

Reaction Condition Effects in the Melt Preparation of Poly(phenylene sulfide) from *p*-Iodophenyl Disulfide

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SYNOPSIS

High melt viscosity poly(phenylene sulfide) (PPS) can be prepared via melt condensation of *p*-iodophenyl disulfide analogous to the solution condensation previously reported by other investigators. Depending upon reaction conditions, the material contained varying amounts of gels, whereas under all conditions, anywhere from 1 to 3 mol % disulfide linkages were present. Solution in 1-chloronaphthalene allowed separation of soluble and gel fractions and also cleaved the disulfide linkages, which allowed better quantitation of the disulfide content than did elemental analysis. Cleavage of the disulfides with 1-chloronaphthalene was verified via a model reaction. Branching in the preparations was related to the level of iodine in the melt reaction and also the reaction temperature. A branching mechanism is proposed based on model experiments that showed a complex reaction order and an initial rate of branching that was dependent on iodine concentration. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Poly(phenylene sulfide) (PPS) has found numerous applications owing to its excellent combination of chemical resistance and thermal properties. We have recently reported a new melt-phase polymerization process for the preparation of PPS involving reaction of *p*-diiodobenzene and sulfur¹⁻³ and some of the characteristics of the resultant polymer. The model compound of this new melt method, *p*-iodophenyl disulfide, has also been recently reported to undergo polymerization in solution to give high molecular weights as determined from iodine analysis.⁴ We report here work done on the melt polymerization of this same monomer in a melt reaction system that was directed toward understanding several important effects in the melt synthesis reaction of PPS from *p*-diiodobenzene and sulfur. In particular, we examine the effects of temperature and melt iodine level on branching during the melt reaction process.

EXPERIMENTAL

General

Phenyl sulfide (ca. 98%) from Aldrich Chemical Co. was used as received. GC/MS analysis showed the major impurities to be thiophenol (0.11 wt %), biphenyl (0.37%), dibenzothiophene (0.91%), and phenyl disulfide (0.11 wt %). Iodine was Mallinkrodt AR grade and biphenyl and 1-chloronaphthalene were Eastman White Label and yellow label, respectively. Phenyl disulfide was obtained from Aldrich Chemical Co. and was recrystallized from ethanol before use. Authentic samples of *o*- and *p*-bis(phenylthio)benzene were prepared according to a literature procedure.⁵

The model reaction of phenyl disulfide (0.10 g, 4.58×10^{-4} mol) with 1-chloronaphthalene (20.00 g, 0.123 mol) was conducted at 230°C in the presence of air for a period of 7.5 h with 0.25 mL samples extracted from the solution at various times. Reaction progress was followed by GC as detailed below. The model reactions of phenyl disulfide were conducted in a magnetically stirred long-neck flask immersed in a temperature-controlled (to within 1°C) oil bath at 230°C.

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Solutions of the polymers were prepared by heating in 1-chloronaphthalene, ca. 10 wt % polymer concentration, at 230°C for 6–7 h. At usually less than 1 h heating time, the solution seemed to be complete; no apparent solution darkening or reduction of gel volume seemed to occur for samples containing gelled material. Filtration was accomplished with a preheated coarse frit Büchner funnel. The filtrate was diluted with a three- to fivefold volume of methanol and the white-to-off-white precipitate filtered with suction, boiled in methanol, and rinsed with hot methanol after suction filtration. Gel samples were boiled multiple times in methanol, decanting the hot methanol between treatments. The products were dried in a vacuum oven at ca. 150 Torr pressure at about 100°C for a 2 day minimum.

Preparation of *p*-Iodophenyl Disulfide

A significant improvement on the literature procedure⁶ for preparation of this compound was as follows: Into a 1 L, three-neck flask with thermowell, stirrer, and addition funnel was weighed 101 g 48% HBr (0.60 mol) and 100 mL of glacial acetic acid. Three hundred milliliters (3.2 mol) of acetic anhydride were then added through the addition funnel with good stirring to the mixture at a rate to keep the temperature of the mixture at 60°C or less. When addition of the anhydride was complete, 10.3 g (0.11 mol) of phenol were added and allowed to dissolve; then 30.2 g (0.10 mol) of *p*-iodobenzenesulfonyl chloride ("PIPSYL chloride") were added. The mixture was stirred and maintained at 60°C by a controller connected to a 250 W infrared heating lamp trained on the flask. The reaction was continued for about 20 h, during which time the product separated from solution. The mixture was cooled to room temperature and the product collected by filtration, washed with small portions of cold methanol, and air-dried on a Buchner funnel. The yield was 20 g (0.0425 mol, 85% of theory) of white crystals; mp: 125–127°C; accurate mass 469.815897; calculated for C₁₂H₈S₂I₂: 469.815698 (0.4 ppm error). The ¹³C-NMR showed four peaks at $\delta = 92.7, 129.7, 136.8, \text{ and } 138.2$ ppm. Scale up of this procedure to 3.30 mol of PIPSYL chloride gave the same yield and product purity as did this laboratory-scale procedure.

