

Electrochemical Doping of Polyaniline: Effects on Conductivity and Optical Spectra

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Polyaniline was electrochemically doped to three electrically and spectroscopically distinctive forms: the closed valence-shell oxidized and reduced forms and the radical cation intermediate form.

We report here the electrochemical-doping-induced changes of the conductivity and optical spectra of polyaniline (PAN). The correlations suggest that PAN is reversibly doped into three forms: (i) a closed valence-shell reduced form, (ii) a radical cation intermediate form, and (iii) a closed valence-shell oxidized form. PAN is the first known conducting polymer that is stable in aqueous solution for all these three forms. The radical cation form is highly conductive. The closed valence-shell oxidized and reduced forms, however, are insulating. This study provides a molecular mechanism for the conductivity switching property of PAN first reported by Paul *et al.*¹ in their PAN-based micro-electronic devices.

PAN films of 100 nm thickness were electrochemically synthesized under the conditions similar to those reported by Kobayashi *et al.*² Films were electrochemically doped in pH 5 phthalate buffer and then vacuum dried for 4-probe conductivity measurements. Figure 1(a) shows the conductivity as a function of the electrochemical potential. The conductivity is highest for an intermediate range of oxidation. It decreases by at least 4 orders of magnitude for either the oxidized (+0.4 V) or the reduced form (-0.3 V). We found that: (i) the doping was reversible within this range of potentials; (ii) the conductivity was electronic rather than ionic for the dried films.

The resistance switching of PAN was previously reported under somewhat different conditions by Paul *et al.*¹ In this

work the samples were immersed in pH 1 solutions while in the current work the samples were vacuum dried from pH 5 solutions. Our conductivity-*vs.*-doping curve at pH 5 is shifted by about 0.24 V to the negative with respect to ref. 1. The -60 mV/pH shift of the potential is consistent with a deprotonation process in the electrochemical oxidation.

The inverted-U-shape curve in Figure 1(a) for PAN is in contrast with the saturation-curve behaviour of other conducting polymers. For polyacetylene³ or any other conducting polymer studied so far, the conductivity increases monotonically with doping and levels off at the highest attainable dopant concentration.

Figure 2 shows the electrochemical-doping-induced changes of the absorption spectra of PAN in a pH 5.9 phthalate buffer solution. When the applied potential was gradually decreased from +0.36 to -0.34 V (*vs.* standard calomel electrode, S.C.E.), the two-band spectrum in Figure 2(a) was first changed into a three-band spectrum which, in turn, was changed into a one-band spectrum [Figure 2(b)]. In addition to a 320 nm band which is common to all spectra, the three-band spectrum has two more transitions at 420 and 800 nm; the two-band spectrum has one more transition at 580 nm. Since the band positions are shifted by doping, there is no focused isosbestic point in Figure 2.

The absorbances at 800, 420, and 580 nm for a film in pH 5.0 solution are plotted against the electrochemical potential in Figure 1(b). The intersection of curves in the 0.3-0.2 V region signifies the transformation of the most oxidized form to the intermediate form. The decrease of the 420 nm band in the -0.15 to -0.3 V region signifies the transformation from the intermediate form to the reduced form. These spectral transformations occur at potentials coincident with the conductivity changes in Figure 1(a).

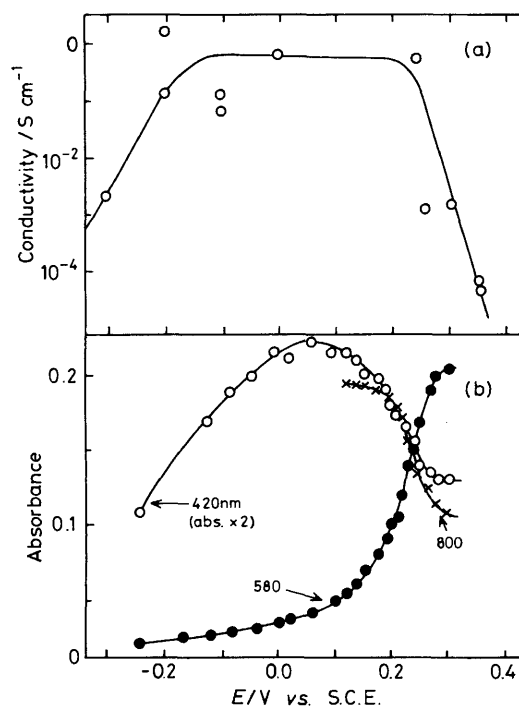


Figure 1. (a) Conductivity of electrochemically generated polyaniline as a function of the extent of electrochemical doping. (b) Changes in optical absorbance at 800 (x), 580 (●) and 420 nm (○), as a function of the extent of electrochemical doping (the absorbance at 420 nm has been multiplied by a factor of two).

