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Kinetic Study on Chemical Oxidation of Leucoemeraldine Base Polyaniline to Emeraldine Base

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ABSTRACT: Leucoemeraldine base form polyaniline, $[C_6H_4—NH]_n$ (PLM), dissolved in *N*-methylpyrrolidone undergoes oxidation promoted by O_2 and H_2O_2 in the presence of $FeCl_3$ and $CuCl_2$ catalysts to give emeraldine base form polyaniline, $[C_6H_4—NH—C_6H_4—NH]_n[C_6H_4—N{=}C_6H_4{=}N]_n$ (PEM), as revealed by the UV-vis spectra of the reaction mixtures. The reaction with O_2 follows first-order kinetics which shows the rate constant of 6.8×10^{-5} s^{-1} at 30 °C. Activation energy of the reaction is determined as 50.4 kJ mol^{-1} from temperature dependence of the rate constants. Oxidation of PLM with H_2O_2 in the presence of $FeCl_3$ proceeds smoothly to give PEM, and UV-vis spectroscopy reveals the presence of clear isosbestic points during the oxidation reaction. The initial rates of the reaction are proportional to the concentration of $FeCl_3$ catalysts and increase with H_2O_2 concentration at $[H_2O_2]$ below 40 mM, while they level off at about 40 mM of $[H_2O_2]$. Further oxidation of PEM to give fully oxidized polyaniline does not occur under the reaction conditions. $CuCl_2$ also serves as an effective catalyst for the oxidation of PLM to PEM by H_2O_2, and in this case, the rate of reaction increases with increase in the concentration of H_2O_2 over a wide range of $[H_2O_2]$ (33–490 mM). The reaction of PLM with a limited amount of dibenzoyl peroxide proceeds rapidly to give PEM, while an excess amount of dibenzoyl peroxide causes formation of uncharacterized product by further oxidation of the initially formed PEM.

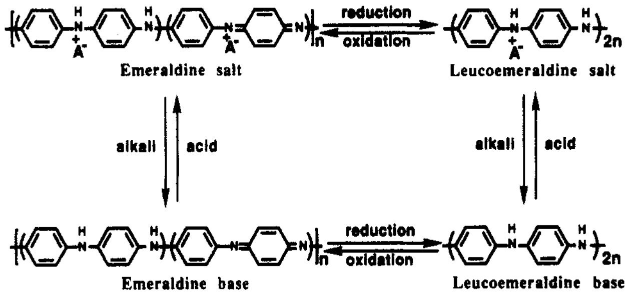
Introduction

Polyaniline has attracted much attention as a promising material for electrodes of batteries,[1,2] electric and optical devices,[3-6] and electrochromic display.[7] Recent studies on polyaniline revealed several molecular structures of the polymer depending on the oxidation state and on the degree of protonation; they include leucoemeraldine base ($[C_6H_4—NH]_n$, abbreviated PLM), emeraldine base ($[C_6H_4—NH—C_6H_4—NH]_n$ $[C_6H_4—N{=}C_6H_4{=}N]_n$, abbreviated PEM), which showed high electrical conductivity on doping with protonic acid, and pernigraniline base ($[C_6H_4—N{=}C_6H_4{=}N]_n$).[8-11]

Physical properties such as electrical conductivity and optical properties are seriously influenced by the structure of the polymer.[1,11,12] The structures of polyaniline (Scheme I) have been established by means of solid-state NMR spectroscopy,[13,14] titration by $TiCl_3$,[8] IR spectroscopy,[31] and XPS measurement.[15,16] A recent advance in the characterization of the polymer backbone structure was achieved also by the observation that polyaniline is moderately soluble in polar organic solvents such as *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and *N*-methylpyrrolidone[17-19] (NMP) since it made it possible to measure NMR and UV-vis spectra and GPC of polyaniline in solutions[20-23] as well as those of aniline oligomers that are regarded as the model compounds of polyaniline.[24-27] The soluble polyaniline is of great advantage also in the preparation of casting films which are suited as materials for practical use.[28]

Chemical reactivity including oxidation and reduction of the soluble polyaniline has attracted less attention than the physical properties. MacDiarmid and co-workers noticed, on the basis of titration of the product, that undoping of the polyaniline in the air was accompanied by O_2-promoted oxidation of PLM.[23a] They also observed a change of the UV-vis spectrum of polyaniline during chemical changes among the various chemical species of polyaniline.[23b,c]

Scheme I



However, there have been few studies on kinetic aspects of such oxidation of the polymer in solution. Elucidation of the reaction mechanism of the oxidation of PLM to PEM is of interest since the reaction is involved in the preparation of polyaniline, where control of the oxidation stage of the polymer is indispensable to obtain desired physical properties of the product. Emeraldine acid form polyaniline, which shows high electrical conductivity, has been prepared by chemical and electrochemical oxidation of aniline under carefully controlled conditions to avoid further oxidation of PEM. Furthermore, PLM is potentially a useful reducing reagent against inorganic and organic compounds.

