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THERMOOXIDATION STUDIES OF THE QUINOXALINE SYSTEM AND CERTAIN BENZIMIDAZOLE COPOLYMER SYSTEMS

PART I

INITIAL STUDIES ON THE MECHANISM OF THERMOOXIDATION OF THE QUINOXALINE SYSTEM

PART II

SYNTHESIS AND EVALUATION OF THERMOOXIDATIVE PROPERTIES OF A SERIES OF BENZIMIDAZOLE COPOLYMERS

Robert T. Conley

James J. Kane

Subrata Ghosh

S. L. Lu

Department of Chemistry, Wright State University

~ Sept, 72

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FOREWORD

This report was prepared by Wright State University, Dayton, Ohio under Department of the Air Force Contract F33615-68-C-1277. The work was administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio with Dr. G.F.L. Ehlers (AFML/LNP) as Project Scientist.

This report covers work from February 1, 1971 to January 31, 1972.

This technical report has been reviewed and is approved.

R. L. Van Deusen

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

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ABSTRACT

A number of model compounds related to the polyquinoxaline system have been synthesized and subjected to solution and pyrolytic oxidation. The pyrolytic oxidation of the model compounds at temperatures between 450 and 500°C produced benzonitrile, the oxides of carbon and cyanogen. Controlled solution oxidation of phenylquinoxaline model compounds produced the related pyrazinedicarboxylic acids. Subsequent pyrolytic oxidation of the pyrazinedicarboxylic acid (the product of solution oxidation) yielded benzonitrile, carbon dioxide, cyanogen and the parent, phenylpyrazine. These results parallel those obtained in our previous studies with the benzimidazole system and are discussed in terms of an initial oxygenation mechanism for thermal oxidation of the quinoxaline system.

Dramatic evidence for thermal oxidation intermediates oxygenated at the carbocyclic ring is presented by product isolation and spectral data. These findings are used for verification of a thermal oxidation mechanism involving (as in the case of the benzimidazole system) initial oxygenation at the carbocyclic ring adjacent to the heterocyclic ring in the quinoxaline and phenylquinoxaline systems.

A series of copolymers containing the benzimidazole unit in conjunction with aromatic amides, benzimides and benzimidazolones was synthesized by condensation reactions and evaluated for their thermooxidative stabilities and solubility properties.

Each copolymer exhibited the solubility characteristics of its least soluble component. Thus the copolymeric benzimidazole/benzimide and benzimidazole/benzimidazolone were completely insoluble in the highly polar aprotic solvents such as DMSO and DMAc.

Thermooxidative stabilities of the copoly(benzimidazole/amide) series and the copoly(benzimidazole-imide) were determined by spectral monitoring of isothermally (350°C) aged film samples cast from DMSO. The results revealed all to be comparable or slightly superior to PBI homopolymer film. Those variations observed were interpreted in terms of the electronic effect of the copolymer unit on formation of or stabilization of the benzimidazole free radical, an intermediate in the proposed mechanism of benzimidazole thermooxidative degradation. The benzimidazole/benzimidazolone copolymer, the benzimidazolone homopolymer (BBB) and the benzimidazole homopolymer (PBI) were cast into films from concentrated sulfuric acid providing tough, flexible films for subsequent thermooxidative studies. The results revealed that PBI/BBB copolymer is comparable to but less stable than BBB homopolymer and vastly superior to PBI homopolymer and the other copolymers in the series. Interestingly, PBI homopolymer cast from sulfuric acid exhibits a thermooxidative stability considerably superior to that of the same polymer cast from DMSO. These results are discussed in terms of possible chemical modifications effected by the concentrated sulfuric acid solvent.

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SECTION I

INTRODUCTION

During the past ten years considerable research effort has been directed toward the synthesis and stability studies of various polyquinoxaline systems. The high degree of research activity in this area of all aromatic-heterocyclic polymers is a reflection of the intensity of interest in the application of polyquinoxalines (PQ) to those uses usually associated with polymeric systems which are candidates for high temperature-high performance tasks.

In our laboratories our continuing studies into the mechanisms of thermooxidative degradation of all aromatic-heterocyclic systems has led us to postulate that benzheterocyclic systems degrade thermooxidatively by very similar if not identical mechanisms. This proposal is based on our observation that the benzimidazole, benzimidazolone and benzimide systems on oxidative degradation all produce similar gaseous and condensible products. The specifics of the oxygenation steps forming the observed volatile products was conclusively shown in the case of the benzimidazole system to result from initial attack by oxygen at the carbocyclic ring adjacent to the heterocyclic ring. Thus it is of interest to include in our thermooxidative mechanism studies the PQ system in order to test further the generality of our postulate concerning the parallelism between mechanisms in oxidative degradation of the benzheterocyclic systems.

The following paragraphs will include a discussion of work done by previous investigators in the synthesis, evaluation, and degradation studies in the polyquinoxaline system.

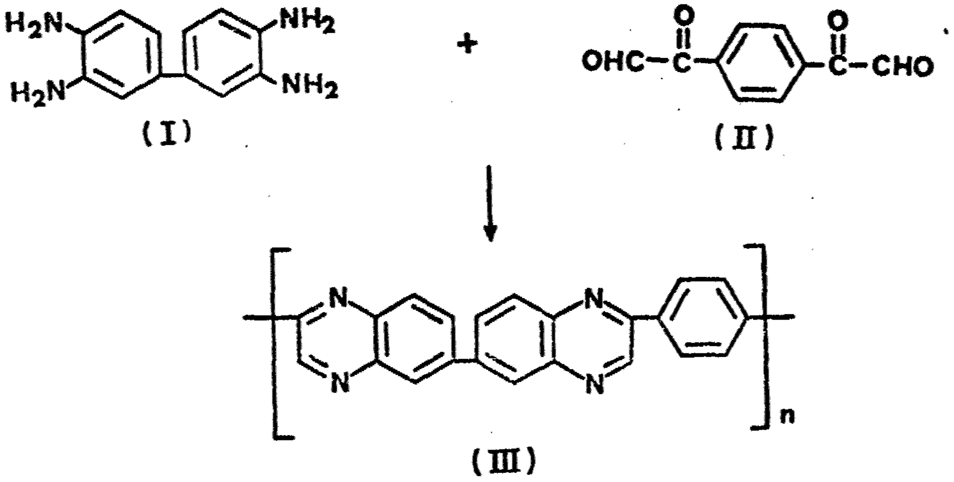
SECTION II

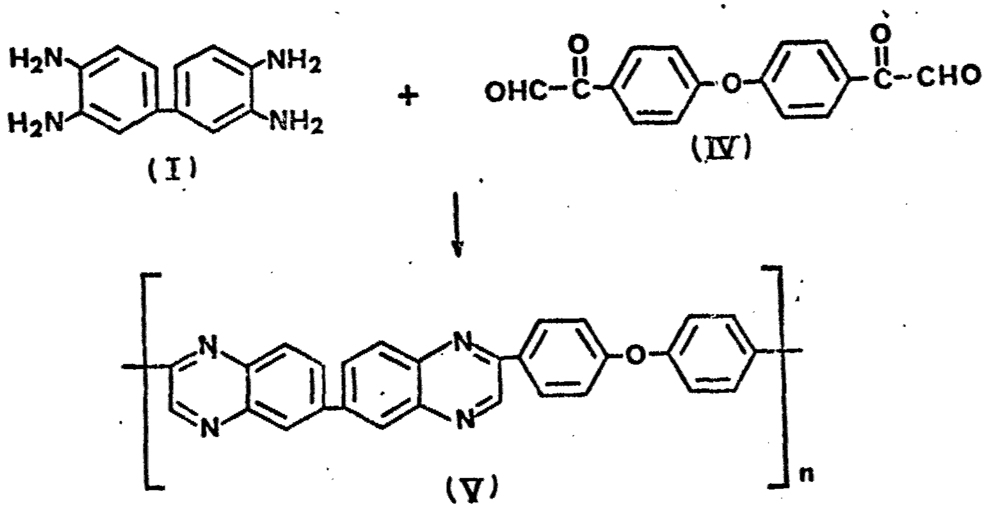
PREVIOUS INVESTIGATIONS

1. Synthesis

a. All aromatic Polyquinoxaline

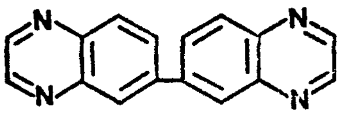
Quinoxalines were first prepared independently by Korner[1] and Hinsberg[2] by the cyclocondensation of an aromatic o-diamine with 1,2-dicarbonyl compounds. The reaction, commonly called the Hinsberg reaction, was proposed[3] as a potential route to polymeric quinoxalines and so applied in 1964 when Stille and Williamson[4] reported synthesis of poly[2,2'-(p-phenylene)6,6'-diquinoxaline] (III) by condensation of 3,3'-diaminobenzidine (I) and 1,4-diglyoxalylbenzene. By a similar condensation of diaminobenzidine (I) and 4,4'-diglyoxalyldiphenyl ether (IV), polymer V was synthesized[5].



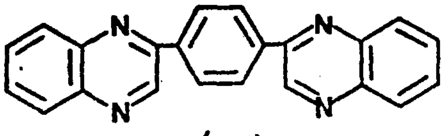


In order to determine the optimum conditions for the polymerization reaction involving phenylglyoxal and 1,2-diaminobenzene type monomers, Stille and Williamson[6] synthesized the series of model compounds VI, VII, and VIII. In particular, formation of VII and VIII, separately utilized the monomers 3,3'-diaminobenzidine (I) and 1,4-diglyoxalylbenzene (II), which were employed in the polymer syntheses. Reaction of diglyoxalylbenzene, II with o-phenylenediamine in solution or in the melt afforded high yields of quinoxaline VII. Reaction of diaminobenzidine, I, with phenylglyoxal produced a low yield of VIII. However when the tetrahydrochloride was used, a high yield of VIII was obtained. Curiously the reaction proved to be stereospecific since VIII was the only isomer produced.

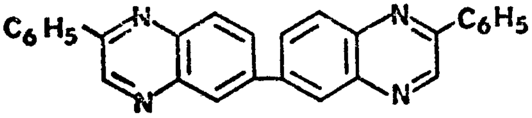
The reaction of stoichiometric amounts of 1,4-diglyoxalylbenzene (II) with 3,3'-diaminobenzidine (I) afforded nearly quantitative yields of poly[2,2'(p-phenylene)6,6'-biquinoxaline] (III). Reaction of monomers I and II in the absence of a solvent with heating at 250°C or reaction of the monomers in a solvent to form a prepolymer and subsequent heat treatment of the prepolymer at 250°C, provided soluble polymer with identical properties. However, further heating of these polymers at higher temperatures considerably decreased the solubility and increased the molecular weight. The decrease in solubility



(VI)



(VII)

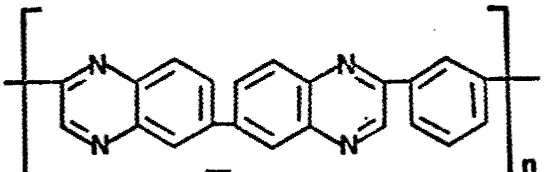


(VIII)

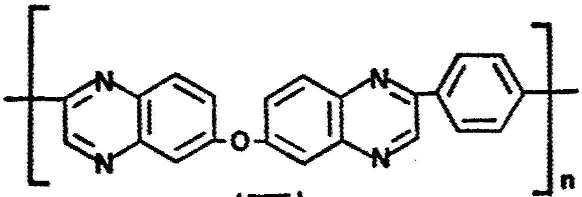
of these polymers was thought to be due to crosslinking. Thus the polymers were insoluble in common organic solvents and only sparingly soluble in solvents like hexamethylphosphoramide (HMP). Films of the polymers were somewhat brittle.

b. Polyquinoxalines with Heteroatoms in Polymer Backbone

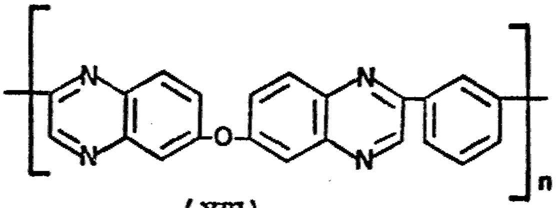
In order to impart increased flexibility to the polymer chain and provide a more soluble and less brittle polymer amenable to fabrication, polymers V, XII, XIII, and XIV all containing oxygen ether linkages in the polymer chain were prepared[5,7] and evaluated[7]. Polymer X was included in this study and all were compared to III which contains the p-phenylene linkage.



X



(XII)



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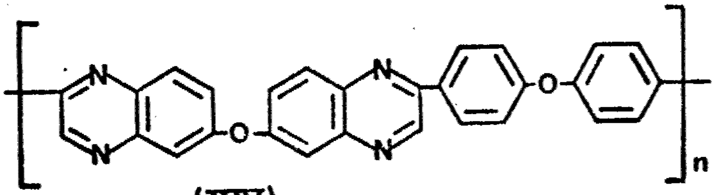
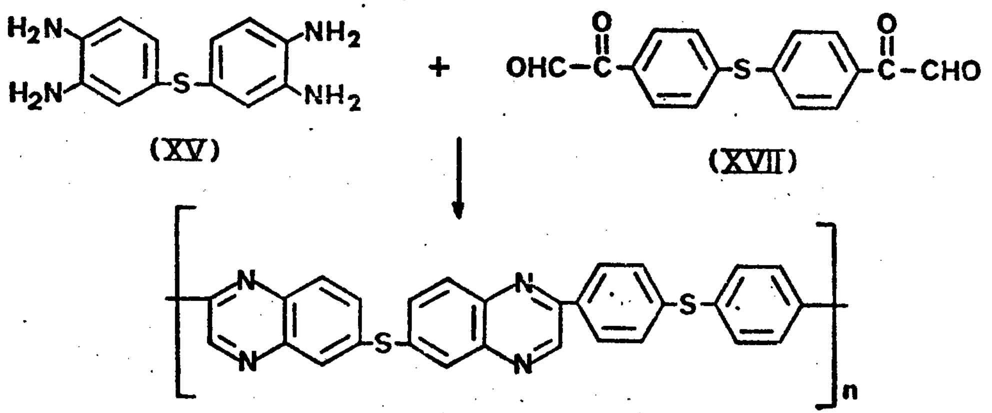


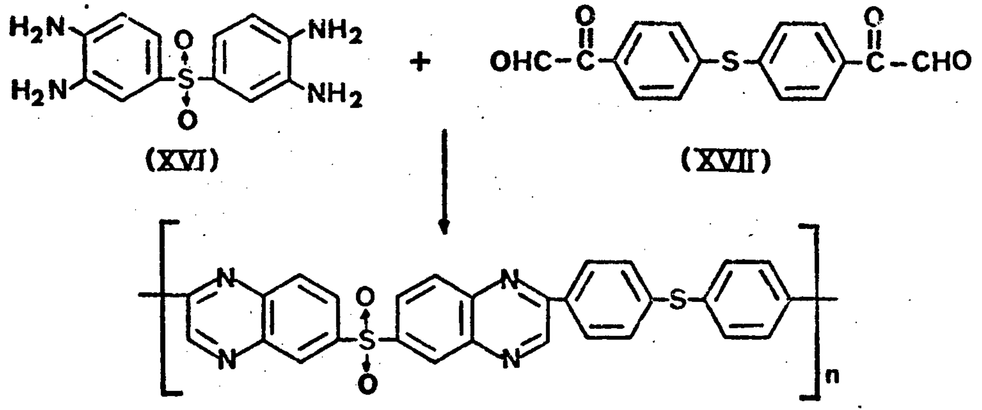
(XIV)

These polymers showed greater solubility than poly[2,2'(p-phenylene)6,6'-biquinoxaline] (III). Of these polymers, poly[2,2'(4,4'-oxydiphenylene)6,6'-oxydiquinoxaline] (XIV), which is expected to possess the highest chain flexibility, demonstrated the greatest solubility and a tough, translucent film could be cast from this polymer. Interestingly, no sacrifice in thermal stability, as might be anticipated, was observed. In a continuation of the study Stille and Arnold[8] prepared six thermally stable polyquinoxalines containing other heteroatoms in the polymer chain backbone (sulfides and sulfones) between the aromatic and quinoxaline segments.

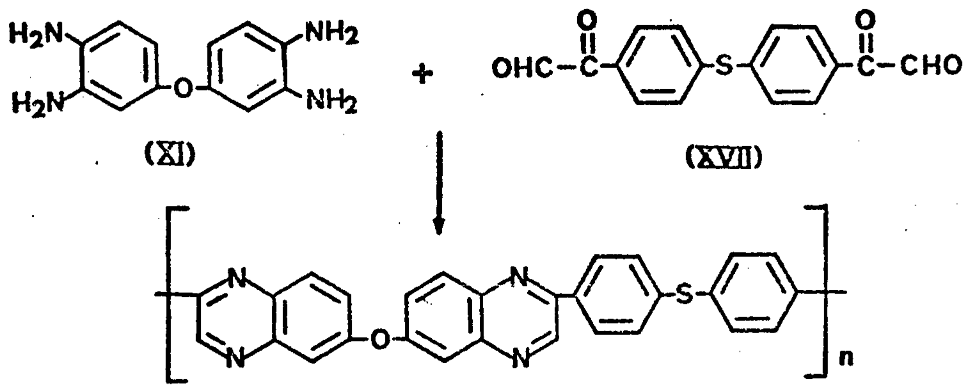
Four new monomers, 3,3',4,4'-tetraaminodiphenylsulfide (XV), 3,3,4,4'-tetraaminodiphenylsulfone (XVI), 4,4'-diglyoxalyldiphenylsulfide (XVII) and 4,4'-diglyoxalyldiphenylsulfone (XVIII) were synthesized. By the polymerization of XVII and XVIII with the tetraamines, XV, XVI, and XI, the six polymers XIX, XX, XXI, XXII, XXIII, and XXIV were synthesized as shown below. The polymerizations were carried out in two stages: In the first stage, a solution polymerization produced a prepolymer. This was followed by the second stage which involved heating the prepolymer under reduced pressure to 375°C.



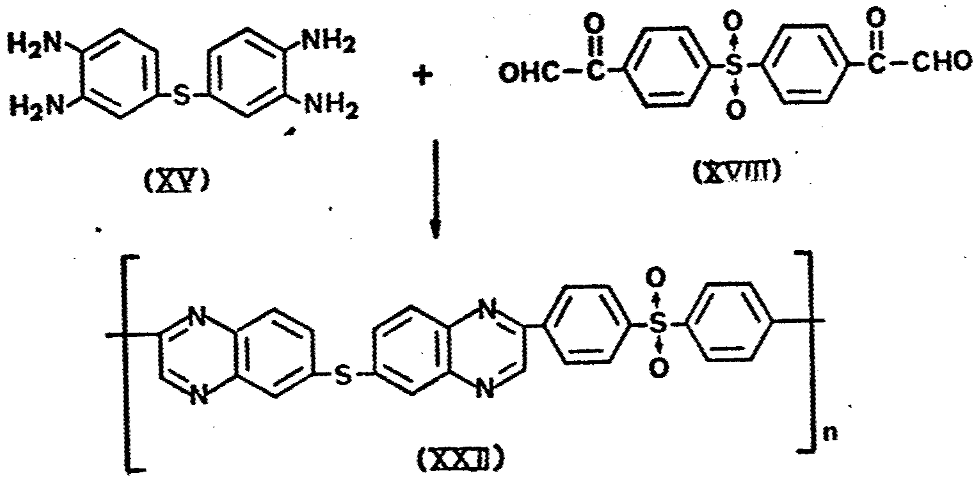
XIX

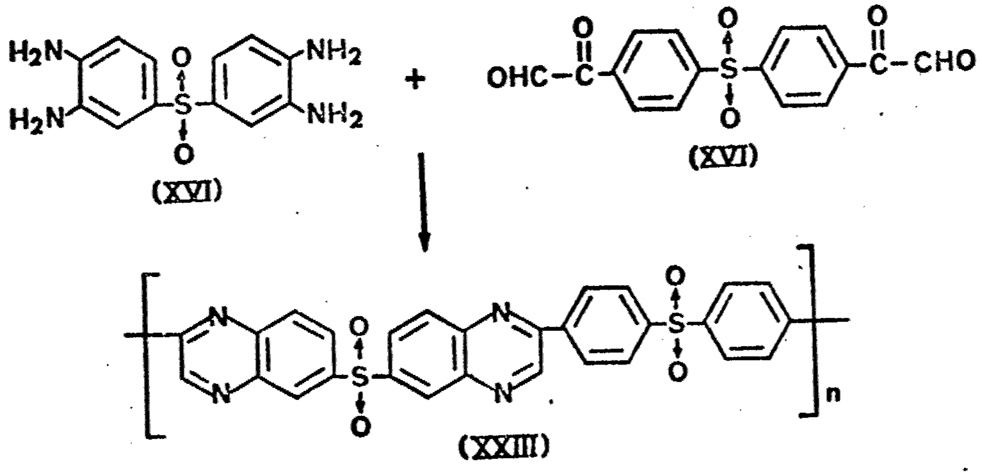


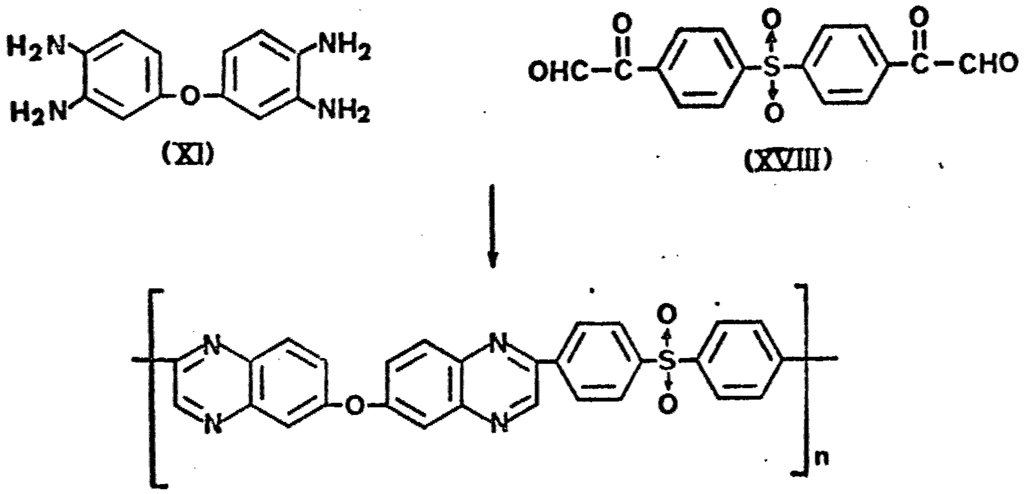
(XX)



(XXI)

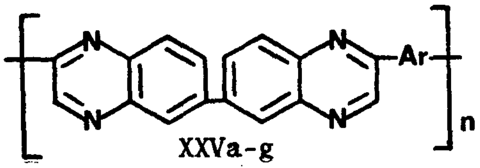

(XV)
(XVIII)
(XXII)


(XVI)
(XVI)
(XXIII)


(XI)
(XVIII)
(XXIV)

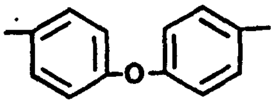
The six polymers exhibited excellent thermal stability characteristics. The solubilities of these polymers containing sulfide or sulfone groups was improved to a greater extent than those polymers containing ether groups. However, these polymers were still difficultly soluble in common organic solvents and sparingly soluble in HMP or concentrated sulfuric acid. However, the prepolymers, from the solution polymerization, were completely soluble in HMP. The solubility decreased only after the second stage polymerization process was carried out. The decrease in solubility was again attributed to crosslinking in the polymer chain[8].

Hergenrother and Kiyohara[9] prepared another series of quinoxaline polymers XXVa-g some of them containing ether linkages in the polymer backbone. By treating stoichiometric quantities of 3,3'-diaminobenzidine with the appropriate bisglyoxal, relatively high molecular weight intermediate polymers were initially formed. The prepolymers were cured by heating at 350°C. All the

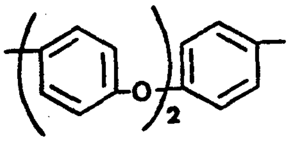


XXVa-g

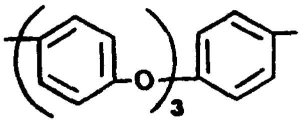
a,Ar =



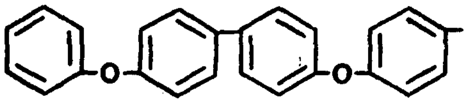
b,Ar =



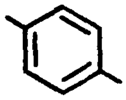
c,Ar =



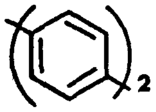
d,Ar =



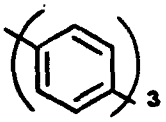
e,Ar =



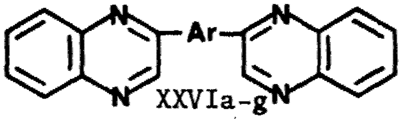
f,Ar =



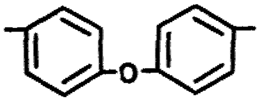
g,Ar =



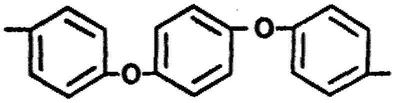
In order to aid in polymer characterization a series of model compounds XXVIa-g were also prepared using o-phenylenediamine.


XXVIa-g

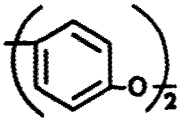
a,Ar =



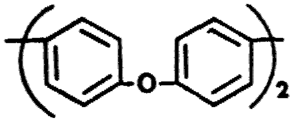
b,Ar =



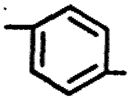
c,Ar =



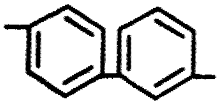
d,Ar =



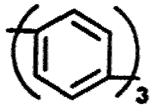
e,Ar =



f,Ar =

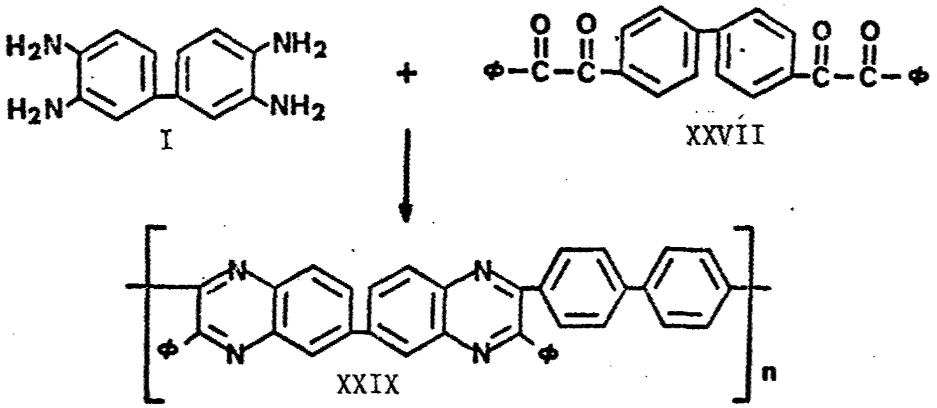


g,Ar =



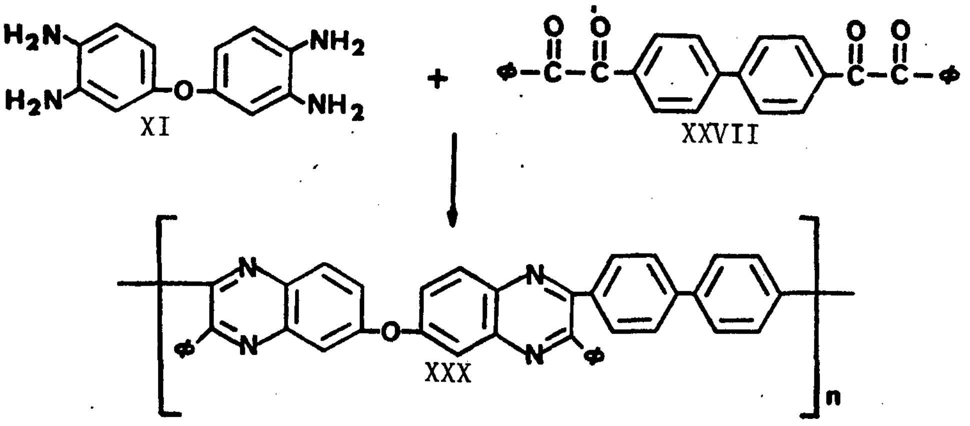
c. Phenyl-Substituted Polyquinoxalines

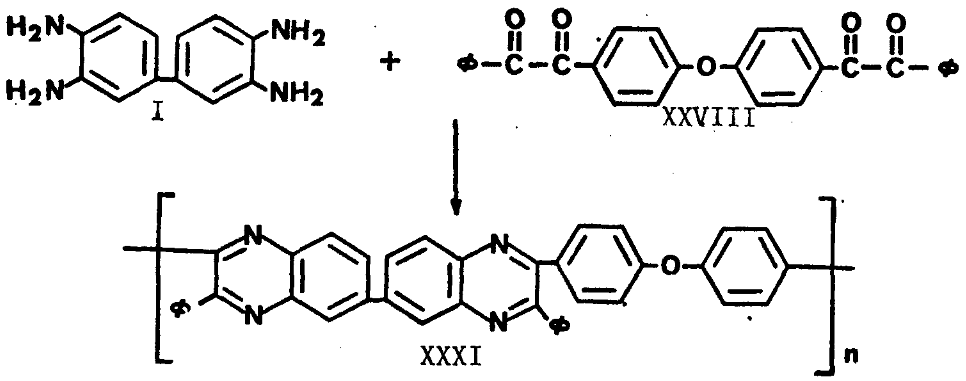
Four polymers have been prepared by the reaction of combinations of two tetraamines, 3,3'-diaminobenzidine (I) and 3,3',4,4'-tetraaminodiphenyl ether (XI) with two bisbenzils, 4,4'-dibenzil (XXVII) and 4,4'-oxydibenzil (XXVIII).

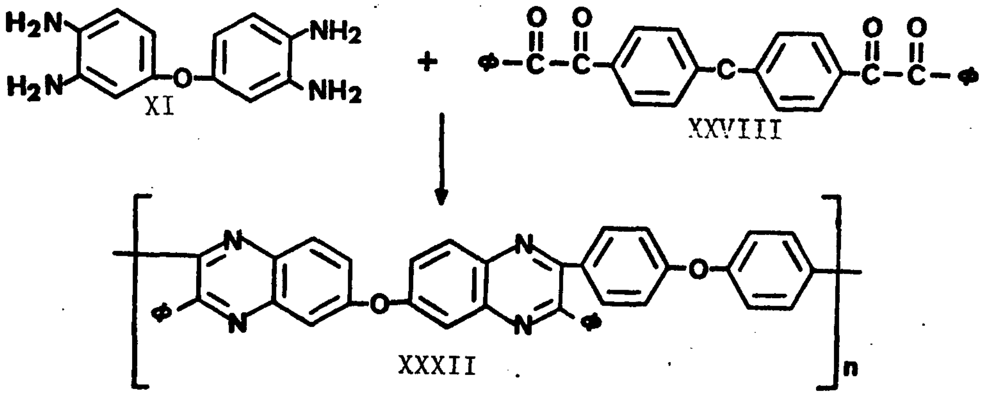

I

XXVII

XXIX

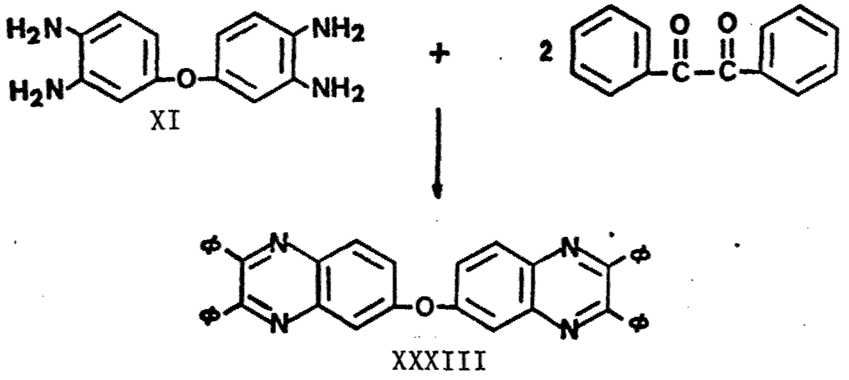




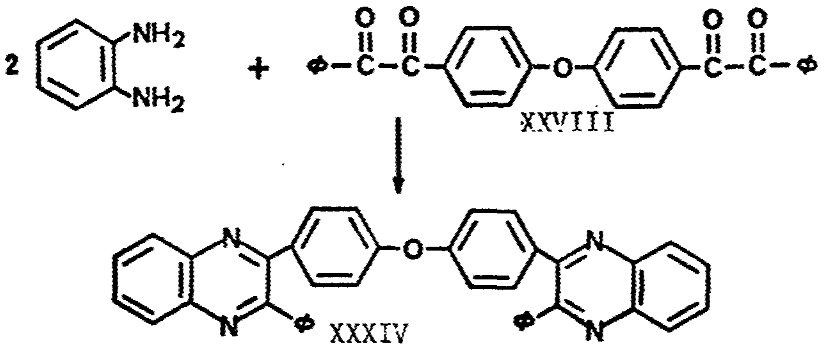


The polymerizations were carried out both in the melt and in solution. The polymerization again consisted of two stages, initially forming a prepolymer which was advanced at 400°C to polymer. The polymers XXIX, XXX, XXXI, and XXXII formed tough, flexible, clear yellow films. The synthesis of model compounds XXXIII and XXXIV in virtually quantitative yields was also reported by melt condensation[10]. The phenyl-substituted polyquinoxalines were reported to possess excellent oxidative and thermal stabilities. It is also interesting to note that the least stable phenyl-substituted polymer (XXXII) was prepared from monomers, each having a diphenyl ether linkage. The observation that the phenyl-substituted polyquinoxalines are more stable than the monosubstituted polymers has been supported by further studies by Wrasidlo and his coworkers[11].

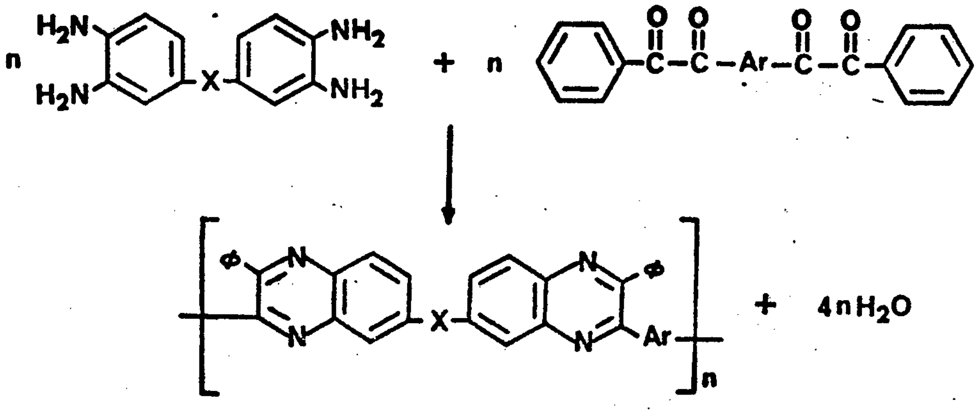
Due to their unusually high thermooxidative stability phenylated polyquinoxalines have recently received considerable attention. In 1969 Wrasidlo and Augl[12,13] synthesized a series of phenylated polyquinoxalines by the one-step solution condensations of aromatic bis(o-diamines) with 1,3 or 1,4-bis(phenylglyoxaloyl)benzene by the following general equation:


XI

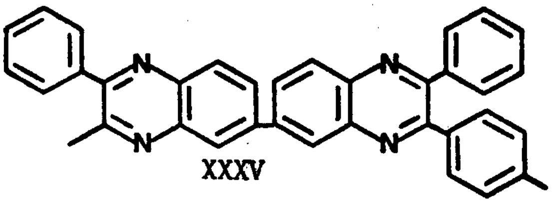
XXXIII

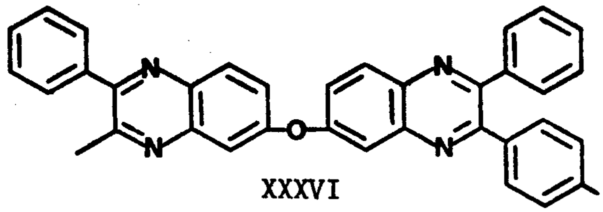

XXVIII

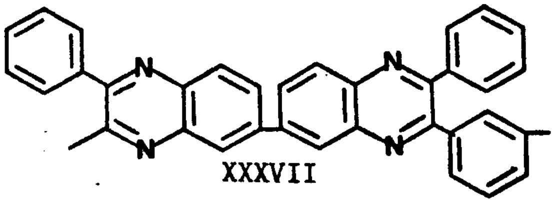
XXXIV

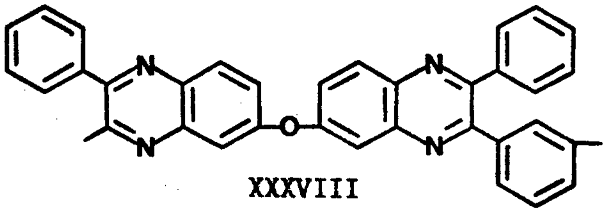


where x may be simply a bond between the phenyl rings or an oxygen atom, and Ar is the p-phenylene or m-phenylene group. In all cases high-molecular-weight linear polymers were obtained within one hour at room temperature. The polymers reported in that study[12,13] are the following:

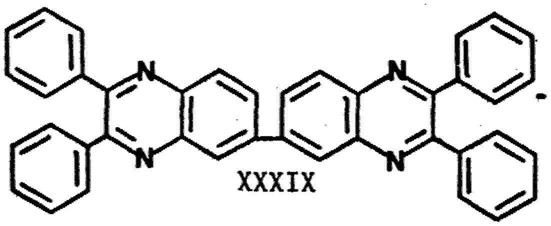

XXXV


XXXVI

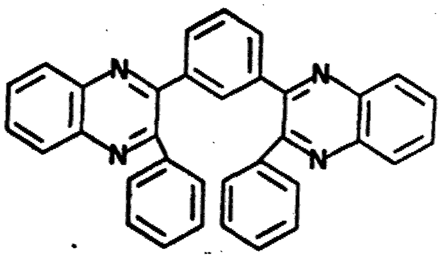

XXXVII


XXXVIII

The corresponding model compounds XXXIX and XL were prepared to determine which segment in the polymer chain contributed to the unusual solubility characteristics found for these polymers. Both the model compounds could be obtained in almost quantitative yield. However, compound XXXIX was completely insoluble in chloroform, while compound XL was very soluble and exhibited many characteristics similar to those of the polymer XXXVII.



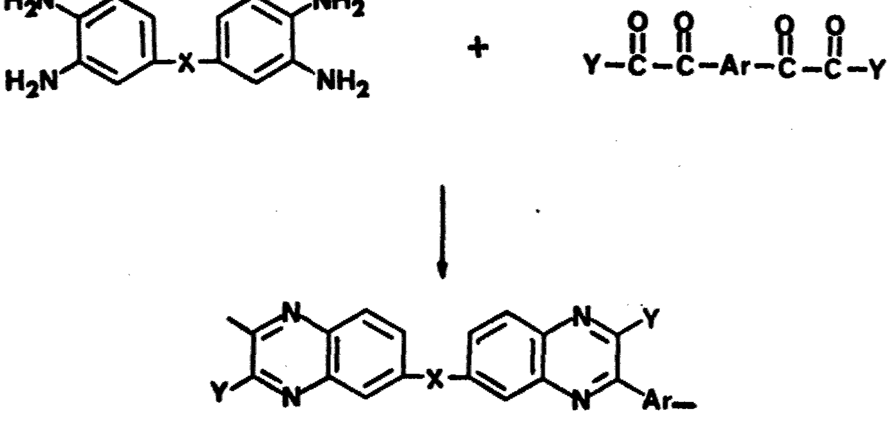
XXXIX



XL

It was observed[13] that polymers with phenyl side-groups exhibit improved solubility and can be readily dissolved in both chlorinated solvents and phenols. The polymers having hydrogen atoms in place of the phenyl groups were found to be completely insoluble in these solvents. The presence of ether groups in the polymer chain apparently does not improve the solubility in chlorinated solvents but increases the solubility in phenols.

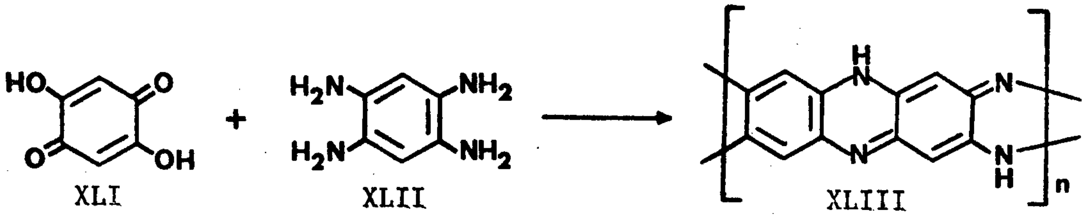
It has been mentioned earlier that polyphenylquinoxalines exhibited superior solubility, thermal stability and processing characteristics when compared to their non-phenylated analogs. In addition to the beneficial effects derived from phenyl group substitution[11,12,13], the introduction of ether groups into the main polymer chain resulted in improved melt characteristics[14]. However, the presence of ether groups results in a substantial decrease in the thermooxidative stability of these polymers[11]. Wrasidlo and Augl[15] examined some of these effects with polymers containing sulfone and carbonyl groups. The formation of the polyquinoxalines is illustrated by the following equation:



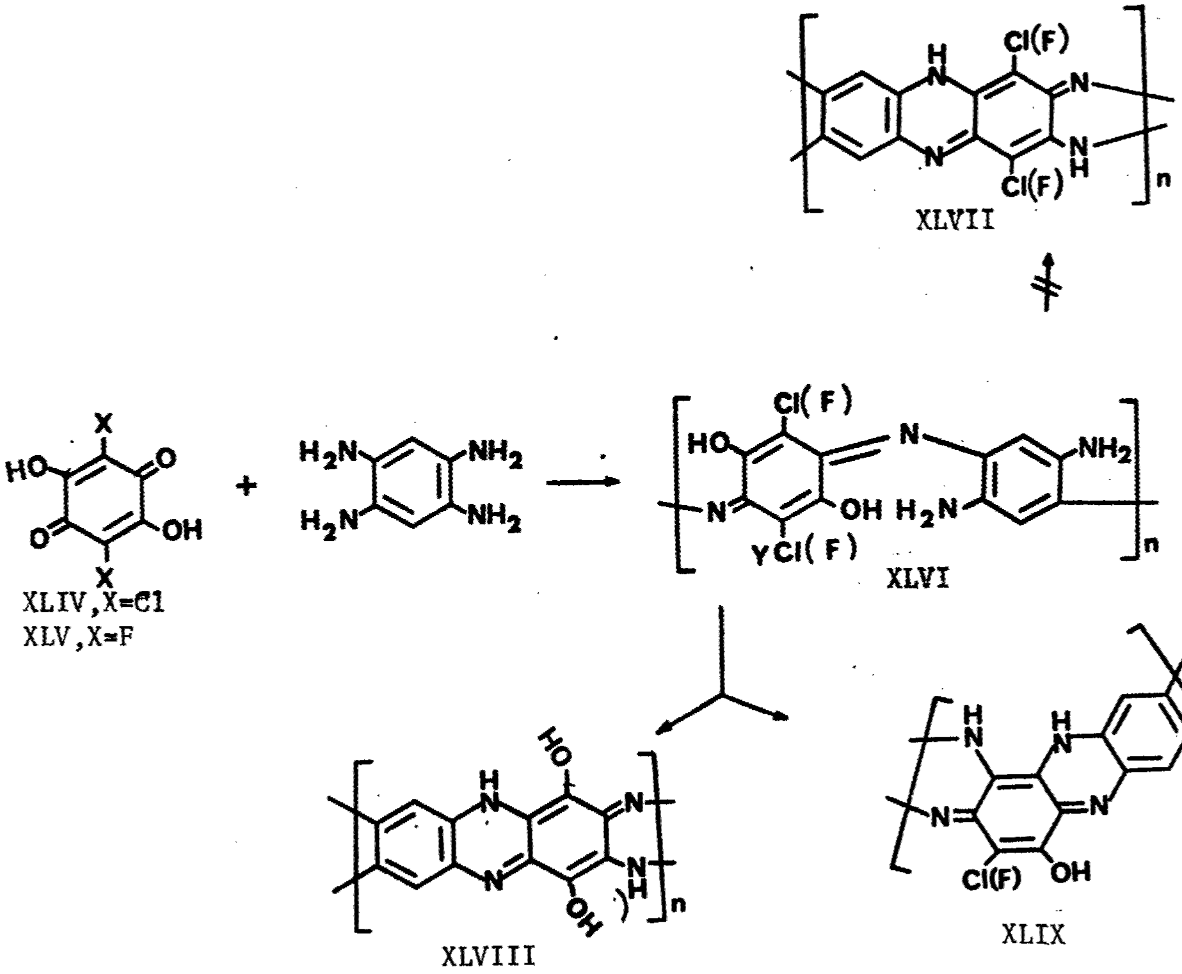
Where x = CO, SO_2, y = H, C_6H_5, Ar = p-phenylene, 4,4'-diphenylether, 4,4'-diphenylsulfone. The reaction of bis-benzels (Y = C_6H_5) with either 3,3'4,4'-tetraminodiphenylsulfone or 3,3',4,4'-tetraaminobenzophenone proceeded at room temperature to yield high-molecular weight soluble polyphenylquinoxalines.

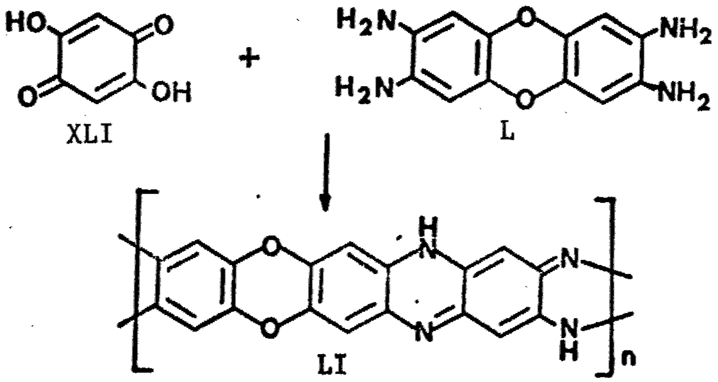
d. Ladder Type Polyquinoxalines

Incorporation of the quinoxaline nucleus into ladder or double strand polymers in order to enhance thermal stability was reported by Stille and Mainen[16-18]. The polymerization of 2,5-dihydroxy-p-benzoquinone (XLI) with 1,2,4,5-tetraaminobenzene (XLII) in HMP or phosphoric acid gave XLIII.

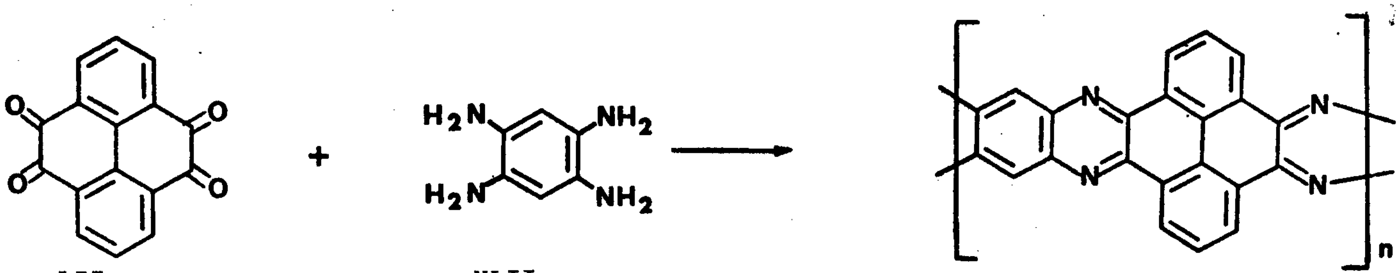

XLI XLII XLIII

The degree of polymerization was markedly dependent on the polymerization medium. Low degrees of polymerization were thought to be due to the formation of a solvent-growing polymer complex. When 3,6-dichloro-2,5-dihydroxy-p-benzoquinone (XLIV) or the 3,6-difluoro derivative XLV were used instead of XLI the corresponding halosubstituted dihydroquinoxalines XLVII were not obtained. Instead polymers XLVIII and XLIX were formed. The presence of the hydroxyl group noticeably decreased the thermal stability of the polymers (decomposition at 200-225°C). The double strand polyquinoxaline polymer LI was synthesized by condensation of XLI and the tetrahydrochloride of amine L[18].

