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In Situ EPR Spectroscopy of Aromatic Diyne Cyclopolymerization

Nicolas Mifsud,[†] Veronique Mellon,[†]
K. Prasanna U. Perera, Dennis W. Smith, Jr.,* and
Luis Echegoyen*

*Department of Chemistry and Center for Optical Materials
Science and Engineering Technologies (COMSET),
Clemson University, Clemson, South Carolina 29634*
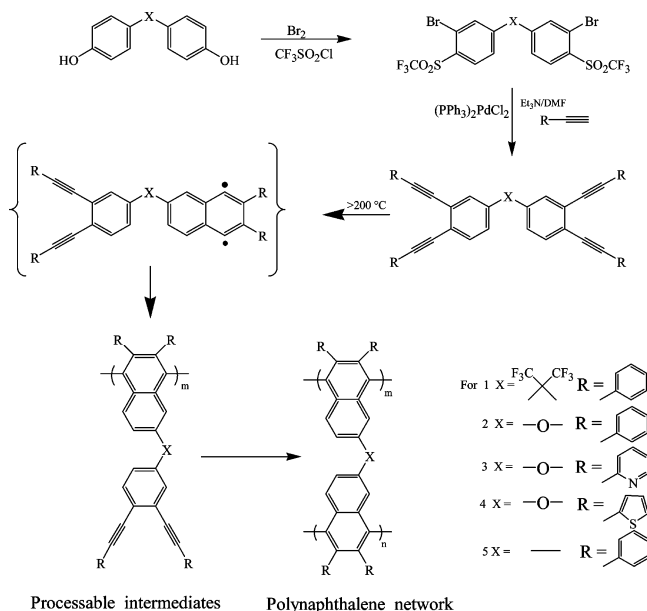
dwsmith@clemson.edu

Abstract: Electron paramagnetic resonance (EPR) spectroscopy was successfully used for the first time to follow the Bergman cyclization of bis-*ortho*-diynyl arene (BODA) compounds. Five BODA monomers with different spacer (X) and terminal groups (R) were compared. In situ polymerization via EPR spectroscopy yielded first-order rate expressions. Monomers with spacer −O− or −C(CF$_3$)$_2$ and terminal group R = Ph exhibited similar kinetic behavior upon thermal polymerization, whereas monomers with pyridine and thiophene terminal groups gave significantly higher rates of polymerization over phenyl-terminated derivatives. A model compound, 1,2-bis(phenylethynyl)benzene, was used to probe the polymerization mechanism, and radical intermediates were found to be stable indefinitely at room temperature.

The Bergman[1,2] cyclization of enediynes to reactive diradical intermediates has been studied extensively for the development of antitumor drugs. More recent work has shown that the thermal cyclorearrangement can also be used to synthesize linear[3] and network polynaphthalenes and precursor resins for glassy carbon micro-/nanostructures.[4−6] Since linear polynaphthalenes are difficult to process, our synthetic strategy has been focused on bis-*ortho*-diynyl arene (BODA) compounds, which polymerize to form branched intermediates around 200 °C with variable intact latent enediyne functional groups (Scheme 1).

Here we report the first EPR spectroscopic results that begin to reveal the nature of the diradical species involved during BODA polymerization.

Bergman cyclopolymerization of BODA monomers afford branched and ultimate network polymers via diradical intermediates (Scheme 1). To date, very little work has been reported concerning EPR studies of radicals

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(6) Shah, H. V.; Brittain, S. T.; Huang, Q.; Hwu, S.-J.; Whitesides, G. M.; Smith, D. W., Jr. *Chem. Mater.* **1999**, *11*, 2623. Perpall, M.; Perera, K. P. U.; DiMaio, J.; Ballato, J.; Foulger, S. H.; Smith, Jr., D. W. *Langmuir* **2003**, *19*, 7153.

