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**PREPARATION AND PROPERTIES OF MODIFIED
POLY-m-PHENOXYLENES**

*ROBERT C. EVERS
GERHARD F. L. EHLERS*

TECHNICAL REPORT AFML-TR-66-134

JUNE 1966

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FOREWORD

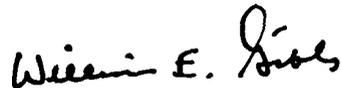
This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734004, "New Organic and Inorganic Polymers". It was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, for which Dr. G. F. L. Ehlers was project engineer.

This report covers work conducted from December 1964 to February 1966.

The authors wish to thank the Analytical Branch, Air Force Materials Laboratory, for performing the elemental analysis and molecular weight determinations.

The differential thermal analysis data were determined by the U.S. Rubber Company under Air Force contract.

This technical report has been reviewed and is approved.



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

ABSTRACT

A series of modified poly-m-phenoxylenes was prepared by the introduction of substituents into the aromatic rings of the polymer. This was achieved by the preparation of a sulfonyl chloride derivative which could undergo reaction with various amines and alcohols to form sulfonamide or sulfonate derivatives.

These modified polymers were characterized by their infrared spectra, elemental analyses, and inherent viscosities. The effect of the various substituents upon the thermal behavior of the polymers was determined by softening range determination, thermogravimetric analysis, and differential thermal analysis.

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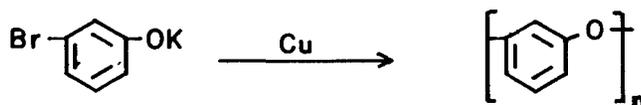
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SECTION I

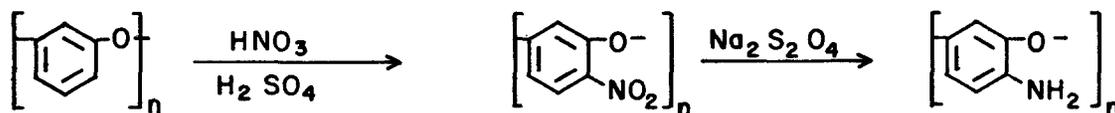
INTRODUCTION

Although the polyphenyl ethers have been known for some time (References 1 and 2), it has been only recently that investigators have been able to obtain any of these polymers in high molecular weights (References 3 through 6). Among the notable investigations in this area is that of Brown and Goldman who reported the preparation of poly-*m*-phenoxyene with molecular weights approaching 10,000 (References 6 and 7). This was achieved by the self-condensation of the potassium salts of *m*-halophenols in the presence of a copper catalyst:



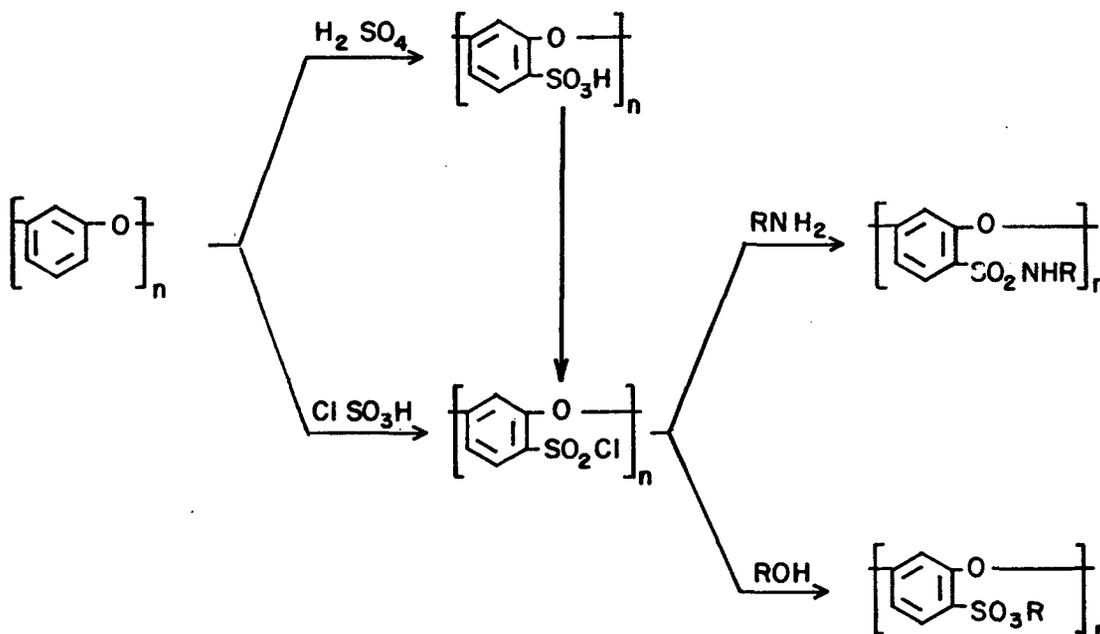
This polymer also exhibited appreciable thermal stability; that is, thermogravimetric analysis (TGA) under nitrogen showed breakdown in the region of 500°-550°C (Reference 7).

A current area of interest is the modification of poly-*m*-phenoxyene by the introduction of various substituents into the phenyl rings of the polymer. The introduction and subsequent reduction of a nitro group has been reported (Reference 8).



The resulting amino derivative is reported to have potential use as an adhesive.

The introduction of sulfur-containing substituents into poly-*m*-phenoxyene has not been previously reported. A variety of sulfur-containing substituents are known but one of the more reactive is the sulfonyl chloride group which could conceivably be introduced either directly or via the sulfonic acid derivative. It could be converted into sulfonamide or sulfonate derivatives according to the following reaction scheme:



It was felt that with a judicious choice of alcohols and amines, valuable information regarding the effect of the various substituents upon the thermal stability of poly-m-phenoxyene could be obtained. Also, the possibility existed that some of the resulting polymers might have useful thermal or mechanical properties.

Accordingly, poly-m-phenoxyene was converted to its sulfonic acid and sulfonyl chloride derivatives. The sulfonyl chloride derivative was reacted with a variety of aliphatic and aromatic amines and alcohols. The resulting products were characterized and their thermal behavior studied.

SECTION II

DISCUSSION

PREPARATION OF STARTING MATERIALS

Poly-*m*-phenoxyene was prepared by the Wyandotte Chemical Company (Reference 9) according to the procedure of Brown and Goldman (References 6 and 7).

4-Amino-*p*-terphenyl was prepared by the Monsanto Research Corporation (Reference 10) by the chemical reduction of 4-nitro-*p*-terphenyl.

The remainder of the starting materials were obtained through commercial sources and purified when necessary.

PREPARATION OF MODIFIED POLYMERS

The key step in the proposed synthetic scheme was the preparation of the sulfonyl chloride derivative of poly-*m*-phenoxyene since this polymer would serve as a starting material for the remaining modification reactions. Initially, it was to have been prepared by chlorination of the corresponding sulfonic acid derivative. Accordingly, the sulfonic acid group was introduced into poly-*m*-phenoxyene by means of sulfuric acid in acetic anhydride as the sulfonating agent. However, attempts to convert the sulfonic acid to the sulfonyl chloride derivative met with only fair success. Although a variety of methods were used, elemental analyses indicated conversions of less than 40 percent in all cases. This lack of success could be attributed partly to difficulties encountered during work-up of the reaction mixtures and the subsequent hydrolysis of the sulfonyl chloride groups during these purification procedures.

As an alternate route, the sulfonyl chloride was prepared by reaction of poly-*m*-phenoxyene with chlorosulfonic acid. If protolytic solvents were avoided during the work-up procedures, as high as 85 percent of the sulfur-containing groups were present as sulfonyl chloride groups. The products of a number of these reactions were combined to form a uniform starting material which was then carefully purified. The sulfonyl chloride derivative was reacted with ammonia and a series of amines - aniline, carbazole, 4-amino-*p*-terphenyl, dodecylamine, and allylamine - to form sulfonamide derivatives. It was also reacted with phenol and dodecyl alcohol to form sulfonate derivatives.

Pyridine was used as an acid acceptor in the majority of the reactions. The resulting pyridine hydrochloride could be eliminated from the polymer more easily than the hydrochloride salts of a number of other potential acid acceptors.

A small amount of insoluble, crosslinked polymer was isolated from some of the reactions. It was found that crosslinking was held to a minimum if reaction temperatures of less than 65°C were used.

In the majority of the reactions, dimethylsulfoxide (DMSO) was used as a reaction medium since the products were soluble in that solvent and stayed in solution during the course of the reaction. Attempts to use tetrahydrofuran (THF) as a solvent resulted in the formation of crosslinked products.

PHYSICAL PROPERTIES OF MODIFIED POLYMERS

The poly-*m*-phenoxyene used in this investigation was a tan powder with an inherent viscosity in benzene of 0.16. Vapor pressure osmometry molecular weight determinations in that solvent indicated a molecular weight of approximately 5100.

In general, the various derivatives were tan or olive-colored powders. The sulfonic acid derivative, however, ranged in color from bright yellow to a golden brown and was somewhat hygroscopic. Elemental analysis indicated approximately 1.3 sulfonic acid groups per phenyl ring. It darkened and decomposed upon prolonged heating in air at 110°C and yielded a partially insoluble product. Elemental analysis of the heat-treated polymer showed a sharply reduced sulfur content.

Analysis of the sulfonyl chloride derivative indicated approximately 1.4 sulfur-containing substituents per repeating unit with 1.0 of these being a sulfonyl chloride group. The remaining sulfur-containing substituents were probably sulfonic acid groups which either were formed as an intermediate in the sulfonyl chloride synthesis or resulted from hydrolysis during the work-up procedure.

This assigned structure was used as a basis for the determination of the polymer structures resulting from the reaction of the sulfonyl chloride derivative with the various amines and alcohols. Elemental analyses of the products indicated that conversion of the sulfonyl chloride group to the desired substituent varied from 60 to 100 percent (0.6 to 1.0 of the desired substituent per repeating unit). It is to be remembered, however, that such values are only approximate due to the complex nature of the modified polymers and the presence of substituents resulting from side-reactions. For instance, elemental analysis of the product from the reaction with dodecyl alcohol indicated the presence of a substantial amount of nitrogen in the polymer. This would seem to indicate that the acid acceptor, pyridine, had incorporated itself into the polymer with some of the substituent groups being pyridinium derivatives.

The various modified polymers exhibited inherent viscosities in dimethylsulfoxide ranging from 0.25 to 1.74. This wide range in values can be attributed partly to the varying degrees of interactions of the different substituents with the solvent. In addition, many of the products were inadvertently fractionated during the purification procedures with the higher molecular weight fractions being retained.

Molecular weight determinations by vapor pressure osmometry were found to be unreliable and gave widely scattered, non-reproducible results. Since the polymers exhibited relatively high inherent viscosities and were not subjected to reactions which would ordinarily cleave the diaryl ether linkage, it appears that no degradation of the polymer chain occurred. If such were the case, molecular weights of greater than 10,000 should have been achieved in most of the reactions.

