580 *Chem. Mater.* **2000,** *12,* 580−585

Preparation and EPR Spectroscopic Investigation of Conjugated Oligomers Containing Semiquinone Repeat Units

David A. Shultz* and Martha G. Hollomon[†]

Department of Chemistry, North Carolina State University,
Raleigh, North Carolina 27695-8204

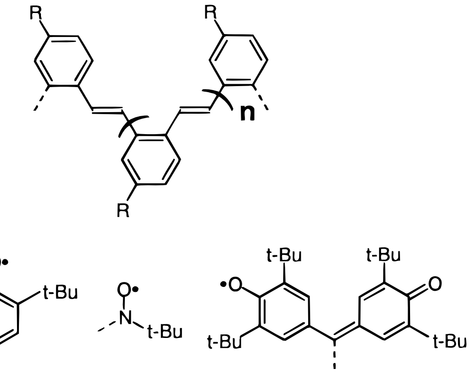
Received November 9, 1999. Revised Manuscript Received December 20, 1999

Three protected catechol-containing conjugated oligomers have been prepared using Pd-mediated coupling reactions. Two of the oligomers are poly[*o*-phenylenevinylene] type while the other is poly[*o*-phenyleneethynylene] type. One of the poly[*o*-phenylenevinylene]-type oligomers is regioregular while the other is regiorandom. The repeat units can be deprotected and oxidized to yield orthoquinone groups, which were subsequently reduced electrochemically to yield paramagnetic semiquinone repeat units. At spin concentrations greater than $\sim$0.25 per repeat unit, precipitation occurs preventing preparation of oligomers with greater spin concentrations using electrochemical methods. The frozen solution EPR spectra for all of the soluble semiquinone-containing oligomers exhibit fine structure, indicating the existence of high-spin ($S > {}^1/_2$) states that arise from exchange coupling (J) of semiquinone groups through the oligomer backbone. Consistent with the π-connectivity of two of the oligomers, the intensities of their EPR signals vary linearly with inverse absolute temperature suggesting $J \geq 0$. Unexpectedly, the same result was obtained for the regiorandom oligomer for which antiferromagnetic coupling was expected. The latter result is explained by the low-spin concentration.

Introduction

Organic Polymers as Polyradicals. The preparation of organic polymers with stable, paramagnetic repeat units has produced several novel materials. Nishide, Lahti, Dougherty, and several other groups reported the preparation of a variety of poly[*o*-phenylenevinylene] (PoPV), poly[*o*-phenyleneethynylene] (PoPE), and other organic polymers with paramagnetic repeat units, three of which are shown in Scheme 1.[1−25] The first two examples in Scheme 1 have delocalized electronic structures due to the positioning of radical atoms

Scheme 1. Paramagnetic Phenylenevinylene Polymers



---

* To whom correspondence should be addressed. E-mail: shultz@chemdept.chem.ncsu.edu. Facsimile: (919) 515-8920. Voice: (919) 515−6972. Web: http://www2.ncsu.edu/ncsu/chemistry/das.html.

[†] Current address: Senior Research Chemist, Hercules Inc., Wilmington, DE 19808-1599.

(1) Misurkin, I. A.; Ovchinnikov, A. A. *Russ. Chem. Rev. (Engl. Transl.)* **1977**, *46*, 967.

(2) Kamachi, M.; Akimoto, H.; Mori, W.; Kishita, M. *Polym. J.* **1984**, *16*, 23.

(3) Nishide, H.; Yoshioka, N.; Inagaki, K.; Tsuchida, E. *Macromolecules* **1988**, *21*, 3119.

(4) Kahn, O. *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*; Kluwer Academic Publishers: Netherlands, 1990.

(5) Nishide, H.; Yoshioka, N.; Kaneko, T.; Tsuchida, E. *Macromolecules* **1990**, *23*, 4487.

(6) Abdelkader, M.; Drenth, W. *Chem. Mater.* **1991**, *3*, 598.

(7) Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 9803−9810.

(8) Kaisaki, D. A.; Chang, W.; Dougherty, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 2764.

(9) Kamachi, M. *Polym. News* **1992**, *17*, 198.

(10) Miura, Y.; Inui, K.; Yamaguchi, F.; Inoue, M.; Teki, Y.; Takui, T.; Itoh, K. *J. Polym. Sci., A.* **1992**, *30*, 959.

