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Synthesis and Properties of Poly(3-hydroquinonylpyrrole)

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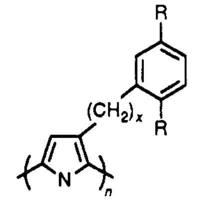
Poly(3-hydroquinonylpyrrole) was synthesized by electrochemical polymerization and characterized by cyclic voltammetry and spectroelectrochemistry. The polymer was made by direct electropolymerization of the monomer and by demethylation of poly(3-(2,5-dimethoxyphenyl)pyrrole). The positive shift of over 60 mV in the oxidation potential of hydroquinone in poly(3-hydroquinonylpyrrole) compared to related substituted hydroquinones is evidence of electronic interaction between the substituent and the polypyrrole backbone. The spectroelectrochemistry revealed an absorption at 360 nm at the potential at which the hydroquinone was oxidized to quinone. For films with comparable charge storage, poly(3-quinonylpyrrole) absorbs only 15% as much light in the visible portion of the spectrum as oxidized polypyrrole. A convenient synthesis is given for a pyrrole monomer with a protected hydroquinone in the 3-position.

Introduction

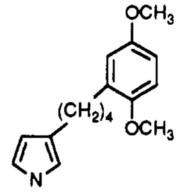
Since the initial report by Diaz et al.[1] that electrooxidation of pyrrole forms a conductive film, the field of conductive polymers has become an area of active research because of their potential applications, including high-energy density batteries, electrochromic displays and windows, sensors, electrocatalysts, and electroregenerative ion-exchange or redox resins.[2] One of the advantages of organic conductive polymers is the possibility of modifying their properties by incorporating different functional groups on the monomer. Functionalization of the monomer has been used to make the resulting polymers self-doping,[3,4] to improve their solubility,[5] to change their optical properties,[6] and, as discussed here, to incorporate redox-active substituents. Polymers which have been formed from monomers with quinone moieties connected through alkyl linkages include those with benzoquinone at the 3-position of thiophene[7] and anthraquinone at the N-position of pyrrole.[8] The quinone substituted polymers show the expected electrochemical reactions and pH dependence of the redox potential of the quinone when cycled in an electrolyte. Similar results are obtained when quinoid molecules are incorporated as dopants into films of polypyrrole (PP).[9,10] In this case, however, because the electroactive species are not covalently bonded to the polymer chain, they can be lost during cycling by exchange with anions in the electrolyte, leading to reduced stability.

For polymers based on pyrrole, functionalization has generally been done at the N-position, which results in a large decrease in the conductivity of the polymer relative to PP.[2,8,11,12] In addition substitution at this position hinders their use in aqueous solutions because they require more positive potentials to make them conductive. Substitution at the 3-position, on the other hand, has little effect on the oxidation potential of the polymer and generally leads to a less severe reduction in the conductivity of the polymer.

Chart I



cmpd	x	R
1a	1	OCH_3
1b	1	OH
2a	4	OCH_3
2b	4	OH
3a	0	OCH_3
3b	0	OH



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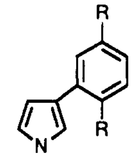
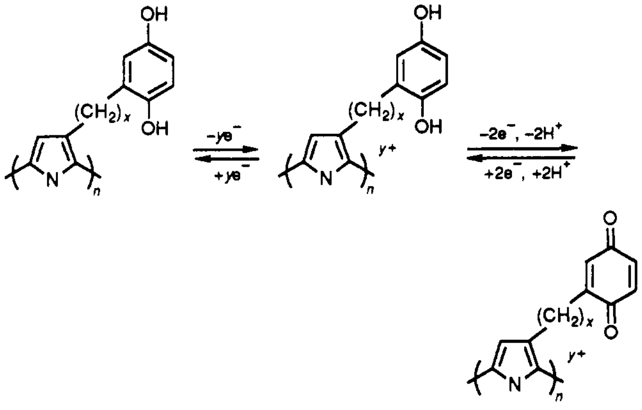


5a, R = OCH_3
5b, R = OH

Scheme I



Work done in other laboratories have investigated the properties of PP substituted in the 3-position with *n*-alkyl chains,[13] ferrocene,[14] alkylsulfonates,[4] α-ketones,[15] alcohols,[16] alkyl thiols[17] and carboxylate.[18] Our earlier report on the electrochemical properties of the homopolymer poly(3-hydroquinonylmethyl)pyrrole (**1b** Chart I) showed that the quinone substituent can be oxidized and reduced through the polypyrrole backbone.[19,20] Similar results were reported by treating copolymers made from **4** and pyrrole to convert the methyl ethers to electroactive hydroquinone moieties to give **2b**.[21] In acid the hydroquinone is oxidized to quinone at potentials positive of the value at which the

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Scheme II

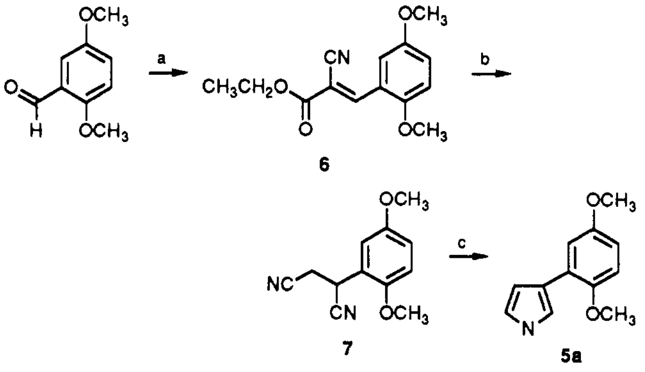
$$\begin{tikzcd} \mathbf{5a} \arrow[r, "BBr_3"'] \arrow[d, "ox\ poly"'] & \mathbf{5b} \arrow[d, "ox\ poly"] \\ \mathbf{3a} \arrow[r, "BBr_3"'] & \mathbf{3b} \end{tikzcd}$$

polypyrrole is oxidized (Scheme I). Thus the redox properties of the hydroquinone/quinone can be utilized with the polypyrrole backbone remaining in the conductive state. Attachment of the hydroquinone increased the charge-storage capacity of the polymers giving them a higher energy storage if employed as a battery electrode or allowing use of thinner films as counter electrodes in transparent electrochromic devices.

In this paper we report on the synthesis and properties of a new pyrrole homopolymer, poly(3-hydroquinonylpyrrole) (PHQP, **3b**). This polymer is the first example of a polypyrrole substituted in the three position with a redox moiety attached *directly* to the polymer backbone without intervening alkyl chains. Such attachment allows investigation of possible conjugation of the quinone with the structure of the polypyrrole backbone.

Pyrroles substituted in the 3-position are more dificult to synthesize than N-substituted pyrroles. Synthetic strategies resulting in a mixture of the 2- and 3-substituted isomers are not desirable because the 2-isomer usually predominates and is difficult to separate from the 3-isomer. We prepared the monomers, therefore, by a procedure that lead solely to the 3-substituted isomer. The synthesis is convenient, and samples of the protected monomer **5a** were obtained in multigram yields. As in our previous work[19] we electrochemically polymerized the monomer **5a** protected with methoxy groups to form **3a** followed by treatment to remove the methyl groups to give PHQP. We have also synthesized the polymer directly from the deprotected monomer, 3-hydroquinoylpyrrole (**5b**). The two routes leading to PHQP are shown schematically in Scheme II. The electrochemical and optical properties of PHQP were investigated by cyclic voltammetry and spectroelectrochemistry.

