^{13}C NMR Study of Poly(N-vinylpyrrolidone)–Cu(II) Complex in Aqueous Solution

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ABSTRACT: Structural and dynamic properties of the poly(N-vinylpyrrolidone)–Cu(II) complex in aqueous solution are studied by ^{13}C NMR relaxation measurements. At pH 4, the spin-lattice relaxation rate of the carbonyl carbon increases remarkably with increasing Cu(II) concentration. This indicates that Cu(II) interacts with the carbonyl group at low pH. The temperature dependence of relaxation rate is explained in terms of the electron–^{13}C dipolar interaction, the ^{1}H–^{13}C dipolar interaction, and the chemical shift anisotropy interaction. The distance between Cu(II) and the carbonyl carbon is evaluated to be 4.0 Å at pH 4.
    KEY WORDS   NMR / ^{13}C / Spin-Lattice Relaxation / Poly(N-vinylpyrrolidone) / Metal Complexes / Cu(II) /

Since the paramagnetic metal ion has a large electronic magnetic moment, the spin-lattice relaxation of nuclei in the neighborhood of the metal ion is greatly enhanced. One can investigate structural and dynamic properties of polymer-metal complex by examining such effects. So far, we examined the interaction of Cu(II) and Mn(II) ions with poly(amino acid)s in aqueous solution.[1–4] It was shown that Cu(II) interacts with the side-chain carboxyl group,[1,3] the side-chain amino group,[2] and the main-chain amide group[1] of poly(amino acid)s, and that Mn(II) interacts with the side-chain carboxyl group and the main-chain carbonyl group.[4]

The oxygen atom of carbonyl group can interact with Cu(II); for example, bis(acetylacetonato)Cu(II) is a well-known complex. In this work, we study the interaction of Cu(II) with poly(N-vinylpyrrolidone) (PVP) which has a carbonyl group in the side-chain pyrrolidone ring and is water soluble.

EXPERIMENTAL

The sample of poly(N-vinylpyrrolidone) (PVP) with a molecular weight of 40,000 was obtained from Polyscience, Inc. PVP was dissolved in water ($D_2O/H_2O = 50/50$) at a concentration of 50 wt%. Aliquots of $CuCl_2$ aqueous solution were added to PVP solution. The concentration of Cu(II) ion is expressed as the molar ratio of Cu(II) ion to PVP residue $f = [\mathrm{Cu(II)}]/[\mathrm{PVP}]$. It varies from 4×10^{-6} to 1×10^{-3}. The value of pH was adjusted by adding HCl or NaOH solutions (pH 4, pH 7, and pH 12). The deuterium effects on pH are not taken into account.

The ^{13}C NMR measurements were carried out on JEOL JNM-FX60Q, FX100, GX270, GX400, and GX500 spectrometers operating at 15 MHz, 25 MHz, 67.8 MHz, 100 MHz, and

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125 MHz, respectively. Most NMR experiments were carried at 67.8 MHz unless otherwise noted. The ^{13}C spin-lattice relaxation rate was measured by the conventional inversion-recovery method. The chemical shift of ^{13}C spectra was measured by taking the dioxane signal as 76.8 ppm relative to tetramethylsilane.

RESULTS AND DISCUSSION

The ^{13}C NMR spectrum of pure PVP in aqueous solution at pH 4 and at 30°C is shown in Figure 1. The assignment is made by off-resonance ^{1}H decoupling experiments and by reference of the spectrum of its monomer.[5] Upon the addition of Cu(II), neither apparent chemical shift change nor line-broadening/narrowing is observed.
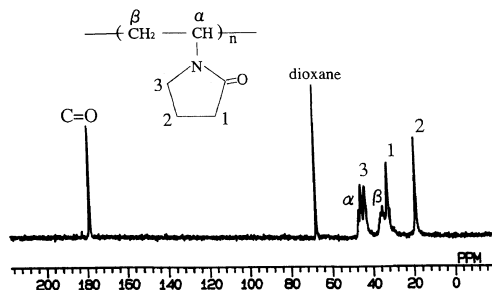
Figures 2 and 3 show the temperature dependence of relaxation rate of the C_2 carbon (Figure 2) and the carbonyl carbon (Figure 3) in aqueous solution at pH 4 and at various Cu(II) concentrations ($f = 1 \times 10^{-3}$ ($\square$), 4×10^{-4} ($\triangle$), 4×10^{-5} ($\times$), and 0 ($\bigcirc$)). Upon the addition of Cu(II), no appreciable change of relaxation rate is observed for the C_2 carbon (Figure 2). Similarly, other carbons except for the carbonyl carbon show relaxation independent of Cu(II) concentration. On the other hand, the relaxation rate of the carbonyl carbon increases with increasing Cu(II) concentration (Figure 3).