SCHEME 1. Synthesis and Cyclopolymerization of BODA Monomers

Processable intermediates   Polynaphthalene network

formed during the cyclization of enediynes.[8] For this study, five different BODA monomers (**1**−**5**, Scheme 1) were used. Monomers were synthesized via a three-step protocol from commercial bisphenols as reported elsewhere (Scheme 1).[4,11] Powdered samples were placed in a quartz EPR tube and then heated between 200 and 210 °C. The EPR spectra of monomers **2** and **4** heated at 210 °C are shown in Figures 1 and **2**, respectively.

Radicals formed during the polymerization of monomers **1**−**4** exhibit EPR signals with significant intensities. The shapes of these signals, however, are different and depend on the terminal group. Monomers with phenyl terminal groups (**1** and **2**, Figure 1) exhibit different EPR spectra with unresolved hyperfine splitting compared to monomers **3** and **4** (Figure 2). The second derivative of the EPR spectrum of monomer **2** suggests the possibility of splitting by two equivalent $M_s = \frac{1}{2}$ nuclei to yield a triplet.

These data also show that the spacer group does not significantly influence the g factor value (Table 1), and therefore it does not appreciably modify the nature of the radical.[9] In some cases, the g factor is sufficiently different from the free-spin radical value (2.0023), thus providing information about spin−orbit coupling and structural information of the paramagnetic species. The g factor value changes with the terminal group and increases from phenyl to thiophene. These values are always lower than the free-spin g factor (2.0023), but the monomer with the thiophene terminal group exhibits a value very close to the reference value (2.0023) (Table

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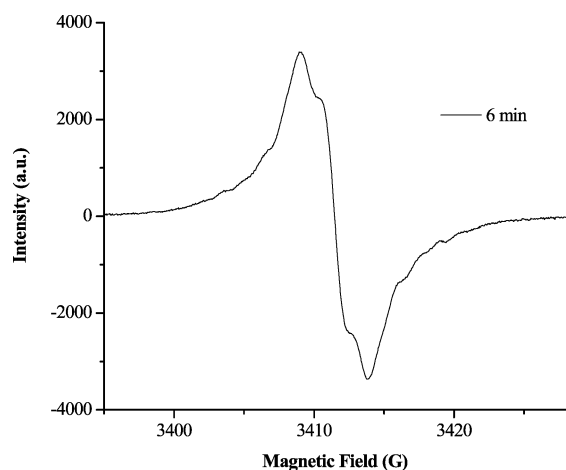
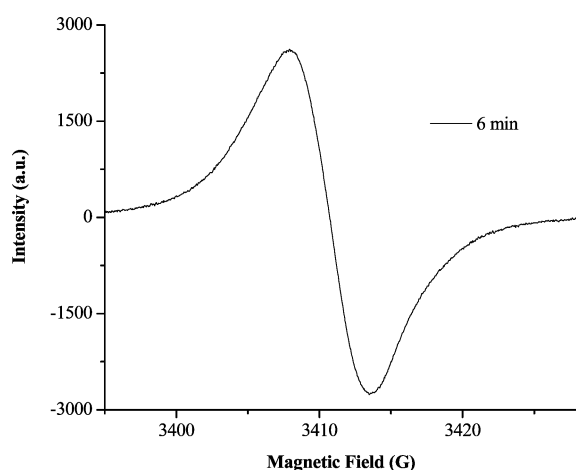**FIGURE 1.** EPR spectrum of **poly-2** at 210 °C.

FIGURE 2. EPR spectrum of **poly-4** at 210 °C.

TABLE 1. EPR Parameter Values for Polymerization of BODA Monomers

BODA monomers	g factor	line width (G)
1	2.0018	4.0
2	2.0018	5.0
3	2.0020	5.4
4	2.0022	6.2
5	2.0018	5.0

FIGURE 3. EPR spectrum of copolymer **poly(2-co-4)** (3/1 mol) after 10 min at 210 °C.

FIGURE 4. EPR spectrum of copolymer **poly(2-co-4)** (1/1 mol) after 10 min at 210 °C.

TABLE 2. EPR Parameter Values for Polymerization of BODA Copolymers

BODA monomers and copolymers	g factor
monomer **2**	2.0018
monomer **4**	2.0022
2-co-4 (50/50)	2.0020
2-co-4 (75/25)	2.0018

1). It appears that only the terminal group influences the nature of the radical for the compounds studied to date.

