

Magnetic Resonance Spectroscopic Investigations of Poly(p-Phenylene Sulfide/Disulfide), PPS/DS

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Introduction

Recently a new process for the synthesis of the commercially important semi-crystalline, engineering thermoplastic poly(p-phenylene sulfide/disulfide), PPS/DS, was presented [1]. This process, based on the reaction of p-diiodobenzene (DIB) and sulfur at elevated temperatures (Figure 1), generates a polymeric material containing para-substituted aromatic groups connected by sulfide and disulfide linkages.

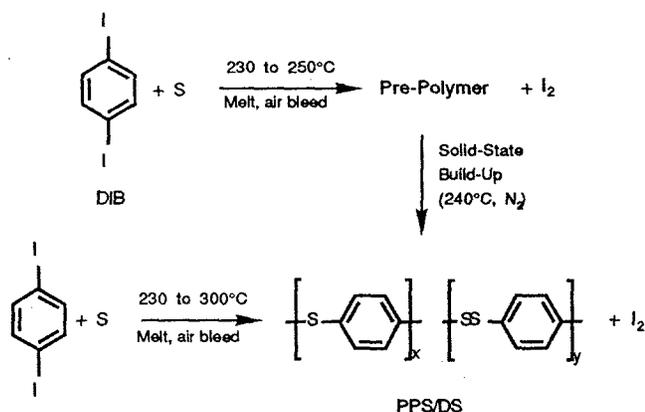


Figure 1. Synthesis of PPS/DS

PPS/DS is not easily characterized by conventional magnetic resonance techniques operating under normal conditions due to its high thermal stability and solvent resistance. Wade and coworkers [2] recently reported on their application of high-temperature solution-

state carbon-13 NMR to commercially available poly(phenylene sulfide), PPS. We have extended this study by examining PPS/DS with epr spectroscopy as well as high-temperature solution-state carbon-13 NMR.

The PPS/DS chemistry is accomplished under conditions that are in certain respects considerably less stringent than those previously employed for other PPS synthetic routes [3,4]. Free radicals have been observed in PPS previously by several workers [5-8] but not under the conditions of synthesis. Since it was anticipated that radicals would play an important role in our chemistry, we examined this reaction process directly employing high-temperature epr spectroscopy under conditions of the reaction. In this report we present evidence for sulfur and carbon radical formation during PPS/DS synthesis.

Experimental

EPR spectra were collected on a Bruker ER 200D SRC EPR spectrometer operating on X-band (9.65 GHz) in the general temperature range of 230 to 300°C and using 3-mm O.D. glass epr tubes with a 200 gauss sweep width, 100 sec sweep time, modulation frequency of 100 KHz and modulation of 40 milligauss. Measurement of *g* values was accomplished in a dual cavity with the resonance of diphenylpicrylhydrazyl (*g* value = 2.0037) as the reference.

PPS/DS synthesis in the epr tube was accomplished in a manner similar to that

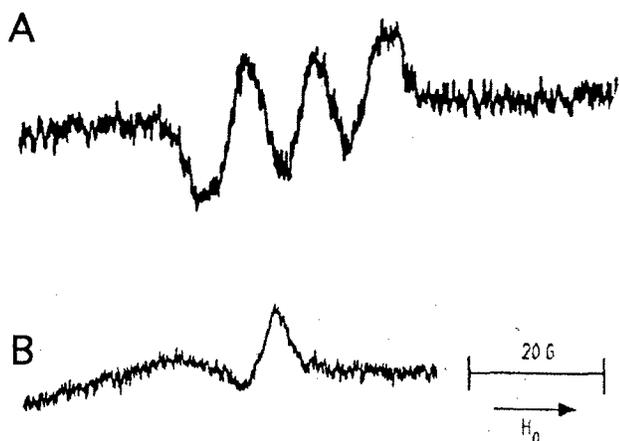


Figure 2. EPR spectra of perdeuterated PPS/DS at (A) 235°C, $g(\text{iso}) = 2.0073$, and (B) 290°C, $g = 2.0042$.

