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STUDIES OF THE BREAKDOWN MECHANISM OF POLYMERS

V. The Thermal Decomposition of Some Polybenzimidazoles

GERHARD F. L. EHLERS
KURT R. FISCH
WILBERT R. POWELL

TECHNICAL REPORT AFML-TR-70-63

MAY 1970

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AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No 7340, "Nonmetallic and Composite Materials", Task No 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. G. F. L. Ehlers (MANP) as Project Engineer.

This report covers work conducted from May 68 to May 69. It was submitted by the authors in December 1969.

The authors wish to thank L. D. Smithson for the high resolution mass spectra of some sublimates.

This technical report has been reviewed and is approved.

William E. Gibbs

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

ABSTRACT

The thermal breakdown of 4 samples of 2,2'-(m-phenylene)-5 5'-bi-benzimidazole and of 6 other polybenzimidazoles was studied between 200 and 650°C.

Unexpectedly high oxygen contents of these polymers first led to a study of moisture adsorption and proper drying conditions. This and the actual decomposition studies showed that polybenzimidazoles not only have a strong tendency to adsorb water, but also contain oxygen in various other forms, possibly end groups, intermediate amide and hydroxy imidazoline structures, secondary ether and phenolic groups, imidazole-water complexes, and unknown oxidation products. Water, carbon monoxide and carbon dioxide are decomposition products of these moieties.

Thermal breakdown of the aromatic rings proceeds via formation of hydrogen and methane, and decomposition of the imidazole structure yields some hydrogen cyanide and ammonia, although most of the nitrogen is retained in the residue, possibly in the form of other heterocyclic, highly condensed structures.

It was interesting to observe that a prepolymer seemed to fragmentize rather than condense on further heating. A polymer with an ether linkage also formed chain fragments. Methyl- and carbomethoxy substitution on the imidazole ring yielded proportionately larger amounts of methane. A polymer with a tetrachlorophenylene moiety lost all of its chlorine as hydrochloric acid, and most of its nitrogen as hydrogen cyanide. And a polybenzimidazole with a polysiloxane-alkylene chain decomposed via fragmentation of this chain.

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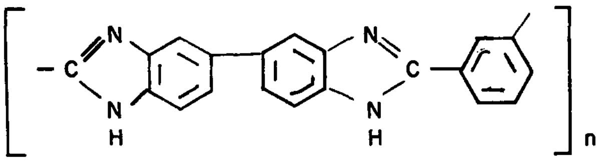
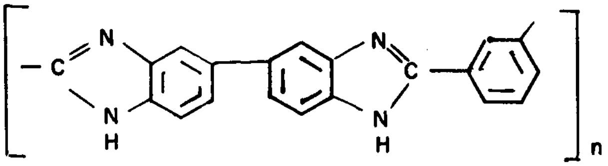
I INTRODUCTION

This work is a continuation of a study of the thermal breakdown mechanism of a variety of novel polymers. Previous reports (AFML-TR-67-89, AFML-TR-67-295, AFML-TR-67-428 and AFML-TR-68-289) covered the thermal decomposition of various "Phenylene-R-" polymers. This report describes the decomposition of the following polybenzimidazoles:

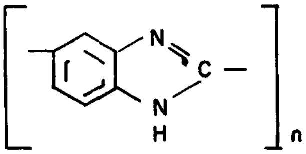
Polymer I-III:



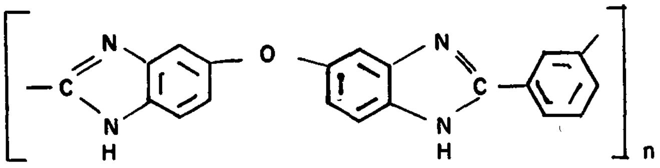
Polymer IV: Prepolymer of



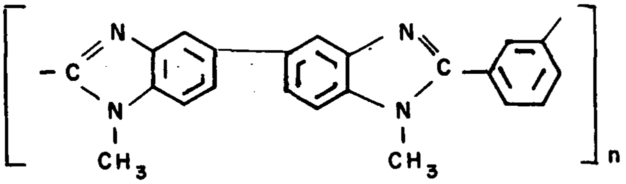
Polymer V:



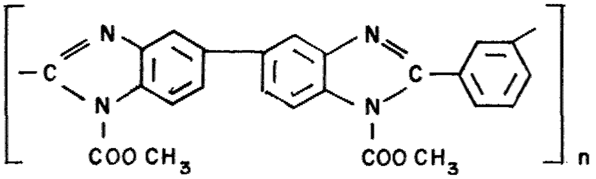
Polymer VI:



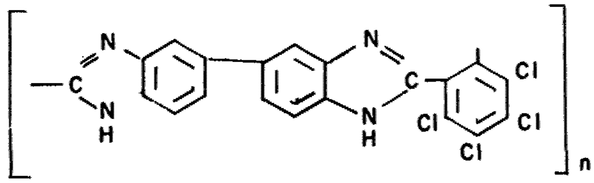
Polymer VII:



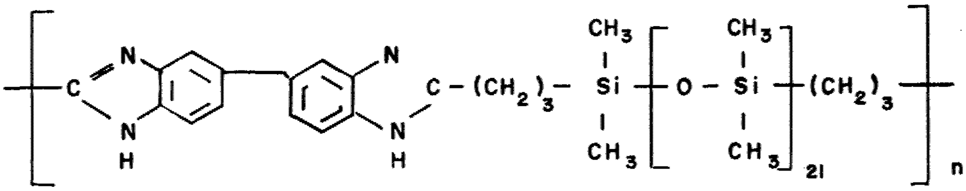
Polymer VIII:



Polymer IX:



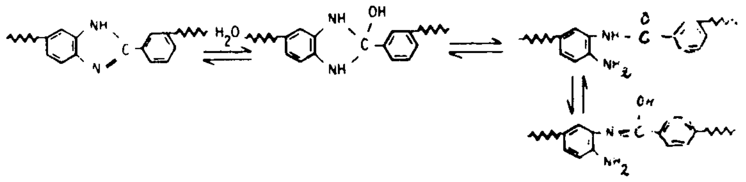
Polymer X:



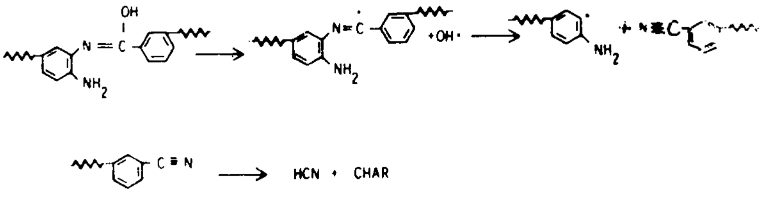
The decomposition studies were conducted under vacuum at three to four different temperature steps, between 200 and 650°C. The gases were analyzed by mass spectroscopy, the residues and sublimates were subjected to elemental analysis and infrared spectroscopy. The application of high resolution mass spectroscopy yielded additional information about the sublimates. Breakdown mechanisms have been postulated on the basis of the results. Experimental details have been given in the earlier reports.

II SURVEY OF RELATED WORK

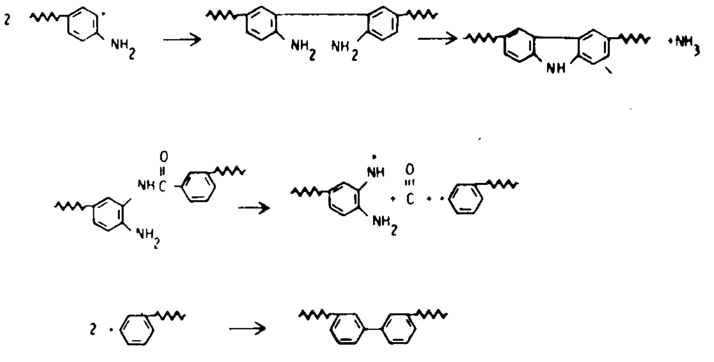
Although a number of authors investigated the thermal properties and the decomposition of polybenzimidazoles, very little work has been concerned with the analysis of the decomposition products, especially the effluent gases. Shulman and Lochte (Reference 1) studied 3 samples of a polybenzimidazole from diaminobenzidine and diphenylisophthalate, with different post-treatment, in programed runs (20-25°C/min) up to 950°C and isothermally between 560 and 604°C. Effluent gases were analyzed by mass spectroscopy, and the chars identified by elemental analysis. The authors found varying amounts of H_2O, CO, CO_2, HCN, NH_3, H_2, and CH_4, with water being the only significant product below 550°C. They believe that the formation of oxygenated products in major quantities from a well-cured polymer suggests that water formed during the condensation reacts with the benzimidazole ring to reverse the final polymerization step, leading to a hydroxy imidazoline. The authors postulated the following mechanism for the thermal degradation of poly-2-2'-(m-phenylene)-5,5'-bibenzimidazole:

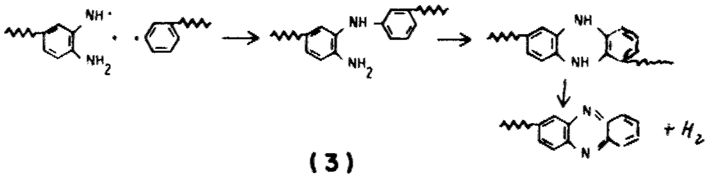


(1)



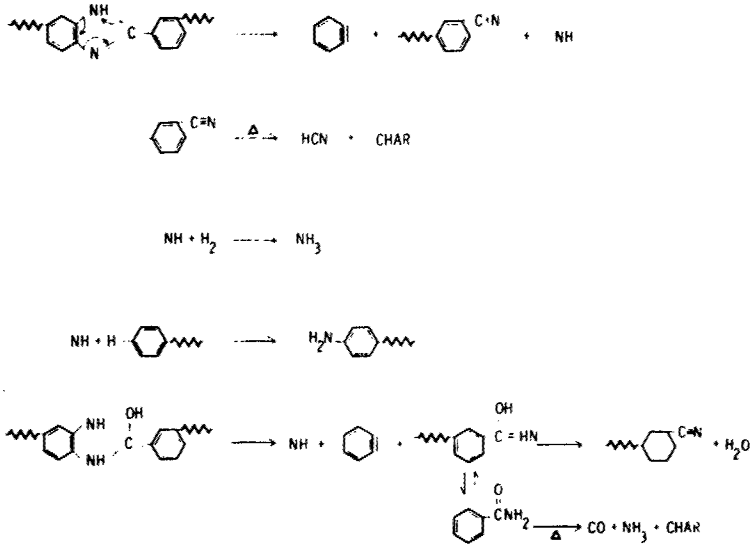
(2)





(3)

As an alternate, but less likely mechanism, they considered degradation via benzene intermediates:



Friedman and coworkers (References 2 and 3) also pyrolyzed samples of polybenzimidazoles from diaminobenzidine and diphenyl isophthalate, in vacuum from room temperature to 1000°C. The effluent gases were continuously analyzed in a time-of-flight mass spectrometer. In addition to the products found by Shulman and Lochte, Friedman observed small amounts of benzene, aniline, benzonitrile, phenylene diamine, aminobenzonitrile, acrylonitrile, and phthalonitrile. Comparison of the work of Shulman and Lochte with that of Friedman and coworkers showed considerable variations in composition and peak temperatures of the effluents. Friedman concludes that differences in sample preparation and the pyrolysis apparatus may have profound effects on the composition of the pyrolysis products. For example, post-heating in air results in increased quantities of water and carbon monoxide, while a closed pyrolysis system may give rise to secondary reactions.

III DISCUSSION

1. The oxygen (water) content of polybenzimidazoles.

The fact that even fully condensed polybenzimidazoles still contain oxygen, was known to us at the beginning of this study. Elemental analyses of the polybenzimidazoles used in this study confirmed this. Originally, we assumed that this oxygen content was indicative of incomplete cyclization, end groups and phenol or water not completely removed during condensation while Shulman and Lochte (Reference 1) believed, that a reversal of the final polymerization step occurred. We, therefore, decided to synthesize a polybenzimidazole sample under conditions (melt polymerization using coldfinger and vacuum throughout the reaction) which were expected to prevent recontamination of the polymer with the phenol formed during the condensation, and which were designed to facilitate the removal of the water formed. It turned out that this polymer, after sending it out for analysis without further drying, had an oxygen content of 7.5%, i.e. of the same order of magnitude as the other samples. It also showed, as did the other polybenzimidazoles, an early (room temp. to 150°C) weight loss in thermogravimetric analysis. This pointed to loosely bound water, and prompted a detailed evaluation of the question of water adsorption, drying conditions and readsorption of water.