In general, the infrared spectra of the polymers were consistent with their assigned structures. In all cases, the spectra exhibited bands at ~ 1450 and ~ 1600 cm^{-1} , indicative of the phenyl nucleus, and at ~ 1250 cm^{-1} , indicative of the diaryl ether linkage. The sulfonic acid derivative gave rise to bands at 1040 and 1200 cm^{-1} , attributable to the sulfonic acid group. These bands could be seen in many of the other spectra thus demonstrating the presence of unreacted $-\text{SO}_3\text{H}$ groups in these polymers. The sulfonyl chloride derivative exhibited bands at 1180 and 1390 cm^{-1} indicative of the $-\text{SO}_2\text{Cl}$ group while the sulfonamide and sulfonate derivatives all gave rise to bands in the regions 1120-1230 and 1310-1420 cm^{-1} attributable to the $-\text{SO}_2-$ stretching vibrations (Reference 12).

The reversal and irreversible thermal transitions of the polymers were determined by subjecting them to softening under load (Figures 12 and 13), thermogravimetric analysis (Figures 14 and 15) and differential thermal analysis (DTA) as shown in Table III. Comparison of the data obtained by these three methods allows one to distinguish between the reversible transitions connected with the melting process and the irreversible transitions from decomposition of the polymers. The starting material and the sulfonic acid derivative melt rapidly between 40°-90°C. The sulfonyl chloride, the sulfonamides and the dodecyl ester soften only to a limited extent within this range; the latter polymer has a second, distinct melting range around 160°C.

The phenyl ester has its highest rates of softening at 145° and 195°C, the rest of the polymers, the sulfonamide derivatives, show the highest softening rates around 200°C.

Strangely enough, the DTA transitions do not reflect the difference in behavior indicated by the softening curves. All of the polymers, with the exception of the phenyl ester, have a transition between 53° and 90°C. The rest of the polymers (with the exception of those containing the $\text{-S-}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{-}$ moiety) show a smaller transition between 130° and 140°C. All of these transitions are endothermic. Only the carbazole derivative has an additional endothermic peak at 220°C which is believed not to be connected with the decomposition.

The decomposition temperature can be derived from the first of the DTA-decomposition transitions (underlined in Table III) and the temperature of the inversion point of the TGA curve. It can be seen that the stability of the original polymer (between 545° and 580°C) is drastically reduced when substituents are introduced. While the primary sulfonamide derivative still has a reasonable stability between 345° and 367°C, the decomposition temperatures of the other polymers range between 215° and 312°C with no apparent relation to the stability of the substituent itself (note the relatively high stability of the dodecyl ester polymer).

SECTION III

EXPERIMENTAL

PREPARATION OF STARTING MATERIALS

Poly-*m*-phenoxyene was prepared by the Wyandotte Chemical Company (Reference 9). The samples ranged in color from tan to dark brown and were found to contain substantial amounts of mineral oil. The polymer was subjected to several dissolution-precipitation procedures with tetrahydrofuran being used as a solvent and pet ether as a precipitant. In order to obtain the polymer in a more tractable condition, it was necessary to carry out a final reprecipitation in methanol. The polymer was dried in a vacuum oven at 35°C for 48 hours.

<u>Analysis:</u>	<u>Calculated</u>	<u>Found</u>
C	78.26	76.34, 76.15
H	4.34	4.48, 4.32
O	17.38	17.36, 17.32
Cl	0.00	0.43, 0.47
Cu	0.00	0.19, 0.20

4-Amino-*p*-terphenyl was prepared by the Monsanto Research Corporation (Reference 10) and was used as received, M.P. 198° -201° C (Lit. 201° C).

Anhydrous dimethyl sulfoxide was obtained from the Matheson, Coleman and Bell Company.

The remaining starting materials were obtained through other standard commercial sources. Allylamine was used as received while aniline, phenol, dodecylamine, and dodecyl alcohol were redistilled under reduced pressure with only the center fraction being retained. Carbazole was recrystallized from acetone prior to use.

PREPARATION OF POLYMERS

The experimental conditions for the various polymer modification reactions are given in Table I. Preparative procedures for the modified polymers are as follows:

Sulfonation of Poly-*m*-phenoxyene

The sulfonation mixture was prepared by the slow addition of 15 ml of sulfonic acid to 60 ml of slowly stirred acetic anhydride. An ice bath was used to keep the solution temperature below 65°C. Then 3 g of poly-*m*-phenoxyene was added in portions to the light yellow sulfonation mixture. Vigorous stirring was maintained and the reaction allowed to continue at 65°C for 15 hours. The polymer was precipitated by the addition of the dark brown reaction mixture to 600 ml of ether. It was redissolved in 60 ml of formic acid and the polymer solution filtered. The polymer was reprecipitated from ether and extracted with ether in a Soxhlet for 24 hours. After drying in a vacuum desiccator for 48 hours and in a vacuum oven at 110°C for three hours, 5.7 g of product was obtained. It was of a dark yellow color and somewhat hygroscopic.

Analysis: Found C, 42.7; H, 3.4; S, 14.3

Reaction of Poly-m-phenoxyene and Chlorosulfonic Acid

Approximately 160 ml of chlorosulfonic acid was cooled to 0-5°C by means of an ice bath. Then 10 g of poly-m-phenoxyene was added slowly with vigorous stirring. The reaction mixture was allowed to warm to room temperature and then heated at 65°C for 18 hours. After being allowed to cool to room temperature, the reaction mixture was added slowly with stirring to 800 ml of cooled absolute ether. The solvent-nonsolvent mixture was decanted off and one liter of chloroform was added to the syrupy residue. After several minutes of stirring, the polymer took on a tan color and could be isolated as fine particles by filtration. The filtrate was stirred with an additional 500 ml of ether. Additional polymer precipitated and was also isolated by filtration. The polymer was dried in a vacuum desiccator for 48 hours. A total of 19.0 g. of product was obtained.

The products of a number of trials similar to the above were dissolved together in THF and reprecipitated from ether. The isolated polymer was redissolved in THF, the polymer solution filtered, and the polymer reprecipitated from petroleum ether. The polymer was isolated by filtration and dried in a vacuum desiccator for 60 hours.

Analysis: Found C, 30.6; H, 1.6; S, 18.4; Cl, 15.5.

Reaction of Sulfonyl Chloride Derivative and Phenol

The sulfonyl chloride derivative (2.0g) was dissolved in 25 g of phenol at 60°C. With vigorous stirring being maintained, dry pyridine (2.0 g) was added dropwise and the reaction allowed to continue for 18 hours. The cooled reaction mixture was slowly added to 300 ml of stirred methanol. The precipitated polymer was redissolved in DMSO and reprecipitated from methanol. It was extracted with methanol in a Soxlet for 20 hours and then washed well with ether. After drying in a vacuum oven at 80°C for 24 hours, 1.8 g of polymer was obtained.

Analysis: Found C, 52.2; H, 3.1; S, 14.9; N, 1.1; Cl, 0.5

Reaction of the Sulfonyl Chloride Derivative with Dodecyl Alcohol

A solution of the sulfonyl chloride derivative (2.0 g) and dodecyl alcohol (2.8 g) in 30 ml of DMSO was stirred vigorously at room temperature. Then a solution of dried pyridine (2.0 g) in 10 ml of DMSO was added dropwise and the reaction heated at 60°C for 18 hours. The polymer was reprecipitated from 10 volumes of THF and isolated by filtration. It was redissolved and reprecipitated twice using formic acid as a solvent and THF as a precipitant. Drying in a vacuum oven at 80°C for 24 hours yielded 2.1 g of product.

Analysis: Found C, 46.6; H, 3.8; S, 17.0; N, 5.1; Cl, 0.6

Reaction of Sulfonyl Chloride Derivative and Ammonia

Gaseous ammonia (2.0 g) was bubbled through 50 ml of DMSO over a 40 minute period. Then with vigorous stirring being maintained, a solution of the sulfonyl chloride derivative (2.0 g) in 30 ml of DMSO was added dropwise through a dropping funnel. Then more ammonia (4.0 g) was added over a period of two hours and the reaction was allowed to continue overnight at room temperature. The polymer was precipitated from 600 ml of acetone, isolated by filtration, and redissolved in formic acid. It was reprecipitated from ether, dried, and extracted in a Soxlet with ethanol for 40 hours. After drying in a vacuum oven at 100°C for 30 hours, 1.5 g of polymer was obtained.

Analysis: Found C, 30.5; H, 3.7; S, 18.8; N, 7.7; Cl, 0.7

Reaction of Sulfonyl Chloride Derivative and Aniline

The sulfonyl chloride derivative (2.0 g) was added in portions to 30 ml of vigorously stirred aniline at room temperature. The resulting dark solution was heated at 55°C for 20 hours. After being allowed to cool to room temperature, the reaction mixture was slowly added to 10 volumes of vigorously stirred ether and the precipitated polymer isolated by filtration. It was redissolved in THF and reprecipitated from petroleum ether. After being dried it was extracted with water in a Soxlet for 72 hours. The polymer was then redissolved in formic acid, the polymer solution filtered, and the polymer reprecipitated from ether. After drying in a vacuum oven at 100°C for 72 hours, 1.1 g of product were obtained.

Analysis: Found C, 45.6; H, 4.2; S, 15.2; N, 4.9; Cl, 0.6

Reaction of Sulfonyl Chloride Derivative with Carbazole

The sulfonyl chloride derivative (2.0 g) was dissolved in 20 ml of DMSO at room temperature. Then a solution of carbazole (2.0 g) and dry pyridine (2.0 g) in 20 ml of DMSO was added dropwise with vigorous stirring being maintained. After two hours, the reaction temperature was raised to 65°C and maintained there for 24 hours. After being allowed to cool, the reaction mixture was added slowly to eight volumes of vigorously stirred THF. The precipitated polymer was redissolved in 97 percent formic acid and reprecipitated from THF. This dissolution-precipitation procedure was repeated twice. Drying of the isolated polymer in a vacuum oven at 80°C for 72 hours yielded 2.2 g of product.

Analysis: Found C, 49.2; H, 3.7; S, 14.6; N, 4.5; Cl, 0.6

Reaction of Sulfonyl Chloride Derivative with 4-Amino-p-terphenyl

The sulfonyl chloride derivative (2.0 g) was dissolved in 30 ml of DMSO at room temperature. With vigorous stirring being maintained, a solution of 4-amino-p-terphenyl (2.0 g) and dried pyridine (2.0 g) in 20 ml of DMSO was added dropwise. A precipitate formed almost immediately but dissolved when the reaction temperature was raised to 60°C. After two hours, the reaction mixture was allowed to cool to room temperature and was stirred for four more hours. The polymer was precipitated from 500 ml of acetone and was isolated by filtration. It was then redissolved in 100 ml of DMSO and reprecipitated from 800 ml of THF. After drying, the polymer was extracted in a Soxlet with THF for 75 hours and methanol for 8 hours. After drying in a vacuum oven at 100°C for 125 hours, 2.1 g of product were obtained.

