Poly[1,4-bis(pyrrol-2-yl)phenylene]: A New Electrically Conducting and Electroactive Polymer Containing the Bipyrrole-Phenylene Repeat Unit

John R. Reynolds,*,† Alan R. Katritzky,‡
Jadwiga Soloducho,‡ Sergei Belyakov,‡
Gregory A. Sotzing,† and Myoungho Pyo†

Center for Macromolecular Science and Engineering and Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, Florida 32611

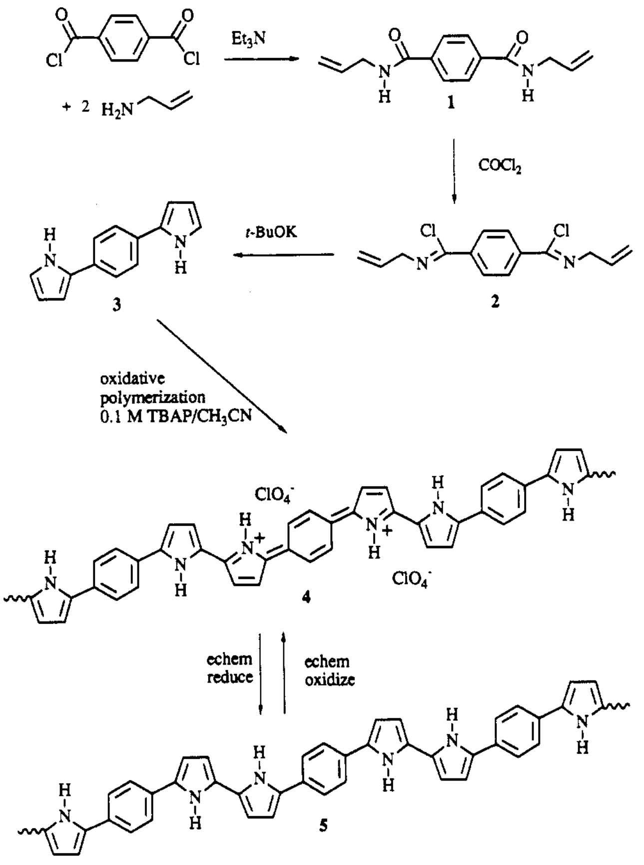
Received May 31, 1994
Revised Manuscript Received September 21, 1994

The electropolymerization of heterocyclic monomers to form electrically conductive and redox active polymers is highly dependent on the monomer's oxidation potential. In some cases, the monomer oxidizes at potentials that cause polymer degradation, leading to defect-containing materials and, in the extreme, inhibiting polymerization completely. In the case of thiophene polymerization, this has been termed the polythiophene paradox.[1] Reduction of the monomer oxidation potential by the electropolymerization of short conjugated oligomeric molecules has provided a simple route to synthesizing polyheterocycles of higher purity both by reducing the monomer's oxidation potential and by predetermining most of the linkages between the heterocyclic rings.[2] We,[3] and others,[4] have utilized these concepts in the synthesis of a series of 1,4-bis(2-furanyl)- and 1,4-bis(2-thienyl)benzenes which form electrically conducting polymers via both chemical and electrochemical polymerization routes. These monomers contain external heterocycles with open α positions available for oxidative coupling polymerization and yield polymers having an alternating 2,2′-biheterocycle/*p*-phenylene repeat unit. They exhibit significantly lower oxidative polymerization potentials than either the parent heterocycle or benzene. Oxidative polymerization of symmetrically derivatized monomers yields isoregically substituted polymers which are significantly more ordered, and exhibit higher electrical conductivities in their doped form, than their unsymmetrically substituted analogs.[3d]

The electropolymerization of pyrrole has proved to be an excellent method for obtaining highly conducting and electroactive polyheterocycles as the monomer oxidizes at a significantly lower potential than either thiophene or furan, and the polymer's redox processes are generally found between −0.5 and 0.0 V vs Ag/AgCl.[2a] With this low oxidation potential to form the conducting state, the polymer is quite stable as a conductor and can be subjected to a high number of redox switches with little degradation in charge response.[5] As such, oligomeric electropolymerizable derivatives, where pyrrole rings are accessible and activated for polymerization, may prove especially useful.