Preparation of PPS from *p*-Iodophenyl Disulfide

Into a three-neck, 125 mL round-bottom flask fitted with a stirrer shaft seal, an inlet tube for a slow flow of air, and a vacuum jacketed distillation head lead-

ing to a flask cooled in dry ice to act as an iodine trap was weighed 35 g (0.0744 mol) of *p*-iodophenyl disulfide. The reaction flask was immersed into a Belmont alloy metal bath controlled at 245 or 260°C and the mixture stirred under the selected pressure according to the following sequences: (1) for the 245°C reactions, the bath temperature and system pressure were maintained at the starting values until 2.5 h elapsed time, after which the system pressure was reduced to < 1 Torr. After 45 min under these conditions, the bath controller was raised to 300°C and reaction continued with slowed stirring for an additional 30–40 min. (2) For the 260°C reactions, the bath temperature and system pressure were maintained at the starting values until 2.5 h elapsed time, after which the system pressure was reduced to 300°C and reaction continued with slowed stirring for an additional 30–40 min. At the end of the reaction sequence, the flask was removed from the metal bath and the polymer allowed to cool under nitrogen at atmospheric pressure (theoretical yield 16.10 g). Distillation of iodine from the reaction mixtures showed a peak head temperature at 25–30 min into the run for the 260°C runs, whereas the peak occurred at ca. 40–50 min in the 245°C runs. Reactions made to determine iodine melt levels were started at the selected pressure and temperature, but the run was terminated after 30 min in the 260°C runs and 60 min in the 245°C runs.

Analytical

Percent carbon, hydrogen, sulfur, and iodine in the final products was determined by standard combustion analysis methods. Differential scanning calorimetry (DSC) was measured on a DuPont 9900 thermal analyzer at a scan rate of 20°C/min using a sample that had been previously melted at 320°C for 2 min and then quenched on a metal block cooled in dry ice. Upon reaching 320°C, the melt was cooled at 20°C/min to obtain the crystallization upon cooling. Melt stability vs. time and complex viscosity were determined using a Rheometrics mechanical spectrometer at 300°C oven temperature, taking measurements over a period of 35 min at a shear rate of 25 radians/s. Extrapolation of the plot of the log of the melt viscosity vs. linear time was used to determine the intercept, which was taken as the melt viscosity at zero testing time. Free iodine in the reaction mixture was determined by a titrimetric method after multiple extractions of the solid with mixed xylenes. Gas chromatography was performed with a DB-5 capillary column with a beginning oven temperature of 100°C programmed at 1.0°C/min

Table I Properties of PPS from Melt Reaction of *p*-Iodophenyl Disulfide

Sample	Pressure (Torr)	Yield ^a (g)	%C	%H	%S	%I	Disulfide ^b (mol %)	T_g (°C)	T_{ch} (°C)	T_{cc} (°C)	T_m (°C)
260C preps											
1	7.5	16.31	64.05	3.41	28.64	6.687	0.5	85	138	188	273
2	15.0	16.21	66.12	3.60	31.80	0.844	9.0	96	175	154	264
3	30.0	16.54	64.27	3.19	30.22	0.924	5.7	94	158	162	259
4	60.0	16.74	65.57	3.62	30.44	0.739	4.3	93	150	167	263
5	120.0	17.05	65.48	3.62	31.89	0.831	9.5	91	164	146	255
6	240.0	16.64	65.78	3.46	30.41	1.146	3.9	87	154	146	252
245C preps											
7	7.5	16.57	64.90	3.64	30.14	1.821	3.7	95	167	146	265
8	15.0	16.91	64.18	3.76	29.40	1.378	3.0	97	173	148	264
9	30.0	16.70	64.95	3.61	30.17	1.679	4.4	94	163	141	260
10	60.0	17.39	64.25	3.81	29.86	0.903	4.4	94	158	161	269
11	120.0	16.65	64.76	3.54	29.87	1.903	4.4	93	163	146	258
12	240.0	17.28	65.41	3.47	30.37		4.4	94	164	155	264

^a All preparations started with 35.00 g *p*-iodophenyl disulfide.