Samples of the Polymers I, II and III (see Introduction) were sent out for oxygen analysis with the following instructions for each:

a) analyze as received;

b) dry at 120°C in vacuum for 4 hours;

c) dry at 200°C in vacuum for 4 hours, then analyze immediately while transferring the sample under nitrogen.

The following results were obtained:

Treatment	Polymer I	Polymer II	Polymer III
a)	7.5	8.6	8.4
b)	4.4	3.5	2.6
c)	2.6	2.7	1.2

Another sample of Polymer I, after drying it as under b), was left in the open and showed a weight gain of 3.7% from readsorbed moisture within a 21 hour period.

The above results show that polybenzimidazoles have a strong tendency to adsorb water. Quite unexpectedly, we found that the decomposition residues retained this behavior. A sample of a 450°C residue, dried 4 hours under vacuum at 120°C and left standing in the open, gained 2.2% in 3½ hours. A 550°C residue gave the following analysis results under the conditions listed above:

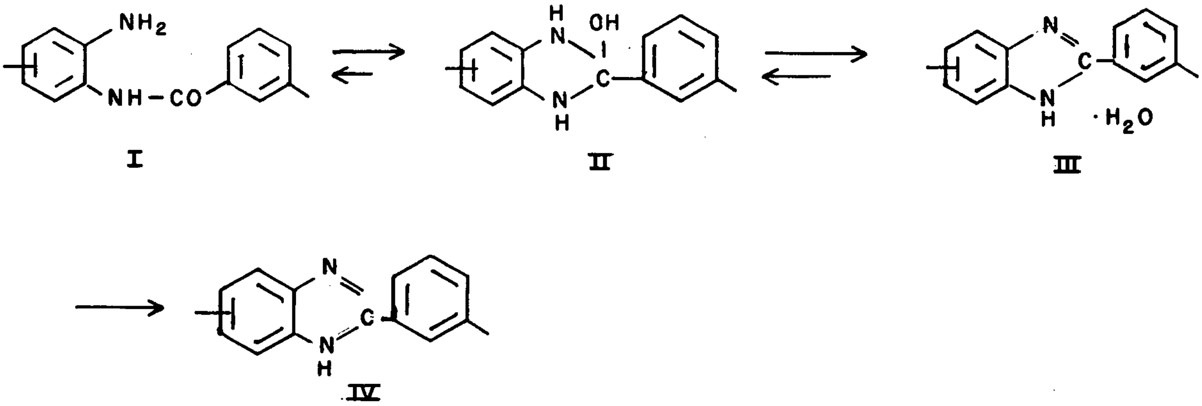
Residue 550°C, treatment a):

C, 74.4; H, 3.81; N, 13.0; O, 5.1.

Same residue, treatment b):

C, 81.1; H, 2.8; N, 15.0; O, 1.1.

It is interesting to note that one of our samples, which had been submitted to us as a prepolymer, and which apparently has been subjected only to a limited postheating (Polymer IV) did not show early weight loss under the conditions of thermogravimetric analysis and therefore did not seem to contain adsorbed water. The infrared spectrum of this prepolymer (Figure 6), when compared to one from a fully heated polymer showed that a number of bands which Feairheller and Katon (Reference 4) attribute to the benzimidazole ring, are weak, while others (at 1094 and 1167 cm^{-1}) are missing, in spite of the otherwise good resolution. This suggests that the prepolymer has essentially the structural elements I and/or II of the following sequence:



This, and the previously mentioned fact that the prepolymer did not seem to contain adsorbed water, point to the benzimidazole ring as the cause for the water adsorption. Water adsorption may lead to the adduct III, the imidazoline structure II, or imidazole-water complexes.

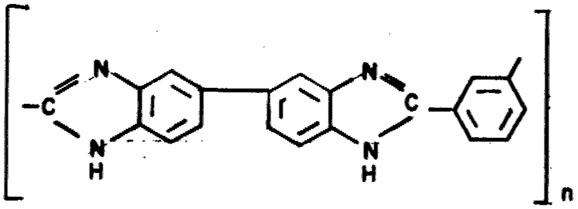
Covalent hydration in heterocyclic compounds is known (Reference 5). Not only water, but other nucleophilic reagents, such as organic solvents are easily added to a carbon-nitrogen double bond. We evaluated a large number of polymer samples which had been kept in vials for several months to years by differential thermal analysis. While vinyl- and "Phenylene-R" polymers were free of water, most of the heterocyclic polymers (all of them containing nitrogen) gave endotherms in the 120 to 140°C range, which disappeared on drying and were indicative of water.

Polybenzimidazoles, however, seem to be outstanding in their tendency to adsorb or retain water. Indications are, that in addition to the effect of the C = N double bond, the imino hydrogen is a contributing, if not the major factor. Polymers VII and VIII, with the imino hydrogen substituted by $-CH_3$ and $-COOCH_3$, formed less water than the other polymers, with the exception of the siloxane containing polymer X. It seems that this strong tendency of the polybenzimidazoles to adsorb water is not sufficiently known, and that not enough attention has been paid to the oxygen content of these polymers. Even Shulman and Loch e, in their previously cited paper on the decomposition of polybenzimidazoles, reported C, H and N analyses of a polybenzimidazole and its residues with 10 to 16% unaccounted for.

In addition to adsorbed and easily removed water, the polymers also contained oxgen which is not eliminated under normal drying conditions, and not even at temperatures as high as 650°C, as the analyses of the residues in Table I indicate (the oxygen analyses were obtained using the drying conditions under c) mentioned above). End groups alone cannot account for the amount of this "stable" oxygen, which is only partially removed as carbon monoxide, along with water and carbon dioxide, at the highest temperature step. It is likely that some intermediate amide-amine I of above sequence is present. The possibility of ether oxygen and phenolic/quinoid oxygen must also be considered. These moieties could form if phenoxy radicals from the diphenylisophthalate and hydroxy radicals from structure II combine with a free radical site on a phenyl ring. Finally, oxidation products of unknown nature may have formed, if the polymer was postheated in an atmosphere not completely free of oxygen.

2. Decomposition Studies

Polymers I-III were obtained from the melt reaction of diaminobenzidine with diphenylisophthalate (Polymers I and II) or isophthalic acid diamide (Polymer III). Their expected structure is



Polymer I was prepared in this laboratory from 0.0075 mole of diaminobenzidine and 0.0075 mole +5% of diphenylisophthalate in a reaction vessel fitted with a coldfinger, by heating the components under slight vacuum at 270°C for 20 minutes, then applying full vacuum for another 20 minutes. After cooling, the polymer was ground and reheated at 400°C for 1 hour at 50μ. This polymer was ground again in a Wig-L-Bug and heated at 400°C for another 3 hours in vacuum. The inherent viscosity in DMSO was 0.47.

Polymer II was obtained from Celanese Research Company under Air Force contract. The polymer was prepared in pilot lot quantities. The first stage involved heating to 235°C within 155 minutes and subsequent cooling, the second stage heating to 396°C within 284 minutes. The polymer had an inherent viscosity of 0.84 in sulfuric acid. A sample of this batch, used in our studies, was purified by T. Helminiak of this laboratory, by dissolving it in DMAC, precipitating it with MEK and washing it with MEK/methanol mixtures and subsequently methanol/ether mixtures each in the following proportions: 80/20, 60/40, 40/60 and 20/80. The polymer was dried at 120°C at 20μ. The oxygen content, however, was actually increased in this procedure.

Polymer III was received from Whittaker Corporation under Air Force contract and was prepared by melt reaction of diaminobenzidine with isophthaldiamide at 270-280°C and postheating it to 400°C.

As Figure 1 shows, the TGA curves of Polymers I-III are very similar and show a small early weight loss. The analyses of the volatiles in Table I and II confirm, that the gas fraction at 200°C is essentially water.

In the intermediate temperature range (200-550°C), the formation of H_2 and CH_4 is indicative of the breakdown of the aromatic ring, and the evolution of HCN and NH_3 representative of the degradation of the benzimidazole ring.

Below 450°C, the degradation of the aromatic ring seems to be more prominent than that of the benzimidazole ring. Polymer I loses much more CO and CO_2 than do the other polymers up to 550°C, although this polymer does not seem to contain more oxygen. We do not have an explanation for this fact, unless the intermediate temperature step at 450°C, which has been used only for Polymer I, is responsible for it. The formation of CO and CO_2 (which occurs in small amounts with the other polymers, too) may have several causes:

a) from end groups $-COOC_6H_5$ or -COOH;

b) from the intermediate structures I and II in the scheme shown previously;

c) from secondary ether linkages or phenolic groups, as explained before;

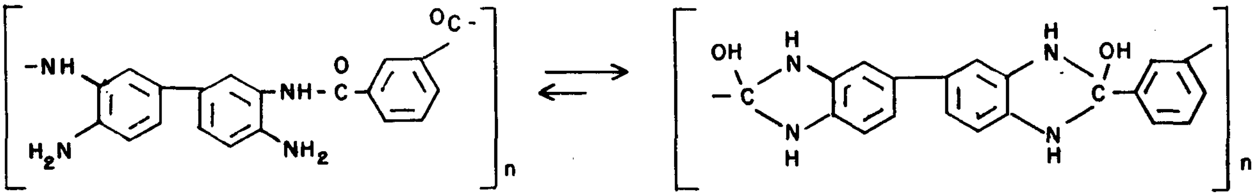
d) from oxidation products formed during synthesis and postheating in an atmosphere not completely free of oxygen.

At the highest temperature step (650°C), a distinct increase in the nitrogen-containing gases, especially HCN, can be observed. The analysis of the residues (Table I) indicates that the polymer loses most of its hydrogen, but only some nitrogen and little oxygen (the scattering of the oxygen results can be considered to be within limits of error). The residue at 650°C corresponds to a composition $C_{20}H_{4.7}N_{2.8}O_{0.4}$, compared to $C_{20}H_{12.9}N_{3.9}O_{0.5}$ of the original polymer.

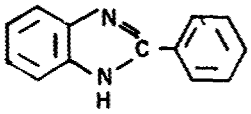
The infrared spectra of the polymers and their residues (Figures 2-5) show little beyond the decrease of all bands with increasing temperatures. (The spectra of Polymer II and its residues show much more resolution than those of I and III; Polymer II has been reprecipitated and is finely divided, while the other two polymers have been obtained directly from melt reactions).

Some sublimate was isolated during the decomposition of polymer III. Its spectrum differs from that of the polymer. It displays a distinct carbonyl band at 1730 cm^{-1} (only a shoulder in the polymer), which may result from carboxylic end groups or from amide linkages, still present or possibly reformed in a reverse polymerization step from a hydroxy imidazoline structure (Reference 1). A sharp and strong doublet at 2900/2970 cm^{-1} indicates CH-stretching frequencies, possibly from aliphatic fragmentation products. Mass spectrometric analysis revealed a considerable number of fragmentation products up to m/e = 500. Some of these could be tentatively identified as aromatic or aliphatic fragments with amine or nitrile groups from the decomposed imidazole ring.

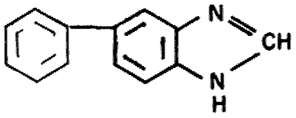
Polymer IV is a prepolymer from Whittaker Corporation, and was synthesized from diaminobenzidine and either diphenylisophthalate or isophthaldiamide. Details of the preparation are not known. The polymer is different in several respects from the other three polymers. Thermogravimetric analysis of this polymer does not show early loss of water. Elemental analysis is close to the structure of an intermediate polyamide or polyhydroxybenzimidazoline:



The infrared spectrum of the polymer (Figure 6) shows a distinct C-O stretching adsorption for alcohols or phenols at 1010 cm^{-1} which disappeared in the spectrum of the 200°C residue (Figure 7). This bond could be indicative of the polyhydroxybenzimidazoline, but also of residual phenol. Most remarkable is the observation that, on further heating, the polymer loses very little water, much less than expected if further condensation occurred. Instead, a sublimate forms, which could not be identified further. Its infrared spectrum is in-conclusive, and its mass spectrographic analysis reveals many of the peaks which were found for the sublimate of Polymer III. The strongest peak occurred at m/e 194 and may be representative of

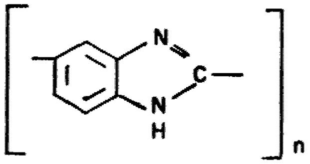


or



In addition to these four samples of poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole, a number of other experimental polybenzimidazoles were studied. Of most of these only limited amounts were available. Elemental analyses of polymers and residues, and the total weight losses at the different temperatures are, therefore, incomplete. However, the analyses of the volatiles alone are of sufficient interest to merit inclusion into this study.

