



Synthesis of self-doped polyaniline bearing phosphonic acid moiety via Pd-catalyzed phosphonation of poly(2-bromoaniline)

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ABSTRACT

Self-doped conducting polyaniline bearing phosphonic acid moiety was synthesized via the Pd-catalyzed phosphonation of poly(2-bromoaniline) as a key reaction.

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Self-doped conducting polymers (p-type), in which anionically charged functional groups are bound via covalent bonds (Scheme 1a), are attractive for a wide range of applications, including electronics materials, biosensor materials, etc.¹ The properties of self-doped conducting polymers include water solubility, efficient doping, etc. Most commonly used functional group in self-doped conducting polymers is sulfonic acid.² On the other hand, phosphonic acid is considered to be attractive because two acidic protons are available. More specifically, the second acid moiety not used for doping would provide the features, such as acid/base complexation with keeping the doping state. However, research on self-doped conducting polymers possessing phosphonic acid moiety has been still limited compared to those with sulfonic acid.³

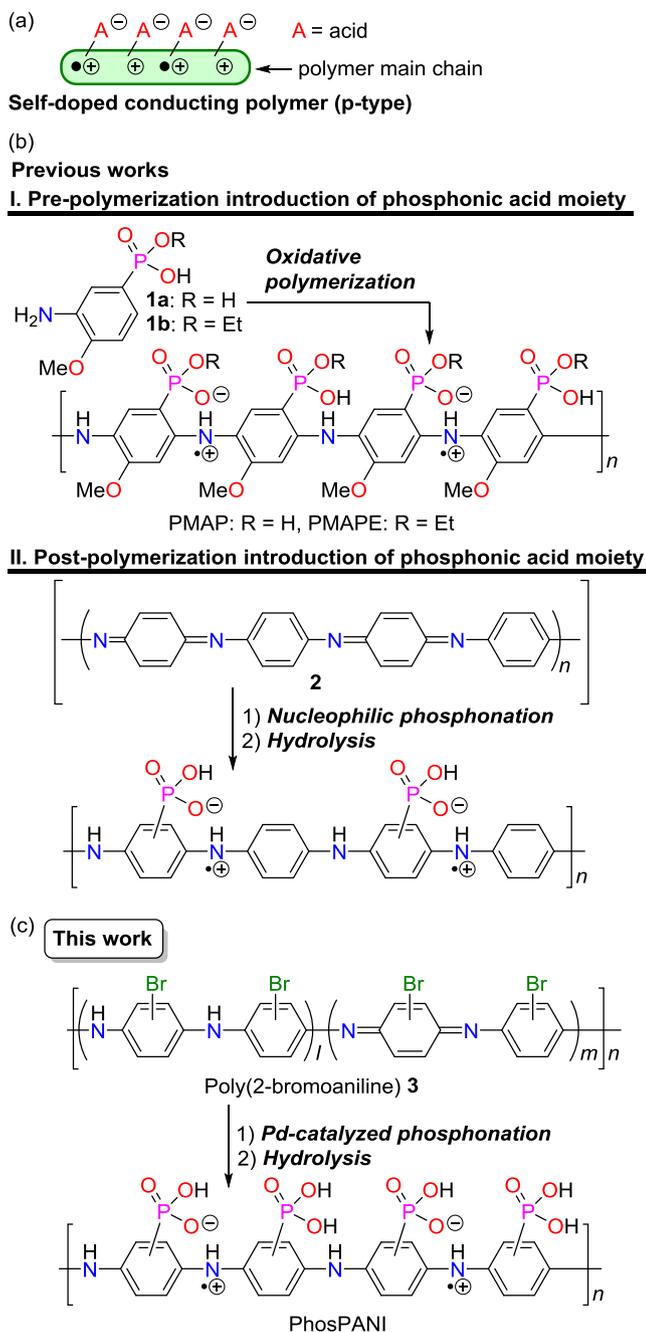
Under such a background, we have developed self-doped conducting polyanilines (PANIs) bearing phosphonic acid moiety, poly(2-methoxyaniline-5-phosphonic acid) (PMAP) (Scheme 1b-I).⁴ This is the first example of PANI where phosphonic acid moiety directly bonds to the main chain. Poly(2-methoxyaniline-5-phosphonic acid monoethyl ester) (PMAPE),⁵ which has phosphonic acid monoethyl ester, was also synthesized and characterized. The conductive properties of various amine complexes of PMAP were investigated and the charge dissipation properties of some PMAP/amine complexes in the electron-beam lithography were reported.⁶ Deprotonation-induced efficient delocalization of polaron is also suggested in PMAP.⁷ Furthermore, an organic

solvent soluble self-doped PANI was prepared via salt formation of PMAP with didodecyldimethylammonium bromide.⁸

