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Water-Soluble Rigid-Rod Polyelectrolytes: A New Self-Doped, Electroactive Sulfonatoalkoxy-Substituted Poly(*p*-phenylene)

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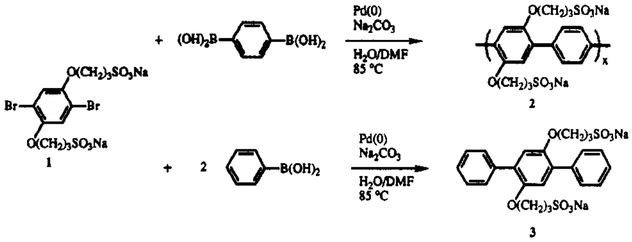
Introduction. The synthesis of polyphenylenes[2] has attracted a great amount of attention due to the rigid-rod character of the backbone, high thermal stability of the neutral polymers, and ability of the π system to be redox doped to high levels of electrical conductivity. As an electroactive polymer, research on poly(*p*-phenylene) (PPP) served as an impetus for the study of a broad variety of aromatic polymers.[3] The direct synthesis of polyphenylenes from benzene has been accomplished by a variety of methods; however, most routes lead to highly insoluble materials containing irregular structures which are quite difficult to characterize. The preparation of polyphenylene films containing exclusively 1,4-linkages has been attempted by the electroreduction of dihalobenzenes in the presence of a nickel catalyst.[4,5] Again, the insolubility of the polymer products made the unambiguous characterization of their structures impossible.

In order to increase the degree of polymerization, induce solubility, and obtain polyphenylenes with well-defined structures, the polymerization of substituted benzenes has received attention. Rehahn et al.[6] utilized the palladium-catalyzed cross coupling of arylboronic acids with aryl bromides in the presence of aqueous base[7,8] for the synthesis of a number of alkyl-substituted PPP's with degrees of polymerization of approximately 30–50. A major advantage of this method, which is commonly termed Suzuki coupling, is the high tolerance of the reaction to functional groups and water. Subsequently, a water-soluble catalyst system was developed, enabling the homogeneous polymerization of water-soluble monomers.[9] Novak and Wallow have utilized this catalyst system with Suzuki coupling to produce water-soluble, carboxy-substituted poly(*p*-phenylenes)[10] with an average of one carboxylic acid group for every two phenylene rings. Using zero-valent nickel, Kaeriyama et al.[11,12] have synthesized poly(2-carboxyphenylene-1,4-diyl) containing one carboxylic acid group per ring. This polymer is soluble in aqueous base and could be converted to PPP by treatment with CuO. During revision of this manuscript, a *p*-phenoxycarboxymethylene-substituted PPP was reported as a rigid-rod polyelectrolyte.[13]

In this study, a water-soluble, electroactive, and electrically conductive, sulfonatoalkoxy-substituted poly(*p*-phenylene), poly[2,5-bis(3-sulfonatopropoxy)-1,4-phenylene-*alt*-1,4-phenylene] (PPP-$ORSO_3$), has been synthesized by the homogeneous Suzuki coupling method. The terminal sulfonate functionality induces water solubility to the rigid-rod backbone and serves as the charge-compensating dopant ion during redox switching. Thus, PPP-$ORSO_3$ is the first PPP-based "self-doped" conducting polymer,[14–17] The steric barriers to planarity of the ring system are reduced by the oxygen on the propoxy spacer groups relative to direct attachment of sulfonate, carboxylate, or alkyl groups to the poly(*p*-phenylene) backbone. We have previously demonstrated that alkoxy groups significantly lower the energy barriers to planarity of ring torsional angles in substituted phenylene–thiophene copolymers relative to alkyl pendants.[18,19] In addition, coupling of benzeneboronic acid with 1-bromo-2-methoxybenzene has been shown to proceed to high yields, indicating a minimal steric limitation to coupling of phenylenes with *o*-alkoxy groups.[20] Finally, the electron-donating nature of the alkoxy substituents serves to balance the greater steric distortions relative to the unsubstituted analog, giving PPP-$ORSO_3$ an electronic band gap (3.0 eV) identical with that of PPP.

Scheme 1



Results and Discussion. PPP-$ORSO_3$ (**2**) was synthesized by the reaction of 1,4-benzenediboronic acid and the disodium salt of 1,4-dibromo-2,5-bis(3-sulfonatopropoxy)benzene (**1**) as outlined in Scheme 1. At the same time, to assist in the spectroscopic identification of the target polymer, a terphenyl model compound, 1,4-diphenyl-2,5-bis(3-sulfonatopropoxy)benzene (**3**) was synthesized from **1** and phenylboronic acid. The absorption maximum in the optical spectrum of **3** in aqueous solution was found to be 3.9 eV (317 nm) which is interestingly equivalent to the value for terphenyl.[21] While the steric interactions of the alkoxy substituents force the molecule to be less planar than when unsubstituted and should cause a blue shift in the absorption, this effect is counterbalanced by the substituent's electron-donating behavior.

