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Chemistry of the Cure of Poly(*p*-phenylene sulfide)

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ABSTRACT: The cure in air of poly(*p*-phenylene sulfide) has been studied. A new synthesis of low molecular weight oligomers thereof has been developed to provide model compounds $C_6H_5S(C_6H_4S)_nC_6H_5$, wherein n averages 6–8. Thus, thermolysis of *p*- as well as m-$C_6H_5SC_6H_4SC_6H_5$ provides oligomers with complete retention of catenation. Oligomers with mixed meta and para linkages have also been prepared. Curing of the oligomers has also been investigated. The simultaneous reactions for cure of polymers or oligomers include: (1) chain extension; (2) oxidative cross-linking; (3) thermal cross-linking; and (4) oxygen uptake followed by loss of SO_2. During the course of this study, the thermal disproportionation of aryl phenyl sulfides has been established.

Several studies have been published on thermal behavior, oxidative degradation, stability, aging, etc., of poly(phenylene sulfide) (PPS).[1-9] Much less has appeared concerning mechanisms of curing.[4,5,7-9] Poly(*p*-phenylene sulfide) is customarily cured in the air: at 260 °C for molding precure, and at 371 °C for coatings. The otherwise moderate mechanical properties of poly(*p*-phenylene sulfide) may be upgraded significantly this way. Studies of thermal behavior of poly(*p*-phenylene sulfide) in air or inert atmospheres are of chief interest to the present work. In addition, studies of high-temperature reactions of simpler model compounds as well as aryl sulfides, especially oxidative and free-radical reactions, should increase insight into the complex changes during cure.

Smith and Handlovits studied the use of chemical agents to cross-link PPS.[4] They also cited evidence for thiyl and aryl free radicals generated by thermal treatment of PPS with attendant cross-linking and biphenyl-type coupling. Black and co-workers[5] concluded that "the mechanism of aging appears to involve a combination of cross-linking, chain scission, and oxidation reactions". They noted evidence for further polymerization, loss of H as well as S, and uptake of O during a three-stage aging process. These workers postulated four types of reactions: cross-linking by loss of H and formation of C–S links, evolution of lighter S compounds such as phenyl sulfide, oxidation of S to sulfoxides and sulfones (although none were sought), and oxidative attack on the benzene rings. Ehlers and co-workers[7] reported evidence for homolysis of C–S bonds and abstraction of H, yielding free radicals for further reactions such as cross-linking and recombination. They also observed lower molecular weight dimeric and trimeric chain fragments along with other S compounds as volatile condensate. Hill and co-workers[8,9] commented on the complexity of curing reactions and postulated a chain-extension reaction wherein lower molecular weight members could be volatilized by scission of a chain near the end. In addition, they also suggested oxidative coupling of aromatic rings, and ionic reactions at S or benzene rings.

Smith and Handlovits[4] reported one of the few studies[10] of model compounds such as 1,4-bis(phenylthio)benzene. When this was heated for 24 h under Ar, volatile products were found to be benzene, thiophenol, phenyl sulfide, phenyl disulfide, and biphenyl. No residue was mentioned or characterized. The results were interpreted to be consonant with results obtained from PPS.

Studies of the thermal and oxidative behavior of simple aryl sulfides and related substances have been reported.[11-14] Bateman and Cunneen[15] discussed the direct, uncatalyzed interaction of sulfides and molecular oxygen and concluded that, at least at moderate temperatures, aryl sulfides such as phenyl sulfide were inert. Singlet oxygen has been reported to interact efficiently with organic sulfides[16] but the excited state of O cannot be implicated in this study. Finally, generation of thiyl radicals by thermolysis of sulfides,[4,6,7] disulfides,[17,18] and mercaptans[19] is established.

The evolution of SO_2 from sulfoxides and sulfones has been investigated. Levy and Ambrose studied the gas-phase decomposition of phenyl sulfoxide, phenyl sulfone, and phenyl sulfide and concluded that they showed increasing stability in that order.[11] Benzene and high molecular weight polymers were observed as decomposition products. In addition, the sulfoxide yielded sulfur dioxide and phenyl sulfide; the sulfone yielded sulfur dioxide; and the sulfide yielded hydrogen, hydrogen sulfide, and dibenzothiophene. Ehlers and co-workers observed sulfur dioxide as one of the decomposition products from a polysul-

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fone[7] and so did Dashevskaya et al.,[20] in amounts said to be "significant". This appears to be a general observation, especially with aliphatic sulfones.

