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**STUDIES OF THE BREAKDOWN MECHANISM OF POLYMERS:
I. THE THERMAL DECOMPOSITION OF SOME
PHENYLENE-R-POLYMERS**

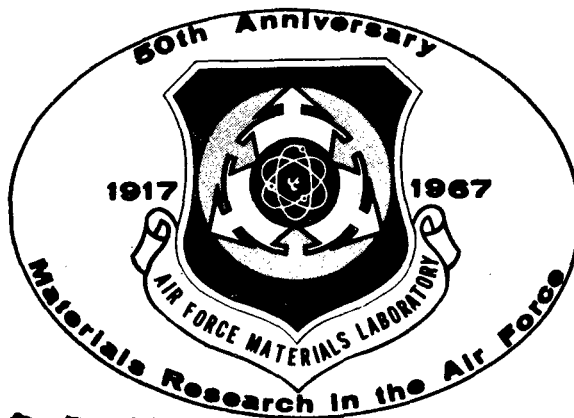
GERHARD F. L. EHLERS
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TECHNICAL REPORT AFML-TR-67-89

MAY 1967

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I. THE THERMAL DECOMPOSITION OF SOME
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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," 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, Research and Technology Division, for which Dr. G. F. L. Ehlers was project engineer.

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

This report covers work conducted from October 1965 to October 1966. This technical report has been reviewed and is approved.



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ABSTRACT

Samples of eight different phenylene-R polymers were subjected to isothermal heating in three progressive steps. The gaseous decomposition products were collected and analyzed by mass spectroscopy. The corresponding residues were obtained in separate, identical runs and identified by weight, elemental analysis, and IR spectra. The data collected were used to postulate an overall breakdown mechanism.

The first reaction occurring during the decomposition of these polymers at lower temperatures (below 450°C) is the removal of pendant groups, and the cleavage of the linkage between the rings. Polyphenylene sulfide shows the least amount of ring breakdown, as indicated by very little methane formation. Sulfur is removed as hydrogen sulfide, and the ruptured bond may partially heal, forming C-C-bonds. Sulfones appear to behave in a similar manner, the SO₂ linkage being removed as sulfur dioxide. The breakdown of ethers and phenols is always accompanied by a considerable amount of ring cleavage and destruction, the decomposition products being CO, CO₂, and H₂O. Crosslinking with evolution of hydrogen is the predominant reaction of all polymers at the higher temperatures (up to 620°C).

The end products, which may contain some O and especially S in the form of stable, fused ring systems, are crosslinked polymer carbons with unsaturated, aliphatic chains rather than completely aromatic, fused ring systems. Possible exceptions are polyphenylene sulfide and polyphenylene.

From the results, it is concluded that polyphenylene sulfide may be of interest as an ablative material.

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INTRODUCTION

Thermogravimetric analysis (TGA) has been used in this laboratory over the past 6 years to examine the stability of experimental polymers. It has been used as a screening device to obtain an overall picture of the relative stability of polymer systems. Results and conclusions of general applicability have, however, been rather limited. In many cases, this was caused by the unknown purity, and even the uncertainty about the structure of many of the new polymers. Another reason, however, is the limited information a TGA curve can provide. It informs us only about the degree of instability, expressed as weight loss, under certain temperature-time conditions. Knowledge about the processes leading to this instability would be of considerable importance.

Mass spectroscopy of the gaseous decomposition products and elemental analysis of the residues provide us with the basic data leading to the required information. A complete clarification of the decomposition mechanism of a new polymer, however, is extremely difficult and time-consuming. This is particularly true in the case of condensation polymers, since their mode of decomposition seems to be much more complex than that of addition polymers. Amazingly little is known about the breakdown mechanism of phenol-formaldehyde resins and similar condensation polymers, considering that more than 60 years have elapsed since their discovery.

The purpose of the present study is to obtain more information of general applicability which would be helpful in the selection and design of promising novel polymer systems. It can fulfill this purpose only if it is capable of keeping pace with the synthesis of new polymers, giving us the most up-to-date information as quickly and comprehensively as possible. The approach used in this study was to subject selected polymers to decomposition under vacuum at successively higher temperature levels. Mass spectrographic analysis of the evolved gases and elemental analysis data of the residues are used to tentatively postulate an overall breakdown mechanism. In those cases where the data are too inconclusive or incomplete to establish a breakdown mechanism, they nevertheless almost always permit the determination of the order and magnitude of instability of certain components or groups within the polymer. This in itself is quite important for future planning. It should be emphasized, however, that the postulation of breakdown mechanisms in this study is meant to be a first approach to the problem, subject to changes should additional information become available.

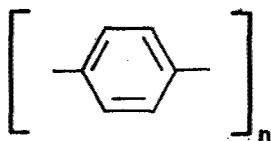
DISCUSSION

Eight polymers of the "phenylene-R-" type have been subjected to thermal decomposition under vacuum. They were: poly-1,4-phenylene, poly-2-hydroxy-1,4-phenylene, poly-1,4-phenylene sulfide, poly-1,4-phenylene sulfoxide, poly-1,3-phenylene oxide, poly(-2,6-dimethyl-1,4-phenylene oxide), poly(-2,5-dimethoxy-1,4-phenylene oxide) and Poly-sulfone "Phenoxy T Blend 5."

The decomposition was run in three consecutive temperature steps. At each temperature, the sample was heated until no further pressure increase was noted in two consecutive readings, not less than two minutes apart. Using the TGA curve as a guide, three temperatures were selected, representing the beginning, the peak, and the end of the decomposition. The final temperature selection however, was dependent upon the necessity to generate a minimum amount of gas sufficient for mass spectroscopy.

The gases generated in this fashion at each temperature step were analyzed by mass spectroscopy (see experimental part for instrumentation and detailed procedure). The final residue was weighed and characterized by elemental analysis and infrared spectroscopy. Two additional decomposition runs were then carried out, duplicating the temperature-time profile up to the point where the first and the second gas sample had been collected. This time, only the residues were isolated and analyzed by weight loss, elemental analysis, and infrared spectroscopy.

From the composition of the gases by mole percent, as well as from the known volume of the instrument and from the pressures obtained, the total weight of the volatiles of each step was calculated. Nongaseous decomposition products seemed to form essentially around 400 to 450°C and deposited all over the instrument, including the manometer. They were not further analyzed except for the determination of infrared spectra, which were generally similar to the original polymer, indicating low molecular weight fragments.

Poly-1,4-phenylene

Related Literature. Kovacic (Reference 1) noted that p-polyphenyl (in this case obtained from benzene with aluminum chloride-cupric chloride) on pyrolysis in vacuo yielded volatile lower p-polyphenyls including biphenyl, terphenyl, quaterphenyl, and quinquephenyl in addition to residual material. Straus and Wall (Reference 2) found that the principal volatile product, in the decomposition of polyphenyl, was hydrogen.

Background Information. The polyphenylene used in this study was prepared in this laboratory according to the method of Kovacic and co-workers (References 3 to 5) from 2 moles of benzene with 1 mole of ferric chloride and 1 mole of water. The product was washed with conc. hydrochloric acid, water, N/2 sodium hydroxide solution and again several times with water, and was dried for 2 hours at 140°C. The chlorine content was 6.2%, which is lower than Kovacic's results under the same conditions (References 3 to 5). The polymer, on combustion, contained 1.6% ash, apparently iron oxide. The C: (H + Cl) ratio corresponded to a summary formula of $\left[\text{C}_6(\text{H} + \text{Cl})_{3.5} \right]_n$. The results suggest a polyphenylene with one chlorine every 7th ring and one crosslink at every 2nd ring.

TABLE I
ANALYSES OF VOLATILES AND RESIDUES OF POLY-1,4-PHENYLENE

	C	H	O	Cl	Ash
Analysis calc. for $(C_6H_4)_n$:	94.7	5.3	-	-	-
found for polymer :	87.5	4.1	1.2	6.2	1.6
found for residue 450°C:	92.3	4.4	0.2	0.5	1.5
found for residue 550°C:	94.5	3.0	0.3	-	2.7
found for residue 620°C:	94.9	1.8	0.6	-	1.6

Temp. Range (°C)	H ₂	CH ₄	H ₂ O	Volatile Products (mole %)			Weight Volatiles (%) *)	Total Weight loss (%) *)
				CO	HCl	CO	C ₆ H ₆	
20-450	36.9	6.5	16.6	4.5	23.5	8.3	3.7	8.0
450-550	88.5	5.4	2.2	1.4	-	-	2.5	10.5
550-620	85.6	8.9	1.9	3.1	-	-	~2.2	2.2

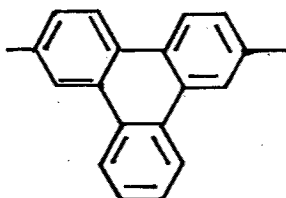
*) of starting materials

Decomposition Study. Thermogravimetric analyses of the polymers are shown in Figure 1, while the temperature-time and pressure-time profiles (used in the decomposition study) are shown in Figure 8. Figures 15 and 16 give the IR spectra. Table I gives the mass spectrographic results of the gaseous decomposition products, the analyses of the corresponding residues, and the percent weight loss at the three temperature ranges.

From these data and the IR spectra, the following conclusions may be reached:

The extent of formation of H_2O , CO , and CO_2 during the first step seems to be rather high for the low oxygen content of the polymer. However, since no nitrogen was detected in the decomposition product (which would point to air being present) no other source of oxygen can be visualized than that contained in the polymer. Some of the water found in the first decomposition step may result from water bound to the polymer.

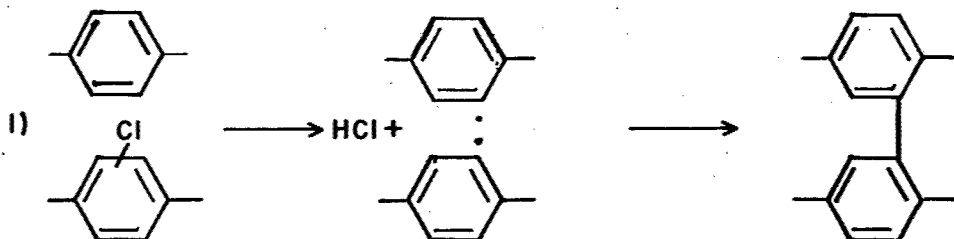
Chlorine seems to leave the molecule first, and almost completely during the first temperature step. It abstracts hydrogen and evolves as hydrogen chloride. A small amount of benzene is given off. Since the amount decreases with higher temperature, it is believed that it results from weak links within the polymer. One possibility would be the decomposition of fused ring systems which may be present (Reference 3):

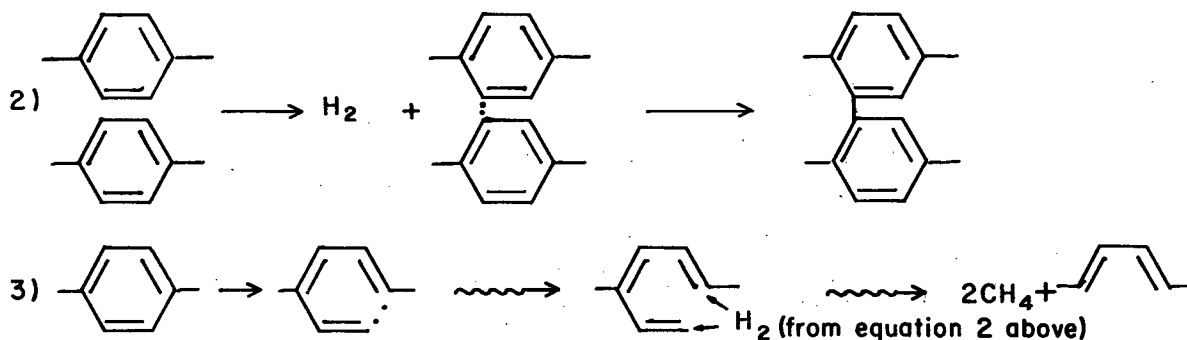


The formation of methane, although relatively small, shows that the benzene rings must begin to break down below $450^\circ C$. Apparently, a bond next to the chain link cleaves, forming a free (bi-)radical, which, under abstraction of hydrogen, forms an alkene system. More abstraction of hydrogen and chain cleavage may lead to the formation of methane. The hydrogen abstraction causes the formation of more free radical sites, which may partially combine (crosslink).

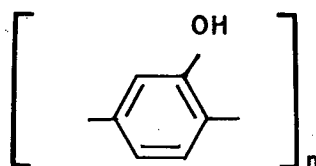
The major decomposition reaction (with its peak occurring at higher temperatures) is the formation of hydrogen. The remaining polymer radicals may at first crosslink, but under ring cleavage and recombination may later form nonaromatic, partially unsaturated, crosslinked polymer carbon networks. The atomic ratio C/H increases from 1.8/1 for the first residue to 4.2/1 for the final residue. The decrease in aromaticity can be seen by comparing the IR spectra (Figures 15 and 16). The aromatic ring absorption at 1460 , as well as the aromatic substitution bands at 810 , 1000 , and 1090 cm^{-1} decrease and finally disappear completely. New bands emerge at 695 and 865 cm^{-1} . The former is probably caused by the formation of alkene moieties, while the latter can be attributed to crosslinking.

The major decomposition reactions may be represented, highly simplified, by the following scheme:

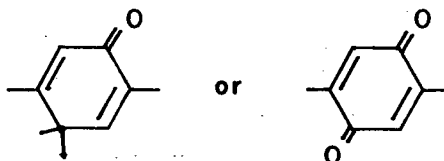




Poly-2-hydroxy-1,4-phenylene



Background Information. Poly-2-hydroxy-1,4-phenylene or polyphenol has been prepared (Reference 6) similar to polyphenylene, described above. Phenol was treated with an excess of ferric chloride at temperatures between 40 and 90°C. The black polymer is infusible but soluble in dimethylformamide. The inherent viscosity of this fraction is only 0.07, corresponding to a molecular weight of approximately 1400. Although the NMR spectrum is consistent with the above structure, the IR spectrum (Figure 17) shows a band at 1640 cm^{-1} attributed to a carbonyl group, and only about 50% of the oxygen reacts as phenolic hydroxyl. It is, therefore, likely that part of the polymer structure can be represented by:



Decomposition Study. The thermogravimetric analysis of the polymer can be seen in Figure 2 and the temperature-time and pressure-time profile in Figure 9. Table II lists the results of the mass spectrographic analysis of the gaseous decomposition products and the elemental analysis of the residues.

Carbon monoxide is the major decomposition product at the lower temperature range and hydrogen at the higher temperature range. No water is formed initially while some is present above 450°C. It will be shown later that polyphenyleneoxides yield water on decomposition, and it has been postulated (see under Poly-1,3-phenylene oxide) that an intermediate phenol has to be formed first. Poly-dimethoxyphenylene oxide produces some methanol on decomposition. The fact that hardly any water is present in the decomposition products of polyphenol, can lead only to the conclusion that no phenolic groups are present in the solid state and/or at higher temperatures. This can be construed to represent strong evidence for tautomerism between (possibly) quinoid and phenolic oxygen, with the equilibrium shifted to approximately 50% phenol, if the polymer is in solution, while it decreases to a few percent only if the polymer is in the solid state. The IR spectra (Figure 17) show that new bands appear at 1020, 1090, and 1250 cm^{-1} in the spectrum of the residue at 450°C. These bands are characteristic for aryether linkages, indicating that intermediate ether links do form to a certain extent.

TABLE II

ANALYSES OF VOLATILES AND RESIDUES OF POLY-2-HYDROXY-1,4-PHENYLENE

	C	H	O	Cl
Analysis calc. for $(C_6H_4O)_n$:				
found for polymer :	78.2	4.4	17.4	-
found for residue 450°C :	74.9	4.0	17.0	0.5
found for residue 550°C :	85.7	3.0	7.4	-
found for residue 620°C :	90.4	2.0	1.8	-
	93.8	1.5	1.1	-

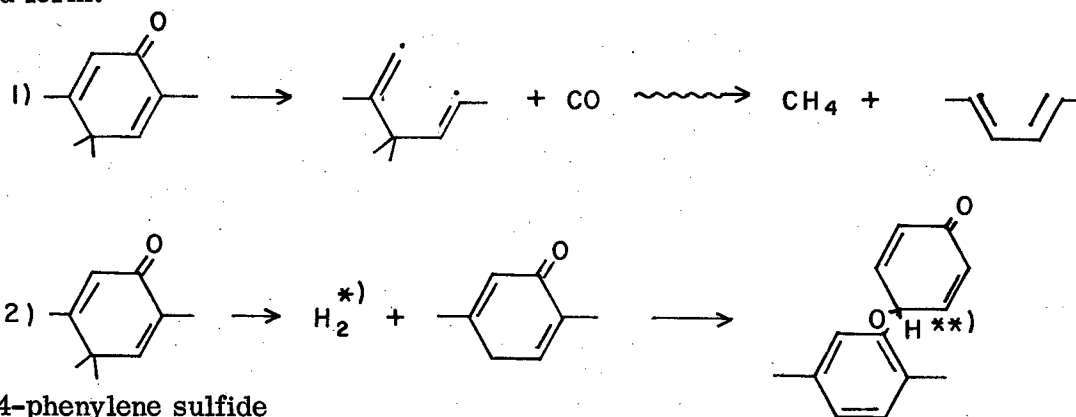
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Temp. Range (°C)	Volatile Products (mole %)							Weight Volatiles (%) *)	Total Weight Loss (%) *)
	H ₂	CH ₄	H ₂ O	CO	C ₂ H ₆	CO ₂	C ₆ H ₆		
20-450	10.0	7.7	-	64.3	-	17.7	0.3	10.0	26.2
450-550	22.7	10.5	2.9	58.3	0.1	5.4	0.1	~3.0	3.0
550-620	71.4	6.8	0.8	20.5	-	0.5	-	3.2	10.8

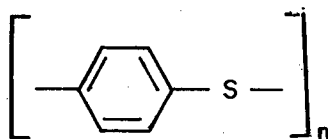
*) of starting materials

These decompose partially via phenolic groups to form some water, which is noticeable in the second gas fraction. While a considerable amount of ring breakdown occurs in connection with the formation of carbon monoxide at the lower temperatures, crosslinking is the prevalent reaction at the higher temperatures, as is the case with polyphenylene.

The scheme below may be representative of the major decomposition reactions, in a highly idealized form:



Poly-1,4-phenylene sulfide



Related Literature. Levy and Ambrose (Reference 7) studied the decomposition of diphenylsulfide. They found benzene and hydrogen sulfide, along with some hydrogen, as the major volatile decomposition products at temperatures between 500 and 560°C. Some dibenzothio-
 phenone was obtained, and traces of free sulfur. Russian authors (References 8 and 9) pyrolyzed diphenylsulfide in the presence of a catalyst and obtained benzene, hydrogen sulfide, and thianthrene.

