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SYNTHESIS AND PROPERTIES OF ACETYLENE TERMINATED SULFONE (ATS)

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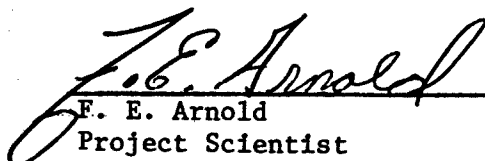
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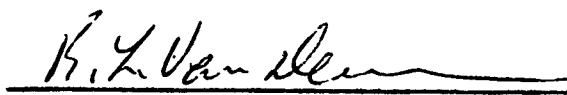
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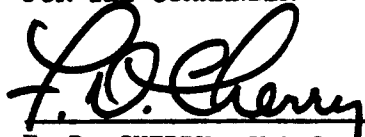
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The utilization of acetylene end-groups on phenylquinoxaline oligomers has provided a wide variety of new and improved matrix resins. The cured thermoset quinoxaline systems exhibit excellent moisture resistance which demonstrated the moisture insensitivity of the polyene product of the acetylene cure reaction. In an effort to use this technology in systems which process and handle like current state-of-the-art epoxies, the thermoset system 4,4' -bis(3-ethynyl-phenoxy)diphenylsulfone (ATS) was synthesized for characterization and evaluation as 350°F matrix system. (Continued)		

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Thermal analytical data obtained on ATS indicated a Tg at 0°C and a strong polymerization exotherm maximizing at 240°C. Cured ATS samples exhibited excellent thermal oxidative properties as evidenced by isothermal aging in air at 500°F and 600°F. Synthetic routes to ATS are included as well as physical properties of the system before/after cure.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419 "Aerospace Structural Materials," Task No. 241904 Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F. E. Arnold as the AFML Project Scientist. Co-authors were G. A. Loughran and Dr. F. E. Arnold, Air Force Materials Laboratory, (AFML/MBP).

This report covers research conducted from April 1977 to April 1979.

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SECTION I

INTRODUCTION

A substantial effort in our laboratory has been directed toward the synthesis and properties of aromatic heterocyclic polymers for utilization as high temperature matrix and adhesive resins. The primary limitation associated with heterocyclic systems is that those which possess the best thermal oxidative stability are formed by polycondensation reactions and the water of condensation evolved during polymerization gives rise to the formation of voids in the cured matrix or adhesive resin. Work in our laboratory circumvented the limitation of this class of polymeric materials by uncovering a new addition reaction based on the thermal treatment of acetylene terminated heterocyclic oligomers.

Our in-house research program first demonstrated the new technology based on the thermal homopolymerization of acetylene terminated heterocyclic systems with the synthesis (References 1 through 4) and evaluation (References 5 through 8) of acetylene terminated quinoxaline oligomers (ATQ's). Quinoxaline oligomers were selected for synthesis since they exhibited excellent thermal properties and moisture resistance (Reference 9). With the utilization of two end-capping agents, 3-(3,4-diaminophenoxy)phenylacetylene (References 3,4) and 4-(3-ethynylphenoxy)benzil (References 10,11), a wide variety of reactive oligomeric materials have been prepared (References 12,13) showing excellent potential for 450-500°F applications. Of most importance, is the fact that all the ATQ's that have been evaluated were shown to be moisture insensitive. This means that the homopolymerization of acetylene end-groups provide a moisture insensitive moiety since the quinoxaline portion of the oligomers was shown not to be moisture insensitive prior to our studies.

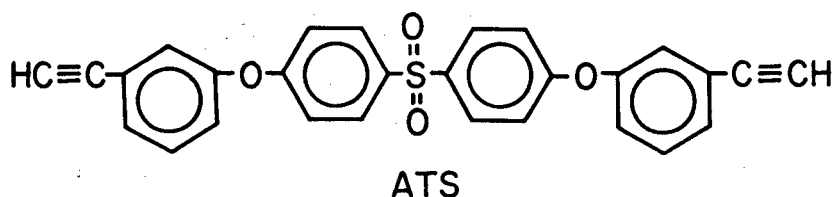
The quinoxaline work established and demonstrated the AT technology and generated a thermally induced addition reaction which formed a moisture insensitive product. It was felt that the initial quinoxaline work

should be pursued in an effort to solve other Air Force problems associated with matrix and adhesive resins. The moisture sensitivity of epoxy matrix systems is one such problem. Could one design and synthesize a 350°F matrix resin that would retain all the processing, handling, and performance characteristics of epoxies, while significantly reducing sensitivity to moisture? This report describes an effort to answer that question with the objective of obtaining a potential candidate system for development as an Air Force matrix and adhesive resin.

SECTION II

RESULTS AND DISCUSSION

The design of a new matrix resin from the standpoint of molecular structure entails primarily two factors, use-temperature and fabrication criteria. In the temperature region of 350°F, the molecular structure must perform for extended periods of time at saturated moisture conditions. We have previously showed that the addition reaction of primary acetylenes leads to a product that was moisture insensitive (Reference 6). The aromatic ether sulfone polymer backbone, as a thermoplastic, has also been shown to perform well under adverse moisture conditions (Reference 14). A thermoset system containing an ethersulfone backbone and acetylene end-groups was selected for synthesis to provide a potential candidate system for a 350° matrix resin.



The fabrication criteria of a 350°F matrix resin entails:

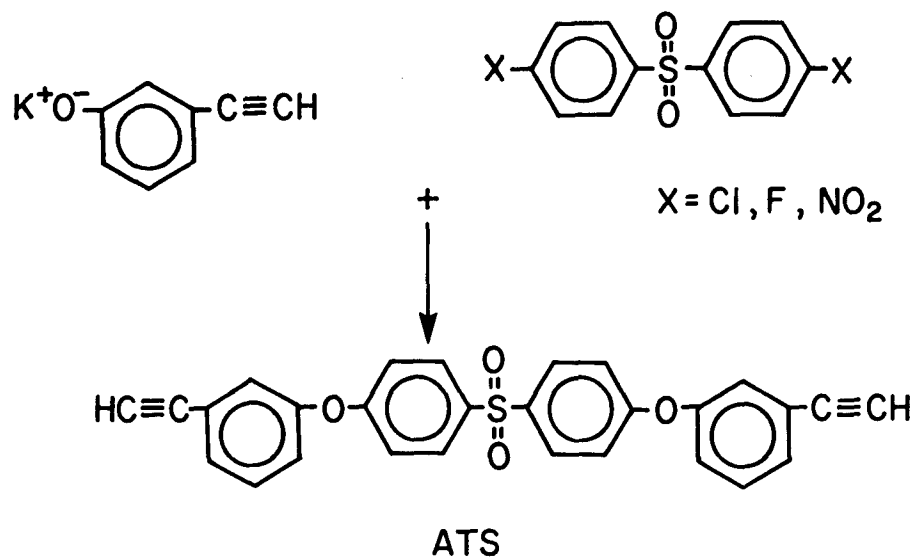
- (1) Melt processability,
- (2) Room temperature tack and drape,
- (3) 350°F maximum cure temperature (100 psi),
- (4) 400-450°F maximum postcure temperature.

The first two are involved with the glass transition of the oligomer; the latter two are concerned with the cure chemistry of the end groups. The acetylene terminated sulfone system (ATS) was structurally designed to provide an amorphous material (meta-oxyethynyl functionality) with a

glass transition temperature well below room temperature, thus allowing melt processability and providing room temperature tack and drape to the prepreg.

