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# A NOVEL REDOX SYSTEM CONSISTING OF π-CONJUGATED POLYMERS AND TRANSITION METALS

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***Abstract***: Coordination of π-conjugated polymers to transition metals constructs a novel redox system due to interchangeable various oxidation states of the polymers, which permits transition metals to interact with each other through a π-conjugate chain. The redox characteristics were found to depend on the electronic interaction with metals and the doping. A combination of copper(II) or iron(III) chloride and polyanilines afforded the complex catalysts with the higher oxidation capability for dehydrogenative oxidation. A catalytic system was also realized in the transition-metal-induced oxidation reaction, in which π-conjugated polymers serve as redox-active ligands participating in the reversible redox cycle. The Wacker oxidation of terminal olefins proceeded catalytically in the presence of a catalytic amount of polyaniline or polypyrrole derivative under oxygen.

## INTRODUCTION

π-Conjugated polymers have received wide interest due to their high potential in a variety of applications as conducting polymers (Ref. 1). The electronic properties are related to their π-conjugate structure (Ref. 2). Doping is able to modify the electronic properties; for example, protonic acid doping converts a semiconducting emeraldine base of polyaniline to the conducting derivative (Ref. 3). Various oxidation states in the π-conjugated polymers interconvert each other. These properties allow to construct a reversible redox cycle for catalytic reactions. In our previous papers (Refs. 4, 5), π-conjugated polymers have been demonstrated to serve as synthetic metal catalysts in dehydrogenative oxidation. The catalytic dehydrogenation of benzylamines proceeds on treatment with a catalytic amount of polyaniline under oxygen to give the *N*-benzylidenebenzylamines. This catalytic system has been applied to the oxidation of 2-phenylglycine and 2,6-di-*t*-butylphenol. The catalytic activity is revealed to be controlled by protonic acid doping. Polypyrroles also constitute a catalytic redox system like polyanilines.

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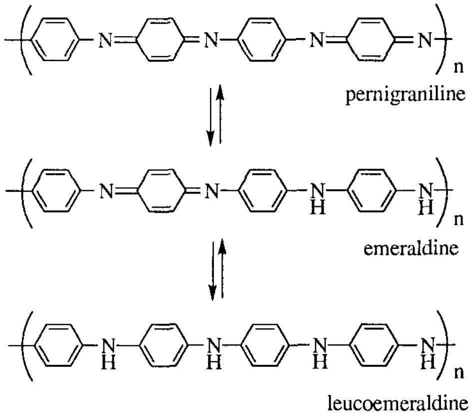
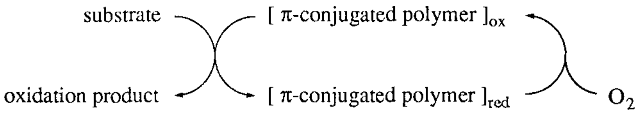
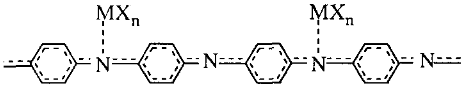


The synthetic metal catalytic system provides a novel method for oxidation reactions. Catalysis depends on a reversible redox cycle of the polymers under oxygen.



π-conjugated polymer = polyanilines, polypyrroles

Coordination of transition metals to the nitrogen atoms of polyanilines or polypyrroles are envisaged to afford the complexes, in which transition metals are considered to interact through a π-conjugate chain. The characteristics of π-conjugated polymers are reflected on the complexes, which are expected to provide a novel complex catalytic system.

