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APPROACHES TO LADDER STRUCTURES

VI. CONDENSATION POLYMERIZATION OF SOME DIFUNCTIONAL DERIVATIVES RELATED TO [4H], 3, 1-BENZOXAZINE-4-ONE WITH CERTAIN AROMATIC DIAMINO DICARBOXYLIC ACIDS, ESTERS OR AROMATIC TETRAAMINES

GERARD A. LOUGHRAN

TECHNICAL REPORT AFML-TR-70-233

FEBRUARY 1971

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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 Mr. G. A. Loughran as Project Scientist.

This report covers work conducted from March 1967 to August 1969. The manuscript was released by the author in March 1970 for publication as a technical report.

The author wishes to thank Dr. G. F. L. Ehlers, Polymer Branch (LNP), Air Force Materials Laboratory, for the TGA curves; Mr. Jerald L. Burkett, University of Dayton Research Institute for running the viscosity determinations and some of the infrared spectra, Mr. Lee Smithson of the Analytical Branch (LPA) for the mass spectral data; and the Analytical Branch (LPA), Air Force Materials Laboratory for the microanalyses.

This technical report has been reviewed and is approved.



RICHARD L. VAN DEUSEN
Acting Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

2,7-dimethyl-[4H,9H], 3,1,8,6-benzobisoxazine-4,9-dione, and 6,6'-bis-(2-methyl-[4H],3,1-benzoxazine-4-one) condense on heating at 300°C either in the melt or in solution in sulfolane or molten benzophenone to give insoluble highly condensed cross-linked polymers whose empirical formulae are the same as the starting materials from which they were prepared. High molecular weight or cross-linked materials were obtained when 2,7-bis-(tri-fluoromethyl)-[4H,9H], 3,1,8,6-benzobisoxazine-4,9-dione, and 6,6'-bis-(2-trifluoromethyl-[4H],3,1-benzoxazine-4-one) were similarly treated. The reaction appears to be accompanied by loss of hydrogen fluoride.

2-methyl-[4H],3,1-benzoxazine-4-one reacted with methyl anthranilate in refluxing xylene to give 2-methyl-3-(\bar{o} -carboxymethyl)-phenylquinazoline-4-one. Polyquinazolinones in the medium molecular weight range, with viscosities in the 0.25 region were obtained when 2,7-dimethyl-[4H,9H], 3,1,8,6-benzobisoxazine-4,9-dione was reacted with either 2,5-diamino-terephthalic acid or its diethyl ester in sulfolane or diphenylether up to 300°.

2,7-dimethyl-[4H,9H], 3,1,8,6-benzobisoxazine-4,9-dione and 3,3'-diaminobenzidine were reacted in dimethylformamide, diethyl cellosolve, and trimethylene glycol dimethyl ether at temperatures from 120° to 310°C to give a soluble low molecular weight linear polyamide expected to use as a prepolymer for subsequent conversion to the corresponding quinazoline and benzimidazo-[1,2c]-quinazoline polymers.



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SECTION I
INTRODUCTION

The polycondensation reactions involving equimolar quantities of a difunctional 2-methyl substituted benzoxazinone and an aromatic diamine are well known (Reference 5). The monomers were either melted together and heated at 180° in an inert atmosphere, or heated in solutions of solvents such as dimethylformamide, dimethyl sulfoxide, or m-cresol at reflux temperatures (152 - 200°C). The resulting products were poly-2-methyl substituted quinoxalones, with inherent viscosities (η_{inh}) up to 1.01 in m-cresol. The polymers appear to exhibit good thermal stability characteristics. Under TGA conditions the onset of decomposition occurred between 400 and 500°C (under nitrogen) with about 75% weight residue remaining at 600°C. These polymers, however, do not appear to be as stable as certain fully aromatic polybenzoxazinones, VII, (References 6, 9 and 10) or polyquinazolinediones, XI, (References 7 and 8) which begin to break down between 500 and 650°C. This is probably due to the presence of an alkyl group attached to the carbon atom in position 2 of the oxazine ring (Figure 1). One might expect that substitution of a CF_3 or phenyl group at this position would result in enhanced thermal stability. This appears to be illustrated by a comparison of the TGA curves (under nitrogen) of the polybenzoxazinone VII (Reference 9), the poly-2-methyl substituted quinoxalene, V (Reference 5) and the polyquinazoline-2,4-dione XI (Reference 10). The curves are illustrated in Figure 1.

One might expect that a more highly condensed polymer system XIII such as one related to benzimidazo-[1,2c]-quinazoline, XXII, would possess a higher degree of thermal stability than the polymers described above, and should at least be as stable as the poly-(imidazopyrrolones), XII, (Reference 11) or the poly-bisbenzimidazobenzophenanthroline-diones, XIV (Reference 12). A comparison of their structures is shown in Figure 2.

6-substituted benzimidazo-[1,2c]-quinazolines XXII, have been previously synthesized by several methods, usually starting with 2-(o-aminophenyl)-benzimidazole, XVII, which is conveniently obtained by reaction of anthranilic acid, XVI, with o-phenylene diamine, XV, in polyphosphoric acid (Reference 13).

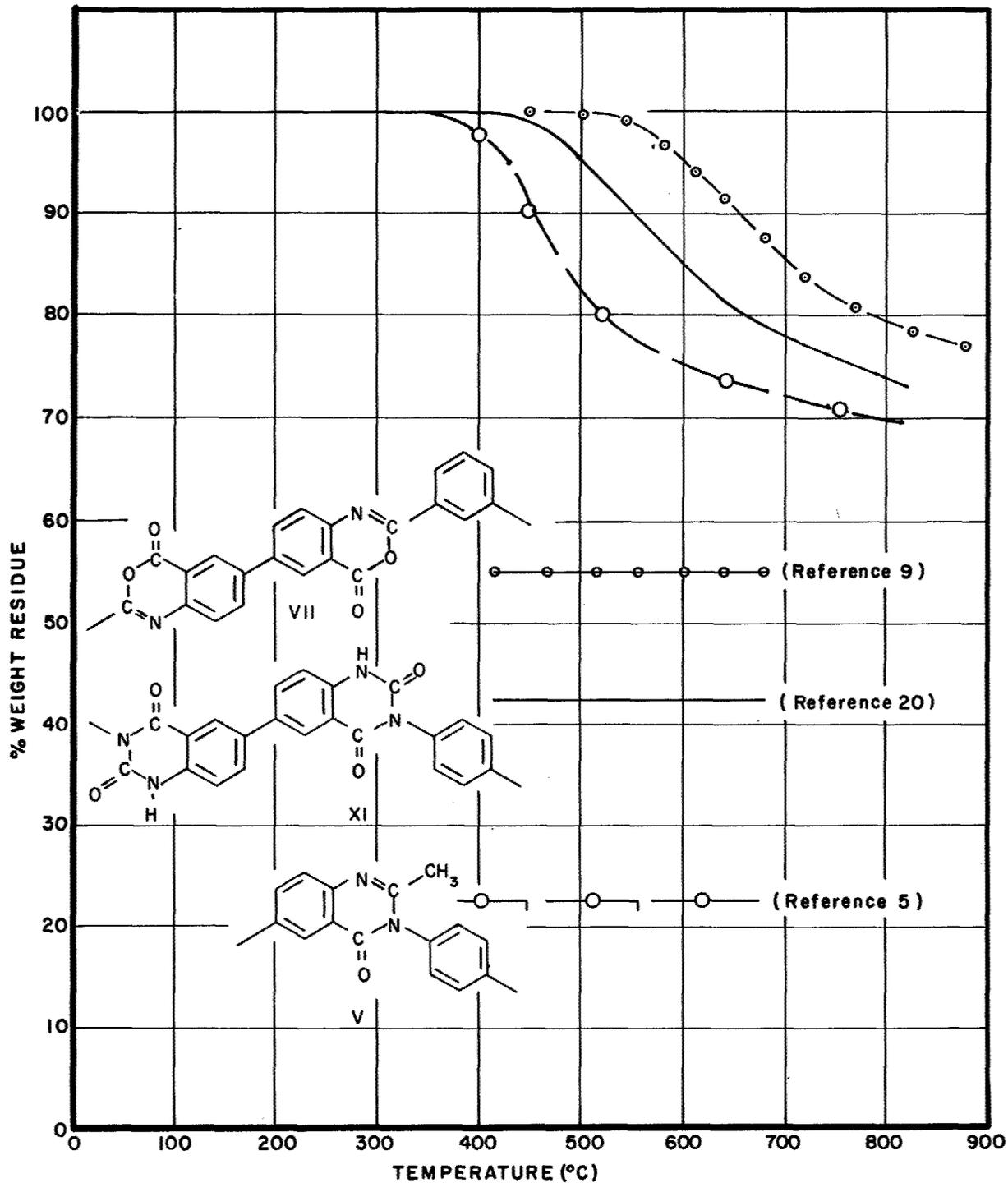


Figure 1. Comparison of TGA Curves from a Poly-(2-Methyl Substituted)-Quinazolinone, V; a Polybenzoxazinone, VII; and a Polyquinoxaline-2,4-Dione, XI

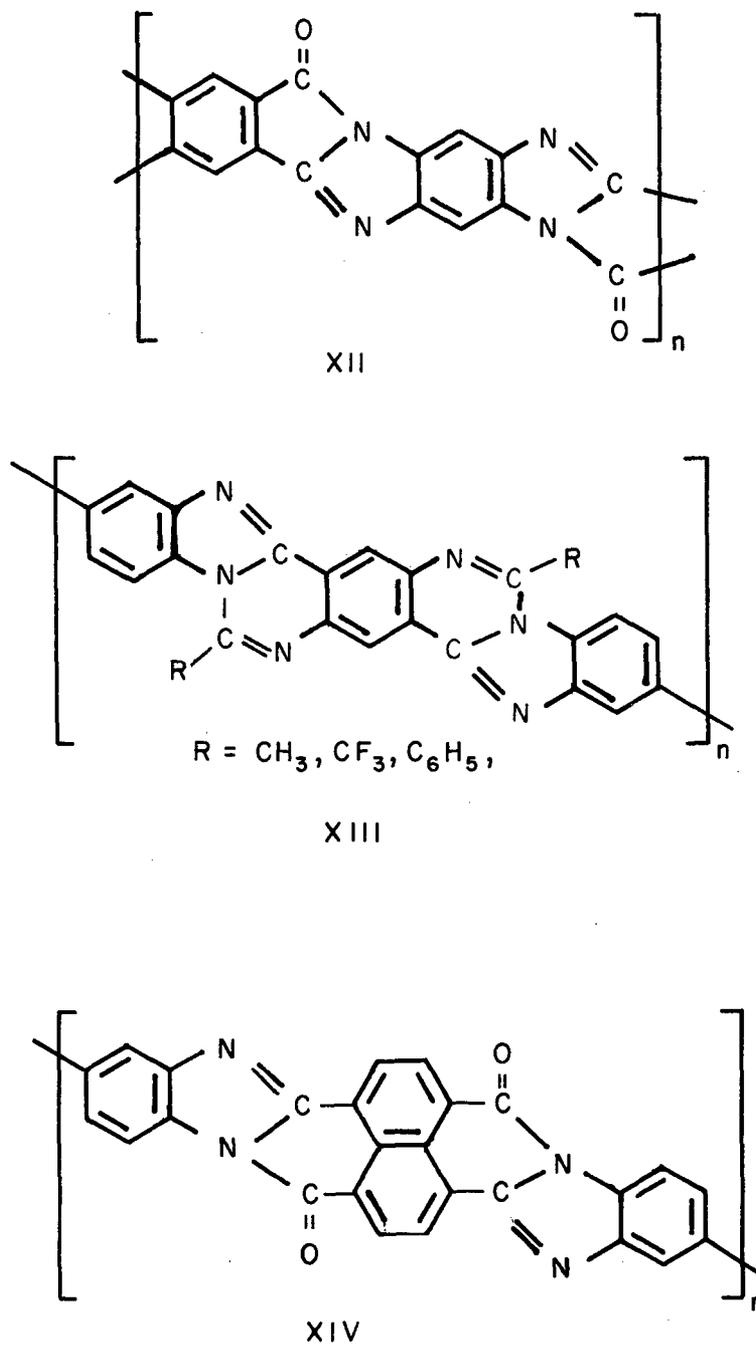


Figure 2. Comparison of Structures of a Polyimidazopyrrolone, XII, a Benzimidazo-[1,2c]-Quinazoline, XIII, and a Bisbenzimidazobenzophenanthrolinedione, XIV

2-(*o*-aminophenyl)-benzimidazole, XVII, is readily acylated with a suitably substituted benzoyl chloride, XVIII, in pyridine to give high yields of the acylated derivative, XX. This can be cyclized by heating at 280°C under reduced pressure to the corresponding benzimidazoquinazoline, XXII. Cyclization also can be effected in a P₂O₅-pyridine mixture, or with polyphosphoric acid (Reference 14). Another convenient preparation involves the reaction of 2-(*o*-aminophenyl)-benzimidazole, XVII, with a suitable ortho substituted aromatic aldehyde, XIX. The resulting azomethine, XXI, then was readily oxidized with a boiling solution of potassium permanganate in acetone to the benzimidazoquinazoline, VII, (Reference 14). This is analogous to the preparation of 2-arylquinazolines by oxidation of certain *o*-(benzylideneamino)-benzamides (Reference 15). The reactions involving the preparation of model 6-substituted benzimidazo-[1, 2c]-quinazolines, XXII are illustrated in Figure 3.

Recently, a benzimidazoquinazoline polymer system, AFR-500, XXVI, was developed by Levine and his coworkers (Reference 16) for use as a laminating resin and as an adhesive. The system involves the initial preparation of a suitable monomer, such as 2,2'-bis-(*o*-aminophenyl)-5,5'-bibenzimidazole, XXIV, or 2,2'-bis(*o*-aminophenyl)-5,5'-oxybibenzimidazole, XXIVb, by reaction of the corresponding tetraamine, XXXIII, with anthranilic acid, XXII, in polyphosphoric acid, or by a melt reaction between the tetraamine, XXIII and phenyl anthranilate, XVIa. Subsequently, the purified bibenzimidazole derivative (XXIV) was heated in a melt reaction with an equimolar quantity of diphenyl isophthalate, XXV. The resulting polymer, XXVI, had very good thermal and oxidative stability. The reaction scheme for its preparation is illustrated in Figure 4.

It is the purpose of this work to briefly explore certain reactions leading to the formation of linear prepolymers of the polyamide type, XXVII, which are designed for subsequent conversion to the quinazolinone structure, XXVIII, and ultimately to a polymer of the fully condensed benzimidazo-[1, 2c]-quinazoline structure, XXIX. Particularly, this involves an initial study of the condensation polymerization of certain 2,7-disubstituted-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-diones; or of a suitable 7,7'-bis-(2-substituted-3,1-benzoxazine-4-one) with either a substituted aromatic diamine such as diethyl-2,5-diaminoterephthalate, XXX, or an aromatic tetraamine such as diaminobenzidine, XXIII.

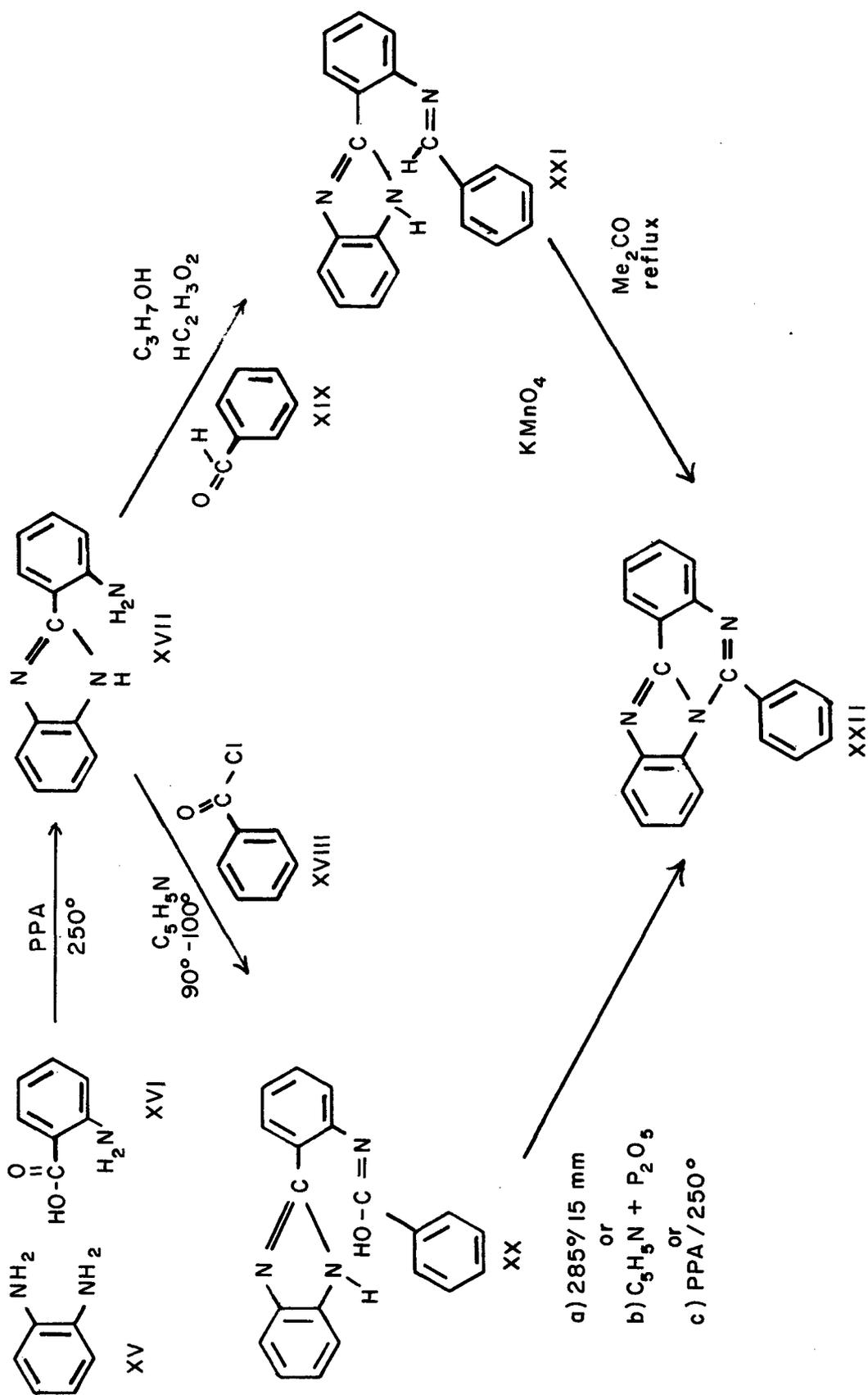


Figure 3. Preparation of Benzimidazo-[1,2c]-Quinazoline, XXII

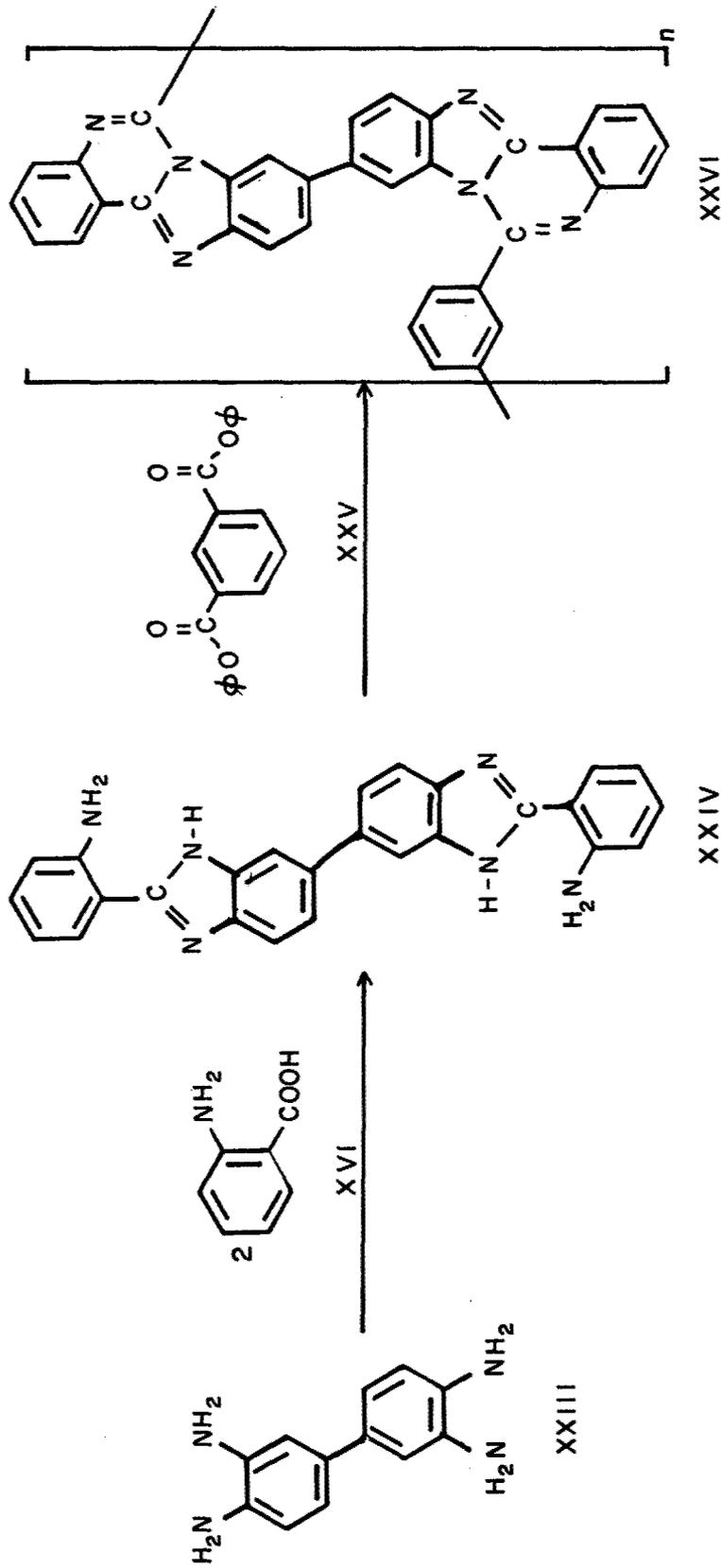


Figure 4. Preparation of Benzimidazo-[1, 2c]-Quinazoline Polymer System, AFR-500, XXVI

Because of their ease of preparation, 2-methyl and 2-trifluoromethyl-substituted benzoxazinone derivatives were initially employed. Later phenyl substituted derivatives will be used since the polymers therefrom can be expected to have a higher degree of thermal stability than their methyl substituted counterparts. A proposed reaction scheme is illustrated in Figure 5. The reactions were carried out in solution in organic solvents such as xylene, diethyl cellosolve, dimethylformamide, diphenylether, trimethylene glycol dimethylether, or sulfolane at temperatures varying from 120°C up to 300°C. The reactions are illustrated in Figures 5 and 10.

Since it has been previously shown that compounds such as [2H], 3, 1-benzoxazine-2, 4, [1H]-dione, XXXI, [2H, 7H], 3, 1, 8, 6-benzobisoxazine-2, 4, 7, 9-[1H, 6H]-tetraone, XXXII, and 6, 6'-bis-([2H], 3, 1-benzoxazine-2, 4, [1H]-dione), XXXVI, undergo thermal disproportionation at 250 - 360°C followed by condensation to highly dense cross-linked products (Reference 4), it might be expected that the benzoxazinones used here might behave similarly. Such a "side reaction" of course might be detrimental to the desired polymerization reaction. Therefore, the behavior of 2-methyl-[4H], 3, 1-benzoxazine-4-one, XXXIV; 2, 7-dimethyl-[4H, 9H], 3, 1, 8, 6-benzobisoxazine-4, 9-dione, I; 2, 7-bis-(trifluoromethyl)-[4H, 9H]-3, 1, 8, 6-benzobisoxazine-4, 9-dione, XXXVI; 6, 6'-bis-(2-methyl-[4H], 3, 1-benzoxazine-4-one), XXXVII; and 6, 6'-bis-(2-trifluoromethyl-[4H], 3, 1-benzoxazine-4-one), XXXVIII were also studied as melt reactions or in solution in solvents such as sulfolane or molten benzophenone at temperatures up to 300 - 325°C. The planned thermal decomposition of [4H], 3, 1-benzoxazine-4-one, XXXV, was not carried out.

SECTION II

DISCUSSION OF RESULTS

1. PREPARATION OF MODEL COMPOUNDS AND MONOMERS

2-methyl-[4H], 3,1-benzoxazine-4-one, XXXIV, was prepared in 75% yield by reaction of anthranilic acid, XVI, in excess acetic anhydride at 120°C (Reference 1). A small amount of N-acetylanthranilic acid, XXXIX, was obtained in the reaction as a by-product. Their infrared spectra are shown in Figures 12 and 13.

Since N-formylanthranilic acid, XL, is readily prepared by heating anthranilic acid, XVI, with formic acid (Reference 2), the reaction of 2,5-diaminoterephthalic acid, XLI, with formic acid was tried. The reaction was carried out at 101°C with a large excess of formic acid and a good yield of the desired product, 2,5-(N,N'-diformylamino)-terephthalic acid, XLII, was obtained. The compound appears to darken near 300°C and decompose and/or sublime without melting. Its softening point curve (Figure 14) reveals a dip near 300°C followed by a leveling off of the curve between 300 and 400°C. This could mean that melting and polymerization may be occurring in this region. The sharp drop in the curve near 450°C probably indicates decomposition. Its infrared spectrum (Figure 15) shows typical absorption in the 2500 cm^{-1} to 3300 cm^{-1} due to -COOH groups.

2,5-diformylaminoterephthalic acid, XLII, was converted to [4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, XLIII, by heating in boiling dimethylformamide containing acetic anhydride. Its infrared spectrum is shown in Figure 16. Absorption attributed to the carbonyl group of the oxazine ring system is observed at 1754 cm^{-1} .

2,7-dimethyl-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, I, was obtained from 2,5-diaminoterephthalic acid, XLI, in refluxing acetic anhydride. The compound appears to darken and sublime or decompose without melting at 300°C. This is illustrated by a sharp dip in its softening point curve (Figure 17) at this temperature. Its infrared spectrum is shown in Figure 18. Typical absorption due to the carbonyl band of the oxazine ring system is observed at

1754 cm^{-1} . When the reaction was carried out in a mixture of acetic acid and acetic anhydride, some 2,5-[N,N'-diacetylamino]-terephthalic acid, XLIV, was obtained. Its infrared spectrum is shown in Figure 19. This compound also appears to darken and decompose and/or sublime near 300°C. A sharp dip appears in its softening point curve (Figure 20) at this temperature. It is interesting to note that early weight loss under TGA conditions occurs close to 300°C. Its TGA curve is shown in Figure 21.

2,5-dicarbethoxyaminoterephthalic acid, XLV, was prepared by reaction of ethyl chloroformate with the disodium salt of 2,5-diaminoterephthalic acid, XLI, at room temperature. Its softening point curve (Figure 22) appears to suggest that melting occurs near 200°C followed possibly by polymerization and/or decomposition between 300 and 400°C. A second dip in the curve near 450°C may indicate the onset of decomposition of any polymer which may have formed. The infrared spectrum of 2,5-dicarbethoxyaminoterephthalic acid, XLV, is shown in Figure 23.

An attempt was made to prepare 2,7-diethoxy-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, XLVI, by running the reaction in refluxing tetrahydrofuran, using triethylamine as acid acceptor, and subsequently distilling off the solvent and finishing off the reaction in boiling dioxane. The product, after removal of the solvent, was a golden viscous oil which became a brittle brown resin after heating in a vacuum oven at 60°C/0.02 mm. Apparently, a polymerization reaction had taken place, the course of which may be similar to that postulated (Figures 7 and 8) for the thermal polymerization of other benzoxazine diones described below.

2,7-bis-(trifluoromethyl)-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, XXXVI, was prepared from 2,5-diaminoterephthalic acid, XLI, by refluxing in excess trifluoroacetic anhydride. This new compound melted at 224 - 225°C. Its infrared spectrum is shown in Figure 24. Absorption attributable to the carbonyl group of the oxazine ring system appears at 1786 cm^{-1} . Usually this band appears in the 1724 to 1754 cm^{-1} range in the spectra of compounds substituted with alkyl groups in number two position of the oxazine ring (Reference 3). Except for fluorine, the analytical values for the other elements are quite good. A molecular weight determination by the VPO method in dioxane gave a

value of 348 which is quite satisfactory for a compound with a molecular formula $C_{12}H_2O_4N_2F_6$. The presence of the molecular ion peak in its mass spectrum at m/e 352 confirms its structure XXXVI.

4,4'-diformylaminodiphenyl-3,3'-dicarboxylic acid, XLVII, was obtained as expected by heating 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid, II, with formic acid. Its infrared spectrum is shown in Figure 25. Absorption attributable to amide I carbonyl absorption appears to be located near 1695 cm^{-1} , although absorption due to the carbonyl group of aryl acids also appears in this region.

4,4'-diformylaminodiphenyl-3,3'-dicarboxylic acid, XLVII, was converted to 6,6'-bis-($[4H]$), 3,1-benzoxazine-4-one), XLVIII, by boiling the compound in dioxane in the presence of excess thionyl chloride. Its infrared spectrum (Figure 26) reveals an absorption band at 1754 cm^{-1} probably due to the carbonyl group of the oxazine ring system.

6,6'-bis(-2-methyl- $[4H]$), 3,1-benzoxazine-4-one), XXXVII was prepared in the usual way by refluxing 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid, II, with excess acetic anhydride. The compound appears to melt and sublime or decompose at $316 - 318^\circ\text{C}$. Its softening point curve (Figure 27) exhibits a sharp dip at about 275°C which could mean melting and/or decomposition. Its TGA curve (Figure 28) shows what appears to be the onset of degradation at about 310°C . Some of this might be due either to elimination of a gaseous by-product or to sublimation. However, after about 20% weight loss, the curve begins to level out so that the weight loss at 500°C is only 25%. Even at 900°C the weight loss is only 38%. This behavior suggests that a polymerization process may be taking place. Its infrared spectrum (Figure 29) exhibits the usual band due to the carbonyl group of the oxazine ring system at 1754 cm^{-1} .

6,6'-bis (2-trifluoromethyl- $[4H]$), 3,1-benzoxazine-4-one, XXXVIII, was prepared by refluxing a mixture of 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid, II, and trifluoroacetic anhydride. Analytical data indicates that the compound, m. p. , $287 - 288^\circ\text{C}$ has a molecular formula, $C_{18}H_6O_4N_2F_6$, although the values for %F is lower than expected. A molecular weight determination by the VPO method in dioxane gave a value of 438 which is quite close to theory, and the

appearance of the molecular ion peak in its mass spectrum at m/e 428 confirms its structure. Its infrared spectrum (Figure 30) exhibits the band due to the carbonyl group of the oxazine ring system at 1786 cm^{-1} which is to be expected.

2. THERMAL CONDENSATION OF 2-METHYL-[4H], 3,1-BENZOXAZINE-4-ONE, XXXIV

It has been established previously (Reference 4) that the thermal decomposition of [2H], 3,1-benzoxazine, 2,4[1H]-dione, involves the loss of carbon dioxide and initial formation of cyclotrimeric and tetrameric arylamides, followed by dehydration to more highly condensed structures. This information was useful in the characterization of the structures of the polymers obtained by thermal decomposition of such difunctional derivatives as [2H, 7H], 3,1,8,6-benzobisoxazine-2,4,7,9, [1H, 6H]-tetraone and 6,6'-bis-([2H], 3,1-benzoxazine-2,4-[1H]-dione) (Reference 4).

