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Electron Paramagnetic Resonance Spectroscopic Investigation of the Synthesis of Poly(*p*-phenylene sulfide/disulfide), PPS/DS

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ABSTRACT: A new process for the synthesis of the commercially important semicrystalline, engineering thermoplastic poly(*p*-phenylene sulfide/disulfide), PPS/DS, based on the reaction of diiodobenzene and sulfur in air at elevated temperatures (230–300 °C), has been introduced. Since it was anticipated that radicals would play an important role in this process, the reaction was examined by high-temperature electron paramagnetic resonance spectroscopy (EPR). This paper includes the first direct observation of radicals under conditions of PPS/DS synthesis. Radicals observed include both a sulfur radical and a carbon radical. EPR experiments with monomers indicate the importance of polysulfide linkages, such as disulfide, with and without iodine or iodo substitution for the formation of these radical species. Even though these results indicate that radicals are easily formed in our process, comment on the importance of the observed radical species in this polymerization mechanism is impossible.

Introduction

Recently a new process, referred to as the RFWL process, for the synthesis of the commercially important semicrystalline, engineering thermoplastic poly(*p*-phenylene sulfide), PPS, was presented (Figure 1).[1] This process, based on the reaction of *p*-diiodobenzene (DIB) and sulfur at elevated temperatures (230–300 °C), generated a polymeric material containing para-substituted aromatic groups connected by sulfide and disulfide linkages, i.e., poly(*p*-phenylene sulfide/disulfide), PPS/DS. Prior to that report, synthesis of PPS was accomplished via several routes which were summarized in two earlier reports.[2,3] Fahey and Ash[2] presented an excellent summary of the state of knowledge of the synthetic routes and the mechanisms for formation of PPS by these routes as well as discussed the mechanism of formation of PPS based on the chemistry of Edmunds and Hill[4] who synthesized the first commercially useful PPS. Lopez and Wilkes[3] presented a good review of PPS properties and preparations, also.

The RFWL process chemistry to produce PPS/DS is accomplished under conditions that are in certain respects considerably less stringent than those previously employed for other PPS synthetic routes. Since it was anticipated that radicals would play an important role in the RFWL process, we examined this reaction process directly by employing high-temperature electron paramagnetic resonance spectroscopy (EPR) under conditions of the reaction, i.e., between 230 and 300 °C in air. Both sulfur and carbon radicals could be envisioned in this process. However, polymer chain growth resulting from the presence of delocalized carbon radicals would not be consistent with the previously reported reaction specificity.[1]

Sulfur radicals are reported to exhibit anisotropic **g** values which result from an anisotropic **g** tensor and have been well-characterized in EPR spectra of mono- and disulfides.[5–10] Sulfur radicals are reported to be observable at temperatures of 100 °C[6] and above.[8] Ma and coworkers[11] employed EPR to investigate the mechanism of chain extension and cross-linking reactions induced by free radicals for commercial PPS heated in air to elevated temperature. Hill and co-workers[12] have reported the study of free radicals at 77 K formed in commercial PPS by γ-irradiation. Kreja and co-workers[13] reported room-temperature EPR spectra of commercial PPS annealed to 778 and 863 K and of commercial PPS doped with iodine. Kispert and co-workers[14] reported a weak, broad EPR resonance from commercial PPS.

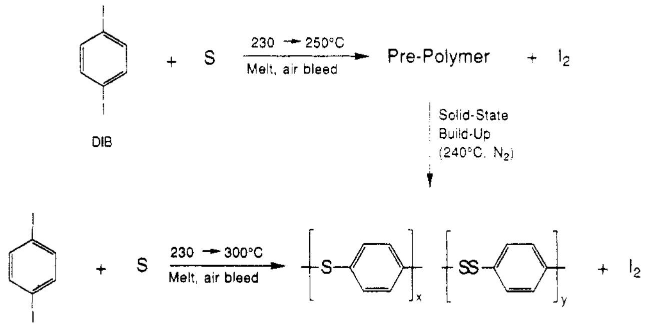

Figure 1. Scheme for the synthesis of PPS/DS.

For a related polymer, Russian researchers[15] examined the course of the reaction of poly(1,3-dimethylphenylene sulfide) with sulfur using EPR. The reaction was followed both as a function of time and as a function of reaction temperature. The polymer product was reported to contain both sulfide and disulfide linkages. These authors interpreted their data in terms of two radical species: a sulfur radical exhibiting an asymmetric EPR resonance and a carbon radical exhibiting a symmetric EPR resonance. Over the course of the reaction either as a function of temperature (from 240 to 280 °C) or as a function of time, the initially observed sulfur radical converted to a carbon radical.

In this paper, we report results based on high-temperature EPR in support of the presence of free radical species during the synthesis of PPS/DS by the RFWL process. This is the first full report of the first direct observation of radicals under conditions of PPS/DS synthesis.[16] We also present evidence for the importance of disulfide linkages relative to the formation of free radicals in PPS/DS.

