

Carbon-13 Relaxation of Methyl Derivatives of Polystyrene in Solution

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ABSTRACT: Carbon-13 spin-lattice relaxation times and line-widths have been measured for solutions of *o*-, *m*-, and *p*-methyl derivatives of polystyrene at temperatures ranging between 30 and 60°C. Spin-lattice relaxation times of these polymers are intimately related with molecular motions, namely, the segmental motion and two internal motions of the phenyl and methyl groups. With respect to the internal rotation of the phenyl group, a transition change was observed in the vicinity of 50°C for poly(*o*-methylstyrene), 45°C for poly(*m*-methylstyrene) and 40°C for poly(*p*-methylstyrene), respectively. In comparison with the model of a freely rotating methyl group, it is concluded that the mobility of the methyl group decreases from the *para* to the *ortho* position of the substituent. This result suggests that the trend of the steric hindrance between the hydrogens bonded to the methyl carbon and those in the backbone has an effect on the segmental motion and the rotation of the phenyl group. The finding that the activation energies for the segmental motion and the rotation of the phenyl group in poly(*m*-methylstyrene) were larger than those in poly(*o*-methylstyrene) and smaller than those in poly(*p*-methylstyrene) is in accord with the above suggestion.

KEY WORDS Methyl Derivatives of Polystyrene / ¹³C-NMR / Spin-Lattice Relaxation / Internal Rotation / Transition / Line-Width / Correlation Time /

In polystyrene and its derivatives, the rotational transition of the phenyl group has been investigated at several laboratories.¹⁻⁴ Bach Van *et al.* measured the temperature dependency of the UV molar extinction coefficients of dilute solutions of polystyrene and its derivatives, and the transitional anomalies for the rotation of the phenyl groups of the methyl substituted polystyrenes were obtained at temperatures ranging from 30 to 80°C.²

Recently, Lanpretre *et al.* compared the intramolecular mobility of halogenated and methylated polystyrenes with that of polystyrene in solution, using the results of measurements of ¹³C spin-lattice relaxation times, but no information of the rotational transitions of the phenyl groups could obtain since these relaxation time measurements were carried out at 30°C.⁵

This paper reports the temperature dependences of ¹³C spin-lattice relaxation times and line-widths for individual carbons of monomer units in methyl derivatives of polystyrene in CDCl₃ solution, the rotational transitions of the phenyl groups and the steric hindrance effect of the methyl groups.

EXPERIMENTAL

Samples

Polymerizations of *o*-methylstyrene, *m*-methylstyrene and *p*-methylstyrene, obtained from Tokyo Kasei Co., Ltd., were initiated by butyllithium in benzene at 25°C. The number average molecular weights for poly(*o*-methylstyrene) (P(*o*-MS)), poly(*m*-methylstyrene) (P(*m*-MS)) and poly(*p*-methylstyrene) (P(*p*-MS)), measured by GPC, were 2.0×10^4 , 1.0×10^4 , and 2.3×10^4 , respectively.

Methods

¹³C-NMR spectra were recorded at 25.05 MHz using a JEOL FX-100 spectrometer equipped with an internal ²D lock and a noise modulated ¹H-decoupler. The 90° pulse width was about 15 μs, and its recycle time was chosen as 10 s. The samples were prepared as 20% (w/v) CDCl₃ solutions in egg-shaped microcells, which were inserted in 10 mm O.D. glass tubes. The normal proton-decoupled ¹³C-NMR spectra of P(*o*-MS), P(*m*-MS) and P(*p*-MS) are shown in Figure 1. The values of the chemical

