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^1H NMR spectra of polyanilines and dynamic exchange of NH hydrogen with H_2O

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Introduction

Polyaniline has attracted much attention as a promising material for electrodes of batteries$^{1)}$, electric and optical devices$^{2)}$, and electrochromic displays$^{3)}$. 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 $\left(C_6H_4-NH\right)_n$ (abbreviated as PLM), emeraldine base $(-C_6H_4-NH-C_6H_4-NH-/-C_6H_4-N=C_6H_4=N-)_n$ (abbreviated as PEM), and their salts with acids$^{4)}$.

In spite of the extensive studies on the chemical and physical properties of polyanilines, clear assignment of ^1H NMR signals of the polyanilines has not been made presumably due to the low solubility of the polymers in usual ^1H NMR solvents and overlapping of the signals of NH and aromatic protons. Recently preparation of highly soluble polyaniline has been reported$^{5)}$ and it has become possible to assign the signal of the NH hydrogen of PLM by using the highly soluble polyaniline and by using an H-D exchange technique between PLM and D_2O. We now report upon (a) the assignment of the signal of the NH proton in PLM by this method and (b) the rapid exchange of the NH proton with H_2O on the NMR time scale.

Experimental part

Materials

Aniline, iron(II) sulfate and iron(III) chloride were purchased from Koso Chemical Co. Ltd., diphenylamine and H_2O_2 (31% aq.) were purchased from Tokyo Kasei Kogyo Co. Ltd. and Mitsubishi Gas Chemical Co. Inc., respectively. All reagents were reagent grade and used without further purification. Dimethyl sulfoxide (DMSO)-d_6 (99,8% D) was purchased from Euriso-top Group and dried with calcium hydride, and D_2O (99,8%) was purchased from Cea-Oris.

Polymerization experiments

Emeraldine base was synthesized according to the previously reported method$^{5)}$. Leucoemeraldine base was prepared by modifying the method of Green and Woodhead$^{5)}$.

Measurements

The ^1H NMR spectra were recorded on a Jeol JNM-FX 100 NMR spectrometer using DMSO-d_6 as solvent at various temperatures.

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Results and discussion

Fig. 1 shows the temperature-dependent ^{1}H NMR spectrum of PLM in dimethyl sulfoxide-d_6 (DMSO-d_6) which contains a small amount of water. Chen and Jenekhe[6)] took ^{1}H NMR spectra of analogues of PLM in DMSO-d_6 and assigned signals in the range $\delta = 4,88-5,66$ to the NH protons of the polymers. Actually, the signal of the NH proton of diphenylamine (DPA) $C_6H_5NHC_6H_5$, a low-molecular-weight model compound of PLM, appears at $\delta = 5,42$ in $CDCl_3$ as reported in the literature[7)].

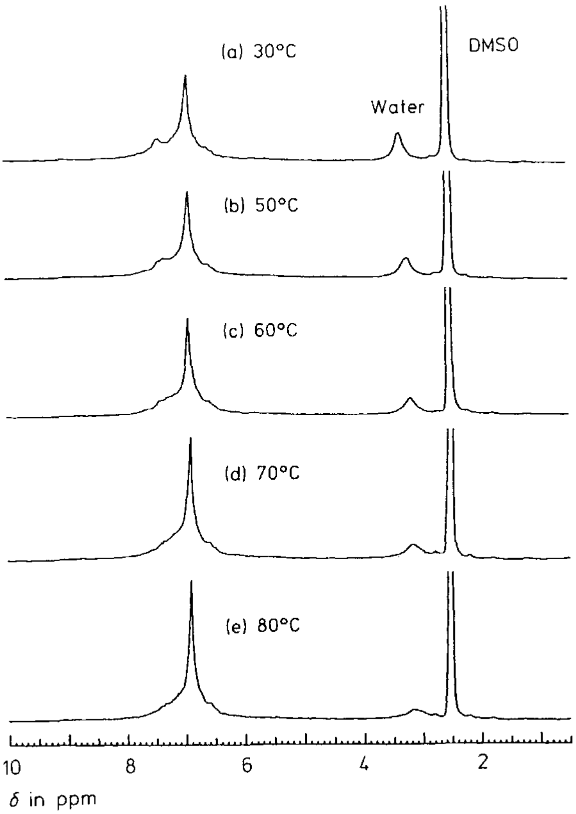

Fig. 1. Temperature-dependent 100 MHz ^{1}H NMR spectrum of PLM in DMSO-d_6

However, DPA gives rise to a ^{1}H NMR signal at much different position in DMSO-d_6. As shown in Fig. 2, the ^{1}H NMR spectrum of DPA exhibits a peak at about δ = 8,0 in DMSO-d_6, and this peak is assigned to the NH proton since this peak disappears almost completely on addition of D_2O to the DPA/DMSO-d_6 solution (Fig. 3(a)).