Background Information. The polymer (batch CB-8-57-2,3, and 4) has been prepared by Dow Chemical Company under Air Force Contract (Reference 10). Cuprous p-bromothiophen-oxide was heated in sealed ampoules under argon at 200°C for two days. The gray polymer was only slightly soluble in hot diphenylether, had a melting range between 282 and 288°C and a melt viscosity of 2×10^3 poises. From melt viscosity, solution viscosity, and bromine end group relationships, a molecular weight of the order of 7000 has been estimated. The polymer contained between 1 and 3% copper. Differential thermal analyses performed in our laboratory, indicated a second order transition at 256°C and an endothermic transition, equivalent to the crystalline melting point, at 282°C.

A reevaluation of the polymer by the U. S. Rubber Company under Air Force Contract (Reference 11) revealed that the polymer was highly crystalline. A newly prepared one-half pound sample of the polymer, reprecipitated from 1-chloronaphthalene had only 0.2% copper and an intrinsic viscosity of 0.04 in diphenylether at 230°C. From end group analysis, a molecular weight of 4000 has been estimated for this polymer. The polymer was soluble in a number of solvents at 200°C, at a concentration of up to 5.9%. Fractionation from solutions resulted in

*) Abstraction from the ring, see previous scheme

**) For further decomposition of the ether linkage (formation of H_2 , CH_4 , H_2O , CO , and CO_2) see poly-1,3-phenylene oxide.

fractions with intrinsic viscosities ranging from 0.01 to 0.25. From freezing point depressions, a number average molecular weight of 1400 to 1500 has been estimated for a fraction with an inherent viscosity of 0.09.

Decomposition Study. Thermogravimetric analyses of polyphenylene sulfide are shown in Figure 3, and the temperature-time and pressure-time profile of the decomposition study can be seen in Figure 10. Table III lists the results of the mass spectrographic analyses of the gaseous decomposition products and the elemental analyses of the residues. The major decomposition products are hydrogen sulfide and hydrogen, the former being obtained in amounts decreasing with increasing temperatures, the latter increasing with increasing temperatures. Above 450°C, a small but noticeable quantity of methane points to some ring breakdown, and some free benzene (possibly from free radical chain ends, see below) also forms. The small amount of oxygen present in the polymer is responsible for the formation of some water, carbon dioxide, carbon monoxide, and sulfur dioxide.

The overall breakdown mechanism, based on mass spectroscopy, elemental analysis, infrared spectroscopy, and the above mentioned literature dealing with the decomposition of diphenylsulfide, can be postulated as follows: The S-linkage breaks first, resulting in two free radical polymer fragments. The sulfide radical abstracts a hydrogen atom, possibly from the ortho-position, to form a mercapto group. After breakage of the C-S bond and further abstraction of hydrogen, hydrogen sulfide is formed. Some of the free phenyl radicals combine to form phenyl-phenyl links and crosslinks. The infrared spectrum (Figure 18) of the 450°C residue seems to indicate a considerable number of phenyl end groups (bands in the 720 to 750 cm^{-1} range), in addition to two neighboring hydrogen atoms (p-substitution, band at 790 cm^{-1}) and single hydrogen (crosslinks, band at 850 cm^{-1}).

Above 450°C, the evolution of hydrogen becomes the predominant reaction, resulting in extensive crosslinking of the so-formed free radicals. The bands at 720 and 750 cm^{-1} have almost disappeared at 550°C, while those at 850 and 790 cm^{-1} (see above), are still present. At 620°C, the residue contains one sulfur per three benzene rings, corresponding to an empirical formula of $(\text{C}_{18}\text{H}_4\text{-S})_n$. This could be represented by a crosslinked, fused ring polyphenylene-polybenzothiophene, such as:

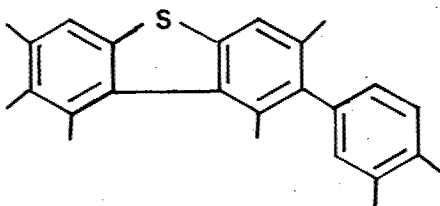


TABLE III

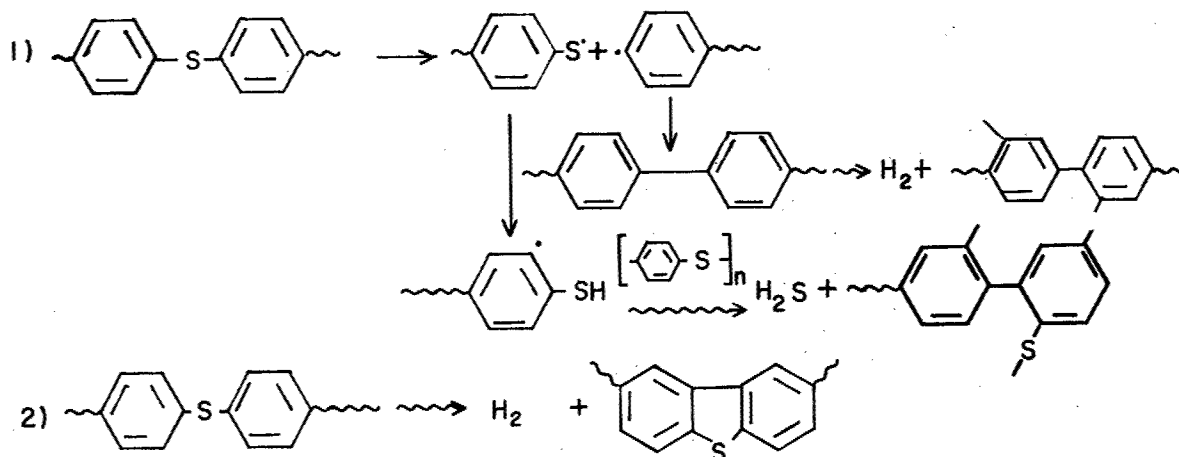
ANALYSES OF VOLATILES AND RESIDUES OF POLY-1,4-PHENYLENE SULFIDE

	C	H	S	Ash
Analysis calc. for $(C_6H_4S)_n$:	66.7	3.7	29.6	-
found for polymer :	66.2	3.7	27.4	2.2
found for residue $450^\circ C$:	71.4	2.8	17.2	4.2
found for residue $550^\circ C$:	72.6	2.1	15.5	3.5
found for residue $620^\circ C$:	75.6	1.5	12.3	4.3

Temp. Range (°C)	H ₂	CH ₄	H ₂ O	CO	H ₂ S	CO ₂	SO ₂	C ₆ H ₆	Weight Volatiles (%) *	Total Weight Loss (%) *
20-450	8.5	0.4	1.4	1.0	84.5	1.1	1.8	1.3	9.3	56.5
450-550	59.7	3.1	1.2	2.9	29.8	0.2	-	3.1	~ 2.5	2.5
550-620	61.4	2.8	1.4	2.3	28.7	0.2	-	3.2	2.8	3.0

*) of starting material

Polyphenylene sulfide shows the least amount of ring breakdown of the polymers investigated in this study. The relatively simple breakdown mechanism is shown below in an idealized form:

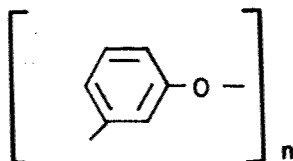


Decomposition Study with an Oxidized Poly-1,4-phenylene sulfide ("Polyphenylene Sulfoxide"). In connection with the poly-phenylene sulfide, we received another sample of this polymer, which had been subjected to conc. nitric acid in acetic anhydride for 48 hours at 0 to 5°C (Reference 10). The polymer showed an infrared absorption near 1050 cm^{-1} , believed to be caused by the sulfoxide group, and from the analysis (different from ours) the authors concluded that the polymer contained 56% sulfide and 46% sulfoxide linkages.

This polymer was subjected to the same kind of decomposition study as described previously with the results shown in Table IV.

The results show that there is an insignificant difference between the oxygen content of the polyphenylene sulfide and the "polyphenylene sulfoxide." The analysis of the latter, however, was short by 4%, and this may possibly account for more oxygen not accessible to analysis. The IR spectra of both polymers were almost alike. The kind and quantities of the volatile products are also very similar. The most notable difference is the much higher sulfur dioxide content in the first decomposition step of the sulfoxide.

Poly-1,3-phenylene oxide



Related Literature. Two papers describe the oxidative degradation of polyphenylethers. Wilson et al. (Reference 12) postulated from the controlled oxidation of two model polyphenylethers that molecular oxygen attacks at the ether linkage. This results in cleavage yielding phenoxy and peroxy intermediates. Dibenzofuran- and dibenzodioxin-containing intermediates were also postulated. Observed decomposition products were carbon dioxide, water, phenol, m-phenoxyphenol, and higher molecular weight products. Archer and Bozer (Reference 13) degraded m and p-phenyleneoxide tetramers and pentamers in air at 600°F. They found arylothers, arylphenols, benzofuran, quinones, carbon dioxide, and water to be the main products of degradation. They postulated that oxygen attacks a ring, followed by cleavage of the ether linkage.

TABLE IV
ANALYSES OF VOLATILES AND RESIDUES OF "POLYPHENYLENE SULFOXIDE"

	C	H	S	O
Analysis found for polymer:				
found for residue 400 C:	62.7	3.7	27.7	1.9
found for residue 550 C:	67.3	2.7	17-20*	0.9
found for residue 620 C:	73.9*	2.2	10.9*	0.8*
	71.3	2.1	14.6	1.4

*results questionable due to insufficient amount of material

Temp. Range (°C)	H ₂	CH ₄	H ₂ O	CO	H ₂ S	C ₃ H ₆	CO ₂	O=C=S	SO ₂	CS ₂	C ₆ H ₆	Weight Volatiles (%) *	Total Weight Loss (%) *)
20-400	5.5	4.4	3.2	4.4	47.8	0.8	6.6	1.9	23.1	1.4	0.9	3.3	68.0
400-550	44.6	2.5	0.6	2.0	47.3	-	0.4	0.1	-	0.5	2.0	2.1	9.5
550-620	75.9	3.9	0.7	3.0	14.5	-	0.5	0.06	-	0.2	1.2	0.8	0.5

*) of starting material

Background Information. The polymer was prepared by Wyandotte Chemicals Corporation under Air Force contract (Reference 14), by a method described by Brown et al. (Reference 15). The procedure involved the reaction of the potassium salt of m-chlorophenol with copper powder in mineral oil at 200°C for 24 hours. The polymer was prepared in 22 batches, yielding 3 to 28 gm each. The batches were combined and thoroughly purified by extraction and precipitation. The following properties have been determined by the U. S. Rubber Company under Air Force contract (Reference 11):

The polymer had an intrinsic viscosity in chloroform at 30°C of 0.20 (the original batches had inherent viscosities in benzene ranging from 0.07 to 0.40). The number average molecular weight, by vapor phase osmometry in benzene solution, was 7580 ± 200 . Weight average molecular weights by light scattering were erroneous because of precipitation of the polymer from diluted solutions. But the discrepancy between results obtained by osmometry, viscometry, and light scattering suggested a broad distribution of molecular weights. Chlorine (end group) analysis pointed to molecular weights of the order of 9000. The polymer was largely amorphous. Our own measurements suggested a T_g between 40 and 50°C and a DTA decomposition exotherm at 502°C; inversion points of the TGA curves, under nitrogen and vacuum, were at 550 and 560°C, respectively. The polymer melted at 45°C and was soluble in a number of solvents, such as chloroform, benzene, and carbon disulfide.

Decomposition Study. Thermogravimetric analyses can be seen in Figure 4, and the temperature-time and pressure-time profile of the decomposition in Figure 11; IR spectra are shown in Figure 19. Results of the mass spectrographic analysis of the gaseous decomposition products and the elemental analyses of the residues are shown in Table V.

The major decomposition products are water (decreasing with higher temperatures), carbon monoxide (peak of formation at 450 to 550°C), and hydrogen (increasing with increasing temperatures). Smaller amounts of methane and carbon dioxide, and some benzene are also formed.

It can be postulated that, at temperatures below 450°C, the ether linkage cleaves first, and two free radicals form. Abstraction of hydrogen leads to a phenol, further hydrogen abstraction (after cleavage of the C-O bond) to the formation of water. The remaining free radicals may combine to form phenyl-phenyl crosslinks. Ring cleavage concomitant with cleavage of the ether linkage under formation of carbon monoxide takes place simultaneously and increasingly at higher temperatures. Another product of the ring cleavage is a relatively small amount of methane, and also carbon dioxide which may have originated from an intermediate peroxide linkage formed from two phenoxy radicals. Hydrogen formation occurs in increasing amounts at higher temperatures, similar to the previously described decompositions. The end product at 620°C corresponds to an empirical formula of $C_{60}H_{16}O$ and may be a cross-linked structure with a considerable number of hydrogen deficient aliphatic pendant and/or linking chains. The high ratio of $CO-CO_2/CH_4$ formed also points to aliphatic chains left in the systems. Furthermore, the IR spectrum of the 550 and 620°C residues indicates the appearance of an alkene band at 695 cm^{-1} . The end product contains some oxygen probably in

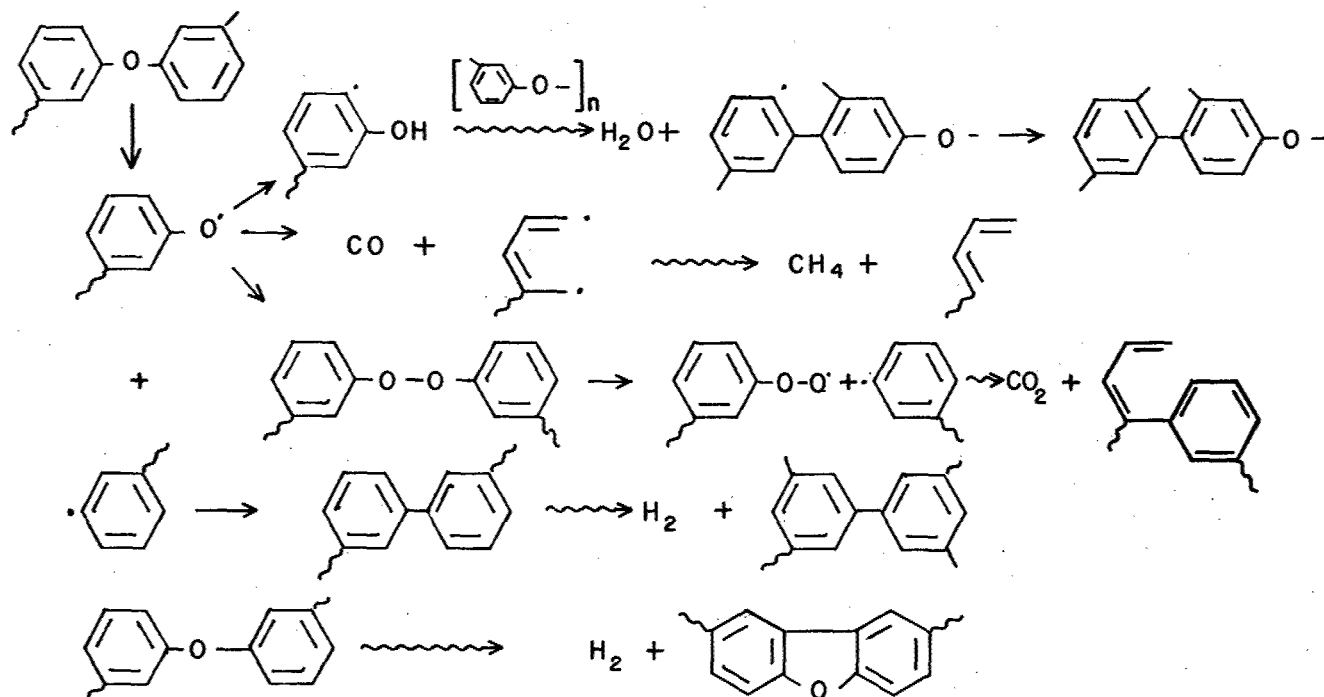
TABLE V
ANALYSES OF VOLATILES AND RESIDUES OF POLY-1,3-PHENYLENE OXIDE

	C	H	O	Cl	Ash
Analysis calc. for $(C_6H_4O)_n$:	78.3	6.3	17.4	-	-
found for polymer :	76.6	4.6	16.4	0.3	1.3
found for residue 450°C :	83.0	3.6	10.1	-	1.0
found for residue 550°C :	89.4	2.8	4.1	-	1.9
found for residue 620°C :	92.0	2.0	2.0	-	2.7

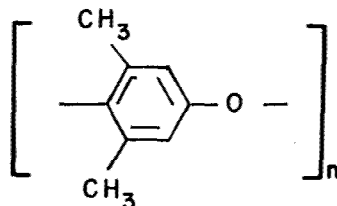
Temp. Range (°C)	Volatile Products (mole %)				Weight Volatiles (%) *	Total Weight Loss (%) *)
	H ₂	CH ₄	H ₂ O	CO	CO ₂	C ₆ H ₆
20-450	26.0	7.3	32.8	23.2	9.6	1.1
450-550	37.3	7.2	16.4	35.1	3.7	0.3
550-620	61.5	7.5	7.7	21.8	1.4	0.1

*) of starting material

the form of dibenzofuran or dibenzodioxin units (References 12 and 13). The major breakdown reactions are shown below (again, as in previous cases, in a highly idealized and simplified form):



Poly(2,6-dimethyl-1,4-phenyleneoxide)



Background Information. The polymer was received from the General Electric company, under the trade name PPO, and in the form of tan pellets. It was dissolved in benzene and reprecipitated from methanol, to give a fibrous-powder material. The polymer dissolved in chlorinated aliphatics, benzene, toluene, and chlorobenzene. DTA curves obtained at this laboratory in triplicate runs suggested a very weak second order transition at 242, 235, 238°C, and a decomposition exotherm at 345°C. Romeyn (Reference 11) found two shallow endotherms, probably second order transitions, at 100 and 210°C, and no evidence of other transitions below 400°C. The same author found an intrinsic viscosity in chloroform of 0.52, a number average molecular weight (membrane osmometer) of 24,000 and a weight average molecular weight (light scattering) of 55,000. X-ray diffraction indicated that the polymer is essentially amorphous.

Decomposition Study. See Table VI. *) Figure 5 contains the thermogravimetric analyses, Figure 12 the temperature and pressure profile, Figures 20 and 21 the IR spectra.

*) Mass spectrographic data of the 20 to 375°C fraction are from a crude sample. The reprecipitated materials showed 16.5 mole % of benzene, which was obviously due to solvent that strongly adhered to the material despite extended drying under vacuum at 80°C.