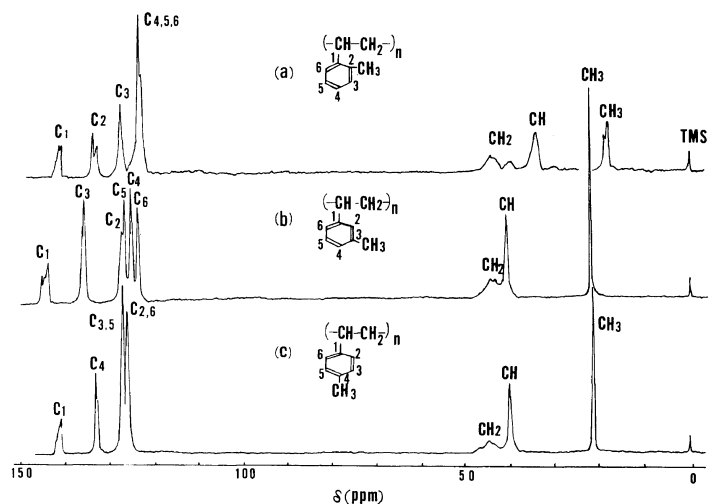


Figure 1. ^1H -decoupled ^{13}C -NMR spectra of 20% (w/v) methyl derivatives of polystyrene in CDCl_3 at 25.05 MHz and 30°C . Each spectrum is the result of 500 accumulations with a recycle time of 10 s: (a) P(*o*-MS); (b) P(*m*-MS); (c) P(*p*-MS).

shift of the spectral lines in Figure 1 are in a good agreement with those measured by Evans, *et al.*⁶

Nuclear Overhauser enhancement values were determined from peak areas obtained initially with complete proton decoupling and finally with the decoupling unit suppressed. The latter was obtained by using pulse-modulated proton decoupling which involves gating the decoupler "on" during data acquisition and "off" during the remaining time.

Spin-lattice relaxation time (T_1) for each carbon was determined from proton-decoupled partially relaxed Fourier transform (PRFT) spectra obtained by $(180^\circ\text{-}\tau\text{-}90^\circ)_n$ pulse sequences. The intensities measured from a set of PRFT spectra were used to determine T_1 , according to the equation,

$$M(t) = M_0[1 - 2 \exp(-t/T_1)] \quad (1)$$

where M_0 is the equilibrium intensity in a normal FT spectrum measured with delayed time t .

RESULTS AND DISCUSSION

Nuclear Overhauser Enhancement

For the case of ^{13}C nuclei under conditions of proton-decoupling, the nuclear Overhauser enhancement (*NOE*) is given by,⁷

$$\text{NOE} = 1 + \frac{\gamma_{\text{H}}}{\gamma_{\text{C}}\chi} \left[\frac{6\tau_{\text{C}}}{1 + (\omega_{\text{H}} + \omega_{\text{C}})^2\tau_{\text{C}}^2} \right]$$

$$\left[\frac{\tau_{\text{C}}}{1 + (\omega_{\text{H}} - \omega_{\text{C}})^2\tau_{\text{C}}^2} \right] \quad (2)$$

where

$$\chi = \frac{\tau_{\text{C}}}{1 + (\omega_{\text{H}} - \omega_{\text{C}})^2\tau_{\text{C}}^2} + \frac{3\tau_{\text{C}}}{1 + \omega_{\text{C}}^2\tau_{\text{C}}^2} + \frac{6\tau_{\text{C}}}{1 + (\omega_{\text{H}} + \omega_{\text{C}})^2\tau_{\text{C}}^2} \quad (3)$$

In the extreme narrowing limit, eq 2 reduces to the well-known expression,

$$\text{NOE} = 1 + \frac{\gamma_{\text{H}}}{2\gamma_{\text{C}}} = 1 + \eta = 2.987 \quad (4)$$

Table I lists the *NOE* factor ($1 + \eta$) for each carbon of the methyl substituted polystyrenes. The *NOE* values obtained at 70°C in Table I are smaller than the theoretical maximum of 2.987. Similar discrepancies have already been obtained by Schaefer and Natusch for several polymer relaxations with by a purely dipolar ^{13}C - ^1H mechanism,⁸ and they suggested that the unknown correlation function describing the actual motion may not differ greatly from that due to isotropic motion described by a single average correlation time.