Therefore, it was considered desirable to try and obtain some information on the course of reaction involving the thermal condensation, rearrangement or decomposition of 2-methyl-[4H], 3,1-benzoxazine-4-one, XXXIV, and if possible, to characterize and determine the structures of the reaction products.

The melt reaction of 2-methyl-[4H], 3,1-benzoxazine-4-one, XXXIV was studied first. The compound was heated at 300°C over nitrogen for about 66 hours. A yellow compound, amounting to about 40% of the weight of the starting material, sublimed on the cooler, upper walls of the apparatus. This product was soluble in benzene. It melted at $79 - 81^{\circ}\text{C}$. Results from vapor phase chromatography and from spotting techniques using thin layer chromatography, indicate that the compound probably contains small amounts of at least two possibly higher molecular weight components. The main component of the material, however, appears to have the molecular formula $\text{C}_{16}\text{H}_8\text{O}_2\text{N}_2$. This appears to be confirmed by what may be its molecular ion peak in its mass spectrum at m/e 260. No significant lines appear in the mass spectrum above this peak. Two possible structures, XLIX and L, having a molecular formula $\text{C}_{16}\text{H}_8\text{O}_2\text{N}_2$ at first appeared worthy of consideration. It was tentatively assumed that either structure (Figure 6) could have been produced by self-condensation of two moles of 2-methyl-[4H], 3,1-benzoxazine-4-one, $\text{C}_9\text{H}_7\text{O}_2\text{N}$,

XXXIV, with elimination of $C_2H_6O_2$ to give $C_{16}H_8O_2N_2$. The compound, L, dehydroindigo, was ruled out since its melting point is known to be in this 215 - 218°C range. However, a compound such as XLIX, can be expected to melt much higher than 81°C.

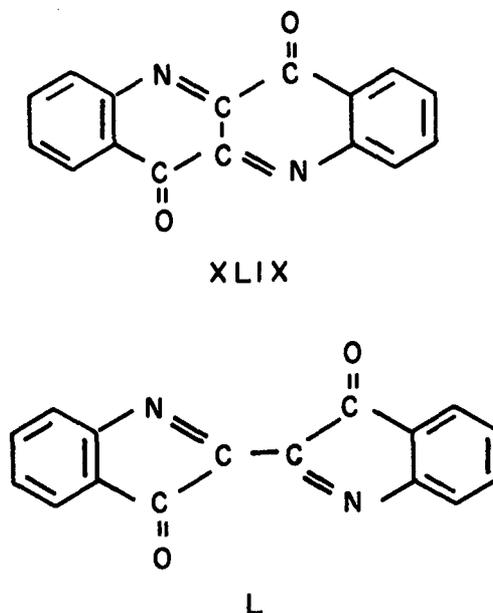


Figure 6. Possible Reaction Products from Thermal Condensation of 2-Methyl-[4H], 3, 1-Benzoxazine-4-One, XXXIV

The infrared spectrum of the main component of the reaction, $C_{16}H_8O_2N_2$, is shown in Figure 31. Its tentative structure XLIX remains to be confirmed by further study.

The condensation of 2-methyl-[4H], 3, 1-benzoxazine-4-one, XXXIV, in molten benzophenone at 300°C appears to be more complex. One of the components of the reaction mixture has an infrared spectrum (Figure 32) identical with that from the benzene soluble melt reaction product, XLIX described above (Figure 30). Analytical results in this case seem to point to a molecular formula approaching $C_{18}H_{10}O_2N_2$ which is different from that obtained from the melt reaction product, XLIX. Obviously, though, on the basis of their infrared spectra both products are identical. Analytical results obtained in the latter case from the reaction product from benzophenone may be doubtful because of the difficulty of purification. A lesser component of the reaction was insoluble in benzene. Its infrared spectrum (Figure 33) was different from those from the melt reaction product, XLIX and from the benzene soluble product

obtained from the reaction in molten benzophenone. Analytical results appear to indicate that this product, LI, has a molecular formula close to $C_{16}H_8O_2N_2$. No further attempts were made to characterize these products.

3. THERMAL CONDENSATION OF SOME DIFUNCTIONAL DERIVATIVES RELATED TO 2-METHYL-[4H], 3,1-BENZOXAZINE-4-ONE

The thermal "condensation" of 2,7-dimethyl-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, I, was carried out in solution in both sulfolane at 320 - 325°C, and in molten benzophenone at 300°C under nitrogen. Analytical values indicate that in both cases the products appear to have a molecular formula approaching $C_{12}H_8O_4N_2$. Their infrared spectra (Figures 34 and 35) are identical. This seems to indicate that a rearrangement has taken place, since the empirical formulae of both the starting monomer and the products of the reaction are the same. The reaction product is probably polymeric and since it is insoluble in methane sulfonic acid and in concentrated sulfuric acid, it can be considered to be cross-linked. A tentative structure, LII, representative of the product is depicted in Figure 7.

Next the thermal behavior of 6,6'-bis-(2-methyl-[4H], 3,1-benzoxazine-4-one), XXXVII, was studied in molten benzophenone at 300°C. Here again the molecular formula of the product, $C_{18}H_{12}O_4N_2$, as calculated from analytical results appears to be identical with that of the starting material. The product is probably a cross-linked polymer since it is insoluble in both methane sulfonic acid and concentrated sulfuric acid. Its possible structure, LIII, is shown in Figure 8 and its infrared spectrum is illustrated in Figure 36.

2,7-bis-(trifluoromethyl)-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, XXXVI, was similarly heated in benzophenone at 300°C under nitrogen. Analytical results indicate that the product has an empirical formula approaching $C_{12}H_5O_4N_2F_4$. The analyses for %H may be high since it seems likely that the loss of two fluorine atoms from the starting material, XXXVI, $C_{12}H_2O_4N_2F_6$, may have occurred as the result of the splitting out of two moles of hydrogen fluoride during the reaction. On this basis one might expect the reaction product to be a low molecular weight compound, $C_{12}O_4N_2F_4$ with a structure depicted by LVa in Figure 7. However, it seems more likely that the material is a cross-linked product, LVb, resulting from intermolecular loss of hydrogen fluoride. Its infrared spectrum is shown in Figure 37.

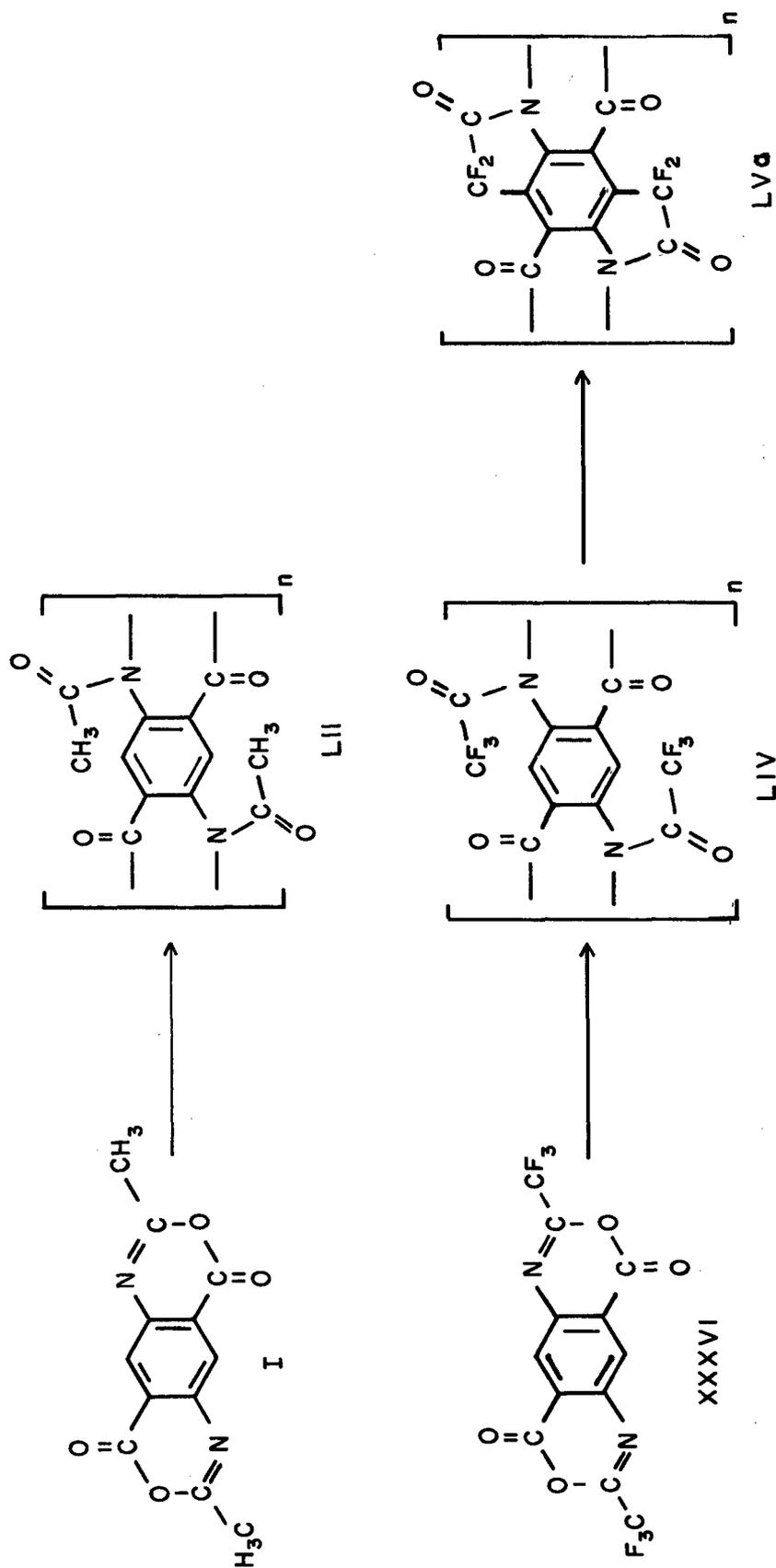


Figure 7. Condensation Products from 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I, and from 2,7-Bis-(Trifluoromethyl)-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, XXXVI

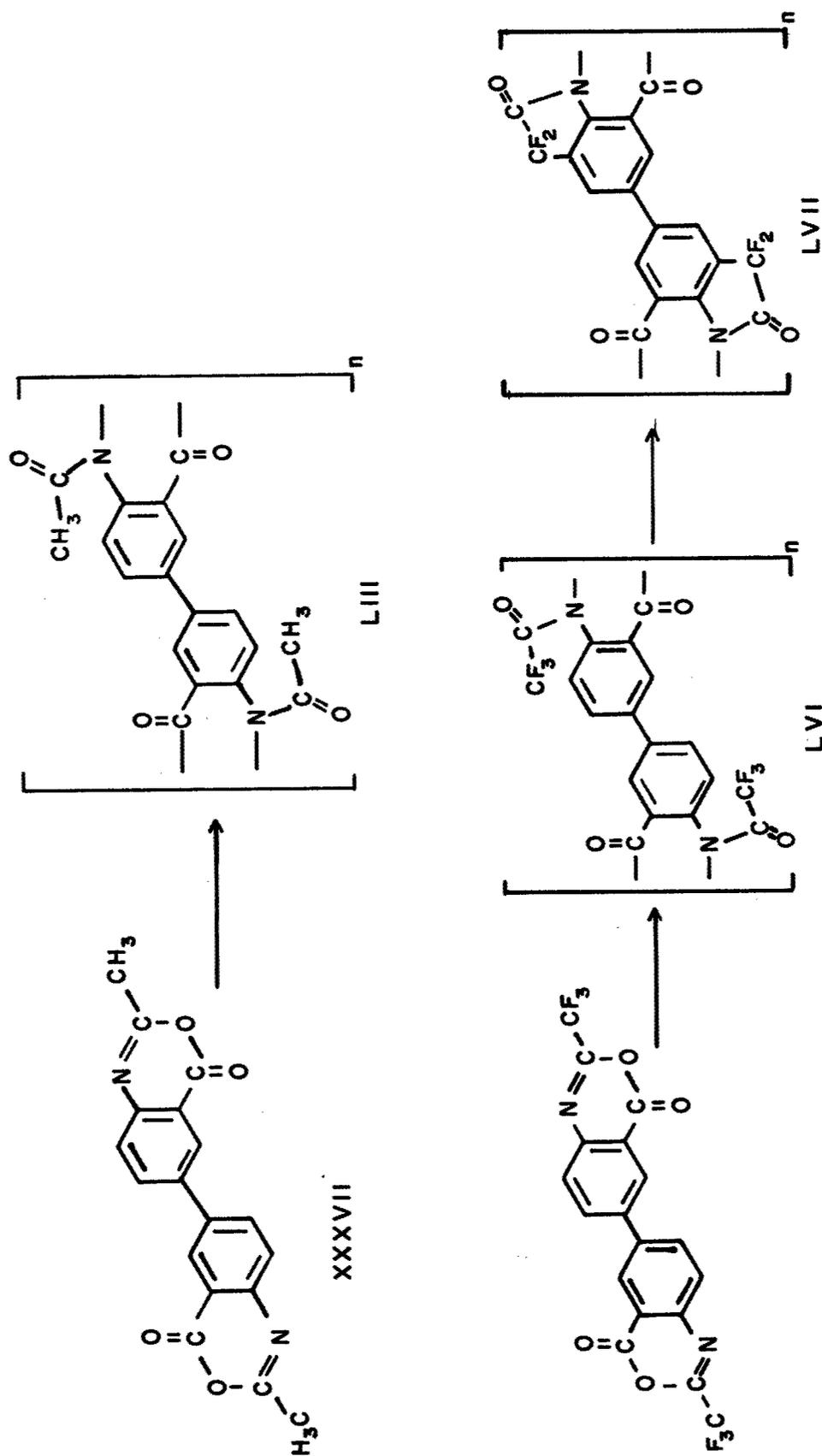


Figure 8. Condensation Products from 6,6'-Bis-(2-Methyl-1,3,4-Benzoxazine-4-One), XXVII, and from 6,6'-Bis-(2-Trifluoromethyl-1,3,4-Benzoxazine-4-One), XXVIII

Somewhat similar results were obtained upon heating 6,6'-bis-(2-trifluoromethyl-[4H]), 3,1-benzoxazine-4-one, XXXVIII, in benzophenone at 300°C under nitrogen. The resulting product had an empirical formula approaching $C_{18}H_6O_4N_2F_4$, indicating loss of two fluorine atoms from the starting material, $C_{18}H_6O_4N_2F_6$. This probably occurred by elimination of hydrogen fluoride and hence the empirical formula can be expected to be $C_{18}H_4O_4N_2F_4$. The product was soluble in toluene and had a molecular weight of 1132 suggesting that it is a low molecular weight polymer with a degree of polymerization of about three. A suggested structure, LVII, is depicted in Figure 8. Its infrared spectrum is shown in Figure 38.

These products were not further investigated because none appears to be of sufficient molecular weight, or to possess desirable solubility characteristics.

4. CONDENSATION OF 2-METHYL-[4H], 3,1-BENZOXAZINE-4-ONE, XXXIV, AND SOME OF ITS DIFUNCTIONAL DERIVATIVES WITH CERTAIN AROMATIC AMINO CARBOXYLIC ACIDS AND ESTERS

2-methyl-[4H], 3,1-benzoxazine-4-one, XXXIV, reacted with methyl anthranilate, LVIII, in refluxing xylene to give the expected 2-methyl-3-(\bar{o} -carboxymethyl)-phenylquinazoline-4-one, LX, m. p. 249 - 251°C as the chief product along with a small amount of the intermediary, N-acetyl-(\bar{o} -aminophenyl)-2-carboxymethylbenzamide, LIX, m. p. 178 - 180°C. Their infrared spectra are shown in Figures 39 and 40. A suggested reaction scheme and structures of the products are shown in Figure 9.

Next, several exploratory reactions were conducted between 2,7-dimethyl-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, I, and 2,5-diaminoterephthalic acid, XLI, and its diethyl ester, XXX, in order to study ring closure to the quinazolinone structure and polymer formation.

When an equimolar mixture of 2,7-dimethyl-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, I, and 2,5-diaminoterephthalic acid, XLI, was heated in sulfolane at 200 - 300°C under nitrogen a brown polymer $(C_{20}H_{12}O_6N_4)_n$, LXII, was produced. Its infrared spectrum is shown in Figure 41. It retains about 60% of its weight under TGA conditions up to 900°C. Its TGA curve is shown in Figure 42. Although the polymer contains some sulfur, presumably due to the

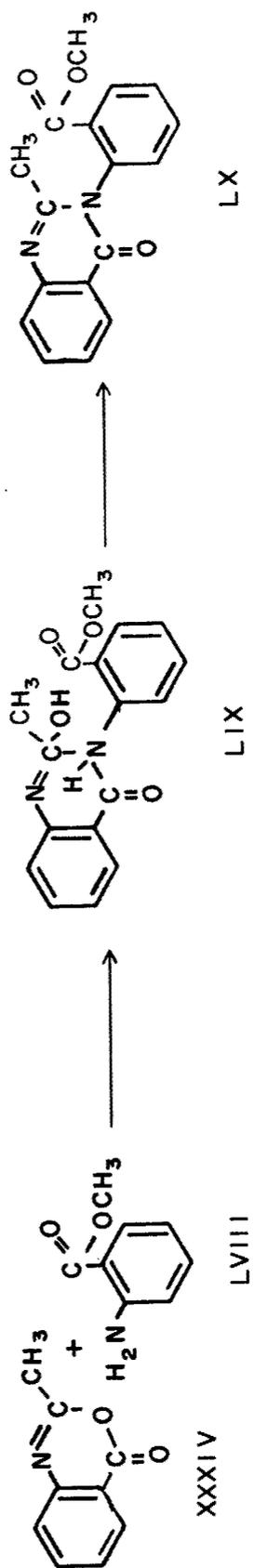


Figure 9. Condensation of 2-Methyl-1,3-Benzoxazine-4-One, XXXIV, with Methyl Anthranilate, LVIII

presence of occluded sulfolane, it is apparent that ring closure to the quinazolinone is fairly complete. The reaction scheme is illustrated in Figure 10. None of the polyamide, LXI, was isolated.

Similar results were obtained when an equimolar mixture of 2,7-dimethyl-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, I, and diethyl-2,5-diaminoterephthalate, XXX, were heated in diphenylether under nitrogen at 225 - 250°C. The resulting polymer, $(C_{24}H_{20}O_6N_4)_n$, LXIV, was apparently ring closed. Its inherent viscosity in methane sulfuric acid was found to be 0.24. Its infrared spectrum and TGA curve are shown in Figures 43 and 44. A suggested reaction scheme is illustrated in Figure 10.

5. CONDENSATION OF CERTAIN BENZOXAZINE DIONES WITH DIAMINOBENZIDINE

The reaction between 2,7-dimethyl-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, I, and diaminobenzidine, XXIII, were investigated under different conditions in order to determine whether "prepolymers" of the polyamide structure, LXV, or the quinazolinone structure, LXVI, could be easily formed in solution. Subsequent conversion of either of these to the fully closed imidazoquinazoline structure, LXVII, can probably be effected in polyphosphoric acid. A reaction scheme is illustrated in Figure 11.

When 2,7-dimethyl-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, I, was reacted with diaminobenzidine, XXXIII, in dimethylformamide, diethyl cello-solve, or trimethylene glycol dimethyl ether at temperatures varying from 120°C to as high as 310°C, a linear polyamide, $(C_{24}H_{22}O_4N_6)_n$, LXV, appears to be the chief product. Its infrared spectra, Figures 45, 46, and 47, are identical. When the reaction was carried out under more drastic conditions, by heating the monomers under nitrogen in solution in molten benzophenone at 310°C for 168 hours in an attempt to produce a polymer of the quinazolone, XXVI, or the imidazoquinazoline, LXVII, structure, the chief product of the reaction LXVIII was a benzene insoluble material with a molecular formula lying close to $C_{37}H_{28}O_3N_6$. This may be reconciled by a polymer of the quinazolinone structure, $(C_{24}H_{18}O_2N_6)_n$, LXVI, which contains one molecule of benzophenone, $C_{13}H_{10}O$, for each unit of the polymer chain. Its infrared spectrum is shown in Figure 48. A small amount of low molecular weight benzene soluble

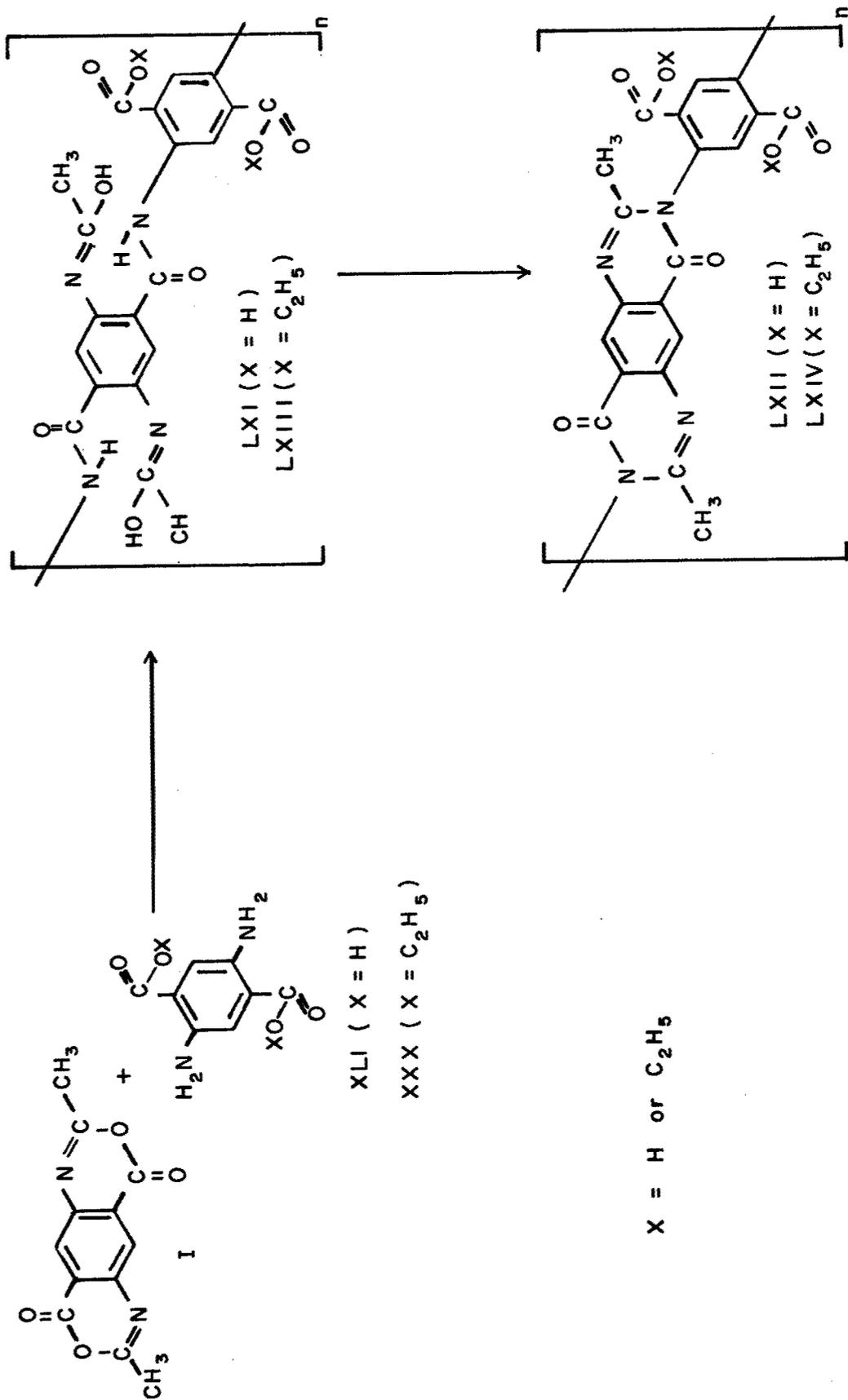


Figure 10. Condensation of 2,7-Dimethyl-1,3,8,6-Benzobisoxazine-4,9-Dione, I, with 2,5-Diaminoterephthalic Acid, XLI, or Diethyl-2,5-Diaminoterephthalate, XXX

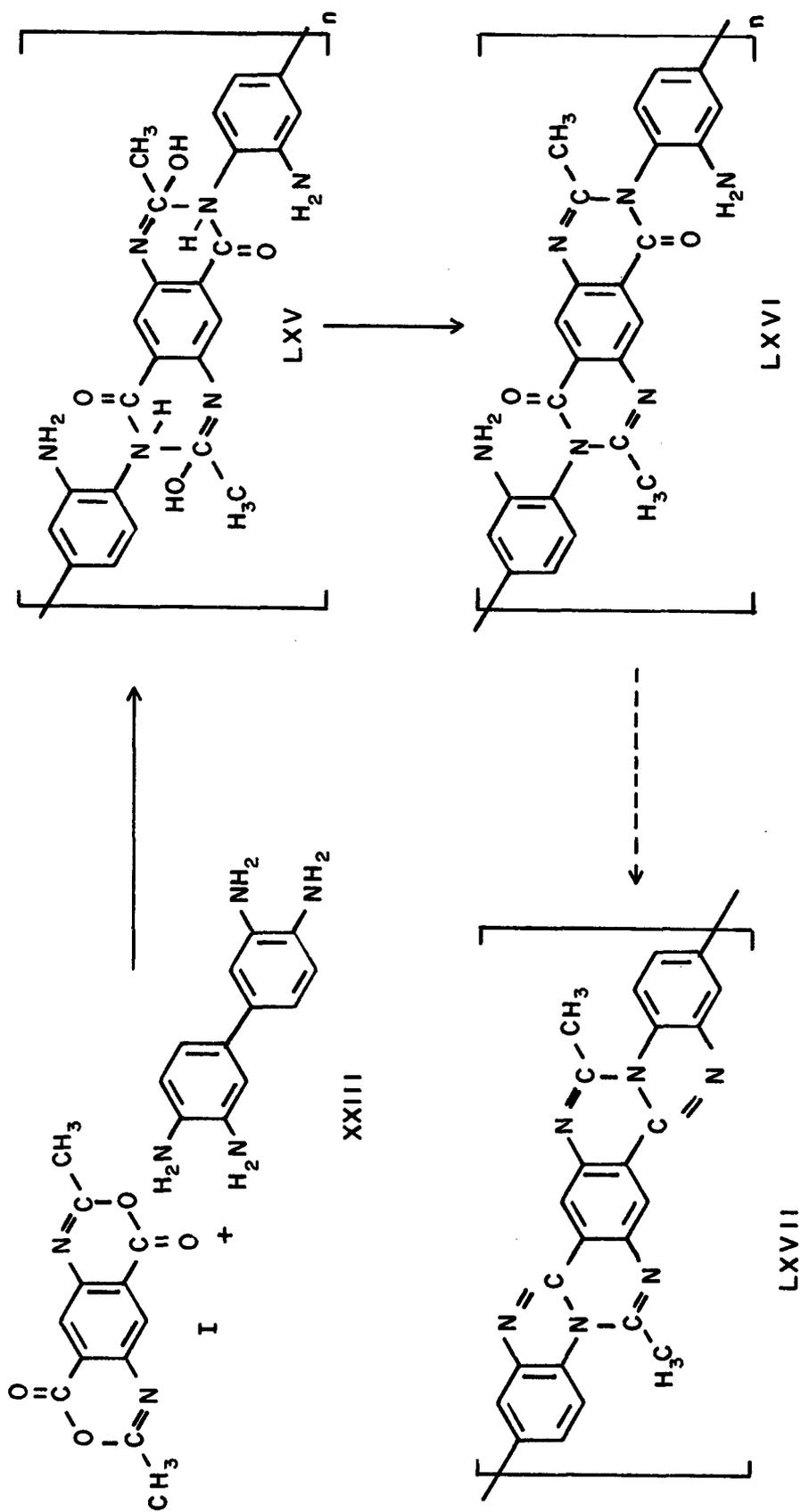


Figure 11. Condensation of 2,7-Dimethyl-4,9-Dione, I, with Diaminobenzidine, XXIII

material, LXIX, (molecular weight, 1559) was obtained from the Soxlet extracts from the above polymer. Analytical results indicate that its molecular formula lies close to $C_{37}H_{24}ON_6$. This also might be reconciled by a polymer of the imidazoquinazolone structure $(C_{24}H_{14}N_6)_n$, LXVII, which contains one molecule of benzophenone, $C_{13}H_{10}O$, for each unit of the polymer chain. Its molecular weight of 1550 indicates that the material is only a trimer. It was not considered worthwhile to further characterize the above described product.

Attempts to obtain an identifiable polymer from reaction of 6,6'-bis-(2-trifluoromethyl-[4H], 3,1-benzoxazine-4-one), XXXVII, and diaminobenzidine, XXIII, in molten benzophenone at 260°C were unsuccessful. Analytical results show that the product, LXX contained very little fluorine. The material apparently has a fairly high degree of thermal stability. It is insoluble in concentrated sulfuric acid and in methane sulfonic acid and is probably highly condensed and is cross-linked. Its TGA curve is shown in Figure 50 and its infrared spectrum is shown in Figure 51.

SECTION III
EXPERIMENTAL

1. GENERAL COMMENTS

a. Starting Materials

Anthranilic acid, XVI, (Eastman No. 29) and methyl anthranilate, LVIII, (Eastman No. 159) were obtained from Distillation Products Industries, Rochester, New York, 14650.

2,5-diaminoterephthalic acid, XLI, was obtained by hydrolysis of diethyl-2,5-diaminoterephthalate, XXX, with aqueous alkali. Diethyl-2,5-diaminoterephthalate, XXX, was obtained by oxidation of diethyl succinoyl succinate diimine with bromine in sulfuric acid. Diethyl succinoyl succinate diimine was obtained by reaction of diethyl succinoyl succinate in molten ammonium acetate. Diethyl succinoyl succinate was prepared by cyclization of diethyl succinate with sodium ethylate (Reference 18).

Diaminobenzidine, XXIII, was obtained from the Celanese Research Company.

Benzidine-3,3'-dicarboxylic acid, II, was prepared from hydrazobenzene dicarboxylic acid by heating with hydrochloric acid (Reference 19). Hydrazobenzene dicarboxylic acid was prepared from *o*-nitrobenzoic acid by the method of Heller (Reference 20).

b. Infrared Spectra

Infrared spectra were obtained by use of a Perkin-Elmer Model 521 Infrared Spectrophotometer from KBr pellets prepared by the window technique (Reference 21).

c. Thermogravimetric Analyses

Thermogravimetric analyses were obtained by heating 500 - 100 mg of the compound under nitrogen in a Chevenard Thermobalance (Adamel, Paris, France) to 900°C at a heating rate of 180°C per hour.

d. Softening Point Determinations

The softening characteristics of the compounds were obtained by means of a modified Vicat apparatus (Reference 22). Heating was performed at a constant rate of 150°C per hour. The softening range was determined from a plot of temperature vs penetration.

e. High Resolution Mass Spectroscopy

The compounds were introduced via the direct introduction probe at temperatures from 130 - 250°C, depending upon the ease of volatility of the compound, into a CEC Model 21-110B Mass Spectrometer at an ionizing voltage of 70 eV and an accelerating voltage of 8 kV.

2. PREPARATION OF MONOMERS AND POLYMERIZATION REACTIONS

a. Acetylation of Anthranilic Acid, XVI. N-Acetylanthranilic Acid, XXXIX, and 2-Methyl-[4H], 3,1-Benzoxazine-4-One, XXXIV

A mixture of 13.7 g of anthranilic acid, XVI, (0.10 mole), and 100 g of acetic anhydride was stirred and heated at 120°C. The amino acid gradually dissolved. After 17 hours 80% of the acetic anhydride was distilled off. On cooling, the liquid solidified to a brown mass. It was stirred with 300 ml of boiling cyclohexane. The insoluble material was filtered off. Yield 0.3 g. It was recrystallized from benzene with charcoal treatment. Its infrared spectrum appears in Figure 13.

