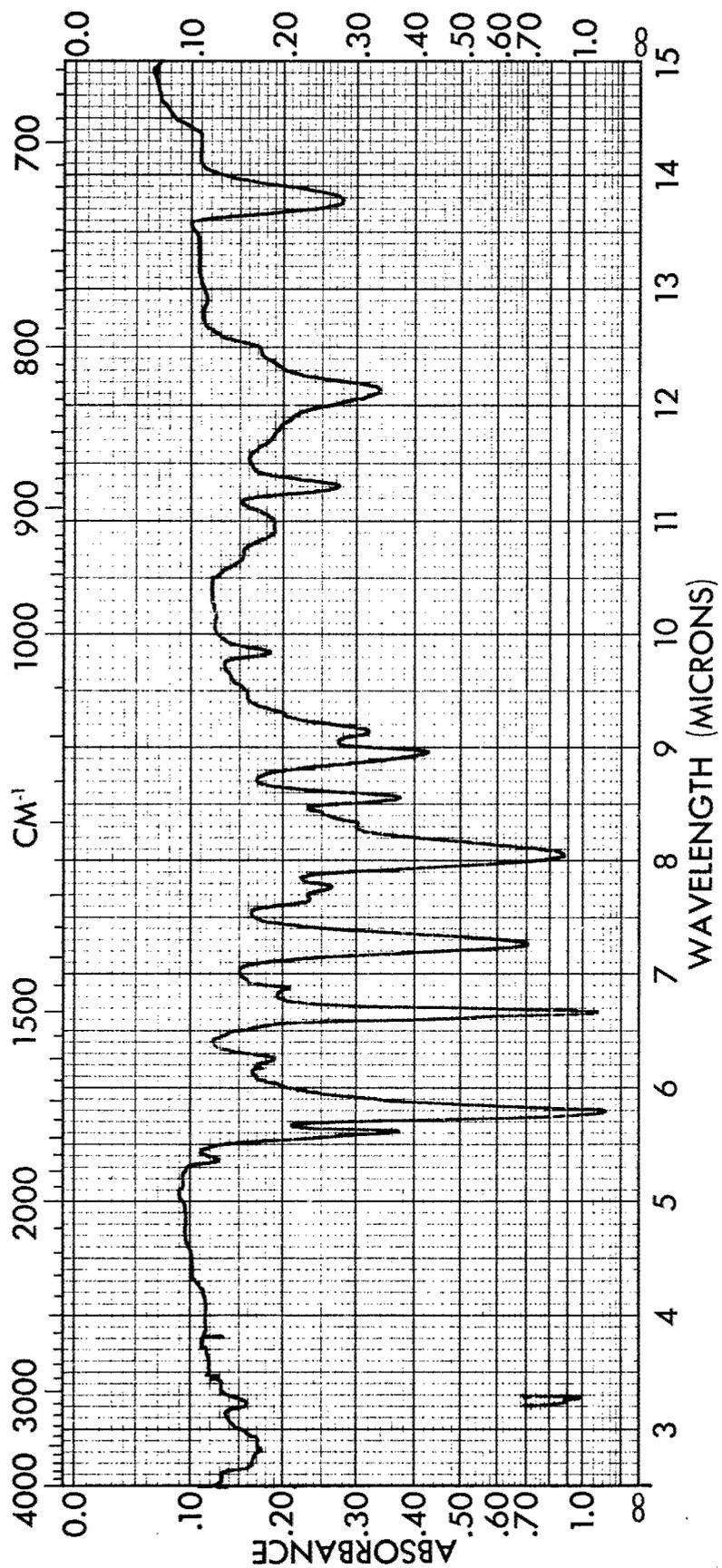


Figure 5. Infrared Spectrum of PI-5 (0-2)

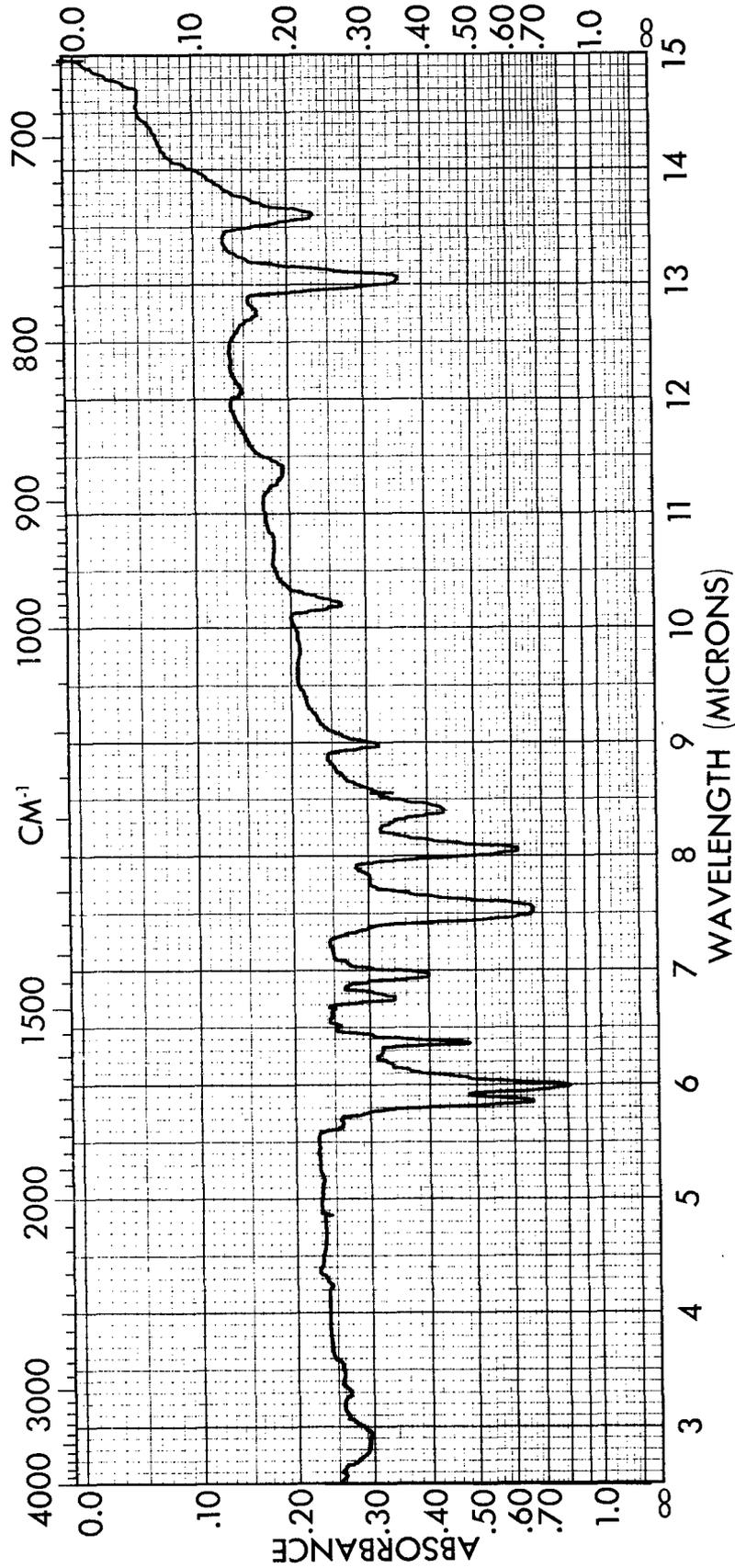


Figure 6. Infrared Spectrum of PI-6 (Reference Polymer A)