(11) Dougherty, D. A.; Jacobs, S. J.; Silverman, S. K.; Murray, M.; Shultz, D. A.; West, A. P., Jr.; Clites, J. A. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 289−304.

(12) Murray, M. M.; Kaszynski, P.; Kaisaki, D. A.; Chang, W.; Dougherty, D. A. *J. Am. Chem. Soc.* **1994**, *116*, 8152.

(13) Kaneko, T.; Toriu, S.; Kuzumaki, Y.; Nishide, H.; Tsuchida, E. *Chem. Lett.* **1994**, 2135.

(14) Kaneko, T.; Toriu, S.; Tsuchida, E.; Nishide, H.; Yamaki, D.; Maruta, G.; Yamaguchi, K. *Chem. Lett.* **1995**, 421.

(15) Tanaka, K.; Ago, H.; Yamabe, T. *Synth. Met.* **1995**, *72*, 225−229.

(16) Nishide, H. *Adv. Mater.* **1995**, *7*, 937.

(17) Nishide, H.; Kaneko, T.; Nii, T.; Katoh, K.; Tsuchida, E.; Yamaguchi, K. *J. Am. Chem. Soc.* **1995**, *117*, 548.

(18) Bushby, R. J.; Ng, K. M. *Chem Commun.* **1996**, 659−660.

(19) Tyutyulkov, N. *Pure Appl. Chem.* **1996**, *68*, 345.

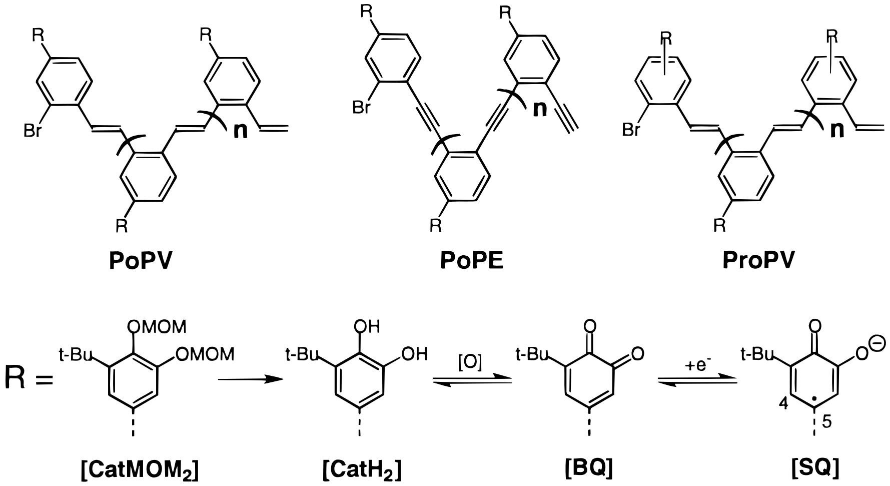
(20) Nishide, H.; Kaneko, T.; Toriu, S.; Kuzumaki, Y.; Tsuchida, E. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 499.

(21) Nishide, H.; Kaneko, T.; Nii, T.; Katoh, K.; Tshuchida, E.; Lahti, P. *J. Am. Chem. Soc.* **1996**, *118*, 9695.

(22) Takahashi, M.; Nishide, H.; Tsuchida, E.; Lahti, P. M. *Chem. Mater.* **1997**, *9*, 11−13.

10.1021/cm9907155 CCC: $19.00

Scheme 2. Quinone-Containing Polymers



with positive spin densities in locations that allow conjugation with the π-system of the polymer chain. Moreover, because of the head-to-tail arrangement of paramagnetic repeat units, nondisjoint, non-Kekulé structures result, and the polymers behave as high-spin ground-state species.[26−28] In other words, the poly[phenylenevinylene] chain serves as the "ferromagnetic coupling unit." [29]

A particularly attractive feature of the PoPV/PoPE design is that connectivity-controlled high-spin coupling persists even in the presence of defects (diamagnetic repeat units) because of the conjugated polymer backbone. Along these lines, Rajca designed and characterized beautiful discrete macrocyclic/polycyclic molecular structures that resist diamagnetic defects.[30−36]

The Utility of Semiquinone Repeat Units. In this study, we wish to further the PoPV/PoPE design to include a paramagnetic, *chelating* ligand as the spin-containing unit as shown in Scheme 2. Semiquinones can be prepared from orthoquinones or catecholates by a one-electron reduction or a one-electron oxidation, respectively. Both calculations and experiment indicate significant spin density on carbons 4 and 5,[37,38] and we have taken advantage of this spin distribution to create high-spin molecules with one or more semiquinone groups.[39−46]

