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POLYPHENYLENESULFONES BY FRIEDEL-CRAFTS TYPE POLYCONDENSATIONS

GERHARD F. L. EHLERS
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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 July to September 1959, January to July 1964 and July to August 1965.

The authors wish to thank J. L. Burkett, University of Dayton Research Institute, Dayton, Ohio who carried out part of the experimental work. Analyses were performed by the Analytical Branch or its contractors.

This manuscript was released by the authors, March 1966 for publication as an RTD Technical Report.

This report has been reviewed and is approved.



W. E. GIBBS
Chief, Polymer Branch
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ABSTRACT

Homocondensation of benzenesulfonylchloride and cocondensation of aromatic disulfonylchlorides with diphenyl, diphenylether and diphenylcarbonate under Friedel-Crafts conditions resulted in polymers with inherent viscosities up to 0.11 and molecular weights probably in the range of 3000-4000.

The polymers are low melting, tan to black powders, soluble in dimethylformamide and tetrahydrofuran. TGA indicates a wide molecular weight distribution. The sulfur content is lower than expected for a 1:1 copolymer; under the reaction conditions used, homocondensation of the aromatic hydrocarbon component could have occurred, according to a cationic oxidative mechanism. It is also possible (and known) that the aromatic disulfonylchlorides, under pyrolysis conditions, condense with evolution of sulfur dioxide and hydrogen chloride. At least 50 percent of the sulfur content of the polymers is present in the form of pending sulfonylchloride (in one case: sulfonic acid) groups. A typical structure of the polymers synthesized is:

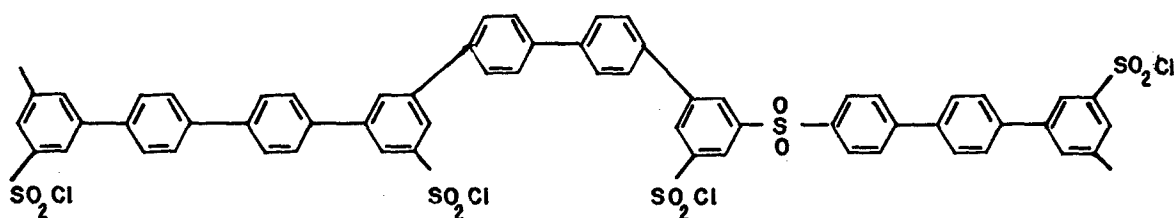


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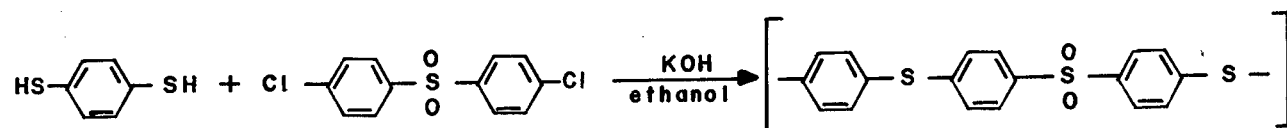
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SECTION I

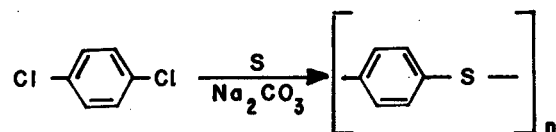
INTRODUCTION

The favorable thermal stability of compounds and polymers containing the diphenylsulfone moiety (such as epoxy compounds being cured with diaminodiphenylsulfone) was the reason to study the synthesis of purely aromatic polymers containing the sulfone linkage.

At the time of the initiation of this program, little related work had been done. Aliphatic or partially aliphatic polysulfones had been made by reacting sulfur dioxide with olefins, or by oxidation of polysulfides. The only aromatic polysulfone described was actually a polysulfide-sulfone and has been prepared by Kreuchunas (Reference 1). He reacted benzenedithiol with p, p'-dichlorodiphenylsulfone in the presence of alkali:

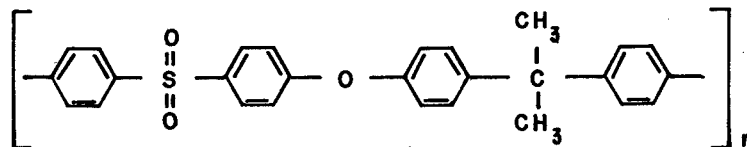


Polymers with 50 to 500 repeating units have been described in this case. Another approach under consideration to this polymer or a pure polyphenylenesulfone was the oxidation of polyphenylenesulfides, which had been obtained through the Macallum process (References 2-6), a heterogeneous reaction between aromatic dihalides, sulfur and sodium carbonate:



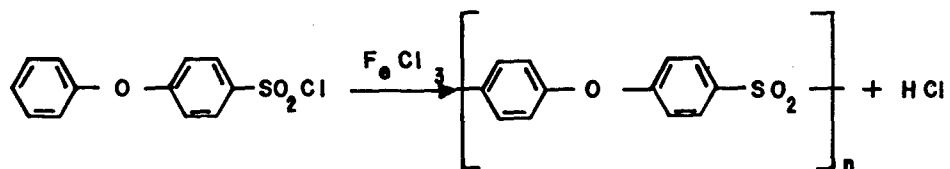
Polymers with a DP of 15 to 170 have been reported. The synthesis of polyphenylenesulfide has subsequently been explored under Air Force Contract (References 7 and 8).

