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Chemical Oxidation of Polyaniline by Radical Generating Reagents, O_2, H_2O_2–$FeCl_3$ Catalyst, and Dibenzoyl Peroxide

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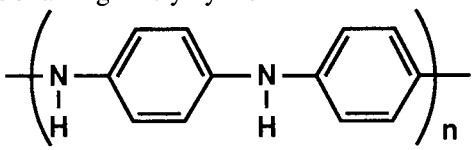
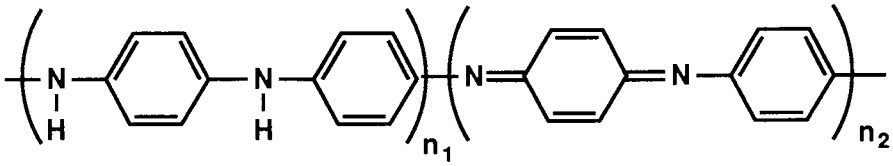
Polyaniline in the reduced form ($-\{-NH-C_6H_4-NH-C_6H_4-\}_n$, leucoemeraldine base form) undergoes oxidation by radical generating reagents such as O_2, H_2O_2–$FeCl_3$ catalyst system, and dibenzoyl peroxide to give the 50% oxidized polymer ($-\{-NH-C_6H_4-NH-C_6H_4-\}_m-\{-N=C_6H_4=N-C_6H_4-\}_n$, emeraldine base form). The oxidation by the H_2O_2–$FeCl_3$ system shows kinetic behaviors characteristic of Fenton–type oxidation.

Despite the wide application of polyaniline as an electrically conducting material,[1] detailed structures and chemical properties of the polymer are still under discussion. As for structures of the fully reduced form (leucoemeraldine base form, abbreviated as PLM) and the 50% oxidized form (emeraldine base form, abbreviated as PEM), they have been determined unambiguously by means of various instrumental analyses.[2-5]



PLM



PEM

Electrochemical oxidation and reduction of the polymers were investigated in detail,[6] however, chemical oxidation and reduction behaviors of polyaniline in solutions have attracted much less attention in spite of the importance of revealing them for use of the polymer. Here we report results of the spectroscopic studies on the oxidation of the PLM polyaniline by O_2, H_2O_2 in the presence of $FeCl_3$ catalyst, and dibenzoyl peroxide. PLM polyaniline prepared from oxidative polymerization of aniline with $(NH_4)_2S_2O_8$ followed by undoping with aqueous ammonia and hydrazine[7] is soluble in (1-methyl)pyrrolidin-2-one (NMP). Contact of the solution with air causes color change due to oxidation of the polymer although the polymer solution is stable under nitrogen and argon. Figure 1 shows change of the UV-visible spectrum on the oxidation of PLM by air. Figure 1 shows

growth of a new peak of PEM at 630 nm[4,8] at the expense of the peak of PLM at 345 nm, and the presence of isosbestic points throughout the reaction is observed in Fig. 1. The reaction followed by the peak intensity at 630 nm at 30 °C under dark (Fig. 1) obeys first order kinetics,

$$\text{PLM} \xrightarrow[\text{with and without } h\nu]{\text{Air (1 atm)}} \text{PEM} \qquad (1)$$

λ_{max} = 630 nm

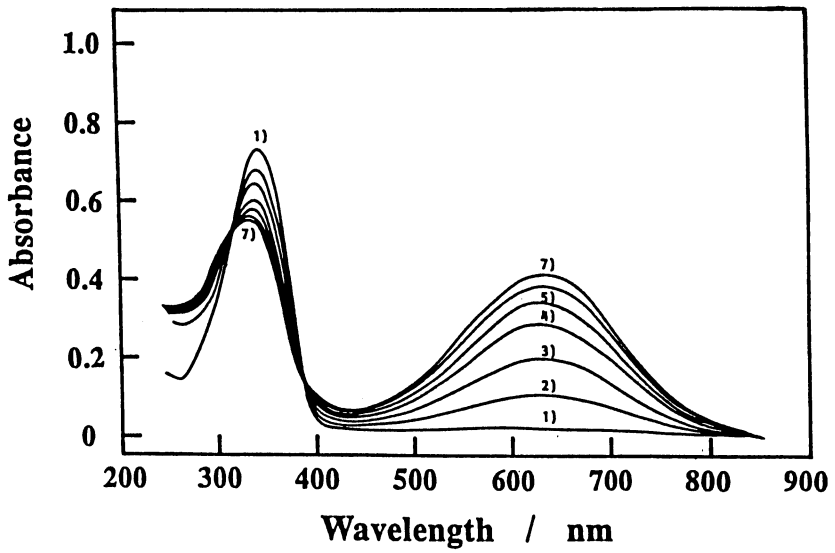


Fig. 1. Change of the UV-visible spectrum during the oxidation of PLM with air in NMP at 30 °C.
Reaction time : 1) 0 min; 2) 240 min; 3) 480 min; 4) 720 min; 5) 960 min; 6) 1290 min; 7) 1590 min.