Analysis: Found C, 55.7; H, 3.9; S, 12.0; N, 3.7; Cl, 0.5

Reaction of Sulfonyl Chloride Derivative with Dodecylamine

The sulfonyl chloride derivative (2.0 g) was dissolved in 30 ml of DMSO at room temperature. A solution of dodecylamine (2.1 g) and dry pyridine (1.0 g) in 30 ml of DMSO were added dropwise over a 75-minute period to the vigorously stirred solution. After being heated for 18 hours at 50°C, the cooled reaction mixture was slowly added to 800 ml of stirred water. The precipitated polymer was isolated by filtration and extracted with water in a Soxlet for 40 hours. After drying in a vacuum oven at 85°C for 60 hours, 2.2 g of product was obtained.

Analysis: Found C, 58.9; H, 9.4; S, 9.8; N, 4.4; Cl, 0.7

Reaction of Sulfonyl Chloride Derivative with Allylamine

The sulfonyl chloride derivative (1.5 g) was dissolved in 30 ml of DMSO at room temperature. A solution of allylamine (0.45 g) in 30 ml of DMSO was then added dropwise with vigorous

stirring being maintained. p-tert-Butyl catechol (0.05 g) was added as a radical inhibitor. After being heated at 65°C for four hours, the reaction mixture was stirred overnight at room temperature. The polymer was precipitated from a 1:1 solution of chloroform and petroleum ether. It was isolated by filtration and redissolved in formic acid. After reprecipitation from THF, the polymer was extracted with THF in a Soxhlet for 8 hours. Drying in a vacuum desiccator for 48 hours yielded 0.9 g of product.

Analysis: Found C, 40.9; H, 5.4; S, 15.6; N, 6.4; Cl, 0.5

PHYSICAL PROPERTIES OF POLYMERS

Viscosity

The inherent viscosities of the polymers were determined at 25°C using solution concentrations ranging from 0.2 g to 0.6 g/100 ml. The viscosities of the respective polymers are summarized in Table II.

Molecular Weight Determinations

The molecular weight of poly-m-phenoxyene was determined by vapor pressure osmometry. Benzene was used as a solvent.

Infrared Spectra

Infrared spectra were obtained on the polymers by use of a Perkin-Elmer Infrared recording spectrophotometer. In all cases potassium bromide pellets of the samples were used. The polymer spectra are shown in Figures 1 through 11.

Softening Range Determination

The softening range of the polymer samples was obtained by use of a modified Vicat apparatus. Heating was performed at a constant rate of 150°C/hour. The softening range was determined from a plot of temperature vs. penetration. Composite plots of the polymers are shown in Figures 12 and 13.

Thermogravimetric Analysis (TGA)

Determinations were carried out in a nitrogen atmosphere on a modified Chevenard thermobalance using a constant heating rate of 150°C/hour. A plot of percent weight residue vs. temperature was made for each polymer. Composite plots are shown in Figures 14 and 15.

Differential Thermal Analysis (DTA)

The instrument used was a specially designed aluminum block connected to an Aminco Thermobalance. The determinations were performed under a helium atmosphere at a heating rate of 8°C/min. The sample was mixed with Al₂O₃ with the reference material also being Al₂O₃.

SECTION IV
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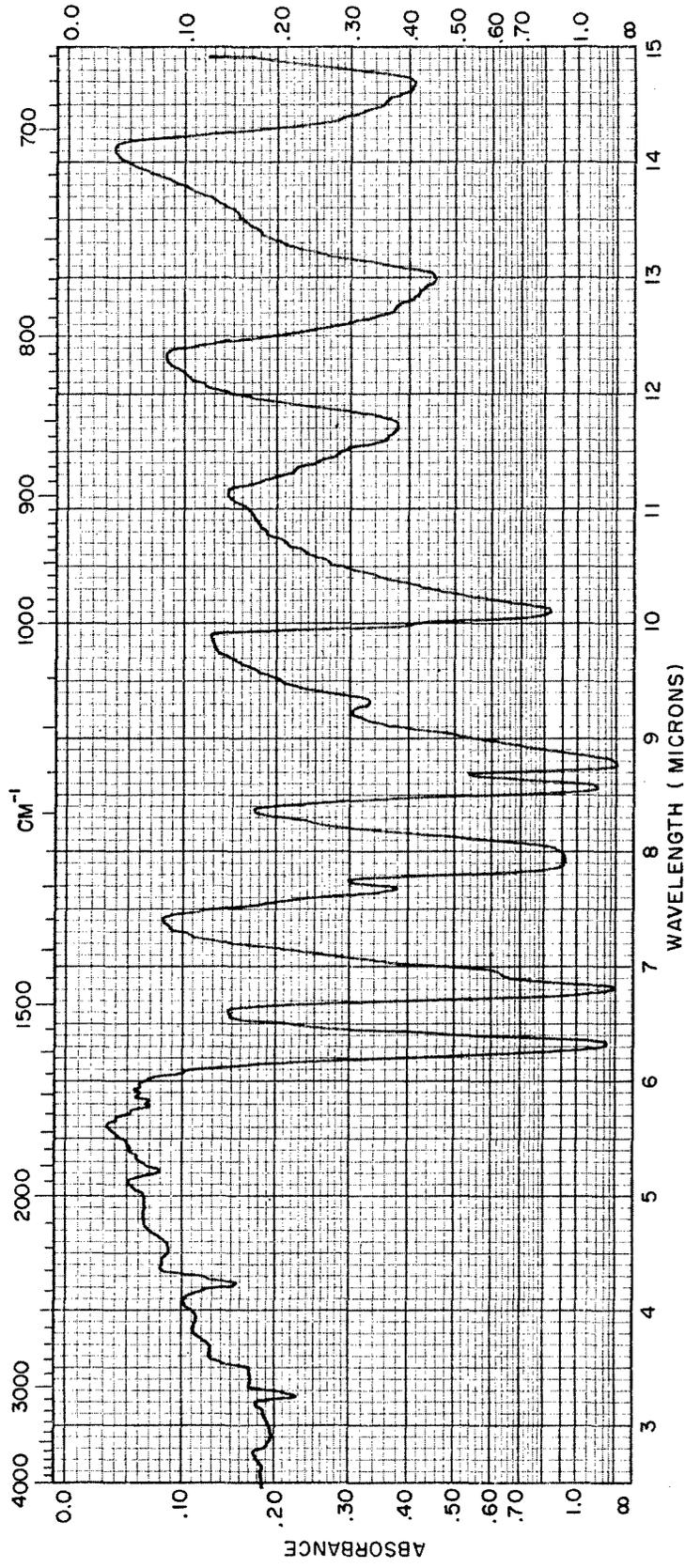


