

Nuclear Magnetic Relaxation of Oligo- and Poly(α -methylstyrene)s in Dilute Solution

Masashi OSA, Hiroshi UEDA, Takenao YOSHIZAKI,[†] and Hiromi YAMAKAWA

Department of Polymer Chemistry, Kyoto University, Katsura, Kyoto 615-8510, Japan

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ABSTRACT: The spin–lattice relaxation time T_1 and nuclear Overhauser enhancement NOE were determined for three samples of atactic oligo- and poly(α -methylstyrene)s (a-P α MS) with weight-average degree of polymerization $x_w = 2, 3,$ and 67.1 in cyclohexane at 30°C . A comparison is made of the present data for T_1 and NOE with the helical wormlike (HW) chain theory, and it is shown that the theory may explain well the data for large x_w ($\gtrsim 10$). For smaller x_w , the rigid sphere model having the radius equal to the apparent root-mean-square radius of gyration of the HW chain fails to give a quantitative explanation of T_1 in contrast to the case of the relaxation time τ_Γ determined from dynamic depolarized light scattering measurements, indicating that the nuclear magnetic relaxation and dynamic depolarized light scattering cannot be described in terms of a common single relaxation time. However, it is shown that there is an effective (mean) magnetic relaxation time τ_M approximately equal to $0.6\tau_\Gamma$. From a comparison of the present results for T_1 for a-P α MS with previous ones for typical flexible polymers, it is also shown that the behavior of T_1 for them, including a-P α MS, may be consistently explained by the use of τ_M (proportional to τ_Γ).

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Time / Nuclear Overhauser Enhancement / Helical Wormlike Chain /

In the preceding paper,¹ we have examined the behavior of the relaxation time τ_Γ defined by the reciprocal of the half-width at half-maximum of the spectrum J_Γ of the excess depolarized component of the light scattered by atactic oligo- and poly(α -methylstyrene)s (a-P α MS) in cyclohexane at 30.5°C (Θ). The quantity τ_Γ represents a mean of relaxation (correlation) times of time-correlation functions of the spherical tensor components of the polarizability tensor affixed to the repeat unit of a polymer chain. In the framework of the dynamic theory for the (unperturbed) helical wormlike (HW) chain,^{2,3} those time-correlation functions are associated with the subspace $L(n) = 2(1)$ (of full Hilbert space) spanned by the basis set with the “total angular momentum quantum number” $L = 2$ and the number of “excited” subbodies $n = 1$. The spin–lattice relaxation time T_1 and nuclear Overhauser enhancement NOE determined from nuclear magnetic relaxation measurements may also be written in terms of the time-correlation functions of the same class $2(1)$,^{2,4,5} and therefore have a close relation to τ_Γ . In the present paper as a continuation of the preceding one,¹ we report results of a nuclear magnetic relaxation study of a-P α MS.

We have already investigated T_1 and NOE for atactic polystyrene (a-PS),⁶ atactic poly(methyl methacrylate) (a-PMMA),⁷ and isotactic (i-) PMMA,⁸ and compared the results with those for τ_Γ ,^{6–8} and found

that T_1 and NOE are closely correlated with τ_Γ , as mentioned in the INTRODUCTION in the preceding paper.¹ Thus the purpose of the present paper is to examine whether such a close correlation holds also for a-P α MS.

EXPERIMENTAL

Materials

All the three a-P α MS samples OAMS2, OAMS3, and OAMS67 used in this work are the same as those used in the preceding study of J_Γ .¹ In Table I are reproduced the values of the weight-average molecular weight M_w , weight-average degree of polymerization x_w , ratio of M_w to the number-average molecular weight M_n , and fraction of racemic diads f_r for the three samples from Table I of ref 1. The details of their preparation have been described in the EXPERIMENTAL section of the preceding paper.¹

The solvent cyclohexane used for nuclear magnetic

Table I. Values of M_w , x_w , M_w/M_n , and f_r for atactic oligo- and poly(α -methylstyrene)s

Sample	M_w	x_w	M_w/M_n	f_r
OAMS2	2.94×10^2	2	1	0.56
OAMS3	4.12×10^2	3	1	0.73
OAMS67	7.97×10^3	67.1	1.04	0.72

[†]To whom correspondence should be addressed (E-mail: yoshizaki@molsci.polym.kyoto-u.ac.jp).

