

## Synthesis of Planar Poly(*p*-phenylene) Derivatives for Maximization of Extended $\pi$ -Conjugation

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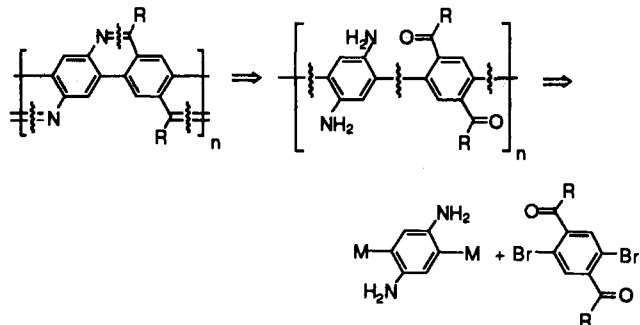
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Poly(*p*-phenylene) (PPP),<sup>1</sup> a highly insoluble polymer that has been studied extensively for its possible electronic and photonic applications, has a 23° twist<sup>1c,2</sup> between its consecutive aryl units due to ortho hydrogen interactions (Figure 1). Attempts to enhance the solubility of PPP by substitution of the rings forces the consecutive aryl units even further out of plane, resulting in a plummet of the extended conjugation (easily observed by the optical spectra).<sup>1i-k</sup> Here we describe a synthetic route to ladder<sup>3</sup> PPP derivatives with bridges that (1) form in high yields upon protonic activation once the PPP backbone is intact, (2) can be substituted so that the newly formed polymer is soluble, unlike many other aromatic ladder polymers, (3) contain a double-bonded unit to keep the consecutive aryl units planar while maximizing extended  $\pi$ -conjugation through the PPP backbone, thereby increasing the bandwidth (lowering the band gap) between the hydroquinoidal and quinoidal forms (Figure 2),<sup>1c</sup> and (4) can be solution-cast into films in the uncyclized form followed by protonic activation to obtain films of the planarized system.

Our retrosynthetic approach involved two key steps (Scheme I, M = metal): first, imine cleavage to the ketoamine function-

### Scheme I



(1) For some recent reviews on polyphenylene, see: (a) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357. (b) Noren, G. K.; Stille, J. K. *Macromol. Rev.* **1971**, *5*, 385. (c) Elsenbaumer, R. L.; Shacklette, L. W. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986. (d) Tourillon, G., in ref 1c. (e) Baughman, R. H.; Brédas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209. For some recent advances in polyphenylene synthesis, see: (f) Ballard, D. G. H.; Courtis, A.; Shirley, I. M.; Taylor, S. C. *Macromolecules* **1988**, *21*, 294. (g) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411. (h) Gin, D. L.; Conticello, V. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3167. (i) Heitz, W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*(1), 327. (j) Percec, V.; Pugh, C.; Cramer, E.; Weiss, R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*(1), 329. (k) Tour, J. M.; Stephens, E. B.; Davis, J. F. *Macromolecules* **1992**, *25*, 499.

(2) We can also accurately calculate the twist angle on a *p*-phenylene decamer to be 22.3° using MMX with extended  $\pi$ -Hückel parameters. For a discussion of twist angle versus degree of extended conjugation, see: (a) Brédas, J. L., in ref 1c. (b) Ferraris, J. P.; Andrus, R. G.; Hrnčir, D. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1318. (c) Gorman, C. B.; Ginsburg, E. J.; Moore, J. S.; Grubbs, R. H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*(3), 714. (d) Orchard, B. J.; Freidenreich, B.; Tripathy, S. K. *Polymer* **1986**, *27*, 1533.

(3) For some discussions of aromatic ladder polymers, see: (a) Overberger, C. G.; Moore, J. A. *Adv. Polym. Sci.* **1970**, *7*, 113. (b) Schlüter, A.-D. *Adv. Mater.* **1991**, *3*, 282. (c) Yu, L.; Chen, M.; Dalton, L. R. *Chem. Mater.* **1990**, *2*, 649. (d) Hong, S. Y.; Kertesz, M.; Lee, Y. S.; Kim, O.-K. *Chem. Mater.* **1992**, *4*, 378. (e) Godt, A.; Schlüter, A.-D. *Adv. Mater.* **1991**, *3*, 497. (f) Yu, L.; Dalton, L. R. *Macromolecules* **1990**, *23*, 3439.