The chelating ability of the semiquinone ligand is widely documented, and a multitude of transition metals complexes has been prepared.[47,48] Semiquinones are unique in their tendency for certain intramolecular electron transfer/spin-crossover equilibria, processes known as valence tautomerism that can lead to bistability and therefore switching behavior.[49−51] In addition, semiquinones often strongly magnetically couple to paramagnetic transition metal ions.[52] Thus, semiquinone-containing polymers could be used to introduce a variety of metal ions into the material and create polymeric materials with new properties. Finally, metal ions can serve to cross-link polymer chains and extend magnetic interactions, thus providing a basis for new molecule-based amorphous ferrimagnets.

Initially, we chose electrochemical methods to prepare the semiquinone groups because the reduction can be carried out in the presence of tetraalkylammonium cation, which is not capable of being coordinated. This choice should (1) allow a higher degree of reduction since alkali metal semiquinones aggregate and precipitate, and (2) decrease the possibility of our EPR results being due to metal ion-induced aggregation.[41,53] In this report,

---

(23) Lu, H. S. M.; Berson, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 1428−1438.

(24) Hayashi, H.; Yamamoto, T. *Macromolecules* **1997**, *30*, 330−332.

(25) Kaneko, T.; Tatsumi, H.; Nishide, H. *J. Polym. Sci., Part A, Polym. Chem.* **1999**, *37*, 189.

(26) Berson, J. A. *Diradicals*; Wiley: New York, 1982.

(27) Rajca, A. *Chem. Rev.* **1994**, *94*, 871.

(28) Shultz, D. A. In *Magnetic Properties of Organic Materials*; Lahti, P., Ed.; Marcel Dekker: New York, 1999.

(29) Jacobs, S. J.; Shultz, D. A.; Jain, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744.

(30) Rajca, A.; Utamapanya, S. *J. Am. Chem. Soc.* **1993**, *115*, 10688−10694.

(31) Rajca, A.; Rajca, S.; Padmakumar, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2091−2093.

(32) Rajca, A. *Adv. Mater.* **1994**, *6*, 605−607.

(33) Rajca, A.; Rajca, S.; Desai, S. R. *J. Am. Chem. Soc.* **1995**, *117*, 806−816.

(34) Rajca, S.; Rajca, A. *J. Am. Chem. Soc.* **1995**, *117*, 9172−9179.

(35) Rajca, A.; Lu, K.; Rajca, S. *J. Am. Chem. Soc.* **1997**, *119*, 10335−10345.

(36) Rajca, A.; Wongsriratanakul, J.; Rajca, S. *J. Am. Chem. Soc.* **1997**, *119*, 11674−11686.

(37) Prabhananda, B. S. *J. Chem. Phys.* **1983**, *79*, 5752.

(38) Wheeler, D. E.; Rodriquez, J. H.; McCusker, J. K. *J. Phys. Chem. A* **1999**, *103*, 4101−4112.

(39) Shultz, D. A.; Boal, A. K.; Driscoll, D. J.; Kitchin, J. R.; Tew, G. N. *J. Org. Chem.* **1995**, *60*, 3578.

(40) Shultz, D. A.; Boal, A. K.; Driscoll, D. J.; Farmer, G. T.; Hollomon, M. G.; Kitchin, J. R.; Miller, D. B.; Tew, G. N. *Mol. Cryst. Liq. Cryst.* **1997**, *305*, 303−310.

(41) Shultz, D. A.; Boal, A. K.; Campbell, N. P. *Inorg. Chem.* **1998**, *37*, 1540−1543.

(42) Shultz, D. A.; Boal, A. K.; Lee, H.; Farmer, G. T. *J. Org. Chem.* **1998**, *63*, 9462−9469.

(43) Shultz, D. A.; Farmer, G. T. *J. Org. Chem.* **1998**, *63*, 6254−6257.

(44) Shultz, D. A.; Bodnar, S. H. *Inorg. Chem.* **1999**, *38*, 591−594.

(45) Shultz, D. A.; Lee, H.; Fico, R. M., Jr. *Tetrahedron* **1999**, *55*, 12079−12086.

