

## Poly(aniline boronic acid): A New Precursor to Substituted Poly(aniline)s

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### EXPERIMENTAL

*Reagents.* 3-aminophenylboronic acid (ABA), bromine and iodine were purchased from Aldrich. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%) and hydrochloric acid (conc.) were purchased from EM Science. The water that was used for all experiments was purified and deionized (18.3 MΩ). All chemicals were used as received.

*Instrumental setup.* Glassy carbon (GC) electrodes (3 mm diameter) were purchased from Bioanalytical Science. Cyclic voltammetry was performed with a potentiostat (EG&G Model: 362). In the voltammetric experiments, a three-electrode configuration was used including a platinum wire (length: 50 cm, diameter: 0.2mm) counter electrode and a Ag/AgCl reference electrode. XPS spectra were recorded with an M-Probe surface spectrometer (Surface Science Instruments). All spectra were recorded with focused and monochromatized Al Kα<sub>1,2</sub> irradiation (hν=1486.6 eV), and the X-ray beam was incident on the surface at an angle of 55° with respect to the surface normal. All binding energies (BE) were referenced to the aromatic C1s peak, which was assigned a value of 284.7 eV according to the protocol described in Beamson G.; Briggs, D. *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*; Wiley and Sons: Chichester, 1992.

*Poly(aniline boronic acid) deposition.* The oxidative polymerization of 3-aminophenylboronic acid was performed producing poly(aniline-3-boronic acid)(PABA) as follows: 3-aminophenylboronic acid (40 mM) and sodium fluoride (200 mM) were dissolved in 25 mL 0.5 M aqueous hydrochloric acid solution. The potential of the GC electrode was scanned between 0.0 and 1.1 V vs. Ag/AgCl at a scan rate of 100 mV/s, and then polymerization was halted at +0.8 V when the charge passed for the reduction of the deposited polymer reached 0.34 mC. PABA film had a deep greenish blue color similar to that obtained upon the formation of poly(aniline). After careful washing of the film with pure water, the electrode was soaked in 0.5 M hydrochloric acid.

*Transformation from PABA to poly(hydroxyaniline).* A beaker was charged with 3 mL H<sub>2</sub>O<sub>2</sub> (30%) containing 0.5 M hydrochloric acid. The PABA electrode was dipped in the solution for 10 min at r.t. (25 °C). The color of the film turned from green to deep blue. The reaction was monitored frequently throughout the course of the transformation with CV in 0.5 M hydrochloric acid by scanning within a potential window of -0.3 to +0.6 V vs. Ag/AgCl at scan rate of 100 mV/sec. After careful washing of the layer with pure water, the electrode was stored in 0.5 M hydrochloric acid.

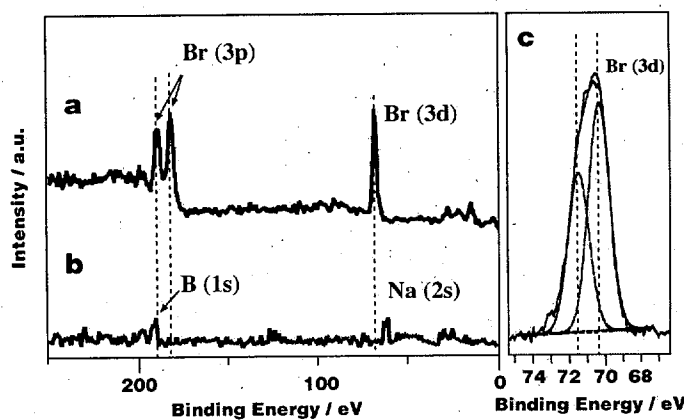
*Transformation from PABA to poly(iodoaniline).* The reaction conditions used were the same as those previously reported (Kuivila, H. G.; Williams, R. T., *J. Org. Chem.* **1954**, *76*, 2679-2682.). A stock solution was made as follows: Iodine (101.5 mg, 4 mM), sodium acetate

(1.969 g, 0.24 M), acetic acid (2.17 g, 0.361 M) were dissolved in 100 mL of an aqueous solution containing 5% methanol. The PABA electrode that was freshly made was dipped in the solution (5 mL) for 50 min at r.t. The reaction was monitored frequently throughout the course of the transformation with CV in 0.5 M hydrochloric acid by scanning within a potential window of 0.0 to +0.8 V vs. Ag/AgCl at scan rate of 100 mV/sec.

