Molecular motion of syndiotactic poly(α-methylstyrene) in solution studied by carbon-13 n.m.r. relaxation measurements

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The carbon-13 n.m.r. spin–lattice relaxation times, nuclear Overhauser enhancement factor (NOE), and line widths have been measured for a syndiotactic poly(α-methylstyrene) in solutions in toluene-d_8 and *o*-dichlorobenzene-d_4 as a function of temperature from 40° to 163°C. The single correlation time model of relaxation is inadequate to explain the data of spin–lattice relaxation time and NOE. But, within experimental error, these relaxation data in two solvents over a full temperature range can be interpreted in terms of either the Cole–Cole or the log-X^2 distributions of correlation times, or a conformational jump model proposed by Monnerie *et al.* The internal rotation of the methyl group is relatively rapid, while that of the phenyl ring is slow and practically overshadowed by the backbone segmental reorientation over the temperature range examined. The solvent dependence of relaxation data was discussed.

Keywords Poly(α-methylstyrene); spin–lattice relaxation time; nuclear Overhauser effect; molecular motion; nuclear magnetic resonance; polymer conformation

INTRODUCTION

In recent years ^{13}C n.m.r. relaxation parameters such as spin–lattice (T_1) and spin–spin (T_2) relaxation times and nuclear Overhauser enhancement factor (NOE) have been used as a probe of molecular motion of polymer[1]. In previous papers, the authors investigated the temperature dependences of ^{13}C n.m.r. relaxation parameters of polystyrene[2] and poly(2-vinylpyridine)[3] in solution and found the transitions at about 50°C and 25°C, respectively, which are attributed to a transitionally increased ease of internal rotation of aromatic side chain around the bond connecting the side chain and the backbone.

In this paper we will present the results of the measurements of ^{13}C relaxation parameters for syndiotactic poly(α-methylstyrene) (PMS) in toluene-d_8 and *o*-dichlorobenzene-d_4 solutions over a wide temperature range from 40° to 163°C. The observed relaxation data for backbone methylene carbon will be analysed in terms of four models of segmental reorientation: (I) single correlation time model[4,5] which is effective for the interpretation of ^{13}C spin–lattice relaxation time of flexible polymer with rapid segmental motion and almost all small molecules, (II) the empirical Cole–Cole distribution[6] and (III) the log-χ^2 distribution of correlation times[7], and (IV) conformational jump model[8].

It is of great interest to investigate the influence of the α-methyl group, which is absent in polystyrene and poly(2-vinylpyridine), on the mobility of backbone and aromatic side group. The ^{13}C spin-lattice relaxation times have been measured for deuterochloroform solutions of PMS (the stereoregularity of polymer has not been shown) at 30°C[9] and α-methylstyrene–alkane copolymers over the temperature range 0° to 50°C[10].

EXPERIMENTAL

Materials

Syndiotactic PMS was prepared at -78°C in toluene with $BF_3O(C_2H_5)_2$ as a catalyst. To avoid the molecular weight dependence of ^{13}C spin–lattice relaxation time[9,11], the fraction of lower molecular weight less than about 15 000 was effectively excluded by fractionation with a benzene–methanol mixed solvent system[12]. The viscosity averaged molecular weight of sample used in this work was 1.14×10^6 and its triad tacticity determined from methyl proton resonance (100 MHz, in *o*-dichlorobenzene) was 88% syndiotactic, 12% heterotactic, and practically 0% isotactic. The deuterated solvents, toluene-d_8 and *o*-dichlorobenzene-d_4 were purchased from Merck Sharp & Dohme Canada Ltd.

^{13}C n.m.r. measurements

^{13}C n.m.r. spectra were measured on a JEOL JNM PS-100 spectrometer equipped with a PFT-100 Fourier transform system, JEC-6 spectrum computer, and JEOL CM-219 IC core memory with 8 k words as an auxiliary memory device, operating at 25.14 MHz. The solvent signals were greatly attenuated and practically negligible compared to the polymer signals, because the repetition time of 90° pulse is much less than the spin–lattice relaxation times of non-protonated carbons in solvent and because the solvent signals were split into multiplet due to ^{13}C–^{2}H spin coupling. ^{13}C relaxation times were measured by means of the 180°–*t*–90° inversion recovery method. The 90° pulse width was $\sim 20\ \mu$s. The values of NOE were measured by comparing the integrals of spectra recorded with and without complete proton noise decoupling. The changes in sample temperature with and without proton decoupling were compensated by temperature controller JES-VT-3. Measurements were

