# Redox Reaction of Polyaniline Film with Aminobenzonitrile

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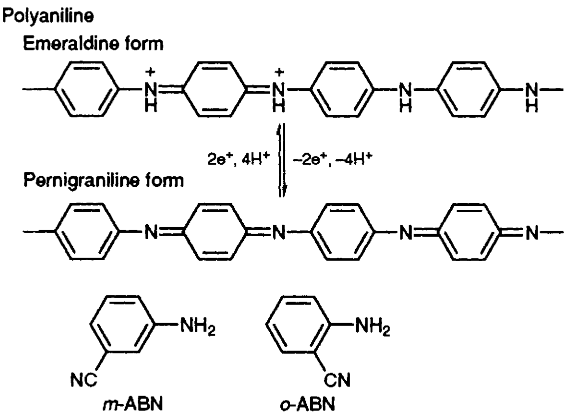
During electrochemical oxidation from the emeraldine form to the pernigraniline form, polyaniline reacts with aminobenzonitrile in solution.

We report the redox reaction of aminobenzonitrile (ABN), a cyanide substituted aniline monomer, with polyaniline film.

Form ESR studies,[1] it was reported that radical species were found in polyaniline film at two potential regions where redox reactions of the film took place; at −0.05–0.15 V where the leucoemeraldine form is oxidised to the emeraldine form, and at 0.65–0.75 V *vs.* SCE, where the emeraldine form is oxidised to the pernigraniline form.[2] [Fig. 1(*a*)]. It was of interest as to whether these radical species would react with monomers in solution.

During electrochemical polymerisation of aniline the propagation reaction to elongate the polymer chain involves reaction between an active species at the polyaniline chain and molecules in solution.[3–5] The active species can be either a neutral or cationic radical, which can react with monomers or dimers in solution,[6,7] which are either neutral or cationic radicals.[4,5] The polymerisation mechanism is complicated and of course, depends on conditions such as pH[7,8] or applied potential.[9] One of our aims was to shed some light on the propagation reaction of polyaniline film.



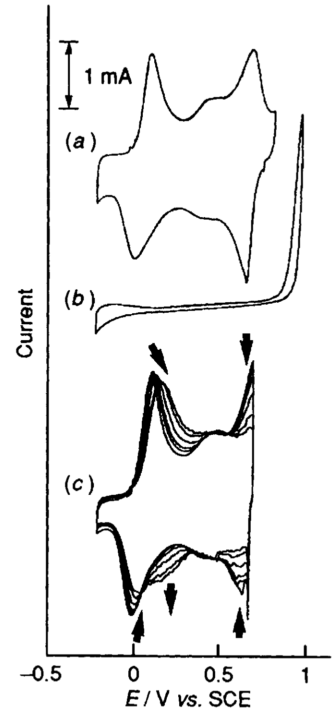


**Fig. 1** Cyclic voltammograms of (*a*) polyaniline film at the surface of Pt (2 cm$^2$), (*b*) *m*-ABN (0.1 mol dm$^{-3}$) in aqueous perchloric acid (1.0 mol dm$^{-3}$) and (*c*) the polyaniline film dipped in an aqueous solution of *m*-ABN; the 1st 5th, 10th, 25th, 50th and 70th potential scans are shown (sweep rate 50 mV s$^{-1}$)

In this study, polyaniline film was dipped into an ABN solution and by applying a potential to the film electrochemically, the reaction between the film and ABN was investigated. ABN was chosen for two reasons. Firstly it has a higher oxidation potential than aniline; the onset potential for the oxidation of *m*-ABN, *o*-ABN, and aniline are 0.80 [see the oxidation current increase in Fig. 1(*b*)], 0.74, and 0.65 V *vs.* SCE, respectively so, at potentials between 0.65 and 0.74 V it is possible to oxidise only the polyaniline film leaving the ABN intact in solution. If unsubstituted aniline were used, the

