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STUDIES OF THE BREAKDOWN MECHANISM OF POLYMERS

III. THE THERMAL DECOMPOSITION OF AROMATIC POLYAMIDES AND POLYIMIDES

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

TECHNICAL REPORT AFML-TR-67-428

APRIL 1968

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STUDIES OF THE BREAKDOWN MECHANISM OF POLYMERS

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FOREWORD

This report was prepared in 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," and under Project No. 7360, "Materials Analysis and Evaluation Techniques," Task No. 736005, "Compositional Atomic and Molecular Analysis." It was administered under the direction of the Air Force Materials Laboratory, for which Dr. G. F. L. Ehlers was project engineer. The authors wish to thank W. J. Crawford for his contributions in interpreting the infrared spectra.

The manuscript was released by the authors in December 1967 for publication as an AFML technical report.

This technical report covers work conducted from January to August 1967. This technical report has been reviewed and is approved.

WE Gibbs

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

ABSTRACT

The breakdown mechanism of an aromatic polyamide and four polyimides has been studied.

The decomposition of the polyamide in the temperature range below 375°C yielded predominantly carbon dioxide, while between 375° and 450°C about equal amounts of carbon dioxide and carbon monoxide formed. Hydrogen is the major product between 450° and 550°C, along with hydrogen cyanide, methane, and carbon monoxide. The major reaction at the lower temperatures seems to be the cleavage of the linkage between the carbonyl group and the ring, with subsequent formation of a carbodiimide linkage via isocyanate intermediates. At higher temperatures, cleavage between the carbonyl and the —NH— group takes place.

The results of the decomposition of the four polyimides are not only quite similar to each other, but also similar to the polyamide. It is remarkable that the polyimides form carbon dioxide to a considerable extent in the lower temperature ranges (below 450°C). The primary cleavage reaction is believed to be the rupture of the imide ring between a carbonyl and nitrogen, with formation of an isocyanate group which reacts with another isocyanate group to form a carbodiimide linkage and carbon dioxide.

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INTRODUCTION

GENERAL

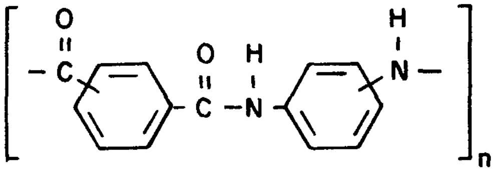
The work reported here is a continuation of a study begun in October 1965. The first report (AFML-TR-67-89) covered the thermal decomposition of polyphenylenes, polyphenylene sulfide, polyphenylene oxides, and polyphenylene sulfone. The second report (AFML-TR-67-295) contained decomposition studies of aromatic and aromatic-fluoroaliphatic polyesters and a polyarylene sulfonate. In the present report, some aromatic polyamides and polyimides were investigated.

As described in the earlier reports, the decomposition studies were conducted under vacuum at several temperatures. The selection of the temperature was based on TGA data but was modified to yield amounts of gases sufficient for mass spectroscopic analysis. The residues were subjected to elemental analysis, and their infrared spectra were taken.

The approximate weight of the volatiles at each step was calculated from the composition of the gases, the known volume of the apparatus, and the pressures obtained. The difference between the total weight loss and the weight of the volatiles can be assumed to be caused by sublimate, other liquids, and solids, all of which were usually deposited on the cell walls during the first temperature step. (In most cases the amounts of the deposits were too small for fractionation and elemental analysis.) The deposits were removed and an IR spectrum of each deposit was taken; the resulting spectrum was usually very similar to the IR spectrum of the original polymer.

The thermal decomposition of the following five polymers was studied:

I



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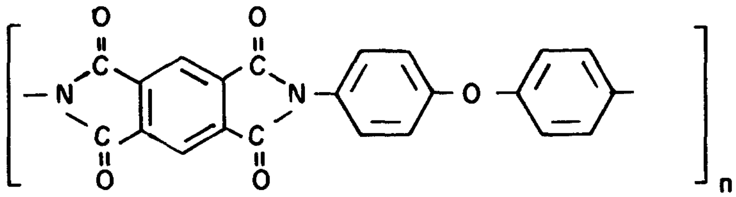

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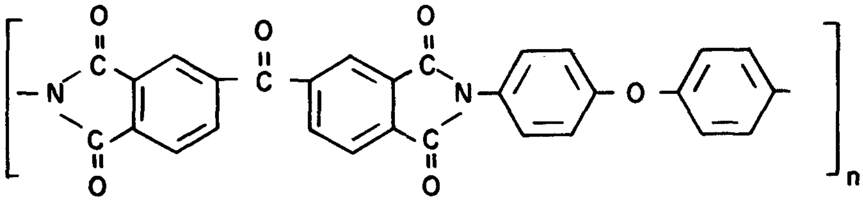
III



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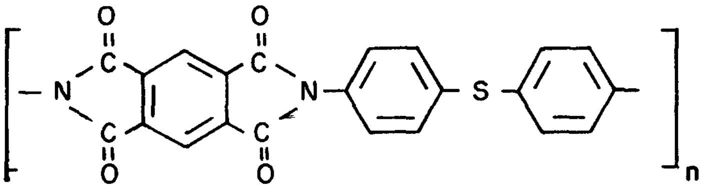
IV



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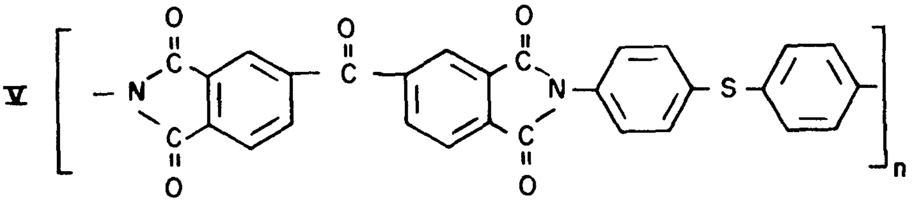
V



Code : Resin I-9

Before describing the results in detail, earlier work on the decomposition of polyamides and polyimides will be reviewed.

PREVIOUS WORK ON THE DECOMPOSITION OF POLYAMIDES AND POLYIMIDES

The decomposition of aliphatic polyamides, especially Nylon 6, Nylon 6, 6, and Nylon 6, 10, has been studied by a number of authors. Only some of this work can be cited here. Achhammer and coworkers (Reference 1) pyrolyzed copolymers of Nylon at 400°C and obtained carbon monoxide, carbon dioxide, hydrocarbons, and cyclopentanone, but no nitrogen compounds. Hasselstrom and coworkers (Reference 2), however, found considerable amounts of ammonia during the pyrolysis of Nylon 6, 6. Kamerbeck and coworkers (Reference 5) pyrolyzed Nylon 6 and 6, 6 at moderate temperatures (305°C) and obtained ammonia, carbon monoxide, and water. Straus and Wall (References 3 and 4) found carbon dioxide and water but no ammonia at pyrolysis temperatures between 310° and 380°C. They ascribed the water formed to water originally absorbed by the material. They also suggested that chain scission occurs in a position β to the carbonyl group as indicated by the dashed lines

$$-CH_2 \vdots CH_2 - CO - NH \vdots CH_2- \tag{1}$$

with the $-NH-CH_2-$ bond being the weaker of the two. Based on this assumption, they postulated the following breakdown mechanism:

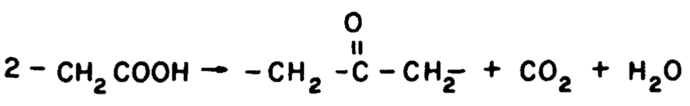
$$\text{Structure (1)} \rightarrow -CH_2-CH_2-CONH_2 + CH_2=CH- \tag{2}$$

$$-CH_2-CH_2-CONH_2 \rightarrow -CH_2-CH_2-C\equiv N + H_2O \tag{3}$$

The water thus formed hydrolyzes another amide linkage

$$-CH_2-CO-NH-CH_2- + H_2O \rightarrow -CH_2-COOH + H_2N-CH_2- \tag{4}$$

Two carboxyl groups may react in the following manner:



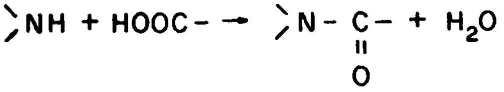
$$2-CH_2COOH \rightarrow -CH_2-\overset{O}{\overset{\|}{C}}-CH_2- + CO_2 + H_2O \tag{5}$$

whereas two amino groups might form a secondary amine and ammonia:

$$2-CH_2NH_2 \rightarrow -CH_2NHCH_2- + NH_3 \tag{6}$$

The carbonyl and secondary amino groups may subsequently react in the following manner:

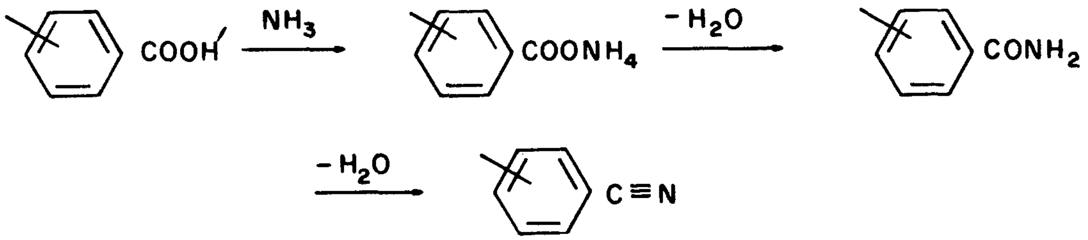
$$>C=O + H_2N- \rightarrow >C=N- + H_2O \qquad (7)$$



$$>NH + HOOC- \rightarrow >N-\overset{}{\underset{\underset{O}{\|}}{C}}- + H_2O \qquad (8)$$

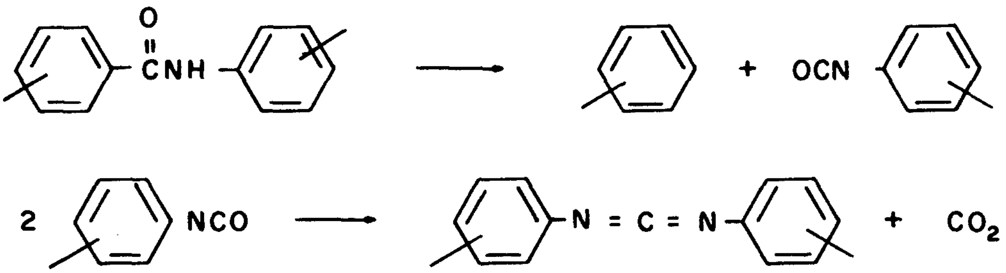
This mechanism accounts for the three major volatiles: CO_2, NH_3, and H_2O, found during the decomposition of aliphatic polyamides.

Little is known about the decomposition mechanism of aromatic polyamides. Krasnov and coworkers (Reference 6) subjected polyamides made from meta- and para-phenylenediamine and iso- and tere-phthalic acid to decomposition under vacuum at temperatures between 320° and 530°C. Semiquantitative results of the mass spectrometric analysis showed carbon dioxide and water as the major volatile products at the lower temperature ranges, and undetermined amounts of carbon monoxide. At the higher temperatures, benzene and hydrogencyanide also formed to a considerable extent, along with toluene, benzonitrile, some hydrogen, and in two out of four cases, also ammonia. The authors concluded that intense hydrolytic reactions of amide bonds occur, with subsequent decarboxylation of the carboxyl end groups. From the formation of benzonitrile, they assumed that the water for the hydrolytic reactions is formed by dehydration of ammonium salt or amide end groups:



(9)

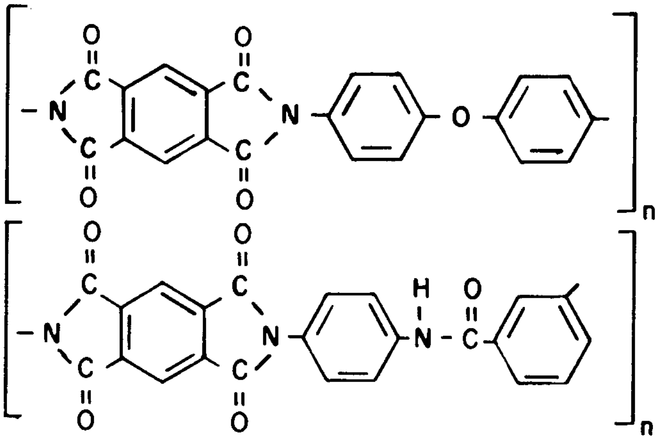
They also considered the possibility of intermediate isocyanate groups with subsequent formation of a carbodiimide linkage:



(10)

Other more complex reactions may also occur, as indicated by the presence of hydrogen, carbon monoxide, hydrogen cyanide, and toluene.

Some work concerning the thermal decomposition and analysis of pyrolysis products of polyimides, has been reported recently. Heacock and Berr (Reference 7), on vacuum pyrolysis of H-film at 540°C, found the following products (mole percent in parentheses): benzene (0.7), carbon dioxide (35.1), carbon monoxide (58.7), water (1.2), hydrogen (2.6), ammonia (traces), hydrogen cyanide (1.2), and benzonitrile (0.5). Forty to sixty percent of the weight loss consisted of gases; the remainder was liquid and solid, containing aminophenolic and phthalimide groups. Bruck (Reference 8) pyrolyzed H-film under vacuum at 600°C and collected mainly carbon dioxide, carbon monoxide, hydrogen, water, hydrogen cyanide, ammonia, and some small amounts of hydrocarbons, such as aniline, benzene, phenol, and benzonitrile. He believed that carbon dioxide results from the thermal decarboxylation and hydrolysis of polyamic acid groups, and that only carbon monoxide results from the imide group. He concluded, therefore, that H-film contains 22% polyamic acid. Scala and Hickam (Reference 9) oxidized the following two polyimide resins

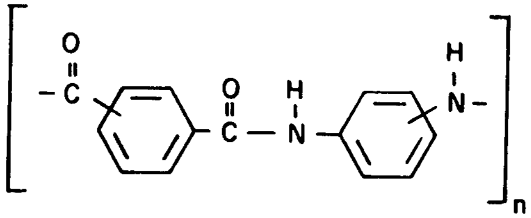


(II)

in air, oxygen, and 0^{18} enriched oxygen. The major decomposition products were carbon dioxide, carbon monoxide, and water. Nitrile groups were identified in the distillate. Hydrogen cyanide and nitric oxide were also observed.