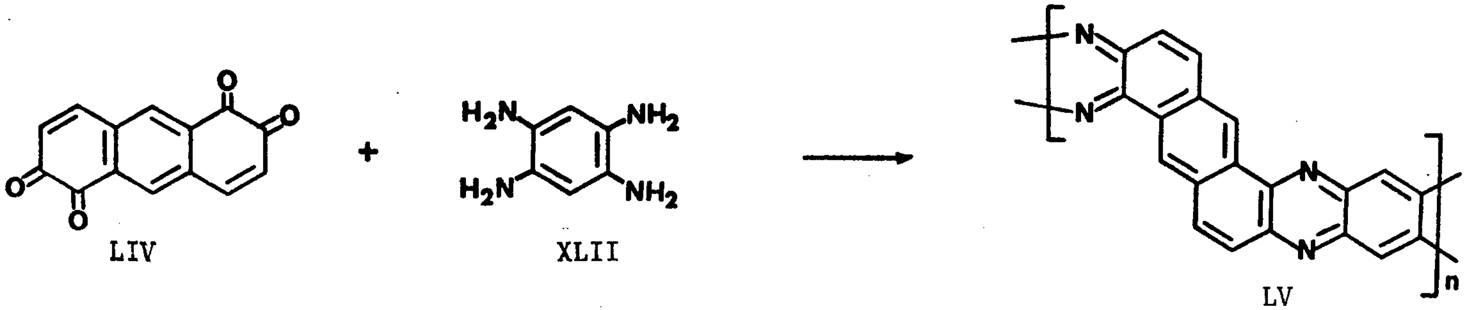

XLVII
Cl(F)
Cl(F)
XLIV, X=Cl
XLV, X=F
XLVI
Cl(F)
Cl(F)
XLVIII
XLIX
Cl(F)


XLI
L
LI

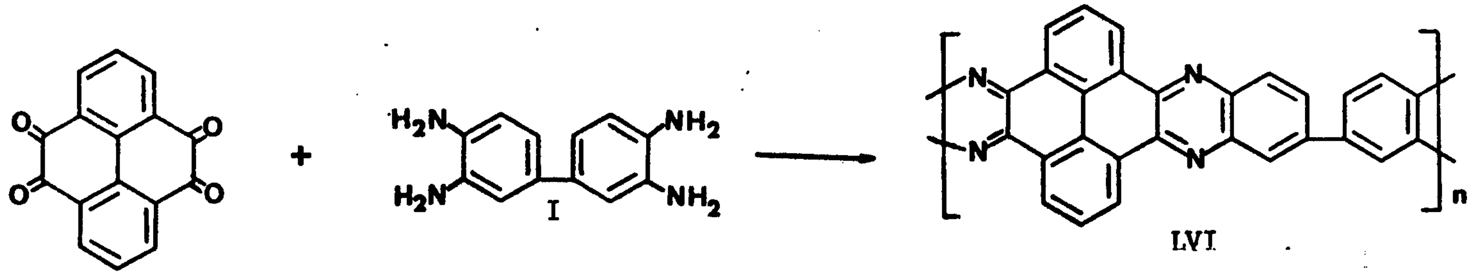
When tetraketones were polymerized with aromatic tetraamines, quinoxaline ladder polymers were obtained. The polymerization of tetraaminobenzene (XLII) with 1,2,6,7-tetraketopyrene (LII) gave polymer LIII[18]. However, reactions of tetraketone LII with the tetramine L failed to produce any polymer. Other polymers synthesized by the condensation of tetraketones and tetraamines are shown below:



LII XLII LIII

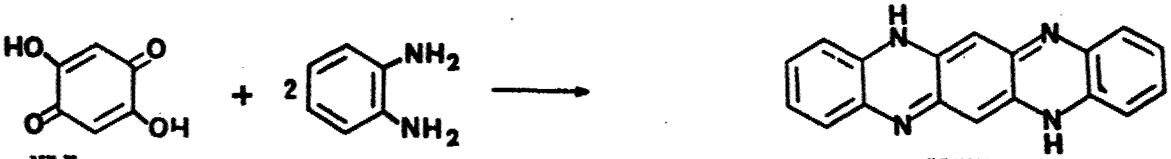


LIV XLII LV



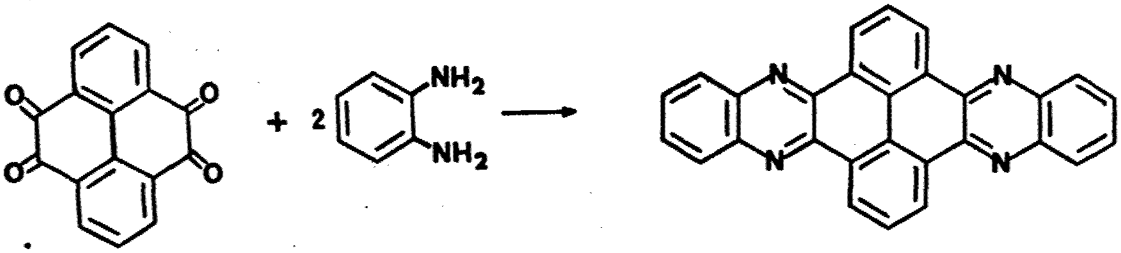
LII LVI

Model Compounds LVII, LVIII, and LIX were also prepared by condensation of the appropriate amines and ketones[18].



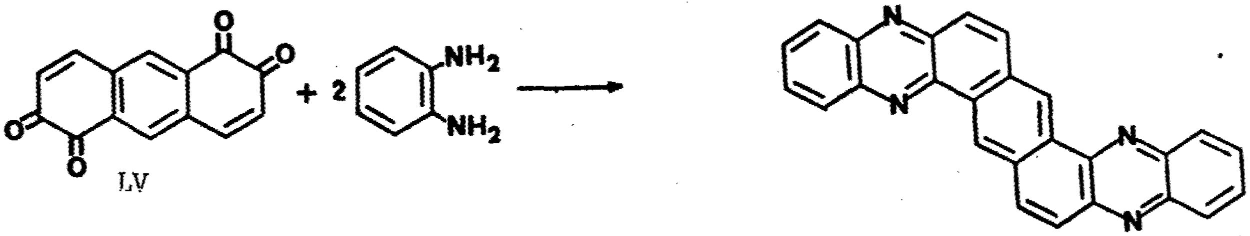
XLI

LVII



LII

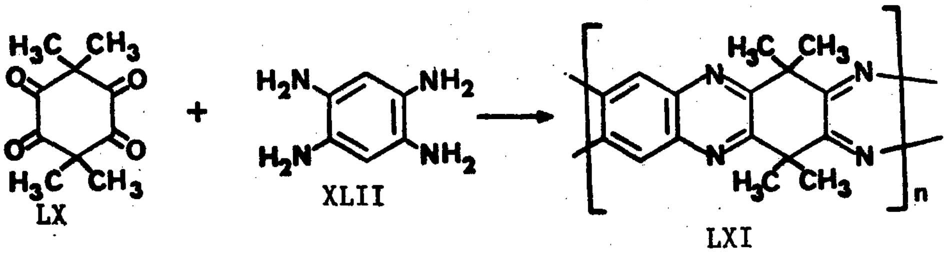
LVIII

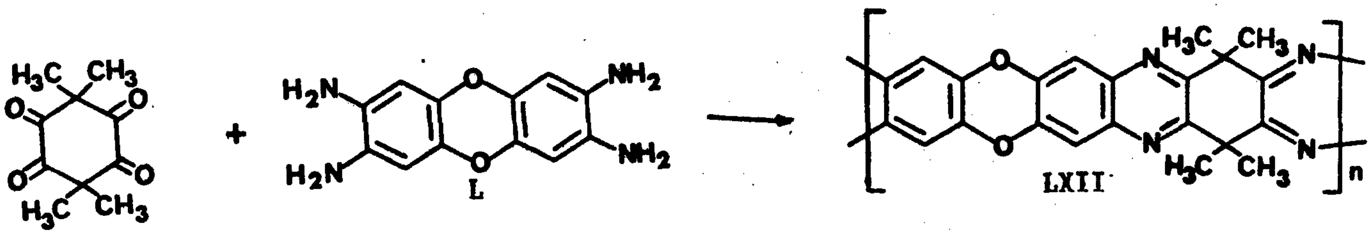


LV

LIX

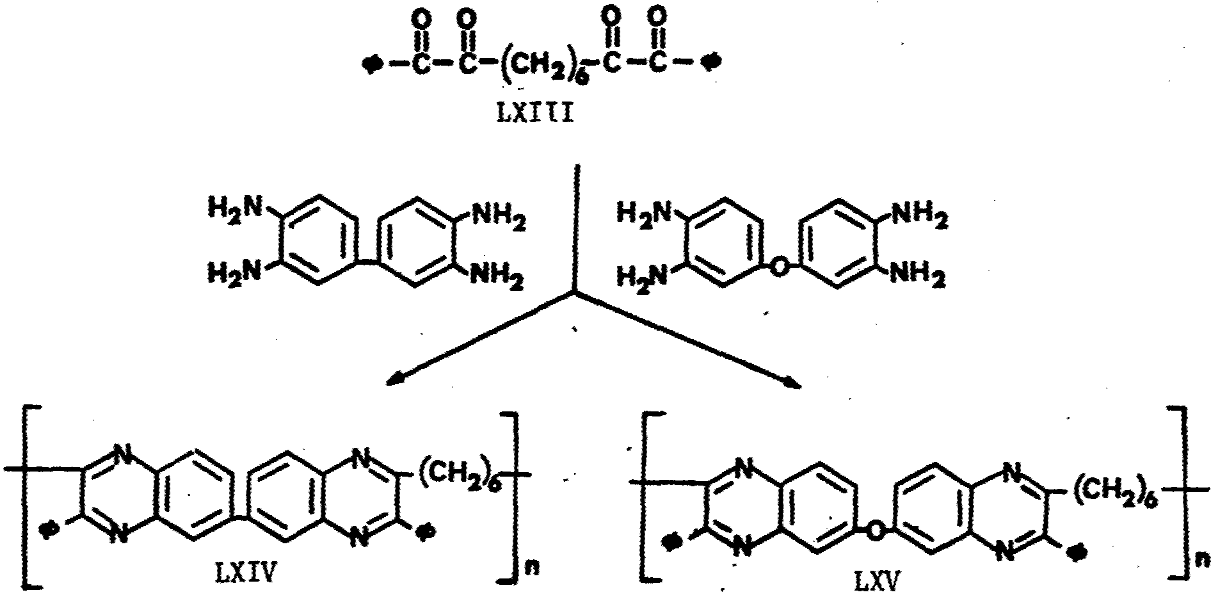
Condensation of 3,3,6,6-tetramethylcyclohexane-1,2,4,5-tetraone (LX) with the tetraamines LII and L produced the ladder polymers LXI and LXII[19] both of which incorporate aliphatic linkages in the polymer double strand. The above two polymers, LXI and LXII, were not found to be as stable as all aromatic polyquinoxalines. In addition LXII was not as stable as LXI.





e. Aliphatic-Aromatic Polyquinoxalines

Research on totally aromatic polyquinoxalines, ladder type polyquinoxalines and the polyphenylquinoxalines has provided high molecular polymers of excellent thermal stability. Although ladder type polyquinoxalines containing aliphatic segments in the polymer chain have been reported[19] the synthesis of aliphatic polyphenylquinoxalines was reported only recently by Hergenrother[20]. The polymerization of 1,10-diphenyldecane-1,2,9,10-tetraone (LXIII) with 3,3'-diaminobenzidine (I) and 3,3',4,4'-tetraaminodiphenyl ether (XI) furnished aliphatic polyquinoxalines LXIV and LXV, respectively. The polymers were found to be extremely tough and to possess excellent adhesion characteristics.

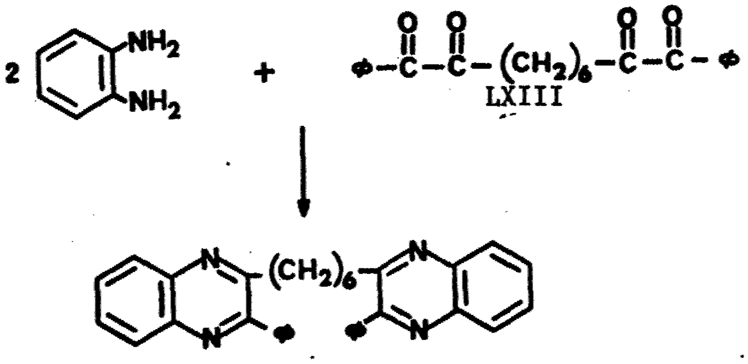


LXIII

LXIV

LXV

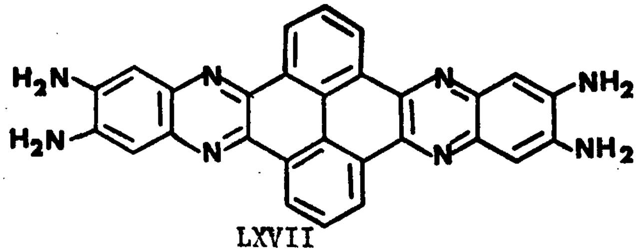
The decomposition temperatures of these materials in both air and in helium were approximately 450°C. The corresponding model compound was prepared in almost quantitative yield by condensation of o-phenylenediamine and 1,10-diphenyldecane-1,2,9,10-tetraone (LXIII).



LXIII

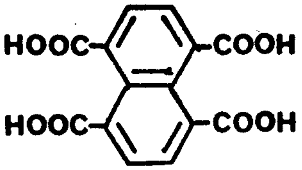
f. Copolymeric Polyquinoxalines

Synthesis of various other types of polymers, polyindoloquinoxalines[21] and polymers with quinoxaline and dioxin units[22] have also been reported. The problem of intractibility of aromatic heterocyclic ladder polymers has been known for some time. Recently, however, it has been shown[23] that soluble high-molecular-weight ladder polymers could be obtained, namely with benzimidazobenzophenanthroline-type ladder polymers (BBL). The aromatic ladder polyquinoxalines which have good thermal stability exhibit unusual solubility characteristics in fluorinated and aprotic solvents. It was considered that a quinoxaline unit in the BBL and pyrone backbone might impart solubility to such systems in aprotic solvents. Using such an approach, Arnold[24] synthesized a new fused aromatic heterocyclic tetraamine, LXVII. Polymerization of LXVII with 1,4,5,8-naphthalenetetracarboxylic acid (LXVIII) formed polymer LXX. LXX was soluble in methanesulfonic acid but exhibited very poor solubility properties in aprotic solvents, such as HMP, DMSO, or NMP. The reaction of LXVII with pyromellitic anhydride (LXIX) in PPA afforded polymer LXXII. Polymer LXXII was partially

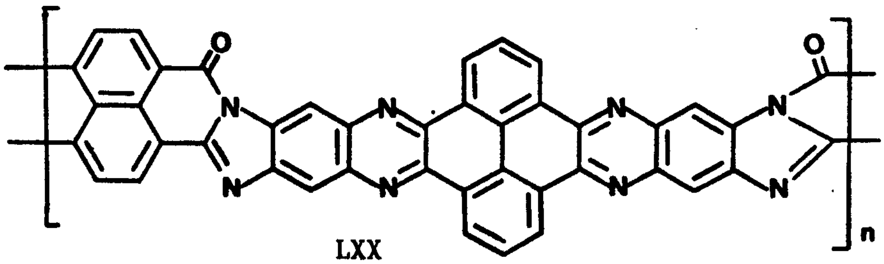


LXVII

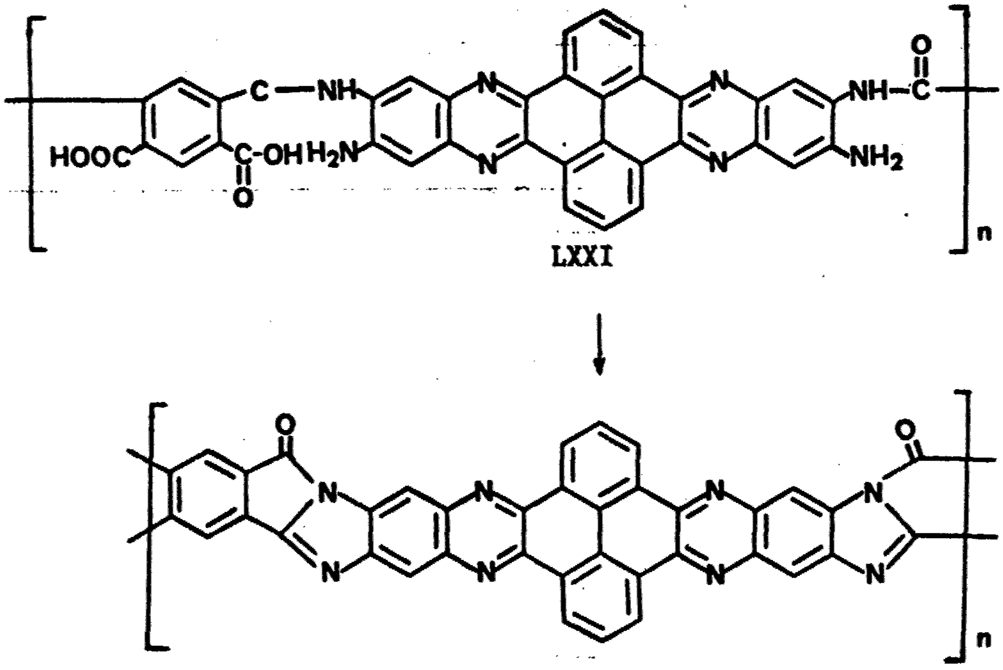
+



LXVIII



LXX



LXXI

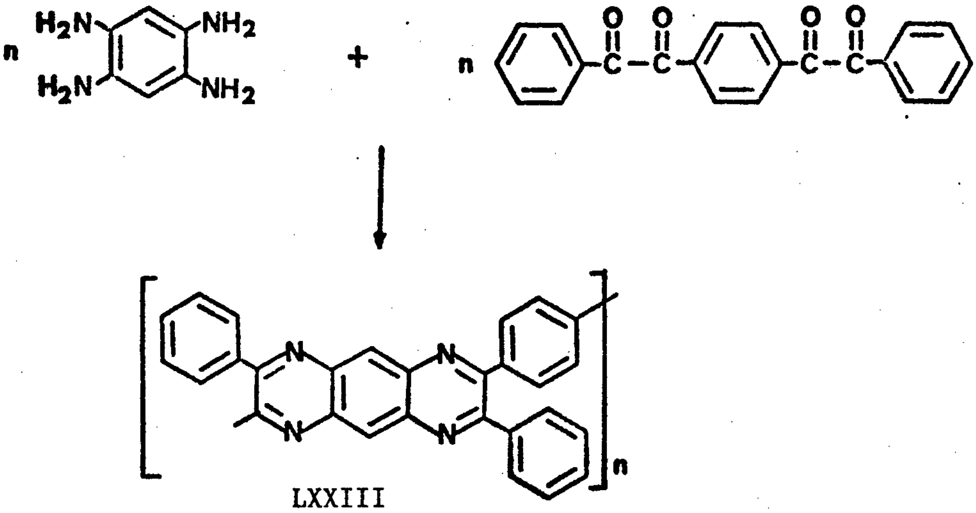
LXXII

soluble in acidic solvents but was found to be virtually insoluble in various aprotic solvents. When the polymerization was carried out in DMAc, the intermediate polyamide-acid-amine LXXI was obtained. On further heating at 250°C, LXXI was converted into LXXII. Both the polymers exhibited thermal stability near 600°C in nitrogen and 450°C in air.

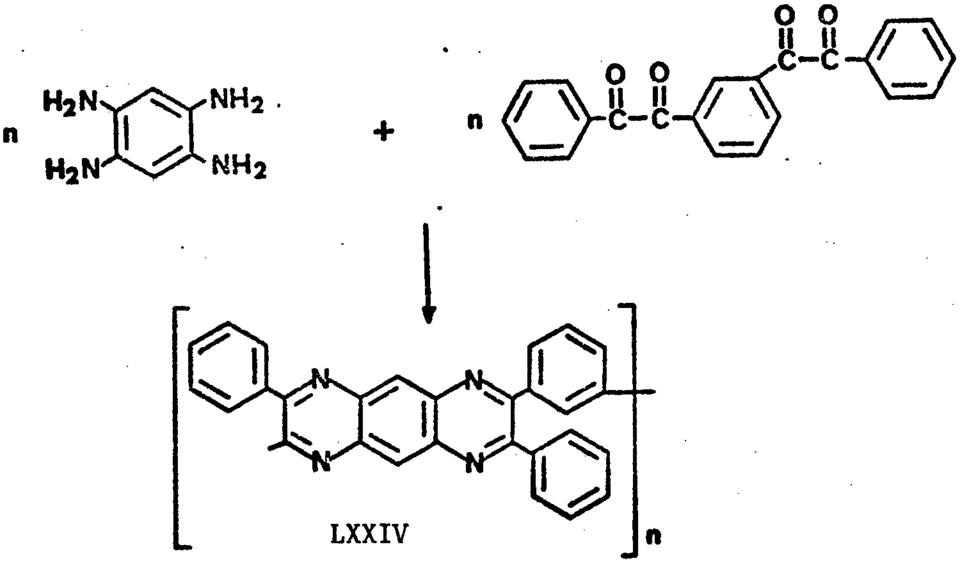
g. Pyrazinoquinoxalines

Wrasidlo and Augl[25] prepared a new type of polymer, phenylated polypyrazinoquinoxalines from the reaction of 1,4-bis(phenylglyoxalyl)benzene or 1,3-bis(phenylglyoxalyl)benzene with 1,2,4,5-tetraaminobenzene to form LXXIII and LXXIV, respectively. Both the polymers, poly[2,7(1',4'-phenylene)-3,8-diphenyl)-pyrazino(2,3-g)quinoxaline] (LXXIII) and poly[2,7(1',3'-phenylene)-3,8-diphenyl)-pyrazino(2,3-g)quinoxaline] (LXXIV) exhibited good thermal stability (polymer decomposition points at about 520°C). The corresponding model compound LXXV was made in 94% yield by reacting two moles of benzil with one mole of tetraaminobenzene.

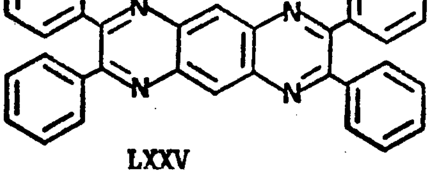
Polymers with chelated polyquinoxaline segments have also been reported[26].



LXXIII



LXXIV

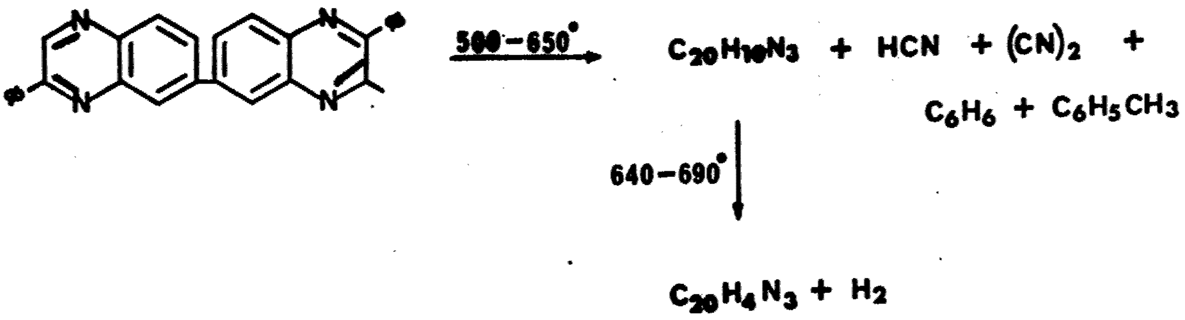


LXXV

2. Thermal Degradation Studies

Until very recently the only information regarding the thermal stability of the various polyquinoxalines was deduced from the reported thermogravimetric analysis (TGA) data or from the polymer decomposition temperatures (PDT). The TGA and PDT of these polymers have been recorded in air, in inert atmosphere, or in vacuum.

Recently, however, the results of an initial investigation of the thermal and oxidative degradation of polyquinoxalines have been reported[11]. When polymer XXXV was pyrolyzed at 640°C in vacuum, hydrogen cyanide, cyanogen, benzene and toluene were obtained as the gaseous products. The thermal degradation occurred over the temperature range of 500-640°C, and resulted in a weight loss of 23%. A pressure maximum was noted but the failure to observe a major endothermic process in this temperature range suggested that bond breaking and recombination mechanisms may be thermodynamically balanced. The main endothermic process was observed between 640-690°C. Analysis of the residue from the decomposition indicated a 64% decrease in hydrogen content with only minor changes in both carbon and nitrogen composition. This led to the conclusion that dehydrogenation constituted the main degradation mechanism. Further, pyrolysis of a thin film of polymer XXXV for 11 seconds at 100°C temperature intervals between 1000 and 1500°C, in an inert atmosphere produced hydrogen, nitrogen, methane, hydrogen cyanide, benzene, toluene and benzonitrile.

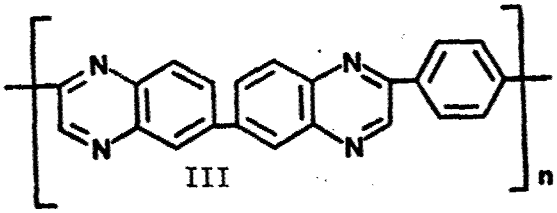


Based on the above data[11] the mechanism by which fully aromatic polyquinoxalines decomposed was considered as a random process. Analysis of the gaseous products obtained from the thermal degradation of the polyquinoxalines examined did not furnish enough information to strongly support a specific mechanism. However, it was postulated that the mechanism involves the opening of the heterocyclic ring with the loss of heterocyclic fragments. At higher temperatures the decomposing polymer undergoes dehydrogenation to produce a nitrogenous residue.[11]

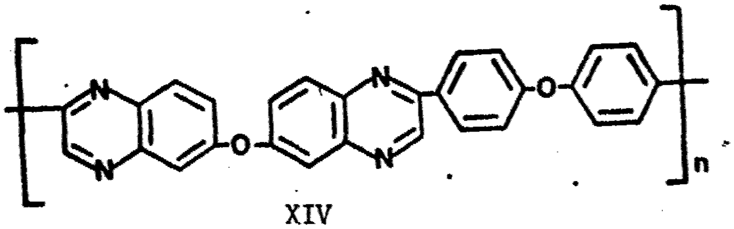
3. Oxidative Degradation Studies

Recent studies on quinoxaline polymers has provided the first available data and observations concerning the oxidative degradation of polyquinoxaline[17].

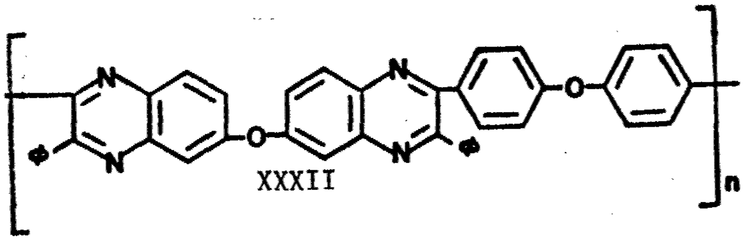
It is known[10,11,12] that phenyl-substituted polyquinoxalines are more stable in air than their unsubstituted analogs. In an investigation of the effect of structure on the oxidative stability of polyquinoxalines it was found[11] that phenyl-substituted polymer XXXV lost 6% of its initial weight after aging at 400°C for 200 hours in static air. The unsubstituted analog, polymer III, lost 58% of its original weight when treated in the same manner. A similar, although less pronounced trend in stability was observed for polymers XXXVI and XII. The phenyl-substituted polymer, XXXVI, lost 49% while polymer XII lost 77% of original weight. In addition to the substituent effect, it was found that the introduction of ether groups into the polymer chain in place of biphenyl or phenylene linkages resulted in a significant decrease in oxidative stability. This effect was demonstrated using three polymers, namely XXXV, XXXVI, and XXXII. The weight loss under the identical experimental parameters were 5, 49, and 74% respectively. Furthermore, it was shown that the greater the number of oxygen atom linkages in the unit structure (polymers XXXII and XIV) the higher the rate and magnitude of the weight loss.



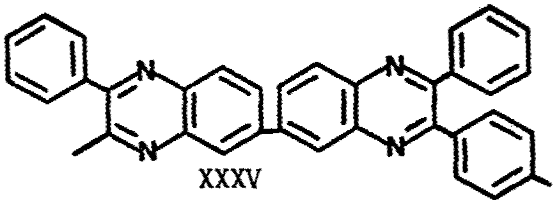
III



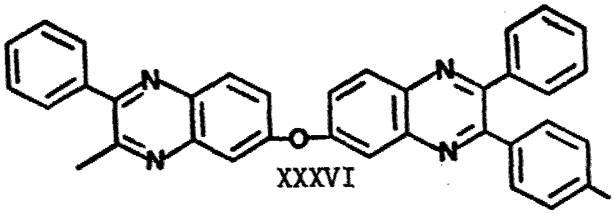
XIV



XXXII



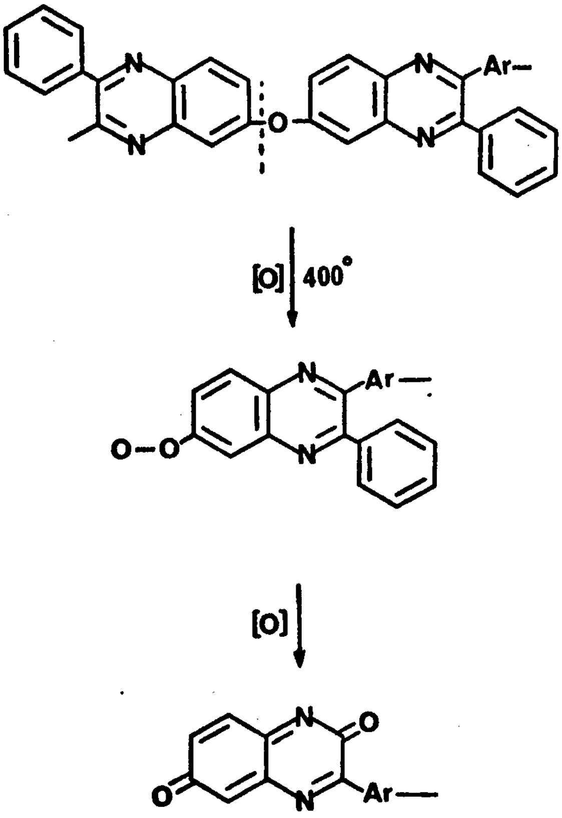
XXXV



XXXVI

On exposure of a film of polymer XXXV to temperatures of 400°C in air for 200 hours, no changes in the infrared spectrum or in the elemental analysis of the sample were observed. In contrast, a film of polymer XXXVI on exposure to the same conditions for about half the time (96 hours) exhibited marked changes in elemental composition, (a two-fold increase in the element oxygen). The infrared spectrum of polymer XXXVI after aging contained a new band at 2225 cm^{-1} (The -C≡N group) and two strong bands at 1740 and 1685 cm^{-1} (both in the region characteristic of carbonyl group absorptions). The oxidative pyrolysis of polymer XXXV was further investigated using simultaneous thermogravimetric analysis (TGA), differential weight loss (DTG) differential thermal analysis (DTA) and sample temperature (T_S) in flowing air.

From the above data it was concluded that the introduction of oxygen linkages into the polymer chain lowers both the thermal and oxidative stability of polyquinoxalines[11]. The formation of two carbonyl bands, the higher rate of weight loss and the two-fold increase in oxygen content of the residue after exposure of oxygen atmospheres in the polymers containing ether linkages suggested a mechanism by which ether containing phenylsubstituted quinoxalines were oxidized[11]. The oxidation is initiated at the ether linkage to produce a peroxy radical. The process was proposed to follow the steps outlined in Figure 1. Attack of oxygen at the ether linkage (or a peroxy radical from prior oxidation at another site) would promote the rupture of the linkage forming a phenoxy radical and a peroxy radical. Further reactions were proposed to lead to the elimination of phenyl side groups and subsequently to the quinonoid product LXXVI.



LXXVI

Figure 1. Mechanism of Thermooxidative Degradation of Poly(ether)phenylquinoxaline)[11]

A different mechanism was proposed for the oxidation of unsubstituted polyquinoxalines[11]. Oxidation was postulated (Figure 2) to be initiated in the heterocyclic ring portion of the molecule (LXXVII) followed by rapid attack by oxygen to form peroxy radicals (structure LXXVIII). Interaction of the peroxy radical with the hydrogen atom of the heterocyclic ring was proposed to produce a more stable hydroperoxide. Decomposition of the hydroperoxide to form the quinonoid structure LXXVII and other products in a slow rate determining step.

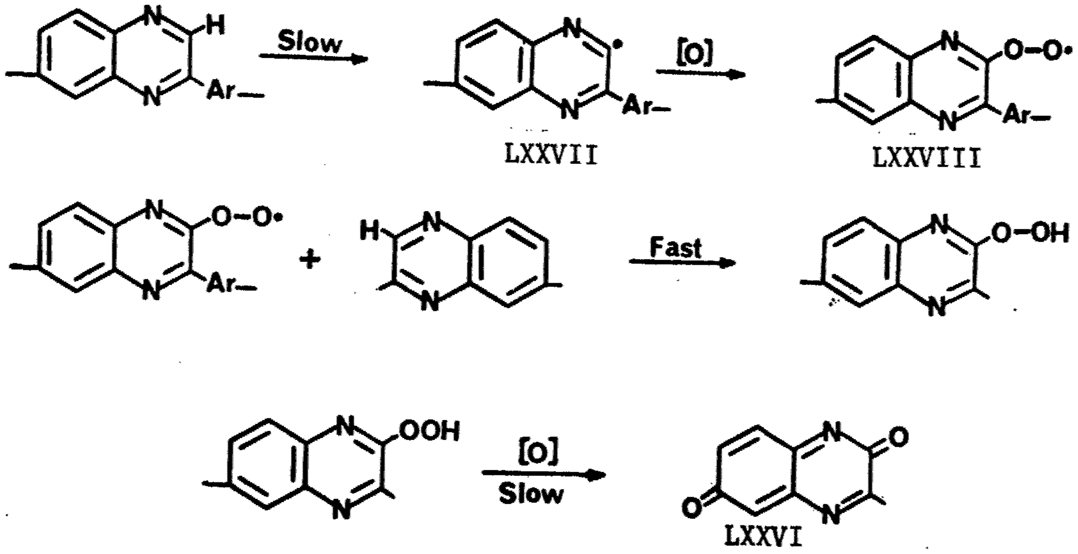
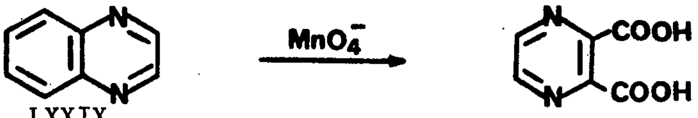


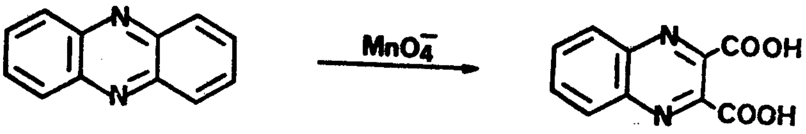
Figure 2. Mechanism of Thermooxidative Degradation of Polyquinoxalines[11]

4. Solution Oxidation of Quinoxalines

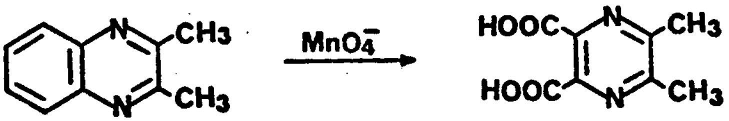
Relatively few reports exist on the solution oxidation behavior of substituted quinoxalines. However, all of them, in contrast to the reported[11] behavior of the polyquinoxalines under thermal oxidation reveal that the carbocyclic ring adjacent to the pyrazine nucleus is considerably more reactive to oxidation than the heterocyclic ring, itself. Thus quinoxaline (LXXIX) has been reported[27,28] to yield pyrazine-2,3-dicarboxylic acid (LXXX) on oxidation with alkaline permanganate. Similarly 2,3-benzoquinoxaline (LXXXI) on similar treatment yields quinoxaline-2,3-dicarboxylic acid (LXXXII)[29]. Surprisingly, 2,3-dimethylquinoxaline (LXXXIII) yields 2,3-dimethylpyrazine-5,6-dicarboxylic acid (LXXXIV)[30]. 2-Methylquinoxaline (LXXXV) according to one report[27] yields 2-methylpyrazine-5,6-dicarboxylic acid (LXXXVI) while others report[31] 2,3,5-pyrazinetricarboxylic acid (LXXXVII). No information has apparently been reported describing the solution oxidation behavior of phenyl-substituted quinoxalines.



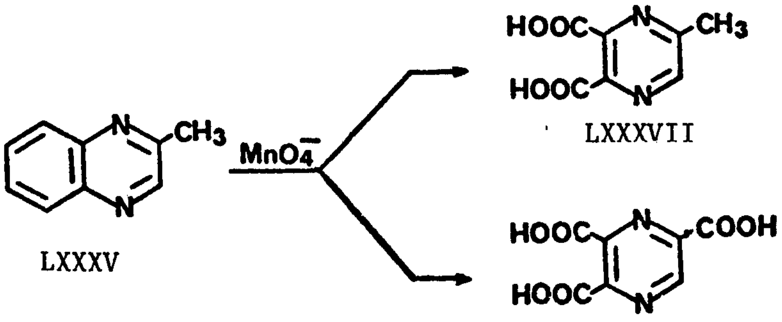
LXXIX LXXX



LXXXI LXXXII



LXXXIII LXXXIV



LXXXV LXXXVII LXXXVII

5. Related Systems: Degradation of Benzimidazoles

The results and conclusions presented in the preceding pages and our finding[32] that the benzimidazole, benzimidazolone and benzimide systems on oxidative degradation all produce similar gaseous and condensable products led us to postulate that a large number of the benzheterocyclic ring systems degrade thermooxidatively by very similar, if not the same, mechanisms. The oxygenation steps forming volatile products results from attack at the carbocyclic ring adjacent to the heterocyclic nucleus.

Therefore it was of interest and somewhat surprising that the polyquinoxaline system was reported[11] to oxidize pyrolytically at the heterocyclic nucleus although in solution oxidation it appears to occur preferentially at the carbocyclic ring adjacent to that heterocyclic nucleus. This behavior appears to contradict the general mechanistic proposal from our laboratories based on data from three other aromatic heterocyclic ring systems which are briefly outlined in the following paragraphs.

Solution and Thermal Oxidations of Benzimidazoles

Previous reports from our laboratories[32] disclosed experimental results providing evidence which supports an oxidation mechanism for polybenzimidazole involving a stepwise oxidation at a specific linkage in the repeat-unit of the the polymer chain.

The suggestion that during the course of thermal oxidation, the m-phenylene segment remains intact longer than the remainder of the repeat unit is supported by the observation that polybenzimidazole, model compound LXXXVIII and model compound LXXXIX yield isophthalonitrile, terephthalonitrile and benzonitrile respectively as the only organic products (Figure 3). Thus by default, the benzimidazole portion of the molecule was selected as the most reactive site for initial oxygenation. Additional experimental evidence for this proposal was obtained by the observation that controlled oxidation

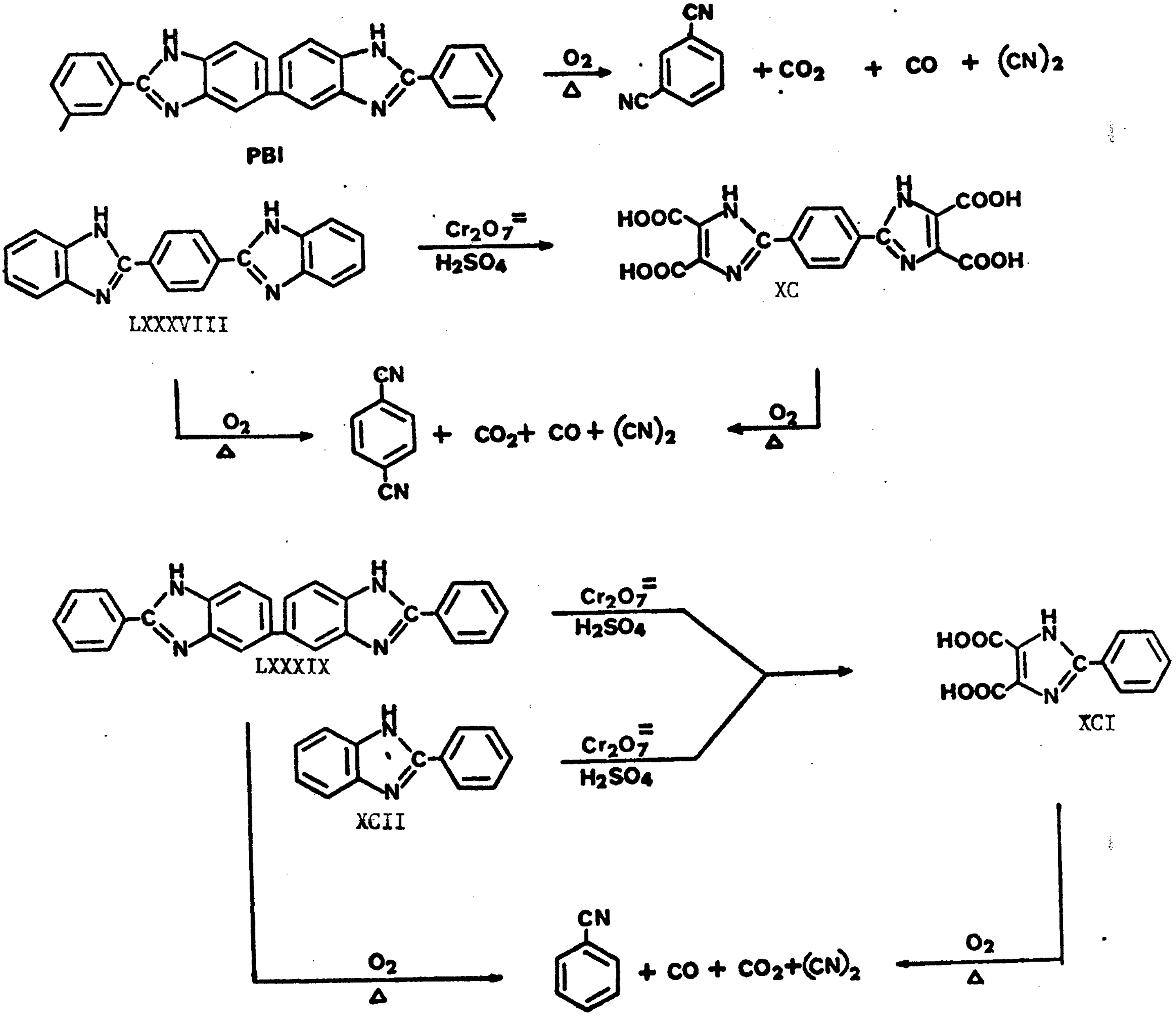


Figure 3. Interrelationship of Solution and Thermal Oxidation in the Benzimidazole System.

of polybenzimidazole film (300°, O_2) resulted in the appearance and gradual increase of nitrile groups in the polymer chain and concurrent gradual disappearance of the biphenyl units. This further suggested the carbocyclic ring adjacent to the imidazole heterocyclic ring is the likely site for initial oxygenation. Figure 3 summarizes the types of reactions found for both the solution and pyrolytic oxidations in polybenzimidazole and typical model compounds.

Oxygenation was thought to occur by reaction of molecular oxygen with the benzimidazole radical formed by homolytic cleavage of the nitrogen-hydrogen bond as shown in Figure 4.

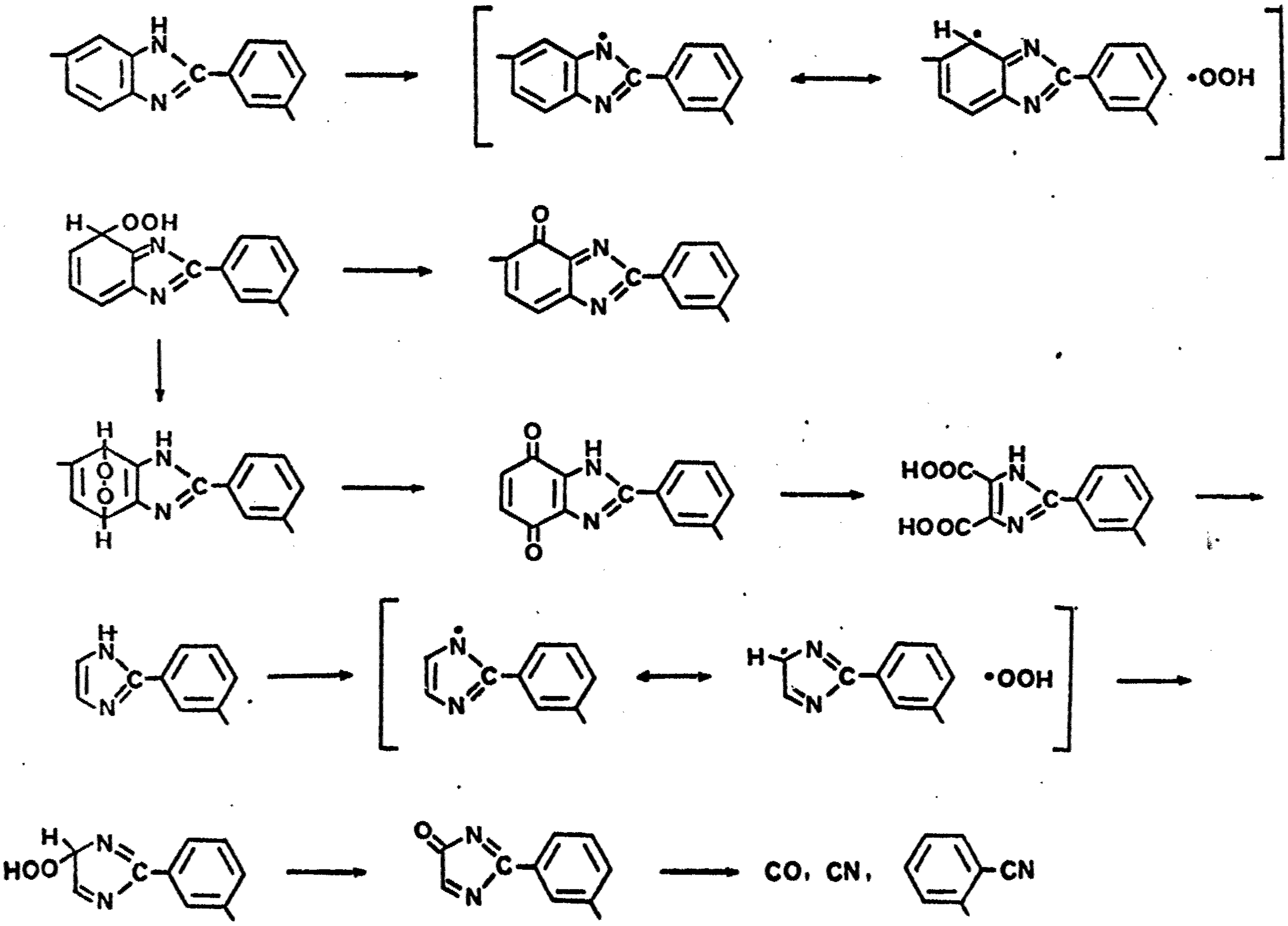


Figure 4. Proposed Mechanism for the Thermooxidation of the Benzimidazole System.

In addition, experimental evidence has been found confirming the postulation that initial oxygenation occurs preferentially at the benzenoid carbocyclic adjacent to the imidazole ring. Thus the fact that model compounds LXXXVIII and LXXXIX undergo oxidation in solution by dichromate to yield the corresponding imidazole tetra-, and dicarboxylic acids, XC and XCI, respectively (Figure 3), confirms previous reports and supports the suggestion that the aromatic heterocyclic ring is more resistant to oxidation than the adjacent aromatic carboxyclic ring.

Subsequent oxidative pyrolysis of the benzimidazole solution oxidation intermediates, such as XCI, 2-phenylimidazole-4,5-dicarboxylic acid, gives products identical (oxides of carbon, cyanogen and benzonitrile) to those obtained from similar thermal oxidation of the parent model compound (Figure 3), confirming that identical, or most probably similar oxygenated intermediates are also likely transitory species in pryolytic oxidation of the 2-arylbenzimidazole system.

Finally pyrolytic oxidation and subsequent mass spectral analysis of the products from model compound LXXXIX labelled in the 2(2') (LXXXIX-H) position and in the terminal ring (LXXXIX-T) confirm that the carbocyclic aromatic nucleus adjacent to the imidazole heterocyclic ring is the most reactive site for initial oxygenation since those carbons initially produce the greatest percentage of carbon dioxide (H and T refers to the heterocyclic-ring carbon and terminal-ring carbon atoms, respectively)[33]. In the same series of experiments, it was found that the terminal phenyl carbon atoms produce (initially) the lowest percentage of carbon dioxide proving that this position is less susceptible to initial attack by oxygen.