Experimental Section

EPR Spectra. EPR spectra were collected on a Bruker ER 200D SRC EPR spectrometer operating on the X-band (9.65 GHz) in the general temperature range 230–300 °C and using 3-mm-o.d. glass EPR tubes. Spectra collected at temperatures outside of this range are noted in the figures. On the basis of these temperatures, the samples were either solid- or melt-phase.

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Individual spectra were recorded generally in 10-deg increments over the specified temperature range with a 200-G sweep width, 100-s sweep time, modulation frequency of 100 kHz, and modulation field of 40 mG. Generally, 20–30 mg of monomer or polymer was weighed into an EPR tube for analysis.

Monomeric and Polymeric Compounds. Phenyl sulfide and phenyl disulfide were obtained from Aldrich Chemical Co. and used without further purification. Iodine and elemental sulfur were obtained from standard commercial sources and used without further purification. DIB[1] and perdeuterated DIB,[17] henceforth referred to as DIB-d_4, were prepared as discussed elsewhere. *p*-Iodophenyl sulfide and *p*-iodophenyl disulfide were prepared and characterized in-house. Phenyl polysulfide, C_6H_5–S_n–C_6H_5 (where n = 3–8) was prepared as described elsewhere[18] and characterized by mass spectrometry and carbon-13 NMR. Experimental PPS/DS polymer samples[1] and perdeuterated PPS/DS polymer samples,[17] henceforth referred to as PPS/DS-d_4, were prepared as discussed elsewhere.

Iodo-terminated PPS (1) with a degree of polymerization (DP) of 9 was prepared according to the previously reported method[1] but employing a 53 mol % excess of DIB during the preparation. The composition was determined by elemental analysis and spectroscopically analyzed by carbon-13 NMR.

Polymer Characterization. Percent carbon, hydrogen, sulfur, and iodine in the final products was determined by standard combustion analysis methods. Sulfur in excess of one sulfur atom per benzene ring was assumed to be present in the form of disulfide linkages.

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.

Carbon-13 NMR of 1 was accomplished using a high-temperature solution-state NMR probe from Doty Scientific Inc. (Columbia, SC) tuned for carbon-13 observation at 100.25 MHz on a JEOL Model GX-400 NMR spectrometer using 10-mm-o.d. NMR tubes. Samples were dissolved in *N*-cyclohexylpyrrolidinone under a blanket of argon and examined at 230 °C. Field/frequency stabilization was accomplished with glyme-d_6 held concentrically in a 5-mm-o.d. capillary tube.

Polymer Synthesis in the EPR Tube. In general, the reactants employed to generate polymer in the EPR tube were weighed directly into the EPR tube. A typical set of conditions for the preparation of PPS/DS in the EPR tube based on the reaction of DIB and sulfur in a manner similar to the synthetic procedure reported elsewhere[1] follows: 49.3 mg of DIB (0.150 mmol) and 4.1 mg of sulfur (0.128 mmol) for a DIB-to-S mole ratio of 1.17:1 were weighed directly into an EPR tube. The EPR tube was placed into the EPR cavity and heated to the initial specified temperature. An EPR spectrum was collected at each specified temperature immediately after sample and cavity thermal equilibration and retuning of the EPR cavity; then the sample was warmed to the next temperature, where the process was repeated, unless additional spectra as a function of time were desired at the present temperature. No special precautions were taken to eliminate air or oxygen since oxygen has been reported to be involved in the RFWL process.[19] Iodine, evolved during this reaction, was not removed from the EPR tube during the reaction but was observed to be condensed in the unheated, top portion of the EPR tube at the end of the temperature experiments.

g Value Measurement. Measurement of **g** values was accomplished in a dual cavity with the resonance of diphenylpicrylhydrazyl (DPPH, **g** value = 2.0037) as the reference.