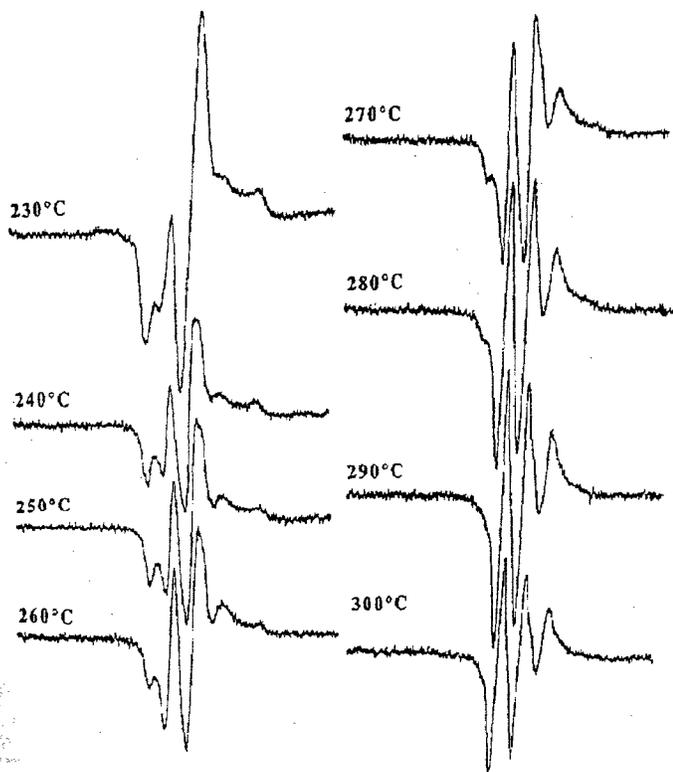


Figure 3. EPR spectra of melting perdeuterated PPS/DS

Table 1. Linkage and end group species found in PPS/DS. Letters and numbers are used in Figure 4 for resonance assignments.

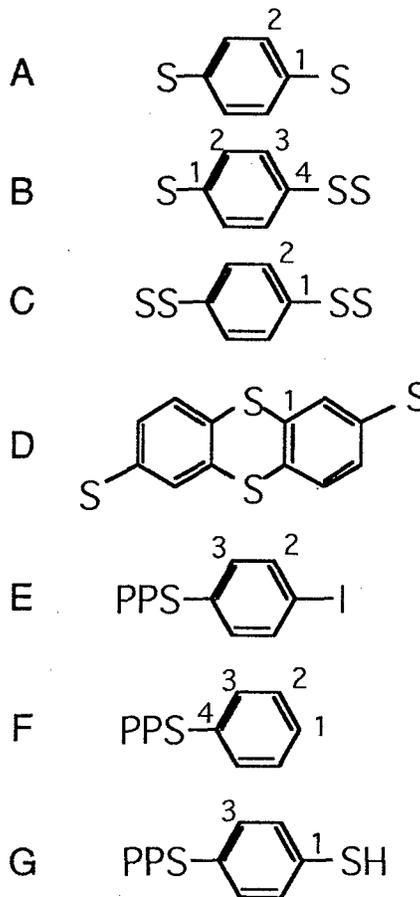


Table 2. Chemical shift assignments in ppm for iodo-terminated PPS (structure shown in Figure 5)