For our own studies, it was decided to use a Friedel-Crafts type approach, forming the sulfone linkage during the condensation reaction. Work on this project had to be interrupted several times because of lack of manpower. In the meantime, additional work on aromatic polysulfones had been published. A class of high molecular weight polymers, with part of its linkages being $-\text{SO}_2-$, became commercially available (Union Carbides "Polysulfone"), for example:



Very recently (shortly before the completion of this work), the synthesis of polyarylenesulfones under Friedel-Crafts conditions was described (References 9 and 10). The authors report that the ferric chloride-catalyzed polycondensation of disulfonyl chlorides with reactive dinuclear aromatic compounds results in polymers which have reduced solution viscosities not greater

than 0.6. Details are presently not available. Another approach (Reference 10) consists of the self-condensation of dinuclear arylsulfonylchlorides:



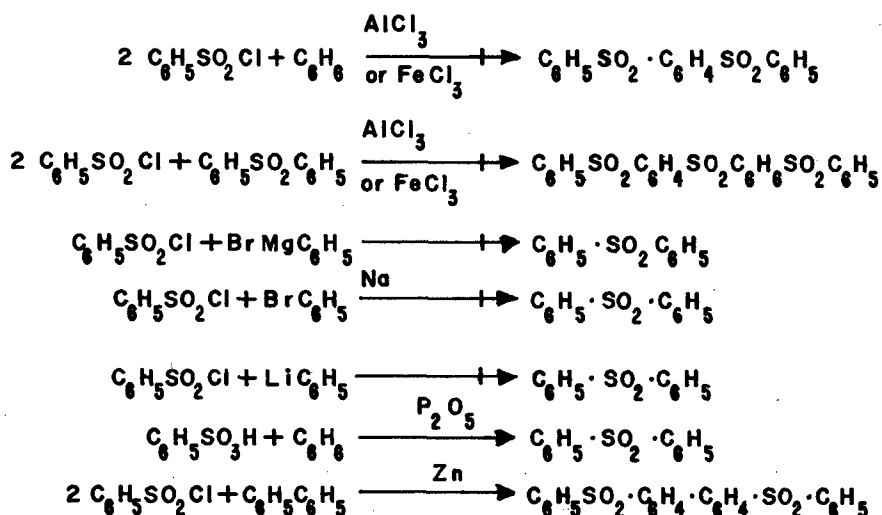
Polymers with reduced viscosities up to 2.0 have been prepared, according to the paper; this seems to be extremely high for a Friedel-Crafts type reaction. The polymers have been characterized by NMR and IR, however, no analysis data were given.

SECTION II

DISCUSSION

1. PROTOTYPE REACTIONS

The Friedel-Crafts approach to polyphenylsulfones was selected since it is the common procedure for the synthesis of the model compound diphenylsulfone. Benzenesulfonylchloride and benzene, in the presence of equivalent amounts of aluminum chloride or catalytic amounts of ferric chloride (Reference 11), form diphenylsulfone in 70-100 percent yield. This was confirmed in a number of experiments with the aim of forming diphenylsulfone and related structures as model compounds. Benzenesulfonylchloride and benzene were reacted with equivalent amounts of a number of Lewis acids, in melt and in solution. Highest yield of diphenylsulfone was obtained using ferric chloride in equivalent amounts in the melt. Other approaches to synthesize diphenylsulfone and related compounds were studied as indicated in the following scheme:



They were unsuccessful with the exception of the last two approaches.

2. POLYMERIZATION REACTIONS

From the preceding studies, it appeared feasible to prepare polyphenylenesulfones either by reacting a monosulfonylchloride, such as benzenesulfonylchloride, with itself or a disulfonylchloride with an aromatic hydrocarbon in the presence of aluminum chloride, ferric chloride or zinc. Another approach was the reaction of disulfonic acids with aromatic hydrocarbons in the presence of phosphorous pentoxide.