Figure 1. IR Spectrum of Poly-m-phenoxylene

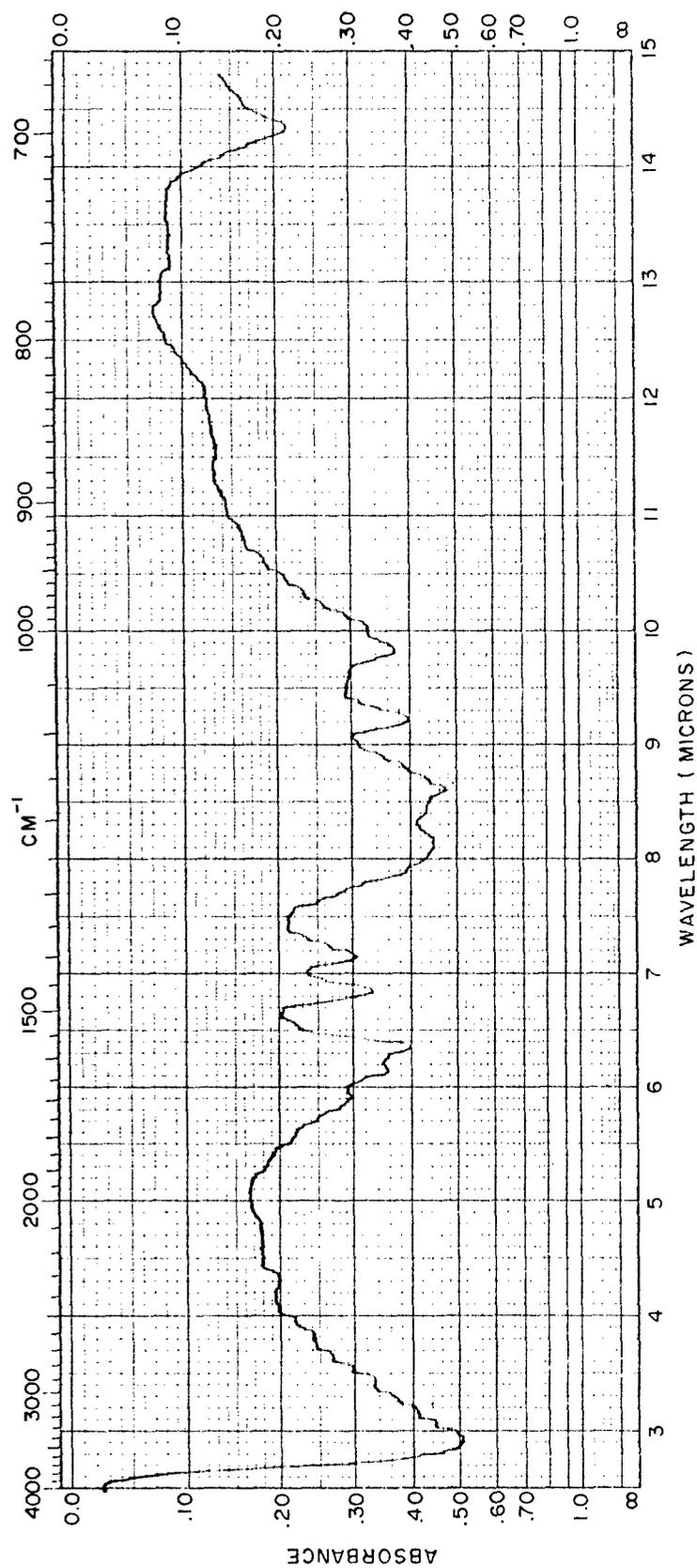


Figure 2. IR Spectrum of Sulfonic Acid Derivative of Poly-m-phenoxylylene

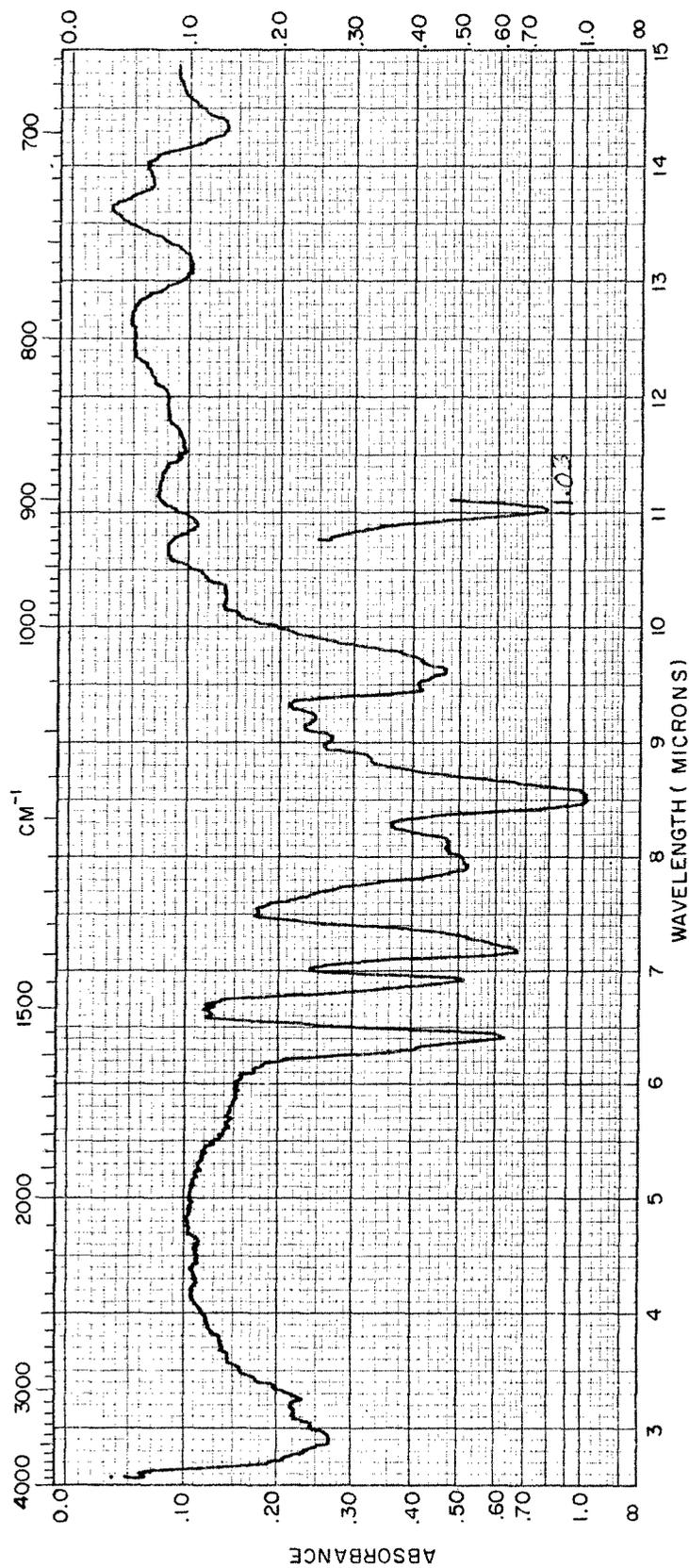


Figure 3. IR Spectrum of Sulfonyl Chloride Derivative of Poly-m-phenoxyflene

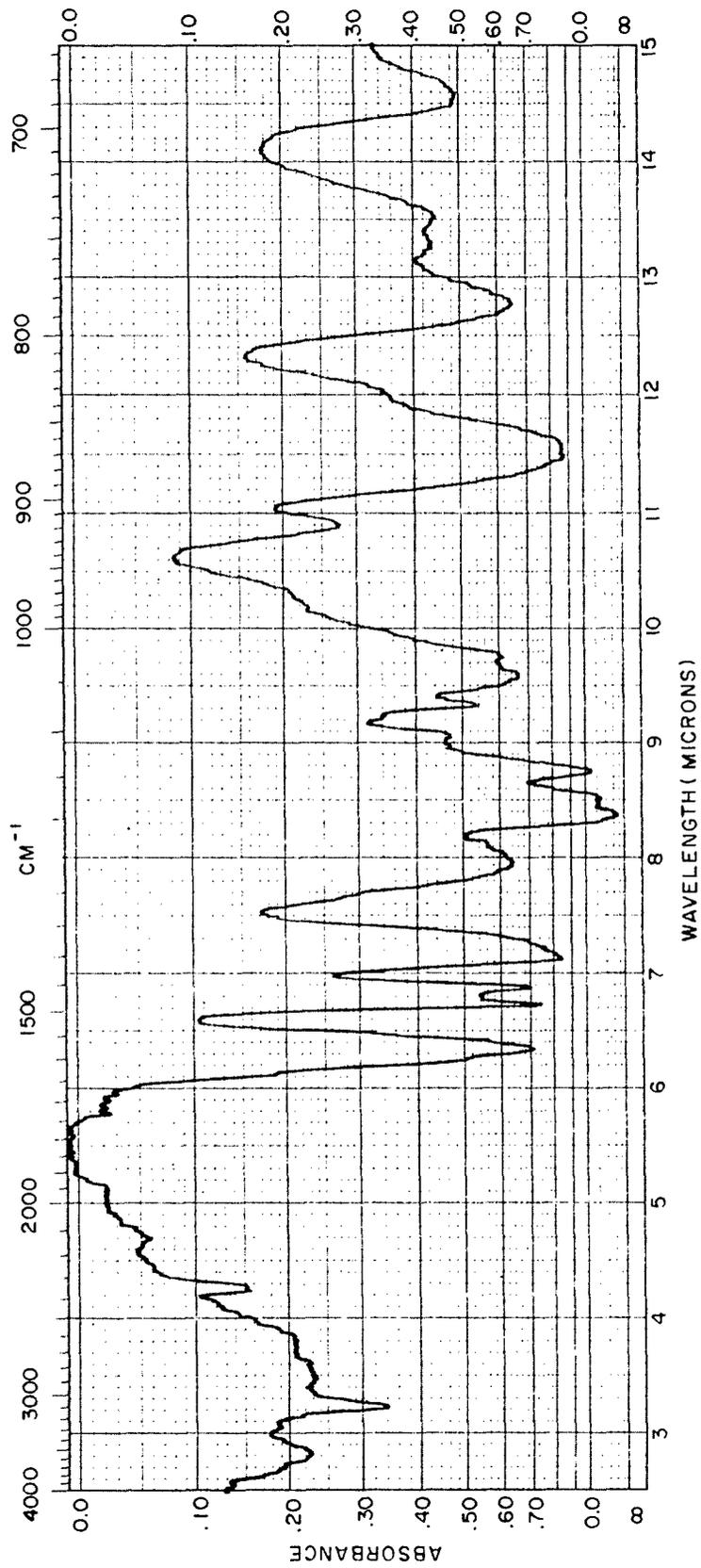


Figure 4. IR Spectrum of Polymer Prepared from Sulfonyl Chloride Derivative and Phenol

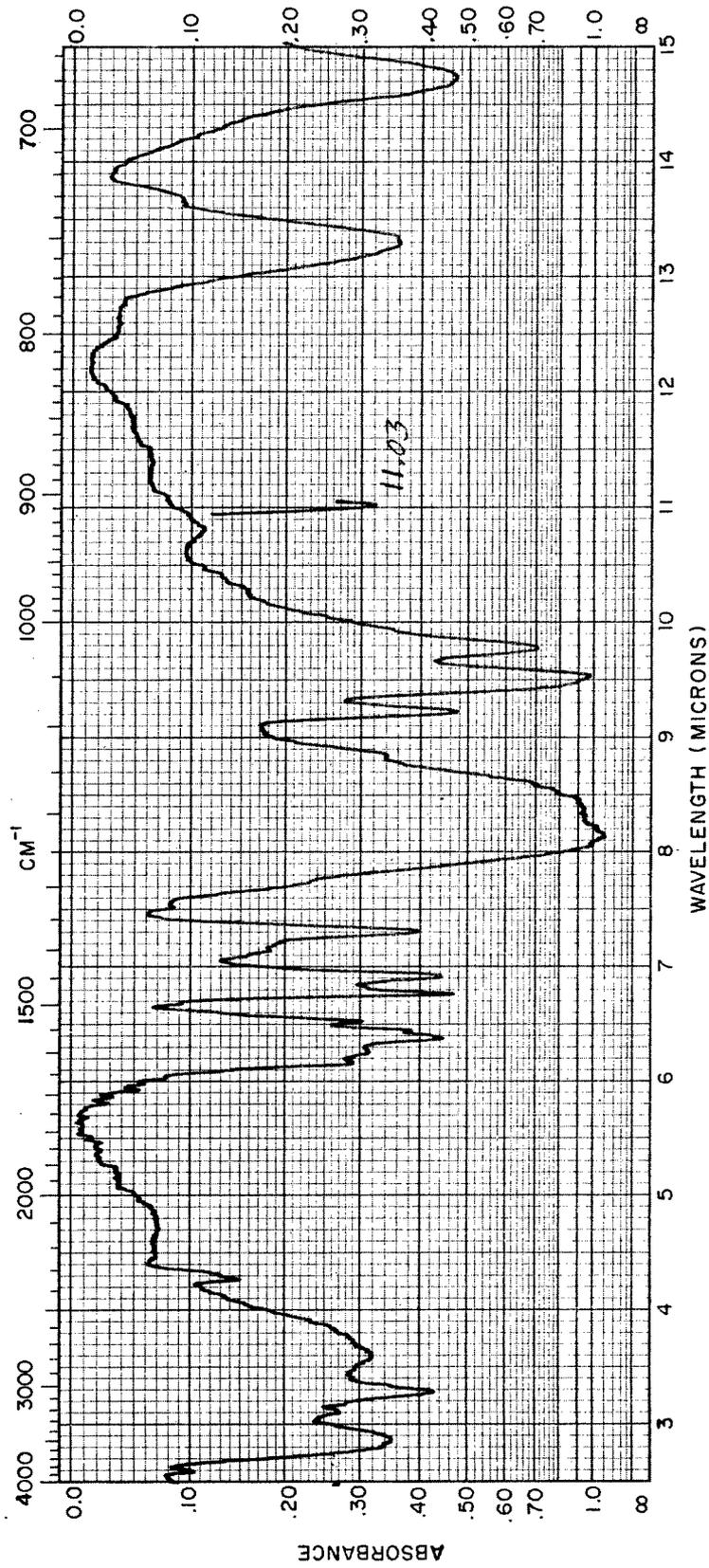


Figure 5. IR Spectrum of Polymer Prepared from Sulfonyl Chloride Derivative and Dodecyl Alcohol