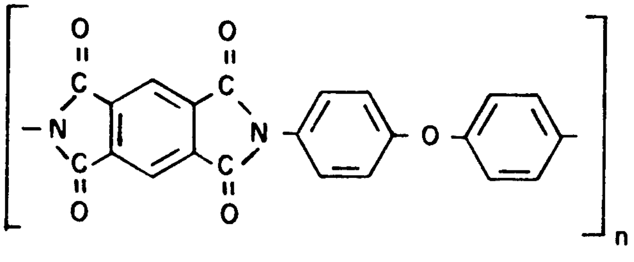
BRIEF DESCRIPTION OF POLYMERS STUDIED IN THE PRESENT REPORT

Polymer I, Sterically Ordered Aromatic Polyamide (Code: X-101)



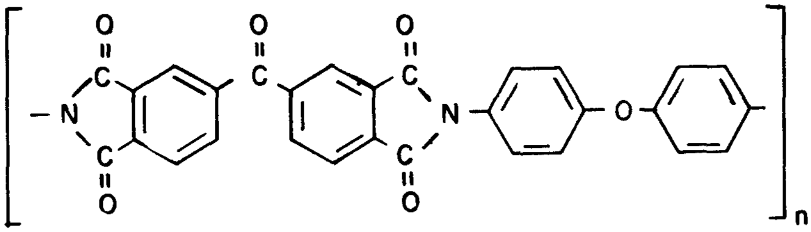
Polyamide X-101 was obtained from Chemstrand Research Center, Inc., in 1964. It is a sterically ordered, fully aromatic polyamide with an inherent viscosity of 1.67, presumably in methane sulfonic acid. Studies conducted by the U. S. Rubber Company under Air Force Contract (Reference 10) showed that the polymer was essentially amorphous. DTA seemed to indicate a second order transition at 275°C and endotherms at 430° and 460°C related to thermal decomposition. Our own DTA measurements showed a second order transition at 277°C and an irregular pattern of endotherms and exotherms beginning at 397°C.

Polymer II, Polyimide from Diaminodiphenylether and Pyromellitic Dianhydride (Code: Resin I-1)



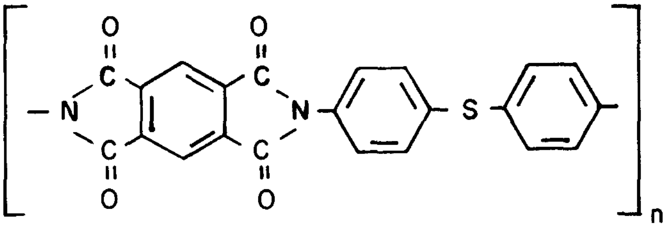
This polymer has been prepared as a film from diaminodiphenylether and pyromellitic dianhydride by the Research Laboratories, Westinghouse Electric Corporation, under Air Force Contract (Reference 13). The polymerization was performed in dimethylacetamide below 60°C. The T_g of the polymer (from dissipation factor increase at 1 kc) was 380°C. Thermogravimetric analysis under nitrogen and air (Figures 19 and 20) shows that the stability of this polymer and that of the other three polyimides is very similar.

Polymer III, Polyimide from Diaminodiphenylether and Benzophenone Tetracarboxylicdianhydride (Code: Resin I-7)



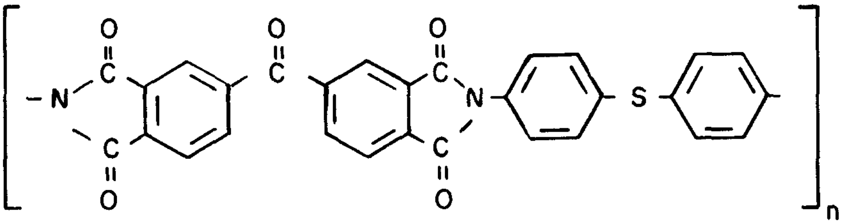
This film sample is a benzophenone analog of the sample described above and has also been prepared by Westinghouse Electric Corporation (Reference 13). Its T_g is 330°C.

Polymer IV, Polyimide from Diaminodiphenyl Sulfide and Pyromellitic Dianhydride (Code: Resin I-6)



Also a film sample, this polymer has been prepared by Westinghouse Electric Corporation from pyromellitic dianhydride and diaminodiphenyl sulfide. It has been extensively investigated as laminating resin. The T_g of the film sample was 350°C.

Polymer V, Polyimide from Diaminodiphenyl Sulfide and Benzophenone Tetracarboxylicdianhydride (Code: Resin I-9)



This is another film sample prepared by Westinghouse (Reference 12). Only limited data are available. Its T_g is 360°C.

DISCUSSION

DECOMPOSITION STUDY OF POLYMER I

Figure 18 shows the results of thermogravimetric analysis of the polymer, with a distinct onset of decomposition at 410°C for the run under nitrogen and at 370°C for the vacuum run. The infrared spectra (Figures 1 and 2) of the original polymer and the residue at 380°C are almost alike, with the exception of a band in the latter at 700 cm^{-1}; this band may result from monosubstituted aromatic rings (more end groups). The spectra of the residues at 450° and 550°C are inconclusive with the exception of the above mentioned bands.

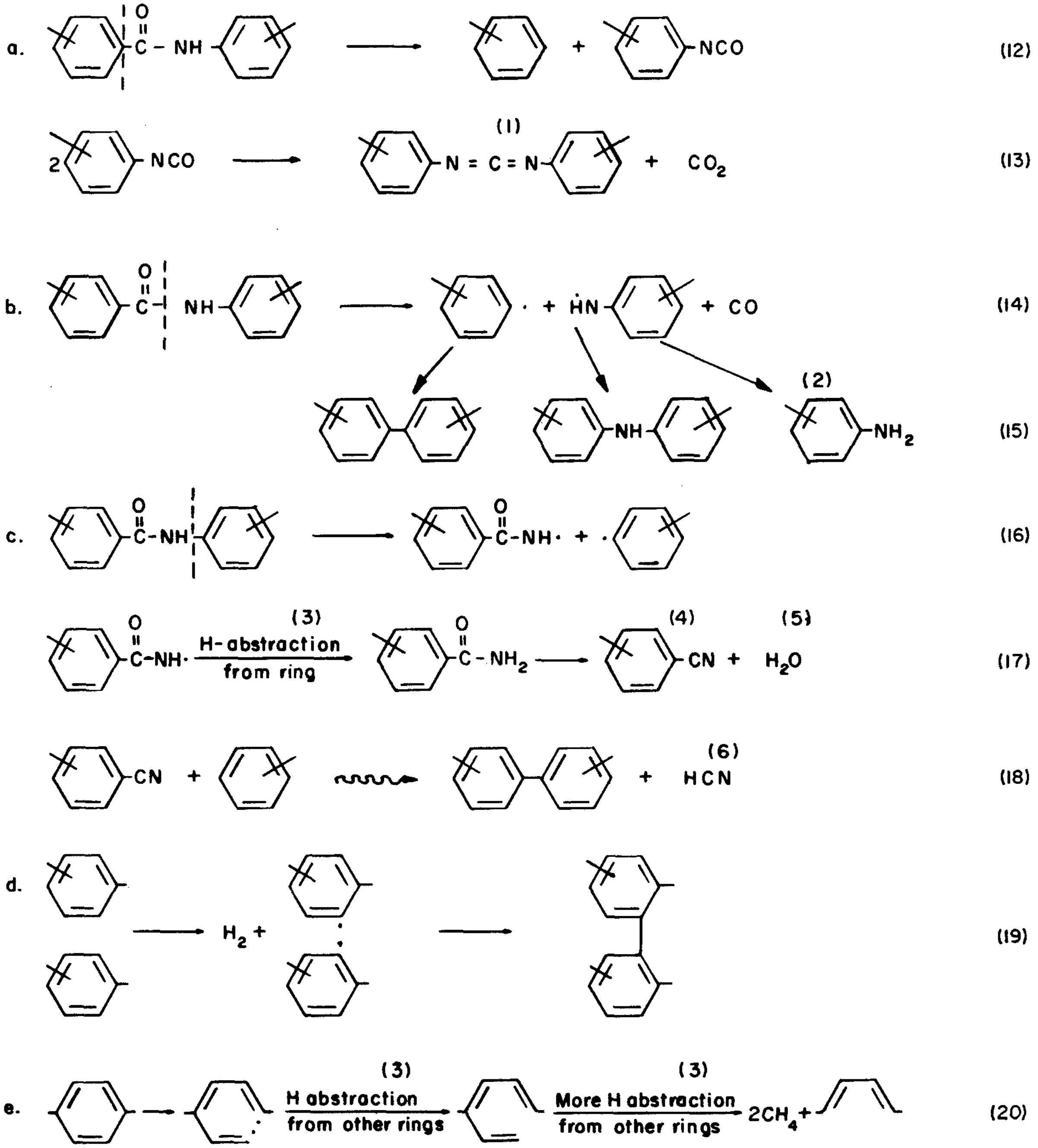
Table I, containing the analytical results of the polymer, the residues and volatiles, shows a lack of agreement between calculated and found data for the original polymer. It also indicates that a major part of the volatile decomposition products must be solids or liquids at room temperature (difference between weight loss of volatiles and total weight loss).

Originally, the sample had been run after keeping it in a vacuum desiccator for several days. The run yielded 8.6% water at 375°C, 4.7% at 450°C, and 1.5% at 550°C. The run was repeated after the sample was dried for 48 hours under vacuum at 80°C. This time, an insignificant amount of water had formed (Table I). Carbon dioxide is the major volatile decomposition product in the lower temperature ranges. Between 375° and 450°C, the carbon dioxide content decreases, while carbon monoxide reaches a peak, and hydrogen formation is noticeably increased. At the highest temperature range, hydrogen is the major product while some hydrogen cyanide, methane, and carbon monoxide are also formed. Nitrogen is given off only in the form of hydrogen cyanide, and no ammonia is formed. The overall loss of nitrogen is low, which is confirmed by the analytical data of the residues.

There may be an inclination to explain the breakdown of aromatic polyamides as being analogous to that of aliphatic polyamides. A rupture of the iminophenyl linkage may occur first. After abstraction of hydrogen from a ring, an amide end group is formed which gives off water to form a nitrile. The water, in turn, hydrolyzes another amide linkage with formation of a carboxyl and an amino end group. The carboxyl group finally decarboxylates to form carbon dioxide as the major volatile decomposition product at lower temperatures.

The following objections can be made against such a mechanism as a major path of breakdown: Since one mole of water is required to form one mole of carbon dioxide, a considerable amount of water must be produced, and a reasonably large part of this would be expected to evolve as free water. However, practically no free water is formed. Furthermore, the above mechanism seems to be rather long and complex for the production of the first and major decomposition product at lower temperatures.

It seems to us that the mechanism considered as a possibility by Krasnov and coworkers (Reference 6), namely the formation of a carbodiimide linkage via isocyanate groups, has merit. Diphenylcarbodiimide, for example, forms with the evolution of carbon dioxide, when phenylisocyanate is heated to 180°C in a sealed tube. The mechanism leading to the five major gaseous decomposition products (carbon dioxide, carbon monoxide, hydrogen, hydrogen cyanide, and methane) would be as follows (superscript numbers pertain to footnotes concerning Equations 12 through 20):



(1) It may form a heterocyclic system at higher temperatures.
(2) Preliminary results of another investigator (Reference 11) show that this polymer forms aniline during decomposition.
(3) A highly crosslinked, carbonaceous structure remains.
(4) Another investigator (Reference 11) found benzonitrile during decomposition of this polymer.
(5) Water may hydrolyze amide linkages as described above.
(6) Another mechanism for the formation of hydrogen cyanide which does not simultaneously yield water is given below (Equation 25 and 26).

From the amounts of volatiles evolved at the different temperature ranges, we can assume that part a) of the mechanism is the preferred route at lower temperatures, and route b) in the medium temperature range, while route c) may occur at higher temperatures.

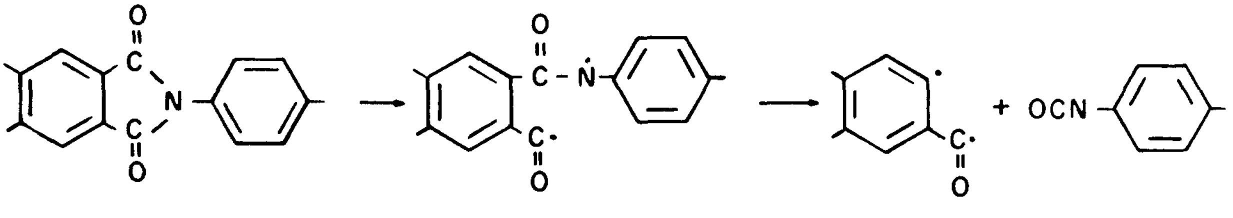
DECOMPOSITION STUDIES OF POLYMERS II THROUGH V

As can be seen from Tables II through V, the results of the decomposition tests are very similar, if the small amount of sulfur-containing decomposition products of polymers IV and V is disregarded. It can even be claimed that there is hardly a significant difference between the data obtained from the polyimides and those from the polyamide I. Polymers III and V, with a benzophenone carbonyl, seem to form more carbon monoxide and less carbon dioxide than the other two polymers. Those with the sulfide linkage produce some hydrogen sulfide especially above 400°C, and some carbonoxysulfide with a peak temperature between 400° and 450°C.

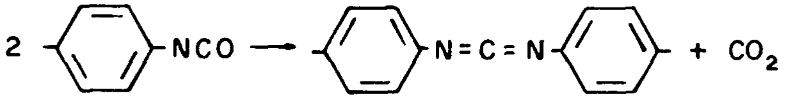
The infrared spectra (Figures 3-17) show very much similarity between the original polymers and the residues at 400°C; as the tables indicate, there is little weight loss up to that point. Changes which occur in the spectra thereafter are the disappearance of bands in the region between 700 and 1200 cm^{-1}. To a large extent, these may be substitution bands which change with bond rupture and crosslinking. In the spectra of polymers III to V, a sharp band appears at 2200 cm^{-1}, which may be a $C \equiv N$ valence band (see the mechanism which follows).

The imide band at 1775 cm^{-1} and the imide substitution band at 723 cm^{-1} (Reference 14) disappeared at 550°C. In the case of polymer V, one of the two bands (723 cm^{-1}) had disappeared already at 450°C.