1. SYNTHESIS

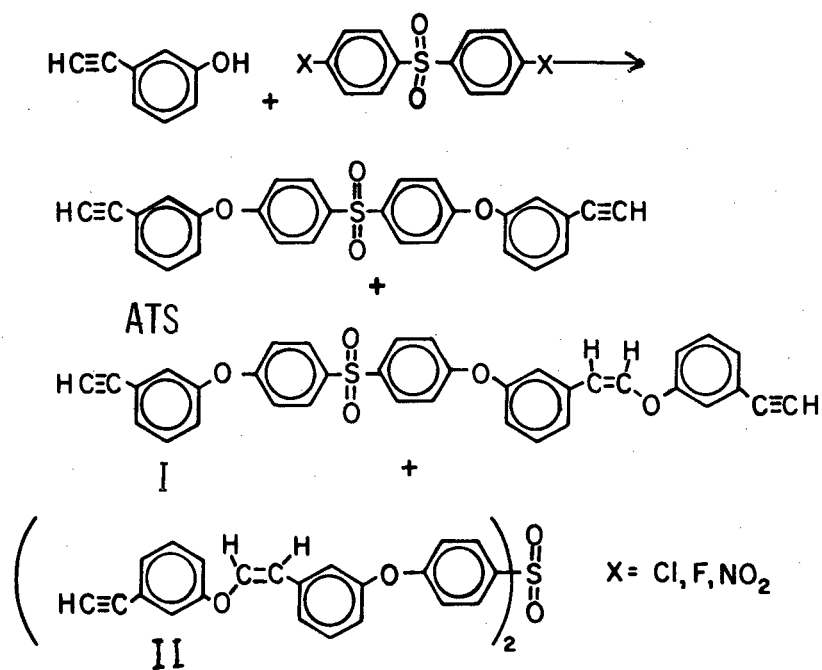
Several different synthetic routes were investigated in order to find the most facile and economical route for the preparation of 4,4'-bis-(3-ethynylphenoxy)-diphenylsulfone (ATS). Initial attempts were concentrated on the nucleophilic displacement reaction of various leaving groups in the 4,4' positions of diphenylsulfone with the metallic salt of m-hydroxyphenylacetylene. The synthesis was carried out in highly aprotic solvents such as dimethylsulfoxide, N,N dimethylacetamide, and sulfolane at temperatures between 75 and 100°C.



Leaving groups such as chloro, fluoro, and nitro groups were employed in the synthesis. Low yields of the desired ATS were obtained utilizing the nitro group in the displacement reaction. The primary product was a white crystalline compound, identified as 3-(p-nitrophenoxy) phenylacetylene resulting from displacement at the sulfone linkage in contrast

to the nitro. The most facile displacement occurred using fluoro as a leaving group. A 63% yield of ATS was obtained using the fluoro in dimethylsulfoxide at only 75°C. The most economical leaving group for the nucleophilic displacement reaction was the chloro group and was therefore studied in depth.

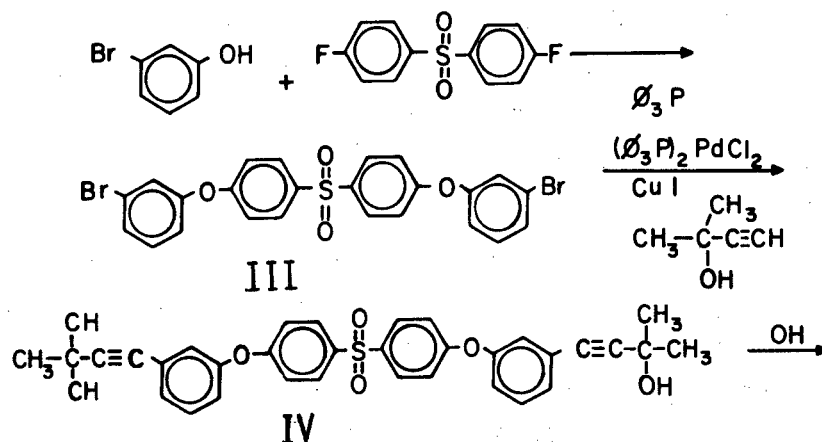
In general, the reactions were carried out under a nitrogen atmosphere at temperatures ranging from 60°C to 100°C. The products, after isolation of the crude reaction mixture, were purified by column chromatography. At 60°, even after 120 hours, the reaction was incomplete, and unreacted 4,4'-dichlorodiphenyl-sulfone was found along with the mono and diethynyl products. In order to allow complete conversion of the mono to the diethynyl product, the temperature was increased to 100°C and reactions were conducted for as long as 168 hours. The primary products were ATS (85%), along with smaller amounts of I (10%) and II (<5%) which were separated from the major product by column chromatography. Structural determinations were made from



analytical analysis, VPO molecular weight, infrared spectra, mass spectra and proton and C^{13} nuclear magnetic resonance spectra. It is known that cis- β -alkoxy styrenes have been readily obtained by the reaction of sodium alkoxides and phenylacetylene (Reference 15). The coupling constants of both protons of I and of cis- β -alkoxy-styrenes, have a magnitude of 7Hz which is consistent for a cis-configuration for the vinyl hydrogens (Reference 16). Therefore, it seems consistent that I and II are produced by the reaction involving the anion of 3-ethynylphenol (excess in all reactions), with the terminal acetylene groups of ATS, as well as I.

The direct displacement of an aryl substituent with an acetylenic species was investigated in an effort to circumvent side reactions of excess hydroxyphenylacetylene, and long reaction times. A recent investigation (Reference 17) into the direct displacement of activated brom-aromatics with methylbutynol was shown to be very effective utilizing the catalyst system composed of bis-triphenylphosphine palladium chloride, cuprous iodide, and triphenylphosphine. The secondary acetylene could be converted into the primary by caustic hydrolysis.

The bis-bromo precursor 4,4'-(3-bromophenoxy)-diphenylsulfone III was prepared by the reaction of 4,4'-difluorodiphenylsulfone with the potassium salt of m-bromophenol in dimethylsulfoxide. Treatment of III with 2-methyl-3-butyn-2-ol in triethylamine, catalyzed by bis-triphenylphosphine palladium chloride, cuprous iodide and triphenylphosphine provided a 94% yield of the bis-butynol intermediate IV. Conversion of IV to the primary acetylene ATS was carried out by the hydrolytic displacement of acetone with potassium hydroxide in toluene. Purification of ATS by this method involved a simple filtration through activated silica gel.



2. PROPERTIES

Analysis of ATS by DSC ($\Delta = 20^\circ\text{C}/\text{min}$) shows an initial strong baseline shift attributed to the T_g (0°C) of the material, a strong exotherm initiating at 140°C and maximizing at approximately 240°C , for the polymerization of the terminal acetylene groups. A weak baseline shift at the higher temperatures, associated with the T_g of the cured polymer, could only be detected on DSC scans with the cure being accomplished during the scan. Samples of ATS, cured at 350°F for four hours followed by a one hour heat treatment at 425°F , exhibited a T_g of 360°F by thermal mechanical analysis (TMA). For the determination of the T_g after cure, the TMA expansion (change of rate of expansion) and for penetration modes (point of highest rate of penetration) were used, also at a rate of ($\Delta = 20^\circ\text{C}/\text{min}$).

