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Synthesis of Poly(phenylenes) by a Rapid Polymerization of 1-Bromo-4-lithiobenzene Using HMPA

by

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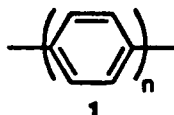
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) A synthesis of poly(phenylene) is described by the treatment of 1-bromo-4-lithiobenzene with hexamethylphosphoramide (HMPA). The polymerization occurred nearly instantaneously even at -78°C. Conditions have been optimized using dioxane as a solvent and HMPA addition at 70-80°C to afford poly(phenylenes) that are predominantly <i>para</i> -linked. The polymers are soluble in THF, dichloromethane, and chloroform. Analysis of the initially formed polymers showed that there was a high bromide content (approximately one bromide for every three aryl rings). Debromination of the material was achieved by treatment with butyllithium and quenching with water. The M_w of the debrominated polymer was 3178 by SEC analysis.					
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SYNTHESIS OF POLY(PHENYLENES) BY A RAPID POLYMERIZATION OF 1-BROMO-4-LITHIOBENZENE USING HMPA

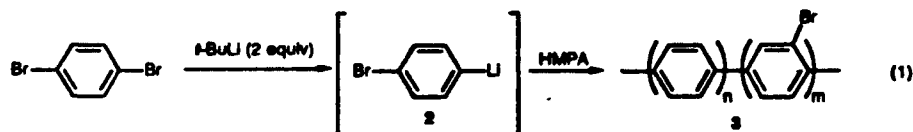
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Poly(*p*-phenylene) (PPP) (1) has attracted much interest since



it can act as an excellent organic conductor upon doping.² The conductivity of doped PPP has reached beyond the semiconducting and into the conducting region with values of $500 \Omega^{-1}\text{cm}^{-1}$ being reported for the pressed pellets (films could not be formed due to the insolubility). There have been numerous syntheses of PPP, however, in nearly all cases, the materials are insoluble and intractable in organic solvents.³⁻¹⁰ The most widely used methods for PPP formation involve the Kovacic and Yamamoto approaches that afford materials with degrees of polymerization of 10-15.²

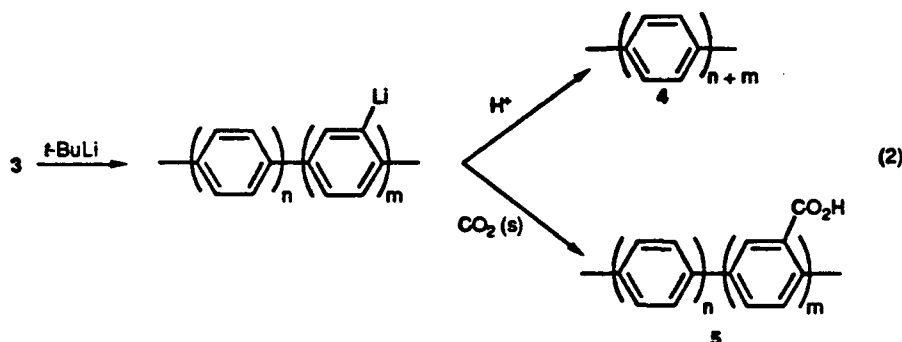
We recently developed a method for the polymerization of 1-bromo-4-lithiobenzene (2) by a facile aryl-aryl coupling scheme which is nearly instantaneous even at -78°C . Though the reaction does occur at -78°C , the optimal method involves the treatment of 1,4-dibromobenzene (1 equiv) in dioxane at 0°C with *t*-butyllithium (2 equiv) to form (2). The intermediacy of 2 was confirmed in a separate experiment by the addition of chlorotrimethylsilane to form 1-bromo-4-(trimethylsilyl)benzene in nearly quantitative yield. The second equivalent of the *t*-butyllithium was necessary for the elimination of the *t*-butyl bromide to afford lithium bromide, isobutylene, and isobutane. This conveniently made all the by-products innocuous. The solution containing 2 was heated to 75°C and hexamethylphosphoramide (HMPA)¹¹ was added all at once. The polymerization to 3 was complete immediately upon completion of the HMPA addition (eq 1). Polymer (3) had one



bromide group (%C, H, Br = 68.94, 4.11, 25.22, respectively) for approximately every three aryl rings in 25-30% yield after one fractional precipitation from ether. It is clear from the FTIR analysis that predominantly *para*-linked material is formed by the strong band at 808 cm^{-1} with weak bands at 882 and 790 cm^{-1} attributed to the *meta*-linkages.¹² Likewise, the

C-Br stretch was evident at 1074 cm^{-1} .⁵ The polymer was soluble in THF, dichloromethane, and chloroform. Though powder X-ray diffraction (XRD) signals have been reported for Kovacic^{2b} and Yamamoto PPP,⁵ no diffraction pattern was observed for **3**, consistent with the solubility of the material. Likewise, scanning electron microscopic (SEM) analysis showed a globular morphology pattern. Size exclusion chromatography (SEC) showed that **3** had a $M_w = 2404$ and $M_w/M_n = 2.33$ relative to polystyrene and oligo(*p*-phenylenes).¹³ There was little, if any, aliphatic material present in the polymer by ^1H NMR.