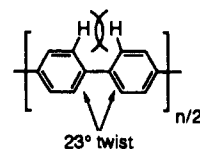


Figure 1. Structure of PPP, with a 23° twist between consecutive aryl units due to ortho hydrogen interactions.

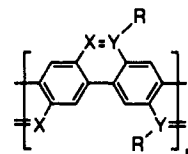
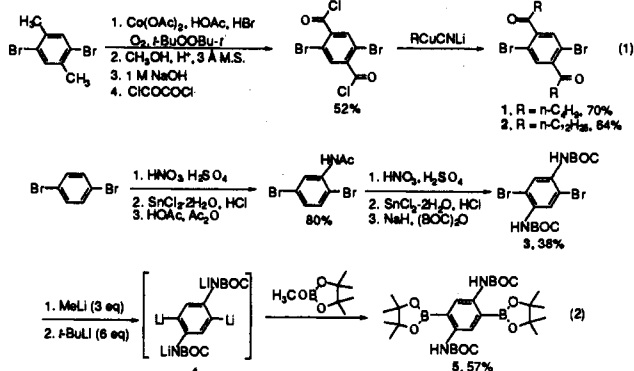


Figure 2. The consecutive benzenoid rings are held planar by the double bonded bridging units so as to maximize the extended  $\pi$ -conjugation. The R groups permit solubility of the planar system.

alized PPP, and second, bond cleavage to the two arene systems shown. Since Pd(0)-catalyzed oxidative addition reactions are facilitated by electron-deficient ring systems,<sup>4</sup> we chose to keep the halides on the ketoaromatic portion.

After several nearly quantitative model reactions, we synthesized the two key monomers needed for the desired AB-type step growth polymerization (eqs 1 and 2).<sup>5</sup> It is remarkable that while



3 was nearly insoluble in ether, it could be tetralithiated in ether to form a soluble intermediate (4) in almost quantitative yield (checked by addition of TMSCl and isolation of the arylbis(silane) after aqueous workup). Treatment of 4 with methyl pinacolborate afforded the monomer 5, which could be purified by passage through a flash chromatography column containing a mixture of activated charcoal and Celite as the stationary phase (silica gel or neutral alumina caused rapid decomposition of the intermediate) and  $\text{CH}_2\text{Cl}_2$  as the eluant followed by recrystallized to form pure 5.<sup>6</sup>

Reaction of 1 or 2 with 5 in the presence of a Pd(0) catalyst yielded the soluble polymers 6 and 7, respectively, from which size exclusion chromatography (SEC) could be used to determine the hydrodynamic volumes relative to polystyrene (6, 63% yield after fractional precipitation,  $M_n = 9850$  with  $M_w/M_n = 1.85$ ; 7, 97% yield after fractional precipitation,  $M_n = 28400$  with  $M_w/M_n = 3.70$ ). Upon exposure of 6 or 7 to trifluoroacetic acid (TFA), quantitative loss of the BOC protecting group and cyclization afforded 8 (90% yield) and 9 (97% yield), respectively

(4) (a) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513. (b) Siddiqui, M. A.; Snieckus, V. *Tetrahedron Lett.* **1988**, *29*, 5463. (c) Gronowitz, S.; Lawitz, K. *Chem. Scr.* **1984**, *24*, 5.

(5) (a) The *tert*-butylperoxide-modified Co-based oxidation was far superior to several permanganate oxidations attempted. See: Hay, A. S.; Blanchard, H. S. *Can. J. Chem.* **1965**, *43*, 1306. The dicarboxylic acid was then converted to the diester to facilitate purification. (b) Doornbos, T.; Strating, J. *Org. Prep. Proced.* **1969**, *1*, 287.

(6) The arylbis(boronic acid) analog of 5 could not be adequately purified for the step growth polymerization.

