

Poly(*o*-aminobenzylphosphonic acid): a Novel Water Soluble, Self-doped Functionalized Polyaniline

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A novel self-doped polymer having alkylphosphonic acid moieties on polyaniline is synthesized from persulfate oxidative coupling of *o*-aminobenzylphosphonic acid **3**; the resulting polymer, apart from being water soluble in its self-doped monosodium salt form, demonstrates excellent redox stability when subjected to potentiometric cycling between 0.0 and 1.0 V.

Polyaniline (PANI) in its insulating emeraldine base form can be converted to a conductor by external protonic dopants.¹ Recently, several reports^{2,3} have focused on the generation of self-doped conducting PANI functionalised with moieties incorporating sulfonic acid which does not require external acid doping. However, these approaches invariably involve post-synthetic transformation of PANI which consequently affords polymeric materials with structures which cannot be unambiguously assigned. Herein, we report the successful preparation of a novel self-doped polyaniline, poly(*o*-aminobenzylphosphonic acid) (PABA) **4** arising from the chemical polymerisation of *o*-aminobenzylphosphonic acid **3** in aqueous solution. PABPA can be cast into free-standing film from an aqueous solution of its salt [from 0.5 mol equiv. NaOH per mol PO(OH)₂], which has a conductivity of *ca.* 10⁻³ S cm⁻¹, independent of pH in the range 0–6. This represents the first documented example of a self-doped PANI not generated by post-synthetic modifications. In addition, this material is water soluble in its conducting self-doped form and possesses excellent redox stability when subjected to potentiometric cycling between 0.0 and 1.0 V; these properties are not generally associated with other self-doped PANI.

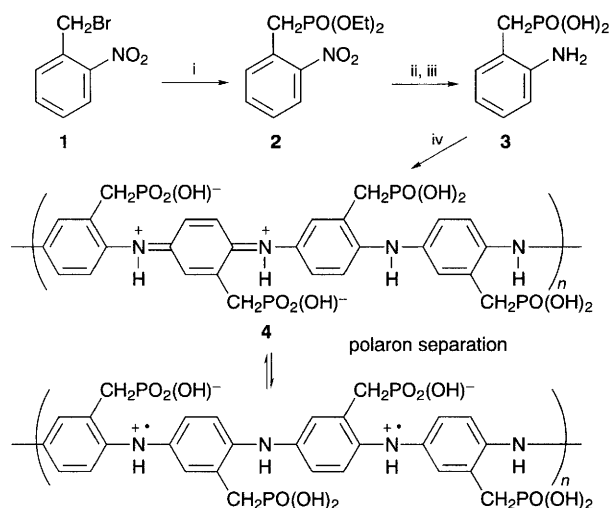
The synthesis of monomer **3** was accomplished in three steps from the commercially available *o*-nitrobenzylbromide **1** in good overall yield (30%)[†] (Scheme 1). Polymerisation to the self-doped polymer was effected by oxidative coupling of **3** in an acidic medium, based in part on established synthetic procedures for polyaniline:⁴ to a 0.4 mol dm⁻³ solution of *o*-aminobenzylphosphonic acid in 3.5 mol dm⁻³ HCl chilled to 0–5 °C was added over 4 h a 0.5 mol dm⁻³ aqueous solution of Na₂S₂O₈. The mixture was allowed to stand overnight (16 h) at 0–5 °C, whence the polymer particles were filtered, rinsed with 2 mol dm⁻³ HCl and eluted with distilled water until the eluate gave a negative AgNO₃ test. After drying *in vacuo*, the polymer **4** was obtained as a dark green powder. Conductivity measure-

ments of polymer pellets which were pre-equilibrated at different pH values, revealed an essentially constant conductivity value at $(1.1 \pm 0.3) \times 10^{-3}$ S cm⁻¹ over the range pH 0–6.

PABPA dissolves in dilute (20 mmol dm⁻³) aqueous ammonia to afford an intense green solution owing to partial deprotonation of the PO(OH)₂ moieties on the polymer backbone to form an ionomer that interacts strongly with H₂O. Without sufficient addition of base, *e.g.* when distilled water or very dilute (2 mmol dm⁻³) NH₃ are used, **4** is completely insoluble, despite the intrinsic presence of zwitterions in the polymer chain. Addition of 0.5, 1.0 and 2.0 mol equiv. of 0.12 mol dm⁻³ aqueous NaOH per mol of PO(OH)₂ to PABPA resulted in complete dissolution of polymer particles in the volume of base used, giving intensely green solutions in the first two instances and a dark blue solution in the last. From these solutions, stable free standing films could be cast by slow evaporation of water in a partially evacuated desiccator (*ca.* 30 mmHg). Upon exposure to HCl vapour, the films became insoluble.