It has been shown (Reference 18) that the initial polymerization of ATS involves the formation of low molecular weight conjugated polyenes. Polymerization kinetics (Reference 19) suggest a free-radical chain mechanism in which molecular weight is governed by a first-order termination reaction. It is felt that subsequent higher temperature reactions occur with the conversion of the conjugated polyene to various aromatized products.

The thermal properties for the cured ATS were quite good as shown by isothermal aging studies at 500 and 600°F in air (Figure 1). The material was cured as above under a nitrogen atmosphere. The TGA weight loss curves (Figure 2) show breaks in the region of 475°C and 500°C in air and nitrogen, respectively.

ATS meets all the processing criteria of a 350°F matrix material. Since the material exhibits a T_g below room temperature, it can be melt prepregged at 155°F and the prepreg has excellent room temperature tack and drape. Preliminary composite data (References 20 and 21) have shown that ATS on unsized Celion 6000 retains 90% of its strength properties when tested at 350°F, after being moisture saturated at 165°F, 95% relative humidity.

SECTION III
EXPERIMENTAL

1. 3 ETHYNYLPHENOL

A solution was prepared from 198g of potassium hydroxide dissolved in 300ml of distilled water. This was added to a solution containing 128g (0.468 mole) of 3-ethynylphenoxy-p-toluene sulfonate in 300ml of methanol. The mixture was distilled under nitrogen with the removal of 300ml of distillate. The reaction mixture was cooled to ambient temperature and added to a slurry of 200ml of concentrated sulfuric acid and 1500g of crushed ice. The cloudy solution was extracted with three 200ml portions of ether and the combined extracts were washed with three 50ml portions of distilled water. The ether solution was filtered through a bed of silica gel and on removal of the solvent a 53g (96%) yield of light yellow oil was obtained.

Anal. Calc'd for C_8H_5O : C, 82.03; H, 4.30

Found: C, 82.30; H, 4.21

2. 4-CHLORO-4'-(3-ETHYNYLPHENOXY) DIPHENYLSULFONE

To a solution containing 12.9g (0.109 mole) of 3-ethynylphenol in 150ml of N,N'-dimethylacetanilide (DMAC) was added 53g of anhydrous potassium carbonate. The solution was stirred under a nitrogen atmosphere for three hours and 10.4g (0.036 mole) of 4,4'-dichlorodiphenyl-sulfone dissolved in 100ml of DMAC was added dropwise over a period of three hours. The reaction mixture was heated to 100°C and maintained at that temperature for 24 hours and on cooling added to distilled water. The product was extracted with ether and chromatographed on a dry column of silica gel, eluting with 3:1 hexane: methylene chloride to give 11g (90% yield), m.p. 140-141°C. Infrared Spectrum (Figure 3) C^{13} NMR Assignment (Table 1).

Anal. Calc'd for $C_{20}H_{13}O_3SCl$: C, 65.12; H, 3.55; S, 8.69

Found: C, 65.31; H, 3.36; S, 8.54

3. 4,4'BIS (3-ETHYNYLPHENOXY) DIPHENYLSULFONE (ATS) FROM 4,4'-DICHLORODIPHENYLSULFONE

To a solution containing 52g (0.448 mole) of 3-ethynylphenol in 300ml of dry dimethylsulfoxide (dried over calcium hydride) was added, under a nitrogen atmosphere, 243g (1.76 mole) of anhydrous potassium carbonate. The reaction mixture was stirred at room temperature overnight. Then the temperature was raised to 50°C and 44.8g (0.156 mole) of 4,4'-dichlorodiphenyl sulfone in 200ml of dry dimethylsulfoxide was added slowly over a period of one hour. The reaction mixture was heated at 100°C under nitrogen for 168 hours; then it was cooled and filtered. The filtrate was added to 1500ml of cold water and the resulting cloudy solution was extracted with 500ml of ether. The ether extract was washed with two 250ml portions of water and filtered through a one-inch thick bed of silica gel. On removal of the ether, under reduced pressure, a 54g (74%) yield of a light yellow viscous resin was obtained. High pressure liquid chromatography indicated that the product consisted of 85% ATS, 10% I and 5% II. Repetitive column chromatography on activated silica gel, eluting with hexane (2):ether (1), provided analytical samples of ATS and the monovinylether I.

(ATS) $T_g = 0^\circ\text{C}$ (DSC)

Proton NMR (Figure 4), C_{13} NMR carbon assignments (Table 2)
 Infrared Spectrum (Figure 5) MW = 450 (VPO-434) (mass spectrum, $[M]^+$ 450)
 Anal. Calc'd for $C_{28}H_{18}O_4S$: C, 74.65; H, 4.03; S, 7.12
 Found : C, 74.74; H, 4.10; S, 7.33

Monovinylether I $T_g = 1^\circ\text{C}$ (DSC)

C_{13} NMR carbon assignments (Table 3)

Infrared Spectrum (Figure 6)

MW = 568 (VPO-528)

Anal. Calc'd for $C_{36}H_{24}O_5S$: C, 76.03; H, 4.28; S, 5.25
 Found: C, 76.01; H, 4.18; S, 5.22

4. 4,4'-BIS (3-BROMOPHENOXY) DIPHENYLSULFONE III

To a solution of 19g (1.1 mmole) m-bromophenol in 100ml of methanol and 100ml of benzene, under nitrogen was added 100ml of a 1N methanolic potassium hydroxide solution. The mixture was heated to distill the solvents off to almost dryness, maintaining the temperature below 100°C. A 100ml of dry benzene was added in the above procedure repeated to yield a light tan solid. To the benzene moist salt was added 12.7g (0.5 mmole) of 4,4'-difluorodiphenyl sulfone dissolved in 120ml of dry dimethylsulfoxide. The reaction mixture was slowly heated to 140°C and maintained at that temperature for four hours. Extraction with methylene chloride followed by washing with 10% aqueous potassium hydroxide, water, and removal of the methylene chloride provided 22g (70% yield) of product M.P. 150-151°C. Infrared spectrum (Figure 7).

Anal. Calc'd for $C_{24}H_{16}O_4$ SBR: C, 51.46; H, 2.86

Found: C, 51.35; H, 2.76

5. 4,4'-BIS 3-(3-METHYL-3-HYDROXY-1-BUTNYLPHENOXY) DIPHENYLSULFONE (IV)

A mixture of 25g (4.46 mmoles) of 4,4'-(3-bromophenoxy) diphenylsulfone, 10.7g (12.7 mmoles) of 2-methyl-3-buten-2-ol and 300ml of triethylamine was degassed by passing nitrogen through the solution for 20 minutes. To the reaction mixture was then added 0.24g of triphenylphosphine, 0.06g of dichloro (triphenyl-phosphine) palladium (II) and 0.06g of cuprous iodide. The reaction mixture was heated to 80°C and maintained at that temperature for 20 hours. It was then cooled to room temperature, filtered, and the triethylamine removed under reduced pressure. The residual oil was dissolved in 300ml of methylene chloride and treated with a 10% solution of sulfuric acid, then washed with distilled water. On removal of the methylene chloride 23.7g (94% yield) of a light yellow oil was obtained. This material thus obtained could be used directly for the next step, or could be purified by chromatography on a column of silica gel (elution with 2:1 hexane, ethylacetate), m.p. 62-67°C. Infrared Spectrum (Figure 8).