(46) Caneschi, A.; Dei, A.; Lee, H.; Shultz, D. A.; Sorace, L. Submitted for publication.

(47) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

(48) Pierpont, C. G.; Lange, C. W. *Prog. Inorg. Chem.* **1994**, *41*, 331.

(49) Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951−4957.

(50) Adams, D. M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 11515−11528.

(51) Gütlich, P.; Dei, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *37*, 22734-2736.

(52) Gatteschi, D.; Dei, A. *Inorg. Chim. Acta* **1992**, *198−200*, 813.

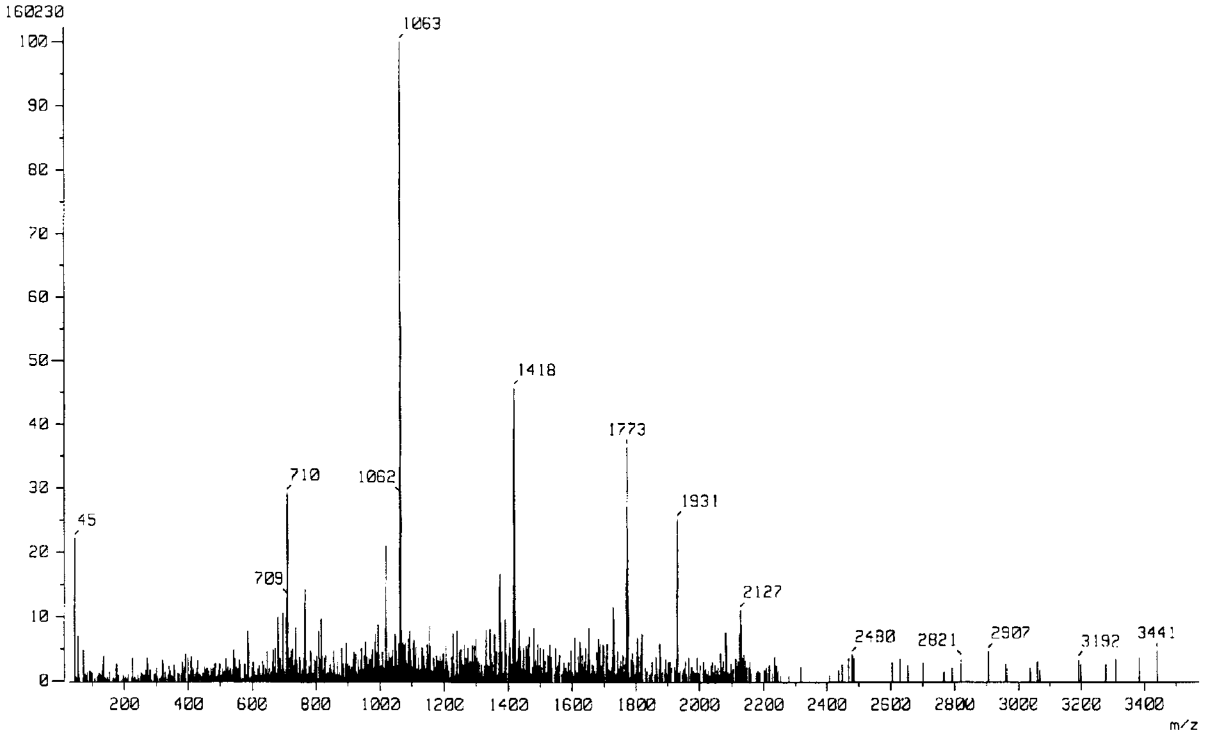


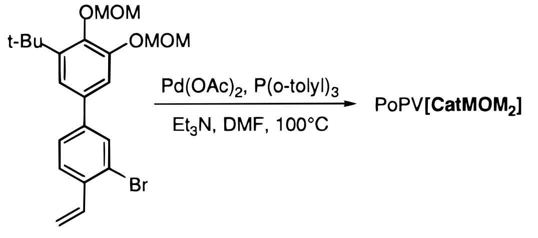
Figure 1. Field desorption mass spectrum of PoPV**[CatMOM$_2$]** polymerized at [monomer] = 0.3 M.

we are interested in demonstrating the creation of semiquinone repeat units on conjugated oligomer backbones, as opposed to the preparation of high molecular weight materials. Moreover, the chelating ability of semiquinones allows the preparation of extended solids without the necessity of high molecular weight polymer.

