Makromol. Chem. **194**, *3149–3155 (1993)*

Chemical reduction of the emeraldine base of polyaniline by reducing agents and its kinetic study

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(Received: December 28, 1992; revised manuscript of February 12, 1993)

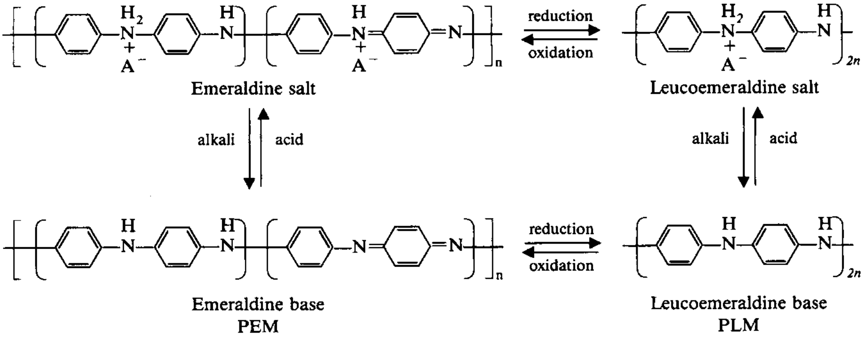
SUMMARY:

The reduction of the emeraldine base form of polyaniline (PEM) by *N,N*-diethylhydroxylamine, sodium tetrahydroborate, sodium dithionite, and hydrazine monohydrate proceeds smoothly at room temperature to give the leucoemeraldine base form of polyaniline (PLM). The reduction of PEM to PLM with these reducing agents obeys a pseudo-first-order kinetics with respect to the concentration of PEM. The pseudo-first-order rate constants, k, of the reduction with hydrazine monohydrate ($5{,}0 \cdot 10^{-1}$ mol · L^{-1}), *N,N*-diethylhydroxylamine ($6{,}2 \cdot 10^{-2}$ mol · L^{-1}), and $NaBH_4$ ($1{,}13 \cdot 10^{-3}$ mol · L^{-1}) are $1{,}46 \cdot 10^{-4}$ s^{-1}, $2{,}50 \cdot 10^{-4}$ s^{-1}, and $1{,}7 \cdot 10^{-3}$ s^{-1} at 20 °C, respectively. In the case of sodium dithionite, which has a higher reducing ability, the reduction proceeds very rapidly at room temperature. Plot of $\ln(k/[\text{reductant}])$ against the electrochemically measured half-wave potential $E_{1/2}$ affords a linear correlation with a slope of 20 V^{-1}.

Introduction

Polyaniline has attracted much attention as a promising material for electrodes of batteries[1,2], electric and optical devices[3], and electrochromic displays[4]. Although a large number of studies have been made on the application of polyaniline to devices, only little attention has been paid to the chemical reactivity of polyaniline in the oxidized and reduced state. Polyaniline has been found to have a variety of structures, depending on the oxidation and reduction state, or the doping and undoping state, as shown in *Scheme 1*[5–8].

Scheme 1:



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Polyaniline prepared by oxidative polymerization of aniline using ammonium peroxodisulfate consists of the emeraldine base form $\{(C_6H_4{-}NH{-}C_6H_4{-}NH)(C_6H_4{-}N{=}C_6H_4{=}N)\}_{\bar{n}}$ (PEM), and complete reduction of PEM converts the structure to the leucoemeraldine base form $(C_6H_4{-}NH)_{4n}$ (PLM). Reduction of PEM with phenylhydrazine also produces PLM, as reported by Green and Woodhead$^{5)}$. On the other hand, we have reported that PLM is oxidized with several oxidizing agents, such as O_2 and H_2O_2 in the presence of $FeCl_3$, to give PEM, and UV-VIS spectroscopy is useful for the kinetic study of the oxidation of PLM to PEM$^{9)}$.