Anal. Calc'd for $C_{34}H_{30}O_6S$: C, 72.06; H, 5.33

Found: C, 71.98; H, 5.27

6. 4,4'-BIS (3-ETHYNYLPHENOXY) DIPHENYLSULFONE (ATS)

To a solution containing 23.7g (4.18 mmole) of (IV) in 250ml of toluene was added, under a nitrogen atmosphere, 12g of sodium hydroxide and 100ml of methanol. The methanol and 100ml of toluene were then removed by distillation. The reaction mixture was washed with 2 x 200ml portions of distilled water, dried over magnesium sulfate and then passed through a fritted glass funnel containing 700g of activated silica gel. The product 17.3g (92% yield) was removed from the silica gel by eluting with methylene chloride.

Anal. Calc'd for $C_{28}H_{18}O_4S$: C, 74.64; H, 4.02

Found: C, 74.32; H, 4.00

SECTION IV

CONCLUSIONS

The goals set forth in the introduction of this report have been realized with the synthesis of the acetylene terminated sulfone (ATS) 350°F thermoset system. The resin meets all the fabrication criteria of the state-of-the-art 350°F epoxide systems. The terminal acetylene groups homopolymerize by addition reactions with the formation of a moisture-insensitive product. The ATS polymer system is the first thermosetting 350°F matrix material found to exhibit high temperature (350-400°F) moisture resistance. It is recommended that the material be fully explored in a composite or adhesive development program.

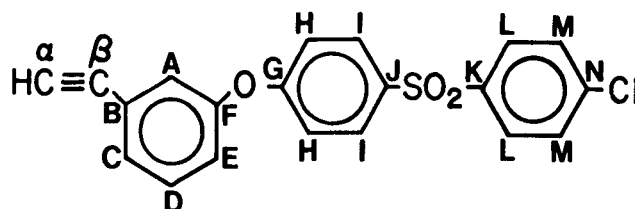
REFERENCES

1. R. F. Kovar, G. F. L. Ehlers, and F. E. Arnold, Polymer Preprints, 16 (2) 246 (1975).
2. R. F. Kovar, G. F. L. Ehlers, and F. E. Arnold, AFML-TR-76-71 (1976).
3. R. F. Kovar, G. F. L. Ehlers, and F. E. Arnold, J. of Polymer Sci., Poly. Chem. Ed., 15, 1081 (1977).
4. R. F. Kovar and F. E. Arnold, U.S. Patent 3,975,444 (1976) and U.S. Patent 3,966,729 (1976).
5. C. E. Browning, A. Wereta, Jr., J. T. Hartness, and R. F. Kovar, Soc. Adv. Mat'r and Process Eng. Vol. 21, (1976).
6. R. F. Kovar and F. E. Arnold, Soc. Adv. Mat'r and Process Eng. Vol. 8, 106 (1976).
7. M. G. Maximovich, S. C. Zockerby, R. F. Kovar, and F. E. Arnold, Soc. Adv. Mat'r and Process Eng. Vol. 22, 713 (1977).
8. M. G. Maximovich, S. Z. Zockerby, R. F. Kovar, and F. E. Arnold, Adhesive Age, 40, (1977).
9. P. M. Hergenrother, J. Macromol. Sci., Revs. Macromol. Chem., C6, 1 (1971).
10. F. L. Hedberg and F. E. Arnold, AFML-TR-78-142 (1978).
11. F. L. Hedberg and F. E. Arnold, U.S. Patent 4,098,825 (1978) and U.S. Patent 4,147,868 (1979).
12. F. L. Hedberg and F. E. Arnold, Polymer Preprints, 18, (1), 826 (1977).
13. F. L. Hedberg, R. F. Kovar, and F. E. Arnold, Contemporary Topics In Poly. Sci. Vol. 2, Plenum Publishing Corporation, New York, 235 (1977).

REFERENCES (CONTINUED)

14. M. G. Maximovich, AFML-TR-75-181, (1975).
15. John E. Baldwin and Leigh E. Walker, J. Org. Chem., 31, 3985 (1966).
16. S. T. Miller, J. Am. Chem. Soc., 73, 6091 (1956).
17. E. T. Sabourin, Petroleum Chem. Preprints, 20, (1), 233 (1979).
18. J. M. Pickard, S. C. Chatteraj and M. T. Ryan, Polymer Preprints, 20, (2), 375 (1979).
19. J. M. Pickard, E. G. Jones, and I. J. Goldfarb, Polymer Preprints, 20, (2), 370 (1979).
20. M. G. Maximovich, S. C. Lockerby, G. A. Loughran, and F. E. Arnold, Soc. Adv. Matr's and Proc. ENg., 23, 490 (1978).
21. M. G. Maximovich and S. C. Lockerby, AFML-TR-78-32, Vol. II, April (1978).
22. J. B. Stothers, "Carbon-13-NMR Spectroscopy," Academic Press, 197 (1972).
23. W. F. Reynolds and R. A. McClelland, Can. J. Chem., 55, 536 (1977).

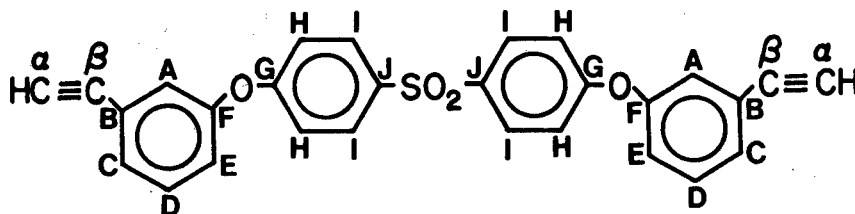
TABLE 1
 C^{13} NMR ASSIGNMENTS* FOR
 4-CHLORO-4'-(3-ETHYNYLPHENOXY)-DIPHENYLSULFONE



	No of C Atoms	PPm		$J^{C^{13}H}$	Intensity Ratio Obs.
		Calc'd	Obs.	Obs.	
α	1.0	--	78.8	253	1.2
β	1.0	--	82.7	--	--
A	1.0	122.9	124.1	165	0.8
B	1.0	124.0	124.6	--	--
C	1.0	127.2	129.3	168	1.7
D	1.0	130.4	130.4	162	1.4
E	1.0	118.9	121.4	165	0.8
F	1.0	158.1	155.4	--	--
G	1.0	162.4	162.3	--	--
H	2.0	119.9	118.5	164	1.7
I	2.0	129.2	130.5	164	2.1
J	1.0	136.5	135.6	--	--
K	2.0	139.6	140.3	--	--
L	2.0	130.6	129.4	168	2.0
M	1.0	129.5	130.1	165	1.6
N	1.0	139.6	141.0	--	--

* Assignments for the C^{13} NMR spectra were made on the basis of additivity rules for substituted benzenes (References 22 and 23).