Figure 4 shows the temperature dependence of relaxation rate of the carbonyl carbon at

Figure 1. 67.8 MHz ^{13}C NMR spectrum of poly(N-vinylpyrrolidone) in water in the absence of Cu(II) at pH 4 at 30°C. Chemical shift is measured in ppm units from the internal standard dioxane at 76.8 ppm.
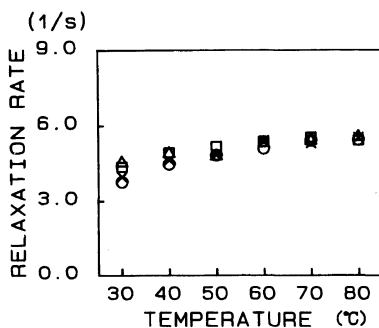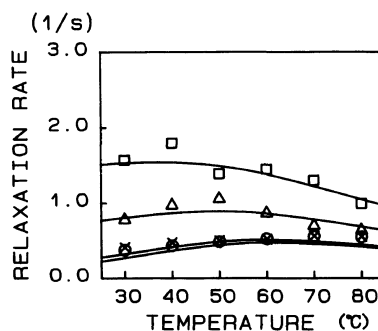

Figure 3. Relaxation rates of carbonyl carbon of poly-(N-vinylpyrrolidone) as a function of temperature at pH 4 and at $f = [Cu(II)]/[PVP] = 1 \times 10^{-3}$ ($\square$), 4×10^{-4} ($\triangle$), 4×10^{-5} ($\times$), and 0 ($\bigcirc$).

Figure 2. Relaxation rates of C_2 carbon of poly(N-vinylpyrrolidone) as a function of temperature at pH 4 and at $f = [Cu(II)]/[PVP] = 1 \times 10^{-3}$ ($\square$), 4×10^{-4} ($\triangle$), 4×10^{-5} ($\times$), and 0 ($\bigcirc$).

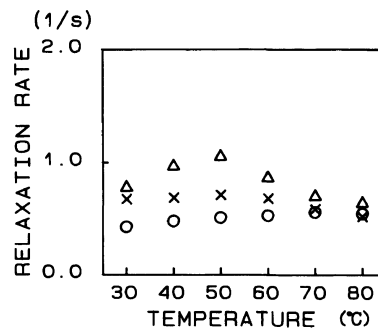**Figure 4.** Relaxation rates of carbonyl carbon of poly-(N-vinylpyrrolidone) as a function of temperature at $f = [Cu(II)]/[PVP] = 4 \times 10^{-4}$, at pH = 4 ($\triangle$), 7 ($\times$), and 12 ($\bigcirc$).

pH 12 ($\bigcirc$), pH 7 ($\times$), and pH 4 ($\triangle$) at $f = 4 \times 10^{-4}$. The change of relaxation rate by the addition of Cu(II) at pH 12 is not so remarkable as that at pH 4. These results indicate that Cu(II) interacts with the carbonyl group at low pH.

The spin-lattice relaxation rate observed in the presence of Cu(II) (R_1^{Cu}) is the sum of the paramagnetic contribution of Cu(II) to the spin-lattice relaxation rate (R_1^p) and the spin-lattice relaxation rate observed in the absence of Cu(II) (R_1^{pure}):

$$R_1^{Cu} = R_1^p + R_1^{pure} \tag{1}$$

The carbonyl carbon undergoes an exchange between the bound ($C=O\cdots Cu(II)$) and free states ($C=O$) with a life time τ_m of the bound state. We can write R_1^p as follows[6]:

$$R_1^p = fq/\{(1/R_1^m) + \tau_m\} \tag{2}$$

Here, q is the number of equivalent carbon nuclei coordinated to Cu(II), and R_1^m is the spin-lattice relaxation rate of the complex governed by the electron–[13]C dipolar interaction[2,7,8]:

$$R_1^m = A\{\tau_c/(1 + \omega_c^2\tau_c^2)\} \tag{3}$$

with

$$A = (3/10)\gamma_C^2 g^2 \beta^2 / r_0^2 \tag{4}$$

Here, ω_C is the Larmor frequency of ^{13}C, r_0 denotes the distance between the carbonyl carbon and the Cu(II) ion in the bound state, and γ_C is the magnetogyric ratio of ^{13}C spin. g and β are the g-factor and the Bohr magneton of the electron spin, respectively. The correlation time of the electron-^{13}C dipolar interaction of the complex τ_c can be given as:

$$1/\tau_c = 1/\tau_R + 1/\tau_m \tag{5}$$

where τ_R is the correlation time of tumbling motion of Cu(II)–carbon bond of the complex. We assume that τ_R has the Arrhenius dependence on temperature,

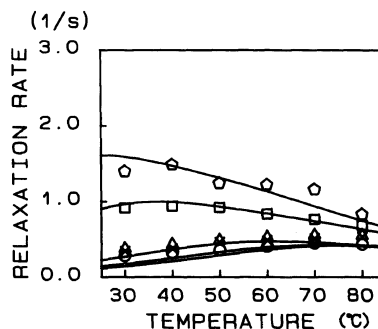$$\tau_R = \tau_{R0} \exp(E_a^R/RT) \tag{6}$$

Figure 5. Relaxation rates of carbonyl carbon of poly-(N-vinylpyrrolidone) in the absence of Cu(II) as a function of temperature at pH = 4 (^{13}C resonance frequency of 15 MHz ($\bigcirc$), 25 MHz ($\square$), 67.8 MHz ($\triangle$), 100 MHz ($\times$), and 125 MHz ($\bigcirc$)).

where τ_{R0} is the correlation time at infinite temperature and E_a^R is the activation energy of molecular motion. If we assume that the molecular motion is not greatly affected by the formation of Cu(II) complex, τ_R can be obtained by analyzing R_1^{pure}. This assumption is acceptable, because the metal ion is so small that it does not affect the mobility of polymer, and because the concentration of Cu(II) ion is very low ($f \leq 10^{-3}$).

We also assume that in the temperature range of this study τ_m obeys the Arrhenius equation:

$$\tau_m = \tau_{m0} \exp(E_a^m/RT) \tag{7}$$

where τ_{m0} is the correlation time at infinite temperature, and E_a^m is the activation energy of the exchange.

Figure 5 shows the temperature dependence of relaxation rate of the carbonyl carbon at pH 4 in the absence of Cu(II) at various observing frequencies (R_1^{pure}: 125 MHz ($\bigcirc$), 100 MHz ($\times$), 67.8 MHz ($\triangle$), 25 MHz ($\square$), and 15 MHz ($\bigcirc$)). It is found that the temperature dependence of R_1^{pure} of the carbonyl carbon at various observing frequencies can not be explained in terms of only the proton-carbon dipole-dipole interaction (R_{1d}). We include the relaxation due to the anisotropic chemical shift interaction (R_{1c}), because the

Table I. Best fit parameters to R_1^{pure} and R_1^p data of carbonyl carbon

τ_{R0}/s	$E_a^R/kcal\,mol^{-1}$	B/s^{-2}	C/s^{-2}
1.2×10^{-14}	8.0	8.0×10^7	3.0×10^{-10}

τ_{m0}/s	$E_a^m/kcal\,mol^{-1}$	A/s^{-2}
4.0×10^{-11}	2.5	1.1×10^{12}

Figure 6. Relaxation rates of C_2 carbon of poly(N-vinylpyrrolidone) in the absence of Cu(II) as a function of temperature at pH$=4$ (^{13}C resonance frequency of 25 MHz ($\square$), 67.8 MHz ($\triangle$), 100 MHz ($\times$), and 125 MHz ($\bigcirc$)).