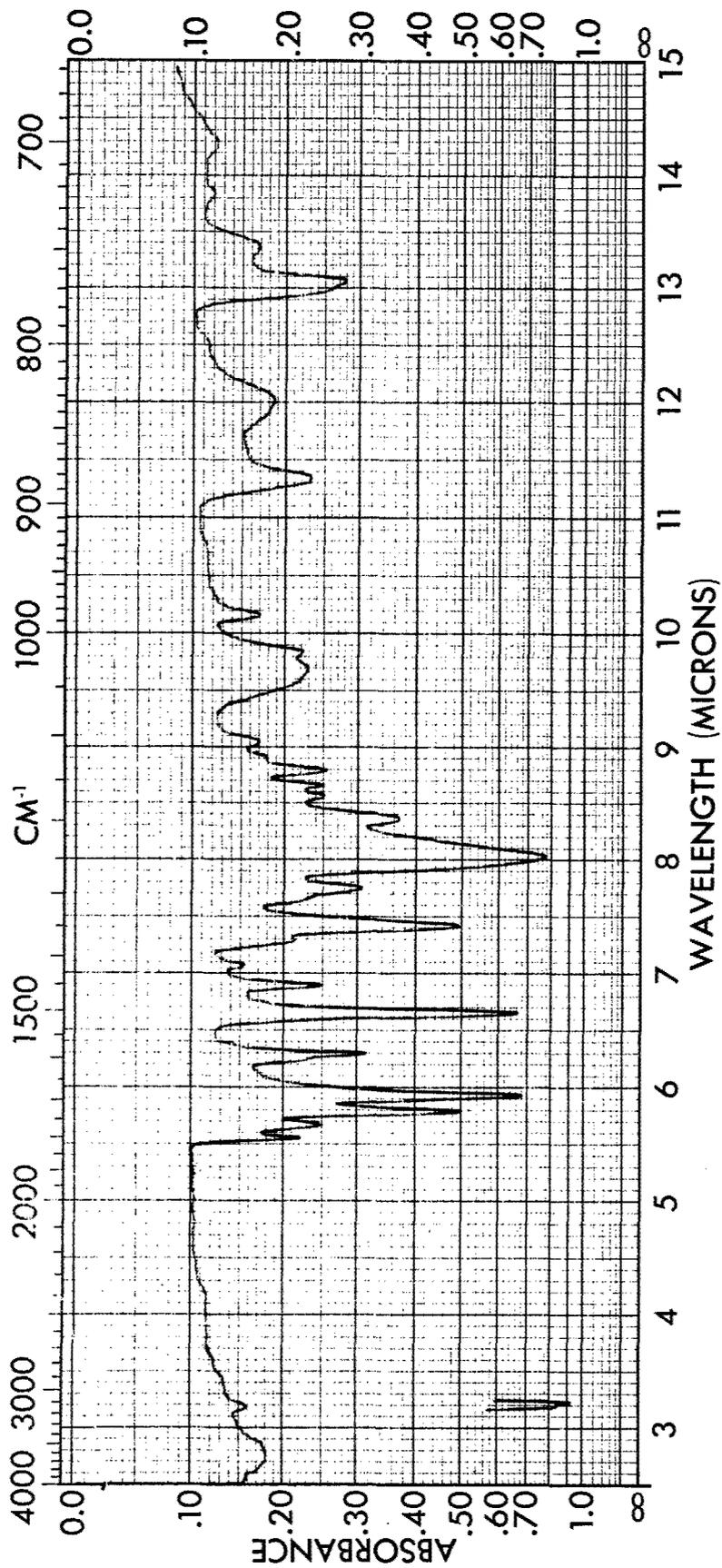


Figure 7. Infrared Spectrum of PI-6 (0-3)

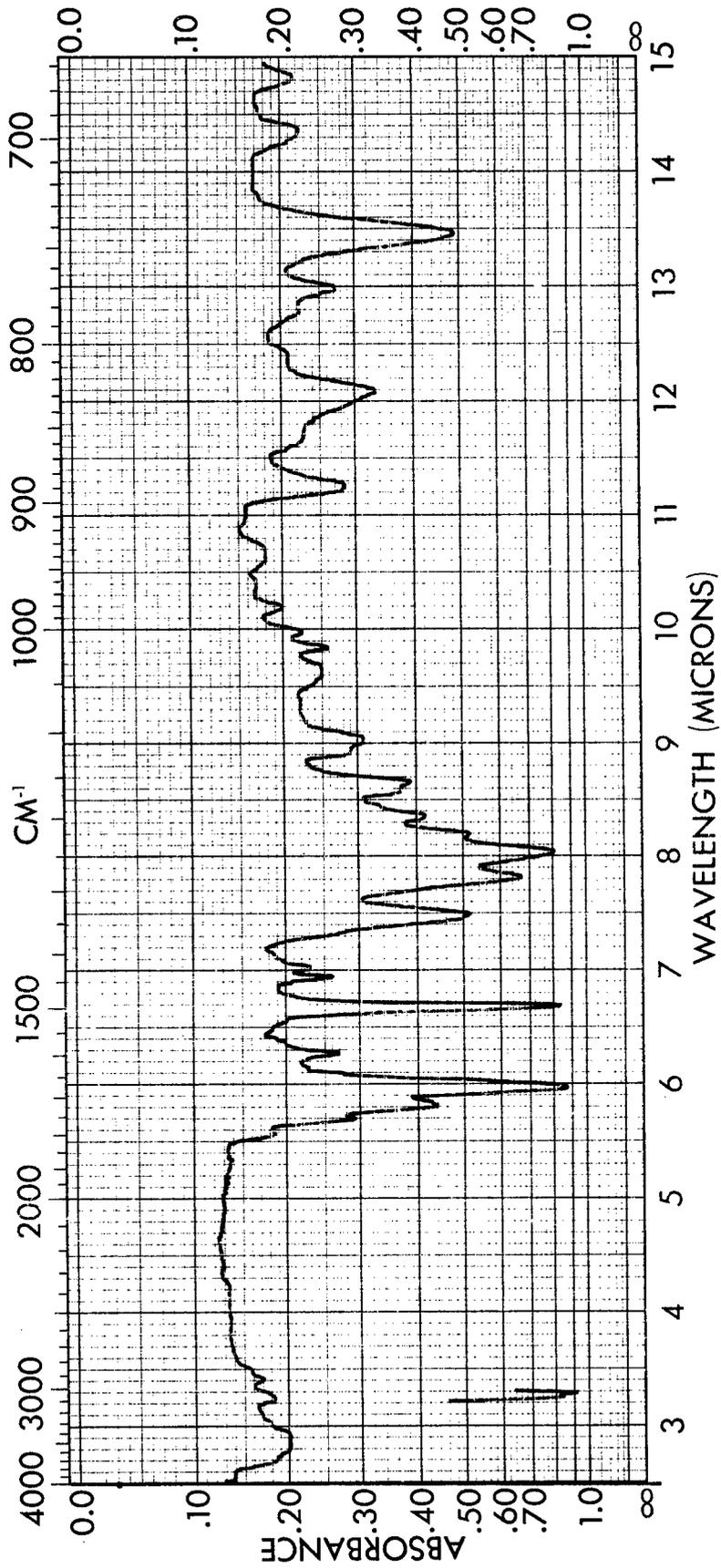


Figure 8. Infrared Spectrum of PI-7 (0-4)

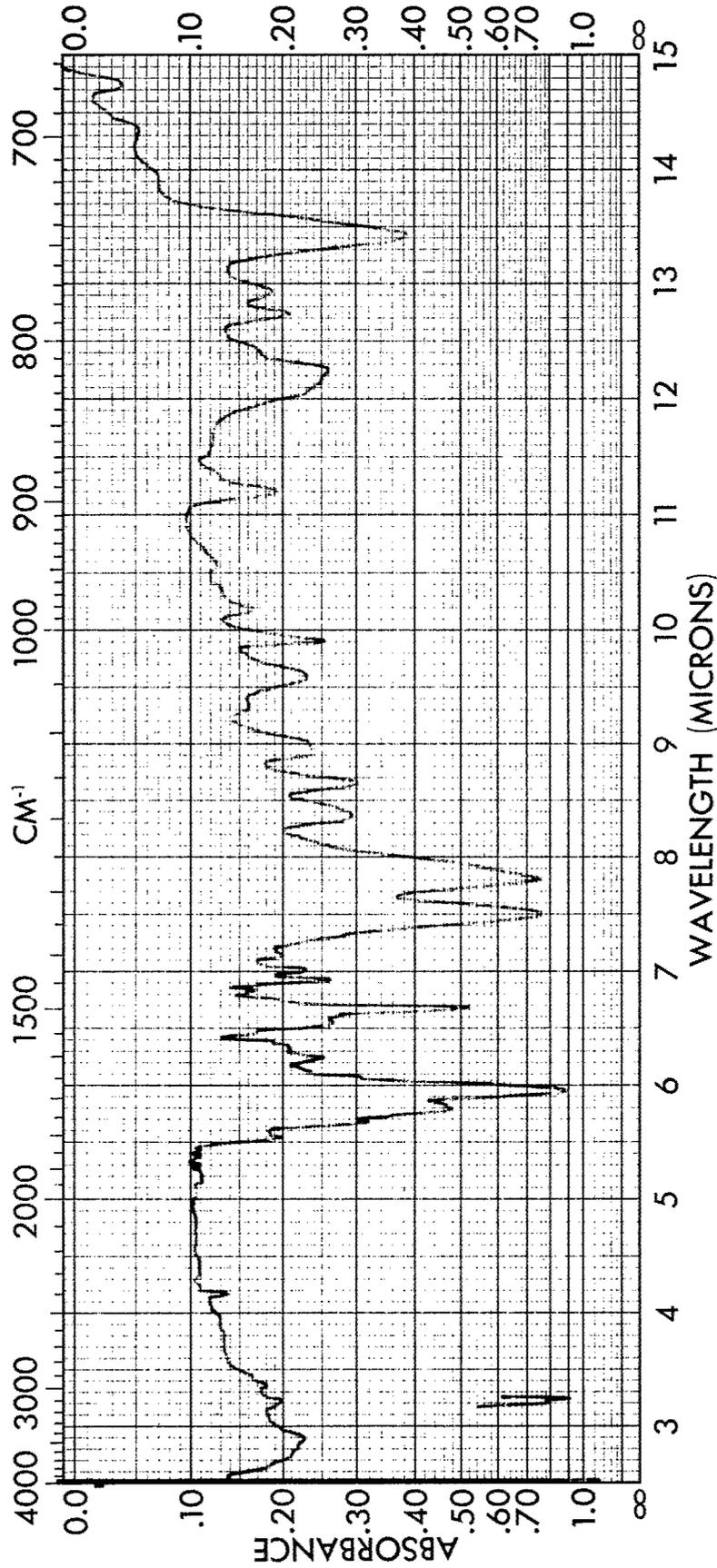


Figure 9. Infrared Spectrum of PI-7 (B-1)