In Table I, the *NOE* value for the methyl carbon in

Table I. NOE of methyl derivatives of polystyrene

Line	NOE (1 + η)	
	70°C	40°C
P(o-MS)		
Ring-carbon		
Substituted (1,2)	2.3 ± 0.2	
Unsubstituted (3)	2.4 ± 0.2	
(4,5,6)	2.5 ± 0.2	
α -carbon	2.6 ± 0.2	
Methyl-carbon	2.7 ± 0.3	
P(m-MS)		
Ring-carbon		
Substituted (1,3)	2.5 ± 0.2	
Unsubstituted (4)	2.7 ± 0.3	
(6)	2.7 ± 0.3	
α -carbon	2.7 ± 0.3	
Methyl-carbon	2.5 ± 0.2	
P(p-MS)		
Ring-carbon		
Substituted (1,4)	2.3 ± 0.2	2.3 ± 0.2
Unsubstituted (3,5)	2.6 ± 0.2	2.4 ± 0.2
(2,6)	2.6 ± 0.2	2.4 ± 0.2
α -carbon	2.7 ± 0.3	2.3 ± 0.2
Methyl-carbon	2.3 ± 0.2	2.2 ± 0.2

P(*p*-MS) is smaller than those for P(*m*-MS) and P(*o*-MS). This evidence demonstrates that the relaxation mechanism of a freely rotating methyl carbon in P(*p*-MS), as stated in correlation time, has substantial contributions from spin-rotation effects.⁹ If the relaxation mechanism of the methyl carbon in P(*p*-MS) is attributed to both the dipole-dipole and spin-rotation interaction, the relationship of the relaxation times due to the former and the latter is given by⁹

$$\frac{T_1(SP)}{T_1(DD)} = \frac{\eta}{1.987 - \eta} \quad (5)$$

where $T_1(DD)$ and $T_1(SP)$ are the relaxation times due to the dipole-dipole and the spin-rotation interaction, respectively. In P(*p*-MS), $T_1(SP)/T_1(DD) \approx 1.9$ from $\eta = 1.3$ in Table I.

Line-Width

Since Bach Van *et al.*² demonstrated a transitional change for the rotation of the phenyl group of the methyl derivatives of polystyrene in the temperature range from 30 to 70°C, it is of interest to measure the line-width ($\Delta H_{1/2}$) within this tempera-

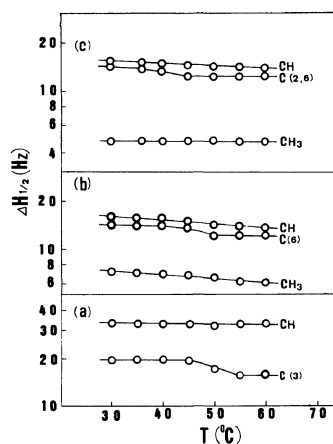


Figure 2. A semilog plot of the line-widths deduced from normal spectra as a function of temperature: (a) P(*o*-MS); (b) P(*m*-MS); (c) P(*p*-MS).

ture range. From the temperature dependence of $\Delta H_{1/2}$ s in Figure 2, transition phenomena are observed for protonated ring carbons; the transition occurs at about 40°C for P(*p*-MS), 45°C for P(*m*-MS) and 50°C for P(*o*-MS).