Anal. Calc'd for $C_9H_9O_3N$; XXXIX:

%C, 60.50; %H, 5.06; %O, 26.70; %N, 7.80

Found:

%C, 61.40; %H, 5.20; %O*, 25.77; %N^K, 7.65

The cyclohexane filtrate was treated with charcoal and filtered while hot. On cooling, white crystals were deposited from the filtrate. The product was filtered off, washed with cold hexane, and vacuum dried at 80°C/0.1 mm. Yield, 11.93 g (74%), m. p. 78 - 80°C. The molecular ion peak appeared in its mass spectrum at m/e 161. Its infrared spectrum is shown in Figure 12.

Anal. Calc'd for $C_9H_7O_2N$, XXXIV:

%C, 67.07; %H 4.38; %O, 19.86; %N, 8.69

Found:

%C, 67.15; %H, 4.64; %O⁺, 20.06; %N^K, 8.53

K-Nitrogen by the Kjeldahl Method. *-Oxygen by the Untersaucher Method,
+-Oxygen by Difference.

b. Preparation of 2,5-N,N'-Diformylaminoterephthalic acid, XLII, and Conversion to [4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, XLIII, by Heating with Thionyl Chloride

(1) 2,5-N,N'-Diformylaminoterephthalic Acid, XLII

A mixture of 4.9 g of 2,5-diaminoterephthalic acid, XLI, (0.025 mole), and 250 ml of formic acid was stirred at the boiling point of formic acid under reflux for two hours. The color of the reaction mixture changed from green in color to light tan. The light tan precipitate was filtered off, washed with benzene, and dried. Yield of crude product, 5.9 g (94%). The crude product was recrystallized from 275 ml of dimethylformamide with charcoal treatment. On cooling the filtered solution, white granules began to form. These were filtered off, washed with ether, and dried at 80°C/0.02 mm/6 hours. Yield 4.4 g (70%). Its infrared spectrum is shown in Figure 15.

Anal. Calc'd for $C_{10}H_8O_6N_2$, XLII:

%C, 47.62; %H, 3.21; %O, 38.06; %N, 11.11; Mol. Wt., 252.2

Found:

%C, 48.01; %H, 3.07; %O*, 38.06; %N^K, 10.98; Mol. Wt.^X, 228

*-Oxygen by the Untersaucher Method. K-Nitrogen by the Kjeldahl Method.
X-Molecular Weight by the VPO Method in DMF at 37°C.

(2) [4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, XLII

A solution from 0.20 g of 2,5-N,N'-diformylaminoterephthalic acid, XLII and 10 ml of dimethylformamide, and 4 ml of acetic anhydride was heated

at 139°C for five minutes. The clear solution was allowed to cool. The white granular crystals were filtered off, washed with benzene, then hexane, and dried at 110°C/0.02 mm. Yield 0.15 g. The compound darkens on heating at 240 - 260°C. It does not melt up to 360°C. Its infrared spectrum is shown in Figure 16.

Anal. Calc'd for $C_{10}H_4O_4N_2$, XLIII:

%C, 55.63; %H, 1.86; %N, 12.98; Mol. Wt., 216.15

Found:

%C, 57.11; %H, 2.65; %N^K, 11.81; Mol. Wt.^X, 185

K-Nitrogen by the Kjeldahl Method. X-Molecular Weight by the VPO Method in DMF at 100°C.

c. Acetylation of 2,5-Diaminoterephthalic Acid, XLI, 2,5-(N,N'-Diacetylamino)-Terephthalic Acid, XLIV, and 2,7-Dimethyl-[2H, 7H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I

A solution was prepared from 1.96 g of 2,5-diaminoterephthalic acid, XLI, and 10 ml of acetic anhydride. The mixture was refluxed for one hour. Then 10 ml of additional acetic anhydride and 25 ml of glacial acetic acid was added. Later after three more hours 25 ml of additional glacial acetic acid was again added. After refluxing for 16 hours longer, the reaction mixture was cooled. A green insoluble solid was filtered off and air dried. Yield 2 g. It was recrystallized from 200 ml of boiling dioxane (with charcoal treatment) giving light brown crystals. Yield 1.25 g. It darkened near 300°C and appears to decompose/or sublime without melting. This is verified by its softening point which is shown in Figure 20. Its infrared spectrum is shown in Figure 19 and its TGA curve is shown in Figure 21.

Anal. Calc'd for $C_{12}H_{12}O_6N_2$; XLIV:

%C, 51.40; %H, 4.30; %N, 10.00

Found:

%C, 51.54; %H, 4.52; %N^K, 10.11

K-Nitrogen by the Kjeldahl Method.

The filtrate on evaporation left a greenish-black solid, 0.75 g. It was recrystallized from benzene as light yellow crystals, 0.48 g. It darkened above 300°C and appears to sublime or decompose without melting. When the temperature is raised slowly (at about 1/2 degree per minute) the material darkens and becomes molten without flowing. When the temperature is raised rapidly (at about two degrees per minute) the compound melts at 324 -325°C to a dark liquid which then appears to bubble. Its softening point curve shown in Figure 17 suggests that melting accompanied by sublimation and polymerization may be taking place near 300°C. Its infrared spectrum is shown in Figure 18.

Anal. Calc'd for $C_{12}H_8O_4N_2$; I:

%C, 59.08; %H, 3.29; %N, 11.48

Found:

%C, 59.05; %H, 3.52; %N,^K 11.77

K-Nitrogen by the Kjeldahl Method.

In another run from 9.81 g of 2,5-diaminoterephthalic acid, XLI, and excess acetic anhydride and no acetic acid, 9.2 g of I was obtained. No XLIV was found.

d. Preparation of 2,5-(N,N'-Dicarbethoxyamino)-Terephthalic Acid, XLV

A solution was prepared from 3.92 g of 2,5-diaminoterephthalic acid (0.02 mole), XLI, and 1.6 g of sodium hydroxide (0.04 mole) in 10 ml of water. The solution then was treated with 30 ml of ethyl alcohol to help hasten formation of the granular solid disodium salt. The water and alcohol were allowed to evaporate in a hood air stream at room temperature. The residue was dried in a vacuum oven at 40°C/0.02 mm. The salt was stirred with 125 ml of tetrahydrofuran. Ten ml of ethyl chloroformate was added and the mixture was stirred for 1 1/2 hours at room temperature. Three ml additional ethyl chloroformate was added. The mixture was allowed to stand overnight in a flask protected from moisture in the atmosphere. The tan solid (mostly NaCl) was filtered off. The filtrate was treated with charcoal and filtered again. The filtrate was evaporated in a hood air stream to a yellow residual powder. Yield, 6.1 g (90%).

The product was dried in a vacuum oven at 40°C/0.10 mm. Its softening point curve, shown in Figure 22, appears to indicate that melting and/or polymerization occurs in the 200 - 250°C range. Its infrared spectrum is shown in Figure 23.

Anal. Calc'd for $C_{14}H_{16}O_8N_2$, XLV:

%C, 49.41; %H, 4.74; %N^K, 8.23; Mol. Wt., 340.28

Found:

%C, 51.28; %H, 4.73; %N^K, 8.04; Mol. Wt.^U, 353

K-Nitrogen by the Kjeldahl Method. U-Molecular Weight by the VPO Method in THF at 34°C.

e. Attempted Preparation of 2,7-Diethoxy-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, XLVI

A mixture of 3.92 g (0.02 mole) of 2,5-diaminoterephthalic acid, XLI, 4.78 g of ethyl chloroformate, and 160 ml of tetrahydrofuran were stirred at refluxing temperature and treated with 4.5 g (6.2 ml) of triethyl amine. After stirring for one hour 150 ml of dioxane was added. The tetrahydrofuran was distilled off. The temperature was raised to 100°C after stirring for another hour the triethyl amine hydrochloride, 6.9 g was filtered off. The filtrate was treated with charcoal, and the new dioxane filtrate was evaporated at 50°C to a golden oil. This oil after heating in a tared dish in a vacuum oven at 60°C/0.02 mm for three days, became a brittle brown resin. Yield, 6.3 g.

f. Preparation of 2,7-Bis-(Trifluoromethyl)-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, XXXVI

A mixture of 9.7 g of 2,5-diaminoterephthalic acid, XLI, (0.005 mole) and 80 ml of trifluoroacetic anhydride was refluxed in a flask protected from atmospheric moisture. After three hours the mixture was cooled. The crystalline product was filtered off, washed with ether, and air dried. It was purified by sublimation at 100°C/0.05 mm as a yellow crystalline solid. Yield, 6.66 g, m.p. 224 - 225°C. The molecular ion peak appears in its mass spectrum at m/e 352. Its infrared spectrum is shown in Figure 24.

Anal. Calc'd for $C_{12}H_2O_4N_2F_6$; XXXVI:

%C, 40.90; %H, 0.57; %N, 7.95; %F, 32.37; Mol. Wt., 352

Found:

%C, 41.21; %H, 0.69; %N^D, 8.25; %F, 30.69; Mol. Wt.^X, 348
m/e 352

D-Nitrogen by the Dumas Method. X-Molecular Weight by the VPO Method in Dioxane.

g. Preparation of 4,4'-Diformylaminodiphenyl-3,3'-Dicarboxylic Acid, XLVII, and Conversion to 6,6'-Bis-($[4H]$), 3,1-Benzoxazine-4-One), XLVIII

A mixture of 6.81 g of 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid, II, and 200 ml of formic acid was stirred at 104°C for two hours and allowed to stand. The gray solid was filtered off, washed with ether, and dried at 100°C/0.02 mm. Yield, 7.0 g. The product was insoluble in boiling benzene, very slightly soluble in hot dioxane or hot diethyl cellosolve. It was soluble in boiling diethylene glycol monoethyl ether. A small sample was recrystallized from a mixture of N,N-dimethylformamide (1) and formic acid (1). Its infrared spectrum is shown in Figure 25.

Anal. Calc'd for $C_{16}H_{12}O_6N_2$, XLVII:

%C, 58.55; %H, 3.68; %O, 29.24, %N, 8.53

Found:

%C, 58.37; %H, 3.95; %O*, 28.47; %N^D, 8.64

*-Oxygen by the Untersaucher Method. D-Nitrogen by the Dumas Method.

About 0.2 g of the diformylamino compound, XLVII, was boiled with 50 ml of dioxane and 15 ml of thionyl chloride. Evaporation left a white residue. This material was taken up in 50 ml of dioxane. The solution was treated with charcoal and filtered. The volume of the filtrate was reduced to 10 ml and cooled in an ice chest until the dioxane began to freeze. The resulting cloudy solution was filtered. The product was a white granular solid. Yield, 0.1 g. Its infrared spectrum is shown in Figure 26.

Anal. Calc'd for $C_{16}H_8O_4N_2$, XLVIII:

%C, 65.75; %H, 2.76; %O, 21.90; %N, 9.59

Found:

%C, 66.19; %H, 3.92; %O*, 22.05; %N^D, 8.94

*-Oxygen by the Untersaucher Method. D-Nitrogen by the Dumas Method.

h. Preparation of 6,6'-Bis-(2-Methyl- [4H], 3,1-Benzoxazine-4-One).
XXXVII.

A mixture of 13.6 g of 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid, II, and 102 g of acetic anhydride were refluxed for two hours. 48 ml of the solvent (ie, a mixture of acetic acid and acetic anhydride) were distilled over and replaced by 100 ml of fresh acetic anhydride. After three hours longer the reaction mixture was cooled. A tan solid precipitated. It was filtered off and dried. Yield, 14.6 g (91%). The compound was recrystallized from dioxane. It melted at 316 - 318°C to a clear liquid which slowly began to bubble as sublimation began. Its softening point curve, Figure 27, indicates that softening accompanied by sublimation and polymerization may be occurring near 300°C. This appears to be verified by its TGA curve, Figure 28. Its infrared spectrum is shown in Figure 29.

Anal. Calc'd for $C_{18}H_{12}O_4N_2$, XXXVII:

%C, 67.49; %H, 3.78; %N, 8.75

Found:

%C, 67.69; %H, 3.75; %N, 8.64

i. Preparation of 6,6'-Bis-Trifluoromethyl- [4H], 3,1-Benzoxazine-4-One, XXXVI

A mixture of 5 g of 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid, II, and 50 ml of trifluoroacetic anhydride was refluxed for four hours in a flask protected from atmospheric moisture. Then the mixture was cooled and the crystalline product was filtered off, washed with ether, and air dried. It was

subsequently recrystallized from 150 ml of boiling acetic anhydride. Yield, 5.53 g. Its molecular ion peak appears in its mass spectrum at m/e 428. Its infrared spectrum is shown in Figure 30.

Anal. Calc'd for $C_{18}H_6O_4N_2F_6$, XXXVI:

%C, 50.48; %H, 1.41; %N, 6.55; %F, 26.60; Mol. Wt., 428

Found:

%C, 50.53; %H, 1.44; %N^D, 6.49; %F, 25.92; m/e , 428

D-Nitrogen by the Dumas Method.

j. Melt Polymerization of 2-Methyl-[4H], 3,1-Benzoxazine-4-One, XXXIV

2-methyl-[4H], 3,1-benzoxazine-4-one, XXXIV, 1.5 g (0.009 mole) was heated in a tube, 25 mm x 140 mm in a slow stream of nitrogen. The tube was heated up to 300°C in an aluminum block encased in a Glas-col heating mantle over a period of three hours. The temperature was controlled by means of a Thermocap relay. Sublimation was observed after the temperature had reached 200°C so a heat gun was used to melt the sublimate causing it to flow back into the bulk of the molten reaction mixture. After three hours the temperature had reached 300°C. Liquid had begun condensing on the upper walls of the tube and adaptor, but no crystalline sublimate was noted. Gradually a yellow oily substance began to form on the upper walls of the tube. After 66 hours, the sublimed yellow material was scraped from the walls of the tube and adaptor. Yield, 0.6 g. Its mass spectrum exhibits what may be its molecular ion peak at m/e 260 with other significant peaks at m/e 246, m/e 236, m/e 221, m/e 143, m/e 193, m/e 77, and m/e 69. Its melting point was taken at 79 - 81°C. The product was soluble in acetone and alcohol. It was precipitated from aqueous methanol, filtered, and dried at 108°C/0.005 mm. Its infrared spectrum is shown in Figure 31.

Anal. Calc'd for $C_{16}H_8O_2N_2$, XLIX:

%C, 73.85; %H, 3.10; %N, 10.77

Found:

%C, 74.22; %H, 4.71; %N, 10.62

A dilute solution of the sample was prepared in toluene and examined by vapor phase chromatography. The solution was injected into a column packed with silicone gum rubber. The temperature was programmed at an increase of 5°C per minute beginning at 160°C. A sharp strong peak appeared at 194°C and appears to be due to the major component. In a separate run under the same conditions the retention time of triphenyl carbinol, b p, 380°C, was found to be of the same order, and a strong peak also appeared near 194°C. The unknown had been programmed up to 270°C, and several smaller peaks appear in the region above 228°C and up to 240°C. This appears to indicate the presence of higher molecular weight components.

The solution was spotted on Eastman Chromatogram paper, alumina absorbent, without fluorescent indicator and developed with ethyl acetate. Two yellow spots (in addition to the third spot at the origin) indicate that the material is probably a mixture of at least three compounds. The compound of lower R_f value appears to be the main component. The compound of the highest R_f value (ie, farthest from the origin) appears to be identical with the main component (in this case the highest R_f value) of the material obtained from condensation of 2-methyl-[4H], 3,1-benzoxazine-4-one, XXXIV, in solution in molten benzophenone.

The residue remaining in the tube after sublimation was a brown resinous material. It was extracted with 500 ml of hot benzene and filtered. The filtrate was treated with charcoal and filtered again. This second filtrate gave an orange precipitate on treatment with water. It was dried 180°C/0.005 mm for 64 hours. Yield, 0.76 g.

Anal. Calc'd for $C_{16}H_8O_2N_2$:

%C, 73.85; %H, 3.10; %N, 10.77; Mol. Wt., 260

From:

%C, 71.49; %H, 4.08; %N, 9.46; Mol. Wt., 871*

k. Solution Polymerization of 2-Methyl-[4H], 3,1-Benzoxazine-4-One XXXIV, in Molten Benzophenone

A mixture of 2-methyl-[4H] 3,1-benzoxazine-4-one, XXXIV, (0.02 mole), and 35 g of benzophenone was heated in a tube 25 mm x 40 mm in a slow

stream of nitrogen at 300°C for 24 hours. Then 25 g of benzophenone was distilled from the reaction mixture. The residue in the tube solidified on cooling. It was stirred into 200 ml of petroleum ether and the brown solid was filtered and then extracted with 200 ml of hot dioxane. Yield 0.34 g. The dioxane filtrate was evaporated to dryness to an orange powder. Both products were combined and extracted with 250 ml of hot benzene. The insoluble brown solid was filtered off and dried. Yield, 0.33 g. Its infrared spectrum is shown in Figure 33. It is different from that of the melt reaction product (Figure 31).

Anal. Calc'd for $C_{16}H_8O_2N_2$, LI:

%C, 73.85; %H, 3.10; %N, 10.77

Found:

%C, 73.50; %H, 3.97; %N, 10.78

The clear red benzene filtrate was evaporated to dryness. The red resinous material remaining behind was stirred with 100 ml of cold methanol. The insoluble orange solid was filtered off, washed with methanol, and dried at 90°C/0.05 mm. Yield 0.82 g. Its infrared spectrum is shown in Figure 32 and is identical with that of the melt reaction product (Figure 31).

Anal. Calc'd for $C_{18}H_{10}O_2N_2$, XLIX:

%C, 75.50; %H, 3.54; %N, 10.02

Found:

%C, 75.65; %H, 3.85; %N, 9.61

Its molecular weight was determined by the VPO method in dioxane to be 488.

A dilute solution of the orange solid in toluene was spotted on Eastman Chromatogram paper, alumina absorbent, without fluorescent indicator, and developed with ethyl acetate. Two spots (in addition to the third spot at the origin) indicate that the material is probably a mixture of two components. The compound with the highest R_f value appears to be the main component of the mixture.

A light yellow solid precipitate gradually appeared in the methanol washings from the above product. It was filtered off and dried at 110°C/0.05 mm. Yield, 0.12 g. Its infrared spectrum is shown in Figure 32.

Anal. Calc'd for $C_{18}H_{10}O_2N_2$, XLIX:

%C, 75.50; %H, 3.54; %N, 10.02

Found:

%C, 75.10; %H, 3.74; %N, 9.81

The benzene insoluble material above was Soxhlet extracted with benzene. Yield 0.32 g. Its mass spectrum exhibited lines at m/e 362, 216, 215, 190, 163, 149, 140, 131, and 113. Its infrared spectrum is shown in Figure 33.

Anal. Calc'd for $C_{16}H_8O_2N_2$, LI:

%C, 73.85; %H, 3.10; %N, 10.77

Found:

%C, 74.11; %H, 3.25; %N, 10.70

1. Thermal Decomposition and Polymerization of 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I

(1) In Sulfolane

A suspension of 0.73 g of 2,7-dimethyl-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, I, and 30 ml of sulfolane was heated in a tube, 25 mm x 140 mm, under a slow stream of nitrogen at 320 - 325°C. The compound slowly dissolved above 200°C to give a clear yellow solution and gradually darkening over a period of several hours as the temperature was increased. A dark brown precipitate gradually was produced. After 27 hours the reaction mixture was cooled, and the brown polymer was filtered off. The filtrate was yellow. The polymer was washed with benzene, then acetone, and dried at 168°C/0.05 m for three hours. Yield 0.55 g. It is insoluble in all organic solvents and in sulfuric acid. Its infrared spectrum is shown in Figure 34.

Anal. Calc'd for $C_{12}H_8O_4N_2$; LII:

%C, 59.08; %H, 3.29; %N, 11.48; %S, 0.00

Found:

%C, 61.33; %H, 3.05; %N, 12.24; %S, 2.82

(2) In Molten Benzophenone

A mixture of 0.976 of the compound and 30 g of benzophenone was heated under nitrogen in the apparatus described above. A clear yellow solution resulted at 250°C. The temperature was raised to 300°C, and the reaction mixture was heated at this temperature for 24 hours. The reaction mixture at this point was a dark brown "gel." The contents of the tube were diluted with 250 ml of acetone. The brown polymer was filtered off, washed with acetone, and air dried. Yield, 0.7 g. Its infrared spectrum is shown in Figure 35. The polymer is insoluble in organic solvents and in concentrated sulfuric acid.

Anal. Calc'd for $C_{12}H_8O_4N_2$, LII:

%C, 59.08; %H, 3.29; %N, 11.48

Found:

%C, 57.68; %H, 3.63; %N^K, 12.15

K-Nitrogen by the Kjeldahl Method.

m. Thermal Decomposition and Polymerization of 6,6'-Bis-(2-Methyl-[4H], 3,1-Benzoxazine-4-One), XXXVII, in Molten Benzophenone

A mixture of 1.28 g of 6,6'-bis-(2-methyl-[4H], 3,1-benzoxazine-4-one), XXXVII, and 30 g of benzophenone were heated in a tube in a slow stream of nitrogen. At 250°C the compound had completely dissolved giving a clear brown solution. The temperature was raised to 300°C and kept at this temperature for 50 hours. The mixture then was cooled, and the polymer was isolated by adding the contents of the tube to 100 ml of acetone. After filtration the brown polymer was washed with acetone and dried. Yield 0.6 g. Its infrared spectrum is shown in Figure 36. The product was insoluble in sulfuric acid and in methane sulfonic acid.

Anal. Calc'd for $C_{18}H_{12}O_4N_2$, LIII:

%C, 67.50; %H, 3.78; %N, 8.75

Found:

%C, 67.06; %H, 3.81; %N, 8.57

More of the product, 0.67 g was obtained from the acetone filtrate by evaporation to dryness and Soxhlet extraction with n-heptane to remove the benzophenone.

n. Thermal Decomposition and Polymerization of 2,7-Bis-(Trifluoromethyl)-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9,Dione, XXXVI, in Molten Benzophenone

A mixture of 1.4 g of 2,7-bis-(trifluoromethyl)-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, XXXVI and 30 g of benzophenone was heated at 300°C for 115 hours. The dark brown liquid was cooled and added to 250 ml of heptane. The upper heptane layer was decanted from the thick brown oil. 150 ml of ether was added giving a turbid solution which then was stirred into 150 ml of heptane. The ether was distilled off. The volume was reduced to 100 ml by distillation. The brown granular product was filtered off, washed with heptane, and dried. Yield 0.25 g. Its infrared spectrum is shown in Figure 37.

Anal. Calc'd for $C_{12}H_0N_4F_4$; LV:

%C, 46.15; %H, 0.00; %N, 8.92; %F, 24.35

Found:

%C, 45.11; %H, 1.54; %N, ^K8.79; %F, 25.05

K-Nitrogen by the Kjeldahl Method.

o. Thermal Decomposition of 6,6'-Bis-(2-Trifluoromethyl)-[4H], 3,1-Benzoxazine-4-One), XXXVIII

A solution from 1.2 g of 6,6'-bis-(2-trifluoromethyl)-[4H], 3,1-benzoxazine-4-one), XXXVIII, and 30 g of benzophenone was heated at 300°C for 144 hours under a slow stream of nitrogen. Most of the benzophenone was distilled over at 0.6 mm. The residue in the tube was extracted with petroleum

ether. The insoluble material was filtered off. Yield, 0.85 g. It was extracted with boiling petroleum ether for six hours. Yield, 0.65 g. The product was stirred with 200 ml of cold toluene. The insoluble material, 0.15g, was found to be a starting material. The toluene filtrate was treated with charcoal, reduced in volume to 15 ml, and poured into 150 ml of petroleum ether. The light tan solid was filtered off and vacuum dried. Yield 0.4 g. Its infrared spectrum is shown in Figure 38.

Anal. Calc'd for $C_{18}H_4O_4N_2F_4$, LVII:

%C, 55.70; %H, 1.04; %N, 7.22; %F, 19.60; Mol. Wt., 1170

Found:

%C, 55.29; %H, 1.54; %N^D, 7.17; %F, 19.40; Mol. Wt.*, 1132

*-Molecular Weight by the VPO Method in Toluene. D-Nitrogen by the Dumas Method.

p. Reaction Between 2-Methyl- [4H]-3,1-Benzoxazine-4-One, XXXIV, and Methyl Anthranilate, LVIII

A mixture from 3.22 g of 2-methyl- [4H], 3,1-benzoxazine-4-one, XXXIV, (0.02 mole), 13 ml of methyl anthranilate, LVIII, and 50 ml of xylene was refluxed for four hours, then cooled. The solution remained clear. 40 ml of distillate was collected, and the remainder of the reaction mixture was stirred with 50 ml of hexane and 300 ml of cold benzene. A white granular precipitate was formed. It was filtered off and dried at 100°C/0.1 mm. Yield, 1.7 g, m p 249 - 251°C. Its infrared spectrum is shown in Figure 39.

Anal. Calc'd for $C_{17}H_{14}O_3N_2$, LX:

%C, 69.45; %H, 4.76; %N, 9.53

Found:

%C, 69.29; %H, 4.57; %N, 9.66

The filtrate was evaporated to an oily residue containing some unreacted methyl anthranilate. This was left in an open petri dish over a hot plate in the hood at 100°C and evaporated down to a tacky orange material. It was

taken up in 25 ml of benzene. Treatment with 400 ml of hexane gave a cloudy orange liquid which was filtered. The filtrate was treated with charcoal and filtered. The filtrate was evaporated to dryness to a tan residue. It was stirred with 100 ml of ether giving white crystals. These were filtered off and dried. Yield, 0.8 g., m p 178 - 180°C. Its infrared spectrum is shown in Figure 40.

Anal. Calc'd for $C_{17}H_{16}O_4N_2$, LIX:

%C, 65.40; %H, 5.16; %N, 8.97

Found:

%C, 65.58; %H, 5.18; %N, 9.10

q. Reaction Between Equimolar Quantities of 2,7-Dimethyl- [4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I, and 2,5-Diaminoterephthalic acid, XLI, in Sulfolane

A mixture from 0.45 g of 2,7-dimethyl- [4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, I (0.002 mole); 0.36 g of 2,5-diaminoterephthalic acid, XLI, and 30 ml of sulfolane was heated in a tube under a slow stream of nitrogen at 200°C for 17 hours, at 250°C for 4 1/2 hours, and at 300°C for 168 hours. The reaction mixture was poured into 400 ml of benzene. The brown resinous product was filtered off, washed with benzene, and dried at 180°C/0.05 mm/8 hours. Yield, 0.60 g. It was partly soluble in sulfuric acid and in methane sulfonic acid. Its infrared spectrum is shown in Figure 41. Its TGA curves are shown in Figure 42.

Anal. Calc'd for $C_{20}H_{12}O_6N_4$, LXII:

%C, 59.50; %H, 2.97; %N, 13.90; %S, 0.00

Found:

%C, 59.46; %H, 3.37; %N^D, 12.40; %S, 2.93

D-Nitrogen by the Dumas Method.

r. Reaction Between Equimolar Quantities of 2,7-Dimethyl- [4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I, and Diethyl-2,5-Diaminoterephthalate

A mixture of 1.221 g of 2,7-dimethyl- [4H, 9H], 3,1,8,6-benzobisoxazine, I (0.005 mole), 1.2613 g of diethyl-2,5-diaminoterephthalate (0.005 mole); and 100 ml of diphenylether was heated in a slow stream of nitrogen up to 225°C

and maintained at this temperature for 18 hours. Then the temperature was raised to 250°C and the reaction mixture was heated at 250°C for 120 hours. The red-brown polymer was filtered off and Soxhlet extracted with methanol for 48 hours and dried at 100°C/0.1 mm. Yield, 1.84 g. The polymer was insoluble in m-cresol and dimethylformamide. It was soluble in warm methane sulfonic acid. $\eta_{inh} = 0.24/0.5\%/MeSO_3H$. Its infrared spectrum is shown in Figure 43 and its TGA curve is shown in Figure 44.

Anal. Calc'd for $(C_{24}H_{20}O_6N_4)_n$, LXIV:

%C, 62.55; %H, 4.39; %N, 12.20

Found:

%C, 62.83; %H, 3.91; %N^D, 12.63

D-Nitrogen by the Dumas Method.

s. Reaction Between 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I, and Diaminobenzidine, XXIII, in Dimethylformamide

A mixture of 0.7327 g of 2,7-dimethyl-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, I (0.003 mole), and 50 ml of dimethylformamide was stirred at 100°C. The compound did not appear to dissolve. A solution of 0.6428 g of diaminobenzidine, XXIII, was added. A clear tan solution resulted. The solution was heated at 120°C for 48 hours. The reaction mixture was reduced in volume to about 10 ml and 200 ml of benzene was added. The brown-black polymer was filtered off, washed with benzene, and dried at 60°C/0.1 mm/2 hours. Yield 1.22 g. The product is soluble in dimethylformamide, dimethylacetamide, and concentrated sulfuric acid at room temperature. The product was extracted with acetone for 48 hours. Its infrared spectrum is shown in Figure 45.

Anal. Calc'd for $(C_{24}H_{22}O_4N_6)_n$, LXV:

%C, 62.87; %H, 4.84; %N, 18.33

Found:

%C, 63.55; %H, 4.60; %N^D, 18.03

D-Nitrogen by the Dumas Method.

t. Reaction Between 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I, and Diaminobenzidine, XXIII, in Trimethylene Glycol Dimethyl-ether.

A mixture from 1.23 g of 2,7-dimethyl-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, I, (0.005 mole), 1.03 g of diaminobenzidine, XXIII (0.005 mole), and 40 ml of trimethylene glycol dimethylether was heated at 300°C in a slow stream of nitrogen for 24 hours. The product was then filtered off, washed with ether, and dried. Yield, 2.07 g. The product was Soxhlet extracted with dioxane for eight days. Then the orange polymer was extracted with six 100 ml portions of hot dimethylformamide. The filtrates appear to be substantially colored indicating some solubility in this solvent. The insoluble product was filtered off and dried at 100°C/0.05 min/18 hours. Yield, 0.32 g. Its infrared spectrum is shown in Figure 46.

Anal. Calc'd for $C_{24}H_{22}O_4N_6$, LXV:

%C, 62.87; %H, 4.84; %N, 18.33

Found:

%C, 61.10; %H, 4.89; %N, 17.52

More of the polymer, LXV, was obtained as a fine brown powder when the dimethylformamide filtrates were concentrated to a volume of 30 ml by distilling off the solvent. This clear brown liquid was diluted with 200 ml of benzene to give a brown precipitate. The product was filtered off, washed with benzene, and dried at 100°C/0.05 mm. Yield, 0.23 g.

u. Reaction Between 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I, and Diaminobenzidine, XXIII, in Diethyl Cellosolve

A mixture of 1.22 g of 2,7-dimethyl-[4H, 9H], 3,1,8,6-benzobisoxazine, I, (0.005 mole), 1.07 g of diaminobenzidine, XXIII, and 250 ml of diethyl cellosolve was stirred at 130 - 150°C for 18 hours. The reaction mixture was cooled and the brown solid product was filtered off and dried at 100°C/0.1 mm. Yield 1.33 g. The polymer was soluble in dimethylformamide. Its infrared spectrum is shown in Figure 47.

Anal. Calc'd for $C_{24}H_{22}O_4N_6$, LXV:

%C 62.87; %H, 4.84; %N, 18.33

Found:

%C, 63.23; %H, 5.11; %N^K, 15.14

K-Nitrogen by the Kjeldahl Method.

v. Reaction Between 2,7-Dimethyl- [4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I, and Diaminobenzidine, XXXIII, in Molten Benzophenone

A mixture of 2,7-dimethyl- [4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, I; 1.071 g of diaminobenzidine, XXXIII; and 50 g of benzophenone were heated under nitrogen at 310°C for 168 hours. The mixture was cooled to 60°C and added to 500 ml of petroleum ether. The brown product was filtered off, and then washed with petroleum ether and benzene. Subsequently the product was Soxhlet extracted with benzene for four days and dried at 110°C/0.01 mm. Yield, 1.05 g. Its infrared spectrum is shown in Figure 48.