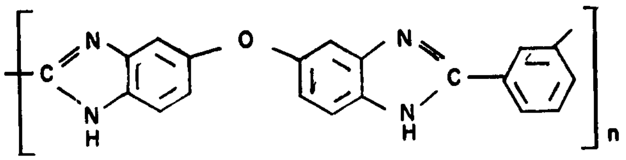
Polymer V was received from Whittaker Corporation under Air Force contract and was prepared by melt polymerization of 3,4 diamino-benzamide. It is expected to have the following structure:



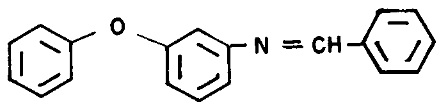
As would be expected, the composition of volatile products (Table IV) resembles that of Polymers II and III. Thermogravimetric analysis (Figure 8) shows considerable water adsorption for the polymer "as received".

Polymers VI to X were prepared by the University of Arizona under Air Force contract. Polymer VI was obtained by melt condensation of diphenylisophthalate and 3,3',4,4'-tetraaminodiphenyl ether; 90% of it was soluble in DMAC, and had an inherent viscosity of 0.48.

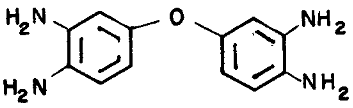
The polymer, with the structure



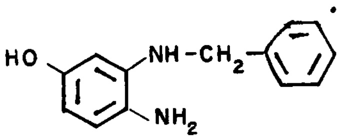
could be expected to show a decomposition behavior somewhat similar to polyphenylene oxides (Reference 6). This proved to be the case. As can be seen from Table IV (weight % volatiles between 20 and 650^{o}C), this polymer produces much more carbon monoxide and dioxide than do the other polymers. The infrared spectrum of the sublimate, compared to the one of the polymer (Figure 9), shows that a strong bond in the spectrum of the polymer at 955 cm^{-1}, which was repeatedly observed with benzimidazole structures, all but disappeared in the spectrum of the sublimate, and the arylether band at 1240 cm^{-}1 decreased considerably, with the other bands remaining strong. The substitution band at 855 cm^{-1} disappears due to cross-linking, while a new band at 740 cm^{-1}, representative of 5 adjacent free hydrogen atoms (more phenyl end groups) emerges. High resolution mass spectroscopy of the sublimate shows a variety of mass peaks up to approximately m/e 492. Some of the m/e peaks could be related to the following structures:



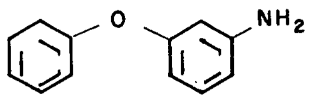
m/e = 273



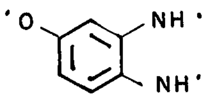
m/e = 229



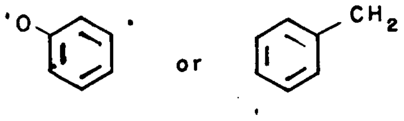
m/e = 213



m/e = 185

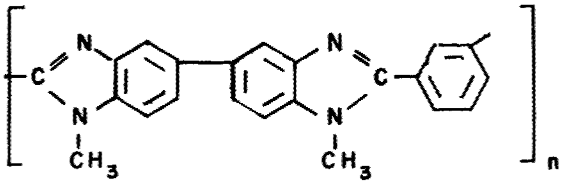


m/e = 121



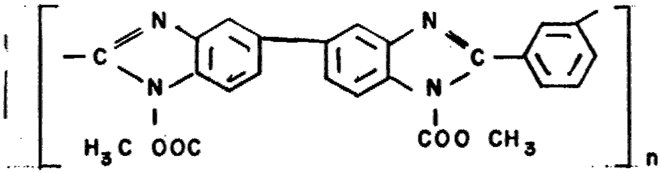
m/e = 92

Polymer VII was obtained by the methylation of a sample of poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole (η_{inh} 0.55 in DMSO) (Reference 7). The polymer was dissolved in DMSO, sodium hydride was added and the solution stirred for 164 hours at 30°C. Methyl iodide was then added and the solution stirred for an additional 72 hours. The polymer was precipitated from water. From the elemental analysis data (Table V) it is difficult to estimate the degree of substitution. The expected structure is



Small amounts of acetone, ethanol, benzene and sulfur-containing compounds (from DMSO) in the 200°C gas fraction probably can be traced to solvents used in the preparation. No explanation can be given for a relatively large amount of methyl chloride. The only feature of interest is the increased amount of methane, apparently from the methyl groups.

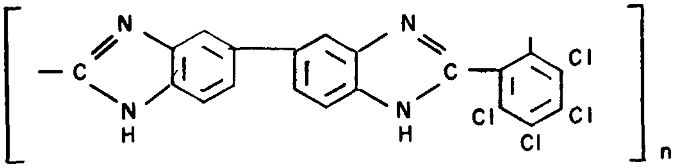
Polymer VIII was synthesized through carbomethoxylation of poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole (Reference 8). The polymer was dissolved in DMAC, sodium hydride was added, it was stirred for 118 hours at 25°C, methyl chloroformate added and the solution stirred for another 74 hours. The polymer was precipitated from water, dissolved in DMAC, and reprecipitated from benzene. The analysis data as supplied by the contractor differed sharply from ours, and both sets of data did not agree with the proposed structure



A low oxygen content in both cases indicates that the conversion of the original polybenzimidazole to the carbomethoxy derivative was incomplete (Table VI). It is, however, interesting to note that the polymer yields increased amounts of methane from the methoxy group, but no methanol.

Polymer IX formed when diaminobenzidine and tetrachlorophthalic anhydride were heated in phenol to 165°C for 6 hours, followed by a temperature increase to 205°C under vacuum (Reference 9). The polymer was washed with methanol, ethanol, and acetone. Its inherent viscosity in sulfuric acid was 0.11.

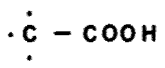
The polymer, with the proposed structure



contains a noticeable amount of oxygen (Table VII). Since thermogravimetric analysis does not reveal an early weight loss, and little water if formed during decomposition, the oxygen content seems to be indicative of uncyclized amide groups and carboxyl end groups; the infrared spectrum of the polymer (Figure 11) is not quite conclusive in this respect.

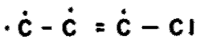
As can be seen from the list of volatiles in Table VII, the breakdown mechanism of this polymer seems to differ considerably from that of the polybenzimidazoles investigated before. Although thermogravimetric analysis (Figure 10) indicates little decomposition below 200°C, the 200°C gas fraction contains a high percentage of fragments which point to some breakdown of the basic polymer structure already at that temperature. The major component of the volatiles has a m/e peak of 81. This fragment was present in very small amounts in various other polybenzimidazoles. A satisfactory assignment has not as yet been made. Discrepancies between the calculated total weight of the volatiles and the overall weight loss point to m/e 81 as a possible impurity, which was not originally present in the polymer.

At 450°C, the major part of the chlorine is removed as hydrochloric acid, the hydrogen being supplied by the benzimidazole moiety. Part of the chlorine, however, may be eliminated in form of a sublimate, which accounts for 50% of the weight balance of the first two fractions. The infrared spectrum of this sublimate (Figure 11) is quite different from that of the polymer. Its most important features are the OH stretching frequency at 3500 cm^{-1}, a (aliphatic) C-H stretching mode at 2980 cm^{-1}, a very strong carbonyl band at 1750 cm^{-1} and the C-O stretching frequency at 1180 cm^{-1}. Mass spectroscopic analysis of the sublimate gave m/e peaks, some of which were assigned as follows:



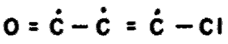
$\cdot\underset{\cdot}{\dot{C}}-COOH$

m/e = 57



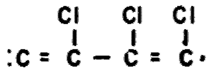
$\cdot\dot{C}-\dot{C}=\dot{C}-Cl$

m/e = 71



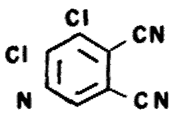
$O=\dot{C}-\dot{C}=\dot{C}-Cl$

m/e = 87

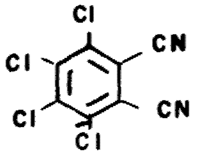


$:C=\overset{Cl}{\dot{C}}-\overset{Cl}{\dot{C}}=\overset{Cl}{\dot{C}}\cdot$

m/e = 153



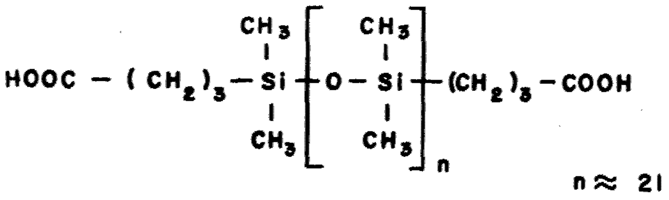
m/e = 196



m/e = 266

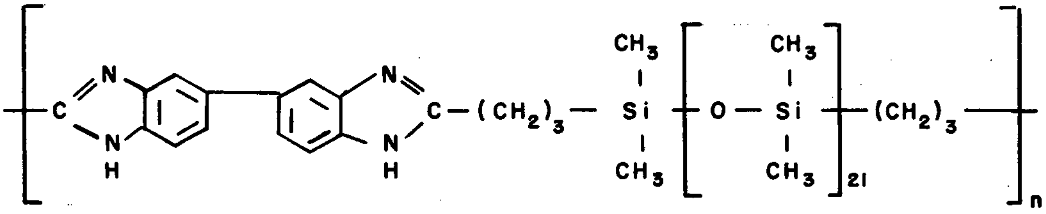
The other prominent volatile product at 450°C is carbon monoxide. At 550 and 650°C, CO and HCN are more prominent than usual, as compared to hydrogen; the reason is the low hydrogen content of this polymer, and the depletion of hydrogen due to the formation of hydrogen chloride. It is also remarkable that the polymer residue at 650°C retains only 3.7% nitrogen, in contrast to 13.6% in the case of Polymer I.

Polymer X is a condensate of a dimethylsiloxane dicarboxylic acid,



$$HOOC-(CH_2)_3-\overset{CH_3}{\underset{CH_3}{Si}}\left[-O-\overset{CH_3}{\underset{CH_3}{Si}}-\right]_n(CH_2)_3-COOH \qquad n \approx 21$$

molecular weight about 2000, which had been reacted with diaminobenzidine in phenol at 250°C for 2 hours. Reheating to 280°C gave a material with an inherent viscosity of 0.66 in tetrahydrofuran (Reference 10). The analysis of the polymer approaches the structure



(Table VIII), but seems to contain some oxygen which may result from incomplete ring closure and which is the cause for the formation of carbon monoxide. Relatively large amounts of methane as well as other alkanes and alkenes are formed by the fragmentation of the aliphatic linkages and the methyl side groups. Some unknown peaks on the mass spectrum may be formed from various siloxane or silane fragments. It is of interest that no nitrogen-containing volatiles are formed; after the breakdown of the aliphatic and siloxane chain, the benzimidazole moieties are apparently removed in form of a sublimate before they reach temperatures high enough for decomposition. In contrast with the other polybenzimidazoles, this polymer decomposes leaving hardly any residue.

IV CONCLUSIONS

Polybenzimidazoles have a strong tendency to adsorb water. This tendency seems to be typical for most N-containing heterocyclic polymers, but is especially pronounced for PBI. Even its decomposition residues rapidly adsorb water in the open atmosphere.

