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Carbon-13 Relaxation Times of Poly(vinylnaphthalene)s in Solution

Kazuhiko Seki* and Yoshio Imamura
Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

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Synopsis. Carbon-13 spin-lattice relaxation times and nuclear Overhauser enhancement factors were measured at 25.03 MHz and 40 °C for a solution of poly(1-vinylnaphthalene)(P1VN) and poly(2-vinylnaphthalene)(P2VN). The backbone motions in P1VN and P2VN were characterized by a distribution of correlation times. The relative mobilities of P1VN, P2VN, and polystyrene were as follows: $\bar{\tau}_{\text{polystyrene}} < \bar{\tau}_{\text{P2VN}} < \bar{\tau}_{\text{P1VN}}$ for the average correlation times. These results were explained on the basis of the energy contour maps for polystyrene, P2VN, and P1VN.

In our previous papers,[1-3] we explained the conformational characteristics of poly(1-vinylnaphthalene) (P1VN) and poly(2-vinylnaphthalene) (P2VN), by estimating the steric compression energies of the rotational isomeric states (RIS) of the naphthyl side groups and the conformational energies of the skeletal bonds.

The revealed differences of the characteristics between P1VN and P2VN corresponded well with the difference of the solution properties of P1VN and P2VN, such as in transition[1] phenomenon, NMR spectra patterns[2] and in fluorescence spectra of the solution.[3]

Futhermore, some information about the molecular dynamics of P1VN and P2VN can be also drawn from the previous calculations. The segmental motion of P1VN chain may undergo the steric restriction of the neighboring 1-naphthyl groups. Since the P2VN chain is not so spatially crowded by neighboring 2-naphthyl groups as the chain in P1VN is, the motion of the main chain in the former would not be so influenced by the restriction of neighboring groups. Consequently, the relative mobilities of P1VN, P2VN, and polystyrene chains can be predicted as follows: $\tau_{\text{polystyrene}} < \tau_{\text{P2VN}} < \tau_{\text{P1VN}}$ for the correlation time τ. These correlation times can be estimated by the measurement o carbon-13 spin relaxation time and nuclear Overhauser enhancement. The purpose of this paper is to discuss the segmental motion in P1VN and P2VN chain as characterized by a distribution of the correlation times.

Experimental

Samples of P1VN and P2VN were prepared by radical polymerization, using α,α'-azobisisobutyronitrile as an initiator. The number-average molecular weights of these polymers were determined using a "KUNAUAR's Membrance Osmometer" in chloroform solution at 37 °C. The average molecular weights of P1VN and P2VN were 4.0×10^4 and 7.5×10^4, respectively. In the vinyl aromatic polymers with this range of the degree of polymerization, the T_1 values are almost independent of the chain lengths.[4,5]

Natural abundance ^{13}C NMR spectra were obtained at 25.03 MHz by Fourier transform techniques using a JEOL JNM PS-100 spectrometer; details described before.[2] Spin-lattice relaxation times T_1 were measured from PRFT spectra obtained from 180°-t-90° sequences. The spectra of the polymer solutions of *ca.* 30% concentrations in dioxane-d_8 were observed at 40 °C. Nuclear Overhauser enhancements (NOE) were measured by comparison of coupled and decoupled spectra. The maximum errors in T_1 and NOE were within $\pm10\%$.

Calculation

Assuming only the dipolar interactions between a methine carbon and the proton bonded to it, the ^{13}C T_1 and NOEF (NOE-1) are given by[6,7]

$$1/T_1 = 2.190\times10^9(f(\omega_1)+3f(\omega_2)+6f(\omega_3))\ \mathrm{s}^{-1}, \tag{1}$$

$$\mathrm{NOEF} = \frac{(-f(\omega_1)+6f(\omega_2))}{(f(\omega_1)+3f(\omega_2)+6f(\omega_3))}\times 3.976, \tag{2}$$

$$\omega_1 = \omega_{\mathrm{H}} - \omega_{\mathrm{C}}, \tag{3}$$

$$\omega_2 = \omega_{\mathrm{C}}, \tag{4}$$

and

$$\omega_3 = \omega_{\mathrm{H}} + \omega_{\mathrm{C}}, \tag{5}$$

where ω_{C} and ω_{H} are the Larmor frequencies for ^{13}C and ^{1}H, respectively and for ^{13}C measurement at 25.03 MHz, $\omega_1=4.682\times10^8$ rad s^{-1}, $\omega_2=1.573\times10^8$ rad s^{-1}, $\omega_3=7.828\times10^8$ rad s^{-1}. As the backbone motion in a polymer is characterized by a distribution of correlation times, the spectral density function $f(\omega_{\mathrm{i}})$ is written by considering a log $-\chi^2$ distribution,[8,9] as follows:

$$f(\omega_{\mathrm{i}}) = \frac{\bar{\tau}\Gamma^{(p)}(s)(b^s-1)\mathrm{d}s}{(b-1)(1+\omega_{\mathrm{i}}^2\bar{\tau}^2((b^s-1)/(b-1))^2)} \tag{6}$$

$$\Gamma^{(p)}(s) = \frac{1}{\Gamma(p)}(ps)^{p-1}\exp(-ps)p\mathrm{d}s, \tag{7}$$

and

$$s = \log_b(1+(b-1)\tau/\bar{\tau}) \tag{8}$$

where Γ function, $\Gamma(p)$, normalizes $\Gamma^{(p)}(s)$ to unity, and the width of the distribution is characterized by p. The value of log base $b=1000$ is used. The $\bar{\tau}$ represents an average correlation time. Using Eqs. 1—8, T_1 and NOEF were computed by varying the width parameter p from 1 to 100 in 1-unit steps, and by varying the average correlation time $\bar{\tau}$ from 1.0×10^{-7} to 1.0×10^{-12} s^{-1}.