Table II. Values of T_1 and NOE for OAMS2 in cyclohexane at 30 °C

Carbon atom no.	$(T_{1,mm}, T_{1,rm}, T_{1,mr}, T_{1,rr})$		$(\text{NOE}_{mm}, \text{NOE}_{rm}, \text{NOE}_{mr}, \text{NOE}_{rr})$
	$c = 0.092 \text{ g/cm}^3$	$c = 0.183 \text{ g/cm}^3$	$c = 0.092 \text{ g/cm}^3$
5	(1.1 ₅ , 0.93 ₉ , 1.1 ₆ , 1.1 ₆)	(0.90 ₉ , 0.89 ₃ , 1.0 ₁ , 0.98 ₆)	(3.0 ₄ , 2.8 ₀ , 2.7 ₇ , 2.9 ₀)
8	(0.90 ₉ , 0.86 ₈ , 1.0 ₄ , 1.0 ₁)	(0.93 ₈ , 0.89 ₂ , 0.99 ₆ , 0.99 ₈)	(3.0 ₆ , 3.0 ₄ , 3.1 ₀ , 3.0 ₃)

relaxation measurements was purified according to a standard procedure prior to use.

Nuclear Magnetic Relaxation

T_1 for ^{13}C was determined for aliphatic carbon atoms of the samples OAMS2, OAMS3, and OAMS67 by the inversion-recovery method with a pulse sequence $\pi-\tau-\pi/2$ on a JEOL JNM-A500 spectrometer at 125.8 MHz. NOE for each of those carbon atoms for the three samples was evaluated from the ratio of the integrated intensity of its peak obtained with complete noise decoupling of protons to that obtained with gated decoupling only during data acquisition. A pulse delay was taken to be longer than 5 times as long as the largest T_1 of the aliphatic carbon atoms under observation. The pulse delay adopted here is somewhat shorter than the one proposed by Opella *et al.*⁹ which is longer than 8 times as long as the largest T_1 . As they have noted, an insufficient pulse delay may lead to an underestimate of NOE for small molecules. As shown in the next section, however, the values of NOE for the sample OAMS2 with the smallest x_w are found to be *ca.* 3, indicating that the pulse delay adopted here has not led to any appreciable underestimate of NOE.

Measurements were carried out on solutions in cyclohexane at 30 °C with a lock signal obtained from an external C_6D_{12} tube. The solutions were not degassed since T_1 's of interest rarely exceeded 2 s, as shown later.

RESULTS

In the case of a-PS⁶ (without α -methyl group), the nuclear magnetic spins of all main-chain (aliphatic) ^{13}C atoms relax due to the dipolar interactions with bonded hydrogen atoms. In the case of a-P α MS as well as of a- and i-PMMAs,^{7,8} however, the spins of the methylene ^{13}C atoms relax by the same mechanism as above, while those of the α - ^{13}C atoms do not since the latter have no bonded hydrogen atoms, so that we consider T_1 and NOE only for the methylene ^{13}C atoms. We note that the nuclear magnetic re-

laxation of its methyl ^{13}C atoms does not directly reflect local motions of its main chain, and is not considered, for simplicity.

The values of T_1 and NOE for the sample OAMS2 in cyclohexane at 30 °C are given in Table II. The aliphatic carbon atoms have been numbered as explicitly shown in its caption, and the x th carbon atom is designated by C_x ($x = 1, \dots, 10$). The sample OAMS2 has the two methylene carbon atoms C_5 and C_8 and is a mixture of the four stereoisomers denoted by *mm*, *mr*, *rm*, and *rr*, where *m* and *r* denote meso and racemic diads, respectively, and the first and second letters (*r* or *m*) indicate the stereoisomeric states of the $\text{C}_3\text{--C}_5\text{--C}_6$ and $\text{C}_6\text{--C}_8\text{--C}_9$ diads, respectively. In its methylene ^{13}C NMR spectra, therefore, we are concerned with eight resonance peaks. We have identified each peak by the use of the assignments previously determined for the same sample.¹⁰ We note that although we could not precisely estimate experimental errors in the raw data, those in the evaluation of T_1 from the spectra are at most *ca.* $\pm 2\%$. It is seen that the values of NOE obtained for the sample OAMS2 are *ca.* 3 for all ^{13}C atoms, corresponding to the narrowing limit.