Scheme III[a]



[a] Key: (a) ethyl cyanoacetate, piperidine, absolute EtOH, heat; (b) KCN, H_2O, EtOH, heat; (c) (1) DIBAL-H, benzene, (2) $NaH_2PO_4 \cdot H_2O$, heat.

Experimental Section

Apparatus. The electrochemical polymerization and testing was done with a Pine Instruments RDE4 potentiostat, Hewlett-Packard Model 7015B x–y recorder, and a Electrosynthesis ESC 630 coulometer. IR spectra were obtained with an IBM 9000 FTIR spectrometer. NMR spectra were recorded on a Varian XL-300 spectrometer at Brandeis University. UV–vis spectra were obtained with a Hewlett-Packard 8452A diode array spectrophotometer. Micrographs were taken on a Cambridge Stereoscan 120 SEM. Conductivities were determined with an Allessi four-point probe, a constant-current source, and a voltmeter. The elemental analyses were done by Galbraith, Knoxville, TN.

Monomer Synthesis. The synthesis of the protected and deprotected functionalized pyrrole monomers is outlined in Scheme III and described below. All reagents and solvents were obtained from Aldrich in the highest purity available and were used as received unless otherwise stated.

Ethyl (2,5-Dimethoxybenzal)cyanoacetate (6).[22] Eleven drops of piperidine were added to a stirred, room-temperature solution of 2,5-dimethoxybenzaldehyde (15.0 g, 90 mmol) and ethyl cyanoacetate (9.6 mL, 90 mmol) dissolved in 32 mL of absolute ethanol. After stirring for 15 min, the solution containing orange crystals was immersed in an ice water bath for 1 h prior to isolation of the crystals by vacuum filtration and washing with cold ethanol. The product was recrystallized from ethanol. The yield of **6** was 21.8 g (93%): mp 84 °C (lit.[22b] mp 85 °C); IR (KBr pellet) 3071, 3023, 2990, 2944, 2909, 2836, 2216, 1703, 1591, 1497, 1092, 1047, 812, 764, 718 cm^{-1}.

2-(2,5-Dimethoxyphenyl)succinonitrile (7).[23] Potassium cyanide (10.9 g, 167 mmol) and 21.8 g of **6** (83.5 mmol) were added to 90% ethanol (260 mL) and heated to reflux, whereupon both the cyanide and cyanosulfate dissolved completely. Reflux with stirring was continued for 4 h. The cooled solution was then evaporated and suspended in water (27 mL). The water was extracted with dichloromethane (2 × 40 mL), and the combined organic layers were dried over sodium sulfate. After evaporation of the solvent, **7** was isolated by Kugelrohr distillation (0.060 mmHg, 130 °C) as a light golden syrup: yield 11.6 g (64%). IR (NaCl plates) 3086, 3009, 2990, 2973, 2940, 2838, 2251, 1509, 1466, 1231, 1181, 1038, 820, 777, 737 cm^{-1}.

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3-(2,5-Dimethoxyphenyl)pyrrole (5a).[24] Product 7 (11.6 g, 53.7 mmol) and 1.5 M diisobutylaluminum hydride (DIBAL-H) toluene solution (93.5 mL, 140 mmol) were dissolved in 375 mL of anhydrous benzene in an argon-filled drybox and stirred with a magnetic stirring bar for 3 h. The solution was removed from the box, 935 mL of 1.5 M aqueous $NaH_2PO_4 \cdot H_2O$ was added, and the mixture was refluxed for 30 min. After the solution had cooled, 1.5 L of diethyl ether was added. The solution was filtered under vacuum, and 2.3 L of 19% aqueous NaCl solution was added to the filtrate. When the layers had separated, the organic layer was washed with 2.3 L each of 15% aqueous NaCl and saturated brine. The organic layer was then dried over $MgSO_4$ and evaporated. Product **5a** was obtained from Kugelrohr distillation at 130 °C and 0.060 mmHg as a clear, light yellow syrup with a yield of 5.35 g (49%). The product gradually turns yellow over several weeks even when stored under Ar. Storage at 0 °C retards the deterioration. Dilute solutions of **5a** in propylene carbonate yellow very slowly. IR (NaCl plates) 3385, 2994, 2938, 2834, 607, 1509, 1277, 1217, 1181, 1048, 1024, 806, 735, 664 cm^{-1}. NMR ($CDCl_3$) δ 3.75 (s, 3 H), 3.82 (s, 3 H), 6.62 (m, 1 H), 6.70 (dd, $J = 3.9$ Hz, 1 H), 6.82 (m, 1 H), 6.87 (d, $J = 9$ Hz, 1 H), 7.13 (d, $J = 3$ Hz), 7.36 (m, 1 H), 8.37 (m, 1 H). Anal. Calcd for $C_{12}H_{13}NO_2 \cdot 0.15H_2O$: C, 69.92; H, 6.51; N, 6.79; O, 16.70. Found: C, 69.95; H, 6.52; N, 7.21; O (by difference), 16.32.

3-Hydroquinonylpyrrole (5b). Five mL of 1.0 M BBr_3 (5 mmol) in CH_2Cl_2 was added to 334 mg of **5a** (1.64 mmol), and the solution was stirred for 1 h. After this time analysis of the solution by TLC (4:1 petroleum ether:ethyl acetate) indicated that almost all of **5a** had reacted. The solution was evaporated, and the residue taken up in water which was saturated with NaCl. Nearly all the residue dissolved in the aqueous solution. The solution was repeatedly extracted with CH_2Cl_2 (4 × 20 mL, 10 × 10 mL). The combined CH_2Cl_2 extractions were dried over $MgSO_4$ and evaporated to give a syrup identified as **5b** with a yield of 91 mg (31%): IR (NaCl plates) 3372, 2961, 2928, 1617, 1507, 1443, 1260, 1202, 1080, 1030, 858, 806, 735, 664 cm^{-1}. Although the NMR spectrum was weak due to the poor solubility of **5b** in $CDCl_3$, peaks were evident at all the chemical shifts listed above for **5a** except the singlets at δ 3.75 and 3.82 due to the methyl groups. Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 60.86; H, 6.64; N, 5.20; B, <0.31.

Electropolymerization. Unless otherwise indicated, the 3-substituted polypyrroles were synthesized by electropolymerization of the monomers in a three-electrode cell. The cell was a 10- or 25-mL beaker containing 0.1 M $LiClO_4$ (Alfa, 99.5%, dried overnight at 170 °C) in propylene carbonate (PC, Burdick & Jackson, 0.015% H_2O) used as received and stored under Ar. The monomer concentration was 0.067 M. The counter electrode was a 1 cm^2 Pt flag, and the reference electrode was a small strip of Li metal immersed in the solution after the surface was freshly exposed by scraping off any surface film. Potentials in PC are given relative to the Li/0.1M Li^+ potential. The potentials vs a saturated calomel electrode (SCE) can be obtained by subtracting 3.1 V from the values obtained vs Li.[25] The electropolymerization was done in a drybox under an Ar atmosphere.

The substrates for the electropolymerization were a Pt foil, a 1-mm-diameter Pt wire sealed in glass, or an optically transparent electrode (OTE) consisting of tin oxide (TO) coated glass (30 Ω/sq, Practical Products, Cincinnati, OH) on which a thin, transparent layer of Pt had been deposited by dc sputtering to improve adhesion of the polymer. The Pt wire substrate was polished for about 1 min with 600-grit alumina sandpaper prior to each electrodeposition.

