

A mild, copper catalyzed route to conducting polyaniline†

H. V. Rasika Dias,*^a Xiaoyu Wang,^a R. M. Gamini Rajapakse^{ab} and Ronald L. Elsenbaumer^a

Received (in Columbia, MO, USA) 3rd October 2005, Accepted 3rd January 2006

First published as an Advance Article on the web 20th January 2006

DOI: 10.1039/b513938d

The aniline dimer, *N*-(4-aminophenyl)aniline has been polymerized cleanly under mild conditions to obtain an emeraldine base form of polyaniline using [MeB(3-(Mes)Pz)₃]CuCl as the catalyst and H₂O₂ as the oxidant, while the subsequent acidification of the emeraldine base gives the conducting emeraldine salt form of polyaniline.

Polyaniline (PANI) is one of the most widely studied conductive polymers during the past two decades.^{1–6} It has good environmental stability, interesting optoelectronic features, and controllable electrical and electrochemical properties. As a result, many technological applications have been demonstrated with polyaniline. The most common route to polyaniline utilizes harsh reagents such as a strong oxidant (*e.g.*, peroxydisulfate) and a strong mineral acid.⁴ Some other oxidants capable of polymerizing aniline to yield polyaniline are Fe³⁺, Cr₂O₇²⁻, MnO₄⁻ and IO₃⁻. All these reactions usually require more than stoichiometric amounts of the oxidant and excess acid. The most widely used route to polyaniline which uses (NH₄)₂S₂O₈ also generates significant amounts of (NH₄)₂SO₄ by-product.⁷ Thus, environmentally benign, and preferably catalytic processes for the synthesis of PANI are of significant interest. The recent reports on the PANI synthesis involving Horseradish peroxidase is an important development in this regard.^{8,9}

In this paper, we describe a metal catalyzed route to polyaniline starting from *N*-(4-aminophenyl)aniline and H₂O₂ (Fig. 1). The tris(pyrazolyl)boratocopper adduct, [MeB(3-(Mes)Pz)₃]CuCl (Mes and Pz stand for mesityl and pyrazolyl, respectively) serves as the catalyst. It was characterized using several methods including X-ray crystallography (see Supporting Information: Figure S1† and crystal structure data‡). [MeB(3-(Mes)Pz)₃]CuCl is a relatively robust, readily accessible metal complex with a sterically and electronically tunable ligand system.¹⁰ It is also noteworthy that the related tris(pyrazolyl)boratocopper–oxygen complexes have been used as models for oxyhemocyanin (an oxygen carrying metalloenzyme in some invertebrates) and oxytyrosinase (a monooxygenase capable of oxidizing phenols).¹¹ There are a limited number of reports on the use of inorganic Cu(II) salts¹² and *cis*-bis(glycinato)copper(II) complex¹³ for the PANI synthesis. However, these systems produce an overoxidized pernigraniline form of polyaniline with various other by-products. The use of

sterically demanding tris(pyrazolyl)borate ligand with copper(II) has the advantage over these in producing better polymers as demonstrated in this PANI work, and also in the phenol polymerization reactions.¹⁴ For example, the use of copper/diamine catalyst for phenol polymerization leads to C–C bonded dimers whereas [HB(3,5-(Ph)₂Pz)₃]CuCl produces stereo-regular C–O coupled poly(1,4-phenylene oxide) polymer.¹⁵

The PANI synthesis route is summarized in Fig. 1, which involved the catalytic oxidative polymerization of aniline dimer, *N*-(4-aminophenyl)aniline using hydrogen peroxide as the oxidant. For example, a mixture containing aniline dimer : catalyst : H₂O₂ : HCl at 1 : 0.05 : 1.5 : 1 ratio in 1 : 1 CH₃CN : H₂O gave good quality polyaniline in about 50% yield, after 24 h at room temperature.§ The reaction carried out under identical conditions, but *without the copper catalyst* (*i.e.*, dimer : catalyst : H₂O₂ : HCl mole ratio of 1 : 0 : 1.5 : 1) did not produce a detectable amount of solid material. The resulting PANI from the metal catalyzed process is soluble only in *N*-methylpyrrolidinone (NMP) giving bluish-purple solutions, which upon addition of an NMP solution containing camphor sulfonic acid turned greenish.