BODA copolymerization with different monomer concentrations gives EPR spectra with significantly different shapes. When 25 mol % monomer **4** and 75 mol % monomer **2** are used, signals can be observed (Figure 3) that are similar to the spectrum of monomer **2** and the *g*-value is exactly the same as that of monomer **2**, (2.0018). For a 50/50 molar ratio, the signal is a smooth curve (Figure 4), however, with a *g*-value of 2.0020 (Table 2), which is between the *g*-value for the homopolymerization of monomers **2** and **4**.

Polymerization was also performed with model enediyne 1,2-bis(phenylethynyl)benzene at 200 °C, and in this case hyperfine splitting is clearly resolved (Figure 5). In the presence of a radical trap, *N-tert*-butyl-α-phenyl-nitrone, the spectrum observed corresponds to
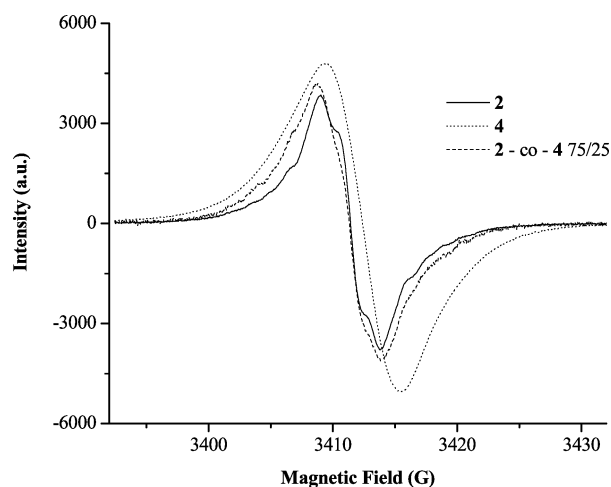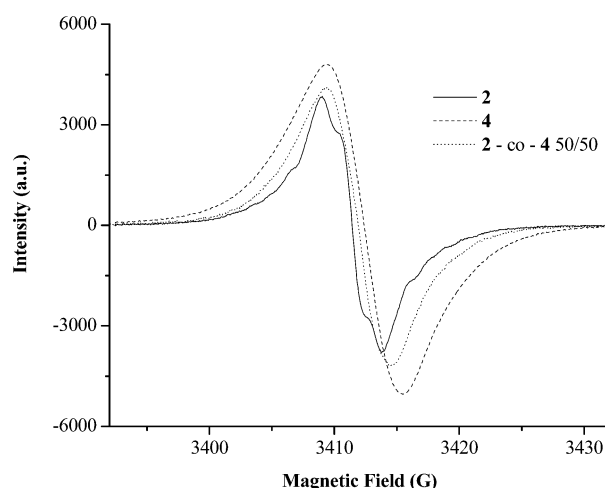
that of the nitroxide group (Figure 6).[10] Moreover, to reveal if there are one or at least two different species involved in the polymerization, experiments at 210 °C were recorded at three different microwave power settings (Figure 7). These results indicate that the ratio of the two central peaks depends on the attenuation, while others do not, suggesting the presence of at least two different radical species, the concentration of which depends on the polymerization time. Experiments were then followed at two different powers over time (Figures 8 and 9). By comparison, it is clear that although an increase in the concentration in one of the species with