Anal. Calc'd for $(C_{37}H_{28}O_3N_6)_n$, LXVIII:

%C, 73.49; %H, 4.64; %N, 13.93

Found:

%C, 73.79; %H, 3.97; %N^D, 14.21

Concentration of the benzene extracts to 100 ml followed by cooling gave a yellow product. Yield, 0.96 g. Its infrared spectrum is shown in Figure 49. Its molecular weight was found to be 1559 by the VPO method in dimethylformamide.

Anal. Calc'd for $(C_{37}H_{24}ON_6)_n$, LXIX:

%C, 78.15; %H, 4.26; %N, 14.80

Found:

%C, 76.84; %H, 5.00; %N^D, 15.59

D-Nitrogen by the Kjeldahl Method.

w. Reaction Between 6,6'-Bis-(2-Trifluoromethyl-[4H]), 3,1-Benzoxazine-4-One), XXXVIII, and Diaminobenzidine, XXIII, in Molten Benzophenone

A solution was prepared from 35 g of molten benzophenone at 90°C and 0.53 g of diaminobenzidine, XXIII. Then 1.07 g of 6,6'-bis-(2-trifluoromethyl-[4H]), 3,1-benzoxazine-4-one), XXXVIII, was added. The compound did not readily dissolve. The temperature was increased gradually and a slow stream of nitrogen was passed through the apparatus. In 30 minutes the temperature reached 200°C, and the liquid became clear. The mixture was heated for six days at 260°C under nitrogen, then cooled, and stirred into 400 ml of petroleum ether. The dark product was filtered off and extracted with acetone in a Soxhlet apparatus for 24 hours, then with dioxane for 24 hours. The product was dried at 100°C/0.1 mm. Yield, 1.4 g. It was insoluble in dimethylformamide, dimethyl sulfoxide, concentrated sulfuric acid, or methane sulfonic acid. Its TGA curve is shown in Figure 50 and its infrared spectrum is shown in Figure 51.

Anal. Found ----- %C, 73.69; %H, 3.89; %N^D, 11.25; %F, 4.28

SECTION IV

CONCLUSIONS

1. 2-methyl-[4H], 3,1-benzoxazine-4-one, XXIV, when heated in the melt under nitrogen at 300°C appears to decompose with loss of $C_2H_6O_2$. The resulting product, XLIX, m p 79 - 81°C apparently has a molecular formula approaching $C_{16}H_8O_2N_2$. When the reaction was run in molten benzophenone at 300°C, XLIX was obtained along with a by-product, LI. The identities of XLIX and LI have not clearly been established.

2. When difunctional 2-alkyl substituted benzoxazinones such as 2,7-dimethyl-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, I, or 6,6'-bis-(2-methyl-[4H], 3,1-benzoxazine-4-one), XXVII, are heated at 300°C in a melt reaction, or in solution in sulfolane or in molten benzophenone, what appears to be a rearrangement followed by further condensation takes place. The resulting products are insoluble, highly condensed cross-linked polymers whose empirical formulae are the same as the starting materials from which they were prepared. When 2,7-bis-(trifluoromethyl)-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, XXXVI, or 6,6'-bis-(2-trifluoromethyl-[4H], 3,1-benzoxazine-4-one), XXXVIII were similarly treated, the reactions were apparently accompanied by loss of hydrogen fluoride. The resulting polymeric products were either cross-linked, or of low molecular weight.

3. 2-methyl-[4H], 3,1-benzoxazine-4-one, XXXIV, reacted with methyl anthranilate in refluxing xylene to give 2-methyl-3-(o-carboxymethyl)-phenyl quinazoline-4-one, LX, as the chief product.

4. 2,7-dimethyl-[4H, 9H], 3,1,8,6-benzobisoxazine-4,9-dione, I, condenses with equimolar quantities of 2,5-diaminoterephthalic acid, XLI, or its diethyl ester, XXX, at 200 - 300°C in sulfolane or in diphenylether to give the corresponding quinazolone polymers, LXII or LXIV, with inherent viscosities in the 0.24 range. The thermal stability of these polymers appears to be good.

5. When 2,7-dimethyl-[4H, 9H]-3,1,8,6-benzobisoxazine-4,9-dione, I, was condensed with equimolar quantities of 3,3'-diaminobenzidine, XXXIII, in solution in dimethylformamide, diethyl cellosolve, or trimethylene glycol dimethylether at 120 - 310°C, a linear polyamide $(C_{24}H_{22}O_4N_6)_n$, LXV, appears

to be the chief product of the reaction. The presence of a polymer of the quinazolone structure, LXVI, or the benzimidazo-[1,2c]-quinazoline structure was not demonstrated. When the reaction was carried out in molten benzophenone at 310°C, the polymeric product had apparently reacted with benzophenone in some way. These products were difficult to characterize. When 6,6'-bis-(2-trifluoromethyl-[4H],3,1-benzoxazine-4-one), XXXVII, was heated with diaminobenzidine, XXIII in molten benzophenone at 260°C, a low molecular weight material, LXX, containing very little fluorine, was obtained. TGA results indicate that the product possesses a fairly high degree of thermal stability.

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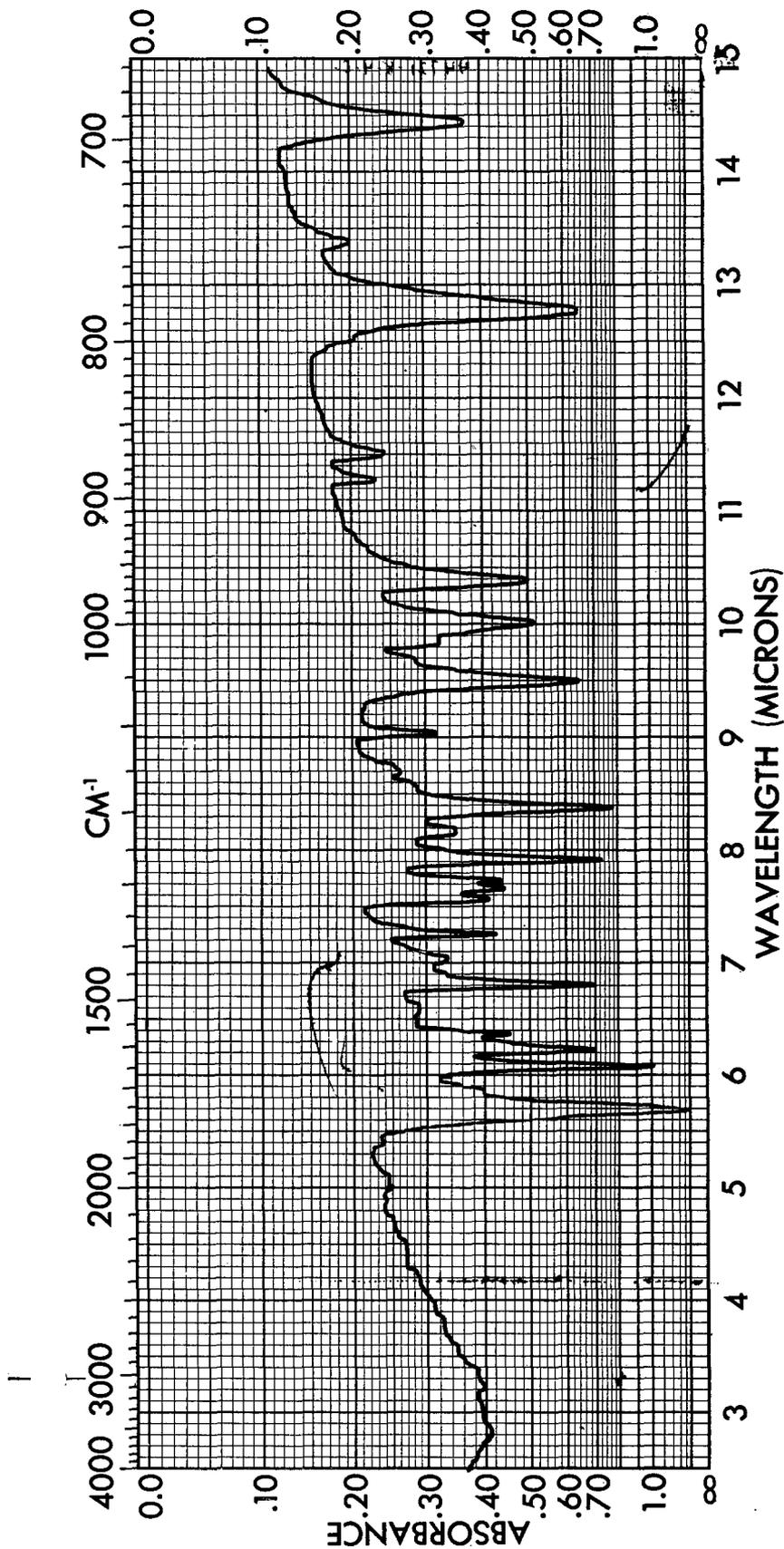


Figure 12. Infrared Spectrum of 2-Methyl-3,1-benzoxazine-4-one, XXXIV

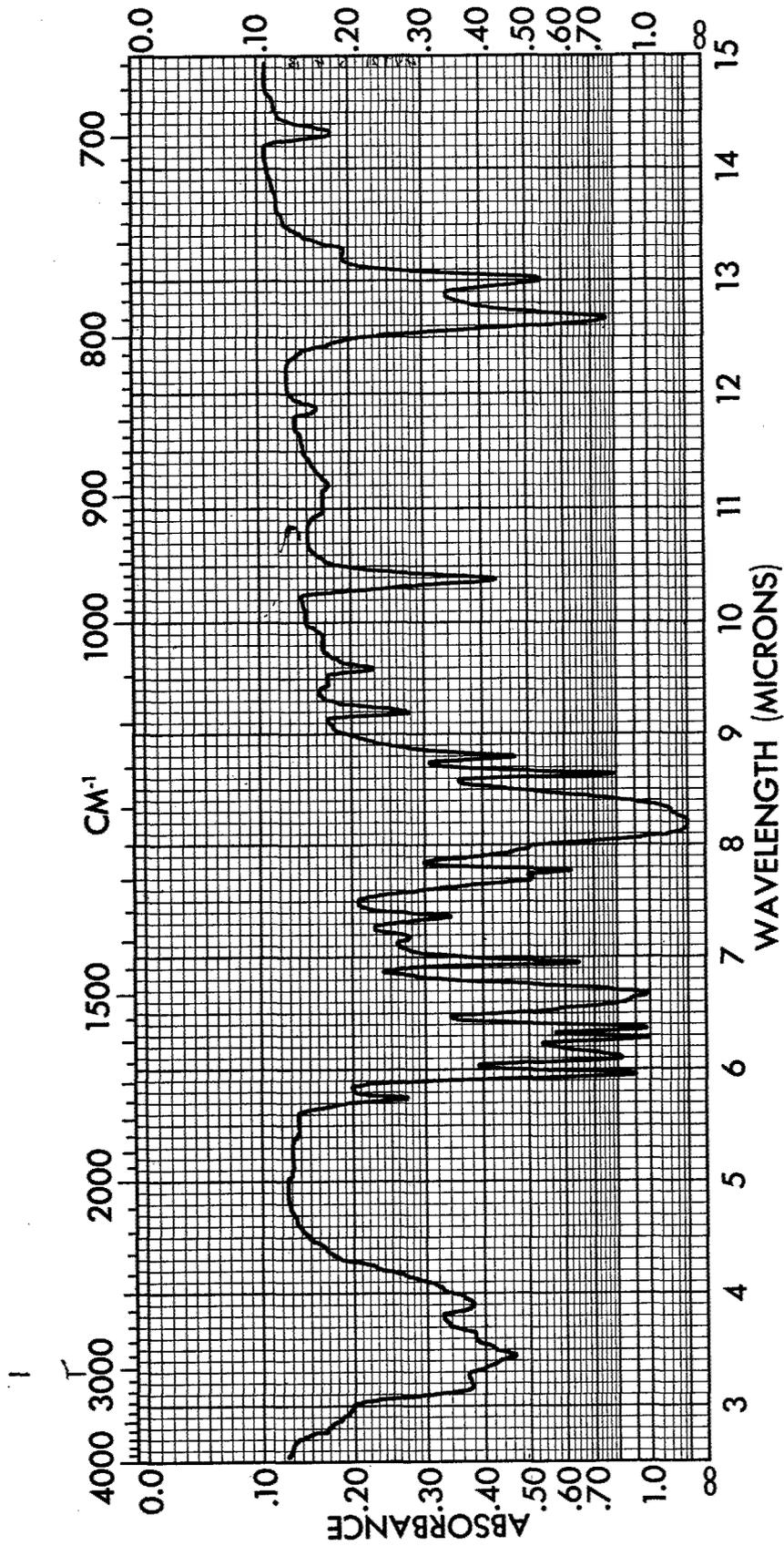


Figure 13. Infrared Spectrum of N-acetylanthranilic Acid, XXXIX

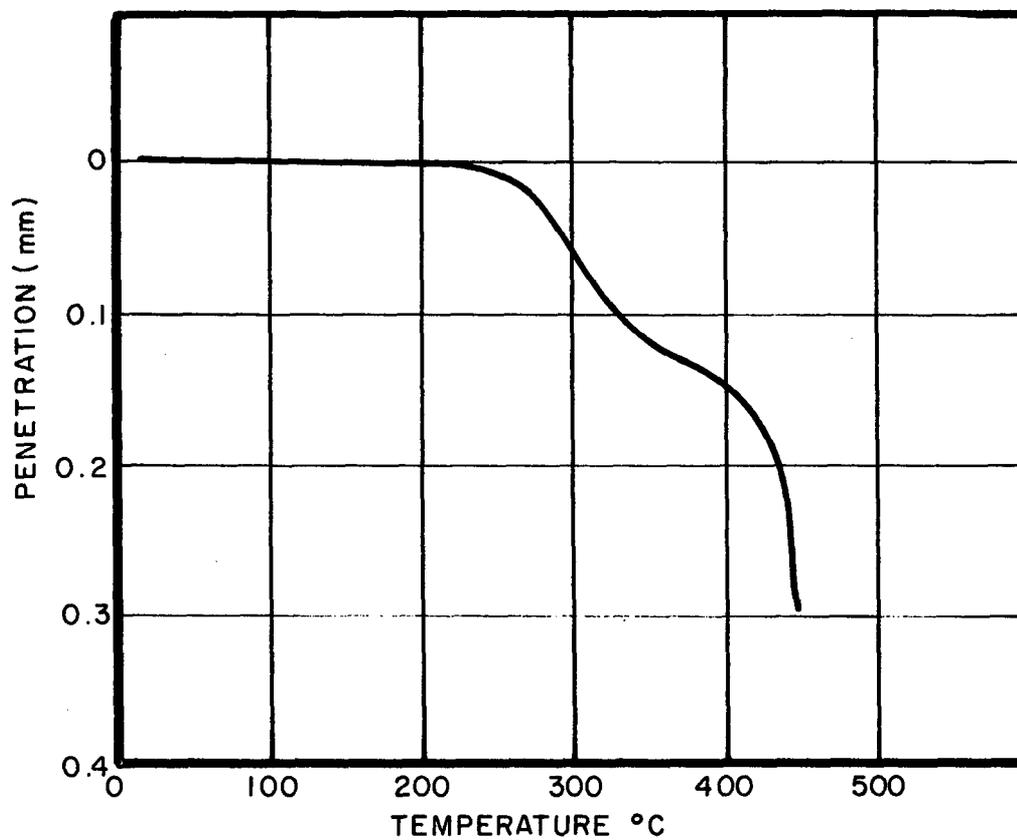


Figure 14. Softening Point Curve of 2,5-(N,N'-Diformylamino)-Terephthalic Acid XLII

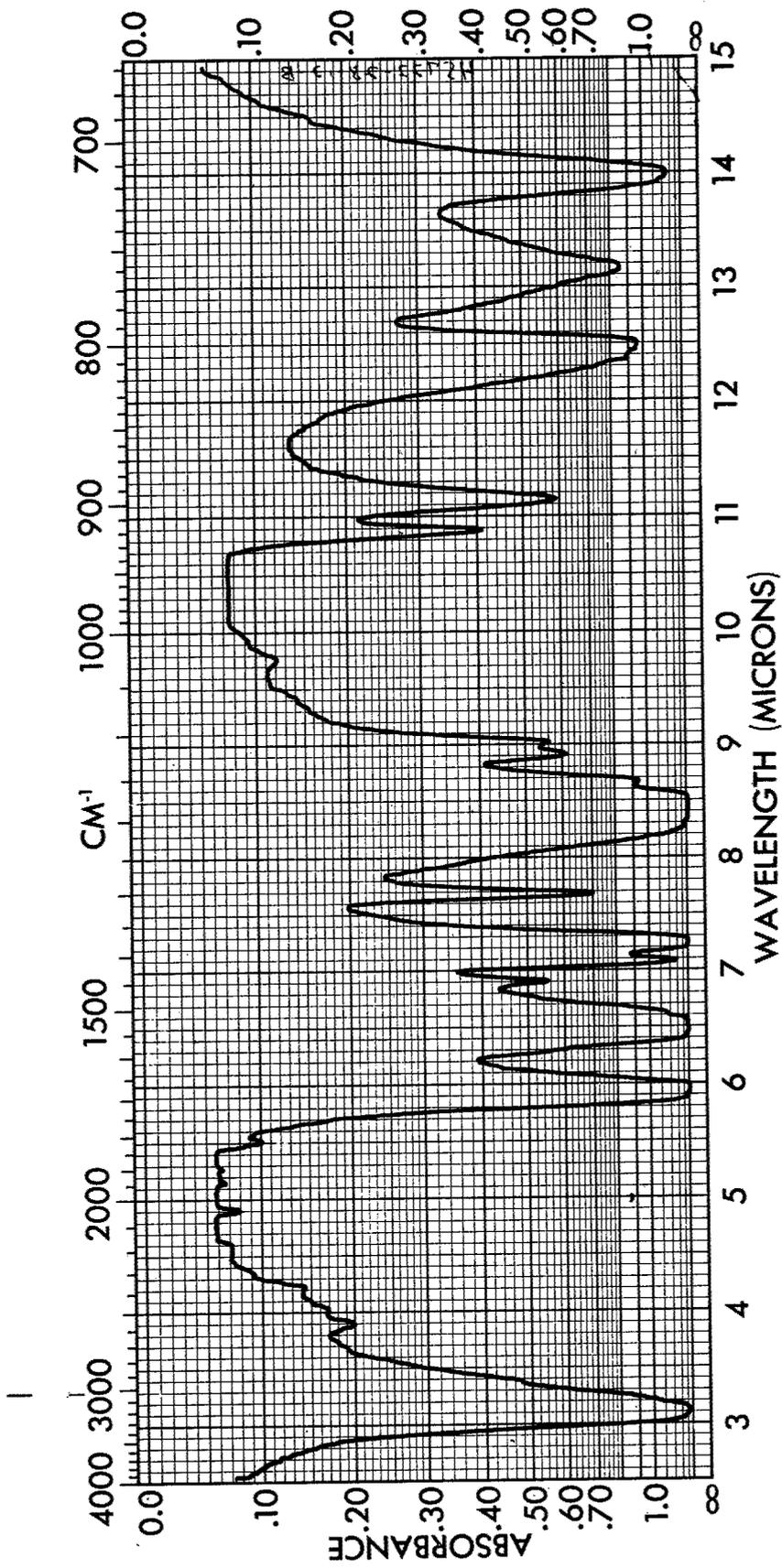


Figure 15. Infrared Spectrum of 2,5-(N,N'-Di-formylamino)-Terephthalic Acid, XLI

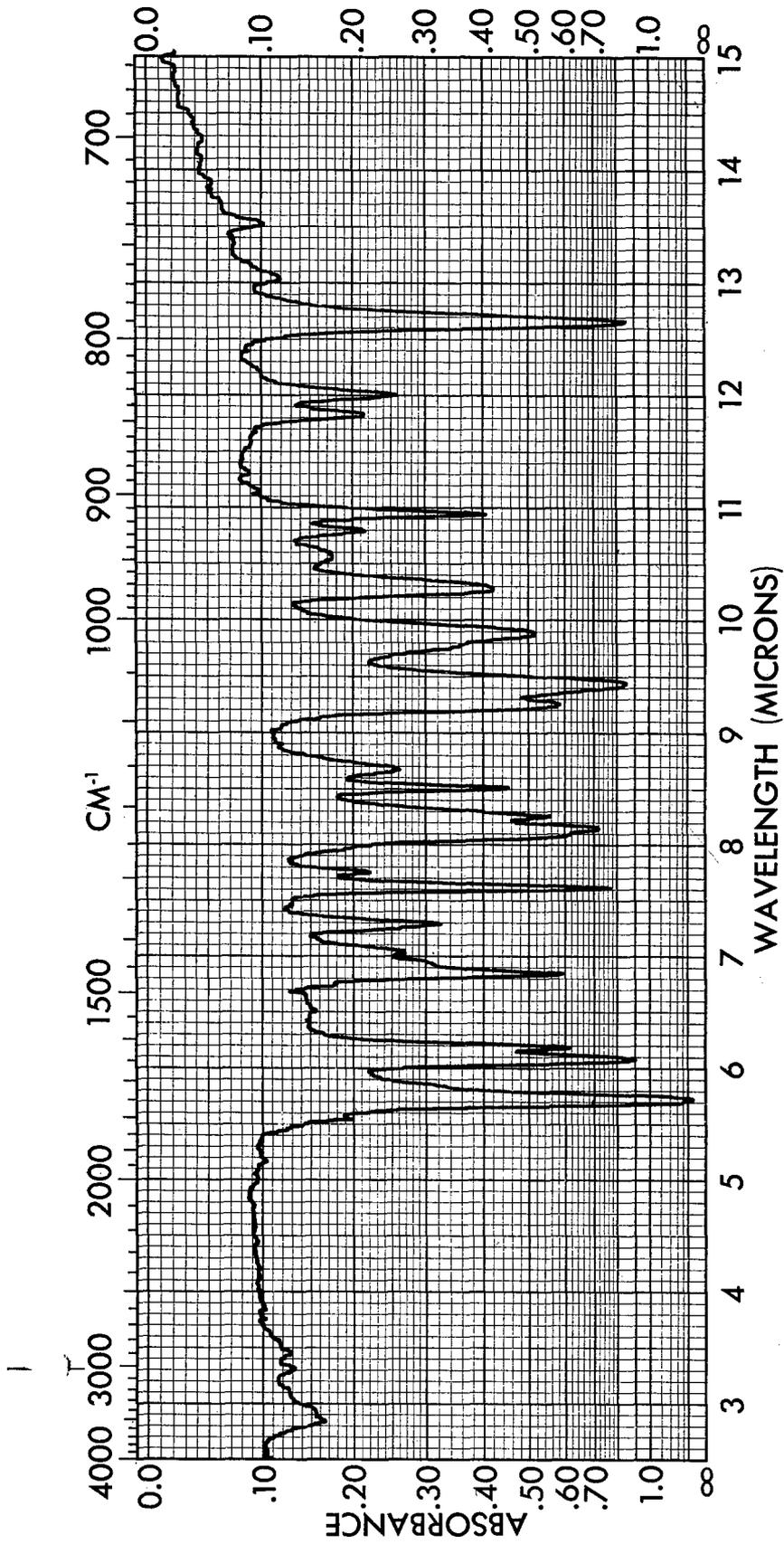


Figure 16. Infrared Spectrum of [4H, 9H], 3, 1, 8, 6-Benzobisoxazine-4, 9-Dione, XLIII

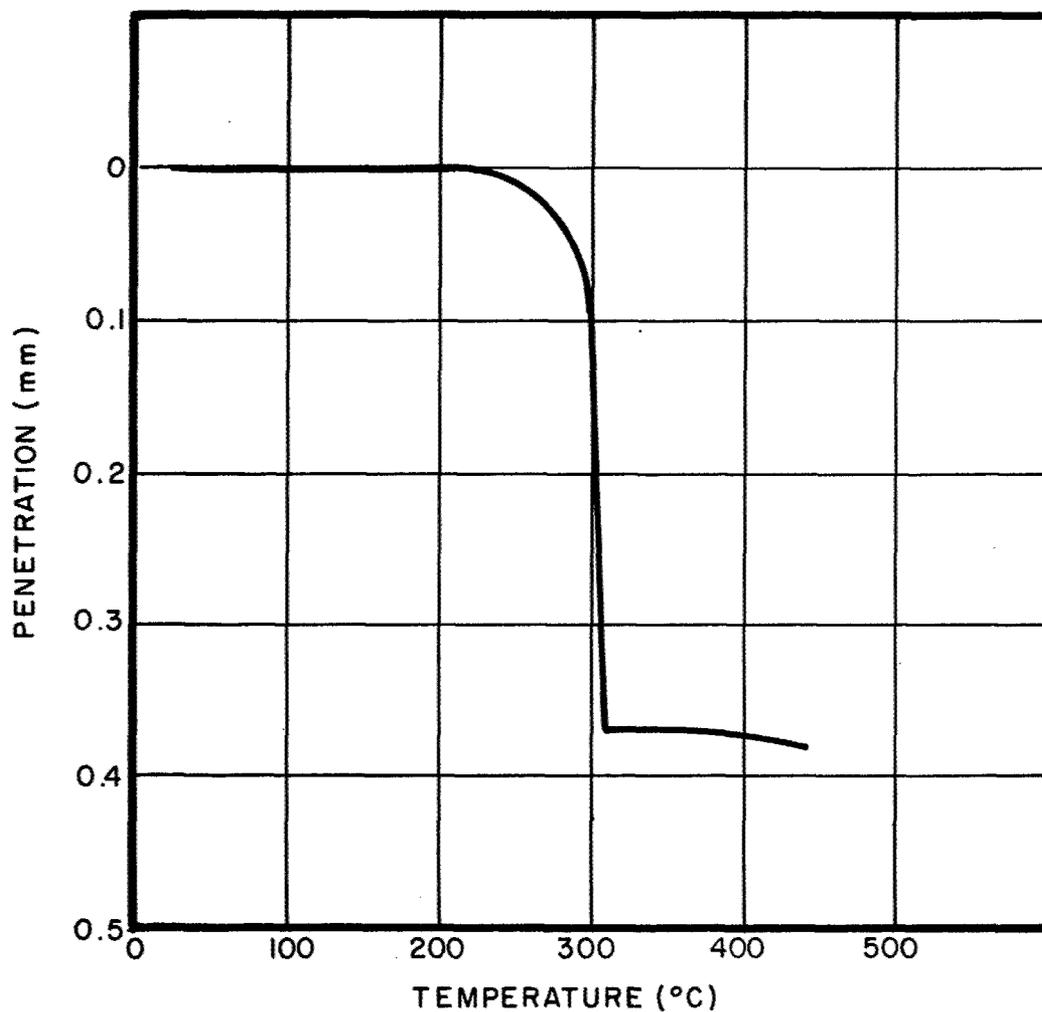


Figure 17. Softening Point Curve of 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I

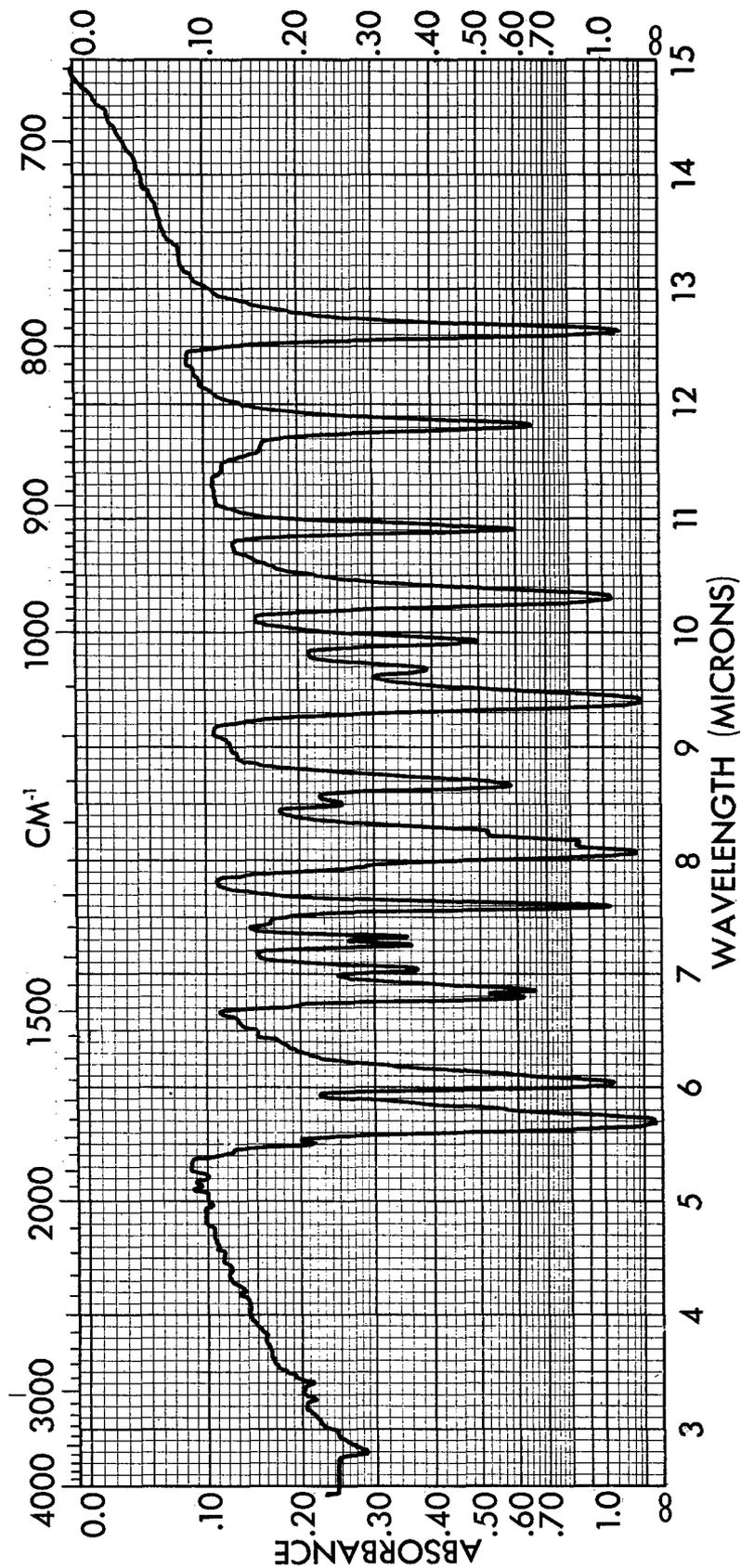


Figure 18. Infrared Spectrum of 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I

