Synthesis of Planar Poly(*p*-phenylene) Derivatives for Maximization of Extended π -Conjugation

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Poly(p-phenylene) (PPP),¹ a highly insoluble polymer that has been studied extensively for its possible electronic and photonic applications, has a 23° twist^{1c,2} 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).^{1i-k} Here we describe a synthetic route to ladder³ 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 π -conjugation through the PPP backbone, thereby increasing the bandwidth (lowering the band gap) between the hydroquinoidal and quinoidal forms (Figure 2), 1c 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



 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) Tourillion, 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 π -Hückel parameters. For a discussion of twist angle versus degree of extended conjugation, see: (a) Brédas, J. L., in ref lc. (b) Ferraris, J. P.; Andrus, R. G.; Hrncir, 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.



L $\mathbf{R} = \mathbf{J}_{\mathbf{n}}$ Figure 2. The consecutive benzenoid rings are held planar by the double bonded bridging units so as to maximize the extended π -conjugation. The

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,⁴ we chose to keep the halides on the ketoaromatic portion.

R groups permit solubility of the planar system.

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).⁵ 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 CH_2Cl_2 as the eluant followed by recrystallized to form pure 5.⁶

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

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

^{(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 disetre to facilitate purification. (b) Doornbos, T.; Strating, J. Org. Prep. Proced. 1969, 1, 287.

(eq 3).^{7.8} All stretches for the ketone, carbamate, and amine in 6 and 7 were absent in the FTIR spectrum of 8 and 9.



Samples of 8 and 9 can be solubilized with CH_2Cl_2/TFA (3:2) mixtures. Additionally, 7 can form THF solution-cast films and then be cleanly cyclized by suspension of the film in anhydrous HCl/EtOAc followed by proton removal with $Et_3N/NaOH$ to afford 9 as a flexible free-standing film. Again, this film was devoid of ketone, carbamate, and amine absorptions in the FTIR spectrum. Therefore, the dodecyl groups are apparently exerting a plasticizing effect so that even this planar rigid rod polymer can possess good film-forming properties.

Powder X-ray diffraction (XRD) of annealed 8 showed a broad pattern at 14 and 41 Å, while 9 showed a similar pattern at 27 and 45 Å. Differential scanning calorimetry (DSC) (50-350 $^{\circ}$ C, 20 deg/min, N₂) thermograms of 8 and 9 were featureless on both the first and second heating cycles. Thermogravimetric analysis (TGA) (50-900 °C, 20 deg/min, N₂) of 9 showed an onset of major weight loss at 400 °C, 10% weight loss at 434 °C, and 50% weight loss at 550 °C. The TGA thermogram of 8 was similar. Most exciting are the optical absorption data showing enormous bathochromic shifts in the polymers upon cyclization (conversion of 6 to 8 and 7 to 9), an observation consistent with the proposed ladder formation (Table I). Also interesting is the large hypsochromic shift in the spectrum of protonated 9 (solution) relative to 9 in the neutral form (solid), suggesting that cationic nitrogen atoms retard the extended conjugation. The absorptions of these planar polymers are far more bathochromically-shifted than those of the planar trimers,⁹ oligo(p-phenylenes), and PPP,¹⁰

(7) The twist in 8 and 9 is <1° between the consecutive phenyl rings calculated by MMX with extended π -Hückel parameters.

(8) Highest molecular weight samples of 6 and 7 were obtained when the Pd-catalyzed coupling was done for ~24 h using an equimolar mixture of 1:5 or 2:5, respectively, followed by the addition of a 5-10 mol % excess of 5 with continued heating for 1-2 days. We thank a reviewer for suggesting this monomer addition sequence. 6: Anal. Calcd for $(C_{22}H_{42}N_2O_6)_n$: C, 69,79; H, 7.69; N, 5.09. Found: C, 70.55; H, 7.25; Br, <0.5; N, 5.13. 7: Anal. Calcd for $(C_{24}H_{74}N_2O_6)_n$: C, 69,79; H, 9.40; Br, <0.5; N, 3.55. 8: Anal. Calcd for $(C_{22}H_{22}N_2)_n$: C, 84.04; H, 7.05; N, 8.91. Found: C, 79.13; H, 6.77; Br, <0.5; N, 8.56. 9: Anal. Calcd for $(C_{34}H_{54}N_2)_n$: C, 84.70; H, 10.10; N, 5.20. Found: C, 81.45; H, 9.64; Br, <0.5; N, 5.22.

(9) The planar trimers were prepared during our model studies for the polymerizations described here using Pd-catalyzed couplings.

(10) Ried, W.; Freitag, D. Angew. Chem., Int. Ed. Engl. 1968, 7, 835. (11) Drs. R. Gaudiana and P. Mehta of Polaroid Corporation kindly provided the solid-state UV-vis data.

Table I. Optical Absorption Data



 $^{a} \lambda_{max}$ is underlined; (sh) is shoulder, (ed) is tailing edge at ~10% of λ_{max} intensity. b Also a strong carbonyl absorption at 196 nm. c Spectrum recorded on the acid solubilized, therefore, multiprotonated system. d These λ_{max} values were recorded on a series of four different polymer samples of 9 in order to ensure their reproducibility.¹¹

while the λ_{max} values are in the range of other near-planar PPP derivatives that have been synthesized.¹²

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Supplementary Material Available: Detailed synthesis procedures and characterization data for compounds 1–3 and 5–9 (6 pages). Ordering information is given on any current masthead page.

⁽¹²⁾ The near-planar benzenoid ladder polymers were prepared by Pdcatalyzed couplings. See: Scherf, U.; Müllen, K. Makromol. Chem., Rapid Commun. 1991, 12, 489. Scherf, U.; Müllen, K. Synthesis 1992, 23. Scherf, U.; Müllen, K. Macromolecules 1992, 25, 3546.