Results and Discussion

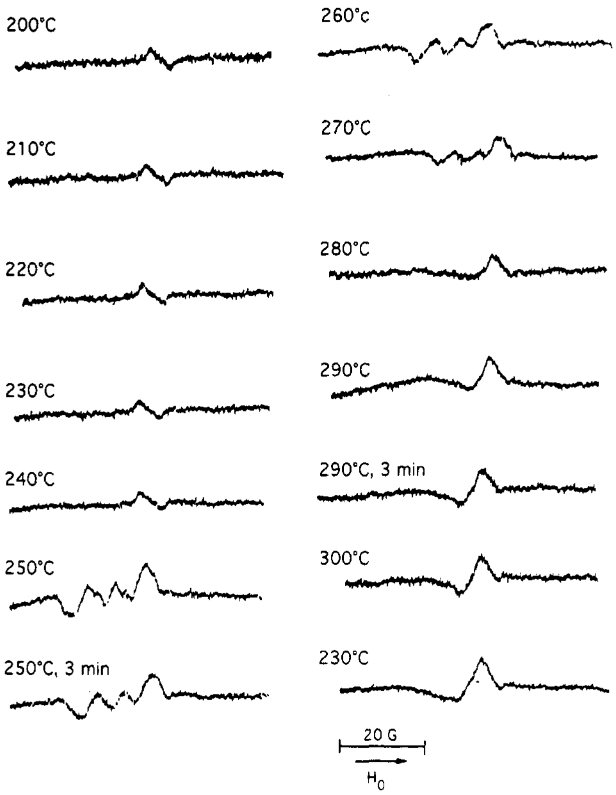

Figure 2. EPR spectra from the reaction of DIB and sulfur (1.17:1 mole ratio) as a function of temperature.

Reaction of DIB and Sulfur. Figure 2 shows EPR spectra obtained during the reaction of DIB and sulfur in the DIB-to-S mole ratio of 1.17:1. Spectra were recorded in 10-deg increments over the temperature range 200–300 °C. At temperatures below 250 °C, no radicals from the reaction are observed. The resonance that is detected (**g** value = 1.9936) results from an impurity in the EPR tube. Between 250 and 270 °C, an anisotropic, multiplet resonance is observed. As the temperature is increased from 250 to 270 °C, the multiplet resonance decreases in intensity until it is replaced at 280 °C by a broad, singlet resonance. The broad resonance remains the only resonance in the spectrum up to 300 °C and is sufficiently stable to be observable after lowering the temperature to 230 °C. The broad resonance exhibits a Dysonian-like line shape which is characteristic of the line shapes of an EPR resonance from an electrically conductive material.[20] This is consistent with a radical delocalized within a conjugated aromatic π system.

g values for the three components of the multiplet resonance are 2.0033 ± 0.0002 ($\mathbf{g}_1$), 2.0072 ± 0.0001 ($\mathbf{g}_2$), and 2.0113 ± 0.0001 ($\mathbf{g}_3$). The isotropic **g** value is 2.0073. The multiplet resonance is assigned to a sulfur radical species. The isotropic **g** value is in excellent agreement with **g** values of 2.0079 and 2.0076 reported by Murray and co-workers[20] for a sulfur radical in two AsF_5-doped PPS samples with different AsF_5-to-PPS mole ratios.

The singlet resonance with a **g** value of 2.0048 is assigned to a carbon radical. Kreja and co-workers[13] report that the **g** value for thermally-treated PPS samples fluctuates about 2.0045 and that iodine doping results in an increase of the **g** value to a degree dependent upon iodine content; i.e., heavily doped samples exhibit a **g** value about 2.006.

It is possible to obtain an EPR spectrum of just the sulfur radical without any interference from the carbon radical (Figure 3) if DIB is reacted with a 31 mol % excess of sulfur under very carefully controlled temperatures. A decrease in intensity of this resonance with increasing temperature can be explained by either a recombination reaction or rapid rearrangement of the sulfur radical to the carbon radical or broadening of the sulfur radical resonance into the baseline due to relaxation effects at elevated temperatures or a combination of these effects.

The multiplet resonance for the sulfur radical is broad and of low intensity. It is likely that some of the broadness is due to unresolved hyperfine splittings to protons on the

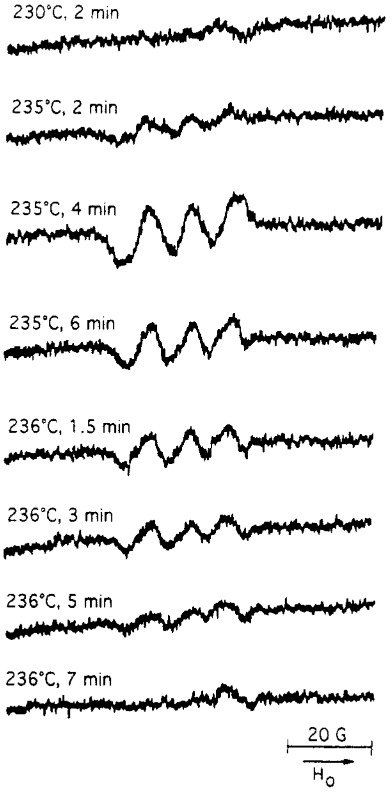

Figure 3. EPR spectra from the reaction of DIB and sulfur (1:1.31 mole ratio) as a function of temperature.