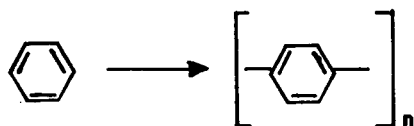
The polymerization reactions are summarized in Tables I and II. Homopolymerization of benzenesulfonylchloride in the presence of aluminum chloride, ferric chloride or zinc yielded only very small amounts of reaction products, which were not investigated further. Reactions of m-benzenedisulfonylchloride and 4, 4'-diphenyldisulfonylchloride with biphenyl, diphenyl-ether and diphenylcarbonate in the presence of ferric chloride and zinc yielded light brown to dark gray reaction products which could be separated into tetrahydrofuran-soluble and insoluble fractions. Inherent viscosities were low, and the sulfur content too low for the expected polymer structure. Reactions of the above disulfonylchlorides with biphenyl in the

presence of aluminum chloride and in various solvents gave again polymers with low inherent viscosities and sulfur content, however, some of the polymers were black in color. The reaction of 4, 4'-diphenylsulfonylchloride with biphenyl and diphenylether in the presence of phosphorus pentoxide gave essentially insoluble material in one case, and white, water soluble and insoluble products in the other case.

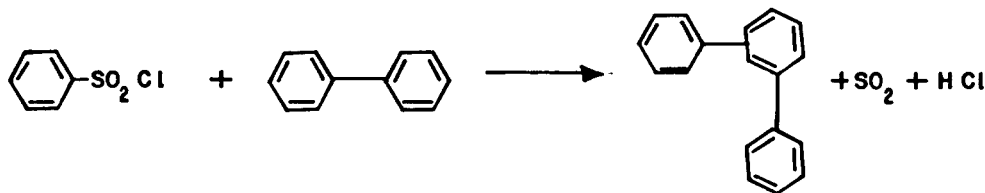
3. INTERPRETATION OF RESULTS AND CONCLUSIONS

A selected group of the polymers, namely Nos. 6, 11, 15 and 21, was investigated more thoroughly in order to obtain a better insight into structure and behavior of these polymers. In addition to complete analysis, they were subjected to alkali fusion, which converts only the pending $-\text{SO}_2\text{Cl}$ or $-\text{SO}_3\text{H}$ groups to $-\text{OH}$; molecular weight, IR, TGA, DTA and softening behavior have also been determined.

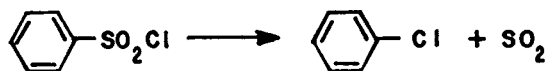
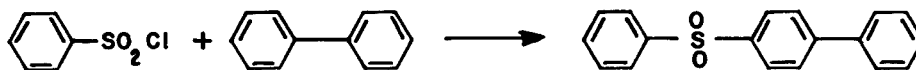
The analysis data indicate that the sulfur content is too low for a polymer with a 1:1 ratio of the two components. The recent literature provides a clue of what might have happened. Extensive work by Kovacic and coworkers (References 12-18 and others) shows that benzene and other aromatic hydrocarbons, in the presence of a Lewis acid and an oxidizing agent (FeCl_3 or $\text{AlCl}_3\text{-CuCl}$) form polyphenylenes:



It has also been found (Reference 19) that aromatic sulfonylchlorides or disulfonylchlorides under pyrolysis conditions, for example in boiling biphenyl, can react in the following manner:

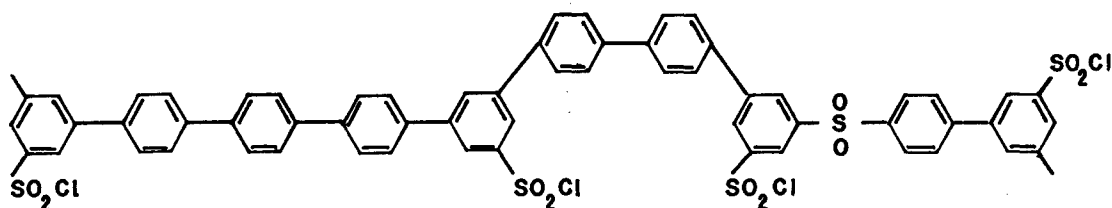


with side reactions such as



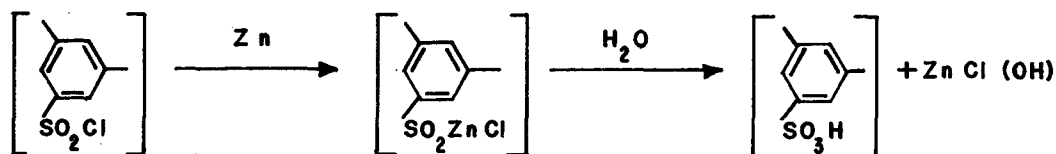
The side reactions are minimized when the solution is kept dilute in sulfonylchloride, and in the presence of copper and some other metal salts, while even trace amounts of aluminum and iron encourage the side reactions.

On the basis of the foregoing and the analyses, alkali fusion tests and the color of the polymers, average structures can be assigned as given in Table III. Following is a specific example for polymer 16:

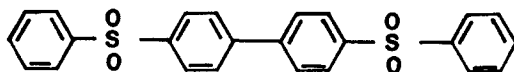


The polymers actually are mixed polyphenylene-polyphenylenesulfones, with pending $-\text{SO}_2\text{Cl}$, or in case of polymer 11, $-\text{SO}_3\text{H}$ groups. The color of the polymers (see Table III) becomes darker with increased aromaticity, that is, with decreased S-content.

