Alternative concept of the transition emeraldine base–emeraldine salt

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The transition of the emeraldine base (EB) to the emeraldine salt (ES) form of polyaniline (PANI) is in fact a redox process

$$\text{'EB'} \underset{-e}{\overset{+e}{\rightleftharpoons}} \text{ES}$$

where 'EB' does not represent the emeraldine oxidation state. This redox process itself is an intermediate stage in the transition of insulating pernigraniline to conducting emeraldine. Generally, transition of PANI from insulating (leucoemeraldine, L, or pernigraniline, PN) to conducting (emeraldine, E) state could be represented by the following scheme:

$$\text{PN} \underset{-e}{\overset{+e}{\rightleftharpoons}} \text{'EB'} \underset{-e}{\overset{+e}{\rightleftharpoons}} \text{ES(E)} \underset{-e}{\overset{+e}{\rightleftharpoons}} \text{L}$$

(Keywords: polyaniline; polyaniline dispersion; emeraldine base–emeraldine salt transition)

Introduction

It is known that the conductivity of polyaniline (PANI) depends on the oxidation state (the ratio of amine to imine nitrogen) and the extent of protonation[1–5]. The conducting form of PANI is an emeraldine salt (ES)[6], i.e. protonated form of emeraldine base (EB). Conductivity may be alternately changed between 10^{-8}–10^{-10} S cm^{-1} (EB) and ~ 1 S cm^{-1} (ES) by treating PANI successively in solutions with pH = 6–10 and pH $\approx$ 1[7,8]. Generally, the process may be described as follows:

$$\text{EB} \underset{-\text{H}^+}{\overset{+\text{H}^+}{\rightleftharpoons}} \text{ES}$$

On the basis of magnetic susceptibility experiments[9–11], it was suggested that the electronic structure changed from semiconductor in the EB to a metal in the protonated ES due to the formation of a polaron band resulting from the proton-induced spin-unpairing mechanism[11,12], described as an internal redox reaction[13]. Therefore, corresponding changes in the electronic absorption spectrum of EB (310–344, 620 nm) during the transformation to ES (330, 420, 800 nm) should not be connected with the change of oxidation state. However, this is inconsistent with the electrochemical-doping-induced changes of the absorption spectra of PANI film at pH = 5.9[14] and pH $\approx$ 1[15,16]. The absorption spectrum of PANI film at 0.16 V *versus* standard calomel electrode (s.c.e.) and pH = 5.9[14] corresponds to the spectrum of ES, although it should correspond to EB under these conditions; and vice versa, the absorption maxima in the spectra of PANI film at 0.8[15] and 1.4 V[16] *versus* s.c.e. at pH $\approx$ 1 are characteristic of EB, while the oxidation state should actually be higher than emeraldine.

The possibility of obtaining PANI as a stable aqueous dispersion with particles smaller than 200 nm in size[17–19] enabled us to follow easily, by optical absorption spectroscopy, both the intermediate and the final polymerization products *in situ* and at various pH values of the medium. We first found that the main reaction steps of the polymerization of aniline are pH dependent[19]. It was shown that, while reaction step 1 (oxidation) proceeds both in acidic and alkaline media, reaction step 2 (reduction) takes place only in acidic medium (see *Figure 1*). The presence of residual monomer and oxidant in chemically prepared PANI enables different steps of the post-polymerization process (determining the interconversion of oxidation states of PANI), to proceed depending on the pH of the medium.

These results are consistent with the well known pH–potential dependences of the conductivity of electrochemically synthesized PANI[8,14–16,20]. In contrast to the chemically prepared PANI, this polymer does not contain residual oxidant. It might be expected that electrochemically synthesized ES would not change its oxidation state (due to the absence of oxidant) or its conductivity under conditions when, according to MacDiarmid *et al.*[21], it has to be deprotonated, i.e. transformed into insulating EB.

Actually[8], when electrochemically synthesized in 1 M HCl, PANI reveals conductivity of 5 S cm^{-1} at pH = 6.

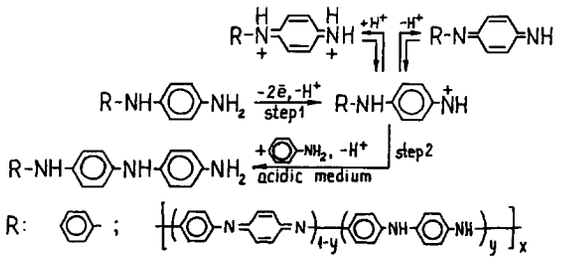

Figure 1 Reaction steps of oxidative polymerization of aniline

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Moreover, electrochemically prepared PANI, initially oxidized in alkaline medium at a particular potential, could be reduced later at the same potential solely by decreasing the pH of the medium. In fact[20], when PANI film was held at a potential of 0.4 V *versus* s.c.e. and pH = 9, it oxidized to pernigraniline. During the following titration with acid, transformation of pernigraniline to the emeraldine oxidation state was observed.

In this paper we present new experimental results which, in combination with our previous data[19], enable us to suggest a new concept of the transition EB–ES. PANI dispersions (and free-standing films cast from them), prepared as described previously[17,18], were studied by optical absorption spectroscopy. Both dispersions, and aqueous solutions wherein the free-standing films had been immersed, were acidified and alkalized by means of 1–4 M solutions of HCl and NaOH. After equilibrating at different pH values, spectra were recorded on Specord M42 (Carl Zeiss).