In Table III are given the values of T_1 and NOE for the sample OAMS3 along with its chemical structure with the numbering system for the aliphatic carbon atoms. It has the three methylene carbon atoms C_5 , C_8' , and C_8 and is a mixture of the eight stereoisomers denoted by *mmm*, *rmm*, *mmr*, *rrm*, *mmr*, *rmr*, *mrr*, and *rrr*, where the first, second, and third letters indicate the stereoisomeric states of the $\text{C}_3\text{--C}_5\text{--C}_6$, $\text{C}_6\text{--C}_8'\text{--C}_6'$, and $\text{C}_6'\text{--C}_8\text{--C}_9$ diads, respectively. In its methylene ^{13}C NMR spectra, therefore, we are in principle concerned with 24 resonance peaks. We have identified each peak by the use of the assignments previously determined for the same sample.¹⁰ However, the intensities of the 12 peaks for the stereoisomers *mmm*, *rmm*, *mmr*, and *rmr* are very weak, and therefore we have only considered the peaks for *rmr*, *rrm*, *mrr*, and *rrr*. We note that the assignments for *rmr* and *rrm* and also those for *mrr* and *rrr* can be interchanged.¹⁰ It is seen that the values of NOE ob-

Table III. Values of T_1 and NOE for OAMS3 in cyclohexane at 30 °C

Carbon atom no.	$(T_{1,mrm}, T_{1,rrm}, T_{1,mrr}, T_{1,rrr})$		$(NOE_{mrm}, NOE_{rrm}, NOE_{mrr}, NOE_{rrr})$
	$c = 0.092 \text{ g/cm}^3$	$c = 0.180 \text{ g/cm}^3$	$c = 0.092 \text{ g/cm}^3$
5	(0.50 ₃ , 0.49 ₁ , 0.49 ₁ , 0.49 ₁)	(0.42 ₈ , 0.41 ₈ , 0.42 ₃ , 0.41 ₈)	(2.7 ₄ , 2.7 ₄ , 2.7 ₄ , 2.7 ₄)
8'	(0.47 ₃ , 0.45 ₀ , 0.46 ₆ , 0.48 ₄)	(0.38 ₀ , 0.38 ₃ , 0.39 ₆ , 0.38 ₈)	(2.7 ₆ , 2.8 ₀ , 2.8 ₉ , 2.8 ₄)
8	(0.48 ₁ , 0.45 ₂ , 0.50 ₃ , 0.46 ₈)	(0.38 ₈ , 0.39 ₅ , 0.40 ₃ , 0.40 ₈)	(2.9 ₄ , 2.7 ₈ , 2.8 ₇ , 2.8 ₆)

Values of T_1 and NOE for the stereoisomers *mrm* and *rrm* and also *mrr* and *rrr* can be interchanged.

Table IV. Values of T_1 and NOE for OAMS67 in cyclohexane at 30 °C

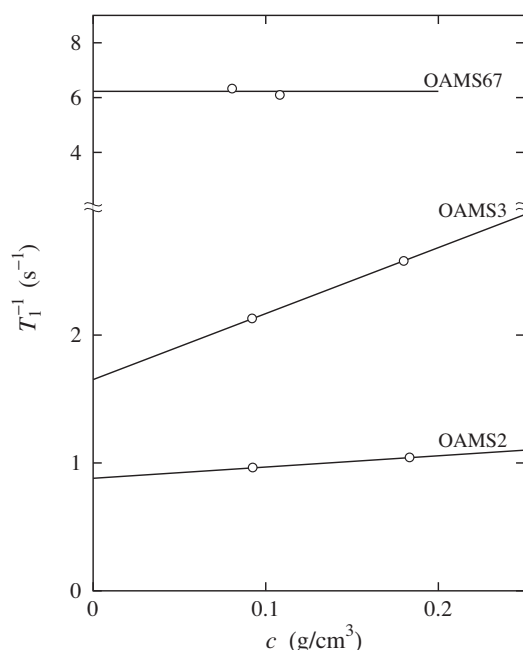
c (g/cm ³)	T_1 (s)	NOE
0.081	0.15 ₈	
0.108	0.16 ₄	
0.106		1.4 ₇

tained for the sample OAMS3 are somewhat smaller than those for the sample OAMS2.