Results and Discussion

Monomer syntheses are described in Supporting Information.

PoPV[CatMOM$_2$] and ProPV[CatMOM$_2$] Syntheses. Monomer **14** was polymerized via the Heck reaction using Pd(OAc)$_2$ as the catalyst in the presence of tri-*o*-tolylphosphine and triethylamine in DMF at 100 °C:



14

In our hands, this Heck polymerization repeatedly produced low molecular weight material, despite several reports of higher molecular weight polymers of similar monomers.[13,14,16,17,20−22,25] PoPV**[CatMOM$_2$]** was purified by SE chromatography and precipitated from methanol to produce an amorphous yellow powder. Gel permeation chromatography (GPC, polystyrene standards) gave $\bar{M}$ of 1300−2700 with 1.4−1.7 as the polydispersity ($\bar{M}_w/\bar{M}_n$). This molecular weight ($\bar{M}_w$) corresponds to a degree of polymerization of 3−6 monomeric units. The MOM-protected PoPV was a yellowish powder, which was soluble in DMF, CH_2Cl_2, $CHCl_3$, toluene, THF, and acetone, but insoluble in alcohols.

The FTIR spectrum of PoPV**[CatMOM$_2$]** displays peaks at 980 cm^{-1}, indicating an out-of-plane bending mode of the *trans*-vinylene bond.[54] FT-Raman spectrum shows peaks at 1623 and 1598 cm^{-1} associated with C=C bond stretch in the vinyl and aromatic rings of PoPV, respectively.

The UV−vis spectrum of PoPV**[CatMOM$_2$]** shows an absorption maximum (λ_{max}) at 298 nm in $CHCl_3$, while the fluorescence emission spectrum shows a maximum at 452 nm ($\lambda_{excitation}$ = 270 nm) which is consistent with the *trans*-stilbene moiety.

When the monomer was polymerized at a concentration less than or equal to 0.3 M, field desorption mass spectrum (FDMS) shows evidence for a mixture of cyclic oligomers, since the masses observed are M-HBr as seen in Figure 1.[55] All attempts at isolating cyclic oligomers were unsuccessful. The ^{1}H NMR spectrum of PoPV**[CatMOM$_2$]** polymerized in dilute solution lacks end group signals, which should be evident for $\bar{M}_w$ of ~2000. FDMS of the monomer **15** shows the distinctive bromine pattern: the molecular ion, M$^+$, for $C_{22}H_{27}O_4{}^{79}Br$ appeared at *m*/*z* 434 and that for $C_{22}H_{27}O_4{}^{81}Br$ at *m*/*z* 436. When the monomer was polymerized at higher monomer concentration (3 M), no cyclic oligomers were observed in the FDMS.

ProPV**[CatMOM$_2$]** was prepared by Heck polymerization between difunctionalized monomers **24** and **25**

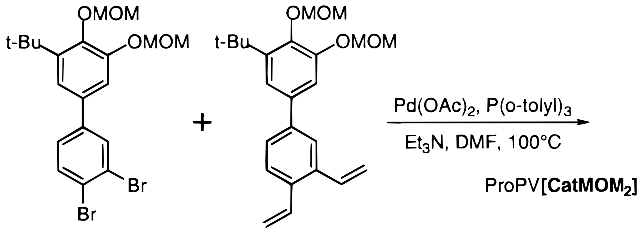
---

(53) Brown, M. A.; McGarvey, B. R.; Ozarowski, A.; Tuck, D. G. *J. Am. Chem. Soc.* **1996**, *118*, 9691−9694.

(54) Heitz, W. *Pure Appl. Chem.* **1995**, *67*, 1951−1964.

(55) Cyclic phenyleneethynylene oligomers have been reported, see: Baldwin, K. P.; Simons, R. S.; Rose, J.; Zimmerman, P.; Hercules, D. M.; Tessier, C. A.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1257.