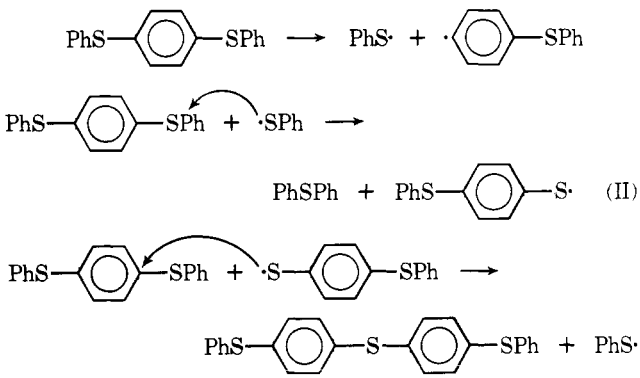
Oligomerization Reaction

Para Oligomers. A new oligomerization reaction has been developed which yields low molecular weight oligomers of PPS with only phenyl end groups. In accordance with the general formula, $C_6H_5S(C_6H_4S)_nC_6H_5$ (I), this oligomerization occurs when starting materials with n greater than 0 are heated to about 370 °C. Phenyl sulfide, I (n = 0), is evolved in substantial quantities and the chain length increases. Benzene-insoluble oligomers are obtained with n averaging 6–8. See eq I.

$$2PhSC_6H_4SPh \rightarrow PhS(C_6H_4S)_2Ph + PhSPh$$

$$PhS(C_6H_4S)_mPh + PhSC_6H_4SPh \rightarrow PhS(C_6H_4S)_{m+1}Ph + PhSPh \quad (I)$$

The reaction is observed to proceed at reasonable rates at 300–395 °C and to be promoted by air. Under nitrogen it is generally slower and the yields of oligomer are smaller. The reaction is promoted by phenyl disulfide and almost totally inhibited by a free-radical trap such as 2,6-di(*tert*-butyl)-4-methylphenol; it appears to be free radical in nature. A mechanism has been proposed involving homolytic scission of C–S bonds to provide thiyl and aryl free radicals, followed by thiyl radical attack on C, displacing another thiyl radical. The thiyl radicals are proposed to attack C of end groups and repeat units alternately as in eq



II. The mechanism suggests a dynamic equilibrium with para yielding only para catenation, as is observed. In view of the high temperature of the reaction, the observed retention of catenation is noteworthy.

The reaction is remarkably clean, side products are minimal, and its course can be monitored readily by infrared and gas chromatographic techniques. It does yield a series of closely related homologues, however; separation and characterization of these can pose problems especially as n increases.

Details are given for several oligomerizations in the Experimental Section, including representative analytical data in Table II to show the spectrum of products obtained from the oligomerization reaction, plus certain additives in Table III, as well as other starting materials in Table IV.

With starting material I (n = 2), the same reaction was observed, thus demonstrating the general nature of the reaction. Oligomers obtained from I (n = 2) were indistinguishable from those from I (n = 1).

Oligomers Other Than Para. When the oligomerization reaction was applied to 1,3-bis(phenylthio)benzene similar results were obtained. In this case, the oligomers proved to be too soluble to separate by means of benzene extraction. The ethanol solvent used probably removed a smaller fraction of lower molecular weight oligomers, compared to benzene. It is instructive to note that, in the infrared spectra of the oligomers, there was no evidence for disubstitution other than meta. This suggests that there had been no scrambling of linkage patterns on benzene rings during the oligomerization reaction. This lack of scrambling virtually excludes the possibility of a benzyne mechanism during the oligomerization.

Oligomers with mixed meta and para linkages were obtained when the oligomerization conditions were applied to a mixture of 1,3- and 1,4-bis(phenylthio)benzenes.

When the oligomerization conditions were applied to 1,2-bis(phenylthio)benzene, thianthrene and phenyl sulfide were obtained in high yields, a result not surprising in view of the favorable juxtaposition of the S functions on the benzene ring and the driving force toward ring closure with its attendant stability.

When the oligomerization conditions were applied to a mixture of 1,2- and 1,4-bis(phenylthio)benzene, in an effort to intercept some reactive ortho species and provide oligomers with mixed ortho and para linkages, the ortho reacted to yield thianthrene and the para to yield para homo-oligomer.

Disproportionations of Phenyl Sulfides. If the oligomerization reaction is considered to be disproportionation of phenyl sulfides, then one might predict it to be a special case of the more general reaction showing disproportionation of unsymmetrically substituted sulfides as in eq III.

$$2ArSC_6H_5 \rightarrow ArSAr + C_6H_5SC_6H_5 \quad (III)$$

Accordingly, phenyl-*p*-tolyl sulfide and 4-biphenylylphenyl sulfide were tested as model compounds. The data in Table I show typical results. When phenyl-*p*-tolyl sulfide was heated at about 280 °C under nitrogen, essentially no reaction was observed; with catalytic amounts of phenyl disulfide added, significant amounts of phenyl sulfide were produced. When 4-biphenylylphenyl sulfide was heated in nitrogen at about 360 °C, a large amount of phenyl sulfide was detected; indeed, the starting material and the two cross-products were present in ratios approaching 1:1:1. When 4-biphenylylphenyl sulfide was heated in air, even more phenyl sulfide was detected.