carbonyl carbon has a large chemical shift anisotropy. The contribution of the chemical shift anisotropy to the ^{13}C relaxation of the carbonyl carbon has been reported for poly(methyl methacrylate) (PMMA).[9] The total relaxation rate is given as:

$$R_1^{pure} = R_{1d} + R_{1c} \qquad (8)$$

with

$$R_{1d} = B[\tau_R/\{1+(\omega_C-\omega_H)^2\tau_R^2\} \\ +3\tau_R/\{1+\omega_C^2\tau_R^2\} \\ +6\tau_R/\{1+(\omega_C+\omega_H)^2\tau_R^2\}] \qquad (9)$$

$$B = N\gamma_C^2\gamma_H^2\hbar^2 S(S+1)/10r^6 \qquad (10)$$

$$R_{1c} = C\omega_C^2\{2\tau_R/(1+\omega_C^2\tau_R^2)\} \qquad (11)$$

and

$$C = (\sigma_\perp - \sigma_\parallel)^2/15 \qquad (12)$$

Here, N is the number of protons which interact with the observing carbon, γ_H is the magnetogyric ratio of ^{1}H spin, $\hbar$ is the Planck constant divided by 2π, ω_H is the Larmor frequency of ^{1}H, and r is the distance between proton and carbon spins. $\sigma_\perp$ and $\sigma_\parallel$ are, respectively, the perpendicular and parallel components of the chemical shielding tensor. For simplicity, we assume that the chemical shielding tensor is axially symmetric.

The solid curves in Figure 5 are calculated by taking τ_{R0}, E_a^R, B, and C as fitting parameters (Table I). The $\sigma_\perp-\sigma_\parallel$ value of the carbonyl carbon calculated from the fitting parameter C (Table I) by using eq 11 is about 70 ppm. This value is somewhat smaller than that expected
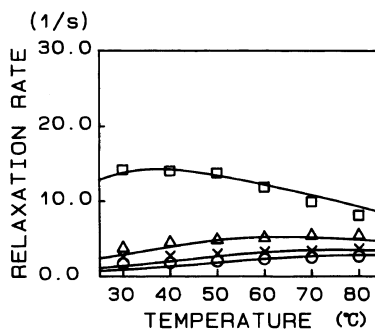
for the carbonyl carbon. The anisotropic nature of motion of the carbonyl group may reduce the efficiency of relaxation due to the chemical shift anisotropy.

Figure 6 shows the temperature dependence of relaxation rate of the C_2 carbon in the absence of Cu(II) (R_1^{pure}s) at pH 4 and at various observing frequencies (125 MHz ($\bigcirc$), 100 MHz ($\times$), 67.8 MHz ($\triangle$), and 25 MHz ($\square$)). The solid lines are calculated using eq 9 with $B=1.2 \times 10^9$ and using the same τ_{R0} and E_a^R listed in Table I. The observed temperature dependence of relaxation rate in the absence of Cu(II) (R_1^{pure}) for other protonated carbons is successfully realized by the same τ_{R0}, E_a^R. The contribution of the anisotropic chemical shift interaction (R_{1c}) for other carbons is negligibly small.

The solid curves in Figure 3 are calculated from eq 1, 2, 3, 5, and 6. By taking τ_{m0}, E_a^m, and A as fitting parameters for R_1^p (Table I) and adopting R_1^{pure} calculated by using parameters in Table I, we can successfully reproduce the observed temperature dependence of relaxation rate of the carbonyl carbon interacting with Cu(II). From the best-fit parameter A and eq 4, the distance between the carbonyl carbon and Cu(II) (r_0) is calculated to be 4.0 Å at pH 4. Similarly, the distance between the carbonyl carbon and Cu(II) is evaluated to be 4.4 Å at pH 7 and

$\sim 7\,\text{Å}$ at pH 12.

The evaluated distance of $4.0\,\text{Å}$ at pH 4 is longer than that of $3.0\,\text{Å}$ reported for poly(glutamic acid) at pH 7.[3] Furthermore, the activation energy of the exchange between the bound and free states E_a^m ($2.5\,\text{kcal mol}^{-1}$) is smaller than those found for poly(L-lysine) ($6\,\text{kcal mol}^{-1}$).[2] The long r_0 distance and the small E_a^m suggest that the interaction between the carbonyl group and Cu(II) is week as compared to that with the side-chain carboxyl group of poly(amino acid)s.

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