SECTION III

PRESENT INVESTIGATION

1. Purpose

The observations reported[11] for thermal oxidation of the polyquinoxaline systems lend themselves to alternative interpretations. One such interpretation would support the generalization that oxygenation occurs not at the heterocyclic but at its adjacent carbocyclic ring.

The observation that a film of polymer XXXVI exhibited absorption bands at 1740 and 1685 cm^{-1} in its infrared spectrum after isothermal aging at 400°C is the only experimental evidence presented in support of the suggestion that extended quinoid structures such as LXXVI are common to all of the polyquinoxaline systems studied[11]. Indeed, the observed infrared absorptions are equally consistant with the intervention of a pyrazine-5,6-dicarboxylic acid intermediate. Such an intermediate diacid would be formed by a series of steps which are parallel to those proposed for thermal oxidation of the benzimidazole system as described in Figure 5.

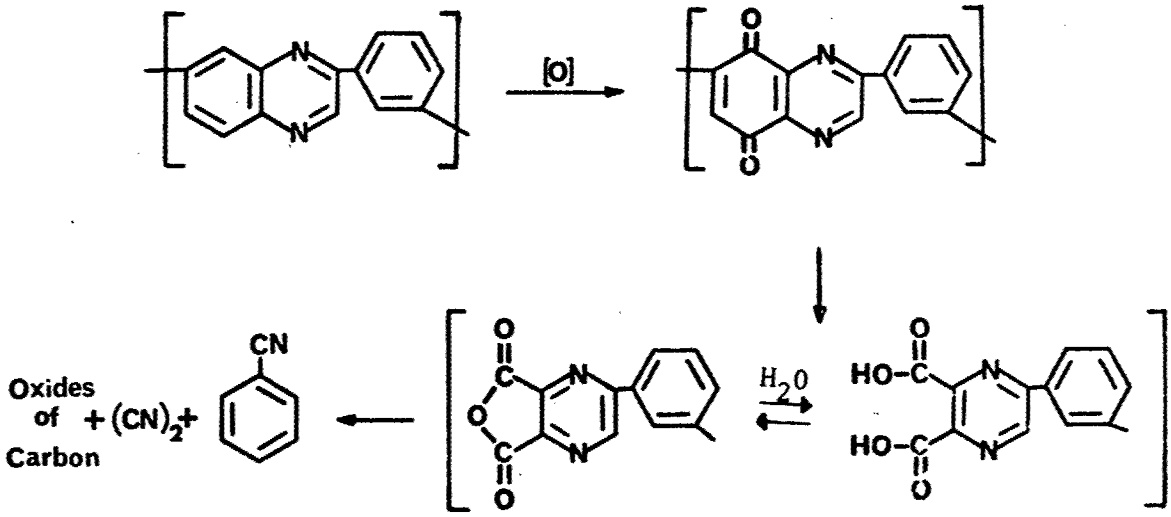
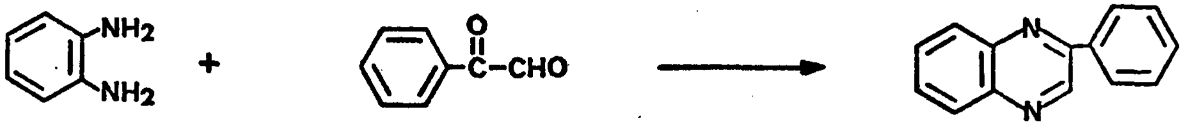


Figure 5. Proposed Thermal Oxidation Mechanism for the Quinoxaline System.

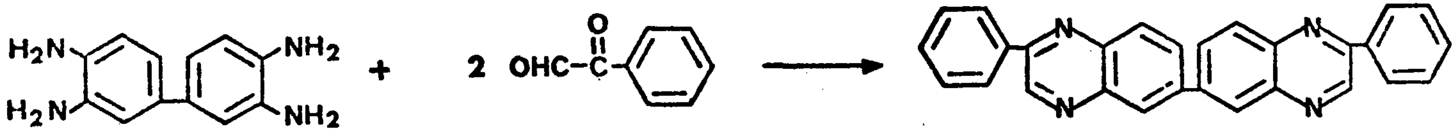
A program has been initiated which parallels the experimental methods employed with the benzimidazole system in order to determine the mechanism by which the quinoxaline system degrades in oxygen atmospheres at elevated temperatures. Our goal is to test the generality of the initial oxidation mechanism demonstrated in the benzimidazole polymer series by extending its scope to include the quinoxaline system. This system was expected to provide counterpart solution oxidation intermediates, the pyrazinedicarboxylic acids enabling ready study of the quinoxaline system.

2. Synthesis of Model Compounds

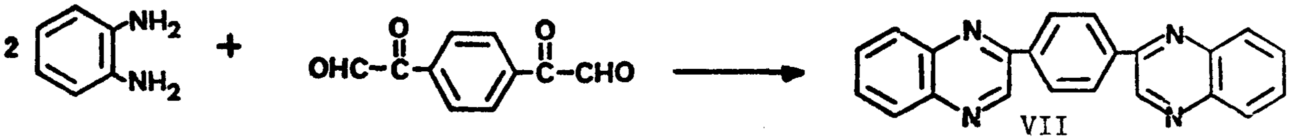
The synthesis of polyquinoxalines and related model compounds was discussed in previous paragraphs. The model compounds prepared in the present investigation were synthesized by condensation reactions between benzil or phenylglyoxal and the appropriate di- or tetra-amine in the melt phase or in solution as summarized in the following equations.



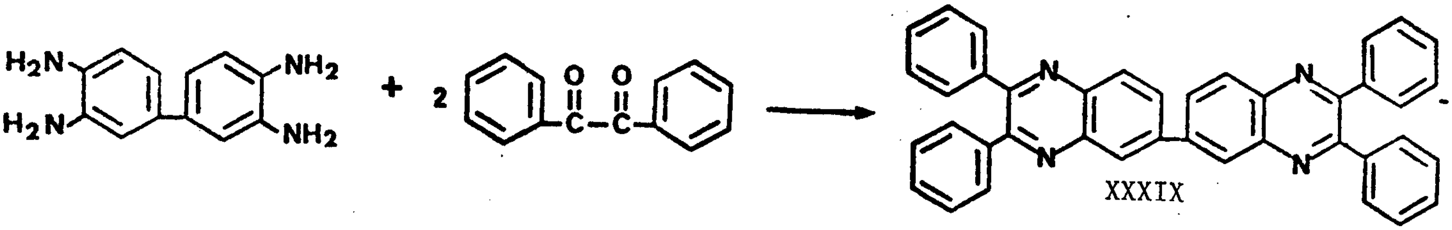
XCVI



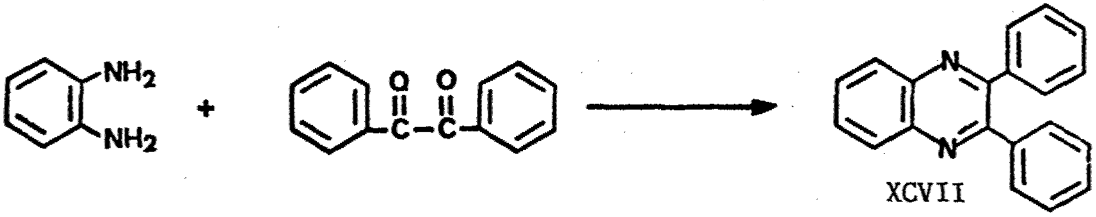
VIII

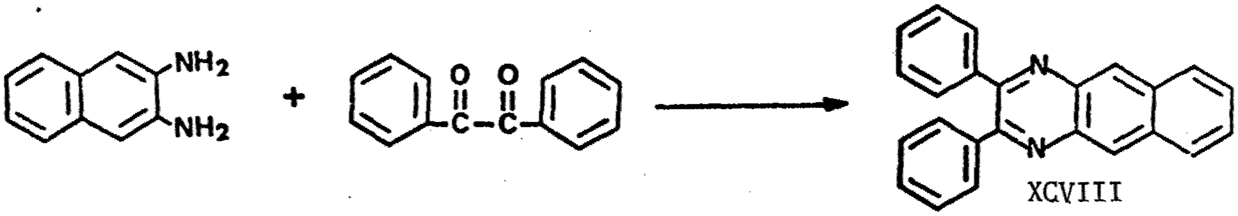


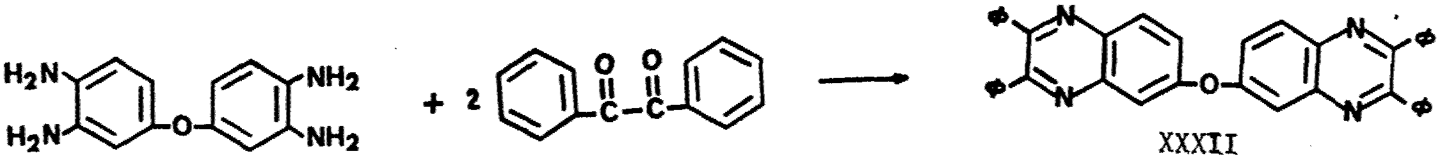
VII

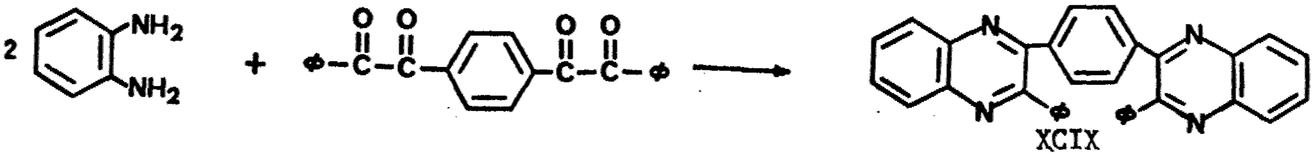


XXXIX


XCVII


XCVIII


XXXII


XCIX

With the exception of VIII all of the above model compounds were obtained in high yield and as sharp melting compounds. Compound VIII is reported[6] as the only isolatable isomer (m.p. 314-5°C) from condensation of 3,3-diaminobenzidine tetrahydrochloride and phenylglyoxal hydrate. However, in our hands the product obtained melted over a broad range (220-245°C) suggesting a mixture of the isomers: 2,2'-diphenyl-6,6'-bisquinoxaline, 2,2'-diphenyl-7,7'-bisquinoxaline and 2,2'-diphenyl-6,7'-bisquinoxaline. The difference in melting behavior may also be due to polymorphism in this compound*.

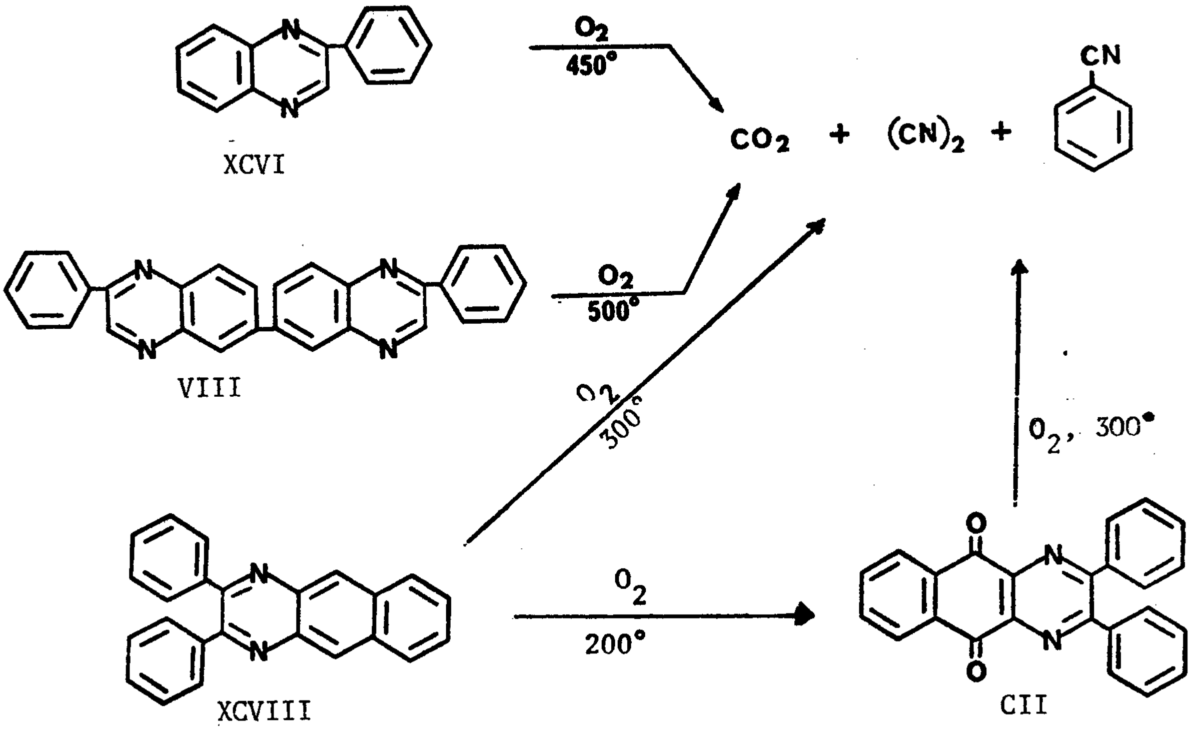
---

* The corresponding 2,2'-diphenyl-5,5'(6,6')-bibenzimidazole and 2,2'-di-p-aminophenyl-5,5'(6,6')-bibenzimidazole exhibited polymorphism when on differential thermal analysis they exhibited dual melting endotherms at 345, 425°C and 355, 451°C respectively[34].

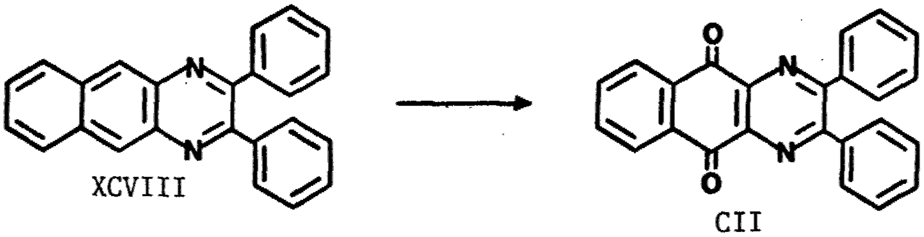
3. Oxidative Pyrolysis of Model Compounds

When 2-phenylquinoxaline (XCVI) was heated in flowing oxygen for 90 minutes at 300°C, no evidence of degradation was observed. No carbon dioxide or cyanogen was found in the off-gases and the only condensable found was sublimed 2-phenylquinoxaline. Similar treatment of XCVI at 450°C for 90 minutes produced cyanogen (collected as a silver salt), carbon dioxide (collected as the barium salt) and the condensable benzonitrile (identified by its infrared spectrum).

Similar pyrolytic oxidation of 2,3-diphenylbenzo[g]quinoxaline (XCVIII) and its quinone (CII) at 300°C produced volatile products identical to those obtained on similar treatment of XCVI, VIII and the series of benzimidazole and benzimide model compounds[32]. Isothermal aging of 2,3-diphenylbenzo[g]-quinoxaline (XCVIII) at 200°C for 400 hours in oxygen produced the corresponding quinone (CII). (IR spectra of reaction mixture shown in Figure 51.) This



result is quite dramatic in that it represents the first instance in which an oxygenated product has been isolated from oxidation of any of the model compounds included in our program. The structure of quinone (CII), 2,3-diphenylbenzo[g]quinoxaline-5,10-dione was established by independent synthesis from 2,3-diphenylbenzo[g]quinoxaline (XCVIII) by reaction with chromic anhydride in acetic acid. The quinone product was bright yellow and revealed infrared carbonyl absorptions at 1678 cm^{-1}.

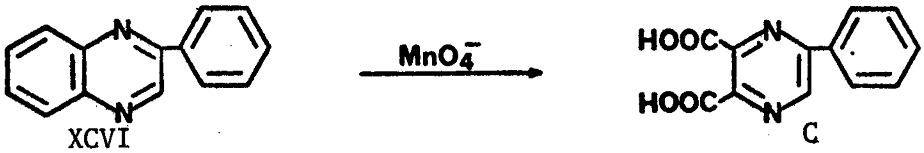

XCVIII

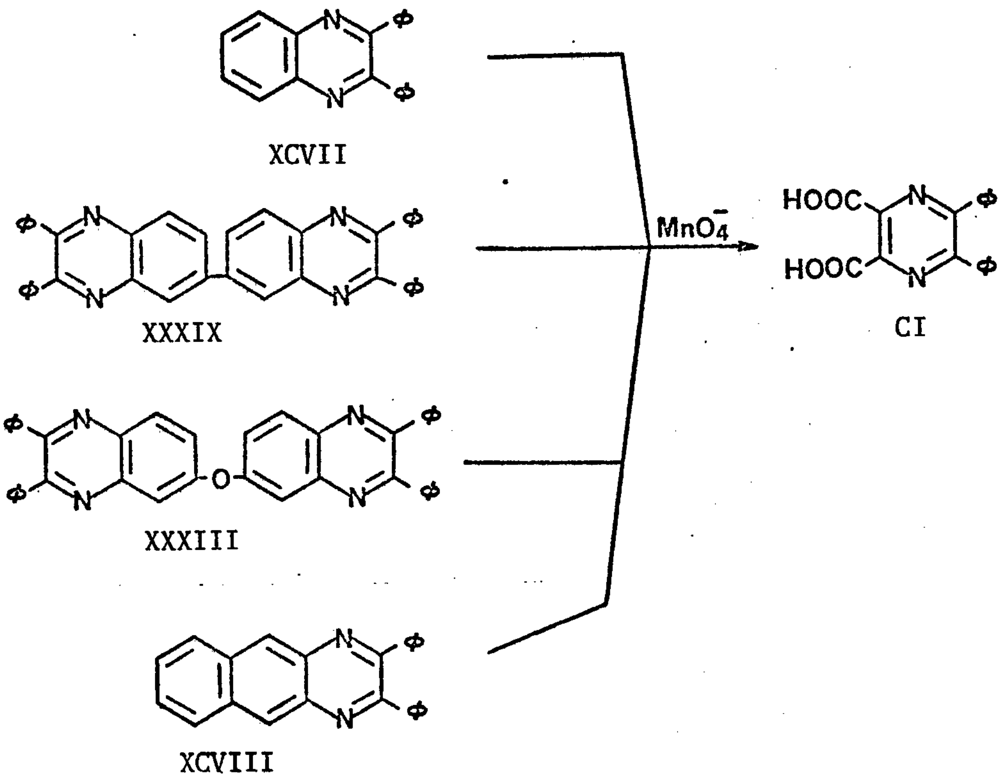
CII

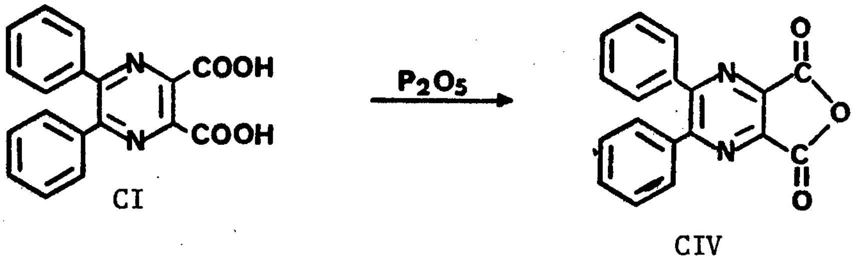
4. Solution Oxidation of Model Compounds

The quinoxaline model compounds were reacted with aqueous alkaline permanganate at 75-85°C to effect oxidation. In most cases, the oxidation product isolated resulted from oxidation of the carbocyclic ring adjacent to the heterocyclic ring to produce the pyrazine dicarboxylic acids. Thus solution (alkaline permanganate) oxidation of 2-phenylquinoxaline (CXVI) produces 2-phenylpyrazine-5,6-dicarboxylic acid (C) in fifty percent yield. The structure assignment was made on the basis of neutralization equivalent, infrared analysis (Figure 50) and decarboxylation to the corresponding 2-phenylpyrazine.

2,3-Diphenylquinoxaline (XCVII), 2,3-diphenyl-benzo[g]quinoxaline (XCVIII), 2,2',3,3'-tetraphenyl-6,6'-biquinoxaline (XXXIX) and 2,2',3,3'-tetraphenyl-6,6'-oxidiquinoxaline (XXXIII) all produced the expected 2,3-diphenylpyrazine-5,6-dicarboxylic (CI) acid on solution oxidation with alkaline permanganate. The structure of the pyrazine dicarboxylic acid product (CI) verified by its neutralization equivalent, infrared spectrum (carbonyl absorptions at 1710 and

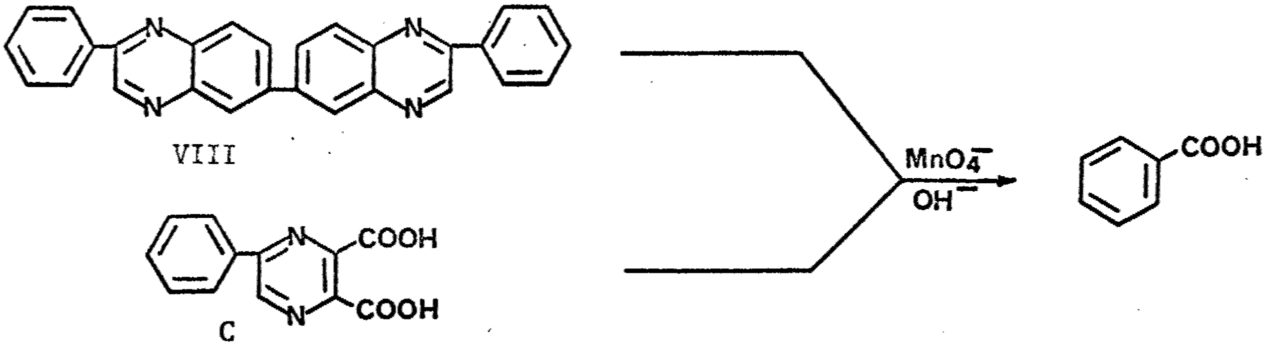

XCVI
MnO_4^-
HOOC
HOOC
N
C


XCVII
XXXIX
XXXIII
XCVIII
MnO_4^-
HOOC
HOOC
Φ
N
CI


COOH
COOH
CI
P_2O_5
O
C
N
CIV

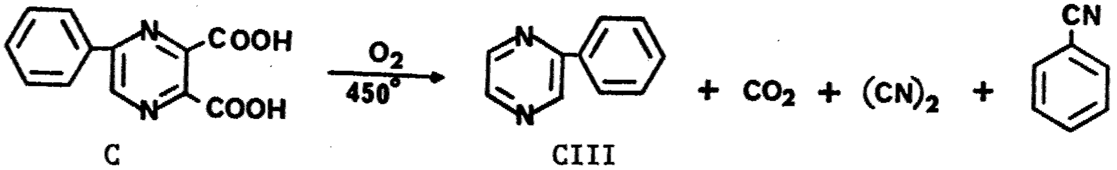
1745 cm^{-1}, Figure 40). Further, the dicarboxylic acid was readily converted to its cyclic anhydride (CIV) by treatment with phosphorous pentoxide. The infrared spectrum of the anhydride was consistent with its proposed structure showing a carbonyl doublet at 1800 and 1864 cm^{-1} (Figure 49).

Model compound VIII, 2,2'-diphenyl-6,6'-biquinoxaline displayed somewhat anamolous behavior on treatment with alkaline permanganate. The product isolated from this reaction was benzoic acid rather than the expected 2-phenylpyrazine-5,6-dicarboxylic acid.



5. Oxidative Pyrolysis of Solution Oxidation Products

When 2-phenylpyrazine-5,6-dicarboxylic acid (C), the solution oxidation product of 2-phenylquinoxaline (XCVI) was pyrolyzed in an oxygen atmosphere at 450°C, the products obtained were carbon dioxide, cyanogen and 2-phenylpyrazine (CIII).



6. Discussion of Results

Those model compounds subjected to solution oxidation by aqueous alkaline permanganate revealed by the products isolated that the carbocyclic ring adjacent to the heterocyclic pyrazine ring is the more labile to oxidation. Thus 2-phenylquinoxaline (XCVI) produced 2-phenylpyrazine-5,6-dicarboxylic acid (C). Similarly, 2,3-diphenylpyrazine-5,6-dicarboxylic acid (CI) was produced by 2,3-diphenylquinoxaline (XCVII), 2,2',3,3'-tetraphenyl-6,6'-biquinoxaline (XXXIX), 2,2',3,3'-tetraphenyl-6,6'-oxydiquinoxaline (XXXIII), and 2,3'-diphenylbenzo[g]quinoxaline (XCVIII). This behavior parallels that observed during oxidation of 2-phenylbenzimidazole model compounds with acidic dichromate resulting in formation of the corresponding 2-phenylimidazole-4,5-dicarboxylic acids.

The model compound 2,2'-diphenyl-6,6'-biquinoxaline (XCVIII) yields benzoic acid instead of the expected 2-phenylpyrazine-5,6-dicarboxylic acid when reacted with alkaline permanganate. The fact that the pyrazine dicarboxylic acid is probably an intermediate (or similar in structure to involved intermediates) in this reaction is supported by the fact that 2-phenylpyrazine-5,6-dicarboxylic acid when subjected to alkaline permanganate yields benzoic acid. There is no apparent explanation for this unusual behavior of 2,2'-diphenyl-6,6'-biquinoxaline at the present time.

Little is known about the mechanism of oxidation of the aromatic nucleus by permanganate in basic solution. It is known[52] that in fused systems the more electron rich ring is preferentially oxidized. Thus 1-nitronaphthalene yields 3-nitrophthalic acid while 1-naphthylamine yields phthalic acid. From the results obtained in the present study it can also be stated that quinone type intermediates are not involved since reaction of 2,3-diphenylbenzo[g]quinoxaline-5,10-dione (CII) with alkaline permanganate yields benzoic acid (no phthalic acid was found) although the quinoxaline itself (XXVII) yields, 2,3-diphenylpyrazine-5,6-dicarboxylic acid.

Pyrolytic oxidation of the model compounds 2-phenylquinoxaline (XCVI) at 450°C; 2,2'-diphenyl-6,6'-biquinoxaline (VIII) at 500°C; and 2,3-diphenylbenzo[g]quinoxaline (XCVIII) at 300°C yielded products similar to those obtained by similar treatment of benzimidazole, benzimidazolone and benzimide model compounds: carbon dioxide, cyanogen and benzonitrile. This result supports the suggestion that all of the benzheterocyclic systems undergo oxidative degradation by similar mechanisms in which the key step is initial oxygenation of the carbocyclic ring adjacent to the heterocyclic ring. Further, the fact that the solution oxidation intermediates 2-phenylpyrazine-5,6-dicarboxylic acid also yields carbon dioxide, cyanogen and benzonitrile* supports the suggestion that pyrolytic oxidation of the quinoxaline system involves oxygenated intermediates similar to the pyrazine dicarboxylic acids. The most compelling experimental evidence in support of this hypothesis is the finding that 2,3-diphenylbenzo[g]quinoxaline when thermally degraded in oxygen at 200°C produces the corresponding 5,10-dione (CII). Subsequent pyrolysis of the dione or the quinoxaline at 300°C yields the usual carbon dioxide, cyanogen and benzonitrile. The formation of 2,3-diphenylbenzo[g]quinoxaline-5,10-dione represents the first example of isolation of an oxygenated intermediate in the pyrolytic oxidation of any of the benzheterocyclic polymers or model compounds included in this study. The fact that this intermediate is indeed oxygenated on the carbocyclic ring adjacent to the heterocyclic ring is compelling and dramatic evidence in support of the proposed mechanism of thermo-oxidative degradation for the quinoxaline system.

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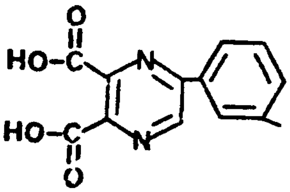
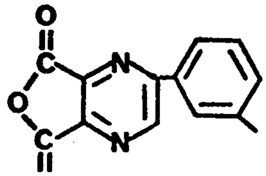
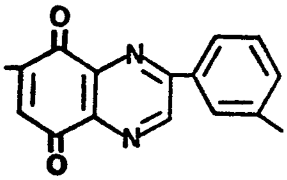
* 2-Phenylpyrazine is also a product of this reaction and probably results from di-decarboxylation of the diacid and subsequent entrainment of the 2-phenylpyrazine from the pyrolysis zone before oxidation occurs.

The only previous direct evidence for oxygenated intermediates in the oxidative degradation of the quinoxaline system was disclosed by Wrasidlo[11] and coworkers when they reported that infrared examination of a film of polymer III revealed absorptions at 1740 and 1685 cm^{-1} during thermooxidative degradation. Those workers assigned the quinoid structure LXXVI to the species responsible for carbonyl absorptions at 1685 and 1740 cm^{-1}. Alternatively, however, other oxygenated species with the pyrazine nucleus still intact should be considered. In light of the results obtained in the present work such structures would include the pyrazine dicarboxylic acid (XCIV), the anhydride (XCV) and the quinone (XCIII).


XCIV


XCV


XCIII

These structural assignments were tested by examination of spectra of molecules containing these structural units which were prepared in the current investigation. Thus 2,3-diphenylpyrazine-5,6-dicarboxylic acid revealed carbonyl absorptions at 1710 and 1745 cm^{-1}, 2,3-diphenylbenzo[g]quinoxaline-5,10-dione (CII) shows carbonyl absorption at 1678 cm^{-1} and the anhydride (CV) shows carbonyl absorptions at 1800 and 1864 cm^{-1}. Thus structures such as the anhydride (XCV) are ruled out as oxygenated intermediates in pyrolytic oxidation of quinoxaline while both the dicarboxylic acid and quinone structural assignments may be further considered. Thus the band observed at 1685 cm^{-1} during thermooxidative degradation of polymer III may well be a broad poorly resolved doublet composed of the 1710 and 1678 cm^{-1} or the 1710 cm^{-1} shifted to a lower frequency by environmental effects in the polymer film.

SECTION IV

SUMMARY AND CONCLUSIONS

In summary, the results of the experimental work outlined for thermo-oxidative degradation studies on the quinoxaline system can be best viewed in terms of the mechanism proposed and shown in Figure 5. The key step in this mechanism involves initial oxygenation at the carbocyclic ring adjacent to the heterocyclic pyrazine ring to form oxygenated intermediates structurally identical or similar to the quinone and pyrazine dicarboxylic acid. This proposal is supported by the following summary of experimental findings (also summarized in Figure 6): (1) Pyrolysis of the model compounds yields products identical to those obtained on pyrolysis of benzimidazoles, benzimidazolones and benzimides, (2) solution oxidation of quinoxaline model compounds yields the corresponding pyrazine dicarboxylic acids, (3) pyrolysis of the pyrazine dicarboxylic acid solution oxidation products yields the same products (carbon dioxide, cyanogen, and benzonitrile) as obtained on pyrolysis of the model compounds themselves, (4) pyrolytic oxidation of XCVIII yields the quinone CII which on subsequent pyrolysis at higher temperatures yields the usual products (carbon dioxide, cyanogen and benzonitrile), (5) the carbonyl absorption bands observed for pyrazine dicarboxylic acids and the quinone 2,3-diphenylbenzo[g]quinoxaline-5,10-dione are very close and similar to those observed[11] during oxidative pyrolysis of film samples of polyquinoxaline III, and (6) infrared nitrile absorptions are observed[11] during oxidative pyrolysis of film samples of polyquinoxaline.

Observation (1) suggests that the mechanism of degradation for the quinoxaline system is similar to the other benzheterocyclics mentioned. More specifically, since initial oxygenation at the carbocyclic adjacent to the

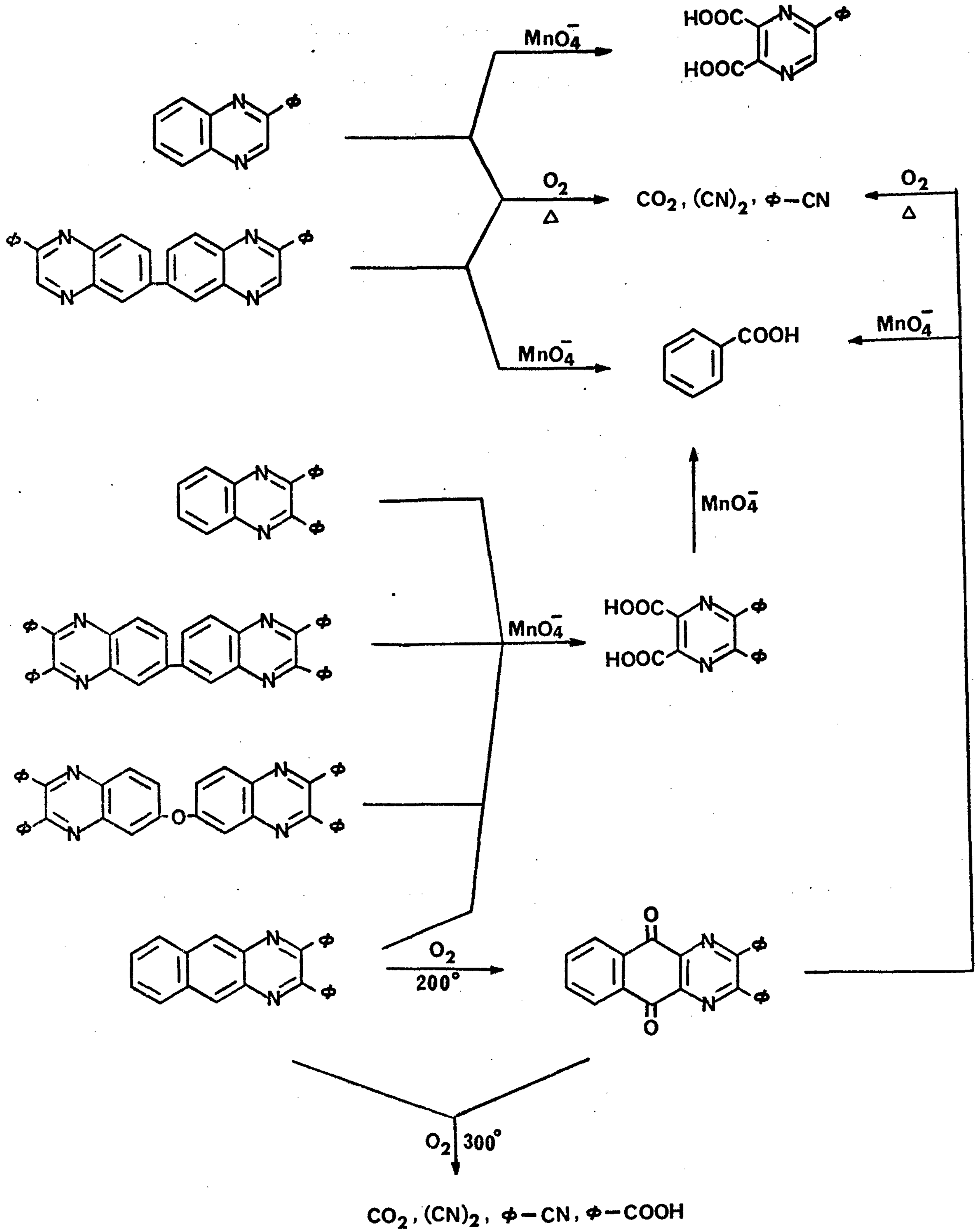


Figure 6. Summary of Solution and Thermal Oxidation in the Quinoxaline System.

heterocyclic ring has been demonstrated for the benzimidazole system, then such a mechanism is strongly suggested for the phenylquinoxaline system. Observation (2) lends further support to the proposal that the carbocyclic ring is the more labile to initial oxygenation. Observation (3) supports the proposal that the oxygenated species are intermediates while observation (4) and (5) provide the first direct observation of oxygenated intermediates in the quinoxaline or any of the benzheterocyclic systems*. Finally, observation (6) supports the formation of chain bound nitrile functions as required by the proposal in Figure 5.

---

* Figures 57-59 show spectra of films of polymer XXXVI with admixtures of 2,3-diphenylbenzo[g]quinoxaline-5,10-dione(CII) and 2,3-diphenylpyrazine-5,6-dicarboxylicacid (CI). These mixtures are simulations of partially degraded polymer (PQ) with the oxygenated intermediates proposed in the present report. The fact that these spectra are similar to those of partially degraded polymer (Figure 56) is offered as added proof to the likelihood that those oxygenated species are indeed intermediates.

SECTION V

EXPERIMENTAL DETAILS

Phenylglyoxal hydrate. Phenylglyoxal hydrate was prepared by the selenium dioxide oxidation of acetophenone according to the procedure of Riley and Grey[53]. The reaction product was crystallized from water to provide 90 g (76% yield) of phenylglyoxal hydrate, m.p. 82-84°C.

1,4-Bis(phenylglyoxal)benzene. 1,4-Bis(phenylglyoxal)benzene was prepared by the selenium dioxide oxidation of 1,4-bis(phenylacetyl)benzene according to the procedure described by Wrasidlo and Augl[13]. The reaction product was recrystallized three times from ethyl alcohol to give 10.2 g (44% yield) of 1,4-bis(phenylglyoxal)benzene, m.p. 121-124°C.

2-Phenylquinoxaline (XCVI). An oxygen free solution of 0.912 g (0.006 mole) of phenylglyoxal hydrate in 60 ml of water was added to an oxygen free solution of 1.04 g (0.006 mole) of o-phenylenediamine dihydrochloride in 60 ml of water. The reaction mixture was refluxed four hours under helium and then filtered to collect the off-white crystals of crude product. Recrystallization from ethyl alcohol furnished 1.18 g (85% yield) of pure 2-phenylquinoxaline (XCVI), m.p. 77-78°C (lit.[2], m.p. 78°C).

2,3-Diphenylquinoxaline (XCVII). A mixture of 4.2 g (0.02 mole) of benzil and 2.16 g (0.02 mole) of o-phenylenediamine was heated on a steam bath for ten minutes by which time the initially molten mixture had turned to a tan solid. The product was then cooled and crystallized from methanol to give 5.21 g (95% yield) of 2,3-diphenylquinoxaline (XCVII) m.p. 125-127°C (lit.[54], m.p. 125-126°C).

2,2'-Diphenyl-6,6'-biquinoxaline (VIII). To an oxygen free solution of 1.083 g (0.003 mole) of 3,3'-diaminobenzidine tetrahydrochloride in 20 ml of water, a solution of 0.912 g (0.006 mole) of phenylglyoxal hydrate in

15 ml of oxygen free water was added. A yellow precipitate was formed immediately. The reaction mixture was refluxed under nitrogen for four hours, cooled and filtered. The crude product was first digested with methanol and then recrystallized from dioxane to afford 1.02 g (85% yield) of a brown crystalline product, m.p. 220-240°C (lit.[6], m.p. 314-316°C). The UV and IR spectra were consistent with the structure 2,2'-diphenyl-6,6'-biquinoxaline.

<u>2,2',3,3'-Tetraphenyl-6,6'-biquinoxaline(XXXIX)</u>. Compound XXXIX was prepared by the condensation of 3,3'-diaminobenzidine and benzil in chloroform according to the procedure described by Wrasidlo and Augl[13]. Crystallization of the crude reaction product from alcohol-toluene-chloroform (50;50;25) provided pure 2,2',3,3'-tetraphenyl-6,6'-biquinoxaline, m.p. 309-310°C (lit.[13], m.p. 309-310°C).

<u>2,3-Diphenylbenzo[g]quinoxaline (XCVIII)</u>. A mixture of 1.58 g (0.01 mole) of 2,3-diaminonaphthalene and 2.10 g (0.01 mole) of benzil was heated at 120°C under helium for five minutes. The temperature was then slowly raised to 200°C and maintained there for 15 minutes before the reaction product was cooled to provide 2.66 g (80% yield) of crude product. Crystallization from toluene furnished pure 2,3-diphenylbenzo[g]quinoxaline (XCVIII), m.p. 187-189°C (lit.[51], m.p. 187-188°C).

Anal Calcd for $C_{24}H_{16}N_2$:	C, 86.72; H, 4.82; N, 8.43%
Found	C, 86.72; H, 4.80; N, 8.40%

<u>2,2',3,3'-Tetraphenyl-6,6'-oxidiquinoxaline (XXXIII)</u>. Compound XXXIII was prepared by the condensation of benzil with 3,3'4,4'-tetraaminodiphenylether in chloroform according to the procedure described for the preparation of Compound XXXIX above. The reaction afforded a 98% yield of crude product which after crystallization from chloroform provided pure 2,2'3,3'-tetraphenyl-6,6'-oxybiquinoxaline, m.p. 258-261°C (lit.[10], m.p. 264.5-265.5°C).

1,4-Bis[2,(3-phenylquinoxalyl)]benzene (XCIX). Compound XCIX was prepared by the condensation of 1,4-bis(phenylglyoxaloyl)benzene and *o*-phenylenediamine in chloroform according to the procedure described for the preparation of Compound XXXIX above. The reaction afforded an 88% yield of 1,4-bis[2,(3,-phenylquinoxalyl)]benzene, m.p. 252-256°C.

Oxidation and Degradation Studies. All solution oxidations were done in 5% aqueous sodium hydroxide solution, with vigorous stirring at 75-85°C for 8-12 hours.

All pyrolytic oxidations were done in a Lindberg Heavy Duty Furnace. The temperature in the sample area was continuously recorded and found to vary by ± 2°C. The sample to be oxidized was weighed and placed into the cool zone of the pyrolysis chamber for 15 minutes while a flow of oxygen was maintained over it. The sample was then moved into and out of the hot zone with a nichrome wire. Exit gases for analysis were passed first through a cold trap containing ether and then through an aqueous silver nitrate solution followed by a barium hydroxide solution trap.

Oxidation of 2-Phenylquinoxaline (XCVI). To 2.28 g of 2-phenylquinoxaline in a solution of 0.8 g of sodium hydroxide in 240 ml of water at 80°C was added a solution of 17.6 g of potassium permanganate in 160 ml of water. The addition was carried out over a ten hour period with vigorous stirring. The reaction mixture was then cooled and excess potassium permanganate was decomposed by the addition of sodium bisulfite. After filtration and concentration to half volume, the reaction mixture was acidified with dilute hydrochloric acid and cooled to -10°C. The off-white crystals of 2-phenylpyrazine-5,6-dicarboxylic acid oxidation product (C) were filtered off, washed with water and dried to yield 1.11 g (50% yield) of the dicarboxylic acid, m.p. 182-185°C. The structure of 2-phenylprazine-5,6-dicarboxylic acid was confirmed by the following facts: (a) Its neutralization equivalent was consistent with that of a dibasic acid with molecular weight of 244 amu; (b) Its infrared spectrum (Figure 50) revealed a strong absorption at 1675 cm^{-1} (carbonyl stretching); (c) Thermal decarboxylation provided 2-phenylpyrazine m.p. 71-72°C.

Anal. Calcd for $C_{10}H_8N_2$: C, 76.92; H, 5.13; N, 17.94%

Found: C, 76.83; H, 5.12; N, 17.72%

Oxidation of 2,3-Diphenylquinoxaline (XCVII). A mixture of 1.2 g of 2,3-diphenylquinoxaline in 200 ml of 5% aqueous sodium hydroxide solution at 85°C was reacted with a saturated solution of potassium permanganate in the manner described above for oxidation of compound XCVI. After twelve hours the reaction mixture was cooled and the excess potassium permanganate was decomposed with sodium bisulfite. The reaction mixture was then filtered, concentrated to 50 ml, acidified with dilute HCl and finally filtered. The resulting crude solid oxidation product was washed with water, dissolved in 5% aqueous sodium hydroxide solution and precipitated by acidification with dilute HCl to provide 120 mg of 2,3-diphenylpyrazine-5,6-dicarboxylic acid (CI), m.p. 135 C (dec.). This structure assignment was confirmed by neutralization equivalent (consistent with a dicarboxylic acid with molecular weight of 320 amu), infrared analysis (carbonyl doublet at 1710 and 1745 cm^{-1}), and the fact that it (CI) was readily converted to a cyclic anhydride as described below.

Preparation of 2,3-Diphenylpyrazine-5,6-dicarboxylic acid anhydride (CIV). To a solution of 100 mg of 2,3-diphenylpyrazine-5,6-dicarboxylic acid (CI) in 100 ml of anhydrous benzene 100 mg of phosphorous pentoxide was added. The reaction mixture was then filtered and the filtrate on evaporation of the solvent afforded 78 mg (96%) of (CIV) m.p. 148°C. The infrared spectrum of this compound was consistent with the anhydride with strong absorption bands at 1800 and 1864 cm^{-1} (Figure 49) characteristic of the aromatic cyclic anhydride group.

Oxidation of 2,2',3,3'-Tetraphenyl-6,6'-biquinoxaline (XXXIX) 2,3-Diphenylbenzo[g]quinoxaline (XCVII) and 2,2',3,3'-Tetraphenyl-6,6'-oxydiquinoxaline (XXXIII). These three model compounds XXXIX, XXXII and XCVII were oxidized with potassium permanganate under the reaction conditions identical to those used for oxidation of (XCVII). The product obtained from these model compounds was identified as 2,3-diphenylpyrazine-5,6-dicarboxylic acid (CI) by mixed melting point determination and comparison of infrared spectrum with that of an authentic sample.

Chromium trioxide oxidation of 2,3-Diphenylbenzo[g]quinoxaline (XCVIII). To 600 mg of 2,3-diphenylbenzo[g]quinoxaline (XCVIII) in 15 ml of glacial acetic acid, a solution of 550 mg of chromium trioxide in 6 ml of 1:1 dilute acetic acid was added. The reaction mixture was heated at 75°C for 20 minutes and then poured into ice. The resulting bright yellow solid was filtered, washed with water and then dried to obtain 500 mg (77%) of CII m.p. 272-273°C (lit.[55] m.p. 268-269°C). The infrared spectrum (Figure 52) indicated (CII) was a quinone with strong absorption at 1678 cm^{-1}(carbonyl stretching).

Anal. Calcd. for $C_{24}H_{14}N_2O_2$: C, 79.56; H, 3.87; N, 7.73%

Found: C, 79.41; H, 3.86; N, 7.79%

Oxidation of 2,3-Diphenylbenzo[g]quinoxaline-5,10-dione (CII). All attempts to oxidize CII with potassium permanganate to 2,3-diphenylpyrazine dicarboxylic acid under the reaction conditions used for oxidation of XXXIII, XXXIX and XCVII were unsuccessful. The final oxidized product was identified as benzoic acid (mixed melting point and infrared spectrum).

Oxidation of 2,3-Diphenylpyrazine-5,6-dicarboxylic acid (CI). To a solution of 100 mg of CI in 50 ml of 5% aqueous sodium hydroxide at 75°C a saturated solution of potassium permanganate was added portionwise. During the addition, the reaction mixture was vigorously stirred. After the addition was complete (10 hours) excess permanganate was decomposed by addition of sodium bisulfite. The crude reaction products were taken up in ether and the organic layer was washed with water and dried over anhydrous magnesium sulfate. The product obtained after removal of the solvent was identified as benzoic acid (mixed melting point and infrared spectrum). The yield was 32 mg (50%).

Oxidation of 2-phenylpyrazine-5,6-dicarboxylic acid (C). Upon potassium permaganate oxidation of C using the identical conditions described for oxidation of XCVII, the product isolated was benzoic acid in 70% yield. The product was identified by infrared analysis and mixed melting point.

Pyrolytic Oxidation of 2-phenylquinoxaline (XCVI) at 300°C. Approximately 250 mg of 2-phenylquinoxaline (XCVI) was pyrolyzed at 300°C for 1 hour in a stream of flowing oxygen (20 ml/minutes). The exit gases were first passed through a cold ether trap, followed by aqueous silver nitrate solution and finally a trap containing barium hydroxide. When the pyrolysis was complete, no residue remained in the boat. A substantial amount of XCVI sublimed and collected at the cold exit end of the pyrolysis tube. There was no sign of cyanogen or benzonitrile evolution. A very small barium carbonate precipitate was obtained.

Pyrolytic Oxidation of 2-Phenylquinoxaline (XCVI) at 400°C. 2-Phenylquinoxaline was pyrolyzed as described above except that the temperature was adjusted to 400°C. Products isolated from this pyrolysis were carbon dioxide (precipitated as barium carbonate), cyanogen (precipitated as silver salt) and benzonitrile (isolated from and identified in the cold ether trap by glc and infrared analysis).

Pyrolytic Oxidation of 2,2'-Diphenyl-6,6'-biquinoxaline (VIII) at 400°C. 2,2'-Diphenyl-6,6'-biquinoxaline was pyrolyzed at 400°C in oxygen (20 ml/minute) for 90 minutes. A strong odor of benzonitrile was apparent in the exit flow stream. However, the presence of benzonitrile could not be confirmed. No silver cyanide precipitate resulted and the presence of turbidity in the barium hydroxide trap suggested that no more than trace quantities of carbon dioxide were evolved.