The key to the breakdown mechanism of polyimides is the formation of carbon dioxide. Bruck (Reference 8) believes, as has already been pointed out, that carbon dioxide results from the decarboxylation and hydrolysis of polyamic acid groups, whereas carbon monoxide is contributed by the imide group. If this reasoning is applied to the polyimides evaluated, it would mean that in view of the considerable carbon dioxide evolution, a large amount of polyamic acid should still be present. The analyses of the polymers, however, especially the oxygen analyses, do not confirm this. Furthermore, we would expect that, on heating, the polyamic acids would continue to cyclize rather than to decarboxylate. As far as hydrolysis is concerned, the question arises concerning the origin of the required water. Our polymers did not contain any appreciable amount of water. We believe, therefore, that the following mechanism applies:

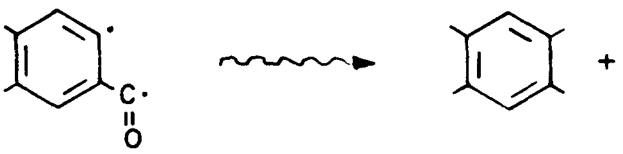


(21)



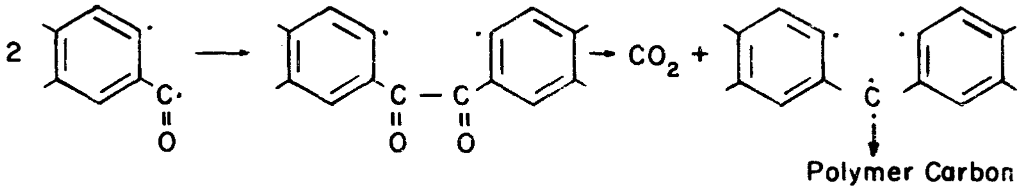
(22)

The carbodiimide linkage may convert to a heterocyclic system at higher temperatures.



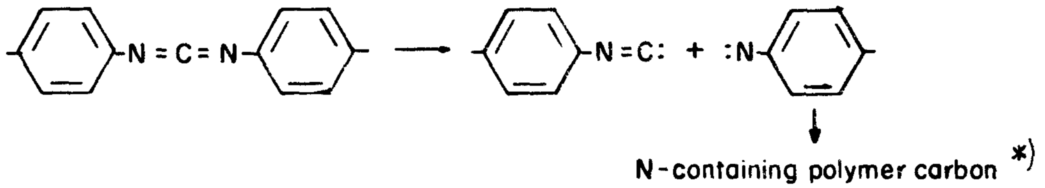
(23)

According to this mechanism the carbon monoxide/carbon dioxide ratio should be 2. Rough calculations based on total amount of volatiles and mole percent of gases place the actual ratio at approximately 1.1 to 1.5. Only the two polymers with a carbonyl linkage (III and V) approach the above ratio; here, the carbonyl linkage contributes to the formation of carbon monoxide. Carbon monoxide formation also occurs when the ether linkage in polymers II and III degrades (Reference 12). Therefore, an additional path of formation of carbon dioxide must exist. The following mechanism seems to be feasible at higher temperatures:

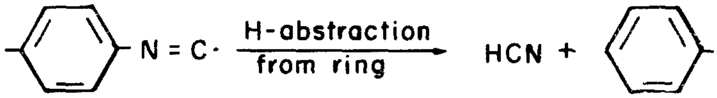


(24)

The formation of hydrogen cyanide may occur according to:

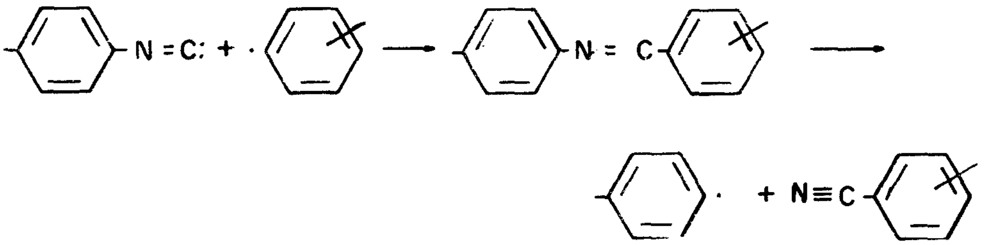


(25)



(26)

Nitrile formation may occur according to the following mechanism:



(27)

The hydrogen sulfide in the sulfur-containing polymers IV and V can be expected to form according to the mechanism explained earlier (Reference 12) and the carbonoxysulfide may result from the reaction of hydrogen sulfide with carbon dioxide. The contribution of the carbonyl and ether linkages to the formation of gaseous products has been mentioned before. The formation of hydrogen and methane occurs essentially according to the mechanisms in Equations 19 and 20.

---

*) As can be seen from Tables II to V, the polymer residues retain the major part of the nitrogen.

EXPERIMENTAL PROCEDURE

The apparatus used for the decomposition studies has been described previously (Reference 12). It consisted of a Vycor test cell (the remainder of the apparatus being Pyrex), fitted with a thermocouple well and connected to a sample cell, manometer, vacuum pump, and nitrogen inlet. The test cell was heated by means of a 750W furnace, controlled by an F&M Model-240M Power Proportioning Temperature Programmer; the temperature control was within ±5°C.

The polymer was dried under vacuum at 110°C overnight and 0.2 g was weighed into a porcelain crucible. The crucible was placed into the test cell and the system was twice evacuated and flushed with nitrogen. The sample cell was degassed by heating with a heat gun. The system was then evacuated to 30-50μ and the valves closed. The controller was set at the desired temperature, the furnace was turned on, and temperature, time, and pressure were recorded at 2-minute intervals. When no further pressure increase was noted between two consecutive readings, the accumulated gases were permitted to diffuse into the sample cell. The sample cell was taken off, a new cell attached, and the system again evacuated and twice flushed with nitrogen. After reestablishing a vacuum of approximately 30-50μ, the furnace temperature was raised to the next higher temperature and the procedure repeated. Selection of the test temperatures was based on information from TGA and from an exploratory run, in order to obtain an appropriate amount of pressure. The final residue was collected and subjected to elemental analysis, weight loss determination, and infrared spectroscopy. Residues for the first two temperature steps were obtained by subjecting two separate samples to the identical history of the original sample up to the first two temperatures, respectively. They were also analyzed as indicated above. In connection with the collection of the first residue, the sublimate formed was isolated, whenever possible, and examined at least by infrared spectroscopy.

MASS SPECTROSCOPY

The gas samples were analyzed in a Consolidated Electrodynamics Corporation Model 21-103B (modified) mass spectrometer. An ionizing voltage of 70 volts and an ionizing current of 10 microamperes were used.

INFRARED SPECTROSCOPY

Infrared spectra were obtained by use of a Perkin-Elmer Infrared recording spectrophotometer Model 137 and potassium bromide pellets. The polymers and especially the residues were shaken 1-4 min. in steel vials in a Wig-L-Bug and sifted through brass sieves. The part with a particle size below 74μ was collected. Depending upon the darkness of the materials, 0.25 to 0.7% of the polymer in KBr were used. The infrared spectra shown in Figures 2, 4, and 13 were originally run singly and then transposed onto a single chart for comparison.

ELEMENTAL ANALYSIS

Elemental analyses were performed by the Analytical Branch, Air Force Materials Laboratory, in duplicate. The data given represent mean values.

REFERENCES

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TABLE I

ANALYSES OF VOLATILES AND RESIDUES OF POLYMER I

	C	H	O	N
Analysis calc. for $(C_{14}H_{10}O_2N_2)_n$:	78.6	4.2	11.8	13.4
Analysis found for polymer:	65.5	4.6	16.9	11.0
Analysis found for residue 375°C:	71.4	4.3	10.1	12.0
Analysis found for residue 450°C:	80.0	3.7	1.9	12.2
Analysis found for residue 550°C	83.4	2.9	2.6	10.0

Temp. Range °C	Volatile Products (mole %)								Weight Volatiles (%)*	Total Weight Loss (%)*
	$C_6H_5CH_3$	C_6H_6	CO_2	CO	HCN	H_2O	CH_4	H_2		
20-375	-	0.3	86.6	11.5	0.4	0.6	0.1	0.5	9.2	26.5
375-450	0.2	1.7	40.2	44.4	1.5	0.4	1.8	0.8	8.0	22.5
450-550	-	0.8	2.7	8.0	12.4	0.5	9.1	66.5	3.9	5.5

* Percent of starting material

TABLE II

ANALYSES OF VOLATILES AND RESIDUES OF POLYMER II

	C	H	O	N
Analysis calc. for $(C_{22}H_{10}O_5N_2)_n$:	69.1	2.7	20.9	7.3
Analysis found for polymer:	67.8	2.8	20.1	7.6
Analysis found for residue 400°C:	69.4	2.9	18.9	7.9
Analysis found for residue 450°C:	75.5	3.4	9.9	8.4
Analysis found for residue 550°C:	80.8	2.9	2.5	7.7
Analysis found for residue 620°C:	83.2	2.1	2.6	6.3

Temp. Range °C	Volatile Products (mole %)							Weight Volatiles (%)*	Total Weight Loss (%)*
	C_6H_6	CO_2	CO	HCN	H_2O	CH_4	H_2		
20-400	0.2	78.0	19.7	0.2	0.5	0.4	1.0	~ 3.4	3.4
400-450	0.1	43.7	53.0	0.2	-	0.4	2.6	17.4	27.5
450-550	0.2	11.1	46.3	4.3	0.4	5.6	32.1	8.8	9.8
550-620	1.2	1.0	23.6	3.7	0.3	8.6	61.6	4.1	5.1

* Percent of starting material

TABLE III

ANALYSES OF VOLATILES AND RESIDUES OF POLYMER III

	C	H	O	N
Analysis calc. for $(C_{29}H_{14}O_6N_2)_n$:	71.6	2.9	19.7	5.8
Analysis found for polymer:	70.6	3.1	18.8	5.8
Analysis found for residue 400°C:	70.9	2.9	17.8	6.4
Analysis found for residue 450°C:	75.0	3.1	12.4	6.2
Analysis found for residue 550°C:	85.4	2.4	2.3	5.6
Analysis found for residue 620°C:	87.0	1.9	1.5	5.2

Temp. Range °C	Volatile Products (mole %)							Weight Volatiles (%)*	Total Weight Loss (%)*
	C_6H_6	CO_2	CO	HCN	H_2O	CH_4	H_2		
20-400	no data, insufficient amount of volatiles							-	2.8
400-450	0.2	37.7	60.1	0.3	0.8	0.1	0.8	18.3	18.9
450-550	0.4	20.7	52.3	2.0	0.6	3.8	20.2	~17.3	17.3
550-620	0.2	1.1	21.3	3.0	0.7	9.0	64.7	3.7	4.0

* Percent of starting material

TABLE IV

ANALYSES OF VOLATILES AND RESIDUES OF POLYMER IV

	C	H	O	N	S
Analysis calc. for $(C_{22}H_{10}O_4N_2S)_n$:	66.3	2.5	16.1	7.0	8.1
Analysis found for polymer:	insufficient material				
Analysis found for residue 400°C:	66.4	2.6	15.4	7.4	7.6
Analysis found for residue 450°C:	70.2	2.8	9.6	7.6	5.8
Analysis found for residue 550°C:	79.0	2.5	1.7	6.9	4.2
Analysis found for residue 620°C:	80.9	1.7	1.3	7.4	3.3

Temp. Range °C	Volatile Products (mole %)										Weight Volatiles (%)*	Total Weight Loss (%)*
	C_6H_6	CS_2	OCS	CO_2	H_2S	CO	HCN	H_2O	CH_4	H_2		
20-400	0.2	-	0.3	82.1	1.1	14.5	0.5	0.4	0.7	0.4	~ 4.2	4.2
400-450	0.2	-	3.8	41.0	5.9	45.9	1.0	0.8	0.1	1.2	23.4	24.8
450-550	0.4	0.1	1.6	24.7	6.5	49.2	4.8	0.2	1.1	11.4	~12.8	12.8
550-620	0.2	0.1	0.2	2.4	7.9	18.0	9.2	0.4	6.4	55.2	3.4	4.7

* Percent of starting material

TABLE V

ANALYSES OF VOLATILES AND RESIDUES OF POLYMER V

	C	H	O	N	S
Analysis calc. for ($C_{29}H_{14}O_5N_2S$) :	69.3	2.8	15.9	5.6	6.4
Analysis found for polymer:	68.3	2.8	16.2	5.6	6.7
Analysis found for residue 400°C:	73.8	3.1	14.2	5.9	4.1
Analysis found for residue 450°C:	70.1	3.0	10.0	5.8	3.8
Analysis found for residue 550°C:	80.5	2.6	2.2	5.5	3.6
Analysis found for residue 620°C:	79.8	2.2	2.2	4.5	3.0

Temp. Range °C	Volatile Products (mole %)									Weight Volatiles (%)*	Total Weight Loss (%)*
	C_6H_6	OCS	CO_2	H_2S	CO	HCN	H_2O	CH_4	H_2		
20-400	-	0.6	64.3	5.2	27.8	0.4	1.0	0.4	0.3	5.4	7.2
400-450	0.4	2.6	26.5	6.4	60.3	0.9	0.5	0.2	2.2	~11.7	11.7
450-550	0.5	0.9	19.1	3.9	48.6	4.4	0.5	2.4	19.7	16.1	20.6
550-620	0.3	0.1	1.3	5.2	12.8	4.9	0.7	8.4	66.3	3.8	5.3