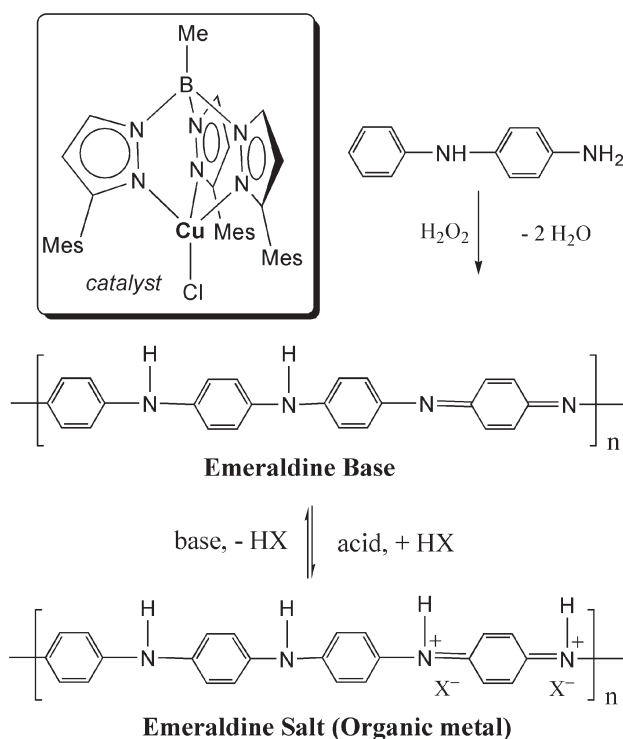


Fig. 1 The chemical structure of the catalyst tris(pyrazolyl)boratocopper(II) complex [MeB(3-(Mes)Pz)₃]CuCl together with the polymerization reaction.

^aDepartment of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019-0065, USA. E-mail: dias@uta.edu

^bDepartment of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka

† Electronic supplementary information (ESI) available: Full experimental details for the synthesis of the catalyst and of polyaniline, and characterization of the materials by cyclic voltammetry, impedance spectroscopy, and scanning electron microscopy. See DOI: 10.1039/b513938d

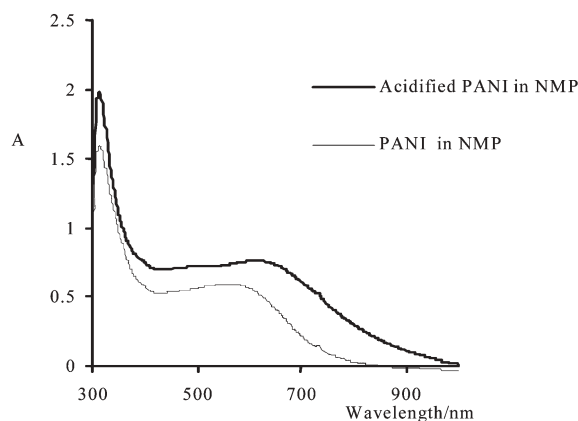


Fig. 2 The UV-visible absorption spectra of PANI Sample (Bottom spectrum: As-prepared sample in NMP, Top spectrum: PANI Sample in NMP acidified with camphor sulfonic acid).

The PANI sample dissolved in NMP shows the characteristic UV-visible absorption spectrum, and indicates that as-prepared samples are mostly in emeraldine base (EB) form possibly due to the flushing of protons during the repeated washing of the product (See Fig. 2 for UV-visible absorption spectra). In general, the emeraldine base form of PANI dissolved in NMP contains two characteristic absorptions, a broad band with λ_{max} at 634 nm (1.96 eV) corresponding to molecular exciton transition, and a sharp strong absorption centered at 320 nm (3.75 eV) due to the $\pi \rightarrow \pi^*$ transition. The spectra of both fully oxidized (pernigraniline base) and fully reduced (leucoemeraldine base) PANI also exhibit the $\pi \rightarrow \pi^*$ transition at 320 nm. However, the 634 nm band tends to disappear when EB is reduced while it red-shifts to Peierls gap band upon complete oxidation.^{2,16-19}