PPP-$ORSO_3$ was purified by dialysis of an aqueous solution using a 3500 g mol^{-1} cutoff membrane and characterized by both ^1H- and ^{13}C-NMR spectroscopies, along with elemental analysis (see the Experimental Section). The results are consistent with the polymer structure shown in Scheme 1. The polymer is composed exclusively of 1,4-linkages with no discrete peaks attributable to end groups evident. Elemental analyses, though somewhat low in S content, are consistent with a dihydrate per repeat unit structure and showed no Br present. While the detection limit for Br is 0.5%, this analysis did not show any color indicative of Br, which indicates the actual Br content is much lower than this limit. These results suggest that the polymer has a substantial degree of polymerization, though, at this time, it cannot be quantified. GPC analyses were attempted but led to strong absorption of the polymer on the columns from the aqueous phase. After thorough drying, a TGA under N_2 shows an onset of decomposition at *ca.* 250 °C. The polymer loses 30% of its mass between 300 and 350 °C and retains 60% of its mass at 800 °C. These TGA results are consistent with initial side-chain degradation from a highly thermally stable polymeric backbone. The wavelength maximum of the π to π^* absorption for the polymer in aqueous solution is red shifted 0.3 eV relative to the terphenyl model compound to 3.6 eV (344 nm) due to extended conjugation. This absorption maximum is quite close to that observed for poly(*p*-phenylene) (3.5 eV).[22]

Thin films of PPP-$ORSO_3$ on indium tin oxide (ITO) glass were prepared by spin coating from an aqueous solution and were found to be capable of both p-type and n-type doping. Similar to many conducting polymers with high redox potentials, cyclic voltammetry was not able to

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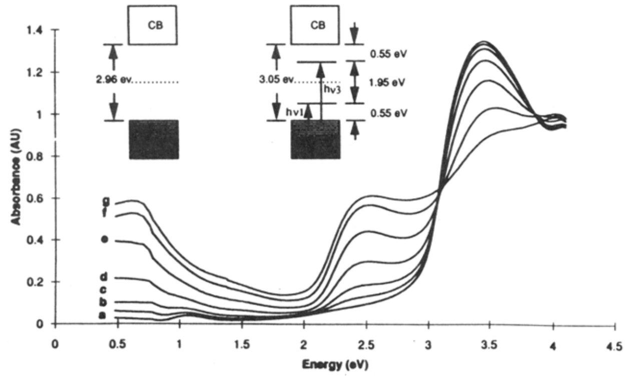

Figure 1. Optoelectrochemical spectra and band structure of poly[2,5-bis(3-sulfonatopropoxy)-1,4-phenylene-*alt*-1,4-phenylene] during electrochemical oxidation: (a) 0.0, (b) 0.90, (c) 0.95, (d) 1.00, (e) 1.05, (f) 1.10, (g) 1.15 V.

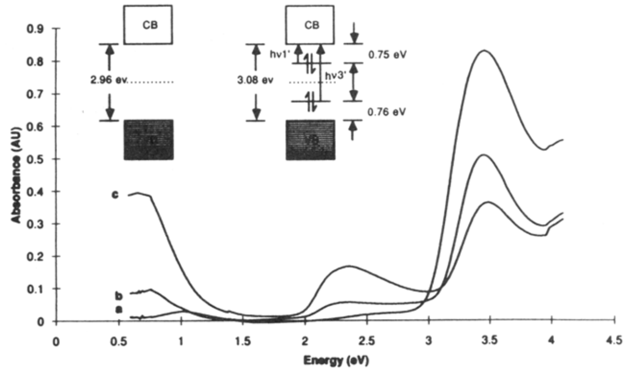

Figure 2. Optoelectrochemical spectra and band structure of poly[2,5-bis(3-sulfonatopropoxy)-1,4-phenylene-*alt*-1,4-phenylene] during electrochemical reduction: (a) −2.20, (b) −2.30, (c) −2.40 V.