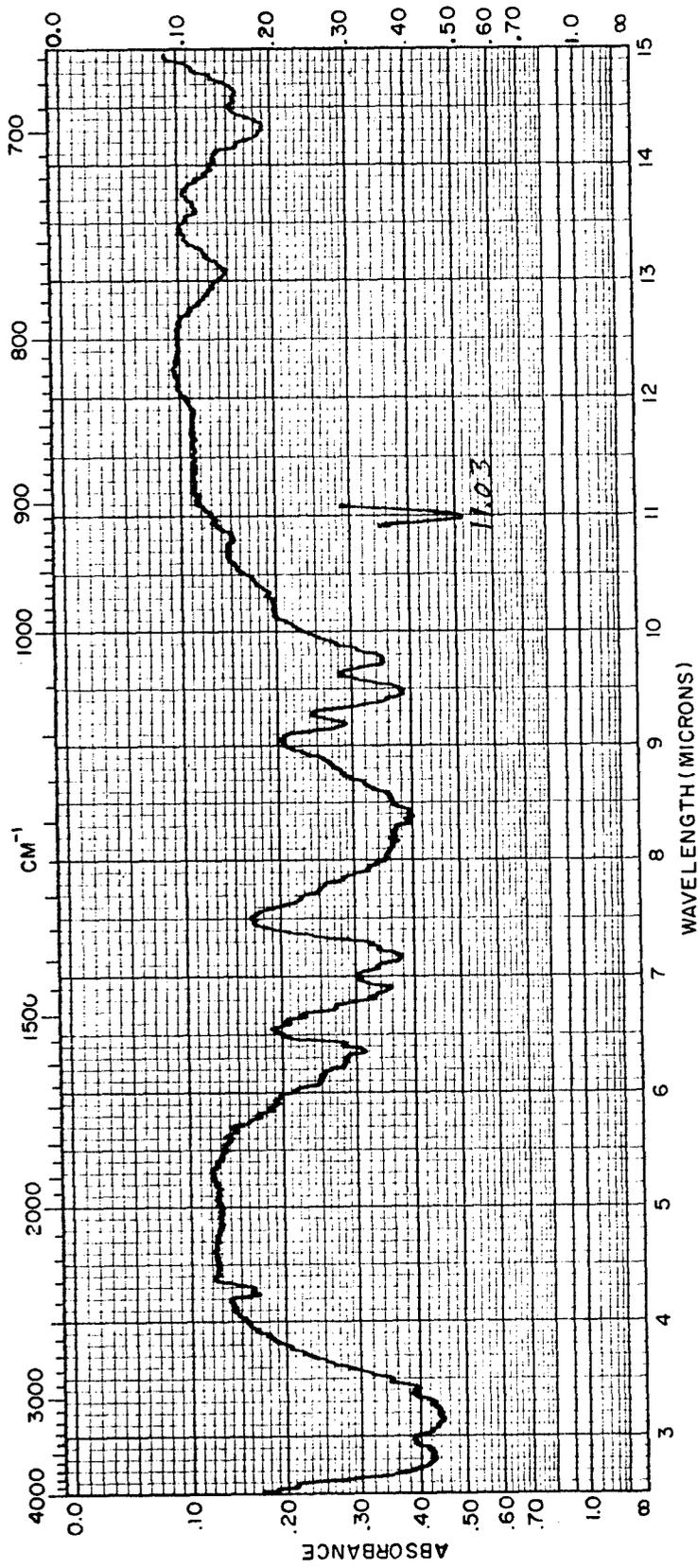


Figure 6. IR Spectrum of Polymer Prepared from Sulfonyl Chloride Derivative and Ammonia

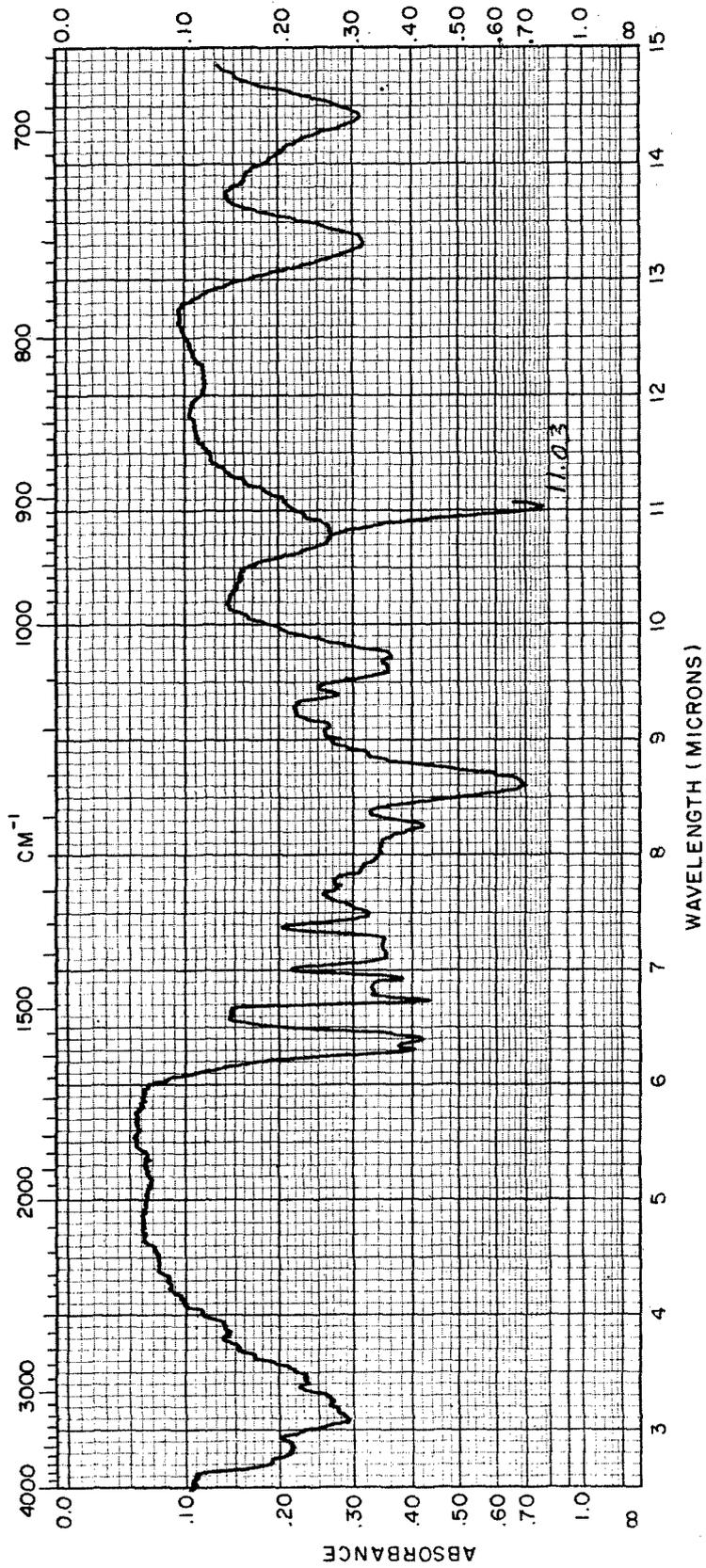


Figure 7. IR Spectrum of Polymer Prepared from Sulfonyl Chloride Derivative and Aniline

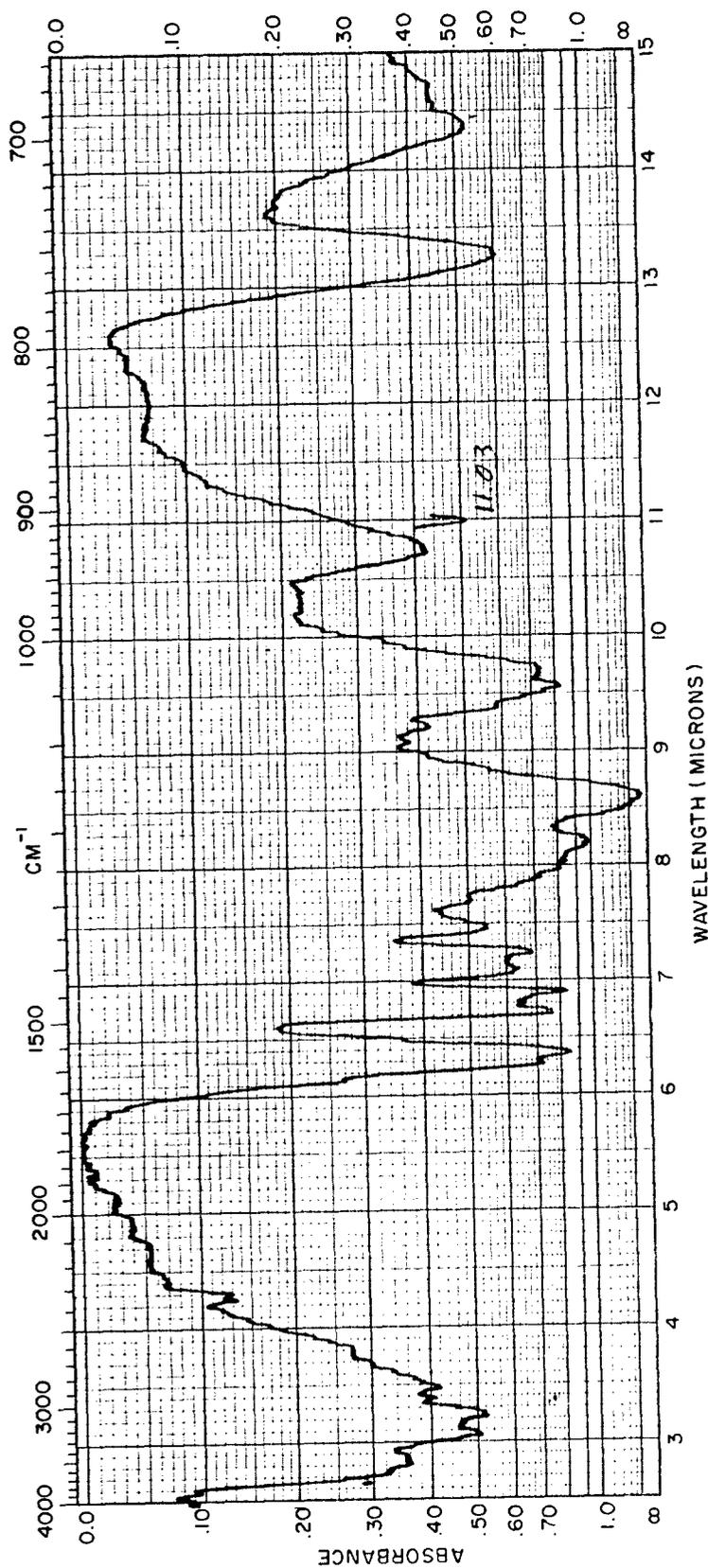


Figure 8. IR Spectrum of Polymer Prepared from Sulfonyl Chloride Derivative and Carbazole