On these bases we have investigated the oxidation reaction of PLM to give PEM using several oxidizing agents under mild conditions, mainly focusing on its kinetic aspects. A part of this work has been reported in preliminary form.[29]

Experimental Section

General Procedure and Materials. All of the manipulations of polyaniline, including that applied for taking UV-vis spectra, were carried out under nitrogen using the standard Schlenk technique[30] if not otherwise stated. NMP was distilled under reduced pressure twice and stored under a nitrogen atmosphere. Aniline, ammonium peroxydisulfate, H_2O_2 (31% aqueous), hydrazine monohydrate, and dibenzoyl peroxide were purchased and used without further purification. $FeCl_3$ and $CuCl_2$ were dried under vacuum for 24 h before use.

Preparation of PEM and PLM and Characterization. The emeraldine salt form of polyaniline was prepared by chemical

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oxidative polymerization of aniline with ammonium peroxodisulfate in an aqueous solution (HCl-H_2SO_4) using the literature method[18] and was subsequently converted to the emeraldine base form (PEM) by treatment of NH_4OH solution (28%). The fully reduced form of polyaniline, leucoemeraldine base (PLM), was obtained by the reduction of PEM with excess hydrazine monohydrate using a modified method of Green and Woodhead.[8] To avoid oxidation, leucoemeraldine samples were handeled under a nitrogen atmosphere. The IR spectra of PEM and PLM are identical with those previously reported.[31] The UV-vis spectra of PEM and PLM in NMP were also essentially identical to those of previously prepared PEM and PLM.[23c,d,25]

Determination of Molar Absorption Coefficient (ϵ_{630}) of PEM and (ϵ_{345}) of PLM. Absorption spectra of five NMP solutions of PEM and PLM were measured under nitrogen using an optical cell equipped with a nitrogen inlet. Absorbance at 630 nm of PEM (molarity calculated on the basis of the sum of the molecular weight of the quinoid [C_6H_4—N=C_6H_4=N] and two benzenoid units [C_6H_4—NH]$_2$): 0.030 (1.37×10^{-6} M); 0.065 (2.75×10^{-6} M); 0.125 (5.49×10^{-6} M); 0.250 (1.10×10^{-5} M); 0.640 (2.75×10^{-5} M). Absorbance at 345 nm of PLM (molarity calculated on the basis of the molecular weight of the four benzenoid units [C_6H_4—NH]$_4$): 0.30 (6.91×10^{-6} M); 0.45 (1.037×10^{-5} M); 0.650 (1.50×10^{-5} M); 0.860 (2.00×10^{-5} M); 2.100 (4.99×10^{-5} M).

Kinetic Measurements for Oxidation of PLM by O_2. Typical measurement was carried out as follows. To an optical cell equipped with a nitrogen inlet was added an NMP solution of PLM (concentration, ca. 6.5×10^{-3} g L^{-1}; volume, ca. 5 mL; amount of aniline monomer unit, ca. 3.3×10^{-5} g or 3.6×10^{-7} mol) under nitrogen stream. The cell was set in a UV-vis spectrometer equipped with a water jacket for circulating water thermostated at 27 °C around the cell. After 20 min, oxygen (1 atm, about 20 mL or about 0.8×10^{-3} mol) was introduced to the system. Kinetic data were obtained by periodical measurement of absorption spectra or measurement of absorbance at 630 nm. After the reaction in the UV-vis cell was completed, the cell was allowed to stand under the same conditions for an extra 24 h and the completion of the reaction was confirmed by taking the UV-vis spectra after 24 h. Oxidation of PLM by O_2 under irradiation of light was carried out with a Mitsubishi FLR 40 SW/M fluorescent lamp and a Toshiba H-400 high-pressure Hg light source.