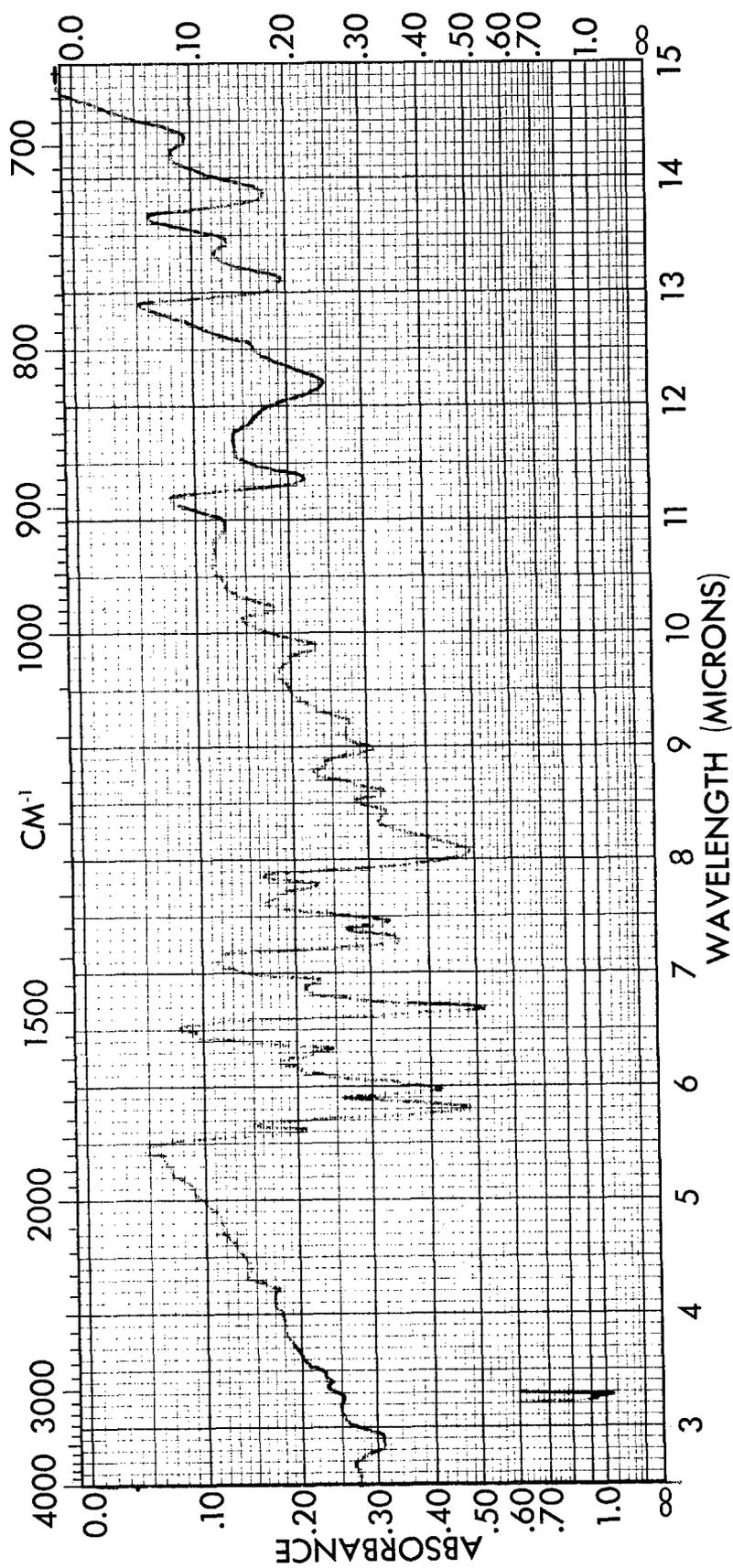


Figure 10. Infrared Spectrum of PI-5/6 (0-2)