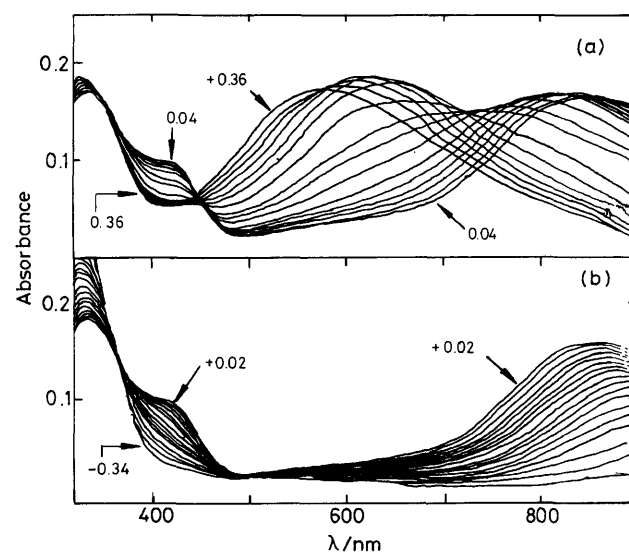


Figure 2. Absorption spectra of polyaniline film in pH 5.9 solution with *in situ* potential control. The potentials were decreased in steps of 0.02 V: (a) from +0.36 to +0.04 V *vs.* S.C.E.; (b) from +0.04 to -0.34 V *vs.* S.C.E.

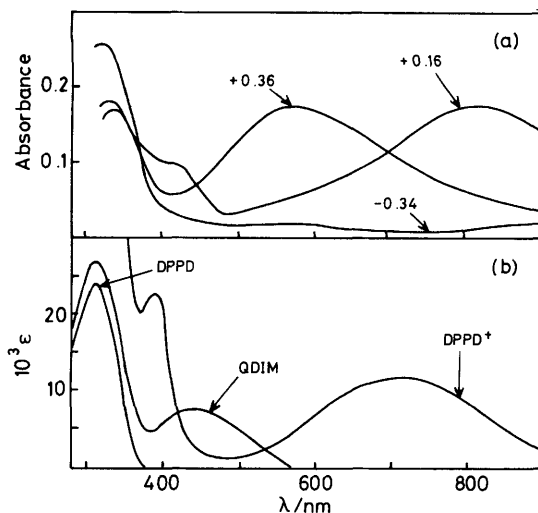
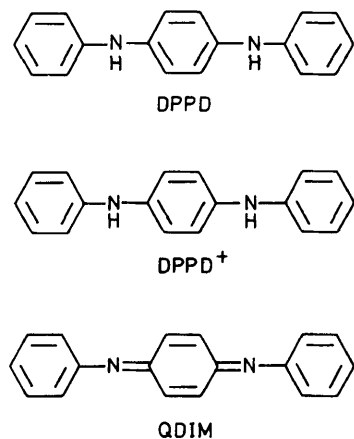


Figure 3. (a) Optical spectra of polyaniline films held at -0.34 , $+0.36$, and $+0.16$ V vs. S.C.E. with pH 5.9 buffer solution. (b) Absorption spectra of DPPD, QDIM, and DPPD^+ (ref. 4).

Spectra of films held at -0.34 , $+0.16$, and $+0.36$ V vs. S.C.E. in pH 5.9 solutions are reproduced in Figure 3(a). They are representative for the three oxidation states of PAN. Figure 3(b) shows the spectra of the three model compounds⁴ DPPD, DPPD^+ , and QDIM. A comparison of Figures 3(a) and 3(b) indicates the spectral patterns that correlate the three oxidation stages of PAN with the three model compounds. These spectral features are also seen in various oxidation states of other molecules^{5,6} with $-\text{N}-\text{ph}-$ linkages, and their absorption bands are assignable.⁵ The broad, long wavelength band (800 nm) of the intermediate oxidation state is characteristic of a radical cation.⁵ Based on these correlations, we suggest that the reduced, the intermediate, and the oxidized forms of polyaniline have the structures $(-\text{ph}-\text{NH}-)_x$, $(-\text{ph}-\text{NH}-)_x^{\cdot+}$, and $(-\text{ph}-\text{N}=\text{Q}=\text{N}-)_{x/2}$, respectively. Here ph and Q stand for *p*-phenylene and quinoid rings.

MacDiarmid *et al.*⁷ have previously suggested the existence of the closed-shell structures (1A and 2A forms in their paper). However, the radical cation with intermediate extent



of oxidation between these two closed-shell structures has not received attention in the literature. The results presented in this paper indicate that the radical cation is stable in aqueous solution, and it is much more conductive than the limiting oxidized and reduced forms. The existence of such an intermediate structure is the important molecular mechanism for the resistance switching of PAN.¹

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