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Rate of Exchange of NH Hydrogen of Polyaniline, Poly(1-naphthylamine), and Diphenylamine with H_2O Hydrogen on NMR Time Scale

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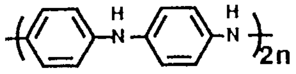
NH hydrogen of polyaniline, poly(1-naphthylamine), and diphenylamine undergoes rapid exchange with H_2O hydrogen in dimethyl sulfoxide on NMR time scale with life time of H_2O hydrogen of about 0.04-0.30 s at 70 °C and activation energy of 13-35 kJ mol^{-1}.

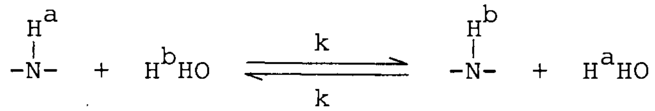
Polyaniline is one of the most promising polymers for electric devices, and a number of papers on the preparation, characterization, chemical reactivities and application of polyaniline have been published.[1-3] However, chemical reactivity of the NH hydrogen in polyaniline has not been revealed well except for its behavior against redox reactions and formation of salts with acids. We now report comparison of the rate of exchange of the NH hydrogen of polyaniline with H_2O hydrogen[4] with those of related compounds.

Figure 1 shows temperature dependent ^{1}H-NMR spectrum of the PLM type polyaniline[5] and diphenylamine DPA in dimethyl sulfoxide-d_6 (DMSO-d_6).



PLM type polyaniline

As shown in Fig. 1b, both the NH and H_2O peaks of DPA is broadened on raising the temperature, and the broadening is reasonably accounted for by assuming rapid exchange between the NH hydrogen and H_2O hydrogen on the NMR time scale.



$$\overset{H^a}{\underset{|}{}}\!\!-N- + H^bHO \underset{k}{\overset{k}{\rightleftharpoons}} \overset{H^b}{\underset{|}{}}\!\!-N- + H^aHO \qquad (1)$$

The NH hydrogen of PLM type polyaniline at δ7.39 ppm (at 30 °C) also undergoes a similar exchange with the H_2O hydrogen to cause the broadening of the both signals at the high temperatures (Fig. 1a), although at 60 °C or higher temperature the broadening of the NH signal is not clear due to the overlapping of the signal with those of aromatic hydrogens. Because of the rapid exchange between the NH hydrogen with H_2O, the NH signal of DPA at δ8.11 ppm and that of PLM type polyaniline at δ7.39 ppm are distinguished by addition of D_2O in the solution, thus unequivocally revealing the peak position of the NH hydrogen of PLM type polyaniline, which has not been clarified yet.

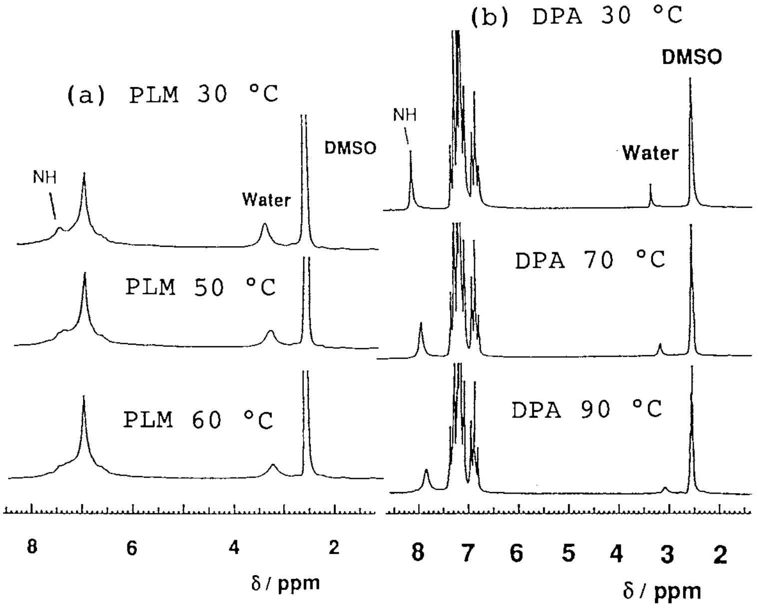


Fig. 1. Temperature variable ^1H-NMR spectra of (a) PLM type polyaniline and (b) DPA in DMSO-d_6.

The life time of NH and H_2O hydrogens can be calculated from the half width of the peaks,[6)] and life time of the H_2O hydrogen under the conditions for Fig. 1a ([NH] = 0.0067 M, $[H_2O]$ = 0.0029 M)[7)] are 0.070 s, 0.055 s, 0.049 s, and 0.40 s at 30 °C, 50 °C, 60 °C, and 70 °C, respectively.