Spin-Lattice Relaxation Times

The temperature dependences of T_1 s for the carbons in P(*o*-MS), P(*m*-MS), and P(*p*-MS) are shown in Figure 3, 4, and 5, respectively. The signal for the methyl carbon of P(*o*-MS) splits into two peaks owing to the effect of tacticity as shown in Figure 1, and the temperature dependence of these T_1 s is presented in Figure 3. In Figure 3, 4, and 5, each T_1 for the methine carbon (C(α)) and the methyl carbon increases linearly with temperature, while

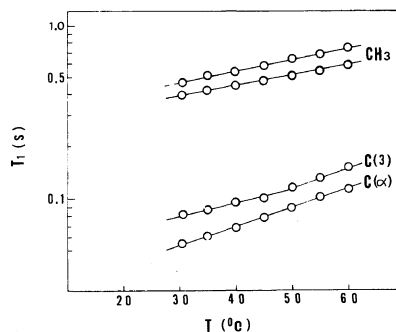


Figure 3. A semilog plot of the spin-lattice relaxation times for the carbons of P(*o*-MS) as a function of temperature.

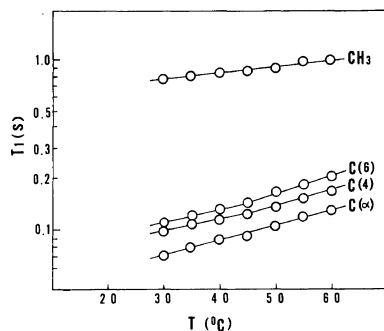


Figure 4. A semilog plot of the spin-lattice relaxation times for the carbons of P(m-MS) as a function of temperature.

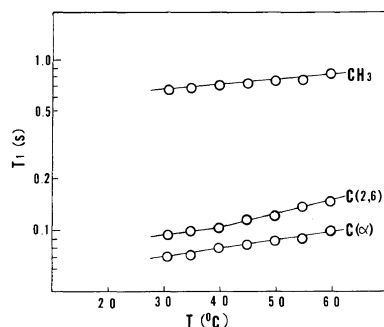


Figure 5. A semilog plot of the spin-lattice relaxation times for the carbons of P(p-MS) as a function of temperature.

those for the protonated ring carbon do not.

Correlation Time

Assuming purely intramolecular interaction between ^{13}C and ^1H , T_1 can be approximated by,¹⁰

$$\frac{1}{T_1} = \frac{1}{10} \hbar^2 \gamma_C^2 \gamma_H^2 \sum_i r_i^{-6} [f(\omega_H - \omega_C) + 3f(\omega_C) + 6f(\omega_H + \omega_C)] \quad (6)$$

where

$$f(\omega) = \tau_R (1 + \omega^2 \tau_R^2)^{-1} \quad (7)$$

and τ_R is the single rotational correlation time for ^{13}C - ^1H coupling, and r_i is the distance between the i th proton and the ^{13}C nucleus in question. In the extreme narrowing limit, eq 6 yields the well-known expression:

$$\frac{1}{T_1} = \hbar^2 \gamma_C^2 \gamma_H^2 \sum_i r_i^{-6} \tau_R \quad (8)$$

For a group bonded to a backbone undergoing isotropic reorientation, the dipolar relaxation rate ($1/R_1(J)$) is given by the following equation,¹⁰

$$\frac{1}{T_1(J)} = \hbar^2 \gamma_C^2 \gamma_H^2 \sum_i r_i^{-6} \chi \tau_R \quad (9)$$

where τ_R is the single correlation time for the backbone carbon and,

$$\chi = \frac{1}{4} (3 \cos^2 \theta - 1)^2 + 18(5 + \rho)^{-1} \sin^2 \theta \cos^2 \theta + \frac{9}{4} (1 + 2\rho)^{-1} \sin^4 \theta \quad (10)$$

The expressions in eq 10 are defined as follows.

$$\rho = \frac{D_{||}}{D_{\perp}} \quad (11)$$

$$D_{\perp} = (6\tau_R)^{-1} \quad (12)$$

$$D_{||} = (6\tau_R)^{-1} + (6\tau_G)^{-1} \quad (13)$$

τ_G is the correlation time for a group rotation, and $D_{||}$ and D_{\perp} represent the diffusion constants for rotational diffusion parallel and perpendicular to the axis for internal motion, respectively, and θ is the angle between the axis for internal rotation and the C-H bond vector.