In addition to adsorbed and loosely bound water, which is readily removed by vacuum drying at temperatures of about 120°C, the polymers retain oxygen which is removed only at higher temperatures, and some of it not even at 650°C. The fact that it evolves as carbon monoxide and carbon dioxide, as well as water, suggests that a variety of structures may be present:

Water bound in form of complexes;

Intermediate polymer structures, such as polyamide-amines or polyhydroxy-imidazolines;

End groups $-COOC_6H_5$ or $-COOH$;

Ether linkages and phenolic/quinoid oxygen from secondary reactions;

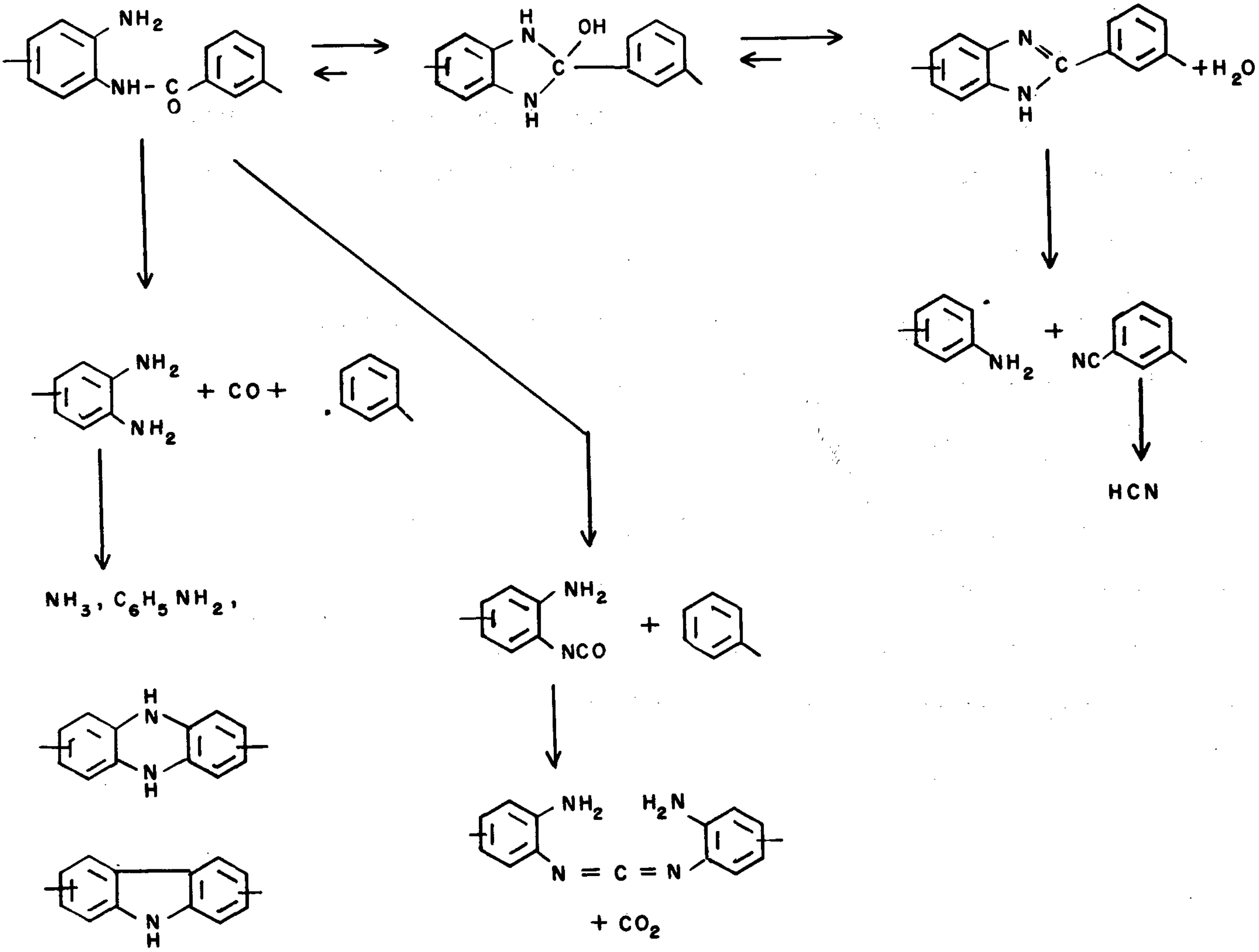
Unknown oxidation products from postheating in the presence of oxygen.

Aside from these factors, the decomposition of a typical polybenzimidazole and its intermediates may, in a simplified manner, be described as follows:

A. Removal of loosely adsorbed water;

B. Cross-linking and breakdown of aromatic rings with formation of hydrogen and methane, according to mechanisms described earlier (References 6, 11 and 12).

C. Breakdown of the imidazole ring and its intermediate stages with evolution of hydrogen cyanide and ammonia. This may occur according to the following scheme:



In connection with the above scheme, it should be pointed out that the formation of carbon dioxide via isocyanates and carbodiimides has been postulated earlier for polyamides and -imides(Reference 11). This mechanism seems to explain satisfactorily the formation of carbon dioxide in these polymers.

Some observations on some of the other polybenzimidazoles are of interest.

A prepolymer of poly 2,2'-(m-phenylene)-5,5'-bibenzimidazole did not seem to condense on further heating, since very little water was formed. Instead, cross-linking occurred (H_2-formation) and some fragmentation (sublimate).

A polybenzimidazole with an ether linkage formed much more carbon monoxide and carbon dioxide than the other polybenzimidazoles.

Imino-methyl groups produced increased amounts of methane, and imino substituted carbomethoxy groups seemed to yield CO, CO_2, and CH_4, but no methanol.

A polybenzimidazole with a tetrachlorophenylene moiety lost not only all of its chlorine as hydrochloric acid, but also most of its nitrogen, in contrast to the other polybenzimidazoles.

A polybenzimidazole with a polysiloxane-alkylene chain decomposed via fragmentation of this chain, while the benzimidazole moiety apparently was removed, more or less intact, as a sublimate, since no nitrogen-containing volatiles were observed, and since the polymer volatilized almost completely.

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TABLE I

ANALYSES OF VOLATILES AND RESIDUES OF POLYMER I

	C	H	N	O
Analysis calc for $(C_{20}H_{12}N_4)_n$:	77.9	3.9	18.2	---
Found for polymer:	76.2	4.1	17.3	2.6
" " residue at 200°C:	77.2	4.2	17.5	2.6
" " " " 450°C:	77.4	4.3	17.3	2.0
" " " " 550°C:	76.9	3.4	15.2	3.4
" " " " 650°C:	82.6	1.6	13.6	2.4

Temp Range (°C)	Volatile Products (Mole %)											Total
	toluene	benzene	CO_2	CH_3CN	CO	HCN	H_2O	NH_3	CH_4	H_2	Volatiles (Weight %)*	Volatiles + Condensables (Weight %)*
20-200	---	---	3.6	---	0.7	0.8	87.1	---	0.8	0.6	0.5	0.7
200-450	0.1	0.3	50.4	0.4	18.1	1.0	4.2	0.3	4.7	20.4	1.0	4.1
450-550	0.1	0.8	0.1	0.4	1.9	7.4	0.7	0.8	9.6	78.3	3.3	6.7
550-650	---	0.1	0.1	0.2	3.8	17.0	0.6	1.4	8.1	68.8	3.9	6.7
	Volatile Products (Weight %)*											
20-650	0.04	0.34	0.82	0.12	0.89	3.00	0.59	0.17	1.34	1.37	8.7	18.2

* of starting material

TABLE II

ANALYSES OF VOLATILES OF POLYMERS II AND III

Polymer II

Temp Range (^oC)	Volatile Products (Mole %)									Total	
	benzene	acetone	CO_2	CO	HCN	H_2O	NH_3	CH_4	H_2	Volatiles (Weight %)*	Volatiles + Condensables (Weight %)*
20-200	0.1	---	2.6	---	0.7	94.9	---	0.8	0.5	0.6	1.2
200-550	0.4	---	0.1	2.0	3.8	0.9	1.4	8.5	82.9	1.5	5.4
550-650	0.1	---	---	1.1	15.6	0.8	7.7	10.2	64.6	3.5	8.2
	Volatile Products (Weight %)										
20-650	0.12	---	0.05	0.28	1.93	0.60	0.58	1.02	0.96	5.6	14.8

Polymer III

Temp Range (^oC)	Volatile Products (Mole %)									Total	
	benzene	acetone	CO_2	CO	HCN	H_2O	NH_3	CH_4	H_2	Volatiles (Weight %)*	Volatiles + Condensables (Weight %)*
20-200	---	0.8	2.8	---	0.2	95.1	---	0.7	0.3	0.9	8.1
200-550	0.3	---	0.3	1.0	5.4	8.4	0.3	11.6	72.7	3.0	
550-650	---	---	0.1	1.9	10.9	3.2	0.8	4.5	78.7	2.8	5.4
	Volatile Products (Weight %)										
20-650	0.10	0.02	0.13	0.35	1.90	1.72	0.08	1.10	1.30	6.7	13.5

* of starting material

TABLE III

ANALYSES OF VOLATILES AND RESIDUES OF POLYMER IV

	C	H	N	O	Ash
Analysis calc for $(C_{20}H_{12}N_4)_n$:	77.9	3.9	18.2	---	---
" " " $(C_{20}H_{16}N_4O_2)_n$:	69.5	5.0	16.2	9.2	
Found for Polymer:	71.0	4.7	17.1	7.2	
" " residue at 200°C:	71.9	4.4	16.1	7.1	
" " " " 550°C:	74.3	3.5	13.9	7.1	
" " " " 650°C:	78.9	2.0	11.4	7.2	

Temp Range (°C)	Volatile Products (Mole %)									Total	
	toluene	benzene	acetone	CO_2	CO	HCN	H_2O	CH_4	H_2	Volatiles (Weight %)*	Volatiles + Condensables (Weight %)*
20-200	---	---	5.2	3.5	---	1.0	89.0	0.7	0.5	1.3	3.3
200-550	---	0.7	---	0.1	1.8	12.9	0.5	12.2	71.7	1.2	15.6
550-650	---	0.1	---	0.2	2.3	13.5	0.5	12.7	70.7	4.6	5.3
20-650	---	0.13	0.19	0.15	0.45	2.67	1.06	1.49	1.04	7.1	24.2

* of starting material

TABLE IV

ANALYSES OF VOLATILES OF POLYMERS V AND VI

Polymer V

Temp Range (°C)	Volatile Products (Mole %)								Total	
	benzene	CO_2	CO	HCN	H_2O	NH_3	CH_4	H_2	Volatiles (Weight %)*	Volatiles + Condensables (Weight %)*
20-200	---	5.0	---	0.1	94.0	---	0.2	0.6	1.9	**
200-550	---	0.4	2.0	3.4	0.9	0.6	4.8	87.8	1.3	**
550-650	---	0.1	2.6	24.8	0.8	1.0	2.3	68.5	2.8	**
	Volatile Products (Weight %)									
20-650	---	0.28	0.38	2.23	1.73	0.08	0.34	0.93	6.0	12.9

Polymer VI

Temp Range (°C)	Volatile Products (Mole %)								Total	
	benzene	CH_3CN	CO_2	CO	HCN	H_2O	CH_4	H_2	Volatiles (Weight %)*	Volatiles + Condensables (Weight %)*
20-200	---	---	5.6	1.0	0.3	92.4	0.5	0.5	1.7	31.7
200-550	0.2	0.2	4.8	14.0	0.5	2.8	5.9	71.6	1.5	
550-650	---	0.1	0.8	10.0	11.4	1.1	3.9	72.7	2.6	3.2
	Volatile Products (Weight %)									
20-650	0.03	0.02	0.66	1.51	0.95	1.56	0.35	0.67	5.8	34.9

* of starting material   ** not determined

TABLE V

ANALYSES OF VOLATILES OF POLYMER VII

	C	H	N	O	Ash
Analysis calc for $(C_{22}H_{16}N_4)_n$:	78.5	4.8	16.7	---	---
" " " $(C_{20}H_{12}N_4)_n$:	77.9	3.9	18.2	---	---
Found for Polymer:	75.3	4.7	15.9	1.1	2.5
" " " (contractor's results)	76.0	5.2	18.7	0.1*	