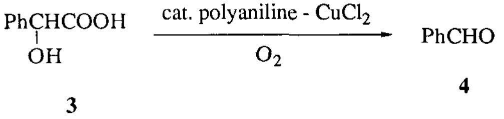


## DEHYDROGENATIVE OXIDATION WITH POLYANILINE-TRANSITION METAL COMPLEXES

Doping of polyaniline with copper(II) chloride formed an efficient catalyst for the dehydrogenation of cinnamyl alcohol (**1**) to cinnamaldehyde (**2**) in DMF (eq 1). A poor result was obtained with each individual component, indicating that a combination of synthetic metal catalyst with copper(II) chloride is required for the oxidation. Iron(III) chloride was similarly used instead of copper(II) chloride as shown in Tab. 1.

$$\underset{\mathbf{1}}{PhCH{=}CHCH_2OH} \xrightarrow[O_2]{\text{cat. polyaniline - metal salt}} \underset{\mathbf{2}}{PhCH{=}CHCHO} \qquad (1)$$

The catalytic system was applicable to the decarboxylative dehydrogenation of mandelic acid (**3**) to give benzaldehyde (**4**, eq 2). The cooperative catalysis of polyaniline and copper(II) chloride is essential as mentioned above. Use of the less doped polyaniline led to the better yield, indicating that the catalysis is affected by the doping.



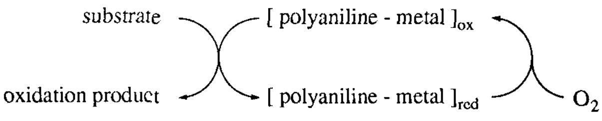
$$\underset{\mathbf{3}}{\underset{OH}{PhCHCOOH}} \xrightarrow[O_2]{\text{cat. polyaniline - }CuCl_2} \underset{\mathbf{4}}{PhCHO} \qquad (2)$$

**Tab. 1.** Oxidation of **1** and **3**[a]

| substrate | polyaniline[b], mg | metal, equiv. | time, h | yield, % |
|---|---|---|---|---|
| **1** | 20 | $CuCl_2$ 0.2 | 10 | 68 |
| **1** | 10 | $FeCl_3$ 0.1 | 20 | 39 |
| **3** | 10 | $CuCl_2$ 0.1 | 50 | 32 |
| **3** | 10[c] | $CuCl_2$ 0.1 | 50 | 55 |

[a] Substrate, 1.0 mmol; DMF, 1.0 mL; reaction at 80 °C under oxygen.
[b] Anal. $C_{6.00}H_{4.50}N_{1.00}(BF_4)_{0.11}$. [c] Anal. $C_{6.00}H_{4.49}N_{0.99}Cl_{0.01}$.

These oxidation reactions did not proceed catalytically under nitrogen. A complex catalyst consisting of polyaniline and metal salt is considered to form a reversible redox cycle under oxygen.



metal = Cu(II), Fe(III)

## COMPLEXATION OF POLYANILINES WITH TRANSITION METALS AND THEIR REDOX BEHAVIOR

The above-mentioned catalysis is based on the complexation with polyanilines (Refs. 5, 7). The insoluble species recovered in the oxidation reaction of **1** in the presence of copper(II) chloride in DMF involved one copper species to two aniline units of polyaniline (anal. $C_{6.00}H_{5.82}N_{1.01}(BF_4)_{0.11}(CuCl_2)_{0.53}$).

Treatment of the undoped polyaniline (anal. $C_{6.00}H_{4.04}N_{0.97}Cl_{0.03}$) with copper(II) chloride afforded the corresponding complex, which was confirmed by UV–vis. spectra. Addition of copper(II) chloride to a solution of the polyaniline in 1-methyl-2-pyrrolidinone (NMP) led to the shift of the absorption around 640 nm, attributable to charge transfer from the benzenoid of polyaniline to the quinoid (Ref. 6), to shorter wavelength, as shown in Fig. 1a. This shift (Δλ) depended on the amount of copper(II) chloride, giving the saturation curve for complexation (Fig. 1b).