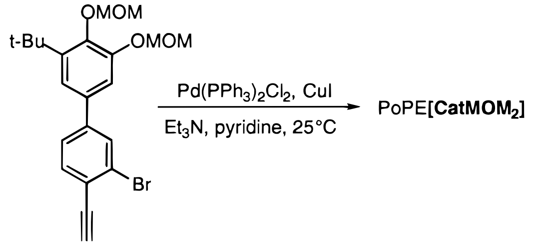
in DMF (0.3 M) at 100 °C using Pd(OAc)$_2$:



24 **25**

ProPV**[CatMOM$_2$]** was purified by SE chromatography and precipitated from methanol to produce an amorphous orange powder. GPC gave a $\bar{M}_n$ of 1300−3200 and a 1.6−2.0 polydispersity ($\bar{M}_w/\bar{M}_n$) was measured. Again, low molecular weight material was produced, with a degree of polymerization (DP) corresponding to the molecular weight is 3−7 monomeric units. ProPV**[CatMOM$_2$]** had similar solubilities as PoPV**[CatMOM$_2$]**.

PoPE[CatMOM$_2$] Synthesis. Polymerization of monomer **15** via the Sonogashira reaction[56−58] using $(PPh_3)_2PdCl_2$ as the catalyst, CuI as the cocatalyst in a 1:1 triethylamine:pyridine solution gave PoPE**[CatMOM$_2$]** in high yield:



15

PoPE**[CatMOM$_2$]** was purified by SE chromatography and precipitated from methanol to gave an orange powder. Gel permeation chromatography (GPC, polystyrene standards, mobile phase 100% THF) was used to determine the molecular weight and molecular weight distribution. During the first polymerizations, we obtained a molecular weight, $\bar{M}_w$, of 9000−11000. This molecular weight corresponds to a degree of polymerization of 22−25 monomeric units—significantly greater than the Heck polymerization of our vinylene monomers. Unfortunately, we could not obtain high molecular weights for the PoPV monomers. To compare structure−property relationships between these oligomers, and since high molecular weights are not our current goal, we desired a lower molecular weight PoPE material. Thus, the polymerization time was decreased from 18 to 6 h and a molecular weight of ~3000 was obtained.

The UV−vis spectrum of PoPE**[CatMOM$_2$]** shows an absorption maximum at 298 nm in CHCl$_3$, while the fluorescence emission spectrum of PoPE**[CatMOM$_2$]** shows a maximum at 452 nm. The FT-Raman spectrum of PoPE**[CatMOM$_2$]** shows a peak at 2209 cm^{-1} associated an internal carbon−carbon triple-bond stretch.

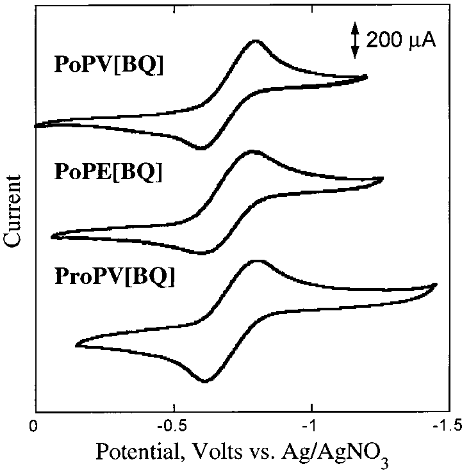
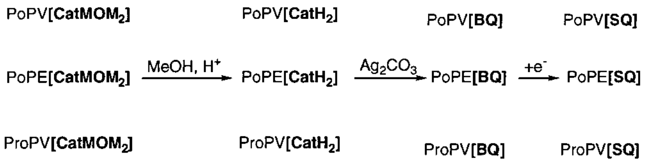


Figure 2. Cyclic voltammograms of orthoquinone-containing oligomers in THF.

Deprotection and Oxidation of Oligomers. Deprotections of PoPV-, ProPV-, and PoPE**[CatMOM$_2$]** to give the corresponding catechol oligomers as red powders were marked by the appearance of strong OH stretches in the IR spectra (~3500 cm^{-1}). Oxidations of the catechol groups were affected using Fétizon's reagent[59] to give the orthoquinone oligomers as red-brown powders.



The sharp peaks near 1650 cm^{-1} associated with an orthoquinone and the disappearance of the catechol OH stretches near 3500 cm^{-1} indicates the formation of the orthoquinone group.