^b Mol % disulfide calculated from elemental analysis results.

for the first 18 min, followed by a rate of 15°C/min for the next 12 min. Retention times and wt % correlation to peak area were established via use of appropriate standards in the usual way.

RESULTS AND DISCUSSION

Direct Polymer Analysis Results

Elemental analysis established that, contrary to the report of the solution preparation of PPS from this monomer,⁴ excess sulfur, presumably in the form of disulfide linkages, was present (Table I) in the melt preparation. Thus, the chain growth was not accomplished by one simple mechanism, but probably through several simultaneous reactions. Such would be expected by analogy to our previously suggested mechanism for the formation of PPS from the melt reaction of *p*-diiodobenzene and sulfur.³

The DSC data (Table I) showed an unexpected decrease in the T_m of the PPS obtained that depended upon the reaction conditions. This decrease was the most notable in the experiments conducted at 260°C. Recently reported data would indicate branching as the source of such melting-point depression.⁷ Additionally, attempted solution of the polymers in 1-chloronaphthalene found gelled material to be present for most of the polymers. Investigation of the cause of this gelation centered first on the melt iodine level during polymer preparation. This reaction mixture iodine level was approximated by stopping the reaction at the time when the head

temperature was just beginning to decrease from the initial peak in iodine distillation and measuring the free iodine in the residue (Table II and Fig. 1). The iodine level thus obtained should be near the peak of the reaction iodine level (Fig. 2), as was found for a second set of 245°C runs with the overall reaction percentage being fairly constant within each of the two temperature series. Although the percentage reaction was not the same for the two series,

Table II Melt Iodine Levels vs. Preparation Conditions

Sample	Pressure (Torr)	Yield ^a (g)	Free I ₂ (wt %)	% $r \times n^2$
260C preps				
1A	7.5	25.46	0.833	51.6
2A	15.0	26.02	1.080	49.0
3A	30.0	27.15	1.046	43.0
4A	60.0	26.86	2.975	47.3
5A	120.0	26.96	4.262	48.6
6A	240.0	29.07	7.025	42.2
245C preps				
7A	7.5	28.31	0.895	36.7
8A	15.0	27.45	1.345	41.9
9A	30.0	28.78	1.189	34.7
10A	60.0	28.13	1.139	38.0
11A	120.0	29.01	2.219	35.1
12A	240.0	29.92	3.832	32.9

^a All preparations started with 35.00 g *p*-iodophenyl disulfide.

^b Calculated from total I₂ liberated.

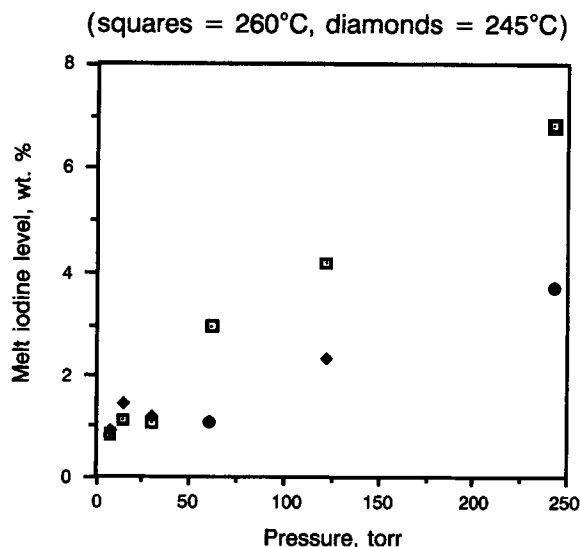


Figure 1 Melt iodine level vs. reaction conditions.