Assuming a purely ^{13}C - ^1H dipolar relaxation mechanism, which has been confirmed by Schaefer and Natusch⁸ for several polymers, τ_R and τ_G can be estimated from eq 9–13. Rotation around the C(x)-C(1) axis leads to relaxation for the *ortho* and *meta* carbons since the C-H bonds in these instances make angles (θ) of 60 and 120° with the rotation axis. In the case of T_1 s for the protonated *ortho* and *meta* carbons, eq 9 is reduced to

$$\frac{1}{T_1(I)} = \frac{1}{64T_1(R)} \left(1 + \frac{216}{6+K} + \frac{81}{3+2K} \right) \quad (14)$$

where $K = \tau_R/\tau_G$, and $T_1(R)$ is the relaxation time of backbone carbons.

Figure 6 shows an expanded view for estimating the rotational ratios of τ_R/τ_G from $64T_1(R)/T_1(I)$ in the methyl substituted polystyrenes. The values of τ_R

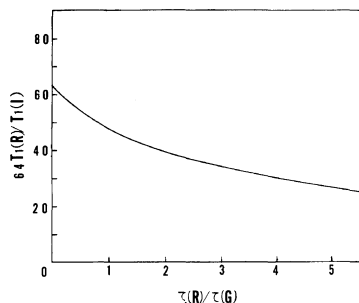


Figure 6. A plot of $64 T_1(R)/T_1(G)$ as a function of $\tau(R)/\tau(G)$.

are calculated by substitution of the observed $T_1(R)$ s in eq 7, while the values of τ_G can be estimated readily from Figure 6 when the values of $T_1(R)$ and $T_1(G)$ are measured at the same temperature. If the methyl rotation is much faster than the backbone and ring reorientations, then eq 10 reduces to¹⁰

$$\chi = \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right)^2 \quad (15)$$

Under this limiting condition, the carbon of a rapidly rotating methyl group ($\theta = 109^\circ$) relaxes 9 times more slowly than in absence of internal rotation.

Figure 7 shows the observed T_1 for a methyl carbon compared with 9 times T_1 for $C(\alpha)$ under the limiting condition described above for P(*o*-MS),

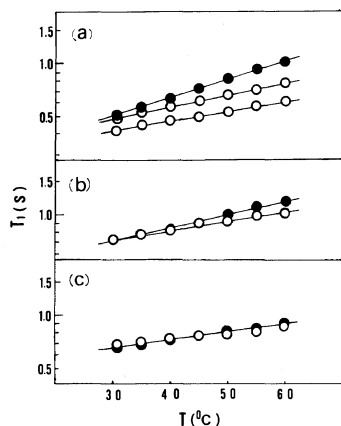


Figure 7. A semilog plot of the spin-lattice relaxation times for the methyl carbon of methyl derivatives of polystyrene as a function of temperature: (a) P(*o*-MS); (b) P(*m*-MS); (c) P(*p*-MS). (○) $T_1(\text{CH}_3)$; (●) $9T_1(\text{C}(\alpha))$.

P(*m*-MS) and P(*p*-MS), within a temperature range from 30 to 60°C.

Consequently, the trend of the discrepancy between the former and the latter is P(*o*-MS) > P(*m*-MS) > P(*p*-MS), and the result for P(*p*-MS) suggests that the methyl group rotates freely about a three fold axis.

Activation Energy

Figure 8 shows the temperature dependences of the correlation times, $\tau(R)$ and $\tau(G)$. The values of $\tau(R)$ were calculated from T_1 s for α -carbon by using eq 8, while those of $\tau(G)$ on P(*o*-MS), P(*m*-MS) and

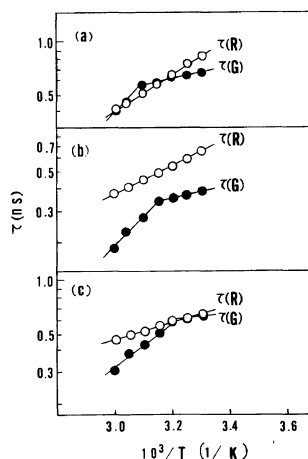


Figure 8. Arrhenius plot of the correlation times for the molecular motions as a function of $10^3/T$ (T being the absolute temp): (a) P(*o*-MS) (b) P(*m*-MS); (c) P(*p*-MS).