TABLE VI

ANALYSES OF VOLATILES AND RESIDUES OF POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)

	C	H	O
Analysis calc. for $(C_8H_8O)_n$:			
found for polymer :	80.0	6.7	13.3
found for residue 375°C :	79.0	6.7	12.5
found for residue 450°C :	81.1	5.4	9.0
found for residue 550°C :	85.1	3.7	5.6
	89.1	2.2	1.9

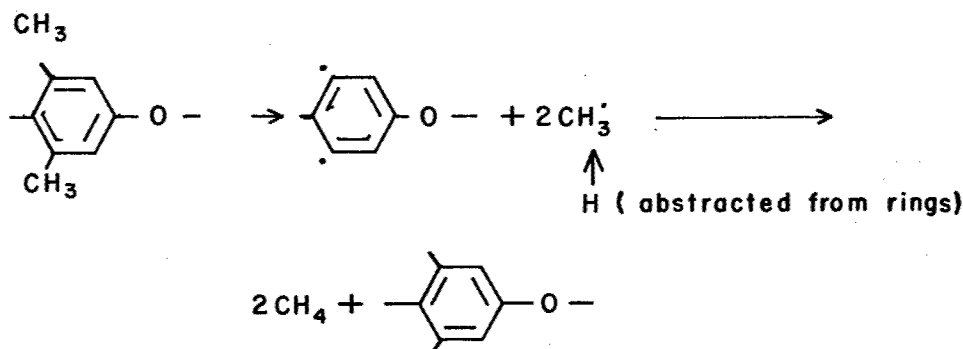
Temp. Range (°C)	Volatile Products (mole %)						C ₆ H ₄ (CH ₃) ₂	Weight Volatiles (%) *)	Total Weight Loss (%) *)
	H ₂	CH ₄	H ₂ O	CO	CO ₂	C ₆ H ₆			
20-375	22.6	43.1	19.0	10.9	3.5	-	0.9	2.1	65.0
375-450	27.6	52.5	2.7	14.7	1.2	0.4	0.8	3.2	5.5
450-550	49.4	28.4	0.5	20.9	0.5	0.2	0.1	~3.0	3.0

*) of starting material

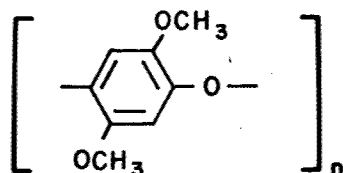
It can immediately be seen that this polymer, on decomposition, gives off much more methane than poly-1,3-phenylene oxide. The major part of the methane is obviously contributed by the methyl groups. Since the amount of methane generated over the entire temperature range is much higher than that generated in previous cases, it can be assumed that the decomposition of the methyl groups takes place during all three decomposition steps.

Apart from the methane generated by the methyl groups, the decomposition pattern of this and the previous polymer are very similar, and the composition of the final residues is almost alike. The IR spectra of the residues of poly(2,6-dimethyl-1,4-phenylene oxide), especially the one at 550°C, have again a strong band at 695 cm^{-1} , believed to be indicative of aliphatic double bonds.

The part of the decomposition reactions involving the methyl groups is shown below:



Poly(-2,5-dimethoxy-1,4-phenylene oxide)



Background Information. The polymer has been synthesized by the Whittaker Corporation, Narmco Research and Development Division, under Air Force contract (Reference 16). The Blanchard polymerization of 4-chloro-2,5-dimethoxy-phenol in the presence of pyridine, cuprous chloride, and oxygen yielded a polymer with an intrinsic viscosity of 0.14 in chloroform and a VPO molecular weight of 6200.

Decomposition Study. Figure 6 shows the thermogravimetric analyses under nitrogen, Figure 13 the temperature-time and pressure-time profile of the decomposition study, and Figures 22 and 23 the IR spectra of the polymer and the residues. Analyses of starting material, residues, and volatile products are given in Table VII.

The main decomposition products at lower temperatures are carbon monoxide, carbon dioxide, methane, and methanol, while at higher temperatures carbon monoxide predominates over hydrogen and methane. For the first time small amounts of ethane and butane, probably along with some higher hydrocarbons, are observed. The formation of methanol from the decomposition of the methoxy group was expected, but its quantity is rather small. The major

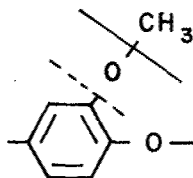
TABLE VII
ANALYSES OF VOLATILES AND RESIDUES OF POLY(2,5-DIMETHOXY-1,4-PHENYLENE OXIDE)

	C	H	O
Analysis calc. for $(C_8H_8O_3)_n$:			
found for polymer :	63.2	5.3	31.5
found for residue 350°C :	60.8	5.2	31.0
found for residue 450°C :	70.4	3.6	21.5
found for residue 450°C :	73.8	3.1	16.6
found for residue 550°C :	86.9	2.2	3.9

Temp. Range (°C)	Volatile Products (mole %)							Weight Volatiles (%) *)	Total Weight Loss (%) *)	
	H ₂	CH ₄	H ₂ O	CO	C ₂ H ₆	CH ₃ OH	CO ₂			
20-350	1.4	25.0	1.1	31.9	1.2	13.6	24.6	0.6	16.2	43.5
350-450	4.9	10.9	1.2	68.1	1.0	0.5	13.4	-	~6.5	6.5
450-550	19.1	12.4	0.5	61.5	0.6	0.1	5.8	-	7.2	9.0

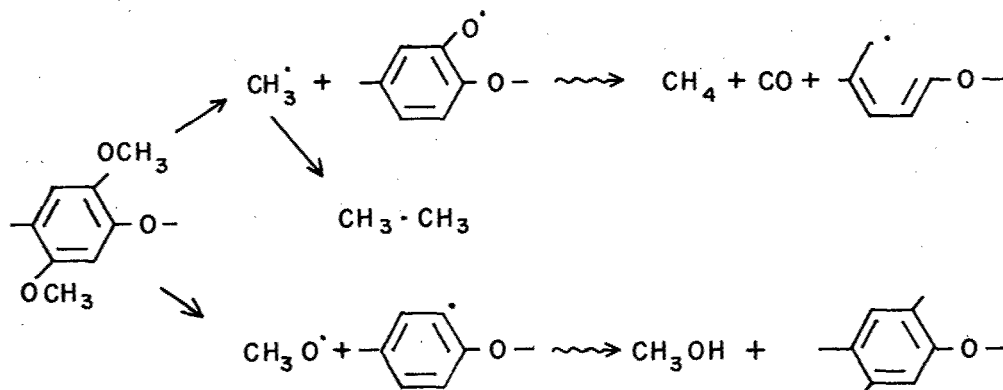
*) of starting materials

decomposition products of the side chain seem to be carbon monoxide and methane. This means that the methoxy group



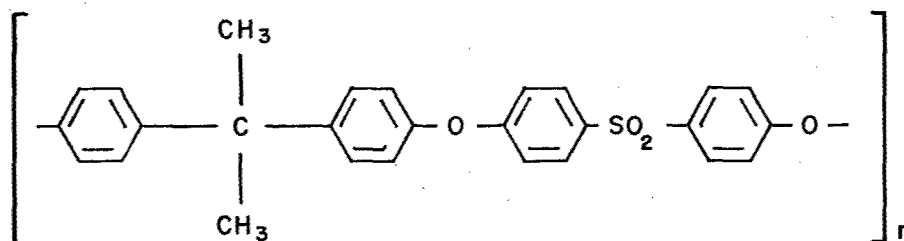
cleaves predominantly as indicated by the solid line, with some cleavage along the dotted line. In the first case the methyl radical probably abstracts hydrogen from the ring to form methane, while a few methane radicals combine to ethane. Some of the phenoxy radicals break down to carbon monoxide, others form peroxide linkages (broad, very weak band at 820 cm^{-1} in the spectrum of residue, Figure 23) which cause the formation of considerable amounts of carbon dioxide. In the second case the methoxy group cleavage results in the formation of methanol and carbon-carbon crosslinks. In addition to this, the postulated breakdown mechanism for poly-1,3-phenylene oxide possibly applies also to this polymer. The analysis of the final residue is similar to those from the other two polyphenylene oxides, although the oxygen content is somewhat higher. Inexplicable at this time is the fact that hardly any water is formed during the decomposition of the ether linkage.

The part of the decomposition reactions involving the methoxy groups may occur, somewhat simplified, in the following manner:

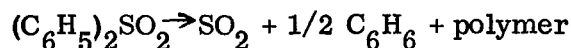


The hydrogen required for the formation of methane and methanol is probably being abstracted from the rings, as in previous cases.

Polysulfone "Phenoxy T Blend 5"



Related Literature. Levy and Ambrose (Reference 17) subjected diphenylsulfone to pyrolysis under vacuum in the temperature range of 472 to 565°C and found benzene, sulfur dioxide, and small amounts of hydrogen, carbon dioxide, and carbon oxysulfide. From the $\text{SO}_2/\text{C}_6\text{H}_6$ ratio of 2, they suggested:



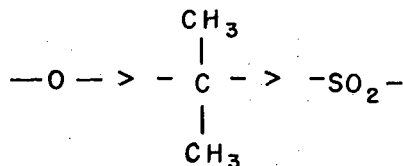
Recently, a decomposition study with polysulfone "Phenoxy T Blend 5" has been reported (Reference 18). Mass spectrographic analyses of the decomposition products revealed that sulfur dioxide was the first measurable decomposition product above 400°C. It can be assumed that the loss of sulfur dioxide is accompanied by the formation of 4,4-diphenylene linkages. Other products below 500°C included phenol, Bisphenol A, and p-isopropenyl phenol. Methane is probably formed by homolytic cleavage of the isopropylidene link via initial formation of a methyl radical. Studies with model compounds, performed by the same authors indicated that the sulfone linkage was more stable than the ether linkage in air, but less stable in an inert atmosphere.

Background Information. The polymer was received in pellet form from the Union Carbide Corporation. For our studies, the polymer has been twice reprecipitated from chloroform-methanol. Elemental analysis confirmed the structure given above. Studies performed by the U. S. Rubber company under Air Force contract (Reference 19) showed that the polymer was soluble in a variety of solvents. It was essentially amorphous. DTA gave a shallow endotherm, probably a second order transition, at 185°C. The intrinsic viscosity in chloroform was 0.62; the molecular weight (from light scattering) has been found to be 84,000.

Decomposition Study. Thermogravimetric analyses are shown in Figure 7, the temperature and pressure profile in Figure 14 and the IR spectra in Figure 24. Table VIII lists the results of mass spectrographic and elemental analysis.

The competing reactions to be expected are scissions at (and removal of) the ether-, sulfone-, and 2,2-propylene linkages, along with the breakdown of the benzene rings. The data indicate an incipient breakdown of all three linkages during the first temperature step. It was hoped that decomposition studies at lower temperatures would permit a distinction between the onset of breakdown of the three linkages. Trials were run at 20 to 350°C and 20 to 400°C, with the results given in Table IX.

Although the onset of breakdown again is uncertain (all three linkages begin to decompose below 350°C), a distinction nevertheless can be made. The removal of the SO_2 linkage is practically completed at 450°C. The methane formation (most of which probably results from the propylene linkage) extends to 620°C, but with a maximum at 20 to 450°C. The decomposition of the ether linkage also extends to 620°C, but its maximum occurs at 450 to 550°C. The order of stability therefore, seems to be



A small part of the sulfur remains in the polymer and is stable at least up to 620°C; it may be present as the di(benzothiophene) moiety. The ether linkage is mainly removed as carbon monoxide under ring cleavage, a smaller part as water and carbon dioxide; the mechanisms have been explained earlier.

TABLE VIII
ANALYSES OF VOLATILES AND RESIDUES OF "POLYSULFONE" (I)

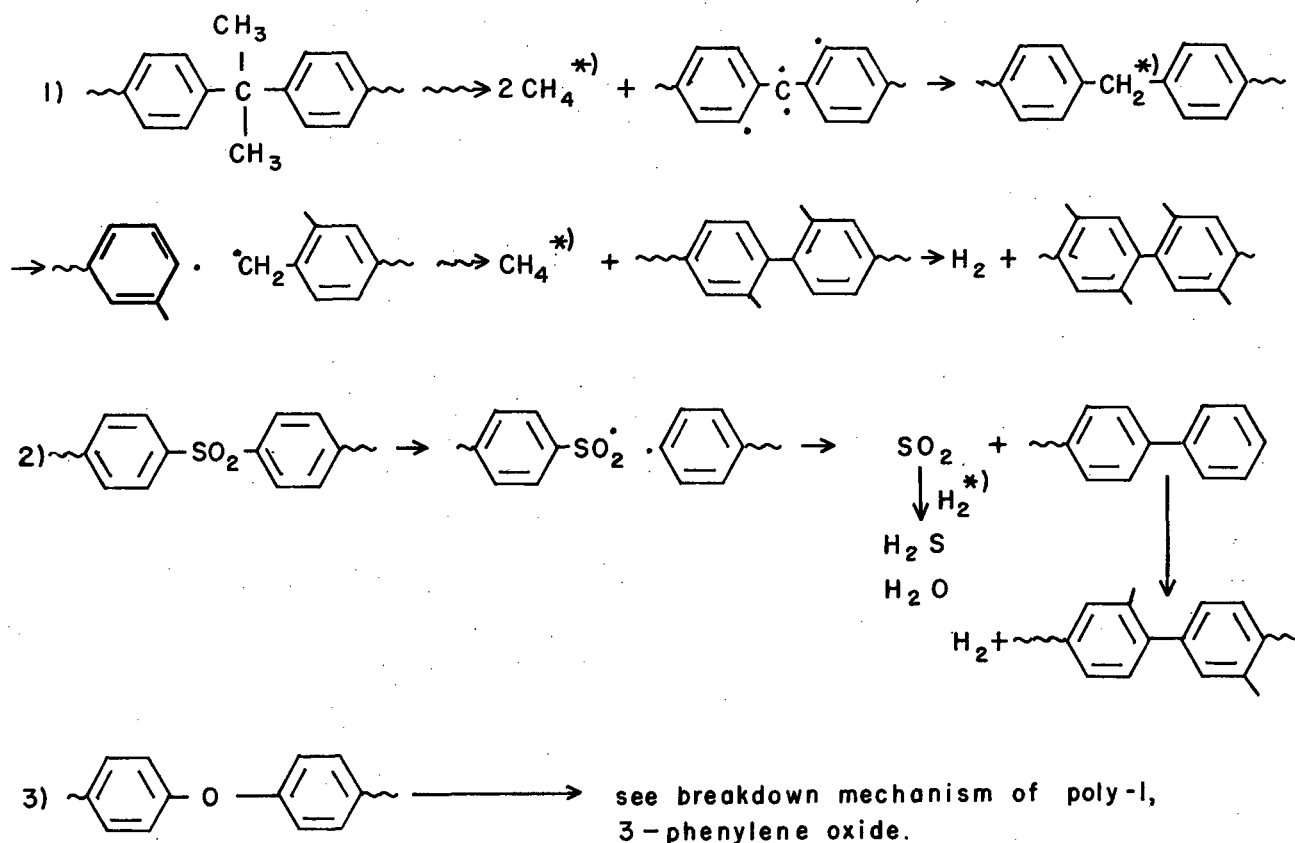
	C	H	O	S
Analysis calc. for $(C_{27}H_{22}O_4S)_n$:	73.3	5.0	14.5	7.2
found for polymer :	73.3	5.4	16.0	7.5
found for residue 450°C :	88.0	4.0	4.5	0.5
found for residue 550°C :	91.6	2.7	1.4	0.5
found for residue 620°C :	93.8	1.6	1.2	0.7

Temp.; Range (°C)	Volatile Products (mole %)							Weight Volatiles (%) *	Total Weight Loss (%) *		
	H ₂	CH ₄	H ₂ O	CO	H ₂ S	CO ₂	SO ₂			C ₆ H ₆	C ₆ H ₅ CH ₃
20-450	9.4	18.3	1.0	6.9	4.9	0.8	57.3	1.0	0.4	23.2	61.0
450-550	61.7	11.4	1.9	22.0	0.8	1.3	-	0.8	0.2	3.9	6.5
550-620	80.0	7.5	0.6	11.6	0.3	0.4	-	0.5	0.1	1.6	0.5

*) of starting material

The evolution of hydrogen occurs predominantly at the upper temperature range. The final residual structure appears to be highly crosslinked, possibly with hydrogen deficient aliphatic chains. Some oxygen and sulfur may be present in the form of stable, fused ring compounds.

The contributions of the three different linkages to the decomposition mechanism are as follows:



*)hydrogen atoms abstracted from rings

TABLE IX
ANALYSES OF VOLATILES AND RESIDUES OF "POLYSULFONE" (II)

[illegible]

*) of starting material
**) questionable

Equilibrium pressure	20 to 350°C:	12 mm
Equilibrium pressure	20 to 400°C:	92 mm

EXPERIMENTAL

General Procedure

The apparatus used for the decomposition studies is shown in Figure 25. A Vycor test cell was used; the remainder of the apparatus was 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 750-watt furnace, controlled by an F&M-240M Power Proportioning Temperature Programmer; the temperature control was within $\pm 5^\circ\text{C}$. The volume of the sample cell was 60.7 ± 0.5 ml; the volume of the evacuated apparatus (without sample cell) was 137 ± 0.5 ml. With increasing pressure, the volume has to be corrected by adding 0.75 ml per 10 ml mercury.

The polymer was dried overnight under vacuum at 110°C , and 0.2 gm 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 to 50μ and the valves closed. After the controller had been set to the desired temperature, the furnace was turned on and temperature, time, and pressure recorded at intervals. After no further pressure increase was noted between two consecutive readings, which were taken every two minutes, 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 establishing a vacuum of approximately 30 to 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. The two residues corresponding to the first two temperature steps were obtained by subjecting two more samples to the first, or the first and the second temperature cycle used in the main experiment. They were also analyzed as indicated above.

Mass Spectroscopy

The gas samples have been 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 have been used.

Infrared Spectroscopy

Infrared spectra were obtained by use of a Perkin-Elmer infrared recording spectrophotometer and potassium bromide pellets. The polymers and especially the residues were shaken 1 to 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 polymer in KBr was used.

Elemental Analysis

Elemental analyses have been performed by the Analytical Branch, Air Force Materials Laboratory.