The polymerization was done by sweeping the electrode potential between the limits of 2.5 and 4.0 V vs Li^+/Li at 100 mV/s or by holding the electrode at 3.9 V vs Li^+/Li. The solution was stirred during the growth. When the polymerization was done by cycling, the growth of the film was followed with the cyclic voltammogram on the *x*–*y* recorder. The charge capacity of the growing film for each cycle was displayed on the coulometer. When the desired charge capacity of the film had been achieved, the cycling was stopped at the negative limit. For formation of the film potentiostatically, the coulometer was used to monitor the total charge passed during the growth. The electrode was then rinsed with PC, immersed in a second cell containing the electrolyte but no monomer, and cycled over the same potential range several times until a steady state was reached.

Films of **3b** were formed in two ways as shown in Scheme II. A solution of **5a** was polymerized to form the protected polymer **3a**. The polymer-coated electrode was then immersed in a 1.0 M BBr_3/CH_2Cl_2 solution for 1 h followed by rinsing with distilled water for 15 min. Alternatively, **3b** could be formed by direct electropolymerization of **5b** onto the electrode. The PC solutions of both protected and deprotected monomer darkened with extended use for film deposition, especially when the 2 cm^2 OTEs were used. The coloration, however, had no apparent effect on rate of film growth or quality of the films.

Bulk samples of **3a** were synthesized by potentiostatic deposition on a 1–2 cm^2 platinum foil electrode. The electrode was held at 3.9 V vs Li in the cell containing the monomer **5a** dissolved in 0.1 M $LiClO_4$ in PC. After sufficient polymer was deposited, it was scraped off, washed with methanol, and dried under vacuum. Anal. Calcd for $C_{12}H_{11}NO_2(ClO_4)_{0.33} \cdot 0.5\ H_2O$: C, 59.42; H, 4.98; N, 5.79, Cl, 4.81; O, 25.14. Found: C, 59.41; H, 4.84; N, 5.40, Cl, 4.81; O (by difference) 25.94. **3a** was converted to **3b** by treatment with the BBr_3/CH_2Cl_2 solution for about 1 h, followed by multiple rinses with CH_2Cl_2 and drying at 0.4 mmHg for 1.5 h. Anal. Calcd for $C_{10}H_7NO_2(Br)_{0.6}$: C, 54.32; H, 3.19; N, 6.33; Br, 21.68. Found: 42.84%; H, 4.27; N, 4.58; Br, 16.45; Cl, <0.5. Pellets for measuring the bulk conductivity of both **3a** and **3b** were pressed in the die used to make KBr pellets.

Films of PP were prepared on the OTE by electropolymerization from a 0.067 M solution of distilled polypyrrole in 0.1 M $LiClO_4$ in PC. The films were grown by cycling the electrode at 100 mV/s between 2.5 and 4.0 V vs Li/Li^+ using the same procedures as described above for formation of 3-substituted polypyrroles on the OTE.

Electrochemical Analysis in Acid. Cyclic voltammograms of polymer films which had been deposited on Pt substrates in the organic electrolyte were measured in 1.0 and 0.01 M H_2SO_4. The cell was a 50-mL beaker with a 2 cm^2 platinum flag counter electrode, and a saturated calomel electrode (SCE) was used as the reference. The working electrode with the polymer was removed from the glovebox, and as much as possible organic solvent was carefully removed with tissue paper from the vicinity of the electrode surface before immersing it the cell and recording the cyclic voltammograms. Films were cycled until a stable cyclic voltammogram was obtained to determine the charge capacity. The charge capacity of a film is measured by integrating the current over the time period of the scan between the potential limits. These values were determined using the coulometer or by graphical integration of the cyclic voltammograms.

Spectroelectrochemical Experiments. The spectroelectrochemical experiments were done in both aqueous and nonaqueous electrolytes. The OTE area was about 2 cm × 1 cm (2 cm^2) defined by covering the remaining glass surface with Teflon adhesive tape. The nonaqueous electrolyte was the same as used to grow the polymer film, 0.1 M $LiClO_4$ in PC. A special cell was designed to hold the electrode for the measurements done in the organic electrolyte. A glass tube extension 2 cm in diameter 3 cm long and sealed at the bottom was fitted to the bottom of a 10-mL three-necked flask. The tube supported two parallel Pyrex flats between which the OTE was placed. The counter and Li reference electrode fitted on either side of the OTE outside of the light beam. The leads were fed through a septum on each neck. The cell was assembled in the glovebox, the electrolyte added, and the septa sealed so that the cell was not exposed to the atmosphere when it was removed from the box.

Spectra in aqueous solutions were obtained with the OTE in a standard rectangular spectrophotometer cell 4 cm long × 1 cm wide × 6 cm deep. The Pt counter electrode was placed in the cell outside the light path. The SCE was in a separate beaker filled with the same aqueous electrolyte and connected to the rectangular cell by a U-tube filled with the electrolyte.

The following procedure was used to measure the spectra. After the cell was placed in the diode spectrometer, a cyclic voltammogram was recorded. The potential on the electrode was then

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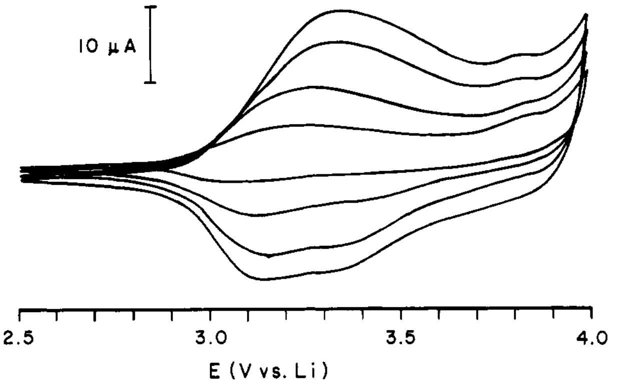

Figure 1. Growth of film of **3a** on Pt electrode (area = 8 × 10^{-3} cm^2) from monomer in $LiClO_4$/PC solution by cycling at 100 mV/s for 40 min.

set at the desired value, and after the current decayed to zero in 1–2 min, the spectrum was measured. The potential was then changed at a rate of 10 mV/s until the new potential value was attained and the next spectrum was measured. Background spectra of the OTE with no polymer film were obtained in the same cell. The reported spectra have been corrected to remove the contribution to the absorption from the OTE.

Results

Synthesis of the 3-Substituted Pyrrole Monomers. The particular usefulness of the synthetic strategy used to prepare the pyrrole monomer **5a** is its exclusive production of the 3-isomer. The synthesis is based on the Knoevenagel condensation of 2,5-dimethoxybenzaldehyde with ethyl cyanoacetate followed by a Michael addition of cyanide to the α,β-unsaturated cyano ester and subsequent decarbalkoxylation. The final step is reduction of the succinonitrile and cyclization to form the pyrrole. The overall yield of the three step synthesis was 29%. The difference between the expected and found values for the elemental analysis for **5a** indicated there was a small amount of water in the final product.