The FT-IR spectrum (on KBr) of the acidified PANI (using HCl) is shown in Fig. 3. The typical absorptions at 1158 cm^{-1} [$\nu(\text{C-N})$ in $\text{B-NH}^+\text{-Q}$], 1313 cm^{-1} [$\nu(\text{C-N})$], 1494 cm^{-1} [$\nu(\text{C-N})$ in N-B-N] and 1586 cm^{-1} [$\nu(\text{C-N})$ in N=Q=N] appear as very strong bands (where B and Q stand for benzenoid and quinoid moieties). The ratio N=Q=N absorption : N-B-N absorption gives an indication of the extent of oxidation in the emeraldine form of the polymer while the ratio $\text{B-NH}^+\text{-Q}$ absorption : N=Q=N absorption gives an indication of the extent of protonation of imine nitrogen atoms in the polymer.^{20,21} This ratio is very close to 1 in the acidified PANI sample suggesting the presence of the emeraldine salt form of structure.

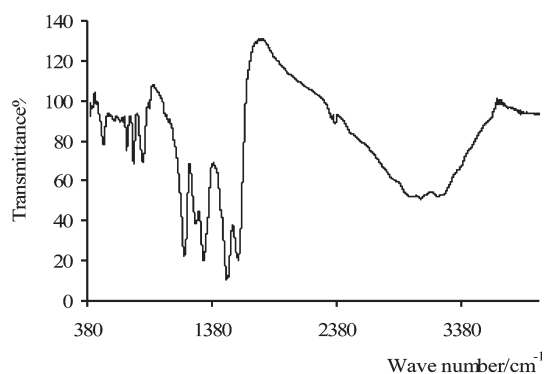


Fig. 3 FT-IR spectrum of PANI sample.

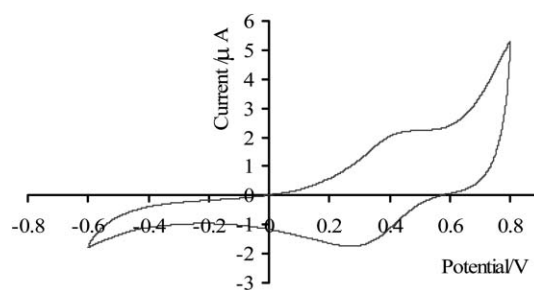


Fig. 4 Cyclic voltammogram at 20 mV s^{-1} of polyaniline on Pt disc electrode in 0.05 mol L^{-1} tetrabutylammonium tetrafluoroborate background electrolyte.

The cyclic voltammetric data suggest the formation of very clean polyaniline with no impurities (Fig. 4). Particularly, Cu impurities are not visible in the CV as there are no peaks corresponding to the Cu^{2+}/Cu couple. The atomic absorption spectroscopic studies of the PANI samples are also in support of negligible amounts of Cu impurities. Electrochemical impedance spectroscopic (EIS) studies²²⁻²⁴ of as-prepared samples indicate an electronic resistance of $2 \times 10^4 \Omega$ which can be lowered to 100Ω by acidification. Ionic conductivity is in the range of $10^3 \Omega$. This is consistent with the scanning electron micrographs (SEM), that show mushroom type nanostructures permeable to solvent molecules (Figure S2a in the Supplementary Information Section†). The DC conductivity of $2.0 \times 10^{-4} \text{ S cm}^{-1}$ for as-prepared samples is in agreement with the electrochemical data.

Another experiment was carried out in which the addition of acid is deliberately avoided during the polymer synthesis but the product obtained was later acidified with 1 mol L^{-1} HCl(aq) or 1 mol L^{-1} camphor sulfonic acid in NMP. Although the amount of PANI precipitated is about five times smaller than those obtained using an acidic medium under similar conditions, it is of high quality. The PANI sample is soluble only in NMP and its FT-IR shows the presence of B-N-B and Q=N=Q moieties but not $\text{B-NH}^+=\text{Q}$ moieties as expected. The latter band appears upon acidification. The CV of the acidified sample shows no Cu impurities and it has the expected signature for regio-regular polyaniline with no branching and no side products or impurities (Figure S3†). Interestingly, the EIS data reveal that²²⁻²⁴(see Figure S4†) the acidified material is highly conducting with an electronic resistance of 980Ω and the ionic resistance of $2.52 \times 10^3 \Omega$ at $+0.7 \text{ V}$. Upon decreasing the DC potential the material remains conducting down to $+0.4 \text{ V}$ though the conductivities gradually decrease (See Figure S5†). The EIS data are not very meaningful at potentials when polyaniline is in its leucoemeraldine form.