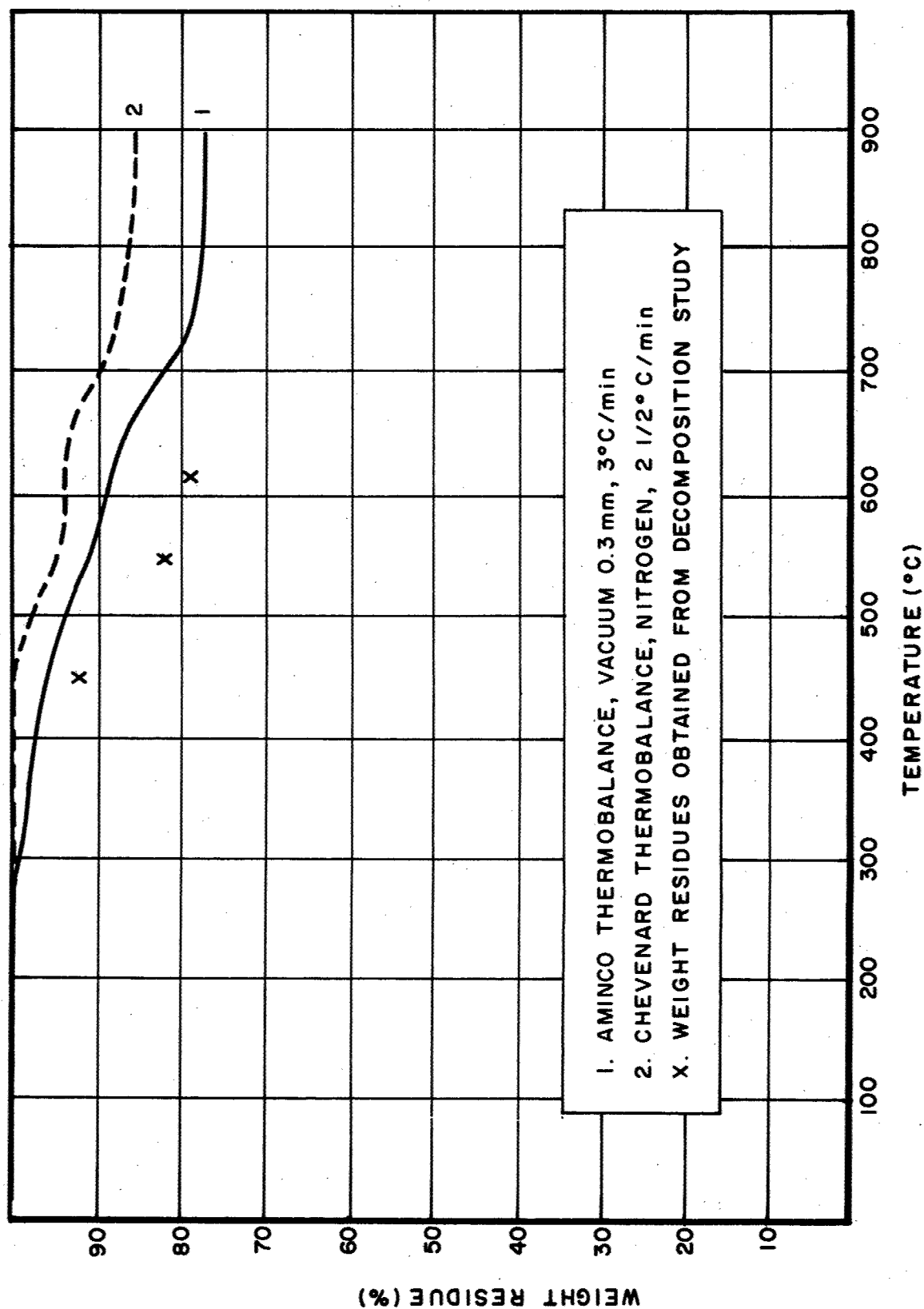


Figure 1. Thermogravimetric Analyses of Poly-1,4-phenylene

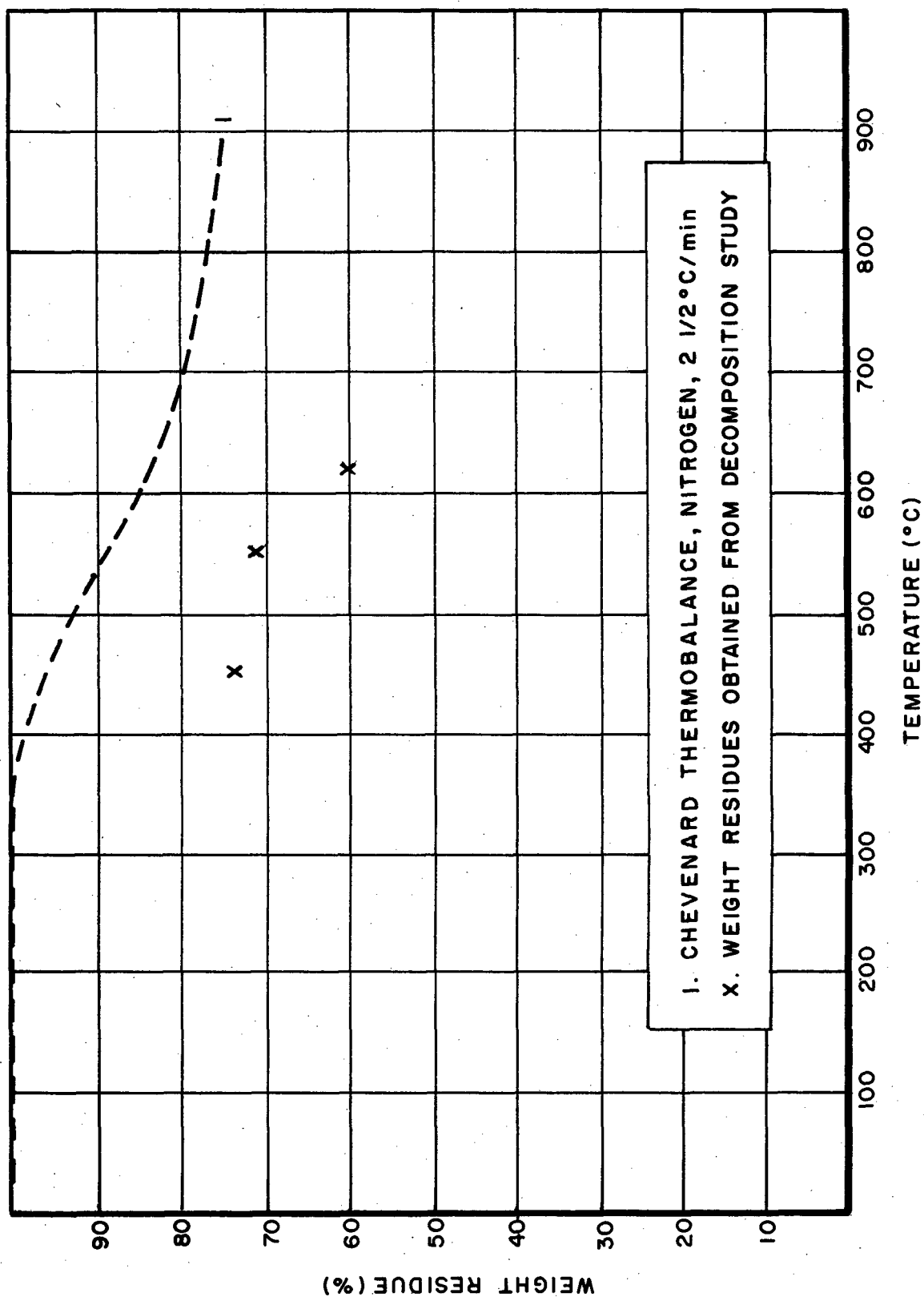


Figure 2. Thermogravimetric Analyses of Poly-2-hydroxy-1,4-phenylene

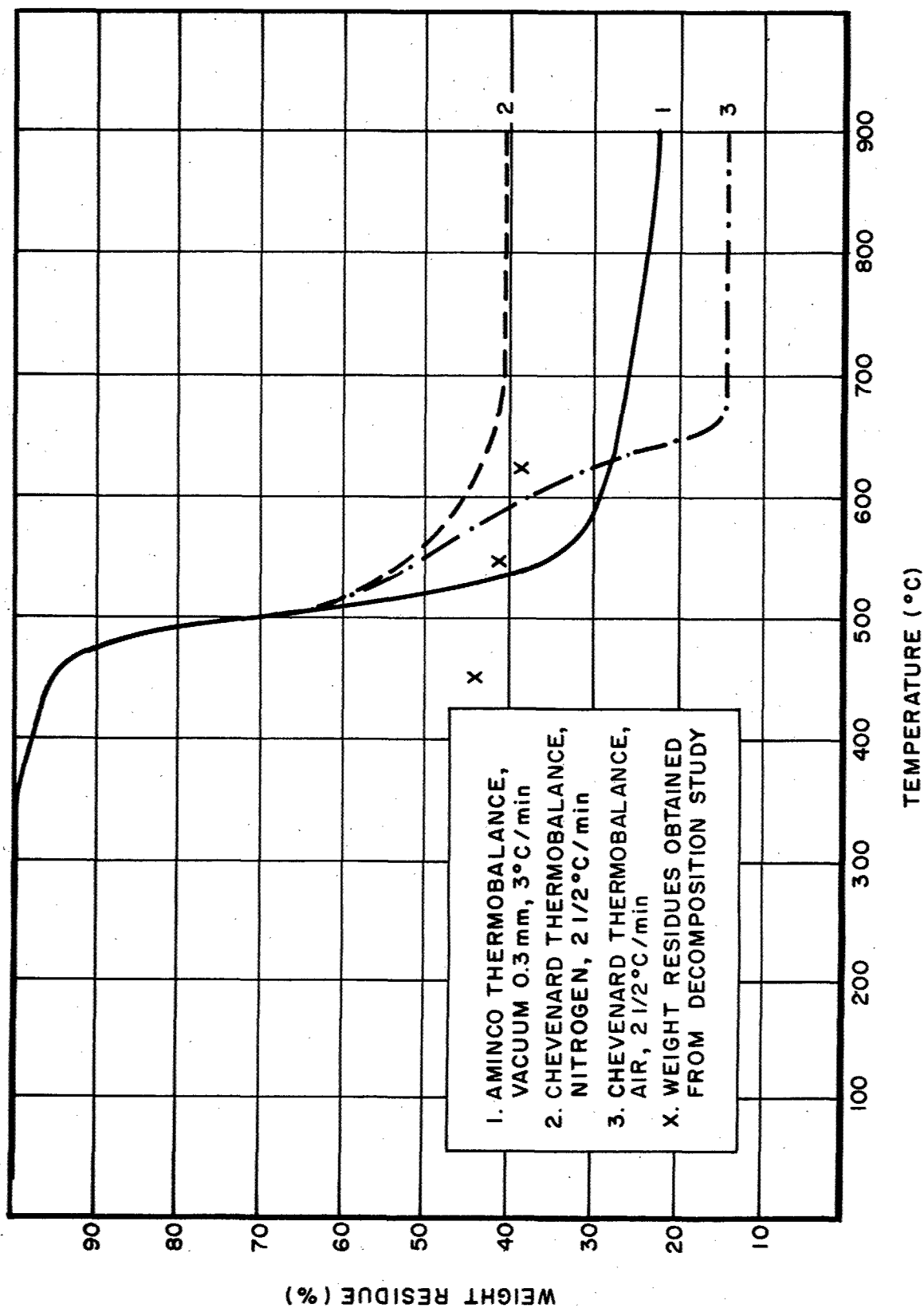


Figure 3. Thermogravimetric Analyses of Poly-1,4-phenylene sulfide

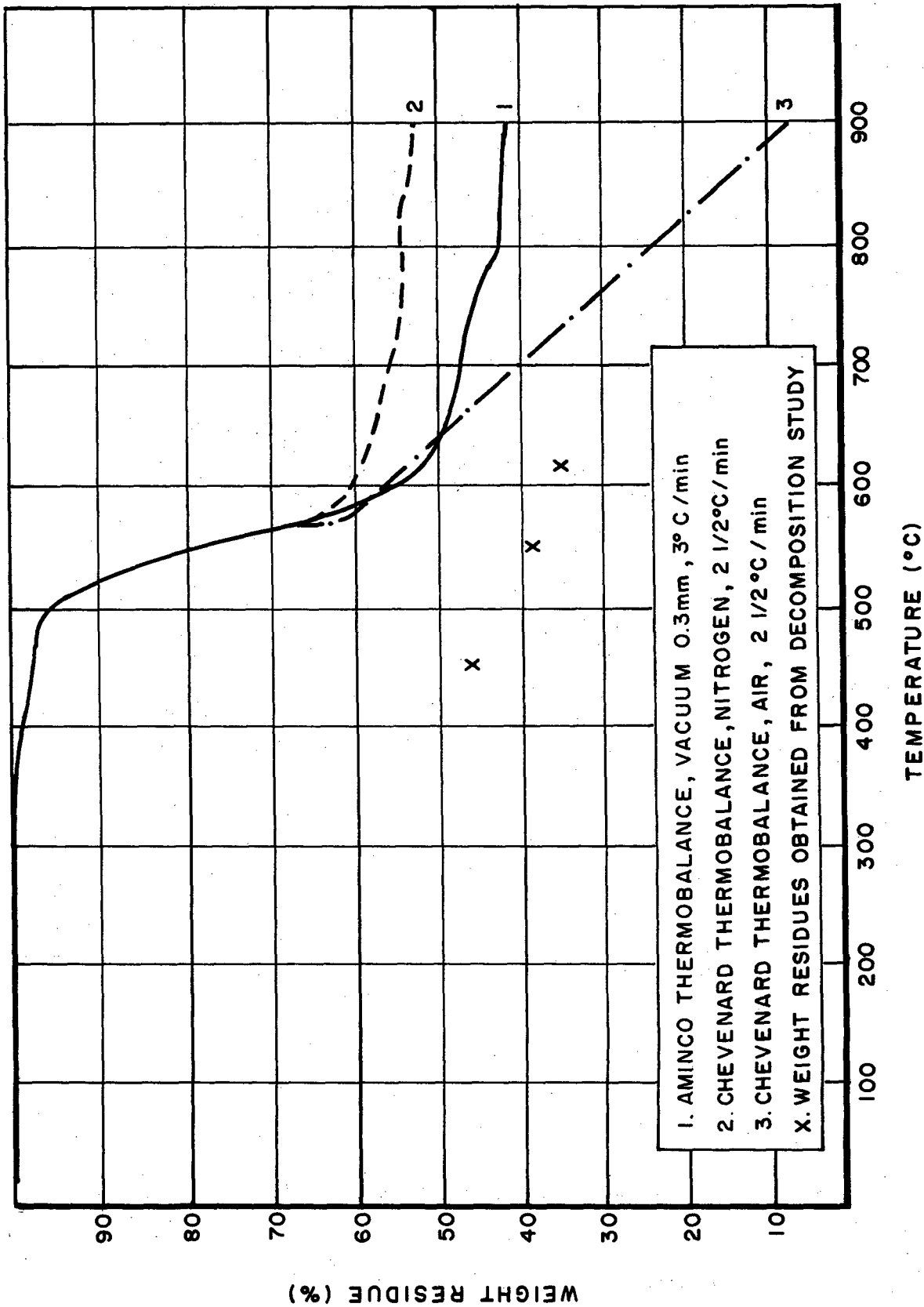


Figure 4. Thermogravimetric Analyses of Poly-1,3-phenylene oxide

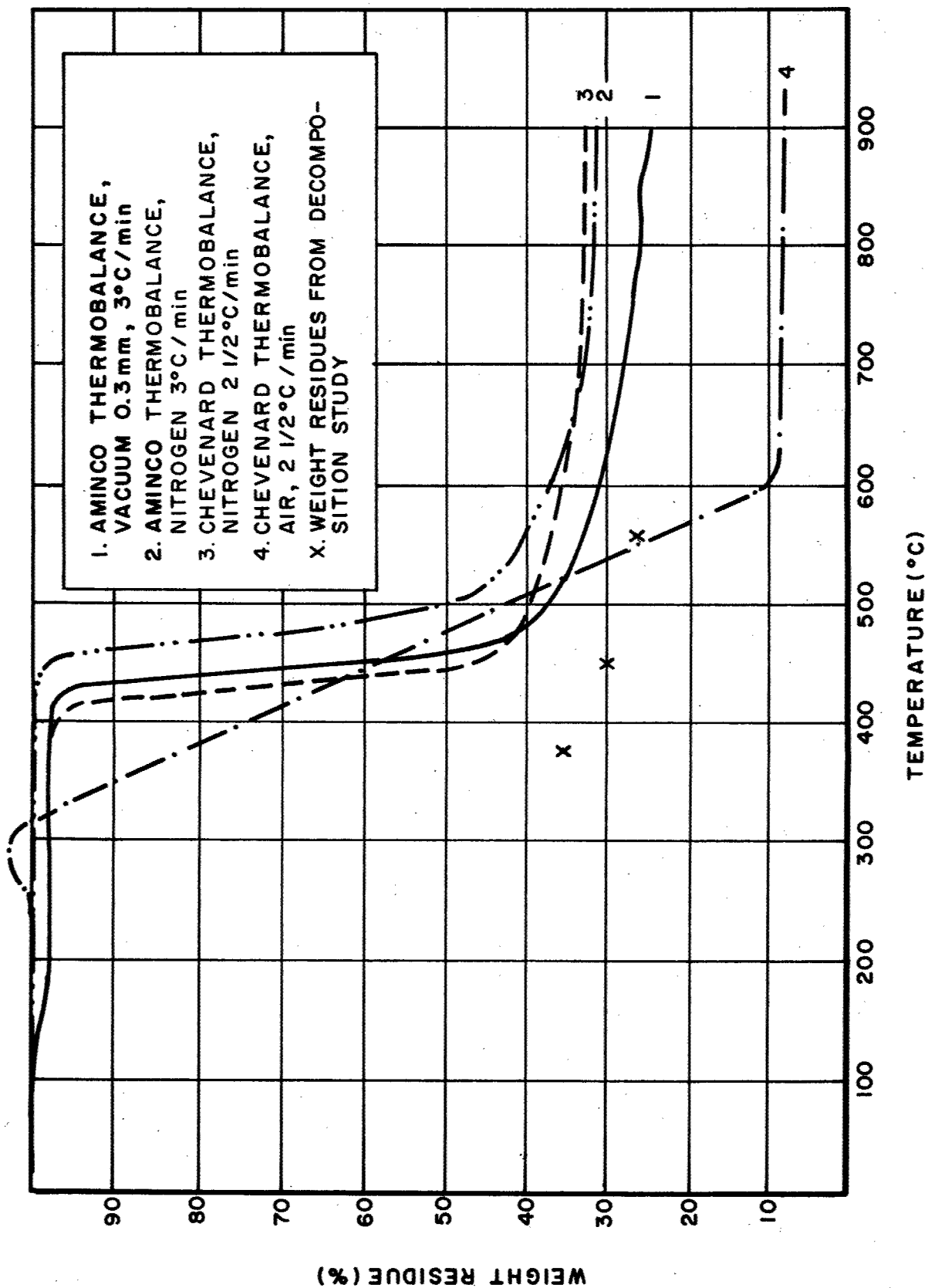


Figure 5. Thermogravimetric Analyses of Poly(2,6-dimethyl-1,4-phenylene oxide)