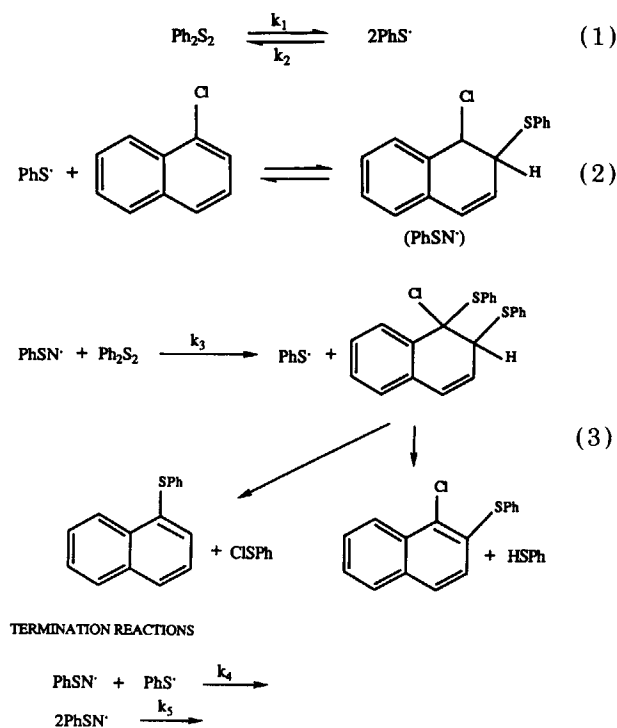
negating direct overall comparisons, nonetheless, the relative conclusions ought still to be valid. The gel fraction (Table III) was related not only to the level of iodine in the melt at a particular temperature but also to the temperature of the reaction. The melt iodine levels at 260°C resulted in branching except for the lowest level (at 7.5 Torr system pressure). At the lower temperature of 245°C, equivalent melt iodine levels did not lead to gelation until appreciably higher values than would have been the case for the higher temperature runs. It is thus apparent that for the best results the reaction temperature needs to be minimized along with the system pressure to avoid gelation. This also means that care must be taken to avoid the higher temperatures of reaction until a large percentage of the iodogroups have reacted to avoid the generation of high levels of melt iodine concentration from rapid further reaction.

The gel fraction of the polymers (Table III) appeared to be only nominally related to the melt iodine level in combination with the melt reaction temperature. The reason, e.g., for the apparently low gel fractions observed at 60 and 120 Torr and 260°C bath temperature relative to the other preparations is not currently understood.

Polymer Dissolution Results

DSC data (Table III) of the soluble fraction of polymer from solution in 1-chloronaphthalene showed large reductions in the polymer T_g compared to the original polymers along with changes in the other transitions that would only be consistent with

shorter polymer chains. This was postulated to be the result of cleavage of the disulfide linkages in the polymer by the 1-chloronaphthalene. This postulate was examined with a single run of the model reaction of phenyl disulfide in excess 1-chloronaphthalene (Fig. 3), which, when plotted as the three-halves power of the concentration of phenyl disulfide vs. time, appeared linear. A compound with mass corresponding to the phenylthio ether of chloronaphthalene was detected as a major product by GC/MS, although there were a number of other GC peaks also observed, another peak of which corresponded to the phenylthio ether of naphthalene. A possible mechanism consistent with a three-halves dependence is as follows:



This mechanism amounts to an induced decomposition of the disulfide and would exhibit the proper three-halves power dependence if reaction 3 is rate-determining. A possible third elimination path for the adduct resulting in HCl elimination is not shown as no odor of HCl was detected over the reaction mixture (a mercaptan odor was, however, evident). However, as this was only a single run, overly great significance should not be attached to the reaction order and other details. The real importance of the data lies in confirmation of the disulfide cleavage by the 1-chloronaphthalene and also that the cleavage would appear to be 95% complete within 450 min. These data also suggest that in the literature report

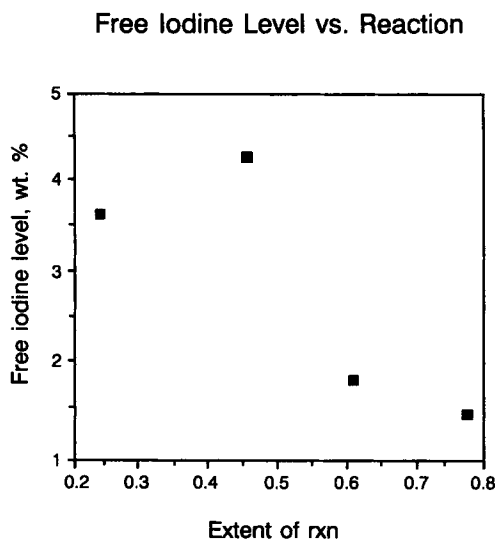


Figure 2 Melt iodine level vs. time for reaction at 245°C and 120 Torr system pressure.