Kinetic Measurements for Oxidation of PLM by H_2O_2 in the Presence of $FeCl_3$ or $CuCl_2$ Catalysts. Typical measurement was carried out as follows. Dried $FeCl_3$ was dissolved in NMP (2.15×10^{-4} M) and stored in a Schlenk tube under nitrogen atmosphere. The NMP solution of PLM (ca. 6.5×10^{-3} g L^{-1}) was added under N_2 to a sealed Schlenk-type glass vessel[30] equipped with mixing tube, nitrogen inlet, and optical cell. The NMP solution of $FeCl_3$ (ca. 1×10^{-7} to 1×10^{-6} M) was first added to the solution of PLM in the mixing tube with stirring, and the PLM solution containing $FeCl_3$ was moved to the optical cell. After 15 min, H_2O_2 (31% aqueous) was added to the NMP solution containing PLM and $FeCl_3$ under nitrogen, and the optical cell was set in a UV-vis spectrometer equipped with a water jacket for circulating water thermostated at 27 °C around the cell. After the hydrogen peroxide was introduced to the system, the oxidation reaction occurred immediately. Kinetic data were collected by periodical measurement of absorption spectra or measurement of absorbance at 630 nm. The oxidation of PLM by the $FeCl_2$–H_2O_2 and $CuCl_2$–H_2O_2 systems and dibenzoyl peroxide was carried out analogously. Completion of the reaction in the UV-vis cell was confirmed as described above.

Results and Discussion

Oxidation of PLM with O_2. PLM and PEM show moderate solubility in polar organic solvents such as DMF and NMP as previously reported. The UV-vis spectrum of the colorless NMP solution of PLM shows a peak at 345 nm, while that of the deep purple solution of PEM shows two peaks at 325 and 630 nm, as shown in Figure 1, respectively. These spectroscopic features of the polyaniline agree well with those in DMF in the previous paper.[25] The peak at 630 nm of PEM was assigned to π–π^* transition of the azaquinoid moiety ([C_6H_4—N=C_6H_4=N]$_n$) in the molecule, while the peak at 325 nm was due to the benzenoid moiety ([C_6H_4—NH]$_n$), and the peak 345 nm of PLM was assigned to π–π^* transition of the benzenoid moiety ([C_6H_4—NH]$_n$) in the molecule.

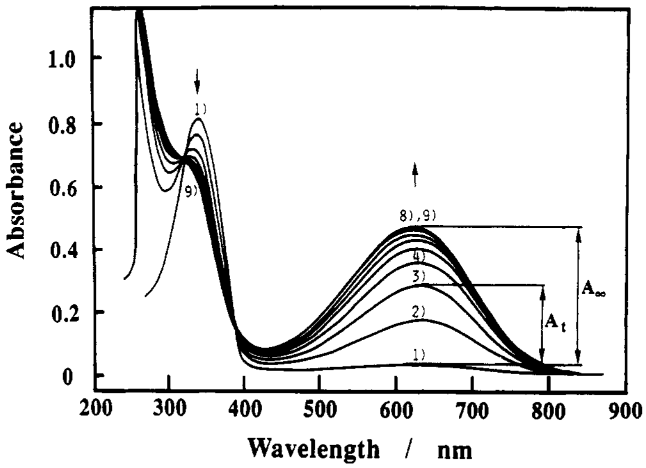


Figure 1. Change of the UV-visible spectrum during the oxidation of PLM with O_2 in NMP at 30 °C. Reaction time: (1) 0 min; (2) 120 min; (3) 180 min; (4) 250 min; (5) 310 min; (6) 370 min; (7) 410 min; (8) 520 min; (9) ∞.

As described under Experimental Section, the molar absorption coefficients of PEM at 630 nm and of PLM at 345 nm are determined to be 2.2×10^4 and 4.3×10^4 M^{-1} cm^{-1} for molarity calculated on the basis of the sum of the molecular weight, respectively {PEM, sum of the azaquinoid ([C_6H_4—N=C_6H_4=N]) and two benzenoid ([C_6H_4—NH]) units (362 = 180 + 182); PLM, sum of four benzenoid ([C_6H_4—NH]) units (364 = 182 + 182)}.