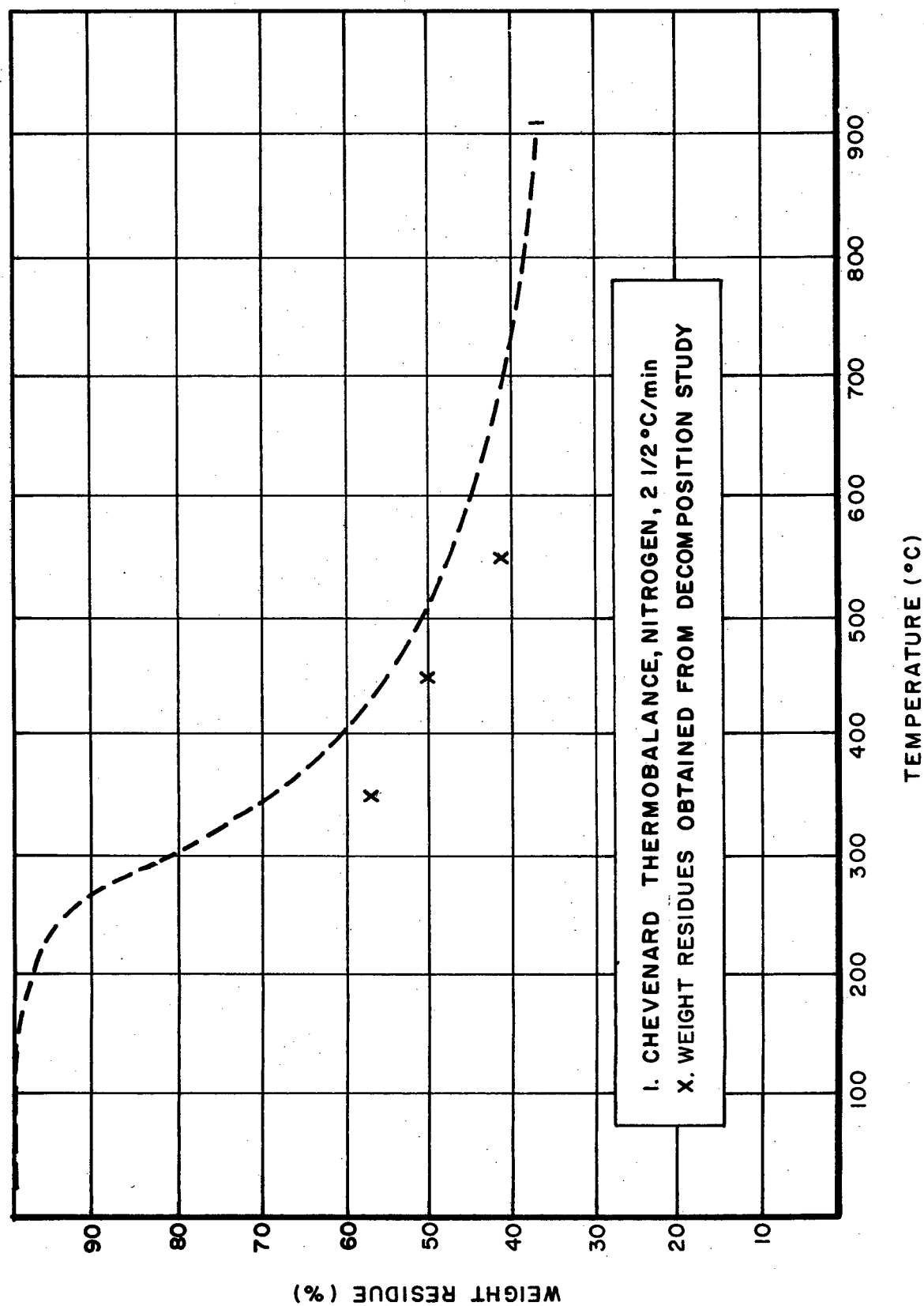


Figure 6. Thermogravimetric Analysis of Poly(2,5-dimethoxy-1,4-phenylene oxide)

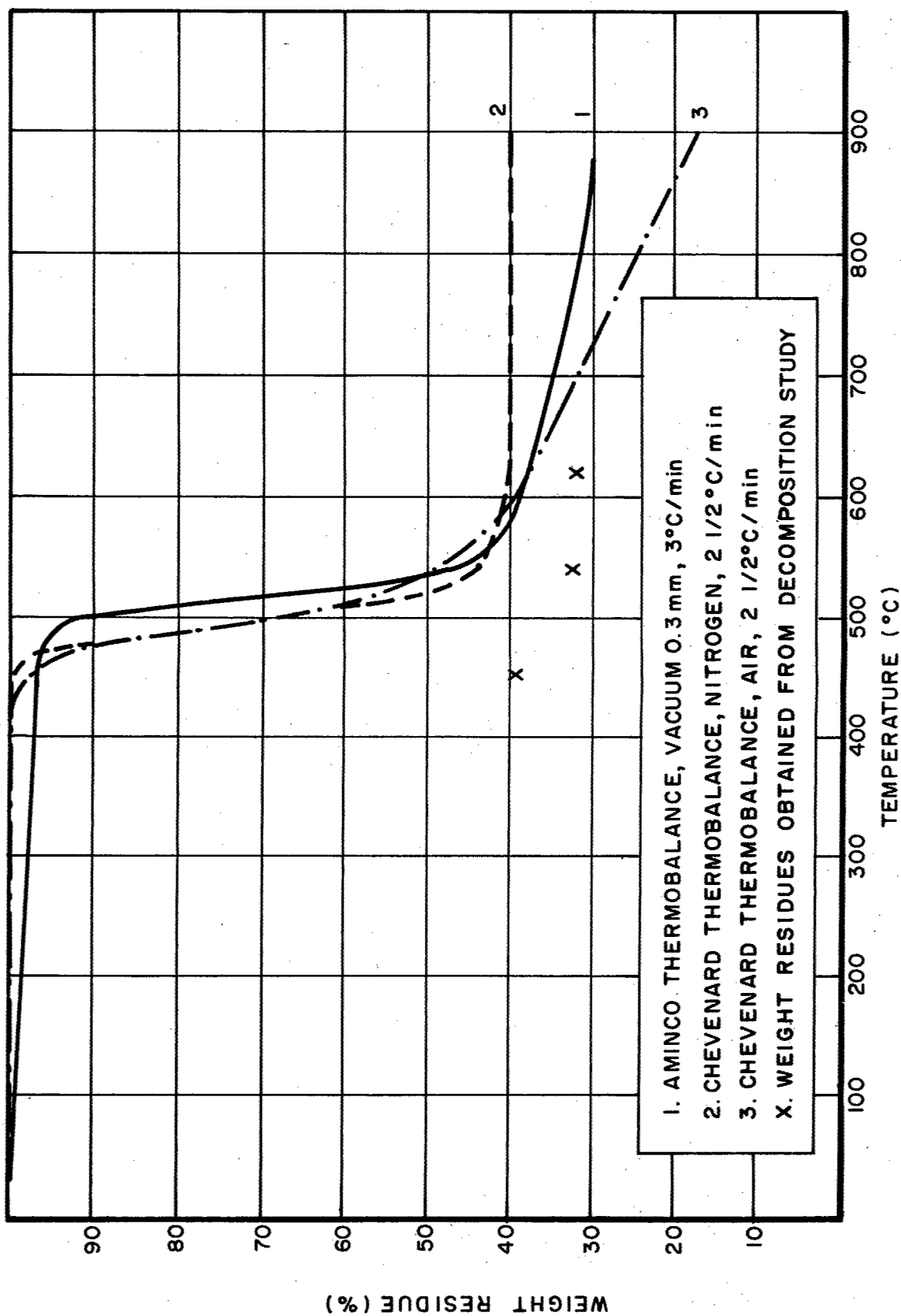


Figure 7. Thermogravimetric Analysis of "Polysulfone"

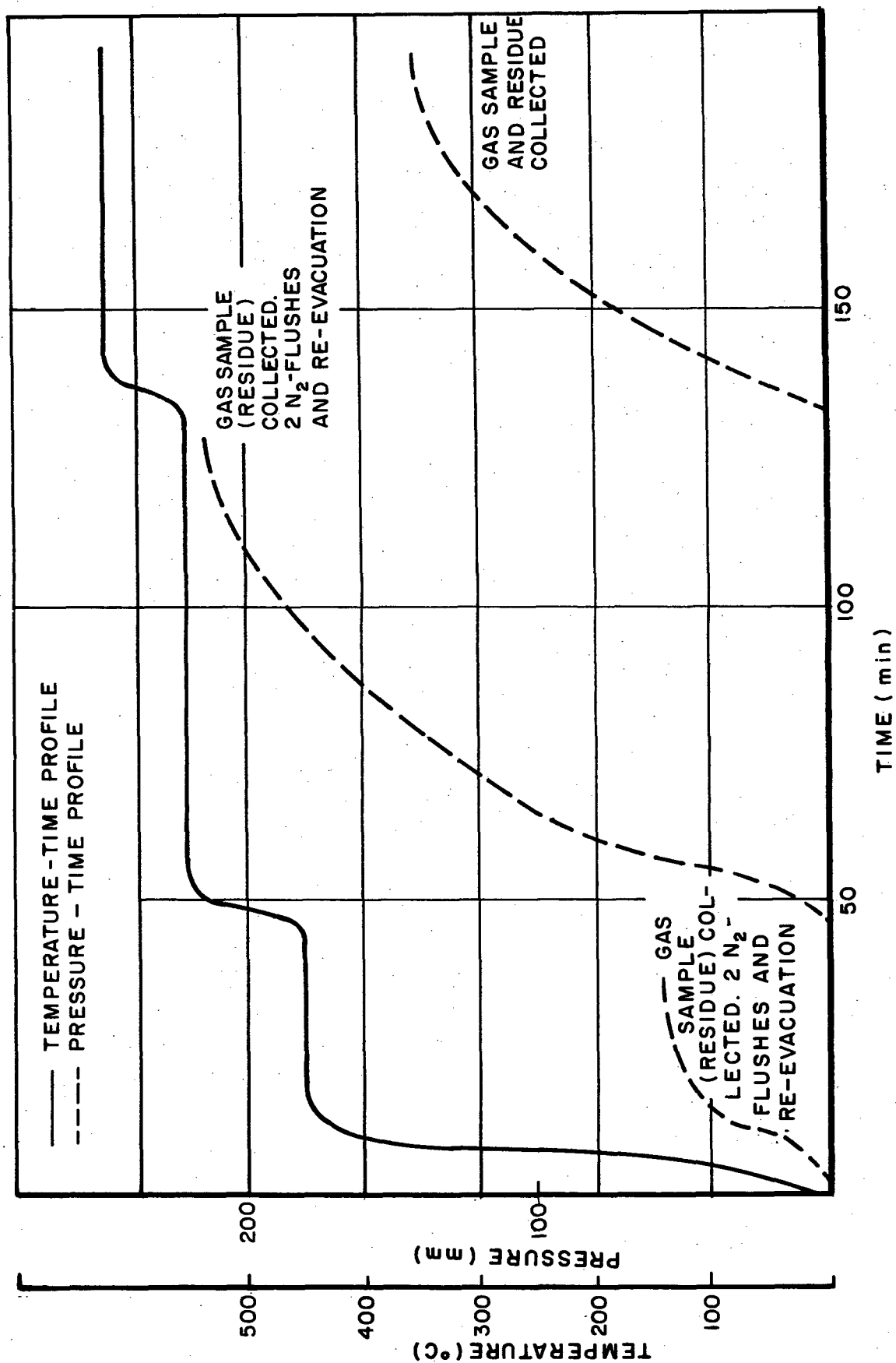


Figure 8. Temperature-Time and Pressure-Time Profile of Decomposition Study of Poly-1,4-phenylene

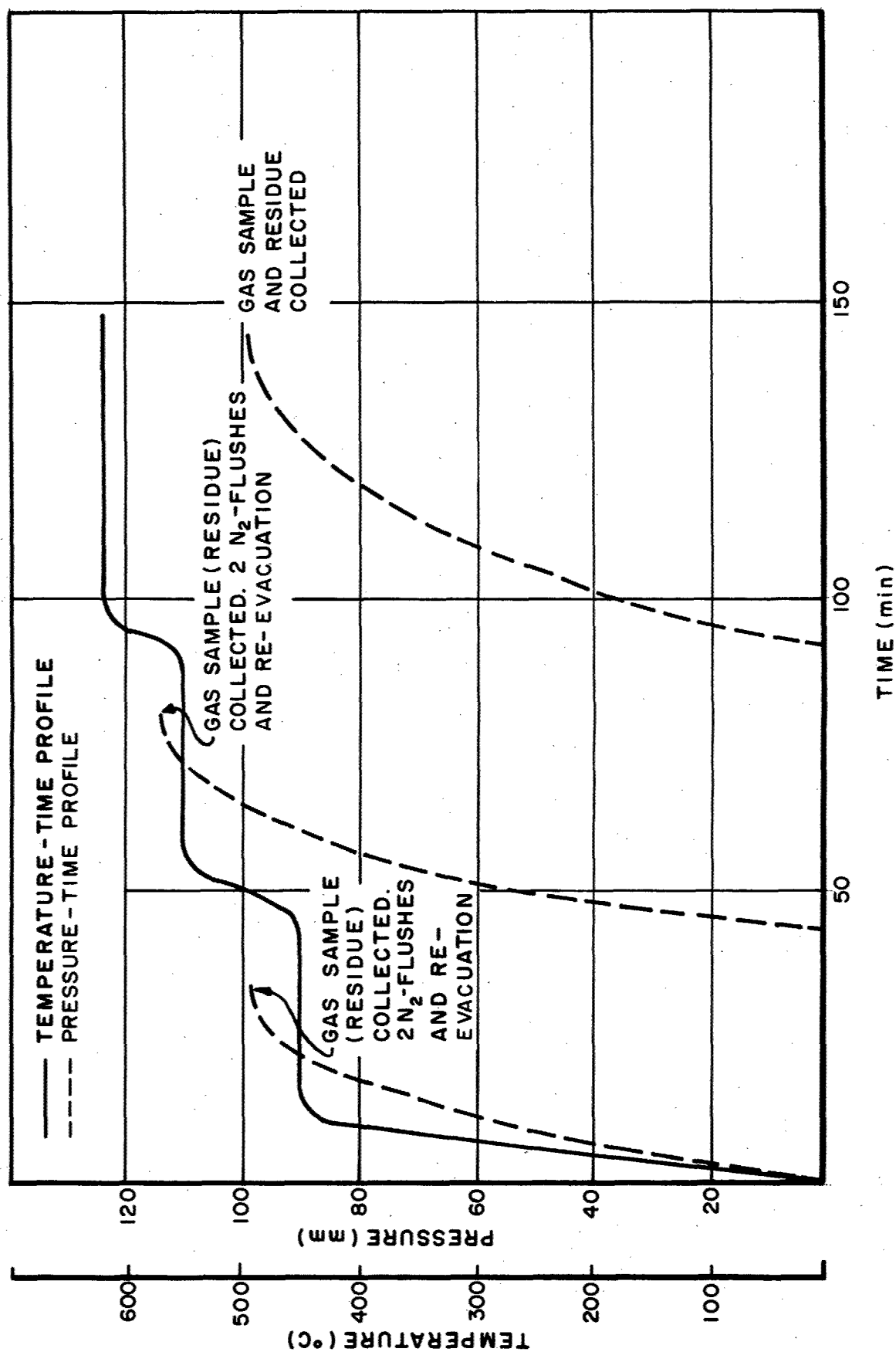


Figure 9. Temperature-Time and Pressure-Time Profile of Decomposition Study of Poly-2-hydroxy-1,4-phenylene

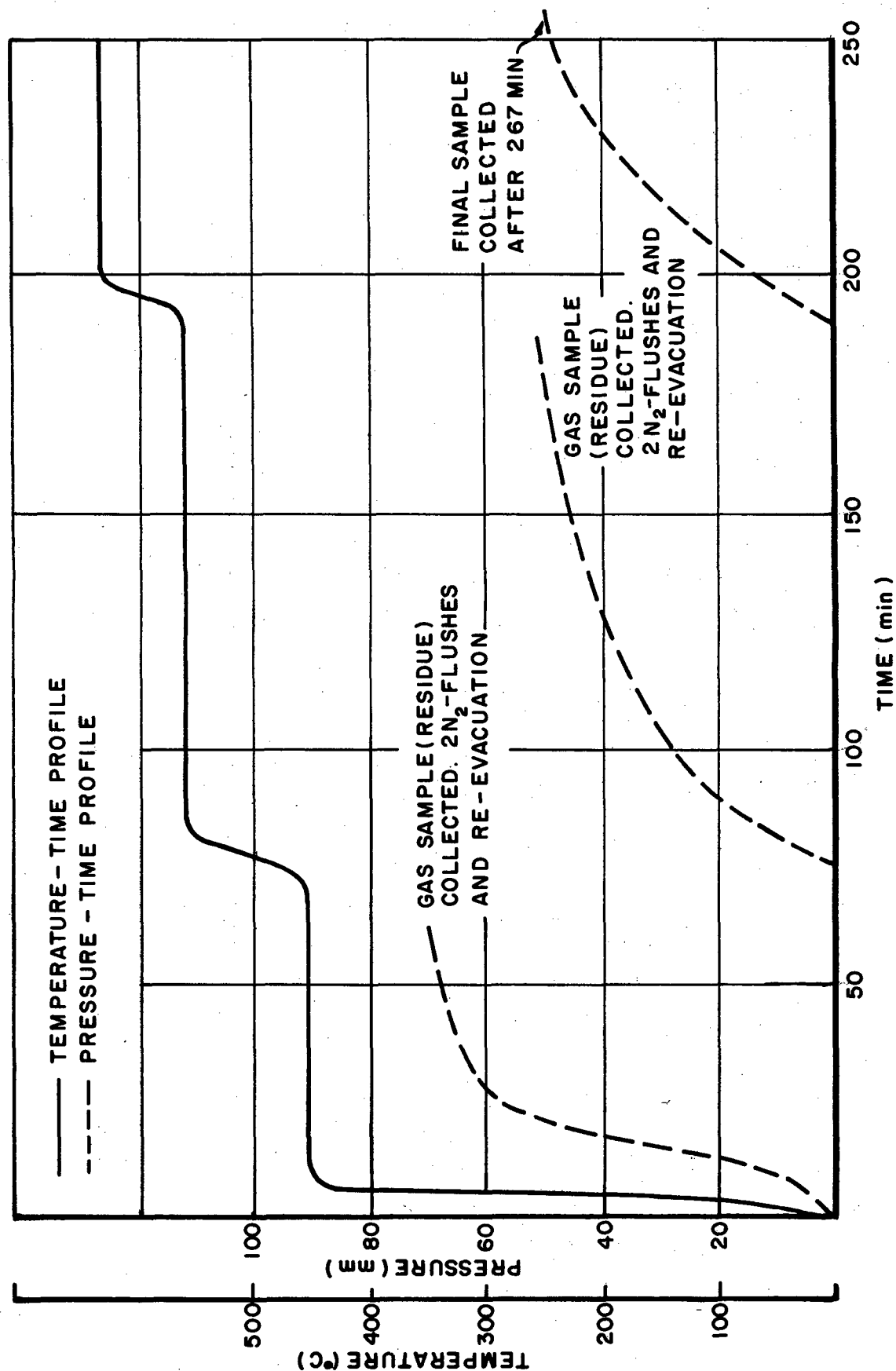


Figure 10. Temperature-Time and Pressure-Time Profile of Decomposition Study of Poly-1,4-phenylene sulfide

