NOTES

^{13}C NMR Relaxation of Poly(acrylic acid) in Aqueous Solution. Effects of Charge Density on Local Chain Dynamics

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A previous paper[1] studied the effects of electrostatic interactions on local chain dynamics by ^{13}C NMR relaxation using poly(2-vinylpyridine) (P2VP) in dioxane-d_8 and fully neutralized P2VP or poly(2-vinylpyridinium chloride) (P2VPCl) in D$_2$O. All experimental data of main chain carbons were found in good agreement with the Dejean–Lauprêtre–Monnerie (DLM) model[2] modified from the Hall–Weber–Helfand model describing the main chain motions in terms of conformational transition[3,4] by introducing libration motions of C–H vectors. The main chain motion of P2VPCl was more restricted than those of P2VP owing to the electrostatic interactions.

When the charge density increases beyond a critical value in polyelectrolytes, counterion condensation or ion-binding takes place so that the effective charge density becomes almost constant or electrostatic interactions are almost saturated. This is characteristic of polyelectrolytes, which plays an important role to determine physicochemical properties such as counterion activity, electric conductivity[5] and intrinsic viscosity.[6] In the previous work,[1] however, we were not able to study the effects of charge density because of the poor solubility of partially neutralized P2VP in D$_2$O. We were not able to have definite conclusion on the activation energy of conformational transition because the solvents of P2VP and P2VPCl were different. To study these problems, poly(acrylic acid) (PAA) is considered a most suitable polyelectrolyte because the charge density can be easily varied by changing the degree of neutralization, α and PAA is dissolved in water irrespective of α.

In this work, we measured ^{13}C NMR relaxation such as spin-lattice relaxation time, T_1, and nuclear Overhauser effect (NOE) of PAAs with different α at two magnetic fields as a function of temperature and analyzed the data of main chains by the DLM model to study the effects of charge density on the local chain dynamics.

EXPERIMENTAL AND DATA ANALYSIS

PAA purchased from Wako Pure Chemical Industries Ltd. was purified by passing its aqueous solution through a mixed ion-exchange resin column of Amberlite IR-120B and IRA-400 and some PAA solutions were partially neutralized by NaOH aqueous solution. The PAA solutions with $\alpha = 0$, 0.2, and 0.8 thus obtained were freeze-dried, followed by drying in vacuum and the dried samples were dissolved in D$_2$O purchased from Aldrich Chemical Co. The polymer concentrations were ca. 10 wt%. All sample solutions were degassed carefully and sealed in NMR sample tubes. The tacticity of PAA sample was found to be almost atactic ($rr = 31\%$, $mr = 48\%$, and $mm = 21\%$, where rr, mr, and mm represent the triad sequences of meso (m) and racemo (r)) from the methine peak intensities of ^{13}C NMR spectra.[7] Molecular weight of PAA ($\alpha = 0$) is ca. 1.2×10^4, determined from the intrinsic viscosity of poly(sodium acrylate) in 1 M NaCl aqueous solution.[8]

^{13}C NMR relaxation measurements were performed at 30—$80 \pm 1°C$ with Varian unity INOVA 500 and Varian Mercury NMR instruments operating at 125.7 and 75.5 MHz for carbon resonance frequency, respectively. Measurements of T_1 and NOE, and data analysis using the DLM model were carried out in the same manner as reported previously.[1,9]

RESULTS AND DISCUSSION

Figures 1, 2, and 3 show temperature dependence of T_1 and NOE for methine carbons of PAAs with $\alpha = 0$, 0.2, and 0.8, respectively. Almost the same data were obtained for methylene carbons. All experimental data were obtained from peaks with the maximum intensity for each group, methine and methylene carbons since the data are independent of tacticity within experimental error as reported by Pierre et al.[7] These data indicate the following specific features. For all samples, T_1 increase with magnetic field or temperature. It should be noted that the temperature dependence of T_1 at $\alpha = 0$ is weaker than at $\alpha = 0.2$ and 0.8 in the high temperature range. This implies that the local chain dynamics of PAA may be affected by electrostatic interactions. NOE are

Figure 1. Temperature dependence of T_1 and NOE for methine carbon of PAA with $\alpha = 0$. Open and filled symbols denote data at the high and low magnetic fields, respectively. Solid lines are calculated by the DLM model with parameters listed in Table I.
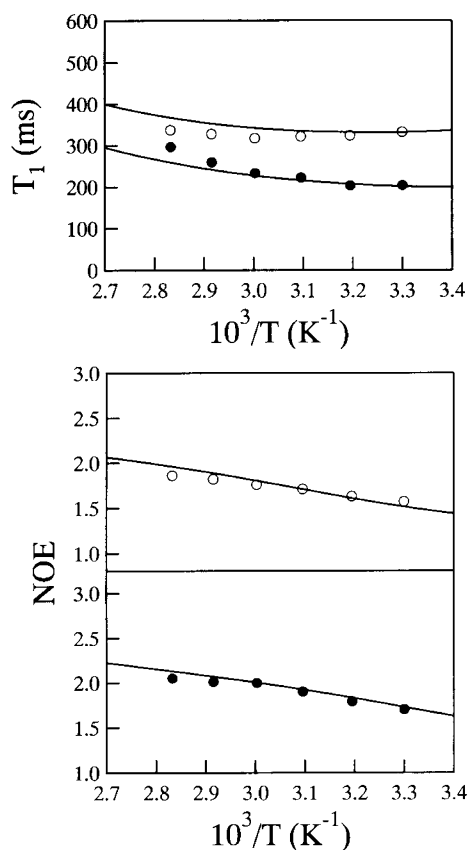