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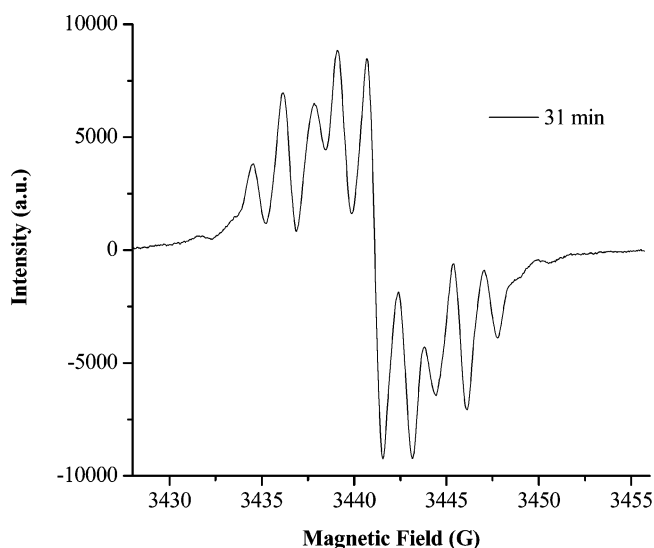
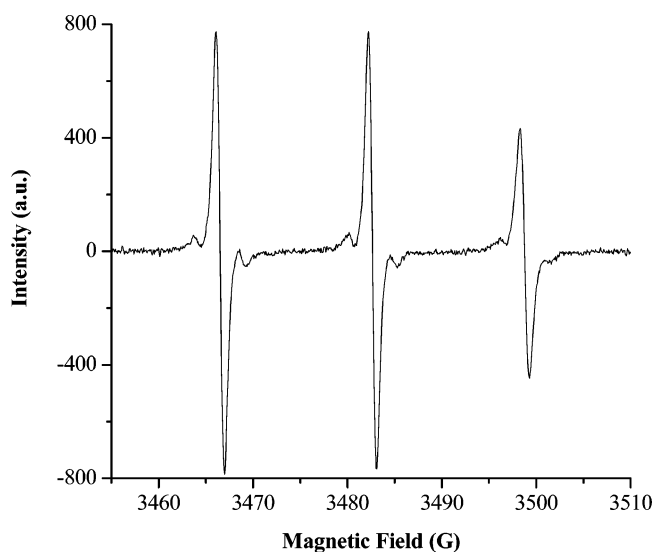**FIGURE 5.** EPR spectrum of poly(1,2-bis(phenylethynyl)-benzene) at 200 °C.

FIGURE 6. EPR spectrum of poly(1,2-bis(phenylethynyl)-benzene) at 200 °C in the presence of *N-tert*-butyl-α-phenyl-nitrone.

time is measured, the ratio of the two central peaks remains constant upon changing the attenuation. The intermediate of the reaction could be a symmetric diradical, or it could be a nonsymmetric diradical due to the polymerization of only one branch. An unambiguous spectral simulation is not reasonable at this time due to the presence of too many species.

Polymerization of 3,3′,4,4′-tetra(phenylethynyl)biphenyl (monomer **5**, Scheme 1) was performed at 210 °C (Figure 10). The spectrum exhibits unresolved hyperfine splittings and is comparable to that observed for monomer **2**. Only 1,2-bis(phenylethynyl)benzene gives distinctive peaks due to a symmetrical environment. On the contrary, with monomers **1−5**, the two radicals do not have exactly the same environment.

Kinetic data were obtained by using double integration of the first derivative spectra, while radical concentrations were normalized against time. The radical concen-
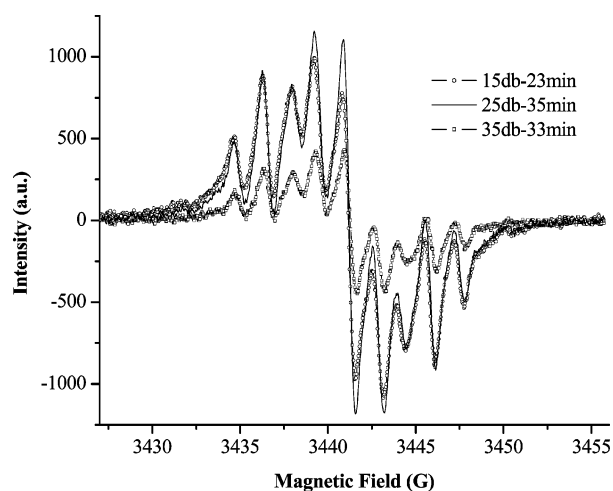