Deprotection is required to utilize the redox behavior of the hydroquinone/quinone couple. Monomer **5a** was treated with BBr_3 following the procedure of McOmie et al.[26] to give **5b**. The low yield of the product extracted from the demethylation reaction may be due to the poor partitioning of the hydroquinone between the CH_2Cl used for extraction and the aqueous solution in which it was formed. The very high C/N ratio of 13.6 from the elemental analysis of the product indicated there were carbon containing impurities in the product, one of which could be the starting dimethoxy monomer. NMR did not indicate the presence of methyl groups, however, and the IR peaks in the regions of 2900, 1215, and 1050 cm^{-1} associated with at methoxy groups in **5a** were very different in the reaction product **5b**. In addition, the product had the broad absorption at 3372 cm^{-1} expected for a compound with hydroxy substituents. On the basis of the similarity of the properties of the films of PHQP made by polymerization of **5b** and by demethylation of polymer **3a**, the impurities did not effect the formation or properties of the resulting polymer.

Poly(3-(2,5-dimethoxyphenyl)pyrrole) (3a). No growth of polymer **3a** from monomer **5a** was evident as the positive limit of the cyclic voltammogram was increased from 3.4 to 3.8 V by 0.1-V intervals. When the limit was raised to 4.0 V vs Li/Li^+, however, steady growth of the polymer commenced as shown in Figure 1. There was no indication of any oxidation of the dimethoxyphenyl group up to this potential limit in agreement with our earlier observations for polymerization of the (dimethoxybenzyl)pyrrole monomer.[19] Continued cycling for 40 min led to film with a cathodic charge capacity of about 15 mC/cm^2. The Pt wire on which the polymer was grown had a pale copper color. When the electrode was washed and transferred to a $LiClO_4$/PC solution without the monomer present, the only significant difference in the cyclic voltammogram was the absence of the small anodic peak at 3.8 V and cathodic peak at 3.35 V observed when the monomer is present. Stable cyclic voltammograms were obtained with repeated cycles in the $LiClO_4$/PC electrolyte.

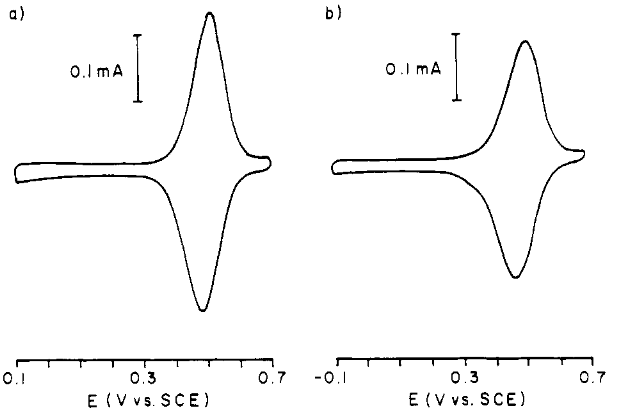

Figure 2. Cyclic voltammograms of PHQP films on Pt electrode (area = 8 × 10^{-3} cm^2) made from (a) treatment of **3a** with $BrBr_3$ and (b) direct polymerization of **5b** in $LiClO_4$/PC. The electrolyte is 1 M H_2SO_4 and the sweep rate is 100 mV/s.

The cyclic voltammograms for the film of **3a** grown potentiostatically at 3.9 V vs Li/Li^+ are indistiguishable from that for the polymer made by potential cycling. Passage of a total charge of 150 mC/cm^2 on the Pt produced films with cathodic charge capacity of about 12 mC/cm^2. The elemental analysis showed that the polymer was doped with 0.33 ClO_4^-/pyrrole. Combining this value with the usual assumption that the growth of polypyrrole films requires two electrons per monomer unit, formation of **3a** with 100% efficiency would produce a charge capacity of 25 mC/cm^2. The polymerization reaction, therefore, proceeds with an efficiency of about 50%, which is comparable to the value of 44% we reported for the formation of the dimethoxy-substituted polymer **1a**.[19]

The elemental analysis of a bulk sample of **3a** made by holding a Pt flag at 3.9 V vs Li/Li^+ for an extended period showed excess hydrogen and oxygen, indicating the presence of water. Excellent agreement between the calculated and found elemental analysis is obtained if the compound contained $0.5H_2O$ and $0.33ClO_4^-$ per monomer unit. The extent of doping of the oxidized polymer is comparable to that reported for other perchlorate doped polypyrroles.[2] The water is probably present as water of hydration in the organic perchlorate salt. The conductivity of a pressed disk of **3a** was $\approx 2 \times 10^{-3}$ S/cm. This value is lower than polypyrrole or polypyrroles substituted in the 3-position with short alkyl chains but is comparable to those reported with bulky substituents. The SEM of **3a** showed it had the bumpy, globular appearance as is commonly observed for electrochemically formed polypyrroles.

Poly(3-hydroquinonylpyrrole) (PHQP, 3b). One method of producing PHQP was the demethylation of films of **3a** by immersing the electrode in BBr_3/CH_2Cl_2 solution and then rinsing in water. The effectiveness of the conversion was evaluated from the charge in the hy-

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[26] McOmie, J. F. W.; Watts, M. L.; West, D. E. *Tetrahedron* 1968, *24*, 2289–2292.

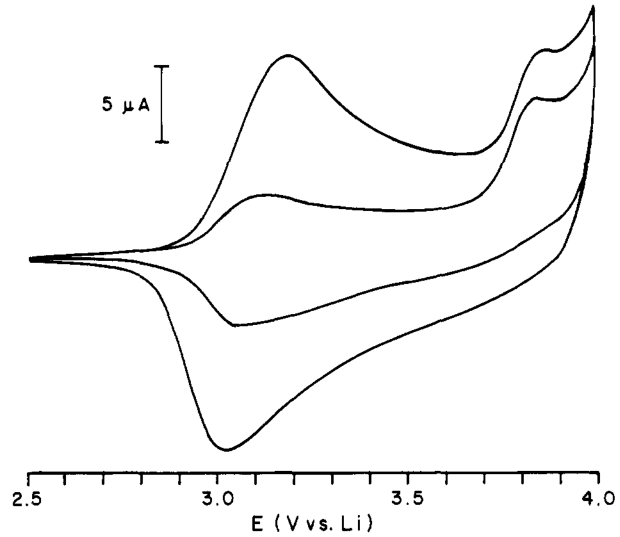

Figure 3. Growth of PHQP on Pt electrode (area = 8 × 10^{-3} cm^2) from monomer **5b** by potential cycling at a sweep rate 100 mV/s in LiCLO$_4$/PC.

Table I. Potentials from Cyclic Voltammograms of 3-Substituted Pyrrole Polymers[a]

compound	$E_{pa/2}$, V	E_{pa}, V	E_{pc}, V	ΔE_p, V
PHQP	3.03	3.20	3.04	0.16
3a	3.00	3.15	2.97	0.18
1a[b]	3.00	3.11	3.08	0.03
PP	2.86	3.04	2.98	0.06

[a] Potential vs Li$^+$/Li measured in 0.1 M LiClO$_4$ in PC at sweep rate of 100 mV/s. [b] Reference 19.

Table II. Total Charge Capacities of Polypyrrole and Derivatized Polypyrrole Films[a]

compound	Q_T in Li/PC (2.5 to 4.0 V vs Li), mC/cm^2	Q_T in 1 M H$_2$SO$_4$ (−0.1 to 0.7 V vs SCE), mC/cm^2
PP	18	16
3a	19	15
PHQP	19	68

[a] Charge capacity, Q_T, is the sum of the absolute value of the anodic and cathodic charge during one cycle at 100 mV/s over the potential range indicated.

droquinone oxidation peak of the cyclic voltammogram measured in 1 M H$_2$SO$_4$ (pH 0.24). Figure 2a shows the cyclic voltammogram in H$_2$SO$_4$ of a film of PHQP prepared by forming polymer **3a** potentiostatically from **5a** in a LiClO$_4$/PC electrolyte and then treating it for 1 h in the boron tribromide solution. The peaks associated with the hydroquinone/quinone redox reaction are evident at ≈0.5 V vs SCE. The charge associated with this reaction increased with longer treatment in BBr$_3$ up to 1 h and then leveled off.