| | |
|----|-------|
| C1 | 92.3 |
| C2 | 138.4 |
| C3 | 132.7 |
| C4 | 135.7 |
| C5 | 135.1 |
| C6 | 131.8 |

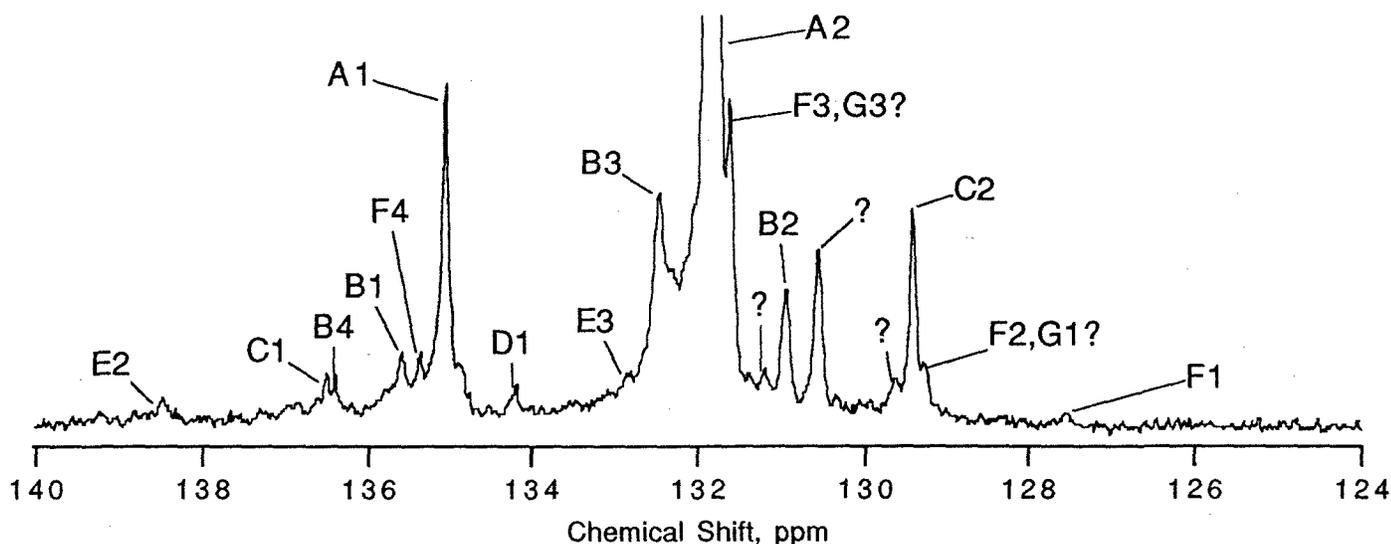


Figure 4. Solution-state carbon-13 NMR spectrum of PPS/DS

previously reported [1]. Perdeuterated PPS/DS (PPS-d₄) (degree of polymerization, DP, of 25) was synthesized in a manner similar to that previously reported [1]. Iodo-terminated PPS (DP of 9) was prepared according to the previously reported method [1] but employing a 53 mole % excess of DIB.

High-temperature solution-state carbon-13 NMR employed a high-temperature 10-mm probe system from Doty Scientific, Inc. (Columbia, SC) on a JEOL Model GX-400 NMR spectrometer. Samples were dissolved in N-cyclohexylpyrrolidinone (CHP) under a blanket of argon and examined at either 230 or 260°C. Field/frequency stabilization was accomplished with glyme-d₆ held concentrically in a 5-mm capillary.

Solid-state NMR spectra were collected on a Varian XL-300 NMR spectrometer.

Discussion

EPR Spectroscopy. During the synthesis of PPS/DS in the epr spectrometer, two distinctly different resonances are observed (Figure 2). At 235°C a triplet resonance is observed. *g* Values for the components of the triplet resonance are 2.0033 ± 0.0002 (*g*₁), 2.0072 ± 0.0001 (*g*₂) and 2.0113 ± 0.0001 (*g*₃). The

isotropic *g* value is 2.0073. This resonance is assigned to a sulfur-centered radical cation. The isotropic *g* value is in excellent agreement with *g* values of 2.0079 and 2.0076 reported by Murray and coworkers [9] for a sulfur-centered radical cation in two AsF₅-doped PPS samples.

Above 280°C, the triplet resonance is replaced by a singlet resonance with a *g* value of 2.0042. This resonance is assigned to an aryl radical.

It is interesting that the melting process for PPS/DS can be easily monitored by epr (Figure 3). Using PPS-d₄, two overlapping triplet resonances are observed at 230°C. The triplet resonance arises from hyperfine coupling between the carbon-centered radical and the deuterium attached to the carbon. The two triplet resonances arise from free radicals being in two different environments. At 230°C, the larger triplet resonance arises from radicals in the solid phase while the smaller triplet resonance arises from radicals in a melted phase. As the temperature is increased, the solid-phase component decreases in intensity until it disappears just above 280°C. The DSC melting point for this polymer is 279°C.

It is unlikely that the carbon radical observed here is mechanistically involved in the synthesis of linear para-substituted PPS/DS since these radicals would produce

