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# Communications to the Editor

## Redox Behavior of Polyaniline−Transition Metal Complexes in Solution

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Application of polyanilines as a conducting polymer has been extensively studied to develop the more useful materials.[1] The electronic properties are related to their $\pi$-conjugate structure.[2] Doping is able to modify the electronic properties of polyanilines; protonic acid doping converts a semiconducting emeraldine base to the conducting derivative.[3] A previous paper demonstrated that polyanilines serve as a synthetic metal catalyst in the dehydrogenative oxidation based on the formation of a reversible redox cycle under oxygen.[4] Protonic acid doping has been revealed to play an important role in the catalytic activity.[5] Coordination of transition metals to the nitrogen atoms is considered to permit transition metals to interact with each other through the $\pi$-conjugate chain. The complexation with copper(II) or iron(III) chloride has been found to contribute to the construction of the more efficient synthetic metal catalytic system in the dehydrogenation reaction. The catalysts consisting of palladium(II) acetate and polyanilines were reported to induce the Wacker oxidation, which provides a novel redox system for the transition-metal-catalyzed reactions.[6] These findings prompted us to investigate the interaction of transition metals with the $\pi$-conjugate chain of polyanilines. We herein report a unique redox behavior of the complex systems.

Treatment of the undoped polyaniline[7] (anal. $C_{6.00}H_{4.04}N_{0.97}Cl_{0.03}$) with $CuCl_2$ afforded the corresponding complex, which was confirmed by UV−vis spectra. Addition of $CuCl_2$ to a solution of the polyaniline in 1-methyl-2-pyrrolidinone led to the shift of the peak around 640 nm, attributable to charge transfer from the benzenoid of polyaniline to the quinoid,[8] into the shorter wavelength, as shown Figure 1a. This shift ($\Delta\lambda$) depended on the molar ratio of $CuCl_2$, giving the saturation curve for complexation (Figure 1b).

The cyclic voltammetry also supports the complexation. The half-wave potential of the undoped polyaniline−$CuCl_2$ complex (aniline unit:copper = 50:1) in 1-methyl-2-pyrrolidinone was 0.46 V vs SCE, in contrast to 0.29 V for that of the undoped polyaniline. The wave shape of the complex was broader. These results appear to be accounted for by the complexation.

Further studies on the redox behavior of the undoped polyaniline−$CuCl_2$ complex (aniline unit:copper = 10:1) in 1-methyl-2-pyrrolidinone were undertaken by *in situ* UV−vis spectra at a given redox potential.[9] At 0.3 V vs SCE, the broad peak around 600 nm based on the charge transfer increased with the blue shift. Concomitantly, the peak around 320 nm based on the $\pi-\pi^*$ transition[8] of the phenyl ring was reduced at the same potential. These spectral changes are presumably explained by the partial electrochemical oxidation of the emeraldine form to the more oxidized one. Such an electrochemical behavior was observed between 0.2 and 0.5 V vs SCE, as illustrated in Figure 2a. A new unassigned peak appeared around 780 nm at 0.6 V vs SCE. On the contrary, at a negative potential below 0.0 V vs SCE, the decrease of the broad peak around 600 nm accompanied the increased peak around 320 nm with isosbestic points (Figure 2b). These changes also indicate that the polyaniline of the complex is partially reduced electrochemically to the leucoemeraldine form. The redox transformation was almost reversible between 0.6 and −0.6 V vs SCE.

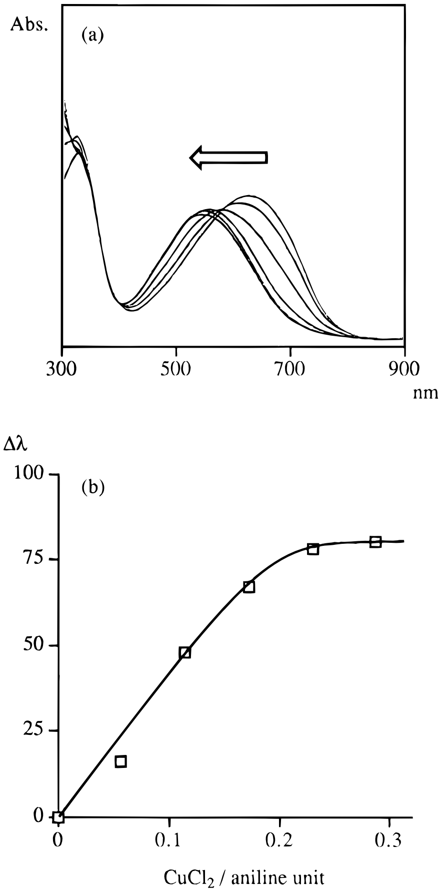

**Figure 1.** (a) UV−vis spectra of the undoped polyaniline (anal. $C_{6.00}H_{4.04}N_{0.97}Cl_{0.03}$) in 1-methyl-2-pyrrolidinone on successive addition of $CuCl_2$ as shown in (b), plots of $\Delta\lambda$ vs the ratio of $CuCl_2$/aniline unit.