Pyrolytic Oxidation of 2,2'-Diphenyl-6,6'-biquinoxaline (VIII) at 500°C. 2,2'-Diphenyl-6,6'-biquinoxaline was pyrolyzed at 500°C in oxygen (20 ml/minute). The pyrolysis products were benzonitrile, cyanogen and carbon dioxide.

Pyrolytic Oxidation of 2,3-Diphenylbenzo[g]quinoxaline (XCVIII) at 300°C. 2,3-Diphenylbenzo[g]quinoxaline was pyrolyzed in oxygen for 60 minutes at 300°C. The pyrolysis products were benzonitrile, cyanogen and carbon dioxide. In addition, trace quantities of benzoic acid were found as sublimate at the cool zone of the pyrolysis tube.

Pyrolytic Oxidation of 2,3-Diphenylbenzo[g]quinoxaline (XCVIII) at 200°C. 2,3-Diphenylbenzo[g]quinoxaline was pyrolyzed in oxygen (10 ml/minute) at 200°C. After 50 hours a trace quantity of benzoic acid was identified in the cool zone of the pyrolysis chamber. Infrared spectral analysis of the boat residue showed it to be only starting material. After 150 hours infrared spectral analysis of the boat residue revealed the presence of a carbonyl absorption. After 250 hours of pyrolysis in oxygen, the boat residue was chromatographed over neutral alumina. After collection of the fractions and fractional crystallization, 2,3-diphenylbenzo[g]quinoxaline-5,10-dione (CII) (mixed melting point and infrared analysis) was isolated and identified. The mother liquor contained only starting material, 2,3-diphenylbenzo[g]quinoxaline. In addition to CII, carbon dioxide was also produced in the pyrolysis of XCVIII at 200°C.

Pyrolytic Oxidation of 2,3-Diphenylbenzo[g]quinoxaline-5,10-dione (CII) at 300°C.

2,3-Diphenylbenzo[g]quinoxaline-5,10-dione was pyrolyzed in oxygen at 300°C. The products isolated and identified were cyanogen, carbon dioxide, benzonitrile and benzoic acid.

Pyrolytic oxidation of 2-phenylpyrazine-5,6-dicarboxylic acid (C).

2-Phenylpyrazine-5,6-dicarboxylic acid (C) was pyrolyzed at 450°C in oxygen (20 ml/minute) for 90 minutes. The following products were isolated and identified; cyanogen, carbon dioxide, benzonitrile and 2-phenylpyrazine, m.p. 71-72°C.

Oxidation of 2,2'-diphenyl-6,6'-biquinoxaline (VIII).

2,2'-Diphenyl-6,6'-biquinoxaline (1.2 g) was added to 200 ml of 5% aqueous sodium hydroxide solution. The reaction mixture was heated at 85°C with vigorous stirring over a ten hour period while solid potassium permanganate (6 g) was added portionwise. Excess permanganate was decomposed by addition of methanol. The reaction mixture was then filtered, concentrated to 50 ml, acidified with dilute HCl and extracted with ethyl ether. The ether layer was washed with water to neutrality and evaporated to yield 38 mg of benzoic acid (mixed melting point and infrared analysis).

PART II SYNTHESIS AND EVALUATION OF THERMOOXIDATIVE PROPERTIES OF A SERIES OF BENZIMIDAZOLE COPOLYMERS

SECTION I

INTRODUCTION

The high temperature thermal and oxidative properties of polymers consisting of aromatic and heterocyclic nuclei, such as aromatic amides, benzimides, benzimidazoles and benzimidazolones have been the focal point of a large number of investigations in recent years.

The high temperature polymers; polybenzimides, polybenzimidazoles (PBI), polybenzimidazolones (BBB) and related model compounds have been prepared and their thermal and thermooxidative degradation have been studied[32]. The determination of weight loss characteristics, product analysis and gaseous products ratio measurement (CO_2/CO) led to the conclusion that oxidation mechanisms were very similar for all of these polymeric systems[32,33]. Mechanisms proposed involved oxygenation of the aromatic carbocycle adjacent to the heterocyclic ring after formation of a free radical by rupture of the nitrogen-hydrogen bond in the imidazole ring of PBI systems or the carbonyl carbon nitrogen bond in BBB and polybenzimide systems.

Subsequent work limited to PBI and related model compounds supported the above interpretations. The first of these involved preparation of proposed thermooxidative intermediates by solution oxidation and their subsequent thermal oxidation proving that such intermediates (2-arylimidazole-4,5-dicarboxylic acid) probably are transitory intermediates in thermal oxidation. The second involved infrared monitoring of PBI films subjected to controlled isothermal oxidation. The results failed to show oxygenated intermediates but did reveal polymer chain-bound nitrile (a proposed intermediate) and did provide a convenient method for following the initial stages of PBI degradation. Thirdly, thermooxidation of carbon-13 labelled model compounds verified that oxygen attacks initially at the aromatic nucleus adjacent to imidazole ring.

The present investigation was aimed at preparing certain high temperature copolymers and to examine their thermooxidative stabilities and solubility properties in comparison to the existing homopolymeric systems. The approach used involves synthesis of copolymers of benzimidazole functions with amides, benzimides and benzimidazolone co-functions. Subsequent evaluation of their thermooxidative stability employs certain of the techniques already developed for the homopolymeric systems.

SECTION II

PREVIOUS INVESTIGATIONS

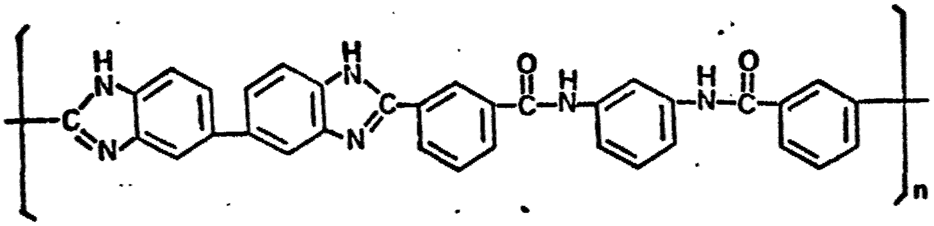
Most of the effort in the area of high temperature polymers has been directed toward studies of homopolymers of aromatic amides, benzimides, benzimidazoles and, more recently, benzimidazolones. Thus, synthetic techniques for preparation of these homopolymer systems are well developed. However, relatively little has been reported on the synthesis and high temperature properties of copolymers incorporating combinations of repeat units of the above homopolymeric systems with benzimidazole repeat units. Those copolymers reported included combinations of benzimidazole-amide and benzimidazole-imide. The synthesis of the former has been reported by two general methods; the low temperature solution condensation of diacid chlorides with diaminophenylbisbenzimidazoles and the melt condensation of tetraamines with diphenylesters containing the amide functions. Preparation of benzimidazole-imide copolymers has been reported by the two stage condensation of diaminophenylbisbenzimidazoles with dianhydrides.

Benzimidazole-amide

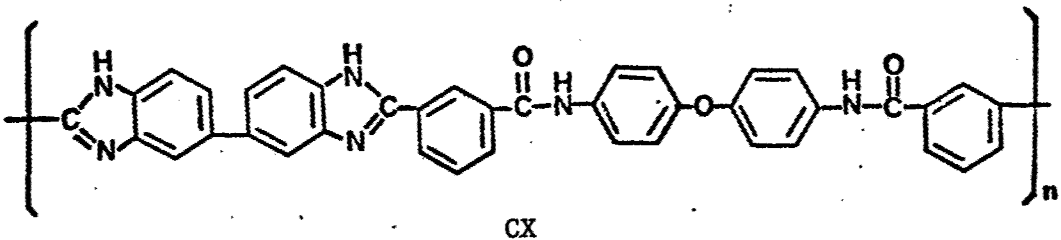
Recently, Iwakura and coworkers[35] synthesized thermally stable benzimidazole-amide copolymers by the condensation of 2,2'-di-*p*-aminophenyl-5,5'-bibenzimidazole with dicarboxylic acid chlorides in dimethylacetamide at -15°C. Thus reaction of 2,2'-di-*p*-aminophenyl-5,5'-bibenzimidazole with terephthaloyl or sebacyl chloride resulted in the preparation of the three poly(amide-benzimidazoles), CVI, CVII, and CVIII.

Melt condensation of diphenyl esters with diamines was also examined by these authors. However, only low molecular weight copolymers were obtained.

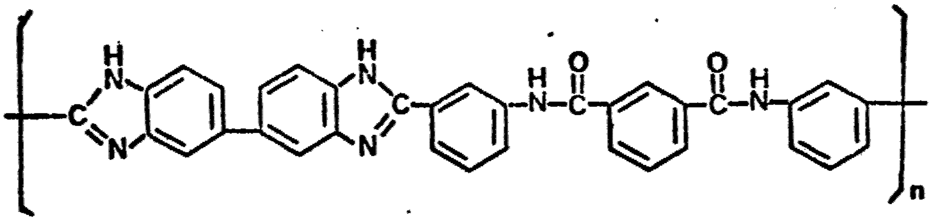
The thermal stability of these polyamides showed only minor loss of weight up to 400°C in air for those derived from aromatic acid chlorides however the copolymer containing the octamethylene chain began to decompose at about 300°C (Figure 7).



CIX



CX



CXI

The copolymers CIX, CX, and CXI synthesized[36] by this method had inherent viscosities of 0.24, 0.19 and 0.20 respectively at 0.5% in conc. sulfuric acid at 30°C. In thermal stability tests with rate of temperature increase of 60°/hr., all three polymers showed an initial weight loss in argon and air at 400°C, reaching 10 and 25-50% loss at 500°C in argon and air respectively (Figures 8 and 9).

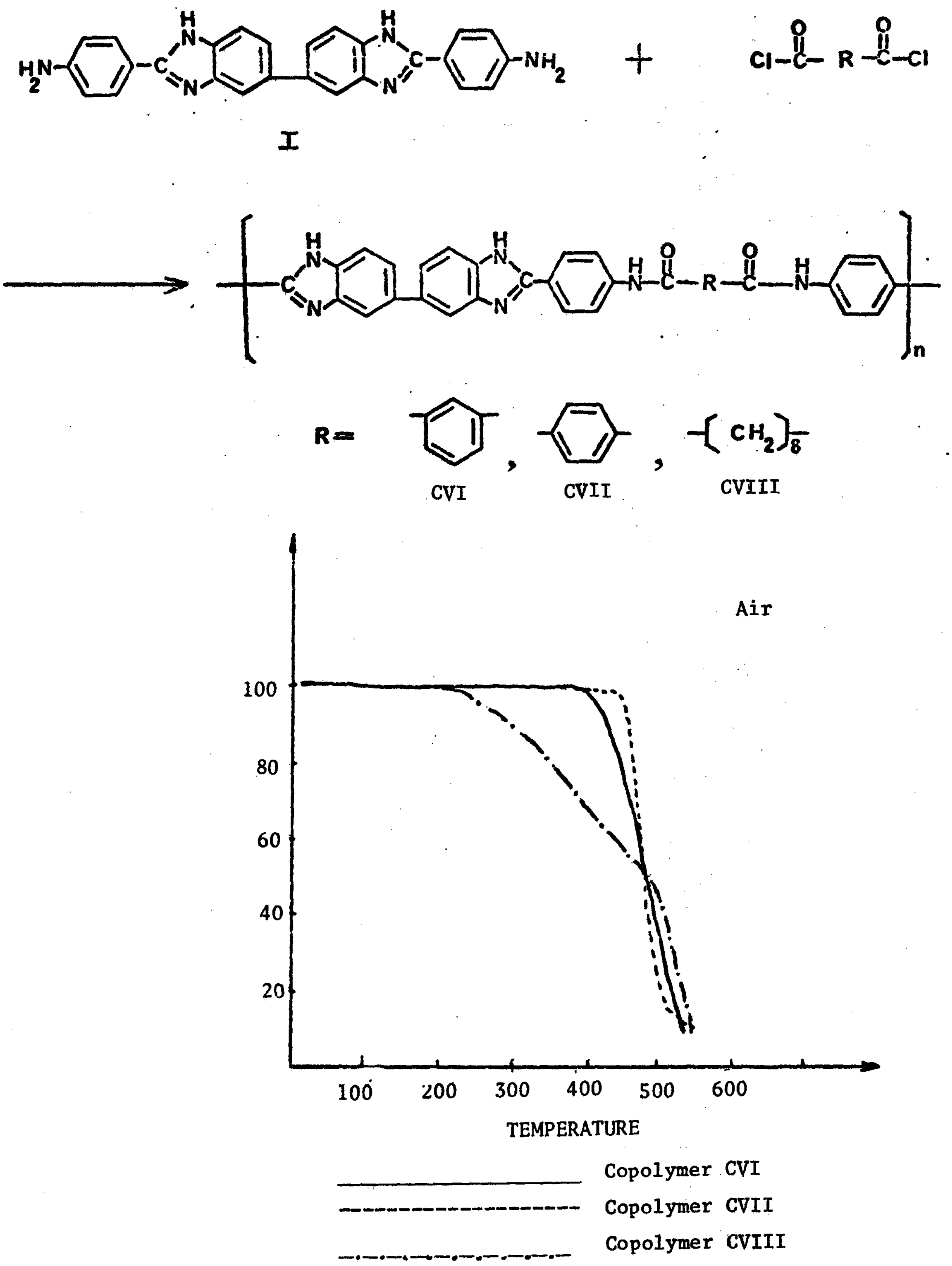


Figure 7 TGA Thermogram of Copoly(Amide-benzimidazoles)[35]

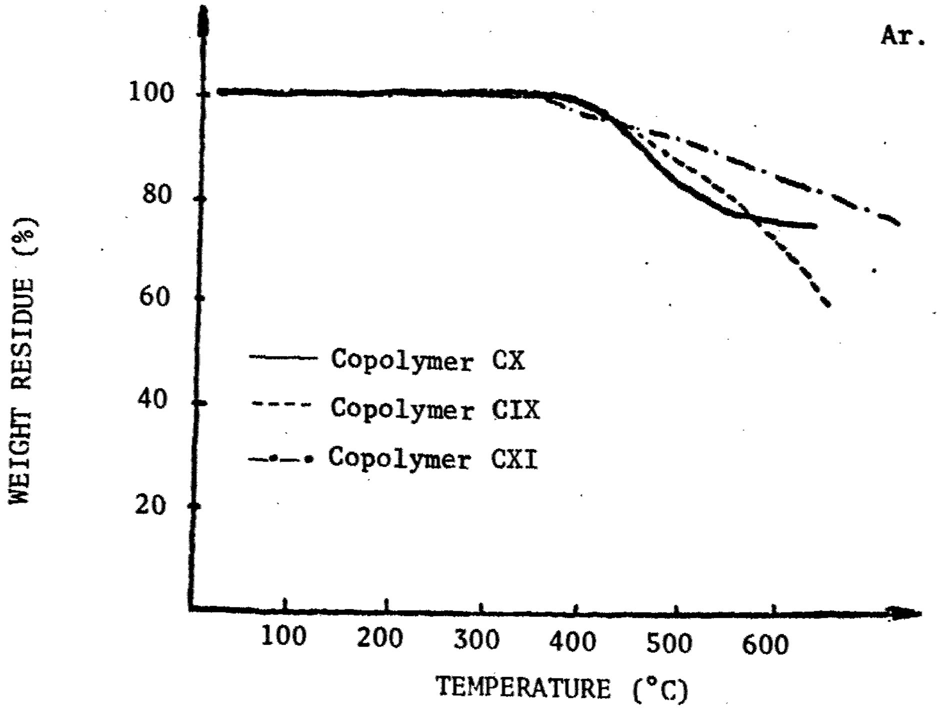


Figure 8 TGA Thermogram of Copoly(Amide-benzimidazoles)[36] CIX, CX, and CXI (in Argon)

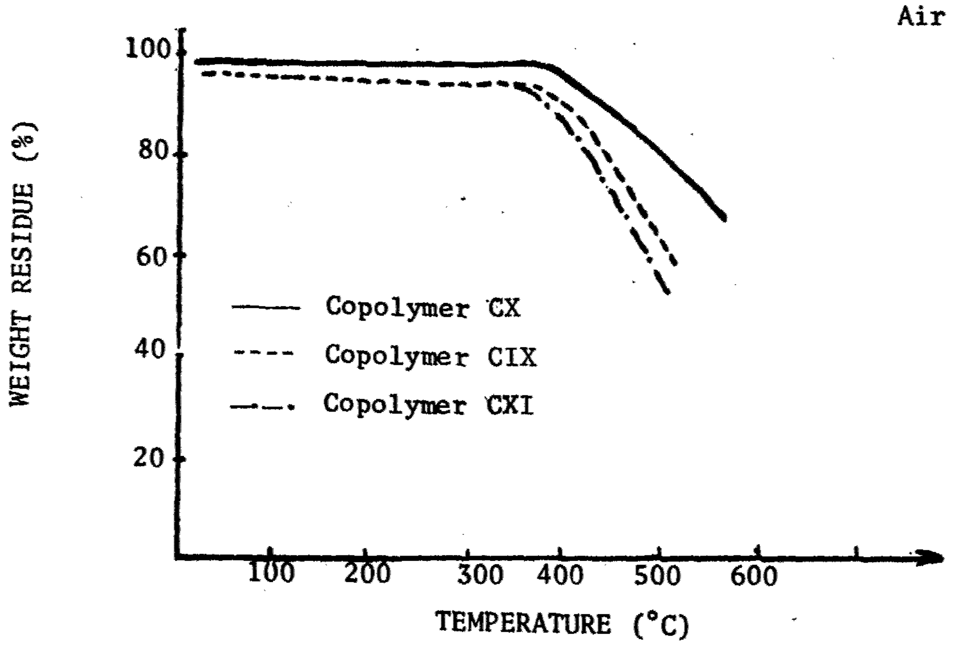
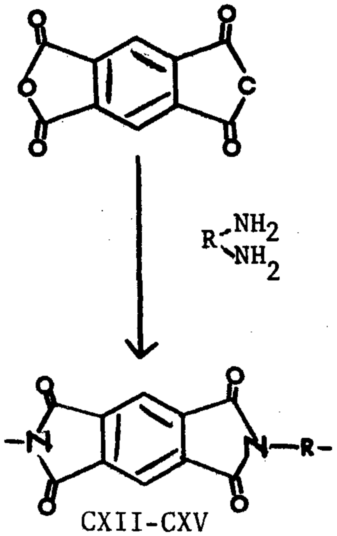


Figure 9 TGA Thermogram of Copoly(Amide-benzimidazoles) CIX, CX, and CXI (in Air)

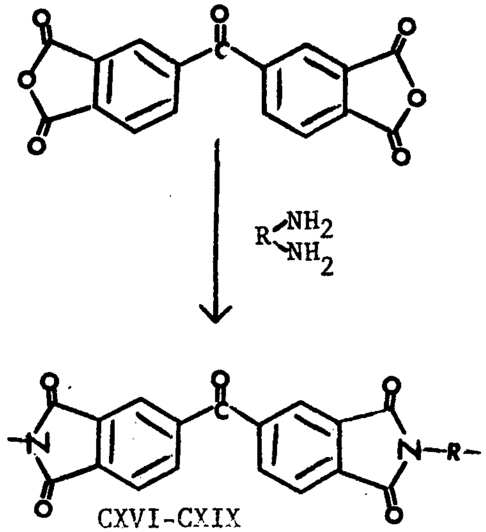
Benzimidazole-imide

More recently[37], it was reported that copolybenzimidazole-imides were prepared by polymerization of diaminobisbenzimidazoles and dianhydirdes to form copoly(benzimidazole-amic acids) which when cast from solution and cured at 280 to 300°C in air gave films showing excellent thermal stability. Combinations of appropriate diamines and dianhydrides resulted in the preparation of eight copolymers, CXII-CXIX.

Thermogravimetric measurements were made both in air (Figures 10 and 11) and in vacuum (Figures 12 and 13) and showed that in air the 15% weight loss levels for diaminobenzidine-derived polymers lies in the 520-550°C range and in the 490-535°C range for tetraaminobenzene-derived polymers.

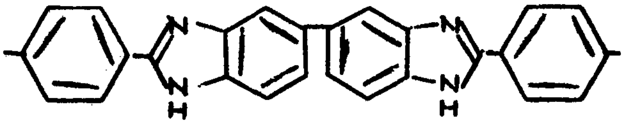


CXII-CXV

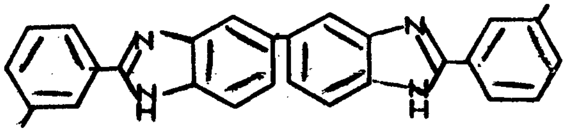


CXVI-CXIX

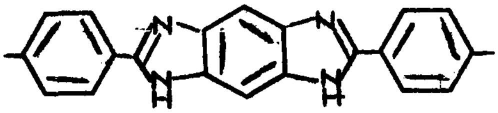
CXII and CXVI; R =



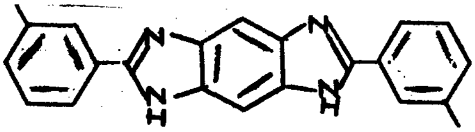
CXIII and CXVII; R =



CXIV and CXVIII; R =



CXV and CXIX; R =



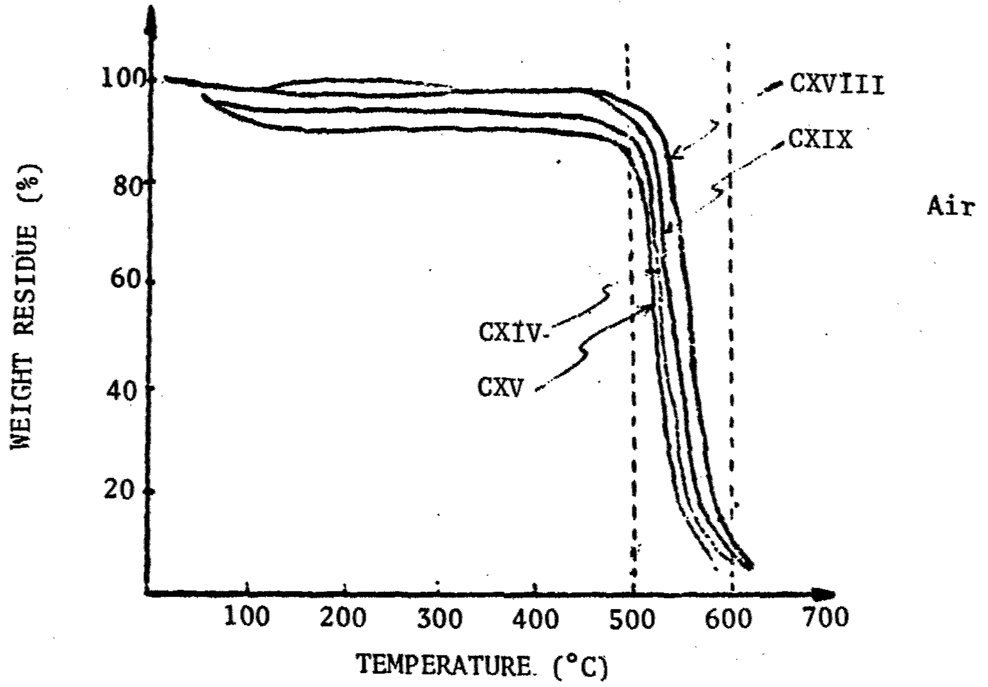


Figure 10 TGA Thermogram of DAB Copolymers[3] in Air

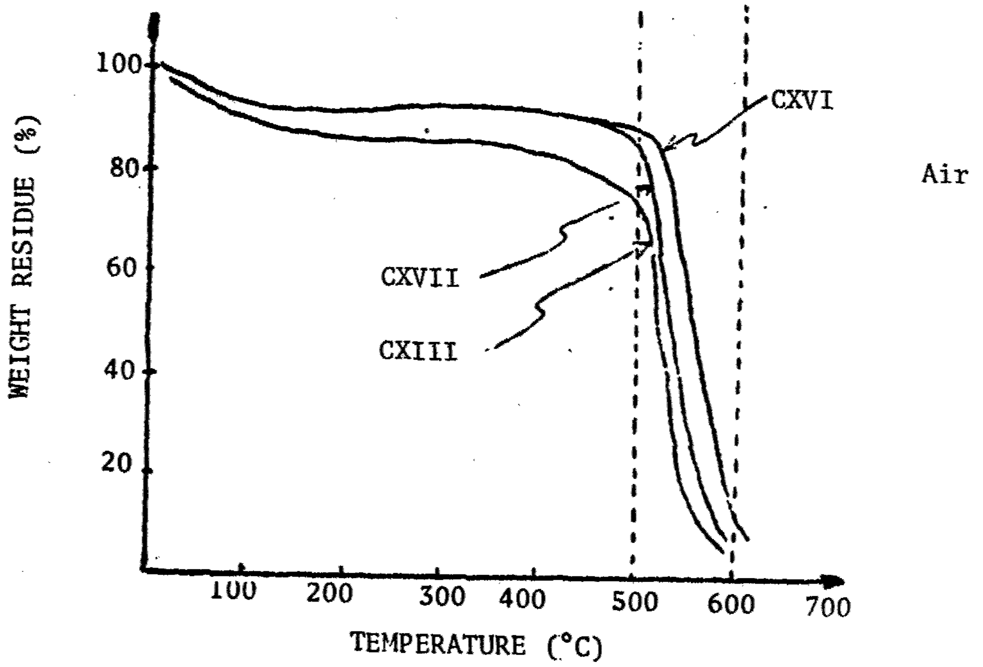


Figure 11 TGA Thermogram of TAB Copolymers[37] in Air

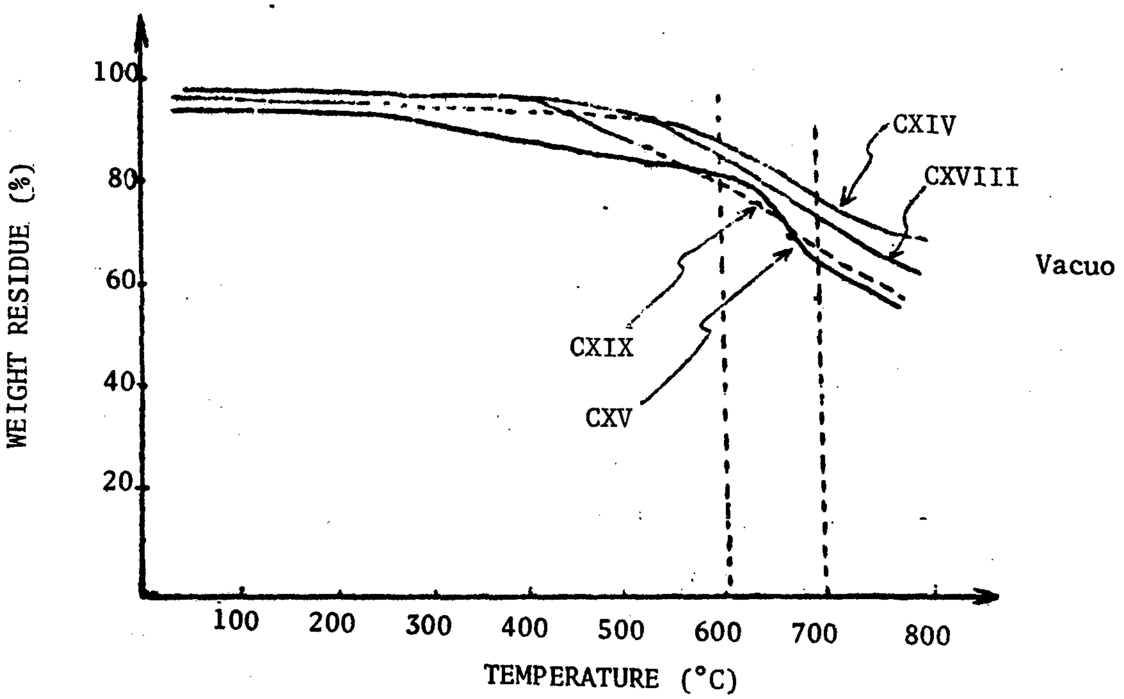


Figure 12 TGA Thermogram of DAB Copolymers[37] *in vacuo*

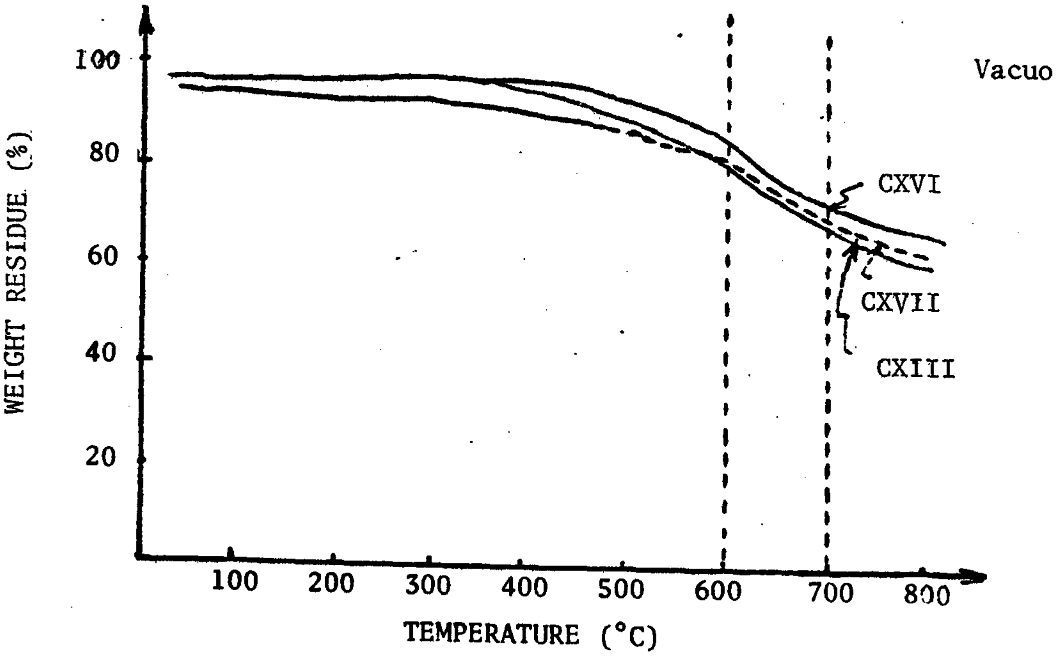


Figure 13 TGA Thermogram of TAB Copolymers[37] *in vacuo*

SECTION III

PRESENT INVESTIGATION

1. Introduction

The results described in the previous section reveal that on the basis of weight loss data, the amide and imide copolymers of benzimidazole exhibit excellent high temperature properties and suggest that this is a fruitful area for further investigation.

In the present investigation our primary interest was to prepare certain copolymers of benzimidazole functions with amide, imide and benzimidazolone functions in the hope of modifying the solubility properties of these systems as compared to the homopolymers (particularly benzimides and benzimidazolones) in order to provide polymeric systems with improved high temperature properties and improved tractability.

In order to evaluate the high temperature stability of the copolymers, they were cast into thin films which were then subjected to isothermal heating in an oxygen atmosphere. Oxidation was interrupted periodically in order to examine the film (infrared scanning) for any structural changes resulting from degradation. This technique was previously applied[38] in our laboratory and was found to be a valuable method for detection of the early stages of degradation in polybenzimidazole homopolymer.

2. Synthesis of Monomers and Polymers

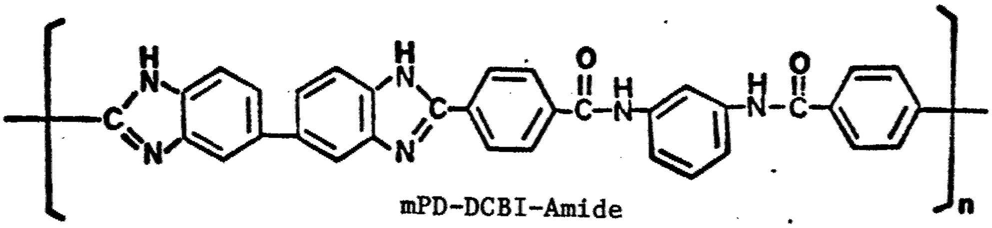
a. Introduction

The copolymers studied in the present investigation were prepared by condensation polymerization reactions between the appropriate amines and carboxylic acids (or derivatives). In each case one of the monomers employed contained one of the co-functions of the resulting copolymers. Thus copolymers containing benzimidazole and amide repeat units were prepared by condensation of a diamine containing benzimidazole functions with a dicarboxylic acid (or acid chloride) or by condensation between a tetraamine and diphenyl ester containing amide functions to form the copolyamide-benzimidazole.

Condensation polymerization at low temperatures in dimethylacetamide (DMAc) between diamines and diacid chlorides was most successful for polymerizations involving formation of amide linkages. Attempts to form copolyamides by condensation of diamines and dicarboxylic acids in 115% polyphosphoric acid (PPA) yielded only low molecular weight polymers. Benzimidazoles and benzimides were successfully prepared in PPA by condensation of a dicarboxylic acid with tetraamine and condensation of a dianhydride with diamine respectively. Benzimides, however, were better prepared by the two step polymerization method. The first step condensation between the dianhydride and diamine in dimethylacetamide (DMAc) produced the polyamic-acid which on subsequent heat treatment in the solid phase yielded the desired imide.

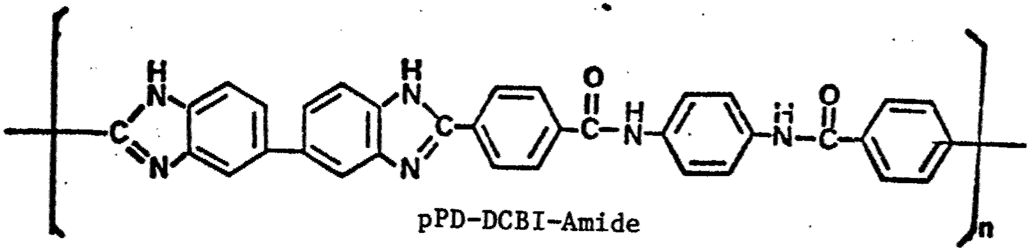
b. Nomenclature

The copolymers prepared and studied in this investigation are shown in Figure 14. Because of the cumbersome nomenclature required for the identification of these copolymers, a code was devised to facilitate identification in the present report. Since all copolymers were synthesized via condensation reactions between amines (di- or tetra-) and di or tetra carboxylic acids or their derivatives, the code system is based on abbreviations assigned to the monomeric amines and carboxylic acids. The monomeric amines and acids are shown in Figure 15 with their assigned abbreviations. The codes assigned to copolymers consist of three segments separated by hyphens. The first segment indicates the amine monomer employed; the second, the acid monomer and the third signifies the type of functionality resulting from the condensation reaction. Thus condensation of 2,2'-di-p-carboxyphenyl-5,5-bibenzimida-



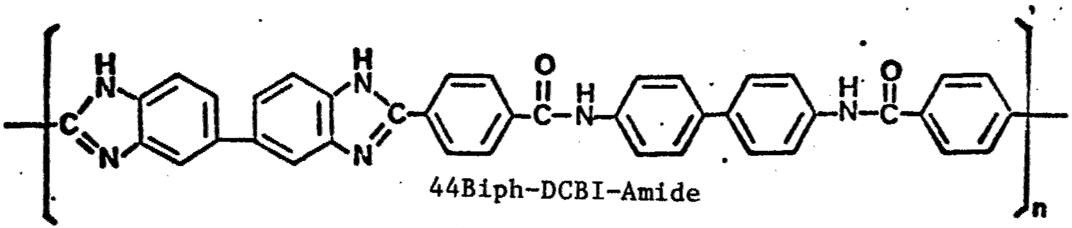
mPD-DCBI-Amide

Poly([5,5'-bibenzimidazole]-2,2'-diyl-p-phenylenecarbonylimino-m-phenyleneiminocarbonyl-p-phenylene)



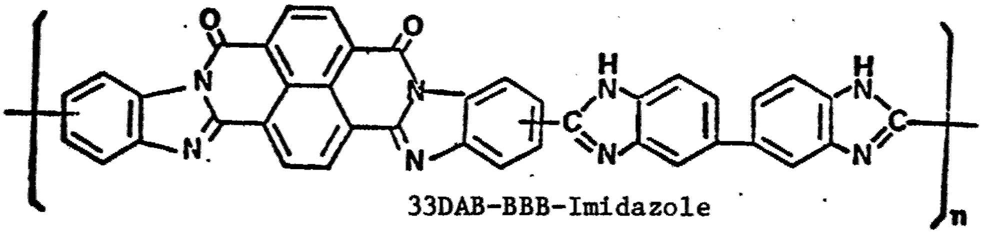
pPD-DCBI-Amide

Poly([5,5'-bibenzimidazole]-2,2'-diyl-p-phenylenecarbonylimino-p-phenyleneiminocarbonyl-p-phenylene)



44Biph-DCBI-Amide

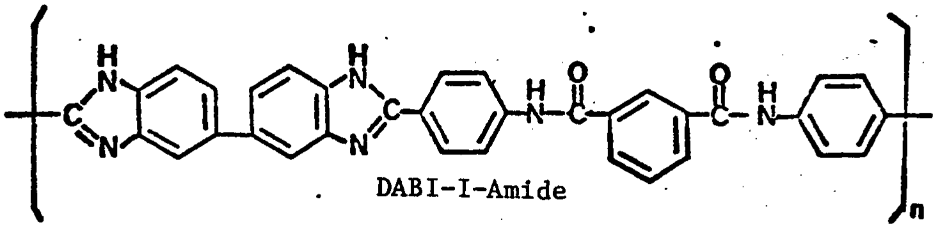
Poly([5,5'-bibenzimidazole]-2,2'-diyl-p-phenylenecarbonylimino-4,4'-biphenyleneiminocarbonyl-p-phenylene)



33DAB-BBB-Imidazole

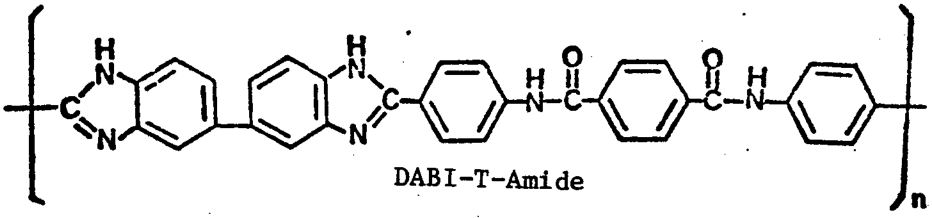
Poly[(6,9-dihydro-6,9-dioxo-bisbenzimidazo[2,1-b:1',2'-j]benzo[lmn][3,8]phenanthroline-3,12-diyl)[5,5'-benzimidazole-2,2'-diyl]

Figure 14 Copolymers prepared in present investigation (structures, names, and codes)



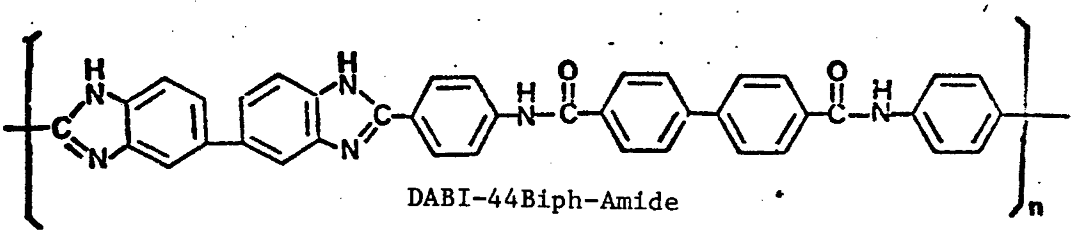
DABI-I-Amide

Poly([5,5'-bibenzimidazole]-2,2'-diyl-*p*-phenyleneiminoisophthaloylimino-*p*-phenylene)



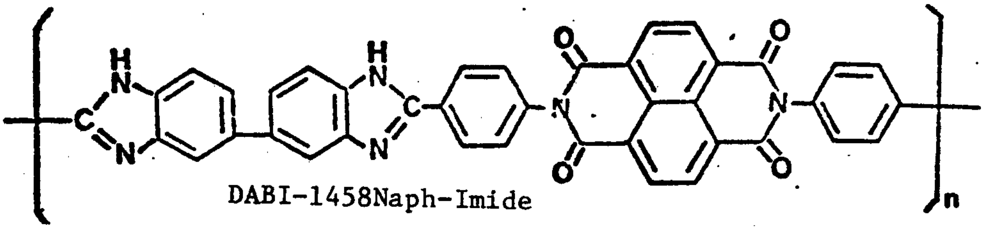
DABI-T-Amide

Poly([5,5'-bibenzimidazole]-2,2'-diyl-*p*-phenyleneiminoterephthaloylimino-*p*-phenylene)



DABI-44Biph-Amide

Poly([5,5'-bibenzimidazole]-2,2'-diyl-*p*-phenyleneiminocarbonyl-4,4'-biphenylenecarbonylimino-*p*-phenylene)



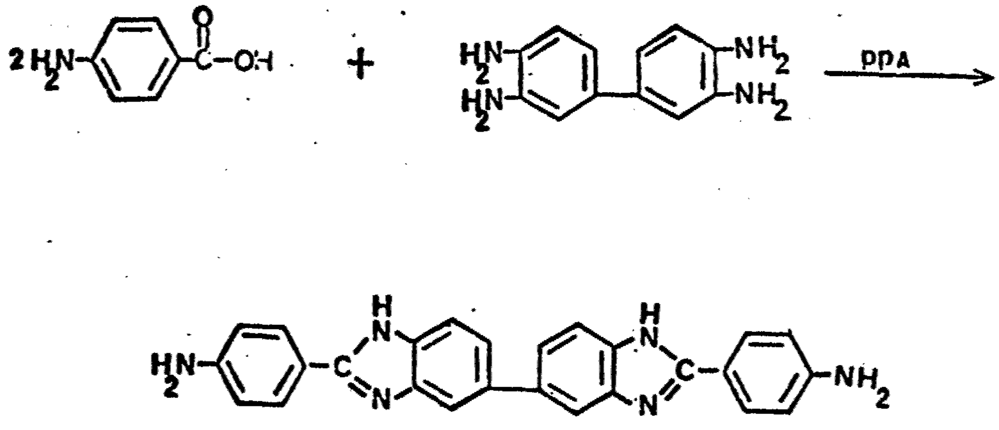
DABI-1458Naph-Imide

Poly[(3,8-dihydro-1,3,6,8-tetraoxobenzo[*lmn*][3,8]phenanthroline-2,7(1*H*,6*H*)-diyl)-*p*-phenylene[5,5'-bibenzimidazole]-2,2'-diyl-*p*-phenylene] zole, DCBI, and m-phenylenediamine, mPD, to produce an amide function copolymer which is designated mPD-DCBI-Amide. The copolymers prepared in this program and their code assignments are shown in Figure 15.

c. Monomers

i. 2,2'-Di-p-aminophenyl-5,5'-bibenzimidazole (DABI)

The aromatic diamine, 2,2'-di-p-aminophenyl-5,5'-bibenzimidazole was prepared by condensation of 3,3'-diaminobenzidine with p-aminobenzoic acid in PPA under nitrogen atmosphere.



DABI

The resulting product forms a solvated complex during the purification process. After heating at 300°C under vacuum, the complex melted with the evolution of volatile material at about 230°C and solidified again. DABI exhibited two melting endotherms (355 and 451°C) on differential thermal analysis (see Figure 38). Similar polymorphic behavior has also been reported for 2,2'-dipehnyl-5,5'-bibenzimidazole[34]. The structure of DABI was deduced from its infrared spectrum (Figure 32) and elemental analysis.

ii. 2,2'-Di-p-carboxyphenyl-5,5'-bibenzimidazole (DCBI)

The dicarboxylic acid, 2,2'-di-p-carboxyphenyl-5,5'-bibenzimidazole, was prepared by condensation of 3,3'-diaminobenzidine and methyl phenyl

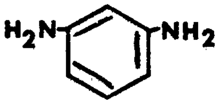
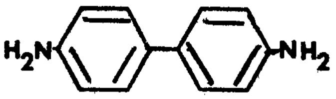
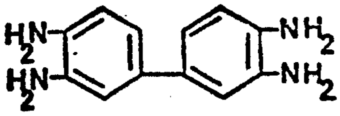
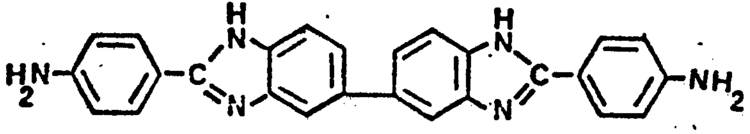
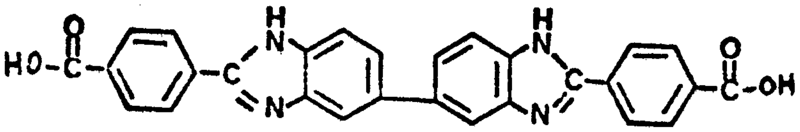
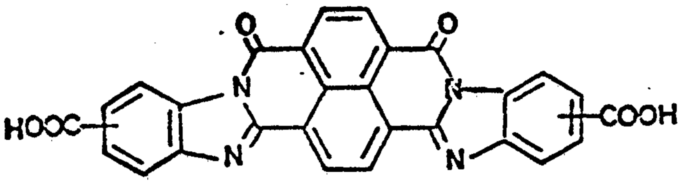
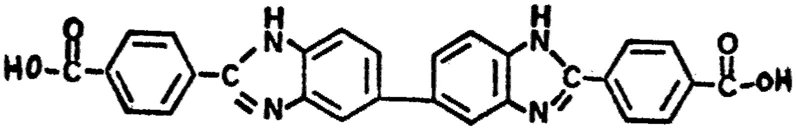
Monomer	Code Abbreviation
	pPD
	mPD
	44Biph
	33DAB
	DABI
	DCBI
	BBB (Acid)

Figure 15 Monomeric Amines and Carboxylic Acids (structures and codes)

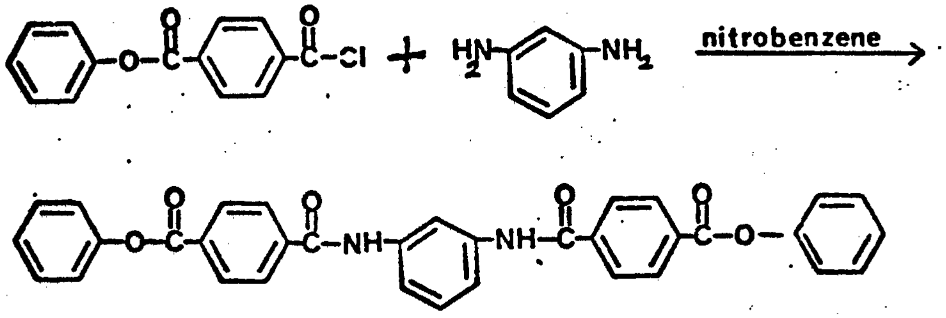
terephthalate to form the benzimidazole with the evolution of phenol leaving the methyl ester intact. Subsequent hydrolysis of the methyl ester gave the diacid monomer. Differential thermal analysis indicates a melting endotherm at 309°C with decomposition probably due to decarboxylation (see Figure 39). Elemental analysis, infrared spectral analysis (Figure 33) and potentiometric titration supported the structure of DCBI. Attempts to prepare the diacid chloride from DCBI by reaction with thionyl chloride, oxalyl chloride and phosphorous pentachloride were unsuccessful.



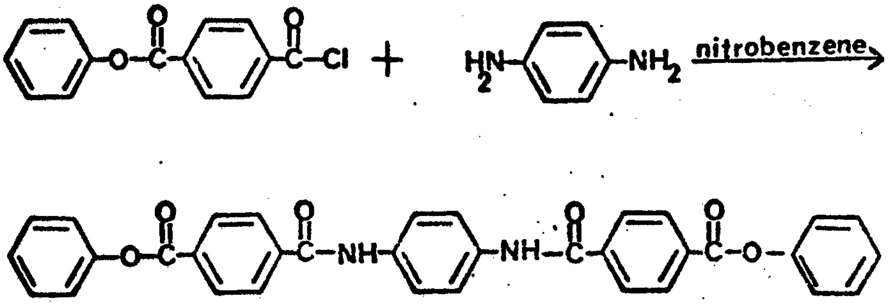
DCBI

iii. 1,3 Bis (4-phenoxycarboxyl-benzoylamino(benzene) (CXX);
1,4 Bis (4-phenoxycarboxyl-benzoylamino(benzene) (CXXI);
4,4'Bis (4-Phenoxycarbonyl-benzoylamino)diphenyl (CXXII)

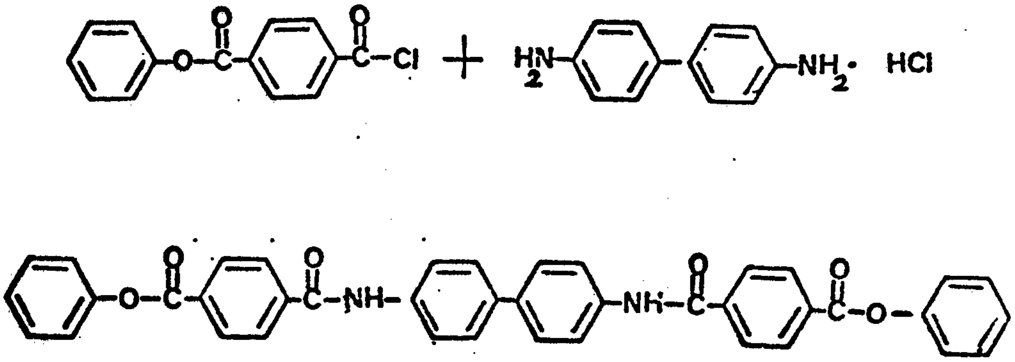
Since the solution polymerization in PPA for preparation of copolyamides produced low molecular weight polymers, another synthetic route based on melt condensation of 3,3'-diaminobenzidine with diphenyl esters CXX, CXXI, and CXXII was employed. For these syntheses a series of new monomers which possess the preformed amide unit with diphenyl ester functions at each end of the molecule were prepared. Compounds CXX, CXXI, and CXXII were prepared according to the following condensation reactions.