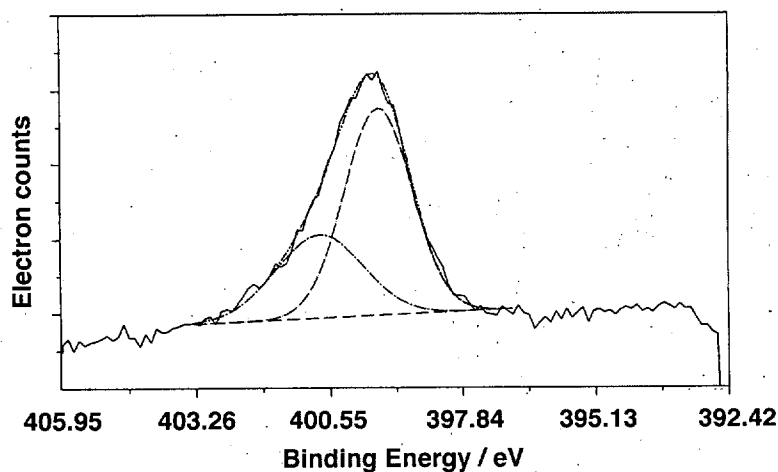
*Transformation from PABA to poly(bromoaniline).* The reaction conditions used were the same as those previously reported (Kuivila, H. G.; Easterbrook, E. K., *J. Org. Chem.* **1951**, *73*, 4629-4632.). A stock solution was made first as follows: Bromine (320 mg, 20 mM) was dissolved in 100 mL 50 wt% acetic acid aqueous solution. The PABA electrode that was freshly made was dipped in the solution (5 mL) for 10 min at r.t. The reaction was monitored frequently throughout the course of the transformation with CV in 0.5 M hydrochloric acid by scanning within a potential window of 0.0 to +0.8 V vs. Ag/AgCl at scan rate of 100 mV/sec.

### XPS

XPS was performed to examine the presence and speciation of Br and N after the transformation of PABA. Figure 1s shows a survey scan and high-resolution spectra in the Br 3p and 3d region. Figure 2s shows the high resolution spectra in the N1s region.

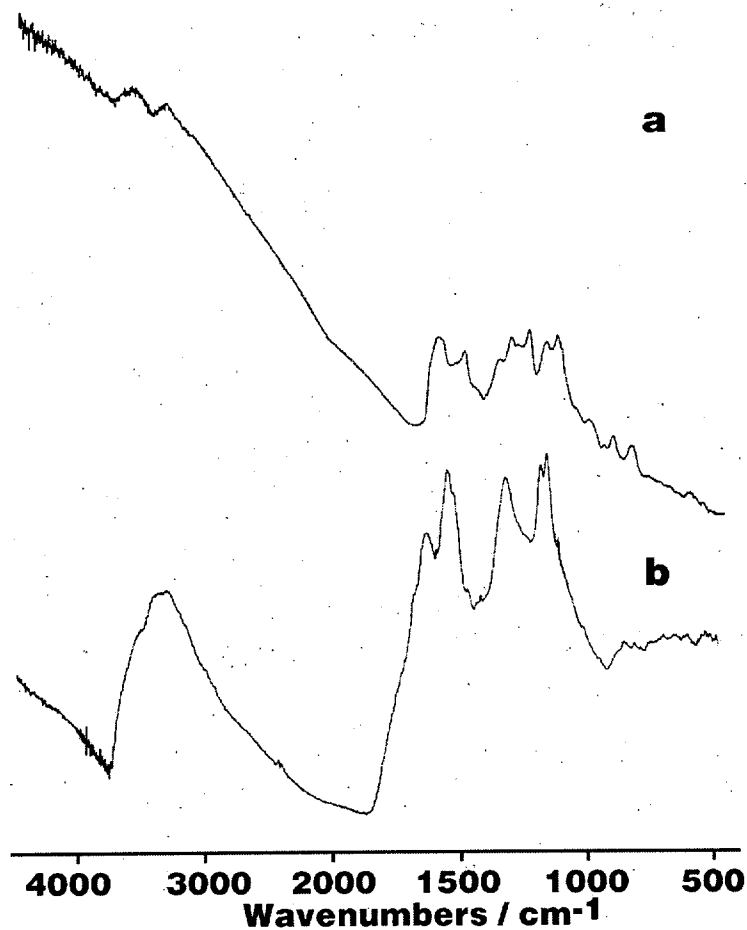


**Figure 1s.** XPS survey scan of PABA (a) after and (b) before ipso-bromination. (c) High-resolution scan after the reaction.



**Figure 2s.** High-resolution XPS spectra of the N 1s region following ipso-bromination.

FT-IR



**Figure 3s.** FT-IR spectra of electrochemically generated PABA (a) before ( $\nu(\text{N}=\text{Q}=\text{N})$ :1595,  $\nu(\text{N}=\text{B}=\text{N})$ :1498, ring deformation (1,2,4 substitution): 920, 880, 816  $\text{cm}^{-1}$ ), and (b) after (hydrogen bonded hydroxygroups  $\nu(\text{O}-\text{H})$ :ca. 3300  $\text{cm}^{-1}$ ) hydroxylation.