Introduction of oxygen (1 atm, excess; cf. Experimental Section) into a vessel containing NMP solution of PLM causes a gradual change of the UV-vis spectrum. Figure 1 shows the change of the spectra during the reaction of PLM with O_2 observed at 30 °C. As shown in Figure 1, the peak at 630 nm assigned to PEM grows with time. The intensity of the peak at 630 nm after completion of the reaction agrees with that of a solution containing PEM in the same molar concentration. Clear isosbestic points are observed at ca. 325 and 390 nm throughout the reaction. There is no indication of further oxidation of PEM to fully dehydrogenated pernigraniline ([C_6H_4—N=C_6H_4=N]$_n$) that will show absorption peak at 500–540 nm. All of these results suggest that PLM undergoes oxidation by O_2 under the conditions to give PEM exclusively. Figure 2 shows first-order plots of the reaction with O_2 obtained from the time-dependent increase in the absorbance at 630 nm. The oxidation reaction follows the pseudo-first-order kinetics with respect to the concentration of PLM up to high conversion (ca. 95%).

$$d[\mathrm{PLM}]/dt = -k[\mathrm{PLM}] \qquad (1)$$

$$d(A_\infty - A_t)/dt = -k(A_\infty - A_t) \qquad (2)$$

$$-\ln\{(A_\infty - A_t)/A_\infty\} = -kt \qquad (3)$$

where A_∞ is the absorption at 630 nm at infinite time and A_t is the absorption at 630 nm at time t (see Figure 1). The temperature dependence of the rate constant k obeys an Arrhenius-type equation

$$k = k_0 \exp(-E_a/RT) \qquad (4)$$

and the activation energy E_a is determined to be 50.4 kJ

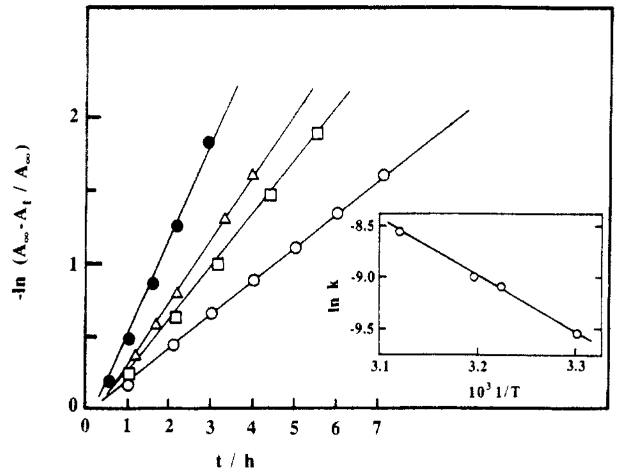


Figure 2. Pseudo-first-order plots of the oxidation reaction of PLM by O_2 at different reaction temperatures. (Inset) Arrhenius plots. (○) 30 °C; (□) 37 °C); (△) 40 °C; (●) 47 °C.

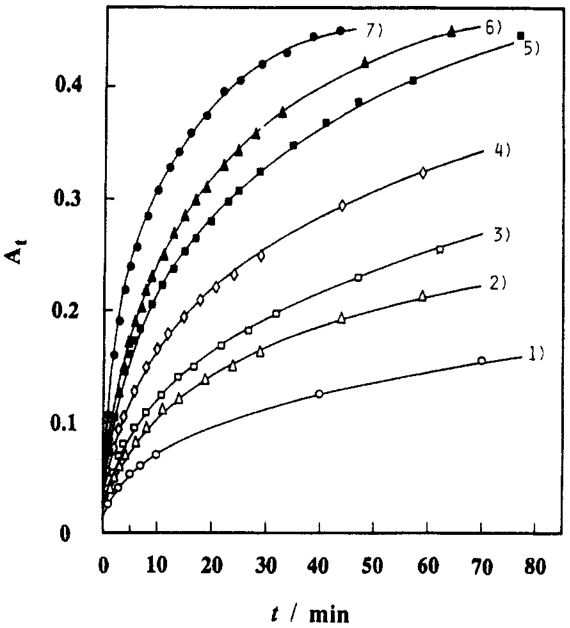


Figure 3. Change of the absorbance A_t at λ_{max} = 630 nm during the oxidation of PLM by the $FeCl_3$–H_2O_2 system with time: dependence on [$FeCl_3$]. [H_2O_2] = 25 mM at 27 °C. [$FeCl_3$] = (1) 1.1 × 10^{-4} mM; (2) 2.15 × 10^{-4} mM; (3) 3.2 × 10^{-4} mM; (4) 4.3 × 10^{-4} mM; (5) 5.4 × 10^{-4} mM; (6) 6.5 × 10^{-4} mM; (7) 1.1 × 10^{-3} mM.

mol^{-1} from the temperature dependence of the rate constants shown in Figure 2.