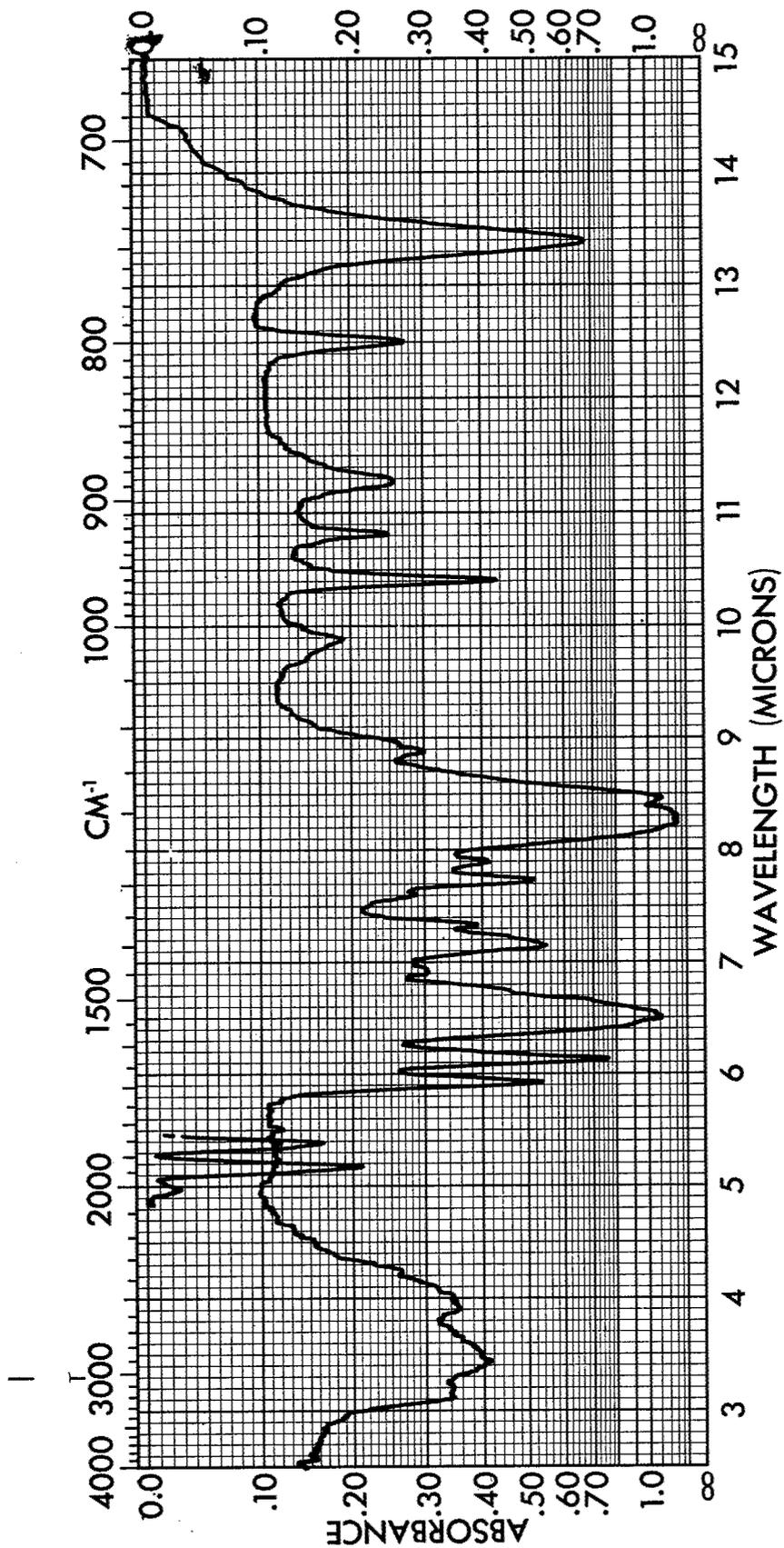


Figure 19. Infrared Spectrum of 2,5-(N,N'-Diacetylamino)-Terephthalic Acid, XLIV

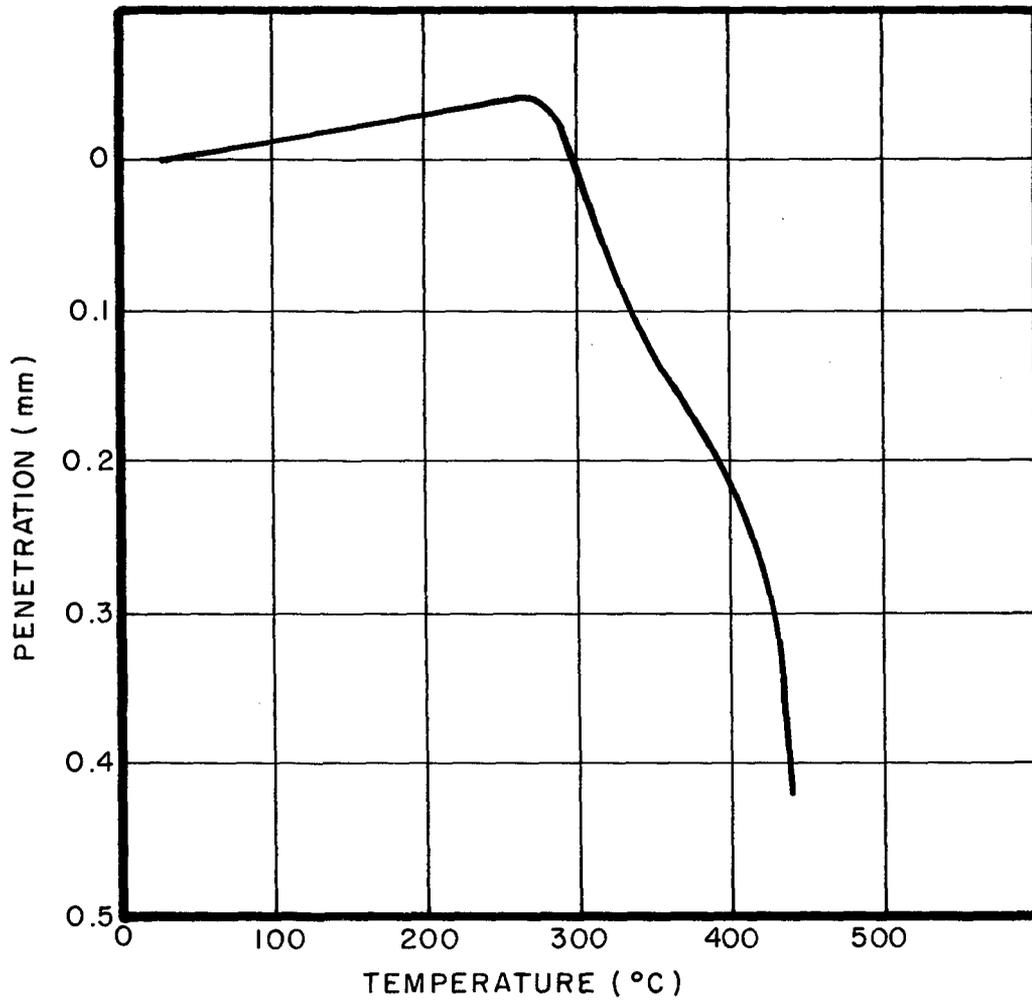


Figure 20. Softening Point Curve of 2,5-(N,N-Diacetylamino)-Terephthalic Acid, XLIV

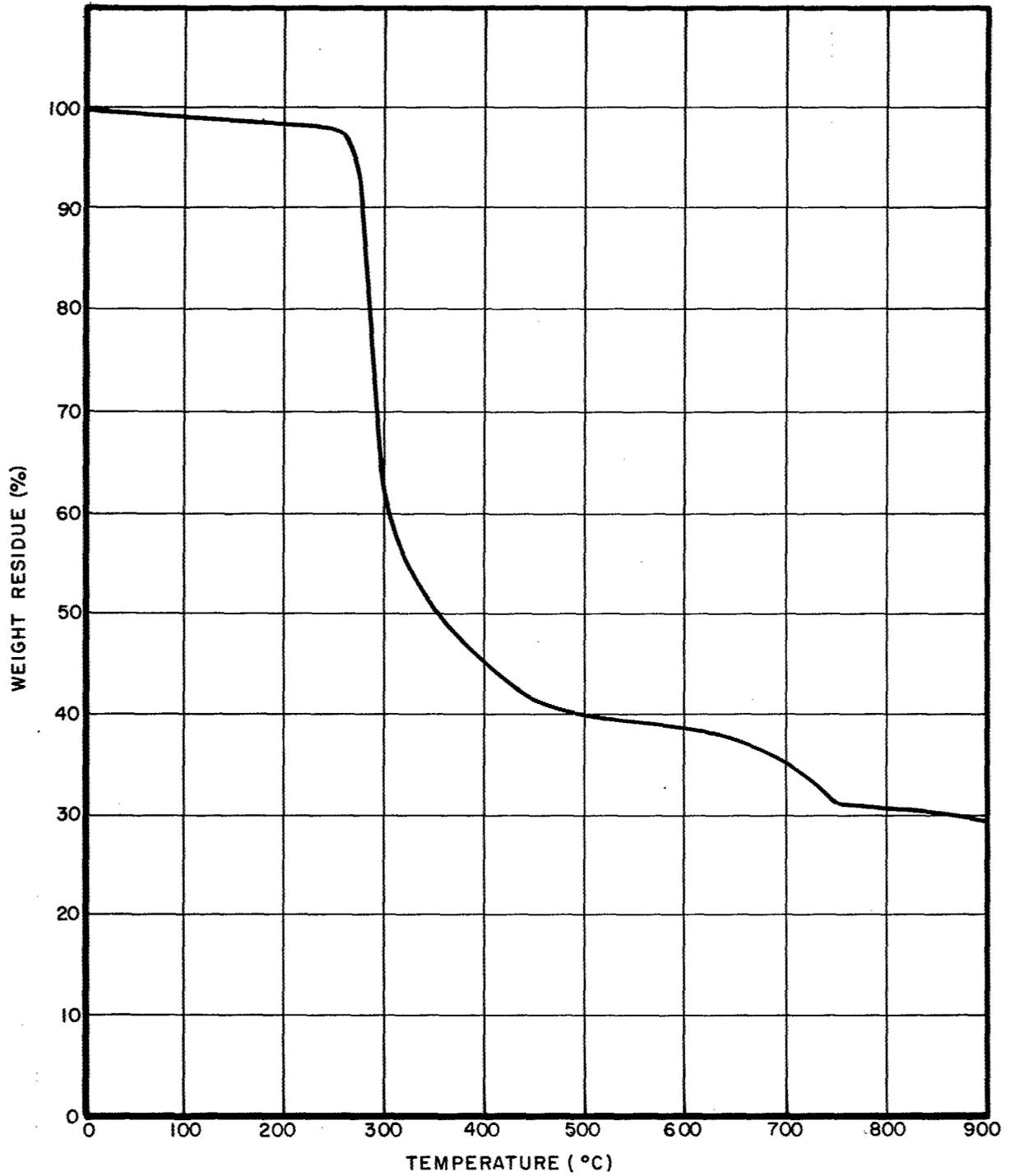


Figure 21. TGA Curve of 2,5-(N,N'-Diacetylamino)-Terephthalic Acid, XLIV

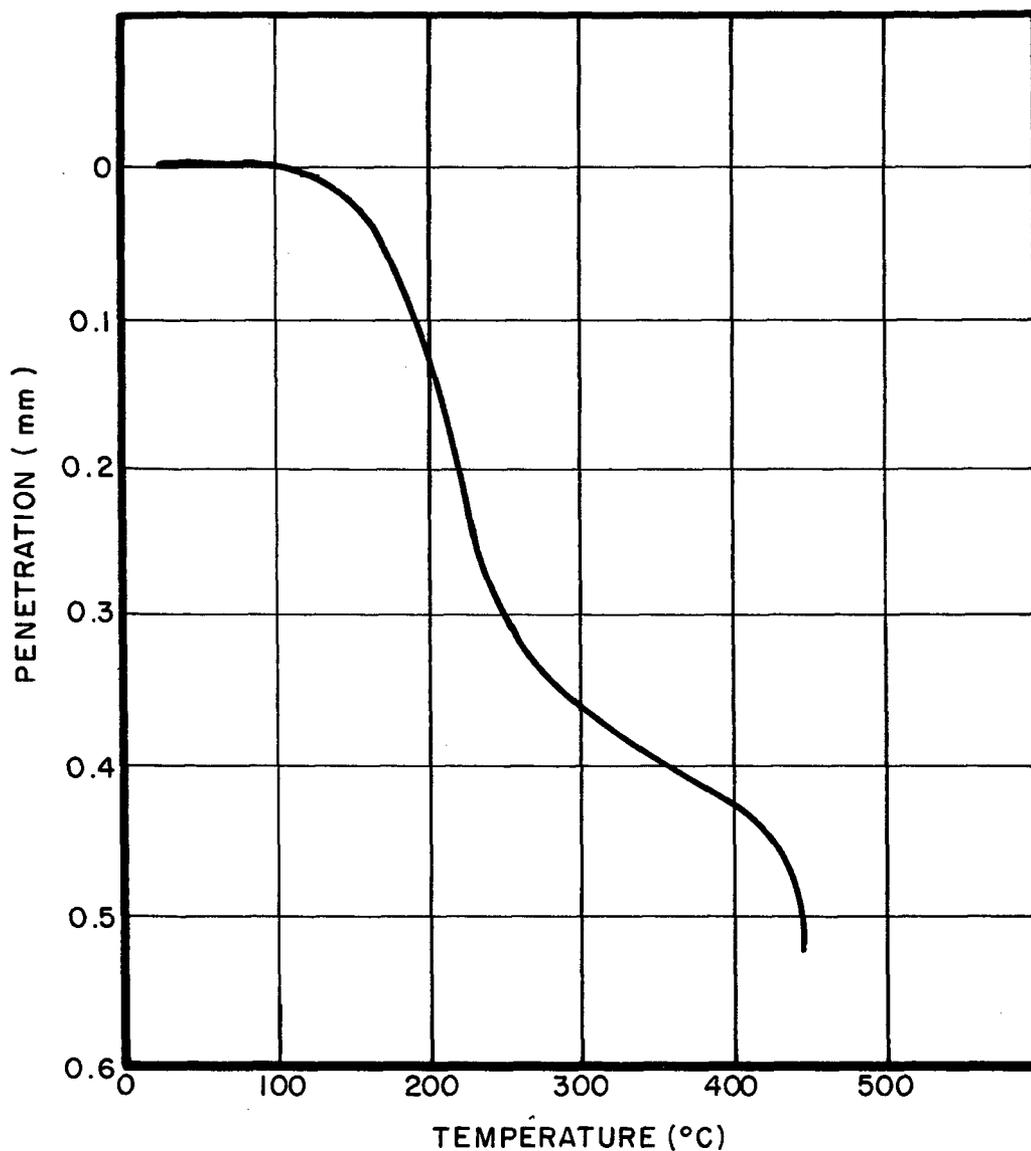


Figure 22. Softening Point Curve of 2,5-(N,N'-Dicarbethoxyamino)-Terephthalic Acid, XLV

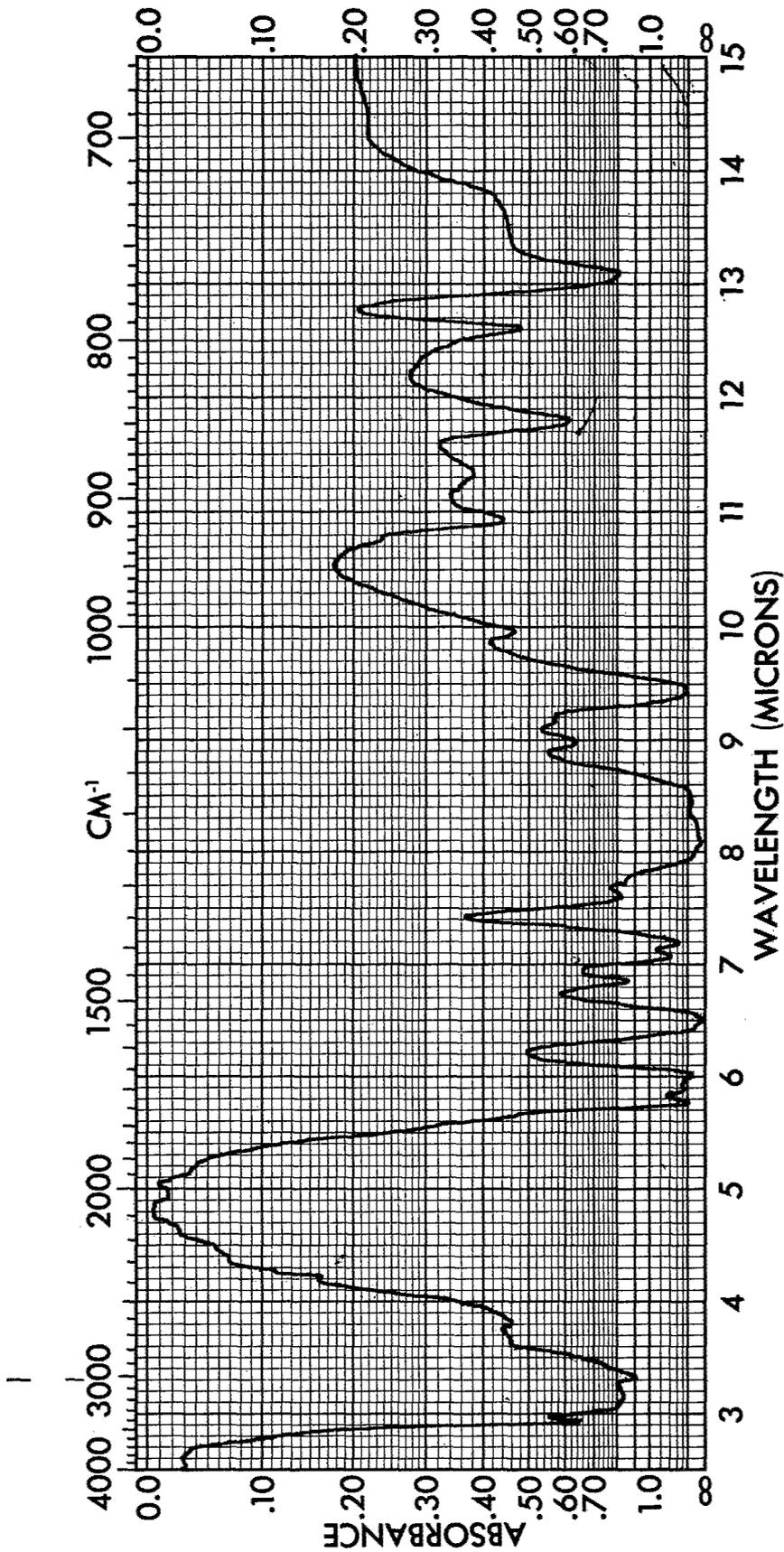


Figure 23. Infrared Spectrum of 2,5-(N,N'-Dicarbethoxyamino)-Terephthalic Acid, XLV

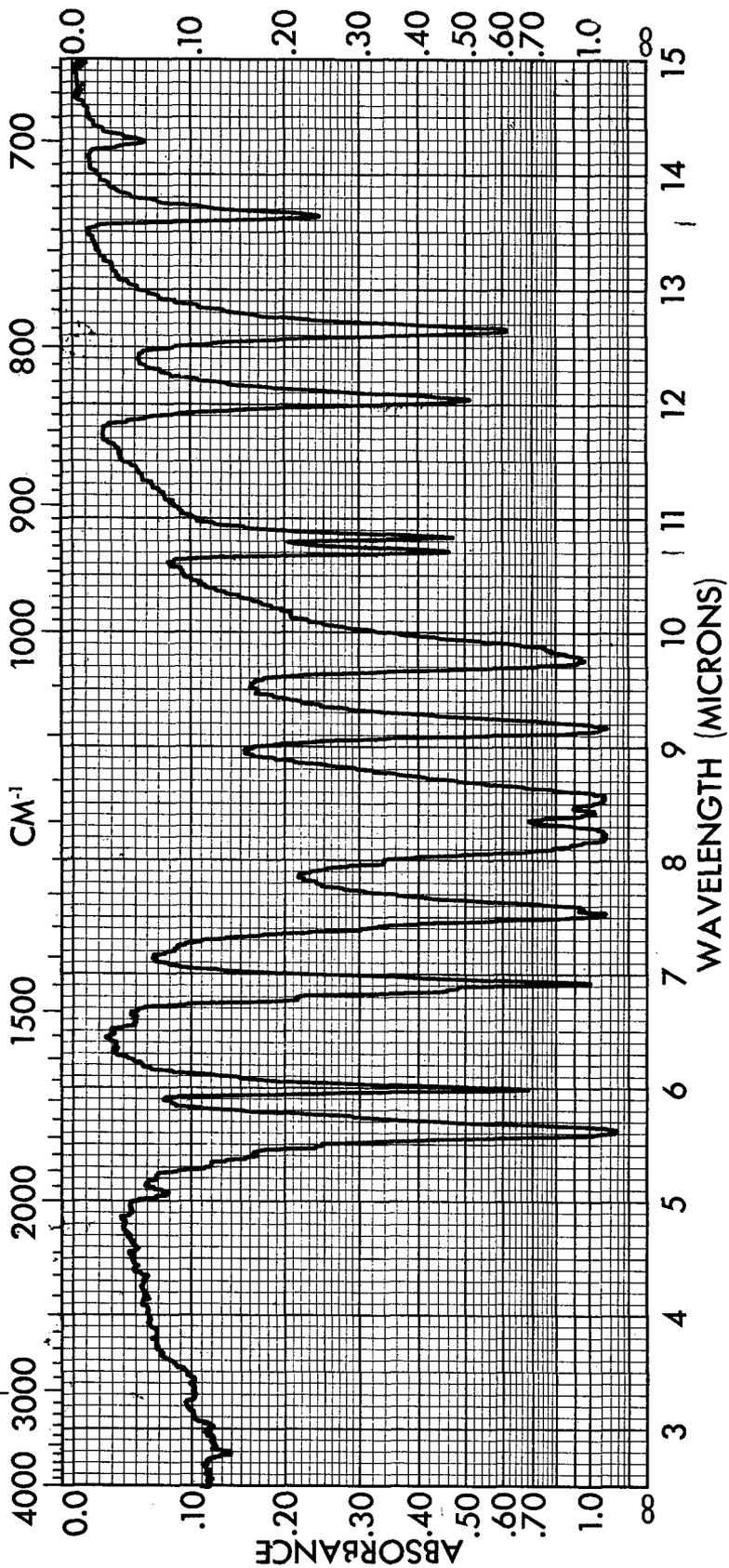


Figure 24. Infrared Spectrum of 2,7-Bis-(Trifluoromethyl)-[4H, 9H],
3,1,8,6-Benzobisoxazine-4,9-Dione, XXXVI

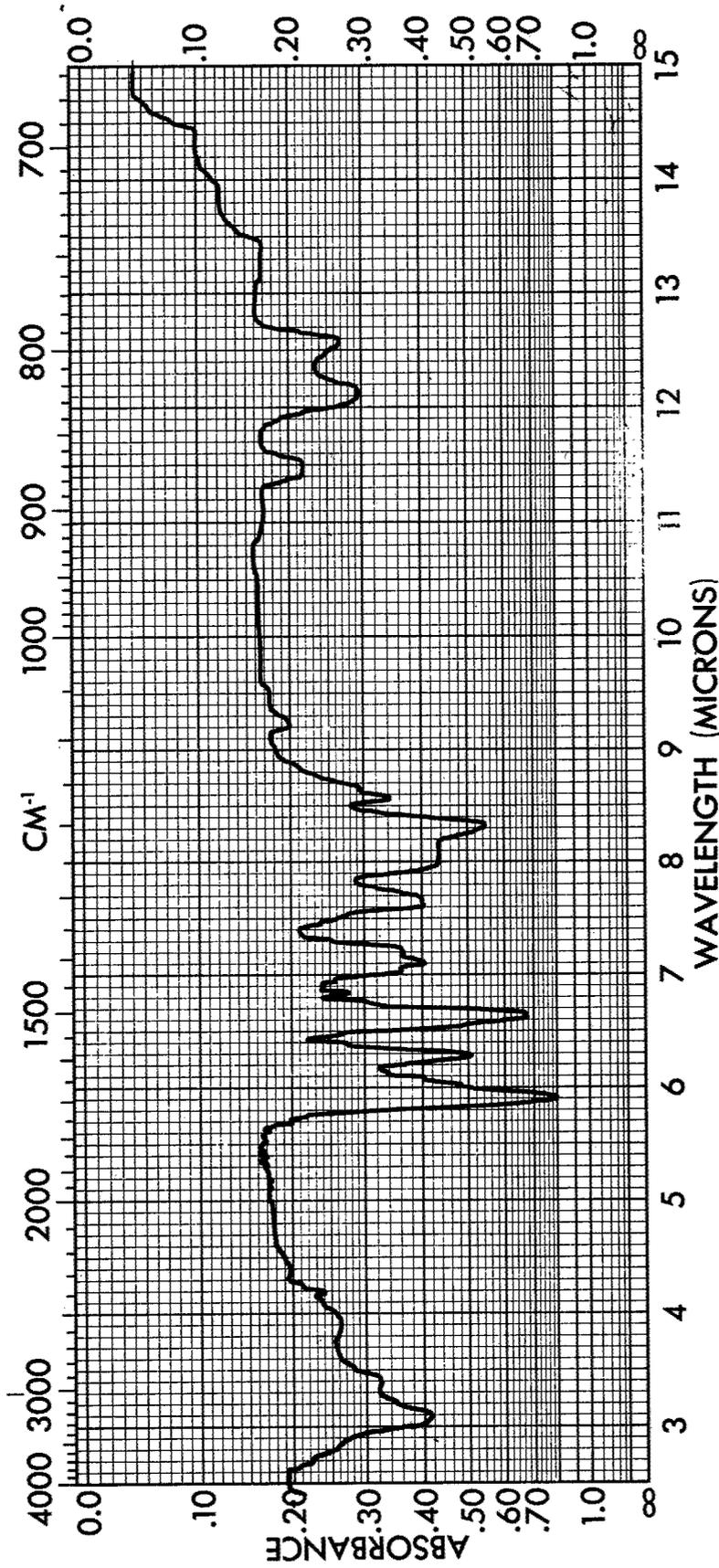


Figure 25. Infrared Spectrum of 4,4'-Diformylaminodiphenyl-3,3'-Dicarboxylic Acid, XLVII

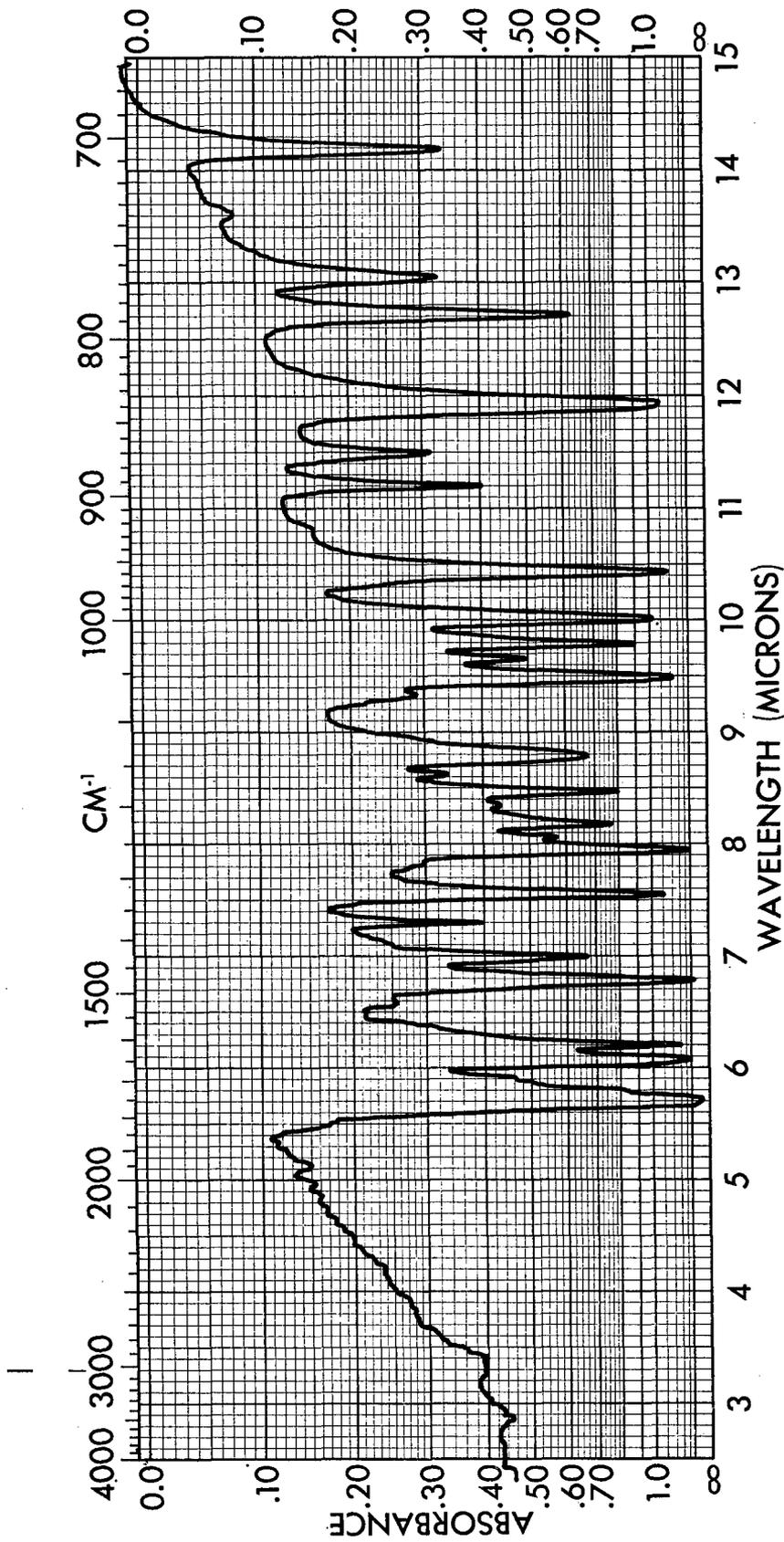


Figure 26. Infrared Spectrum of 6,6'-Bis-(4H),3,1-Benzoxazine-4-One),
XLVIII

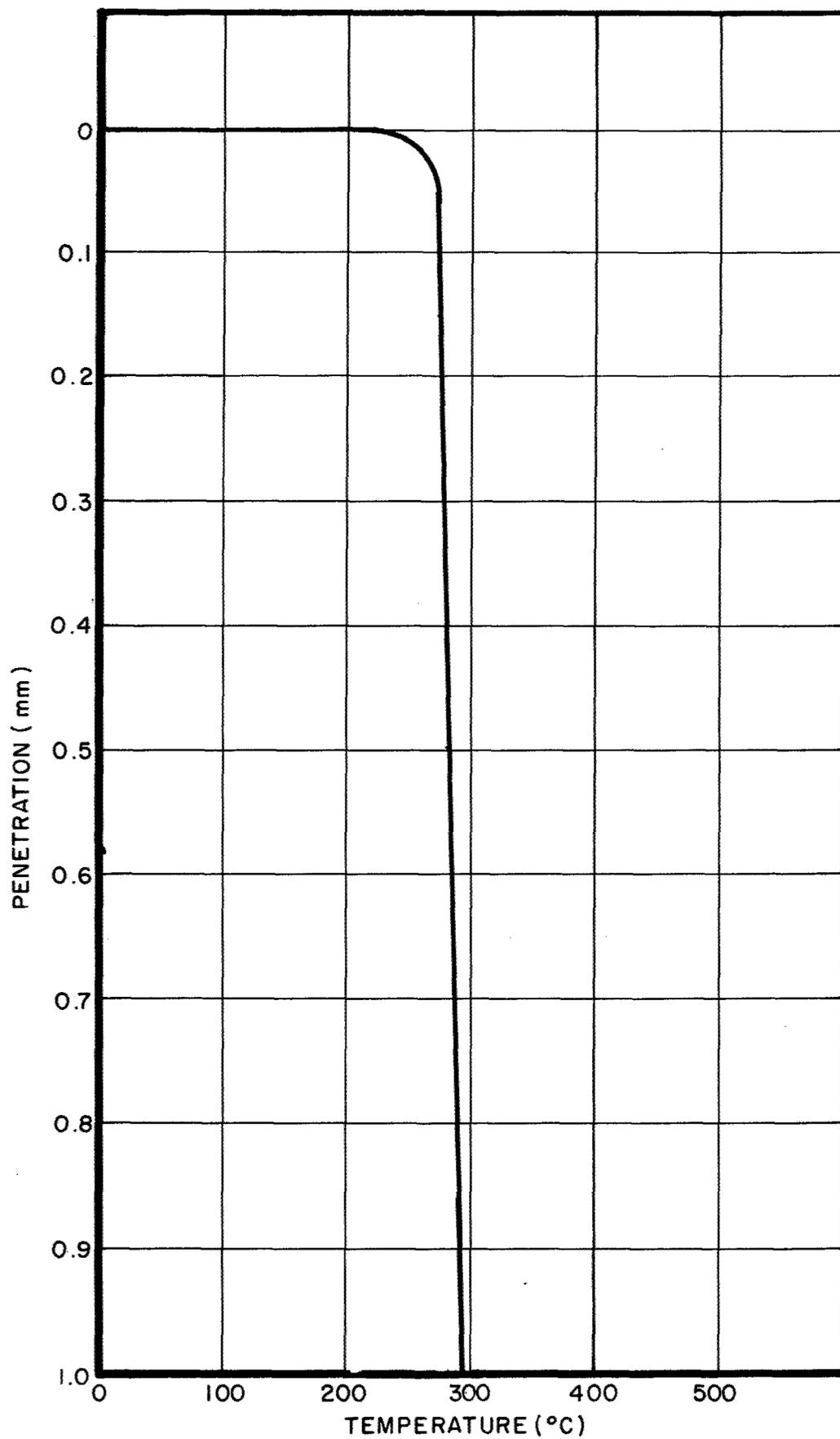


Figure 27. Softening Point Curve of 6,6'-Bis-(2-Methyl-[4H], 3,1-Benzoxazine-4-One), XXXVII