resolve an oxidation peak. The cathodic dedoping peak was resolved at 0.62 V versus Ag wire and is close to the value obtained by Fauvarque for PPP in a similar electrolyte.[23] Upon electrochemical oxidation, the nearly transparent yellow neutral polymer film becomes brick red and significantly more opaque. The changes in the electronic band structure of the polymer during electrochemical oxidation were investigated using *in situ* optoelectrochemistry. Spectra were obtained from 2100 to 300 nm as a function of applied potential and are shown in Figure 1. The neutral polymer exhibits a single strong absorption with an onset (typically denoted as the electronic band gap) at 3.0 eV and a maximum at 3.5 eV. This is 0.1–0.2 eV lower in energy than the absorption observed for the polymer in solution and can be attributed to a solid-state effect which lowers the torsional angle between adjacent rings in aromatic polymers. The close correlation of the band gap of PPP-ORSO$_3$ with PPP suggests that the pendant sulfonatoalkoxy groups impart a similar effect on the polymer's ring torsional angles as seen previously for the thiophene–phenylene-linked polymers.[18,19]

During stepwise electrochemical oxidation, two additional potential-dependent absorptions are observed at 0.55 and 2.50 eV which are consistent with bipolaronic charge carriers, as demonstrated by the band structure inset in Figure 1. This band structure is quite similar to the one calculated for p-doped PPP by Bredas et al.[21,22] where the energy gap between the valence band and the first bipolaron band ($h\nu1$) is 0.56 eV. Experimentally, $h\nu1$ has been determined to be slightly larger (0.8–1.3 eV)[23–26] for p-doped PPP, indicative of a higher degree of distortion which may be due to Coulombic interactions between charge carriers. These interactions are expected to be largely screened in the case of PPP-ORSO$_3$ by the pendant anionic groups.

One of the characteristics of PPP's is their ability to be reversibly electrochemically reduced (n-type doped). Optoelectrochemistry of n-doped PPP-ORSO$_3$ has revealed a band structure consistent with negative charge carrier formation as shown in Figure 2. The intragap states are slightly farther from the band edges in the n-doped polymer than in the p-doped polymer, as illustrated in the figure inset, indicating a larger degree of distortion. This difference in band structure, and the low stability of the n-doped polymer, suggests that the electron-donating sulfonatoalkoxy substituents impart a greater electronic stabilizing effect on positive charge carriers compared to negative charge carriers.

In summary, we have synthesized the first water-soluble, electroactive, self-doped poly(*p*-phenylene) derivative that can be both p-type and n-type redox doped. The ability to utilize a variety of bis(boronic acids) in this polymerization with sulfonate containing aryl halides will lead to a high degree of structural control of the optoelectronic properties of these water-soluble polymers.

Experimental Section. Materials and Methods. 1,4-Benzenediboronic acid,[27] benzeneboronic acid,[28] and tris[(sulfonatophenyl)phosphine]palladium(0) trisodium salt[29,30] were synthesized according to previously published procedures.

NMR spectra were obtained on a Varian XL-200, 200-MHz NMR spectrometer. D$_2$O was used as solvent with deuterated acetone or dioxane as chemical shift standards. FT-IR spectra were obtained using a Biorad/Digilab FTS-40A spectrophotometer. UV–vis–near-IR spectra were obtained using a Varian Cary 5E spectrophotometer. TGA experiments were carried out under N$_2$ on a Perkin-Elmer 7 Series Instrument. Electrochemical studies were carried out using an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat. Cyclic voltammetric and optoelectrochemical experiments were performed as described previously[31] using a 0.1 M NaClO$_4$/acetonitrile electrolyte and ITO working, Pt counter, and Ag wire quasi-reference electrodes. The acetonitrile was distilled from P$_2$O$_5$ prior to use, the NaClO$_4$ dried by multiple freeze/pump/thaw cycles, the electrolyte deoxygenated by bubbling with Ar, and all electrochemical experiments carried out under a blanket of Ar.

1,4-Dibromo-2,5-bis(3-sulfonatopropoxy)benzene Sodium Salt (1). A solution of bromine (50.0 mL, 0.094 mol, in CCl$_4$) was added slowly with stirring to a solution of 1,4-dimethoxybenzene (7.07 g, 0.051 mol) in 100 mL of CCl$_4$. The mixture was allowed to stir for 20 h at room temperature, quenched with aqueous KOH, and washed with water, and the solvent was removed. The 1,4-dibromo-2,5-dimethoxybenzene obtained was recrystallized from ethanol and dried under vacuum. To 14.8 g (0.05 mol) of 1,4-dibromo-2,5-dimethoxybenzene in a 250-mL, round-bottomed flask was added slowly 110 mL of a 1 M solution of BBr$_3$ (0.11 mol) in CH$_2$Cl$_2$, and the reaction was stirred at 40 °C overnight. The reaction was quenched by the dropwise addition of the reaction mixture into a flask containing 250 mL of degassed water at 0 °C. The colorless precipitate obtained was stirred for 30 min, and 2,5-dibromohydroquinone was collected by filtration and dried under vacuum for 24 h. In a three-neck, 300-mL, round-bottomed flask was dissolved 2,5-dibromohydroquinone (1.50 g, 5.06 mmol) in 100 mL of absolute ethanol (Florida Distilleries). A 5% excess of NaOH (0.47 g, 11.7 mmol) in 50 mL of absolute ethanol was added slowly from an addition funnel over 20 min with vigorous stirring at room temperature. Propanesultone (Aldrich) was added neat dropwise in slight excess (1.38 g, 11.3 mmol). After 18 h, the mixture was filtered and a white paste resulted which was recrystallized from 50 mL of water. Yield: 2.56 g (91%). ^{1}H NMR: δ 2.03 (q), 2.96 (t), 3.98 (t), 7.19 (s). ^{13}C NMR: δ 23.91, 47.47, 68.91, 110.37, 118.92, 148.03. Anal. Calcd for $C_{12}H_{14}O_8S_2Na_2Br_2{\cdot}2H_2O$: C, 24.3; H, 3.1; S, 10.8; Na, 7.8; Br, 27.0. Found: C, 24.55; H, 3.06; S, 9.60; Na, 6.57; Br, 27.26.