$$\frac{d\,[PLM]}{dt} = -k\,[PLM] \qquad (2)$$

$$\frac{d\,(A_\infty - A_t)}{dt} = -k\,(A_\infty - A_t) \qquad (3)$$

A_∞ = absorbance at 630 nm at infinite time
A_t = absorbance at 630 nm at time t

which shows the rate constant k of 2.3 x 10^{-5} s^{-1} at 30 °C under air. There was no indication of further oxidation of PEM to fully dehydrogenated polyaniline $\text{-(-N=C}_6\text{H}_4\text{=N-C}_6\text{H}_4\text{-)-}_n$ that shows absorption peak at shorter wavelength of 500 – 540 nm.[2c,4b] All these results indicate clean oxidation of PLM to PEM by O_2. Although the role of oxygen as the oxidizing reagent in the doping of polyaniline has been already suggested,[9] this seems to be the first example showing that PLM is oxidized to PEM with oxygen. 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 light from fluorescent lamp also obeys the first order kinetics with the k value of 1.3 x 10^{-4} s^{-1}at 30 °C. Irradiation of too strong light (e.g., 30000 lux from high pressure Hg light) led to degradation of PEM after the above mentioned normal oxidation. The UV-visible spectra showed essentially the same change as that shown in Fig. 1 in the first stage, however, after the formation of PEM the peak of PEM at 630 nm gradually decreased and a new broad absorption at about 450 nm appeared.

The PLM polyaniline undergoes oxidation also with H_2O_2 in the presence of catalytic amount of $FeCl_3$ under nitrogen atmosphere in the dark.[10] The reaction proceeds much more rapidly than the above reaction with oxygen. The presence of $FeCl_3$ catalyst is indispensable to the oxidation in the dark, while the reaction with H_2O_2 under irradiation of the light proceeds slowly even in the absence of Fe catalyst probably due to photo-assisted decomposition of H_2O_2 to give radical species.

$$\text{PLM} \xrightarrow{FeCl_3\ ,\ H_2O_2} \text{PEM} \qquad (4)$$

The oxidation was followed by the growth of the peak of PEM at 630 nm as shown in Fig. 2. In this case, however, the time course of the oxidation somewhat deviates from the first order kinetics , and kinetic aspects of the $FeCl_3$- catalyzed oxidation have been analyzed in term of the initial oxidation rate of PLM. The initial rate of the reaction,

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

(R_0 = initial reaction rate, ε = molar absorption coefficient [8])

is proportional to the concentration of $FeCl_3$.

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

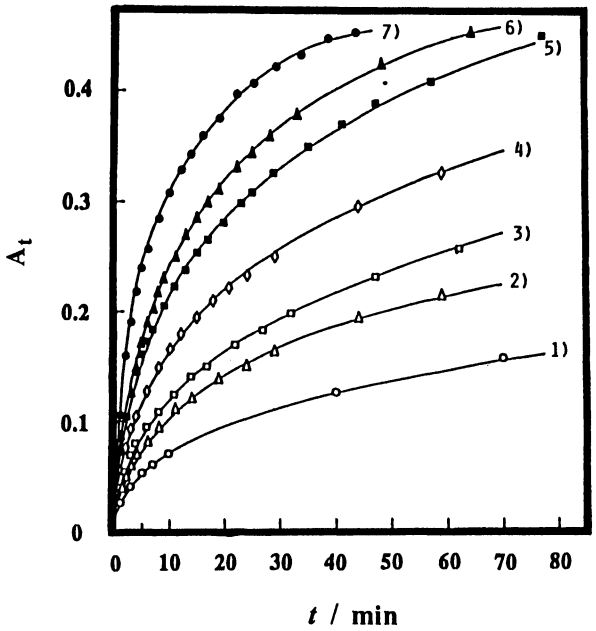


Fig. 2. Change of the absorbance A_t at λ_{max} = 630 nm during the oxidation of PLM by the $FeCl_3$-H_2O_2 system with time. At 27 °C. $[H_2O_2]$ = 25 mM, $[FeCl_3]$ = 1) 1.1 x 10^{-4} mM; 2) 2.2 x 10^{-4} mM; 3) 3.2 x 10^{-4} mM; 4) 4.3 x 10^{-4} mM; 5) 5.4 x 10^{-4} mM; 6) 6.5 x 10^{-4} mM; 7) 1.1 x 10^{-3} mM. (1 M = 1 mol dm^{-3})