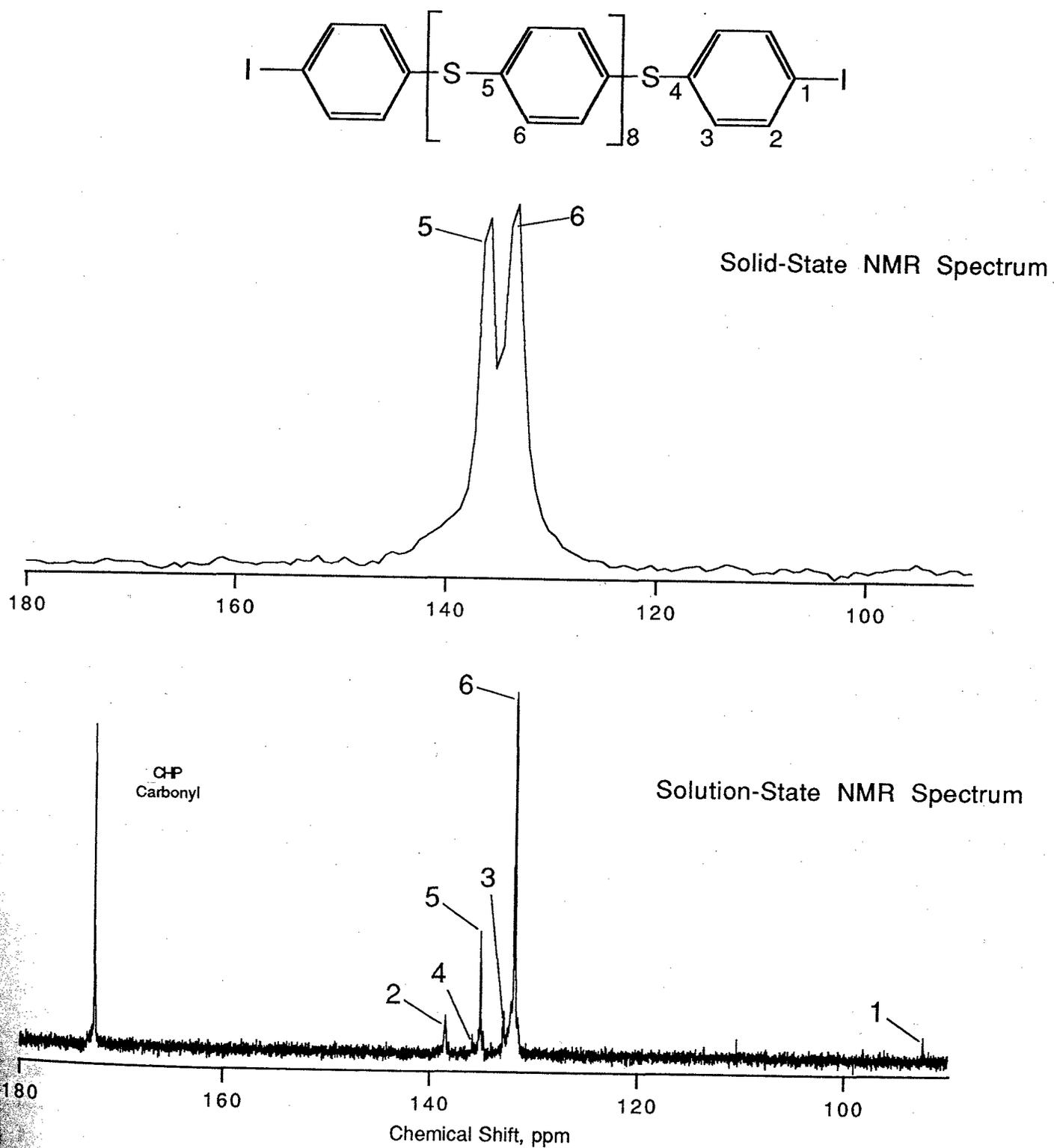


Figure 5. Solid-State and Solution-State Carbon-13 NMR spectra of an Iodo-Terminated PPS

aromatic substitution other than para-substitution. Our PPS/DS chemistry has been shown to produce exclusively para-substituted polymer [10].

NMR Spectroscopy. Solution-state carbon-13 NMR at 260°C in CHP provides high-resolution NMR spectra of PPS/DS that enable an analysis for various linkage groups, such as sulfide and disulfide, as well as numerous end groups of the type p-X-phenyl, where X = H, SH or I. Resonances for the species in Table 1 are assigned in the spectrum shown in Figure 4.

Assignments are based on comparison with spectra for model compounds and analysis of several PPS/DS spectra. Species A, B and C were assigned by comparison of spectra from PPS or PPS/DS with and without excess sulfur as well as model compounds such as diphenyl sulfide and diphenyl disulfide. Based on the thermal history of the synthesis, excess sulfur is expected to be present only as disulfide linkages. Species D was assigned by comparison with the spectrum of thianthrene. Species E assignments are discussed below. Species F and G were assigned based on previous assignments [2]. Several resonance assignments in Figure 4, labelled with "?", have not been made conclusively. Complete assignments await synthesis of appropriate model compounds.

Solution-state carbon-13 NMR of an iodo-terminated PPS polymer (Species E, Table 1) at 230°C in CHP clearly shows sufficient detail to confirm the degree of polymerization of 9 and to assign all resonances in the terminal iodophenyl group (Figure 5, Bottom). The assignments for these carbons are shown in Table 2. By comparison, the room temperature solid-state NMR spectrum of this polymer is not very informative (Figure 5, top).

Conclusions

PPS/DS does not lend itself to study by conventional magnetic resonance techniques operating under normal conditions. Through the use of several magnetic resonance techniques, we have begun to understand some of the limitations to studying PPS/DS by these techniques and to enhance our understanding of the chemistry of this

unusual polymer. We have presented here data on the first direct observation of free radicals generated under conditions of synthesis of PPS/DS and have expanded the applicability of the high-temperature solution-state carbon-13 NMR technique. Solution-state NMR has provided evidence for several linkage groups and end groups in PPS/DS enabling us to better appreciate the chemistry of this polymer. Room temperature solid-state NMR has not proven to be useful in these studies.

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