In order to reveal the redox behavior of polyaniline in more detail, we have now examined reduction of PEM with various reducing reagents. The present research is mainly focused on the kinetics of the reduction, and hydrazine, *N,N*-diethylhydroxylamine$^{10)}$, sodium tetrahydroborate$^{11)}$ and sodium dithionite$^{12)}$, known as good reducing agents for quinones, are used as reducing agents.

Experimental part

Materials

Commercially available hydrazine monohydrate ($NH_2NH_2 \cdot H_2O$), *N,N*-diethylhydroxylamine (DEH), sodium tetrahydroborate ($NaBH_4$) and sodium dithionite ($Na_2S_2O_4$) were used without further purification. The emeraldine base form of polyaniline was prepared by chemical oxidative polymerization of aniline according to the method$^{13)}$ described previously. *N*-Methyl-2-pyrrolidone (NMP) was distilled under reduced pressure twice and stored under nitrogen atmosphere. Water was distilled and stored under nitrogen.

Leucoemeraldine base form of polyaniline (PLM)

The reductions of PEM using the following reducing agents and purification methods were carried out under nitrogen to avoid oxidation of PLM:

(a) With $NH_2NH_2 \cdot H_2O$: PLM was obtained by the reduction of PEM with excess hydrazine monohydrate by modifying a reported method$^{5,9)}$.

(b) With DEH: A mixture of excess DEH (5 mL) and blue-black powder of PEM (75 mg; 0,21 mmol of monomeric units) was stirred for 24 h at room temperature under nitrogen. The suspension gradually turned light purplish blue from initial deep blue-black. The light purplish blue powder was collected by filtration and dried under reduced pressure to give light purple PLM.

(c) With $NaBH_4$: $NaBH_4$ ($1{,}1 \cdot 10^{-1}$ mol) was added to a suspension of PEM (75 mg; 0,21 mmol) in distilled water at room temperature. The suspension of the deep blue-black PEM was stirred for 48 h under nitrogen. After the suspension turned light purplish blue, the reaction mixture was poured into distilled water purged with nitrogen. The light purple powder collected by filtration was washed three times with distilled water and dried under vacuum.

(d) With $Na_2S_2O_4$: The reduction of PEM with $Na_2S_2O_4$ was carried out in way analogous to that described in procedure (c).

Kinetic measurements of reduction of PEM

Kinetic measurements were carried out spectroscopically by a method$^{9)}$ similar to that described previously, although, in the present study, the measurement of the UV-VIS spectra was carried out under nitrogen. Typical measurement was carried out as follows. The concentration of PEM in NMP was determined by using molar absorption coefficients$^{9)}$ ($2{,}2 \cdot 10^4$ $L \cdot mol^{-1} \cdot cm^{-1}$, molarity based on the sum of the molecular weight of the quinoid

(C_6H_4—N=C_6H_4=N) and that of two benzenoid units ($(C_6H_4$—$NH)_2$, MW = 362,42) of PEM at 630 nm. An NMP solution of PEM (ca. $1,8 \cdot 10^{-5}$ mol · L^{-1}) was added into an optical cell under nitrogen, and the cell was kept in water thermostated at 40 °C. After 5 min, a solution of hydrazine monohydrate (ca. $5,0 \cdot 10^{-1}$ mol · L^{-1}) was added to the stirred NMP solution containing PEM under nitrogen, and the optical cell was set in the UV-VIS spectrometer equipped with a water jacket around the cell kept at 40 °C. Kinetic data were obtained by observing the decrease of the absorbance at 630 nm. The reduction of PEM by DEH, $NaBH_4$ and $Na_2S_2O_4$ was carried out analogously.

Although $NaBH_4$ in water rapidly decomposes with evolution of dihydrogen, $NaBH_4$ in aqueous NaOH solution had good stability[14], and the kinetics of the reduction of PEM with $NaBH_4$ was carried out by adding the alkaline solution (ca. $1,0 \cdot 10^{-3}$ mL) of $NaBH_4$ to the NMP solution (ca. 4 mL) of PEM.

In the case of $Na_2S_2O_4$, its aqueous solution was added to the NMP solution of PEM.