FIGURE 7. EPR spectra of poly(1,2-bis(phenylethynyl)ben-zene) at 210 °C at different attenuation.
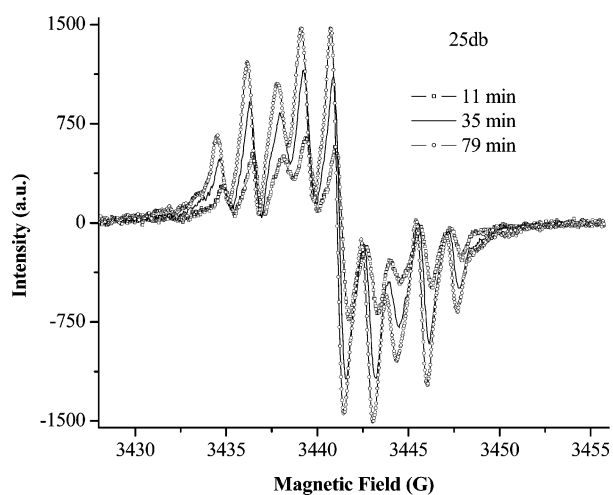

FIGURE 8. EPR spectra of poly(1,2-bis(phenylethynyl)ben-zene) at 210 °C with an attenuation of 25 db.
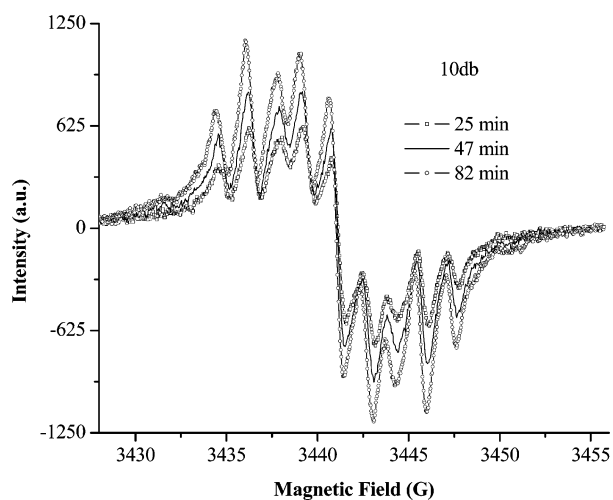

FIGURE 9. EPR spectra of poly(1,2-bis(phenylethynyl)ben-zene) at 210 °C with an attenuation of 10 db.

tration derived from BODA monomers follow a first-order rate expression as described previously using calorimetric techniques.[5] For monomers **1** and **2**, the rate constants
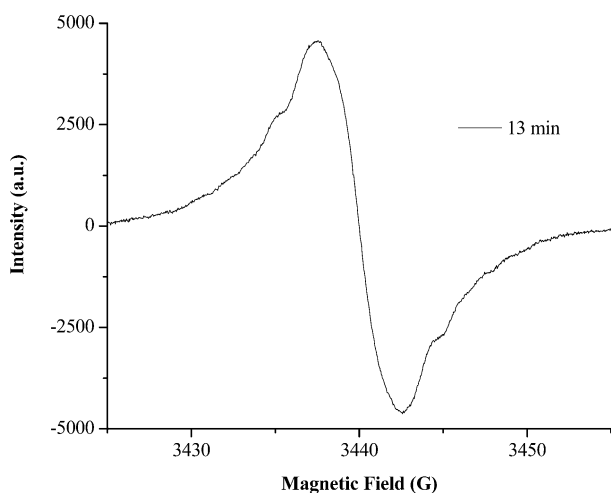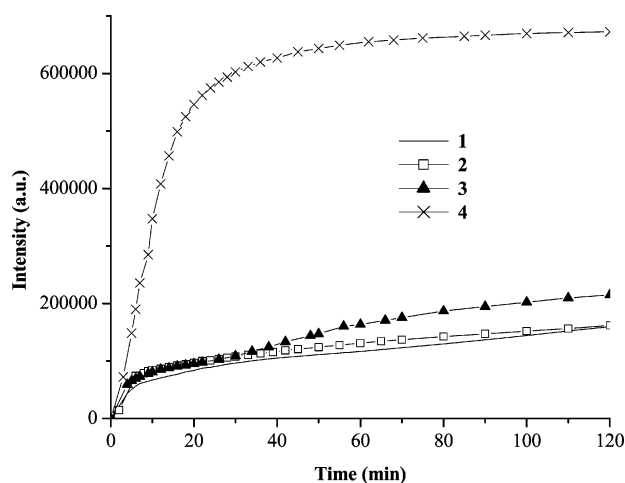
FIGURE 10. EPR spectrum of **poly-5** at 210 °C.