The rate of the exchange, R, most probably follows the following rate equation,

$$R = k[NH][H_2O] \qquad (2)$$

If this equation is applied, the life time of H_2O, τ_{H_2O}, corresponds to a value calculated according to the following equation,

$$\tau_{H_2O} = 2[H_2O]/R$$
$$= 2/k[NH] \qquad (3)$$

and k is thus calculated by the following equation,

$$k = 2/\tau_{H_2O}[NH] \qquad (4)$$

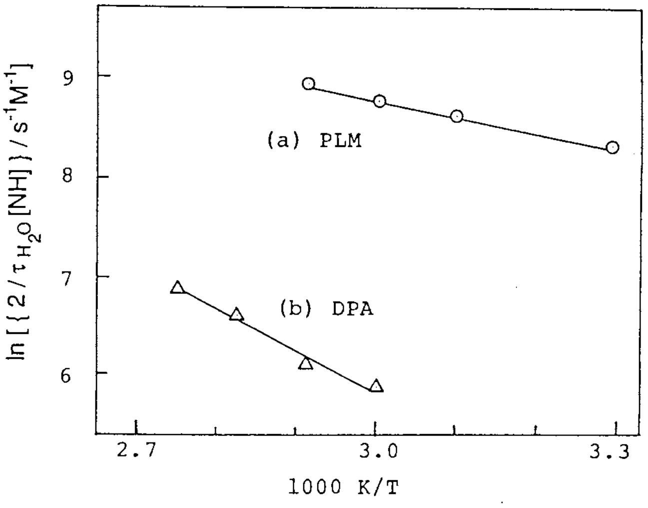


Fig. 2. Arrhenius plot of ln $\{2/\tau_{H_2O}[NH]\}$ against 1/T.

Figure 2 exhibits plot of ln $\{2/\tau_{H_2O}[NH]\}$ value against 1/T, and from the straight line in Fig. 2, the activation energy for the NH-H_2O exchange is obtained; the E_a values as well as $2/\tau_{H_2O}[NH]$ values for the PLM type polyaniline and analogous compounds are summarized in Table 1.

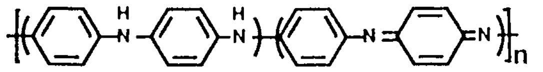
Table 1. The value of $2/\tau_{H_2O}[NH]$ at 70 °C and E_a for various amines

Amine[a]	PLM	DPA	PEM	PNA	NMA	AN	NA
$\{2/\tau_{H_2O}[NH]\}/s^{-1}M^{-1}$	8.1×10^3	4.4×10^2	8.7×10^4	1.5×10^4	b)	b)	b)
$E_a/(kJ\ mol^{-1})$	13	35	34	28	(3.6×10^2)[c]		

a) PLM = PLM type polyaniline. DPA = diphenylamine. PEM = PEM type polyaniline. PNA = poly(1-naphthylamine). NMA = N-methylaniline. AN = aniline. NA = 1-naphthylamine. b) The exchange rate was too small to be measured by the NMR spectroscopy. c) Value for NMA at 80 °C.

Comparison of the $2/\tau_{H_2O}[NH]$ value in Table 1 reveals the following characteristics of the exchange reaction.

PEM type polyaniline exhibits the $2/\tau_{H_2O}[NH]$ value comparable to that of the PLM type polyaniline.



PEM type polyaniline

Both the PLM and PEM type polyanilines give considerably larger $2/\tau_{H_2O}[NH]$ value than diphenylamine. The NH group of the PLM type polyaniline is considered to have higher basicity than the NH group of DPA due to attachment of only one electron-withdrawing phenylene unit per the NH group compared with the attachment of two phenyl groups to the NH group of DPA. If the exchange reaction proceeds through the formation of $-NH_2^+-$ intermediate species with OH^- counter anion, the larger value of $2/\tau_{H_2O}[NH]$ for the PLM type polyaniline than that for DPA is accounted for by the higher basicity of the PLM type polyaniline.

Poly(1-naphthylamine), which is prepared by a method similar to that[5)] applied to the preparation of the PEM type polyaniline and considered to have a structure analogous to that of the PEM type polyaniline,[8)] shows the $2/\tau_{H_2O}[NH]$ value comparable to those of the PLM and PEM type polyaniline.

PLM and PEM type polyanilines, DPA, and PNA having two aromatic groups attached to the NH group undergo much faster exchange reaction compared with those of NMA, AN, and NA having one aromatic group attached to the NH or NH_2 group, in spite of higher basicity of NMA, AN, and NA than that of DPA. This suggests an aromatic ring-assisted exchange mechanism involving formation of an H-aromatic ring complex. Formation of an H-aromatic ring complex by an H-π interaction has been proposed for DPA on the basis of IR spectroscopic and dielectric studies.9)

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