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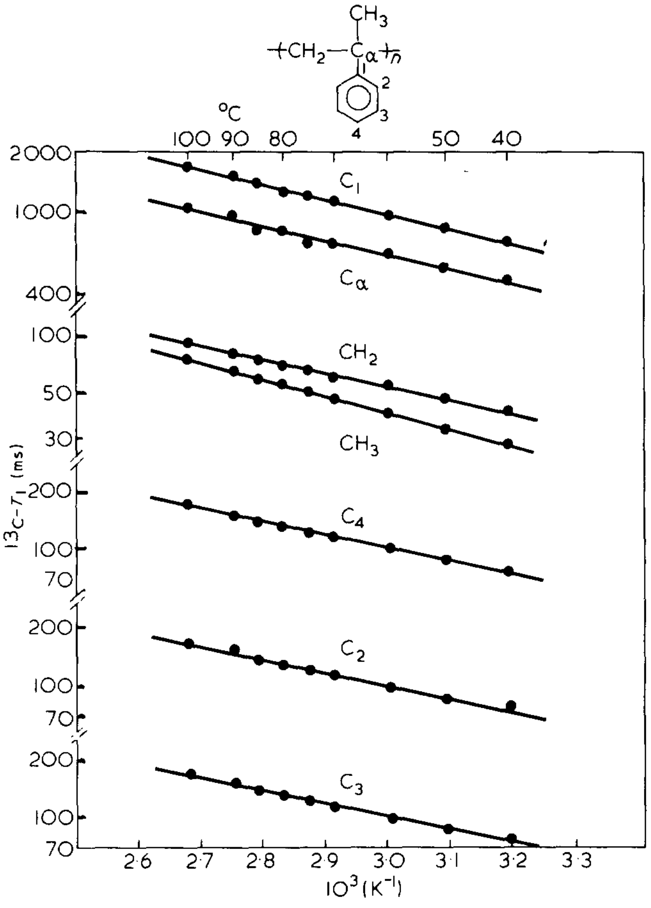

Figure 1 Temperature dependence of ^{13}C T_1 values for syndiotactic poly(α-methylstyrene) in 25% (w/v) solution in toluene-d_8

performed on solutions of 25% (w/v) in deuterated solvents, which also provided the internal ^2H lock signals. The solutions were contained in 8 mm o.d. glass tubes and were first degassed by repeated freeze-pump-thaw cycles and then filled with argon gas. Sample volume was adjusted so that almost the entire sample was contained within the volume of the probe coil. The maximum error in T_1 and NOE was estimated to be ±10% and ±20%, respectively. The determination of relaxation model parameters which gave simultaneous good fits of the values T_1 and NOE were made with the aid of computer HITAC 8700 at the Information Processing Center, Tokyo Institute of Technology.

RESULTS AND DISCUSSION

Temperature dependence of relaxation data

In the previous paper[13], an assignment of the ^{13}C n.m.r. spectrum was reported for PMS. In *Figures 1* and *2* are shown the temperature dependences of the ^{13}C T_1 values for the various carbons of syndiotactic PMS over the temperature range 40° to 100°C in toluene-d_8 and 104° to 163°C in *o*-dichlorobenzene-d_4. ^{13}C T_1 values for all carbons increase linearly with increasing temperatures in both solvents. The corresponding temperature dependences of the NOE values are shown in *Figures 3* and *4*. The NOE values for the methyl and methylene carbons were estimated directly by comparing the integrated intensities of proton-decoupled and proton-coupled resonances. The NOE values for aromatic carbons $C_{2,3,4}$ were obtained from a comparison of total intensity of completely proton-decoupled $C_{2,3,4}$ resonances with that of the methylene resonance. The NOE value of the latter was estimated in advance. Evidently the NOE values increase linearly with increasing temperature and approach the theoretical maximum value of 2.988 at high temperature.

The temperature dependences of the line widths were also measured for all resonances. It was found that the line width for each carbon decreases continuously with increasing temperature, but the reduction was small.