The elemental analysis was done on a bulk sample of PHQP formed by the BBr$_3$ reaction with the methylated polymer **3a**. The presence of Br and absence of Cl indicated that the ClO$_4^-$ dopant had been replaced by Br$^-$. The C/N ratio of 10.9 was above the expected value of 10, but not as high as that for the equivalent monomer **5a** formed by BBr$_3$ treatment. In the polymer case the ratio could be explained by demethylation of about half of the dimethoxyphenyl substituents. The very low weight percent of carbon and nitrogen relative to hydrogen and oxygen pointed to large amounts of water in the polymer as might be expected for a polymer salt that had been immersed in aqueous solutions as part of the treatment.

PHQP was also formed by direct electropolymerization of monomer **5b** in an aprotic solvent. The polymerization appeared to begin even when the positive limit was as low as 3.6 V vs Li$^+$/Li, but the rate of polymerization was much faster when the limit was increased to 4.0 V vs Li$^+$/Li, and this limit was generally used. Figure 3 shows the growth of PHQP from a solution of **5b** in LiCLO$_4$/PC. The anodic peak initially at 3.1 V and cathodic peak at 3.05 V is comparable to those observed for other pyrrole polymerizations, but there is a second peak at 3.84 V which is much more pronounced than in the polymerization of **5a**. As is observed for the oxidation of pyrrole leading to the formation of the polymer, then was no corresponding cathodic peak. This peak was not observed in the cyclic voltammogram of the polymer taken in the absence of the monomer. Oxidation of the hydroquinone substituent in the aprotic solvent is not expected to occur below potentials of 4.2 V vs Li$^+$/Li.[27] The cyclic voltammogram for this film when cycled in 1 M H$_2$SO$_4$ is given in Figure 2b and is seen to be comparable to that given in Figure 2a for the film formed by deprotecting **3a**.

No conductivity measurements were made on material grown directly from the deprotected monomer which would have been doped with ClO$_4^-$ rather than Br$^-$. The conductivity of PHQP made from the bulk sample of the treated **3a** was the same as for the **3a**, ≈2 × 10^{-3} S/cm^{-1}. Because of the suspected high water content of the material, however, the conductivity may be both ionic and electronic. The density of the dark green pellet used for the conductivity measurement was 0.75 g/cm^3. Observation of PHQP in the SEM revealed it had a platelike structure and appeared denser than the protected polymer **3a**.

Cyclic Voltammetric Characterization of the Polymers on Pt. Table I compares the potentials for the oxidation–reduction of the pyrrole backbone for three 3-substituted polypyrroles—**1a**, **3a**, and PHQP—with the unsubstituted PP. All the cyclic voltammograms were measured in PC/0.1 M LiClO$_4$ cycled between 2.5 and 4.0 V vs Li at 100 mV/s. The peak potential values are comparable for the 3-substituted polymers and shifted about 150 mV positive of PP. As observed for other 3-substituted polypyrroles, this shift is less than the value of 0.3 V typically observed for substitution on the nitrogen of the pyrrole.[2k] When films of **3a** were cycled to 4.3 V vs Li, the current began to increase and a reduction peak at 4.13 V vs Li was evident. This new wave is attributed to oxidation of the pendent 2,5-dimethoxyphenyl group. A similar wave was observed in the cyclic voltammogram of **1a**.[19]

In contrast to the cyclic voltammogram in aprotic solvents, the hydroquinone redox chemistry was clearly evident in sulfuric acid solutions as shown in Figure 2. For PHQP a nearly reversible reaction is observed with i_{pa} = i_{pc} and E_{pa} and E_{pc} values of 0.490 and 0.460V vs SCE, respectively. Table II compares the total charge capacity, defined as the sum of the absolute values of the anodic and cathodic charge, for PP, **3a**, and PHQP films in the aprotic electrolyte and in H$_2$SO$_4$. The three polymers had comparable charge capacity in the 0.1 M LiClO$_4$/PC electrolyte. Because of the contribution from the hydroquinone–quinone redox reaction in H$_2$SO$_4$, however, the charge capacity of PHQP was much larger than the other two polymers in the acid electrolyte.

On the basis of the dopant level derived from the elemental analysis of the **3a**, the charge stored when the

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(27) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1970.

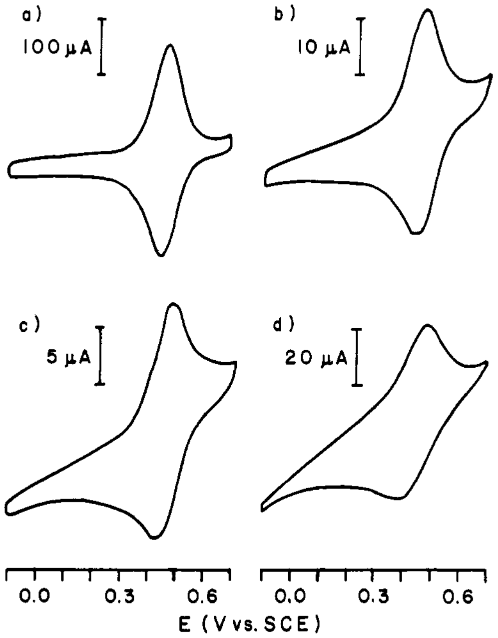

Figure 4. Cyclic voltammogram of PHQP film on Pt electrode (area = 8×10^{-3} cm^2) in 1 M H_2SO_4 as a function of scan rate in mV/s: (a) 100, (b) 10, (c) 5 (d) 2. The current scales are adjusted so the charge under the curves can be compared directly except for (d) for which the charge scale is twice that of the other curves.

polypyrrole backbone is oxidized corresponds to the loss of 0.33 e$^-$/monomer unit, whereas the charge associated with the hydroquinone oxidation is 2 e$^-$/monomer unit (see Scheme I). Thus the expected ratio of the charge in the hydroquinone redox reaction to the charge necessary to oxidize the polymer backbone should be 2/0.33 = 6. In our experiments, the values were variable and reflect the efficiency of the demethylation reaction of either the monomer **5a** or polymer **3a**. Ratios above 3.5 could not be obtained even if the deprotection reaction was run at elevated temperature. Excessive exposure to BBr_3 ultimately degraded the film.