Cure of Oligomers

The oligomers (n averaging 6–8 for para, about 4 for meta) served as model compounds for PPS in curing studies inasmuch as they may be cured in air to tough, flexible films. While degrees of cure may vary, the conversion of a powder to a coherent film represents a convenient dividing line between noncure and cure. For purposes of this study, cure was judged in terms of formation of tough, flexible films rather than simply in terms of modest increases in molecular weight.

Sulfur dioxide was evolved from oligomer samples during cure, apparently concomitant with cross-linking. When samples of oligomer were heated in air at 400 °C, sulfur dioxide was detected continuously throughout a 2-h heating period in one experiment; in another, a total of 0.071% of the weight of the oligomer sample was evolved as sulfur dioxide during a 20-min reaction. Based upon the molecular weight of the sample, this would mean that one sulfide linkage in 764 was converted to sulfur dioxide in that time. In both experiments, other products were also detected. For example, from the first, I (n = 0, 1, and 2) was shown to be evolved, indicating that the oligomerization reaction must be proceeding during cure.

When samples of oligomers were heated under nitrogen at 400 °C, under the same conditions, sulfur dioxide was

Table I
Disproportionation of Phenyl Sulfides

	Conditions				Products by GC, wt %					
Starting material	Atm	H	°C	Added	PhSPh	PhSTol	PhSB	Tol_2S	B_2S	Recovery, %
PhSTol[a]	N_2	70	274–286		1		No reaction			95.5
	N_2	22	270–276	PhSSPh[c]	4	93		2		98.5
	N_2	26	305–311	PhSSPh[c]	12	73		15		97.4
PhSB[b]	Air	68	357–366		51		24		20	98.2
	N_2	68	357–368		33		32		35[d]	99.2

[a] Tol = p-tolyl. Starting material 98% pure; showed by GC 0.8% p-$ClC_6H_4CH_3$, 1.0% PhSPh. [b] B = 4-biphenylyl. Starting material 99% pure; showed by GC 1% 4-$BrC_6H_4C_6H_5$, no PhSPh. [c] Nominally 1%. [d] Isolated, purified to mp 169–171 °C, and identified. For bis(4-biphenylyl) sulfide lit.[29] mp 171–172 °C. This isolated sample showed the same gas chromatographic behavior as higher boiling members of the crude reaction product, but now 98% pure with about 2% 4-bromobiphenyl.

not evolved continuously nor was there cure to tough, flexible films. Slight increases in molecular weight were observed, as judged by the powdery appearance of the residues, and also by the fact that I (n = 0, 1, and 2) was detected in small amounts. The latter observation was taken as evidence that the oligomerization reaction was proceeding although virtually no cross-linking was occurring.

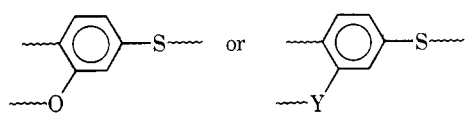
Samples of oligomers were subjected to conditions of increasing cure and the infrared spectra were compared. Many changes were noted, but the most obvious may be interpreted as follows: (1) loss of C_6H_5; (2) increase in aryl C–O; (3) loss of C–S; and (4) greater resemblance with increasing cure to spectra of PPS in comparable states of cure. In addition, there was no evidence for sulfoxide, sulfone, sulfinate, nor hydroxyl species. Apparent loss of phenyl absorption means relatively fewer end groups or substitution onto them. This is interpreted to mean chain extension (the oligomerization reaction proceeding) with lower members such as I (n = 1, 2, etc.) being evolved; or branching onto the phenyl end groups, perhaps oxidatively; or some combination of these. Increase in aryl C–O is demonstrated by uptake of oxygen by PPS during cure. The significant absorptions of 1238 cm^{-1} which increase with increasing cure are consonant with aryl ether absorption. Furthermore, these absorptions coincide with the advent of weak, albeit significant, absorption at 870, attributable to 1,2,4-trisubstitution. The apparent loss of C–S[21] would be consonant with the loss of sulfur dioxide, or alternatively oxidation of sulfide units to sulfoxide or sulfone. In view of the fact that none of these oxidized sulfur units was detected, however, this alternative is considered to be less likely. If any sulfoxide, sulfone, sulfinate, or sulfonic species are formed, they apparently do not survive to be detected.