One of the interesting features of the oxidation of PLM with O_2 is that irradiation of light accelerates the oxidation. For example, the oxidation under irradiation of 450 lux of light from a fluorescent lamp also obeys the first-order kinetics which shows the k value of 1.3 × 10^{-4} s^{-1} at 30 °C. Irradiation of too strong light (e.g., 30 000 lux from a high-pressure Hg light) led to degradation of PEM after the above-mentioned normal oxidation. In the case of this reaction, the UV–vis spectra showed essentially the same change as that shown in Figure 1 in the first stage; however, after the formation of PEM, the peak of PEM at 630 nm decreased gradually and a new absorption appeared at ca. 450 nm. The results indicate that further oxidation of the PEM occurred, although the formed byproduct was not characterized.

Oxidation of PLM with H_2O_2 in the Presence of $FeCl_3$, $FeCl_2$, and $CuCl_2$ Catalysts. PLM polyaniline undergoes facile oxidation with H_2O_2 in the presence of $FeCl_3$ under nitrogen atmosphere in the dark. The reaction proceeds much more rapidly than the oxidation reaction with oxygen. The presence of transition-metal catalyst such as $FeCl_3$, $FeCl_2$, and $CuCl_2$, which have been used as typical catalysts for Fenton-type oxidation,[32-44] is indispensable for the oxidation by H_2O_2 in the dark. The UV–vis spectrum of the reaction mixture shows a change from that of pure PLM to that of pure PEM with clear isosbestic points, similar to those of oxidation with O_2. The change of the UV–vis spectrum with time is analogous to that shown in Figure 1, and the intensity of the peak at 630 nm after completion of the reaction again agrees with that of the solution containing PEM in the same molar concentration. Kinetic aspects of the oxidation in the presence of $FeCl_3$, $FeCl_2$, and $CuCl_2$ are described below.

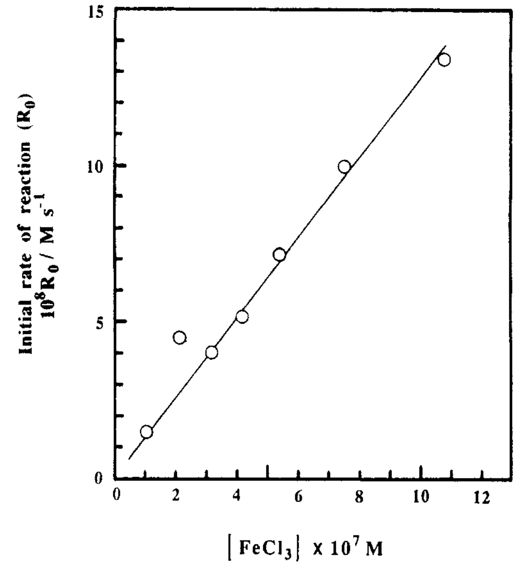


Figure 4. R_0 vs [$FeCl_3$] for the $FeCl_3$–H_2O_2 system at 27 °C. [H_2O_2] = 25 mM.

$FeCl_3$ and $FeCl_2$ Catalysts. The rate of the reaction is followed by the growth of the peak at 630 nm as shown in Figure 3. In this case, the time course of the oxidation somewhat deviates from first-order kinetics, and the change of the UV–vis spectrum with time is analogous to that shown in Figure 1. The intensity of the peak at 630 nm after completion of the reaction again agrees with that of the solution containing PEM in the same molar concentration. Kinetic aspects of the $FeCl_3$-catalyzed oxidation have been analyzed in terms of the initial oxidation rate of PLM. The initial rate of the reaction

$$R_0 = \left(\frac{d[PEM]}{dt}\right)_{t=0} = \left(\frac{1}{\epsilon}\frac{dA_t}{dt}\right)_{t=0} \qquad (5)$$

$$\epsilon = 2.2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$$

is proportional to the concentration of $FeCl_3$ as shown in Figure 4.

$$R_0 = a[FeCl_3] \qquad (6)$$

Figure 5 shows the dependence of the initial rate of the reaction on the concentration of H_2O_2 at [$FeCl_3$] = 0.22 μM. The initial rate increases with increase in [H_2O_2] below 40 mM and levels off above 40 mM.