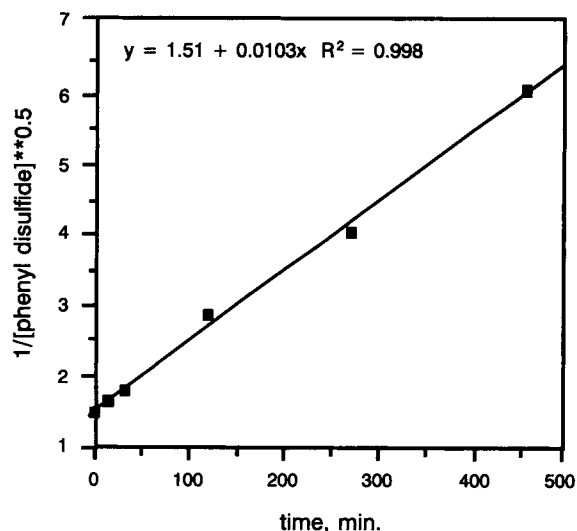


Figure 3 Three-halves order plot for decomposition of phenyl disulfide in 1-chloronaphthalene (230°C).

of the solution polymerization of *p*-iodophenyl disulfide,⁴ if disulfide linkages were present, they might not have been observed depending upon the exact workup procedure that involved polymer dissolution in 1-chloronaphthalene.

By comparison to previously published results,⁷ as a qualitative measure, it can be stated that the

lower the melting point of the polymer isolated from the 1-chloronaphthalene solution experiment the more branched was the PPS. Another possible reason for the observed melting-point depression could be due to a side reaction producing a unit such as a thianthrene linkage. Thianthrene linkages would be expected to have a strong peaks at about 1103, 880,

Table III Results of 1-Chloronaphthalene Dissolution of PPS Samples

Sample	Pressure (Torr)	Gel Fraction	Sample ^a	Soly/ <i>T_g</i>	Soly/ <i>T_{ch}</i>	Soly/ <i>T_{cc}</i>	Soly/ <i>T_m</i>	dp by <i>T_g</i> ^b
260C preps								
1	7.5	0.00	Soly	80	132	215	273	40
2	15.0	0.06	Soly	79	132	207	266	38
			Gel	92	159	169	263	
3	30.0	0.37	Soly	79	127	204	268	38
			Gel	93	170	162	260	
4	60.0	0.01	Soly		229	230	272	
			Gel	86	145	202	274	
5	120.0	0.05	Soly	81	146	195	261	42
			Gel	88	160	167	258	
6	240.0	0.26	Soly	79	142	182	256	38
			Gel	86	165	162	249	
245C preps								
7	7.5		Soly	69	117	221	270	24
8	15.0		Soly	86	136	211	274	53
9	30.0		Soly	79	137	193	264	38
10	60.0		Soly	82	135	210	273	44
11	120.0	0.13	Soly	72	118	201	262	27
			Gel	94	185	139	259	
12	240.0	0.07	Soly	77	130	212	268	34
			Gel	91	158	166	267	

^a Soly = material soluble in 1-chloronaphthalene; gel = insoluble material.

^b Equation is $T_g = 2.1202 + 48.714 \log(dp)$ (see Ref. 9).

and 760 cm^{-1} by analogy to a fully thianthrenic polymer.⁸ The infrared spectra were, however, identical to previous spectra obtained for pure PPS and showed only a very weak peak at 1115 cm^{-1} , which appeared invariant with preparation conditions. The peak at 760 cm^{-1} should also have been in an easily observable position as a shoulder on the weak peak at 742 cm^{-1} . That peak appeared smooth in all preparations. The 880 cm^{-1} peak would appear in an otherwise clear area of the IR spectrum but was also not observed. Thus, varying levels of thianthrenic linkages in the polymer seem unlikely to account for the melting-point decrease, whereas increased branching can.