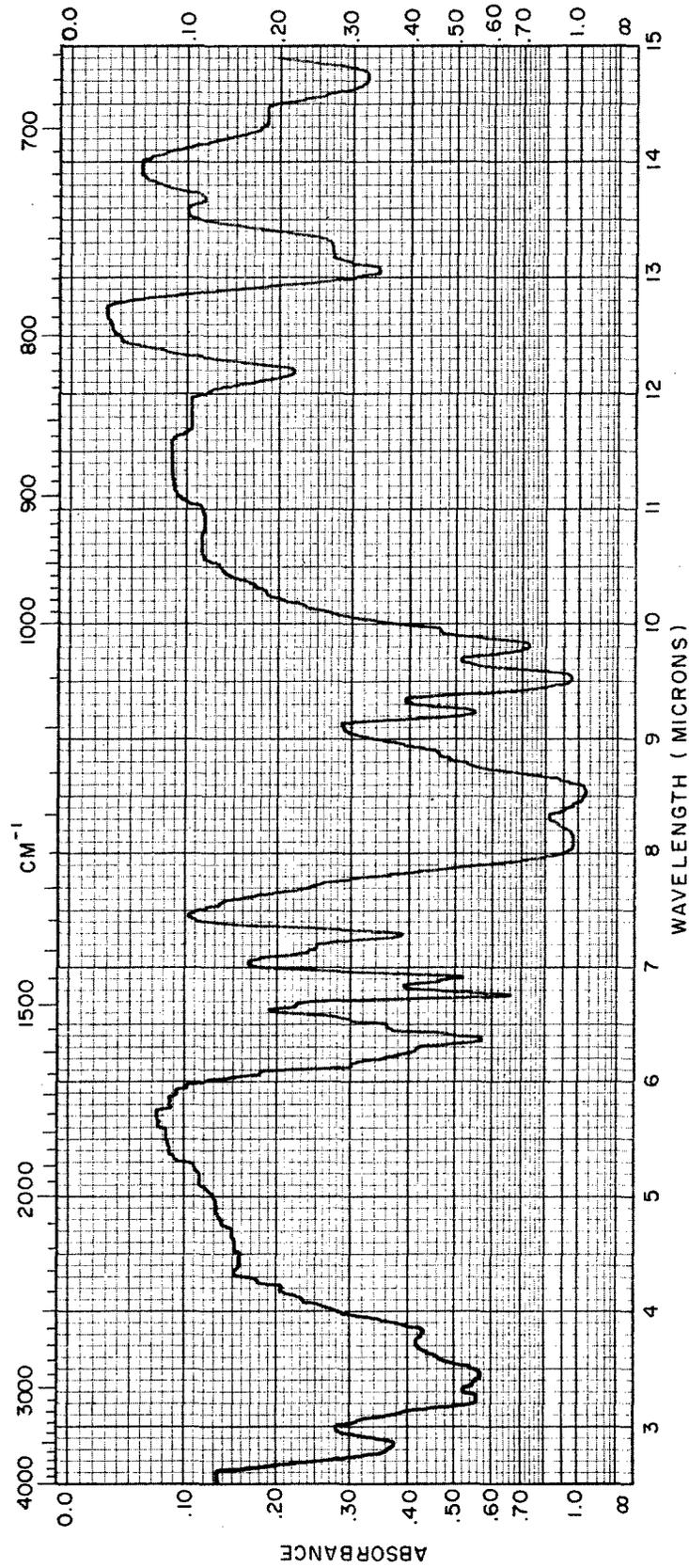


Figure 9. IR Spectrum of Polymer Prepared from Sulfonyl Chloride Derivative and 4-Amino-p-terphenyl

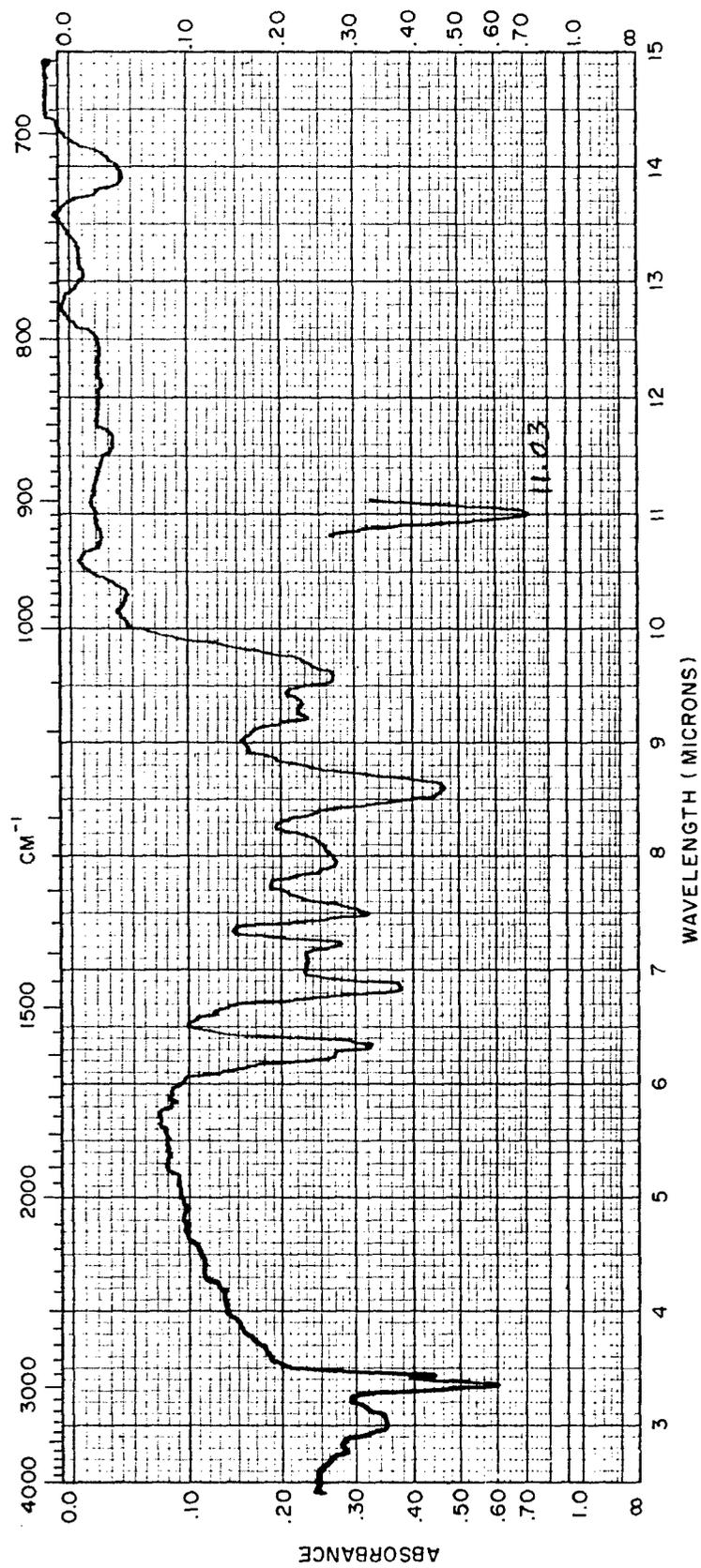


Figure 10. IR Spectrum of Polymer Prepared from Sulfonyl Chloride Derivative and Dodecylamine

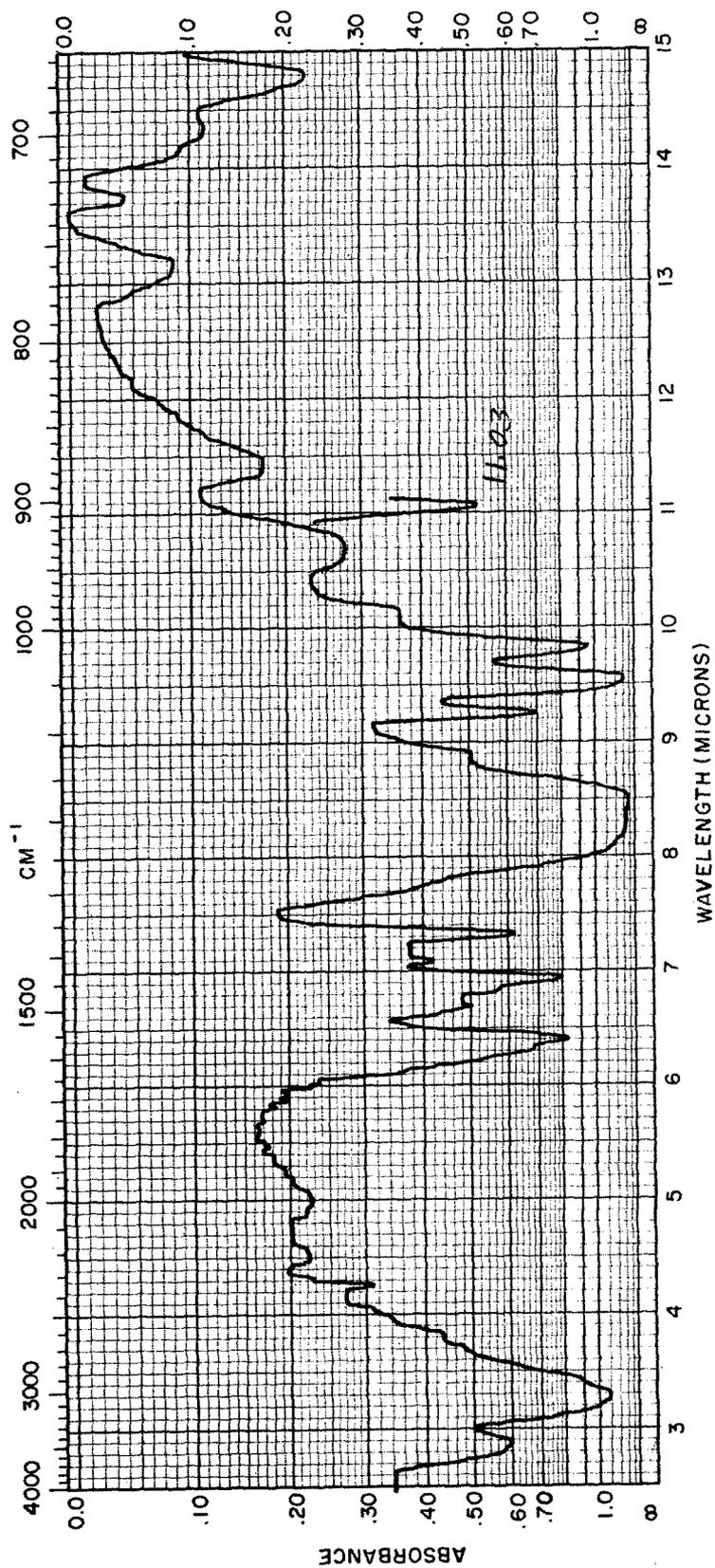


Figure 11. IR Spectrum of Polymer Prepared from Sulfonyl Chloride Derivative and Allylamine