Cure of Poly(p-phenylene sulfide)

Direct experimental evidence supporting the idea of chain extension during cure of PPS[8,9] was obtained by curing a sample of PPS in air and analyzing the heavier volatiles. In addition to other volatile substances, low molecular weight products represented by I (n = 0, 1, and 2) were detected in small amounts. Thus, PPS increases in molecular weight as lower molecular weight units are evolved during cure, whether end groups are C_6H_5 or substituted phenyl, by means of this reaction. That the volatiles were generated by the cure process, and not simply present in the PPS sample initially, was indicated by the failure to detect I (n = 0, 1, or 2) in a benzene extract of the same PPS.

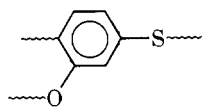
Direct oxygen analyses on a heavily cured sample of PPS were compared to those of the same PPS uncured. An increase of 0.90% O by weight was found. Correcting for typical weight losses during cure, one can calculate this level of oxidation to be sufficient for 1 cross-linking aryl ether linkage per 16 repeat units, more than enough to provide a tightly interlocked three-dimensional network.[5] From infrared data, the O must be present as aryl ether units rather than hydroxyl species or oxidized S units.

Samples of PPS, both cured and uncured, were examined by infrared. With vibrational mode assignments available for PPS,[22] changes in the spectra of samples caused by curing may be interpreted as follows: (1) increasing aryl C–O; (2) increasing 1,2,4-trisubstitution; (3) decreasing para substitution; (4) decreasing C–S; (5) no evidence for sulfoxide, sulfone, sulfinate, nor hydroxyl species; and (6) formation of units such as

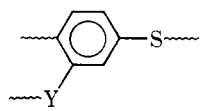


where Y is S or aryl. The uptake of what must be aryl ether O is underscored by increasing absorption at 1235 cm^{-1} and this could lead to 1,2,4-trisubstitution, but not all such units need come from O attack since free radicals such as aryl or thiyl could also lead to trisubstitution. Decrease in para absorption is consonant with conversion of 1,4-disubstituted units to 1,2,4-trisubstitution. Decreasing C–S is consonant with observed loss of SO_2. The alternative (oxidation to sulfoxide, sulfone, etc.) is considered less likely because of lack of evidence for hydroxyl, sulfinyl, or sulfonyl.

The simultaneous reactions observed with cured PPS may be summarized: (1) chain extension (oligomerization); (2) oxidative cross-linking forming units like



(3) thermal cross-linking forming units like



where Y may be aryl or S; and (4) oxygen uptake followed by loss of SO_2. However, more definitive mechanistic proposals, including the initial interaction of S and O, possible sources of SO_2, and the possible intermediacy and subsequent fate of oxygenated S species must await further experimental work.

Experimental Section

Infrared spectra were taken on Perkin-Elmer spectrophotometers, Models 137 and 257. In addition, a Digilab FTS-15 was used for high resolution spectra and, by computer manipulation, difference spectra. Oxygen analyses were obtained by neutron activa-

tion. Inherent viscosities were determined in chloronaphthalene (0.4 g per 100 ml) at 206 °C. Gel permeation chromatography results were obtained in 1,2,4-trichlorobenzene at 130 °C. Most gas chromatographic analyses were performed with a 5-ft SE-30 column (2.5%) programmed from 200 to 325 °C at 25 °C/min. The same column was used at lower temperatures, sometimes isothermally, for more volatile samples. Melting points were determined in capillaries in a Thomas-Hoover melting point apparatus. Proton magnetic spectra were taken on a Varian T-60 spectrometer.

The aryl phenyl sulfides used in this study were prepared from thiophenolates and aryl halides in high-boiling polar solvents[23] at atmospheric pressure or under pressure at elevated temperatures for less reactive halides. Reaction mixtures were poured into water and the organic phases separated. Crude products were then purified by crystallization or distillation. Sulfoxides and sulfones were obtained by oxidation of the corresponding sulfides with hydrogen peroxide in acetic acid solution, at or near room temperature with equivalent proportions of oxidant for the former, at reflux with excess oxidant for the latter. Melting points reported for sulfones are those of reaction products as obtained without further purification. Thiophenol from Aldrich Chemical Co. and 4-chlorophenyl sulfide from K&K Laboratories, Inc., were used as received. Phenyl sulfide and phenyl disulfide were used as obtained from Eastman Kodak Co. Samples of poly(*p*-phenylene sulfide) were prepared according to the method of Edmonds and Hill.[24]