We have also investigated the effect of temperature, the amount of oxidant, and the tris(pyrazolyl)borate ligand. The reaction carried out at higher temperatures ($40 \text{ }^\circ\text{C}$) using excess oxidant (dimer : catalyst : H_2O_2 : HCl mole ratio of 1 : 0.05 : 10 : 1) produced somewhat inferior quality PANI. For example, cyclic voltammetry (CV) signature of the PANI was only obtained when scanned at very slow scan rates suggesting highly compact polymer morphology hindering the accessibility to solvent species. Electrochemical impedance spectroscopic studies also indicate high ionic resistance (the low frequency almost vertical straight line is not visible even at 0.1 mHz) for as-prepared samples.²²⁻²⁵ In fact, scanning electron micrographs of this PANI sample (Figure S2b†)

show densely packed fibril structure in contrast to the mushroom type nanostructure observed for PANI obtained at 20 °C using 1.5 equivalent of H₂O₂ (as described above). Therefore, it can be inferred that drastic conditions such as higher temperatures and excess oxidants give unfavorable results.

The effect of the bulky tris(pyrazolyl)borate ligand was also investigated by performing a reaction using CuCl₂ in place of the [MeB(3-(Mes)Pz)₃]CuCl catalyst in a mixture of dimer : catalyst : H₂O₂ : HCl at a 1 : 0.05 : 1.5 : 1 ratio. The resulting PANI sample gave a complicated CV and contains several redox peaks possibly showing the degraded products such as benzoquinones and benzidenes or cross-linked structure as reported previously.^{26–28} Its EIS data do not show the typical behavior of a conducting polymer as well.

In summary, [MeB(3-(Mes)Pz)₃]CuCl catalyzes the formation of a clean emeraldine base form of polyaniline from aniline dimer and H₂O₂. Presumably, the water is the only by-product of this process. The method described here is also amenable for large scale synthesis. The use of a mineral acid during the polymer synthesis is not essential, but affects the yield. The excess hydrogen peroxide is detrimental and 1 : 1.5 molar ratio of dimer : H₂O₂ is sufficient. Preliminary studies indicate that PANI could be obtained directly from aniline containing 1 mol% of aniline dimer. We are presently exploring a greener route to PANI using aniline as the starting point and O₂ as the oxidant, and the ligand effects on PANI quality.

We acknowledge the financial support from US National Science Foundation (CHE-0314666) and the Texas Higher Education Coordination Board (ATP-003656-0153-2003).

Notes and references

‡ Crystallographic data for [MeB(3-(Mes)Pz)₃]CuCl·CH₂Cl₂, Formula, C₃₈H₄₄BCl₃CuN₆ (765.49), *T* = 100(2) K, triclinic, space group *P* $\bar{1}$, *a* = 12.6899(13) Å, *b* = 18.2468(18) Å, *c* = 18.7138(18) Å, α = 68.8850(10)°, β = 88.916(2)°, γ = 71.5520(10)°, *V* = 3812.3(7) Å³, *Z* = 4, μ = 0.819 mm⁻¹, Final *R* indices [*I* > 2 σ (*I*)] *R*₁ = 0.0610, *wR*₂ = 0.1289. CCDC 293122. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513938d

§ *N*-phenyl-1,4-phenylenediamine (0.921 g, 5.0 mmol) was added to a mixture of HCl (0.50 g, 36.5% HCl, 5.0 mmol), acetonitrile (18 mL) and H₂O (18 mL) under a nitrogen atmosphere and stirred for 10 min. The oxidant H₂O₂ (0.855 g, 30% H₂O₂ solution, 7.5 mmol) was added to this mixture. The resulting mixture was then added to the catalyst [MeB(3-(Mes)Pz)₃]CuCl (0.170 g, 0.25 mmol) dissolved in a minimum amount of 1 : 1 CH₃CN/H₂O. The solution was stirred for 24 h under N₂ at room temperature. A dark precipitate was formed. This precipitate was separated by filtration and washed with MeOH (3 × 30 mL), dilute HCl (0.1 M, 3 ×

30 mL), and CHCl₃ (3 × 30 mL), and dried under reduced pressure to obtain PANI (51% yield).