It can be seen that Cl is practically absent in polymer 11. Since alkali fusion indicates that 50 percent or more of the sulfur is present in the form of pending groups, these must be sulfonic acid rather than sulfonyl chloride groups. Probably (with zinc as catalyst or co-reactant) a zinc salt of the sulfinic acid forms first, which is hydrolyzed during the work-up (washing with water):



The sulfonylchloride group itself is relatively stable against hydrolysis. The analysis of this polymer also suggests the presence of water bound to the sulfonic acid group, as it is the case with benzene sulfonic acid. IR-spectra of polymers 6, 11 and 15 (a good spectrum of polymer 21 could not be obtained) are identical, with the exception of an additional absorption for polymer 11 at 715 cm^{-1} , which probably is related to $-\text{SO}_3\text{H}$ (vs. $-\text{SO}_2\text{Cl}$ for the other polymers). Molecular weights seem to be rather low, although the TGA curves of polymers 6 and 21 suggest a wide molecular weight distribution. Cryoscopic molecular weight determinations in dimethylsulfoxide gave values of only 220; 212 for polymer 6, 161; 166 for polymer 21; these values, which would suggest a molecule with about two benzene rings, are definitely much too low and probably caused by solvent association, possibly in connection with the pending, functional groups of the polymer. The model compound



was synthesized. It has a molecular weight of 434 and an inherent viscosity of 0.017 (in acetophenone), which fits nicely into our empirical plot of molecular weight versus inherent viscosities of "phenylene-R-" polymers and polyheterocyclics. According to this plot, our polymers would have molecular weights in the order of at least 3000 to 4000.

While the TGA curves of polymers 6 and 21 are similar, the one of polymer 11 is considerably different; it has a sharp breakdown and a low final weight residue. It seems feasible that the polymers with pending sulfonylchloride groups crosslink under evolution of hydrogen chloride and form a stable network, while the polymer with sulfonic acid groups, due to the lower reactivity of these groups, does not react further. Its softening range, however, is

somewhat higher than the one of the other two polymers. The following first order endotherms have been found when subjecting the samples to differential thermal analysis:

Polymer 6: 110; 101°C (repeated runs)

Polymer 11: 124; 127°C (repeated runs)

Polymer 21: 220; 228°C (repeated runs)

While the transitions of the first two polymers fall into the respective ranges and are believed to be crystalline melting points, the transition of polymer 21 is much higher. Since this polymer has the lowest S content, no -SO₂- linkages and highest aromaticity (black color) it seems to be reasonable to assume a melting point in this range; surprisingly, the softening curve is not in agreement with this result.

SECTION III

EXPERIMENTAL

MONOMERS

Benzenesulfonylchloride, m-benzenedisulfonylchloride and 4,4'-diphenyldisulfonylchloride have been prepared from the potassium salts of the corresponding acids with phosphorous-pentachloride.

EXAMPLE OF A MELT POLYMERIZATION

A mixture of 9 g. of m-benzenedisulfonylchloride and 5 g. of diphenyl were heated under nitrogen to 90°C, then 10.6 g. of anhydrous ferric chloride added. A vigorous hydrogen chloride evolution started immediately. The temperature was, in the course of several hours, increased to 180°C. The black, solid residue was ground and washed with diluted hydrochloric acid and with water. The light brown powder was separated into a THF soluble (A) and insoluble fraction (B).

A: 4.5 g.; melting range 135-140°C; η inh. (0.5 % in THF): 0.05. Analysis found: C, 65.4; H, 6.1; S, 11.3; Cl, 5.4.

B: 1.9 g.; not melting below 420°C; Analysis found: S, 7.6.

EXAMPLE OF A SOLUTION POLYMERIZATION

A solution of 2.78 g. (0.01 mole) of m-benzenedisulfonylchloride and 1.54 g. (0.01 mole) of biphenyl in 50 ml. of nitrobenzene was added dropwise to a solution of 2.85 g. (0.02 mole) of aluminum chloride in 50 ml. of nitrobenzene at 80°C. The solution turned dark during the addition and was heated to 180°C for 20 hours. The reaction mixture was filtered and the residue (5.2 g.) treated with diluted hydrochloric acid on a steam bath for 1 hour, washed with water and refluxed for 1 hour each in benzene and methanol, 1.2 g. of black powder. η inh. (0.3% in DMF): 0.06. Analysis found C, 57.7; H, 3.6; S, 9.3; Cl, 9.8; Ash, 1.4.