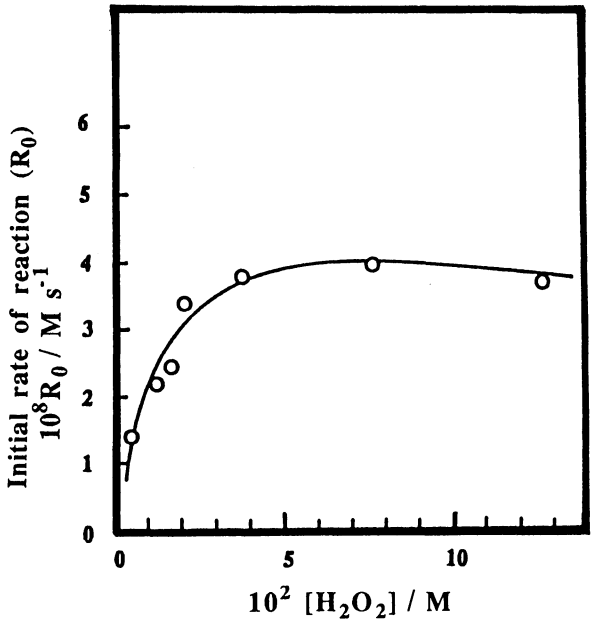


Fig. 3. R_0 vs. $[H_2O_2]$ for the $FeCl_3$-H_2O_2 system. $[FeCl_3]$ = 2.15 x 10^{-4} mM. (1 M = 1 mol dm^{-3})

Since oxidation with H_2O_2 in the presence of Fe catalyst (Fenton reagent) is generally accepted to proceed through Fe catalyzed decomposition of H_2O_2 to give •OH radical or other radical which abstracts H from the substrate,[11] the present reaction is also considered to involve abstraction of the NH hydrogen of PLM to give

PEM. Figure 3 shows dependence of R_0 on the concentration of H_2O_2. As shown in Fig. 3, 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 $[H_2O_2] = 5 \times 10^{-2}$ mol dm^{-3}. At the higher $[H_2O_2]$ region the ·OH radical once formed may be trapped by H_2O_2 or dimerized to regenerate H_2O_2 to afford the kinetic behavior shown in Fig. 3. Barb and his coworkers reported that the rate of generation of O_2 from H_2O_2 catalyzed by Fe^{+3} species also leveled off at the high $[H_2O_2]$ region.[12)]

Oxidation of PLM polyaniline also takes place with dibenzoyl peroxide at room temperature accompanied by spectral change similar to that shown in Fig. 1. The reaction is very rapid, and completed in ca. 30 min even when a stoichiometric amount of dibenzoyl peroxide is used. Use of an excess amount of dibenzoyl peroxide causes appearance of the absorption peak at ca. 570 nm which is assigned to completely dehydrogenated polymer $\text{-}(\text{-N=C}_6\text{H}_4\text{=N-C}_6\text{H}_4\text{-})_n$.

All the above results indicate that the oxidation of PLM by the reagents involves abstraction of NH hydrogen of PLM by radical as a crucial step. Furthermore, as described above, PEM serves as good substrate for studying oxidation by O_2 and the H_2O_2-catalyst system.

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8) Molar absorption coefficient of PEM= 2.2 x 10^4 M^{-1} cm^{-1} (1 M = 1 mol dm^{-3}) at 630 nm for molarity calculated based on the sum of the molecular weight of the $-C_6H_4-N=C_6H_4=N-$ and $-C_6H_4-NH-C_6H_4-NH-$ units (362 = 180+182) (PEM is regarded as a 1:1 mixture of the two units [2-5)]).
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10) Addition of $FeCl_3$ catalyst to the NMP solution of PLM polyaniline followed by addition of H_2O_2 after 15 min causes the smooth oxidation of PLM, while addition of a mixture of $FeCl_3$ and H_2O_2 to the solution of NMP did not cause the oxidation at all. This suggests reaction of PLM with $FeCl_3$ to give active species of the catalysis. Kuhn and Wasserman reported similar effect of the order of addition of Fe^{+3}, 2,2-bipyridyl (bpy), and H_2O_2 on the decomposition of H_2O_2 catalyzed by a Fe^{+3}-bpy system (R.Kuhn, A.Wassermann, *Ann. Chem.*, **503**, 203 (1933)).
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