* Percent of starting material

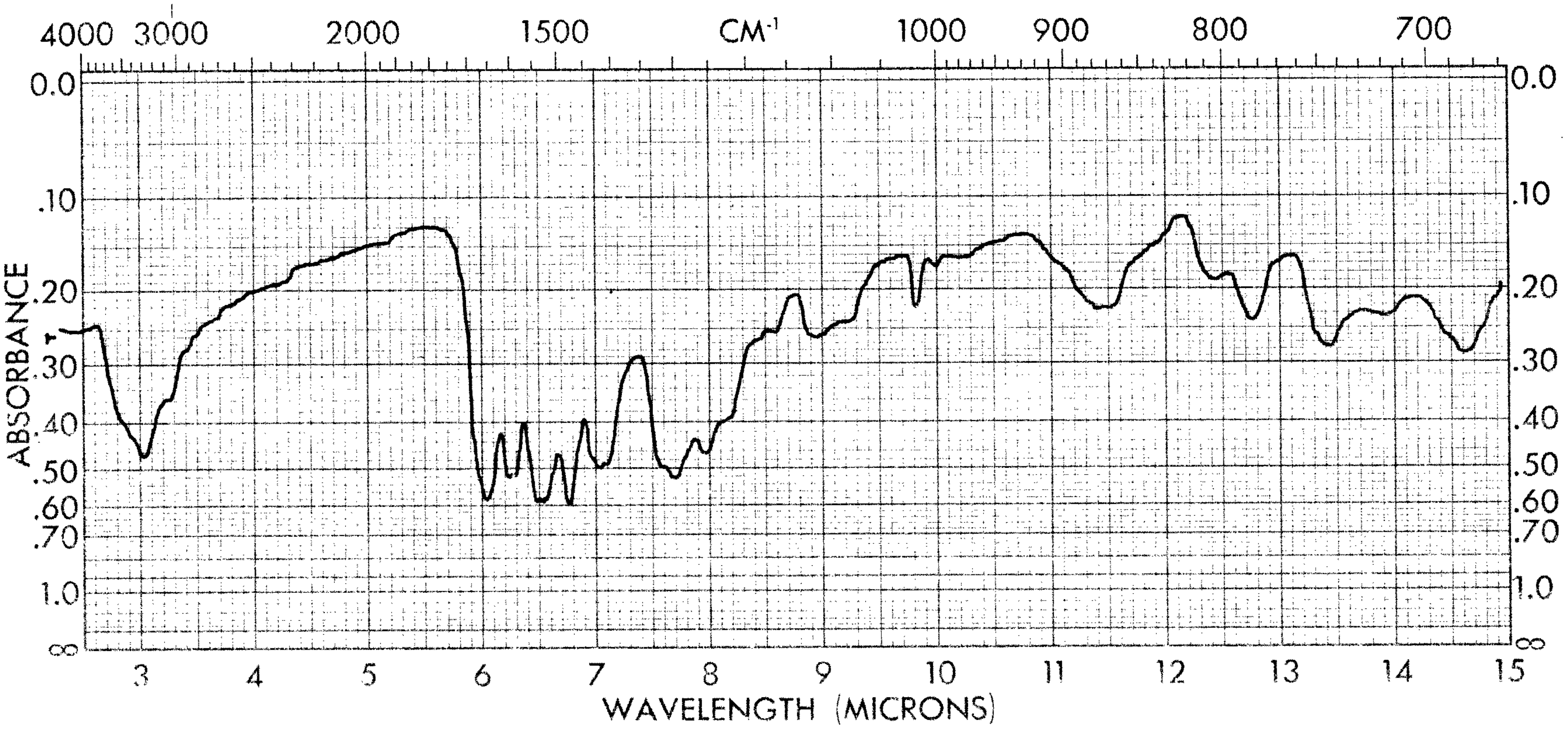

Figure 1. Infrared Spectrum of Polymer I

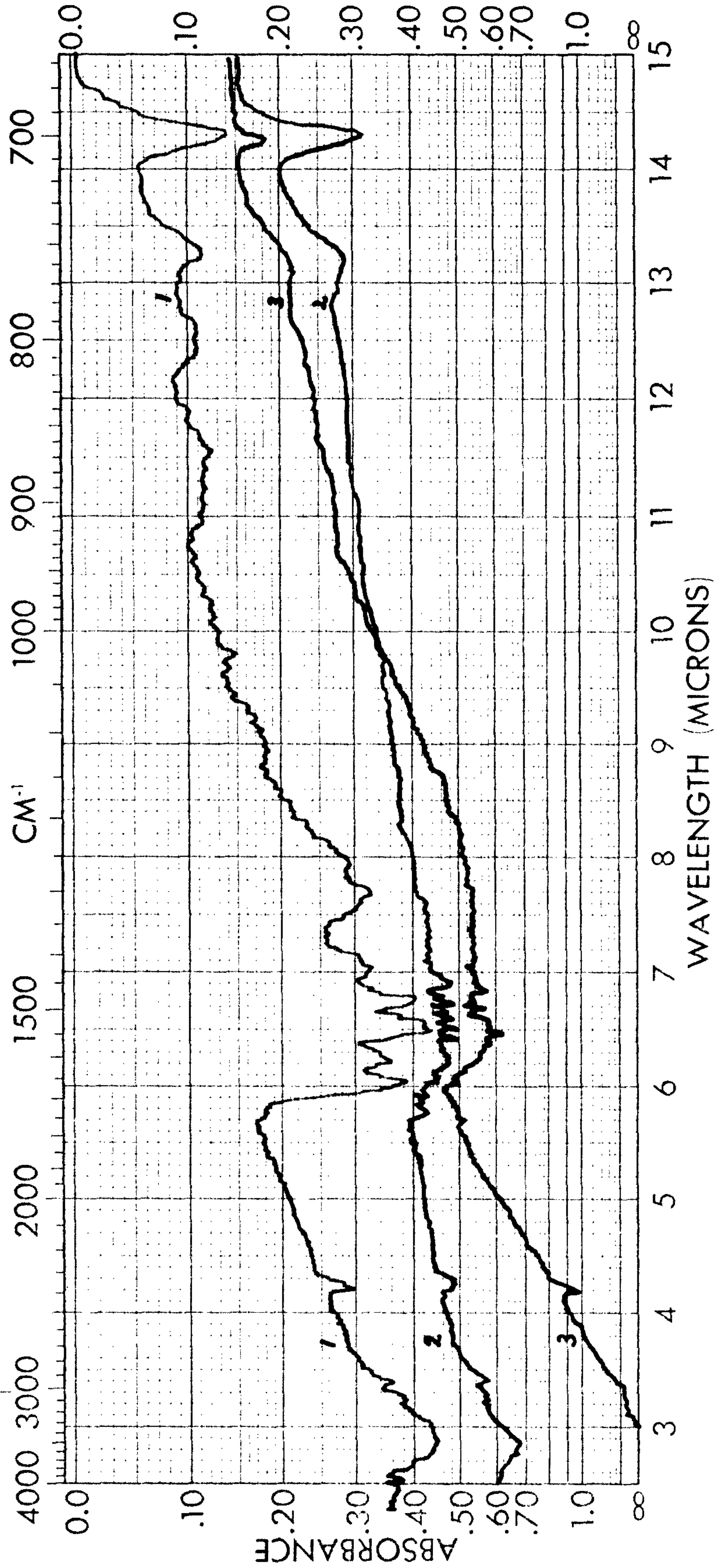

Figure 2. Infrared Spectra of Residues of Polymer I at 1: 380° C; 2: 450° C; 3: 550° C