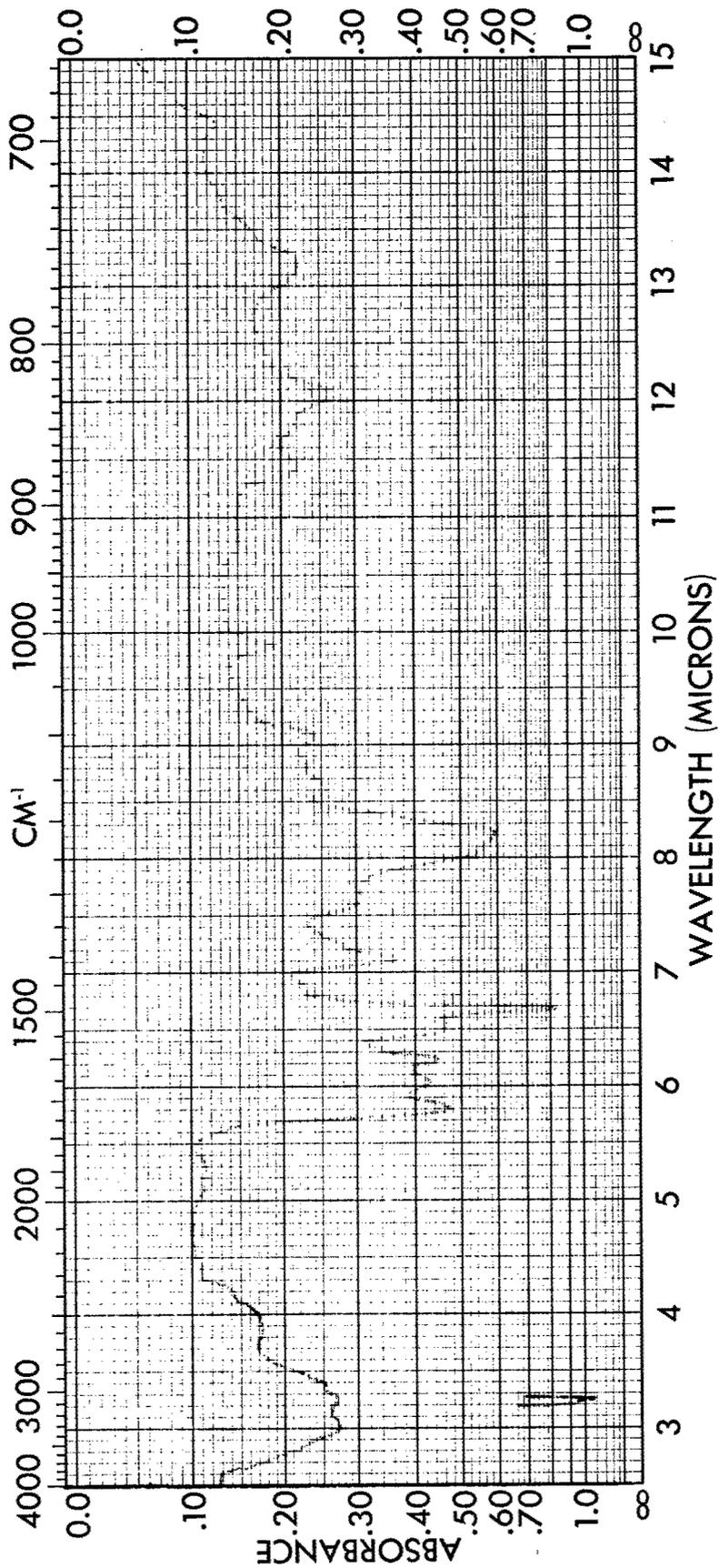


Figure 11. Infrared Spectrum of PI-5/7 (0-2) prepolymer

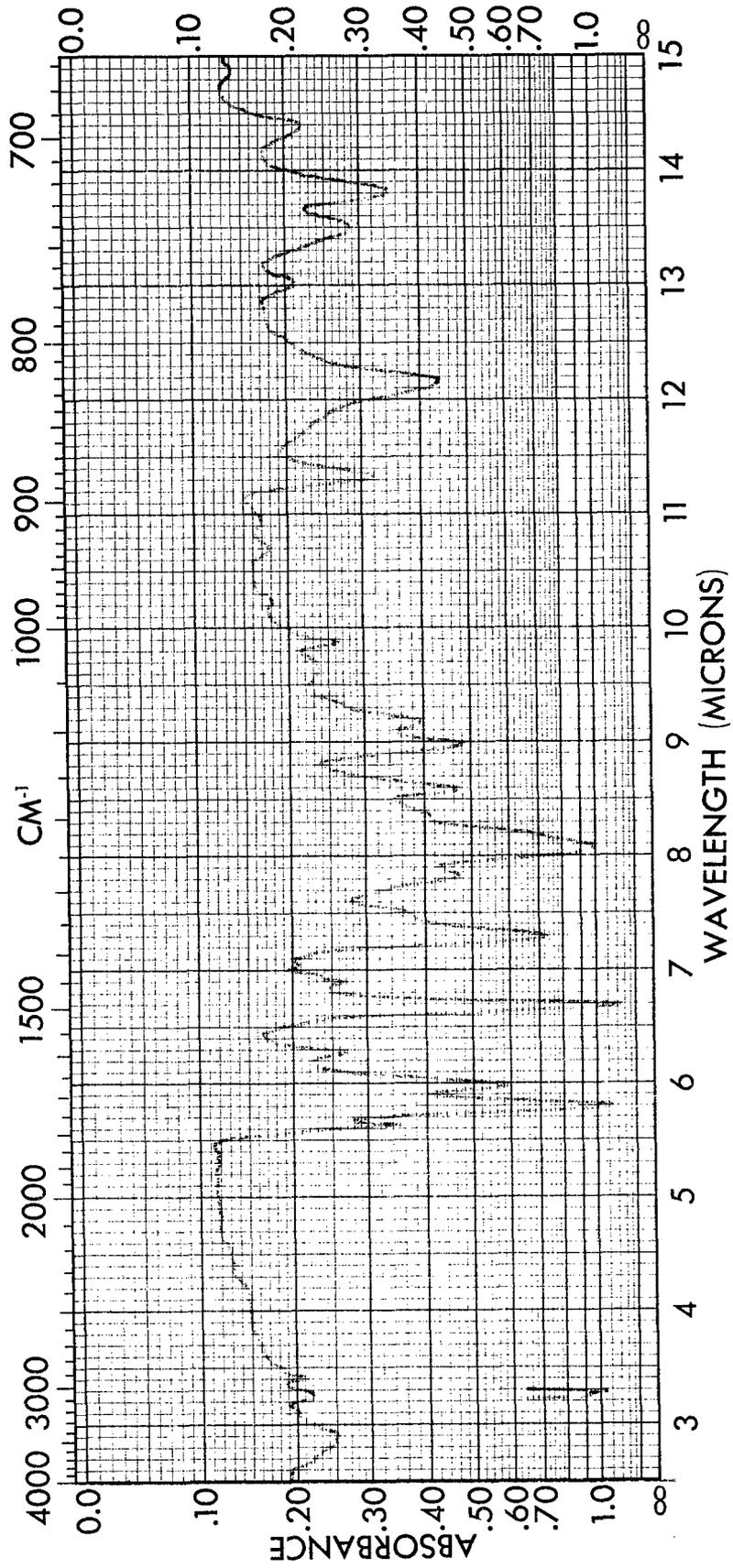


Figure 12. Infrared Spectrum of PI-5/7 (0-2)

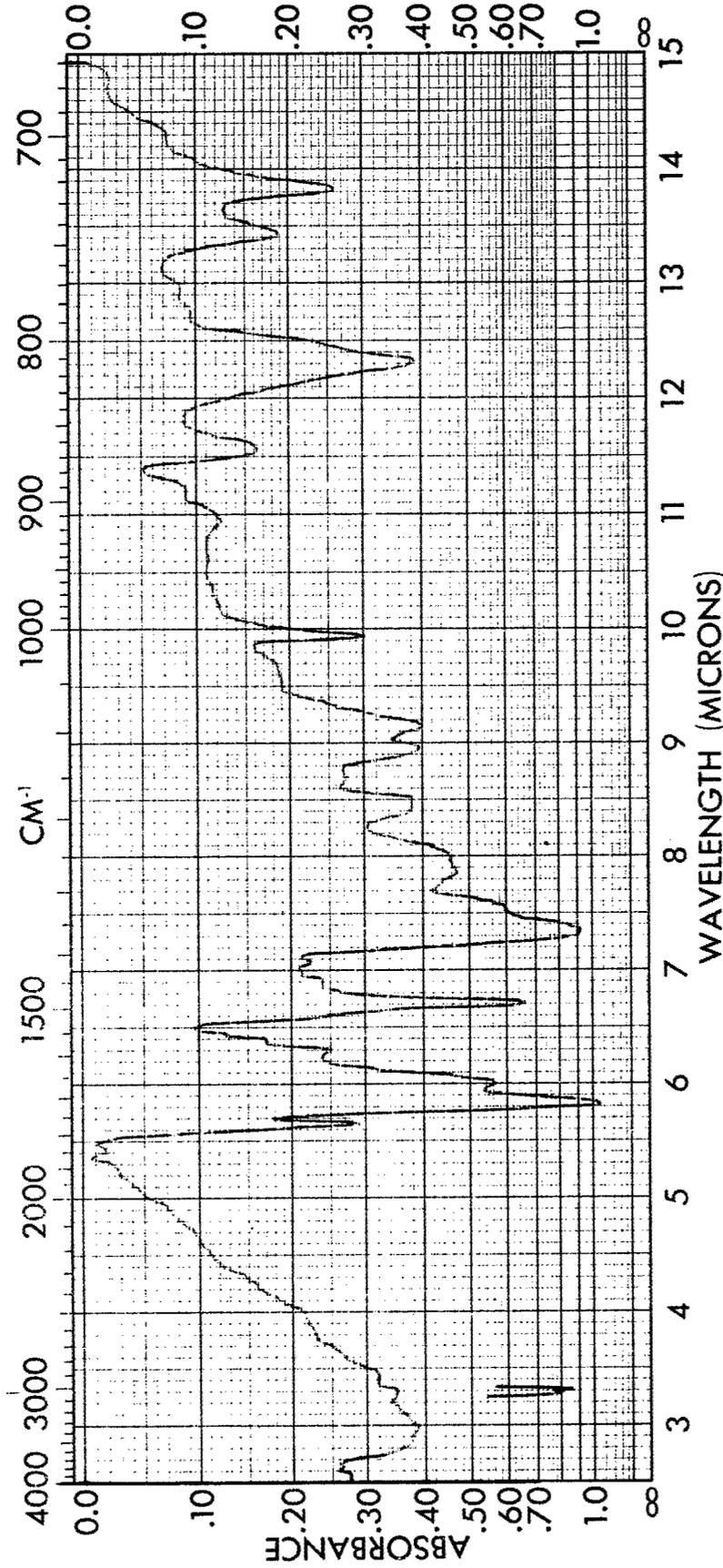


Figure 13. Infrared Spectrum of PI-5/7 (B-1)

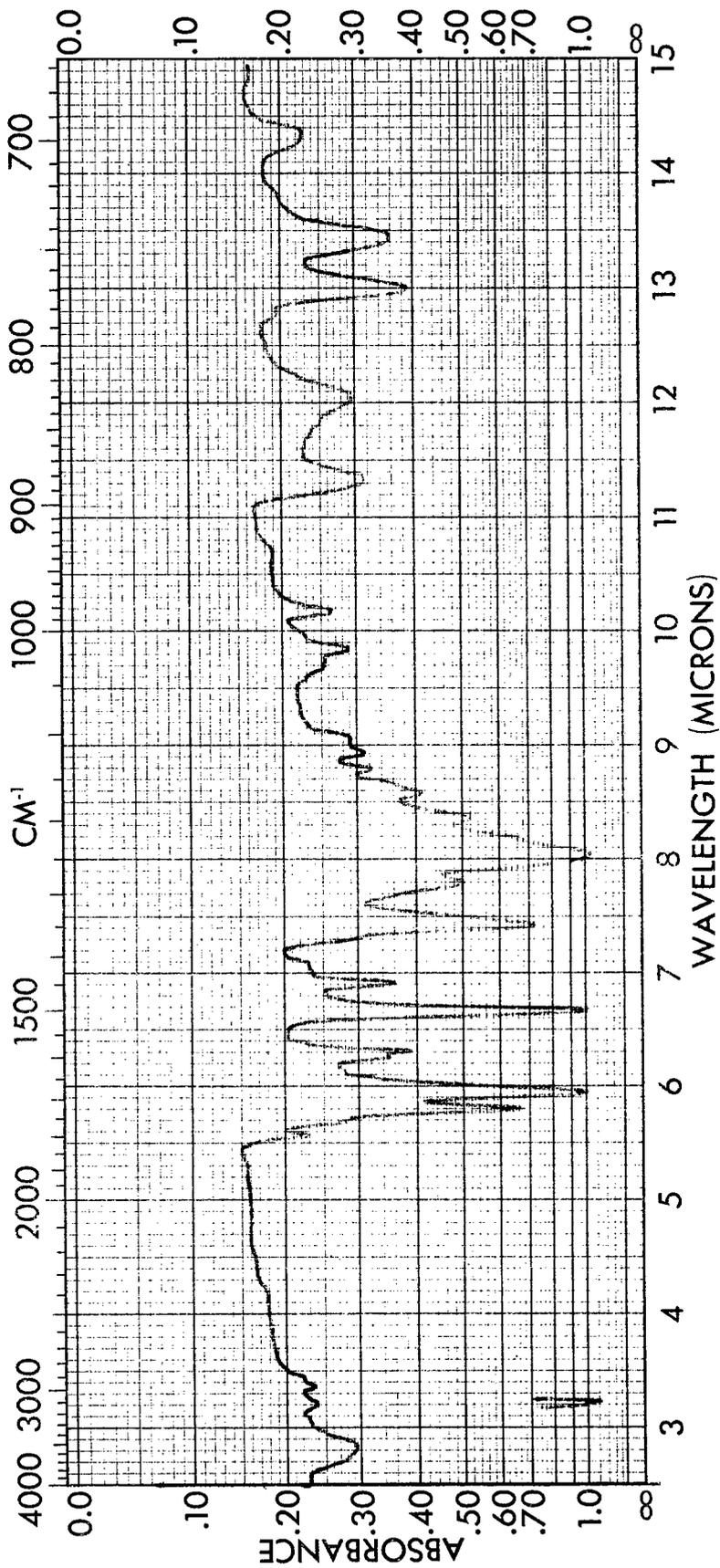


Figure 14. Infrared Spectrum of PI-6/7 (0-2)