The stepwise increase of dispersion pH up to 12–13 results in the gradual oxidation of PANI, as seen from absorption spectra (*Figure 2*). Analogous changes in absorption spectra of PANI have been observed during electrochemical oxidation due to increased potential from 0.16 to 0.36 V at pH = 5.9[14], from 0.3 to 0.8 V in 0.1 M H_2SO_4[15], and from 0.8 to 1.4 V in 1 M HCl[16]. This demonstrates that transformation of the spectra from curve 1 to curve 7 (*Figure 2*) reflects the process of chemical oxidation of PANI. In this case, instead of enhanced potential, increasing pH of the medium leads to decreasing rate of the post-reduction process, and finally, in alkaline medium, results in its total termination (i.e. PANI of the highest oxidation level for the corresponding experimental conditions has been obtained). The opposite situation, gradual acidification of PANI dispersion up to pH = 0.6, results in reduction of PANI, which is reflected in transformation of the absorption spectra from curve 7 to curve 1.

As shown previously[19], 'irreversible' oxidation of PANI can be performed in acidic medium where, in contrast to the alkaline and neutral media, post-reduction accompanied by the aniline consumption proceeds simultaneously with the post-oxidation. In a set of experiments, products having exactly the same absorption spectra as shown in *Figure 2*, curves 1–7, have been obtained by oxidation of free-standing film (cast from PANI dispersion) in 1 M HCl by gradual addition of an increasing amount of oxidant $(NH_4)_2S_2O_8$. The reverse transformation from curve 7 to curve 1 of the spectra of oxidation products of PANI, obtained as described above in acidic medium, were observed only by gradual addition of aniline.

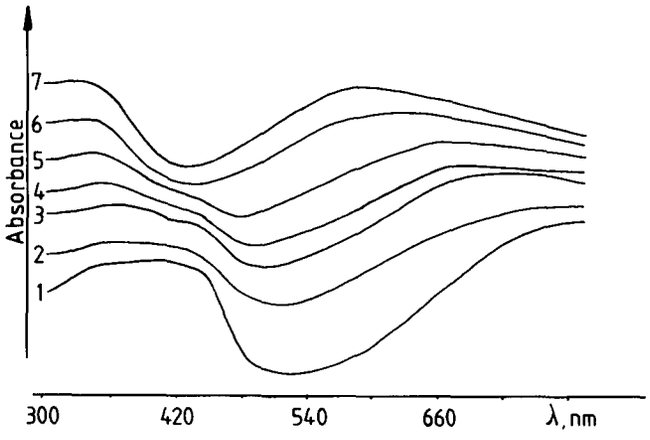

Figure 2 Optical absorption spectra of polyaniline dispersions at different pH vaues: 1, 0.6; 2, 1.2; 3, 3; 4, 4; 5, 5; 6, 6; 7, 13

Therefore the optical absorption spectra of PANI related to its conductivity level, reflect its oxidation state rather than the protonation. In turn, the oxidation state is determined by the probability of the different steps of the post-polymerization (redox) process taking place. This probability depends both on the presence of oxidant and reducer (aniline) and on the pH of the medium. The latter determines whether solely the oxidation step (in alkaline or neutral media), or both the oxidation and reduction steps (in acidic medium) take place. Moreover, the degree of reduction increases on decreasing pH of the medium.

For that reason, either a higher concentration of oxidant (in chemical oxidation) or a higher potential (in electrochemical oxidation) are needed in 'acidic' oxidation of PANI than in neutral or alkaline media.

On the other hand, the increase of the degree of reduction of oxidized PANI from pernigraniline, $(1-y) \approx 1$, or intermediate oxidation state, $0.5 < (1-y) < 1$, (among the latter falls the so-called emeraldine base), up to emeraldine state on decreasing pH from ~4 to 1, determines the enhanced electrical conductivity, as observed by many authors[21] for chemically prepared PANI. (y is as defined in *Figure 1*).

Therefore, the transition

$$\mathrm{EB} \underset{-\mathrm{H}^+}{\overset{+\mathrm{H}^+}{\rightleftharpoons}} \mathrm{ES}$$

is in fact a redox process

$$\text{'EB'} \underset{-e}{\overset{+e}{\rightleftharpoons}} \mathrm{ES}$$

where 'EB' does not represent the emeraldine oxidation state ($1-y \approx 0.5$) but an intermediate oxidation state, where $0.5 < 1-y < 1$. This redox process itself is an intermediate stage in the transition of insulating pernigraniline to conducting emeraldine.

Generally, transition of PANI from insulating (leucoemeraldine, L, or pernigraniline, PN) to conducting (emeraldine, E) state can be represented by the following scheme:

$$\mathrm{PN} \underset{-e}{\overset{+e}{\rightleftharpoons}} \text{'EB'} \underset{-e}{\overset{+e}{\rightleftharpoons}} \mathrm{ES(E)} \underset{-e}{\overset{+e}{\rightleftharpoons}} \mathrm{L}$$

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