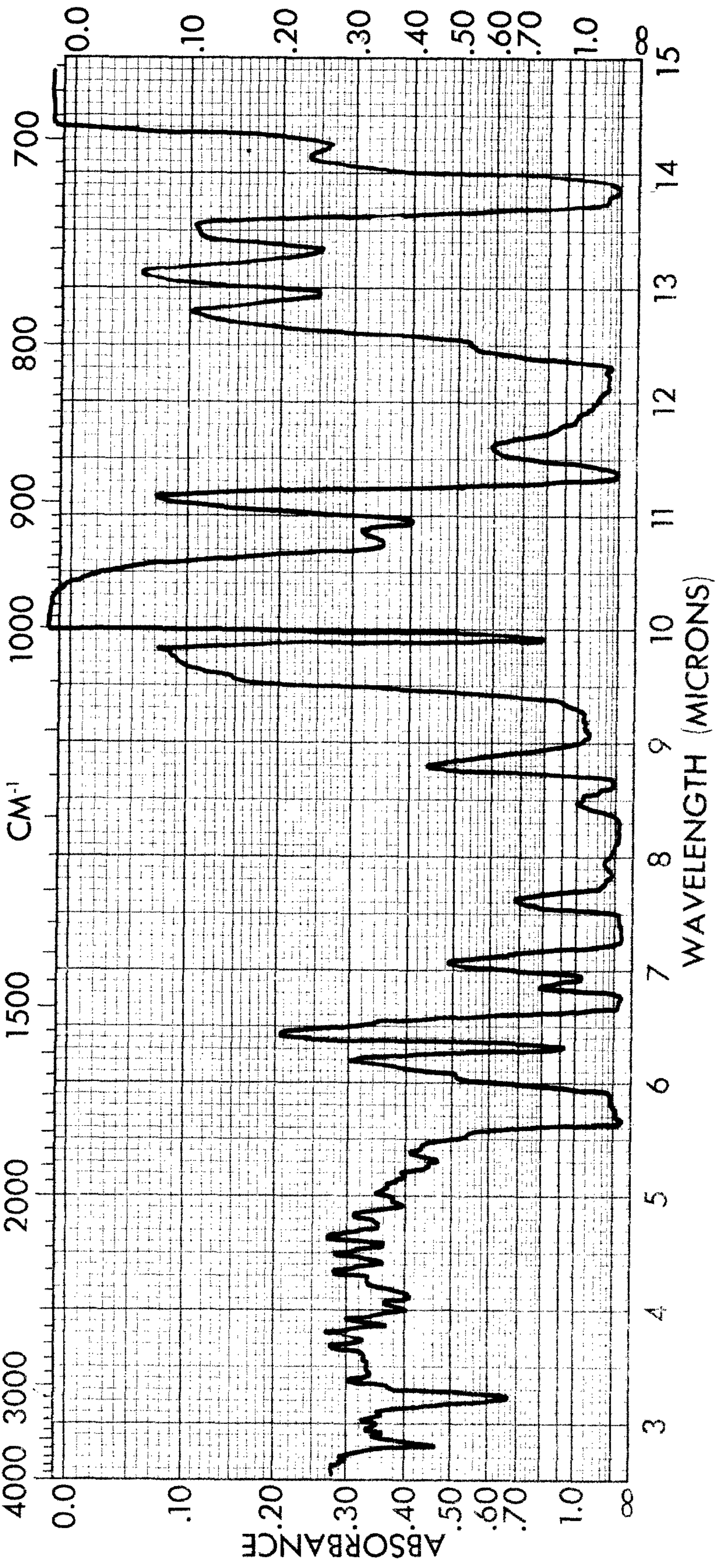

Figure 3. Infrared Spectrum of Polymer II

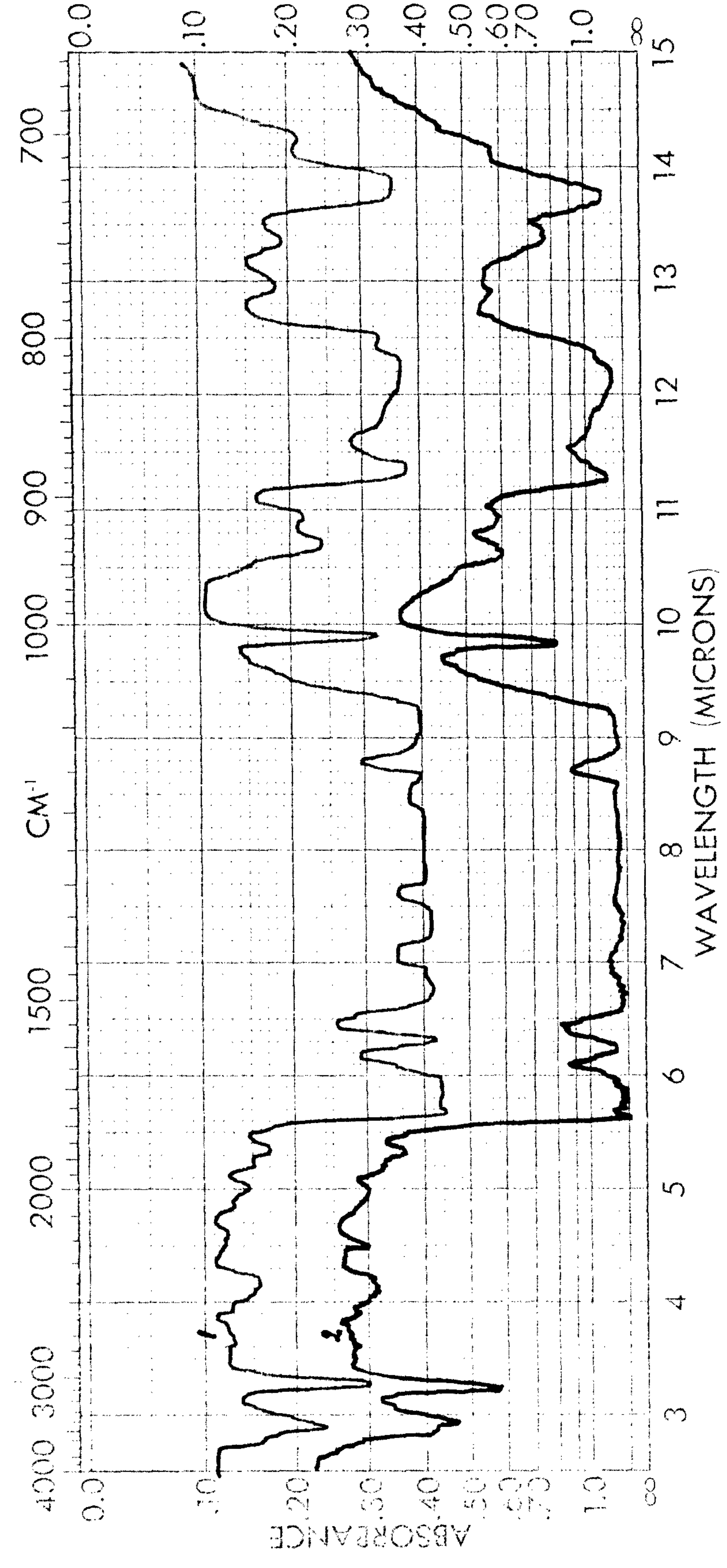

Figure 4. Infrared Spectra of the Residues of Polymer II at 1: 400° C; 2: 450° C

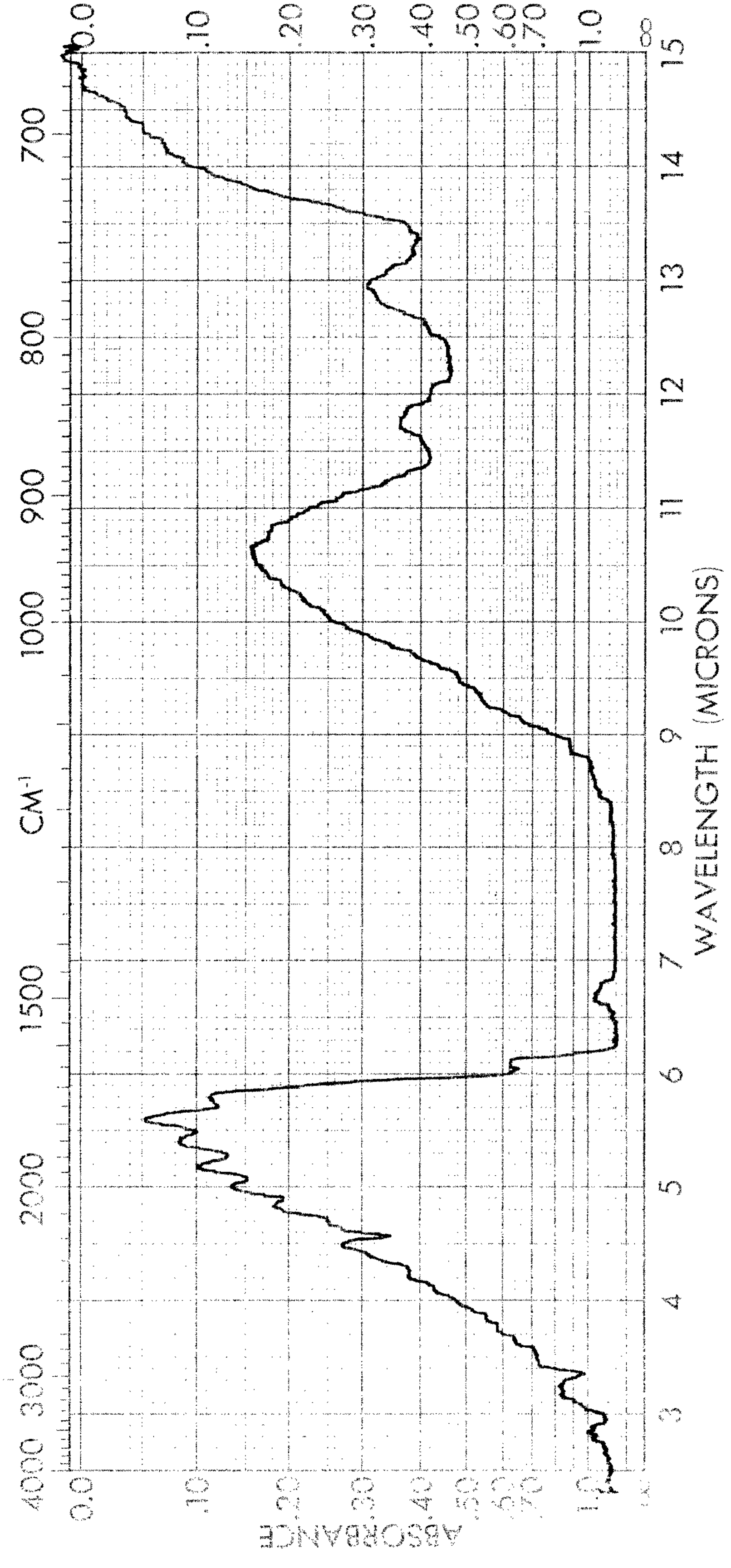

Figure 5. Infrared Spectrum of the Residue of Polymer II at 550° C

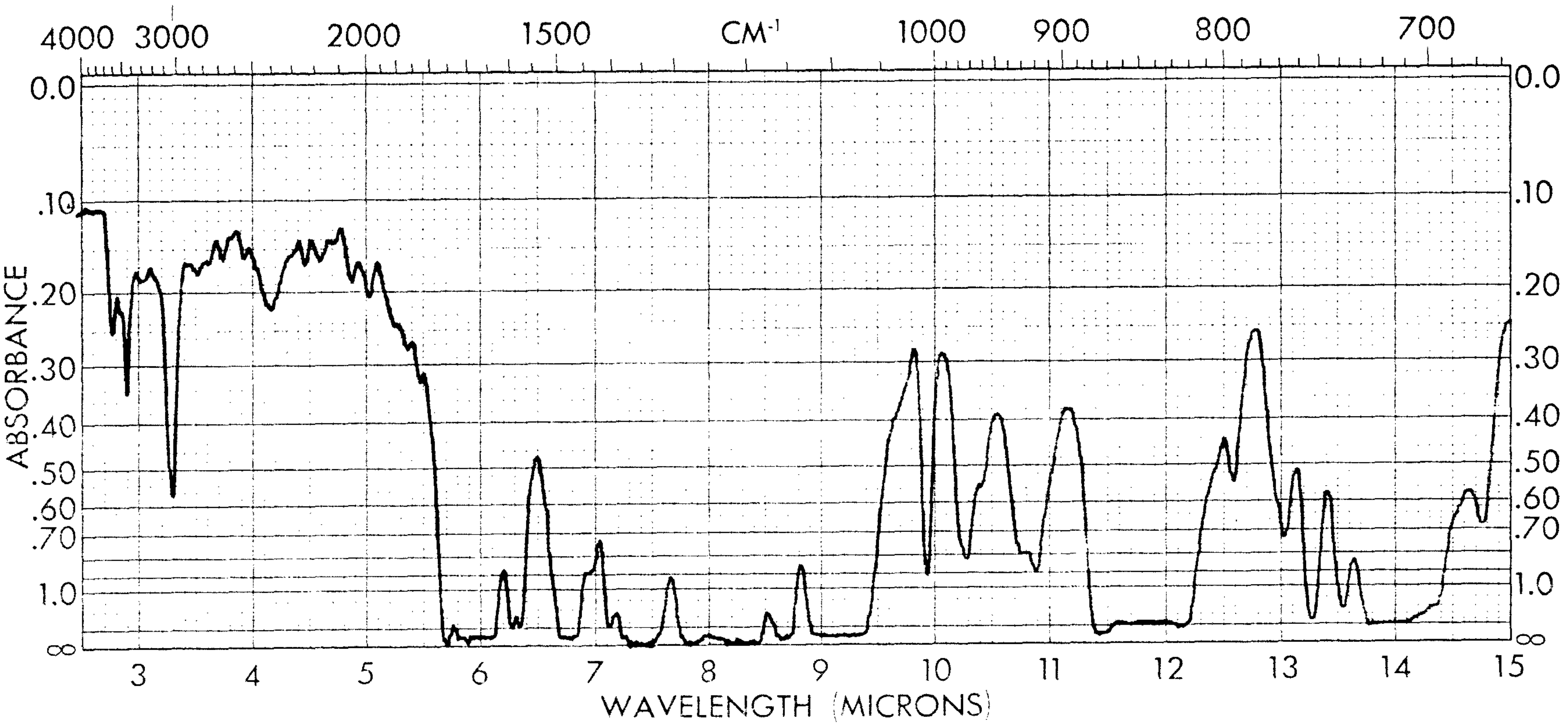

Figure 6. Infrared Spectrum of Polymer III

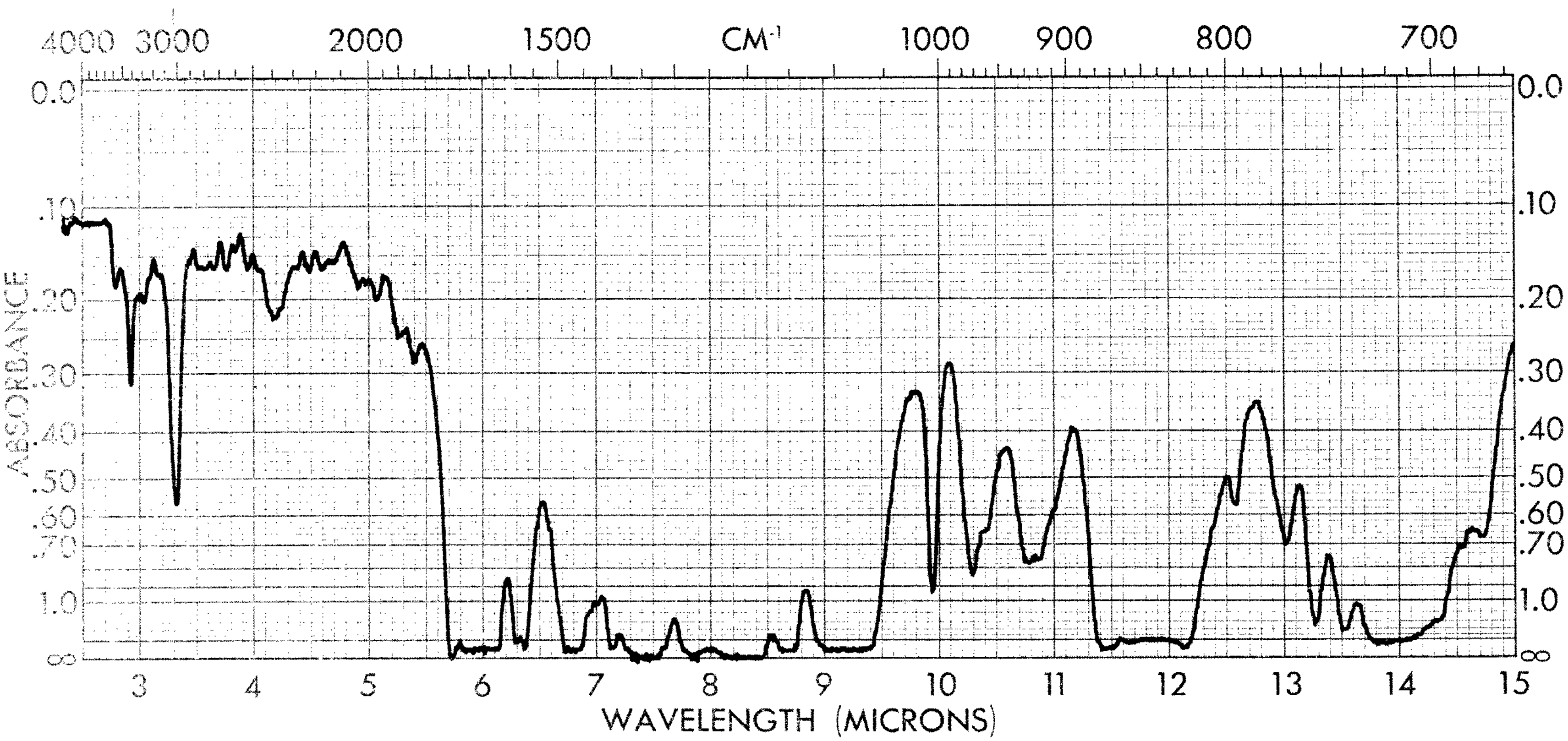

Figure 7. Infrared Spectrum of the Residue of Polymer III at 400° C

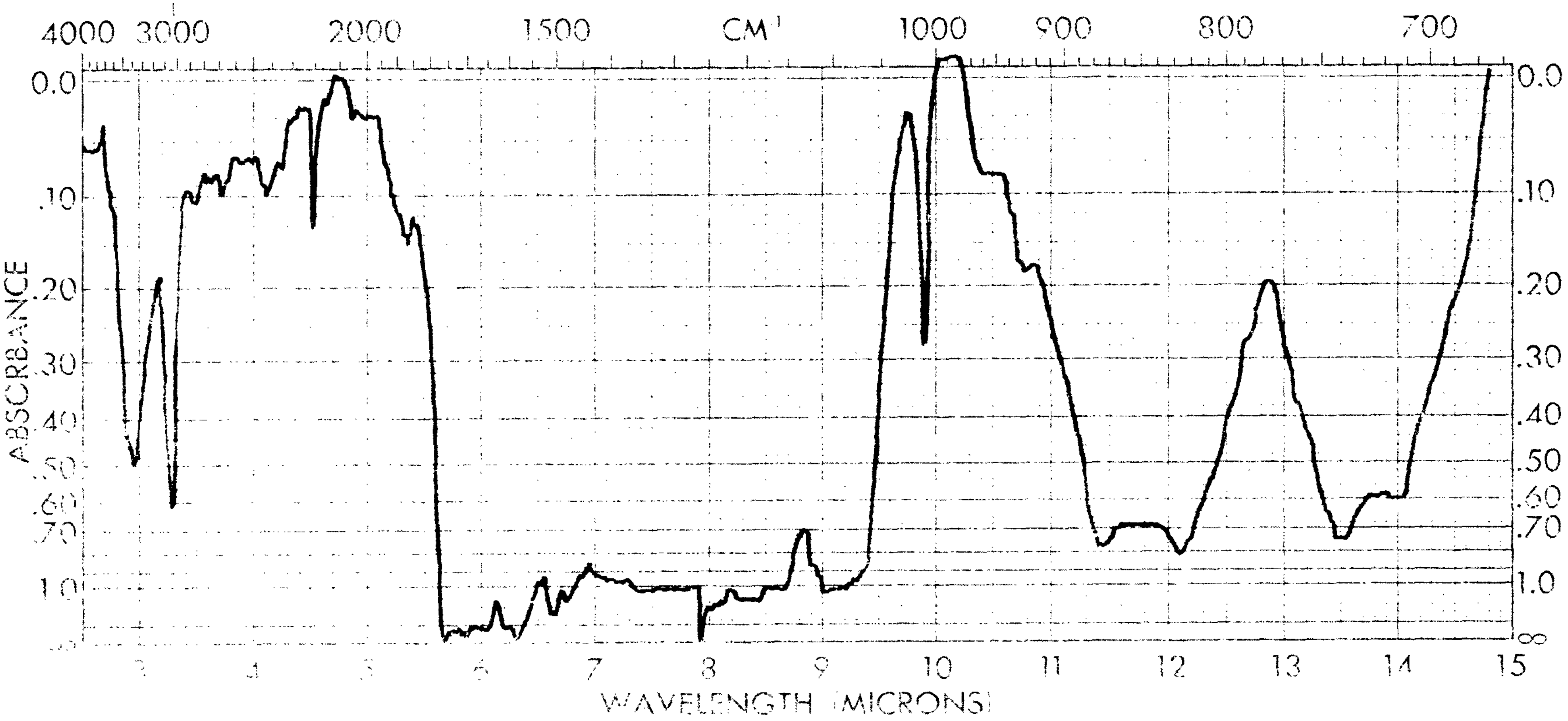