For the sample OAMS67, we have identified the peaks of the methylene ¹³C NMR spectra only for the six kinds of tetrads *mmm*, *mnr*, *rmr*, *mrm*, *mrr*, and *rrr* by the use of the assignments determined by Inoue *et al.*¹¹ The mean values of T_1 and NOE are given in Table IV.

Now it is seen from Tables II and III that for the samples OAMS2 and OAMS3, T_1 and NOE for a given ¹³C atom depend somewhat on the stereoregularity, as is natural. However, since we are interested in their dependences on x_w , we ignore the minor differences between their values for the stereoisomers and simply consider only their mean values for each methylene ¹³C atom over them. For OAMS2, we consider the averages of mean values so evaluated for C5 and C8. As for OAMS3, we consider the mean values for C8', since we are interested in the motion of the central (or intermediate) part of the a-P α MS chain. We note that for the sample OAMS67 the results obtained are just those for the intermediate methylene ¹³C atoms. Figure 1 shows plots of the reciprocal of the mean (or averaged) T_1 against c for the center methylene ¹³C atoms for the samples OAMS2, OAMS3, and OAMS67. Extrapolation is made to infinite dilution from a pair of data at two concentrations for each sample, following the straight line indicated. As for NOE, we regard the mean (or averaged) values obtained above as those at infinite dilution, for convenience.

The values of T_1 and NOE thus obtained at infinite

**Figure 1.** Plots of the reciprocal of the mean T_1 against c for the center methylene ¹³C atoms for the three a-P α MS samples in cyclohexane at 30 °C.**Table V.** Values of T_1 and NOE for atactic oligo- and poly(α -methylstyrene)s in cyclohexane at 30 °C at infinite dilution

Sample	T_1 (s)	NOE
OAMS2	1.1 ₄	2.9 ₆
OAMS3	0.60 ₅	2.8 ₄
OAMS67	0.16 ₁	1.4 ₇

dilution are summarized in Table V. Note that for flexible polymer chains T_1 and NOE in general increase with decreasing relaxation time of the orientation of the C–H internuclear vector. It is seen that T_1 and NOE decrease with increasing x_w . Considering the previous results for a-PS⁶ and a- and i-PMMA^{7,8} the values 0.16₁ s and 1.4₇ for OAMS67 may be re-

garded as the asymptotic values of T_1 and NOE, respectively, in the limit of $x_w \rightarrow \infty$. We note that although Inoue *et al.*¹² reported the values of T_1 and NOE for a syndiotactic P α MS sample with the viscosity-average molecular weight 1.14×10^6 , we have not compared those with the present values, since the solvent condition and the Larmor frequency (strength of external magnetic field) of an NMR spectrometer they adopted are different from ours.

DISCUSSION

HW Theory

Before proceeding to make a comparison of the present results of nuclear magnetic relaxation measurements with the HW theory,^{2,4,5} we briefly summarize its relevant results.

We assume that the nuclear magnetic spin (of a methylene ^{13}C atom in the present case) relaxes due to the heteronuclear dipolar interaction between two unlike spins I and S , with spin I observed and spin S irradiated (*i.e.*, spins of ^{13}C and ^1H atoms, respectively, in the present case, so that $I = S = 1/2$) and with the internuclear distance r between them. Then T_1 and NOE for the single (discrete) HW chain composed of N identical rigid subbodies may be given by^{2,4}

$$T_1^{-1} = (1/20)K^2 r^{-6} \times [J_0(\omega_S - \omega_I) + 3J_1(\omega_I) + 6J_2(\omega_S + \omega_I)] \quad (1)$$

$$\text{NOE} = 1 + \frac{\gamma_S}{\gamma_I} \times \left[\frac{6J_2(\omega_S + \omega_I) - J_0(\omega_S - \omega_I)}{J_0(\omega_S - \omega_I) + 3J_1(\omega_I) + 6J_2(\omega_S + \omega_I)} \right] \quad (2)$$