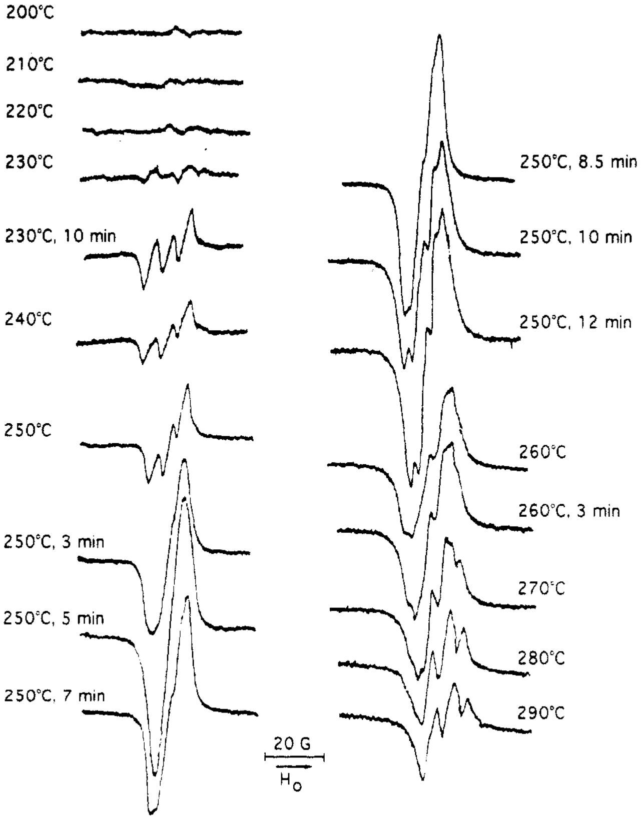

Figure 4. EPR spectra from the reaction of DIB-d_4 and sulfur (1.18:1) as a function of temperature.

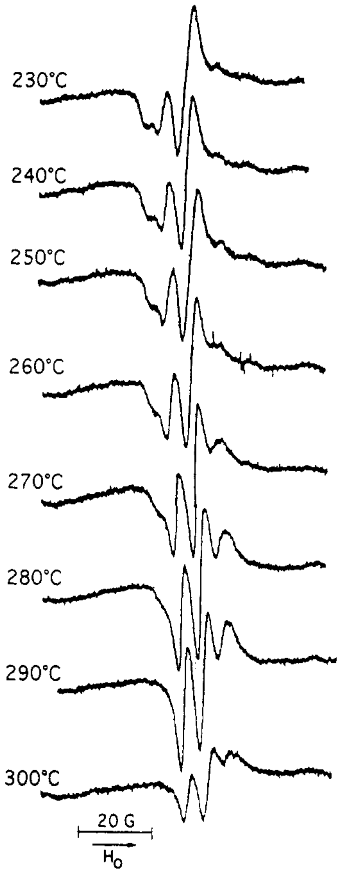

Figure 5. EPR spectra of the melting process for perdeuterated PPS/DS with a DP of 25.

aromatic ring. To investigate this possibility, the reaction between DIB-d_4 and S was examined by employing a DIB-d_4-to-S mole ratio of 1.18:1 and over the temperature range 200–290 °C (Figure 4). Replacement of deuterium for hydrogen should remove the hyperfine splittings to hydrogen and result in sharper resonances. Between 200 and 220 °C, no radical resonances are observed. At 230 °C, a very low intensity multiplet resonance is observed which increases in intensity on standing for 10 min and remains visible up to 250 °C. The intensity of this resonance is larger than the corresponding resonance obtained under similar conditions in Figure 2. Since equal amounts of materials and the same instrumental parameters were used for both reactions, it appears that the multiplet resonance is sharpened by removing the hyperfine interaction with hydrogen via replacing the hydrogens with deuteriums. Therefore, the broad resonances observed during the DIB reaction result from unresolved hyperfine splittings to hydrogen. After standing a short time at 250 °C (Figure 4), the multiplet resonance broadens considerably. This broadening with time is most likely due to spin-spin exchange resulting from increased radical concentration.[20] After standing at 250 °C for a few additional minutes, the resonance broadness is lost, most likely due to the concentration of radicals being decreased by further reaction. From this point in the reaction to the end at 290 °C, several overlapping multiplet resonances are observed. The multiplet character of the carbon radical resonances results from hyperfine coupling to the deuterium nucleus. The different multiplet patterns result from free radicals experiencing a distribution of molecular correlation times within the polymer. The collection of different correlation times results from a distribution of polymer molecular weights resulting from polymer chain growth.