Figure 2. Temperature dependence of T_1 and NOE for methine carbon of PAA with $\alpha = 0.2$. Open and filled symbols denote data at the high and low magnetic fields, respectively. Solid lines are calculated by the DLM model with parameters listed in Table I.

significantly smaller (1.5—2.0) than the maximum value (3.0) at the extreme narrowing limit and decrease with decreasing temperature. A single exponential correlation function may thus not be applied to the data. The ratios of T_1 for methine and methylene carbons, $T_1(\text{CH})/T_1(\text{CH}_2)$, are 1.8—1.9 for all samples, implying that the local dynamics of C–H vectors is not identical for methine and methylene carbons.

The solid lines in Figures 1, 2, and 3 show the best fitting curves of T_1 and NOE vs. temperature, calculated by the DLM model listed in Table I for methine carbons of PAA with $\alpha = 0$, 0.2, and 0.8, respectively, where τ_0, τ_1, and τ_2 are correlation times for damping, propagation and libration, respectively, E_a and A are apparent activation energy and a pre-factor, respectively, in the temperature dependence of correlation time, $\tau_1 = A \exp (E_a/RT)$, and θ is the libration angle of C–H vector.[1,9] In the entire temperature range, experimental T_1 and NOE are in good agreement with the DLM model for all the samples. For methylene carbons these values are well explained by the DLM model. As shown in Table I, the correlation time ratios, τ_0/τ_1, at $\alpha = 0.2$ and 0.8 (4) are smaller than at $\alpha = 0$ (7). Their values are almost equal to those of fully charged (5) and uncharged (8) P2VP, respectively.[1] The small correlation time ratio means that the propagation of local chain motion associated with τ_1 is more restricted by damping associated with τ_0. This indicates that the main chain motion of PAA is restricted by the electrostatic interactions between charges on carboxyl groups, though
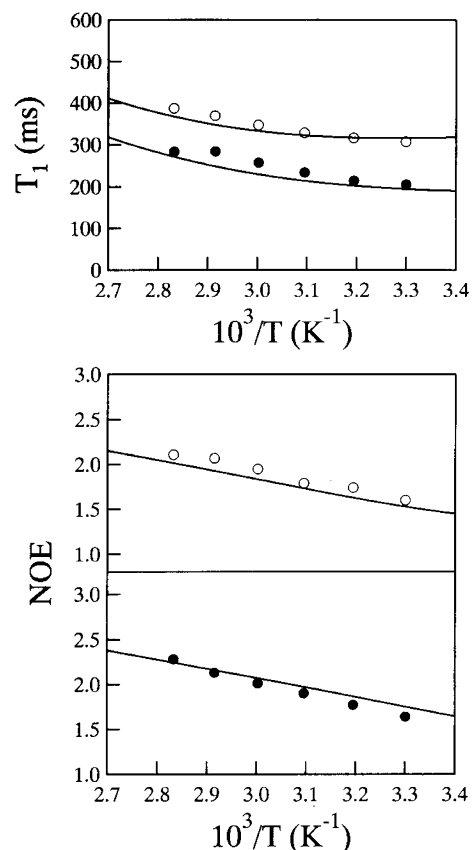
restriction is not different for $\alpha = 0.2$ and 0.8.