with

$$K = \hbar \gamma_I \gamma_S \quad (3)$$

where γ_I and γ_S are the gyromagnetic ratios of spins I and S , respectively, ω_I and ω_S are the respective Larmor angular frequencies, \hbar is Dirac's constant (Planck's constant divided by 2π), and $J_m(\omega)$ ($m = 0, 1, 2$) are the spectral density written in the form^{2,4}

$$J_m(\omega) = 2 \sum_{k=1}^N (Q_{pk}^0)^2 \sum_{j=-2}^2 \frac{A_{2,k}^j \tau_{2,k}^j}{1 + (\omega \tau_{2,k}^j)^2} \quad (4)$$

with p indicating the subbody number and

$$Q_{pk}^0 = [2/(N+1)]^{1/2} \sin[\pi pk/(N+1)] \quad (5)$$

$$\tau_{2,k}^j = 1/\lambda_{2,k}^j \quad (6)$$

We note that J_m is independent of m . The quantities $\lambda_{2,k}^j$ in eq 6 are the eigenvalues of the matrix representation of the diffusion operator associated with the subspace 2(1) (of full Hilbert space) spanned by the

basis set with the "total angular momentum quantum number" $L = 2$ and the number of "excited" subbodies $n = 1$, which have already appeared in J_Γ given by eq 1 (with eq 2) of the preceding paper,¹ and the coefficients $A_{2,k}^j$ in eq 4 are given by eq 26 of ref 4. As in the preceding paper,¹ we use the augmented eigenvalues $\lambda_{2,k}^j$ given by eq 25 of ref 5 which takes partly into account the interactions with the complementary subspace. Thus $\lambda_{2,k}^j$ may readily be calculated for given values of N and six HW model parameters. They are the constant differential-geometrical curvature κ_0 and torsion τ_0 of the characteristic helix, the static stiffness parameter λ^{-1} , the bond length a , and the translational and rotatory friction coefficients ζ_t and ζ_r of the subbody. We note that the coefficient $A_{2,k}^j$ depends on the parameters κ_0 , τ_0 , and λ^{-1} and also on the polar and azimuthal angles α and β which specify the direction of the C–H internuclear vector in the localized coordinate system affixed to the subbody.

Dependences of T_1 and NOE on x_w

Now we proceed to make an analysis of the present results for T_1 and NOE. Figure 2 shows plots of $n_{\text{CH}}T_1$ and NOE against the logarithm of x_w for the center methylene ^{13}C atoms for a-P α MS in cyclohexane at 30 °C, where n_{CH} is the number of C–H bonds attached to the ^{13}C atom under observation and is equal to 2 in the present case. The unfilled and filled circles represent the observed values of T_1 and NOE, respectively, given in Table V, and the solid curves represent

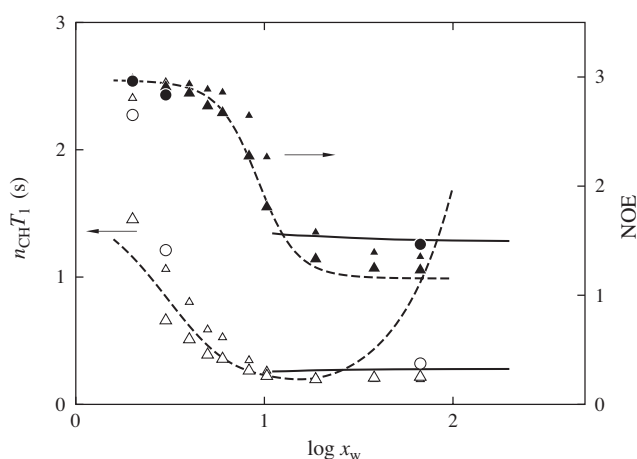


Figure 2. Plots of $n_{\text{CH}}T_1$ and NOE against the logarithm of x_w for the center methylene ^{13}C atoms (with $n_{\text{CH}} = 2$) for a-P α MS in cyclohexane at 30 °C: (○) $n_{\text{CH}}T_1$; (●) NOE. The solid and dashed curves represent the theoretical values for the HW model and the rigid sphere model, respectively. The unfilled and filled large triangles represent the values of $n_{\text{CH}}T_1$ and NOE, respectively, calculated with $\tau_{\text{M}} = C\tau_{\Gamma}^*$ along with $C = 1$, and the small ones represent those with $C = 0.6$ (see the text).