Figure 4 shows the cyclic voltammograms measured at scan rates between 100 and 2 mV/s for films of PHQP formed directly from monomer **5b**. For the fastest three scan rates, the current scale was adjusted so that the charge scale, i.e., the area proportional to the current times the voltage, was the same for the different sweep rates. At the slowest sweep rate of 2 mV/s the charge represented in the figure was twice that of the other curves. The ratio of the charge in the hydroquinone to that in the polypyrrole backbone for this PHQP film was about 1. Since this ratio was nearly independent of sweep rate, the reason for the low ratio was not due to inadequate electronic conductivity to the quinone through the polypyrrole backbone. As the sweep rate decreased, the polypyrrole background underlying the hydroquinone redox peaks became larger and the curve was skewed, indicating an increased surface area and resistivity of the polymer. There was also an increase in the value of ΔE_p between the anodic and cathodic peak potentials. The order of the measurements in Figure 4 were from the fastest to the slowest sweep rate. When the order was reversed on another film, the shape of the cyclic voltammogram at 2 mV/s was similar to that shown in Figure 4a at 100 mV/s, but the charge in the cyclic voltammogram was still twice that obtained at 100 mV/s. For this film the cyclic voltammogram at 100 mV/s was skewed. These changes were indicative of deterioration of the film during the cycling such as detachment from the substrate. We obtained similar results with PP when it was cycled at different scan rates in H_2SO_4. In $LiClO_4$/PC there was no change in the charge capacity or shape of the cyclic voltammogram for PHQP over this range of sweep rates.

The films of PHQP showed a gradual decay of charge capacity and increase in the film resistivity with repetitive cycling at 100 mV/s in 1 M H_2SO_4 between −0.1 and 0.7 V vs SCE. The rate of this decay varied somewhat from film to film. For example, over 150 min of constant cycling, the charge capacity was halved, and the separation between the anodic and cathodic peaks of the hydroquinone redox reaction increased from 30 to >250 mV. The stability was not improved by cycling in 0.01 M H_2SO_4, reducing the scan rate to 10 mV/s, or use of PHQP prepared by deprotection of **5a** rather than direct polymerization of **5b**. Comparable changes were observed when we cycled PP in 1 M H_2SO_4 under the same conditions. The instability of PHQP, therefore, was probably associated with degradation of the polypyrrole backbone rather than due to processes related to the quinone substituent. It was found that if the potential range in the cycling was limited to the redox range of the quinone from 0.3 to 0.6 V vs SCE, the cycling could be continued for 16 h before the charge capacity was halved.

Optical Properties of PHQP on OTE. PHQP was electropolymerized directly onto 2 cm^2 TO–Pt electrodes from solutions of monomer **5b** by potential cycling. Adhesion to either bare, clean indium tin oxide (ITO) or tin oxide coated glass was very poor. Thick polymer deposits either slipped off in one sheet or did not form uniformly. The growth was limited to the edges with much of the center of the substrate remaining bare. Variations in the manner of electrodeposition, i.e., repeated cycling at various scan rates or holding the potential at 3.9 V vs Li, had no affect on the adhesion. By sputtering a layer of platinum of less than 50 nm onto TO, an electrode was attained with good transparency on which uniform polymer films were formed free of adhesion problems. The use of previously deprotected monomer enabled the deposition of good films of PHQP without the adverse effects resulting from the deprotection of films of **3a** in BBr_3 solution. BBr_3 treatment of thin films on bare TO left a gritty, discolored deposit that was electrochemically inactive. The films used for the optical studies on OTE substrates, therefore, were all formed from the unprotected monomer.

The charge capacity in $LiClO_4$/PC of the films electropolymerized on TO/Pt substrates was 50% larger when measured at 10 than at 100 mV/s. The separation between the anodic and cathodic peaks also increased at the higher sweep rate. These observations reflect both significant resistance across the TO/Pt/PHQP layer and rate limitations for migration of the counterion within the film during the cycling. As the scan rate was decreased further from 10 to 2 mV/s, the charge increased by less than 10%. In H_2SO_4 the charge capacity was independent of the scan rate over the range 2–10 mV/s. The cyclic voltammograms of these films, however, exhibited greater separation between the anodic and cathodic redox peaks of the hydroquinone than on the Pt wire substrates, and this separation increased with the thickness of the films and scan rate. In comparing the optical results of different films the total charge capacity was measured at sweep rates of 10 mV/s.

Visual observation of the films of PHQP showed that it had a green color throughout the 2.5–4.0 V vs Li$^+$/Li range when cycled in $LiClO_4$/PC. A distinct lightening of the green color and an increase in transparency, however, was evident when the potential was held at 2.5 V. The results of the spectroelectrochemical measurements over

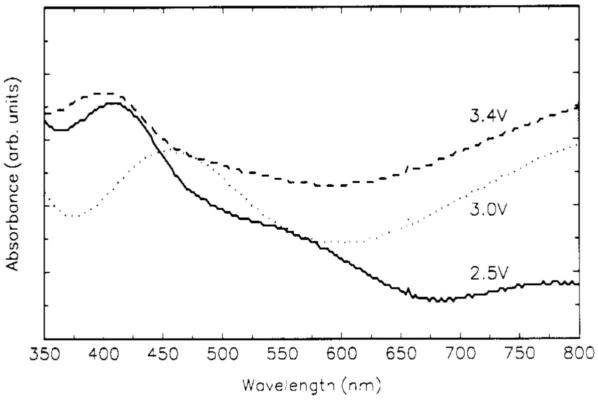

Figure 5. Spectra of a PHQP film (Q_T = 10 mC/cm^2) grown on a OTE in Li/LiClO$_4$ in the fully reduced state (2.5 V), and partially (3.0 V) and fully (3.4 V) oxidized state.

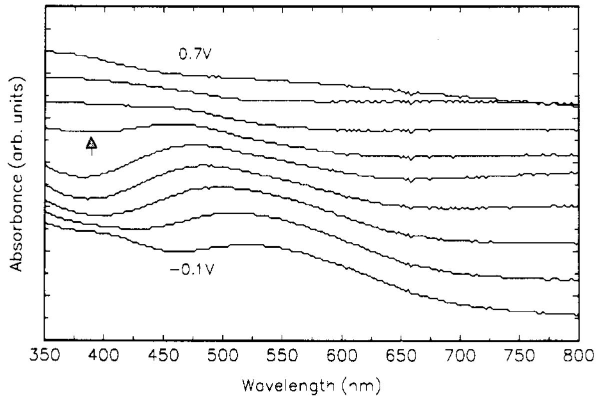

Figure 6. Optical absorption spectra of PHQP film (Q_r = 12 mC/cm^2 in Li/LiClO$_4$ and 45 mC/cm^2 in H$_2$SO$_4$) measured in 0.01 M H$_2$SO$_4$. Spectra were recorded with the applied potential on the electrode increased by 0.1-V steps beginning with the reduced state at −0.1 V and ending with the oxidized state at 0.7 V vs SCE. Each successive spectrum has been displaced upward by 0.1 absorption unit from the previous spectrum. The arrow points to the spectrum obtained with the film held at 0.4 V vs SCE and indicates absorption by the quinone formed by the oxidation of the hydroquinone on the PHQP film.

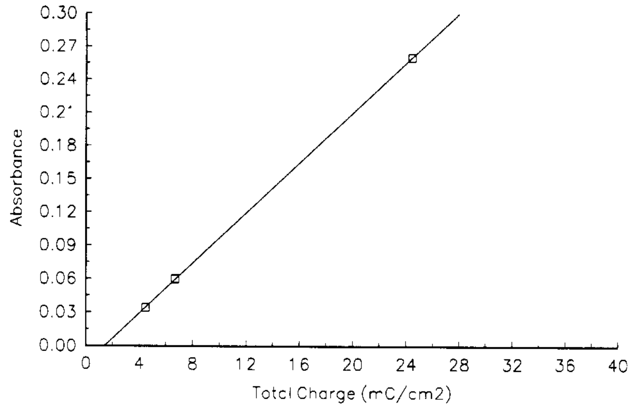

Figure 7. Plot of the absorbance at 600 nm of films of PHQP as a function of their total charge capacity measured in 1 M H$_2$SO$_4$ at 10 mV/s.