Here we report a unique synthesis of 1,4-bis(pyrrol-2-yl)benzene (BPB), its electropolymerization behavior, and properties of the electroactive and electrically conducting polymer obtained. BPB is activated to electropolymerization, forming an electrically conducting polymer at an extremely low oxidation potential. The 2,2′-bipyrrole/*p*-phenylene polymer formed is highly electroactive with a low potential for switching between the conducting and insulating states. This new synthetic route opens up a number of opportunities for the synthesis of derivatized, potentially soluble and processable, pyrrole-containing polymers. Polymers of similar structure have been prepared via boronic acid coupling polymerization[6] and polymer derivatization methodologies.[7]

Scheme 1



BPB was successfully synthesized via a three-step route as illustrated in Scheme 1. The *N*,*N*′-diallylterephthaldiamide (**1**) was obtained by the reaction of terephthaloyl chloride with allylamine and triethylamine in benzene to give **1** in 75% yield. When reacted with phosgene, compound **1** was converted into the imino chloride derivative **2** in 59% yield. The crude compound **2** was used directly for the next step without purification; it was cyclized to BPB (**3**) after reaction with potassium *tert*-butoxide in THF. The crude **3** was purified by column chromatography (phase, silica gel; eluent, cyclohexane/THF) to give the desired BPB (**3**) in 22% yield. The structure of the monomer, which was obtained in an overall yield of 10% based on terephthalic acid as the starting reagent, was confirmed by ^1H and ^{13}C NMR, MS, and FT-IR.

The cyclic voltammetric (CV) scanning electropolymerization behavior of a 10 mM solution of 1,4-bis(pyrrol-2-yl)benzene to form poly[1,4-bis(pyrrol-2-yl)-*p*-phenylene perchlorate] (PBPB-ClO_4) was examined in CH_3CN/0.1 M tetrabutylammonium perchlorate (TBAP) as shown in Figure 1a by a series of multiple CV's. For comparison, the scanning electropolymerization of pyrrole under similar conditions is shown in Figure 1b.

These oxidative polymerizations proceed through an electrochemically activated step-growth mechanism with the initial formation of a monomer cation radical. This cation radical can either react with a neutral monomer, followed by a second electron transfer and proton loss to form a dimer, or it can couple with a second cation radical, forming the neutral dimer again after proton loss. Sub-

---

* Author to whom correspondence should be addressed.
† Center for Macromolecular Science and Engineering.
‡ Center for Heterocyclic Compounds.

0024-9297/94/2227-7225$04.50/0 © 1994 American Chemical Society

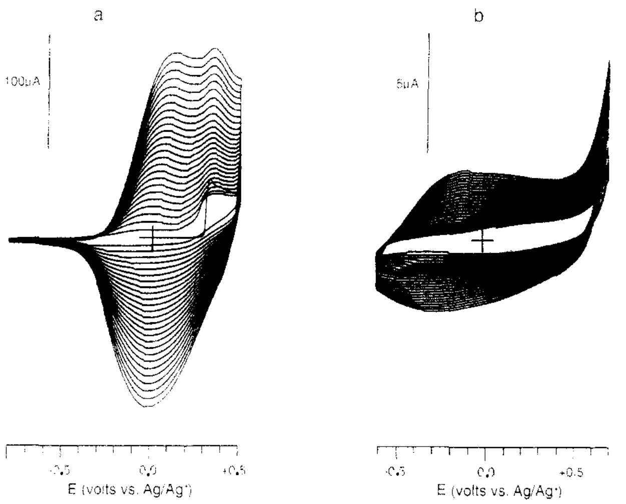


Figure 1. Cyclic voltammetric scanning electropolymerization of (a) 10 mm 1,4-bis(pyrrol-2-yl)benzene in 0.1 M TBAP/CH_3-CN and (b) 10 mM pyrrole in 0.1 M TBAP/CH_3CN.

sequent step oxidation and coupling of the dimers yield oligomers and, ultimately, polymer deposits on the electrode surface in the doped and electrically conducting state **4**. The CV scanning method employed, in which the conducting form **4** is switched to the insulating form **5** during the negative potential sweep of each cycle, was utilized as it tends to yield smooth films and allows the redox activity of the polymer to be monitored with film growth.