Results and discussion

Reduction of deep blue-black PEM with reducing agents such as DEH, $NaBH_4$, and $Na_2S_2O_4$ in water gives light purple PLM. IR spectra of PLM's prepared by using these reducing agents are essentially identical with that of PLM[9] prepared by using NH_2NH_2 as the reducing agent. These PLM's exhibit a very weak peak at 1 590 cm^{-1} and no aborption at 1 160 cm^{-1} which are assigned to the quinoid structure of PEM. UV-VIS spectra of NMP solutions of the obtained PLM's show only one sharp peak at 345 nm which is characteristic of PLM. The absorption spectrum of the NMP solution of PLM is unchanged for a month when stored under nitrogen or argon, and the solution remains colorless. These IR and UV-VIS data indicate that PEM is easily reduced with these reducing agents at room temperature to give PLM, similarly to the case of the reduction with hydrazine.

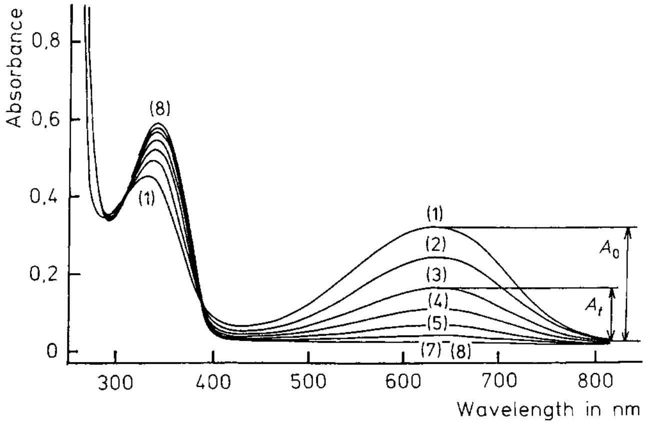


Fig. 1. Change of the UV-VIS spectra during the reduction of PEM with NH_2NH_2 in NMP at 40 °C. Reaction time: (1) 0 min; (2) 10 min; (3) 25 min; (4) 40 min; (5) 53 min; (6) 80 min; (7) 110 min; (8) ∞. $[NH_2NH_2] = 5,0 \cdot 10^{-1}$ mol · L^{-1}

Kinetics of the reduction

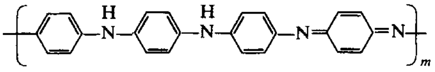
Fig. 1 shows the change of the UV-VIS spectra during the reduction of PEM with NH_2NH_2 in NMP at 40 °C. The absorption peak at 630 nm gradually decreases with time and finally disappears, due to the complete reduction of PEM to PLM. As shown in Fig. 1, the UV-VIS spectrum changes with clear isosbestic points at about 305 and 385 nm, and the reduction follows the following pseudo-first-order kinetics in the presence of an excess amount of reducing reagent.

$$\mathrm{d[PEM]}/\mathrm{d}t = -k\mathrm{[PEM]} \tag{1}$$

$$\begin{aligned} \mathrm{d}A_t/\mathrm{d}t &= -k\,A_t \\ \ln A_t &= -k\,t + \ln A_0 \end{aligned} \tag{2}$$

(A_t = absorption at 630 nm at time t, A_0 = absorption at 630 nm at t = 0 (see Fig. 1))

The abosorption band at 630 nm is considered to be originated from the following block with sufficient chain length *m*:



The observation of the clear isosbestic points indicates that the reduction of the =N— imine nitrogen to —NH— does not proceed at random positions of the imine nitrogens of PEM, but preferentially at all of the imine nitrogens in the above depicted block with chain length *m*. Therefore, the product formed during the reduction is considered to be a mixture of wholly reduced PLM and intact PEM or a block copolymer with the above described block and a reduced $\left(C_6H_4—NH\right)_l$ block.