Analysis of molecular motion

Backbone segmental motion. In the previous ^{13}C relaxation study on polymer[14], it has been shown that T_1 values are largely determined by rapid motions of the chain segment while NOE to some extent and T_2 to a significant extent are affected by lower frequency motions. Thus values of T_2 and NOE, in addition to T_1 values, are necessary to provide a fuller characterization of the chain segmental motion of polymer. It has not been found to be a polymerization condition for obtaining poly(α-methylstyrene) having pure stereochemical configuration. The ^{13}C resonances of PMS, even the highly syndiotactic PMS used in this work which contained 12% heterotactic triad, suffer a line broadening at lower magnetic field arising from chemical shifts dispersion due to the configurationally irregular tactic chain structure[13,15]. In this case, a true value of T_2 cannot be obtained from an observed line width. Thus the segmental motion of the methylene carbon of PMS was analysed by using two relaxation parameters, T_1 and NOE.

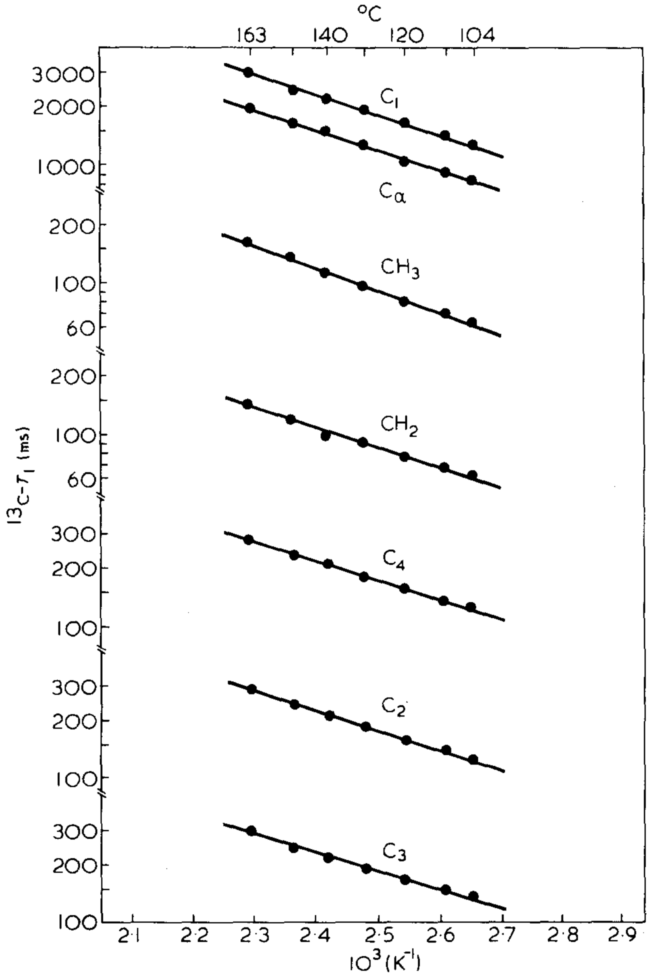

Figure 2 Temperature dependence of ^{13}C T_1 values for syndiotactic poly(α-methylstyrene) in 25% (w/v) solution in *o*-dichlorobenzene-d_4

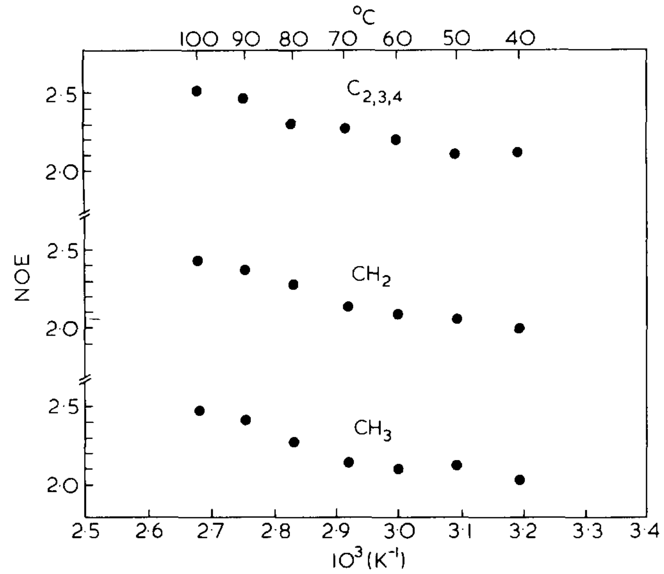

Figure 3 Temperature dependence of NOE values for syndiotactic poly(α-methylstyrene) in 25% (w/v) solution in toluene-d_8