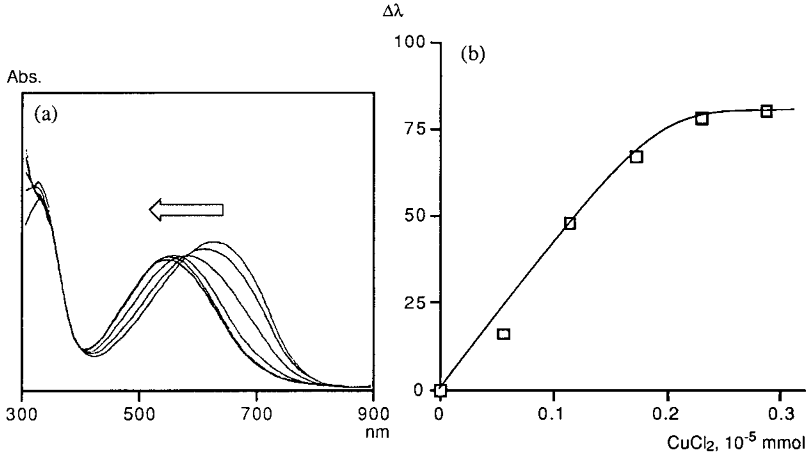


**Fig. 1.** (a) UV-vis. spectra of the polyaniline (anal. $C_{6.00}H_{4.50}N_{1.00}(BF_4)_{0.11}$) in NMP on successive addition of $CuCl_2$ as shown in (b) : plots of Δλ vs the amount of $CuCl_2$.

The cyclic voltammetry also supports the complexation. The half-wave potential of the undoped polyaniline–$CuCl_2$ complex (aniline unit : copper = 50 : 1) in NMP 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 indicate the higher catalytic activity of the complex.

Further studies on the redox behavior of the undoped polyaniline–$CuCl_2$ complex (aniline unit :

copper = 10 : 1) in NMP were undertaken by *in situ* UV–vis. spectra at a given redox potential. At 0.3 V vs SCE, the broad absorption around 600 nm based on the charge transfer increased with the blue shift. Concomitantly, the absorption around 320 nm based on the $\pi$–$\pi^*$ transition 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, as illustrated in Fig. 2a. On the contrary, at a negative potential below 0.0 V, the decrease of the broad absorption around 600 nm accompanied the increased absorption around 320 nm with isosbestic points (Fig. 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.

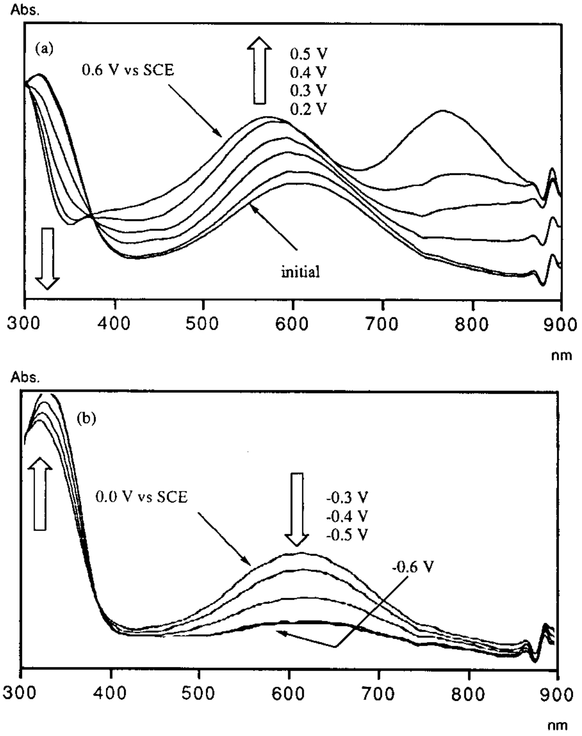


**Fig. 2.** UV-vis. spectra of the undoped polyaniline (anal. $C_{6.00}H_{4.04}N_{0.97}Cl_{0.03}$) - $CuCl_2$ complex in NMP. (a) Electrochemical oxidation. (b) Electrochemical reduction.