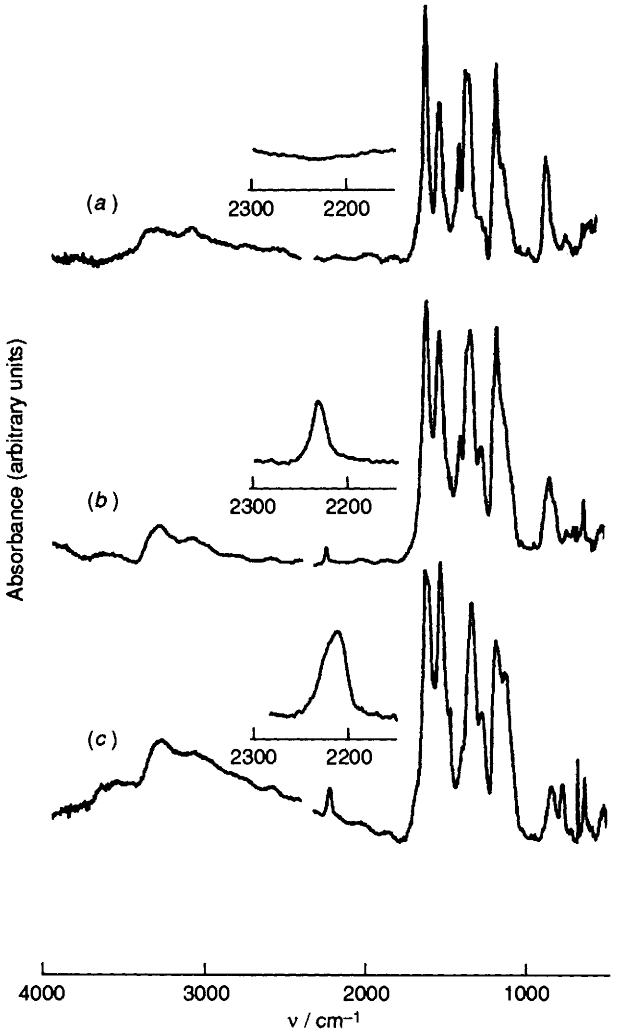
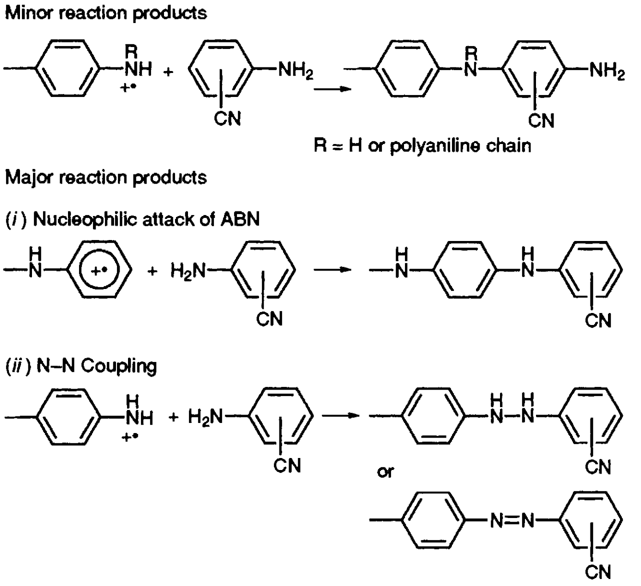


**Fig. 2** FTIR spectra of (*a*) polyaniline film and functionalized polyaniline film with (*b*) *m*-ABN and (*c*) *o*-ABN. The spectra were recorded by the use of a grazing angle (80°) reflectance accessory; insets show absorptions of the cyanide group.



Scheme 1

oxidation of the polyaniline film would be accompanied by oxidation of aniline. Secondly, ABN has a characteristic cyanide group, which is easily detected by FTIR spectroscopy enabling moniterasation of any reaction.

Figs. 1(*a*) and (*b*) show cyclic voltammograms of polyaniline film (thickness *ca.* 80 nm) at a platinum electrode and of *m*-ABN in aqueous acid solution, respectively. Oxidation of *m*-ABN proceeded at potentials >0.80 V.

When the polyaniline film was dipped into the *m*-ABN solution and the applied potential was cycled between −0.2 and 0.6 V, no reaction between the film and *m*-ABN took place. However, when the potential was extended to >0.65 V, progressively increasing changes were observed in the cyclic voltammograms [Fig. 1(*c*)]. Here the polyaniline film began to be oxidised from the emeraldine form to the pernigraniline form. In the resulting cyclic voltammograms, a new redox couple appeared at *ca.* 0.2 V, slightly higher than the potential for the leucoemeraldine–emeraldine redox couple. This shift suggested that the redox properties of the polyaniline film was affected by reaction with *m*-ABN.

After 70 cycles, the *ex situ* FTIR spectrum of the resulting polyaniline film was recorded and is shown in Fig. 2(*b*). A new absorption at 2232 cm$^{-1}$ showed that the cyanide of *m*-ABN had reacted with the polymer. The film was free of *m*-ABN monomer which might diffuse into the film since no IR absorption corresponding to *m*-ABN was found. Using *o*-ABN instead of *m*-ABN led to similar behaviour with the FTIR spectrum of the film shown in Fig. 2(*c*). The cyanide band appeared at 2216 cm$^{-1}$, whereas those of *m*- and *o*-ABN occur at 2234 and 2209 cm$^{-1}$, respectively (an amino nitrogen at the *o*-position weakens the –C≡N triple bond).

The IR absorptions of the out-of-plane bending modes of C–H on the phenyl ring, occurring in the region 750–900 cm$^{-1}$, indicated the mode of reaction between ABN and the polyaniline film.[10,11] The absorption of polyaniline, with 1,4-substituted phenyl rings, occurs at 840 cm$^{-1}$, while those the 1,3- and 1,2-substituted phenyl rings, of *m*- and *o*-ABN occur at 686, 788 cm$^{-1}$ and at 742 cm$^{-1}$, respectively. For the functionalized polyaniline films with *m*- and *o*-ABN, new absorption bands appeared at 805 cm$^{-1}$ (sh) and at 761 cm$^{-1}$, respectively. These are in the region for disubstituted phenyl rings and not for 1,2,4- or 1,3,5-*tri*-substituted rings.[10] Other new absorptions, although weak and not clearly seen, were observed in the trisubstituted region at 850–900 cm$^{-1}$. These small absorptions suggested that the trisubstituted product was formed only as a minor species by an electrophilic attack of polyaniline to ABN.[10,11] The major reaction product is probably formed by a nucleophilic attack of ABN to the phenyl ring of the polyaniline[4] or by an N–N coupling. Possible reaction schemes for these products are shown in Scheme 1. The existence of N–N bonds was supported by a small peak at 1450 cm$^{-1}$, corresponding to ν(N=N).[8] Similar N–N coupling has been proposed in the electrochemical polymerisation of aniline in aqueous acid solution.[5]

Our data suggested that when the polyaniline film was oxidised from the emeraldine form to the pernigraniline form, it reacted with ABN to elongate the polymer chain.

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