Results and Discussion

The proton-decoupled ^{13}C NMR spectra of P1VN and P2VN at 40 °C are shown in Figs. 1a and b, respectively. The signal peaks of naphthyl carbons are denoted by the symbols A, B, C, D, E, and F from the order of the low magnetic field. Table 1 shows the ^{13}C T_1 values for the aromatic peaks in P1VN and P2VN, together with those for polystyrene reported in the literature.[5,10,11] The T_1 for the aromatic carbons suggests that A–C peaks correspond to the nonprotonated carbons, and that D–F for P1VN and D, E for P2VN correspond to the protonated carbons. The line widths of A peaks in P1VN and P2VN are somewhat broader than that of B or C peak. Since this feature is attributed

Table 1. ^{13}C Spin-lattice relaxation times of aromatic carbon in P1VN, P2VN, and polystyrene

Polymer	Solvent	Temp/°C	Aromatic carbons T_1/ms					
			A	B	C	D	E	F
P1VN	Dioxane-d_8	40	968	1320	1520	78	85	86
P2VN	Dioxane-d_8	40	928	1380	1440	91	84	—
			Meta, ortho carbon			Para carbon		Ref.
Atactic polystyrene	Toluene-d_8	30	140			120		10
Atactic polystyrene	Tetrachloroethylene	44	98			89		5
Atactic polystyrene	Tetramethylene oxide	30	126			110		11

Table 2. ^{13}C Spin-lattice relaxation times and NOE of methine carbon in P1VN, P2VN, and polystyrene in solution

Polymer	Solvent	Temp/°C	T_1/ms	NOE	$\bar{\tau}$/s^{-1}	p	Ref.
P1VN	Dioxane-d_8	40	66	1.40	1.6×10^{-8}	20	—
P2VN	Dioxane-d_8	40	64	1.70	5.3×10^{-9}	12	—
Isotactic polystyrene	o-Dichlorobenzene	35	65	1.80	1.0×10^{-9}	18	9
Atactic polystyrene	Pentachloroethane	30			4.5×10^{-9}	20	12

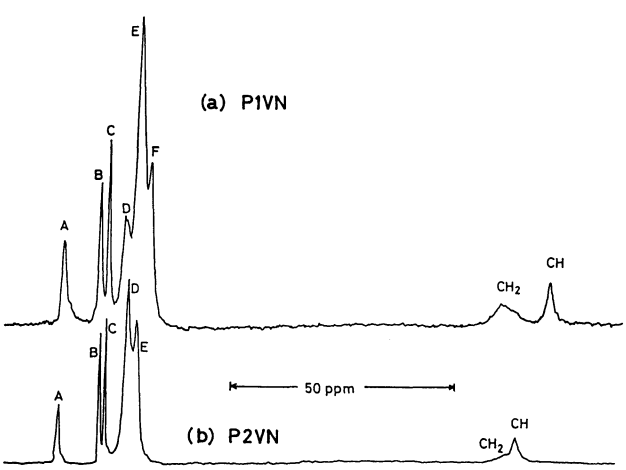

Fig. 1. Proton-decoupled, natural abundance ^{13}C FT NMR spectra of (a) P1VN and (b) P2VN in dioxane-d_8 at 25.03 MHz and 40 °C.

to the tacticity number in the polymer samples used, the A peak can be assigned to the naphthyl carbons, which bond to α-carbon. A similar phenomenon was observed in polystyrene. The other peaks of the aromatic carbons can not be assigned to each carbon in the naphthyl group at the present stage. T_1 values of the protonated carbon in P1VN and P2VN are smaller than that of polystyrene. This observation suggests that the naphthyl ring rotation is perturbed by the neighboring naphthyl rings, CH and CH_2 groups.

The average correlation times $\bar{\tau}$ and width parameter p satisfying the observed values (T_1 and NOE) are given in Table 2. T_1 value of methine carbon in P1VN was approximately equal to that of P2VN or polystyrene. It is apparent that the correlation time can not be adequately approximated by the T_1 value, and the $\bar{\tau}$ values for the segmental motion of these polymer are mainly influenced by the NOEF.

The segmental motion of P1VN was estimated to be slower than that for P2VN and polystyrene, as was expected. The order of the relative mobilities of the polymer chains agreed with that described above. These experimental results are explained as follows. The mobility of the main chain would be correlated to the values of the contour lines of the energy maps, which surround all the minima (tt, gt, tg, and gg) positions, since the energy value of each contour has a influence upon the magnitude of the change in RIS (t and g) of the molecular chain. In a previous paper,[3] all minima in the conformational energy maps of P1VN chain were shown to be surrounded by the contour lines of 9 kcal mol^{-1},[†] in the P2VN chain, the lines were 7—8 kcal mol^{-1}, while in polystyrene, it was sufficient to surround the all minima by contours of 5—6 kcal mol^{-1}. The order of the energy of these contours was found to be that of the chain mobilities described above.

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[†] In SI units: 1 kcal mol^{-1}=4.184 kJ mol^{-1}.