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. Although the increase of the broad absorption around 640 nm and the concomitant decrease of the absorption around 320 nm of the undoped polyaniline were observed with isosbestic points at a positive potential (0.2–0.5 V vs SCE), the hypochromic change did not appear between 0.0 and -0.6 V except for the small red shift. The undoped polyaniline is reduced with great difficulty at a negative potential, conceivably due to the protonic acid doping effect because the hypochromic change was performed from 0.0 V to -0.6 V with the protonic acid doped polyaniline (anal. $C_{6.00}H_{6.34}N_{0.98}Cl_{0.57}$). In addition to its self-redox, the copper salt is considered to play an important role to serve as a similar dopant in the reduction of a quinoid moiety into the corresponding benzenoid one, as observed in the protonic acid doping. Based on the above-mentioned observations, the complexation attains the higher catalytic capability in the oxidation.

The reaction of the undoped polyaniline with low-valent transition metals was investigated from the viewpoint of their redox interaction. On the addition of copper(I) chloride (aniline unit : copper = 2 : 1), the blue solution of the undoped polyaniline in NMP became purple in 3 min, then colorless in 2 h with disappearance of the absorption around 640 nm (Fig. 3). This finding discloses the coordination of a low-valent copper species and the subsequent reduction of the quinoid moiety. The color of the thus obtained solution turned out to be bluish-purple by bubbling oxygen. The absorption 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 low-valent metals such as Fe(II), Mn(II), V(II), and Sm(II).

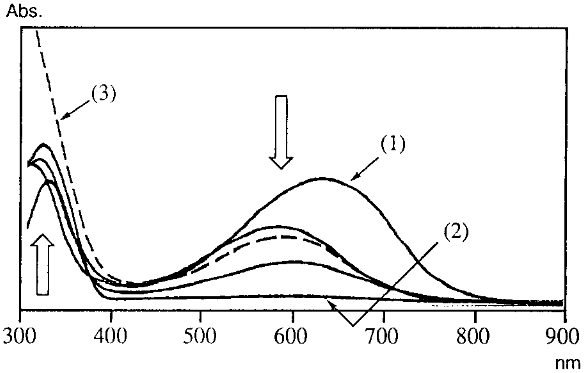
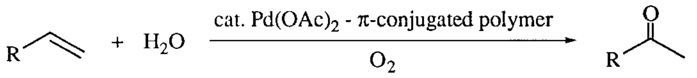


**Fig. 3.** UV-vis. spectra. (1) The undoped polyaniline (anal. $C_{6.00}H_{4.04}N_{0.97}Cl_{0.03}$) in NMP. (2) After CuCl (aniline unit : copper = 2 : 1 ) was added at room temperature under argon, progressive changes were recorded at 20, 60, and 120 min, respectively. (3) Oxygen was bubbled into the solution of (2) at room temperature over 40 min.

## PALLADIUM(II)-CATALYZED OXIDATION BASED ON REDOX OF π-CONJUGATED POLYMER

Efficient catalytic systems for oxidation principally depend on a smooth reversible redox cycle of transition metal complexes. If ligands form a reversible redox cycle, the redox interaction between metals and ligands is envisaged to largely contribute to the catalytic system. The system has not been extensively investigated so far despite the high synthetic potential. Trimethyl ester of coenzyme PQQ has been demonstrated to serve as a ligand forming a reversible redox cycle under oxygen, which provides an efficient catalytic system for the palladium(II)-catalyzed oxidation reactions (Ref. 8).

The Wacker oxidation reaction of 1-decene proceeded catalytically in the presence of a catalytic amount of polyaniline in acetonitrile-water under oxygen to give 2-decanone as a sole oxidized product (eq 3, Tab. 2)(Ref. 9). The catalysis was not observed in the absence of polyaniline derivatives, indicating that π-conjugated polymer participates in the catalytic cycle. Polypyrroles could be used similarly (Ref. 10). Terminal olefins were successfully oxidized to the corresponding 2-alkanones. A difference in the electronic state of the polymer or the complexation affects the catalysis because the catalytic activity depended on protonic acid doping. A reversible redox cycle of the catalyst was found to be achieved only under oxygen.



