Properties of Cyanide-functionalized Polyaniline Prepared by Oxidative Electrochemical Polymerization of *o*-Aminobenzonitrile

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Cyanide-functionalized polyaniline that is redox-active, soluble, and coloured gold, is prepared by the electrochemical oxidative polymerization of *o*-aminobenzonitrile in an aqueous acid solution.

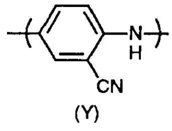
We report the functionalization of polyaniline by the introduction of cyanide into the phenyl rings. Polyaniline is a well known conducting polymer and its electrochemical and physical properties have been reported in detail,[1–3] but the effects of ring substituents on its redox properties have not been established.[4–7] Polyaniline derivatives with electron-withdrawing substituents in the phenyl ring, other than chloride,[4] have been reported to give rise to very thin or unsatisfactory films because of difficulties in the electrochemical polymerization.[4,5]

Here, we describe the preparation and properties of cyanide-functionalized polyaniline (Y), a new polymer having the structure of polyaniline (X) with a cyanide group attached to each phenyl ring. Cyanide is a strong electron-withdrawing substituent, so we expected changes in the properties of the polyaniline.

Our strategy was to bring about electrochemical oxidative polymerization of *o*-aminobenzonitrile (0.5 mol dm^{-3}) in aqueous perchloric acid (1.0 mol dm^{-3}). The functional polyaniline film grew at the surface of a platinum or gold electrode as the applied potential was either cycled between −0.2 and 0.9 V *vs.* a saturated calomel electrode (SCE) or held at 0.9 V *vs.* SCE. Fig. 1(*A*) shows that if the applied potential was only up to 0.7 V *vs.* SCE, a redox reaction did not occur at the electrode, and a polymer film was not formed. With the application of the potential above 0.8 V *vs.* SCE, where the large anodic current began to increase, the monomer, *o*-aminobenzonitrile, in the solution became oxidized at the electrode, was deposited onto the electrode, and gave rise to a film 35 ± 18 nm thick (measured by a multiple-beam interferometer) after 25 potential scans, or 62 ± 11 nm thick after the potential had been held at 0.9 V *vs.* SCE for 3 min. In Fig. 1(*B*), the increase in the redox currents with potential cycling is shown. Once the film had been formed, the redox couples remained [Fig. 1(*C*)], although the positive end of the potential was decreased to 0.7 V *vs.* SCE. The anodic current at 0.72 V and the cathodic current at 0.01 V *vs.* SCE, which corresponded to the redox of the film and not to that of any species in the solution, increased in proportion to the sweep rate from 10 to 50 mV s^{-1}.[8] The film was redox-active only in the aqueous acid solution containing a high concentration (0.5 mol dm^{-3}) of the monomer. When the monomer concentration was 0.1 mol dm^{-3} or zero, the polymer was redox-inactive and served as an insulant layer. Redox activity was found again when the film was returned to the aqueous acid solution of high concentration. An alternative molecule to bring about the film redox activity was phenol. The role of these molecules in the electrolyte is not clear, but their strong dipole moment,[9] in interacting with the functionalized polyaniline, may change the morphology of the film, triggering the redox reaction.

The resulting film was stable and adhered well to the electrode. The colour was gold (the absorption gradually decreased from 380 to 680 nm without any maximum) after application of the potential at 0.6 V *vs.* SCE; it was almost colourless at −0.2 V *vs.* SCE. These colours were different from the yellow, green, blue and violet of polyaniline reported earlier.[1,2,4] The cyanide groups of the phenyl ring remained intact during the electrochemical polymerization, because in the FT IR spectrum of the film, a strong cyanide band appeared at 2228 cm^{-1}, while a carbonyl band, which would appear if the cyanide group had been hydrolysed, was absent. No carbonyl carbon was detected by X-ray photoelectron spectroscopy, either. The cyanide band of the monomer, *o*-aminobenzonitrile, appeared at 2210 cm^{-1}. The film was