- 1 *Handbook of Conducting Polymers*, ed. T. A. Skotheim, R. L. Elsenbaumer and J. Reynolds, Marcel Dekker, New York, 1998.
- 2 A. G. MacDiarmid and A. J. Epstein, *Faraday Discuss. Chem. Soc.*, 1989, **88**, 317–332.
- 3 A. G. MacDiarmid, *Synth. Met.*, 1997, **84**, 27–34.
- 4 A. G. MacDiarmid, J. C. Chiang, A. F. Richter, N. L. D. Somasiri and A. J. Epstein, in *Conducting Polymers*, ed. L. Alcacer, Reidel, Dordrecht, The Netherlands, 1987.
- 5 A. G. MacDiarmid, *Rev. Mod. Phys.*, 2001, **73**, 701–712.
- 6 W. J. Albery, Z. Chen, B. R. Horrocks, A. R. Mount, P. J. Wilson, D. Bloor, A. T. Monkman and C. M. Elliott, *Faraday Discuss. Chem. Soc.*, 1989, **88**, 247–259.
- 7 R. L. Elsenbaumer, C. C. Han, and K. Y. Jen, Thermally Stable Forms of Electrically Conducting Polyaniline, *U. S. Pat.*, 5 160 457, 1992.
- 8 S. Trakhtenberg, Y. Hangun-Balkir, J. C. Warner, F. F. Bruno, J. Kumar, R. Nagarajan and L. A. Samuelson, *J. Am. Chem. Soc.*, 2005, **127**, 9100–9104.
- 9 W. Liu, J. Kumar, S. Tripathy, K. J. Senecal and L. Samuelson, *J. Am. Chem. Soc.*, 1999, **121**, 71–78.
- 10 C. Pettinari and C. Santini, in *Polypyrazolylborate and Scorpionate Ligands*, 2004.
- 11 S. Trofimenko, *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999.
- 12 T. Tushima, H. Yan and M. Ishiwatari, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 1947–1953.
- 13 A. Puzari and J. B. Baruah, *J. Org. Chem.*, 2000, **65**, 2344–2349.
- 14 H. Higashimura, K. Fujisawa, Y. Moro-oka, M. Kubota, A. Shiga, A. Terahara, H. Uyama and S. Kobayashi, *J. Am. Chem. Soc.*, 1998, **120**, 8529–8530.
- 15 H. Higashimura, M. Kubota, A. Shiga, K. Fujisawa, Y. Moro-oka, H. Uyama and S. Kobayashi, *Macromolecules*, 2000, **33**, 1986–1995.
- 16 J. E. de Albuquerque, L. H. C. Mattoso, R. M. Faria, J. G. Masters and A. G. MacDiarmid, *Synth. Met.*, 2004, **146**, 1–10.
- 17 J. G. Masters, Y. Sun, A. G. MacDiarmid and A. J. Epstein, *Synth. Met.*, 1991, **41**, 715–718.
- 18 A. G. MacDiarmid and A. J. Epstein, *Synth. Met.*, 1994, **65**, 103–116.
- 19 F. Wudl, R. O. Angus, Jr., F. L. Lu, P. M. Allemand, D. Vachon, M. Nowak, Z. X. Liu, H. Schaffer and A. J. Heeger, *J. Am. Chem. Soc.*, 1987, **109**, 3677–3684.
- 20 Y. Furukawa, F. Ueda, Y. Hyodo, I. Harada, T. Nakajima and T. Kawagoe, *Macromolecules*, 1988, **21**, 1297–1305.
- 21 B. L. Rivas and C. O. Sanchez, *J. Appl. Polym. Sci.*, 2001, **82**, 330–337.
- 22 W. J. Albery and A. R. Mount, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 1115–1119.
- 23 W. J. Albery and A. R. Mount, *Electroact. Polym. Electrochem.*, 1994, **1**, 443–483.
- 24 X. Ren and P. G. Pickup, *J. Electroanal. Chem.*, 1997, **420**, 251–257.
- 25 J. Jamnik, J. Maier and S. Pejovnik, *Electrochim. Acta*, 1999, **44**, 4139–4145.
- 26 D. Orata and D. A. Buttry, *J. Am. Chem. Soc.*, 1987, **109**, 3574–3581.
- 27 W.-C. Chen, T.-C. Wen and A. Gopalan, *Electrochim. Acta*, 2002, **47**, 4195–4206.
- 28 X. Yang, Q. Xie and S. Yao, *Synth. Met.*, 2004, **143**, 119–128.