In the synthesis of self-doped PANIs, the timing to introduce acid moieties can be classified by before^{1a,2c,3a,3b} or after^{2b,9,10} polymerization. PMAP and PMAPE were synthesized via the oxidative polymerization of the corresponding monomer bearing phosphonic acid moiety (Scheme 1b-I).^{4,5} On the other hand, the post-polymerization introduction is attractive because there is no need to worry about the reactivity of monomers in the oxidative polymerization. For example, the electron-withdrawing group on monomer decreases the reactivity in oxidative polymerization. In fact, (2- or 3-aminophenyl)phosphonic acid moiety which corresponds to the structure (Scheme 1a) without methoxy group showed low reactivity for the oxidative polymerization.^{4a} For the synthesis of PANIs bearing sulfonic acid via post-polymerization introduction, both electrophilic^{2b,9} and nucleophilic¹⁰ (accompanying the reduction of the quinoid moiety) substitution reactions have been reported. Recently, we reported the direct phosphonation at the main chain of PANI via nucleophilic phosphonation to PANI (an oxidized form **2**, Scheme 1b-II).¹¹ In this context, we conceived on Pd-catalyzed phosphonation of poly(2-bromoaniline) (**3**, Scheme 1c). In this approach, one phosphonate can be introduced into one aniline unit in contrast to the nucleophilic phosphonation approach where one or two phosphonates can be introduced at a quinoid moiety (Scheme 1b-II). Here, we report the synthesis of self-doped conducting PANI (PhosPANI) bearing phosphonic acid moiety via the Pd-catalyzed phosphonation as a key reaction.

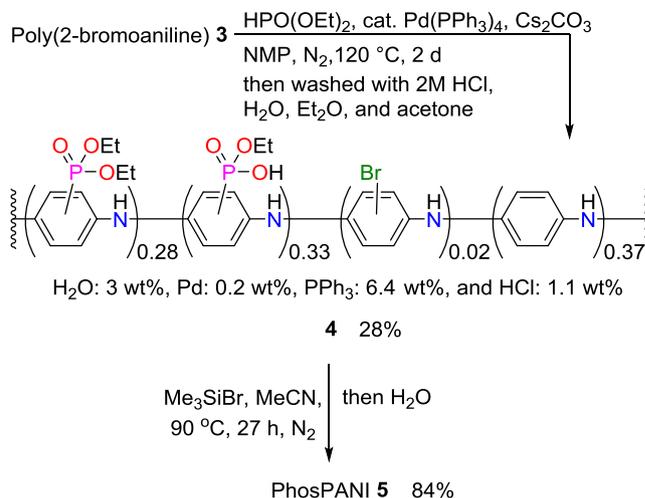
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Scheme 1. (a) Schematic illustration of self-doped conducting polymer (p-type). (b) Previous work. **I:** PMAP and PMAPE synthesized via oxidative polymerization. **II:** Nucleophilic phosphonation of an oxidized form of PANI. (c) This work: Synthesis of PhosPANI via the Pd-catalyzed phosphonation.

Polymer **3** was prepared by using the modified procedure of previously reported one.¹² In order to introduce the phosphonate moiety to **3**, Pd-catalyzed coupling reaction developed in our laboratory was employed.¹³ Polymer **3** was coupled with $\text{HPO}(\text{OEt})_2$ in the presence of $\text{Pd}(\text{PPh}_3)_4$ (4 mol%) and Cs_2CO_3 (1.1 equiv) in NMP under a nitrogen atmosphere at 120 °C for 2 days. After washing the obtained crude product with aqueous 1 M HCl solution, H_2O , Et_2O , and acetone, the phosphonated product **4** was obtained. Partial hydrolysis was indicated due to high reaction temperature and long reaction time in the presence of base. To investigate the composition of **4**, ICP-AES for the analysis of phosphorus and palladium, ion-chromatography for the analysis of chlorine and



Scheme 2. Synthesis of PhosPANI **5** via Pd-catalyzed phosphonation. Each unit should be randomly arranged.