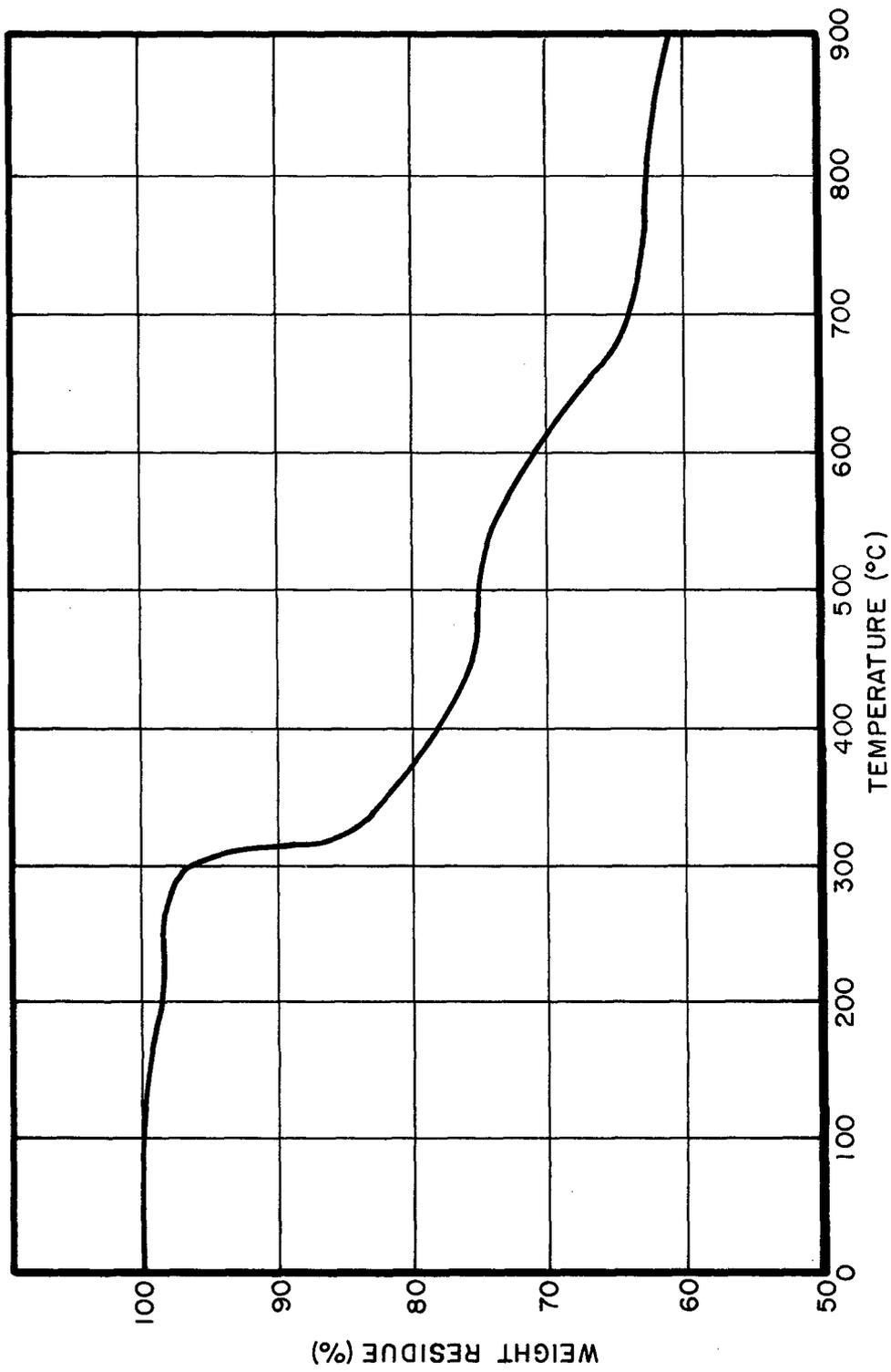


Figure 28. TGA Curve of 6, 6'-Bis-(2-Methyl-[4H], 3, 1-Benzoxazine-4-One), XXXVII

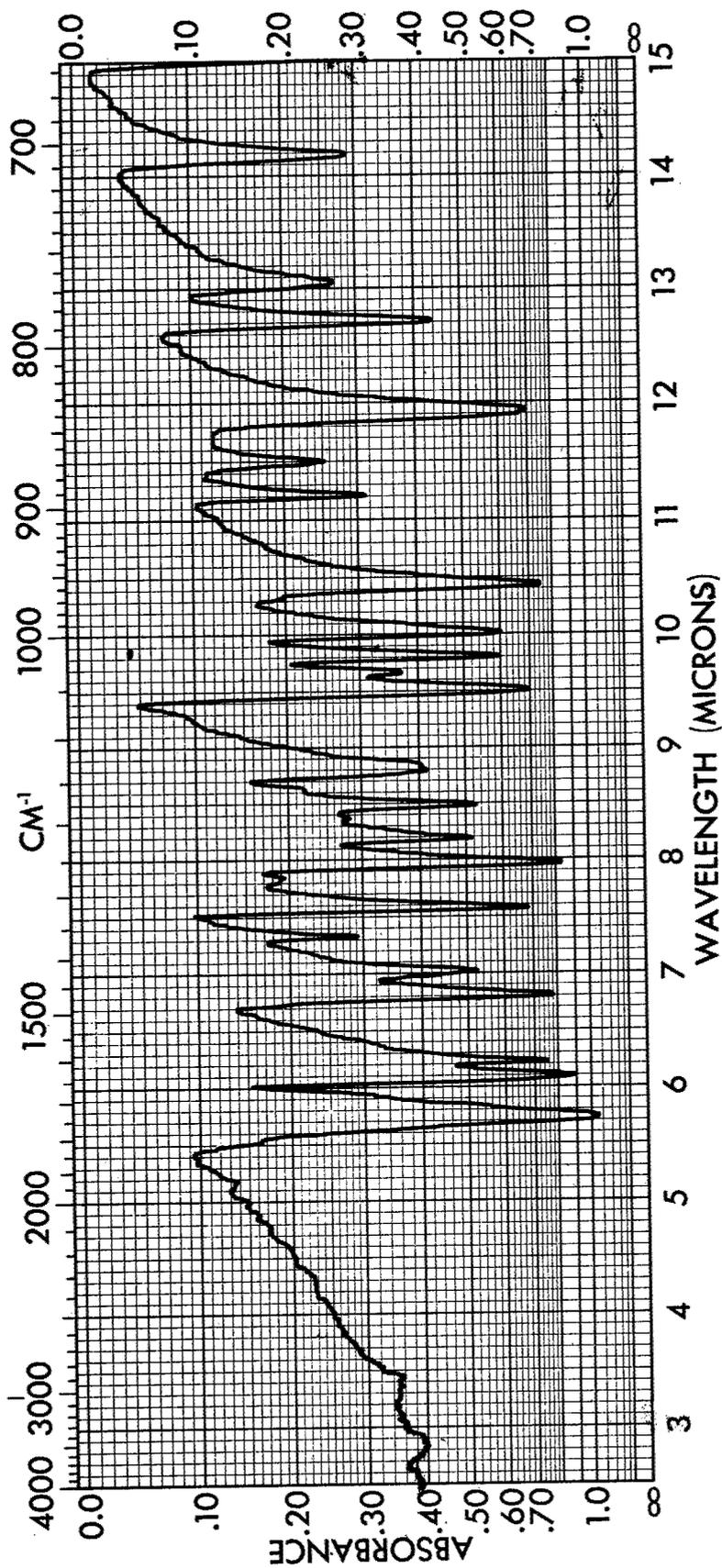


Figure 29. Infrared Spectrum of 6,6'-Bis-(2-Methyl-[4H],3,1-Benzoxazine-4-One), XXXVII

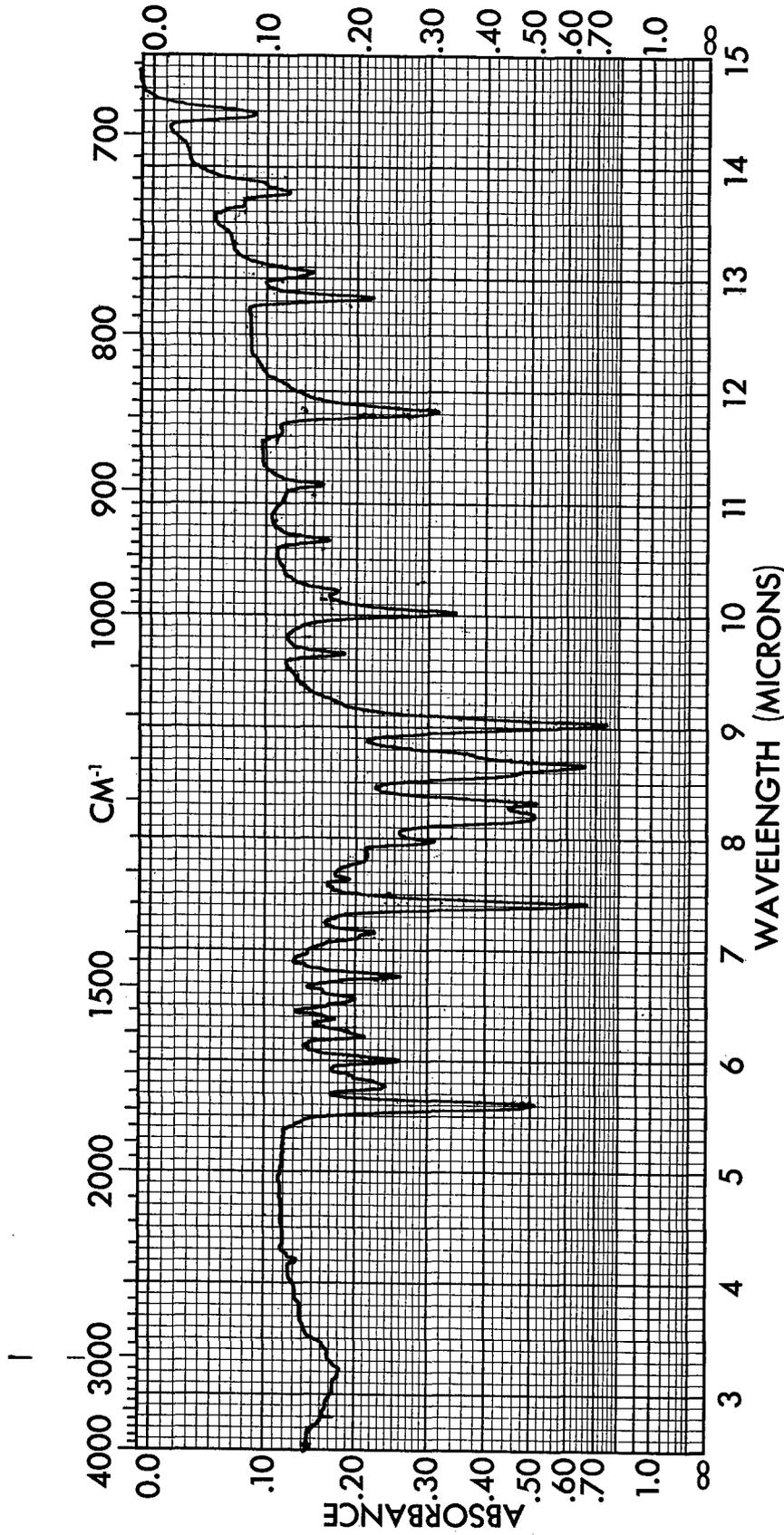


Figure 30. Infrared Spectrum of 6,6'-Bis-(2-Trifluoromethyl-[4H],3,1-Benzoxazine-4-One), XXXVIII

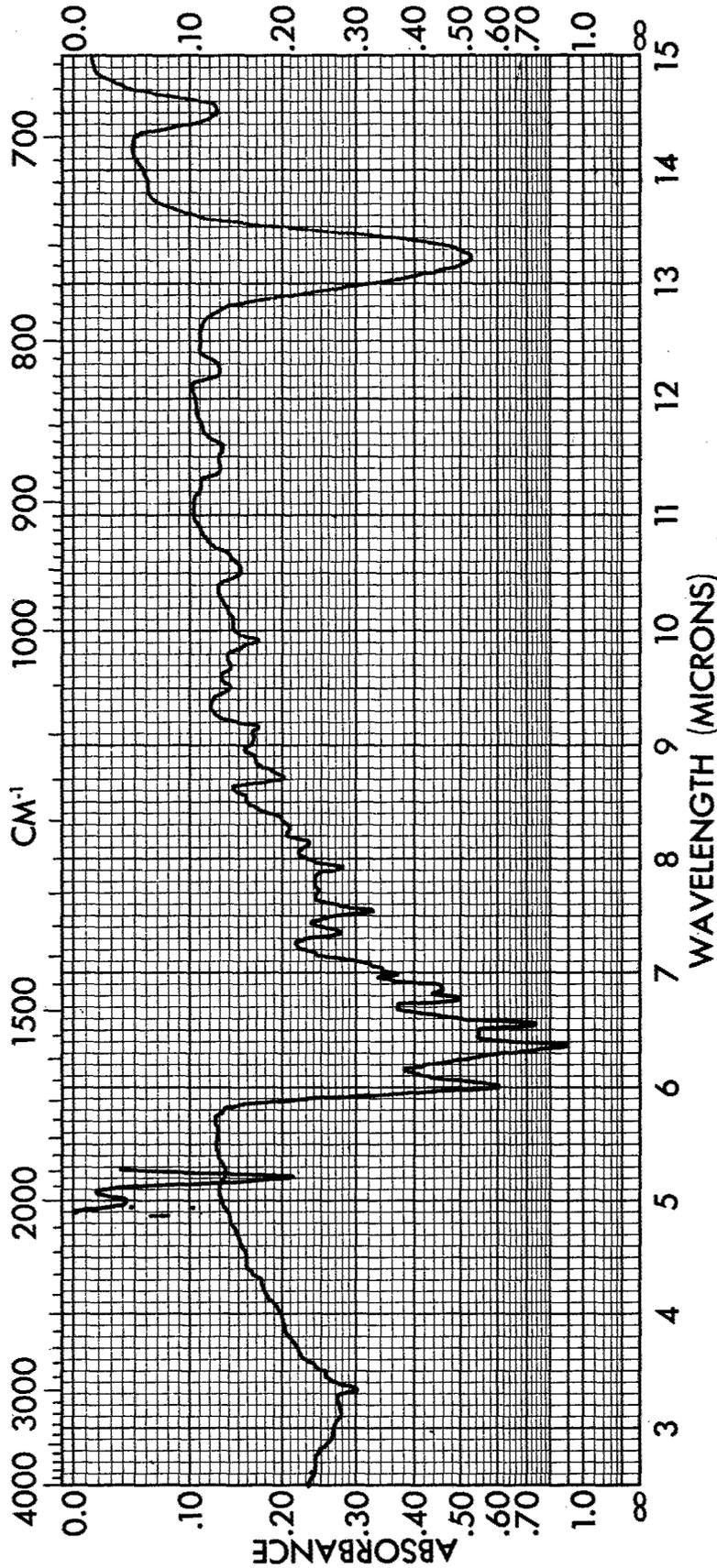


Figure 31. Infrared Spectrum of the Yellow Sublimate, $C_{16}H_{10}O_2N_2$, XLIX, from Melt Condensation of 2-Methyl-[4H], 3,1-Benzoxazine-4-One, XXXIV

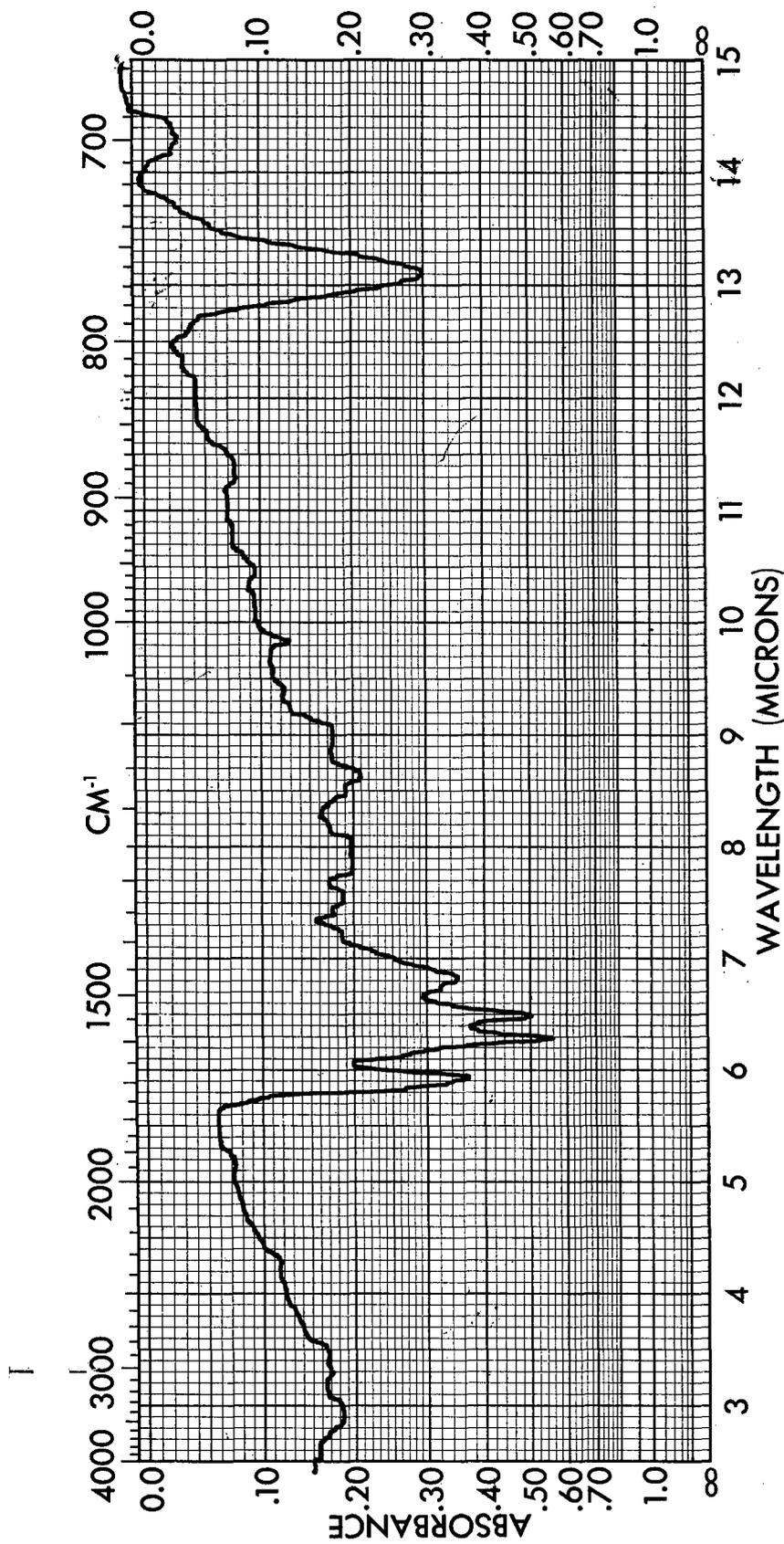


Figure 32. Infrared Spectrum of the Benzene-Soluble Product, $C_{18}H_{10}O_2N_2$,
 XLIX, from Solution Condensation of 2-Methyl-[4H], 3, 1-Benzoxa-
 zine-4-One, XXXIV

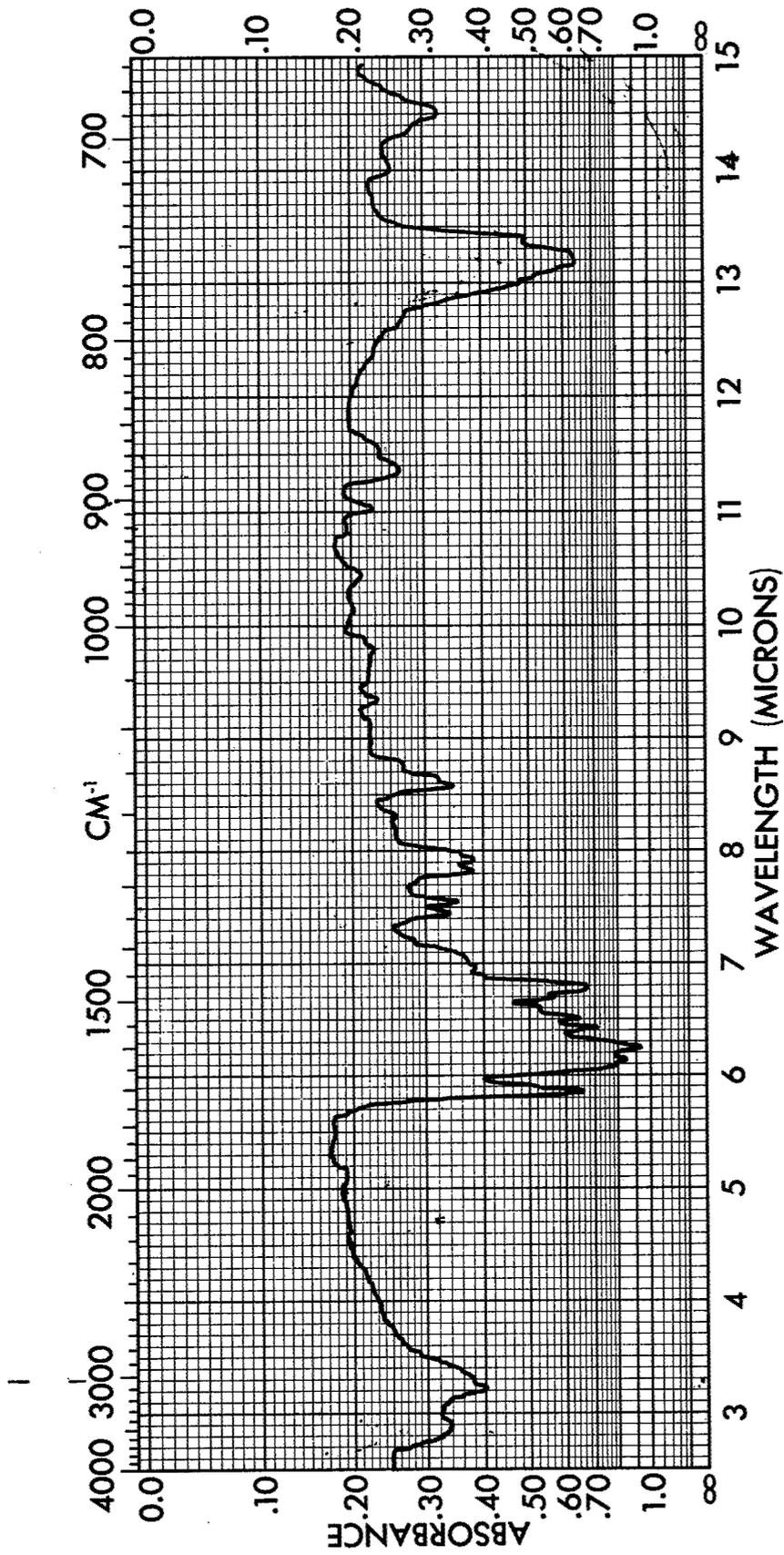


Figure 38. Infrared Spectrum of the Benzene-Insoluble Product LI, from Solution Condensation of 2-Methyl-[4H], 3,1-Benzoxazine-4-One, XXXXIV

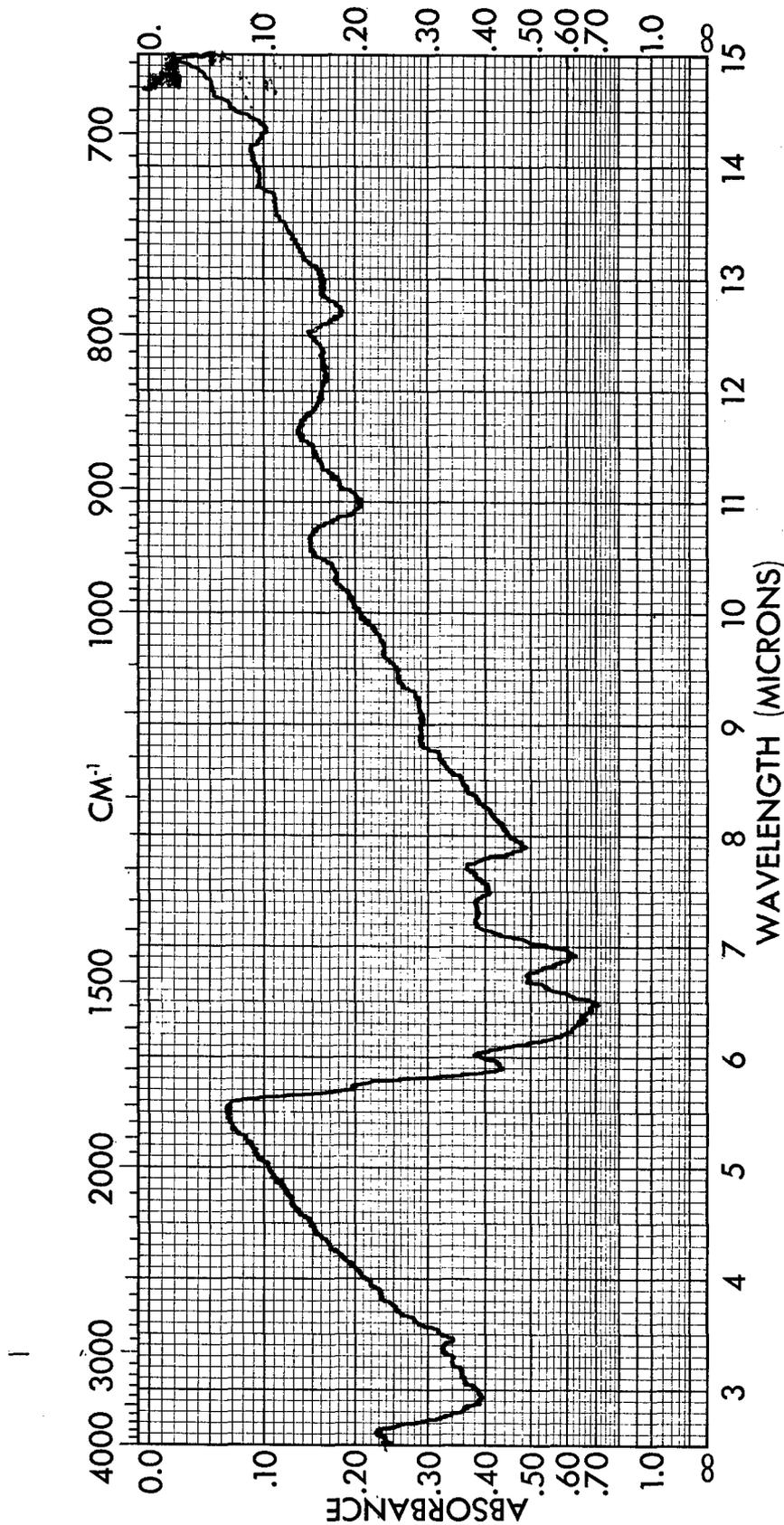


Figure 34, Infrared Spectrum of the Condensation Product, $C_{12}H_{18}O_4N_2$, LII, from 2,7-Dimethyl-[4H, 9H]-3,1,8,6-Benzobisoxazine-4,9-Dione, I, at 320 - 325°C in Sulfolane

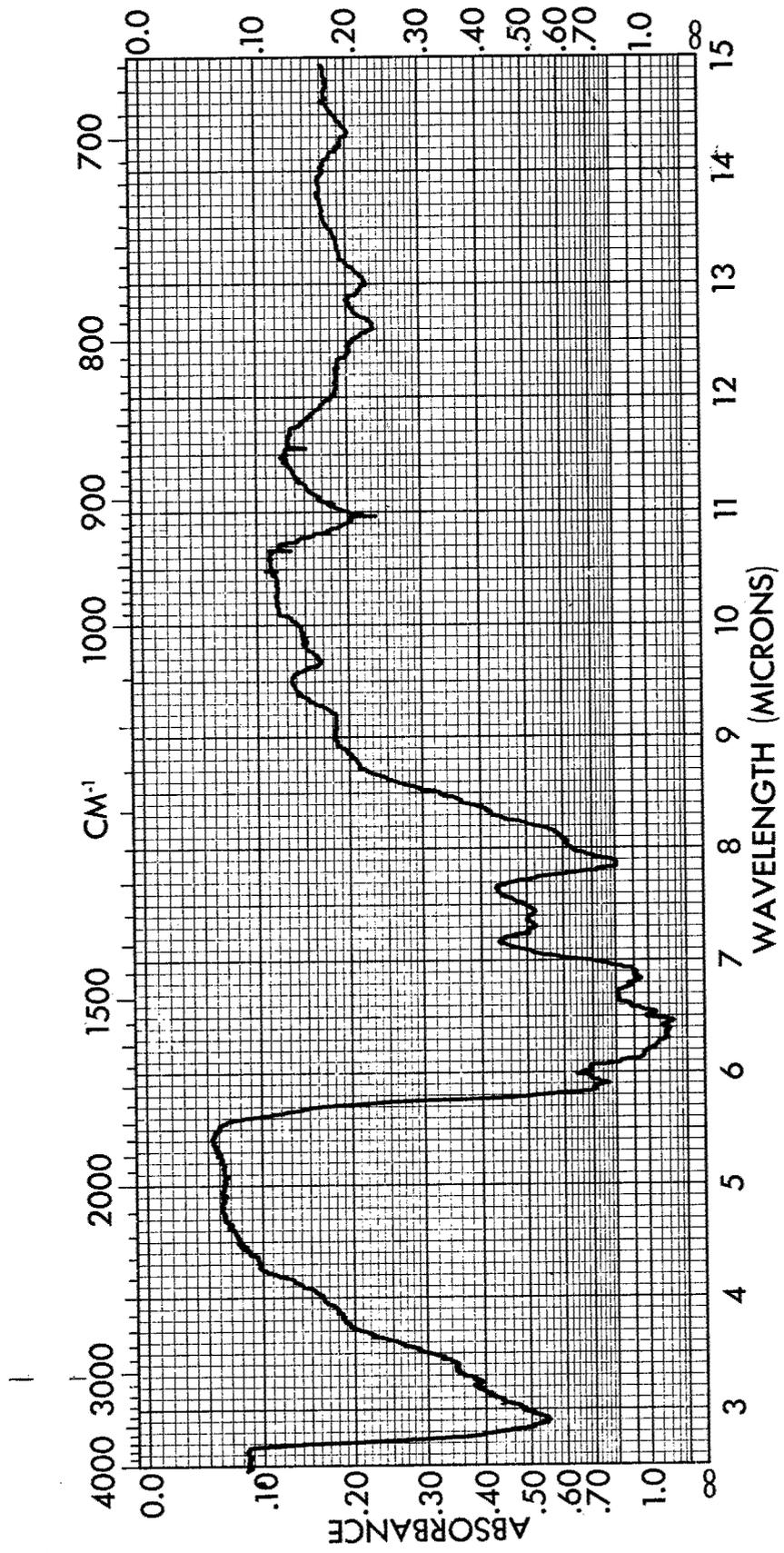


Figure 36. Infrared Spectrum of the Condensation Product, $C_{12}H_8O_4N_2$, II, from 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4-9-Dione, I, at 300°C in Molten Benzophenone