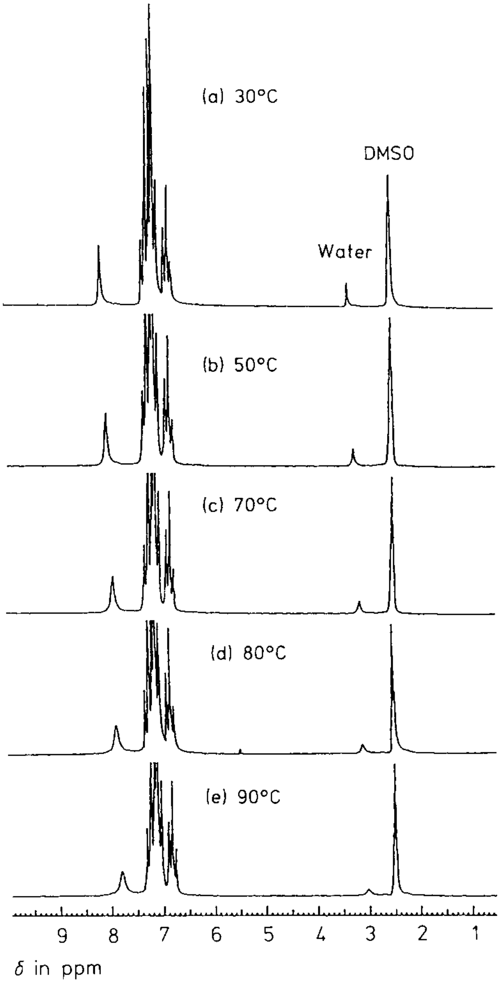

Fig. 2. Temperature-dependent 100 MHz ^{1}H NMR spectrum of diphenylamine in DMSO-d_6

Comparison of the ^{1}H NMR spectrum of DPA (Fig. 2(a)) with that of PLM (Fig. 1(a)) suggests that a somewhat broad signal at about $\delta = 7{,}4$ in Fig. 1(a) is assigned to the NH proton of PLM whereas a band at higher magnetic field (about $\delta = 6{,}8$ in Fig. 1(a)) is assigned to the *p*-phenylene protons of PLM. The peak at about $\delta = 7{,}4$ in Fig. 1(a) is actually extinguished by the exchange with D of D_2O (Fig. 3(b)). These data clearly indicate that the signal at about $\delta = 7{,}4$ in Fig. 1(a) is assignable to the NH proton[a].

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[a] The 500 MHz ^{1}H NMR spectrum of PLM indicates that the peak at about $\delta = 7{,}4$ assigned to the NH proton is overlapped with a broad unidentified absorption band.