CXX 1,3-bis(4-phenoxycarbonyl-benzoylamino)benzene



CXXI 1,4-bis(4-phenoxycarbonyl-benzoylamino)benzene

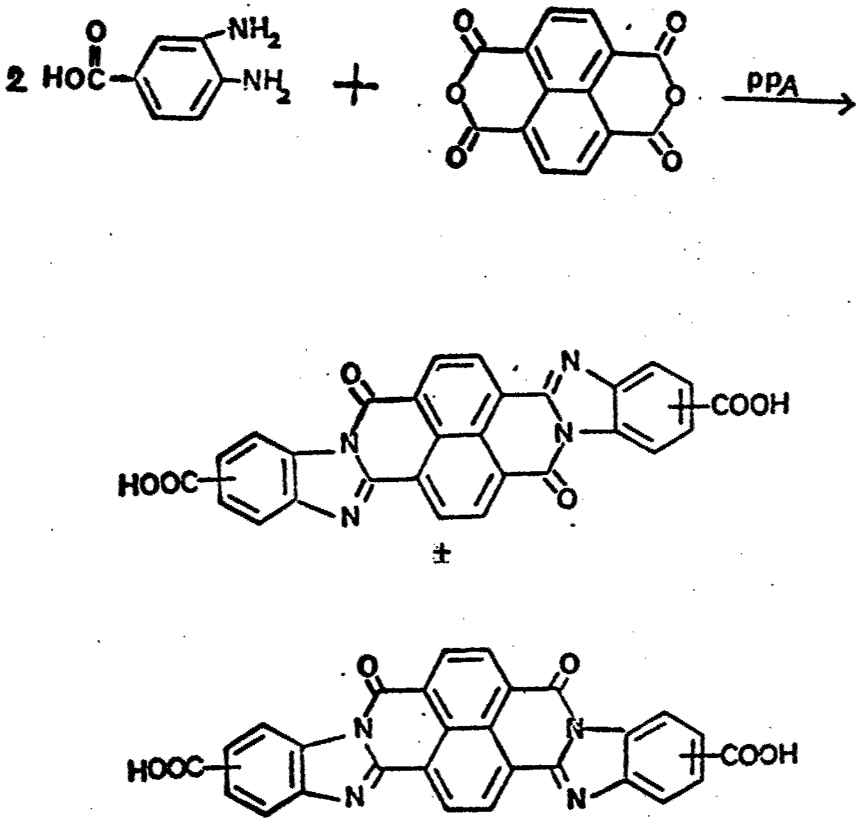


CXXII 4,4'-bis(4-phenoxycarbonyl-benzoylamino)biphenyl

Elemental analysis and infrared spectra (Figures 34, 35, and 36) confirmed the proposed structures for these monomers which were purified by crystallization from hexamethylenephosphoramide (HMP) and methanol.

iv. 6,9-Dihydro-6,9-dioxobisbenzimidazo(2,1-b:1',2'-j)benzo (<u>lmn</u>)(3,8)phenanthridine

Another new monomer, BBB acid was synthesized utilizing condensation of 3,4-diaminobenzoic acid and 1,4,5,8-napthalene-tetracarboxylic dianhydride (NTDA) in PPA under inert gas.



BBB Acid

The product was obtained as a mixture of six possible isomers based on the <u>cis</u>, <u>trans</u> relationships of both the imidazole ring fusions and the positions of the carboxylic acid functions. The structural features of BBB were confirmed by its infrared spectrum (Figure 37). Potentiometric titration and elemental analysis further confirmed the proposed structures. Differential thermal analysis of the mixture showed a broad melting endotherm peaking at 444°C with subsequent decomposition (see Figure 40).

v. 1,4,5,8-Napthalenetetracarboxylic acid Dianhydride

1,4,5,8-Napthalenetetracarboxylic dianhydride (NTDA) was prepared from dehydration of the corresponding tetracarboxylic acid in PPA.

d. Copolymers

The copolymers DABI-I-Amide, DABI-T-Amide mPD-DCBI-Amide, pPD-DCBI-Amide and 44Biph-Amide prepared from solution polymerization in PPA gave products with inherent viscosities over a range of 0.03-0.07 (conc. H_2SO_4) However, the same copolymers synthesized from diacid chlorides and DABI under low temperature conditions (Figure 16) exhibited inherent viscosities of 0.31, 0.32, and 0.30 for DABI-I-Amide, DABI-T-Amide and DABI-44Biph-Amide, respectively. The polymerization was conducted in DMAc containing 0.5% of lithium chloride and 12% triethylamine which functioned both as an acid acceptor and solvent. The initial reaction temperature, -20°C, was slowly raised to 15-25°C after 20 minutes. Quantitative yields were obtained.

Copolymer films of DABI-I-Amide and DABI-44Biph-Amide were cast from DMSO solution for subsequent studies. However, copolymer DABI-T-Amide, because of its poor solubility in both DMSO and DMAc, could not be cast into film. Therefore, polymer film of DABI-T-Amide was cast directly from the polymer solution after filtering off the insolubles.

Copolymer mPD-DCBI-Amide was obtained from melt condensation of compound CXX and 3,3'-diaminobenzidine under reduced pressure to yield copolymer

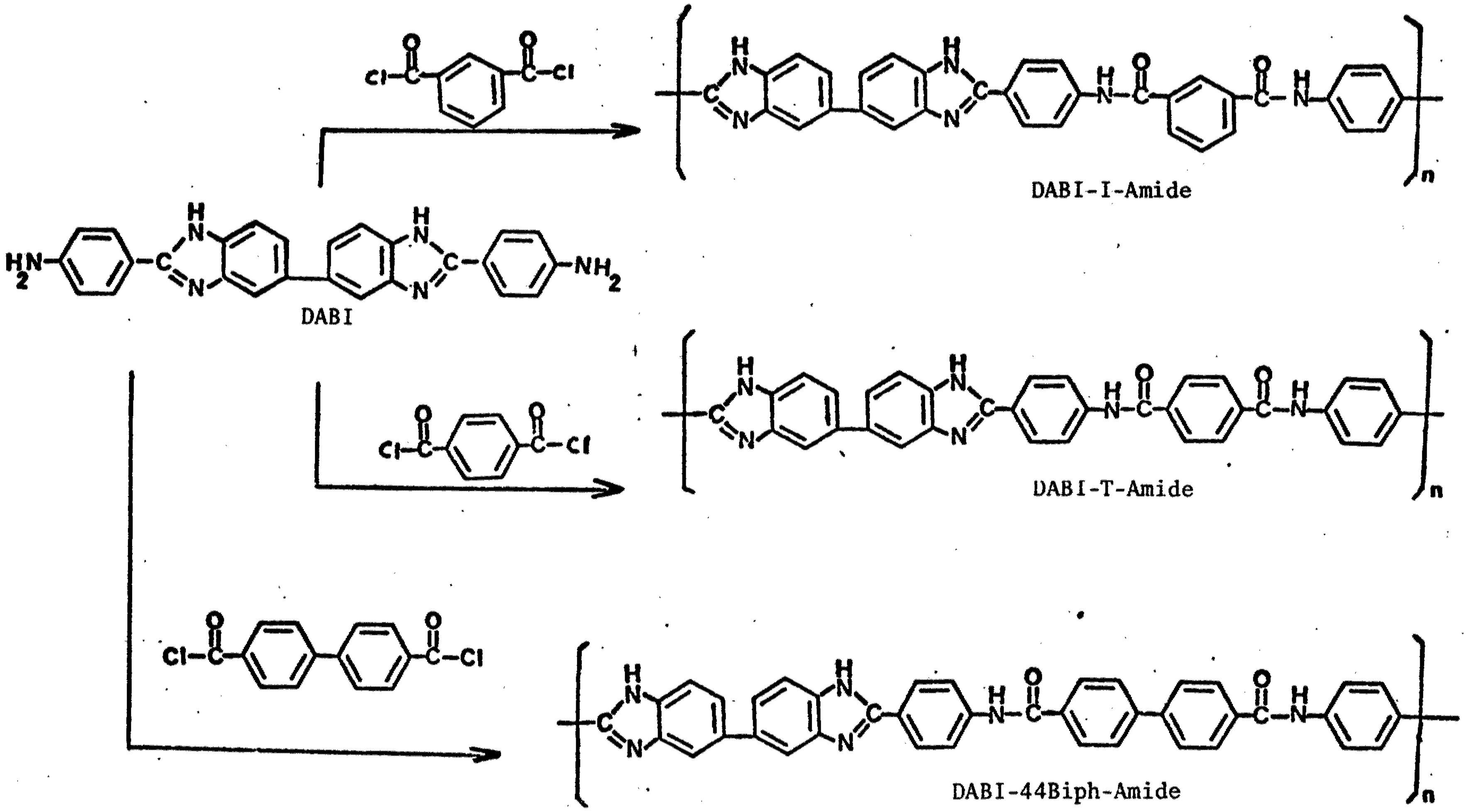
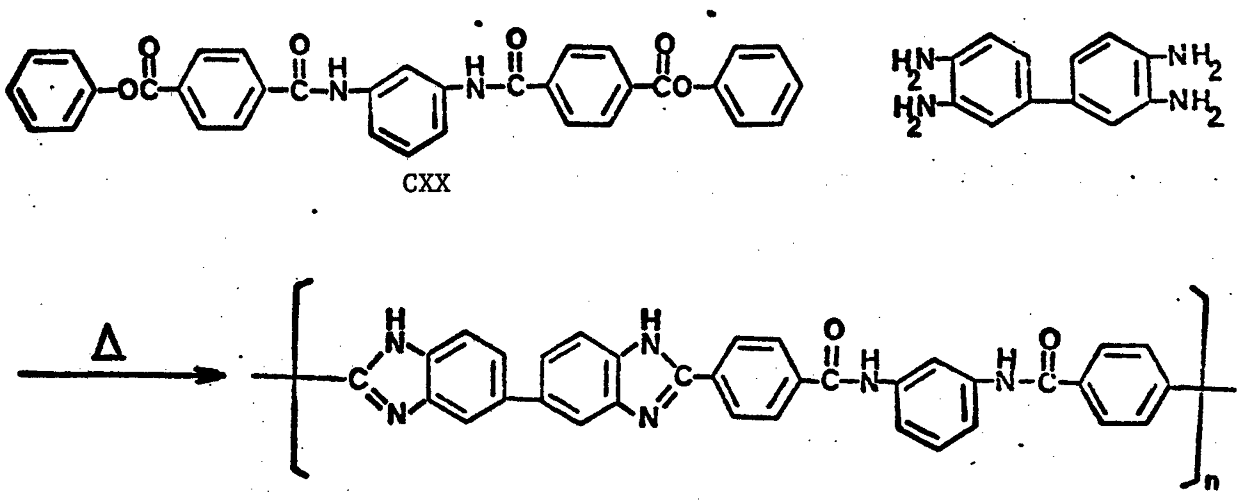


Figure 16 Copolymers prepared by low temperature solution polymerization in DMAc

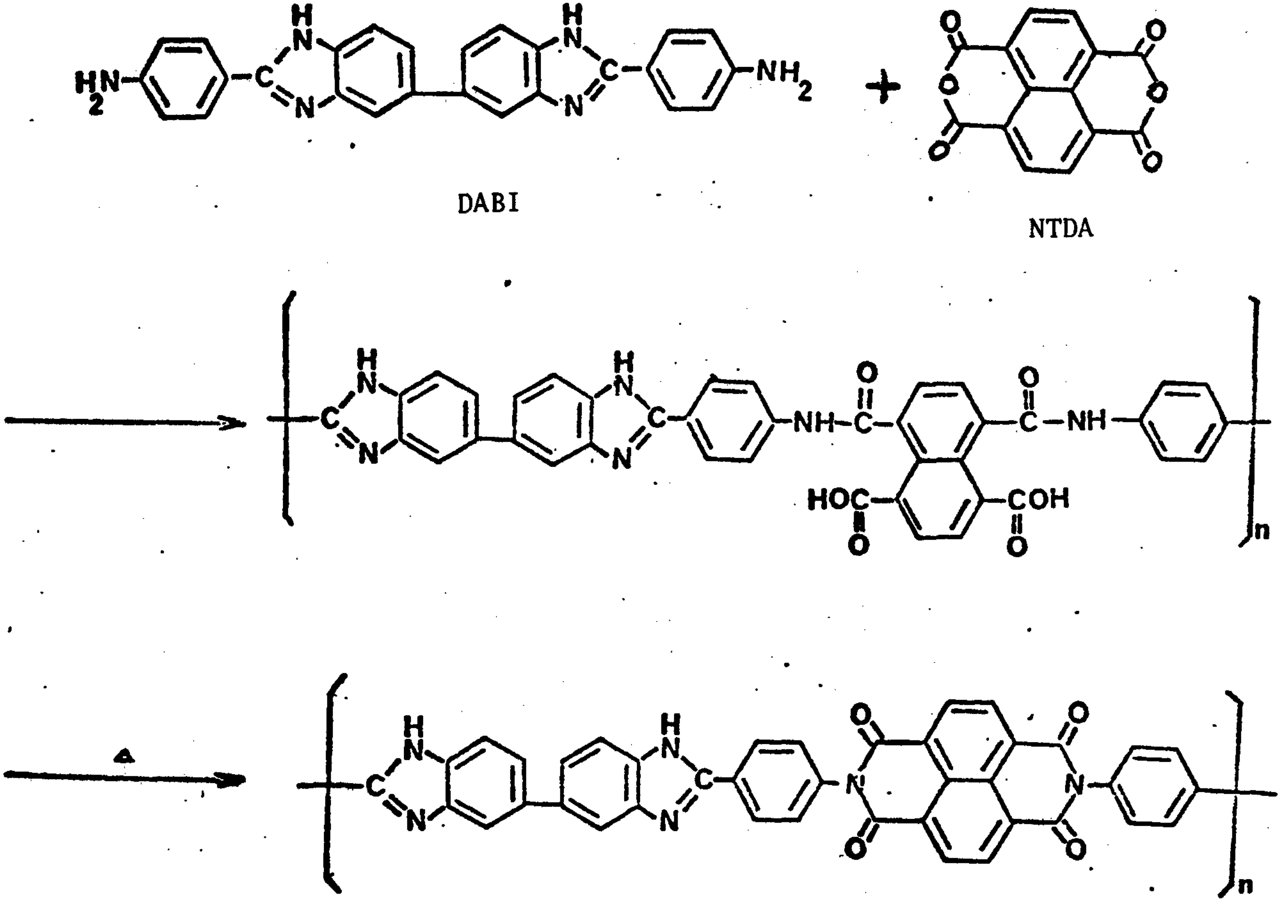
with an inherent viscosity of 0.36.



CXX

mPD-DCBI-Amide

The infusible characteristics of compounds CXXI and CXXII makes melt condensation impossible. Attempts to prepare pPD-DCBI-Amide and 44Biph-DCBI-Amide by solution polymerization in PPA or DMSO were unsuccessful.



DABI

NTDA

DABI-1458Naph-Imide

In the polymerization of DABI-1458 Naph-Imide, the reaction mixture of NTDA and DABI in DMSO formed a polyamic acid prepolymer at room temperature.

Examination of the infrared spectrum of this prepolymer revealed that the amic acid moiety could be characterized by absorption peaks at 1605 and 1375 cm^{-1} which are assigned to the antisymmetrical and symmetrical vibrations of the carboxylate structure[39] (Figure 17).

On heating of this polyamic acid film to 300°C for 0.5 hour, the bands due to the carboxylate group vanished and were replaced by the amide absorption peaks at 1790 and 1710 cm^{-1} (Figure 17).

Copolymer DABI-1458Naph-Imide was also prepared from PPA to give a brown granular solid which is insoluble in common organic solvents and slightly soluble in cold concentrated sulfuric acid. Hot strong sulfuric acid dissolved it to yield a zero viscosity solution indicating degradation during the heat process.

Although PPA was not a suitable condensation medium for production of high molecular weight polyamides, copolymer 33DAB-BBB-Imidazole was prepared in this solvent successfully. The compound BBB acid and 3,3'-diaminobenzidine in PPA gave copolymer with inherent viscosity of 0.35 which can be cast into a tough film from sulfuric acid. The infrared spectrum of this copolymer film was almost identical to the related BBB homopolymer in a KBr pellet and confirmed the proposed structure (Figure 27). All possible *cis* and *trans* arrangements of repeat units can be expected since monomeric BBB acid is a mixture of *cis* and *trans* isomers.

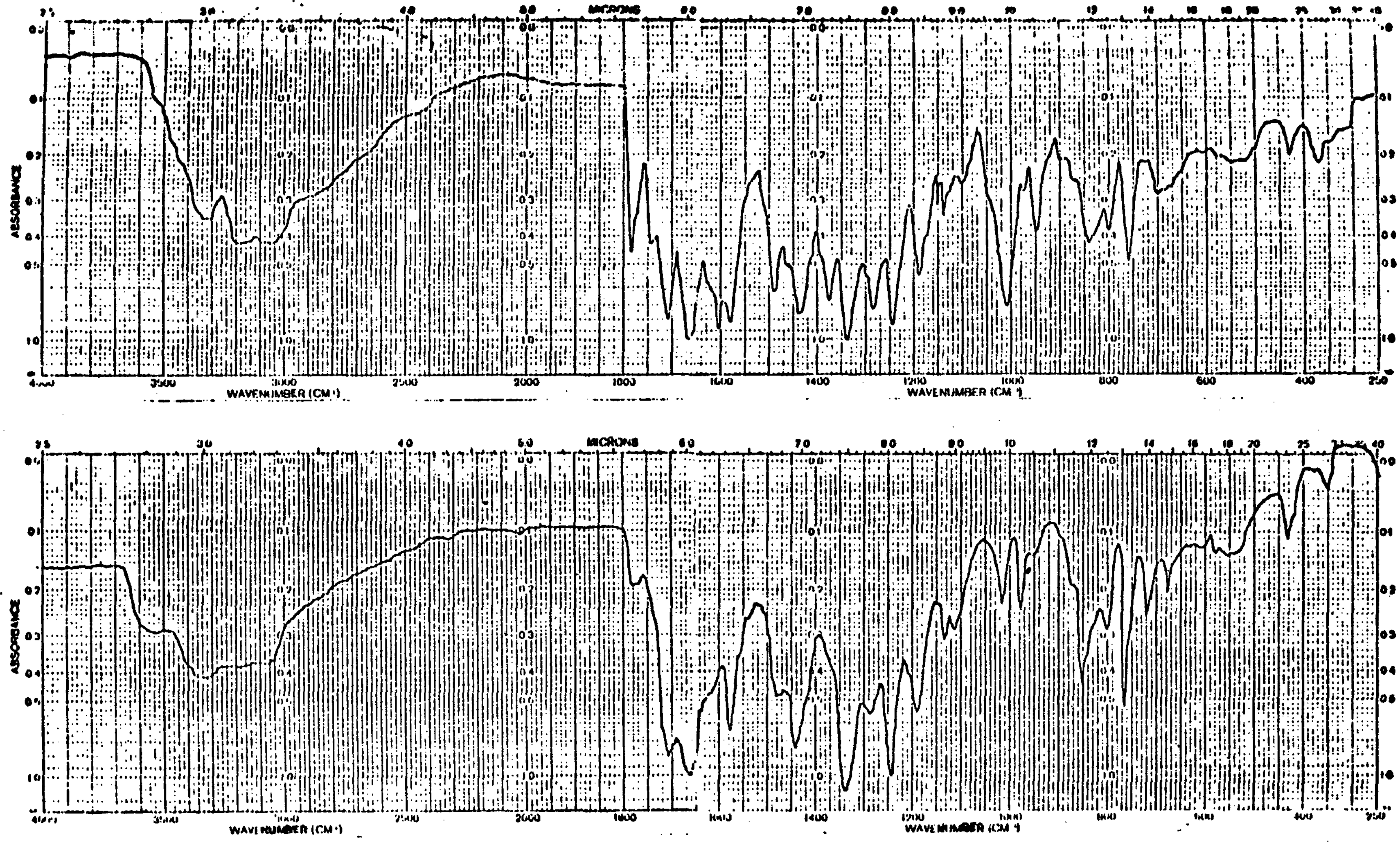


Figure 17 Infrared spectra of DABI-1458Naph-Imide copolymer (Bottom) and prepolymer (Top).

Differential thermal analysis of DABI-T-Amide and DABI-44Biph-Amide were similar showing no endotherms or exotherms up to 500°C (Figures 42 and 44). However, a gradual endothermic slope appeared at 325°C. The copolymer DABI-I-Amide exhibited a sharp exotherm at 375°C which may be due to crystallization followed by a sharp endothermic slope (See Figure 41).

3. Degradation of Copolymers - Thermal Oxidative Stabilities

Copolymer degradations were studied by periodic infrared examination of each film after exposure to an oxygen atmosphere (30 ml/min) at 350°C. The appearance and disappearance of absorption bands characteristic of various functional groups allowed certain conclusions to be drawn about the stability of the copolymers during the early stages of thermooxidation.

The results showed that the most dramatic infrared spectral change was the appearance of three bands at 2220 (assigned to nitrile) 1115 and 615 cm^{-1} (unassigned) for the benzimidazole-amide and benzimidazole-imide copolymers and the appearance of the nitrile absorption for the benzimidazole-benzimidazolone copolymer. The remainder of the spectra revealed a general broadening in intensity with prolonged degradation. The spectra of PBI homopolymer and its copolyamides with the exception of mPD-DCBI-Amide revealed a nitrile absorption after a heating period of three hours. Copolymer mPD-DCBI-Amide revealed the nitrile absorption after seven hours and DABI-1458Naph-Imide after five hours. All of the above films were cast from the aprotic solvents, DMSO and DMAc. Polymer films cast from concentrated sulfuric acid exhibited greater stability to thermooxidation. Thus PBI cast from sulfuric acid did not develop a nitrile function until after twelve hours, 33DAB-BBB-Imidazole after sixty-three hours and BBB homopolymer after eighty four hours. The results based on the time of appearance of the nitrile band for each film sample are summarized in Table I.

TABLE I

Growth of Nitrile Band on Oxidation at 350°C

Polymers	Time of First Appearance
DABI-I-Amide[a]	Third Hour
DABI-T-Amide[b]	Third Hour
DABI-44Biph-Amide[a]	Third Hour
mPD-DCBI-Amide[a]	Seventh Hour
DABI-1458Naph-Imide[c]	Fifth Hour
33DAB-BBB-Imidazole[d]	Sixty-Third Hour
BBB[d]	Eighty-Fourth Hour
PBI[a]	Third Hour
PBI[d]	Twelfth Hour

a. Film cast from DMSO

b. Film Cast from DMAc

c. Film formed by casting pre-polymer from DMSO and subsequent heat curing.

d. Film Cast from conc. H_2SO_4

The above observations reveal a similarity in the thermooxidative behavior for all of the copolymers and suggest that the weakest link along the polymer chain is the benzimidazole unit which has been shown[38] under thermal oxidative conditions to form a nitrile function in the polymer chain. Furthermore the time required for appearance of the nitile function under isothermal conditions and its rate of increase has been shown to be a convenient measure of the reactivity of the PBI system in the early stages of the thermooxidative degradation. The mechanism proposed[46] (Figure 4) for thermal oxidation of PBI involves initial cleavage of the N-H bond to produce the resonance stabilized benzimidazole radical which after oxygenation and subsequent degradation leads to formation of the only spectrally observable intermediate, the nitrile function. Thus, the assumption that the spectral observations in the present study reflect the initial stages of oxidation of the benzimidazole segments is supported by the fact that the behavior of the copolymers parallels that of PBI homopolymer. It is further supported by the fact that no initial decrease in the amide absorptions concurrent with the appearance of the nitrile absorption are observed suggesting that the amide segment remains intact during the initial stages of oxidation of the benzimidazole units in the copolymer chain.

On oxidative pyrolysis copolymer DABI-I-Amide film showed a dramatic change in its infrared spectrum at 2220, 115 and 615 cm^{-1} as a function of time (Figure 18). The remaining absorptions show a decrease in intensity with increasing degradation (see Figure 19). A similar observation was also found in the pyrolyzed films of copolymer DABI-T-Amide and DABI-44Biph-Amide suggesting a slightly superior resistance of the latter two components to thermal oxidation. This greater resistance to oxidation is probably related to the higher degree of order usually found in polymers with para

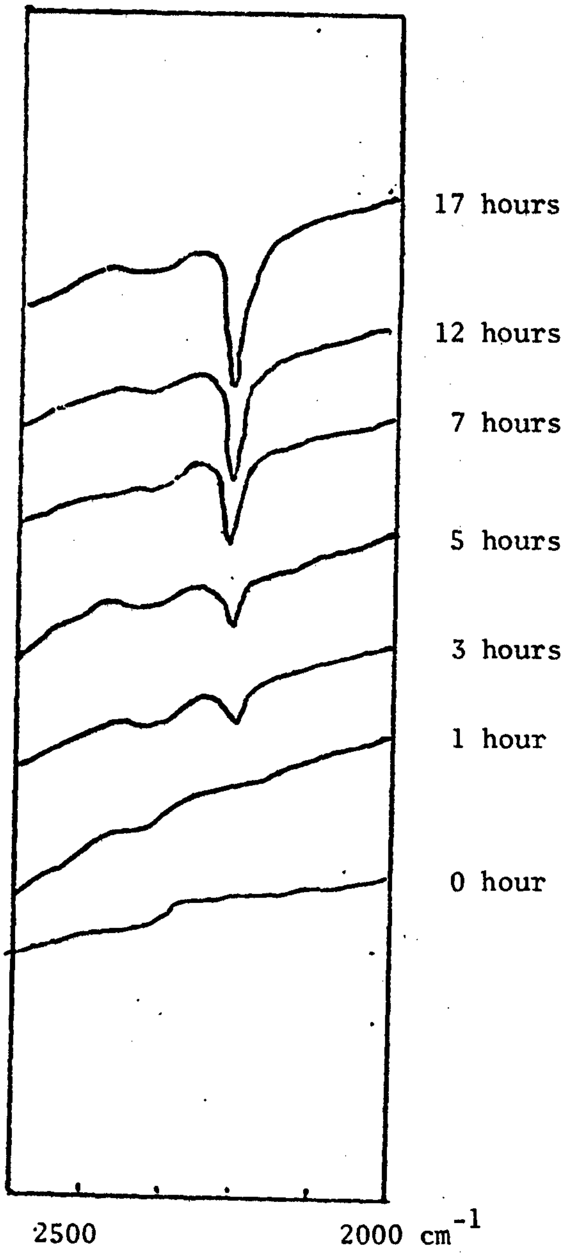


Figure 18 Infrared spectra of DABI-I-Amide at various stages of thermooxidative degradation.

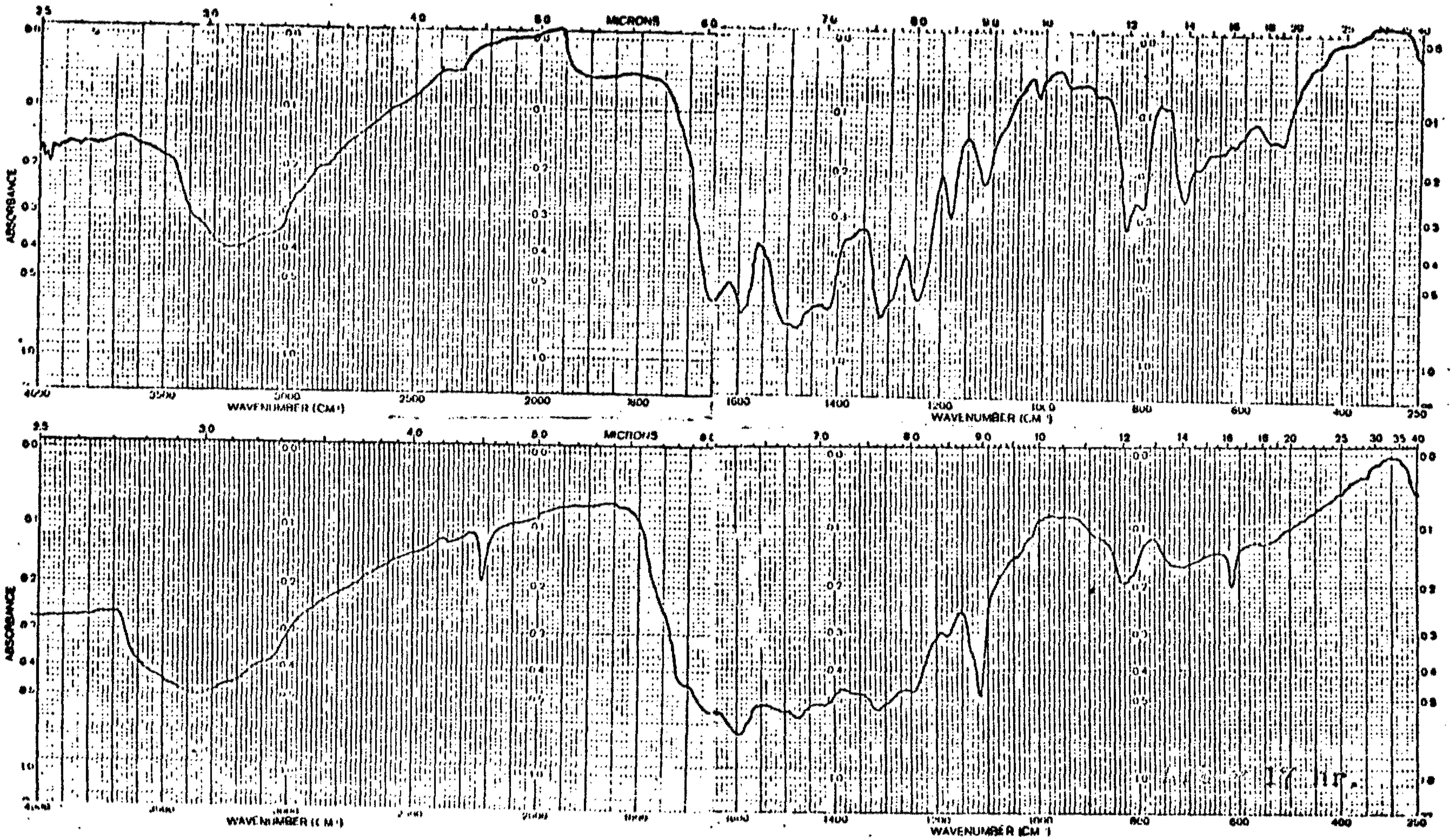


Figure 19 Infrared spectra of copolymer DABI-I-Amide film before and after thermooxidative degradation at 350°C.

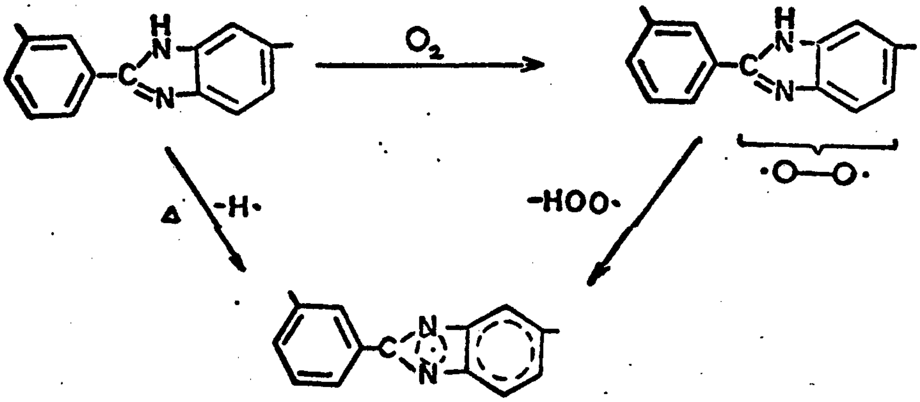
linkages. All three copolymers however are comparable in reactivity and are also comparable to PBI homopolymer which also develops a nitrile function after three hours.

Oxidative pyrolysis of copolymer mPD-DCBI-Amide film revealed the appearance of the nitrile absorption after seven hours (see Figures 20 and 21) indicating that this copolyamide exhibits better thermooxidative stability than DABI-I-Amide, DABI-T-Amide, DABI-44Biph-Amide and PBI homopolymer. This finding is in agreement with a previous report[36] that copolymer mPD-DCBI-Amide showed better thermal stability than copolymer DABI-I-Amide based on thermal gravimetric analysis (Figure 9). The enhanced oxidative stability of copolymer mPD-DCBI-Amide can be interpreted in terms of the effect of the carbonyl group bonded to the benzene ring adjacent to the imidazole system. The electron-withdrawing effect of the carbonyl group would result in overall decreased reactivity of the imidazole N-H bond toward homolytic bond breaking which generates the free radical species, the proposed precursor to oxygenation of the benzimidazole segment.

There are two key reactions which could be involved in the early stage of degradation:

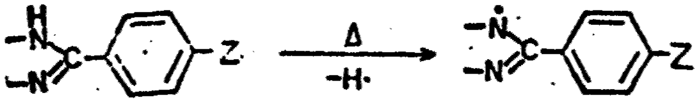
(1) Homolytic cleavage of the imidazole nitrogen-hydrogen bond.

(2) Hydrogen abstraction by an oxygen molecule or by free radical sources which are thermally generated from the functional end groups of polymers.



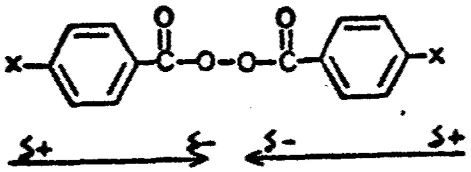
Both of these routes lead to the formation of the same radical species a process which is expected to be facile because of the resonance stabilization afforded to the resulting radical.

If rupture of the nitrogen-hydrogen bond is due to homolytic cleavage, the electron withdrawing group (Z) attached to the benzene ring bonded to the heterocyclic ring will decrease the electron density of the nitrogen-hydrogen bond, strengthening the bond and resulting in a greater resistance to formation of the radical intermediate.



On the other hand, electron-donating groups (e.g. the imino function) are expected to increase the rate of radical formation. Subsequent oxygenation and oxidative destruction would result in a more rapid rate of appearance of the nitrile function.

A similar effect was observed in the unimolecular dissociation of benzoyl peroxide[40]. It was found that electron-donating substituents increased the rate of first order dissociation since they increased the electronegativity difference between the peroxide oxygen and the aromatic ring. The greater negative charge on the oxygens produced a large electrostatic repulsive force between them and a faster rate of dissociation.



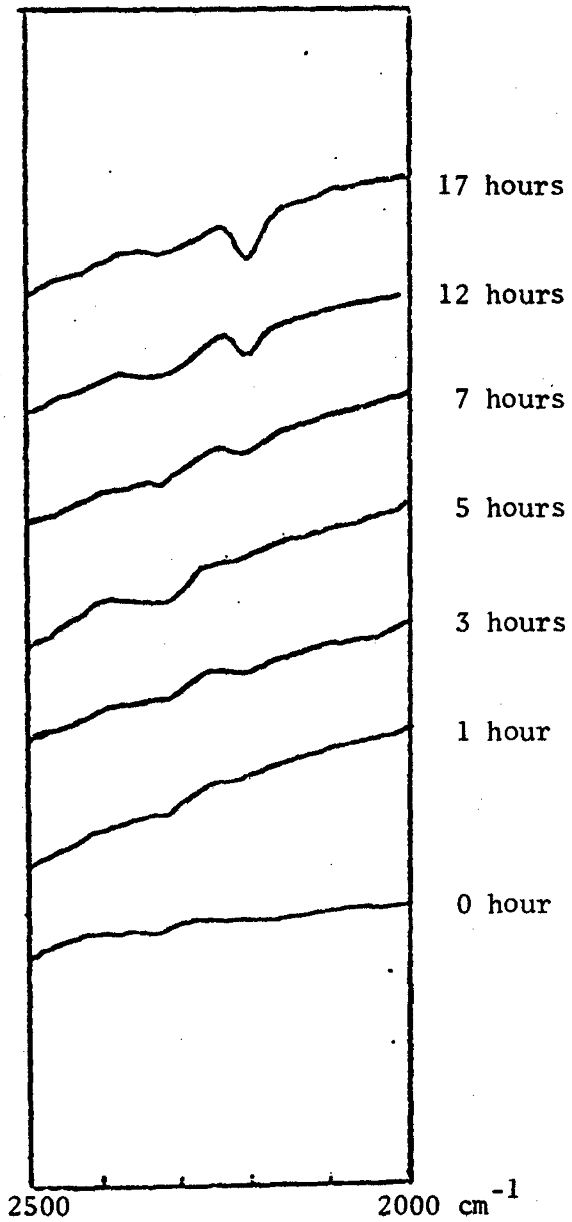


Figure 20 Infrared spectra of mPD-DCBI-Amide at various stages of thermooxidative degradation.

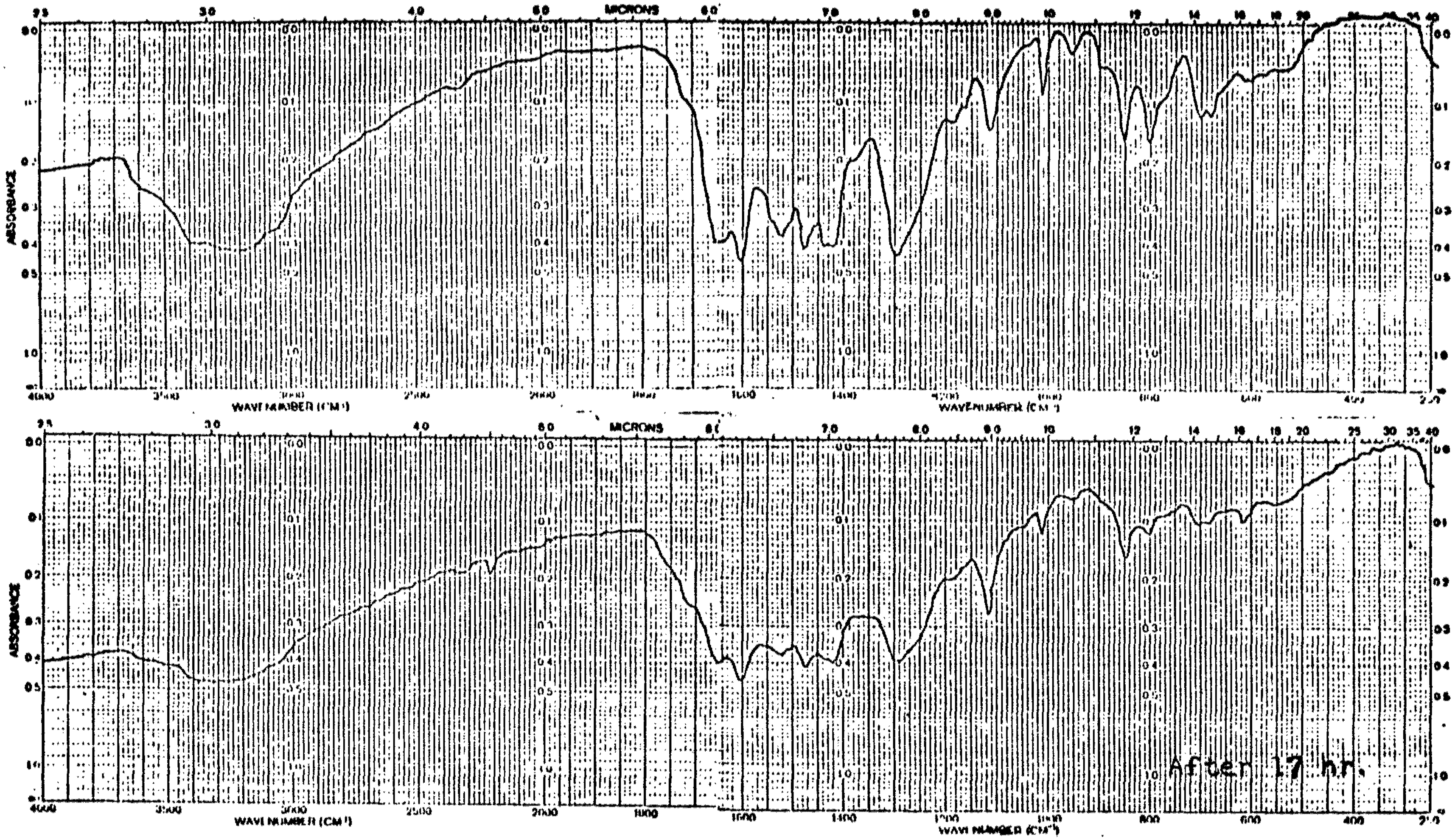


Figure 21 Infrared spectra of copolymer mPD-DCBI-Amide film before and after thermooxidative degradation at 350°C.

Although oxygen itself (a diradical) is too unreactive to be the species which actually abstracts the hydrogen[41], the attack of oxygen on the imidazole ring can also be affected by the characteristics of the substituents. Thus, electron-withdrawing groups reduce the electron density and decrease the likelihood of attack by electrophilic oxygen molecules or free radicals. This effect could be the source of the observed enhanced stability of copolymer mPD-DCBI-Amide which has the relatively strong electron-withdrawing carbonyl substituent.

Studies of oxidation for other systems are in accord with these findings. Kuzminskii and Popova[42] found that styrene butadiene rubber oxidizes faster than polybutadiene, which in turn oxidizes faster than acrylonitrile butadiene rubbers. Increasing the content of acrylonitrile in the nitrile rubber increases the induction period for oxidation of the polymer. This is to be expected since the cyano group is a powerful electron-withdrawing substituent. The empirical fact that polymers with electron-withdrawing groups are less prone to oxidation was noted many years ago[43].

Isothermal oxidation of copolymer DABI-1458Naph-Imide film revealed the appearance of the nitrile band at 2220 cm^{-1} after five hours (see Figure 22) indicating that this copolymer is less susceptible to oxidation than DABI-I-Amide, DABI-T-Amide, DABI-44Biph-Amide and PBI but more susceptible than mPD-DCBI-Amide. The remaining absorptions of the infrared spectrum reveals an overall decrease in intensity with continued degradation (see Figure 23). The lower reactivity of DABI-1458Naph-Imide toward oxidation compared to DABI-I-Amide, DABI-T-Amide, DABI-44Biph-Amide and PBI is probably due to the greater electron withdrawing ability of the imide compared to the amide

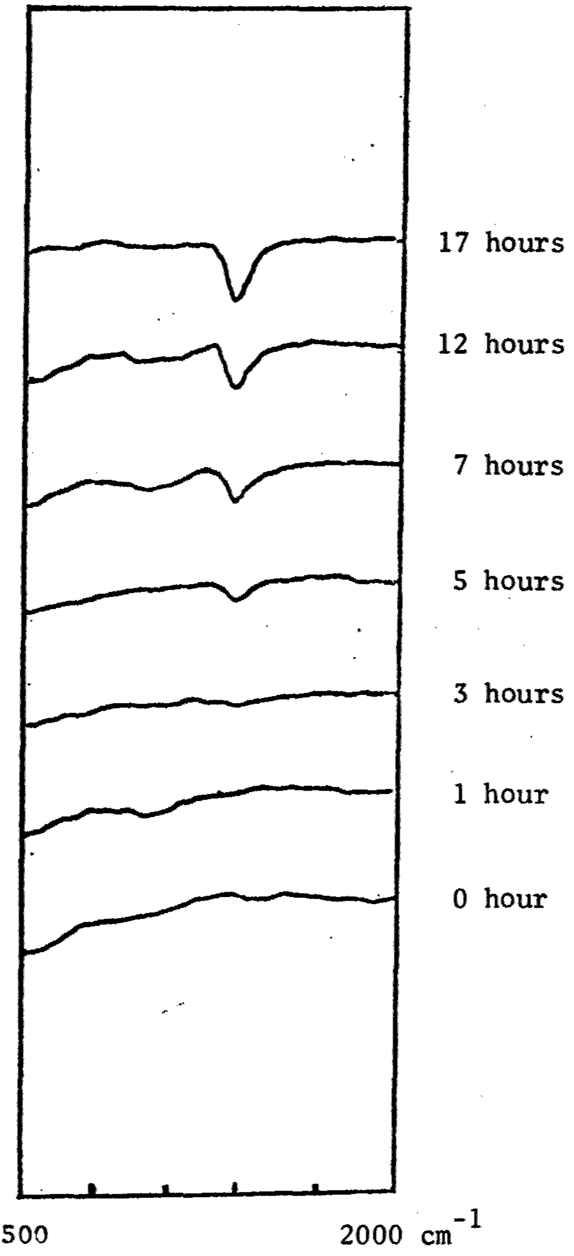


Figure 22 Infrared spectra of DABI-1458Naph-Imide at various stages of thermooxidative degradation.

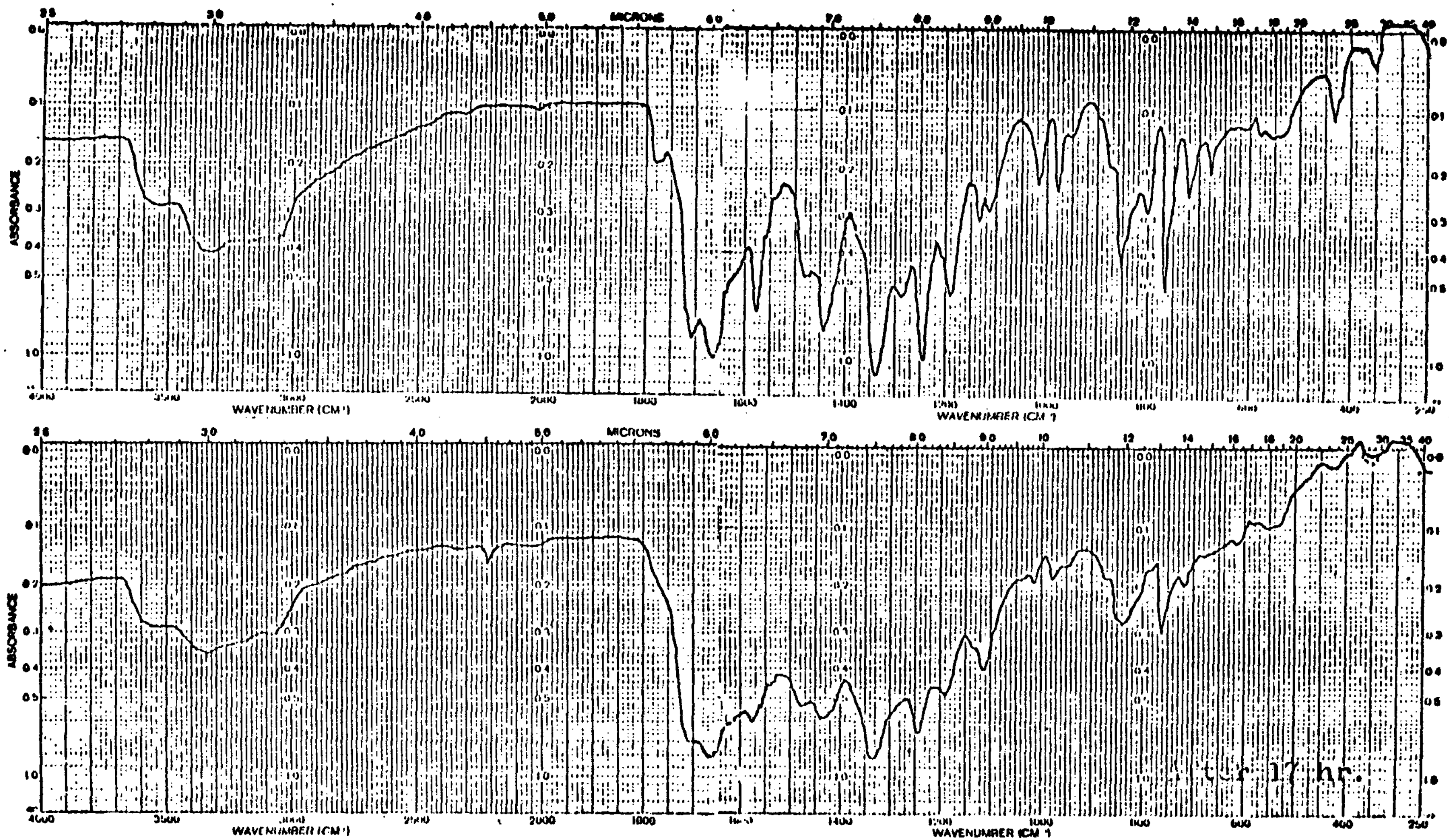
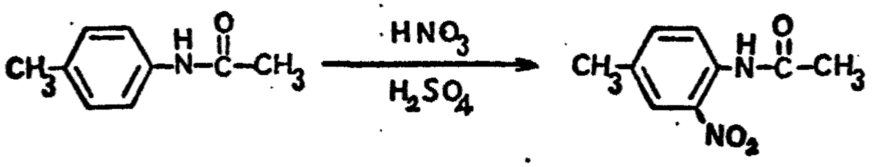
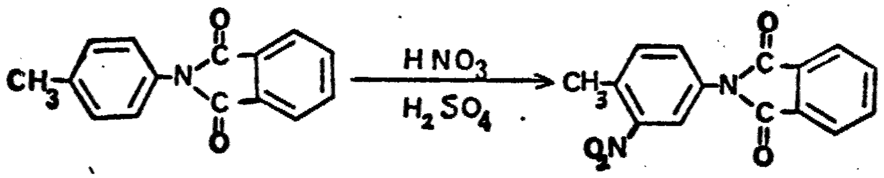


Figure 23 Infrared spectra of copolymer DABI-1458Naph-Imide film before and after thermooxidative degradation at 350°C.

function. This speculation is supported by the report[44] that while a single acyl substituent on nitrogen as in aceto-*p*-toluidide is not sufficient to reduce the orienting effect of the acyl-amino group below that of the methyl group, double acylation, as in phthaloyl-*p*-toluidine will do so. Thus the former compound nitrates ortho to the singly acylated nitrogen while the latter nitrates meta to the double acylated nitrogen.