The gel fraction isolated from the dissolution in 1-chloronaphthalene showed DSC data in accord with expectations of generally higher T_g 's and lower T_m 's (Table III) than those of the soluble material. Recently reported work on the thermal transition behavior vs. chain length of oligomers gave an equation relating T_g to the degree of polymerization (dp) [$T_g = 2.12 + 48.714 \log(dp)$],⁹ which was applied to the soluble, degraded chains from the soluble portion of the polymer. Application of this equation gave degrees of polymerization ranging from 38 to 42 dp for the 260°C and from 24 to 53 for the 245°C runs. This suggests that the disulfide levels of the final polymers are all within the range of 3–1 mol %, with most in the range of 1.5 mol % (obtained from the reciprocal of the dp multiplied by 100 minus 1 mol %) and were definitely nonzero. These numbers varied less than those obtained via elemental analysis and were consistently lower than

the elemental analysis numbers. In one respect, analysis of the polymer disulfide level by this method should be more accurate than results obtained via calculation from the elemental analysis since the elemental results' errors are the sum of both the variability of the carbon analysis and also the sulfur analysis, whereas the degradative method only has a single error. One drawback of this degradative method is that a bias may be inherent in the values obtained, owing to the effect of end groups on the T_g of the chain segments produced. This is, in all probability, not a large effect. The other possible problem with this degradative method for disulfide determination is that the calibration of T_g vs. dp was made for linear chains and this relationship no doubt changes with branching present in the fragments. This leads to potential variability not due to the disulfide but is expected to be a relatively small effect.

It is worth noting that if the excess sulfur in the elemental analysis were present as thianthrene linkages instead of disulfides, then there would be no chain cleavage upon solution in 1-chloronaphthalene.

Melt Rheology Results

Melt viscosity measurements (Table IV) were all uniformly quite high excepting the 7.5 Torr preparation at 260°C . There was no apparent trend in the melt viscosities with preparation conditions. Owing to varying gel content and branching of the soluble polymer fraction that must be present in at least

Table IV Melt Viscosity of PPS from Melt Reaction of *p*-Iodophenyl Disulfide

Sample	Pressure (Torr)	Gel Fraction	MV (poise) ^a	(tan δ) ^b
260C preps				
1	7.5	0.00	3327	3.00
2	15.0	0.06	301786	0.40
3	30.0	0.37	92238	0.40
4	60.0	0.01	316960	0.10
5	120.0	0.05	138567	0.30
6	240.0	0.26	328496	0.08
245C preps				
7	7.5	0.00	39815	1.00
8	15.0	0.00	57031	0.90
9	30.0	0.00	114109	0.40
10	60.0	0.00	137474	0.60
11	120.0	0.13	63849	0.40
12	240.0	0.07	72151	0.60

^a Melt viscosity at 300°C and 25 radians/s.

^b Tan δ = loss modulus, G'' , divided by storage modulus, G' .

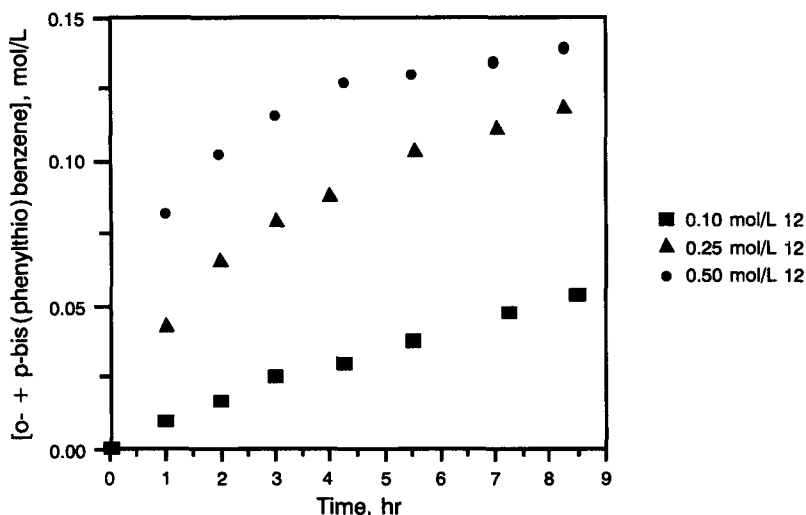


Figure 4 Bis(phenylthio)benzenes vs. time and iodine concentration at 230°C, $[\text{Ph}_2\text{S}_2] \sim 0.05 \text{ mol/L}$.

the samples that contained a gel fraction, nothing can be said about the weight-average molecular weight of the samples from the melt viscosity data. The $(\tan \delta)^2$ for all samples with the lowest melt viscosities were all uniformly low. Values of $(\tan \delta)^2$ of less than 1 indicate a material acting more like a solid than as a liquid. This is, no doubt, a consequence of a high storage modulus from gel content and probably from branching even in samples not showing gel. Thus, the branching induced by the high-temperature preparation of PPS via this route would suggest the necessity to carry out the polymerization at the lowest practical temperature to avoid melt iodine levels that combined with higher temperatures would lead to a branched product.