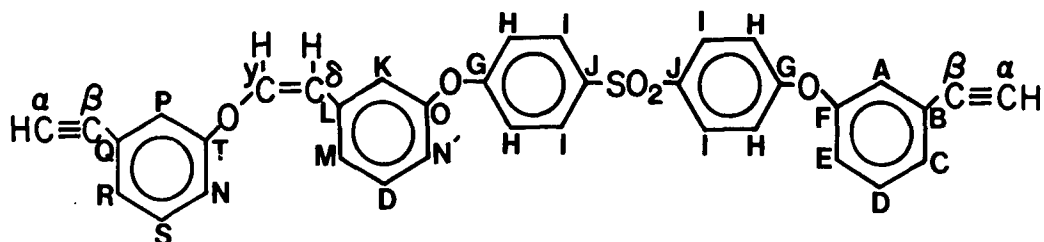
TABLE 2
 C^{13} NMR ASSIGNMENTS* FOR
 4,4'-BIS-(3-ETHYNYLPHENOXY)-DIPHENYLSULFONE



	No of C Atoms	PPm		$J^{C^{13}H}$ Obs.	Intensity Ratio Obs.
		Calc'd	Obs.		
α			78.5	253	2.0
β			82.3	--	--
A	2.0	122.9	123.4	163	2.4
B	2.0	124.0	123.9	--	--
C	2.0	127.2	128.5	165	2.1
D	2.0	130.4	130.0	164	2.4
E	2.0	118.9	120.7	164	2.3
F	2.0	158.1	155.4	--	--
G	2.0	162.4	161.1	--	--
H	4.0	119.9	117.9	164	4.0
I	4.0	129.2	129.6	164	4.0
J	2.0	136.5	135.7	--	--

* Assignments for C^{13} NMR spectra were made on the basis of additivity rules for substituted benzenes (References 22 and 23).

TABLE 3
 C^{13} NMR ASSIGNMENTS* FOR THE
 MONOVINYL ETHER OF ATS



	No of C Atoms	PPm		$J^{C^{13}H}$ Obs.	Intensity RATIO Obs.
		Calc'd	Obs.		
			78.1	253	0.8
α	2.0	78.3	78.5	253	1.2
β	2.0	82.5	82.5	--	--
Y	1.0	147.9	142.2	185	0.9
δ	1.0	94.6	110.1	156	1.0
A	1.0	122.9	123.7	160	1.0
B	1.0	124.0	122.6	--	--
C	1.0	127.2	127.5	165	1.1
D	2.0	130.4	130.3	164	2.4
E	1.0	118.9	120.3	164	0.9
F	1.0	158.1	155.0	--	--
G	1.0	162.4	162.1	--	--
H	4.0	119.9	117.8	166	3.5
I	4.0	129.2	129.9	164	5.5
J	2.0	136.5	135.3	--	--
K	1.0	117.1	118.7	169	1.3
L	1.0	139.5	137.0	--	--
M	1.0	121.4	121.0	164	1.2
N	1.0	118.6	118.1	166	1.0
N'	1.0	116.8	118.7	166	1.0
O		157.9	161.4	--	--
P	1.0	120.8	120.5	164	1.1
Q		123.1	124.2	--	--
R	1.0	126.5	125.6	169	1.0
S	1.0	129.6	128.8	165	1.0
T	1.0	156.7	161.4	--	--

* Assignments for the C^{13} NMR spectra were made on the basis of additivity rules for substituted benzenes (References 22 and 23).