EPR of PPS/DS-d_4 During the Melting Process. The effect of melting on EPR spectra can be seen in spectra from two samples of PPS/DS-d_4 polymer over the temperature range 230–300 °C. One polymer has a DP of 25 (Figure 5), while the other has a DP of 150 (Figure 6). Both sets of EPR spectra indicate the presence of two overlapping multiplet resonances. Each multiplet reso-

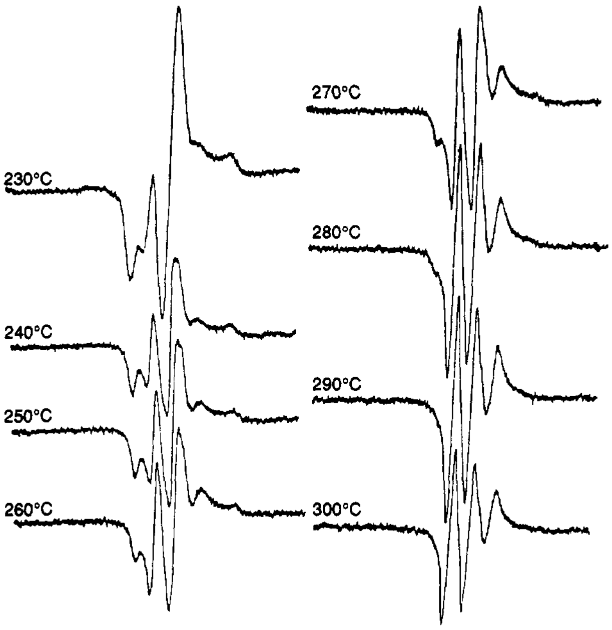

Figure 6. EPR spectra of the melting process for perdeuterated PPS/DS with a DP of 150.

nance consists of three resonances. The components of the two overlapping multiplets can be picked out in the 230 °C spectrum of Figure 6 where five distinct resonances are seen. The central resonance of the five resonances is composed of the two overlapping central resonances of each multiplet pattern. On either side of this large central resonance are two smaller resonances. The two outermost resonances belong to one multiplet resonance, while the inner resonances next to the large central resonance result from the other multiplet resonance.

The outer multiplet resonance decreases in intensity from 230 to 280 °C. This series of spectra is characteristic of EPR spectra resulting from a melting solid containing a spin probe.[21] The DSC-determined melting point of the polymer with DP = 25 is 281 °C and for the polymer with DP = 150 is 279 °C. The **g** values for the components of the multiplet resonance of the inner multiplet resonance at 290 °C are 2.0006 ± 0.0001 ($\mathbf{g}_1$), 2.0042 ± 0.0002 ($\mathbf{g}_2$), and 2.0079 ± 0.0001 ($\mathbf{g}_3$). The isotropic **g** value is 2.0042. This value is in agreement with the **g** value for a carbon radical shown earlier in this work. Details of this melting process are more involved than consideration of only an amorphous and a crystalline phase. Analysis of this melting process based on a discussion of three components within the amorphous phase and a DP-dependent crystalline phase will be provided shortly.[22]

PPS/DS Polymer Containing Excess Sulfur. EPR spectra of polymer samples containing 18% (Figure 7) and 27% (Figure 8) excess sulfur by elemental analysis show strong resonances for both types of radicals observed in this system. The carbon radical resonance maintains a nearly constant intensity at each temperature for the individual samples. The intensity of the sulfur radical increases to a maximum at about 270 °C in Figure 7 and then decreases to nearly no intensity in 300 °C. In contrast, the sulfur radical resonance in Figure 8 is still very large at 300 °C. By comparison of individual spectra at each temperature, it is clear that the intensities of both radical resonances increase with an increase in excess sulfur in the polymer, based on examination of equal amounts of each polymer in the EPR tube.

EPR of Monomeric Materials. Comparison of the EPR spectra of phenyl sulfide (Figure 9) and phenyl disulfide (Figure 10) over the temperature range 230–300 °C indicates no radical resonance from phenyl sulfide and only a very small carbon radical resonance from phenyl disulfide at the upper end of this temperature range.

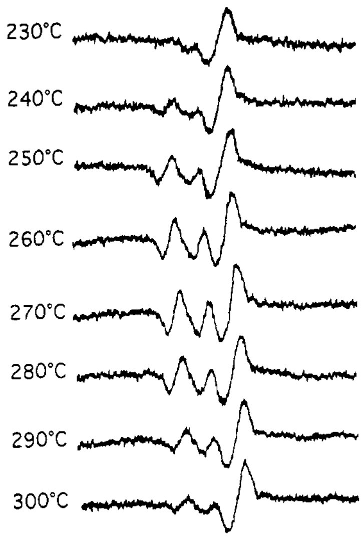

Figure 7. EPR spectra of PPS/DS polymer containing 18% excess sulfur as a function of temperature.