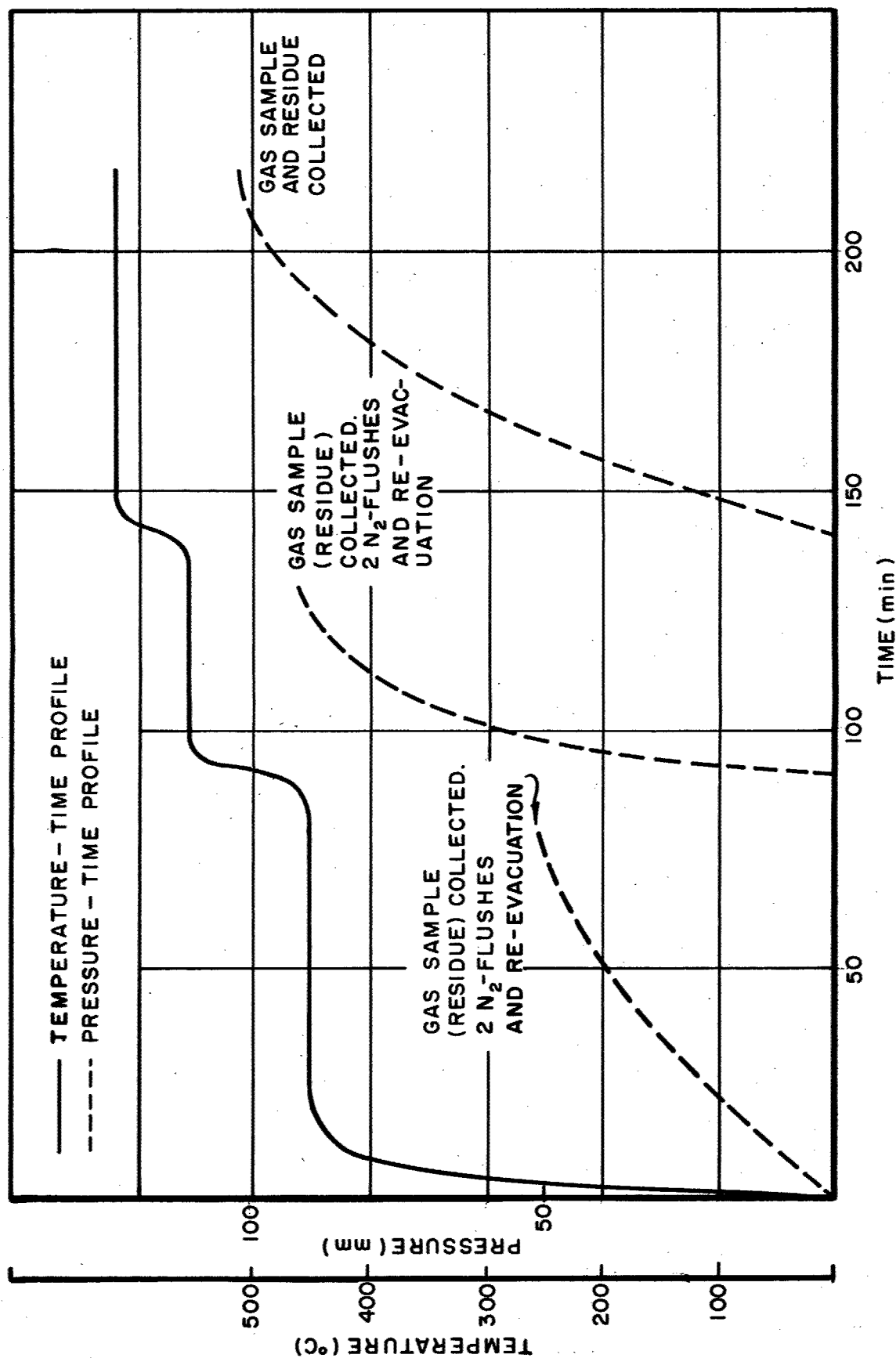


Figure 11. Temperature-Time and Pressure-Time Profile of Decomposition Study of Poly-1,3-phenylene oxide

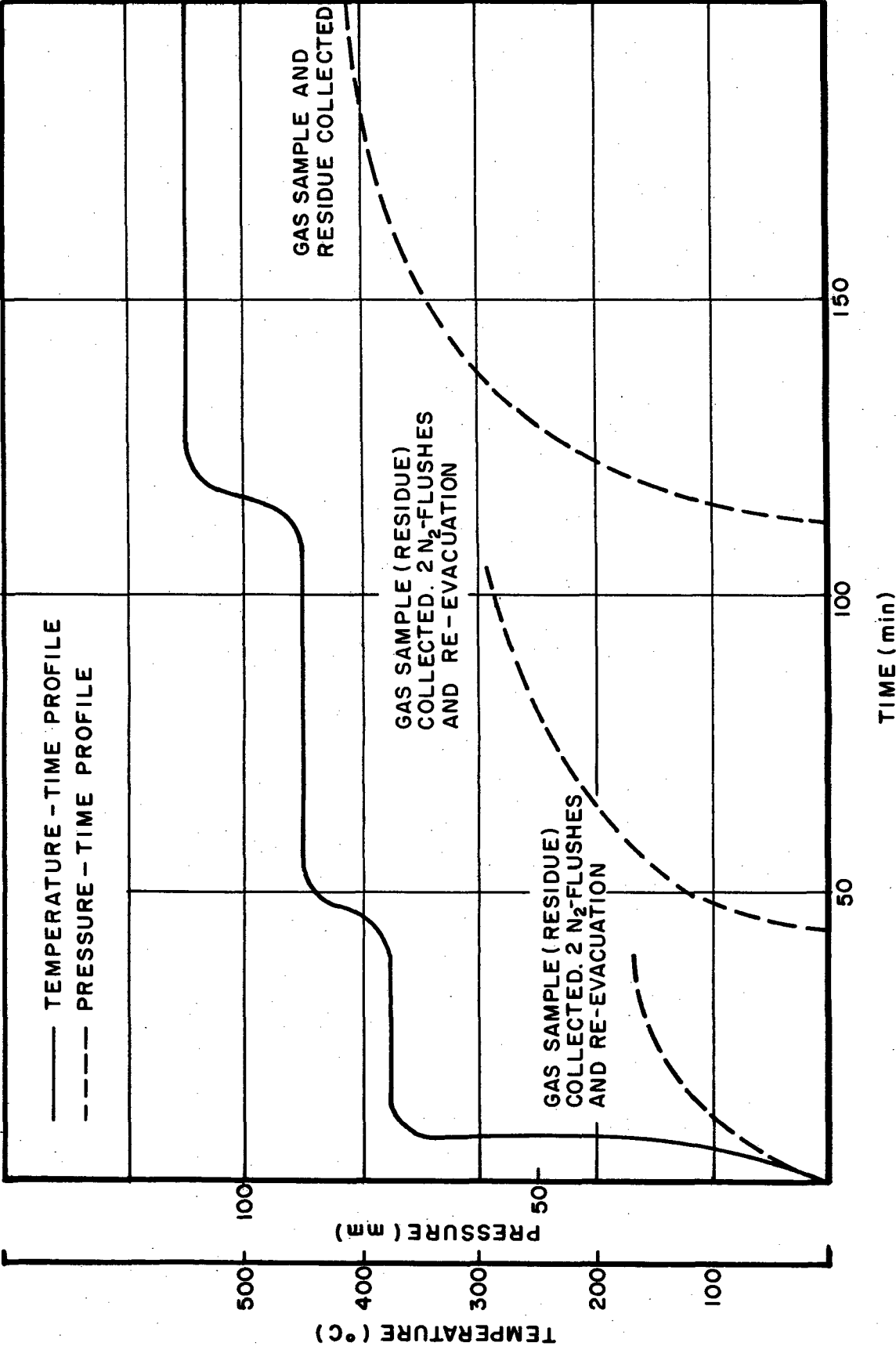


Figure 12. Temperature-Time and Pressure-Time Profile of Decomposition Study of Poly(2,6-dimethyl-1,4-phenylene oxide)

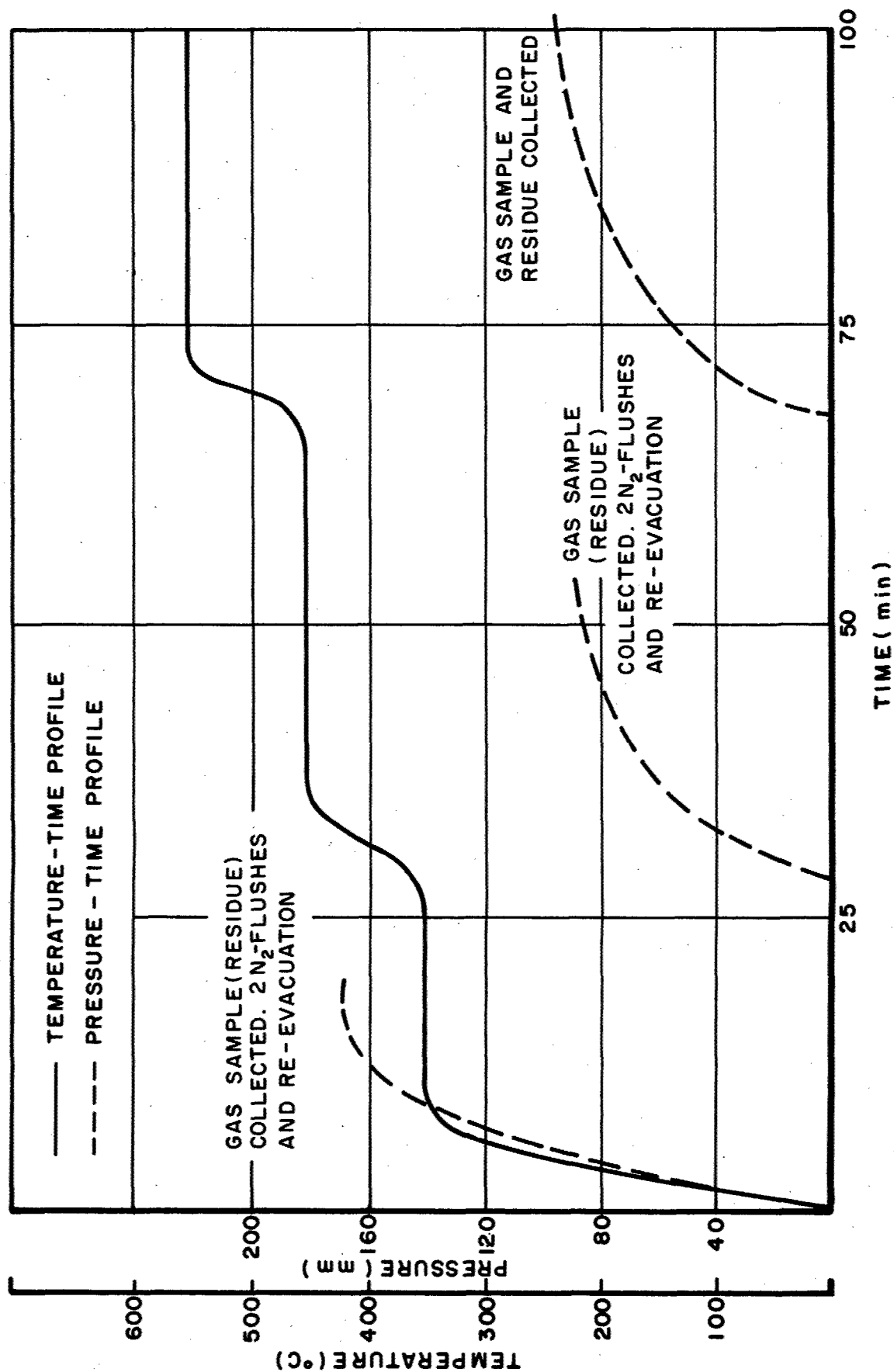


Figure 13. Temperature-Time and Pressure-Time Profile of Decomposition Study of Poly(2,5-dimethoxy-1,4-phenylene oxide)

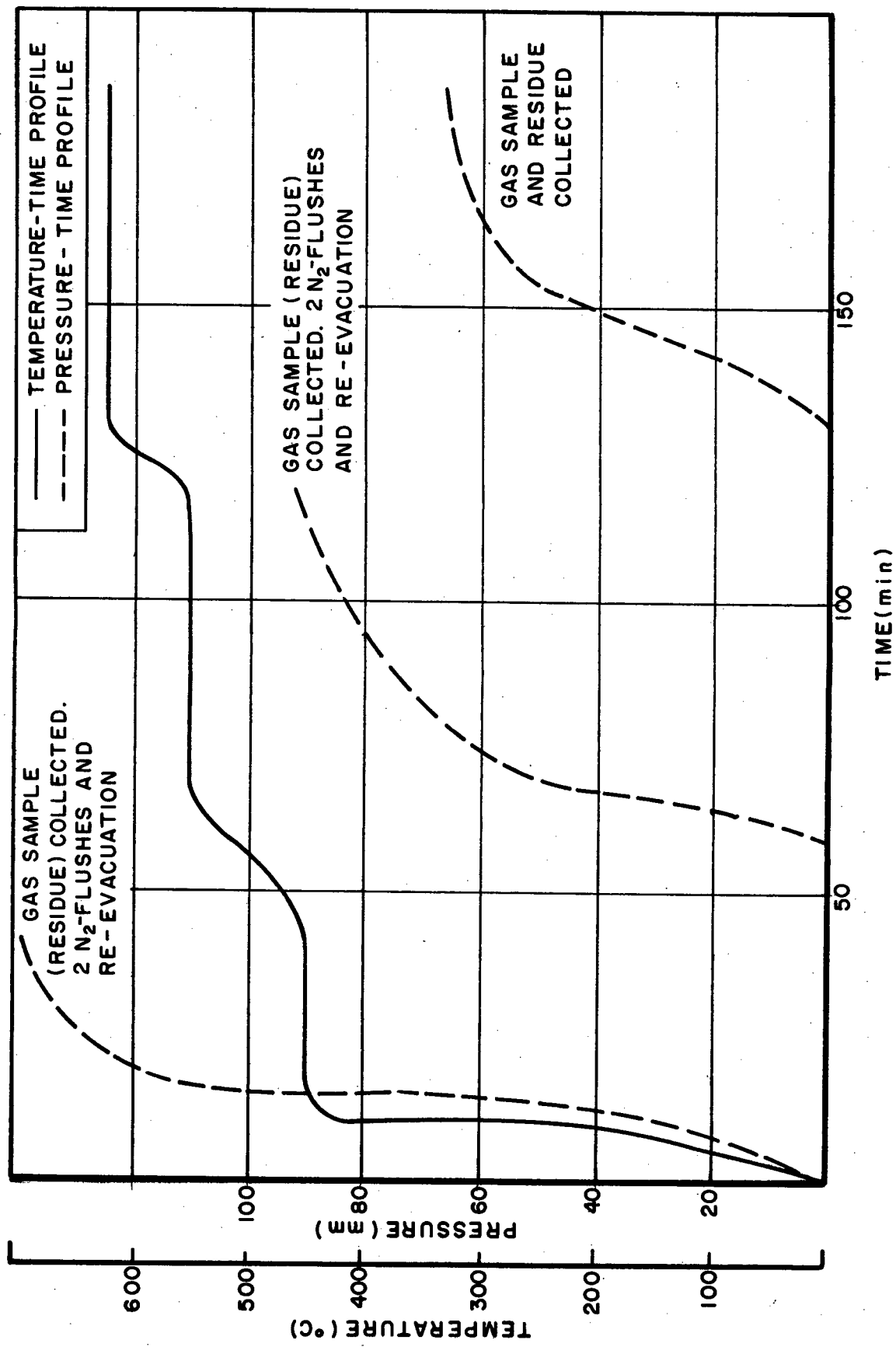


Figure 14. Temperature-Time and Pressure-Time Profile of Decomposition Study of "Polysulfone"

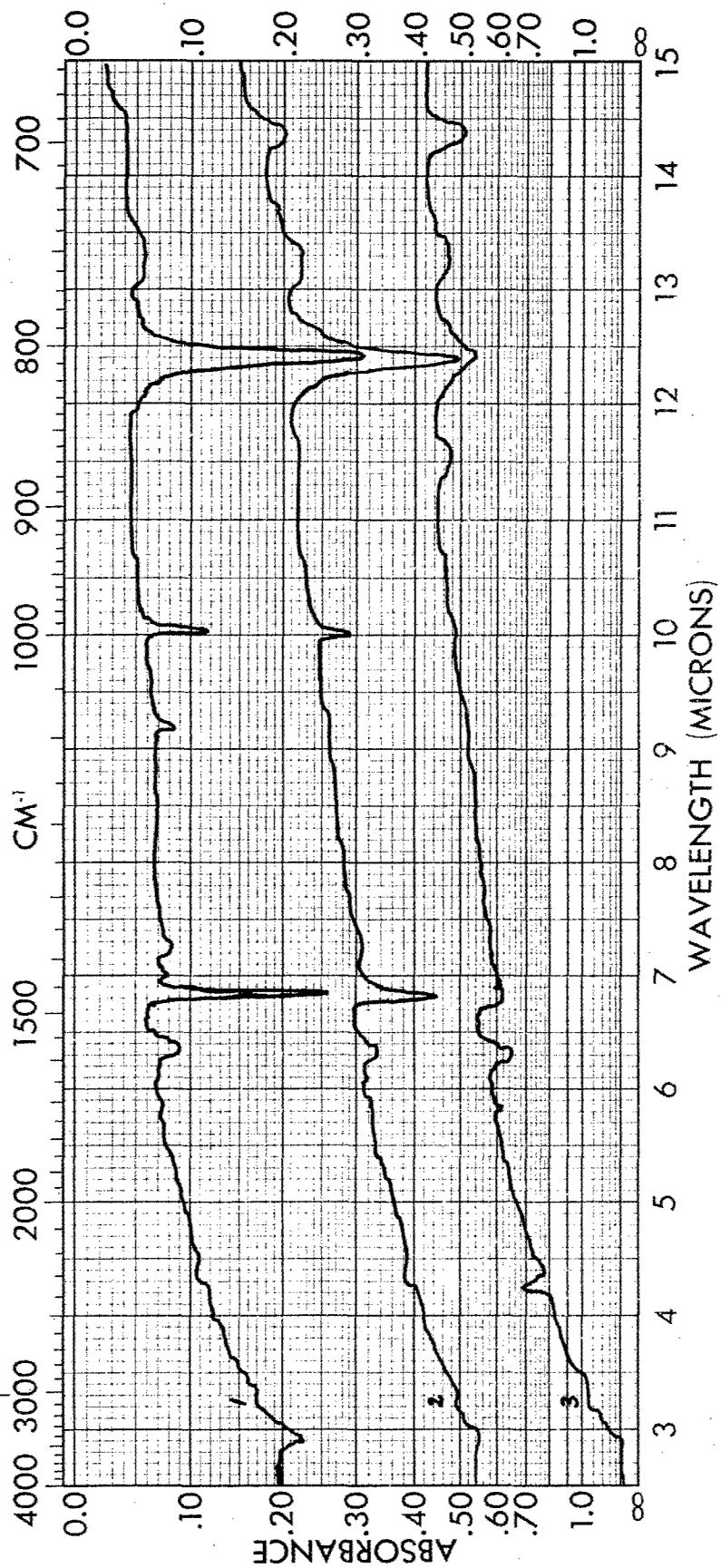


Figure 15. IR Spectra of (1.) Poly-1,4-phenylene; (2.) Residue at 450°C; (3.) Residue at 550°C