bromine, and thermogravimetry analysis (TGA) for H_2O were performed. In ^{31}P NMR spectrum, the two main broad peaks and a small peak (7%) appeared at around 20, 17 (in a range for $\text{ArP} (= \text{O})(\text{OR})_2$), and -6 (PPh_3) ppm, respectively. (Fig. S2). ^1H NMR also showed the presence of the ethyl group derived from the ethyl phosphonate (Fig. S3). UV-vis-NIR absorption spectra of the mixture suggested the reduction of the quinoid moiety (Fig. S1). These analyses (see Supporting Information) resulted in the structure for **4** shown in Scheme 2. Substitution rate of the phosphonate moiety based on all of the aniline units was 61%. The rate of the residual bromide was 2%. Reduction of bromide was indicated as a side reaction (37%). Residual palladium was observed in 0.2 wt%. Presence of HCl (1.1 wt%) was also suggested. Thus, carbon-phosphorus bond formation mainly took place.

Hydrolysis of **4** was conducted by treating with Me_3SiBr , followed by pouring into H_2O .¹⁴ Washing the resulted precipitate with H_2O , Et_2O , and acetone gave the corresponding PhosPANI **5** as a black solid. The washing was performed under air, and main chain seems to be oxidized in some degree because the absorption spectra (Fig. 3 and Fig. S4) shown below suggest the half-oxidized form. PhosPANI **5** was comparatively soluble in aqueous basic solution, but their solubility was low in organic solvents and neutral to acidic aqueous solutions.

Thermal stability of PhosPANI **5** was investigated by TGA (Fig. 1). It suggests that PhosPANI **5** includes approximately 5 wt% of H_2O . From about 100 to 400 °C, gradual weight loss (upto ca. 15%) was observed. Finally, ca. 27% weight loss was observed at 500 °C. This might be due to the cleavage of the phosphonic acid moiety. The values for weight loss at 400 and 500 °C are in a similar level to those for PMAP.^{4c}

The solid of PhosPANI **5** exhibited an ESR signal with a single resonance line at $g = 2.003$, where hyperfine coupling was not observed (Fig. 2). The spectrum is typical for related conducting PANIs,¹⁵ indicating the self-doping. The peak-to-peak line width ΔH_{pp} has been used to estimate the level of delocalization of electrical charge carrier in PANI, where the smaller ΔH_{pp} shows more efficient delocalization.¹⁶ The ΔH_{pp} for **5** was 0.73 mT, which is larger than that of the solid state ESR for PMAP ($\Delta H_{\text{pp}} = 0.18$ mT). These results suggest that the polaron of PhosPANIs **5** is less delocalized than that of PMAP.

Fig. 3 shows an electronic absorption for the films of PhosPANI **5**. The film of **5** was formed on a glass substrate by drop-cast of aqueous NH_3/MeOH suspension of **5** followed by annealing at 100 °C for 1 min. The absorption spectrum of the thus-obtained

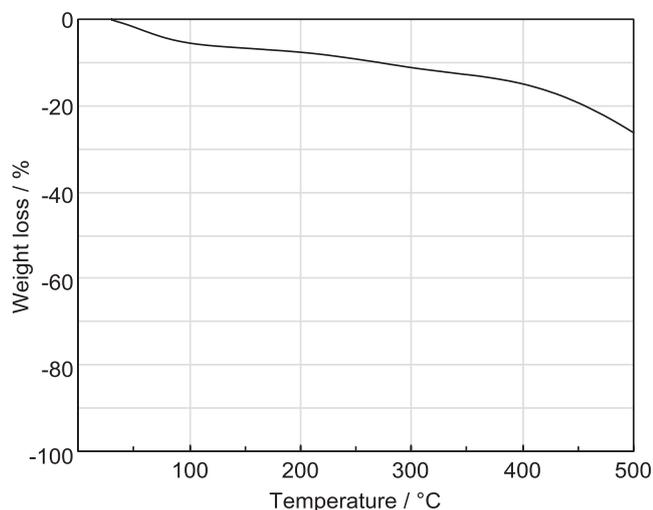


Fig. 1. TGA curve for PhosPANI 5 under a nitrogen atmosphere.