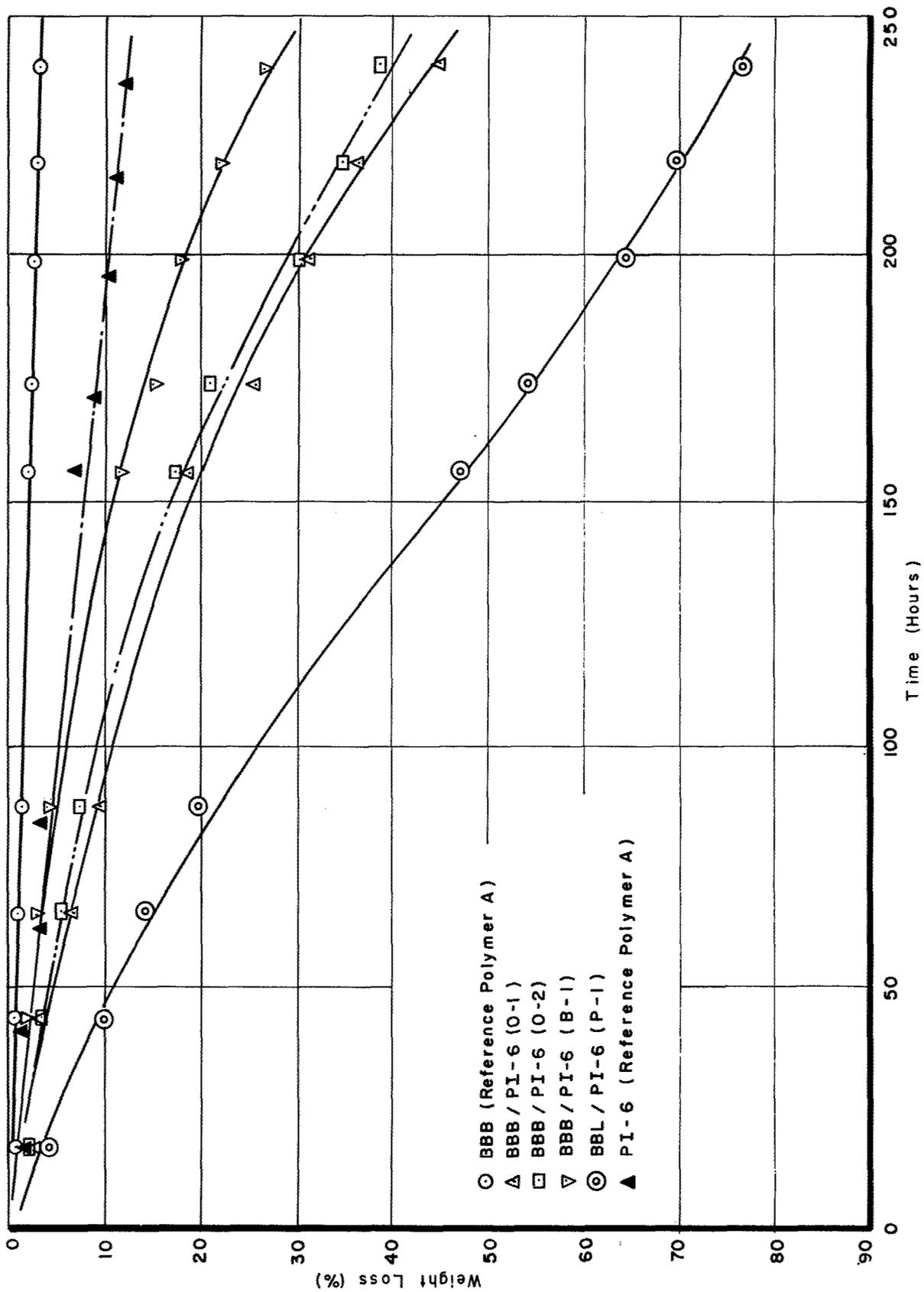


Figure 15. Isothermal Aging Curves for Various BB/PI Polymers at 700°F

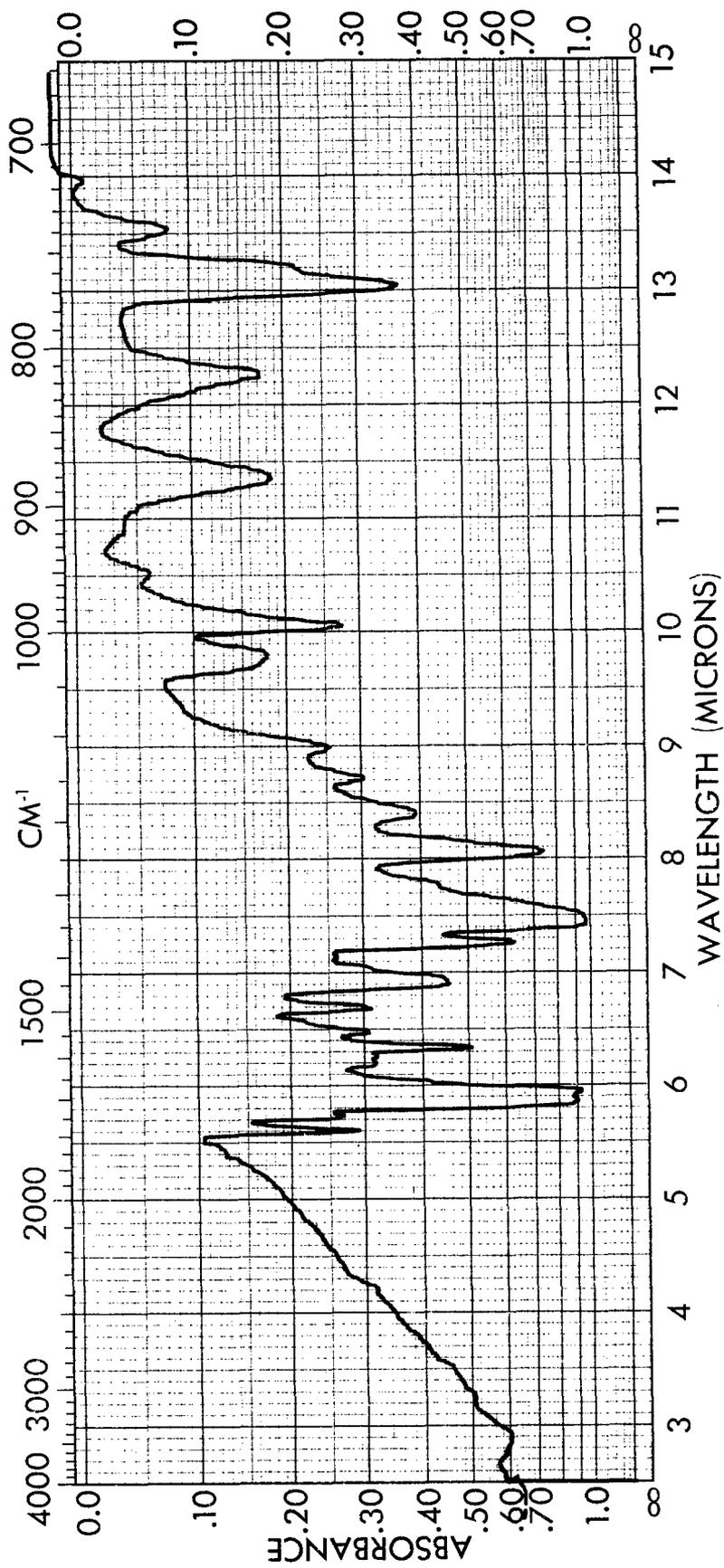


Figure 16. Infrared Spectrum of BBB/PI-6 (P-1)