Temp Range (^oC)	Volatile Products (Mole %)														Total	
	benzene	SO_2	O=C=S	$(CH_3)_2CO$	CH_3Cl	CH_3SH	C_2H_5OH	CO_2	CH_3CN	CO	HCN	H_2O	CH_4	H_2	Volatiles (Weight %)**	Volatiles + Condensables (Weight %)**
20-200	0.1	5.1	0.3	2.3	5.8	2.2	1.2	45.3	0.5	5.4	1.2	14.4	14.1	2.1	1.7	***
200-450								2.3	0.2	1.3	0.5	0.4	89.7	5.5	4.2	***
450-550								0.8	0.2	2.5	6.8	0.6	16.9	72.0	2.0	***
550-650								0.2	0.1	2.1	17.2	0.5	7.6	72.3	3.5	***
	Volatile Products (Weight %)															
20-650	traces	0.15	0.01	0.06	0.13	0.05	0.03	1.34	0.07	0.61	2.55	0.21	5.16	1.05	11.4	18.2

* by difference ** of starting material *** not determined

TABLE VI

ANALYSIS OF VOLATILES AND A RESIDUE OF POLYMER VIII

	C	H	N	O	Ash
Analysis calc for $(C_{24}H_{16}N_4O_4)_n$:	67.9	3.8	13.2	15.1	---
" " " $(C_{20}H_{12}N_4)_n$:	77.9	3.9	18.2	---	---
Found for polymer:	70.7	4.8	*	5.0	
" " " (contractor's results)	68.1	4.7	15.2	11.4**	0.6
" " residue at 650°C:	79.7	1.6	11.8	2.5	4.0

Temp Range (°C)	Volatile Products (Mole %)										Total	
	Xylene	Toluene	Benzene	CO_2	CH_3CN	CO	HCN	H_2O	CH_4	H_2	Volatiles (Weight %)***	Volatiles + Condensables (Weight %)***
20-200	0.2	0.1	9.0	46.4	1.7	18.1	1.3	14.5	7.4	1.4	3.0	*
200-450			0.2	8.6	0.9	6.2	2.3	0.5	68.1	13.1	1.9	*
450-550			0.3	0.8	0.3	1.9	4.3	0.7	12.2	79.5	1.3	*
550-650				0.2	0.2		16.4	0.7	7.0	75.5	2.6	*
	Volatile Products (Weight %)											
20-650	0.02	0.01	0.64	2.15	0.15	0.71	1.89	0.29	2.04	0.90	8.8	30.1

* not determined ** by difference *** of starting material

TABLE VII

ANALYSES OF VOLATILES AND RESIDUES OF POLYMER IX

	C	H	N	Cl	O	Ash
Analysis calc for $C_{20}H_8N_4Cl_4$:	53.8	1.8	12.6	31.8	---	---
Found for polymer:	52.8	2.7	9.2	27.2	5.2	
" " " (contractor's results)	52.8	2.9	12.0	26.7		
" " residue 450°C:	67.4	2.9	15.4	6.0	4.6	4.4
" " " 550°C:	72.6	2.6	16.3	4.8	3.5	
" " " 650°C:	74.4	1.9	3.7	---	7.8	0.7

Temp Range (°C)	Volatile Products (Mole %)										Total
	m/e 81	CH_3Cl	CO_2	HCl	CO	HCN	H_2O	CH_4	H_2	Volatiles (Weight %)*	Volatiles + Condensables (Weight %)*
20-200	64.1	2.6	8.0	---	----	13.8	4.4	6.5	0.6	14.2	31.6
200-450	----	---	8.6	53.7	28.2	2.8	5.4	0.5	0.8	10.5	
450-550	----	---	7.0	1.6	57.3	18.3	0.7	1.3	13.8	2.7	2.7
550-650	----	---	1.1	0.9	10.0	48.5	1.4	4.7	33.4	3.6	5.5
	Volatile Products (Weight %)										
20-650	11.80	0.29	2.43	6.37	4.79	4.19	0.55	0.43	0.17	31.0	37.6

* of starting material

TABLE VIII

ANALYSES OF VOLATILES OF POLYMER X

	C	H	N	O	Si
Analysis calc for $C_{64}H_{132}N_4O_{21}Si_{22}$(n=21):	39.6	7.9	2.8	17.6	32.2
Found for polymer:	33.4	7.9	2.1	21.3*	35.3

Temp Range (°C)	m/e 171	m/e 134	m/e 98	Volatile Products (Mole %)									Total	
				butene	CO_2	propene	ethane	ethene	CO	H_2O	CH_4	H_2	Volatiles (Weight %)**	Volatiles + Condensables (Weight %)**
20-550	5.5	2.9	1.3	1.6	1.2	2.7	1.5	11.0	2.0	0.7	43.7	25.9	1.5	98.0
550-650	-	-	-	-	0.8	-	-	2.9	23.0	1.8	30.3	41.2	0.5	
	Volatile Products (Weight %)													
20-650	0.49	0.20	0.07	0.05	0.04	0.06	0.02	0.19	0.26	0.02	0.54	0.06	2.0	98.0

* by difference

* * of starting material

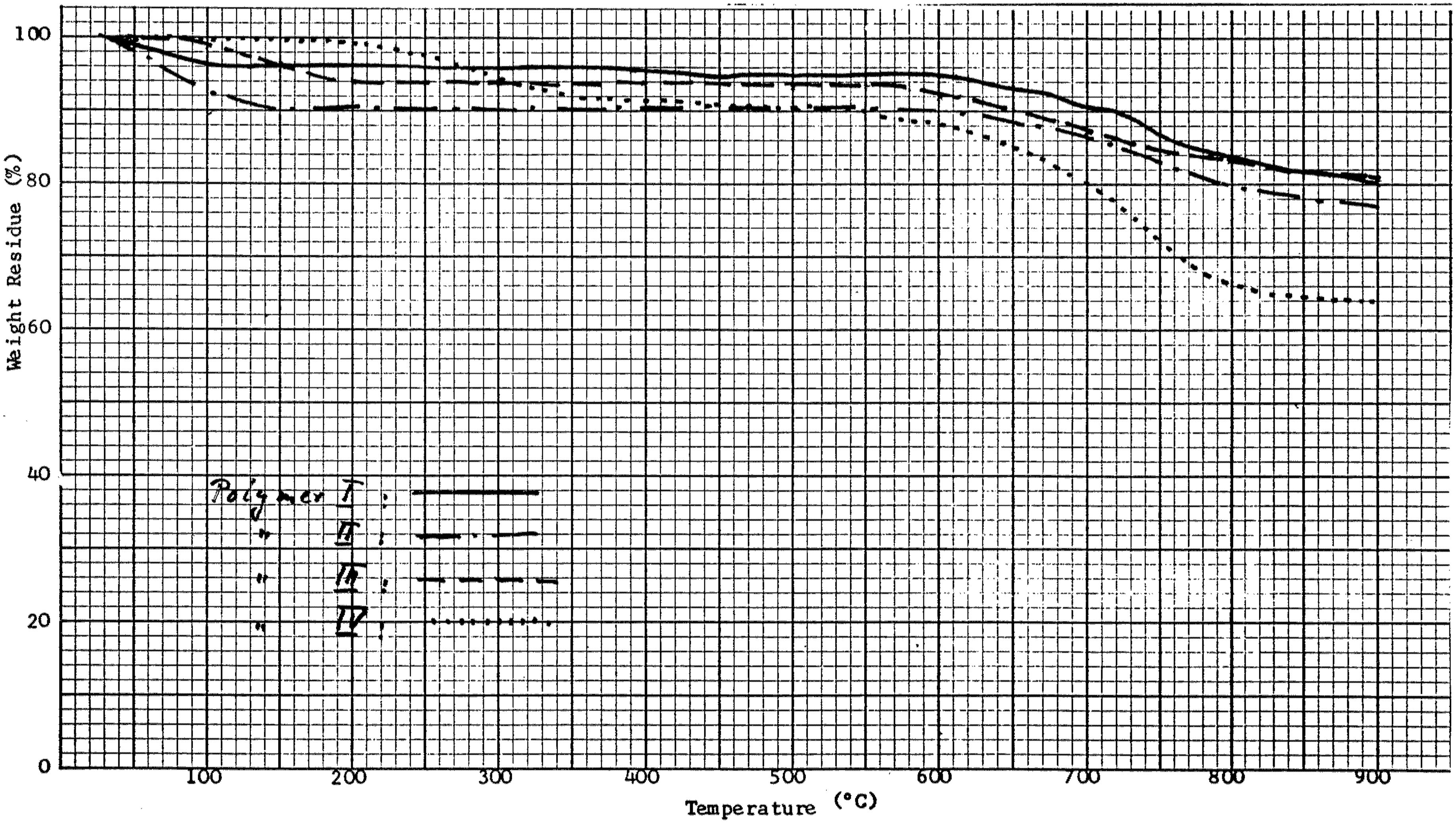

Figure 1 Thermogravimetric Analyses ($3^{o}C$/min, nitrogen) of Polymers I to IV

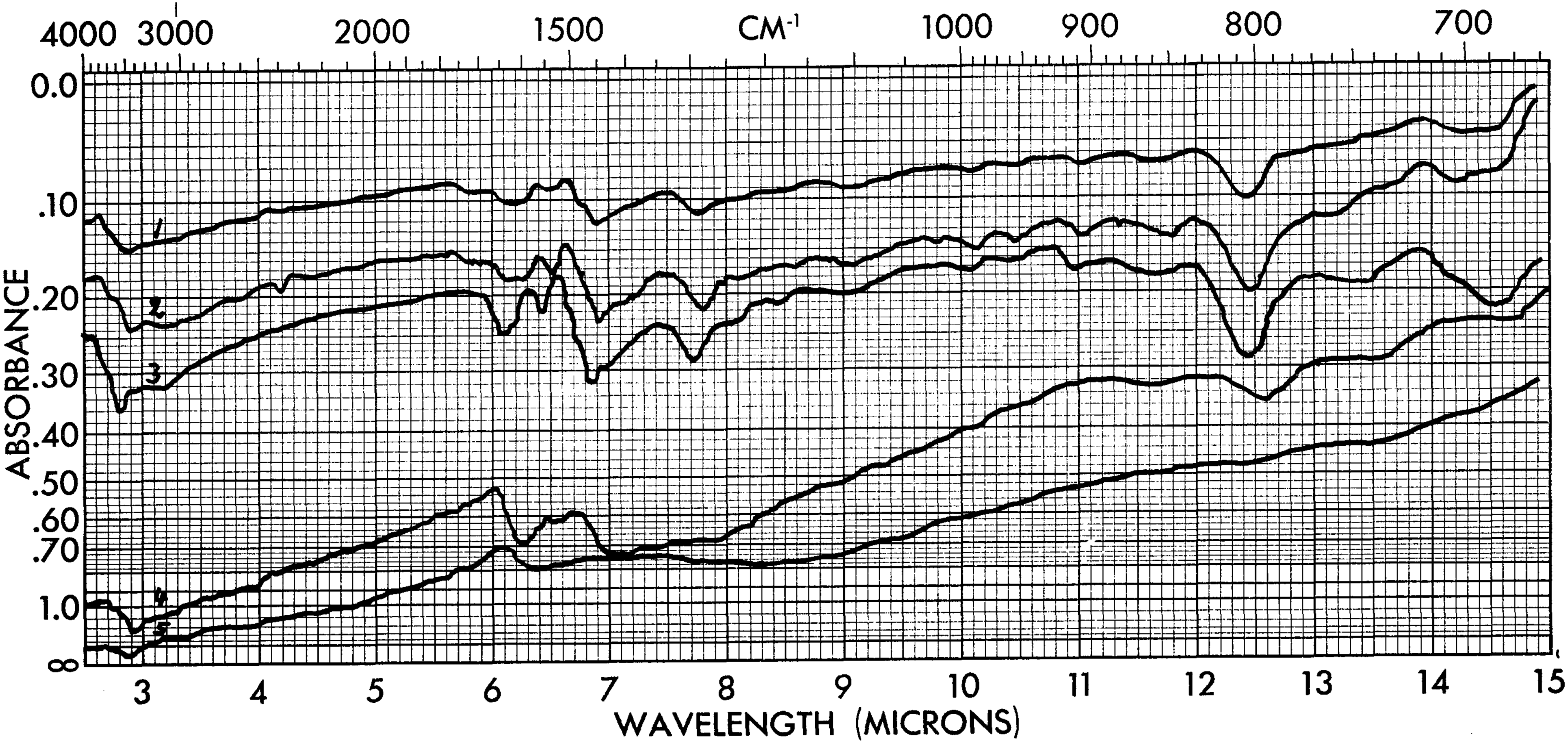

Figure 2 Infrared Spectra of 1: Polymer I; 2: Residue at 200°C; 3: Residue at 450°C; 4: Residue at 550°C; 5: Residue at 650°C