(X)



(Y)

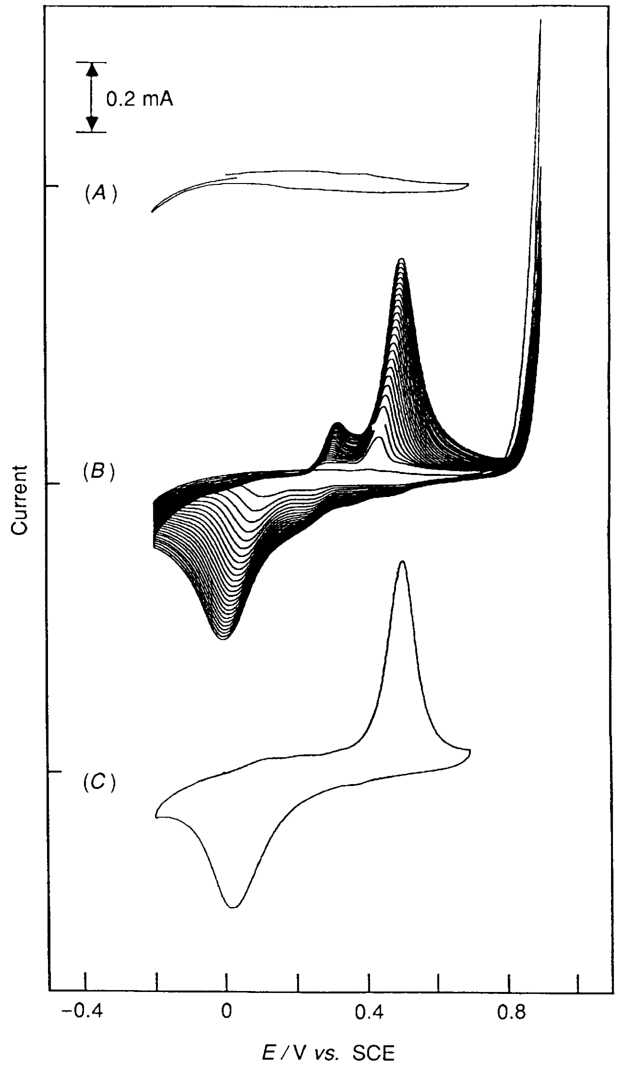
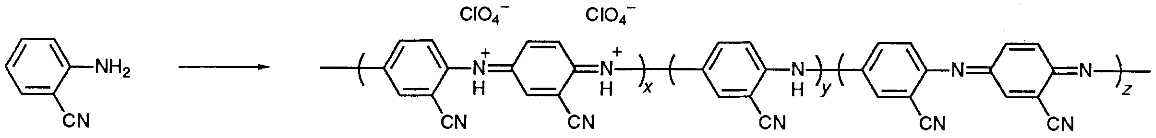


Fig. 1 Cyclic voltammograms of (*A*) aqueous solution containing 0.5 mol dm^{-3} *o*-aminobenzonitrile and 1.0 mol dm^{-3} perchloric acid, (*B*) film gradually grown with potential cycling between −0.2 and 0.9 V *vs.* SCE, and (*C*) the film in the potential region from −0.2 to 0.7 V *vs.* SCE in the same aqueous acid solution as in (*A*) at a platinum electrode (1 × 1 cm) at 25 °C. All scans are at 50 mV s^{-1}.