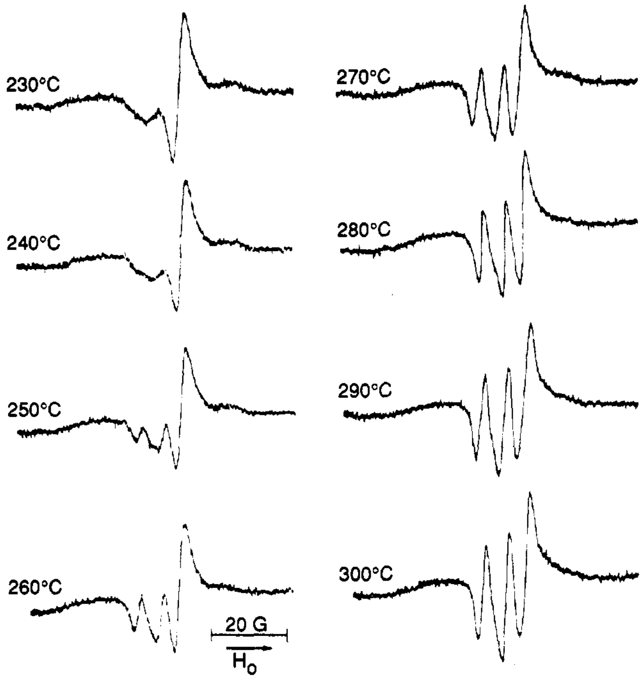

Figure 8. EPR spectra of PPS/DS polymer containing 27% excess sulfur as a function of temperature.

Comparison of the EPR spectra of p-iodophenyl sulfide (Figure 11) and p-iodophenyl disulfide (Figure 12) over the same temperature range indicates no radical resonance from p-iodophenyl sulfide but shows a significant carbon radical resonance from p-iodophenyl disulfide overlapping a second, broader resonance. These overlapping resonances can be seen more clearly in the series of EPR spectra for iodo-terminated PPS polymer (Figure 13) and are similar to the overlapping resonances reported previously[13] resulting from annealed PPS. The melting point of this iodo-terminated polymer is 264 °C, which suggests that the broad resonance is not related to the melting process of this polymer. The source of this multiplet resonance is unclear at this time. Incidentally, p-iodophenyl disulfide was used by Wang and Hay[23] in the solution preparation of PPS oligomers.

Comparison of the EPR spectra of phenyl sulfide (Figure 14) over the 230–300 °C temperature range and phenyl

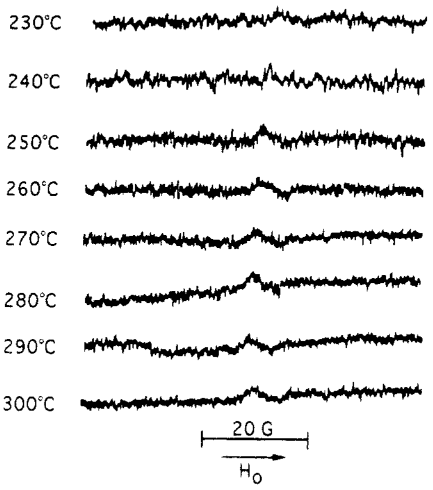

Figure 9. EPR spectra of phenyl sulfide as a function of temperature.

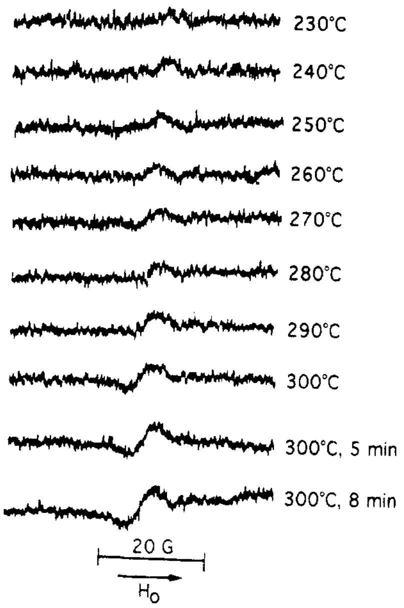

Figure 10. EPR spectra of phenyl disulfide as a function of temperature.

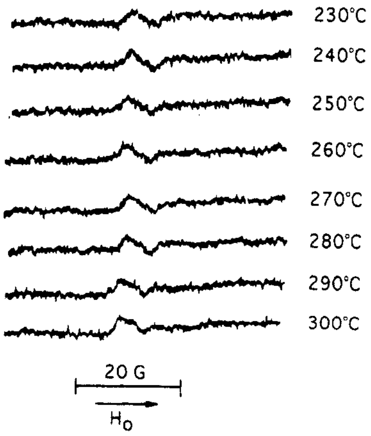

Figure 11. EPR spectra of *p*-iodophenyl sulfide as a function of temperature showing only a resonance from the impurity in the EPR tube over the entire temperature range.

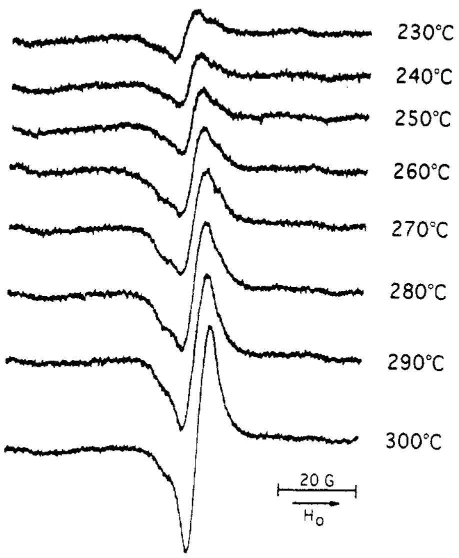

Figure 12. EPR spectra of *p*-iodophenyl disulfide as a function of temperature.