(3)

Tab. 2. The Wacker oxidation of olefins[a]

| olefin | π-conjugated polymer | anal. | yield, %[b] |
|---|---|---|---|
| $H_2C{=}CH(CH_2)_7CH_3$ | polyaniline | $C_{6.00}H_{5.18}N_{0.98}Cl_{0.41}$ | 677 |
| $H_2C{=}CH(CH_2)_7CH_3$ | polyaniline | $C_{6.00}H_{4.40}N_{0.99}Cl_{0.06}$ | 140 |
| $H_2C{=}CH(CH_2)_7CH_3$ | poly(*o*-toluidine) | $C_{7.00}H_{7.89}N_{0.99}Cl_{0.28}$ | 760 |
| $H_2C{=}CH(CH_2)_7CH_3$ | *N,N'*-diphenyl-*p*-phenylenediamine[c] | | 75 |
| $H_2C{=}CH(CH_2)_9CH_3$ | polyaniline | $C_{6.00}H_{5.18}N_{0.98}Cl_{0.41}$ | 601 |
| $H_2C{=}CH(CH_2)_8COOCH_3$ | polyaniline | $C_{6.00}H_{5.18}N_{0.98}Cl_{0.41}$ | 720 |
| $H_2C{=}CH(CH_2)_2COCH_3$ | polyaniline | $C_{6.00}H_{5.65}N_{0.98}Cl_{0.52}$ | 509 |
| $H_2C{=}CH(CH_2)_2COCH_3$ | polypyrrole | $C_{4.00}H_{3.31}N_{0.98}Cl_{0.26}$ | 616[d] |

[a] Olefin, 1.0 mmol; $Pd(OAc)_2$, 0.1 mmol; π-conjugated polymer, 40 mg; MeCN, 1.0 mL; reaction at 70 °C for 24 h under oxygen. [b] Based on the palladium catalyst. [c] 0.1 mmol. [d] Reaction at 40 °C for 90 h.

A real catalyst is considered to be formed by complexation of a palladium species with π-conjugated polymer, which was checked by UV-vis. spectra. A new broad absorption around

635 nm appeared on treatment of poly(*o*-anisidine) with Pd(OAc)$_2$ in NMP (Fig. 4a) and is likely to be attributable to the palladium complex with poly(o-anisidine). This broad absorption disappeared in the reaction with 1-decene and water under argon. Bubbling oxygen through the thus obtained solution gave rise to the broad absorption around 600 nm with isosbestic points (Fig. 4b). The similar spectrum was obtained by bubbling oxygen through the solution of Pd(OAc)$_2$ and poly(*o*-anisidine) (Fig. 4a).

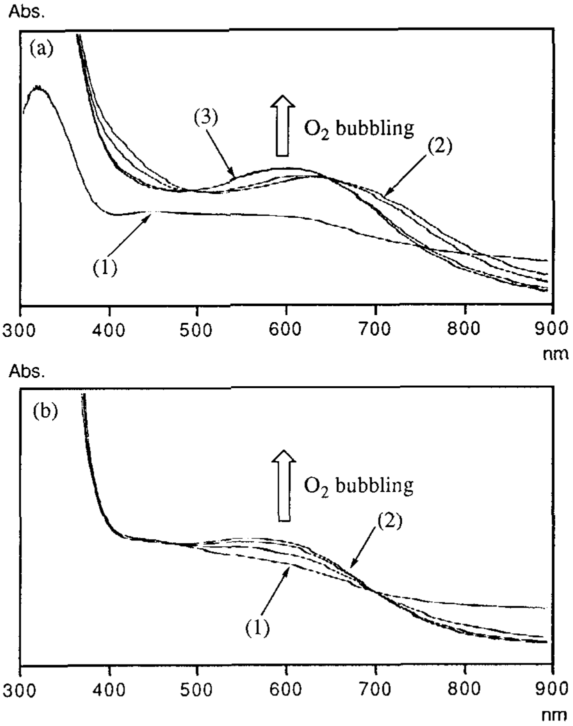
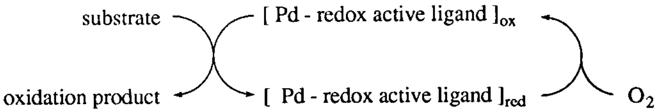