Since addition of a stoichiometric or excess amount of $FeCl_3$ to the NMP solution of PLM leads to a very rapid (almost instant) oxidation of PLM to PEM as proved by the UV–vis spectroscopy, the following redox reaction seems to be the first step of the catalytic oxidation of

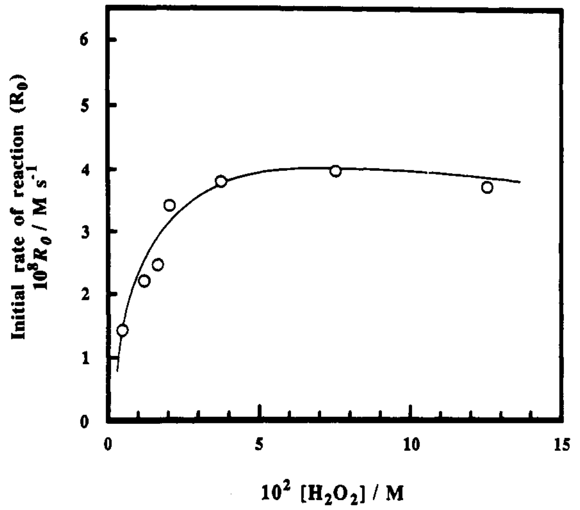


Figure 5. R_0 vs [H_2O_2] for the $FeCl_3$–H_2O_2 system at 27 °C. [$FeCl_3$] = 2.2×10^{-4} mM.

PLM by the H_2O_2–$FeCl_3$ system.

$$\mathrm{PLM} + \mathrm{Fe(III)} \rightarrow \mathrm{PEM} + \mathrm{Fe(II)} \qquad (7)$$

This redox reaction may proceed through initial electron transfer from PLM to the transition-metal species [Fe(III) in this case], as proposed by Seok and Meyer[44] for the oxidation of phenols by Ru(IV) compounds. The Fe(II) species thus formed is expected to regenerate Fe(III) species according to the redox reaction with H_2O_2, which is often proposed to generate radicals such as •OH,[37,40–43] e.g.

$$\mathrm{Fe(II)} + H_2O_2 \rightarrow \mathrm{Fe(III)(OH^-)} + {}^{\bullet}\mathrm{OH} \qquad (8)$$

Aromatic amines and OH compounds have been reported to undergo oxidation by H_2O_2 in the presence of an Fe catalyst (Fenton reagent) through dehydrogenation of the substrate.

The •OH radical thus formed also may cause the oxidation of PLM by abstraction of the H of NH.

$$\mathrm{PLM} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{PEM} + H_2O \qquad (9)$$

One of the interesting features of the present oxidation with the H_2O_2–$FeCl_3$ system is that pretreatment of the $FeCl_3$ by PLM is essential for the high catalytic activity of $FeCl_3$. Addition of the $FeCl_3$ catalyst to the NMP solution of PLM followed by addition of H_2O_2 after 15 min causes the smooth oxidation of PLM to PEM, while addition of a mixture of $FeCl_3$ and H_2O_2 to the NMP solution of PLM does not cause the oxidation at all. This suggests the importance of not only the formation of the Fe(II) species according to eq 7 but also the formation of active species presumably by the coordination of the Fe(II) species to PLM for the high catalytic activity of the Fe species; the coexistence of H_2O_2 with Fe(III) or Fe(II) may prevent the formation of the active Fe species coordinated with PLM. Kuhn and Wassermann reported a similar effect on the order of addition of Fe(III), 2,2′-bipyridyl (bpy), and H_2O_2 on the decomposition of H_2O_2 catalyzed by the Fe(III)–bpy system.[45] Recently, it is also reported that a polyaniline–Fe(III) mixture[46] serves as an effective catalyst for the oxidation of organic compounds with O_2.

As shown in Figure 5, R_0 increases with increase in [H_2O_2] at low [H_2O_2]. However, the rate levels off at higher [H_2O_2] or rather decreases after maximum rate around [H_2O_2] = 5×10^{-2} M. Barb and co-workers reported similar results—that the rate of decomposition of H_2O_2 catalyzed by Fe(III) to generate O_2 also leveled off at the high [H_2O_2] region.[37] At the higher [H_2O_2] region, hydrogen peroxide may compete with PLM for the •OH radical; •OH radicals once formed may be trapped by H_2O_2 or dimerized to regenerate H_2O_2.