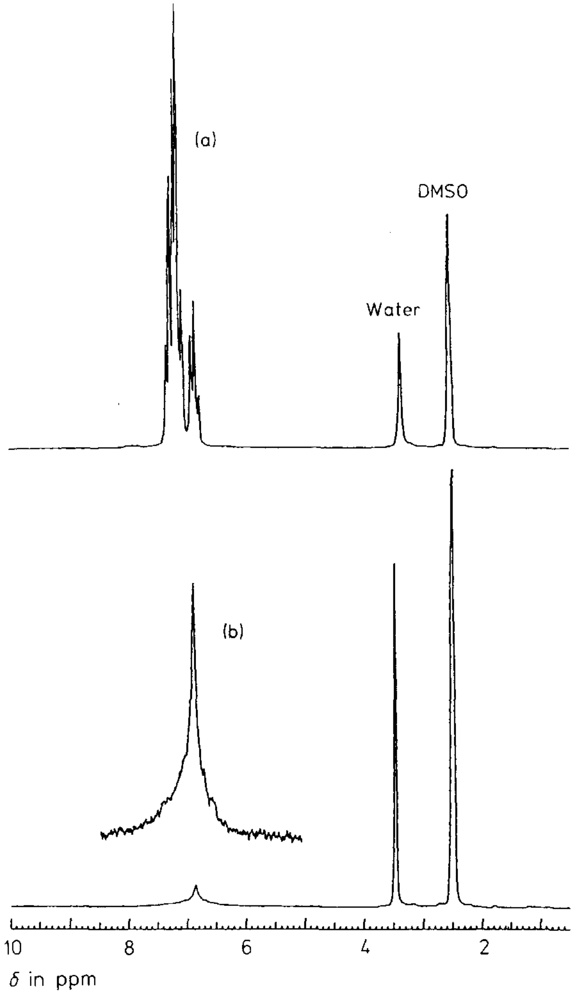
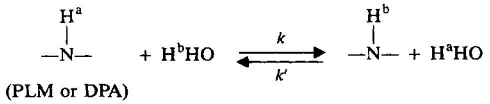


Fig. 3. (a) 100 MHz ^1H NMR spectrum of diphenylamine in a mixture of DMSO-d_6 (ca. 0,4 cm^3) and D_2O (ca. 20 μL) at 25 °C; (b) 100 MHz ^1H NMR spectrum of PLM in a mixture of DMSO-d_6 (0,4 cm^3) and D_2O (15 μL) at 25 °C

The temperature dependence of the ^1H NMR spectra of PLM (Fig. 1) and DPA (Fig. 2) clearly shows broadening of the NH signals and signal of water in DMSO-d_6 at elevated temperature[8]. Besides the broadening of the peaks of H_2O and NH hydrogens, the shift of the H_2O signal (possibly that of the NH signal also) to higher magnetic field is observed on raising the temperature (by about $\Delta\delta = 0{,}07$ and 0,10 from 30 °C to 70 °C for PLM and DPA, respectively). The reason for this shift is not clear at the moment. The H_2O signal in DMSO containing H_2O as impurity also shows a similar temperature-dependent shift of the δ value.

The temperature-dependent broadening of the NH and H_2O signals shown in Figs. 1 and 2 is reasonably accounted for by assuming the following rapid exchange of hydrogen between the NH hydrogen and hydrogen of water on the NMR time scale:



$$\underset{\text{(PLM or DPA)}}{\overset{H^a}{\overset{|}{-N-}}} + H^bHO \underset{k'}{\overset{k}{\rightleftarrows}} \overset{H^b}{\overset{|}{-N-}} + H^aHO \qquad (1)$$

In contrast to the broadening of the —NH— and H_2O signals, the signals of the aromatic hydrogens of PLM and DPA as well as that of DMSO-d_6 become rather sharper on raising the temperature presumably for physical reasons such as the decrease in viscosity of the solvent.

It is difficult to determine an accurate ratio between the amount of H in the —NH— group of PLM and that in water from Fig. 1, since separation of the NH signal and determination of its area is not so easy. However, if we assume the ratio is 1, the life time τ of H^a in —NH— (Eq. 1) is equal to that of H^b and the τ value can be easily obtained from the half-width of the H_2O signal.

When the H_2O hydrogen does not undergo such exchange as in H_2O in DMSO-d_6 which does not contain PLM or DPA, the half-width of the H_2O signal in DMSO-d_6 is about 1,7 Hz as measured with DMSO-d_6 containing only H_2O as impurity. On the other hand, the half-width of the H_2O signal in Fig. 1 (a) – 1 (d) is estimated as 16 Hz, 20 Hz, 22 Hz and 29 Hz, respectively. From the half-width, the values of the life time of H^a at 30 °C, 50 °C, 60 °C and 70 °C are estimated as 0,070 s, 0,055 s, 0,049 s, and 0,040 s; the life time indicates the —NH— hydrogen exchanges with the H_2O hydrogen, for example, at about 14 times per second at 30 °C. If the exchange (Eq. 1) follows the second-order rate equation, $R = k[\text{—NH—}][H_2O]$, the life time of H^a τ corresponds to a value calculated according to the following equation, $\tau = [\text{—NH—}]/R = 1/k[H_2O]$.