The effective charge density becomes almost constant beyond a critical charge density in polyelectrolytes. According to the counterion condensation theory of Manning and Oosawa,[10,11] the effective charge density or effective degree of neutralization, $\alpha_e = \alpha$, if the ratio of Bjerrum length, $\xi_b = e^2/4\pi\varepsilon_0\varepsilon kT$, to charge distance, b/α, $\beta = \alpha\xi_b/b < 1$, while $\alpha_e = b/\xi_b$, if $\beta > 1$, where e is the elementary charge, ε_0 and ε are dielectric constants in vacuum and medium, respectively, and b is the distance between charged groups at $\alpha = 1$. Assuming $b = 0.25$ nm for PAA, we have $\alpha_e = 0.2$ and 0.32—0.35 for $\alpha = 0.2$ and 0.8 in D_2O at 30—80°C, respectively. For PV2PCl, the charge density corresponds to that of PAA with $\alpha = 1$, so that we have $\alpha_e = 0.32$—0.35. Since the difference in effective charge density becomes much smaller than the difference in analytical charge density owing to ion-binding as described above, it is understandable not to observe distinct difference in the local motion of PAAs with $\alpha = 0.2$ and 0.8, and of PV2PCl. Thus, it is concluded that the main chain dynamics of polyelectrolytes can be interpreted through the effective charge density rather than analytical charge density in the same manner as the thermodynamic and transport properties.[5] In this work, to obtain reliable data, NMR relaxation measurement was carried out at relatively high polymer concentrations (ca. 10wt%) or at relatively high ionic strengths (ca. 0.1—0.2), where the electrostatic interactions were significantly screened, so that probably the charge effects on main chain dynamics were further suppressed in this
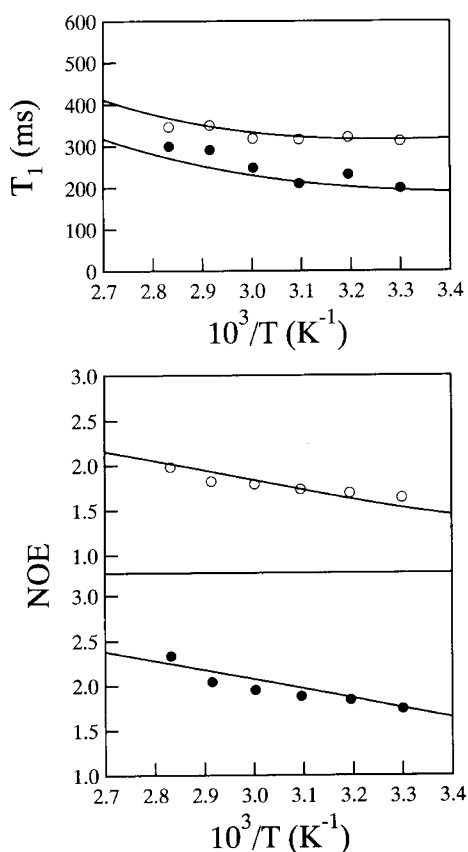
Figure 3. Temperature dependence of T_1 and NOE for methine carbon of PAA with $\alpha = 0.8$. Open and filled symbols denote data at the high and low magnetic fields, respectively. Solid lines are calculated by the DLM model with parameters listed in Table I.

Table I. Fitting parameters of the DLM model for main chain carbons of PAAs with different α

α	0		0.2		0.8	
Groups	CH	CH$_2$	CH	CH$_2$	CH	CH$_2$
τ_0/τ_1	7	7	4	4	4	4
τ_1/τ_2	100	100	100	100	100	100
E_a/kJ mol^{-1}	19.2	19.2	19.2	19.2	19.2	19.2
$10^{12}A$/s	0.50	0.50	0.50	0.50	0.50	0.50
θ/deg	27.0	30.0	27.0	30.0	27.0	30.0

case and the previous case.[1] They became comparable to the steric hindrance effects of moderately bulky side chains.[9] This is consistent with the fact that the static chain stiffness or the persistence length is almost independent of α for PAA at high ionic strength.[12]

Let us examine the activation energy, E^*, associated with a potential barrier for conformational transition. E^* can be evaluated by subtracting the activation energy of solvent viscosity, E_η from the apparent activation energy, E_a as $E^* = E_a - kE_\eta$ where $k = 1$—0.41[13] as

described previously.[1,9] Using $E_\eta = 15.6$ kJ mol^{-1} for water,[14] we have $E^* = 3.6$ kJ mol^{-1} if $k = 1$ and $E^* = 12.8$ kJ mol^{-1} if $k = 0.41$ for all the samples irrespective of α. Thus, E^* is independent of α and the latter value is comparable to the intrinsic torsional potential for C–C bonds.[4,15] This seems inconsistent with τ_0/τ_1 indicating the charge effects. As shown in Table IV in the previous paper,[9] E^* depends on the chain stiffness less than τ_0/τ_1 in the range of low steric hindrance. If this would be the case for the charge effects, the above inconsistency could be understood.

There is a clear difference in libration angles, θ, for methine and methylene carbons for all the samples as shown in Table I. This is consistent with the fact that $T_1(CH)/T_1(CH_2)$ (1.8—1.9) is smaller than 2, which is expected from the number of directly bonded proton. θ for each group is constant irrespective of α. The libration motion of C–H in PAA may thus be affected by the bulky carboxyl group, but not electrostatic interactions. The latter is different from that of P2VPCl affected by electrostatic interactions.

Since plots of $\log(T_1/\omega_c)$ vs. $\log(\omega_c\tau_1)$ are superimposed at the two Larmor frequencies for the methine carbons of PAAs with different α in the same manner as in previous papers,[1,9] the mechanisms of local motion as reflected in the correlation function are independent of temperature, and the above analysis is justified.[16,17]

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