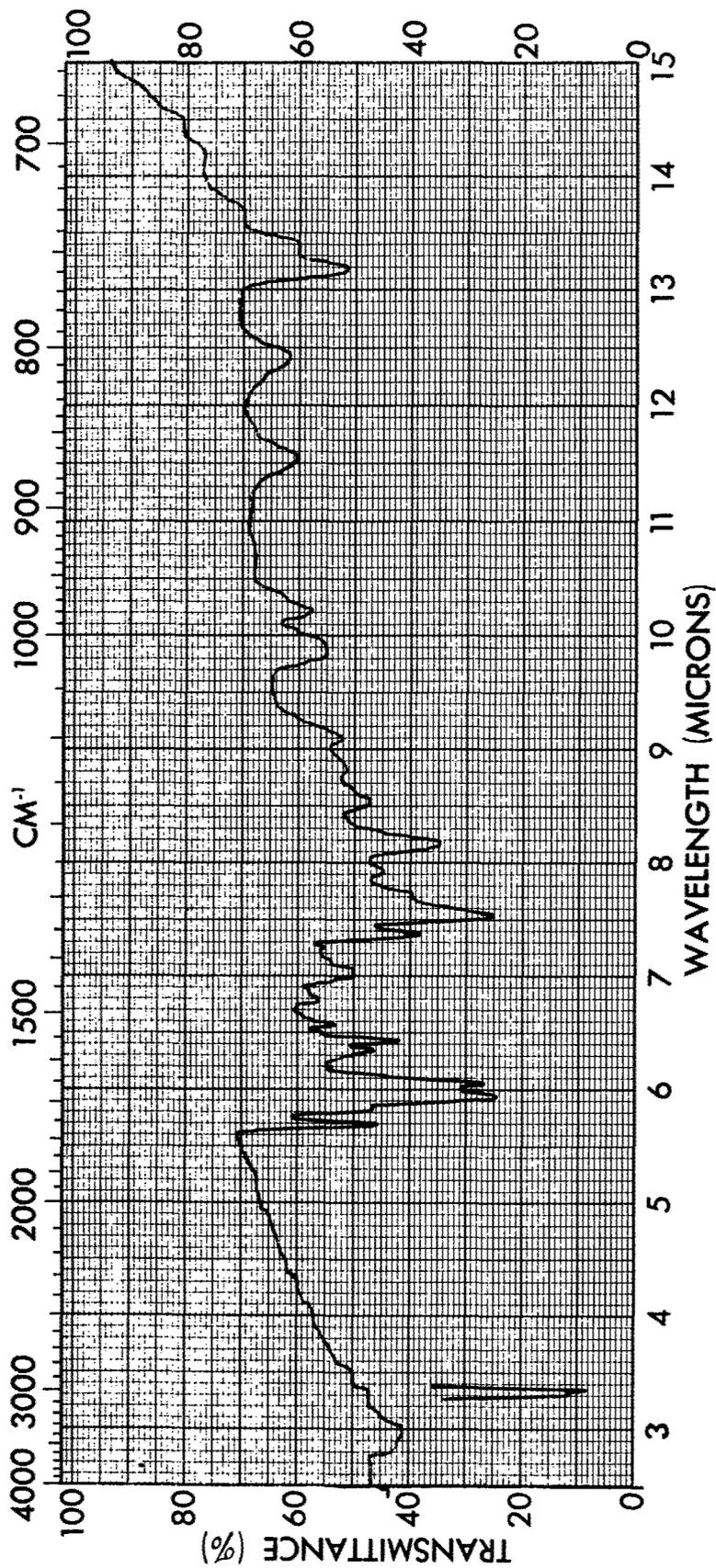


Figure 17. Infrared Spectrum of BBB/PI-6 (P-2)

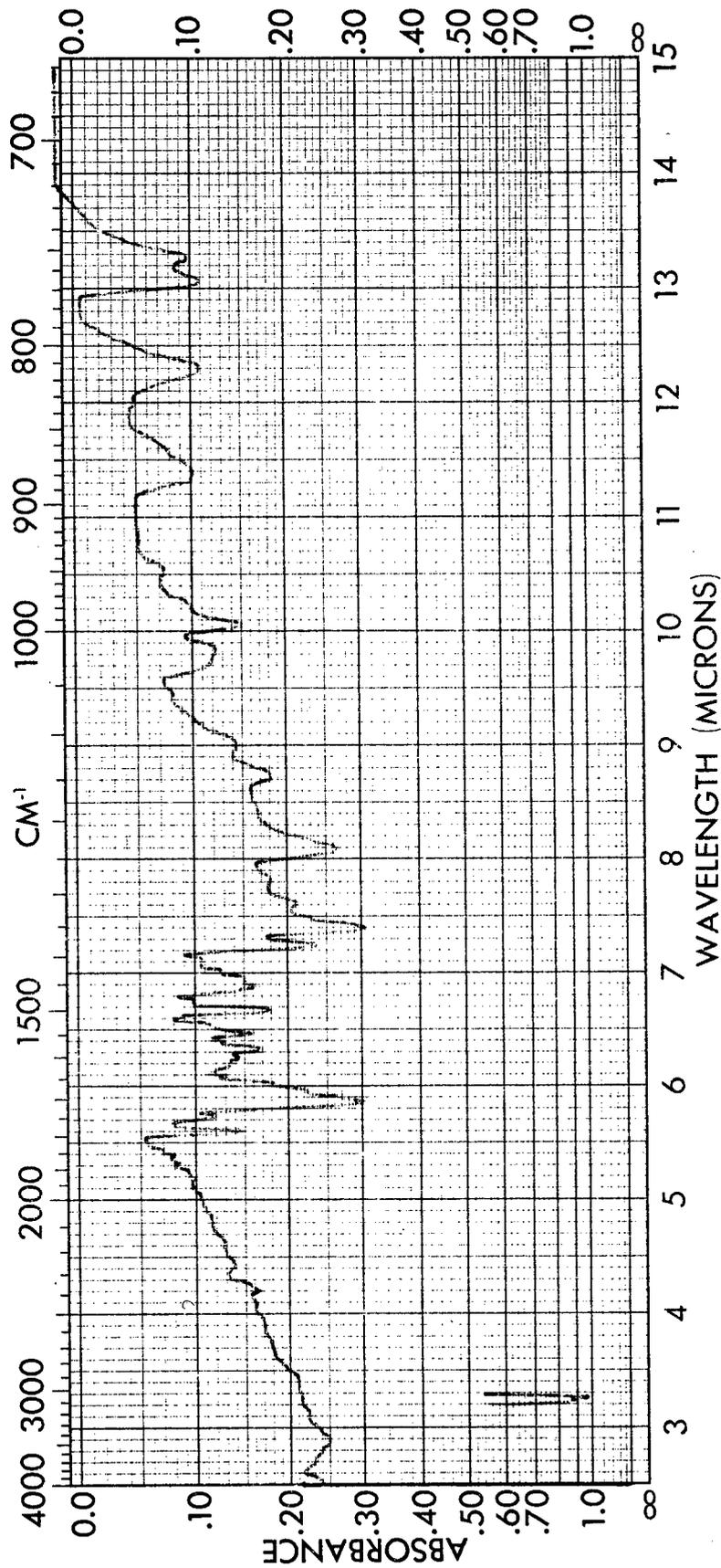


Figure 18. Infrared Spectrum of BBB/PI-6 (0-2)

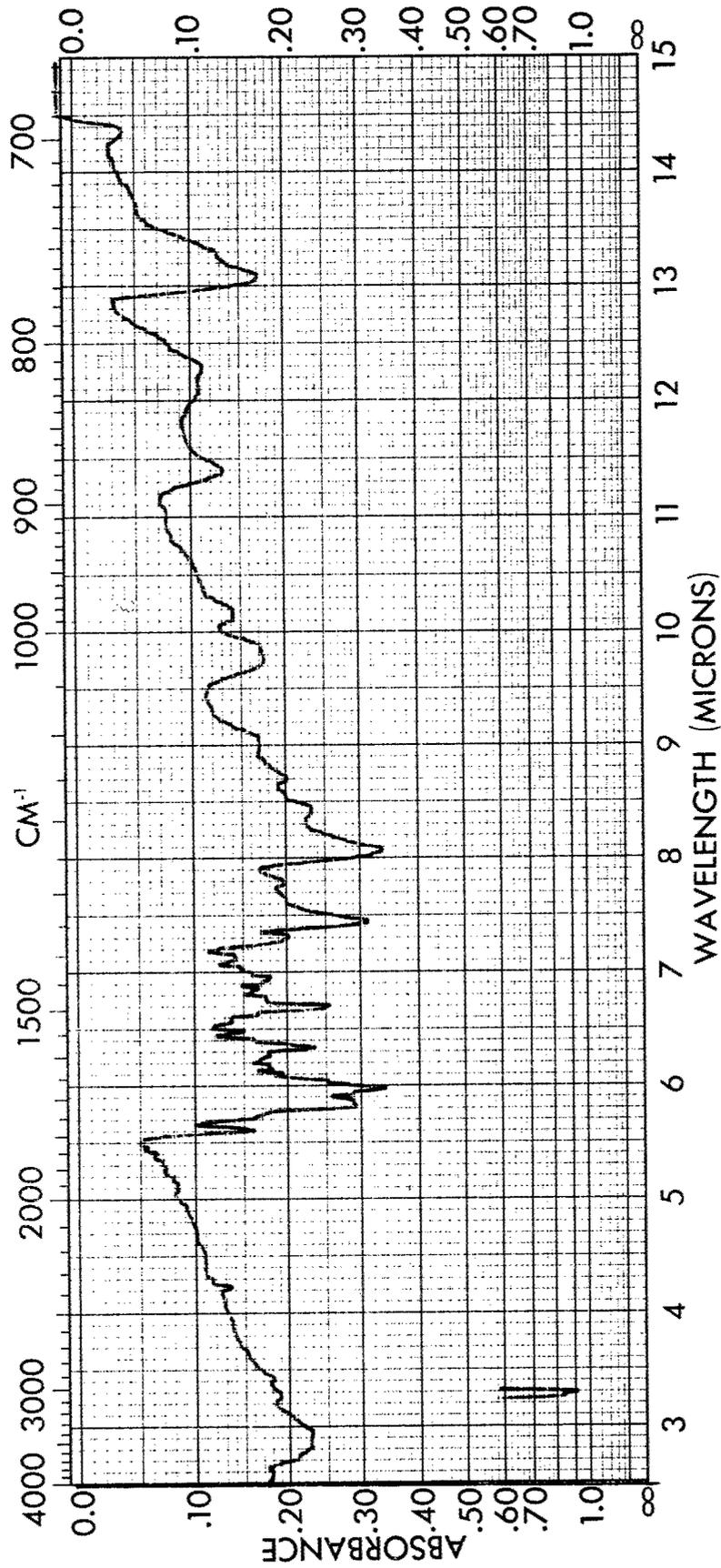


Figure 19. Infrared Spectrum of BBB/PI-6 (0-4)