Preparation of Phenyl-*p*-tolyl Sulfide. This was obtained from sodium thiophenolate and *p*-chlorotoluene in *N*-methyl-2-pyrrolidone at 260 °C. Fractional distillation through a 12-inch Vigreaux column provided a sample boiling at 138–146 °C at 4.0–4.5 Torr (lit.[25] bp 311.5 °C). A portion was oxidized to the sulfone, mp 122–123 °C (lit. mp 124.5,[25] 125–127,[26] 127–128[25]), in 95% yield, with an infrared spectrum identical with that quoted for authentic phenyl-*p*-tolyl sulfone.[26] Gas chromatographic analyses showed the sulfide to be 98% pure, with 0.8% *p*-chlorotoluene and 1.0% phenyl sulfide.

Preparation of 4-Biphenylylphenyl Sulfide. This was obtained from potassium thiophenolate and 4-bromobiphenyl in *N*-methyl-2-pyrrolidone at 155–165 °C.[23] Repeated recrystallizations from ethanol yielded a chromatographically homogeneous sample, mp 67–69 °C (lit.[27] mp 70 °C). A larger sample, mp 66–67 °C, proved to be 99% pure on gas chromatographic analysis, with 1% 4-bromobiphenyl and no phenyl sulfide. The larger sample was used in these studies. A portion of a precursor, mp 66–67 °C, was oxidized to the sulfone, mp 145–147 °C (lit.[28] mp 147 °C), in 98% yield.

Thermal Disproportionation of Aryl Phenyl Sulfides. Preliminary experiments showed that the methyl group of phenyl-*p*-tolyl sulfide was susceptible to oxidation when heated in the air. Therefore, it was heated in the presence of nitrogen with and without added phenyl disulfide as free-radical source. 4-Biphenylylphenyl sulfide could be heated under nitrogen or air; at the higher temperatures it was considered unnecessary to add phenyl disulfide. The sulfide was heated and then the crude reaction mixture was analyzed by gas chromatography. The results of several experiments are summarized in Table I. Some other products were also observed, including volatile materials, e.g., thiophenol and phenyl disulfide, or polymeric and tarry materials, but in minor amounts.

Preparation of 1,4-Bis(phenylthio)benzene. This was prepared from sodium thiophenolate and *p*-dichlorobenzene in *N*-methyl-2-pyrrolidone at 260 °C in appropriate molar ratios. Fractional distillation provided chromatographically homogeneous samples boiling near 200 °C at 3 Torr, and highly crystalline, mp 82–83 °C (lit.[23,30] mp 82–83 °C). Samples melting in the range 80–82 °C were oxidized in 98% yields to the bis(sulfone), mp 228–230 °C (lit. mp 229,[31] 235–238,[32] 237–238[33]); these bis(sulfides) were essentially homogeneous to gas chromatographic analyses. Oxidation of the bis(sulfide) to the bis(sulfoxide) yielded, as expected, mixtures melting over a wide range, mp 136–162 °C (lit. α isomer mp 179–180 °C, β mp 145–146 °C[34]), in 88% yields. No attempt was made to separate the isomers. Infrared analyses assured that no absorptions attributable to sulfoxide appeared in spectra of sulfones and similarly that, at most, only traces of sulfone were present in samples of sulfoxide.

Preparation of 1,3-Bis(phenylthio)benzene. This was prepared from sodium thiophenolate and *m*-dichlorobenzene in *N*-methyl-2-pyrrolidone at 260 °C in appropriate molar ratios. Fractional distillation through a 12-in. Vigreaux column provided a chromatographically homogeneous sample boiling at 198–201 °C at 3.5 Torr (lit.[35] bp 174–181 °C at 0.3 Torr). A portion was oxidized to the bis(sulfone), mp 190–191 °C (lit.[36] mp 187–188, 190 °C).

Preparation of 1,2-Bis(phenylthio)benzene. Similarly, the ortho isomer was obtained from sodium thiophenolate and *o*-dichlorobenzene. Fractional distillation through a 12-in. Vigreaux column provided a sample boiling at 198–202 °C at 3.0 Torr (lit.[23] bp 180–187 °C at 0.25 Torr). Gas chromatographic analyses indicated the sample to be 98% pure, with 2% of an unidentified impurity, possibly an isomer from similarity of retention times. A portion was oxidized to the bis(sulfone), mp 160–163 °C (lit. mp 165.5–166.0 °C,[37] mp 167 °C[38]), in 99% yield, with an infrared spectrum identical with that quoted for authentic 1,2-bis(phenylsulfonyl)benzene.[37]

Preparation of Bis[4-(phenylthio)phenyl] Sulfide, I (n = 2). Sodium thiophenoxide and 4-chlorophenyl sulfide were heated in *N*-methyl-2-pyrrolidone to 175 °C for about 3 h. Typical work-up provided a crude reaction mixture which gas chromatography indicated to be 82% pure. Recrystallization from ethanol (small scale) or from benzene–ethanol (large scale) provided purer sulfide, I (n = 2), mp 101–102 °C (lit.[39] mp 100–102 °C). The small-scale sample was chromatographically homogeneous; the larger-scale sample proved to be 98% pure, with about 2% of an impurity which was probably monosubstitution product from the original reaction.