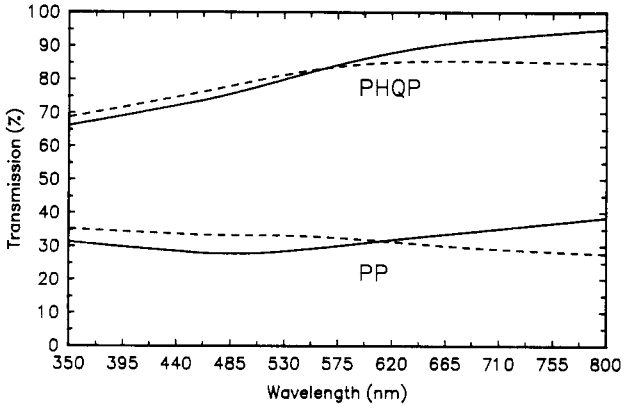

Figure 8. Comparison of the transmission spectra in 1 M H$_2$SO$_4$ for a PHQP and PP film in their oxidized and reduced states. The total charge capacity of the PHQP and PP measured at 10 mV/s were 6.7 and 7.9 mC/cm^2, respectively.

the visible range for a 10.0 mC/cm^2 film held at 2.5, 3.0, and 3.4 V vs SCE are shown in Figure 5. The potentials were held at successively more positive values. When the potential was increased from 3.4 to 3.9 V, a gradual yellowing of the PC solution was observed. When the potential was then returned to 2.5 V and a second spectrum measured, it did not match the original spectra taken with the electrode held at 2.5 V. A cyclic voltammogram of the film after these spectral measurements showed that little, if any, PHQP remained on the substrate.

When a similar experiment on a comparable film was run in H$_2$SO$_4$ and the potential was scanned in stepwise increments between −0.1 and 0.7 V vs SCE, no significant deterioration of the film or solution discoloration occurred. Spectroelectrochemical measurements for a film with total charge capacity of 45 mC/cm^2 are given in Figure 6. All spectra were obtained on the same film. Each successive spectrum has been shifted upward by 0.1 absorbance unit from the previous spectrum so it can be distinguished from the other spectra. When the spectra were not displaced, an isosbestic point at about 600 nm was evident. A plot of absorbance at this wavelength in 1 M H$_2$SO$_4$ for three PHQP films with different total charge storage is given in Figure 7. The expected linear relationship between charge capacity of the films, which is proportional to their thickness, and the absorbance was observed in agreement with Beer's law. The nonzero x intercept showed there was a small error in the correction for the background absorbance of the Pt/TO blank without the polymer film.

Figure 8 compares the spectra from films of PHQP and PP with comparable charge storage capacity. The charge storage of the PHQP and PP films was 6.7 and 7.9 mC/cm^2, respectively, measured at 10 mV/s in 1.0 M H$_2$SO$_4$ over the potential range −0.1 to 0.7 V vs SCE. The spectra for each film are given for the films in the fully reduced and oxidized state. The transmittance for PHQP is significantly higher at all wavelengths. For the thin film of PP, the transmission is nearly wavelength independent over the range 350–800 nm. For PHQP, on the other hand, the transmission increases at longer wavelength for both the oxidized and reduced states. PP has a isosbestic point around 600 nm like the PHQP films. The absorbance of the PHQP film at 600 nm is 0.073 compared to 0.5 for PP. Taking into account the slightly different charge density of the two films, the absorbance of PHQP is one-sixth that of PP.

Discussion

Synthesis. The synthetic strategy in this work is a useful method for making pyrrole monomers substituted at the 3-position. Not only does the new reaction sequence lead to substituents uniquely in the 3-position, but it also allows the introduction of chemically labile species which would react in the more commonly used Friedel–Crafts reaction. The overall yield for the three-step synthesis of **5a** was 29%. This result contrasts sharply with very low yield of 3% and isolation difficulties for our earlier synthesis to prepare 3-(2,5-dimethoxybenzyl)pyrrole, the monomer of **1a**.[19] That synthesis produced the 2- and 3-substituted pyrroles in the ratio of 6:1.

The gradual darkening of **5a** over time, even under argon, indicated some slow spontaneous polymerization or perhaps decomposition leading to impurities. There was some evidence for these in the NMR. The stability was improved by diluting the monomer immediately in PC solution. The gradual darkening of the monomer solution with continued use for the polymerization reactions is attributed to buildup of soluble oligomers of **3a**. This darkening, however, gave no evidence of inhibiting polymer growth on the working electrode or affecting the properties of the polymer films.

This high ratio of C to N in the elemental analysis of PHQP formed by treatment of **3a** with $BrBr_3$ indicated that complete demethylation was not obtained. It is known that this demethylation reaction gives unpredictable yields.[28] There are also reports that the second methyl group on a phenyl is only removed if it is in the meta position.[29] On the other hand, Press reported the yield of demethylation of 3-methoxyphenol is about 46% to analytically pure material.[28] If the reaction with **3a** had proceeded only to the 3-methoxyphenol product, it is expected that the phenol would be oxidized to the hydroquinone during the cycling in H_2SO_4.[30] The dimethoxyphenyl substituent, however, does not undergo a redox reaction in aqueous solution over the potential region evaluated and would not contribute the charge capacity of the film.

The charge associated with the oxidation of the hydroquinone substituent in PHQP did not exceed 3.5 times that due to oxidation of the polypyrrole backbone regardless of which route was used to prepare the PHQP. For the oxidation of polymer **1b** prepared by BBr_3 treatment of the protected polymer **1a**, the value was about 7 times which was closer to that expected if two electrons per hydroquinone substituent were transferred.[19] We conclude from the lower value obtained with PHQP that the demethylation reaction was not complete for either route of the synthesis, i.e., via demethylation of **5a** or **3a**. The lower yield for the demethylation of **3a** could be due to steric hindrance preventing the BBr_3 from reacting when the dimethoxy substituent is directly attached to the pyrrole in polymer backbone chain.

The demethylation of monomer **5a** to **5b** would not be influenced by the steric interference imposed by the polymer structure, but the yield could be low as discussed above. NMR and IR spectra of product **5b** which indicated minimal presence of methyl groups was not supported by the high C to N ratio obtained from the elemental analysis. The extent of the demethylation reaction may be a sensitive function of the reaction conditions and purity of the BBr_3 solution, neither of which were optimized in this work. The material extracted by the methylene chloride from the aqueous solution after the BBr_3 treatment is thus believed to be a mixture of **5a** and **5b**, although the presence of some 2-methyl-5-hydroxylphenyl-substituted pyrrole cannot be ruled out. Electropolymerization from a solution containing monomers **5a** and **5b** would form a copolymer. This copolymer would be expected to have properties comparable to the polymer formed by the partial deprotection of **3a** which is what we observed. Formation of copolymers with different ratios of the demethylated and methylated substituent would explain the variability observed in the ratio of charge in the hydroquinone redox reaction to that of the polypyrrole backbone.

Table III. Potentials for Oxidation of Hydroquinone Attached to the 3-Position of Polypyrrole

compound	E,[a] V	ref
methylhydroquinone	0.37	14b
2b	0.40	14b
1b	0.43	19
hydroquinone	0.46	14b
PHQP	0.49	this work

[a] Potential vs SCS.