Electrochemistry and Polyradical Formation. Cyclic voltammograms (CV) were recorded for the orthoquinone oligomers PoPV**[BQ]**, PoPE**[BQ]**, and ProPV**[BQ]** in THF at room temperature with tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte, and are shown in Figure 2. The CVs reveal two distinct reduction processes, but only the first are shown. These quasireversible couples correspond to the orthoquinone/semiquinone redox processes and are centered near −0.7 V vs Ag/AgNO$_3$. The second reductions that occur near −1.7 V vs Ag/AgNO$_3$ are chemically irreversible and correspond to semiquinone/catecholate couples.[60,61]

The polyradicals were formed by controlled-potential coulometry at ca. −1.1 V vs Ag/AgNO$_3$ at room temperature in a glovebox. Aliquots of the dark green solutions for EPR spectral analysis were taken from the electrochemical cell at set intervals. Unfortunately at ~25%

---

(56) Miura, Y.; Ushitani, Y.; Inui, K.; Teki, Y.; Takui, T.; Itoh, K. *Macromolecules* **1993**, *26*, 3698−3701.

(57) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467−4470.

(58) Sonogashira, K. *Coupling Reactions Between sp2 and sp Carbon Centers*; Pergamon Press: Oxford, 1991; Vol. 3.

(59) Balogh, V.; Fétizon, M.; Golfier, M. *J. Org. Chem.* **1971**, *36*, 1339.

(60) Stallings, M. D.; Morrison, M. M.; Sawyer, D. T. *Inorg. Chem.* **1981**, *20*, 2655−2660.

(61) Jones, S. E.; Chin, D. H.; Sawyer, D. T. *Inorg. Chem.* **1981**, *20*, 2457−4262.

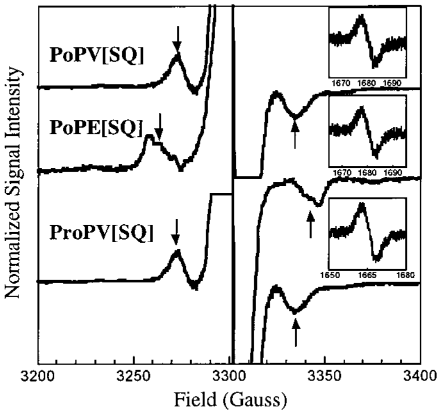


Figure 3. EPR spectra of semiquinone-containing oligomers at 77 K in THF.

of the total number of coulombs passed, the semiquinone oligomers become insoluble in THF despite our use of noncoordinating counterions, demonstrating the limit of bulk electrolysis for the generation of the semiquinones. This insolubility is the result of the formation of salts and can be remedied easily by using soluble metal complexes in place of tetrabutylammonium. There are a multitude of possibilities for soluble metal complexes, including metal tris(cumenyl-methylpyrazolyl)borate),[62] which we used to prepare bis(semiquinone) complexes.[44,46,63] Such efforts will be the focus of future reports.

EPR and VT-EPR Spectra of the Polyradicals. Frozen solution EPR spectroscopy is commonly used to detect unpaired electrons for the study of $S > {}^1/_2$ states in polyradicals.[64−66] In favorable cases, variable-temperature (VT) EPR spectroscopy can be used to estimate the exchange parameter, J ($2J$ is the singlet−triplet gap in a biradical for example), when the coupling is *antiferromagnetic*. For both ferromagnetic coupling and for $J = 0$, a straight line is obtained when EPR signal intensity is plotted against inverse temperature.[67]

The room-temperature EPR spectra of all of the THF-soluble portions of the semiquinone oligomers are single lines, exhibiting unresolved hyperfine structure. However, as shown in Figure 3, the frozen solution spectra of PoPV**[SQ]**, PoPE**[SQ]**, and ProPV**[SQ]** exhibit both fine structure in the $\Delta m_s = 1$ region and show $\Delta m_s = 2$ transitions characteristic of high-spin ($\boldsymbol{S} > {}^1/_2$) states in addition to strong monoradical signals at $g \approx 2$ (~3300 G). We assign the signals marked with arrows in Figure 3 to the X/Y transitions of high-spin species. If these signals are due primarily to biradicals, consistent with both spin count and molecular weight, the zero-field-splitting parameters, $|D/hc|$ are ~0.005 cm^{-1}. From a point−dipole perspective this gives an interelectronic separation of ~8 Å,[68] which is a reasonable value for our oligomers based on molecular models. The appearance of $\Delta m_s = 3$ transitions for triradical or higher spin states were not observed.