Figure 8. Infrared Spectrum of the Residue of Polymer III at 450° C

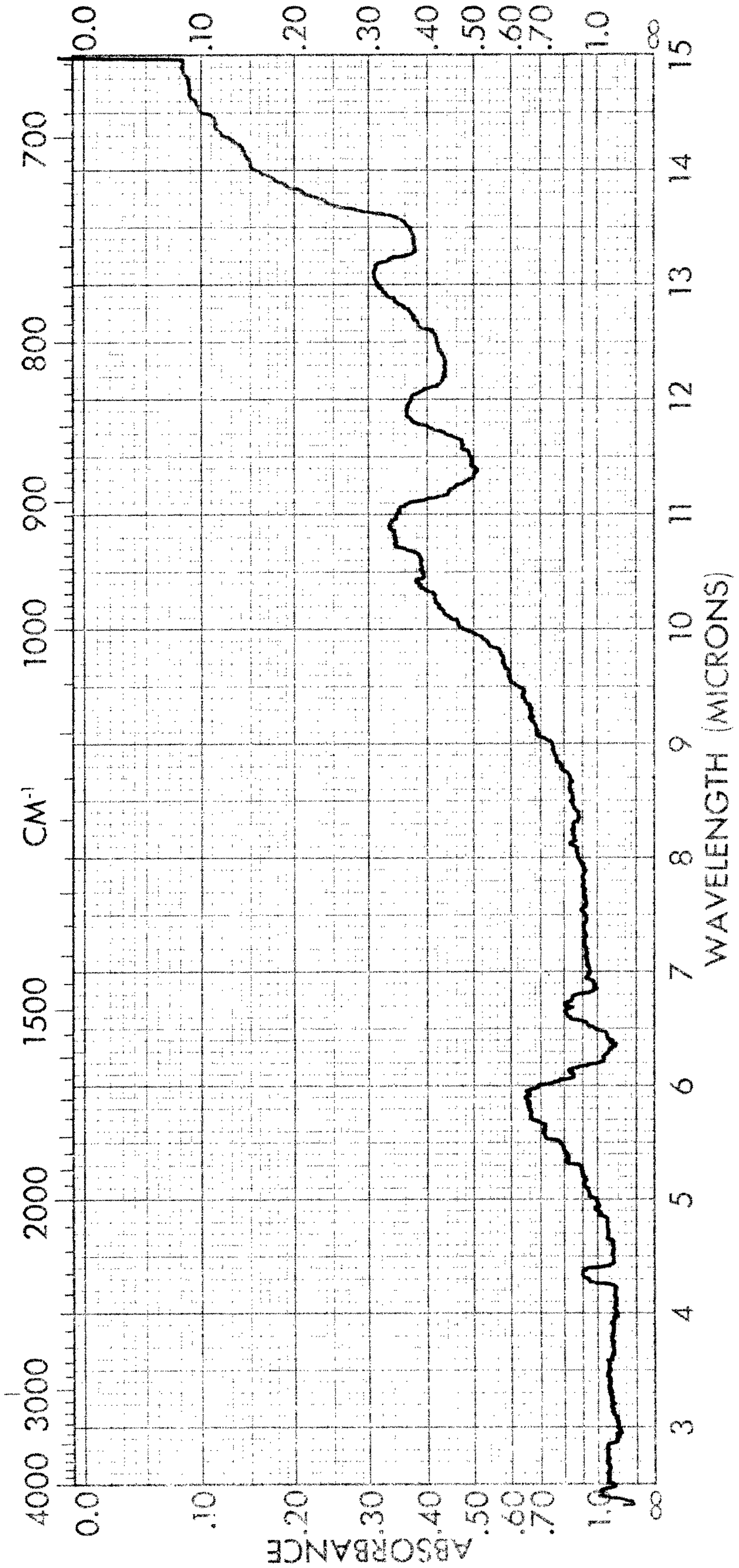

Figure 9. Infrared Spectrum of the Residue of Polymer III at 550° C

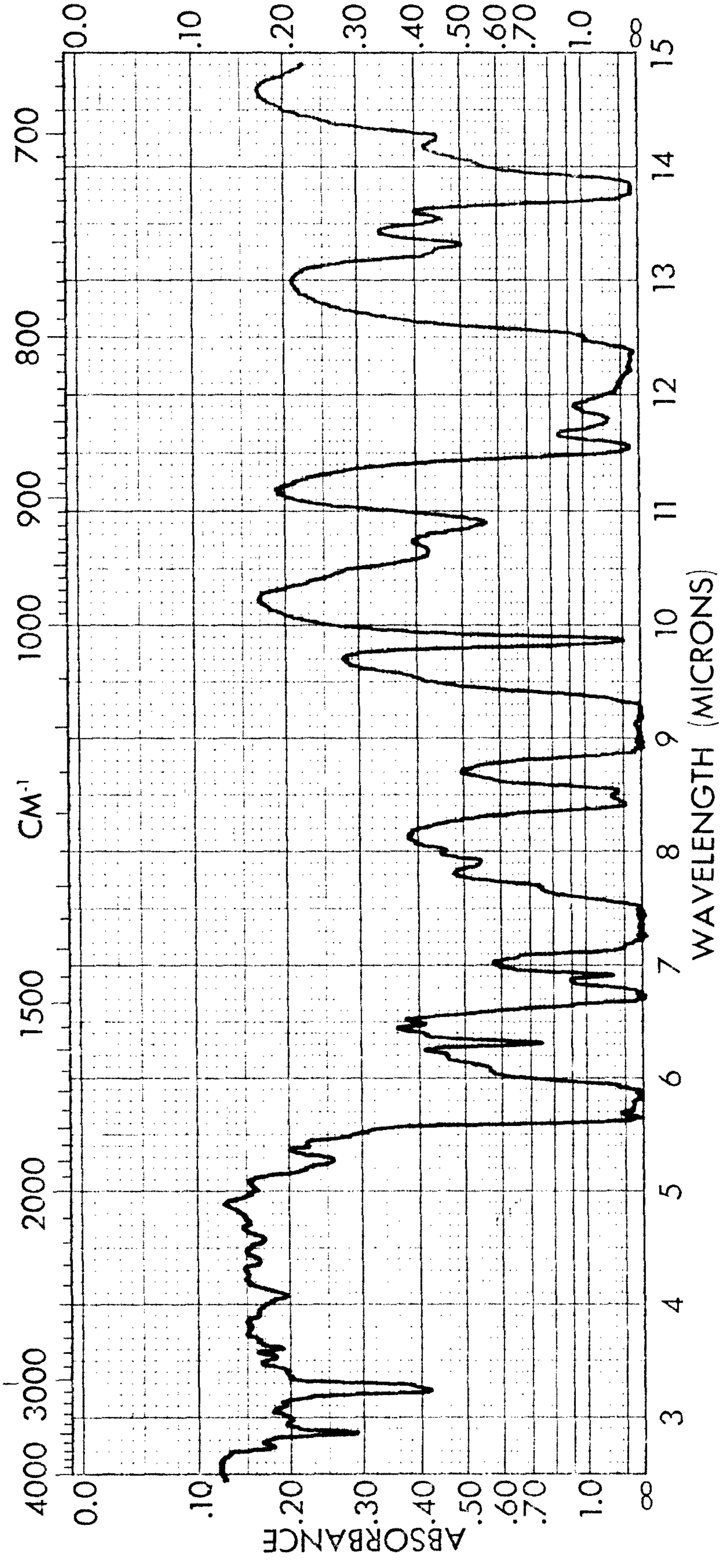

Figure 10. Infrared Spectrum of Polymer IV

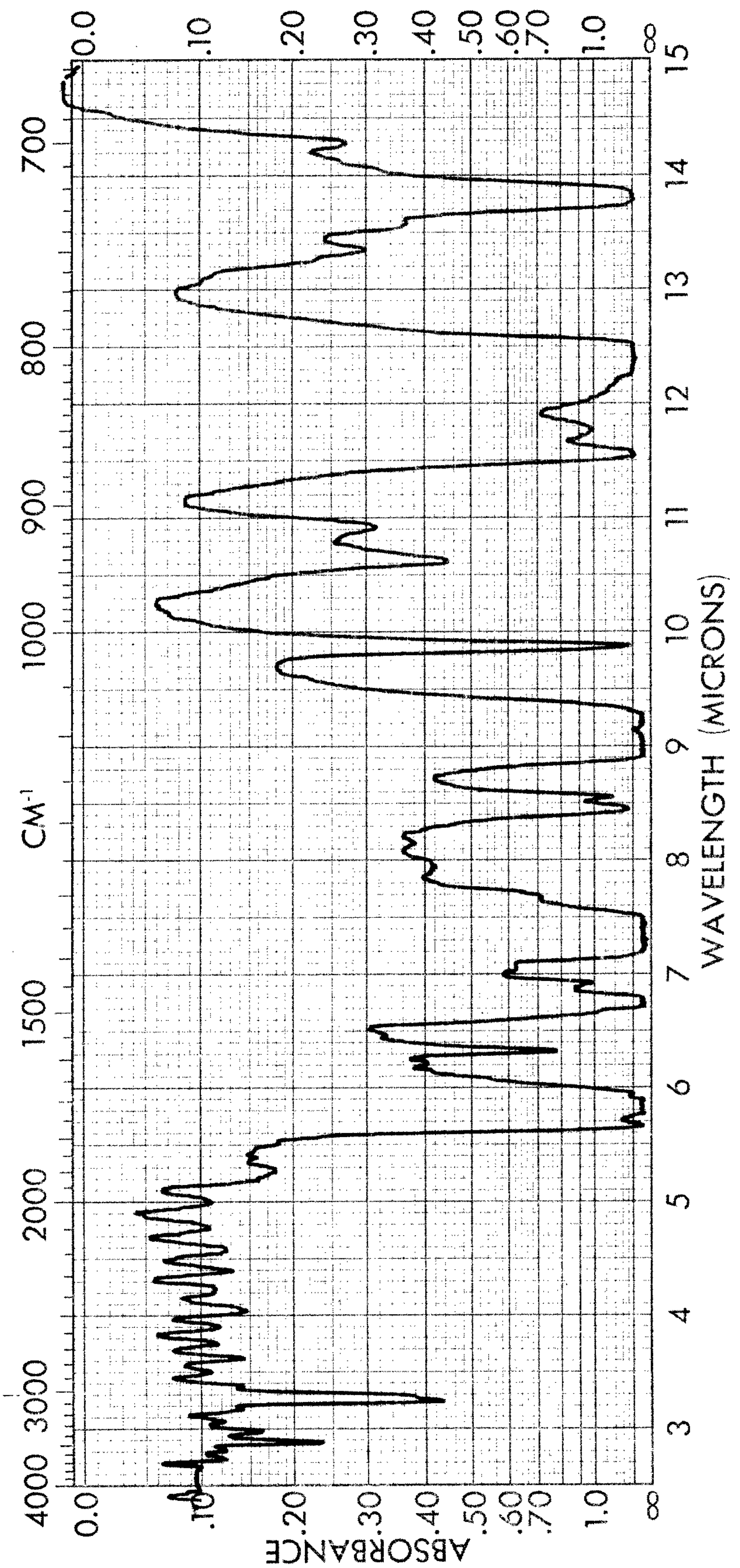

Figure 11. Infrared Spectrum of the Residue of Polymer IV at 400° C

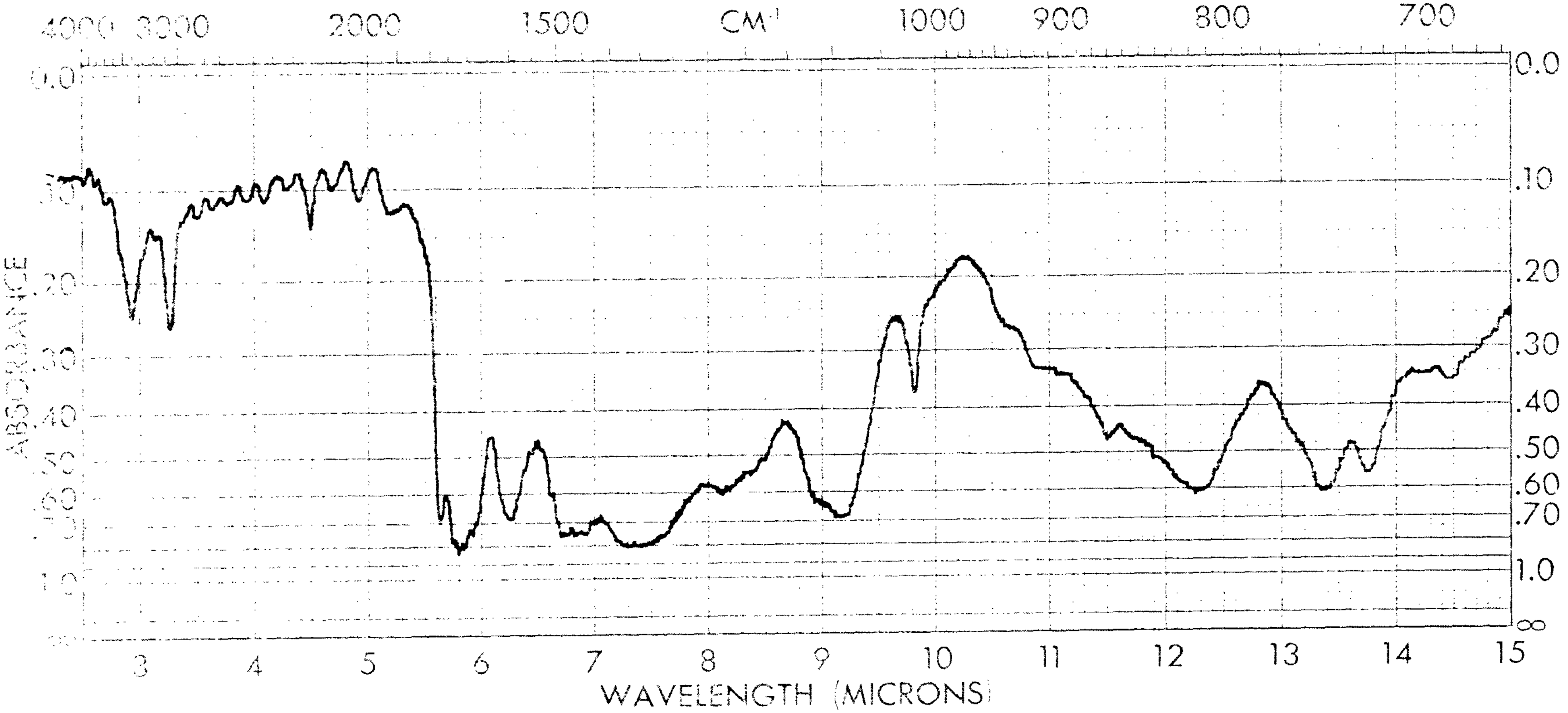

Figure 12. Infrared Spectrum of the Residue of Polymer IV at 450° C

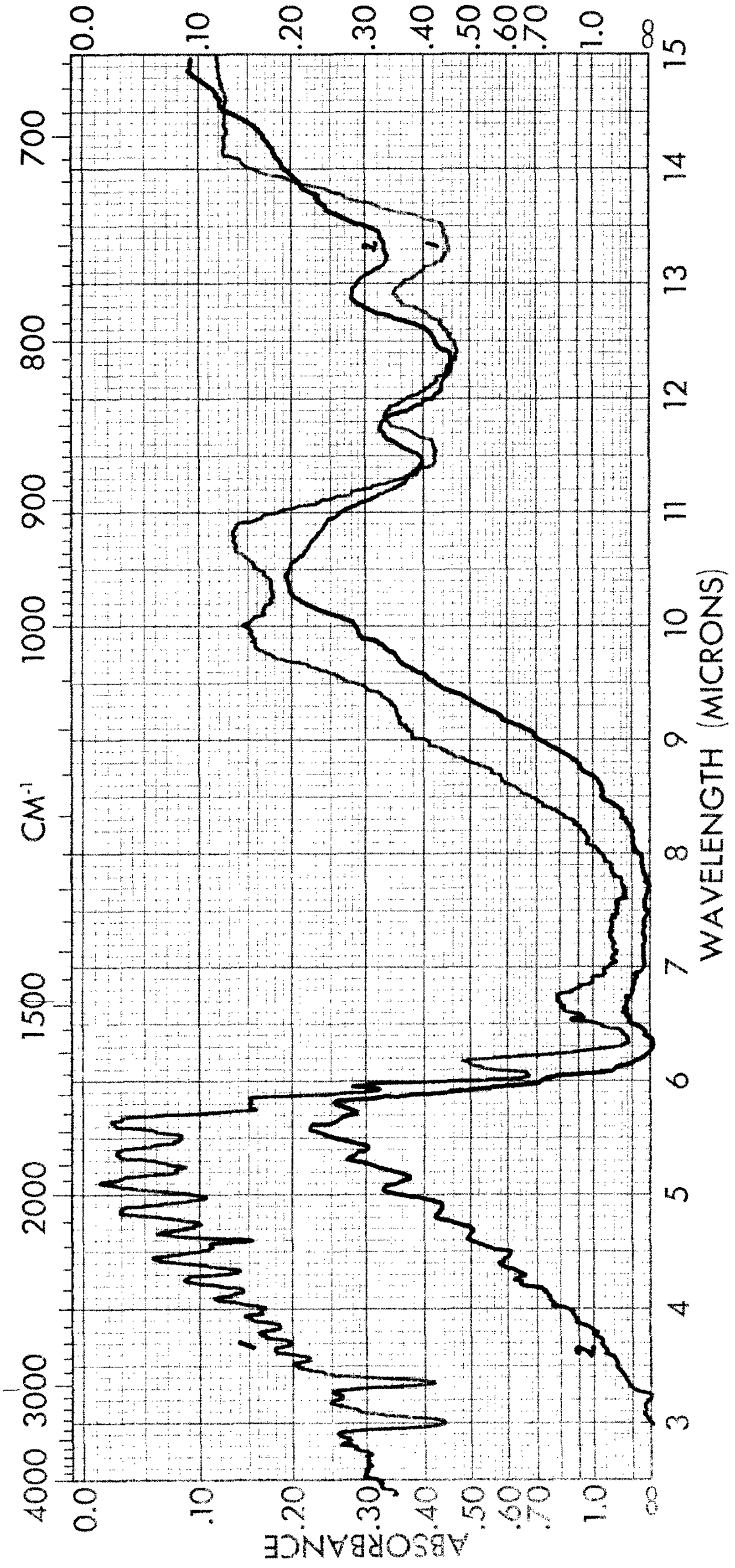

Figure 13. Infrared Spectra of the Residues of Polymer IV at 1: 550° C; 2: 620° C