Copolymer 33DAB-BBB-Imidazole was found to be completely insoluble in common organic solvents including the aprotic solvent DMF, DMAc, DMSO, and HMP. However, a film of this copolymer was cast from concentrated sulfuric acid. The resulting film was subjected to the usual isothermal oxidative aging conditions at 350°C with periodic monitoring by infrared. This copolymer showed unusual oxidative stability in that the nitrile band at 2220 cm^{-1} appeared only after sixty-three hours (Figure 24). Thus it appears that the benzimidazolone segment dramatically enhances the resistance of the

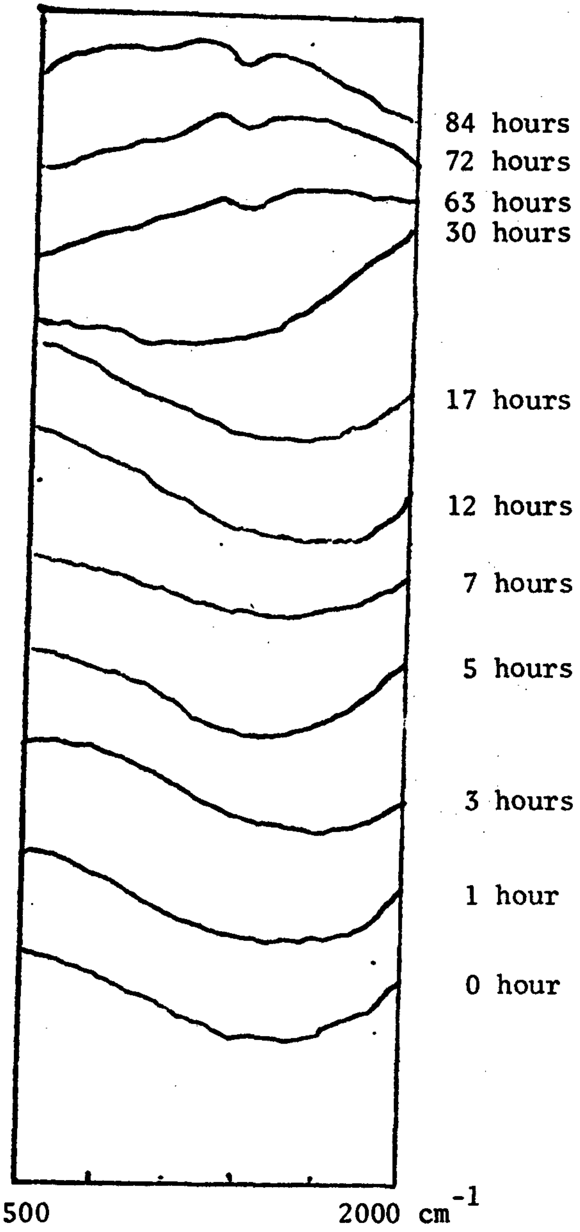


Figure 24 Infrared spectra of 33DAB-BBB-Imidazole at various stages of thermooxidative degradation.

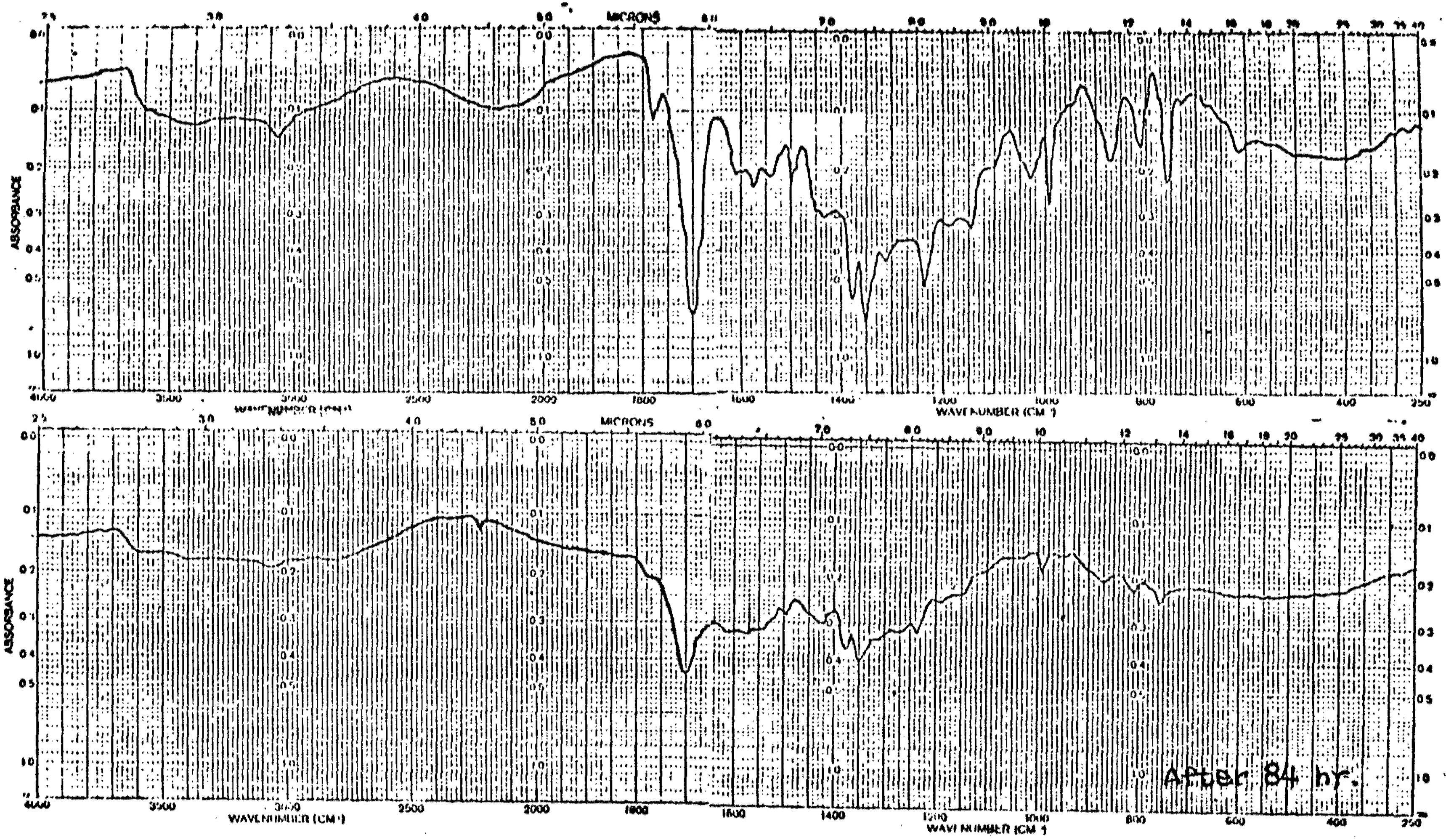


Figure 25 Infrared spectra of copolymer 33DAB-BBB-Imidazole film before and after thermo-oxidative degradation at 350°C.

benzimidazole system to oxidation. However, it is difficult to draw comparisons between this copolymer film and the other copolymers and PBI homopolymer film oxidized in this investigation because of the unusual nature of the film casting solvent, concentrated sulfuric acid. The infrared spectrum of 33DAB-BBB-Imidazole film cast from concentrated sulfuric acid (Figure 25) does not reveal any indication of aromatic sulfonation, any residual sulfuric acid or any sulfate salt. Interestingly the spectrum is identical to that of BBB homopolymer (Figure 26) cast from sulfuric acid, showing only the typical absorption of the benzimidazole segments. Furthermore, the spectra of 33DAB-BBB-Imidazole and BBB films cast from sulfuric acid are practically identical to that of BBB homopolymer[45] (Figure 27).

The infrared spectrum of PBI homopolymer cast from concentrated sulfuric acid (Figure 28) is however dramatically different from that of PBI cast from DMSO (Figure 29) and reveals absorptions at 1040 and 1170 cm^{-1} which are assigned to sulfate[39]. Other absorptions (800, 1280, 1430, 1520, and 1610 cm^{-1}) are shifted and changed in intensity. The spectra of PBI cast from sulfuric acid, although it suggests the presence of sulfate does not reveal whether it is convalently bound through aromatic sulfonation or ionically bound as a salt with the basic imidazole nucleus.

For purposes of comparison with 33DAB-BBB-Imidazole, the homopolymer films BBB and PBI were also subjected to isothermal ageing at 350°C in oxygen with periodic infrared monitoring. The results (Figure 30) disclose the expected high stability of the BBB system which developed a nitrile function only after eighty-four hours. Surprisingly, PBI homopolymer cast from concentrated sulfuric acid developed a nitrile function after twelve hours exposure in contrast to film cast from DMSO which shows

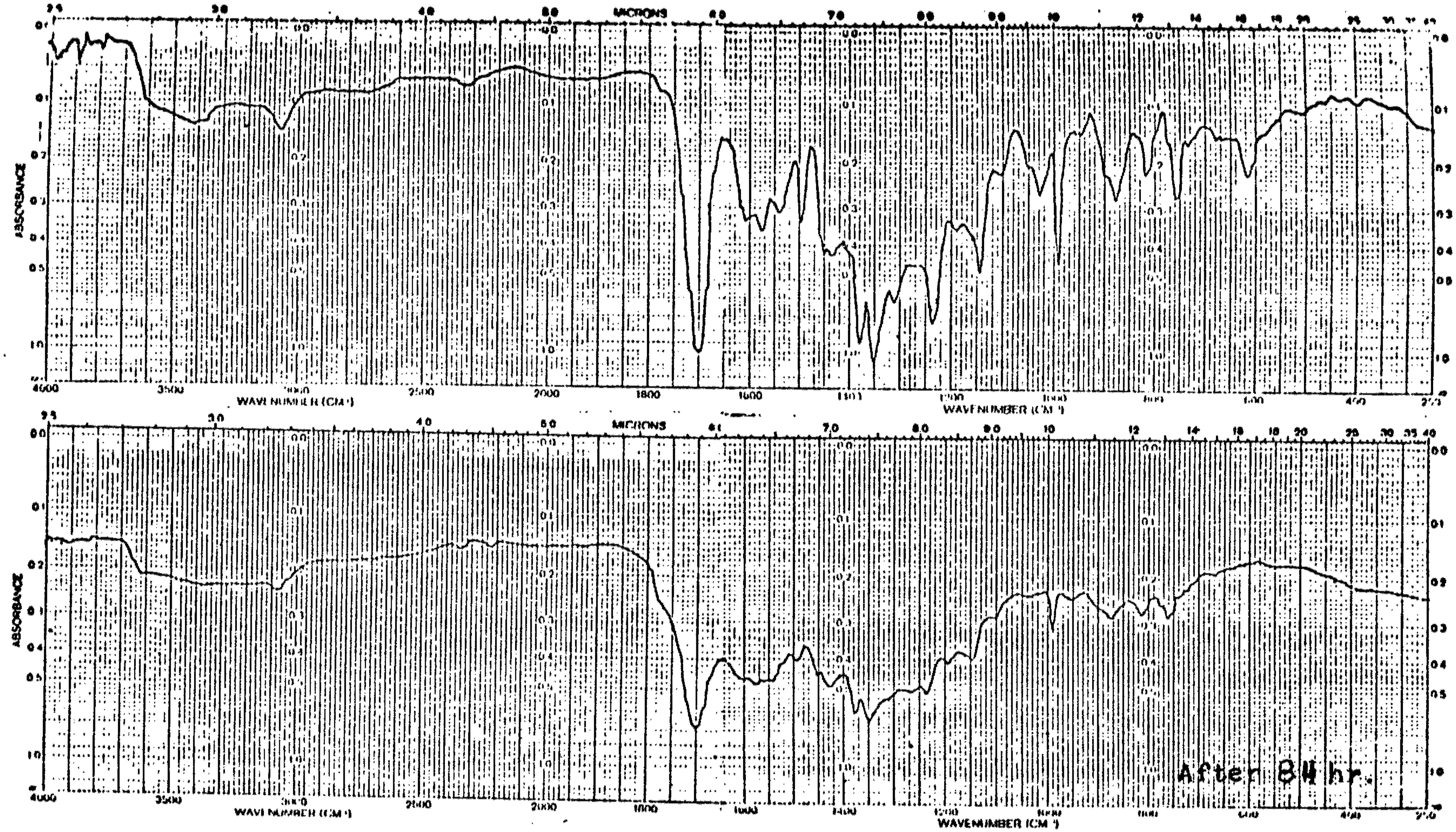


Figure 26 Infrared spectra of homopolymer BBB film before and after thermooxidative degradation at 350°C

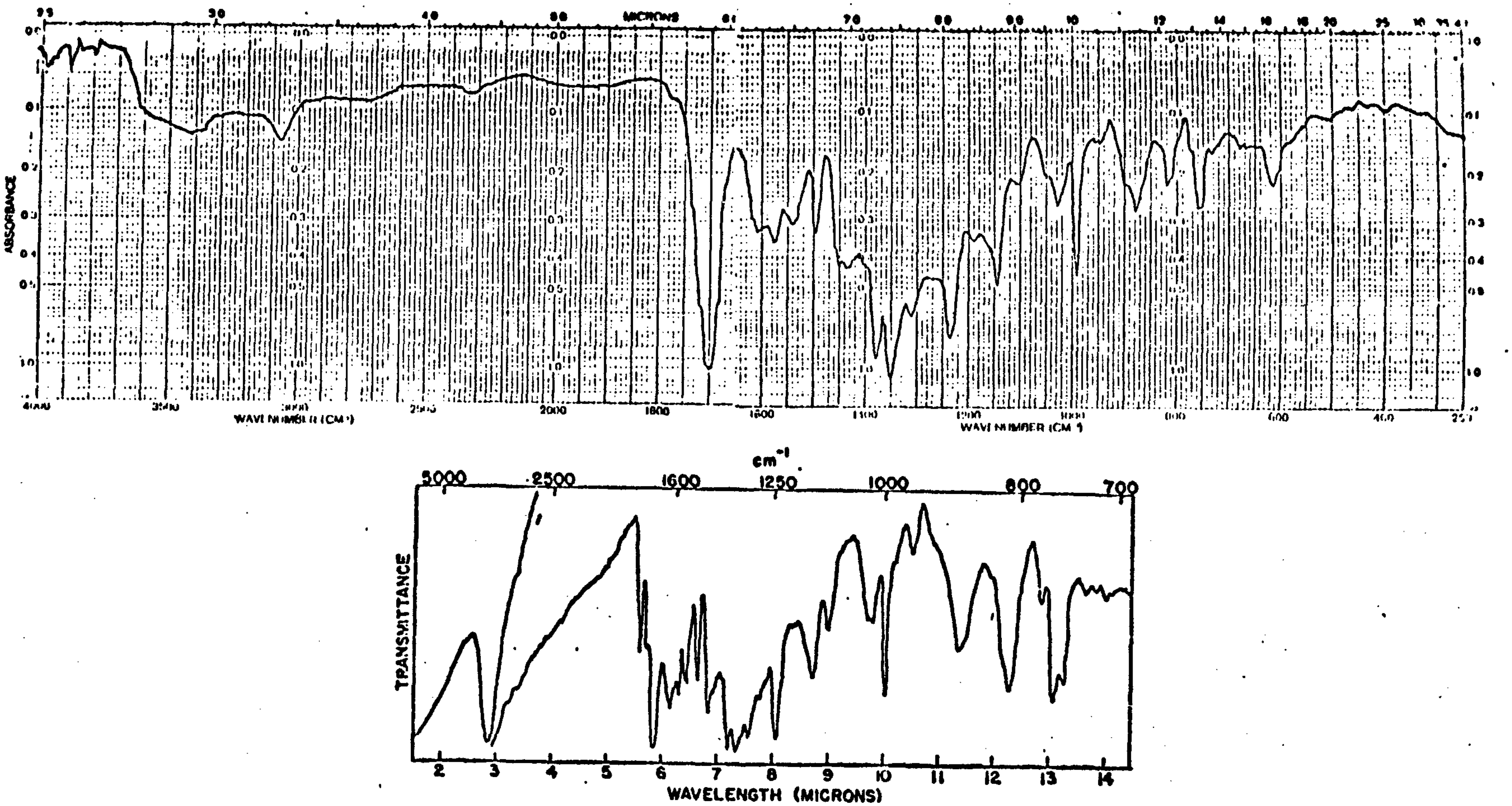


Figure 27 Infrared spectra of BBB film cast from conc. H_2SO_4 (Top) and BBB in KBr pellet (Bottom).

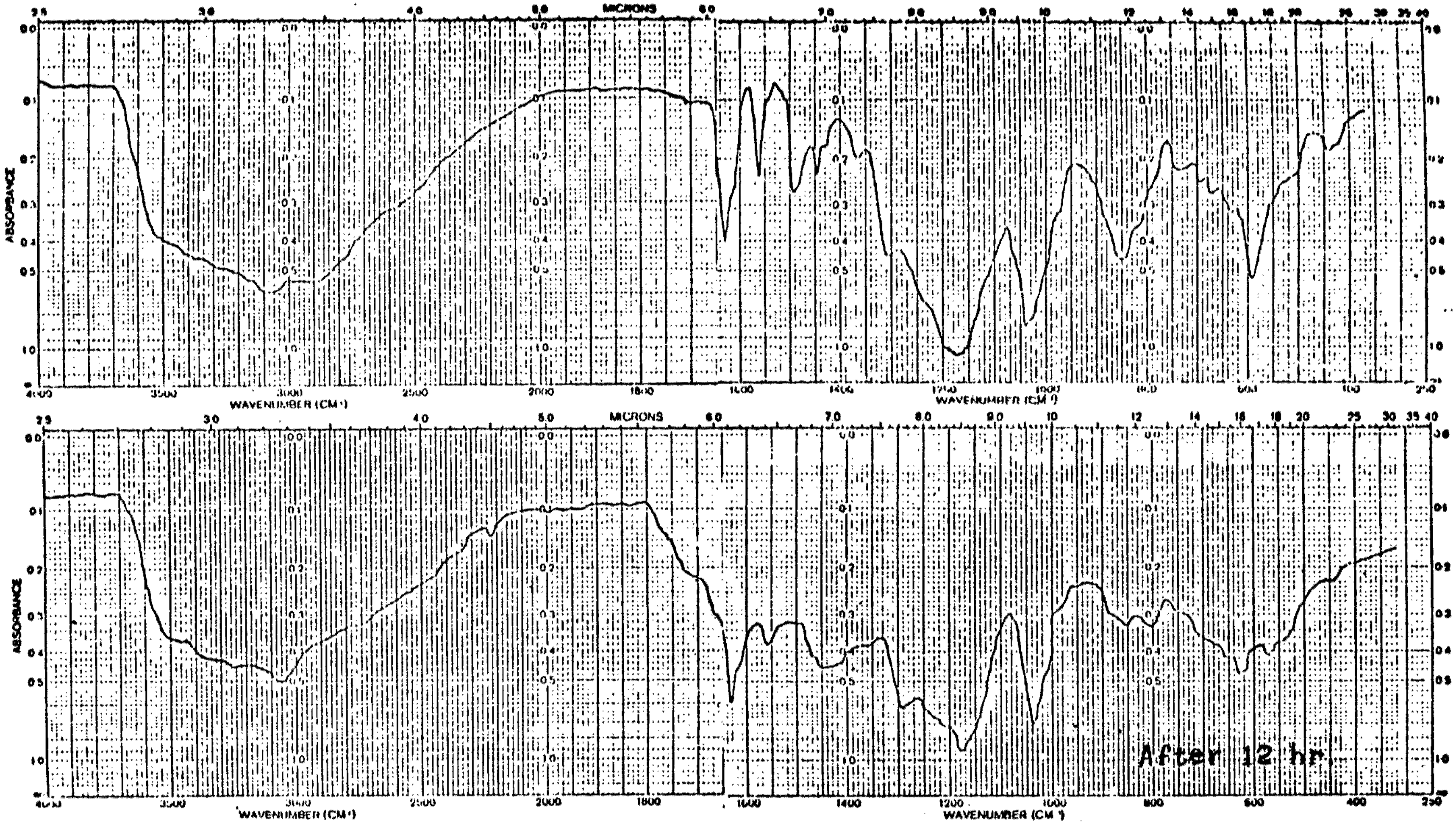


Figure 28 Infrared spectra of PBI film cast from conc. H_2SO_4 before and after thermooxidative degradation at 350°C.

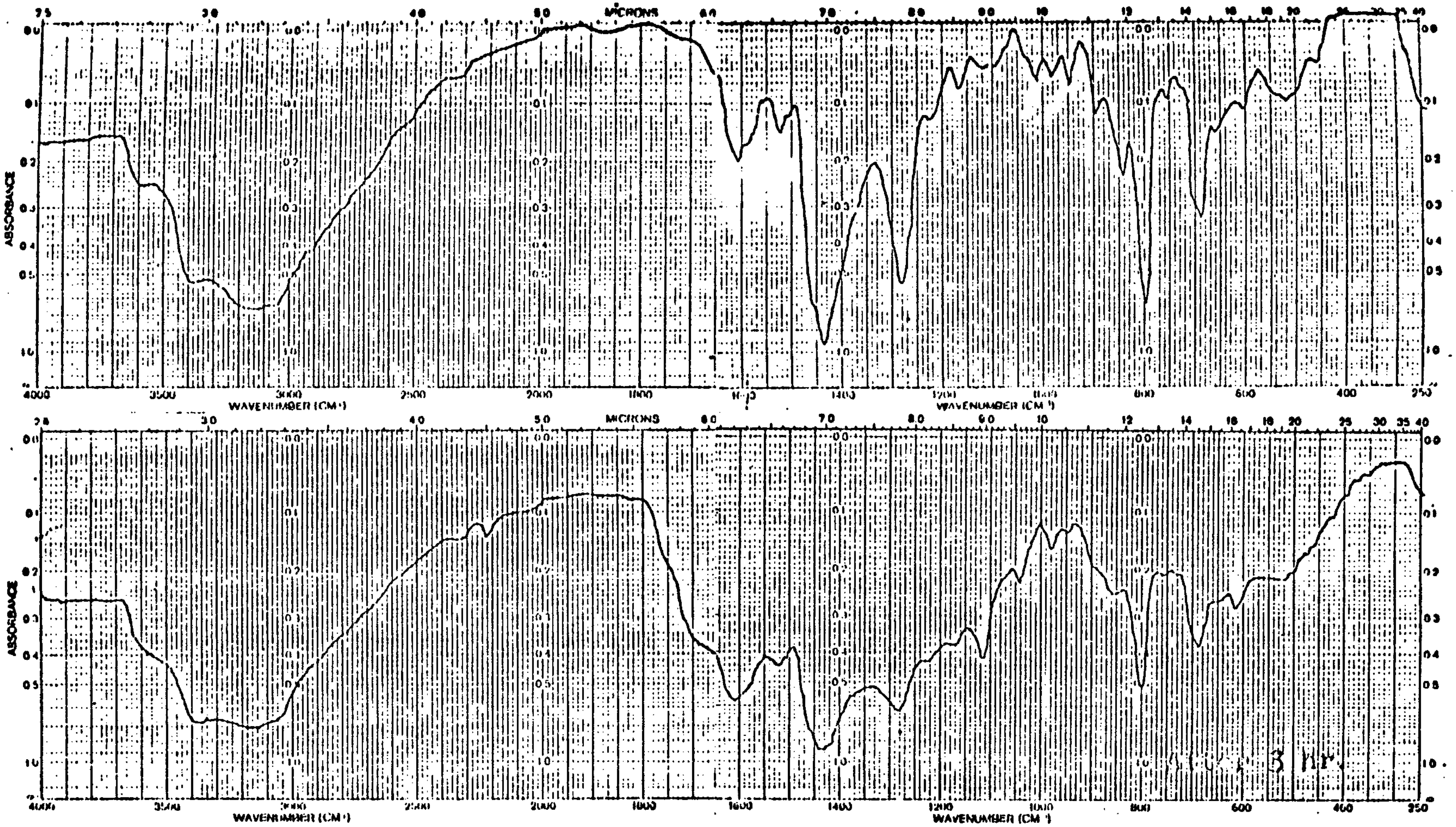


Figure 29 Infrared spectra of PBI film cast from DMSO before and after thermooxidative degradation at 350°C.

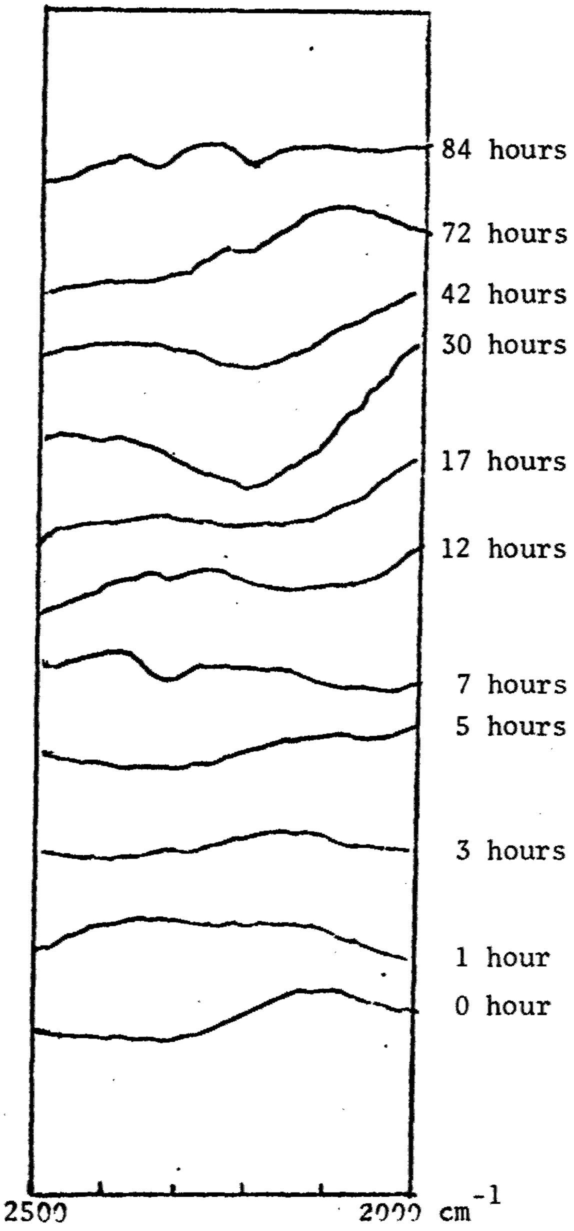


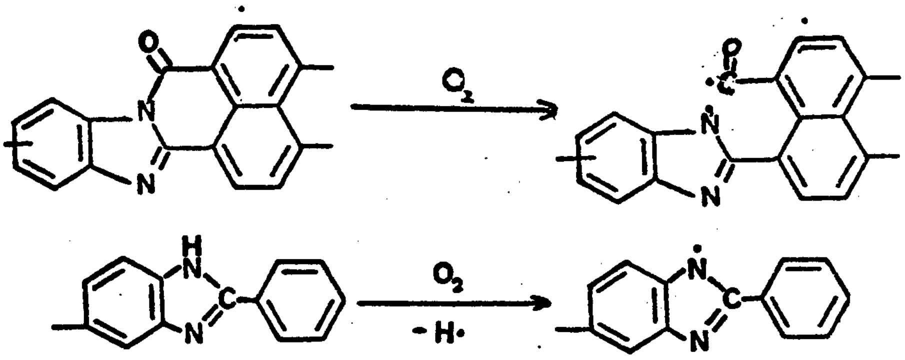
Figure 30 Infrared spectra of BBB at various stages of thermooxidative degradation.

evidence of degradation (appearance of the nitrile function) after only three hours. Moreover, the film cast from sulfuric acid is still tough and intact after twelve hours while the film cast from DMSO is no longer self supporting after similar exposure time.

Comparison of 33DAB-BBB-Imidazole with PBI and BBB all cast from sulfuric acid and showing signs of degradation after sixty three, twelve and eighty-four hours respectively reveals the marked stabilizing effect of the benzimidazolone functions on the benzimidazole segments toward thermal oxidation.

Unfortunately, with the data on hand it is difficult to speculate on the chemical or structural nature of PBI after exposure to concentrated sulfuric acid. However, it does seem reasonable to propose that either salt formation or aromatic ring sulfonation would be expected to stabilize the benzimidazole linkage through the expected decrease of electron density. Whatever the nature of the chemical or structural changes resulting from such treatment, the improvement of the homopolymer oxidative stability is noteworthy and should be further explored.

In the benzimidazolone polymers, the mechanism of degradation was proposed[46] to be similar to that proposed for the benzimidazole system. The initial processes were the abstraction of the hydrogen atom in the benzimidazole system and the opening of the amido bond in the benzimidazolone system.



Further oxidative degradation of the benzimidazolone radical is expected to develop a nitrile moiety which was detectable by the infrared technique upon oxidative degradation (350°C for 84 hours) (see Figure 26). This observation provides the first supporting evidence for development of a nitrile function in the BBB system and thus supports the proposed mechanism which is shown in Figure 31.

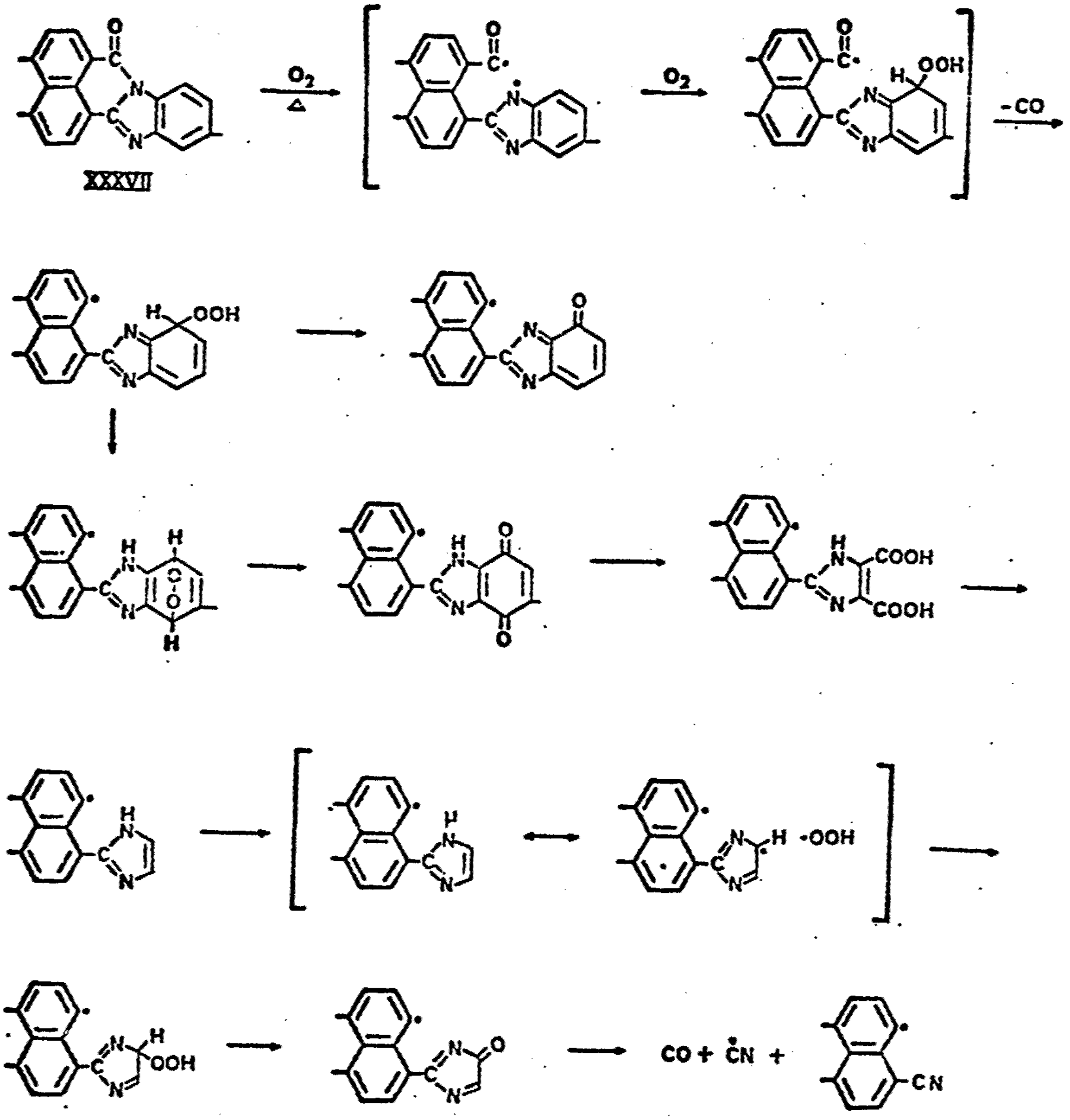


Figure 31. Proposed thermooxidative degradation mechanism for polybenzimidazolones

SECTION IV

SUMMARY AND CONCLUSIONS

The object of the present investigation was to prepare a series of copolymers containing the benzimidazole unit in conjunction with aromatic amides, benzimides and benzimidazolones and to make an exploratory survey of these copolymers from the viewpoint of their thermal oxidative characteristics and their solubility properties.

The copolymers were prepared by condensation reactions between appropriate amines and carboxylic acids (or derivatives). Thus copoly(amide-benzimidazoles) were synthesized either by condensation of a diaminobenzimidazole with a diacid (or diacid chloride) or by condensation of a tetraamine and a diphenyl ester containing amide functions.

Low temperature condensation polymerization in DMAc between diamines and diacid chlorides was found most successful for formation of amide functions. Attempts to form similar copolyamides by condensation of diamines with dicarboxylic acids in 115% PPA yielded only low viscosity polymers. The latter method yielded copoly(amide-benzimidazoles) with inherent viscosities ranging from 0.03-0.07 while the former method gave quantitative yields of products with viscosities ranging from 0.30 to 0.32.

Condensation reactions between tetramines and dicarboxylic acids and diamines with tetracarboxylic acid dianhydrides in 115% PPA to form benzimidazole and benzimide linkages were, as expected, successful routes to certain of the desired copolymers. Similarly melt condensations between tetraamine (diaminobenzidine) and a diphenyl ester containing preformed amide functions produced mPD-DCBI-Amide quantitatively with an inherent viscosity of 0.36. However certain other similar reactions were unsuccessful because of the infusible nature of the amide containing diphenyl ester starting materials.

The preparation of the copoly(benzimide-benzimidazole), DABI-1458 Naph-Imide was equally successful when carried out in 115% PPA or by the two stage process to form first the copoly(benzimidazole-amic acid) in DMSO solvent. After casting into film the prepolymer was converted to the desired imide by heat treatment. The latter method was used to obtain films for the present study.

Preparation of the copoly(benzimidazole-benzimidazolone) was also effected by condensation of a dicarboxylic acid derivative of a bis-benzimidazolone and tetraamine in 115% PPA.

Polybenzimidazoles are generally soluble in the polar aprotic solvents DMSO and DMAc while benzimides and benzimidazolones are generally insoluble in these solvents and require solvents such as concentrated sulfuric acid. Unfortunately the desired solubility effects were not observed in this investigation as the copolymers exhibited the solubility characteristics of their least soluble component. Thus the copolymeric benzimidazole-benzimides and benzimidazole-benzimidazolones were completely insoluble in DMAc, DMF, DMSO and HMP. They were however soluble in concentrated sulfuric acid. The copoly(amide-benzimidazoles) were, as expected, soluble in DMSO and similar solvlents.

In order to carry out the desired oxidative studies on copolymer films with periodic infrared analysis, the samples were prepared by casting films directly on potassium bromide pellets. The pellets with adhered films were then placed in the oven in a flowing oxygen atmosphere and removed periodically for infrared analysis. The most dramatic spectral changes observed were appearances of bands at 2220 cm^{-1} (assigned to nitrile) at 1115 and 615 cm^{-1} (unassigned) for the homopolymer poly-2,2'-(m-phenylene)-5,5'-bebenzimidazole (PBI) homopolymer (the standard) and for the benzimidazole-amide and benzimidazole-imide copolymers. The remainder of the spectra revealed a general broadening in intensity with increased degradation. On the basis of previous work, the time of appearance of the nitrile function was related to the thermo-oxidative stability of the polymeric systems involved. The results gave the following orders of increasing thermal stabilities for the copoly(benzimidazole-amides) and the copoly(benzimidazole-imide): PBI (3 hr) DABI-I-Amide (3 hr), DABI-T-Amide (3 hr), DABI-44 Biph-Amide (3 hr), DABI-1458 Naph-Imide (5 hr), mPD-DCBI-Amide (7 hr). These data reveal that except for the copolyimide and mPD-DCBI-Amide no enhancement of thermal oxidative stability is observed by incorporation of amide functions in the PBI system. However mPD-DCBI-Amide and the DABI-1458 Naph-Imide exhibit a marked improvement in stability of these systems when compared to the standard PBI homopolymer. These results are interpreted in terms of the electronic effect of the imino, imido and carbonyl groups on formation and stability of the benzimidazole free radical. These results fit well into the mechanism previously proposed for thermal oxidation of the benzimidazole system.

The copoly(benzimidazole-benzimidazolone) 33DAB-BBB-Imidazole was not included in the above series because of its insolubility in the film casting solvents DMSO and DMAc. Suprisingly, this copolymer was readily cast into film from concentrated sulfuric acid. This film was used (supported in a frame rather than adhered to a KBr pellet) for thermal oxidation studies. In order to provide homopolymer standards, BBB and PBI films were similarly prepared by casting from concentrated sulfuric acid. The ability of these polymers to withstand hot concentrated sulfuric acid and deposit tough flexible films represents rather remarkable behavior. The infrared spectra of the copolymer and BBB films were identical to those of powdered polymer suggesting that exposure to hot concentrated sulfuric acid resulted in no chemical modification. However, the spectra of PBI cast from sulfuric acid differed from normal PBI suggesting that chemical modification did occur in this system. These suggestions need to be verified by chemical analysis.

The results of thermal oxidative studies gave the following order of increasing stability for the above films: PBI (12 hours), 33DAB-BBB-Imidazole (63 hours), BBB (84 hours). The enhancement of thermooxidative stability of the PBI system by incorporation of benzimidazolone is quite apparent and in fact dramatic in the above data. However, interpretations are difficult to make until it is known what chemical modification, if any, was induced by the exposure to hot sulfuric acid.

Several aspects of the above data are worthy of special comment. The thermal oxidative stability of PBI film cast from DMSO is rated at three hours while film cast from sulfuric acid is rated at twelve hours. Moreover, the film from sulfuric acid was still tough and flexible after twelve hours in oxygen at 350°C while film from DMSO is no longer self supporting after only three hours under the same conditions. Whatever chemical modifications may have occurred in the sulfuric acid treatment, they appear to be beneficial and should be further pursued.

The casting of BBB homopolymer into film afforded the first opportunity for conducting degradation studies of BBB polymer film. The observation of nitrile functions in this remarkably stable film represents the first observation of a degradation intermediate in this system. This observation also represents the first confirmation of the degradation mechanism previously proposed for the benzimidazolone system.

SECTION V

EXPERIMENTAL DETAILS

1. Monomers

Isophthalic acid (Aldrich Chemical Company) was purified by reprecipitation with aqueous HCl from aqueous NaOH solution to give a white crystalline product, m.p. 345-6°C (lit.[47] m.p. 345-7°C).

2. Isophthaloyl Chloride

Isophthaloyl chloride (Aldrich Chemical Company) was purified by vacuum distillation and recrystallization from ethyl ether to give to a white solid, m.p. 41-2°C (lit[47] m.p. 42-3°C).

3. Terephthalic Acid

Terephthalic acid (Aldrich Chemical Company) was purified in the same manner as isophthalic acid, m.p. 300°C (lit.[47] m.p. sub.).

4. Terephthaloyl Chloride

Terephthaloyl chloride was prepared by refluxing 10 g of terephthalic acid in 50 ml of thionyl chloride and 0.2 ml of pyridine until all the solid dissolved (about 15 hours). The excess thionyl chloride was distilled off under vacuum. Terephthaloyl chloride was purified through a Vigreux column by vacuum distillation (b.p. 115-6°C/3mm). The solidified distillate was then recrystallized from hexane to give pure terephthaloyl chloride (8.1 g, 66% yield), m.p. 81-2°C (lit.[47] 82°C).

5. 4,4'-Biphenyldicarbonyl chloride

4,4'-Biphenyldicarboxylic acid (Alfred Bader Chemicals) (1.21 g, 5 m-mole) was dissolved in 5 g of biphenyl. Phosphorous pentachloride (2.1 g, 10 mmole) was added slowly to the hot solution which was refluxed until evolution of HCl was complete (about 1.5 hours). The product was purified by distilling off most of the biphenyl in the vacuum and pouring the residue into hot benzene. The product crystallized from the benzene solution to yield 1.1 g (79% yield) of 4,4'-biphenyldicarbonyl chloride, m.p. 184-5°C (lit.[48] m.p. 184°C).

6. 3,3'-Diaminobenzidine

3,3'-Diaminobenzidine was supplied by the Materials Laboratory, Wright-Patterson Air Force Base and was used without further purification.

7. m-Phenylenediamine

m-Phenylenediamine (Matheson Coleman and Bell) was purified by vacuum distillation, followed by recrystallization from benzene to yield pure m-phenylenediamine, m.p. 63-4°C (lit.[47] m.p. 63-4°C).

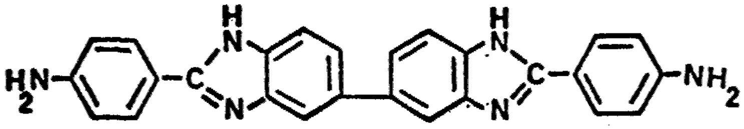
8. p-Phenylenediamine

p-Phenylenediamine was purified by sublimation to yield a white solid, m.p. 139-140°C (lit.[14] m.p. 140°C).

9. Benzidine dihydrochloride

Benzidine dihydrochloride (Fisher Scientific Company) was used without further purification.

10. 2,2'-Di-p-aminophenyl-5,5'-bibenzimidazole (DABI)

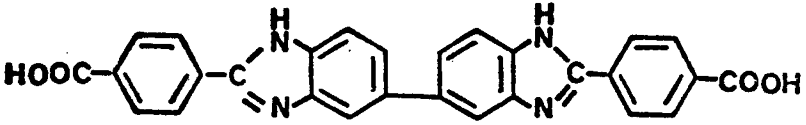


DABI

In a 250-ml three necked flask equipped with a stirrer, nitrogen inlet and calcium chloride drying tube was placed 100 ml of 115% polyphosphoric acid (PPA) which was heated at 150°C under nitrogen atmosphere for 30 minutes. On cooling to 70°C in a thin stream of nitrogen, a mixture of 3,3'-diaminobenzidine (5.000 g, 0.0234 mole) and p-aminobenzoic acid (6.552 g, 0.0468 mole) was added to the solution. The reaction mixture was heated at 150°C under nitrogen for ten hours. The product was precipited by pouring the hot solution into ice-water, collected by filtration, washed several times with water, and reslurried in a dilute solution of sodium bicarbonate. After filtration, the product was washed with water again until the washings were neutral, then dried at 110°C under vacuum.

The crude product (10.5 g) was dissolved in 150 ml of hot methanol, decolorized and reprecipitated by the addition of water. The yellow hydrate product (8.5 g) was collected by filtration, placed in a 25-ml round bottomed flask and heated at 300°C under vacuum for one hour to effect dehydration. The solid melted once with evolution of vapor and solidified again to give DABI, a yellow-brown powder (7.6 g, 98% yield), m.p. 332-4°C (lit.[35] m.p. 321-2°C), Anal. Calc'd for $C_{26}H_{20}N_6$: C, 74.98%; H, 4.84%; N, 20.18%; found: C, 74.88%; H, 4.81%; N, 20.42%.

11. 2,2'-Di-p-carboxyphenyl-5,5'-bibenzimidazole (DCBI)



Preparation of p-carbomethoxybenzoic acid

In a one-liter round bottom flask was placed 260 ml anhydrous methanol containing dimethyl terephthalate (19.4 g, 0.10 mole). To the solution was slowly added potassium hydroxide (4.6 g, 0.12 mole) in 55 ml of anhydrous methanol and refluxed for 10 minutes. After cooling to room temperature, the product was filtered, washed with benzene and dried. The potassium p-carbomethoxybenzoate was dissolved in water. The aqueous solution was filtered and acidified with conc. hydrochloric acid. The resulting precipitate was collected by filtration and recrystallized from hot methanol to yield p-carbomethoxybenzoic acid

(8.6 g, 48% yield), m.p. 214°C (lit[49] m.p. 230° sub.)

Preparation of p-carbomethoxybenzoyl chloride

In a 250-ml round bottom flask was placed 11 ml of thionyl chloride containing *p*-carbomethoxybenzoic acid (5.0 g, 0.0278 mole). The resulting thin paste was heated on the steam bath until evolution of sulfur-dioxide and hydrogen chloride stopped. The excess thionyl chloride was distilled off under vacuum and the product was collected by fractional distillation to give a white solid (5.4 g, 98%) m.p. 50-2°C (lit[50] m.p. 54-55°C).

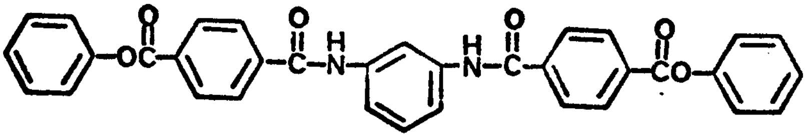
Preparation of methyl phenyl terephthalate

To a solution containing *p*-carbomethoxybenzoyl chloride (4.95 g, 25 m-mole) in 15 ml of toluene was added phenol (2.40 g, 25 mmole) with 1.0 ml of pyridine. The mixture was refluxed at 130°C for four hours. The solid was separated by filtration and washed twice with toluene (10 ml). Both filtrate and washings were evaporated to allow the product to crystallize. Recrystallization from hot methanol gave pure white solid (4.4 g, 67%) m.p. 103-5°C.