Model Reaction Results

Experiments to model the potential branching reaction were conducted by decomposing phenyl disulfide in the presence of phenyl sulfide (as the reactant and solvent) at 230°C as the simplest model of a PPS chain. These were conducted both without and with the presence of added iodine in varying concentrations. Fit of the reaction data, e.g., the appearance of *o*- and *p*-bis(phenylthio)benzene summed (see Fig. 4 for the lowest phenyl disulfide concentration) to simple models proved elusive. In the absence of iodine, the reaction rate was very low (Fig. 5). With the exception of one data point, the initial rate of product production (Fig. 5) vs. initial

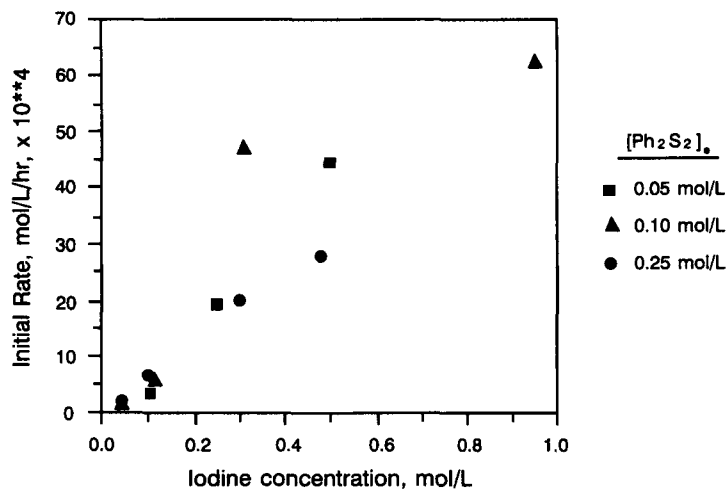


Figure 5 Effect of iodine on initial reaction rate for varying phenyl disulfide concentration.

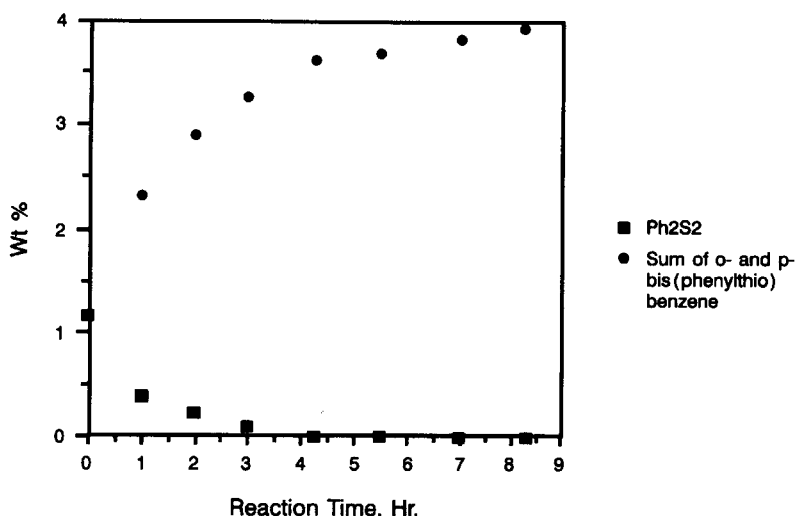
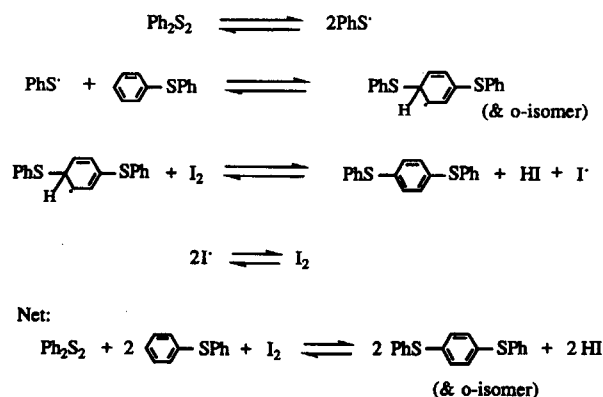


Figure 6 Weight percent phenyl disulfide and combined bis(phenylthio)benzenes vs. time at 230°C, $[\text{Ph}_2\text{S}_2]_0 = 0.05 M$, $[\text{I}_2]_0 = 0.50 M$.