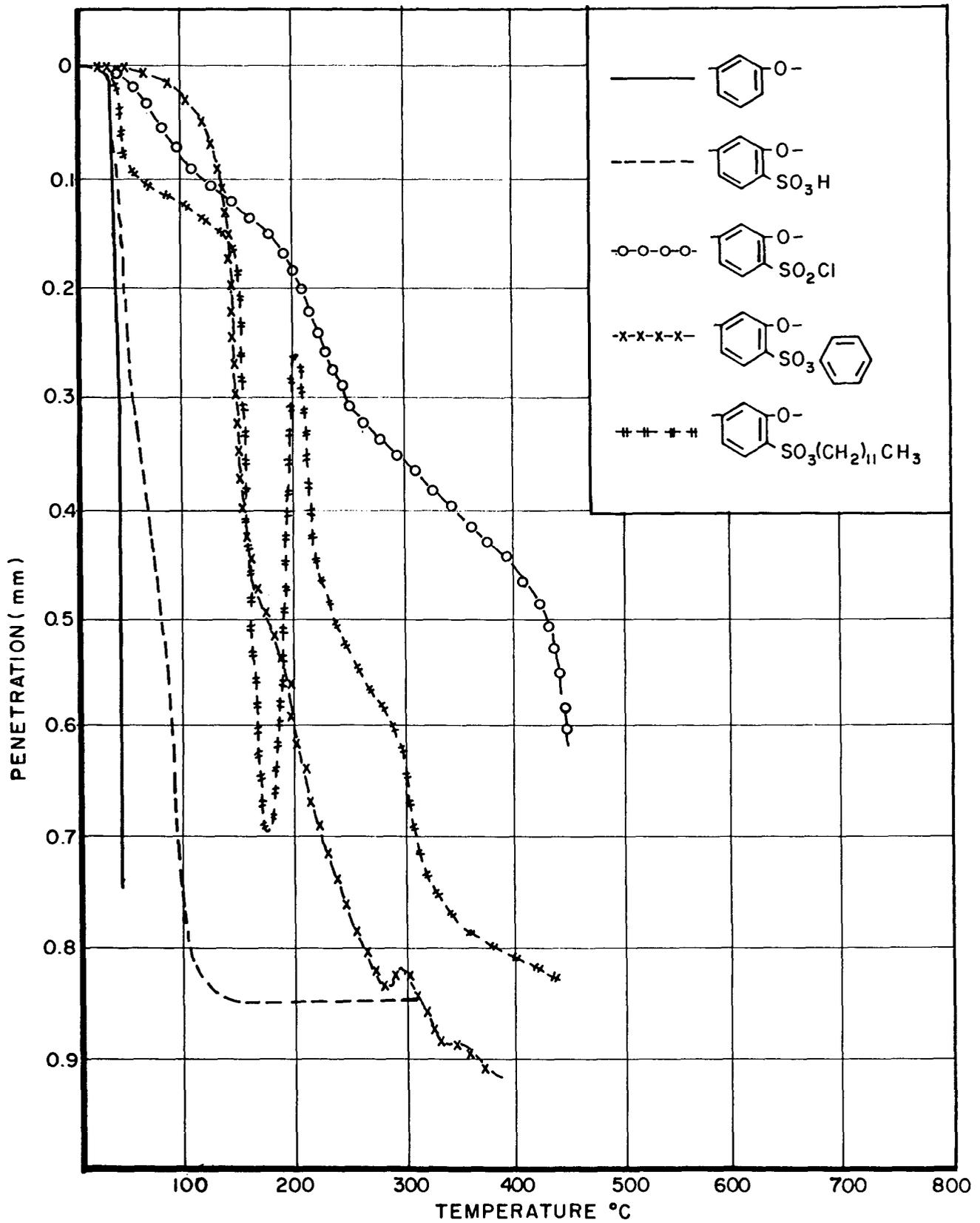


Figure 12. Composite Plot of Softening Curves I

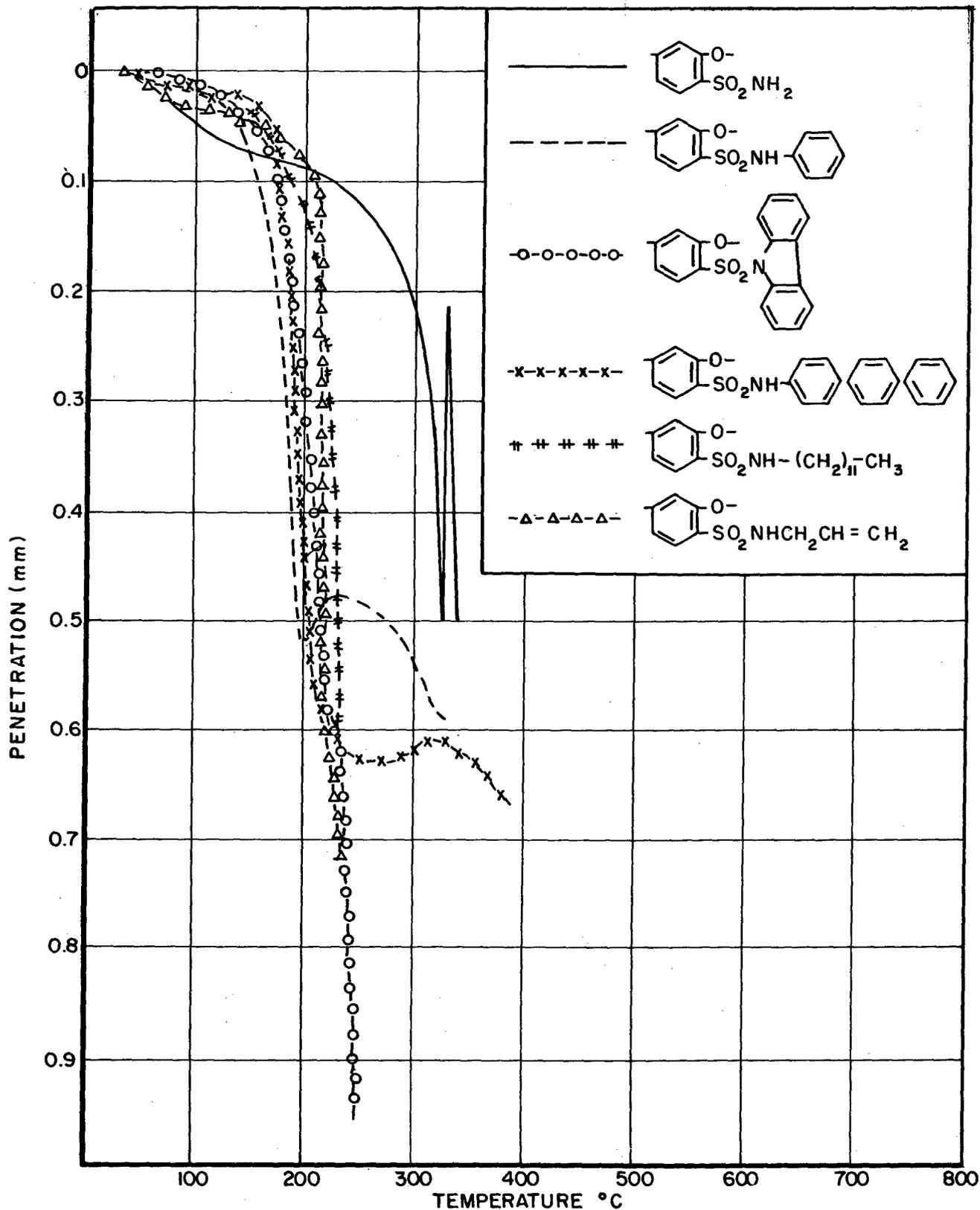


Figure 13. Composite Plot of Softening Curves II

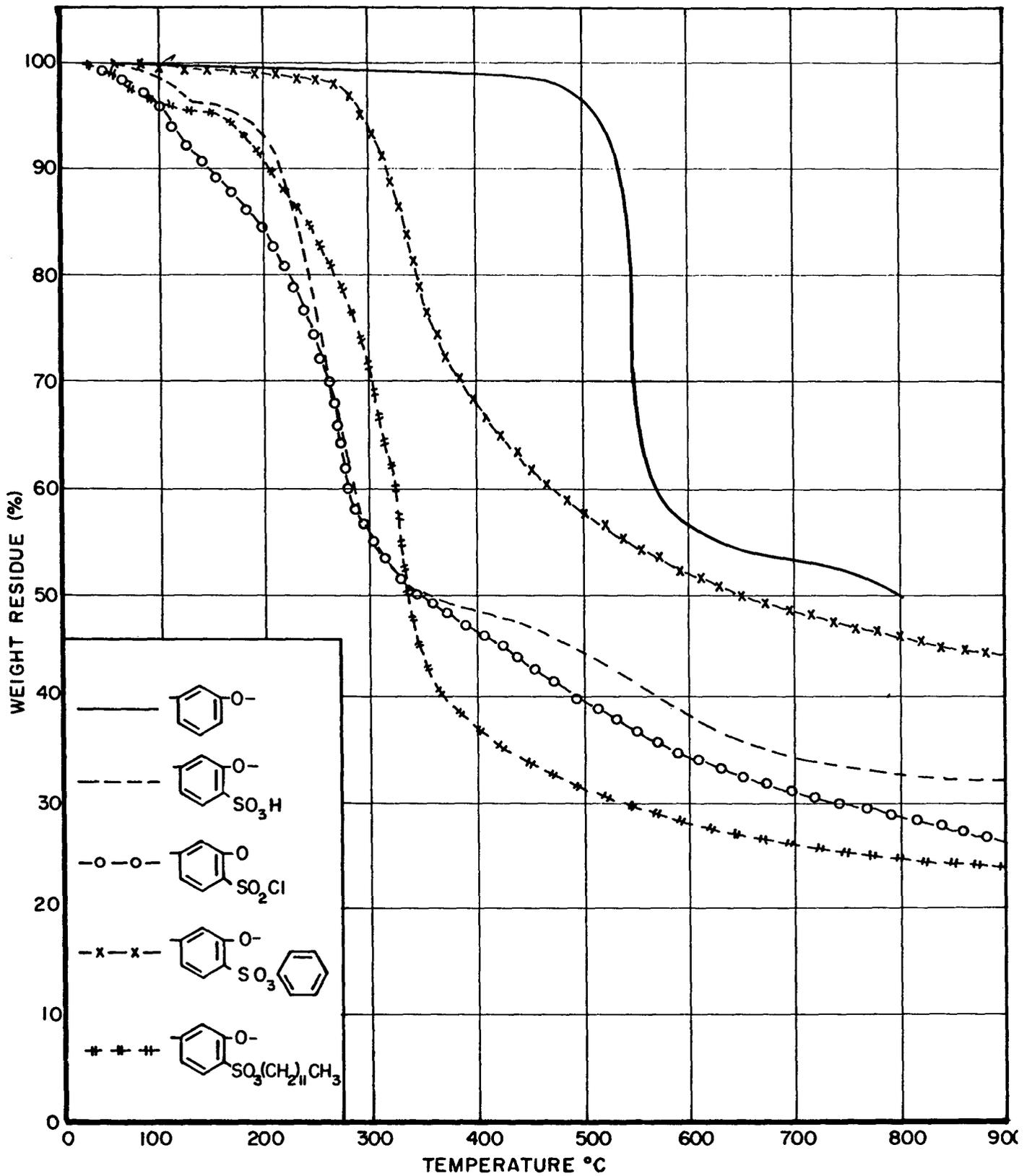


Figure 14. Composite TGA Plot I

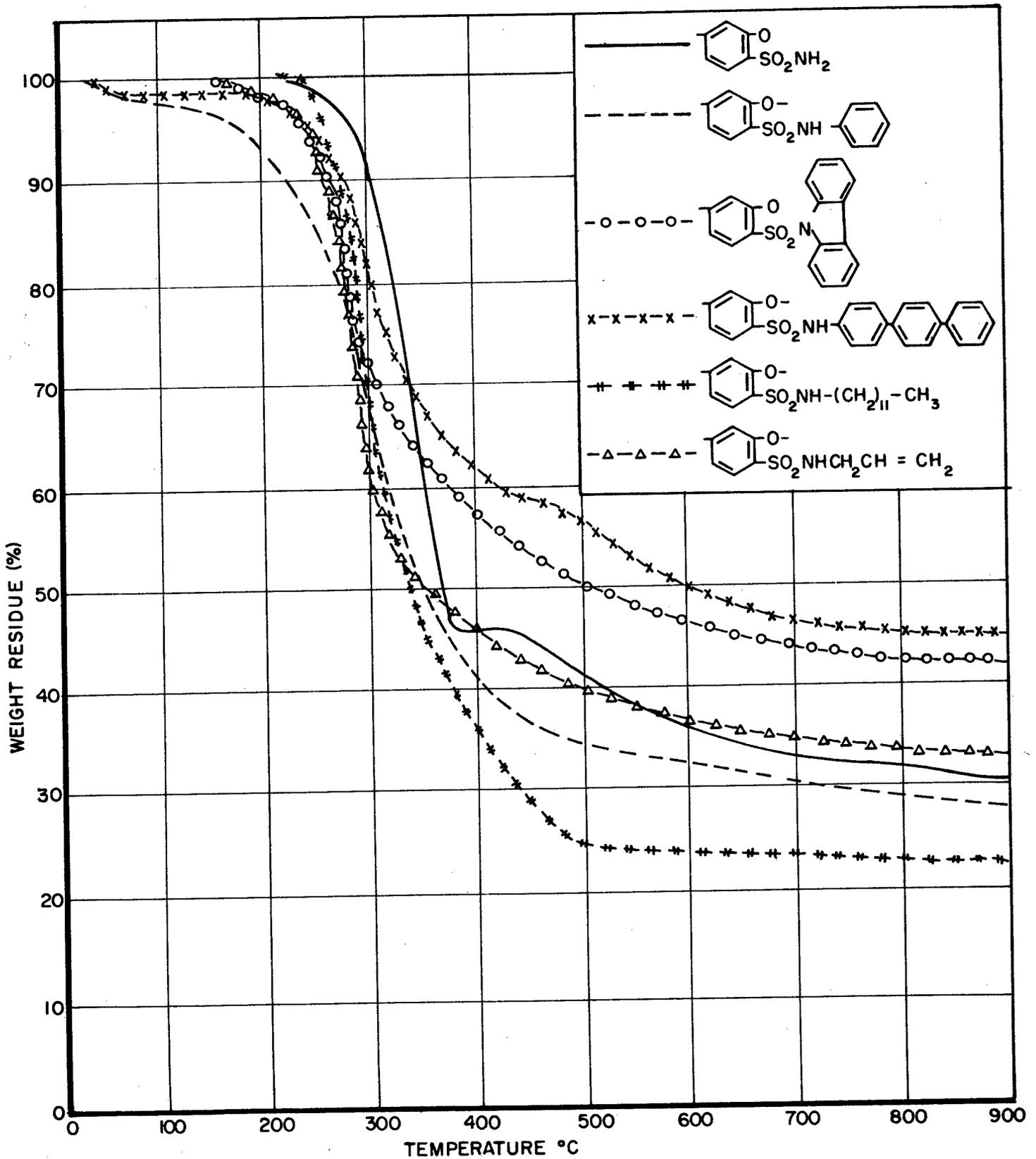


Figure 15. Composite TGA Plot II

TABLE I
REACTION CONDITIONS

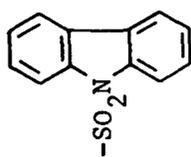
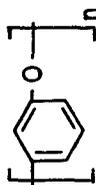
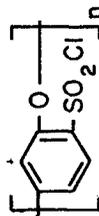
Modified Polymer	Reaction Medium	Acid Acceptor	Reaction Time Hrs.	Reaction Temp. °C	$\frac{\text{g modified polymer}}{\text{g initial polymer}}$
	(CH ₃ CO) ₂ O	--	15	65°	5.7 3.0 (a)
-SO ₂ Cl	HOSO ₂ Cl	--	18	65°	19.0 10.0 (a)
	phenol	pyridine	18	60°	1.8 2.0 (b)
-SO ₃ (CH ₂) ₁₁ CH ₃	DMSO	pyridine	18	60°	2.1 2.0 (b)
-SO ₂ NH ₂	DMSO	NH ₃	18	room temp.	1.5 2.0 (b)
	aniline	aniline	20	55°	1.1 2.0 (b)
	DMSO	pyridine	26	room temp. - 2 hrs 65° - 24 hrs	2.2 2.0 (b)
	DMSO	pyridine	6	65° - 2 hrs room temp. - 4 hrs	2.1 2.0 (b)

TABLE I
REACTION CONDITIONS (Cont'd)

Modified Polymer	Reaction Medium	Acid Acceptor	Reaction Time Hrs.	Reaction Temp. °C	g modified polymer / g initial polymer
$-\text{SO}_2\text{NH}(\text{CH}_2)_3\text{CH}_3$	DMSO	pyridine	18	50°	$\frac{2.2}{2.0}$ (b)
$-\text{SO}_2\text{NHCH}_2-\text{CH}=\text{CH}_2$	DMSO	$\text{CH}_2=\text{CH}-\text{CH}_2\text{NH}_2$	16	65° - 4 hrs. room temp. - 12 hrs	$\frac{0.9}{1.5}$ (b)



(a) initial polymer being



(b) initial polymer being

TABLE II
 PHYSICAL PROPERTIES OF

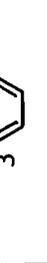

X	Appearance	Solvents	Number of X-Units per ring (a)	η_{inh} (solvent)
-H	tan powder	C ₆ H ₆ , THF, CHCl ₃ , DMF	1.0	0.16 (C ₆ H ₆)
-SO ₃ H	yellow-orange powder	MeOH, DMSO, DMF, HCOOH	1.3	0.56 (DMSO)
-SO ₂ Cl	light tan powder	THF, DMF, DMSO	1.0	0.84 (DMSO)
	tan powder	DMSO, pyridine	1.0	0.69 (DMSO)
-SO ₃ (CH ₂) ₁₁ CH ₃	light tan powder	HCOOH, DMSO	b	1.24 (DMSO)
-SO ₂ NH ₂	light brown powder	HCOOH, H ₂ O, DMSO, DMF	1.0	1.74 (DMSO)
	olive powder	DMSO, HCOOH, DMF, THF	0.9	1.25 (DMSO)
	tan powder	DMSO, HCOOH, DMF	0.6	0.60 (DMSO)

TABLE II
PHYSICAL PROPERTIES (Cont'd)

X	Appearance	Solvents	Number of X-Units per ring (a)	η_{inh} (solvent)
 $-\text{SO}_2\text{NH}_2$	tan powder	DMSO	0.8	0.66 (DMSO)