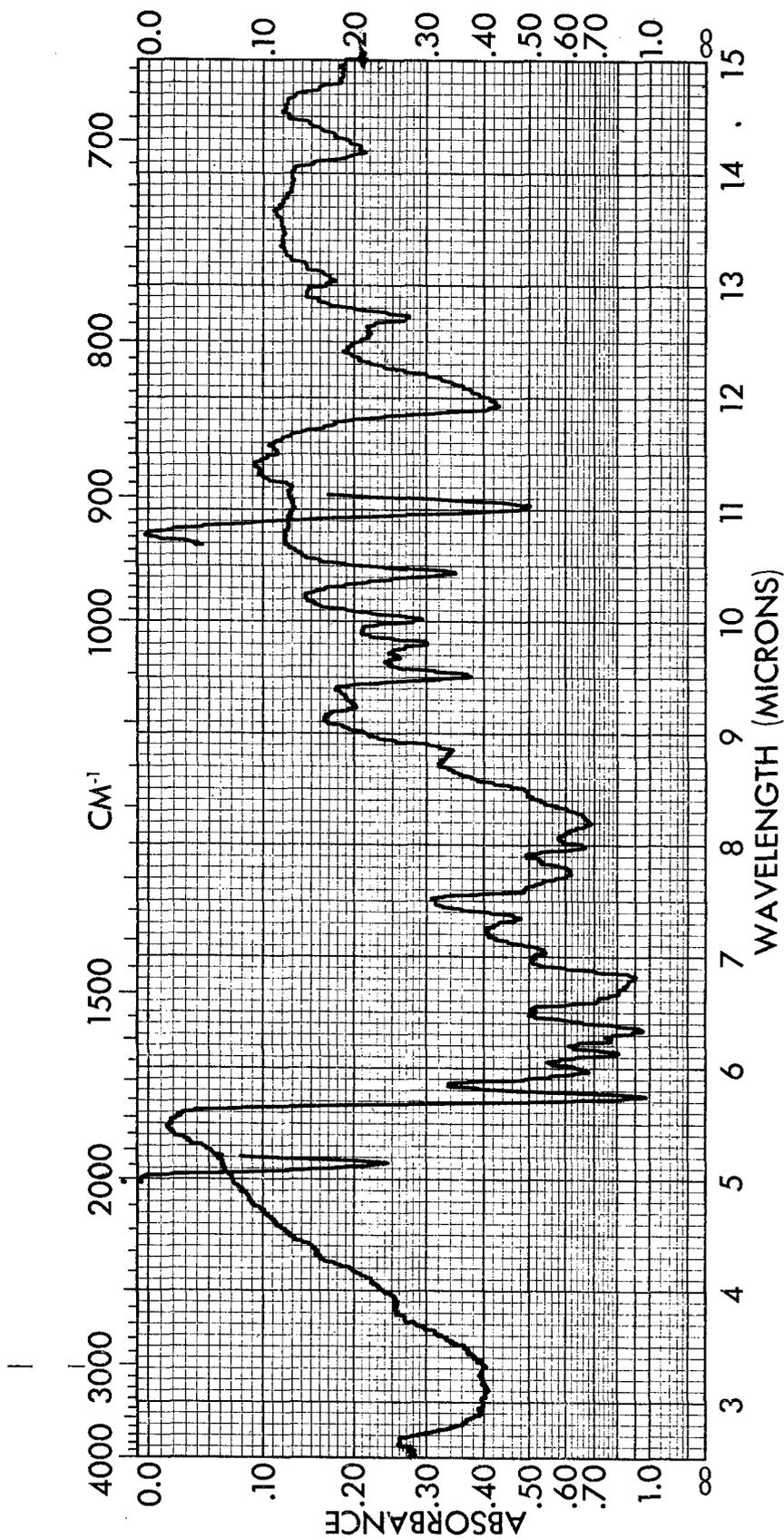


Figure 36. Infrared Spectrum of the Condensation Product, $C_{18}H_{12}O_4N_2$,
 LIII, from 6,6'-Bis-(2-Methyl-[4H],3,1-Benzoxazine-4-One),
 XXXVII

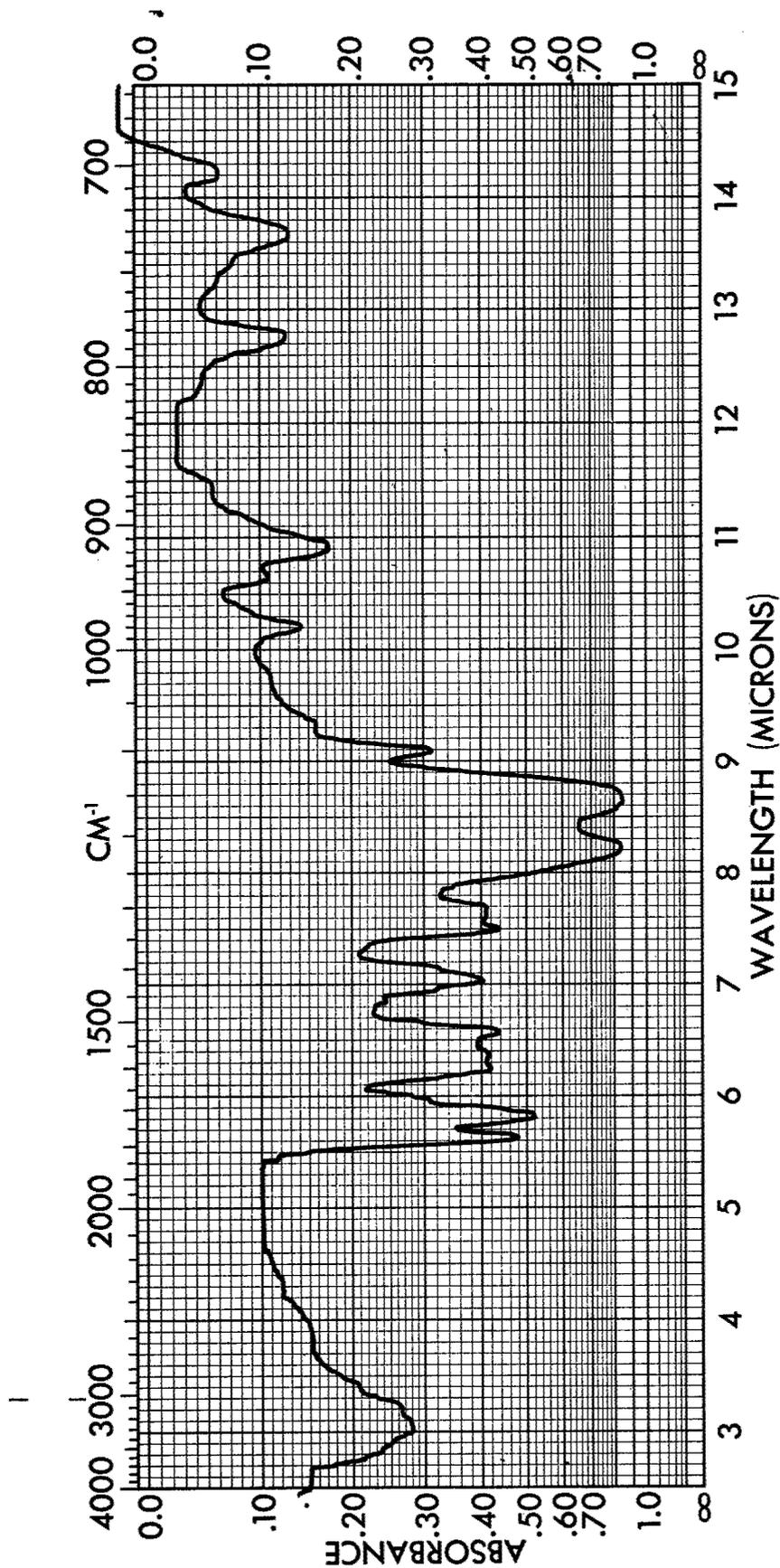


Figure 37. Infrared Spectrum of the Condensation Product, LVb, from
 2,7-Bis-(Trifluoromethyl)-[4H, 9H], 3,1,8,6-Benzobisoxazine-
 4,9-Dione, XXXVI

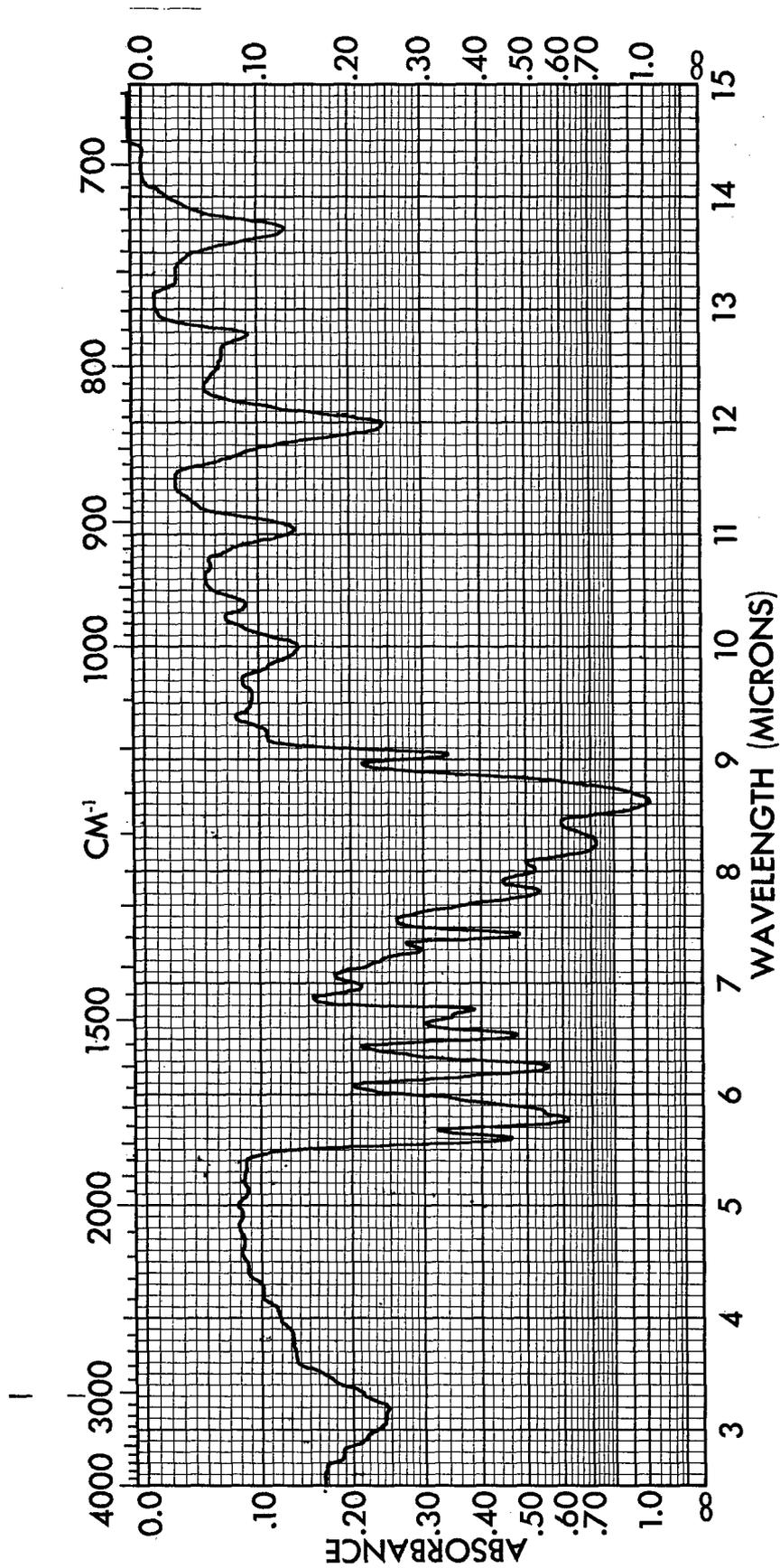


Figure 38. Infrared Spectrum of the Condensation Product, LVII, from
 6, 6'-Bis-(2-Trifluoromethyl-[4H], 3, 1-Benzoxazine-4-One),
 XXVIII

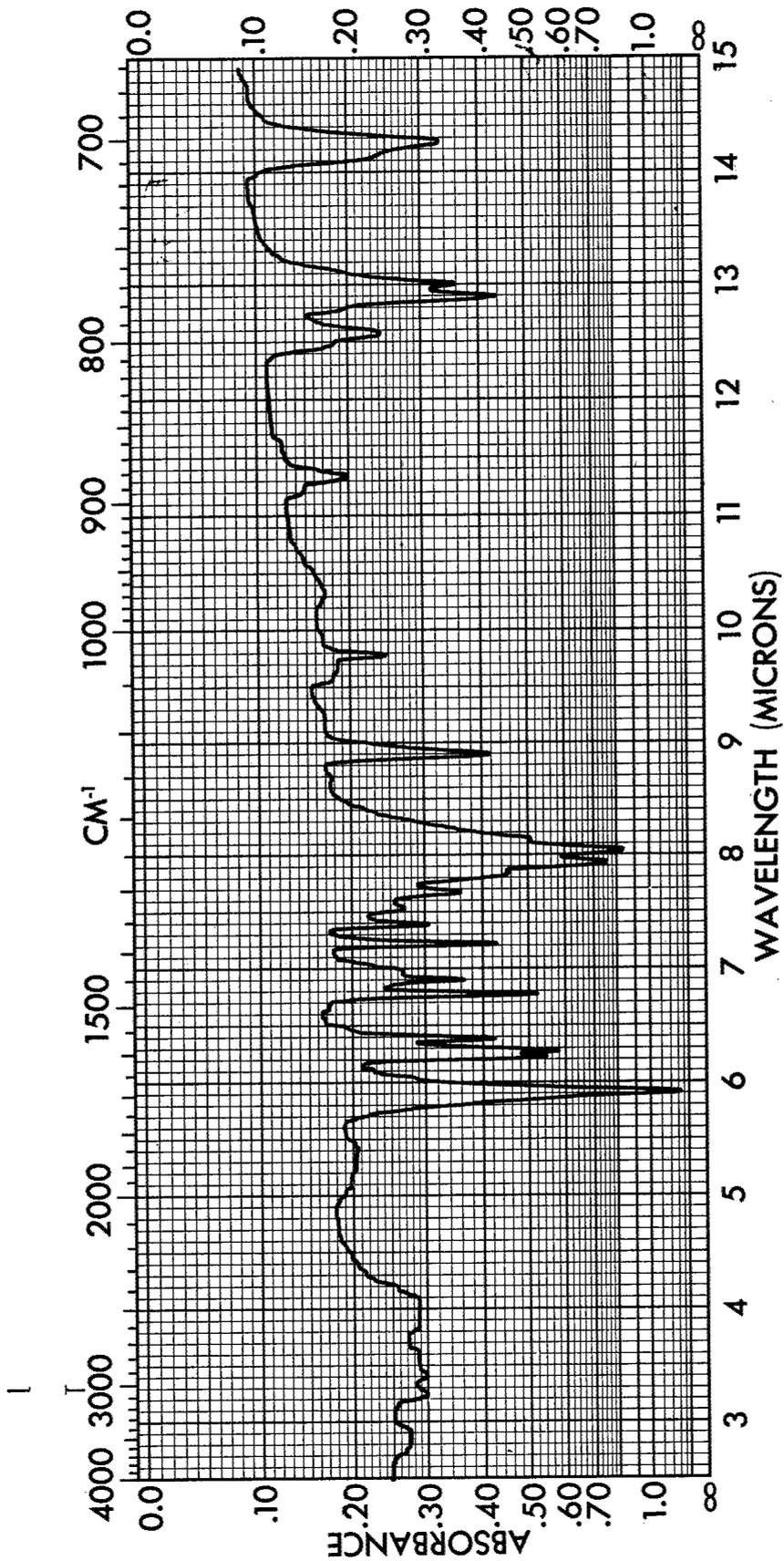


Figure 39. Infrared Spectrum of 2-Methyl-3-(6-Carboxymethylphenyl)-Quinazoline-4-One, LX

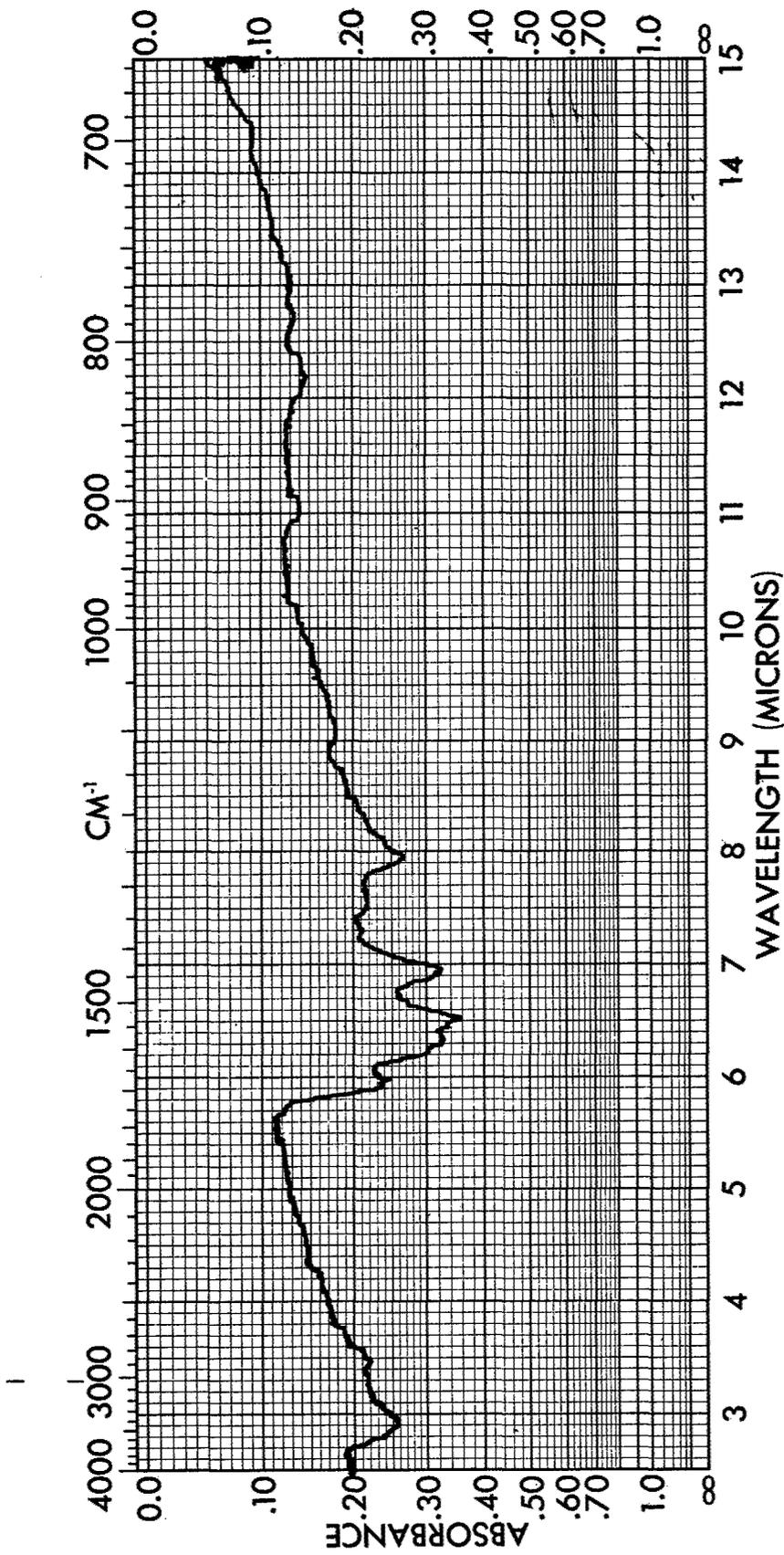


Figure 41. Infrared Spectrum of the Polymer (C₂₀H₁₂O₆N₄)_n, LXII, from Reaction of 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I, and 2,5-Diaminoterephthalic Acid, XLI in Sulfolane at 250 - 300°C

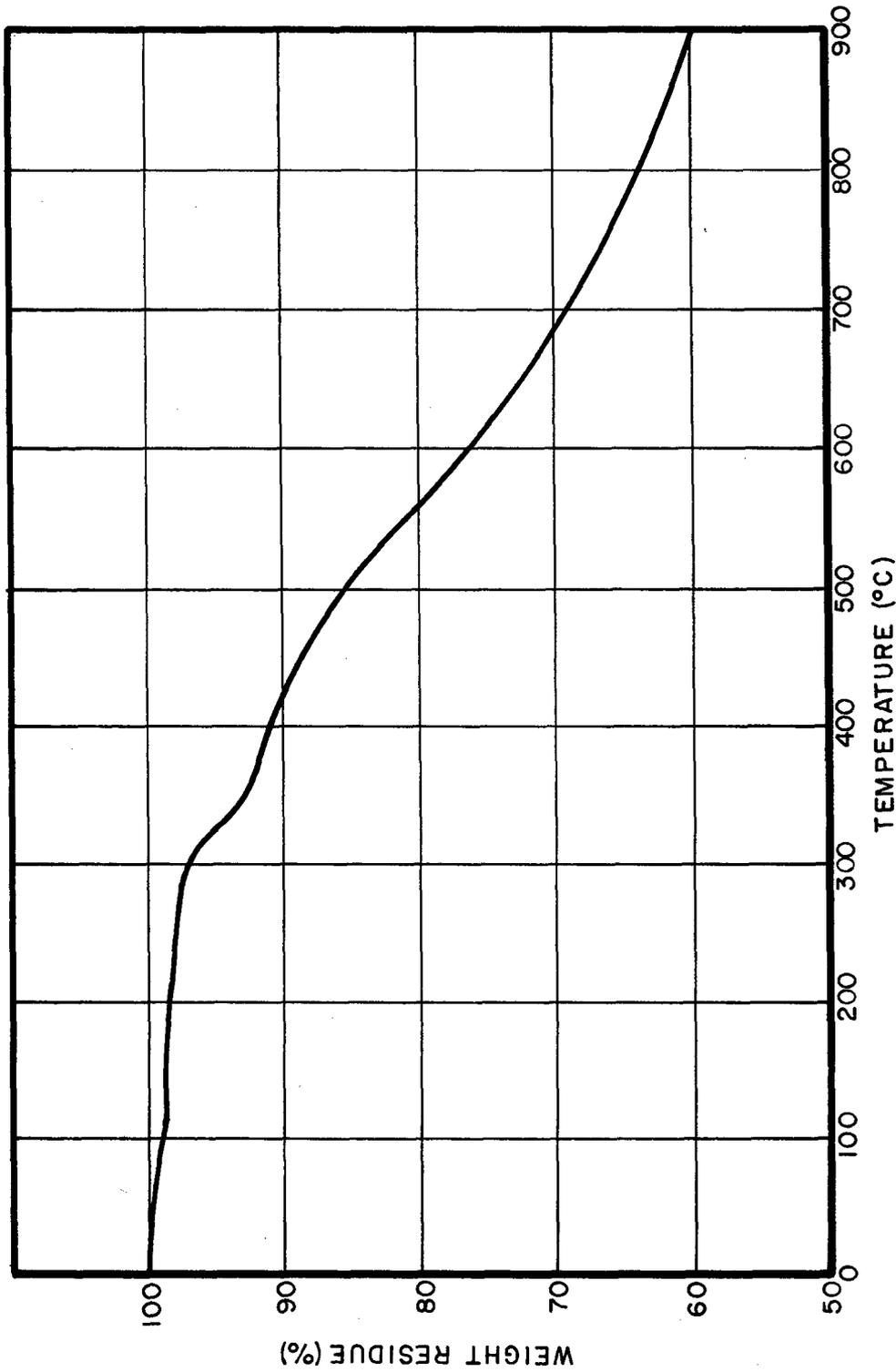


Figure 42. TGA Curve of the Polymer $(C_{20}H_{12}O_6N_4)_n$, LXII, from Reaction of 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I, and 2,5-Diaminoterephthalic Acid, XLI, in Sulfolane at 250 - 300°C

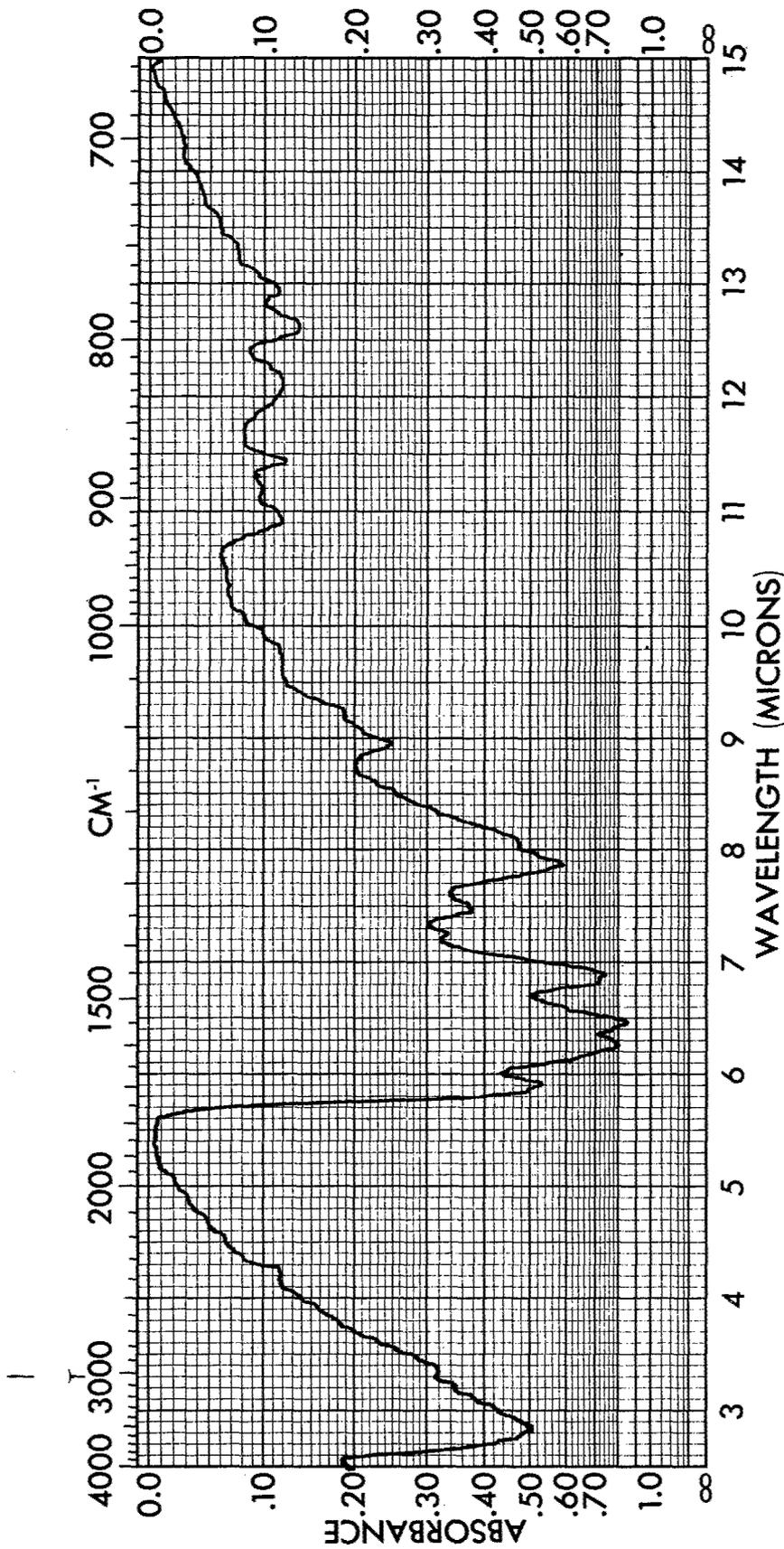


Figure 43. Infrared Spectrum of the Polymer (C₂₄H₂₀O₆N₄)_n, LXIV, from Reaction of 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I, and Diethyl-2,5-Diaminoterephthalate, XXX, in Diphenyl Ether at 225 - 250°C

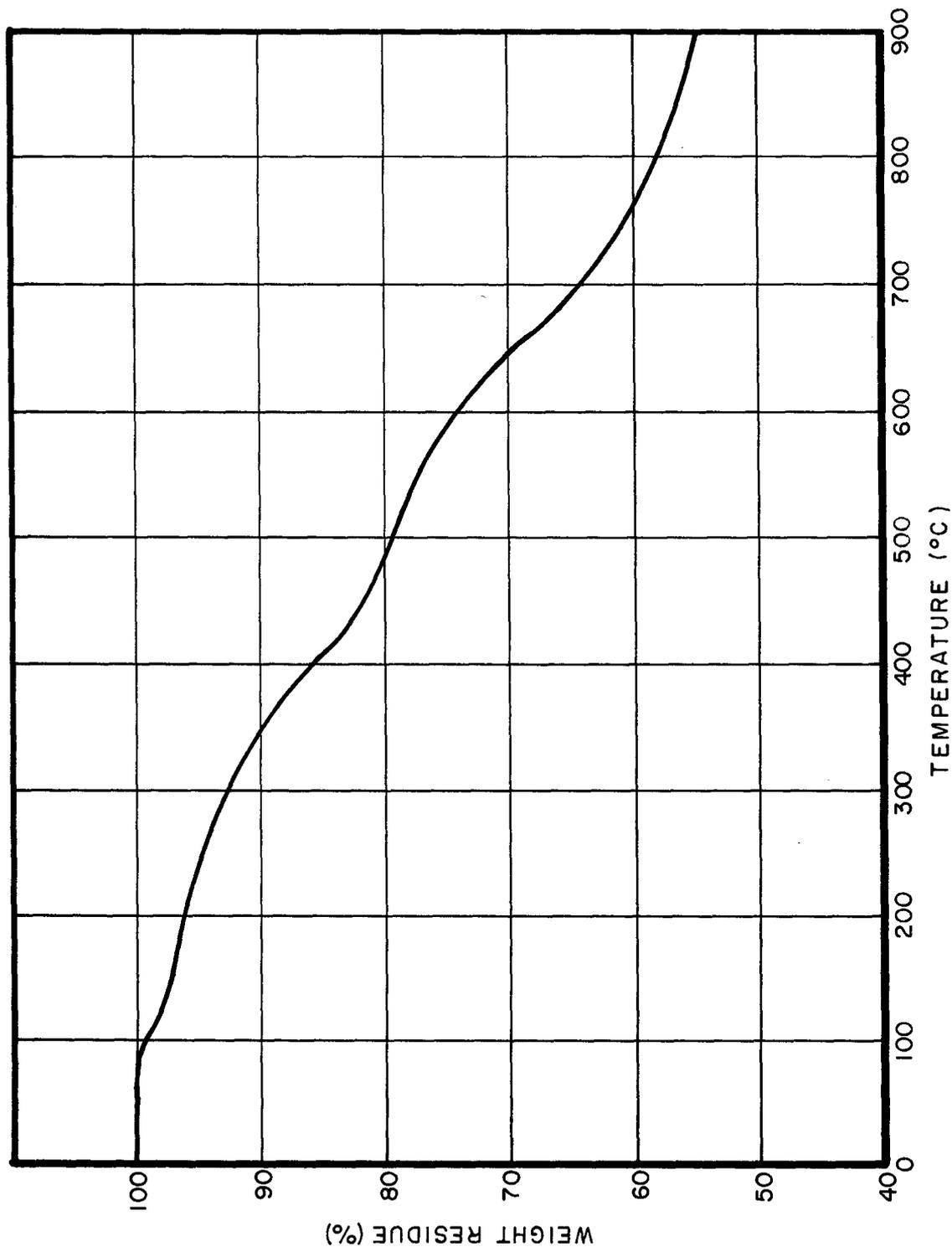


Figure 44. TGA Curve of the Polymer (C₂₄H₂₀O₆N₄)_n, LXIV, from Reaction 2, 7-Dimethyl-[4H, 9H], 3, 1, 8, 6-Benzobisoxazine-4, 9-Dione, I, and Diethyl 2, 5-Diaminoterephthalate, XXX, in Diphenyl Ether at 225 - 250°C