It should be noted that the above-mentioned redox behavior of the undoped polyaniline−$CuCl_2$ complex at a negative potential is different from that of the undoped polyaniline. The similar change in UV−vis spectra of the undoped polyaniline was monitored at a positive potential (0.2−0.5 V vs SCE); the increase of the broad peak around 640 nm and the concomitant decrease of the peak around 320 nm were observed with isosbestic points (Figure 3a). The hypochromic change, however, did not appear between 0.0 and −0.6 V except for the small red shift (Figure 3b). The undoped polyaniline

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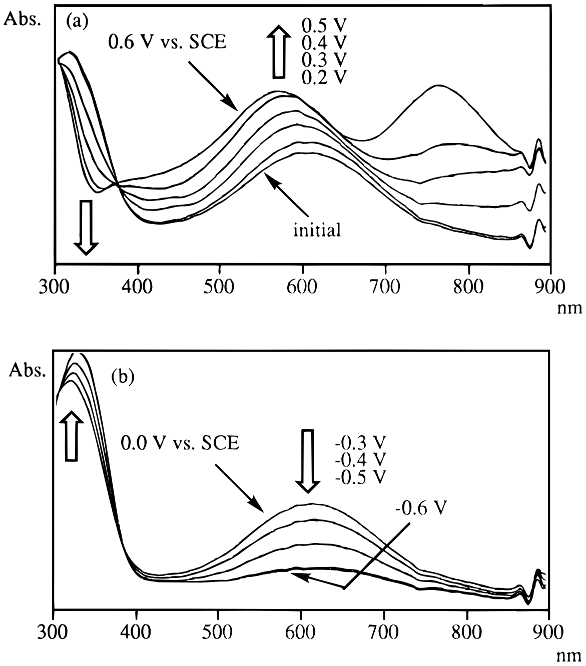

**Figure 2.** UV−vis spectra of the undoped polyaniline−$CuCl_2$ complex (aniline unit:copper = 10:1) in 1-methyl-2-pyrrolidinone: (a) electrochemical oxidation; (b) electrochemical reduction.

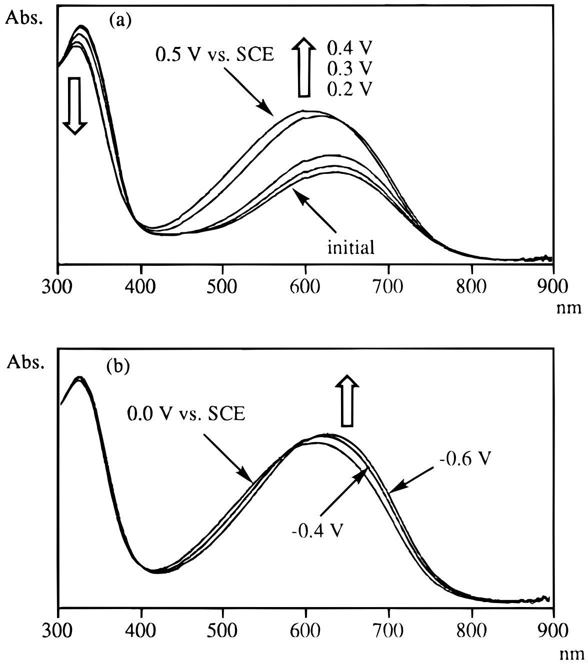

**Figure 3.** UV−vis spectra of the undoped polyaniline in 1-methyl-2-pyrrolidinone: (a) electrochemical oxidation; (b) electrochemical reduction.

is able to be oxidized electrochemically but is reduced with great difficulty at a negative potential. These results are conceivably explained by the protonic acid doping effect, which is supported by the following observation.

In contrast to the redox behavior of the undoped polyaniline, the hypochromic change was performed from 0.0 V to −0.6 V vs SCE with the protonic acid doped polyaniline[7] (anal. $C_{6.00}H_{6.34}N_{0.98}Cl_{0.57}$). The peak around 780 nm (0.6 V vs SCE) observed in the copper complex did not appear in the present oxidation.