Scheme 1 *Conditions*: electrochemical polymerization in aqueous $HClO_4$ solution

soluble in common polar aprotic solvents such as acetonitrile, methylene chloride and dimethyl sulphoxide, and partially soluble in ethanol. The highest molecular weight of the functional polyaniline forming the film was evaluated from its mass spectrum, where the largest fragment peak appeared at m/z 1430. This result was supported by gel permeation chromatography, which showed a peak at 1400. These values correspond to a polymer molecule as large as 12 units of the monomer. Its ^1H NMR spectrum in $(CD_3)_2SO$ solution showed at least four well resolved –NH proton signals, at δ 9.37, 8.33, 7.10 and 6.90, suggesting that protonated imine nitrogens were present in the polymer chain. To compensate the positive charge, perchlorate anions were incorporated into the film. Chlorine was detected by the X-ray photoelectron spectroscopy and the anion content was determined by ion chromatography. The perchlorate content of 5.3 w/w% indicated that 6.5% of the nitrogens that linked the phenyl ring in the polymer were protonated imines and that the rest were amine or deprotonated imine nitrogens. The structure of the cyanide-functionalized polyaniline was therefore as shown in Scheme 1. Other physico-chemical properties are now being examined.

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References

1 D. M. Mohilner, R. N. Adams and W. J. Argersinger, Jr., *J. Am. Chem. Soc.*, 1962, **84**, 3618; A. F. Diaz and J. A. Logan, *J. Electroanal. Chem.*, 1980, **111**, 111; J.-C. Chiang and A. G. MacDiarmid, *Synth. Met.*, 1986, **13**, 193; A. Kitani, J. Izumi, J. Yano, Y. Hiromoto and K. Sasaki, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2254; T. Kobayashi, H. Yoneyama and H. Tamura, *J. Electroanal. Chem.*, 1984, **177**, 281; E. M. Geniès and M. Lapkowski, *Synth. Met.*, 1987, **21**, 117.

2 R. J. Cushman, P. M. McManus and S. C. Yang, *J. Electroanal. Chem.*, 1986, **291**, 335; Y. Li, B. Yan, J. Yang, Y. Cao and R. Qian, *Synth. Met.*, 1988, **25**, 79; D. E. Stilwell and S.-M. Park, *J. Electrochem. Soc.*, 1989, **136**, 427.

3 E. M. Geniès, P. Hany, M. Lapkowski, C. Santier and L. Olmedo, *Synth. Met.*, 1988, **25**, 29; E. W. Paul, A. J. Ricco and M. S. Wrighton, *J. Phys. Chem.*, 1985, **89**, 1441; G. Horányi and G. Inzelt, *J. Electroanal. Chem.*, 1988, **257**, 311; K. Hyodo and M. Nozaki, *Electrochim. Acta*, 1988, **33**, 165; N. Oyama, Y. Ohnuki, K. Chiba and T. Ohsaka, *Chem. Lett.*, 1983, 1759.

4 S. Cattarin, L. Doubova, G. Mengoli and G. Zotti, *Electrochim. Acta*, 1988, **33**, 1077.

5 A. Volkov, G. Tourillon, P.-C. Lacaze and J.-E. Dubois, *J. Electroanal. Chem.*, 1980, **115**, 279; P. Snauwaert, R. Lazzaroni, J. Riga and J. J. Verbist, *Synth. Met.*, 1986, **16**, 245.

6 K. Chiba, T. Ohsaka, Y. Ohnuki and N. Oyama, *J. Electroanal. Chem.*, 1987, **219**, 117; D. MacInnes, Jr., and B. L. Funt, *Synth. Met.*, 1988, **25**, 235; C. Barbero, J. J. Silber and L. Sereno, *J. Electroanal. Chem.*, 1989, **263**, 333.

7 J. Bacon and R. N. Adams, *J. Am. Chem. Soc.*, 1968, **90**, 6596; R. L. Hand and R. F. Nelson, *J. Electrochem. Soc.*, 1978, **125**, 1059.

8 R. W. Murray, in *Electroanalytical Chemistry*, ed. A. J. Bard, Dekker, New York, vol. 13, p. 191.

9 A. L. McClelland, *Tables of Experimental Dipole Moments*, Freeman, San Francisco, 1963; G. L. Findley, T. P. Carsey and S. P. McGlynn, *J. Am. Chem. Soc.*, 1979, **101**, 4511.