Plots of $\ln A_t$ against time at various temperatures are shown in Fig. 2. The pseudo-first-order rate constant k can be calculated from the slope of the linear lines in Fig. 2, and the pseudo-first-order rate constants k at 10 °C, 20 °C, 30 °C, and 40 °C are $1{,}11 \cdot 10^{-4}\ \mathrm{s}^{-1}$, $1{,}46 \cdot 10^{-4}\ \mathrm{s}^{-1}$, $2{,}50 \cdot 10^{-4}\ \mathrm{s}^{-1}$, and $5{,}83 \cdot 10^{-4}\ \mathrm{s}^{-1}$, respectively, at

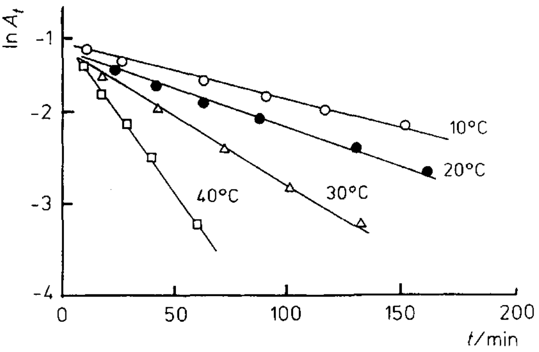


Fig. 2. Pseudo-first-order plots for the reduction of PEM with NH_2NH_2 at various temperatures. $[NH_2NH_2] = 5{,}0 \cdot 10^{-1}$ mol · L^{-1}

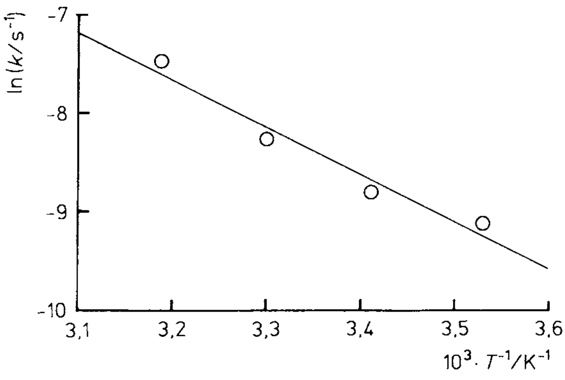


Fig. 3. Arrhenius plot for the reduction of PEM with NH_2NH_2. $[NH_2NH_2] = 5,0 \cdot 10^{-1}$ mol · L^{-1}

$5,0 \cdot 10^{-1}$ mol · L^{-1} of hydrazine. The Arrhenius activation energy E_a for reduction of PEM with hydrazine is determined to be 38 kJ · mol^{-1} from the temperature dependence of the k value shown in Fig. 3.

The reduction with DEH also obeys the pesudo-first-order kinetics with respect to the concentration of PEM, as proved by a similar plot of $\ln A_t$ vs. time. The UV-VIS spectrum of the PEM-DEH system also changes with time, with isosbestic points at about 305 and 385 nm. When the concentration of DEH is $2,1 \cdot 10^{-2}$ mol · L^{-1}, the pseudo-first-order rate constants k at 10 °C, 20 °C, 30 °C, and 40 °C are determined to be $1,52 \cdot 10^{-4}$ s^{-1}, $2,50 \cdot 10^{-4}$ s^{-1}, $5,00 \cdot 10^{-4}$ s^{-1}, and $1,04 \cdot 10^{-3}$ s^{-1}, respectively, and the Arrhenius activation energy E_a is 47 kJ · mol^{-1}.

The UV-VIS spectrum of the reduction system of PEM with $NaBH_4$ varies with time similarly to that shown in Fig. 1, and the reduction of PEM with $NaBH_4$ also follows the pseudo-first-order kinetics. The rate constant at $1,13 \cdot 10^{-3}$ mol · L^{-1} of $NaBH_4$ is determined as $1,7 \cdot 10^{-3}$ s^{-1} at 20 °C; however, the reduction with $NaBH_4$ proceeds too rapidly (within a few minutes) at temperatures higher than 30 °C to be followed by the change of UV-VIS spectrum.