Preparation of (DCBI)

A 100-ml three-necked flask was fitted with a stirrer, an inlet of dry nitrogen and outlet. A mixture of methyl phenyl terephthalate (4.5 g, 17.8 m-mole) and 3,3'-di-aminobenzidine (1.81 g, 8.9 mmole) was thoroughly mixed on a rotator with stainless steel balls. The apparatus was carefully purged with dry nitrogen by repeated evacuation and refilling. The mixture of monomers was heated to 240°C at a rate of 2 degrees per minute. When the melt was formed with the evolution of phenol; high vacuum was applied to the system at 240°C for 0.5 hours. On cooling under a thin stream of dry nitrogen, the solid was ground and washed with aqueous sodium hydroxide solution (10%), filtered and dried. The resulting 2,2'-p-carbomethoxyphenyl 5,5'-bibenzimidazole was then refluxed with 135 ml of methanolic potassium hydroxide solution (5%) for one hour. The potassium salt was separated from the mixture by filtration and dissolved in 35 ml of water. After filtering off the insolubles, the clear filtrate was acidified with conc. hydrochloric acid. The product was purified from aqueous sodium hydroxide and conc. hydrochloric acid to give yellow solid (2.4 g, 57% yield) m.p. 420°C; Neutralization equivalent calc'd for $C_{26}H_{16}N_4(CO_2H)_2$; 237.1; found 229.3; Anal. Calc'd for $C_{28}H_{28}N_4O_4$: C, 70.88%; H, 3.83%; N, 11.18%; found; C, 70.81%; H, 3.83%; N, 11.00%.

12. 1,3-Bis(4-phenoxycarbonylbenzoylamino)benzene (CXII)



CXII

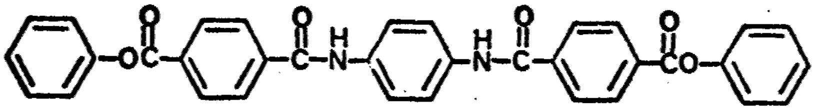
Preparation of phenyl p-chloroformylbenzoate

Phenol(9.4g, 0.10 mole) in 8 ml of pyridine was added dropwise to 80 ml of benzene containing terephthaloyl chloride (20.3 g, 0.11 mole). The mixture was refluxed for two hours and filtered. The solid was then digested with 50 ml of hot benzene to dissolve any phenyl p-chloroformylbenzoate remaining in the solid. The filtrates were combined and evaporated. Recrystallization from hot benzene gave a white crystalline solid (20.2 g, 85% yield), m.p. 167-8°C, Anal. Calc'd for $C_{14}H_9ClO_3$; C, 64.51%; H, 3.48%; Cl, 13.60%; found: C, 64.50%; H, 3.46%; Cl, 13.50%.

Preparation of CXII

Freshly recrystallized m-phenylenediamine (1.08 g, 0.01 mole) was dissolved in 10 ml of nitrobenzene and slowly added to 20 ml of nitrobenzene containing phenyl p-chloroformylbenzoate (5.22 g, 0.02 mole) with stirring. The resulting white precipitate was filtered, dried and reprecipitated from hexamethylphosphoramide (HMP) and methanol to give compound VII (5.1 g, 91% yield) m.p. 289-291°C; Anal. Calc'd for $C_{34}H_{24}N_2O_6$: C, 73.37%; H, 4.35%; N, 5.03%; found: C, 73.12%; H, 4.25%; N, 5.09%.

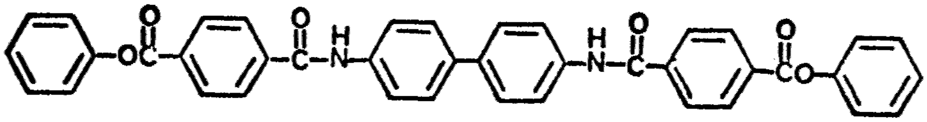
13. 1,4-Bis(4-phenoxycarbonylbenzoylamino)benzene (CXIII)



CXIII

Compound CXIII was synthesized following the procedure for preparation of compound CXII. The product from reaction of p-phenylendiamine (0.01 mole) with phenyl p-chloroformylbenzoate (0.02 mole) in nitrobenzene was isolated by filtration and reprecipitated from HMP and methanol to yield CXIII, a purple red solid (5.0 g, 91% yield), m.p. 470°C; Anal. Calc'd for $C_{34}H_{24}N_2O_6$: C, 73.37%; H, 4.40%, N, 5.03%; Found: C, 73.45%; H, 4.40%; N, 5.11%.

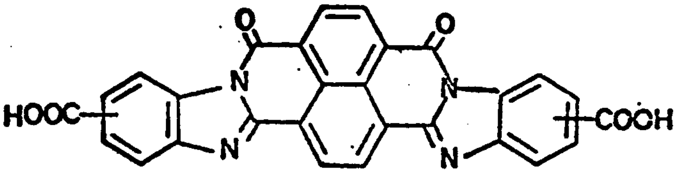
14. 1,4-Bis(4-phenoxycarbonylbenzoylamino)biphenyl (CXIV)



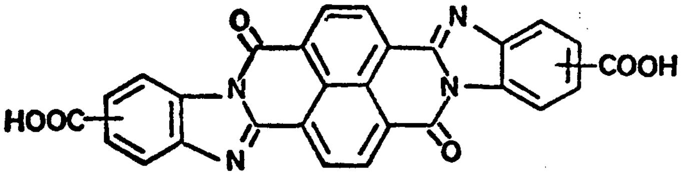
IX

Compound CXIV was made following the procedure for preparation of Compound CXIII. Benzidine dihydrochloride (2.57g, 0.01 mole) was stirred with 20 ml of hot nitrobenzene containing 5 ml of triethylamine. On cooling, the amine salt was filtered off and washed twice with nitrobenzene (5 ml). The filtrate was slowly added to a solution of phenyl p-chloroformylbenzoate (5.22 g, 0.02 mole) in 20 ml of nitrobenzene with stirring. The yellow product was separated by filtration and dried under vacuum at 110°C. Purification was carried out from HMP and methanol to yield CXIV (2.54 g, 40% yield), m.p. 470°C, Anal. Calc'd for $C_{40}H_{24}N_2O_6$: C, 75.94%; H, 4.46%; N, 4,43%; found: C, 75.87%; H, 4.45%; N, 4.27%.

15. 6,9-Dihydro-6,9-dioxobisbenzimidazo[2,1-b:1',2'-j]benzo[lmn]-[3,8]phenanthroline-3,12[(2,13)(2,12)]-dicarboxylic acid and 8,17-Dihydro-8,17-dioxobisbenzimidazo[2,1-b: 2',1'-i]benzo[lmn][3,8]phenanthroine-2,12[(3,11)(2,11)]-dicarboxylic acid, BBB acids



CXV



Preparation of 1,4,5,8-napthalenetetracarboxylic dianhydride (NTDA)

Crude 1,4,5,8-naphthalenetetracarboxylic acid (Aldrich Chemical Company) (10 g) was dissolved in 100 ml of water containing potassium hydroxide (8.4 g). After heating the solution with 10 ml of 5% potassium permanganate solution at 100°C, it was decolorized and filtered. The tetracarboxylic acid was precipitated with 50 ml of conc. hydrochloric acid and separated by filtration. The resulting sticky solid was dried at 110°C under vacuum for one hour to yield 1,4,5,8-napthalenetetracarboxylic acid (NTCA), a pale golden powder (7.0 g, 70% yield), m.p. 300°C (lit[47] m.p. sub.).

A 150 ml portion of 115% PPA was heated to 150°C and stirred under nitrogen while NTCA (5.0 g, 0.017 mole) was slowly added. The temperature was raised to 200°C. After one hour, an examination of the reaction mixture by infrared spectroscopy indicated the disappearance of the carboxylic acid hydroxyl stretching absorption (2700 to 3300 cm^{-1}) and the appearance of a strong band at 1780 cm^{-1} with a shoulder at 1860 cm^{-1} which is assigned to the six-membered cyclic anhydride. The mixture was cooled to 70°C, hydrolyzed, filtered, washed with water until neutral and dried at 110°C to yield NTDA (3.9 g 87% yield) m.p. 320°C (decomp.) (Lit[47] m.p. decomp.).

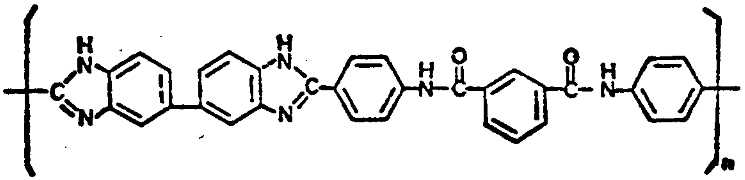
Preparation of BBB Acid

In a 300-ml flask, a portion of 150 ml of 115% PPA was heated at 150°C for 0.5 hours under nitrogen atmosphere. Upon cooling, a mixture of 3,4-diaminobenzoic acid (3.684 g, 24.2 mmole) and NTDA (3.243 g, 12.1 mmole) was added to the solution. The reaction temperature was maintained at 210°C for 3 hours under nitrogen after which the reddish reaction mixture was then poured over ice. The solid product was filtered, washed with water, dissolved with 10% sodium hydroxide and the solution filtered. The crude product was obtained by addition of conc. hydrochloric acid to the basic solution and filtered. Purification was repeated by dissolving in 10% sodium hydroxide and acidifying with conc. hydrochloric acid. The orange crystalline solid was then boiled with water, filtered and washed until the washings were neutral to yield the mixture of BBB acids (2.58 g, 43% yield) after drying at 110°C under vacuum. Neut. equiv.: Calc'd for $C_{26}H_{10}N_4O_2(CO_2H)_2$ 250.2; found: 258; Anal. Calc'd for $C_{28}H_{12}N_4O_6$: C, 67.20%; H, 2.42%; N, 11.20%; found: C, 67.46%; H, 2.59%; N, 11.29%.

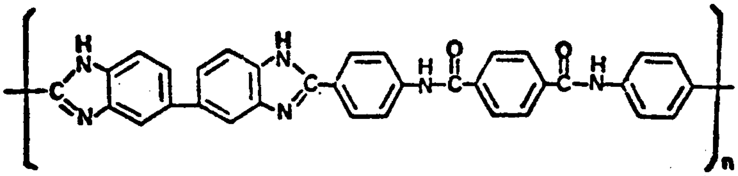
Polymers

1. Poly((5,5'-bibenzimidazole)-2,2'-diyl-p-phenyleneimino-isophthaloylimino-p-phenylene)(DABI-I-Amide), poly((5,5'-bibenzimidazole)-

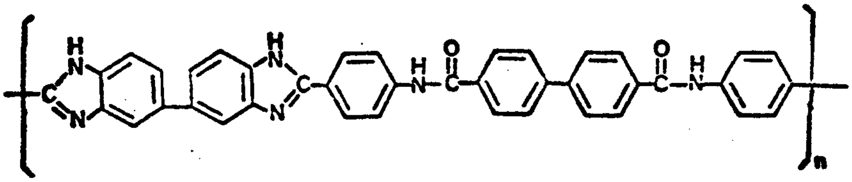
2,2'-diyl-p-phenyleneimino-terephthaloylimino-p-phenylene) (DABI-T-Amide), and poly((5,5'-bibenzimidazole)-3,2'-diyl-p-phenyleneiminocarbonyl-4,4'-biphenylylenecarbonylimino-p-phenylene) (DABI-44Biph-Amide)



DABI-I-Amide



DABI-T-Amide



DABI-44Biph-Amide

Copolymers DABI-I-Amide, DABI-T-Amide and DABI-44Biph-Amide were prepared by solution polymerization at low temperatures which gives higher inherent viscosities than polycondensation in polyphosphoric acid (PPA). The inherent viscosities (ηinh) of polymers were obtained at 30°C with a solution of the polymer (0.2 g) dissolved in 100 ml of conc. sulfuric acid.

Low temperature solution polymerization

Monomer DABI (1.04 g, 2.5 m mole) was dissolved in 10 ml of dimethylacetamide (DMAc) containing 30 mg of lithium chloride and 1.5 ml of triethylamine. The mixture was cooled at -20°C. To the solution was added a solution of isophthaloyl chloride (0.51 g, 2.5 mole) in 3 ml of DMAc under magnetic stirring. After stirring for twenty minutes at room temperature, the resulting viscous solution was poured into a mixture of 50 ml methanol and 50 ml water to precipitate the polymer. Copolymer DABI-I-Amide (ηinh 0.21) was filtered, washed with methanol and dried at 110°C under vacuum. Anal. Calc'd for $C_{34}H_{22}N_6O_2$: C, 74.73%; H, 4.03%; N, 15.38%; found: C, 74.73%; H, 4.17%; N, 15.21%.

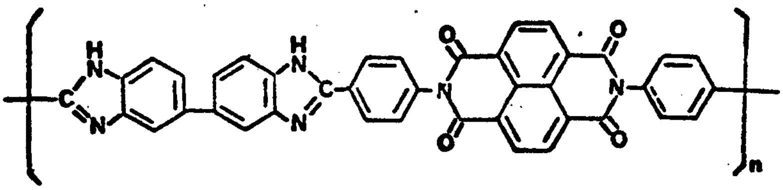
Copolymer DABI-T-Amide (ηinh 0.32) and DABI-4,4'-Biph-Amide (ηinh 0.30) were obtained using the same procedure, except that isophthaloyl chloride was replaced by terephthaloyl chloride and 4,4'-biphenyldicarbonyl chloride respectively. The yield of all three polymers was quantitative. Anal. Calc'd for DABI-T-Amide, $C_{34}H_{22}N_6O_2$: C, 74.73%; H, 4.03%; N, 15.30%; found: C, 75.01%, H, 3.85%; N, 15.31%; Anal Calc'd for DABI-44Biph-Amide, $C_{20}H_{26}N_6O_2$: C, 77.16%; H, 4.21%; N, 13.50%; found: C, 76.93%; H, 4.21%; N, 13.37%.

Attempted polymerization in PPA

To a pretreated 110 ml portion of 115% PPA, a mixture of monomer DABI (5.5g, 13 mmole) and isophthalic acid (2.2 g, 13 mmole) was added with rapid stirring under a blanket of dry nitrogen. The temperature was raised to 200°C (where the mixture turned dark brown) and maintained there for four hours. After cooling, the solution was poured over ice-cold water. A green-yellow solid was isolated, washed several times with water and blended with 20% sodium carbonate. The product was filtered, washed with water until neutral and dried at 110°C under vacuum to give copolymer DABI-I-Amide with ηinh: 0.07; Anal Calc'd for DABI-I-Amide ($C_{34}H_{22}N_6O_6$ see above; found: C, 74.55%; H, 3.99%; N, 15.17%.

Copolymer DABI-T-Amide was prepared by condensation of terephthalic acid with an equivalent amount of monomer I by following the same procedure of preparation for copolymer DABI-I-Amide; ηinh: 0.07.

2. Poly(3,8-dihydro-1,3,6,8-tetraoxobenzo(lmn)(3,8)phenanthroline-2,7(1H,6H)-diyl)-p-phenylene(5,5'-bibenzimidazole)-2,2'-diyl-p-phenylene) (DABI-1458Naph-Imide)



DABI-1458Naph-Imide

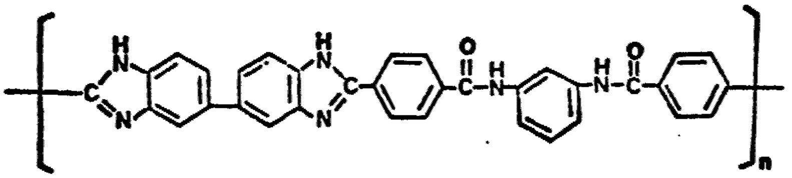
Polymerization in DMSO

In 7 ml of DMSO, monomer DABI (0.3882 g, 0.933 m mole) was dissolved under nitrogen with stirring at room temperature. NTDA (0.2500 g, 0.933 m-mole) was added over a period of 0.5 hour. The resulting dark brown solution was cast on a glass pate and the solvlent was removed by heating at 100°C for 2.5 hour. The infrared spectrum of the resulting prepolymer revealed bands at 1600 and 1375 cm^{-1} (assigned to the carboxylate group). Ring Closure was accomplished by heating the film at 300°C under nitrogen for one hour. Examination of the infrared spectrum of the film after heat treatment showed absorption peaks at 1790, 1720 and 720 cm^{-1} (assigned to the aromatic imide). On this basis the polymer was assigned the structure of copolymer DABI-1458Naph-Imide.

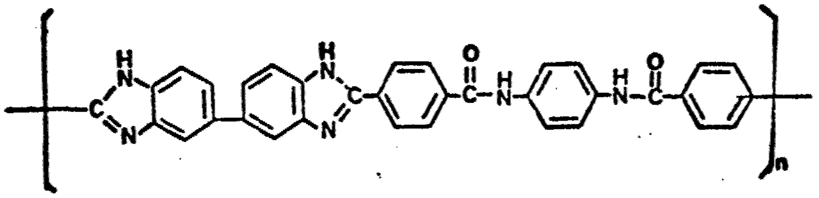
Attempted Polymerization in PPA

A 50 ml portion of 115% PPA was treated as previously described. A mixture of NTCA (1.52 g, 5 mmole) and monomer DABI (2.08 g, 5 mmole) was added under nitrogen atmosphere. The reaction temperature was raised to 300°C and maintained there for 4 hours with stirring. After cooling, the reaction mixture was hydrolyzed, filtered, washed and dried. The resulting material was insoluble in DMAc, DMF, DMSO and HMP and only slightly soluble in cold conc. H_2SO_4.

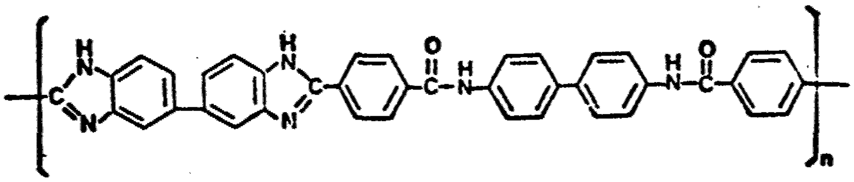
3. Poly((5,5'-bibenzimidazole)-2,2'-diyl-*p*-phenylenecarbonylimino-*m*-phenyleniminocarbonyl-*p*-phenylene)(mPD-DCBI-Amide), poly((5,5'-bibenzimidazole)-2,2'-diyl-*p*-phenylene)(pPD-DCBI-Amide), and poly-(5,5'-bibenzimidazole)-2,2'-diyl-*p*-phenylenecarbonylimino-4,4'-biphenylyleneiminocarbonyl-*p*-phenylene)(44Biph-DCBI-Amide)



mPD-DCBI-Amide



pPD-DCBI-Amide



44Biph-DCBI-Amide

Melt Polycondensation

Under an atmosphere of nitrogen, an intimate mixture of 3,3'-diaminobenzidine (0.107 g, 0.5 mmole) and monomer VII (0.107 g, 0.5 mmole) was heated at 300°C for 15 minutes. The resulting yellowish mass was cooled under nitrogen, ground and reheated at 300°C under vacuum for 0.5 hour. The temperature was raised to 380°C and held for one hour. Examination of the infrared spectrum of the product indicated the appearance of a band at 1605 cm^{-1} (assigned to C-N double bond) and the disappearance of the ester band due to the carbonyl stretching vibration. The resulting copolymer mPD-DCBI-Amide was found insoluble in DMAc, DMF, but partially soluble in DMSO and soluble in conc. H_2SO_4. The inherent viscosity was 0.36.

Attempts to achieve melt condensations for copolymer pPD-DCBI-Amide and 44Biph-DCBI-Amide from the corresponding monomer CXIII and CXIV respectively were not successful.

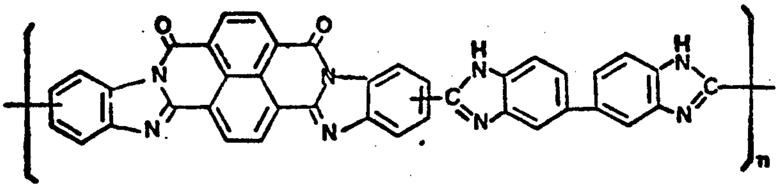
Attempted Polymerization in PPA

The polycondensations were carried out using the previously described procedure of the preparation for copolymer DABI-I-Amide in PPA. Thus DCBI was reacted with m-phenylenediamine, p-phenylenediamine or benzidine dihydrochloride, respectively, to yield low molecular weight copolymer mPD-DCBI-Amide, pPD-DCBI-Amide and 44Biph-DCBI-Amide. ηinh 0.03, 0.04, 0.03 respectively. Anal. for mPD-DCBI-Amide found: C, 74.72%, H, 4.00%; N, 15.10%.

For pPD-DCBI-Amide found: C, 74.99%; H, 4.26%; N, 15.52%.

For 44Biph-DCBI-Amide found: C, 77.20%; H, 4.37%; N, 13.26%.

4. Poly((6,9-dihydro-6,9-dioxobisbenzimidazo(2,1-6:1',2'-j)benzo(lmn)(3,8)phenanthroline-3,12-diyl)(5,5'-bibenzimidazole)-2,2'-diyl)(33 DAB-BBB-Imidazole)



33DAB-BBB-Imidazole

A 25 ml portion of 115% PPA was treated as previously described. When the acid cooled to 70°C, a mixture containing monomer BBB (1.50 g, 3 mmole) and 3.3 diaminobenzidine (0.642 g, 3 mmole) was added to the solution under a nitrogen atmosphere. The reaction mixture was heated over a Wood metal bath. The color of the solution turned to yellow at 100°C, orange at 150°C red at 185°C and dark red at 220°C. The temperature was maintained at 220°C for 2.5 hours, after which the mixture was cooled to 70°C and poured over ice in order to hydrolyze the PPA. The red precipitate was collected, washed several times with water and dried. The black solid was ground and extracted with 10% sodium hydroxide for 30 minutes, followed by washing with water until neutral and dried at 110°C under vacuum to yield 33DAB-BBB-imidazole ηinh 0.35.

Copolymer 33 DAB-BBB-imidazole was insoluble in DMSO, DMAc, and HMP, but slightly soluble in NaOH (20N), and soluble in conc. H_2SO_4 and H_3PO_4 (85%), Anal. Calc'd for $C_{40}H_{18}N_8O_2$: C, 74.76%; H, 2,82%; N, 17.44%; found: C, 74.70%; H, 2.75%; N, 17.81%.

Degradation Studies

1. Film Casting

DABI-I-Amide copolymer prepared by low temperature polymerization was soluble in DMF, DMAc, DMSO. The polymer solutions were cast on glass plates and mercury surface as a thin film but after removal of solvent, the films could not be removed because of their strong adhesion to the glass or mercury surface. In order to carry out the desired oxidative studies of films with periodic infrared analysis, the samples were prepared by casting films directly on to potassium bromide pellets. Then a polymer solution of concentration 1% in DMSO was added dropwise on KBr pellet and baked at 100°C under vacuum for one hour. The color of the resulting polymer film was yellow prior to pyrolysis.

DABI-T-Amide copolymer, precipitated from DMAc and a mixture of methanol and water, is insoluble in most organic solvents. The polymer solution obtained from low temperature polymerization was carefully filtered to remove the insoluble amine salt, diluted to 1% and then cast on a KBr pellet. The solvent, DMAc, was evaporated at 300°C under vacuum for 0.5 hour leaving a thin yellow film on the pellet.

DABI-44Biph-Amide copolymer solution was prepared and cast on a KBr pellet using the procedure described above. Its solubility and adhesive properties were the same as for copolymer DABI-I-Amide.

Examination of polymer films by infrared spectroscopy showed amide bands at 1650, 1520 and 1320 cm^{-1} and the doublet near 800 cm^{-1}. These observations confirmed that copolymer DABI-I-Amide, DABI-T-Amide and DABI-44Biph-Amide consist of amide and benzimidazole units as shown in Figures 19 and 21.

The prepolymer of DABI-1458 Naph-Imide copolymer, polyamic acid, was obtained from mixing stoichiometric amounts of monomers in DMSO as described in the synthesis section. The dark brown solution was cast on a KBr Pellet and baked at 100°C for 2.5 hours followed by heating at 300°C under nitrogen for one hour. The resulting dark brown polymer film on KBr was examined by infrared spectroscopy. Absorptions at 1790, 1720 and 720 cm^{-1} confirmed that the aromatic imide was formed as shown in Figure 17.

mPD-DCBI-Amide prepared by melt condensation is insoluble in DMAc. A 1% polymer solution was obtained by dissolving well ground powder of the copolymer sample in DMSO, and used to make a film on a KBr pellet. After drying at 100°C under vacuum for one hour, the infrared spectrum of the green-yellow film revealed amide bands at 1650, 1530 and 1300 cm^{-1}, and benzimidazole absorptions at 800 and 850 cm^{-1} as shown in Figure 21.

Very few solvents dissolve for 33DAB-BBB-Imidazole copolymer other than strong acid (3.g. conc. H_2SO_4). Five ml of conc H_2SO_4 was utilized to dissolve 100 mg of a well ground sample at 100°C. The insoluble material was separated by centrifugation. The purple red solution was spread on a glass plate and dried at 250°C in air for 3 hours. A clear tough and flexible film was removed after curing at 200°C under vacuum for 2 hours. The film, black by reflected light but very deep red by transmitted light, exhibits a metallic luster. The infrared spectrum is shown in Figure 25.

Polybenzimidazolone (BBB) was supplied by the Material Laboratory, Wright-Patterson Air Force Base. A film of BBB homopolymer was cast by the same technique used for preparing 33DAB-BBB-Imidazole copolymer. The resulting film was flexible, tough, clear, had a metallic luster and was deep red in color. The infrared spectrum obtained from this film is almost identical to that of BBB polymer in KBr (Figure 27).

2. Pyrolysis

All samples to be oxidized as film strips or thin films adhered to KBr pellets were placed in the sample holders and individually moved into the constant temperature preheated pyrolysis tube (using Lindberg oven 54031 and control console 59344) under a constant flow rate of oxygen atmosphere (30 ml/min) for varying periods of time. The effluents were vented into the hood. After specified heating times, the sample was moved to the cool zone of the pyrolysis tube prior to examining by infrared spectroscopy. For each run, the temperature and oxygen flow rate were held constant at 350°C under oxygen atmosphere at a flow rate of 30 ml/min.

3. Examination using infrared spectroscopy

The infrared spectra of DABI-I-Amide, DABI-T-Amide, DABI-44Biph-Amide, mPD-DCBI-Amide, DABI-1458Naph-Imide and 33DAB-BBB-Imidazole at various stages of oxidative degradation were recorded using Perkin-Elmer 457 or 621 Infrared Spectrophotometer.

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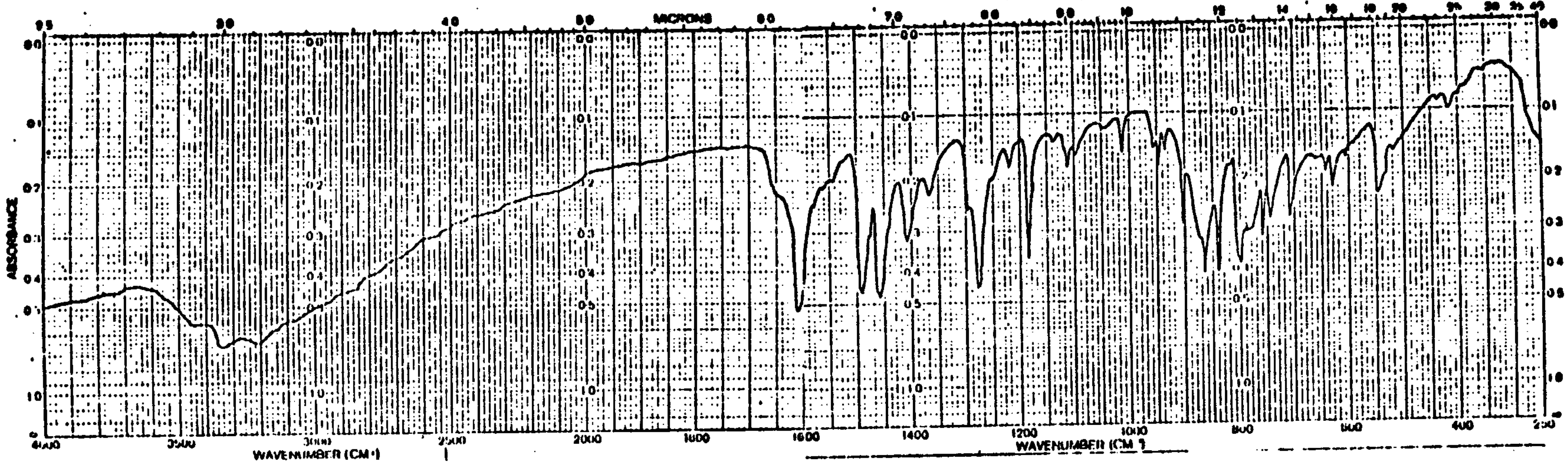
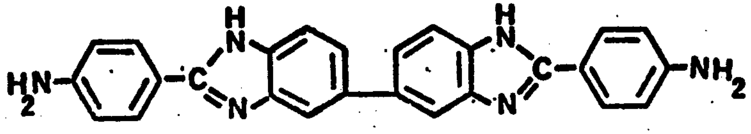
APPENDIX A

INFRARED SPECTRA





I

Figure 32 Infrared spectrum of compound DABI

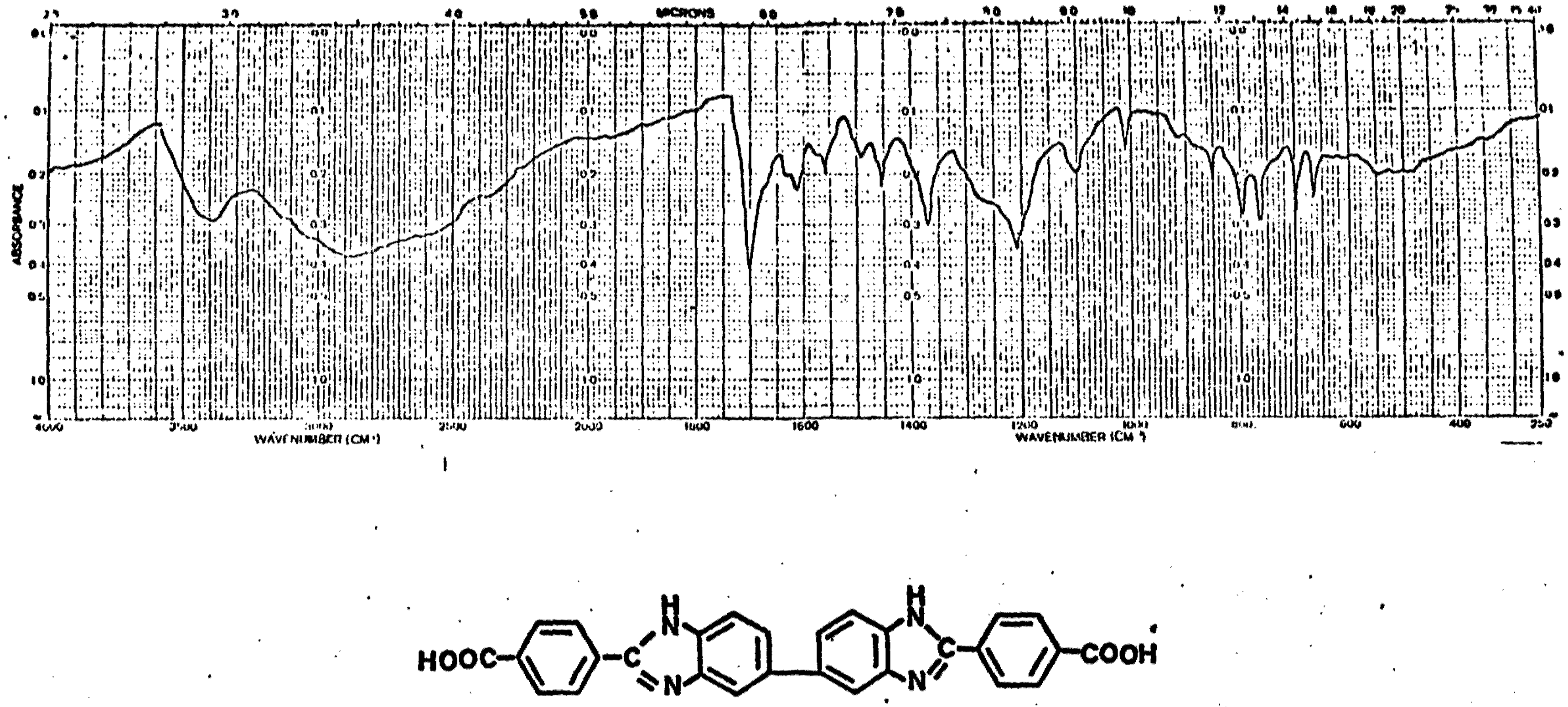
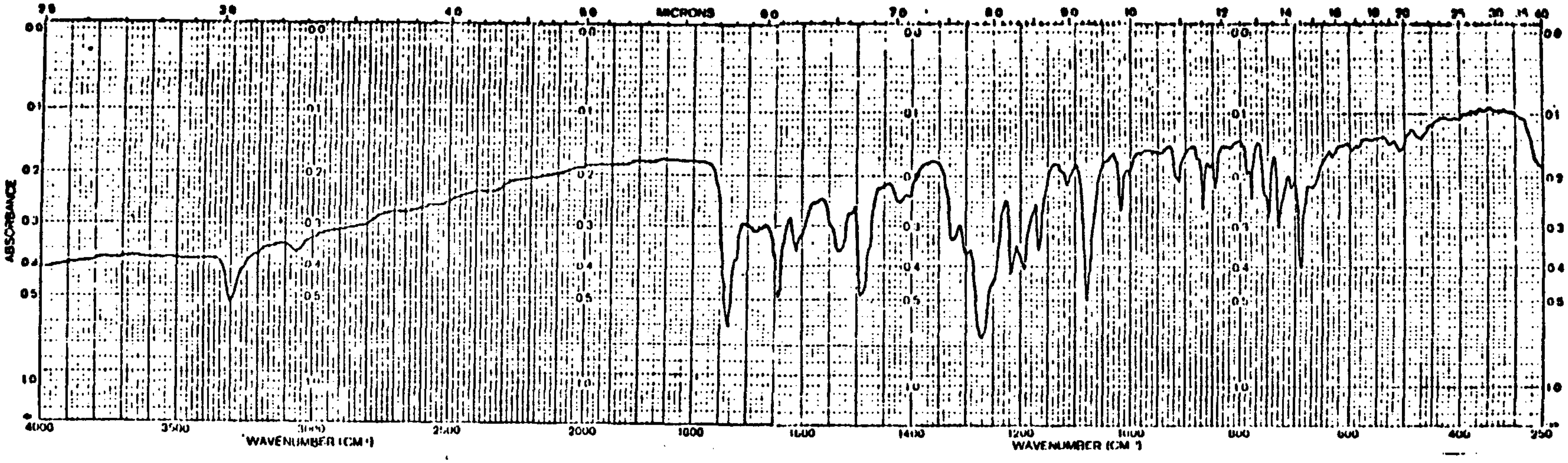
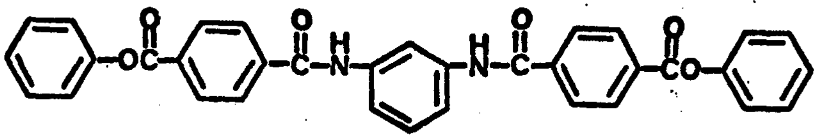


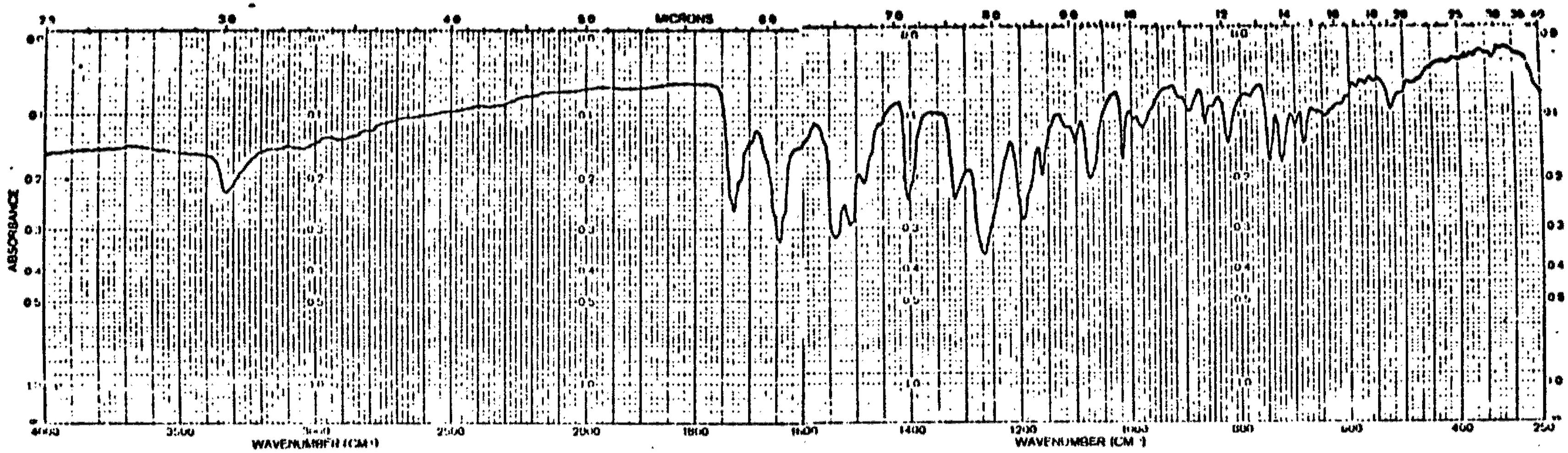
Figure 33 Infrared spectrum of compound DCBI

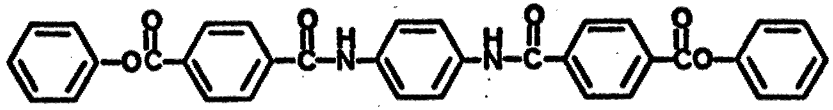




CXX

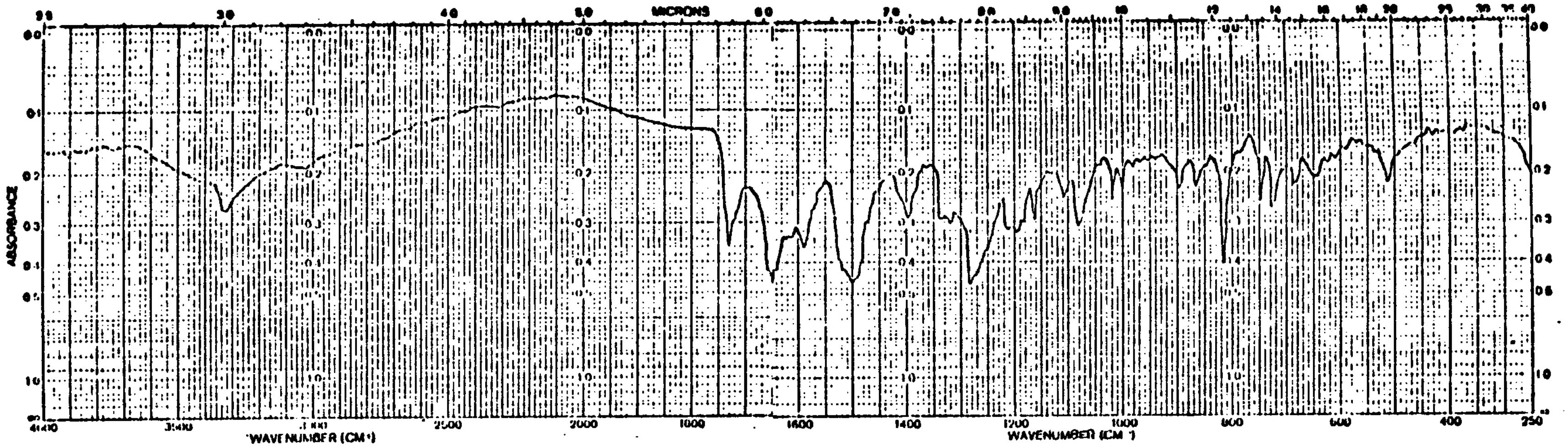
Figure 34 Infrared spectrum of compound CXX.

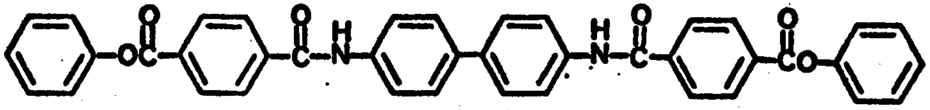




CXXI

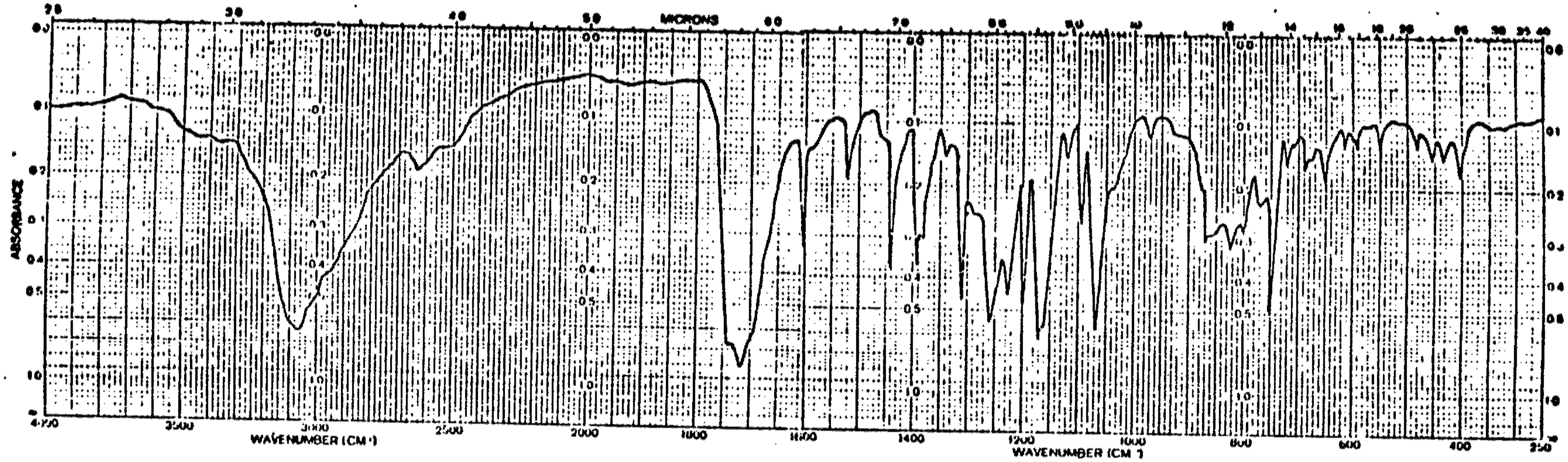
Figure 35 Infrared spectrum of compound CXXI.

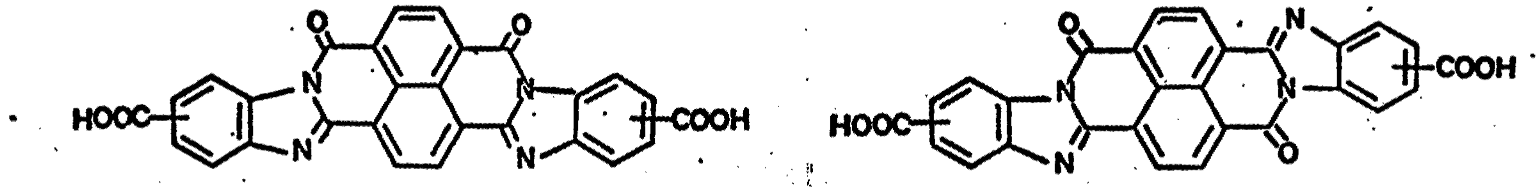




CXXII

Figure 36   Infrared spectrum of compound CXXII.





BBB ACID

Figure 37 Infrared spectrum of compound BBB acid.

APPENDIX B

DTA DIAGRAMS

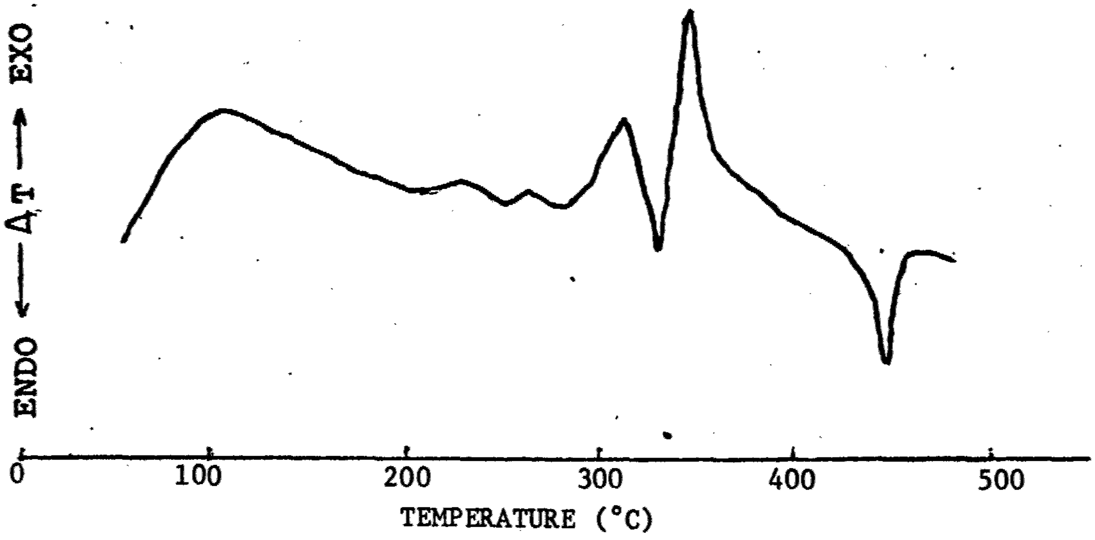


Figure 38 DTA of compound DABI in nitrogen.

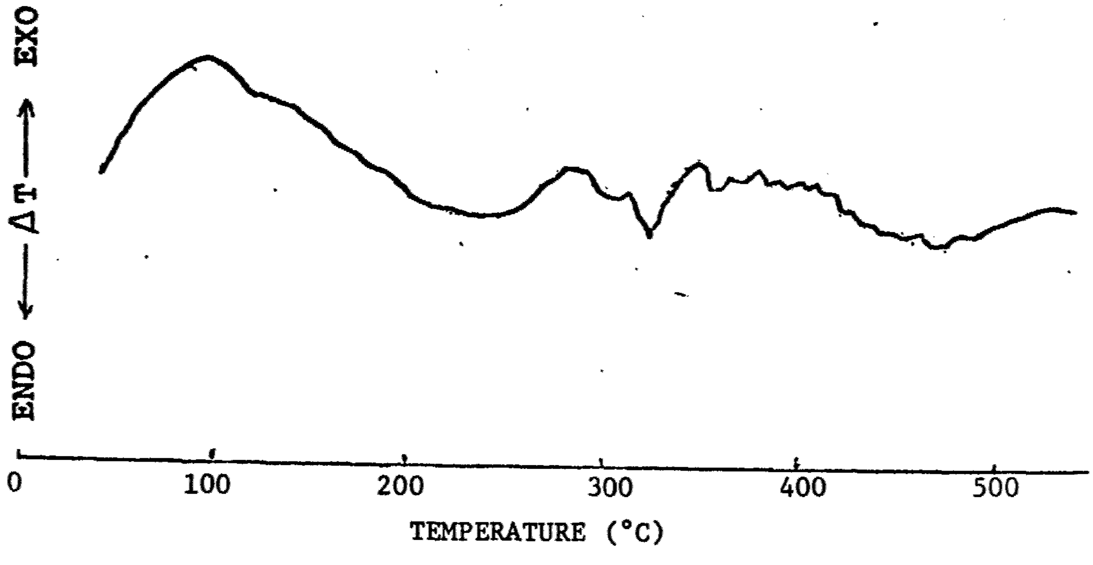


Figure 39 DTA of compound DCBI in nitrogen.

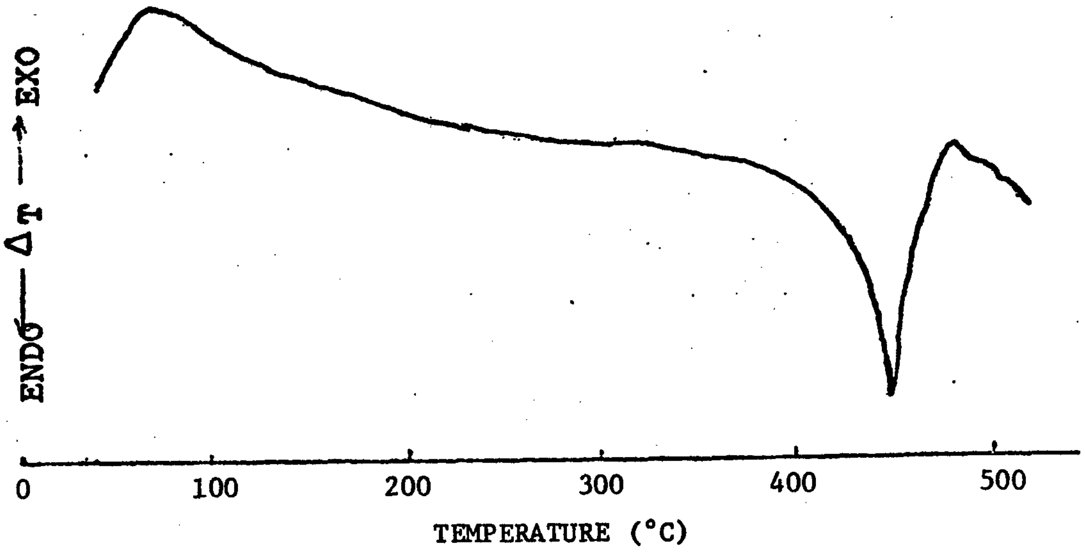


Figure 40 DTA of compound BBB acid in nitrogen.