In the case of DPA, the broadening of the signal on raising temperature is obviously observed with both the NH signal and H_2O signals as shown in Fig. 2, and the life time of the —NH— hydrogen is calculated from the half-width of the —NH— signal. At 30 °C, the exchange between the —NH— hydrogen of DPA and H_2O hydrogen seems to be not fast as judged from considerably sharp NH and H_2O signals at this temperature. Therefore, an intrinsic half-width of the —NH— signal is estimated as about 3,2 Hz (the half-width observed at 30 °C). On raising the temperature to 60 °C, 70 °C, 80 °C, and 90 °C, the half-width of the —NH— signal becomes 5,8 Hz, 6,5 Hz, 8,9 Hz and 10,2 Hz, respectively; from these values the life times of the —NH— hydrogen at 60 °C, 70 °C, 80 °C and 90 °C are estimated as 0,38 s, 0,30 s, 0,18 s, and 0,14 s, respectively. Comparison of the life time of the —NH— hydrogen of DPA with that of PLM reveals that the —NH— hydrogen of PLM is more easily exchanged with the water hydrogen probably due to easier quaternization of the —NH— group ($\text{—NH—} + H_2O \rightleftarrows \text{—}NH_2^+\text{—} + OH^-$) in the polymeric base PLM; the difference in the number of phenyl or phenylene ring(s) per —NH— group between PLM and DPA accounts for a stronger basicity of the —NH— nitrogen in PLM and the easier quaternization for PLM.

Fig. 4 shows the temperature dependence of the ^1H NMR spectrum of PEM. The broadening of the water hydrogen signal at 70 °C suggests that the —NH— hydrogen of PEM is also exchangeable with the water hydrogen. However, the degree of the

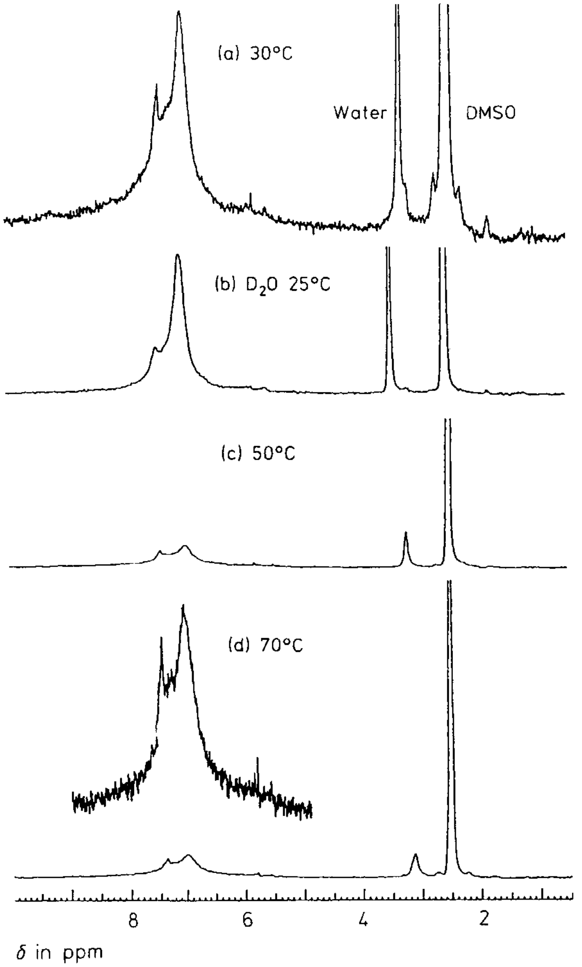


Fig. 4. Temperature-dependent 100 MHz ^{1}H NMR spectrum of PEM in DMSO-d_6

broadening of the water signal at 70 °C is smaller compared with that observed with PEM. This is probably due to the lower basicity of the —NH— group of PEM than that in PLM; the oxidized structure of PEM explains the lower basicity and this lower basicity explains the difficulty of the exchange through the assumed quaternization of the —NH— group by water. The 500 MHz ^{1}H NMR spectrum of PEM shows two broad peaks at δ = 8,12 and 8,23 which disappear on the exchange with D_2O and are assigned to the —NH— hydrogen of PEM. However, the area of the peak is considerably smaller compared with the proposed PEM structure[4] and further experiments to assign the —NH— signal in PEM are now carried out.

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