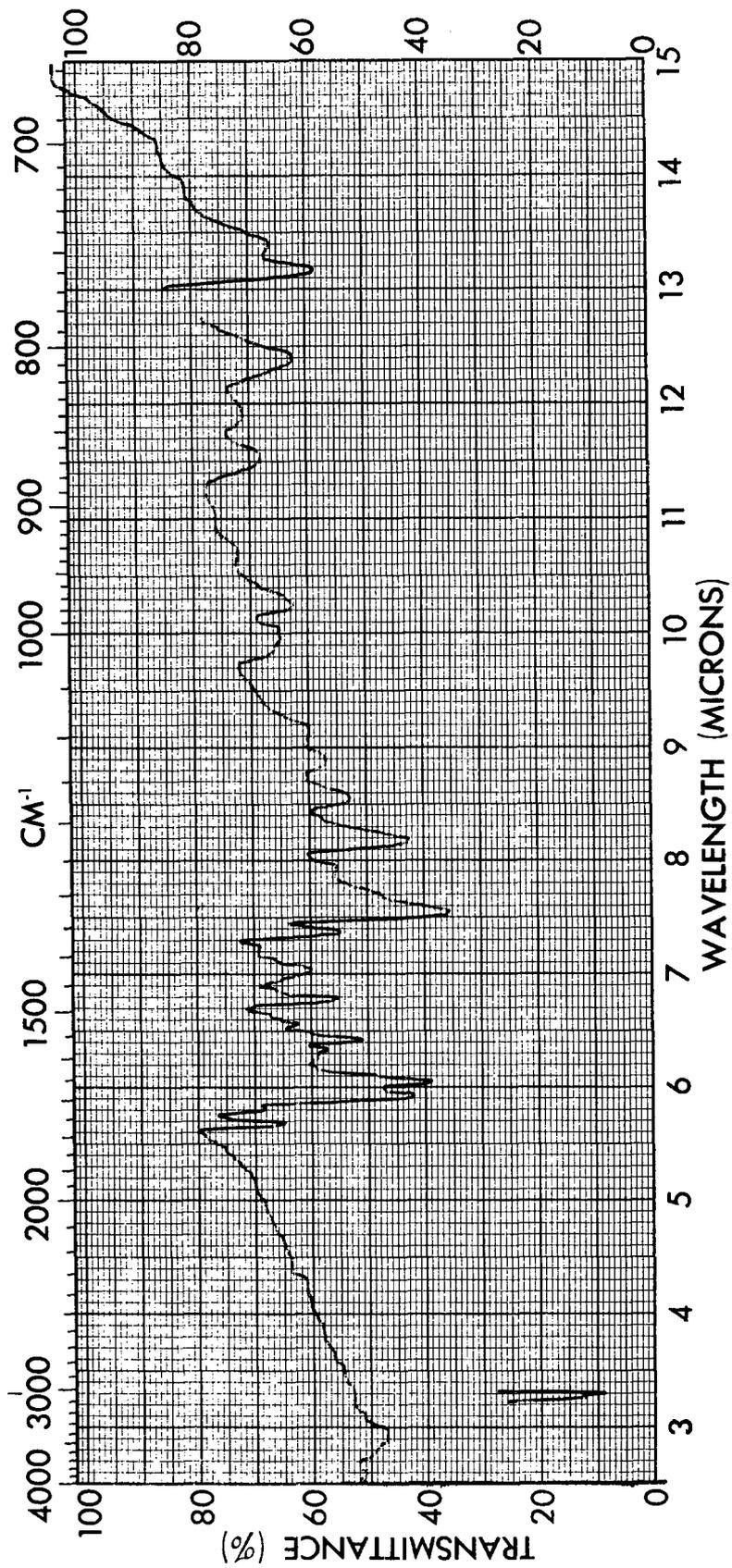


Figure 20. Infrared Spectrum of BBB/PI-6 (B-1)

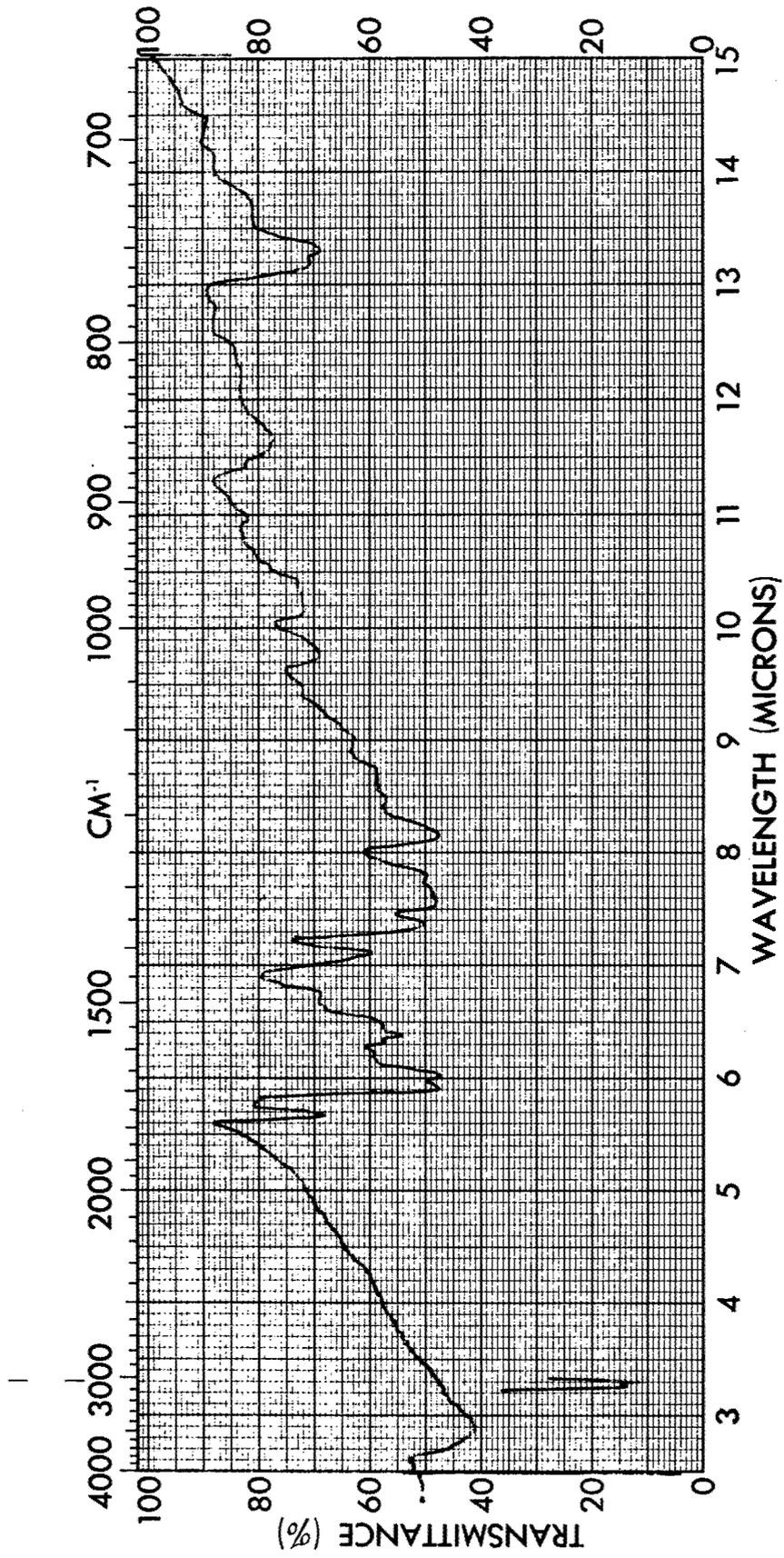


Figure 21. Infrared Spectrum of BBL/PI-6 (P-1)