the respective HW theoretical values calculated from eqs 1–6 with the same values of the static and dynamic model parameters as those used in the preceding paper,¹ *i.e.*, $\lambda^{-1}\kappa_0 = 3.0$, $\lambda^{-1}\tau_0 = 0.9$, $\lambda^{-1} = 46.8 \text{ \AA}$, and $\lambda a = 0.063$ ($a = 2.95 \text{ \AA}$) for the static ones and $r_1 \equiv \zeta_t/3\pi\eta_0 a = 1.0$ and $r_2 \equiv \zeta_r/a^2\zeta_t = 8.0$ for the dynamic ones, where η_0 is the solvent viscosity. Further, we have adopted the values 90° and $\pm 55^\circ$ for the angles α and β , respectively, as before.⁴ We note that the coefficients $A_{2,k}^j$ in eq 4 and therefore J_m given by eq 4 do not depend on the sign of β when $\alpha = 90^\circ$. This means that the two protons of the two bonded hydrogen atoms make equivalent contributions to T_1 , and then T_1 calculated from eqs 1–6 with $\beta = 55^\circ$ is just twice the observed T_1 and therefore corresponds to the observed $n_{\text{CH}}T_1$. For the Larmor angular frequencies ω_I and ω_S , we have used the values $2\pi \times 125.8 \times 10^6$ and $2\pi \times 500.2 \times 10^6$ rad/s, respectively, corresponding to the present measurements. We have also adopted the values 1.09 \AA of r and 0.826 cP of η_0 for cyclohexane at 30°C . The calculation of the theoretical values has been limited to the range of $N (= x_w) \gtrsim 10$ as in the preceding study of J_Γ .¹ For such large N , the values of T_1 and NOE observed for the center (intermediate) methylene carbon atoms are actually the mean values averaged over the position of ^{13}C , so that we have presented the theoretical values averaged over p , which may be obtained by replacing $(Q_{pk}^0)^2$ by N^{-1} in eq 4.

The HW theoretical values of both $n_{\text{CH}}T_1$ and NOE are almost independent of x_w in its range (for $x_w \gtrsim 10$) for which the theory is valid. Their asymptotic values in the limit of $x_w \rightarrow \infty$ are 0.278 s and 1.50 , respectively, which are in rather good agreement with the values 0.32_2 s and 1.4_7 , respectively, observed for the sample OAMS67.

Next, in order to examine the behavior of T_1 and NOE for small x_w , we consider the rigid sphere model² which has the radius equal to the apparent root-mean-square radius of gyration $\langle S^2 \rangle_s^{1/2}$ of the HW chain as before¹ but to which a C–H internuclear vector is affixed in the present case. T_1 and NOE may then be given by eqs 1 and 2, respectively, with J_m given by¹³

$$J_m(\omega) = \frac{2\tau_M}{1 + (\omega\tau_M)^2} \quad (7)$$

where τ_M is identical to the relaxation time τ_Γ associated with J_Γ given by eq 6 of the preceding paper¹ and is given by

$$\tau_M = 4\pi\eta_0 \langle S^2 \rangle_s^{3/2} / 3k_B T \quad (8)$$

with k_B the Boltzmann constant and T the absolute temperature. Note that T_1 so obtained corresponds to the observed $n_{\text{CH}}T_1$ as in the case of the HW theoret-

ical values above. As noted in the preceding paper,¹ $\langle S^2 \rangle_s^{1/2}$ is defined as the coefficient of the squared scattering vector k^2 in the expansion of the scattering function determined from small-angle X-ray scattering measurements and may be regarded as the mean-square radius of gyration of the excess electron density. It may then be given by

$$\langle S^2 \rangle_s = \langle S^2 \rangle + S_c^2 \quad (9)$$

where $\langle S^2 \rangle$ is the (usual) mean-square radius of gyration of the HW chain contour of total length L and is given by eq 5 of ref 14 (or eq 4.83 of ref 2 in units of λ^{-1}) and S_c is the (effective) radius of gyration of the cross section of the excess electron density distributed around the chain contour and has already been evaluated to be $\sqrt{10.7} \text{ \AA}$ for a-P α MS.¹⁴