EXAMPLE OF AN ALKALI FUSION

Approximately 0.2 g. of polymer 15 was heated in a mixture of 3 g. of sodium hydroxide and 3 g. of potassium hydroxide to 215°C for 20 minutes. The melt was diluted in water, acidified, the precipitate filtered off and washed with hot and cold water. Yield approximately 0.1 g. Analysis found: S, 4.42; 4.53.

IR-SPECTRA

IR-spectra were obtained by use of a Perkin-Elmer Infracord recording spectrophotometer, using potassium bromide pellets.

THERMOGRAVIMETRIC ANALYSES

Thermogravimetric analyses were carried out on a modified Chevenard thermobalance under nitrogen at a heating rate of 150°C/hour.

SOFTENING CURVES

Softening curves were obtained in an experimental set. A compacted, powdered sample of the material in the sample holder having a 0.040 in (1 mm) depth and a diameter of 5/16 inch is

heated at a rate of 150°C/hour. A load of 1000 g is applied to a circular, 1/4 inch diameter stainless steel disk, which rests on the sample. Penetration of the load into the sample is plotted in temperature dependence.

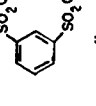
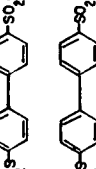
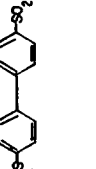
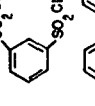
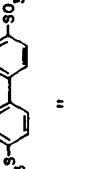
DIFFERENTIAL THERMAL ANALYSIS

Differential thermal analysis data have been obtained in an experimental unit, attached to an Aminco Thermobalance. The heating rate was 180°C/hour, the atmosphere nitrogen.

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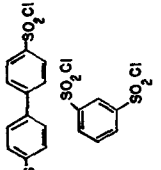
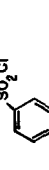
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TABLE I
SYNTHESIS AND PROPERTIES OF POLYPHENYLENESULFONES (GELT REACTIONS)

No.	Sulfonylchloride, g	Hydrocarbon, g	Catalyst g	Molar Relationship	Time hrs	Temp. °C	React. Prod. g	Color	Solubility	Melt Point °C	Analysis				η inh.
											C	H	S	Cl	
1		30	AlCl ₃	1:0.38	1/2	170	< 1	brown		100-125					
2	"	100	FeCl ₃	1:0.14	5	up to 170	7	dark brown							
3	"	30	"	1:0.3	"	"	< 1	light brown		145-160			20.3	17.0	
4	"	35	Zn	1:cat.	29	130	1.0 0.6			180-200 > 400					
5	"	35	Zn	1:cat.	29	180	~ 1.0 ~ 0.5			"					
6		9	FeCl ₃	1:1:2	3	up to 180	4.5 1.9	light brown	THF - sol. " insol.	135-140 > 420	65.4	6.1	11.3 7.6	5.4	0.05 (0.5% in THF)
7	"	9	"	1:1:2	5	up to 150	5.2 2.8	dark gray	THF - sol. " insol.	140-160 280->300			10.5 8.2		
8		7	"	1:1:2	5	up to* 180		brown							
9		7	FeCl ₃	1:1:2	4	220	2.5 2.5 1.5	benzene sol THF sol insol		170-190 part 225 > 450			10.1 8.9 8.1		0.04 (0.5% in benzene)
10	"	3.7	"	1:0.8:1.6	5	220*	0.3 2.0 0.7	benzene sol THF sol insol		70-90 > 125 > 450					
11		2.8	Zn	1:1:1	73 3	180* 300	1.4	light gray	insol.		53.0	3.3	14.1	0.4	0.11 (0.4% in DMF)
12		7.9	P ₂ O ₅	1:1:2	5	up to* 150		white water sol.					7.9		
13	"	7.9	"	1:1:2	5	up to 150		white water insol.					10.8		

* under N₂-blanket
Trial No. 11: 73% of calc. HCl titrated.

TABLE II
SYNTHESIS AND PROPERTIES OF POLYPHENYLENESULFONES (SOLUTION REACTIONS)

No.	Sulfonylchloride, 	g	Biphenyl g	AlCl ₃ g	Molar Relationship	Solvent	Time hrs.	Temp °C	React. Prod. g	Color	Analysis					η inh
											C	H	S	Cl	Ash	
14		1.70	0.76	1.53	1:1:2	Nitrobenzene	48	100	0.2	black	61.1	4.3	9.6		6.7	0.09 (0.3% in N-methylpyrrolidone)
15		5.51	3.06	5.39	1:1:2	Carbondisulfide		46		tan	58.4	3.4	12.5	10.9		0.07 (0.3% in N-methylpyrrolidone)
16	"	5.53	3.06	5.29	1:1:2	Ligroin	24	60-90		tan						0.10 (0.3% in N-methylpyrrolidone)
17	"	5.50	3.09	3.09	1:1:1.2	Nitrobenzene	18	125*		black	61.8	3.5	8.6			0.11 (0.3% in DMF)
18	"	2.75	1.55	2.90	1:1:2	"	22	80-130	1.0	black	59.3	3.1	7.7	10.3	0.9	0.07 (0.4% in DMF)
19	"	2.76	1.55	5.86	1:1:4	"	18	130	1.0	black						0.07 (0.3% in DMF)
20	"	2.78	1.54	2.85	1:1:2	"	20	180	1.2	black	57.7	3.6	9.3	9.8	1.4	0.06 (0.3% in DMF)
21	"	11.02	6.17	11.85	1:1:2	"	24	115	16.9	black	59.9	3.4	7.4	12.7**		0.06 (0.3% in DMF)