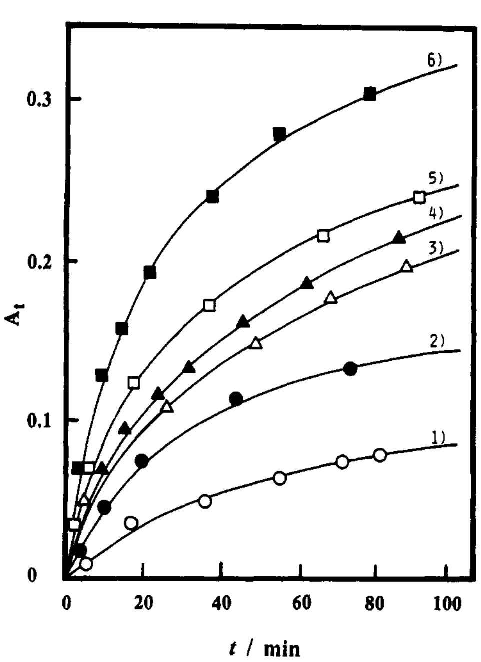


Figure 6. Change of the absorbance A_t at λ_{max} = 630 nm during the oxidation of PLM by the $CuCl_2$–H_2O_2 system with time at 30 °C: dependence on [$CuCl_2$]. [H_2O_2] = 9.8×10^{-2} M. [$CuCl_2$] = (1) 4.0×10^{-5} mM; (2) 1.2×10^{-4} mM; (3) 3.6×10^{-4} mM; (4) 4.4×10^{-4} mM; (5) 4.8×10^{-4} mM; (6) 7.9×10^{-4} mM.

$${}^{\bullet}\mathrm{OH} + H_2O_2 \rightarrow HO_2{}^{\bullet} + H_2O \qquad (10)$$

$FeCl_2$ shows catalytic activity comparable to that of $FeCl_3$. However, in the case of $FeCl_2$, the pretreatment of $FeCl_2$ with PLM is not necessitated for the high catalytic activity, in contrast to the case of $FeCl_3$. The pretreatment of $FeCl_2$ with PLM for 15 min before addition of H_2O_2 (analogous to pretreatment done for $FeCl_3$) gives a catalyst system showing essentially the same catalytic activity (within ±10% difference) as that of the PLM–H_2O_2-pretreated $FeCl_3$ system which is depicted in Figure 3. However, in this case, the catalytic activity of $FeCl_2$ observed on addition of $FeCl_2$ and H_2O_2 to the NMP solution without the pretreatment is somewhat (ca. 30%) higher than that observed on the addition of H_2O_2 to the pretreated Fe(II)–PLM system.

Both the Fe(II) and Fe(III) species are considered to participate in the oxidation of PLM in essentially the same manner through the redox reactions (e.g., eq 8). Since the Fe–H_2O_2 system eventually abstracts H of the NH group of PLM effectively to oxidize PLM, the system is expected to serve as a good reagent to polymerize aniline to polyaniline, which involves similar abstraction of H of the NH_2 group of aniline. Actually, soluble polyaniline can be easily obtained by using the Fe–H_2O_2 system.[47]

$CuCl_2$ Catalyst. The oxidation of PLM with H_2O_2 in the presence of $CuCl_2$ causes a change of the UV–vis spectrum similar to that depicted in Figure 1, with clear isosbestic points. Figures 6 and 7 show time courses of the oxidation of PLM with the H_2O_2–$CuCl_2$ system followed by the UV–vis spectroscopy. As shown in Figures 6 and 7, the initial rate of the oxidation R_0 increases with increase in [$CuCl_2$] and [H_2O_2]. The dependence of R_0 on [H_2O_2] (Figure 7) indicates that R_0 increases with increase in [H_2O_2] over a wide range of [H_2O_2] (3.3×10^{-2} to 4.9×10^{-1} M) in contrast to the case of the oxidation with the H_2O_2–$CuCl_2$ system (Figure 5). Thus, at relatively low