In addition to its self-redox, the copper salt is considered to play an important role in the redox process,

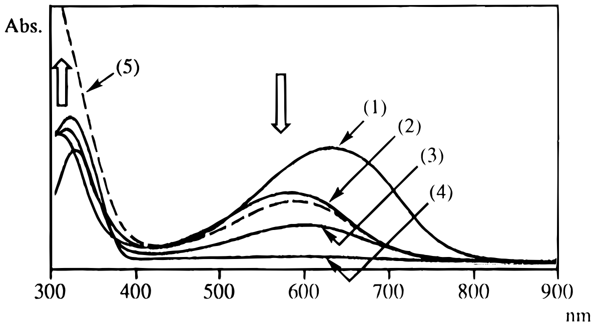

**Figure 4.** UV−vis spectra of (1) the undoped polyaniline in 1-methyl-2-pyrrolidinone. After CuCl (aniline unit:copper = 2:1) was added at room temperature under argon, progressive changes were recorded at 20 (2), 60 (3), and 120 min (4), respectively. (5) Oxygen was bubbled into the solution of (2) at room temperature over 40 min.

as observed in the protonic acid doping. In order to reduce a quinoid moiety of polyaniline into the corresponding benzenoid one, the presence of a proton is essential. In the case of the undoped polyaniline, however, there is not enough of a proton source to perform the reduction. Copper salt is assumed to serve as a similar dopant and furthermore the complexation attains the higher catalytic capability in the oxidation of cinnamyl alcohol.[4] Catalytic oxidation of benzylamine has been revealed to require the use of a protonic acid doped polyaniline under oxygen,[5] which is also consistent with the above-mentioned result.

The reaction of the undoped polyaniline with low-valent transition metals was investigated from the viewpoint of their redox interaction. On the addition of CuCl (aniline unit:copper = 2:1), the blue solution of the undoped polyaniline in 1-methyl-2-pyrrolidinone became purple in 3 min, then colorless in 2 h with disappearance of the peak around 640 nm (Figure 4). This finding discloses the coordination of a low-valent copper species and the subsequent reduction of the quinoid moiety.[10]

The color of the thus obtained solution turned out to be bluish-purple by bubbling oxygen. The peak around 590 nm appeared and gradually increased over 40 min, suggesting the reoxidation of the benzenoid moiety of the copper complex. The spectral shift is assumed to be due to the complexation. Similar redox behaviors were observed with Fe(II), Mn(II), V(II), and Sm(II).

In conclusion, the complexation of polyanilines with transition metals provides a novel reversible redox system. The complex system is expected to form a sequential potential field based on the $\pi$-conjugate characteristic. Further investigation is now in progress.

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(7) Polyaniline was prepared according to the reported method: MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Somasiri, N. L. D. In *Conducting Polymers*; Alcacer, L., Ed.; Reidel Publishing: Dordrecht, The Netherlands, 1987; p 105. A solution of aniline (20.4 g, 219 mmol) in 1 M HCl (300 mL) was placed in an ice/water bath and cooled. A solution of ammonium peroxodisulfate (11.5 g, 50.4 mmol) in 1 M HCl (200 mL) cooled in an ice/water bath was dropwise added to the solution of aniline over about 10 min with vigorous stirring. As the polymerization proceeded, the solution turned dark green and the salt of polyaniline began to precipitate. After the addition of the ammonium peroxodisulfate solution was completed, the mixture was stirred for an additional 2 h. Polyaniline (4.5 g) was filtered using a Büchner funnel, washed with 1 M HCl (300 mL), acetonitrile (300 mL), and then ether (300 mL), and dried in vacuum at room temperature for 24 h. Treatment of the thus obtained polymer with an aqueous solution of 0.1 M sodium hydroxide for 24 h with stirring gave the undoped polyaniline, which was filtered, washed with water (300 mL), acetonitrile (300 mL), and then ether (300 mL), and dried in vacuum at room temperature for 24 h.

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(9) *In situ* UV−vis spectra were measured according to the reported method: Yoneyama, H.; Ii, Y.; Kuwabata, S. *J. Electrochem. Soc.* **1992**, *139*, 28. 1-Methyl-2-pyrrolidinone was distilled under reduced pressure with $CaH_2$ as a drying agent and stored under argon. Copper(I) chloride (Wako Pure Chemical Industries) was used after drying under reduced pressure at 80 °C for 24 h.

(10) The redox interaction in the coordination sphere is assumed to reduce the quinoid moiety of the undoped polyaniline.

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