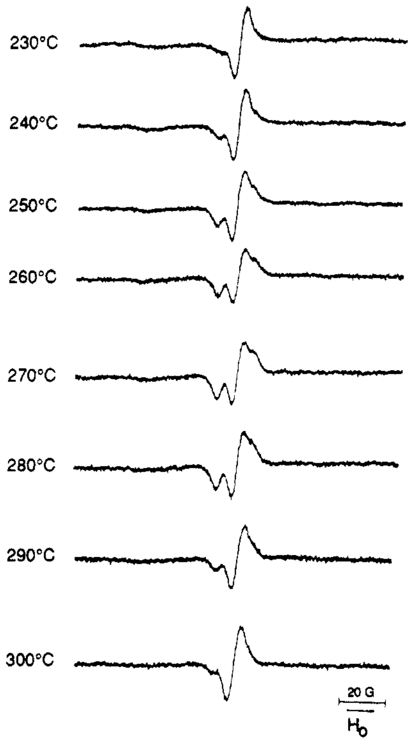

Figure 13. EPR spectra of an iodo-terminated PPS oligomer (DP = 9) as a function of temperature.

disulfide (Figure 15) over the lower temperature range of room temperature to 90 °C, each in combination with iodine, indicates only a small carbon radical resonance from phenyl sulfide interacting with iodine but shows a large carbon radical resonance from phenyl disulfide interacting with iodine at 90 °C. When the sample is held at 90 °C for up to 20 min, the carbon radical resonance increases in intensity from the intensity shown after 3.5 min. In the presence of only a slight excess of iodine (10 mol %, relative) in Figure 14, the carbon radical resonance does not exhibit a shift to higher **g** value. In the presence of a large excess of iodine (over 100 mol %, relative) in Figure 15, the carbon radical resonance is shifted to a higher **g** value. It is well-recognized that doping with iodine results in an increase in the **g** value to a degree dependent on the iodine level.[13]

Examination of the EPR spectra of DIB and sulfur (Figure 16) over the temperature range 230–300 °C indicates no radical resonance from either starting material. Examination of the EPR spectra of phenyl polysulfide (Figure 17) indicates a carbon radical resonance is readily formed at about 160 °C. These spectra suggest that the polysulfide linkage easily cleaves at lower tem-

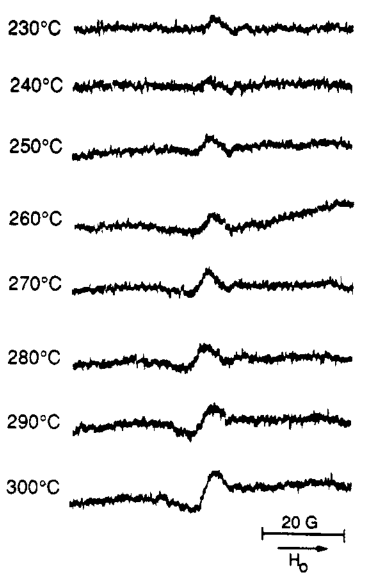

Figure 14. EPR spectra of phenyl sulfide containing a 10 mol % excess of iodine as a function of temperature.

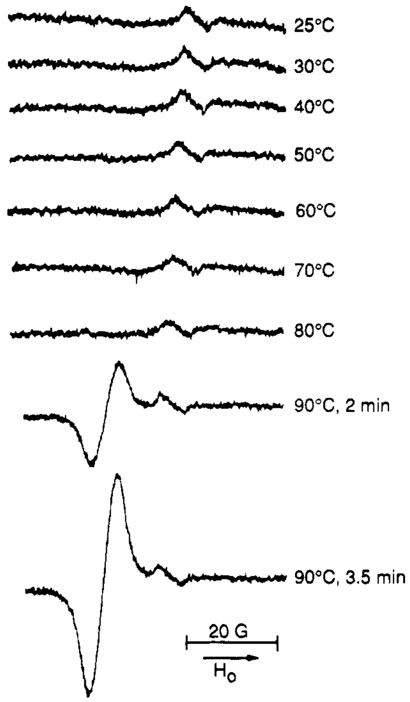

Figure 15. EPR spectra of phenyl disulfide containing a 103 mol % excess of iodine as a function of temperature.

perature than the disulfide linkage to form sulfur radicals that rearrange easily to carbon radicals.