Oligomerization Reactions. A cone-shaped flask, heated by a sand bath, was equipped with a thermometer, a capillary inlet for introduction of gas dipping to the bottom of the flask, and adapters for simple distillation through an air condenser to a receiver arranged for vacuum takeoff. The entire apparatus was arranged to be as compact as possible with efficient heating, and with insulation extending as far as the condenser.

1,4-Bis(phenylthio)benzene (11.71 g) was placed in the flask and melted. A flow of air through the capillary was established at several micro bubbles per second. The bis(sulfide) was heated for about 7 h at 308–375 °C during which time 3.0 ml of distillate was collected. Most of the heating time was near the higher temperatures. The distillate first began to appear about half-way through the reaction. To facilitate its removal, vacuum was applied intermittently and carefully lest the contents of the flask erupt into the receiver. Upon cooling, the residue consisted of a solid moistened by some liquid which had been incompletely removed by distillation.

The total residue was taken into hot benzene and any solids crushed. The benzene slurry was cooled to room temperature and filtered. It tended to filter slowly because the solid oligomer particles were swollen by the solvent and somewhat soft and sticky. The filtrate and washings from the oligomers were stripped by means of a rotary evaporator to a sticky, soft semisolid. The reaction mixture was thus divided into three fractions: the distillate as collected, the benzene-soluble semisolids from the oligomers, and the benzene-insoluble oligomers. The first two products were examined by gas chromatography and all by infrared spectroscopy.

Gas chromatography provided complete analysis of the volatile material collected as distillate. An estimate of the heavier benzene-soluble materials present in the benzene-soluble fraction was obtained. First, gas chromatographic analysis indicated the relative amounts of I (n = 0, 1, and 2) (anything heavier than n = 2 would not go through the column). Then all phenyl sulfide, I (n = 0), was carefully removed from the sample and the relative weight loss was noted. This weight loss was compared to an expected weight loss based upon gas chromatographic analysis assuming that only I (n = 0, 1, and 2) had been present. Since less weight was lost than according to this assumption, the difference was attributed to heavier benzene-soluble materials I (n = 3, 4, . . .).

A summary of this analysis and a tabulation of all the products obtained from the reaction is given in Table II.

The sample of oligomers, a tan powder when thoroughly dried under vacuum, was subjected to analyses. Stoichiometric calculations of repeat units per end group allowed an estimate of degree of polymerization; about 6 repeat units per 2 end groups remained after all lower molecular weight products in Table II had been accounted for. This theoretical estimate was corroborated by combustion analyses for S. Calcd for n = 6 in $C_6H_5S(C_6H_4S)_nC_6H_5$: S, 26.87. For n = 7: S, 27.19. Found: S, 27.07; so that $6 < n < 7$ and mol wt about 900. Gel permeation chromatography indicated a narrow molecular weight distribution with a heterogeneity index of 1.67. Infrared spectra were similar to those of PPS with additional absorption at 1025 cm^{-1}.

When the oligomerization reaction was carried out with 1,4-bis(phenylthio)benzene in the presence of certain additives, insight

Table II
Products of Oligomerization of p-$C_6H_5SC_6H_4SC_6H_5$

	Charge = 11.71 g		Wt, in g, for n in $C_6H_5S(C_6H_4S)_nC_6H_5$					
Fraction	Wt, g	%	0	1	2	3, 4	>4	Remarks
Distillate	3.00	25.6	2.86	0.14				
Benzene soluble	5.62	48.0	1.91	1.52	0.98	1.21		
Benzene insoluble	3.00	25.6					3.00	Mp 178–210 °C
Total	11.62		4.77	1.66	0.98	1.21	3.00	Total in g
		99.2	41	14	8	10	26	% by wt