The monosodium salt of the self-doped polymer has a UV–VIS polaronic band transition at 436 nm (2.85 eV) and 880 nm (1.40 eV), with a π – π^* transition at 312 nm (3.98), whilst elemental analysis[‡] and IR spectra of the as-synthesized polymer are consistent with the structure **4**. The ratio of the IR absorption intensity at 1597 cm⁻¹ (attributed to the quinoid ring) to that at 1489 cm⁻¹ (attributed to the benzenoid ring) is indicative of a predominant emeraldine oxidation state similar to other conventional emeraldine salts.⁵ The presence of absorption peaks at 1139 (PO₂⁻, asym stretching, with overlying P=O stretching), 1056 (PO₂⁻, sym stretching) and 933 cm⁻¹ (P–OH stretching) is consistent with the presence of the phosphonate group,⁶ whilst the absorption bands at 870 and 810 cm⁻¹ relate to a 1,2,4-trisubstituted PANI.²

XPS studies on the N 1s core level indicate that 43% of the nitrogen atoms in the as-synthesized sample have been doped through protonation by the phosphonic acid groups.[§] No further increase in doping level could be achieved through re-



Scheme 1 Reagents and conditions: i, (EtO)₃P, 110 °C, 2 min; ii, cyclohexene, Pd–C, EtOH, reflux, 15 min; iii, conc. HCl, reflux, 6 h; iv, Na₂S₂O₈, HCl (aq), 0–5 °C, 16 h

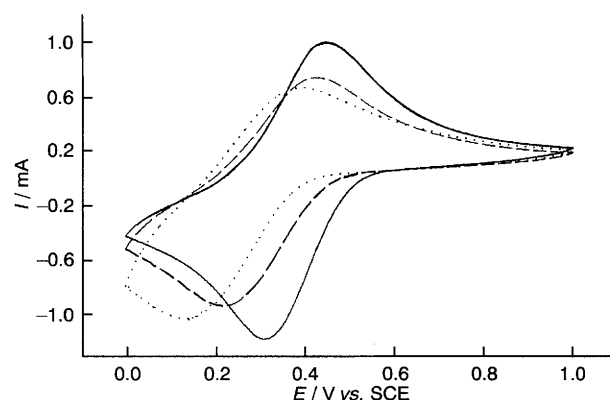


Fig. 1 CV of PABPA at different pH values; scan rate, 50 mV s⁻¹. (—) 10 mol dm⁻³ HCl at pH -0.2; (---) 0.1 mol dm⁻³ HCl + 0.9 mol dm⁻³ NaCl at pH 1.1; (····) 0.01 mol dm⁻³ HCl + 1.0 mol dm⁻³ NaCl at pH 2.1.

equilibration of the polymer in strong HCl. This indicates that the polymer has attained maximum doping under the described synthesis.

Fig. 1 depicts the effect of a pH variation at constant ionic strength on the steady-state multicycle voltammogram of a thin film of PABPA deposited on a Pt working electrode. Interestingly, this polymer displayed only one set of redox peaks at $E_{1/2} = 0.39$ V (vs. SCE) in striking contrast to reported polyaniline systems which show two sets ($E_{1/2} = 0.18$ and 0.74 V in the parent polyaniline⁷). The absence of the second redox process suggests that the present polymer in the emeraldine state is exceptionally resistant to oxidation to the pernigraniline state.⁸ Additionally, repeated cycling between 0.0 and 1.0 V ($> 10^2$ cycles) resulted in only a slight fall in electroactivity. In contrast, irreversible degradation occurs rapidly once the potential reaches 0.8 V in both the parent PANI⁹ and sulfonated polyaniline² with the appearance of a third set of redox peaks between the original two.

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Footnotes

† Selected data for **3**: white crystalline, mp 268°C (decomp.); IR (KBr) ν/cm^{-1} 3050, 2889vs, 2590vs, 2192vs, 1653vs, 1606s, 1588vs, 1536vs, 1498vs, 1464s, 1306m, 1244m, 1186s, 1139vs, 1100vs, 1062vs, 1005vs, 928vs, 856m, 773vs, 745s; ^{13}C NMR (D_2O , SiMe_4) δ 134.9, 132.6, 131.6, 130.7, 126.0, 35.0 (d, $^1J_{\text{PC}}$ 125 Hz); ^1H NMR (D_2O , Me_4Si) δ 7.38–7.33 (4H, m), 3.12 (2H, d, $^2J_{\text{PCH}}$ 20.0 Hz); MS m/z 187 (M^+ , 25%), 169 (100) and 106 (94).

‡ Found: C, 40.9; H, 4.9; N, 6.9. $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_6\text{P}_2 \cdot 2.32\text{H}_2\text{O}$ requires C, 40.9; H, 4.8; N, 6.9%.

§ Corroborating evidence of an internal doping of the benzenamine moiety in the polymer backbone by the pendant phosphonic acid groups is provided from XPS studies where it was shown that the amount of positively charged nitrogen arising from the doping mechanism is counterbalanced by an equivalent amount of the monoanion $\text{P}=\text{O}(\text{OH})\text{O}^-$.

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