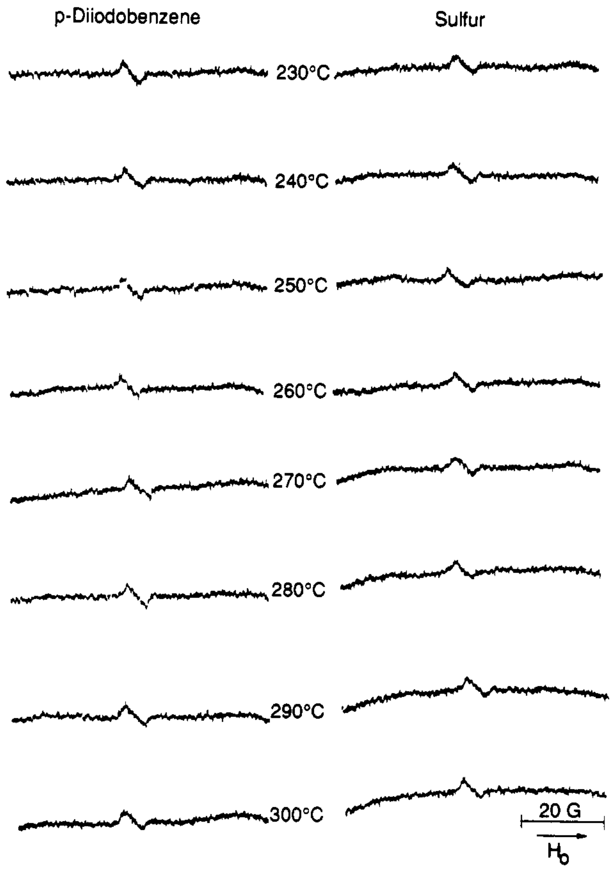

Figure 16. EPR spectra of *p*-diiodobenzene and sulfur, individually, as a function of temperature.

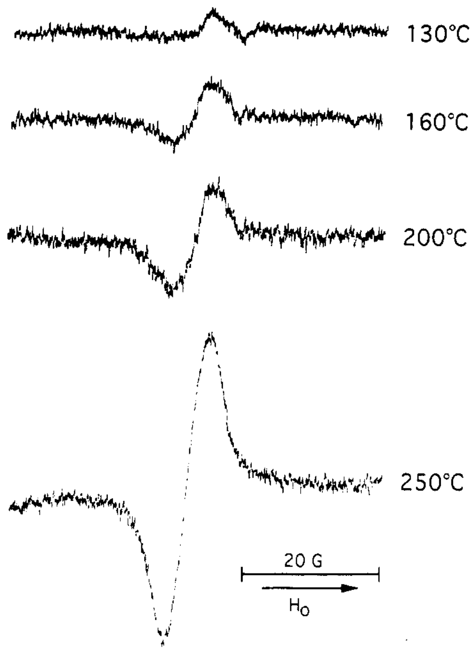

Figure 17. EPR spectra of phenyl polysulfide as a function of temperature.

Summary of These Observations. The EPR spectra of these monomeric materials indicate that iodine or iodo substitution enhances the ability of these systems to generate free radicals thermally, relative to no iodo substitution or iodine being present. Also, radicals are more easily formed with polysulfide linkages than disulfide or sulfide linkages without iodine present or iodo substitution. In the examples with iodine, it is likely that radical formation is initiated by the presence of a very low level of thermally-generated iodine radicals. Even though our results indicate that radicals are easily formed in this process, we cannot say at present whether a radical species, similar to that proposed by Heitz and co-workers,[24,25] is involved in the polymerization mechanism of the RFWL process. Alternatively, the radical species could be formed from the already formed chains reacting with iodine present to generate first a sulfur radical which then rearranges to a carbon radical. In any event, it is worth repeating that a delocalized carbon radical is not indicated in the polymerization mechanism, as that should result in aromatic substitution other than the virtually 100% para substitution observed.[1] That a polysulfide compound produced free radicals at lower temperatures than the disulfide also supports part of the previously proposed mechanism[26] where an initial polysulfide radical attacks an iodo aromatic species followed by subsequent S–S bond cleavage to form radicals for further reaction. Sulfide bonds are the ultimate stable state with disulfide bonds being stable enough to ensure their presence in the final product given the appropriate reactant stoichiometry.

Conclusions

On the basis of EPR evidence, we have provided the first direct observation that free radicals are present during the synthesis of PPS/DS from diiodobenzene and sulfur between 230 and 300 °C in the presence of air. Radicals observed include a sulfur radical and a carbon radical. EPR experiments with monomers indicate the importance of polysulfide linkages, such as disulfide, between phenyl groups with and without iodine for the formation of these radicals. Even though our results indicate that radicals are easily formed in this process, we cannot say at present whether a radical species, similar to that proposed by Heitz and co-workers, is involved in the polymerization mechanism of the RFWL process.

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