Formation of films of PHQP by direct polymerization of **5b** has several advantages over the treatment of films of **3a** with BBr_3. Boron tribromide is a corrosive chemical which during the treatment sometimes degraded the polymer films or adversely affected their adhesion to the Pt substrate. The resistivity of the degraded PHQP films was so high the anodic peak in the cyclic voltammograms was shifted beyond 0.7 V vs SCE in H_2SO_4 electrolyte. Treatment of **3a** on the OTE discolored the film, roughened the film surface, and lead to eventual detachment of the film. On the other hand films produced from the deprotected monomer had cyclic voltammograms with low resistivity and adhered well to the electrode.

The formation of polymers **5a** and **5b** which do not have a flexible alkyl group between the aryl group and the polypyrrole was somewhat unexpected since 3-phenylthiophene does not form films by electrochemical polymerization.[31] We have also been unsuccessful in polymerizing 3-ferrocenylpyrrole.[32] We have no direct information on the molecular weight of PHQP. The conductivity value of PHQP is smaller than those reported for samples of electrochemically polymerized 3-alkypyrroles which had molecular weights of 5000–10000 g/mol.[13] As seen in Figure 5, the absorption maximum of oxidized PHQP is at 400 nm, which agrees with that obtained for PP with short conjugation lengths formed by chemical polymerization.[33] Both of these characteristics of PHQP could be attributed to a polymer with short chain lengths or with short conjugation due to nonplanarity of the polypyrrole backbone. The present data do not allow us to distinguish between these two possibilities.

Electrochemistry. For PHQP the peak potentials for the hydroquinone redox couple in 1 M H_2SO_4 (pH 0.24) at a sweep rate of 100 mV/s were 0.49 and 0.46 V vs SCE for E_{pa} and E_{pc}, respectively. E_{pa} was constant over the scan rate 2–100 mV/s (see Figure 4). In 0.01 M H_2SO_4 (pH 1.85) at 10 mV/s, the E_{pa} value was shifted negatively by 95 mV. The shift of $\approx$58 mV/pH unit is close to the value of 59 mV/pH unit expected for the two-electron-reduction process and comparable to the 54 mV/pH unit reported for polymer **2b** with the hydroquinone attached to the 3-position of polypyrrole though a butyl group.[21] Any effect of conjugation between the oxidized polymer and the hydroquinone substituent in PHQP, therefore, is not sufficient to stabilize the semiquinone intermediate to the degree that the second electron transfer does not take place within the potential range used. These electrochemical results support our assertion that the failure to obtain the expected 2-electron oxidation per pyrrole is due to incom-

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plete demethylation as discussed above.

The potential for hydroquinone oxidation in PHQP is compared in Table III with the formal potentials at pH 0 for hydroquinone, methylhydroquinone, and the two other polypyrroles with hydroquinone substituents attached at the 3-position. PHQP has an oxidation potential higher than the unsubstituted hydroquinone as expected if the positively charged conductive polymer is exerting an electron-withdrawing effect on the hydroquinone. The oxidation potentials of the other two polymers lie between that of the methyl and unsubstituted hydroquinone indicating a reduced, if any, effect on the oxidation potential by the polymer.

For PHQP ΔE_p, the separation between the anodic and cathodic peak potentials was 30 mV and did not change with the scan rate measured except at 2 mV/s, where we suspect some degradation of the polypyrrole chain was occurring. ΔE_p should be zero for a reversible reaction of an adsorbed species on an electrode. Our nonzero value could be due to the reaction being irreversible or to iR effects, but these explanations are ruled out because the current function, i_p/ν, where ν is the scan rate, was constant for the three fastest scan rates. A possible explanation is that the nonzero ΔE_p resulted from the hydroquinone redox current being added to the asymmetric background current of the underlying conductive polymer. The ΔE_p of polymer **2b** was >90 mV at 2 mV/s, and the value increased with increasing scan rate.[21] The different electrochemical response of **2b** and PHQP may reflect poorer electrical conductivity between the conductive polymer backbone and the hydroquinone in **2b** because of the separation by the butyl group.

Optical Properties. The spectra of the PHQP film in $LiClO_4$/PC, Figure 5, was comparable to that reported for PP and other substituted polypyrroles.[2,6] The film degraded, however, during measurement of the spectra when it was held at 3.9 V vs Li^+/Li. Similar problems with PP films at high positive potentials have been reported.[34] In 0.01 M H_2SO_4, however, after measuring the spectra over the range of potentials from –0.1 to 0.7 V, the original spectrum was obtained when the potential was returned to –0.1 V vs SCE. The spectra in Figure 6 show the usual increase in absorption at wavelengths above 600 nm as the film was oxidized between the potentials of –0.1 to 0.3 V vs SCE. The broad peak around 525 nm decreased slightly and shifts to the blue. Above potentials of 0.3 V there was little change in the long-wavelength portion of the spectra. These changes were qualitatively the same behavior reported for as-grown PP films doped with perchlorate.[35]

The absorption changes for PHQP in the 350–425-nm region, however, were different from PP for which the absorption steadily decreases with oxidation. For PHQP the absorption initially decreased with increasing oxidation of the polymer up to potential of 0.3 V as observed on PP. The next spectrum taken with the electrode held at 0.4 V vs SCE, however, showed a distinct increase in the absorption in this region as indicated by the arrow in Figure 6. This potential change was where the oxidation of hydroquinone occurred in 0.01 M H_2SO_4. Subsequent increases in the potential had little effect on the spectra. When the spectra changes were monitored in 1 M H_2SO_4, the new absorption occurred between 0.4 and 0.5 V vs SCE, again where the hydroquinone oxidation occurs. The new absorption, therefore, is attributed to a transition involving the quinone. PHQP provides an example where changes in the spectra of the conductive polymer backbone can be separated from those due to changes in the oxidation state of a covalently attached substituent on the polymer.

Absorption by free quinone is very weak at these wavelengths; ϵ is 20 and 1000 L/(mol cm) at 440 and 300 nm, respectively.[36] Using the charge in the quinone redox reaction of the PHQP to estimate the amount of quinone, the absorption coefficient for the quinone in the film is about 100 L/(mol cm). Thus, while the presence of quinone is detected in the spectra, there was not a significant effect on the absorption coefficient or wavelength which would indicate significant electronic interaction with the conductive polymer.

The slope of the line in Figure 7 is proportional to the absorption coefficient of PHQP at 600 nm. The value of 0.022 cm^2/mC is one-sixth that for PP. The addition of the electroactive substituent, therefore, has had the desired effect of increasing its charge storage without a comparable increase in its absorption. Films of PHQP are thus a potential candidates to fulfill the demanding requirements of the counterelectrode in all polymeric electrochromic cell. It has ion storage capability, reversible electrochemistry, electronic conductivity, and high transparency. These advantages would be enhanced even further if a method for complete demethylation of the polymer or monomer could be found. Trimethylsilyl iodide has been reported as a reagent for mild hydrolysis of ethers.[37] This reaction was used to convert **2a** to **2b** in the copolymer with PP, but the yield of the reaction was not given or discussed.[21] We are currently investigating use of this reagent and other methods of deprotection.

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Registry No. **5a**, 138572-37-9; **5a** (homopolymer), 138572-41-5; **5b**, 138572-38-0; **5b** (homopolymer), 138572-40-4; **6**, 80777-94-2; **7**, 138572-39-1; KCN, 151-50-8; ethyl cyanoacetate, 105-56-6; 2,5-dimethoxybenzaldehyde, 93-02-7.

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