FIGURE 11. Kinetic plots for BODA polymerization at 210 °C.

were calculated to be 4.7×10^{-4} and 2.3×10^{-4} s^{-1} by EPR, respectively, compared to 4.1×10^{-5} and 2.8×10^{-5} s^{-1} by DSC, respectively.[5] These values are reasonably close at this stage of error analysis for the EPR data, and a more rigorous evaluation of the kinetic data will be the subject of another report. First and foremost, the study of BODA monomers **1** and **2** clearly proves that polymerization of monomers with different spacers ($-$O$-$, C(CF$_3$)$_2$) and with the same terminal group (Ph, Scheme 1) does not show significant differences, which agrees well with our earlier report (Figure 11).[5,11] It also appears that the terminal group plays an important role on the *trans*-alkyne distance and also a significant effect on the overall polymerization rate. The rate of polymerization is significantly increased when pyridine replaces phenyl as the terminal group. This is presumably due to the electron-withdrawing nature of pyridine, which leads to less steric repulsion of the incoming π-orbital in the proposed cyclization transition state.[12,13] The increased rate with thiophene as a terminal group provides additional sup-
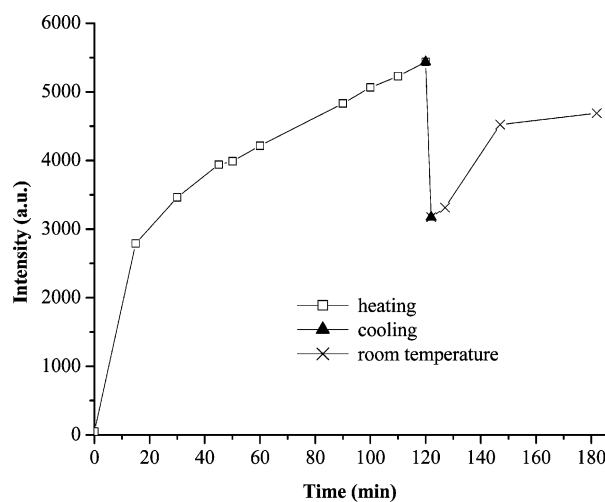

FIGURE 12. Long-lived radical species from monomer **1** after 200 °C for 2 h.

port for this hypothesis. Thus, a larger terminal group will increase the interalkyne distance and decrease the rate of cyclization.

Kinetic and lifetime data of long-lived radicals were also studied by EPR.[14,15] The radicals seem to be very stable and EPR signals could be observed even after three weeks at room temperature. Monomer **1** was heated to 200 °C for 120 min and then cooled to 27 °C (Figure 12) where after 1 h at room temperature, radicals are still present; moreover, their concentration increases significantly for 20 min and remains for at least three weeks for monomers **1**–**4**. The same experiment was repeated for monomer **2** as illustrated in Figure 13 (see Supporting Information).

Radical species involved in Bergman cyclopolymerization of bis-*ortho*-diynyl arenes have been detected by EPR spectroscopy. Kinetic studies clearly indicate that terminal groups play an important electronic and steric role on the polymerization rate. However, spacer groups do not significantly affect the kinetics. Unusual long-lived aromatic radical species were detected for several weeks at room temperature.

Supporting Information Available: Experimental details, structure of 1,2-bis(phenylethynyl)benzene, and Figure 13 showing a graph of the long-lived radical species from monomer **2** after 200 °C for 2 h. This material is available free of charge via the Internet at http://pubs.acs.org.

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