The brominated polymer **3** could be lithiated with *n*-butyllithium in THF at -78°C and protonated to afford polymer **4** or treated with CO_2 (s) to afford the carboxylated derivative **5** (eq 2). Polymer **4** had 0% bromide content by elemental



analysis. Remarkably, the M_w increased from 2404 for **3** to 3178 for **4** ($M_w/M_n = 2.80$) upon debromination while the material remained soluble with degrees of polymerization >40 . Some possible explanations could be that (1) the bromide content in **3** caused the polymer to be retained more tightly by the SEC columns (cross-linked polystyrene) and thus respond as a lower molecular weight material or (2) re-lithiation caused a further coupling and/or crosslinking of the chains. Again, no powder XRD signals were observable and SEM showed a globular morphology. In the UV spectrum, polymers **3** and **4** showed λ_{max} at 274 and 278 nm, respectively. These values are indicative of mixtures of *para*- and *meta*-linked material.¹⁴ Both polymers **3** and **4** are electroactive. A Pt-electrode was coated with films of both compounds **3** and **4**. Anodic peak potentials (E_{pa}) for the oxidation were at 1.44 and 1.45 V, respectively [recorded relative to Ag/AgNO_3 (0.01 M) in CH_3CN at 50 mV/s scan rate with 0.1 N tetraethylammonium perchlorate (TEAP) as the electrolyte and a Pt working electrode].¹⁵

The formation of polymer **5** demonstrates the flexibility of this approach for the synthesis of functionalized derivatives. The FTIR (KBr) spectrum of **5** was free of the C-Br stretch at 1074 cm^{-1} with the major stretch at 1686 cm^{-1} for the carbonyl moiety. The O-H stretch was weak presumable due to restricted hydrogen bonding in the solid. Elemental analysis showed %C, H = 76.10, 4.99. This procedure could have tremendous applications for the synthesis of functionalized polymers for self-doped conducting systems with fast electrochromic switching times and the fabrication of

Experimental

Preparation of polymer 3. To a 25 mL two-necked round-bottomed flask containing a Teflon coated magnetic stir bar and fitted with a reflux condenser was added 1,4-dibromobenzene (0.477 g, 2.0 mmol) and dioxane (2 mL). After cooling the solution to 0°C, *t*-butyllithium (2.4 mL, 4.2 mmol, 1.75 M in pentane) was slowly added. The ensuing white-yellow slurry was stirred at 0°C for 30 min before warming rapidly to 85°C with an oil bath. To the solution was rapidly added HMPA¹¹ (0.35 mL, 1 mmol) (EXOTHERMIC!) and the dark solution was allowed to cool to room temperature. The reaction mixture was poured into 3 N hydrochloric acid (25 mL) and the organic layer was separated. The aqueous phase was extracted with dichloromethane (3x) and the combined organic phase was washed with 3 N hydrochloric acid (10x). The solution was dried over anhydrous magnesium sulphate and removal of the solvent *in vacuo* afforded a tan-brown solid. Ether soluble fraction = 0.1132 g. Ether insoluble but THF soluble fraction = 0.0296 g. See text for additional data.

Trapping of the intermediate 1-lithio-4-bromobenzene (2) to form 1-bromo-4-(trimethylsilyl)benzene. To a solution of 1,4-dibromobenzene (23.6 g, 100 mmol) in ether (150 mL) was added at -78°C *t*-butyllithium (123.5 mL, 210 mmol, 1.7 M in pentane) over 1 h. The solution was stirred for one hour at -78°C and chlorotrimethylsilane (14 mL, 110 mmol) was added over 10 min. The solution was warmed to room temperature for 30 min and poured into water. The aqueous layer was extracted with ether (3 x 30 mL), and the combined organic layers were washed with brine and dried over magnesium sulfate. The solvent was removed *in vacuo* and no further purification was needed to afford 19.6 g (86%) of the title compound as a clear colorless oil. IR (neat) 2956, 1574, 1479, 1376, 1251, 1106, 1067, 1012, 841 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.47 (d, *J* = 8.3 Hz, 2 H), 7.36 (d, *J* = 8.3 Hz, 2 H), 0.24 (s, 9 H).

Debromination of 3 to form 4. To a stirred solution of 3 (0.0329 g) in THF (3.5 mL) was added at -78°C *t*-butyllithium (0.6 mL, 1.0 mL, 1.7 M in pentane). The ensuing brown-black reaction solution was stirred at -78°C for 1 h. To the solution was added at -78°C water (15 mL). The solution was then allowed to warm to room temperature. The solution was then poured into 3 N hydrochloric acid. The organic layer was separated and the aqueous portion extracted with methylene chloride (3x). The combined organic layers were washed with water and dried over magnesium sulphate. Filtration and removal of the solvent *in vacuo* afforded 0.0234 g of a brown solid. See text for additional data.

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