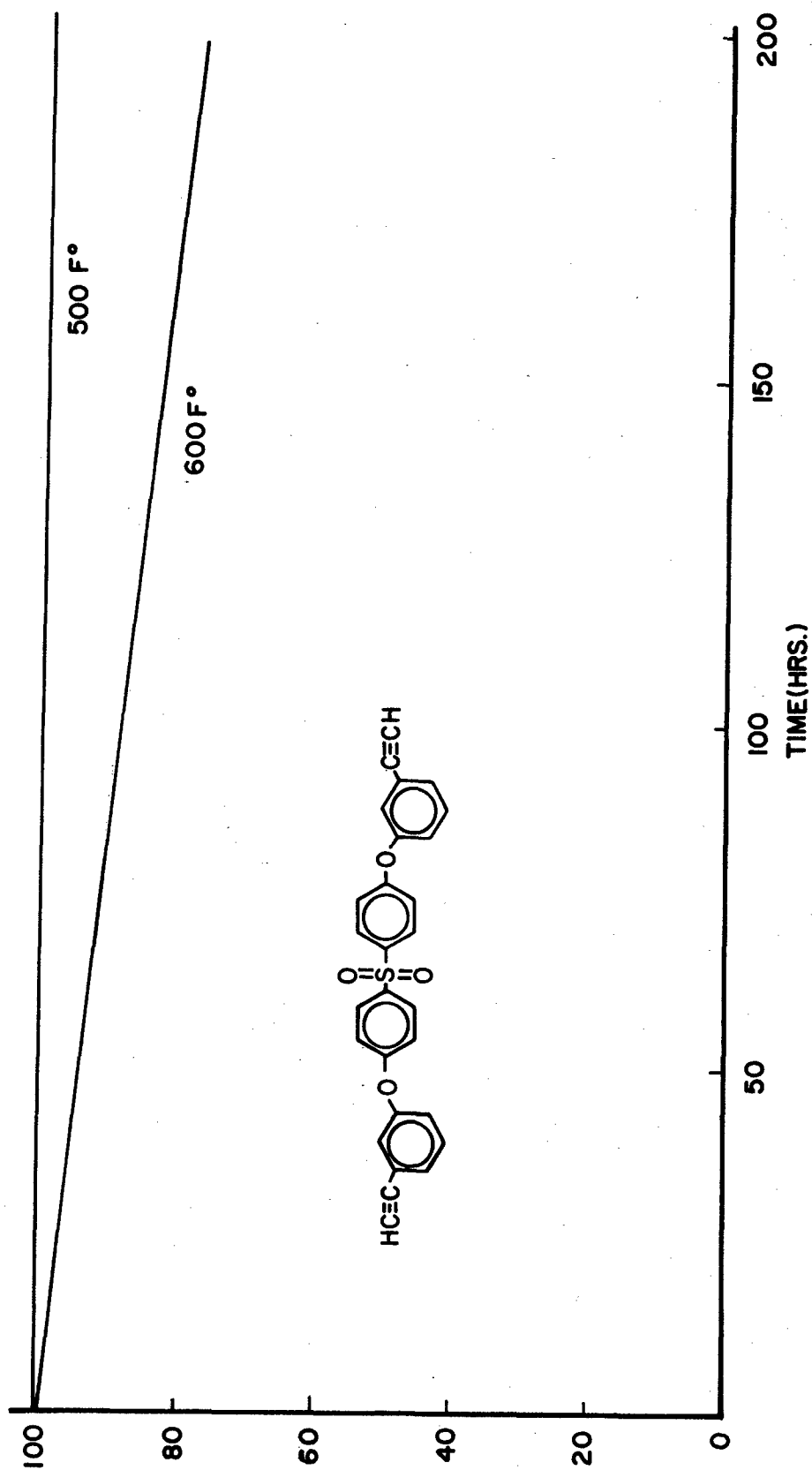


Figure 1. Isothermal Aging in Air at 500°F and 600°F of Cured ATS

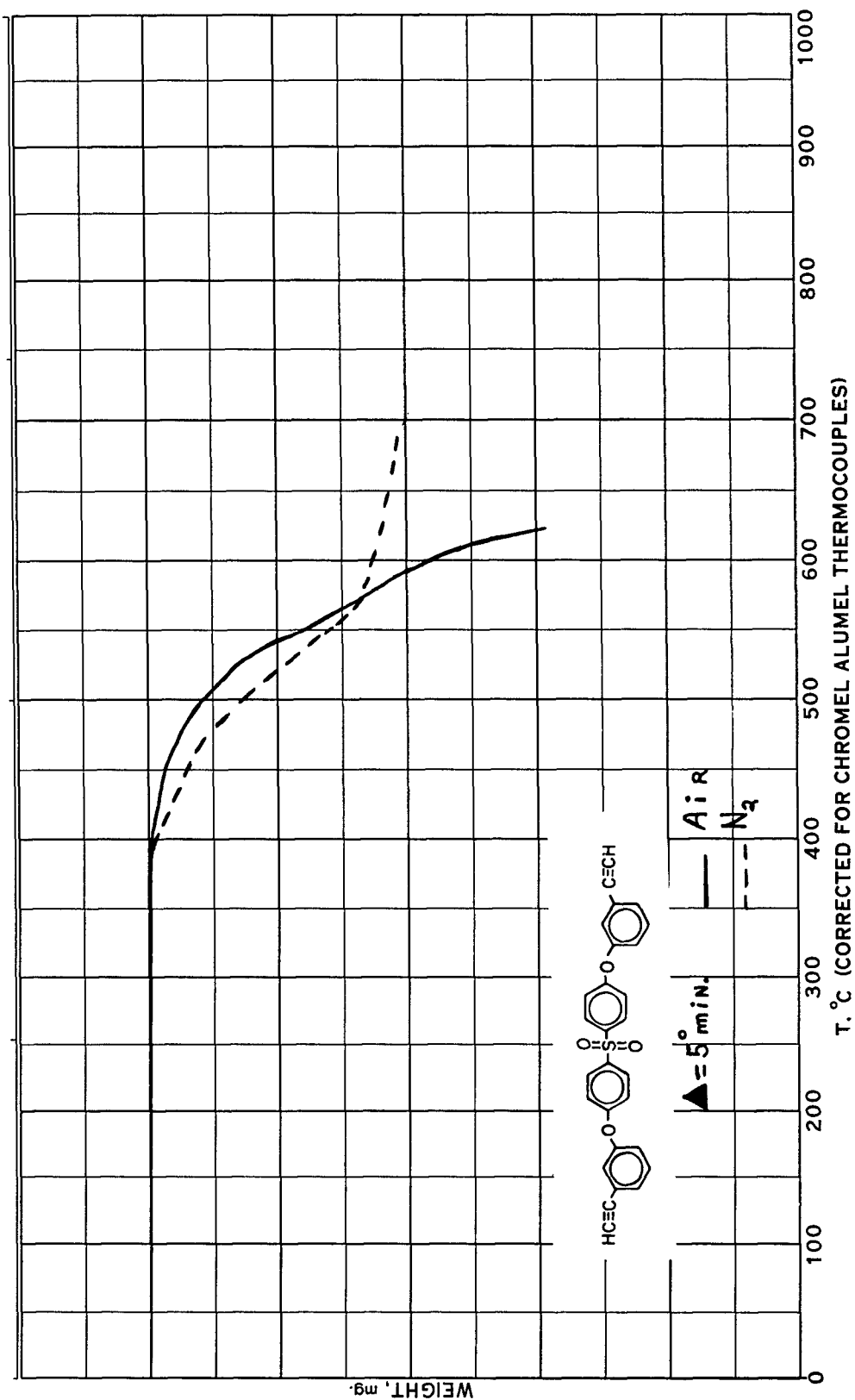


Figure 2. Thermogravimetric Analysis of Cured ATS in Nitrogen and Air

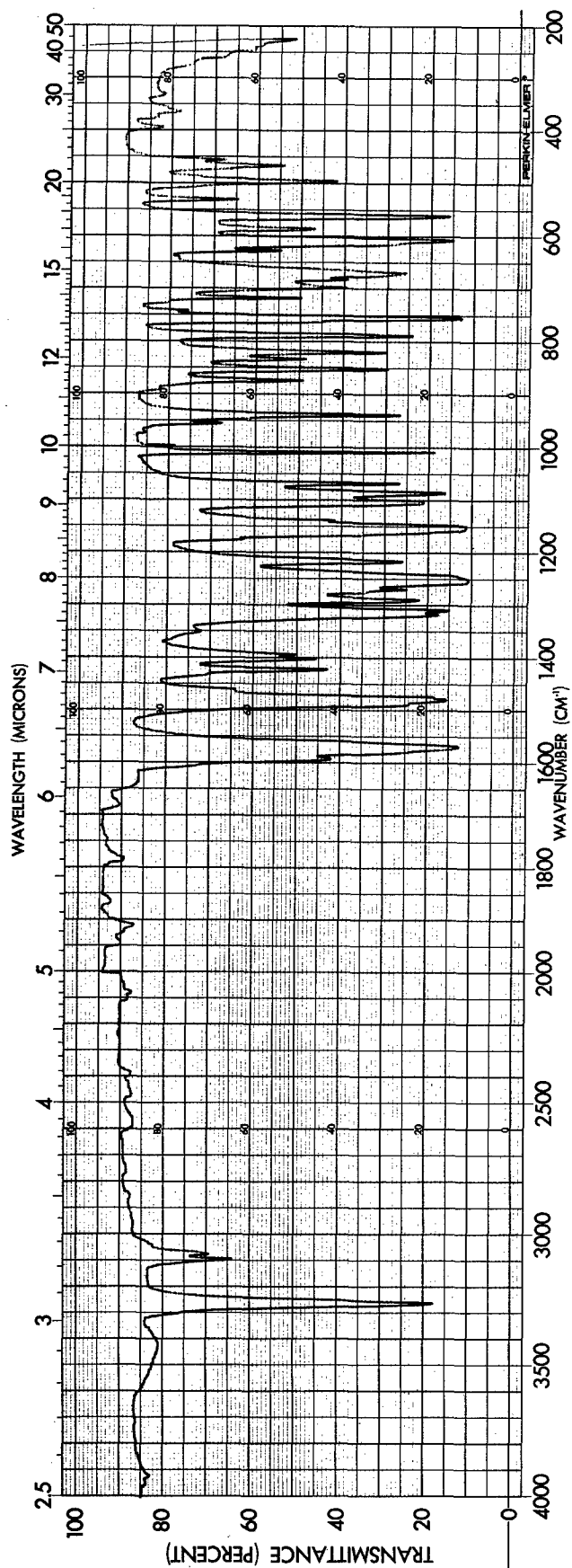