Table II. Activation energy for molecular motion of methyl derivatives of polystyrene in 20% (w/v) solution in CDCl_3

Sample	$\Delta E/\text{kcal mol}^{-1}$ ^a		
	R/motion	G/motion	
		Lower ^b temperature region	Higher ^b temperature region
P(<i>o</i> -MS)	4.7	1.7	7.6
P(<i>m</i> -MS)	3.4	1.6	7.2
P(<i>p</i> -MS)	2.3	0.7	6.3

^a $1 \text{ kcal mol}^{-1} = 4.184 \text{ kJ mol}^{-1}$.

^b From the transition temperature.

P(*p*-MS) were calculated from T_1 s for C(3), C(6) and C(2,6), respectively, by using eq 14. In Figure 8, it can be seen that the Arrhenius plots of $\tau(R)$ for the three compounds fall on the straight lines, and those of $\tau(G)$ show a break in the vicinity at 50°C for P(*o*-MS), 45°C for P(*m*-MS), and 40°C for P(*p*-MS), respectively. The activation energy (ΔE) for each motion can be estimated by the following equation

$$\tau = \tau_0 \exp(\Delta E/RT) \quad (16)$$

where τ_0 is the correlation time at infinite temperature and R is the gas constant.

Table II presents the activation energies for each motion of P(*o*-MS), P(*m*-MS) and P(*p*-MS). The ΔE for the segmental motion of P(*p*-MS) is in good agreement with that for the atactic polystyrene of 2.5 kcal mol⁻³ (10.5 kJ mol⁻³) within an experimental error of $\pm 10\%$, while the ΔE s for the segmental motion of P(*m*-MS) and P(*o*-MS) are larger than that of the latter.

Bach *et al.* have shown that the transition temperatures for the model compounds of the methyl-derivatives of polystyrene, *o*-methyleneethylbenzene, *m*-methyleneethylbenzene, and *p*-methyleneethylbenzene, were 60, 45, and 40°C, on the basis of the behavior of molar extinction coefficients as a function of temperature, and that the transition phenomena of these compounds involved the conformational changes concerning the rotation of the phenyl ring about the C_{arom}-C_{aliph} bond.² The temperature region of the transition phenomena in the methyl-substituted polystyrenes is similar to that in the model compounds, and so it is considered that the activation energy of G-motion in Table II is the difference of the conformational energy between the most stable and the most unstable position of the phenyl ring. By analogy with the conformations of the central ring in 2,4,6-triphenylheptane,² the most probable positions of phenyl ring in P(*o*-MS) are shown in Figure 9. Taking into account the steric hindrance between the methyl group and the backbone, it seems reasonable

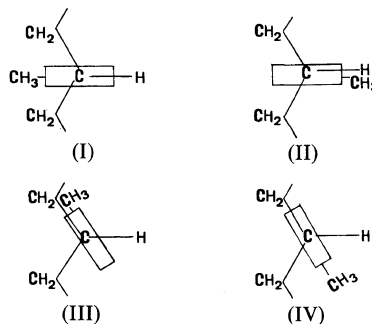


Figure 9. Most probable positions of phenyl rings in P(*o*-MS).

that the most stable conformer is I and that the most unstable conformer is III. The same interpretation can be proposed for P(*m*-MS) and P(*p*-MS), and it seems that the degree of the steric hindrance effect between the methyl group and the backbone determines the trends of the activation energy for the G-motion in Table II.

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