BPB exhibits a low oxidation potential at the bare electrode beginning at +0.27 V and peaks ($E_{p,m}$) at +0.35 V vs Ag/Ag^+ as seen in the first scan of Figure 1a. Figure 1b demonstrates that pyrrole, already known to have a relatively low oxidation potential, does not begin to oxidize until +0.6 V and a peak was not resolved in this experiment. The oxidation potential of BPB is low when compared to most other electropolymerizable monomers.[8] Bipyrrole[2h] and 2,5-bis(2-thienyl)pyrrole,[2f] two monomers with comparably low oxidation potentials, exhibit $E_{p,m}$ values at +0.21 and +0.36 V, respectively. Other monomers for comparison, all of which exhibit higher oxidation potentials, include pyrrole ($E_{p,m}$ = +0.9 V), 3-methylthiophene ($E_{p,m}$ = +1.5 V), bithiophene ($E_{p,m}$ = +1.0 V), 1,4-bis(2-thienyl)benzene ($E_{p,m}$ = +0.9 V), and 1,4-bis(2-thienyl)-2,5-dimethoxybenzene ($E_{p,m}$ = +0.7 V).

With repeated scanning of the BPB solution a reversible PBPB redox process quickly develops with an $E_{1/2}$ at 0.0 V and a narrow peak to peak separation. It is evident that the PBPB redox develops quite rapidly and that the monomer is polymerizing efficiently to form a highly electroactive polymer. Comparison with the current response from the 10 mM solution of pyrrole indicates that this monomer forms electroactive polymer about 40 times faster than pyrrole itself. These results suggest that the terminal pyrrole rings are activated to electropolymerization, and this is the focus of further study.

The redox-doped PBPB-ClO_4 was subsequently cycled between its charged and neutral forms in monomer-free electrolyte. A linear increase of peak current with scan rate was found as expected for an electrode-supported electroactive film. A multiple redox switching experiment was carried out on PBPB-ClO_4, prepared via constant potential electropolymerization at +0.4 V, and subsequently switched in monomer-free 0.1 M TBAP/CH_3CN electrolyte. Double potential steps were carried out by holding the potential at +0.3 V for 10 s, stepping to −0.4 V for 10 s, and then returning to the original potential. The charge for each half cycle was monitored and compared to the original charge response, after equilibration of the redox response, as a function of the number of complete switching cycles. After 900 and 2300 double potential switches the polymer retained 67% and 46% of its original charge response, respectively. For comparison purposes, poly(pyrrole chloride), redox switched in 0.1 M $LiClO_4$ (aqueous), exhibits essentially the same switching stability of 65% retention after 900 double potential steps.

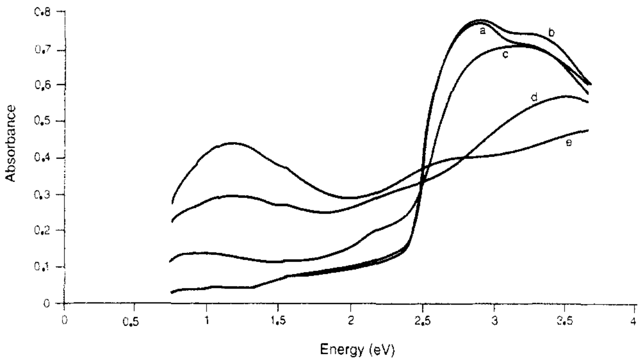


Figure 2. Optoelectrochemical analysis of poly[1,4-bis(pyrrol-2-yl)-*p*-phenylene] in 0.1 M TBAP/CH_3CN. Spectra were run with polymer held at (a) −0.8, (b) −0.4, (c) −0.0, (d) +0.2, and (e) +0.5 V vs Ag wire.

A series of optoelectrochemical studies were carried out and confirmed the bipolaronic nature of the charge carriers as illustrated by Figure 2. The neutral form of the polymer shows a distinct π to π^* transition with a band-gap onset of 2.4 eV (516 nm) and a peak at 2.7–2.8 eV (440–460 nm). Interestingly, this is lower than the values for either polypyrrole or poly(*p*-phenylene). This can be attributed to the highly delocalized nature of the neutral polymer. Theoretical analysis of the polymers' conformation using a complete PRDDO geometry optimization indicates the preferred structure of the polymer to be completely planar.[9] Stepwise oxidation of the polymer shows the growth of bipolaron bands with peaks evolving at approximately 1 and 2.2 eV as the polymer dopes.

A film of PBPB-ClO_4 was electrosynthesized from a 10 mM monomer solution of 0.1 M TBAP/CH_3CN electrolyte. The PBPB-ClO_4 film exhibited a conductivity of 15 S cm^{-1} which is on the same order of magnitude as the conductivities of 10–100 S cm^{-1} found for PP-ClO_4.