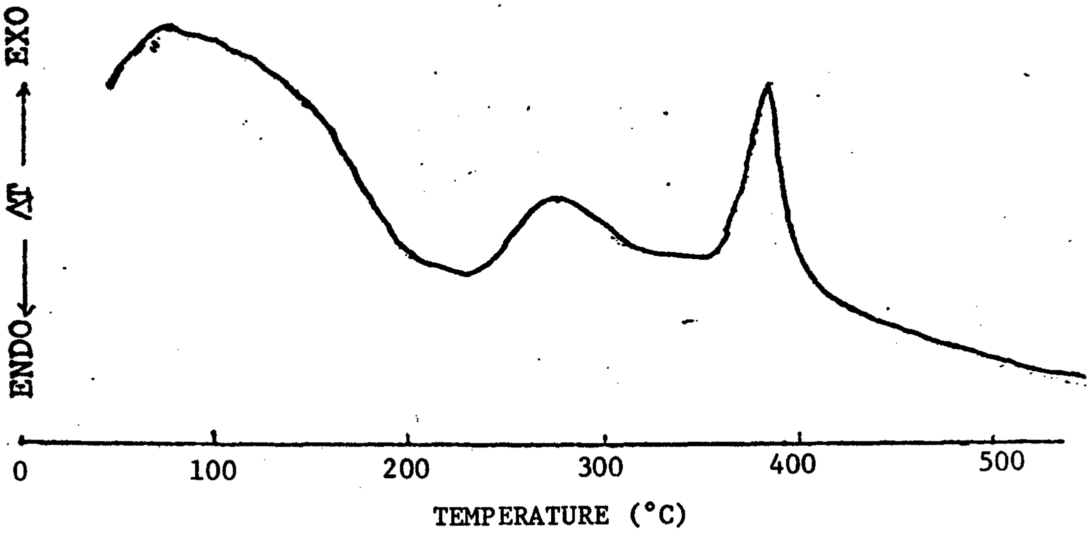


Figure 41 DTA of copolymer DABI-I-Amide in nitrogen.

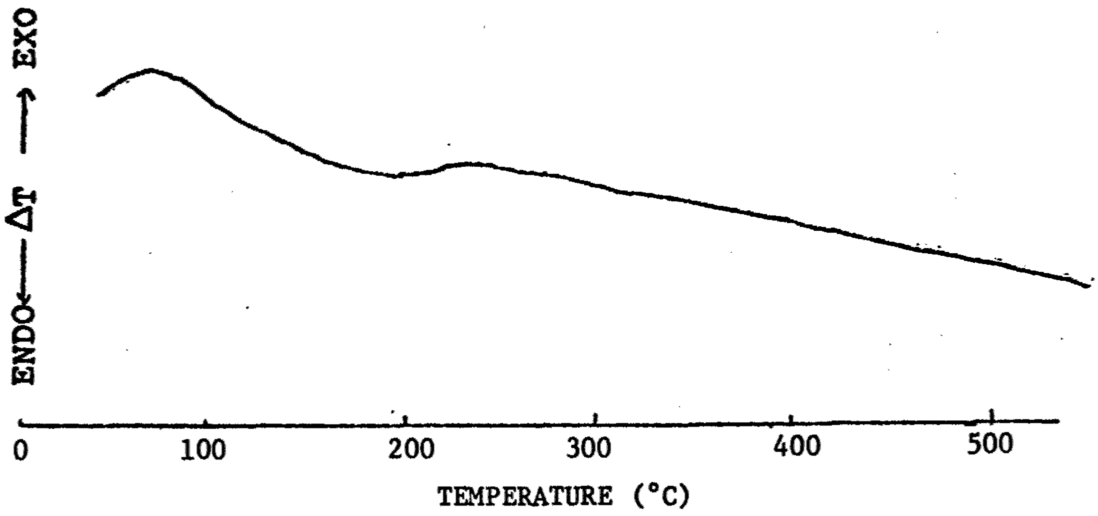


Figure 42 DTA of copolymer DABI-T-Amide in nitrogen.

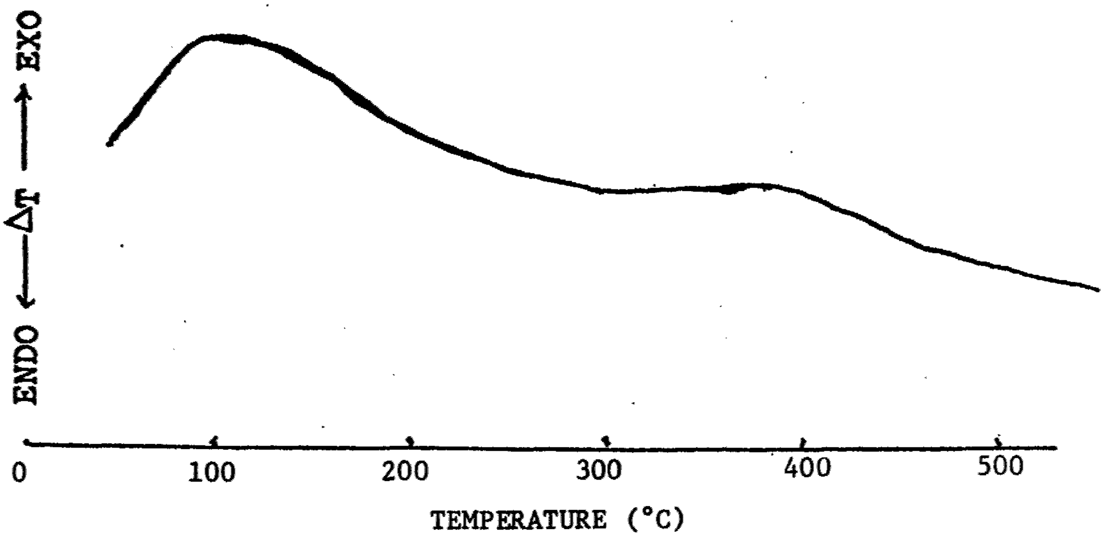


Figure 43 DTA of copolymer DABI-1458Naph-Imide in nitrogen.

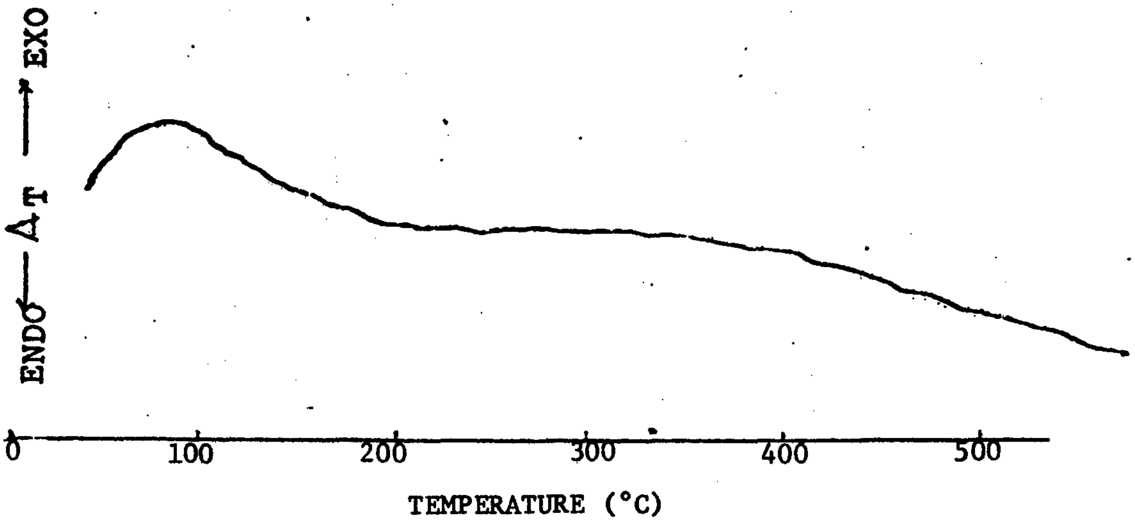


Figure 44 DTA of copolymer DABI-44Biph-Amide in nitrogen.

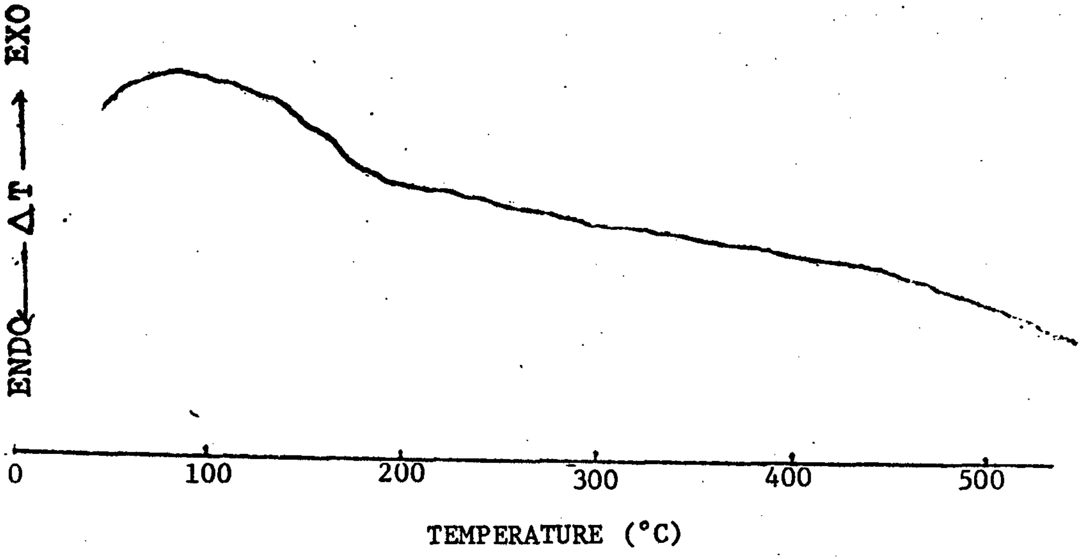


Figure 45 DTA of copolymer mPD-DCBI-Amide in nitrogen.

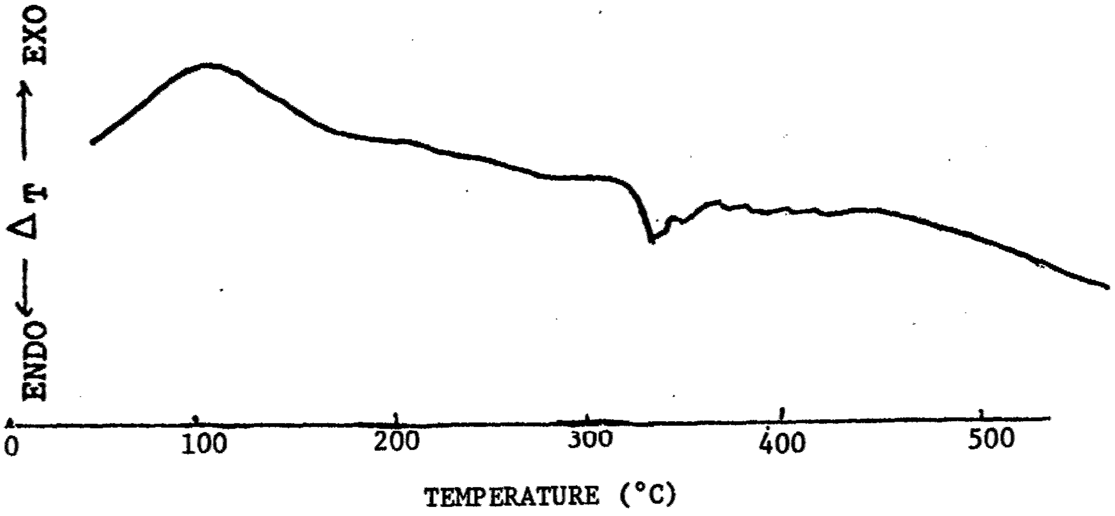


Figure 46 DTA of copolymer pPD-DCBI-Amide in nitrogen.

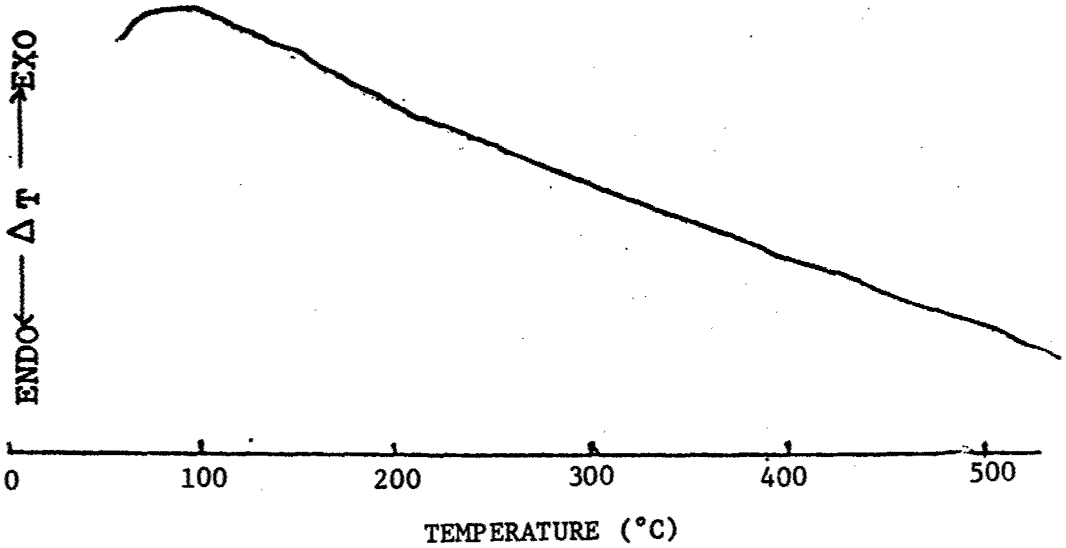


Figure 47 DTA of copolymer 33DAB-BBB-Imidazole in nitrogen.

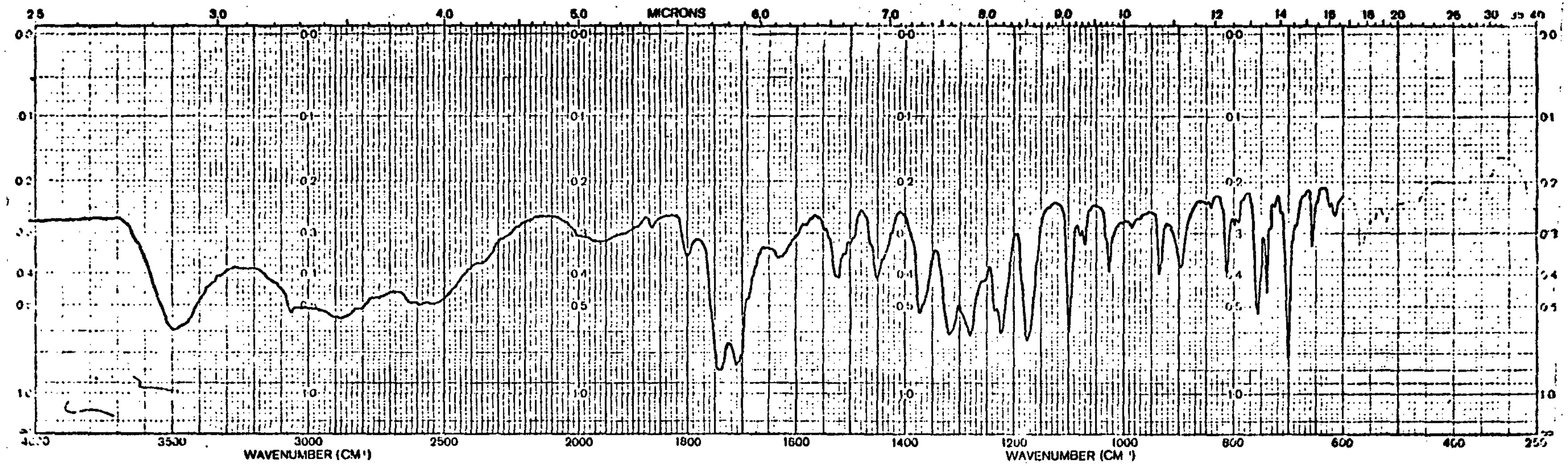


Figure 48

Infrared Spectrum of 2,3-Diphenylpyrazine-5,6-dicarboxylic Acid Anhydride (CIV)

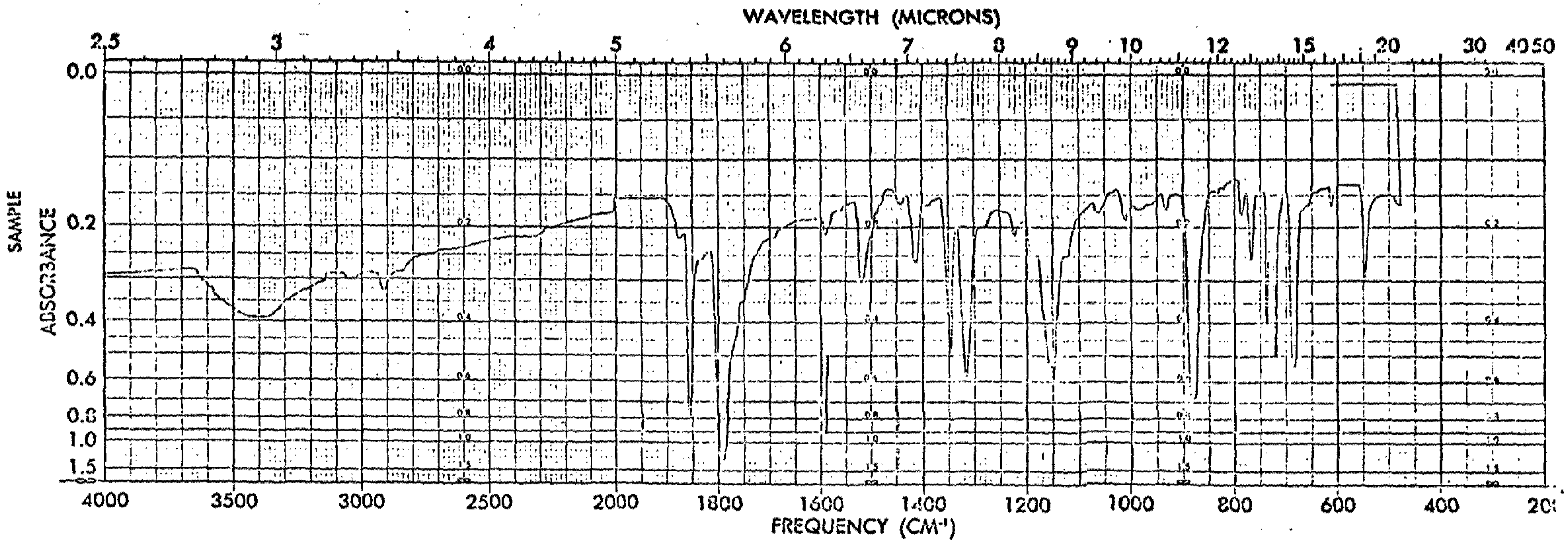


Figure 49

Infrared Spectrum of 2,3-Diphenylpyrazine-5,6-dicarboxylic Acid Anhydride (CIV)

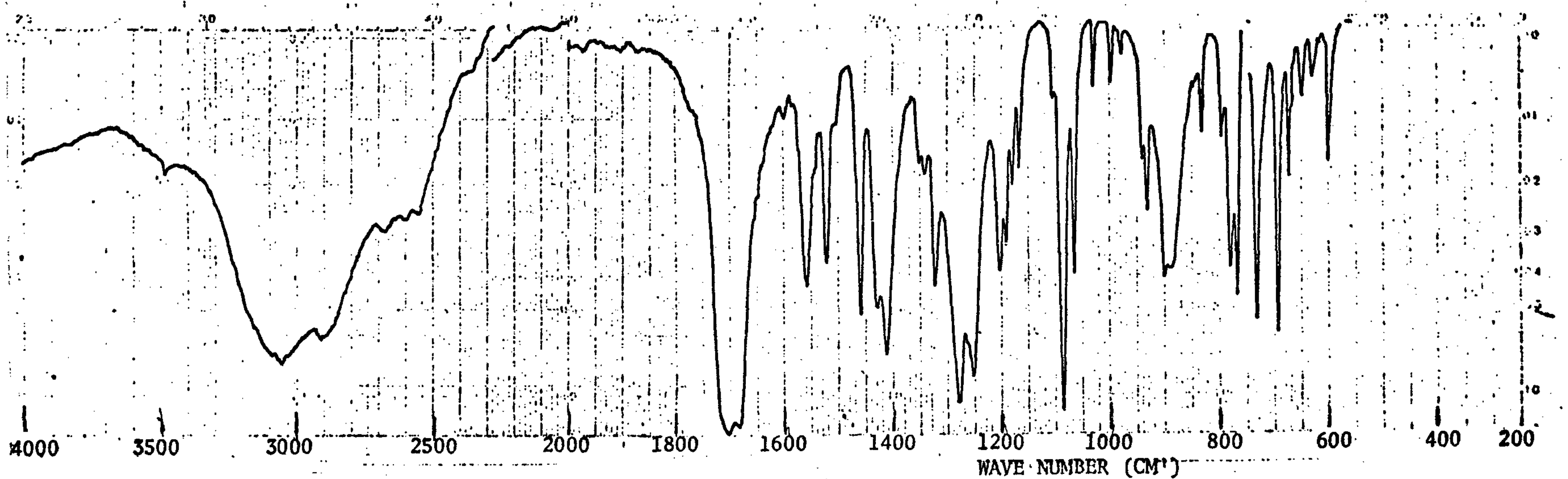


Figure 50

Infrared Spectrum of 2-Phenylpyrazine-5,6-dicarboxylic acid (C)

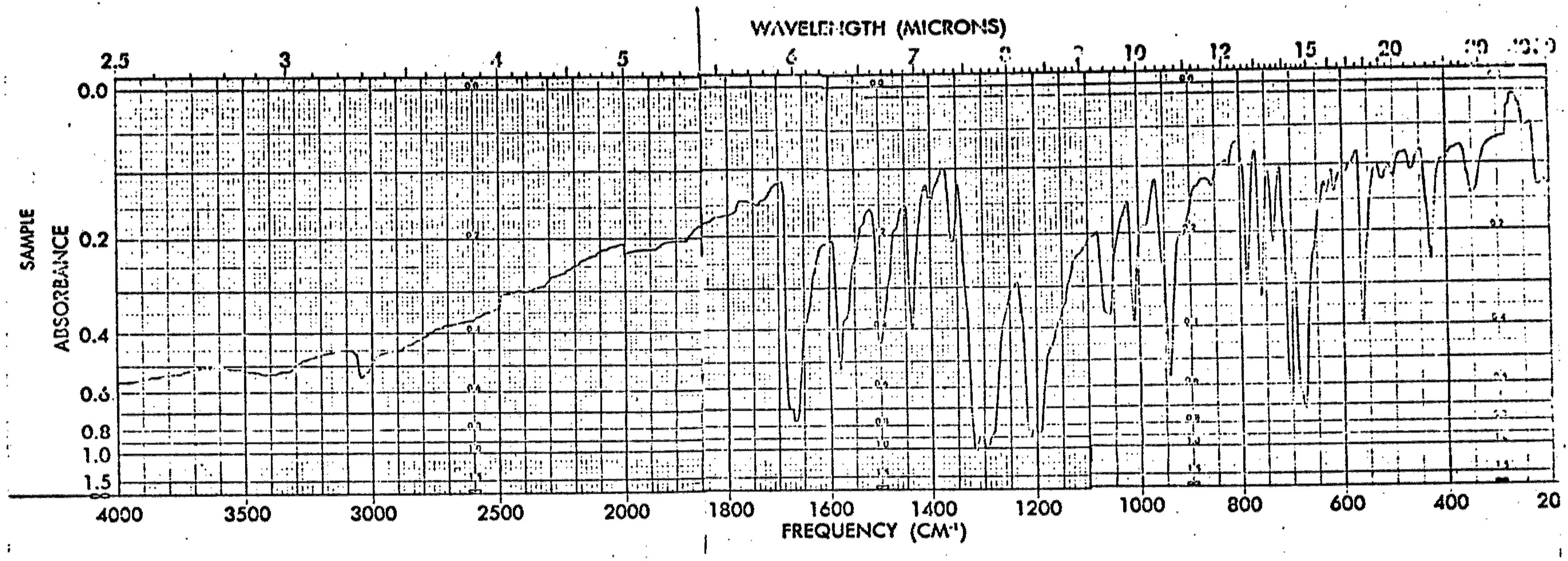


Figure 51

Infrared Spectrum of Product Mixture After Isothermal (200°C) Aging of 2,3-Diphenylbenzo[g]quinoxaline (XCVIII) in Oxygen for 400 Hours

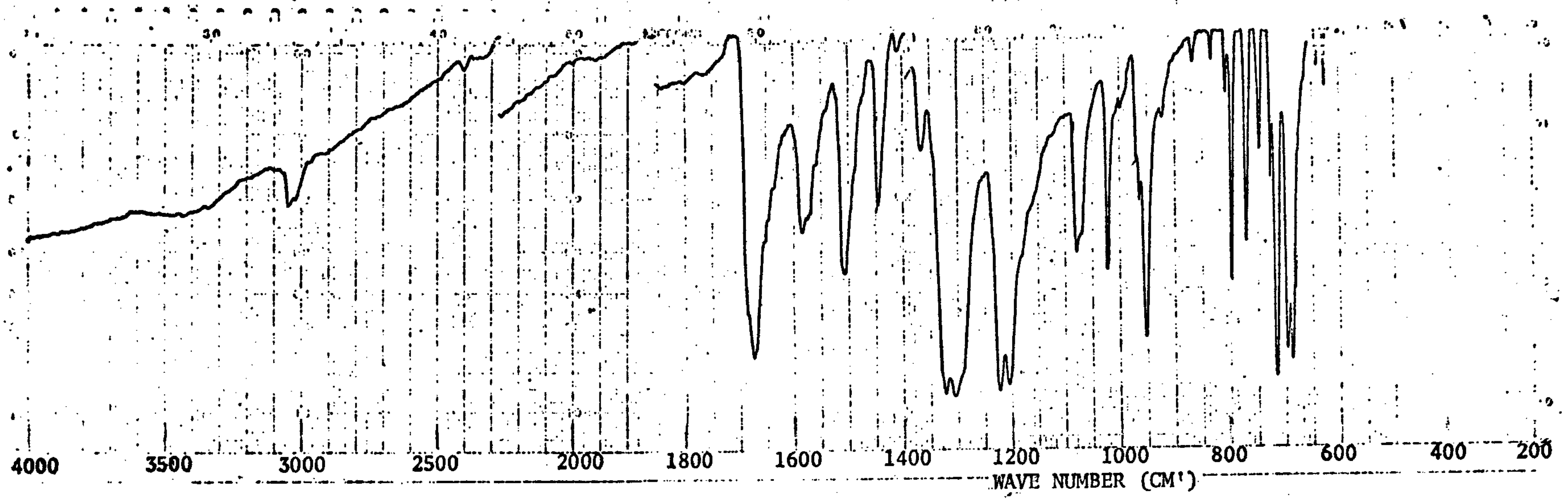


Figure 52

Infrared Spectrum of 2,3-Diphenylbenzo[g]quinoxaline-5,10-dione (CII)

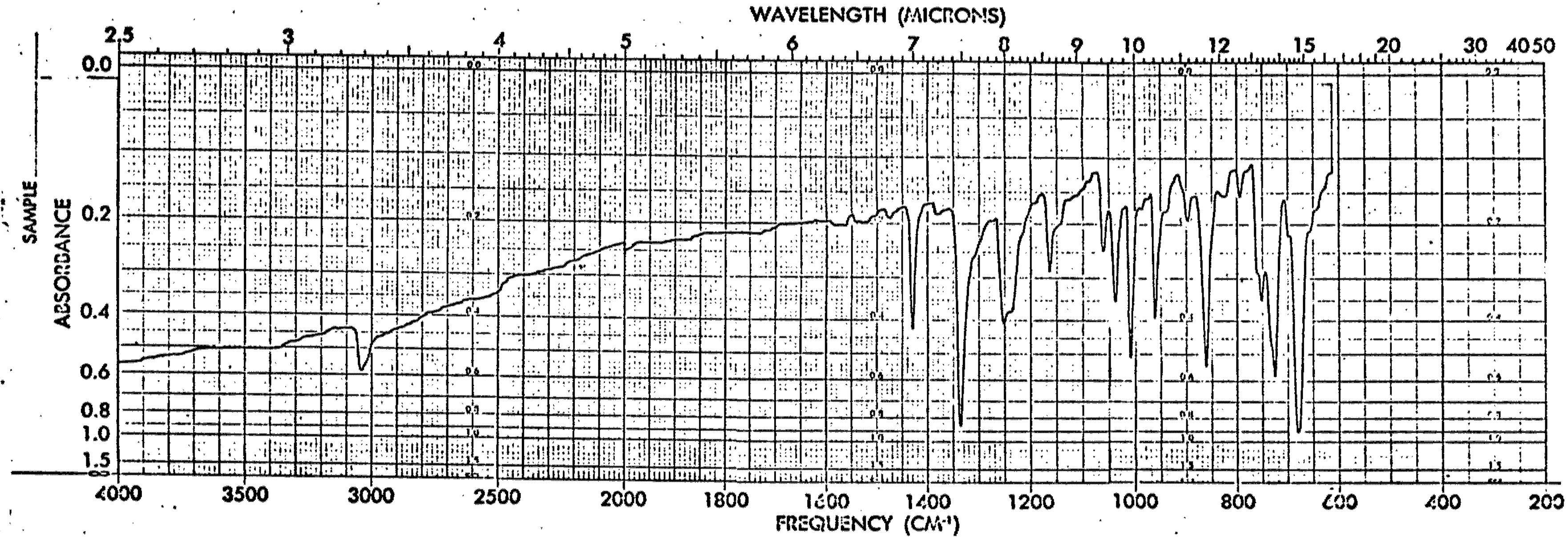


Figure 53

Infrared Spectrum of 2,3-Dipehnylbenzo[g]quinoxaline (XCVIII)

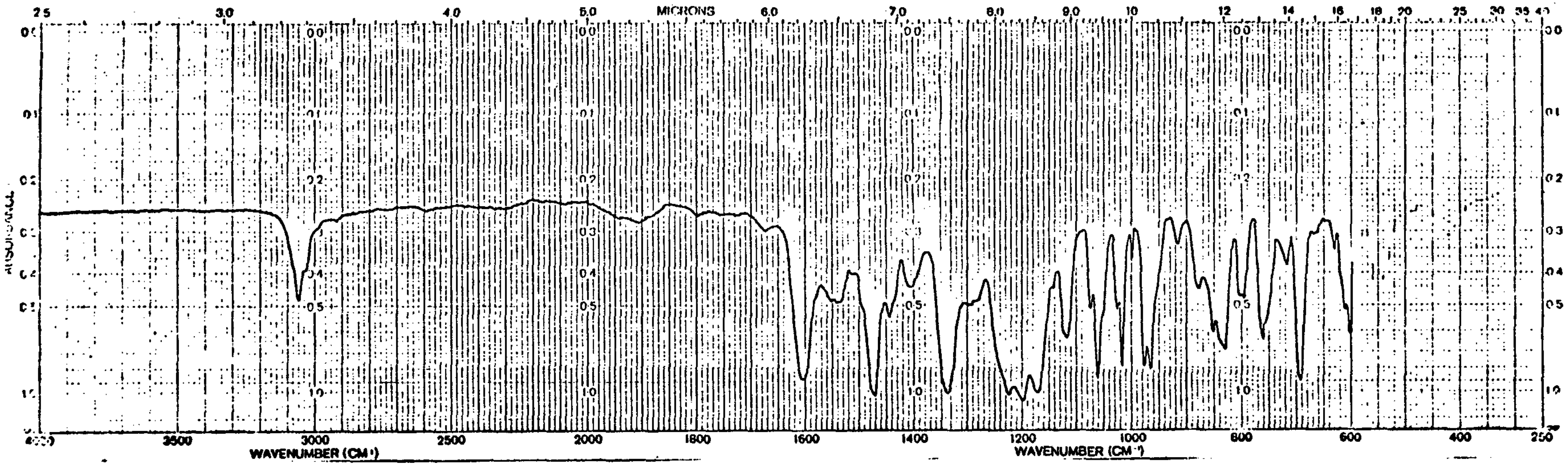


Figure 54

Infrared Spectrum of Polymer XXXVI Film

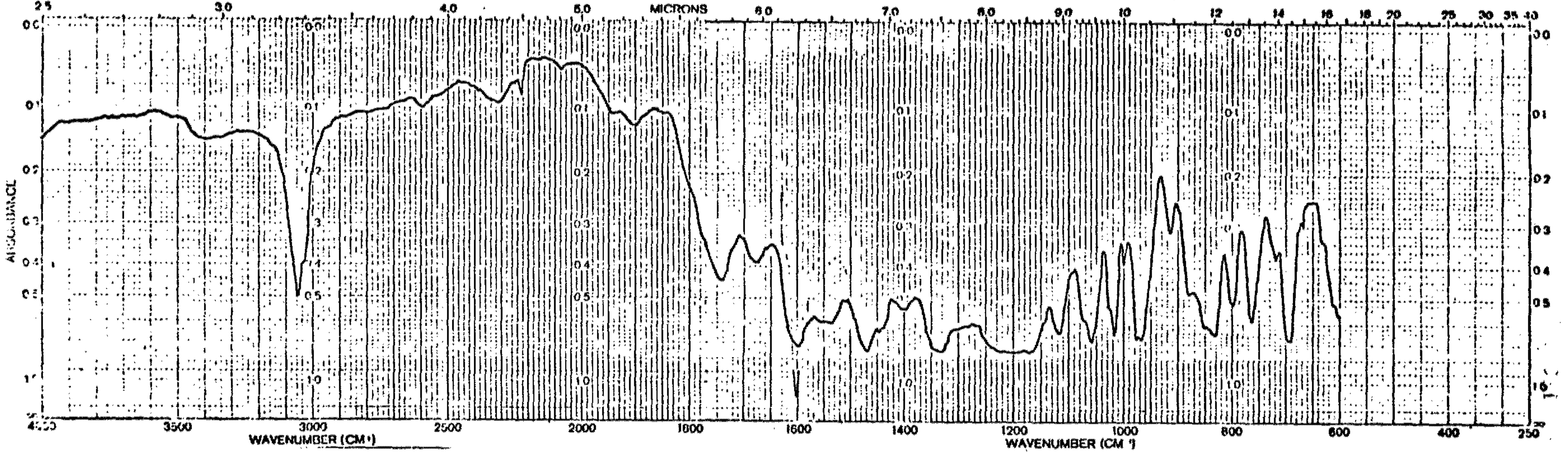


Figure 55

Infrared Spectrum of Polymer XXXVI Film After 120 Hours in Oxygen at 300°C

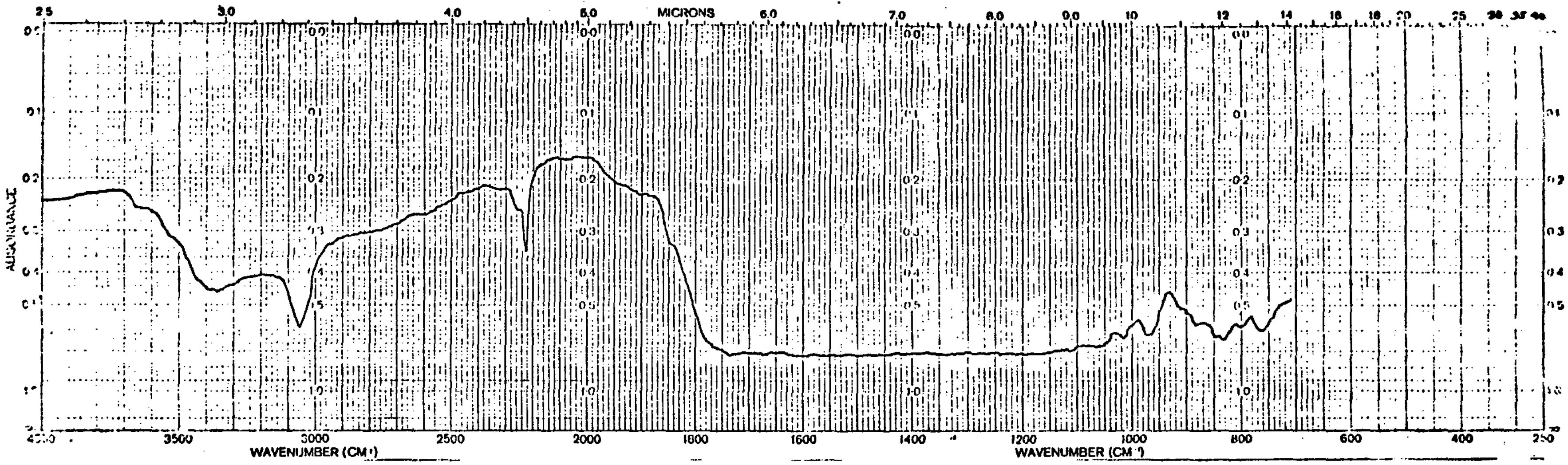


Figure 56

Infrared Spectrum of Polymer XXXVI Film After Four Hours in Oxygen at 400°C

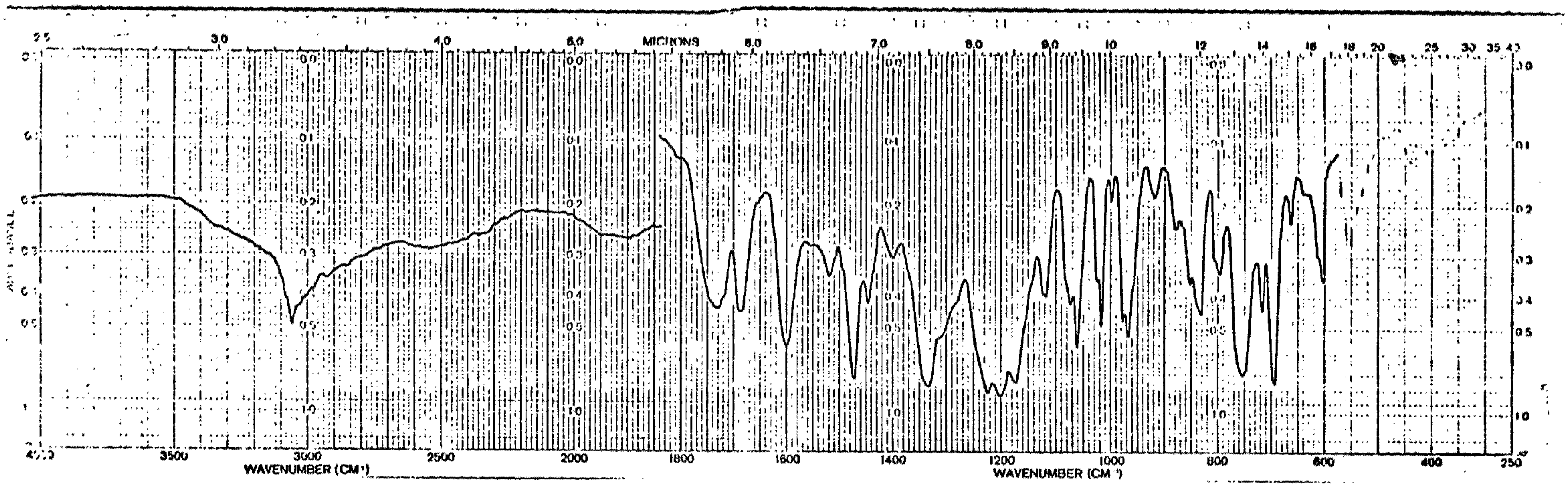


Figure 57

Infrared Spectrum of Polymer XXXVI Film with Admixture of 2,3-Diphenylpyrazine-5,6-dicarboxylic Acid (CI) and 2,3-Diphenylbenzo[g]quinoxaline-5,10-dione (CII)

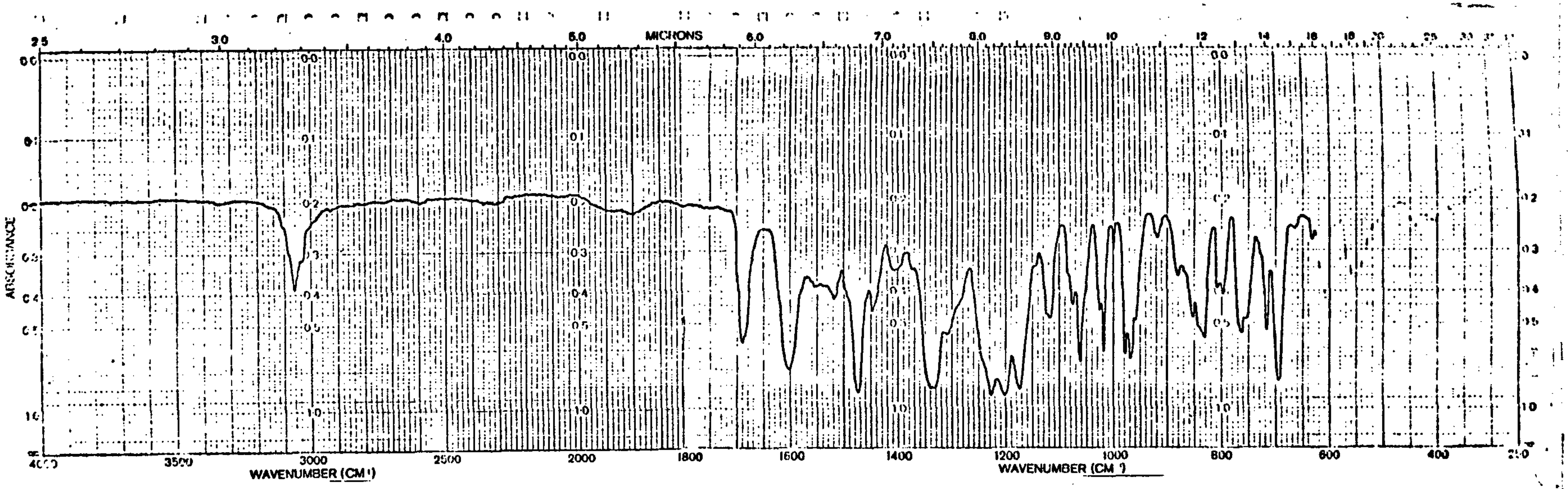


Figure 58

Infrared Spectrum of Polymer XXXVI Film with Admixture of
2,3-Diphenylbenzo[g]quinoxaline-5,10-dione (CII)

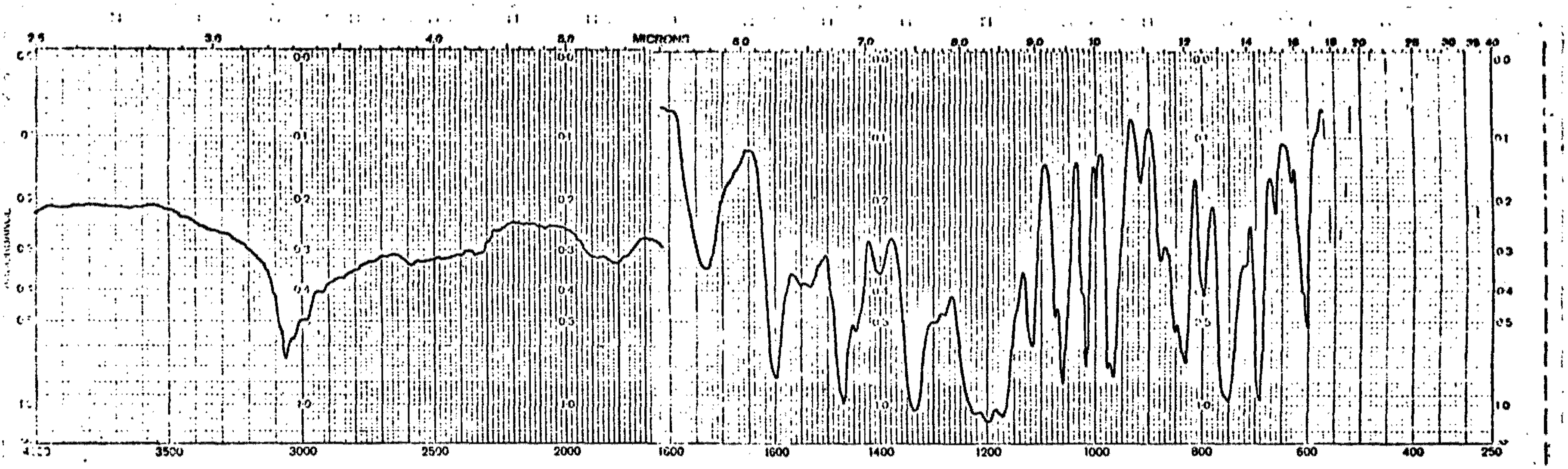


Figure 59

Infrared Spectrum of Polymer XXXVI Film with Admixture of 2,3-Dipehnylpyrazine-5,6-decarboxylic Acid (CI)

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13. ABSTRACT

The synthesis and oxidation (solution and pyrolytic) of certain quinoxaline model compounds is reported. Pyrolytic oxidation (400-500°C) yielded benzonitrile, oxides of carbon and cyanogen. Solution oxidation yielded the corresponding pyrazine dicarboxylic acids. Subsequent pyrolytic oxidation of the pyrazine dicarboxylic acids produced benzonitrile, oxides of carbon, cyanogen, and the corresponding pyrazine derivative.

Evidence for thermal oxidation intermediates oxygenated at the carboxylic ring (adjacent to the heterocyclic ring) is presented by product isolation and spectral data. The results are discussed in terms of an initial oxygenation mechanism for the quinoxaline system.

A series of copolymers of benzimidazole units with amides, benzimides and benzimidazolones was synthesized and evaluated for therooxidative stabilities and solubilities.

Each copolymer exhibited the solubility characteristic of its least soluble component. The benzimidazole/benzimidazolone copolymer exhibited greater thermal stability than PBI homppolymer. Ther other copolymers exhibited stabilities comparable to PBI.

Concentrated sulfuric acid was successfully used as a film casting solvent for polybenzimidazolone (BBB), PBI, and copolymer (PBI/BBB). All three films exhibited superior thermooxidative stabilities.

DD FORM 1 NOV 65 1473

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
1. Oxidative Degradation						
2. High Temperature Polymers						
3. Aromatic Heterocyclic Polymers						
4. Polybenzimidazoles						
5. Polyquinoxalines						
6. Polybenzimidazolones						
7. Copolymers of Benzimidazole						
8. Poly([5,5'-bibenzimidazole]-2,2'-diyl-*p*-phenylenecarbonylimino-*m*-phenyleneiminocarbonyl-*p*-phenylene)						
9. Poly([5,5'-bibenzimidazole]-2,2'-diyl-*p*-phenylenecarbonylimino-*p*-phenyleneiminocarbonyl-*p*-phenylene)						
10. Poly([5,5'-bibenzimidazole]-2,2'-diyl-*p*-phenylenecarbonylimino-4,4'-biphenyleneiminocarbonyl-*p*-phenylene)						
11. Poly[(6,9-dihydro-6,9-dioxo-bisbenzimidazo[2,1-*b*:1',2'-*j*]benzo[*lmn*][3,8]phenanthroline-3,12-diyl)[5,5'-benzimidazole-2,2'-diyl]						
12. Poly([5,5'-bibenzimidazole]-2,2'-diyl-*p*-phenyleneiminoisophthaloylimino-*p*-phenylene)						
13. Poly([5,5'-bibenzimidazole]-2,2'-diyl-*p*-phenyleneiminoterephthaloylimino-*p*-phenylene)						
14. Poly([5,5'-bibenzimidazole]-2,2'-diyl-*p*-phenyleneiminocarbonyl-4,4'-biphenylenecarbonylimino-*p*-phenylene)						
15. Poly[(3,8-dihydro-1,3,6,8-tetraoxobenzo[*lmn*][3,8]phenanthroline-2,7(*1H*,*6H*)-diyl)-*p*-phenylene[5,5'-bibenzimidazole]-2,2'-diyl-*p*-phenylene]						
16. Oxidative Stabilities of Copolymers						
17. Quinoxaline Model Compounds						
18. Thermooxidation of Quinoxaline Model Compounds						
19. Solution Oxidation of Quinoxaline Model Compounds						

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
20. Quinoxaline Stabilities of Copolymers						