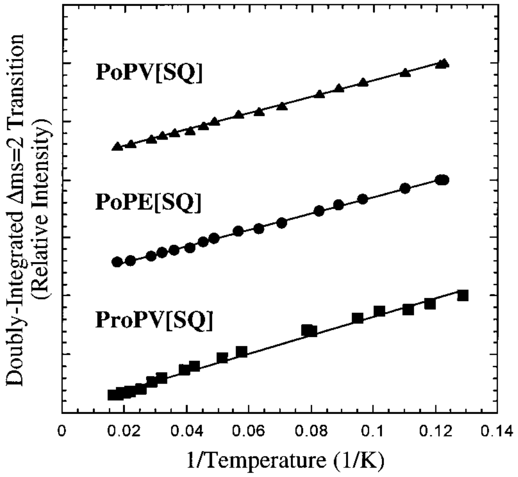


Figure 4. Curie plots for doubly integrated $\Delta m_s = 2$ signals of semiquinone-containing oligomers.

The results of VT-EPR experiments are shown in Figure 4. Plots of the temperature dependences of the doubly integrated $\Delta m_s = 2$ signals are linear within experimental error, suggesting $J \geq 0$. It is noteworthy that ProPV**[SQ]** shows a linear Curie plot despite the lack of a repeated head-to-tail motif along the oligomer chain. This is readily explained by the low spin concentration. For a DP of ~6 and a spin concentration of ~0.25, the average chain has less than two unpaired electrons. However, for those chains that are biradicals, $S = 1$ triplets will exhibit EPR spectra while the $S = 0$ singlets may not if the antiferromagnetic J-coupling is large compared to kT. An alternative is that the antiferromagnetic coupling is weak, and the resulting Curie plot is linear. Oligomers having more than two unpaired electrons apparently do not constitute a large fraction of the material. We believe that we were not able to produce a large enough concentration of semiquinones along the oligomer backbone to observe the effects of antiferromagnetic coupling.

Conclusions

Conjugated oligomers with catechol, orthoquinone, and semiquinone repeat units have been prepared using Pd-mediated coupling reactions. The DPs for the PoPV-type oligomers (DP = 4−7) were lower than the PoPE-type polymer (DP = 22−25). Mass spectral evidence for cyclic oligomer formation during the concentrated polymerization of monomer **14** was presented.

CV of the orthoquinone-containing oligomers showed redox activity analogous to that of nonpolymeric orthoquinones, and controlled-potential coulometry provided soluble semiquinone-containing oligomers having spin concentrations of ~0.25. Unfortunately, continued electrolysis resulted in precipitation. EPR spectra of frozen solutions of the semiquinone oligomers are consistent with $S > {}^1/_2$ species. Curie plots for all the paramagnetic materials are linear, consistent with $J \geq 0$. The unanticipated linear Curie plot for ProPV**[SQ]** is readily explained by the low-spin concentration. Efforts are underway toward preparation of soluble metal complexes of these materials.

---

(62) Ruf, M.; Noll, B. C.; Groner, M. D.; Yee, G. T.; Pierpont, C. G. *Inorg. Chem.* **1997**, *36*, 4860−4865.

(63) Shultz, D. A.; Bodnar, S. H.; Kumar, R. K.; Kampf, J. W. *J. Am. Chem. Soc.* **1999**, *121*, 10664−10665.

(64) Teki, Y.; Takui, T.; Itoh, K. *J. Chem. Phys.* **1988**, *88*, 6134.

(65) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

(66) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; Chapman and Hall: New York, 1986.

(67) *The Chemistry of Quinonoid Compounds*; Berson, J. A., Ed.; John Wiley & Sons: New York, 1988; Vol. II, p 482.

(68) Keana, J. F.; Dinerstein, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 2808.

Experimental Section

General and synthetic details and spectral data can be found in the Supporting Information.

General Procedure for Electrochemical Reduction of Quinone Oligomers. In the glovebox, a 2 mM solution of quinone oligomer in THF containing 100 mM tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was subjected to controlled potential coulometry at −1.1 V vs Ag/$AgNO_3$. Aliquots were removed by pipet for examination by EPR spectroscopy.

Acknowledgment. This work was funded by the National Science Foundation (CHE-9634878). D.A.S. also thanks the Camille and Henry Dreyfus Foundation for a Camille Dreyfus Teacher−Scholar Award. Mass spectra were obtained at the Mass Spectrometry Laboratory for Biotechnology. Partial funding for the Facility was obtained from the North Carolina Biotechnology Center and the National Science Foundation. The MALDI-TOF mass spectrometer was funded in part by the North Carolina Biotechnology Center.

Supporting Information Available: Synthetic discussion and details and spectral data (22 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

CM9907155