Figure 3. Infrared Spectrum of 4-Chloro-4'-(3-Ethynyl)-Phenoxy Diphenylsulfone

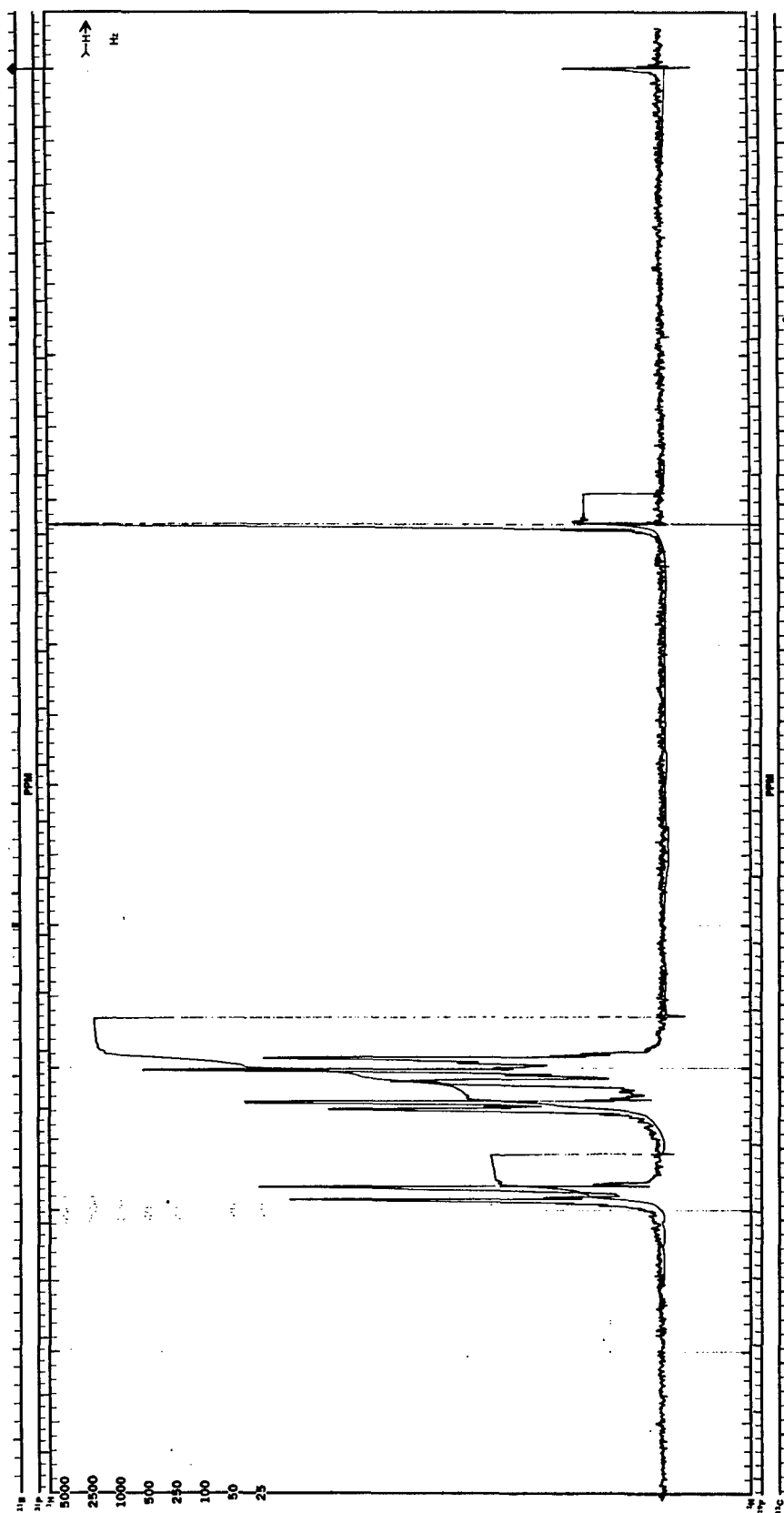


Figure 4. Proton NMR Spectrum of 4,4'-Bis (3-Ethynylphenoxy)-Diphenylsulfone (ATS)

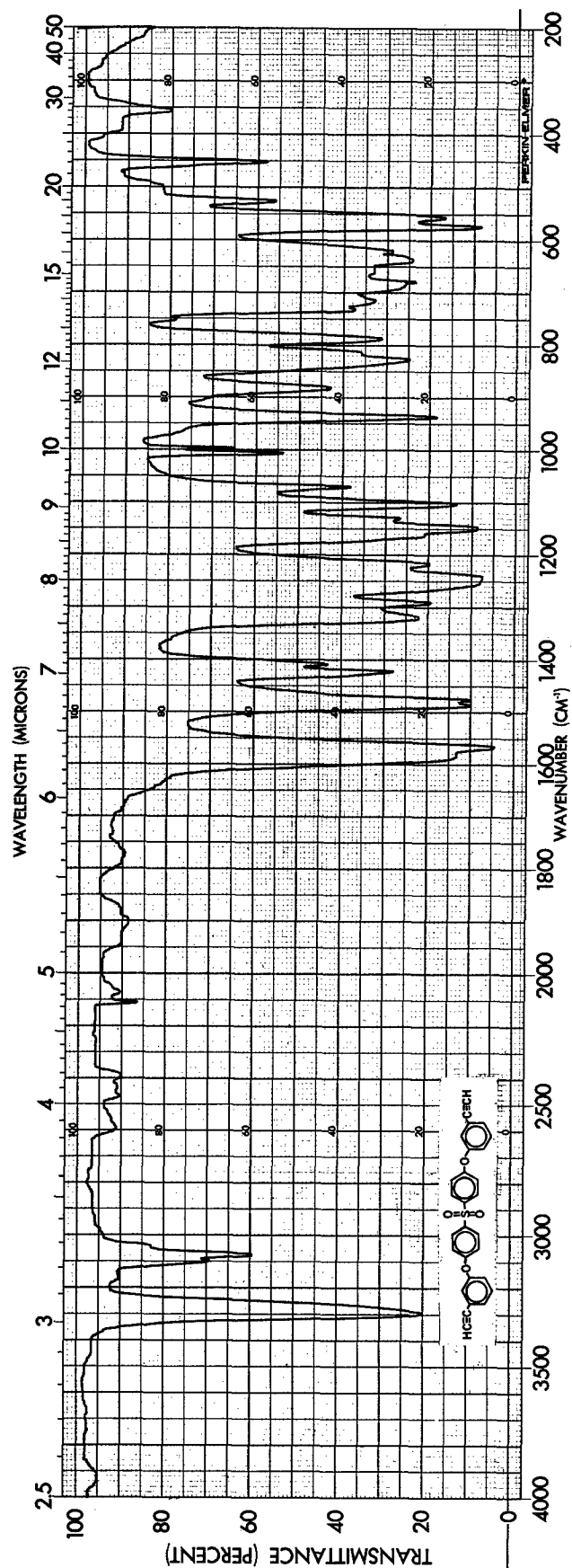


Figure 5. Infrared Spectrum of 4,4'-Bis (3-Ethynylphenoxy)-Diphenylsulfone (ATS)