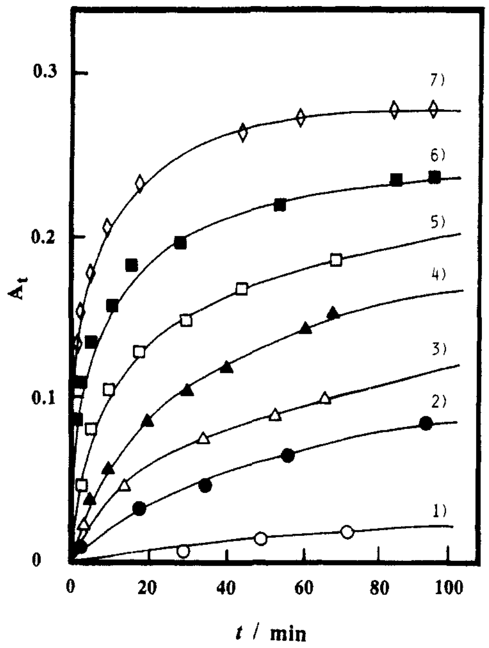


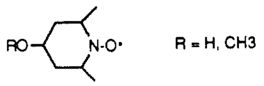
Figure 7. Change of the absorbance A_t at λ_{max} = 630 nm during the oxidation of PLM by the $CuCl_2$–H_2O_2 system with time at 30 °C: dependence on [H_2O_2]. [$CuCl_2$] = 2.0×10^{-4} mM. [H_2O_2] = (1) 3.3×10^{-2} M; (2) 6.6×10^{-2} M; (3) 9.8×10^{-2} M; (4) 1.6×10^{-1} M; (5) 3.3×10^{-1} M; (6) 3.9×10^{-1} M; (7) 4.9×10^{-1} M.

[H_2O_2] (e.g., 1×10^{-3} M) the H_2O_2–$FeCl_3$ system is much more effective for the oxidation of PLM, whereas at relatively high [H_2O_2] the H_2O_2–$CuCl_2$ system shows activity comparable to that of the H_2O_2–$FeCl_3$ system.

Oxidation of PLM with Dibenzoyl Peroxide and Related Radical Sources. Dibenzoyl peroxide is known to generate radicals on heating above 60 °C. Therefore, heating a PLM solution in the presence of dibenzoyl peroxide is expected to cause radical formation which leads to oxidation of PLM by the hydrogen abstraction of the NH group. However, addition of dibenzoyl peroxide (BPO) to an NMP solution even at room temperature instantly caused very rapid growth of the peak at 630 nm in the UV–vis spectrum, revealing a rapid formation of PEM. It is known in radical polymerization of vinyl monomers with BPO that the thermal decomposition of BPO to generate the radical species is accelerated by other radical-generating compounds to lead to a chain reaction (induced decomposition).[48] In the present case, PLM seems to cause such an induced decomposition of BPO. NMP showed no obvious effect on the radical decomposition of BPO at room temperature.

In the case of the oxidation of PLM with BPO, however, use of excess BPO causes another type of oxidation of PLM, giving rise to a new absorption peak at 570 nm. MacDiarmid and co-workers[11b,c] have reported that PEM reacts with excess *m*-chloroperbenzoic acid in the presence of acetic acid in an NMP solution to give the fully oxidized pernigraniline ($[C_6H_4{-}N{=}C_6H_4{=}N]_n$), showing absorption at 520–530 nm, and other oxidized polymers containing an epoxy moiety in the molecule depending on the reaction conditions. Oxidation of aromatic amine to give *N*-oxide products is also reported depending on the reaction conditions. The change of the UV–vis spectrum in the presence of excess BPO seems to indicate further oxidation of the initially formed PEM to give highly oxidized polyaniline.

$NOPF_6$ also causes instant oxidation of PLM to PEM at room temperature. On the other hand, α,α'-azobis(isobutyronitrile) (AIBN) does not cause such a smooth oxidation at room temperature or at 60 °C. In the case of AIBN, such induced decomposition as that observed for BPO is not usually observed in the radical polymerization. Addition of the radical



to the NMP solution of PLM at room temperature did not cause the oxidation of PLM either. The radical seems to be too stable to abstract the hydrogen of the NH group.

Conclusion. Polyaniline in the reduced form PLM undergoes oxidation with H_2O_2 in the presence of Fe(III), Fe(II), and Cu(II) catalysts to give PEM cleanly. In the case of the Fe catalysis, complex formation with PLM seems to be important for the high catalytic activity and the oxidation of PLM is considered to proceed via a redox system intermediated by Fe(II) and Fe(III). The Fe(III) species and radicals (e.g., •OH) produced in the redox system are regarded to abstract hydrogen of the NH group to oxidize PLM to PEM.

PLM is also oxidized easily by molecular oxygen, BPO, and $NOPF_6$, which are also expected to abstract the NH hydrogen of PLM.

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