$-\text{SO}_2\text{NH}(\text{CH}_2)_{11}\text{CH}_3$	tan powder	THF, acetone, DMSO, DMF	1.0	0.25 (DMSO)
$-\text{SO}_2\text{NHCH}_2\text{CH}=\text{CH}_2$	light tan powder	DMSO, HCOOH, DMF	1.0	1.14 (DMSO)

(a) as determined from elemental analysis

(b) could not be determined due to excessive nitrogen content

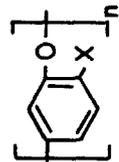
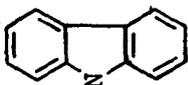


TABLE III
DTA-TRANSITIONS AND TGA-INVERSION POINTS FOR POLYMERS

X	DTA - Transitions (*)						Inversion point (s) of the TGA Curve
-H	53(-)	135(-)	255(-)	580(+)	545		
-SO ₃ H	85(-)			530(+)	(130), 260		
-SO ₃ (CH ₂) ₁₁ CH ₃	90(-)		230(-)	385(-)	(75), 220, (335)		
-SO ₃ - 	90(-)		265(+)	410(-)	335		
-SO ₂ Cl	95(-)	135(-)**	215(+)	430(-)	(120), 270		
-SO ₂ NH ₂	90(-)	135(-)**	367(-)	475(-)	345, 475		
-SO ₂ NH(CH ₂) ₁₁ CH ₃	60(-)**	135(-)**	312(-)		300		
-SO ₂ NHCH ₂ CH=CH ₂	60-80(-)	[135(-)]	265(+)	300(-)	280		
-SO ₂ NH- 	80(-)	140**	235(+)	385(-)	280		
-SO ₂ NH- 	75-85(-)	130(-)	245(+)	350(-)	370(-)		
-SO ₂ N- 	90(-)	135(-)	220(-)	295(+)	315(-)		

* + = exotherm; - = endotherm
 ** this transition could also be a baseline shift (second order transition)
 [] questionable
 = decomposition temperature

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		2b. GROUP	
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11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Research and Technology Division Air Force Systems Command Wright-Patterson Air Force Base, Ohio	
13. ABSTRACT <p>A series of modified poly-m-phenoxylenes was prepared by the introduction of substituents into the aromatic rings of the polymer. This was achieved by the preparation of a sulfonyl chloride derivative which could undergo reaction with various amines and alcohols to form sulfonamide or sulfonate derivatives.</p> <p>These modified polymers were characterized by their infrared spectra, elemental analyses and inherent viscosities. The effect of the various substituents upon the thermal behavior of the polymers was determined by softening range determination, thermogravimetric analysis, and differential thermal analysis.</p>			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Poly-m-Phenoxylenes Modified Polymers Thermal Stability Poly-Sulfonamides Poly-Sulfonates						

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