In Figure 2, the values of $n_{\text{CH}}T_1$ and NOE calculated from eqs 1 and 2, respectively, with eqs 7–9 and with the above values of ω_I , ω_S , r , and η_0 are represented by the respective dashed curves. The differences between the observed and calculated values of T_1 for the samples OAMS2 and OAMS3 are not very small, especially for the former. This disagreement implies that T_1 cannot be explained in terms of the single relaxation time τ_Γ for a-P α MS as well as for a- and i-PMMA^{7,8} (with a given x_w) in contrast to the case of a-PS,⁶ although such an explanation is possible for J_Γ for all of them.

As before,^{6–8} we then examine values of T_1 and NOE calculated from eqs 1 and 2, respectively, with eq 7, where we equate τ_M to the scaled τ_Γ in cyclohexane at 30°C , which we denote by τ_Γ^* , taking account of the differences in η_0 and T by the use of the equation

$$\tau_\Gamma^* = [(\eta_0/T)_{30}/(\eta_0/T)_{30.5}] \tau_\Gamma \quad (10)$$

with the *observed* values of τ_Γ in cyclohexane at 30.5°C given in Table II of the preceding paper.¹ If T_1 and NOE could be explained in terms of this τ_Γ^* , their calculated values would agree well with the observed ones. The values of $n_{\text{CH}}T_1$ and NOE so calculated for all the samples investigated in the preceding paper¹ are represented by the unfilled and filled large triangles, respectively, in Figure 2. Except for the value (≈ 3) of NOE in the narrowing limit, the calculated values (large triangles) are appreciably smaller than the observed ones (circles) as in the cases of a- and i-PMMA^{7,8} and in contrast to the case of a-PS.⁶

As previously mentioned,⁷ the above discrepancy may be regarded as arising from the differences in relative weights of the eigenvalues $\lambda_{2,k}^j$ between J_Γ in the preceding paper¹ and J_m in the present paper and also those among a-P α MS, a-PS, and a- and i-PMMA. Thus we simply relate an *effective* mean (single) magnetic relaxation time τ_M to τ_Γ^* by

$$\tau_M = C\tau_\Gamma^* \quad (11)$$

as before,^{7,8} where C is a constant independent of x_w chosen so that the values of T_1 and NOE calculated from eqs 1 and 2, respectively, with eqs 7, 10, and 11 (and with the observed τ_Γ) are close to the observed ones. In Figure 2, the unfilled and filled small triangles represent the values so calculated with $C = 0.6$, which happens to be the same as that previously used for a- and i-PMMA.^{7,8} As in those cases, these calculated values agree well with the observed ones except for T_1 at large x_w , for which the former values are still *ca.* 40% smaller than the latter.

Comparison with Other Flexible Polymers

Finally, in this subsection we compare the present values of T_1 for the methylene ^{13}C atoms for a-P α MS with the previous ones for a-PS^{6,7} and a- and i-PMMA.^{7,8} Unfortunately, however, the present values were determined at 125.8 MHz but the previous ones at 100.4 MHz, and therefore the former cannot be directly compared with the latter. Thus we try to estimate the values of T_1 for ^{13}C for the a-P α MS at 100.4 MHz by the use of a maneuver on the basis of the theoretical values for the rigid sphere model for the samples OAMS2 and OAMS3 and the HW model for the sample OAMS67. That is, we consider that the value of T_1 at 100.4 MHz is given by the one at 125.8 MHz multiplied by the ratio of the theoretical value of T_1 calculated at 100.4 MHz to that at 125.8 MHz. The values of the ratio calculated for both samples OAMS2 and OAMS3 are 0.99 and that for the sample OAMS67 is 0.78, leading to the values 1.1₃, 0.59₉, and 0.12₆ s of T_1 at 100.4 MHz for the samples OAMS2, OAMS3, and OAMS67, respectively.