In conclusion, electropolymerization of the easily oxidized BPB yields a new conducting polymer, PBPB. The electropolymerization proceeds quite rapidly, and the polymer formed is highly electroactive with a low redox switching potential. The synthetic methodology used to prepare this monomer and polymer open up numerous avenues for the synthesis of derivatized PBPB's and is the subject of continued investigation.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE 9307732).

References and Notes

(1) Krische, B.; Zagorska, M. *Synth. Met.* **1989**, *28*, C263.
(2) (a) Diaz, A. F.; Crowley, J.; Bargon, J.; Gardini, G. P.; Torrance, J. B. *J. Electrochem. Soc.* **1981**, *121*, 355. (b) Chung, T. C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1984**, *30*, 702. (c) Ferraris, J. P.; Skiles, G. D. *Polymer* **1987**, *28*, 179. (d) Laguren-Davidson, L.; Van Pham, C.; Zimmer, H.; Mark, H. B. *J. Electrochem. Soc.* **1988**, *135*, 1406. (e) Hillman, A. R.; Swann, M. J. *Electrochim. Acta* **1988**, *33*, 1303. (f) Ferraris, J. P.; Hanlon, T. R. *Polymer* **1989**, *30*, 1319. (g) Ferraris, J. P.; et al. *J. Chem. Soc., Chem. Commun.* **1989**, 1318. (h) Raymond, D. E.; Harrison, D. J. *J. Electroanal. Chem.* **1990**, *296*, 269. (i) Souto Maior, R. M.; Hinkelmann, K.; Eckert, H.;

Wudl, F. *Macromolecules* **1990**, *23*, 1268. (j) Roncali, J.; Giffard, M.; Jubault, M.; Gorgues, A. *J. Electroanal. Chem.* **1993**, *361*, 145. (k) Glenis, S.; Benz, M.; LeGoff, E.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 12519. (l) Joshi, M. V.; Cava, M. P.; Bakker, M. G.; McKinley, A. J.; Cain, J. L.; Metzger, R. M. *Synth. Met.* **1993**, *55–57*, 948. (m) Musmanni, S.; Ferraris, J. P. *J. Chem. Soc., Chem. Commun.* **1993**, 172.

(3) (a) Ruiz, J. P.; Nayak, K.; Child, A. D.; Marynick, D. S.; Reynolds, J. R. *Mater. Res. Soc. Symp. Proc.* **1990**, *173*, 369. (b) Reynolds, J. R.; Ruiz, J. P.; Child, A. D.; Nayak, K.; Marynick, D. S. *Macromolecules* **1991**, *24*, 678. (c) Child, A. D.; Reynolds, J. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1780. (d) Ruiz, J. P.; Dharia, J. R.; Reynolds, J. R.; Buckley, L. J. *Macromolecules* **1992**, *25*, 849. (e) Reynolds, J. R.; Child, A. D.; Ruiz, J. P.; Hong, S. Y.; Marynick, D. S. *Macromolecules* **1993**, *26*, 2095.

(4) (a) Danieli, R.; Ostoja, R.; Tiecco, M.; Zamboni, R.; Taliani, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1473. (b) Mitsuhara, T.; Tanaka, S.; Kaeriyama, K. *Makromol. Chem.* **1988**, *189*, 1755; *J. Chem. Soc., Chem. Commun.* **1987**, 764. (c) Tanaka, S.; Kaeriyama, K.; Hiraide, T. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 743. (d) Pelter, A.; Maud, J. M.; Jenkins, I.; Sadeka, C.; Coles, G. *Tetrahedron Lett.* **1989**, *30*, 3461. (e) Haynes, P. M.; Hepburn, A. R.; Goldie, D. M.; Marshall, J. M.; Pelter, A. *Synth. Met.* **1993**, *55–57*, 839.

(5) Pyo, M.; Reynolds, J. R.; Warren, L. F.; Marcy, H. O. *Synth. Met.*, in press.

(6) Martina, S.; Schlüter, A.-D. *Macromolecules* **1992**, *25*, 3607.

(7) Pouwer, K. L.; Vries, T. R.; Havinga, E. E.; Meijer, E. W.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1988**, 1432.

(8) Where peak potentials are reported vs SCE in the literature, 0.3 V has been subtracted for direct comparison to Ag/Ag^+.

(9) Hong, S. Y.; Marynick, D. S. *Macromolecules* **1992**, *25*, 3591.