Table III
Oligomerization in the Presence of Additives

Added	%	Yield of oligomers,[a] %	Other products obsd	Remarks
	0	26	n = 0, 1, 2, . . .	Typical control run
Phenyl disulfide	2.2	31	n = 0, 1, 2, . . .	Evidence for radical reaction
Ionol[b]	2.4	3	n = 0, 1, 2, . . . , PhSH	Evidence for radical reaction
Triphenylamine	5.1	14	n = 0, 1, 2, . . . , Ph_3N, PhSH	No evidence for ionic reaction
2-Naphthalenesulfonic acid	5.0	9	n = 0, 1, 2, . . .	No evidence for ionic reaction
1,4-Bis(phenylsulfinyl)-benzene	5.0	10	n = 0, 1, 2, . . .	No sulfoxide nor sulfone observed
1,4-Bis(phenylsulfonyl)-benzene	5.1	0	n = 0, 1, 2, . . . , sulfone	Products soluble in benzene, n remains small, reaction proceeds to small extent

[a] Nonvolatile, benzene-insoluble products. [b] 2,6-Di(*tert*-butyl)-4-methylphenol.

Table IV
Other Oligomerization Reactions

		Insoluble oligomeric products		
Starting material	Added PhSS-Ph, %	Yield, %	Melting range, °C	Insoluble in
1. Para, I (n = 1)	2.2	31.9	205–225	Benzene
2. Para, I (n = 1)	2.4	34.2	224–244	Benzene
3. Para, I (n = 2)	None	38.6	210–228	Benzene
4. Meta, I (n = 1)	2.2	44.2	Low melting	Ethanol
5. Para, I (n = 1) plus meta, I (n = 1) (1:1)	2.1	49.3	Viscous oil	Ethanol

into the nature of the reaction was obtained. Listed in Table III are the additives tested and the results obtained.

The results of several other oligomerization reactions are listed in Table IV, including oligomers containing linkages other than just para. For the oligomerizations listed in Table IV, entry 1 describes a sample with an inherent viscosity of 0.04 and a heterogeneity index, by gel permeation chromatography, of 1.95 with a slightly higher molecular weight than that reported in Table II, and a slightly broader distribution. For entry 2, the molecular weight was slightly higher yet. Calcd for n = 7 in $C_6H_5S(C_6H_4S)_nC_6H_5$: S, 27.19. For n = 8: S, 27.44. Found: S, 27.33; so that $7 < n < 8$ and mol wt about 1000. For entry 3, the starting material was the next higher member of the series, I (n = 2). It is noteworthy that I (n = 1) was definitely shown to be present as by product along with I (n = 0). In fact, an experiment paralleling entry 3 showed by gas chromatography that I (n = 0, 1, and 2) was present in the reaction mixture in the ratio of 17:3:2 along with other products. Entry 4 describes meta oligomers. Analyses indicated that the degree of polymerization was low compared with other examples. Calcd for n = 4: S, 25.90. Found: S, 25.93; so that n = 4 and mol wt about 620. In the disubstitution region of the infrared spectra of this sample, there was no significant evidence for any pattern other than meta. Studies of model systems indicated that, if present, a little para should have been evident under these conditions. Entry 5 describes mixed oligomers. They were very soluble in benzene, unlike the behavior one would predict for a mixture of meta and para oligomers. Indeed, an intimate mixture (1:1) of the homo-oligomers, meta and para, showed drastically different solubility characteristics; the mixture precipitated large amounts of para oligomer although the meta oligomer was soluble.

Cure of Oligomers. A sample of para oligomer was placed in an aluminum boat in an all-glass flow reactor arranged for control of the atmosphere. Moist air was passed over the sample as it was placed in a tube furnace. Volatile material was swept into a dry ice–acetone bath where it was partially condensed. An acidic off-gas, as sensed with moistened litmus paper, was detected and later identified as SO_2; it was evolved throughout the entire 2-h heating period. The residue amounted to 87% of the weight taken, volatiles from the trap comprised about 6%, and about 7% was lost, some presumably as SO_2. By gas chromatographic analysis, I (n = 0, 1, and 2) was detected in the volatiles from the trap in the ratio of 30:7:2 along with other products in a complicated mixture.

Another sample was treated similarly and the off-gas collected, identified, and estimated: 0.071% of the weight of oligomer appeared as SO_2 during 20 min of cure.

When samples of para oligomer were subjected to conditions of cure outlined previously, but in an atmosphere of nitrogen rather than air, no cure to tough, flexible films was observed, and SO_2 was not evolved throughout the heating period of 2 h. By gas chromatographic analysis, I (n = 0, 1, and 2) was detected among volatile products in minute amounts.

On an aluminum substrate, para oligomers were heated in a muffle furnace in air for various times and temperatures to provide samples of oligomers with increasing states of cure. Infrared spectra of the samples were taken and compared. With increasing cure, the following most obvious absorptions were observed to decrease in intensity: 700, 750, 1031, 1099, and 1443 cm^{-1}. The following were observed to increase: 870, 1238, and 1638 cm^{-1}. In addition, there was no evidence for sulfone at 1324 and 1164; nor sulfoxide at 1050; nor sulfinate at 1130; nor OH species in the usual regions.