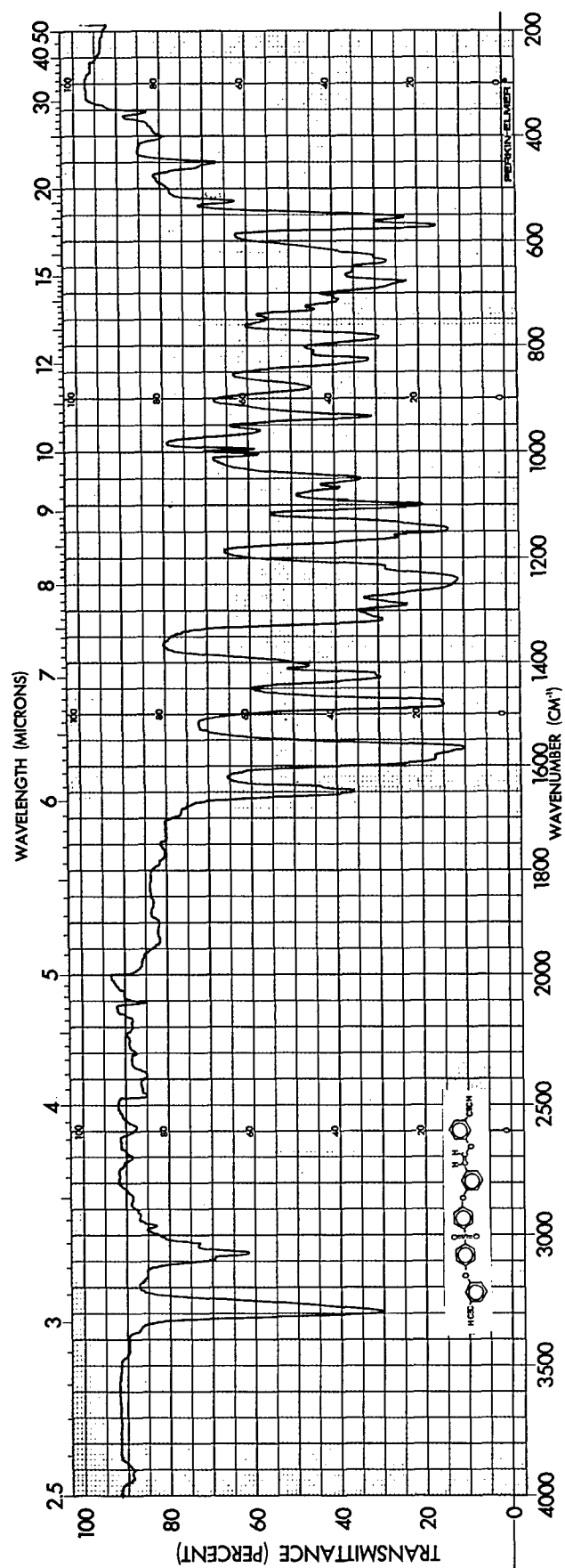


Figure 6. Infrared Spectrum of the Monovinylether of ATS

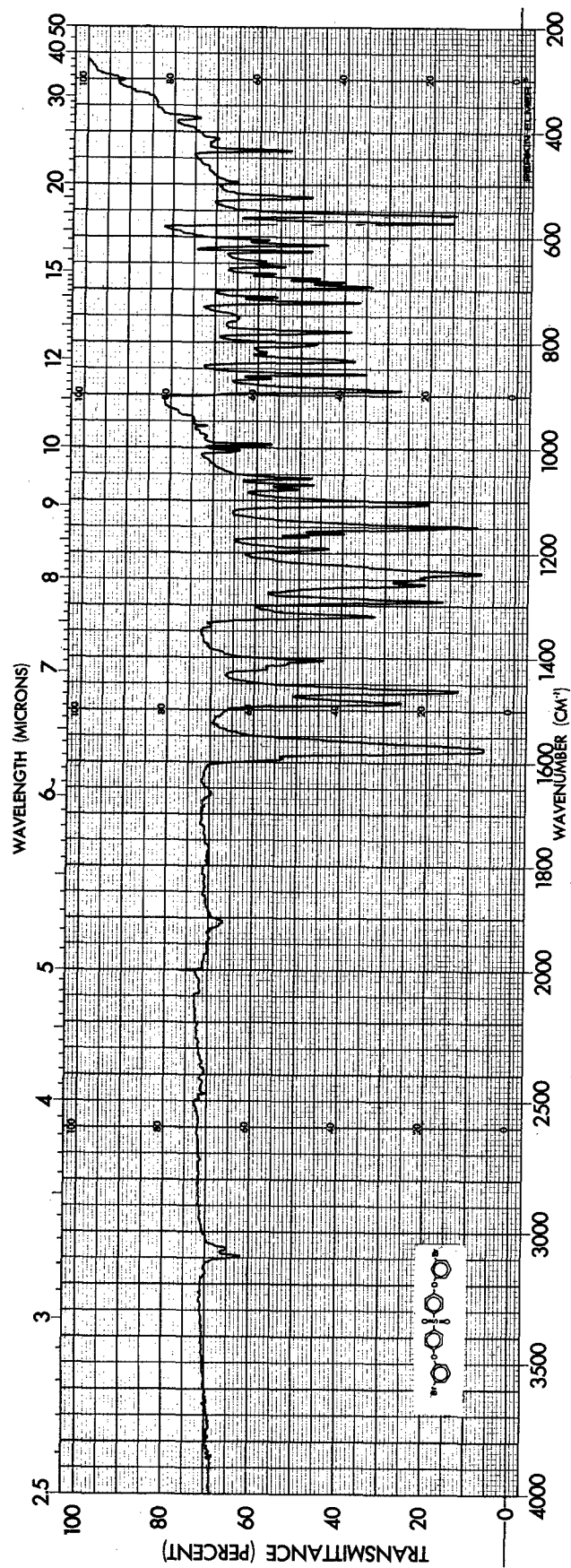


Figure 7. Infrared Spectrum of 4,4'-Bis (3-Bromophenoxy)-Diphenylsulfone

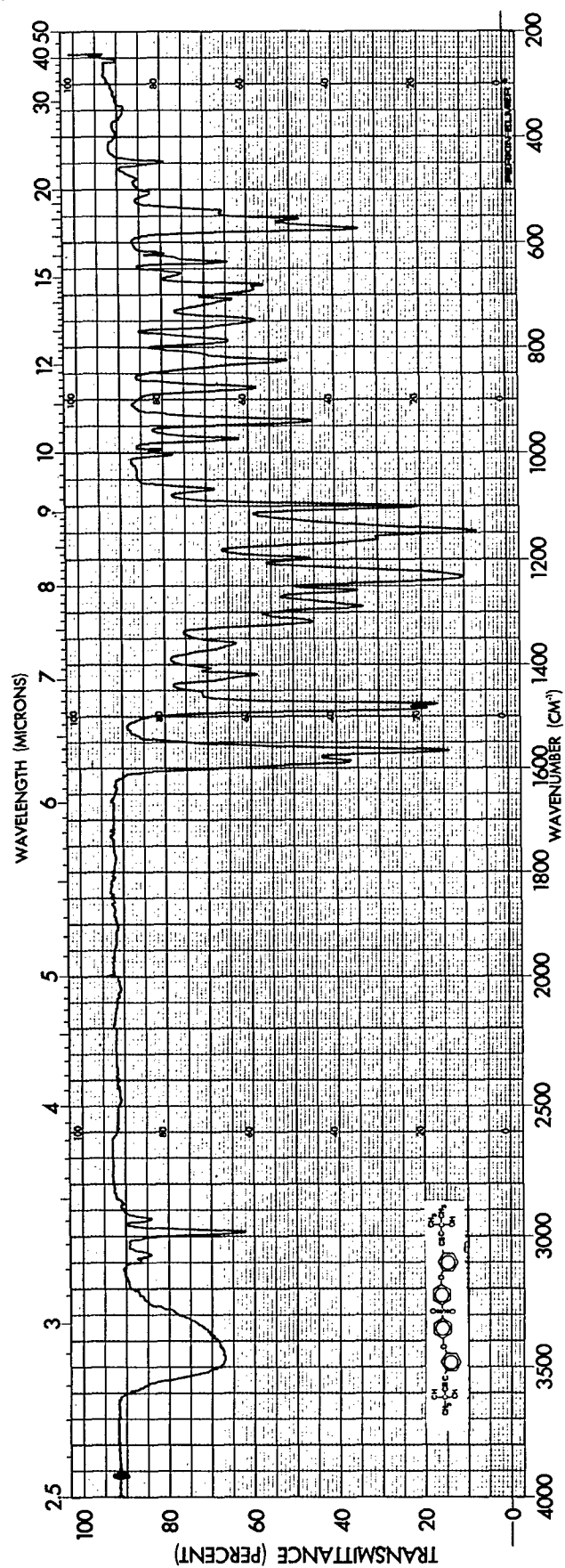


Figure 8. Infrared Spectrum of 4,4'-Bis 3-(3-Methyl-3-Hydroxy-1-Butynylphenoxy) Diphenyl sulfone