* H₂S given off during reaction** O₂:12.7%; Al: 0.1%

TABLE III
STRUCTURE OF SEVERAL POLYPHENYLENESULFONES

No.	Color	S present in pending group as determined from		1 -SO ₂ - linkage every-----rings	1 -SO ₂ Cl- group every-----rings	1 -SO ₃ H- group every-----rings
		Alkali Fusion	Analysis			
6	dark tan	54% or more	50	6	6	--
11	light gray	54% or more	50	3 1/3	--	3 1/3
15	light tan	64% or more	80	10	2 1/2	--
21	black	59% or more	100	--	2 1/2	--

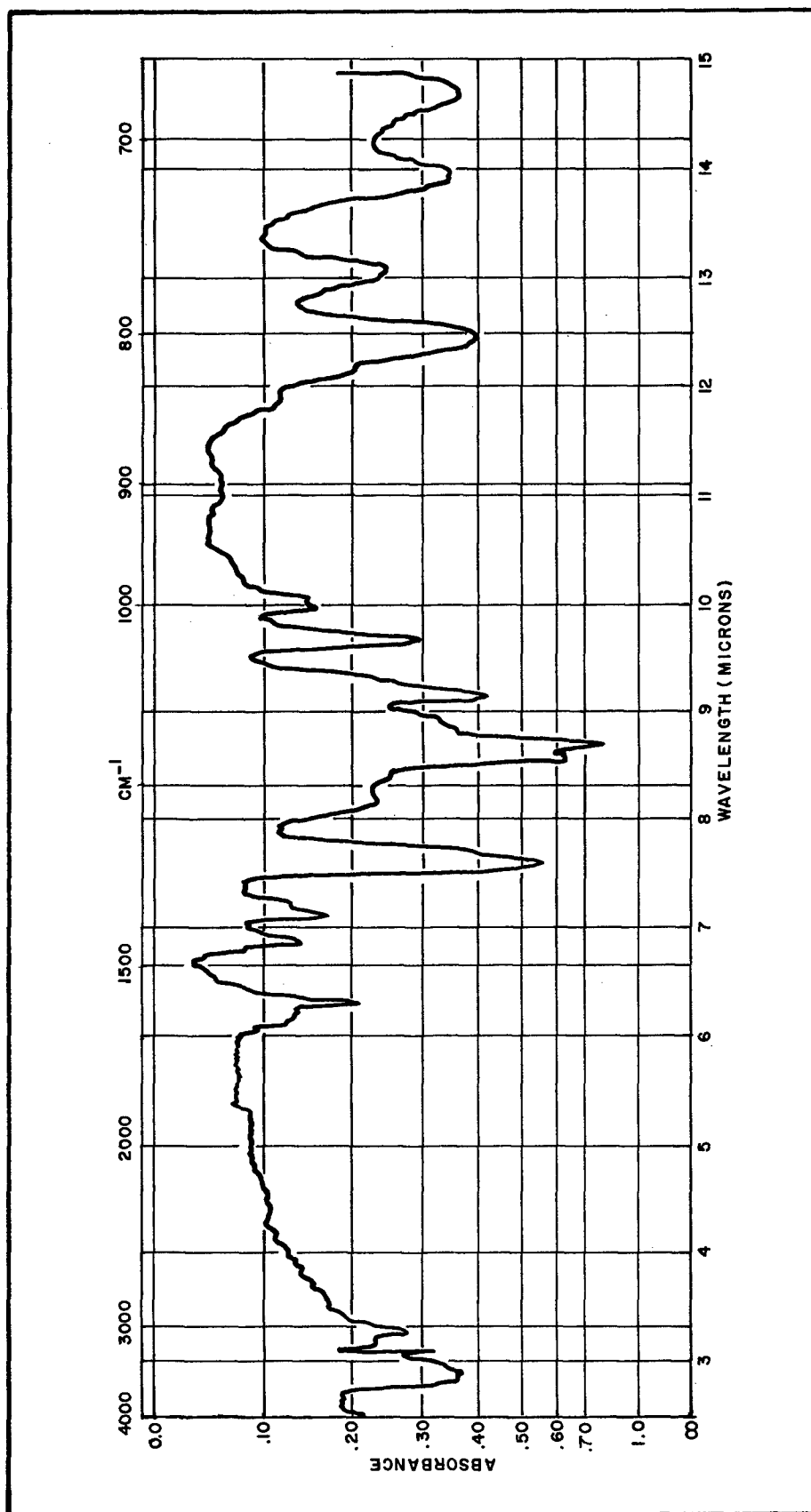


FIGURE 1 IR-Spectrum of Polymer 11

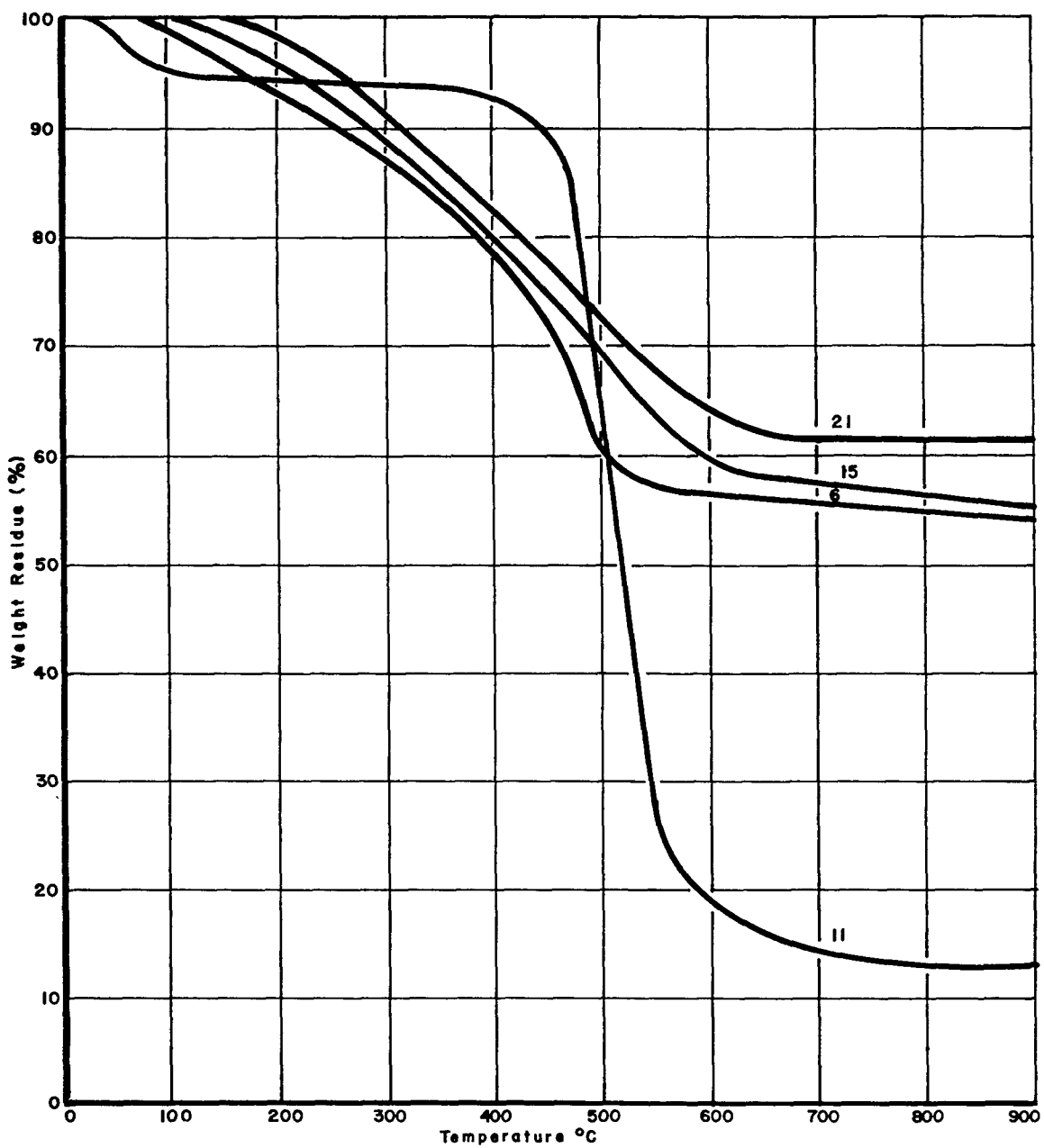


FIGURE 2 Thermogravimetric Analysis (ΔT 150° C/hr., N_2) of Polymers 6, 11, 15 and 21.