In the case of reduction of PEM with $Na_2S_2O_4$, even the addition of only a small amount ($9,2 \cdot 10^{-5}$ mol · L^{-1}, or 5 mol per mol of monomeric unit of PEM) of $Na_2S_2O_4$ to the NMP solution of PEM at room temperature causes very rapid disappearance (within 5 min) of the peak at 630 nm, indicating that $Na_2S_2O_4$ has very strong reducing ability toward PEM. In this case, determination of the k value was not possible. However, the half time of PEM in the reduction was roughly estimated to be 10–20 s at 20 °C by the visual method, and this half time corresponds to a k value of the order of 10^{-1} s^{-1}.

Reducing ability of the reductant and linear free energy relation

As described above, DEH, $NaBH_4$ and $Na_2S_2O_4$, and NH_2NH_2 easily reduce PEM both in heterogeneous and homogeneous systems. The reduction of PEM with N_2H_4, DEH, and $NaBH_4$ obeys the pseudo-first-order kinetics, and the reducing ability of

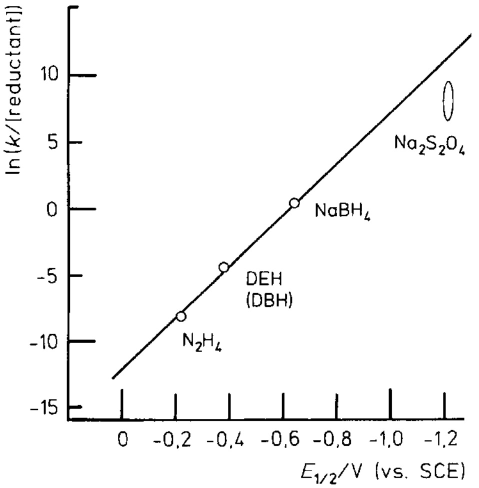


Fig. 4. Plot of the pseudo-first-order rate constant k at 20 °C against the half-wave potential $E_{1/2}$

the reductant increases in the order of NH_2NH_2 < DEH < $NaBH_4$ < $Na_2S_2O_4$.

The reactivity of the reducing agents may be correlated to their half-wave potentials ($E_{1/2}$) obtained by polarographic measurements. The $E_{1/2}$ values (vs. SCE) of NH_2NH_2, *N,N*-dibenzylhydroxylamine, $NaBH_4$, and $Na_2S_2O_4$ are $-0{,}22$ V[15], $-0{,}38$ V[16], $-0{,}64$ V[17], and $-1{,}21$ V[18], respectively. Here the $E_{1/2}$ value of *N,N*-dibenzylhydroxylamine is used as an alternative to that of DEH, and negatively larger $E_{1/2}$ value indicates stronger reducing ability of the reagent.

Plot of ln(*k*/[reductant]) against the $E_{1/2}$ value affords a linear correlation between the two parameters, with a slope of 20 V^{-1}, as shown in Fig. 4.

$$d\ln(k/[\text{reductant}])/d\,E_{1/2} = 20\ V^{-1} \tag{3}$$

According to the Marcus theory[19], the rate constant k' of a reaction involving electron transfer may be correlated with the potential difference ΔE_0 between the oxidant and reductant, by the following equation

$$d\ln k'/d\,(\Delta E_0) = -nF/(2RT) \tag{4}$$

where n, F, R, T stand for the number of electrons transferred in the redox reaction, Faraday constant, gas constant, and temperature, respectively. The meaning of n for such a polymer reaction is not clear; however, comparison of Eq. (3) with Eq. (4) affords an n value of about 1. Although redox reactions of polyaniline have been widely studied, a linear free energy relation (LFER) such as that expressed by Eq. (3) has no precedent. Thus, from the present research, the ease of reduction of PEM to PLM is also revealed to be controlled by the reducing ability of the reductant and essentially follows LFER.

A more detailed study (e. g., with various polyaniline derivatives having substitutents at the phenylene rings[20], with various solvents, etc.) of the reducing reaction, in combination with a close investigation of the oxidation reaction⁹⁾, will render the basis for revealing essential and precise processes in the redox reaction.

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