iodine concentration suggested that the reaction was first order in iodine and a low order ($\frac{1}{2}$ or even 0) in phenyl disulfide. It is important, however, to point out that though these initial rates of the reaction appeared to be quite a regular series, the equations necessary to fit the data varied with iodine concentration and also phenyl disulfide concentration. The reaction system is thus quite complex. The following elementary reactions would be expected to be the principal ones of this system:

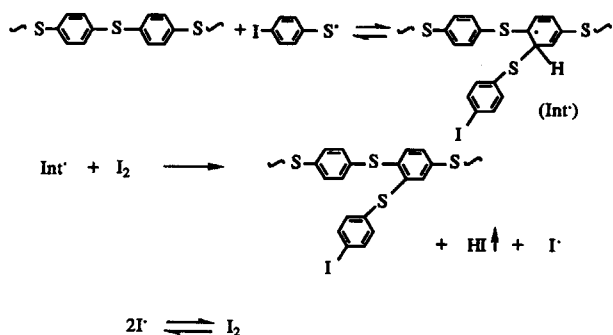


The literature does not provide for direct, simple analogies with this reaction system. Furan¹⁰ and thiophene¹¹ have been found to undergo phenylthiolation when the source of the phenylthiyl radical was thiophenol reacting with Fenton's reagent (hydrogen peroxide and ferrous ion).

In all of the model reactions, a continued, but slowed production of the bis(phenylthio)benzenes was noted after all of the phenyl disulfide was con-

sumed (Fig. 6). This suggests that the hydroiodic acid produced in the reaction is capable of reaction with phenyl sulfide to produce more phenyl disulfide. The mechanism for this is not currently understood. It is, however, apparent that the phenylthiyl radical does attack phenyl sulfide to form thioether products, the rate of which is greatly enhanced by added iodine.

We propose that the polymer branching reaction by analogy to these model reactions is as follows:



The phenylthiyl radical derived from iodophenyl disulfide used in the above equation represents any phenylthiyl radical from whatever source since the end result would be the same.

CONCLUSIONS

Preparation of poly(phenylene sulfide) (PPS) by melt reaction of *p*-iodophenyl disulfide gave, depending upon reaction conditions, varying amounts

of gels via a complex mechanism. Clearly, this method of preparation of PPS is limited by the necessity of operating at lower temperatures and, therefore, longer reaction times, as the branching tendency was dependent on the overall iodine concentration and the reaction temperature at which it was present.

REFERENCES

1. See, e.g., M. Rule, D. R. Fagerburg, J. J. Watkins, and J. S. Fauver, U.S. Pat. 4,786,713 (Nov. 22, 1988); *Chem. Abstr.*, **110**, 174004j (1989), and subsequent patents.
2. M. Rule, D. R. Fagerburg, J. J. Watkins, and P. B. Lawrence, *Makromol. Chem. Rapid Commun.*, **12**, 221-226 (1991).
3. M. Rule, D. R. Fagerburg, J. J. Watkins, P. B. Lawrence, R. L. Zimmerman, and J. D. Cloyd, *Makromol. Chem. Symp.*, **54/55**, 233-246 (1992).
4. Z. Y. Wang and A. S. Hay, *Macromolecules*, **24**, 333 (1991).
5. R. Adams, W. Reifschneider, and A. Ferretti, *Org. Syn., Collective Vol. V*, 107 (1973).
6. V. O. Lukashevich, *Doklady Akad. Nauk S.S.S.R.*, **103**, 627-630 (1955) (Translation of the full article is available from the National Translations Center).
7. D. R. Fagerburg, J. J. Watkins, and P. B. Lawrence, *J. Macromol. Sci. Chem. A*, **30**, 323-330 (1993).
8. F. Bertinelli, P. Costa Bizzarri, C. Della Casa, and M. Fiorini, *J. Polym. Sci. Polym. Phys.*, **26**, 2203-2214 (1988).
9. D. R. Fagerburg, J. J. Watkins, and P. B. Lawrence, *Macromolecules*, **26**, 114-118 (1993).
10. L. Benati, C. M. Camaggi, and G. Zanardi, *J. Org. Chem.*, **40**, 966 (1975).
11. Y. A. Goldfarb, G. P. Pokhil, and L. W. Belenkii, *Doklady Chem.*, **167**, 385 (1966).

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