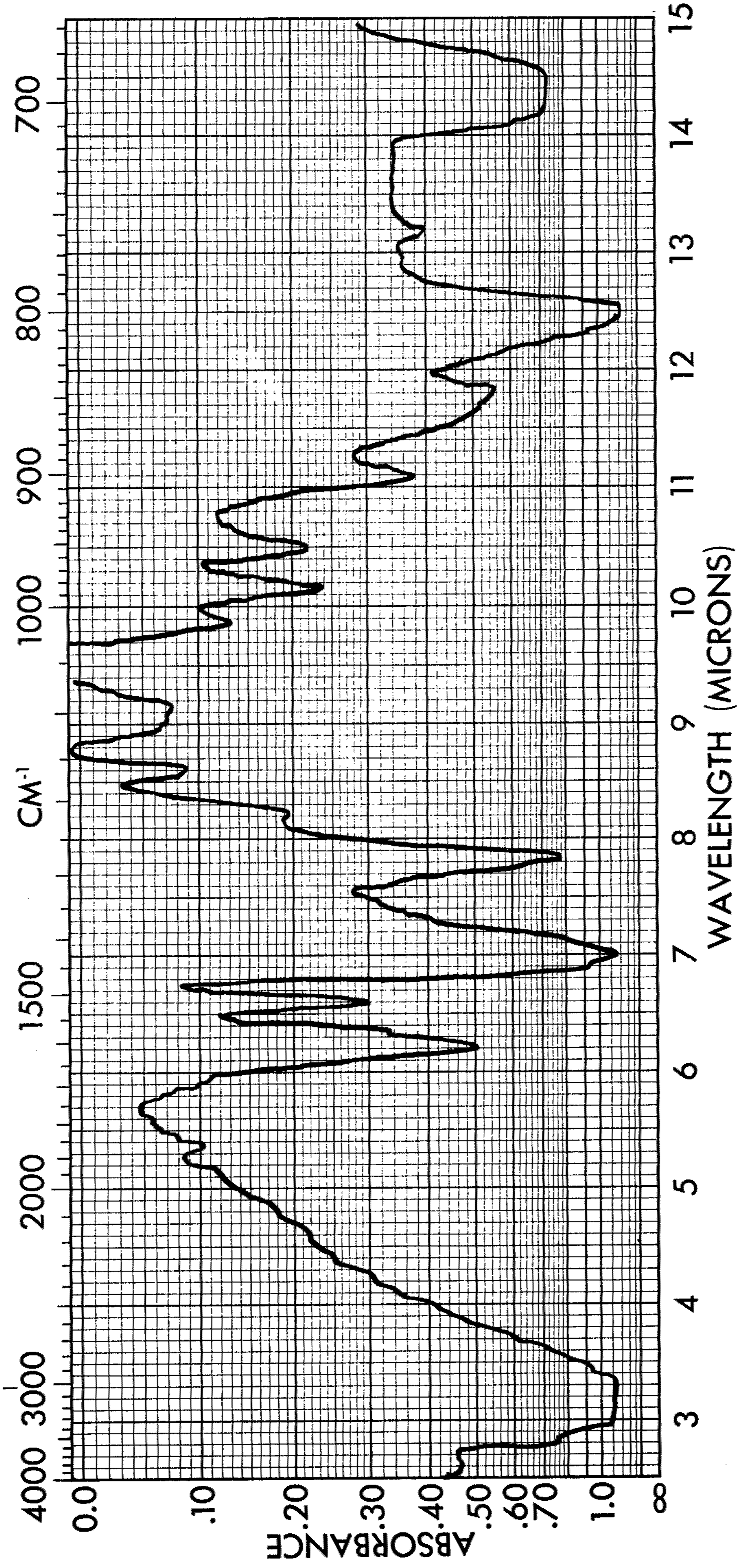

Figure 3 Infrared Spectrum of Polymer II

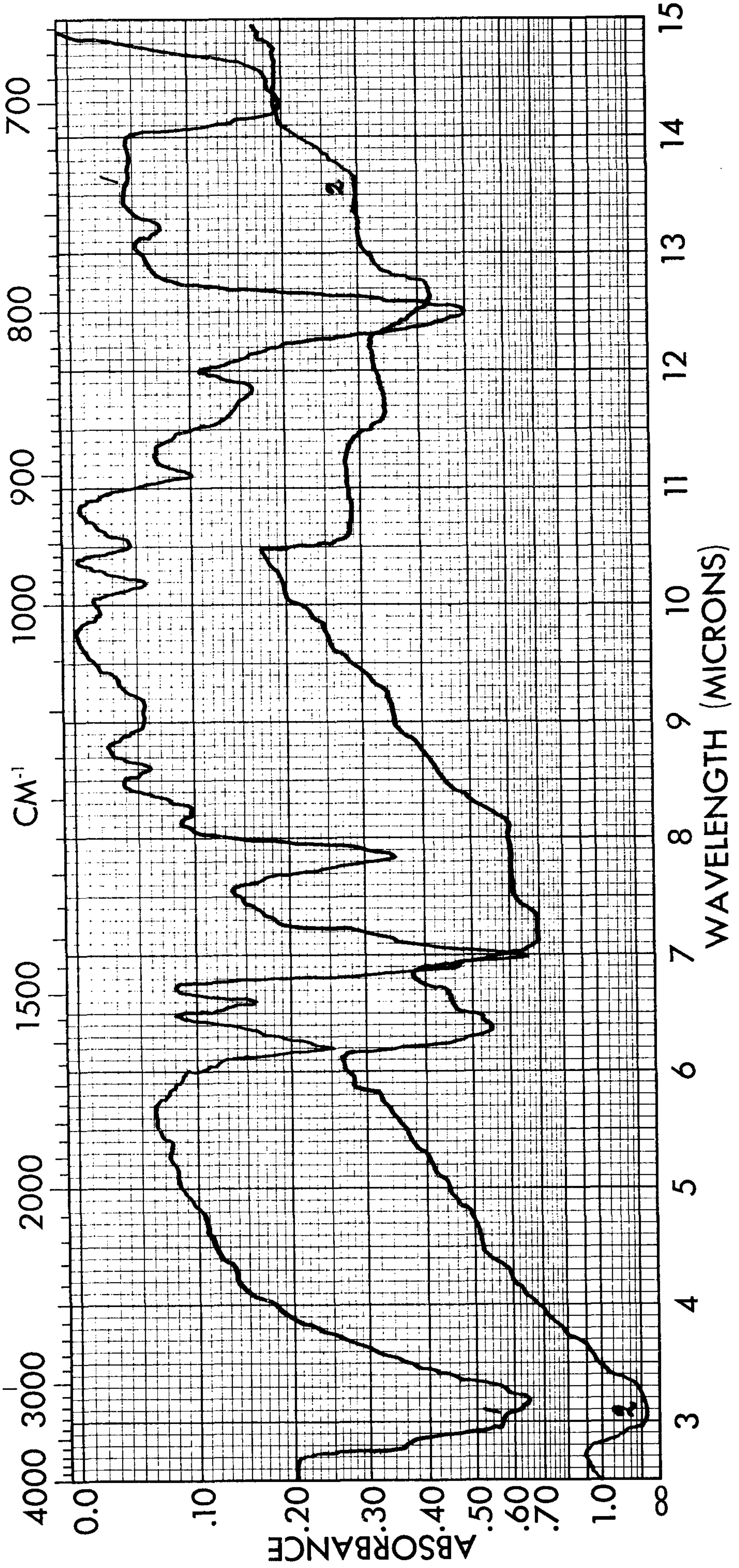

Figure 4 Infrared Spectra of the Residues of Polymer II at 1: 200°C; 2: 550°C

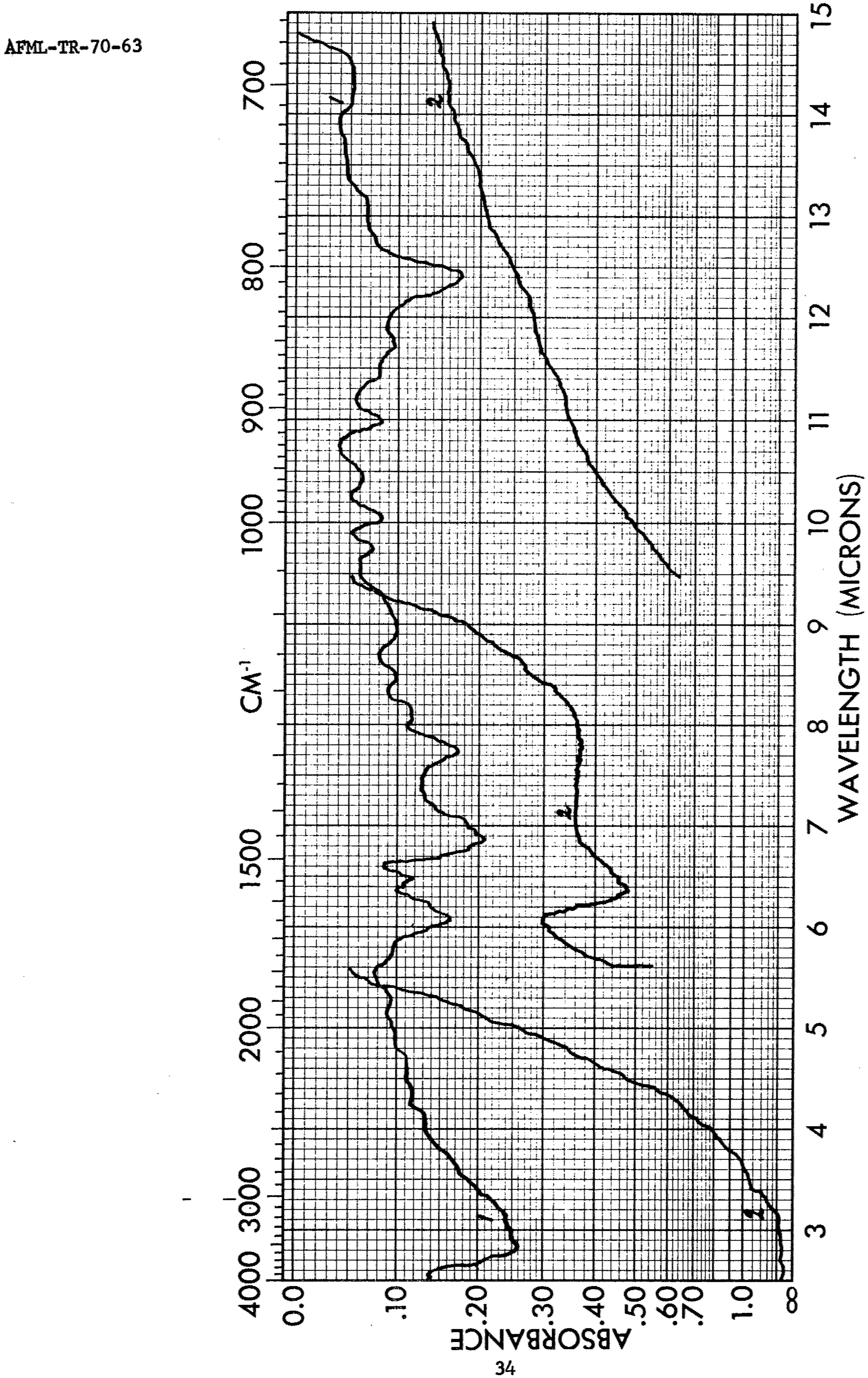

Figure 5 Infrared Spectra of 1: Polymer III; 2: Residue at 550°C

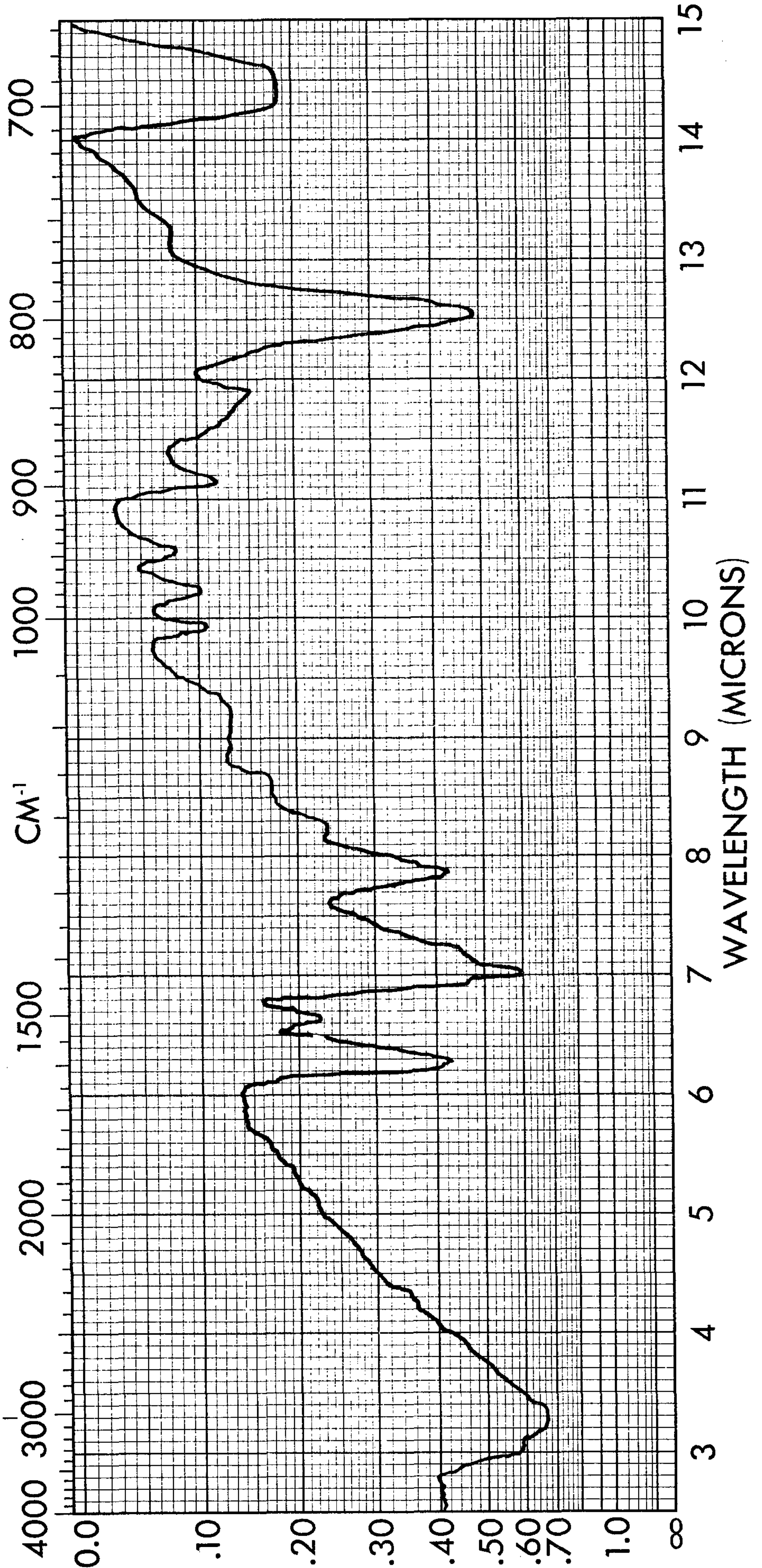

Figure 6 Infrared Spectrum of Polymer IV

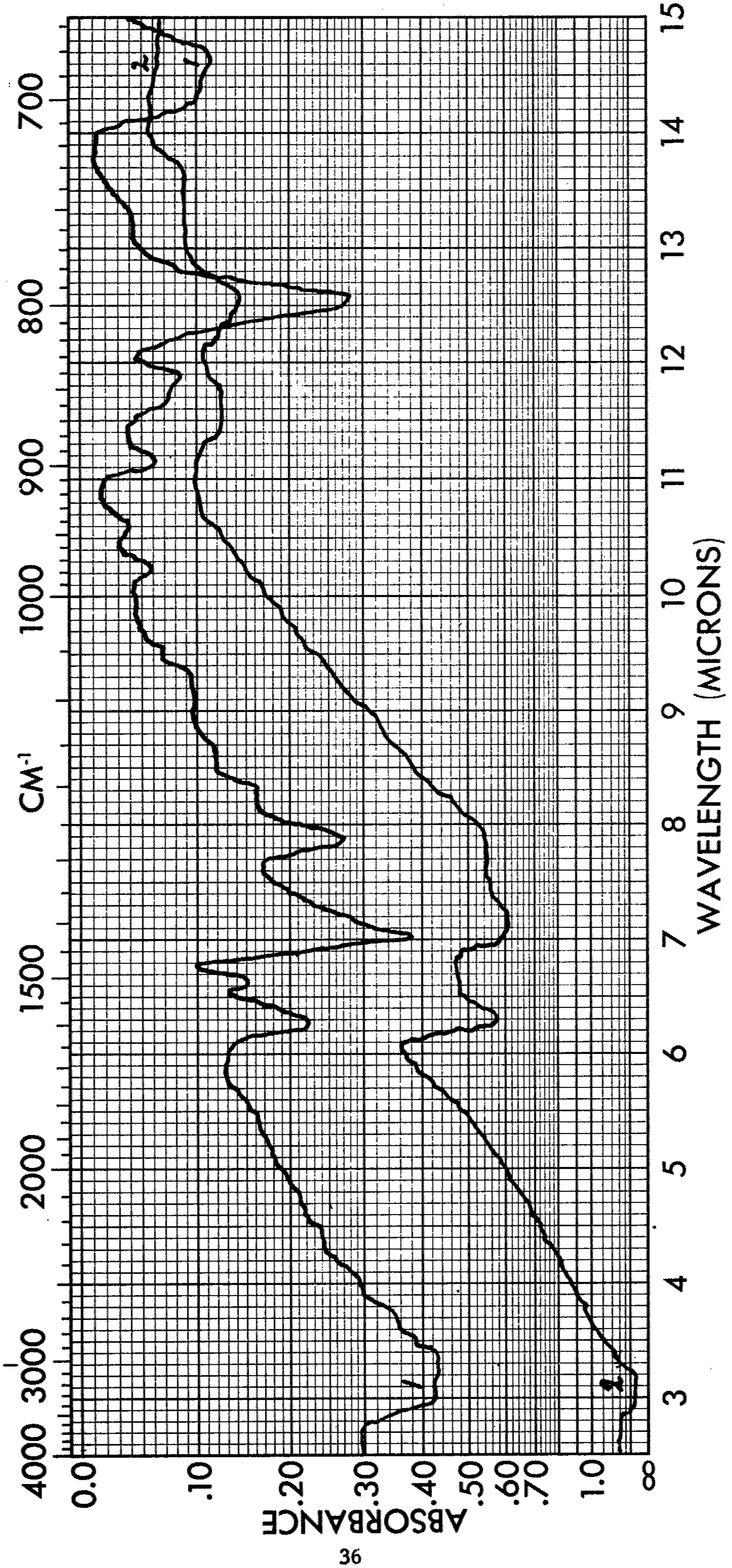

Figure 7 Infrared Spectra of the Residues of Polymer IV at 1: 200°C; 2: 550°C

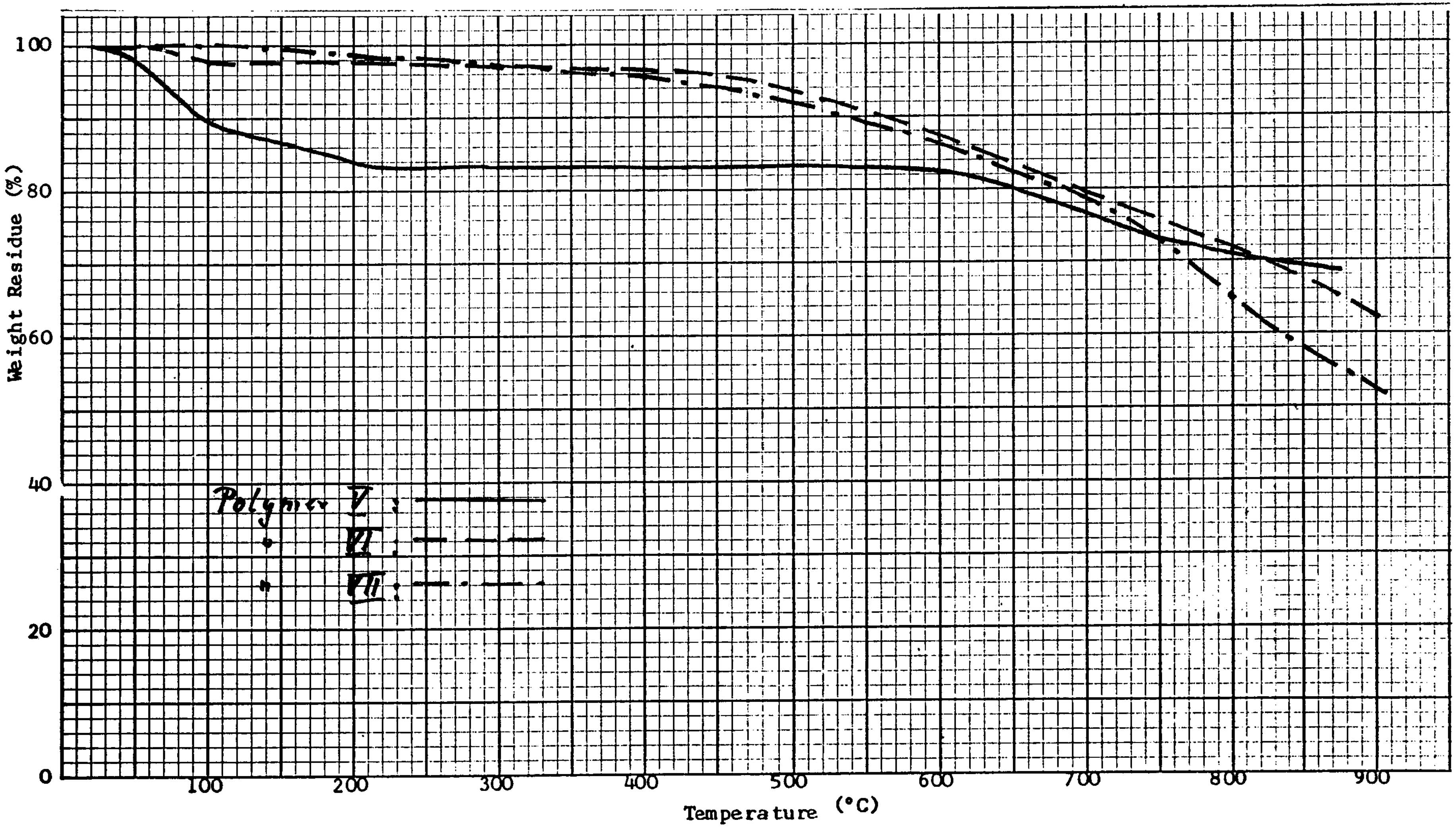

Figure 8 Thermogravimetric Analyses (3°C/min, nitrogen) of Polymers V to VII

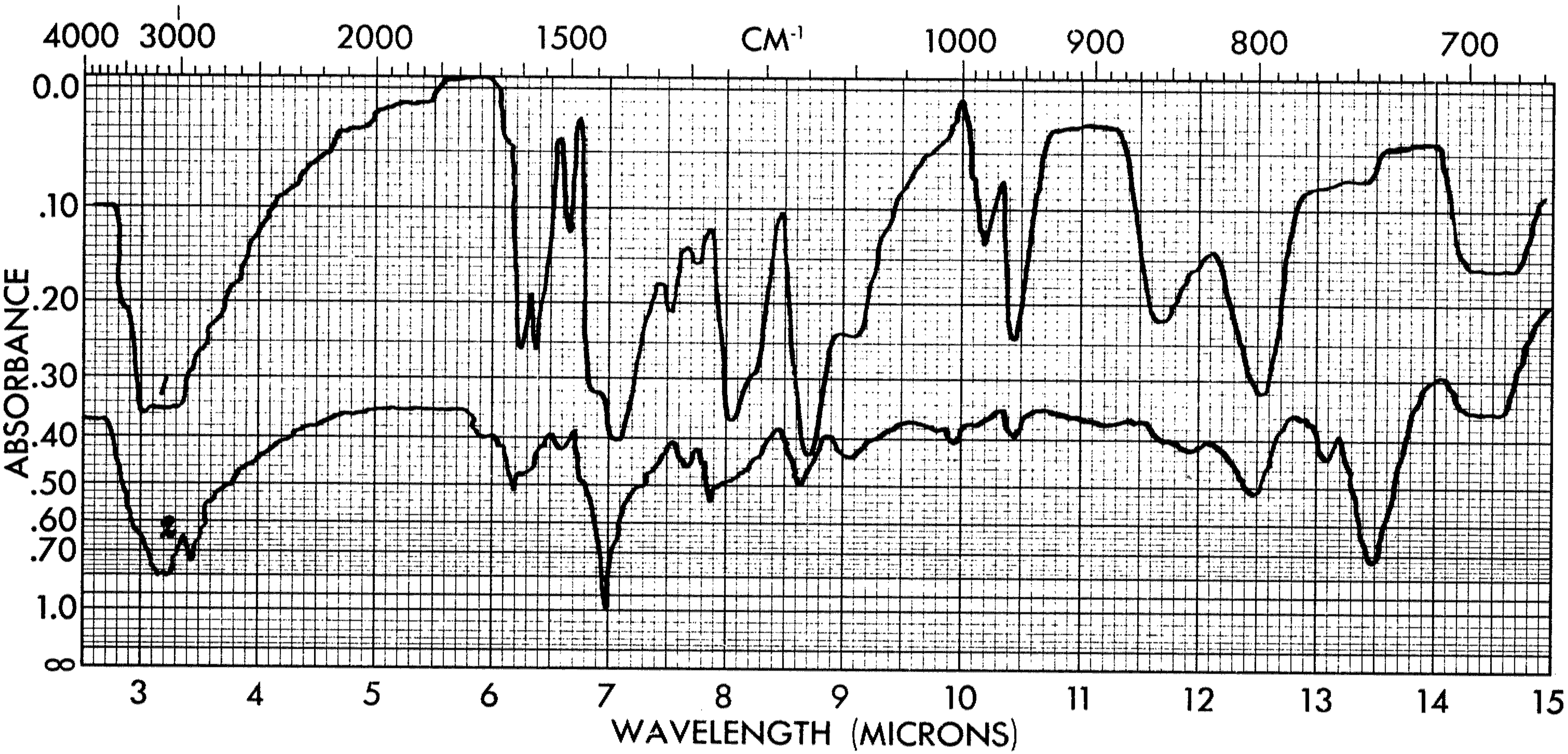

Figure 9 Infrared Spectra of 1: Polymer VI and 2: Sublimate of Polymer VI

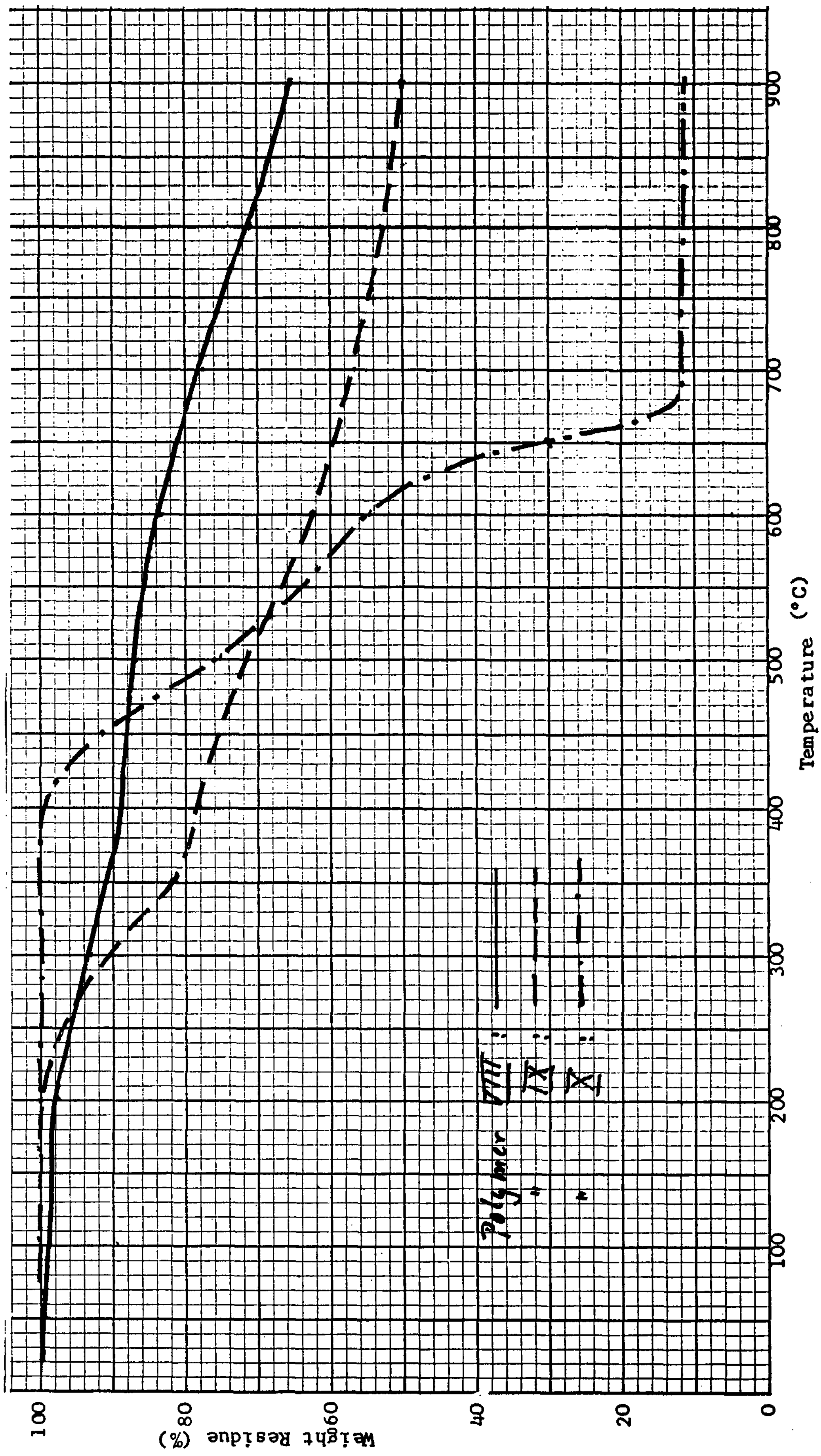

Figure 10 Thermogravimetric Analyses (3^oC/min, nitrogen) of Polymers VIII - X

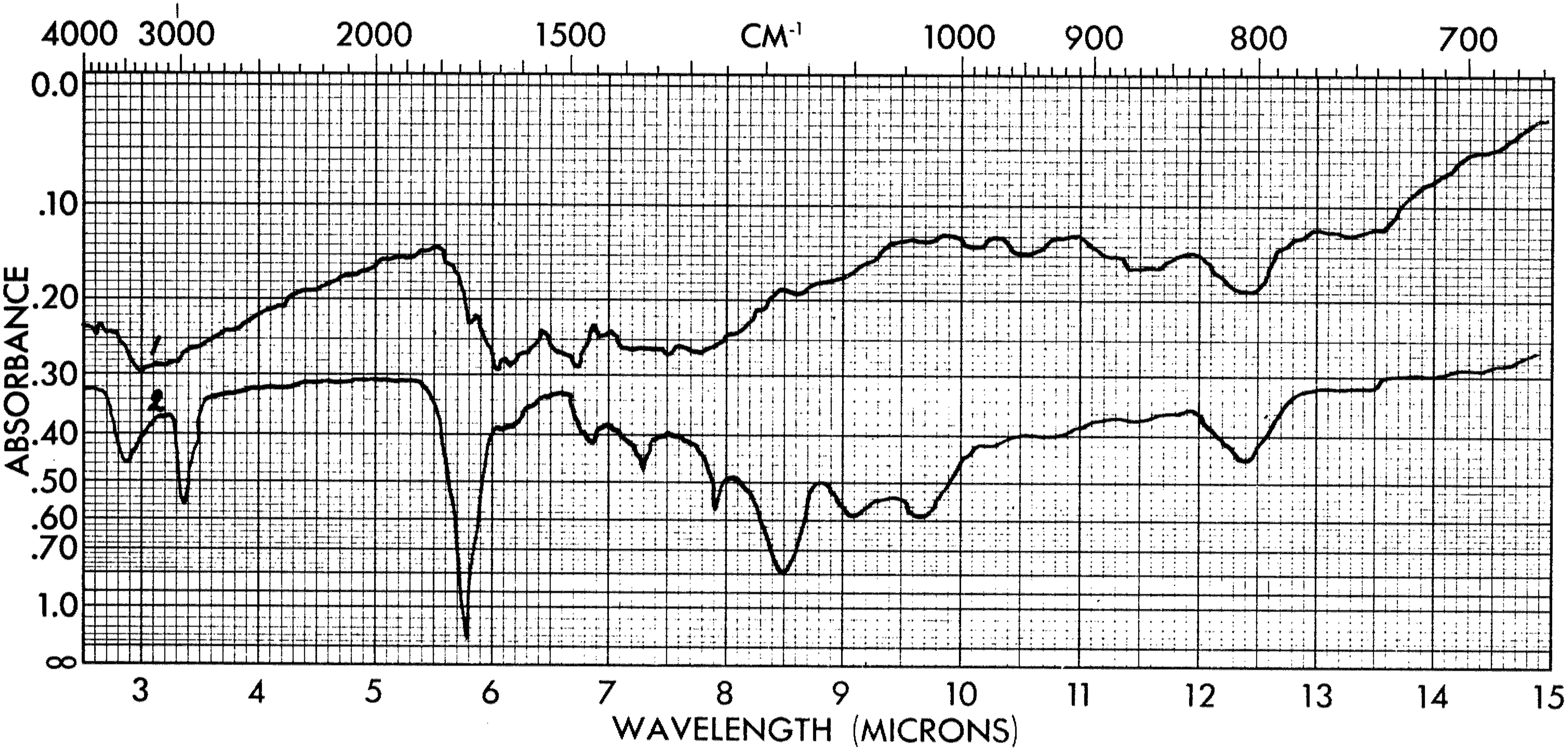