Cure of Poly(p-phenylene sulfide). A sample of PPS was cured under conditions equivalent to those used during the oligomerization reaction. A round-bottom flask was equipped with heating mantle, simple distillation adapter, thermometer, and 3

Table V
Volatiles Obtained from Curing PPS

Fraction	Wt, g	%	Remarks
Benzene-soluble condensate	0.09	0.23	Mostly I (n = 0, 1, 2) (14:7:1) but also phenyl disulfide, thiophenol, and at least 6 other components
Benzene-insoluble condensate	0.03	0.08	Low mol wt PPS
Residue	37.87	97.8	Cured PPS
Total	37.99	98.1	

mm i.d. air inlet tube, all somewhat similar to equipment used for oligomerizations. A 33.72-g sample of PPS was charged to the flask, and a flow of air maintained. The sample was heated 5 h at 308–410 °C during which time the PPS became heavily cured and some light materials were trapped on the cooler walls of the adapter; there was, however, no distillate collected as such nor was any effort made to collect very low molecular weight materials in a trap. The adapter was rinsed thoroughly with benzene and the solvent removed. Solids remaining in the adapter were removed. The products thus obtained, listed in Table V, were separated into benzene-soluble condensate, benzene-insoluble condensate, and residue. The first of these was analyzed by gas chromatography and infrared (see Table V).

A comparable sample of uncured PPS was extracted with hot benzene for 1 h. The extract was filtered and the solvent removed in vacuo by means of a rotary evaporator. The residue, which totaled 1.5% of the charge, consisted of semisolids which were examined by infrared. The residue proved to be low molecular weight PPS, the benzene-soluble fraction, with no evidence for any thiophenol nor I (n = 0, 1, or 2). Thus, I (n = 0, 1, and 2) was observed only from curing PPS.

Direct oxygen analyses were conducted on a sample of PPS both before cure and after 16 hr at 260 °C followed immediately by 24 h at 370 °C in air. The oxygen content of the heavily cured sample showed an increase of 0.90% O by weight. Although it was impossible to obtain good infrared spectra of such a sample heavily oxidized in bulk, the marginal quality spectra obtained were consonant with spectra obtained for films of PPS deposited upon salt plates and cured thereon.

Samples of PPS on salt plates were subjected to cure in air. The infrared scans showed changes with cure. With increasing cure, the following bands showed increasing absorption: 1740, 1278, 1235, 1170, 918, and 875 cm^{-1}. Absorption near 823 showed a shift nearer to 814 cm^{-1}. The following bands showed decreasing absorption: 1560, 1350, 1095, and 965 cm^{-1}. There was no compelling evidence for sulfoxide, sulfone, sulfinate, nor hydroxyl species.

Another series of samples was prepared and examined under conditions of higher resolution with wider range (4 cm^{-1}, Digilab FTS-15). Computer manipulation accentuated differences in the spectra. With increasing cure, the following prominent bands changed: 1235, 1165, and 870 increasing; 1390, 1095, 1075, 740, 560, and 490 decreasing. In addition, with increasing cure, the following less obvious bands changed: 1740, 1585, 1275, 1150, 1115, 915, 660, and 610 cm^{-1} increasing; 1440, 1350, 1180, and 960 cm^{-1} decreasing. There was no compelling evidence for any sulfoxide, sulfone, sulfinate, nor hydroxyl species.

Thermal Stability of Sulfoxides and Sulfones. A sample of 1,4-bis(phenylsulfonyl)benzene was placed in an aluminum boat in an all-glass flow reactor arranged for control of the atmosphere. No attempt was made to trap volatiles. Air was passed over the sample as it was placed in a tube furnace. During 1 h at 400 °C, 59% of the bis(sulfone) slowly distilled from the hot zone, and 22% remained essentially unchanged; the total surviving was thus 81%. However, an acidic off-gas, detected as described previously and probably SO_2, was noted throughout the reaction time. Losses amounted to 19%, presumably as SO_2 and volatile fragments. Thus the sulfone was remarkably stable at 400 °C in air, but some SO_2 was detected.

A sample of 1,4-bis(phenylsulfinyl)benzene was treated similarly. The bis(sulfoxide) proved to be less stable than the bis(sulfone): 48% distilled as very impure sulfoxide, 13% remained as a carbonaceous residue, and 39% was lost, presumably as SO_2 and volatile fragments. Much acidic off-gas, probably SO_2, was detected throughout the experiment, more so than from the bis(sulfone).

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