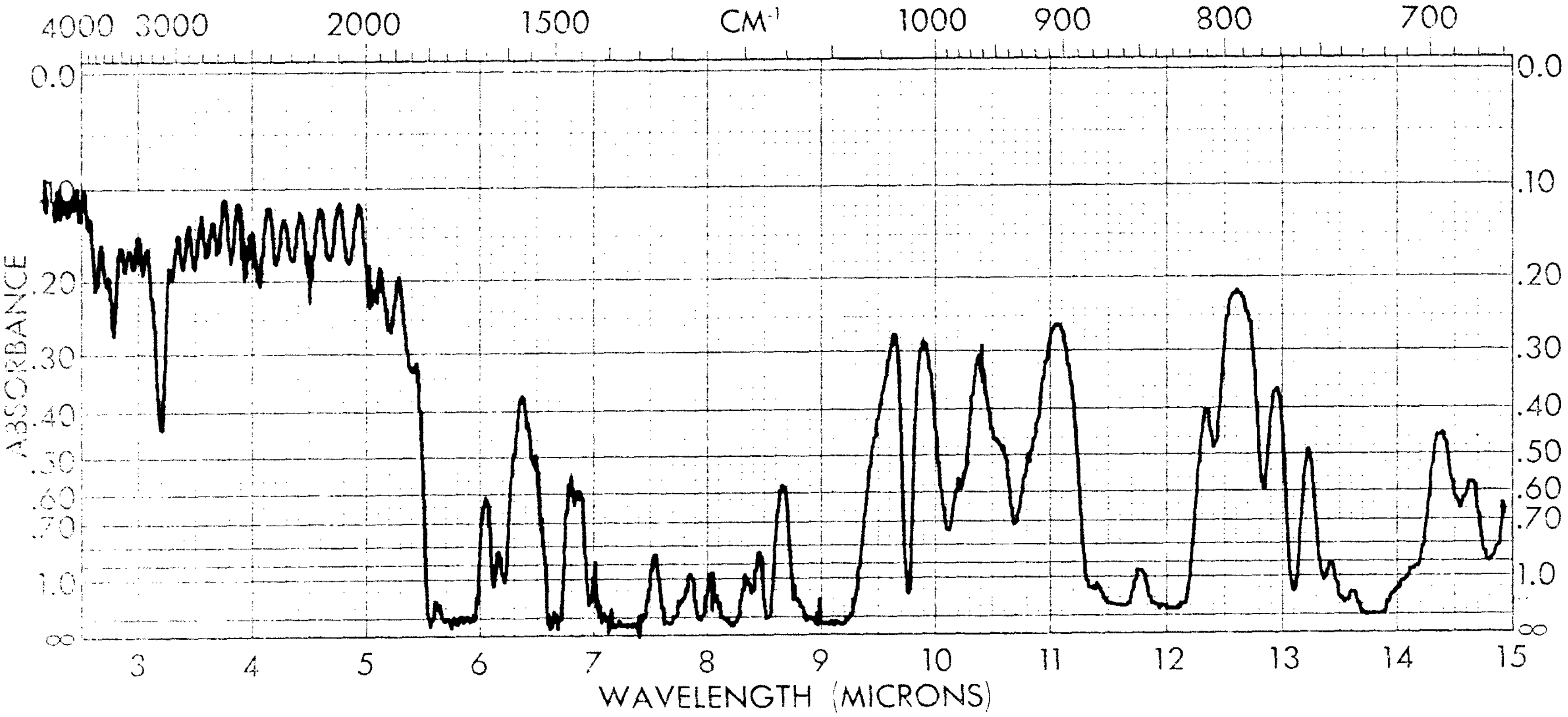

Figure 14. Infrared Spectrum of Polymer V

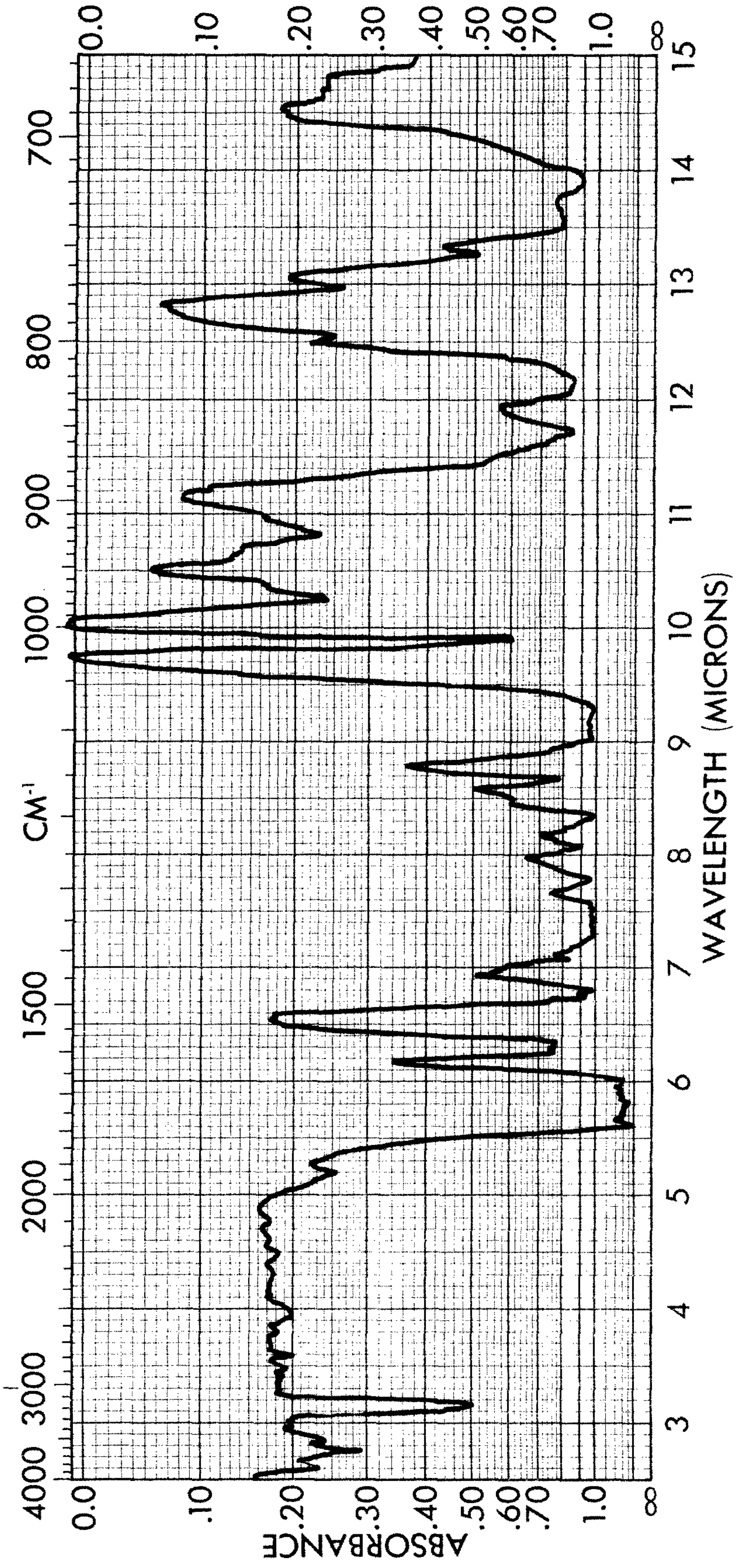

Figure 15. Infrared Spectrum of the Residue of Polymer V at 400°C

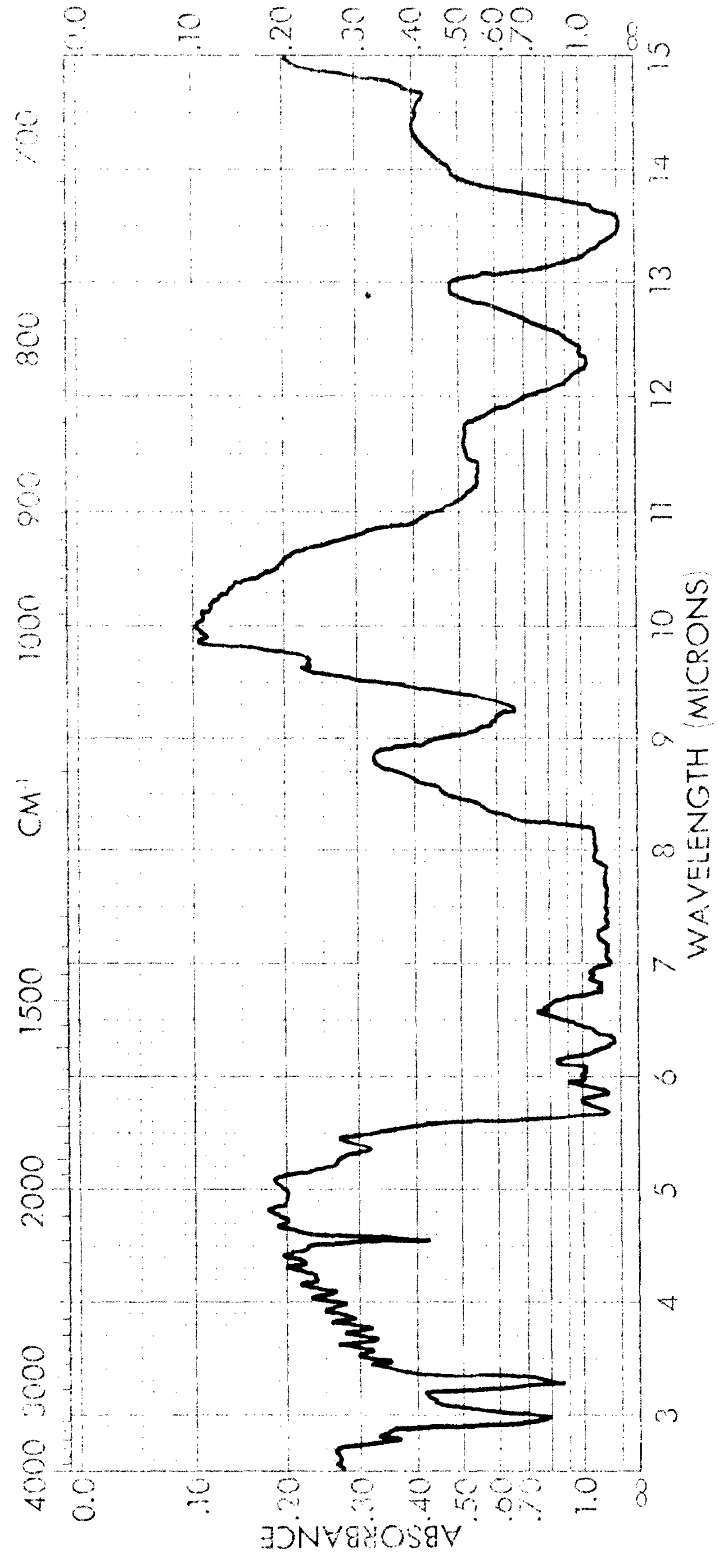

Figure 16. Infrared Spectrum of the Residue of Polymer V at 450° C

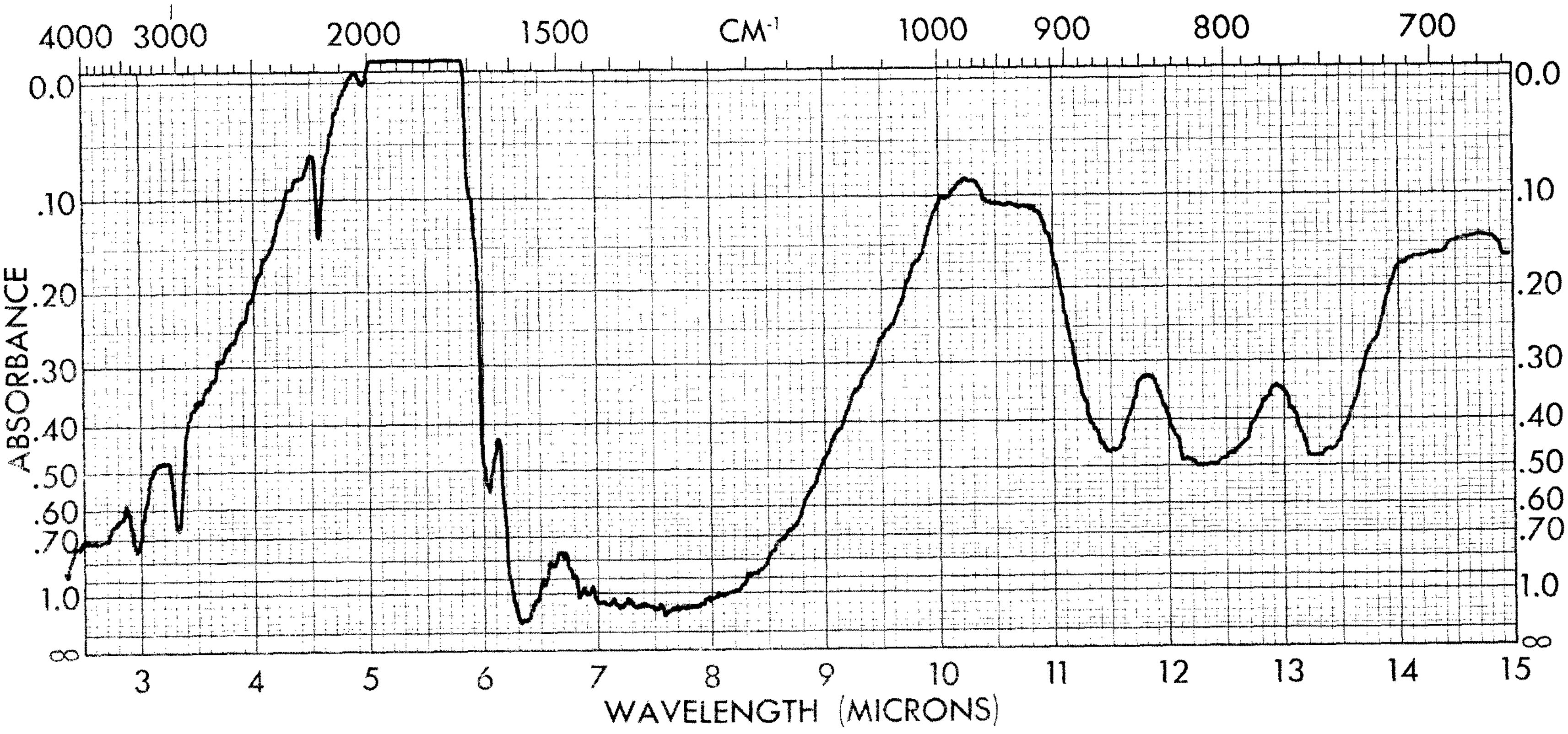

Figure 17. Infrared Spectrum of the Residue of Polymer V at 550° C

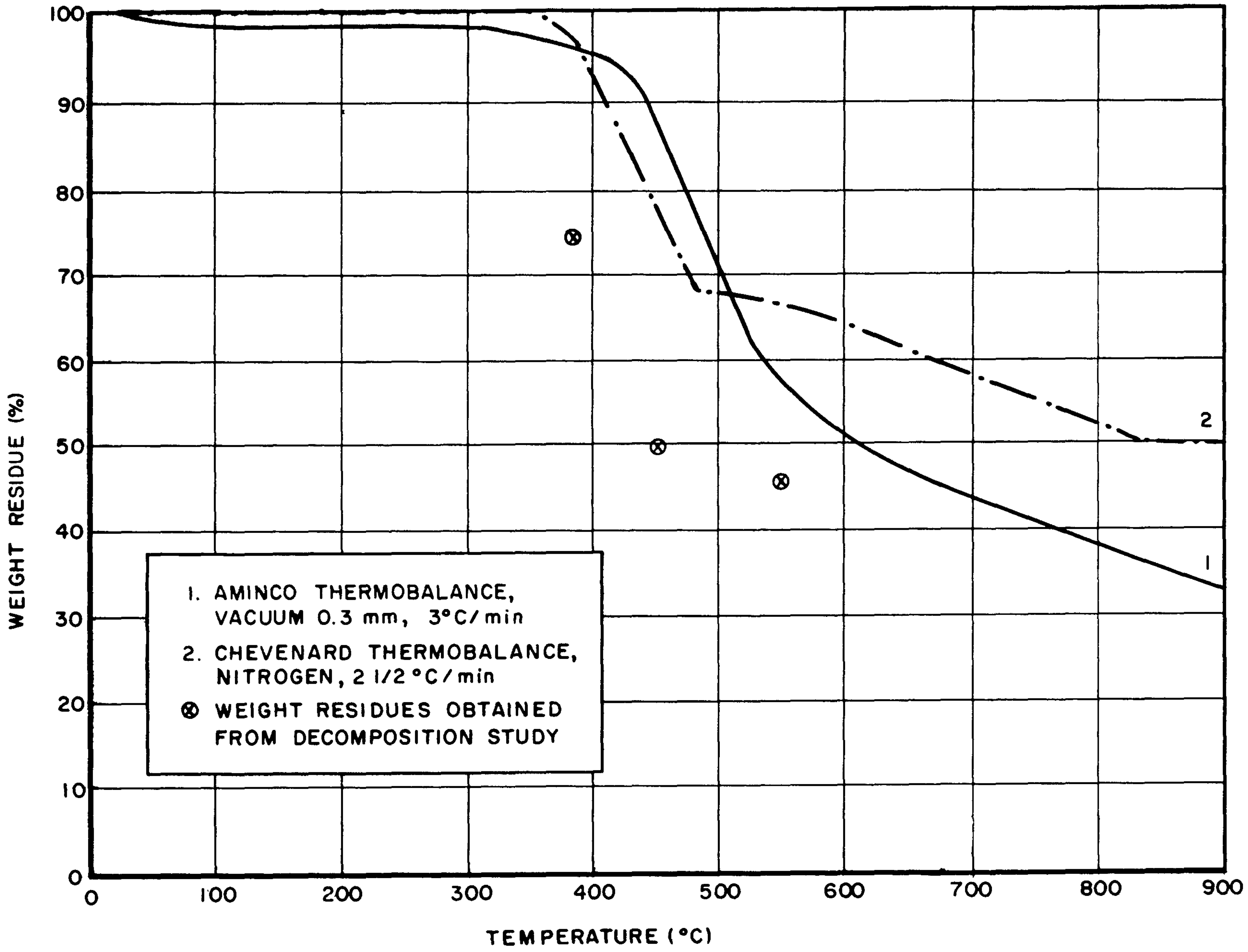

Figure 18. Thermogravimetric Analysis of Polymer I (Vacuum and Nitrogen)

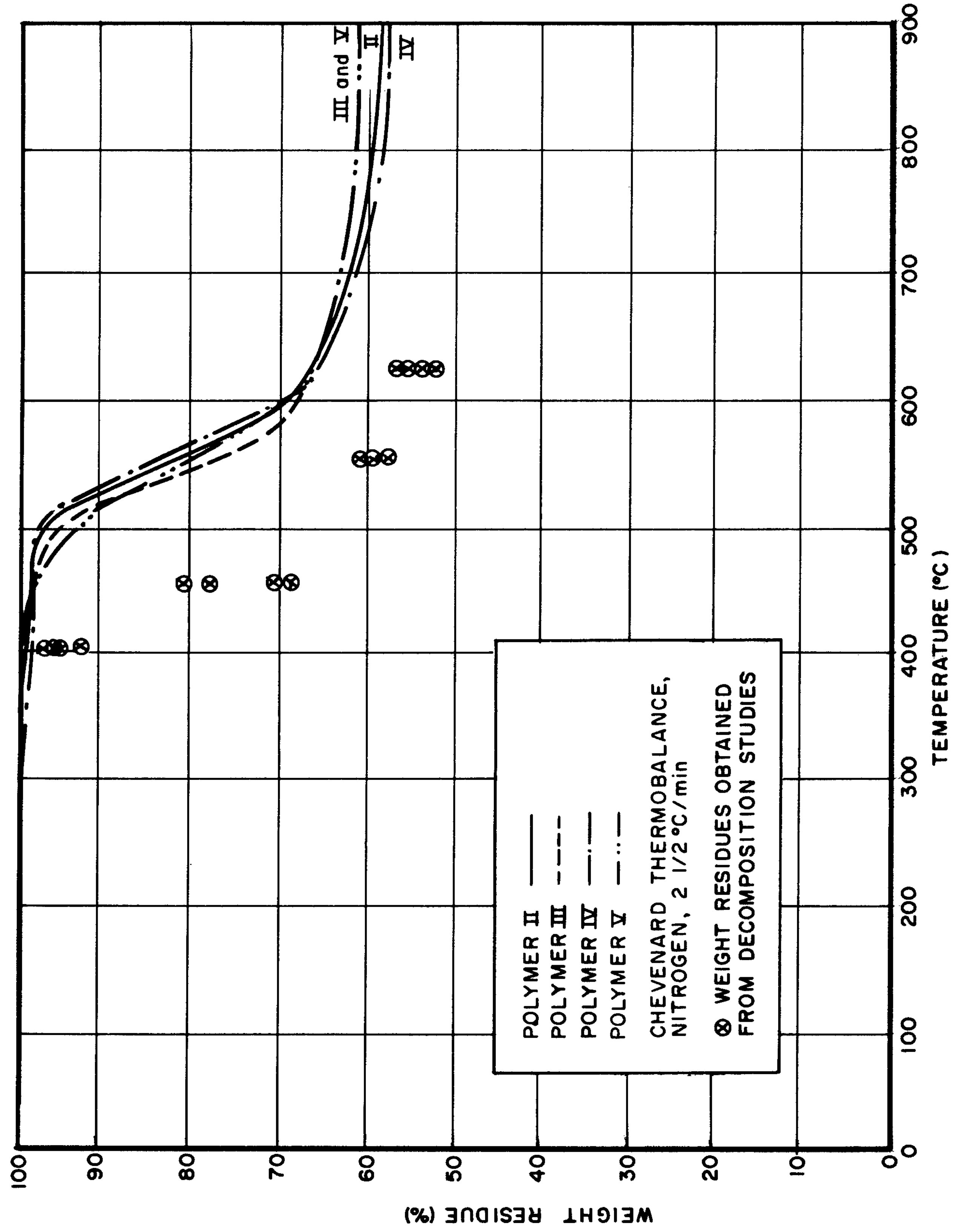

Figure 19. Thermogravimetric Analysis (Nitrogen) of Polymers II, III, IV, and V

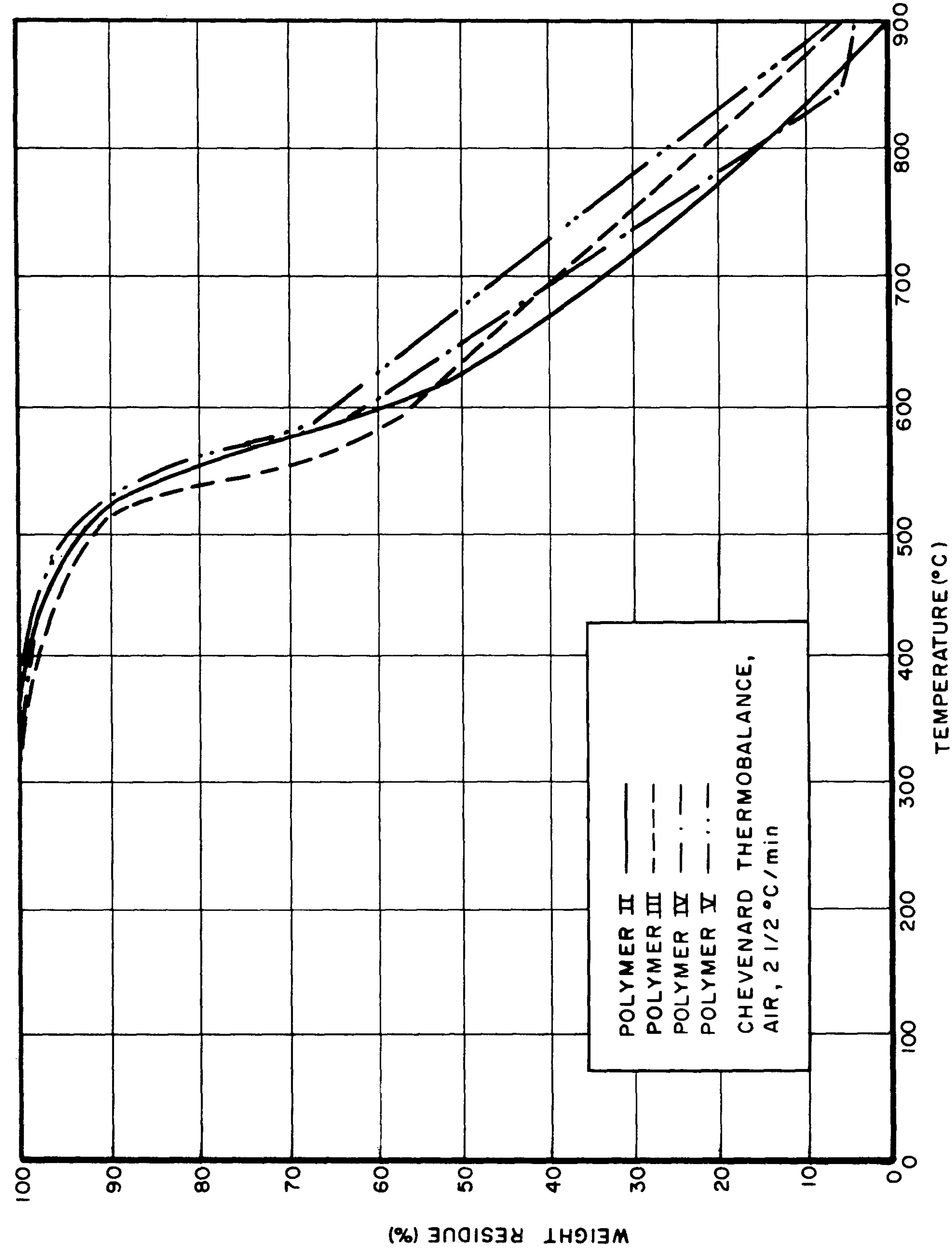

Figure 20. Thermogravimetric Analysis (Air) of Polymers II, III, IV, and V

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The breakdown mechanism of an aromatic polyamide and four polyimides has been studied.

The decomposition of the polyamide in the temperature range below 375°C yielded predominantly carbon dioxide, while between 375° and 450°C about equal amounts of carbon dioxide and carbon monoxide formed. Hydrogen is the major product between 450° and 550°C, along with hydrogen cyanide, methane, and carbon monoxide. The major reaction at the lower temperatures seems to be the cleavage of the linkage between the carbonyl group and the ring, with subsequent formation of a carbodiimide linkage via isocyanate intermediates. At higher temperatures, cleavage between the carbonyl and the —NH— group takes place.

The results of the decomposition of the four polyimides are not only quite similar to each other, but also similar to the polyamide. It is remarkable that the polyimides form carbon dioxide to a considerable extent in the lower temperature ranges (below 450°C). The primary cleavage reaction is believed to be the rupture of the imide ring between a carbonyl and nitrogen, with formation of an isocyanate group which reacts with another isocyanate group to form a carbodiimide linkage and carbon dioxide.

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Decomposition Mechanism						
Mass Spectroscopy						
Polymer						
Polyamide						
Polyimide						

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