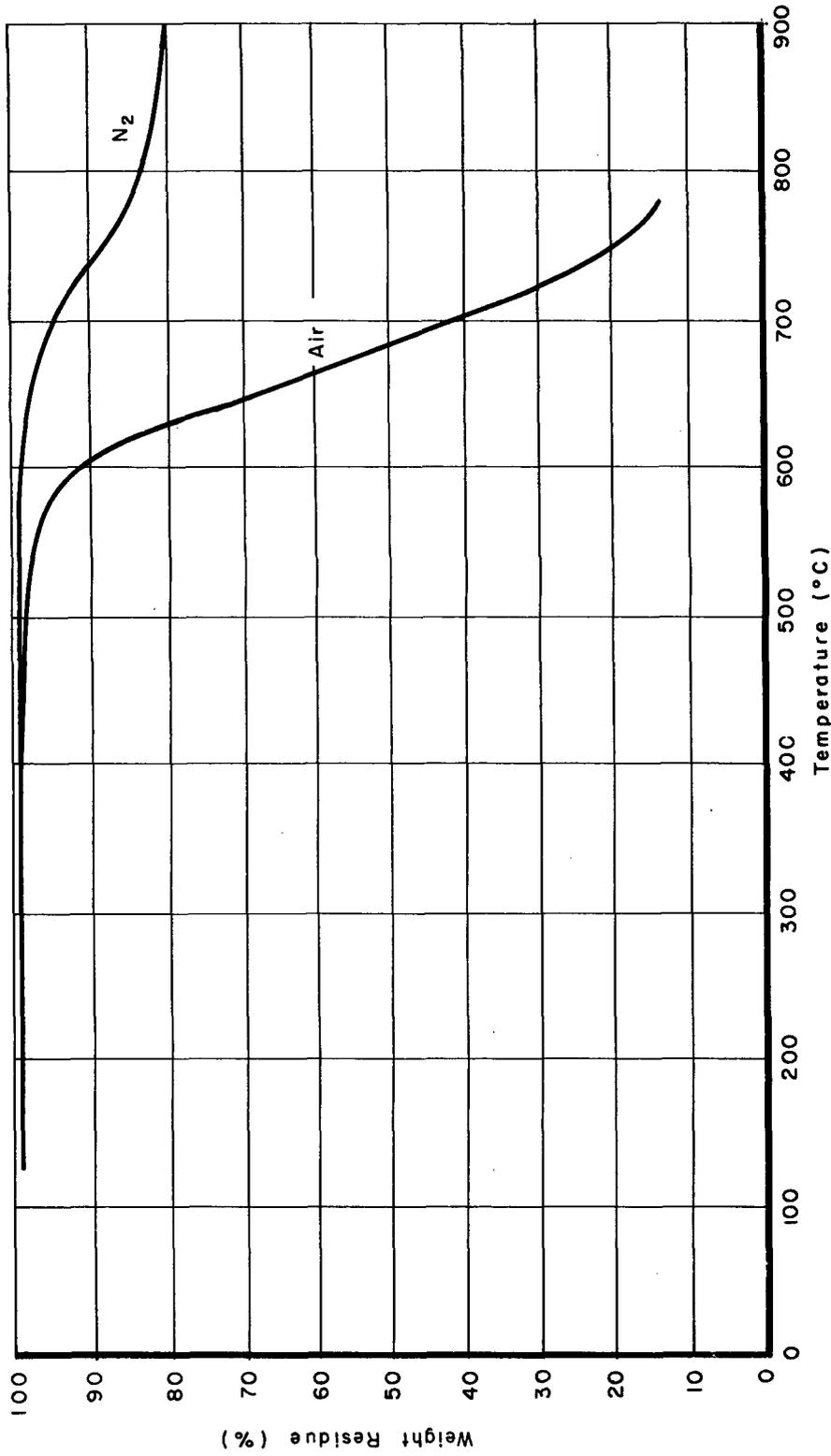


Figure 22. Thermogravimetric Analysis of BBB/BBL-65/35 Copolymer in Inert and Thermooxidative Environment ( $\Delta T = 30^{\circ}\text{C}/\text{min.}$ )

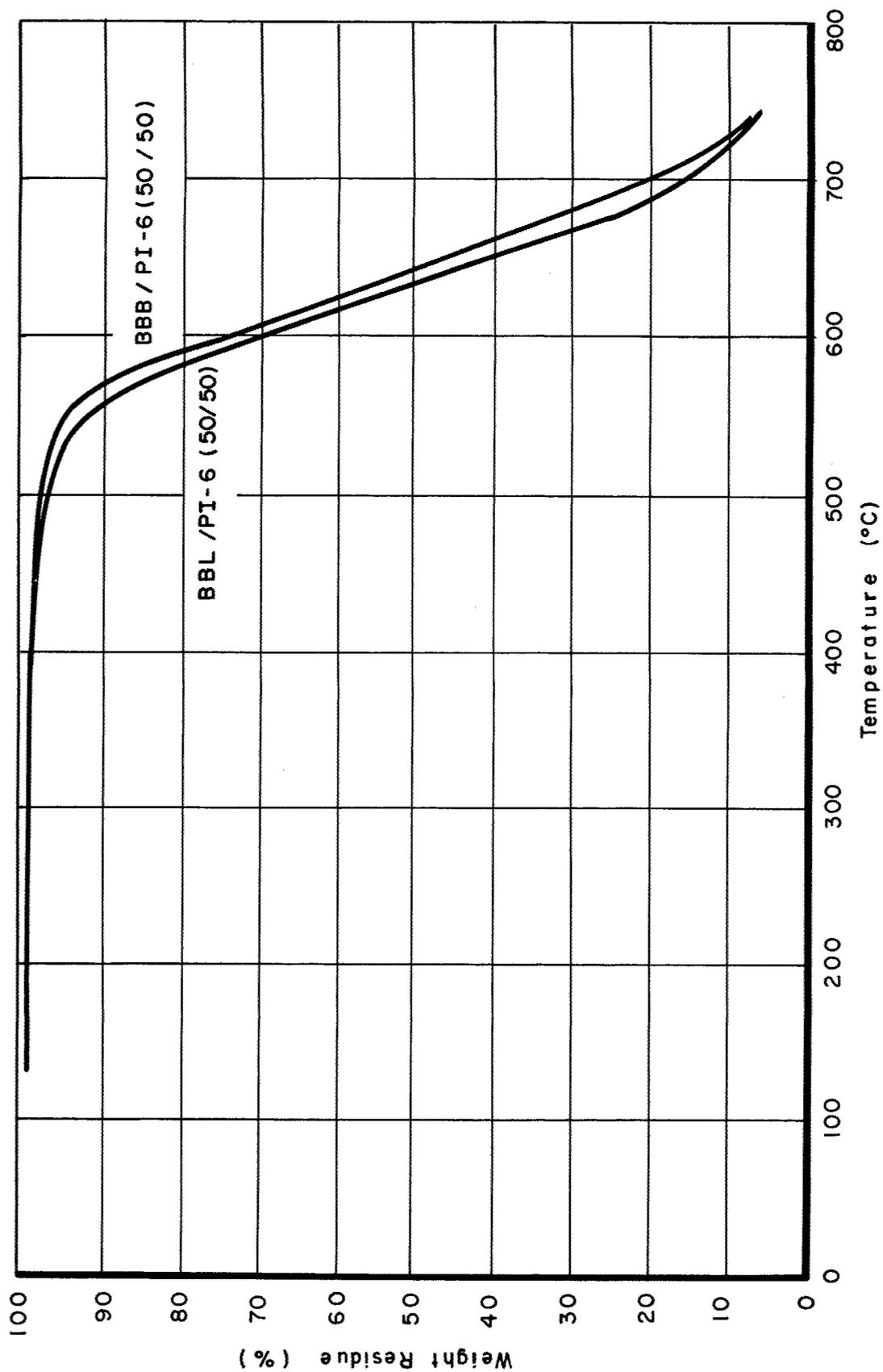


Figure 23. Thermogravimetric Analysis of BBB/PI-6 Copolymers.  
 ( $\Delta T = 3^{\circ}C/min.$  in. Air)

UNCLASSIFIED

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		Air Force Materials Laboratory Wright-Patterson Air Force Base, Ohio 45433	
13. ABSTRACT			
<p>A high molecular weight benzimidazobenzophenanthroline (BB) polymer containing both the "Bis-BB" (BBB) and the "BB-Ladder" (BBL) polymer structures has been prepared. This BBB/BBL polymer was synthesized from 1,4,5,8-naphthalene tetracarboxylic acid (NTCA) and a stoichiometric mixture of 3,3'-diaminobenzidine (DAB) and 1,2,4,5-tetraaminobenzene tetrahydrochloride (TAB.4HCl) by polycondensation in polyphosphoric acid. The polymer was black and amorphous with an intrinsic viscosity of 2.80 dl/gm at 30°C in sulfuric acid and 3.25 dl/gm at 30°C in methane sulfonic acid, and found to be stable to 500°C in air and 600°C in nitrogen by thermogravimetric analyses. Films of this polymer were prepared using both casting and precipitation techniques. This polymer also appeared to have fiber-forming properties.</p> <p>Using a conventional synthetic route for polyimide formation a series of polyimides containing five, six and seven-membered rings were prepared. Then a series of polymers containing a mixture of five- and six-, five- and seven-, and six- and seven-membered imide rings were prepared by reacting aromatic diamines with stoichiometric amounts of pyromellitic dianhydride (PMDA) and/or 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) and/or 2,2',6,6'-biphenyl-tetracarboxylic dianhydride (BPTCDA) in N,N'-dimethylacetamide to give film-forming polyamic acids. These were subsequently converted to aromatic polyimides which possessed thermal properties approaching conventional polyimides.</p> <p>Another series of polymers containing both the "BB" structure and the imide structure were prepared by the condensation of NTCA with stoichiometric amounts of DAB (or TAB.4HCl)</p>			

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and either 4,4'-diaminobiphenylether (oxydianiline), m-phenylene diamine or 4,4'-diaminobiphenyl. These polycondensations were carried out 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 viscosities ranging from 0.08 to 0.29 dl/gm at 30°C in sulfuric acid, and to exhibit stability in air to over 500°C by thermal gravimetric analyses. Isothermal aging studies were performed and the polymers with mixed structures were found to be less resistant to a thermooxidative environment than the most stable parent homopolymers.