Figure 3 shows double-logarithmic plots of $n_{\text{CH}}T_1$ (in s) against τ_M (in s) for the center methylene ^{13}C atoms (with $n_{\text{CH}} = 2$) at 100.4 MHz for a-P α MS in cyclohexane at 30 °C (unfilled circles), a-PS in cyclohexane at 40 °C (filled circles),^{6,7} a-PMMA in acetonitrile at 44 °C (filled triangles),⁷ and i-PMMA in acetonitrile at 35 °C (filled inverted triangles),⁸ where the values of τ_M for the respective polymers have been calculated from eq 11 with the values of τ_Γ^* and with $C = 0.6$ for a-P α MS and a- and i-PMMA^{7,8} and $C = 1$ for a-PS.^{6,7} The heavy and light dashed curves represent the HW theoretical values for a-P α MS and a-PS, respectively, and the heavy and light dot-dashed curves represent those for a- and i-PMMA, respectively, all at 100.4 MHz. The right-end point of each curve bounded by the vertical line segment with the shade corresponds to the asymptotic value of τ_Γ in the limit of $x_w \rightarrow \infty$, and the other end point corresponds to $x_w = 10$. The dotted curve represents the the-

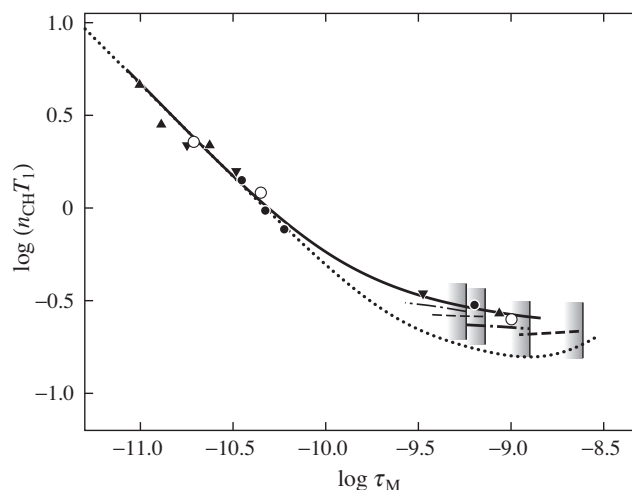


Figure 3. Double-logarithmic plots of $n_{\text{CH}}T_1$ (in s) against τ_M (in s) for the center methylene ^{13}C atoms (with $n_{\text{CH}} = 2$) at 100.4 MHz: (○) present data for a-P α MS in cyclohexane at 30 °C; (●) previous data for a-PS in cyclohexane at 40 °C;^{6,7} (▲) previous data for a-PMMA in acetonitrile at 44 °C;⁷ (▼) previous data for i-PMMA in acetonitrile at 35 °C.⁸ The heavy and light dashed curves represent the HW theoretical values for a-P α MS and a-PS, respectively, the heavy and light dot-dashed curves represent those for a- and i-PMMA, respectively, the dotted curve represents the theoretical values for the rigid sphere model, and the solid curve connects smoothly the data points (see the text).

oretical values calculated from eq 1 with eq 7 for the rigid sphere model at 100.4 MHz. It is seen that all the data points for a-P α MS, a-PS, and a- and i-PMMA form nearly a single-composite curve, as shown by the solid curve, and follow the dotted curve for small τ_M [for $\log(n_{\text{CH}}T_1) \gtrsim -0.2$], as was expected.

CONCLUSIONS

The spin–lattice relaxation time T_1 and nuclear Overhauser enhancement NOE were determined for the methylene ^{13}C atoms for a-P α MS in cyclohexane at 30 °C. It has been shown that the HW theory may explain well their behavior for large x_w ($\gtrsim 10$). In contrast to the case of the preceding study of dynamic depolarized light scattering,¹ the rigid sphere model for smaller x_w fails to give a quantitative explanation of T_1 , indicating that the nuclear magnetic relaxation and dynamic depolarized light scattering cannot be described in terms of a common single relaxation time. However, it has been shown that there is an effective (mean) magnetic relaxation time τ_M approximately equal to $0.6\tau_\Gamma$, and also that the behavior of T_1 for typical flexible polymers, including a-P α MS, may be consistently explained by the use of τ_M (proportional to τ_Γ).

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