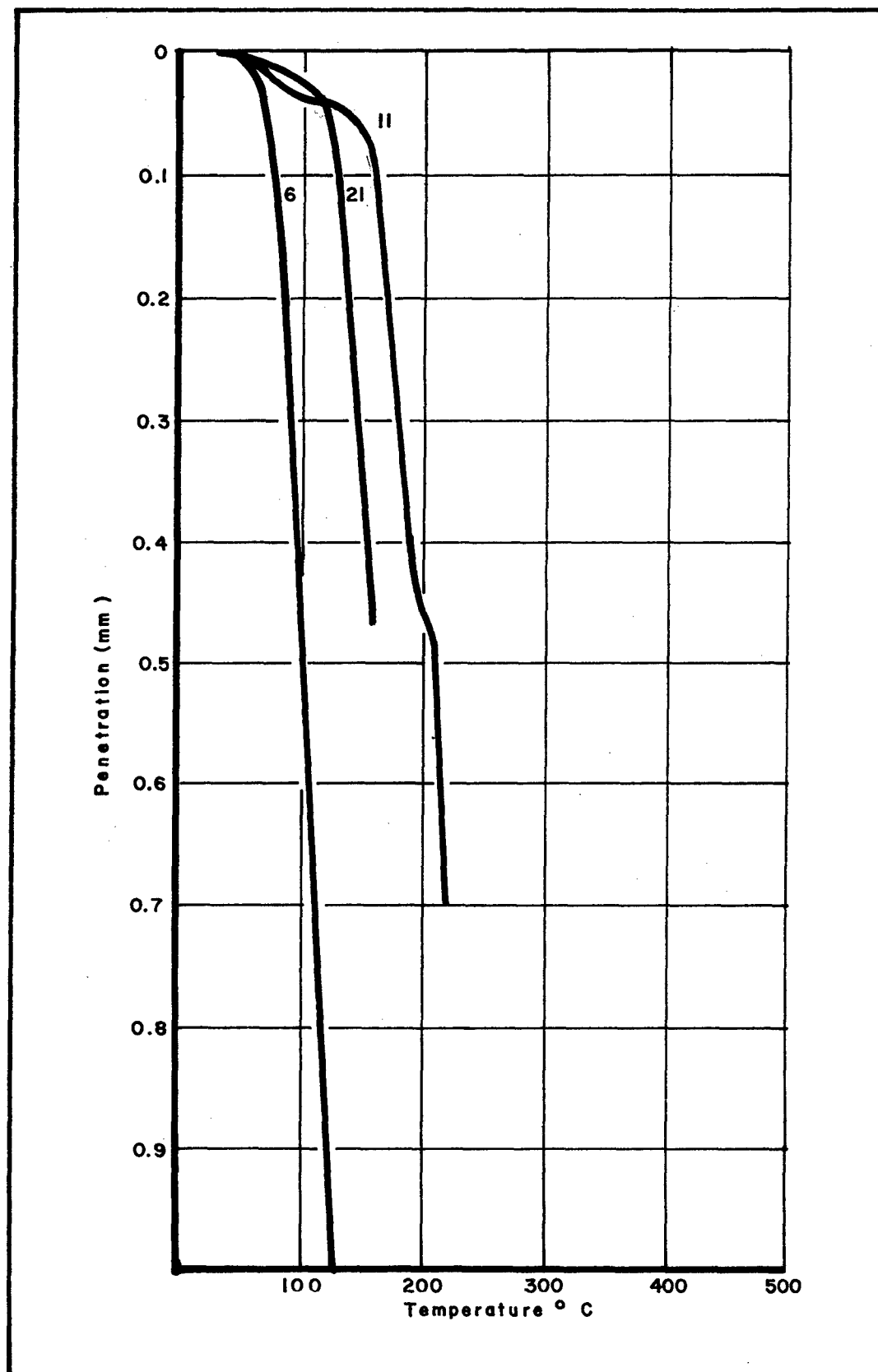


FIGURE 3 Softening Curves of Polymers 6, 11 and 21.

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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 Homocondensation of benzenesulfonylchloride and cocondensation of aromatic disulfonylchlorides with diphenyl, diphenylether and diphenylcarbonate under Friedel-Crafts conditions resulted in polymers with inherent viscosities up to 0.11 and molecular weights probably in the range of 3000-4000. The polymers are low melting, tan to black powders, soluble in dimethylformamide and tetrahydrofuran. TGA indicates a wide molecular weight distribution. The sulfur content is lower than expected for a 1:1 copolymer; under the reaction conditions used, homocondensation of the aromatic hydrocarbon component could have occurred, according to a cationic oxidative mechanism. It is also possible (and known) that the aromatic disulfonylchlorides, under pyrolysis conditions, condense with evolution of sulfur dioxide and hydrogen chloride. At least 50 percent of the sulfur content of the polymers is present in the form of pending sulfonylchloride (in one case: sulfonic acid) groups. The polymers can be considered as copolyphenylenes-polyphenylene sulfones with pending sulfonylchloride groups.		

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Polymers						
Polyphenylenesulfones						
Friedel-Crafts Reaction						
Thermal Stability						

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