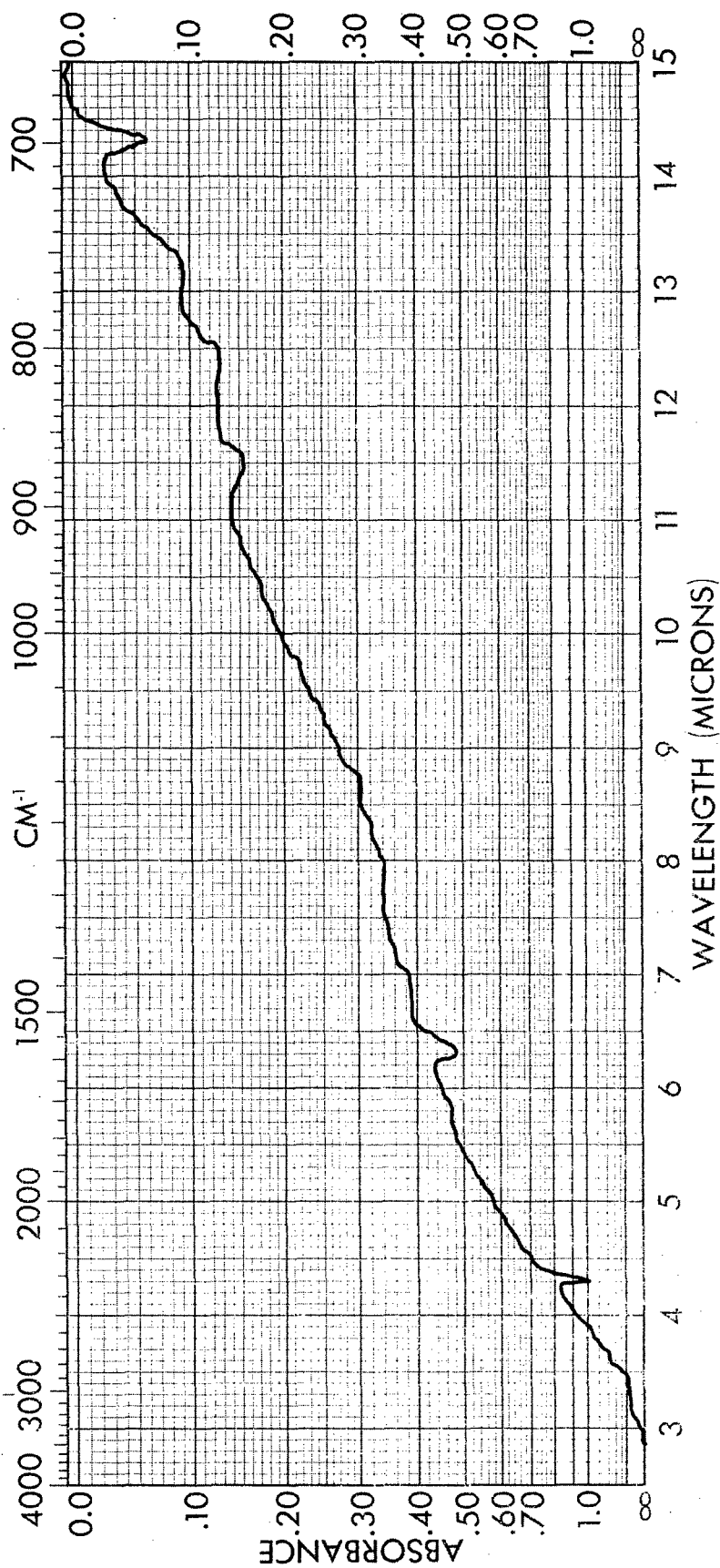


Figure 16. IR Spectrum of the Residue at 620°C of Poly-1,4-phenylene

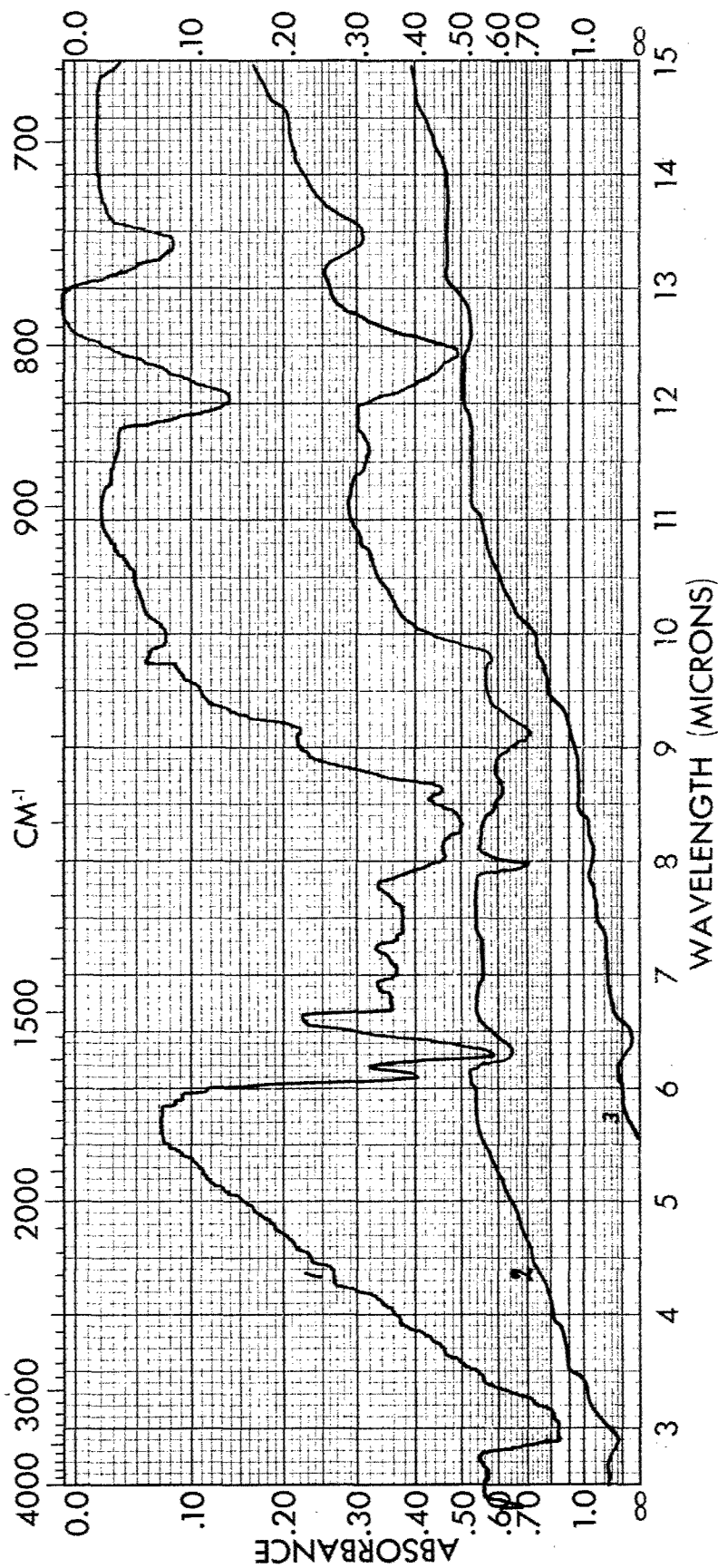


Figure 17. IR Spectra of (1.) Poly-2-hydroxy-1,4-phenylene; (2.) Residue at 450°C; (3.) Residue at 550°C

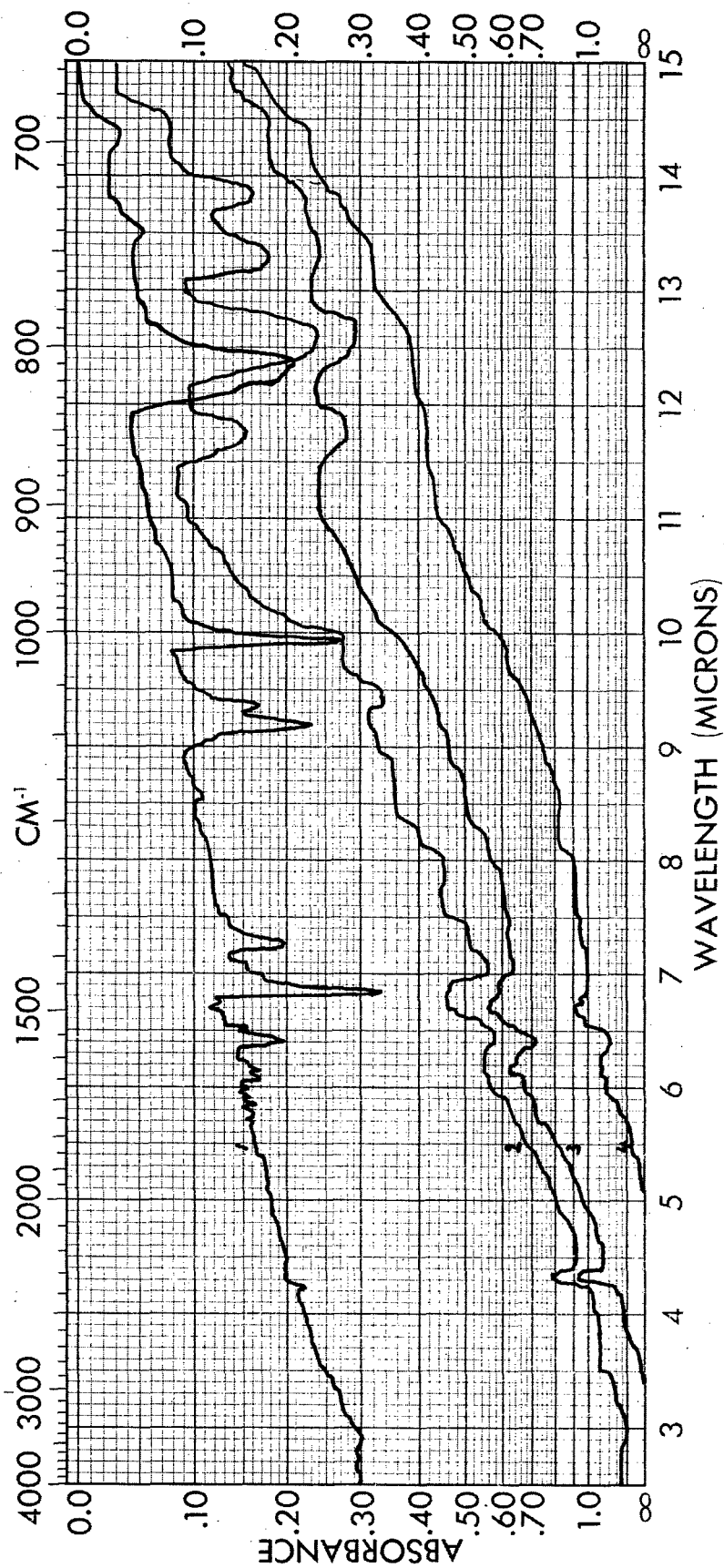


Figure 18. IR Spectra of (1.) Poly-1,4-phenylene sulfide; (2.) Residue at 450°C; (3.) Residue at 550°C; (4.) Residue at 620°C

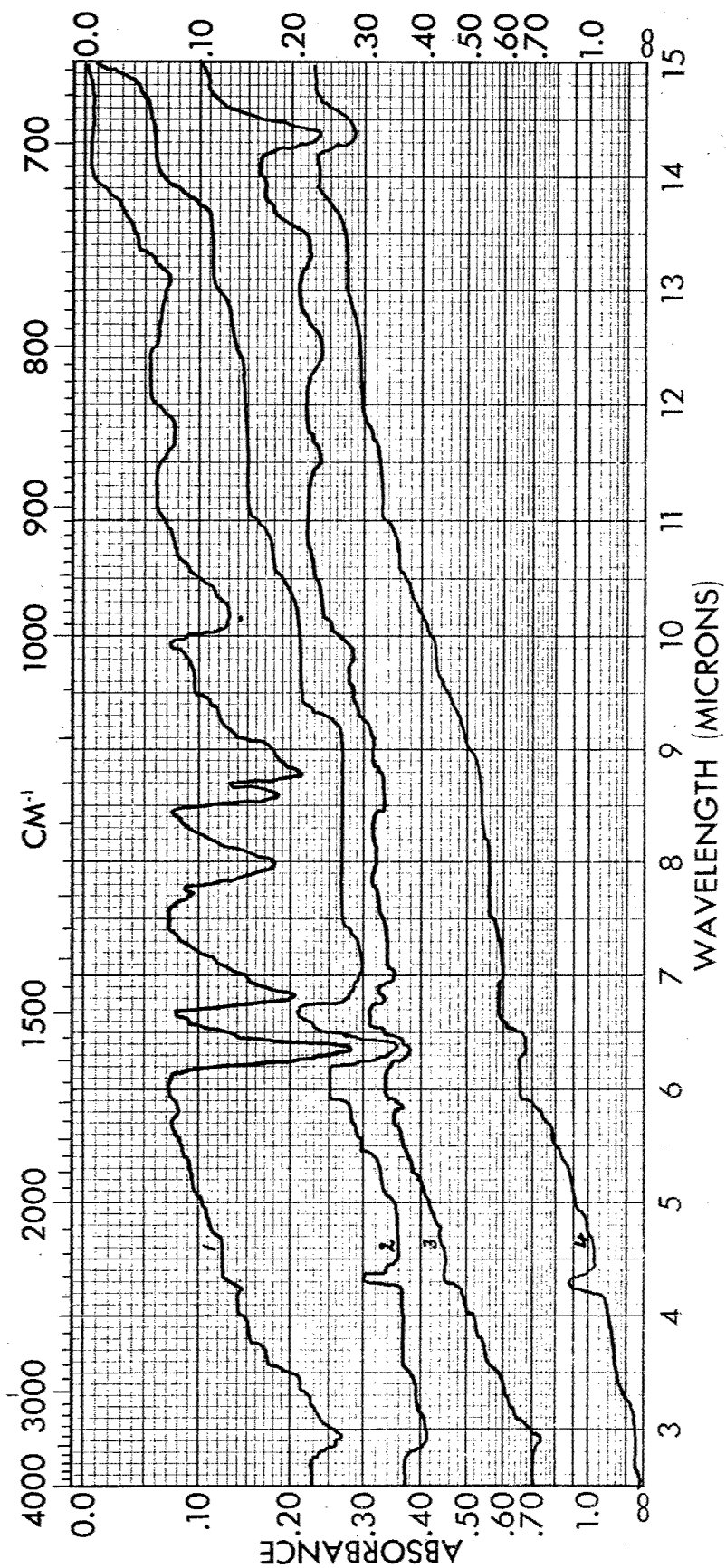


Figure 19. IR Spectra of (1.) Poly-1,3-phenylene oxide; (2.) Residue at 450°C; (3.) Residue at 550°C; (4.) Residue at 620°C

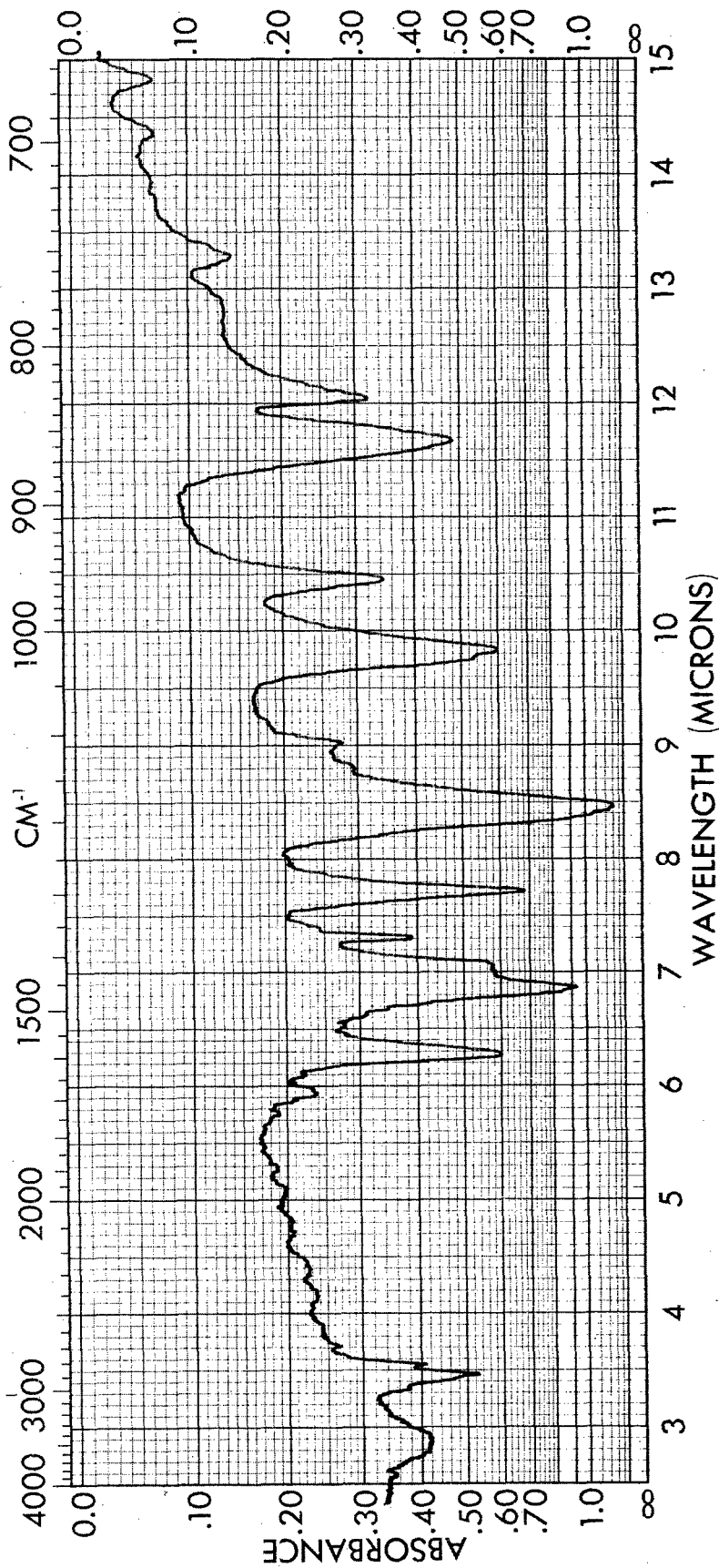


Figure 20. IR Spectrum of Poly(2,6-dimethyl-1,4-phenylene oxide)