1,4-Diphenyl-2,5-bis(3-sulfonatopropoxy)phenylene Sodium Salt (3). Tris[(sulfonatophenyl)phosphine]palladium(0) (45 mg) was transferred in an argon drybox to a 200-mL Schlenk flask with a magnetic stirbar. In a separate 200-mL, round-bottomed flask were dissolved 1,4-dibromo-2,5-bis(3-sulfonatopropoxy)benzene, sodium salt (0.70 g, 1.25 mmol), benzeneboronic acid (0.31 g, 2.56 mmol), and sodium carbonate (0.99 g) in 47 mL of doubly distilled water and 20 mL of DMF. This solution was heated to 85 °C and stirred until the solids were completely dissolved. This solution was degassed with an argon stream and transferred via cannula to the flask containing the catalyst. This solution was allowed to stir under argon at 85 °C for 10 h. After this time, a small amount of black powder was visible in the solution. The reaction mixture was evaporated by boiling until the solution volume was approximately 25 mL. The black precipitate was removed by filtration, and the remaining liquid was added dropwise to 250 mL of cold acetone. A light tan powder precipitated, which was collected by filtration, recrystallized from 50 mL of water, and dried under vacuum. Yield: 0.38 g (55%). ^{1}H NMR: δ 2.02 (q), 2.81 (t), 3.87 (t), 6.96 (s), 7.51 (m). ^{13}C NMR: δ 22.98, 46.69, 66.86, 115.74, 126.32, 127.04, 128.00, 129.77, 135.89, 148.16. FTIR (cm^{-1}): 3059, 3026, 2947, 2877, 1600, 1483, 1388, 1195, 1056, 865, 770, 701, 616. Anal. Calcd for $C_{24}H_{24}O_8S_2Na_2{\cdot}2H_2O$: C, 49.1; H, 4.8; S, 10.9; Na, 7.8; Br, 0.0. Found: C, 47.44; H, 4.82; S, 10.31; Na, 8.98; Br, <0.5.

Poly[2,5-bis(3-sulfonatopropoxy)-1,4-phenylene-*alt*-1,4-phenylene] (2). The polymer was prepared according to the above procedure using phenylenebis(boronic acid) (0.23 g, 1.39 mmol), 1,4-dibromo-2,5-bis(3-sulfonatopropoxy)benzene (0.78 g, 1.39 mmol), and sodium carbonate (0.99 g). A brown/tan precipitate formed and was collected by filtration. The polymer was dissolved in a minimum of hot distilled water, reprecipitated by cooling, and collected by filtration. The polymer was redissolved in a minimum of hot distilled water, reprecipitated by cooling, and collected by filtration. The polymer was redissolved in distilled water, dialyzed for 72 h in 3500 g mol^{-1} cutoff membrane, and vacuum dried. The polymer is highly soluble in water, DMSO, aqueous base, and dilute aqueous acid and is slightly soluble in strong aqueous acid. The polymer is insoluble in acetone, ethanol, methylene chloride, and acetonitrile. Yield: 0.42 g (64%). ^{1}H NMR: δ 1.97, 2.82, 3.90, 6.91, 7.53, all broads peaks. ^{13}C NMR: δ 24.29, 48.03, 67.43, 116.06, 129.81, 137.11, 149.92. FTIR (cm^{-1}): 3030, 2940, 2870, 1598, 1483, 1378, 1168, 1048, 841, 732, 614. Anal. Calcd for $[C_{18}H_{18}O_8S_2Na_2{\cdot}2H_2O]_x$: C, 42.5; H, 4.4; S, 12.6; Na, 9.0; Br, 0.0. Found: C, 43.17; H, 5.02; S, 9.97; Na, 8.33; Br, <0.5.

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