Figure 11 Infrared Spectra of 1: Polymer IX and 2: Sublimate of Polymer IX

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13. ABSTRACT

The thermal breakdown of 4 samples of 2,2'-(m-phenylene)-5 5'-bi-benzimidazole and of 6 other polybenzimidazoles was studied between 200 and 650°C.

Unexpectedly high oxygen contents of these polymers first led to a study of moisture adsorption and proper drying conditions. This and the actual decomposition studies showed that polybenzimidazoles not only have a strong tendency to adsorb water, but also contain oxygen in various other forms, possibly end groups, intermediate amide and hydroxy imidazoline structures, secondary ether and phenolic groups, imidazole-water complexes, and unknown oxidation products. Water, carbon monoxide and carbon dioxide are decomposition products of these moieties.

Thermal breakdown of the aromatic rings proceeds via formation of hydrogen and methane, and decomposition of the imidazole structure yields some hydrogen cyanide and ammonia, although most of the nitrogen is retained in the residue, possibly in the form of other heterocyclic, highly condensed structures.

It was interesting to observe that a prepolymer seemed to fragmentize rather than condense on further heating. A polymer with an ether linkage also formed chain fragments. Methyl- and carbomethoxy substitution on the imidazole ring yielded proportionately larger amounts of methane. A polymer with a tetrachlorophenylene moiety lost all of its chlorine as hydrochloric acid, and most of its nitrogen as hydrogen cyanide. And a polybenzimidazole with a polysiloxane-alkylene chain decomposed via fragmentation of this chain.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Pyrolysis						
Degradation						
Decomposition						
Thermal Stability						
Mechanism						
Mass Spectroscopy						
Polymer						
Polybenzimidazoles						