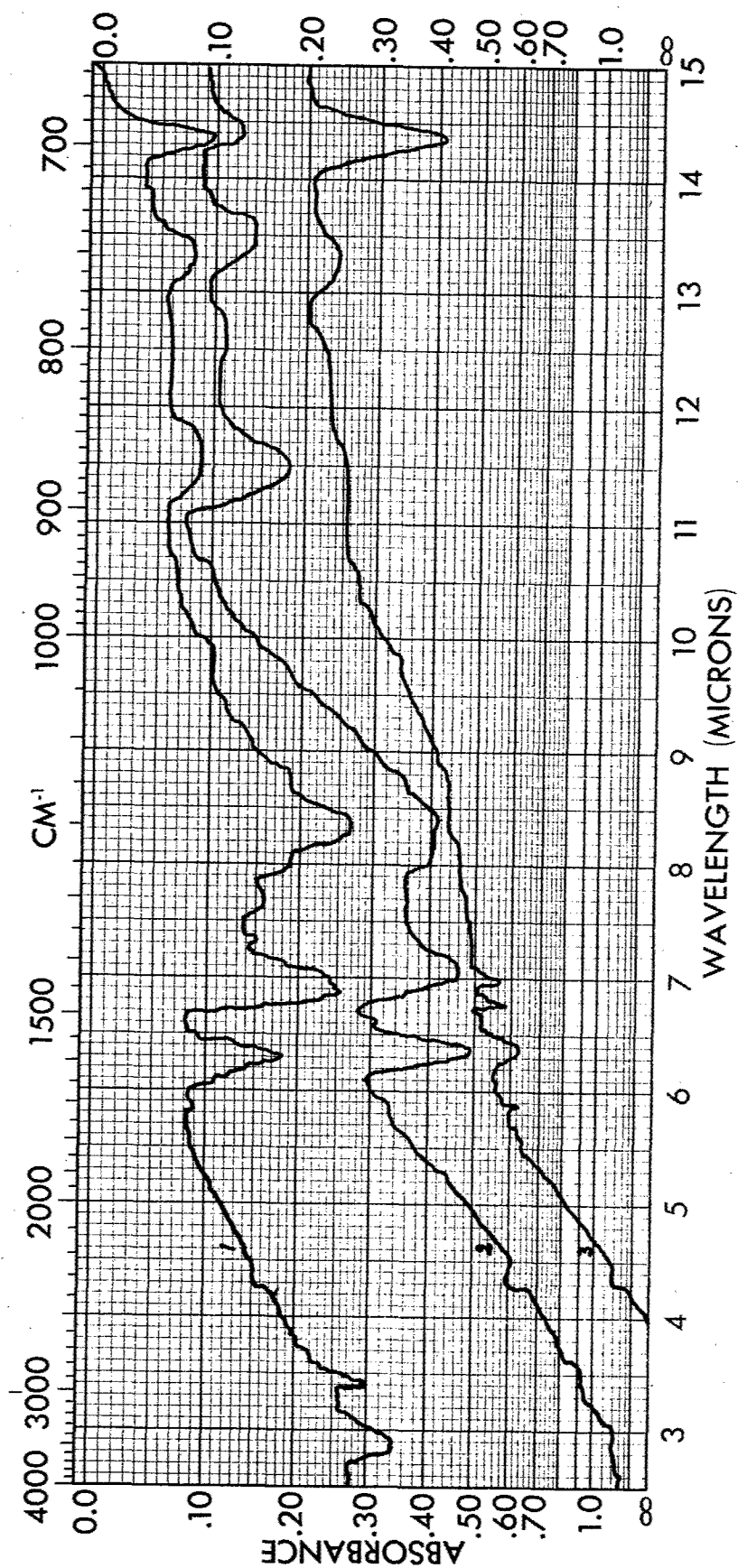


Figure 21. IR Spectra of (1.) Residue of Poly(2,6-dimethyl-1,4-phenylene oxide) at 375°C; (2.) at 450°C; (3.) at 550°C

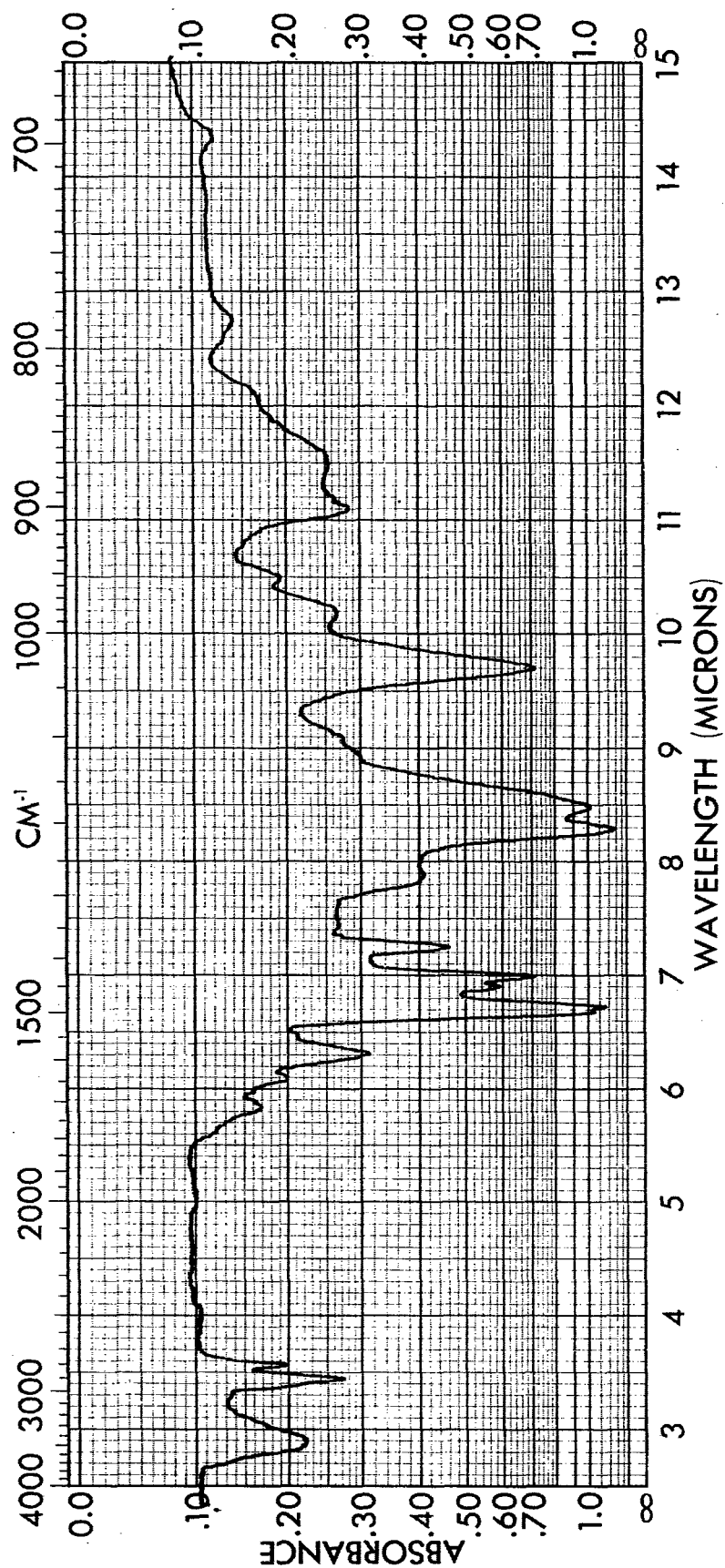


Figure 22. IR Spectrum of Poly(2,5-dimethoxy-1,4-phenylene oxide)

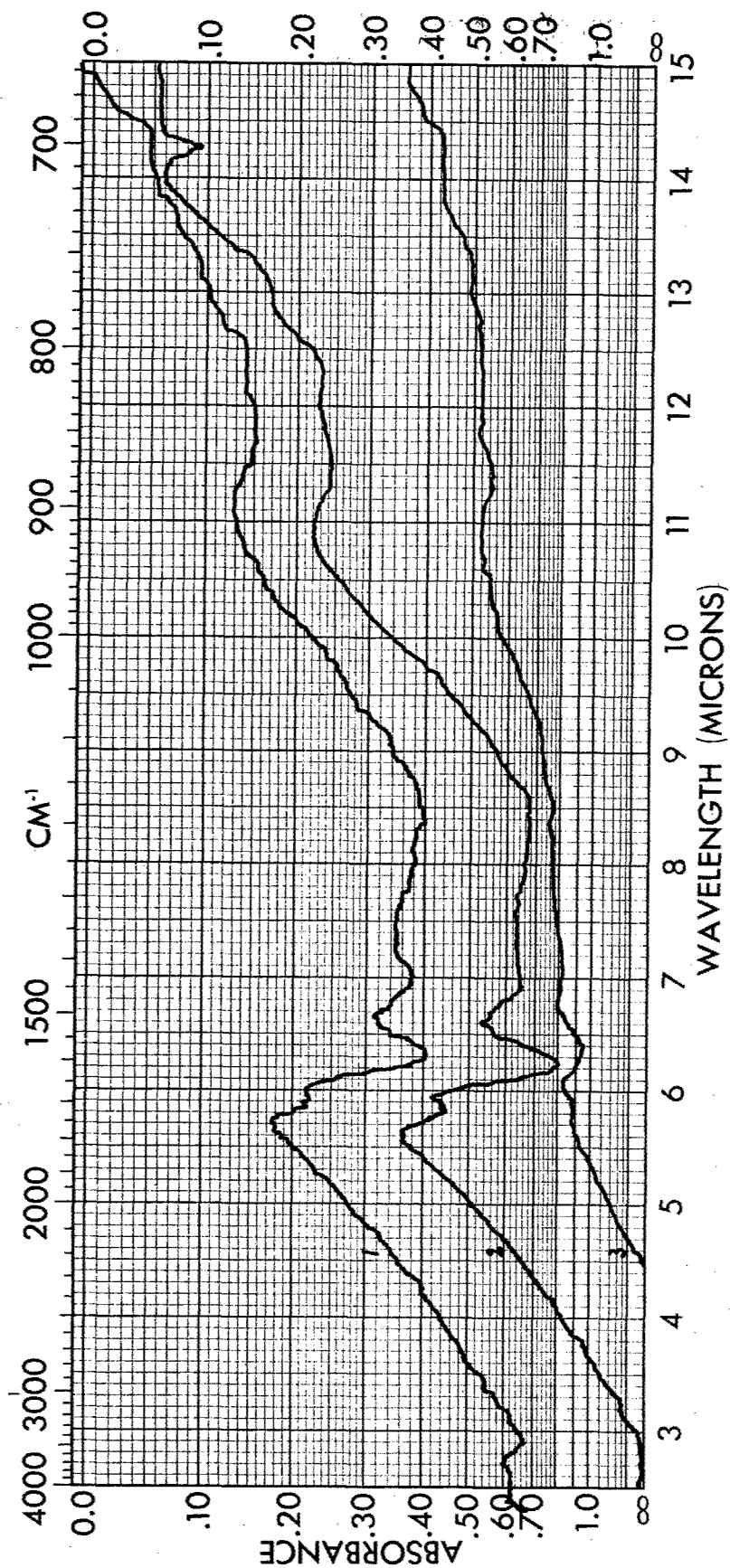


Figure 23. IR Spectra of Residues of Poly(2,5-dimethoxy-1,4-phenylene oxide) at (1.) 350°C; (2.) 450°C; (3.) 550°C

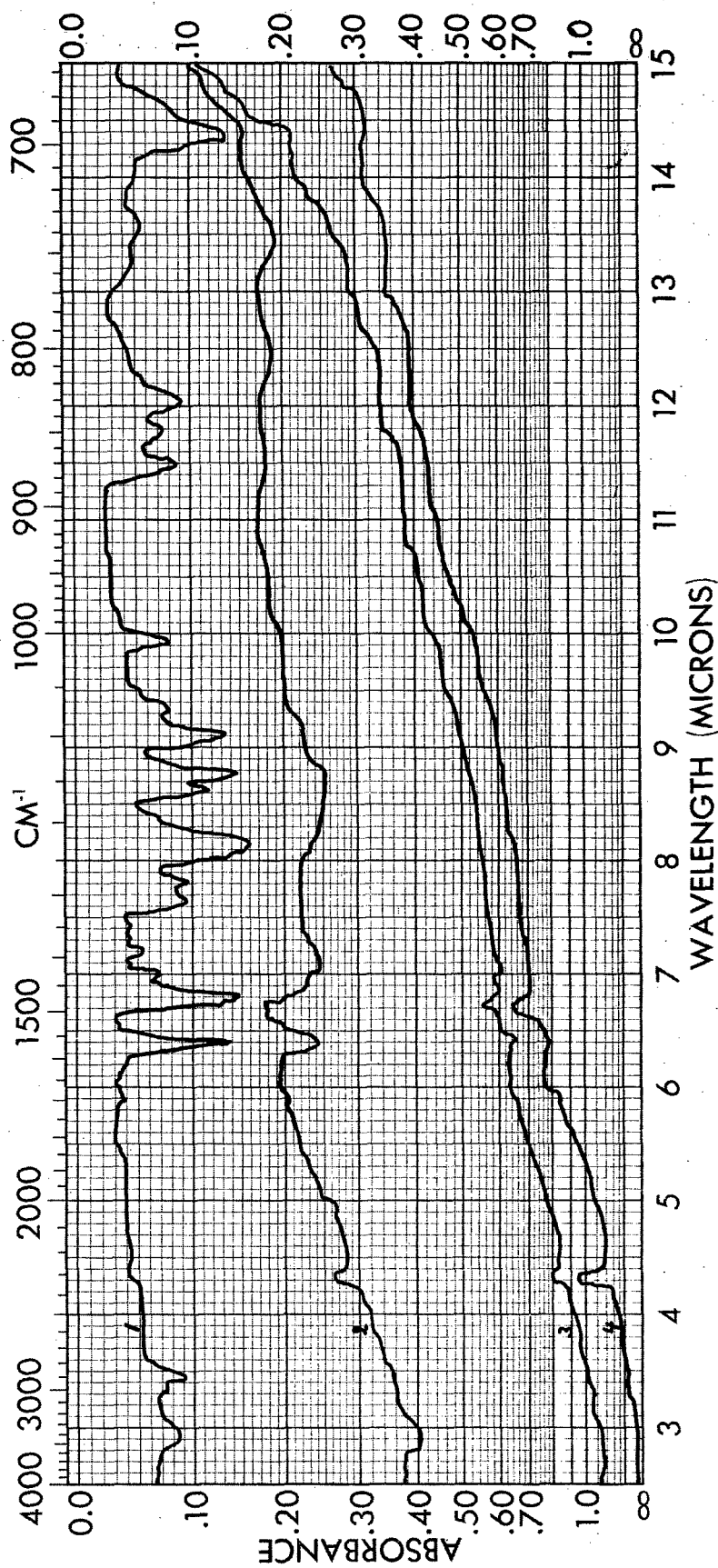


Figure 24. IR Spectra of (1.) Polysulfone "Phenoxy T Blend 5"; (2.) Residue at 450°C; (3.) Residue at 550°C; (4.) Residue at 620°C

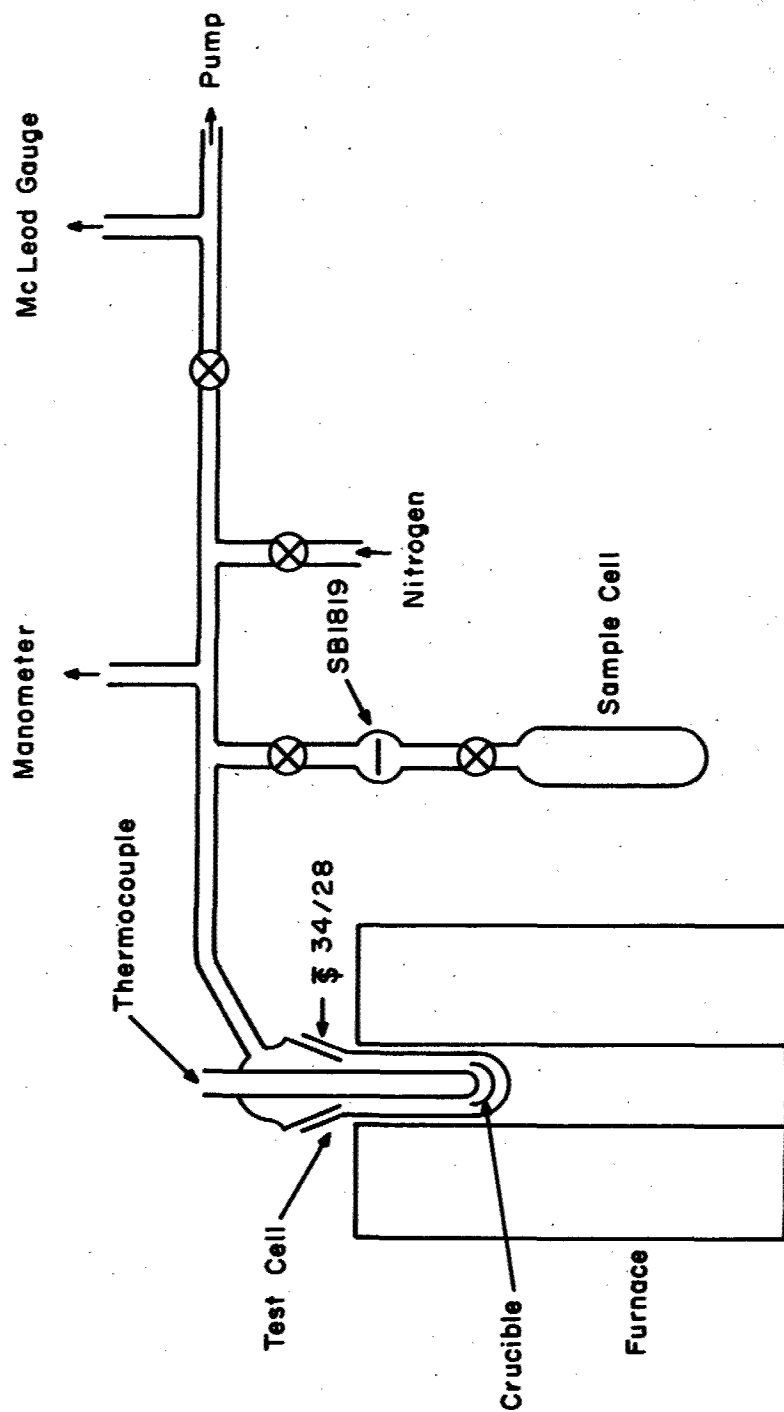


Figure 25. Apparatus Used for the Decomposition Studies

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13. ABSTRACT Samples of eight different phenylene-R polymers were subjected to isothermal heating in three progressive steps. The gaseous decomposition products were collected and analyzed by mass spectroscopy. The corresponding residues were obtained in separate, identical runs and identified by weight, elemental analysis, and IR spectra. The data collected were used to postulate an overall breakdown mechanism. The first reaction occurring during the decomposition of these polymers at lower temperatures (below 450°C) is the removal of pendant groups, and the cleavage of the linkage between the rings. Polyphenylene sulfide shows the least amount of ring breakdown, as indicated by very little methane formation. Sulfur is removed as hydrogen sulfide, and the ruptured bond may partially heal, forming C-C-bonds. Sulfones appear to behave in a similar manner, the SO ₂ linkage being removed as sulfur dioxide. The breakdown of ethers and phenols is always accompanied by a considerable amount of ring cleavage and destruction, the decomposition products being CO, CO ₂ , and H ₂ O. Crosslinking with evolution of hydrogen is the predominant reaction of all polymers at the higher temperatures (up to 620°C). The end products, which may contain some O and especially S in the form of stable, fused ring systems, are crosslinked polymer carbons with unsaturated, aliphatic chains rather than completely aromatic, fused ring systems. Possible exceptions are polyphenylene sulfide and polyphenylene.		

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Polyphenylene oxide						
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From the results, it is concluded that polyphenylene sulfide may be of interest as an ablative material.

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