**Fig. 4.** UV-vis. spectra: (a) (1) Poly(*o*-anisidine) (anal. $C_{7.00}H_{7.60}N_{0.94}Cl_{0.51}$) in NMP, (2) the solution of Pd(OAc)$_2$ and poly(*o*-anisidine), and (3) oxygen was bubbled into the solution at room temperature. (b) (1) The solution of the Pd(OAc)$_2$ and poly(*o*-anisidine) in NMP was treated with 1-decene and water at 70 °C for 20 h under argon and (2) oxygen was bubbled at room temperature into the solution thus obtained.

These findings suggest the involvement of a complex catalyst activated by oxygen in the redox cycle. π-Conjugated polymers are believed to behave as a ligand with reversible redox function under oxygen.



redox active ligand = polyanilines, polypyrroles

## CONCLUSION

Complexes of polyanilines and transition metals serve as synthetic metal complex catalysts in the oxidation reactions. A novel redox system for the palladium(II)-catalyzed oxidation is achieved, in which polyanilines or polypyrroles behave as redox-active ligands. In these systems, transition metals are coordinated to π-conjugated polymers and are considered to interact electronically with each other through a π-conjugate chain. Since π-conjugated polymers are known to form a sequential potential field, a similar kind of field is considered to be attained in the complex system. Furthermore, the above-mentioned systems are envisaged to provide combinatorial catalysis.

## ACKNOWLEDGEMENT

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## REFERENCES

(1) A. Kitani, M. Kaya, K. Sakaki, *J. Electrochem. Soc.* **133**, 1069 (1986); A. G. MacDiarmid, L. S. Yang, W. S. Huang, B. D. Humphrey, *Synth. Met.* **18**, 393 (1987); G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, A. J. Heeger, *Nature* **356**, 47 (1992); D. DeBerry, *J. Electrochem. Soc.* **132**, 1022 (1985)

(2) J. G. Masters, Y. Sun, A. G. MacDiarmid, *Synth. Met.* **41**, 715 (1991); R. R. Chance, D. S.Boudreaux, *Synth. Met.* **18**, 329 (1987); D.-K. Moon, T. Maruyama, K. Osakada, T. Yamamoto, *Chem. Lett.* 1633 (1991)

(3) A. Ray, G. E. Asturias, D. L. Kershner, A. F. Richter, A. G. MacDiarmid, *Synth. Met.* **29**, E141 (1989)

(4) T. Hirao, M. Higuchi, I. Ikeda, Y. Ohshiro, *J. Chem. Soc., Chem. Commun.* 194 (1993); T. Hirao, M. Higuchi, Y. Ohshiro, I. Ikeda, *Chem. Lett.* 1889 (1993)

(5) M. Higuchi, I. Ikeda, T. Hirao, *J. Org. Chem.* **62**, 1072 (1997)

(6) G. Venugopal, X. Quan, G. E. Johnson, F. M. Houlihan, E. Chin, O. Nalamasu, *Chem. Mater.* **7**, 271 (1995)

(7) M. Higuchi, D. Imoda, T. Hirao, *Macromolecules* **29**, 8277 (1996)

(8) T. Hirao, T. Murakami, M. Ohno, Y. Ohshiro, *Chem. Lett.* 785 (1989); T. Hirao, T. Murakami, M. Ohno, Y. Ohshiro, 299 (1991); T. Hirao, *Rev. Heteroatom Chem.* **11**, 207 (1994)

(9) T. Hirao, M. Higuchi, B. Hatano, I. Ikeda, *Tetrahedron Lett.* **36**, 5925 (1995)

(10) M. Higuchi, S. Yamaguchi, T. Hirao, *Synlett* 1213 (1996)