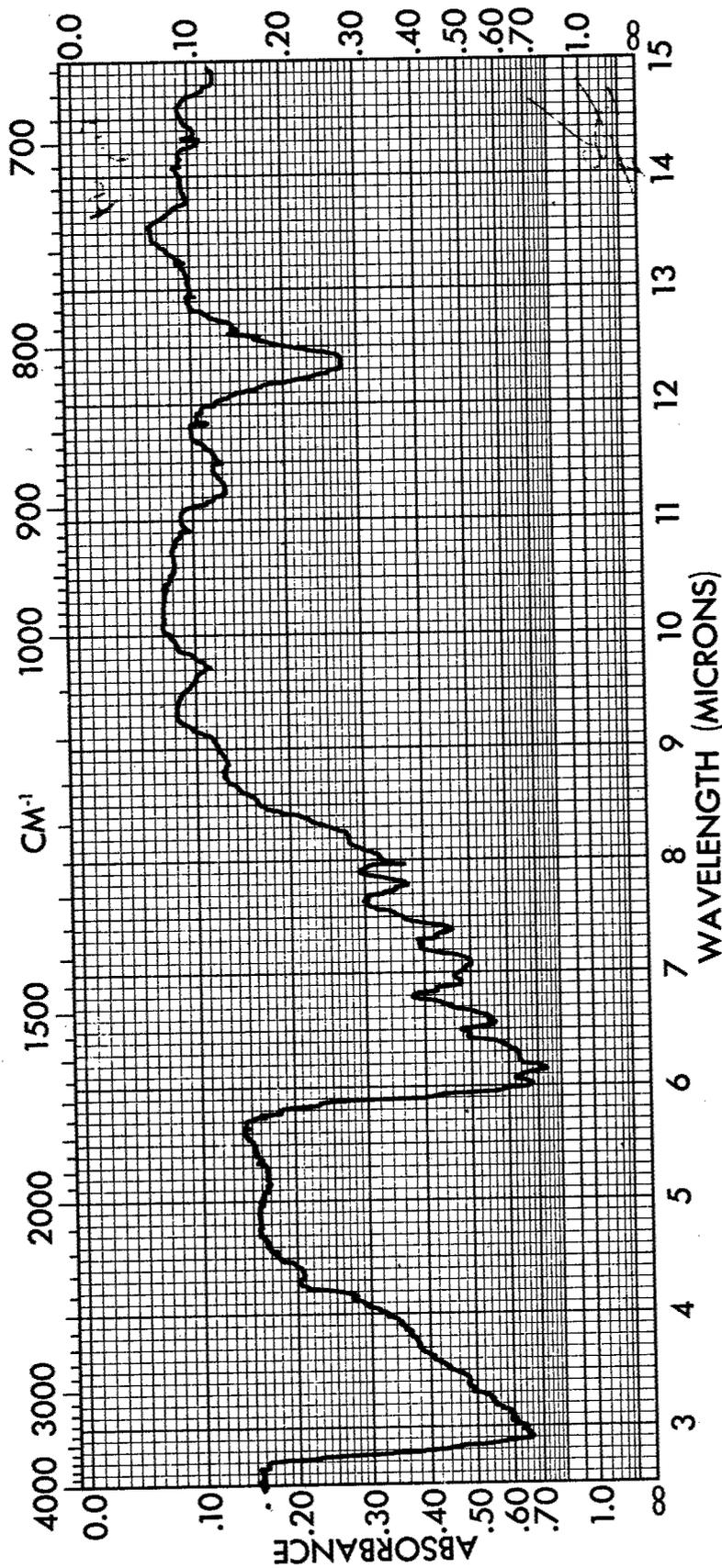


Figure 45. Infrared Spectrum of the Polymer (C₂₄H₂₂O₄N₆), LXV, from Reaction of 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I, and Diaminobenzidine, XXIII, in Dimethylformamide

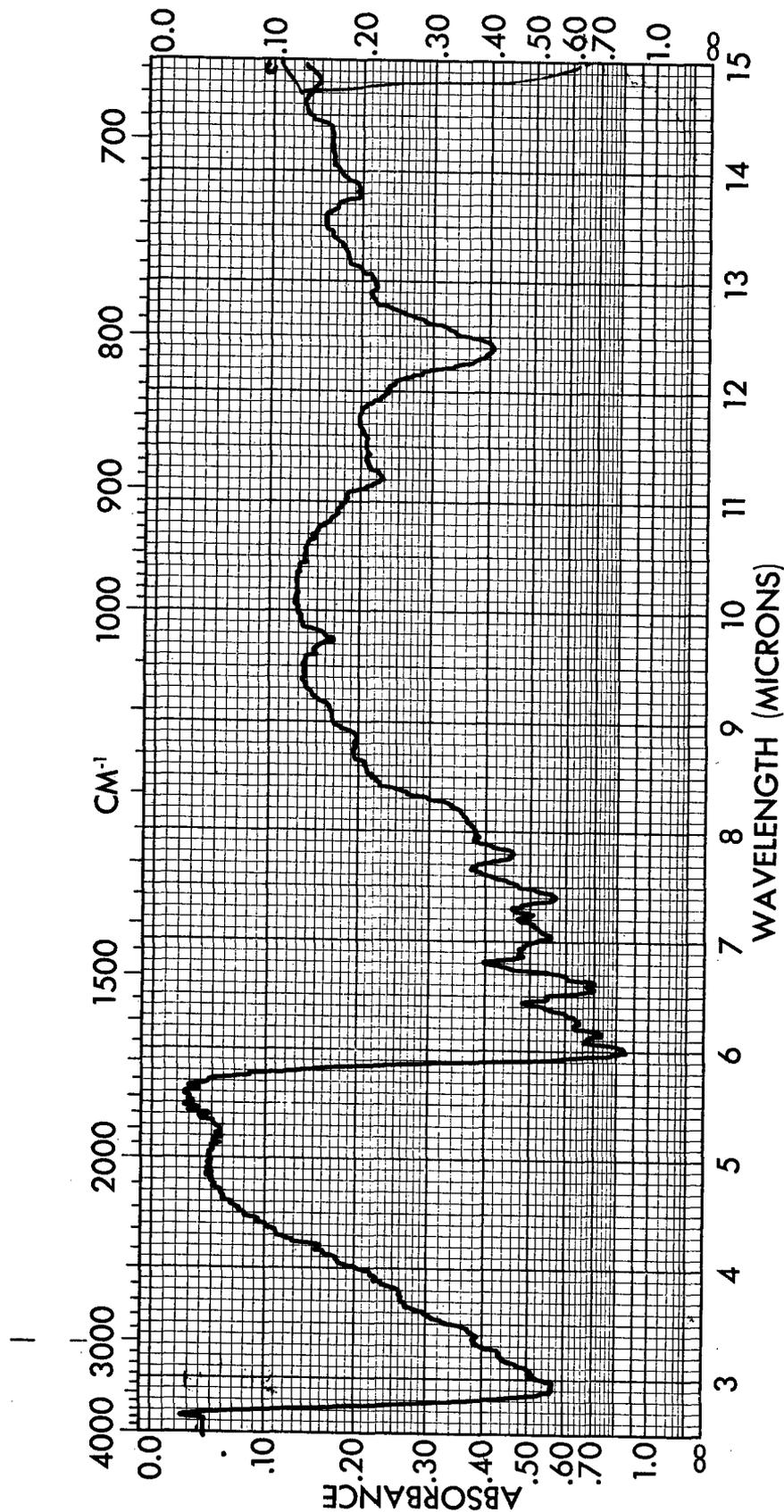


Figure 46. Infrared Spectrum of the Polymer (C₂₄H₂₂O₄N₆)_n, LXV, from Reaction of 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I, and Diaminobenzidine, XXIII, in Trimethylene Glycol Dimethyl Ether

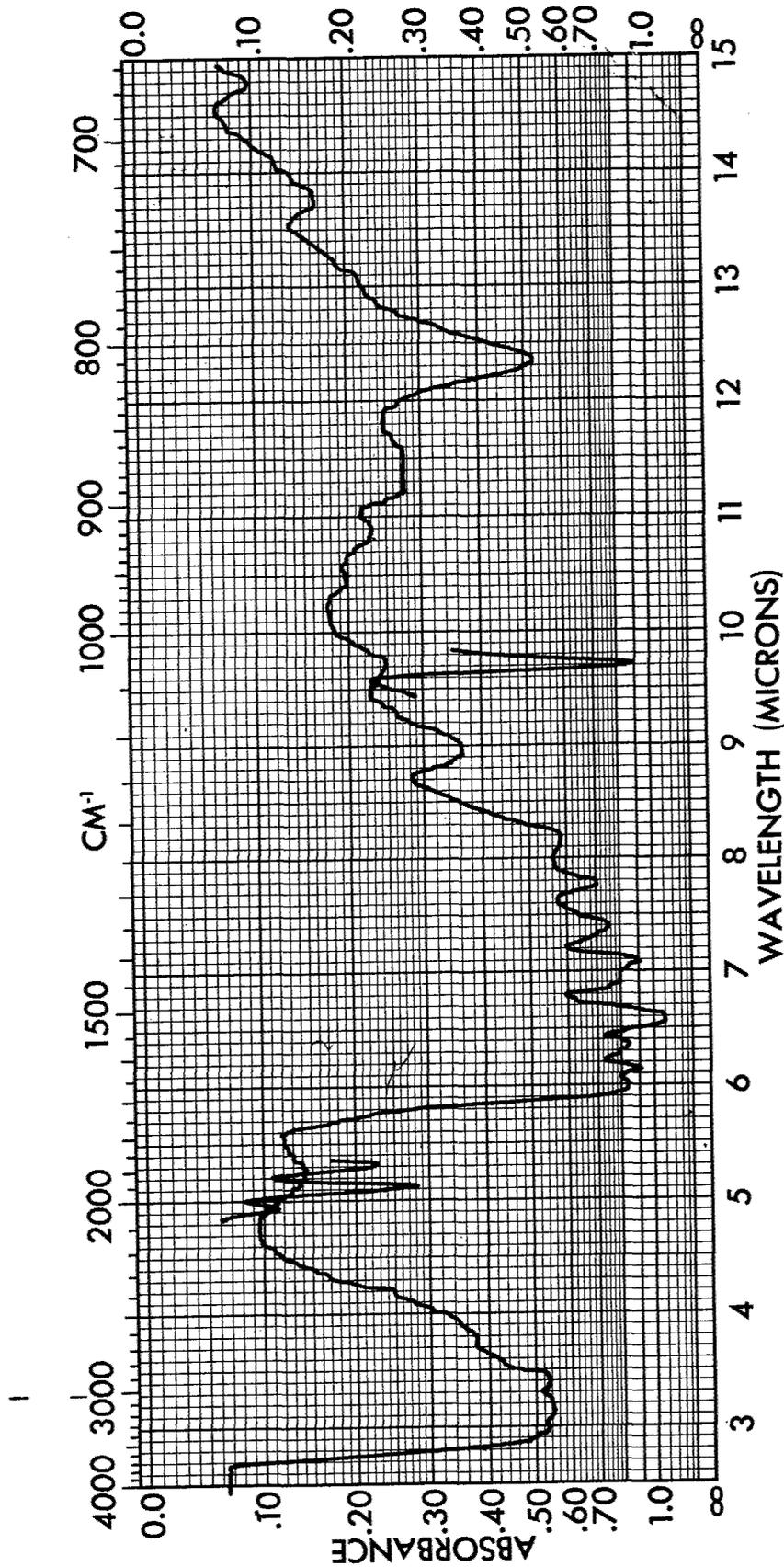


Figure 47. Infrared Spectrum of the Polymer ($C_{24}H_{22}O_4N_6$)_n, LXV, from Reaction of 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I, and Diaminobenzidine, XXIII in Diethyl Cellosolve

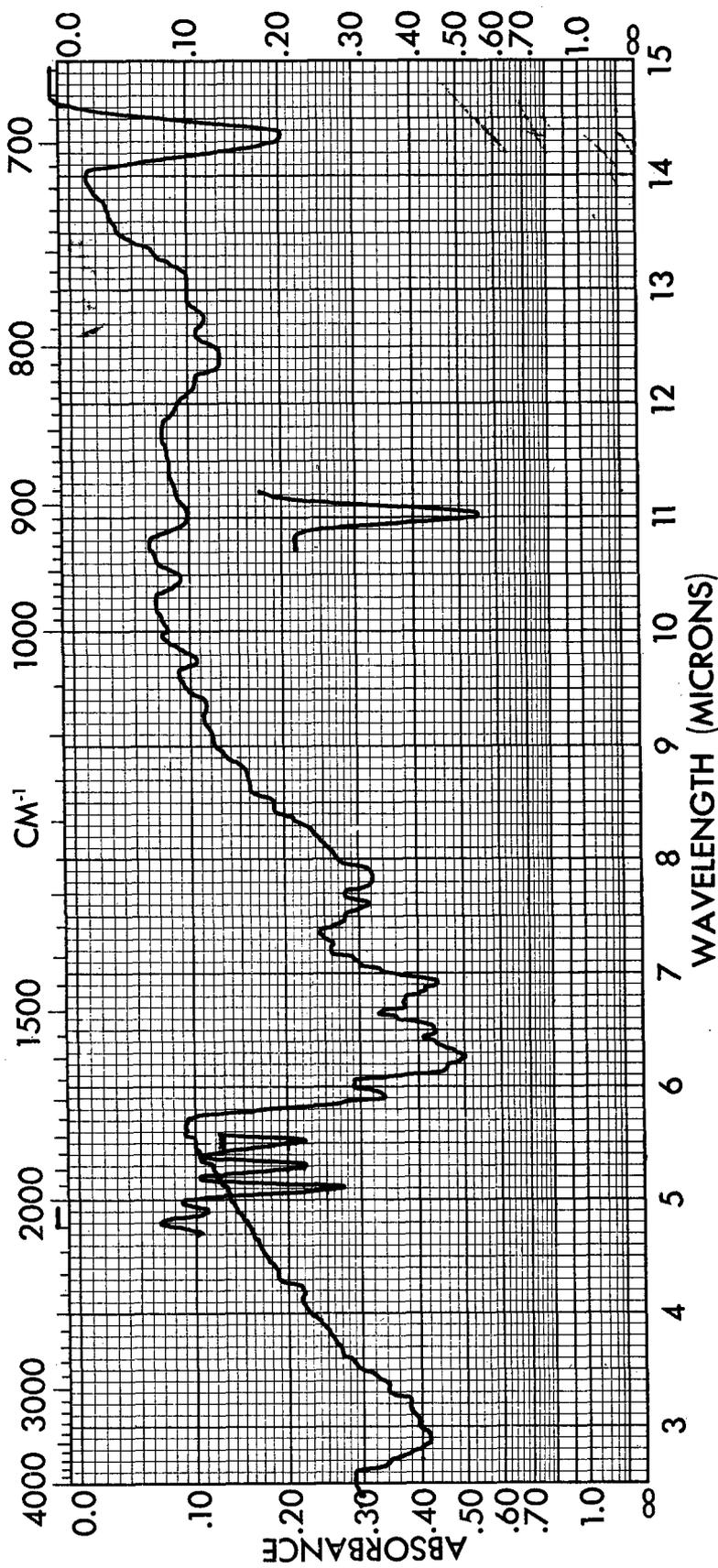


Figure 48. Infrared Spectrum of the Polymer, $(C_{37}H_{28}O_3N_6)_n$, LXX, from Reaction of 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I, and Diaminobenzidine, XXIII, in Molten Benzophenone

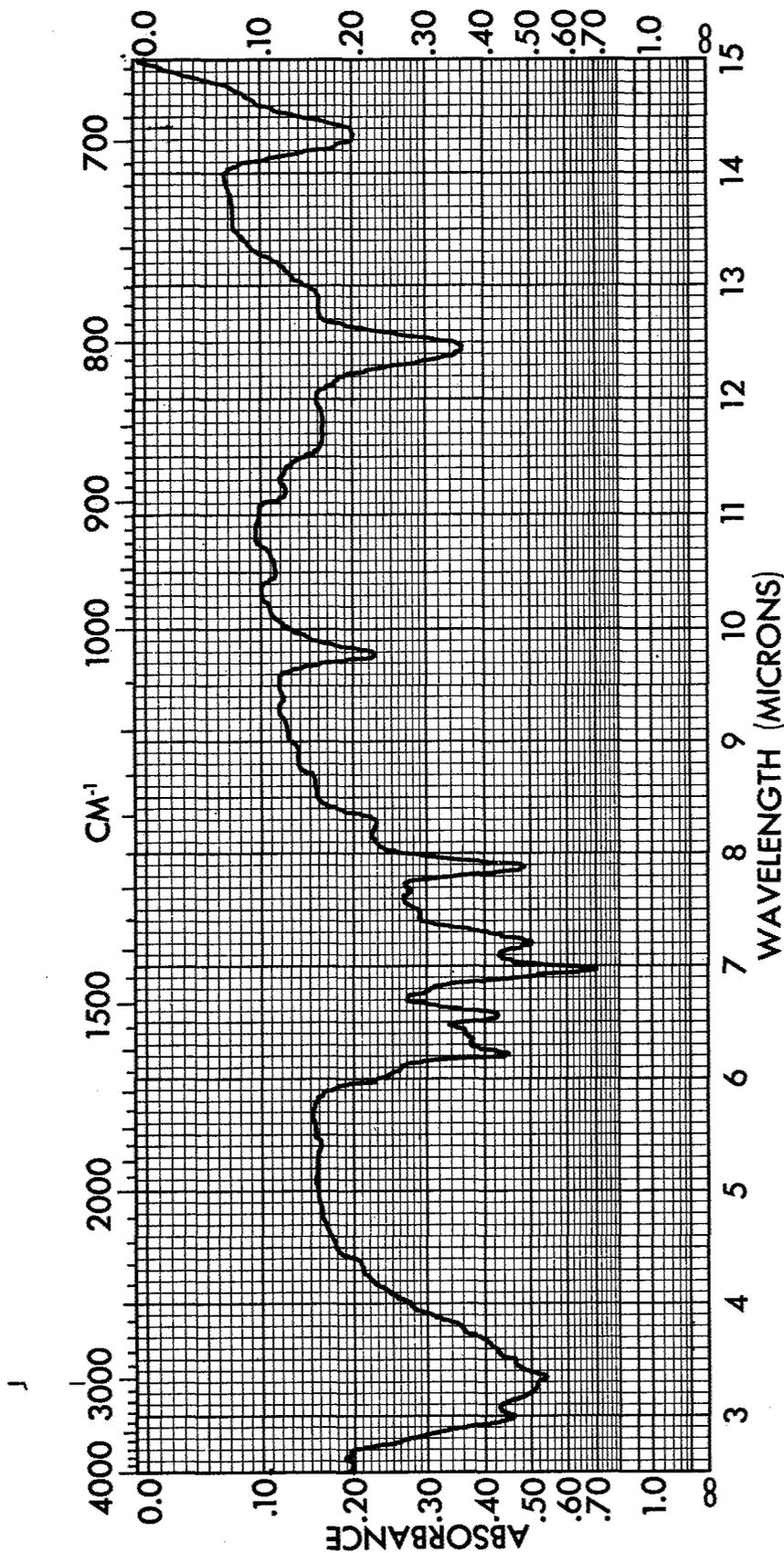


Figure 49. Infrared Spectrum of the Polymer (C₃₇H₂₄ON₆)_n, LXIX, from Reaction of 2,7-Dimethyl-[4H, 9H], 3,1,8,6-Benzobisoxazine-4,9-Dione, I, and Diaminobenzidine, XXIII, in Molten Benzophenone

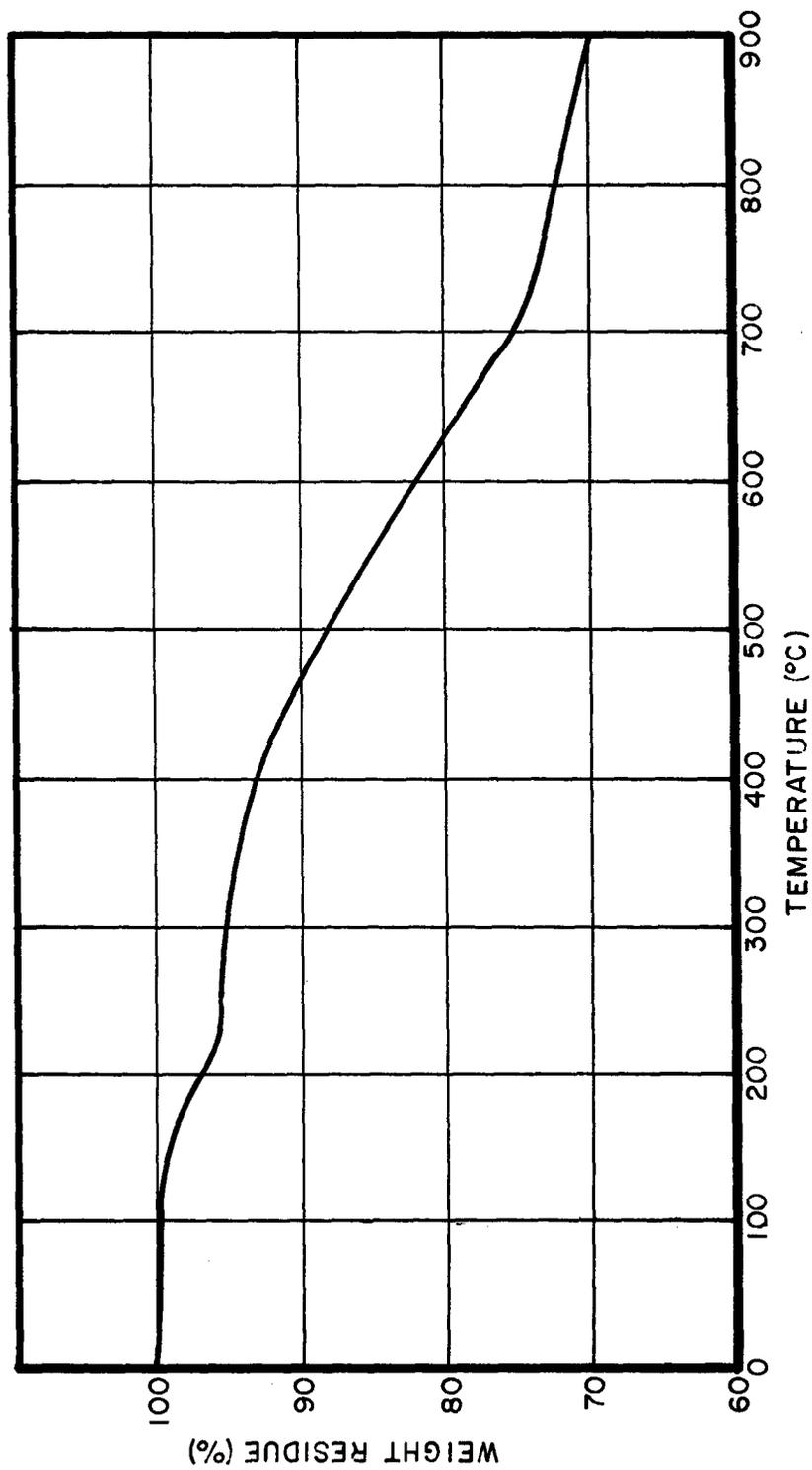


Figure 50. TGA Curve of the Product from Reaction of 6, 6'-Bis-(2-Trifluoromethyl-4H), 3, 1-Benzoxazine-4-One), XXXVII, with Diaminobenzidine, XXIII, in Molten Benzophenone.

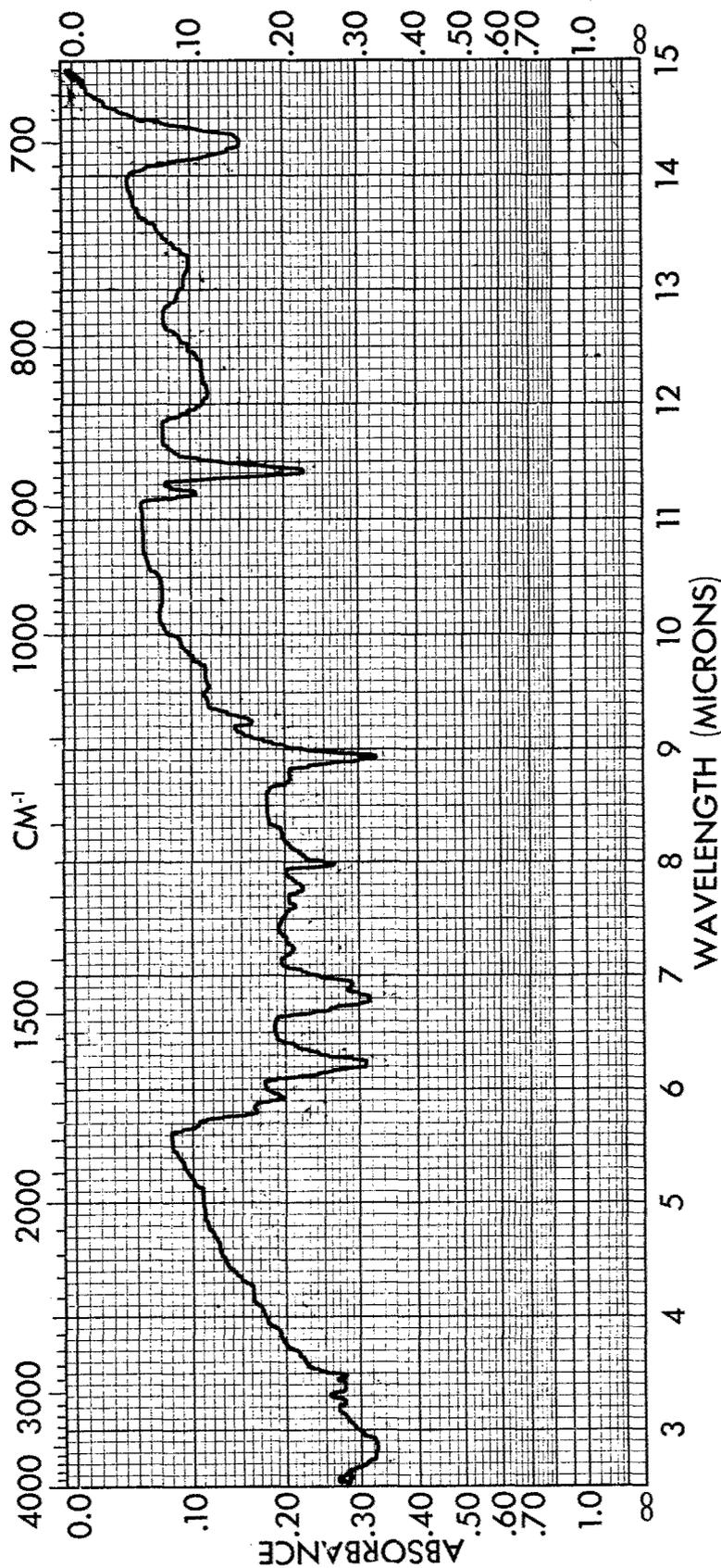


Figure 51. Infrared Spectrum of the Product from Reaction of 6,6'-Bis-(2-Trifluoromethyl-[4H], 3,1-Benzoxazine-4-One), XXXVII with Diaminobenzidine, XXIII, in Molten Benzophenone

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Air Force Materials Laboratory Air Force Systems Command Wright-Patterson Air Force Base, Ohio 45433		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP	
3. REPORT TITLE APPROACHES TO LADDER STRUCTURES VI. CONDENSATION POLYMERIZATION OF SOME DIFUNCTIONAL DERIVATIVES RELATED TO [4H], 3,1-BENZOXAZINE-4-ONE WITH CERTAIN AROMATIC DIAMINO DICARBOXYLIC ACIDS, ESTERS OR AROMATIC TETRAAMINES			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) March 1967 - August 1969			
5. AUTHOR(S) (First name, middle initial, last name) Gerard A. Loughran			
6. REPORT DATE February 1971		7a. TOTAL NO. OF PAGES 99	7b. NO. OF REFS 22
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-70-233	
b. PROJECT NO. 7340		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c. Task No. 734004			
d.			
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11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory (LNP) Air Force Systems Command Wright-Patterson AFB, Ohio 45433	
3. ABSTRACT 2,7-dimethyl-[4H,9H], 3,1,8,6-benzobisoxazine-4,9-dione, and 6,6'-bis-(2-methyl-[4H], 3,1-benzoxazine-4-one) condense on heating at 300°C either in the melt or in solution in sulfolane or molten benzophenone to give insoluble highly condensed cross-linked polymers whose empirical formulae are the same as the starting materials from which they were prepared. High molecular weight or cross-linked materials were obtained when 2,7-bis-(trifluoromethyl)-[4H,9H], 3,1,8,6-benzobisoxazine-4,9-dione, and 6,6'-bis-(2-trifluoromethyl-[4H], 3,1-benzoxazine-4-one) were similarly treated. The reaction appears to be accompanied by loss of hydrogen fluoride. 2-methyl-[4H], 3,1-benzoxazine-4-one reacted with methyl anthranilate in refluxing xylene to give 3-methyl-3-(δ-carboxymethyl)-phenylquinazolinone-4-one. Polyquinazolinones in the medium molecular weight range, with viscosities in the 0.25 region were obtained when 2,7-dimethyl-[4H,9H], 3,1,8,6-benzobisoxazine-4,9-dione was reacted with either 2,5-diamino-terephthalic acid or its diethyl ester in sulfolane or diphenylether up to 300°. 2,7-dimethyl-[4H,9H], 3,1,8,6-benzobisoxazine-4,9-dione and 3,3' diamino-benzidine were reacted in dimethylformamide, diethyl cellosolve, and trimethylene glycol dimethyl ether at temperatures from 120° to 310°C to give a soluble low molecular weight linear polyamide expected to use as a prepolymer for subsequent conversion to the corresponding quinazoline and benzimidazo-[1,2c]-quinazoline polymers.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Polymers Polyaromatics Polyquinazolines Polybenzimidazo-[1,2c]-quinazolines 3-Methyl-3-(o ⁻ -carboxymethyl-)-phenylquinazoline-4-one						