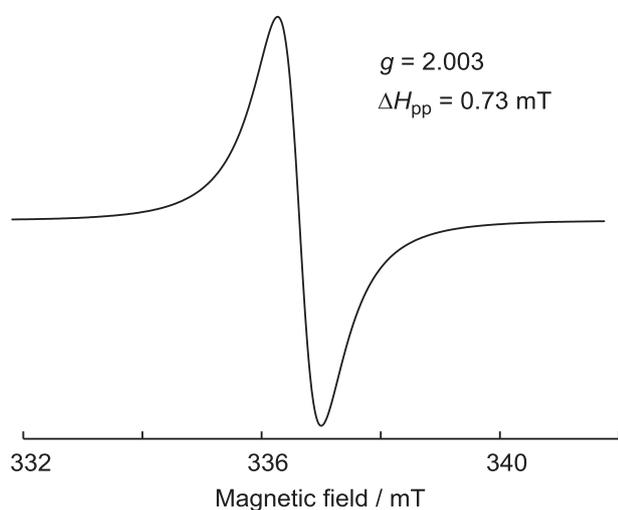


Fig. 2. ESR spectrum of PhosPANI 5 (solid state).

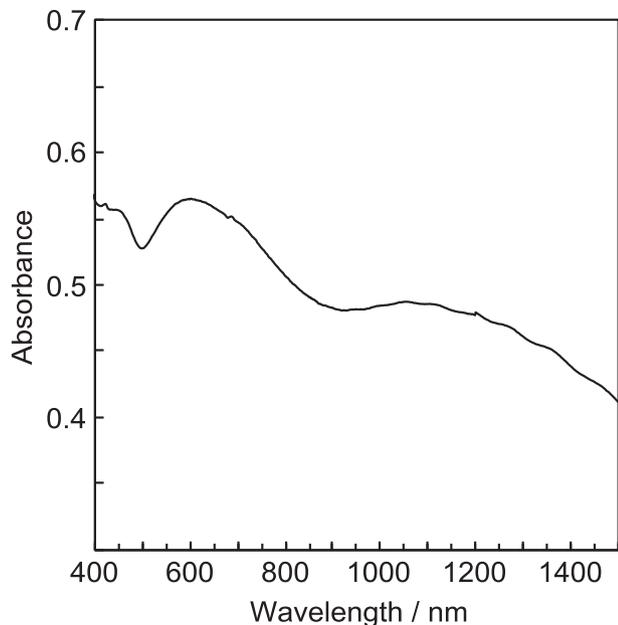


Fig. 3. Absorption spectrum of the drop-casted film of the aqueous NH_3/MeOH suspension of PhosPANI 5 after annealing at 100 °C.

film of **5** showed a broad peak around 450 nm assigned as a polaron band¹⁷ and broad one around 600 nm assigned as a CT transition band.¹⁷ The broad absorption from around 700 nm is considered to include localized polaron band (around 750 nm)¹⁷ and free carrier tail (> around 1000 nm).¹⁷ Absorptions of polaron and CT transition indicate the doped and de-doped states, respectively. Thus, both self-doped and de-doped moieties seem to be present in PhosPANI **5**. Despite the use of basic aqueous suspension of **5** to form the film (absorption spectrum for the suspension clearly showed the complete de-doping, see Fig. S4), the complete de-doping was not observed for the film. This can be explained by removal of NH_3 under annealing conditions.

Electrical conductive property of PhosPANI **5** was investigated in terms of sheet resistance of the drop-cast film. An interdigitated array platinum electrode was used to measure the sheet resistance by a direct-current method. The ca. 10 g/L aqueous NH_3/MeOH suspension of PhosPANI **5** was drop-casted on the electrode. The sheet resistance of PhosPANI **5** was $3.6 \times 10^8 \Omega/\text{square}$ at room temperature. The magnitude of the sheet resistance is a level for charge dissipation materials.¹⁸ The sheet resistance of **5** is smaller than those of PhosPANIs prepared via nucleophilic phosphonation [PhosPANI(52%P): $3.6 \times 10^9 \Omega/\text{square}$; PhosPANI(73%P): $4.0 \times 10^{10} \Omega/\text{square}$, here %P shows the substitution rate of the phosphonate moiety).¹¹ On the other hand, in comparison with PMAP ($2.2 \times 10^7 \Omega/\text{square}$),¹¹ that of **5** is one order of magnitude higher, which might be due to the less efficient doping in **5**.

In conclusion, we have synthesized a self-doped conducting PhosPANI **5** bearing phosphonic acid moiety via the Pd-catalyzed phosphonation of poly(2-bromoaniline) as a key reaction. PhosPANI **5** exhibited the conductive property with the level for charge dissipation materials.

Acknowledgments

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A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.tetlet.2018.03.054>.

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