The methylene carbon of PMS, similar to other related polymers[11,14], is considered to relax only via a dipolar mechanism with the directly attached proton. Assuming that an isotropic reorientational model can apply to describe a backbone segmental motion, ^{13}C T_1 is given by[16]:

$$\frac{1}{NT_1} = \frac{\hbar^2}{10}\gamma_C^2\gamma_H^2 r^{-6}[f(\omega_H-\omega_C)+3f(\omega_C)+6f(\omega_H+\omega_C)] \tag{1}$$

where $f(\omega)=\tau_r/(1+\tau_r^2\omega^2)$, γ_C and γ_H are gyromagnetic ratios for ^{13}C and ^1H, ω_C and ω_H are the Larmor frequencies for ^{13}C and ^1H, respectively, r is the internuclear C–H distance, and τ_r is the single effective rotational correlation time, and N is the number of directly bonded protons. For the methylene carbon of syndiotactic PMS, observed T_1 values ranged from 41 ms at 40°C in toluene-d_8 to 144 ms at 163°C in *o*-dichlorobenzene-d_4. According to equation (1), values of correlation time τ_r are calculated from these T_1 values to be 0.66 ns and 0.16 ns, respectively. The corresponding NOE values predicted from isotropic reorientational model are theoretical maximum (2.988). The measured NOE values (1.98 and 2.79) are considerably smaller than the values predicted. Thus the assumption of isotropic reorientation with single correlation time is inadequate and a distribution of correlation times is suggested to characterize the backbone segmental motion in PMS. This situation has been found to be the case in many polymers[1,7,14,17].

Here we tried to interpret the observed relaxation data T_1 and NOE in terms of three models: (I) the empirical Cole–Cole distribution of correlation times[6,14,17], which is symmetrical about average correlation time τ_0 and is governed by τ_0 and width parameter γ lying in the range 0–1 with 1 being equivalent to a single correlation time model; (II) log-χ^2 distribution of correlation times[7,14], which is unsymmetrical about τ_0 with a tail toward long correlation times and is characterized by τ_0 and width parameter p with $p>100$ being practically equivalent to a single correlation time model; (III) the conformational jump model with the non-exponential correlation function[8], which requires two correlation times ρ and θ, the former characterizing the three-bond jump process in an ideal diamond lattice and the latter reflecting either slower modes of subchains or departure of the real chain from the ideal lattice. For the conformational jump model the crucial factor is the ratio ρ/θ. If $\rho/\theta \geqslant 10$, the model reduces effectively to the single correlation time model. The width parameter p can be related to motional cooperativity[7,14].

These models were applied to the T_1 and NOE data for the methylene carbon and model parameters obtained which gave simultaneous good fits of two relaxation data T_1 and NOE are listed in *Tables 1* and *2*. In these Tables, the effective correlation times estimated by using equation (1) are also listed for a comparison. Within experimental error, the relaxation data T_1 and NOE in two solvents over the wide temperature range examined can be interpreted in terms of either the Cole–Cole and log-χ^2 distributions of correlation times or a conformational jump model of chain dynamics. We cannot judge at present which model is the most adequate to describe the segmental motion of the methylene carbon.

To judge the adaptability of these models, it is necessary to test an ability of obtained model parameters to reproduce independent measurements, e.g., T_2 observed at the same frequency or T_1 and NOE observed at well separated frequencies. In spite of these circumstances, we can discuss some characteristics of the segmental motion of syndiotactic PMS, based on these model parameters. The values of the distribution parameters listed are subject to error because of the difficulty in measuring ^{13}C NOE values accurately and the uncertainty in C–H bond lengths. In spite of these restrictions, clear trends emerge in the temperature dependence of the model parameters.

For both the Cole–Cole and log-χ^2 distribution models, the width parameters increase unsystematically and the average correlation times decrease constantly with increase in temperature. In other words, the segmental motion of PMS at higher temperature is characterized by a narrower and more symmetric distribution and shorter average correlation time than those at lower temperature. Thus at higher temperature the long-range cooperative motions become less important. The same temperature dependence has also been found for many polymers[1]. The width parameters and the average correlation times are

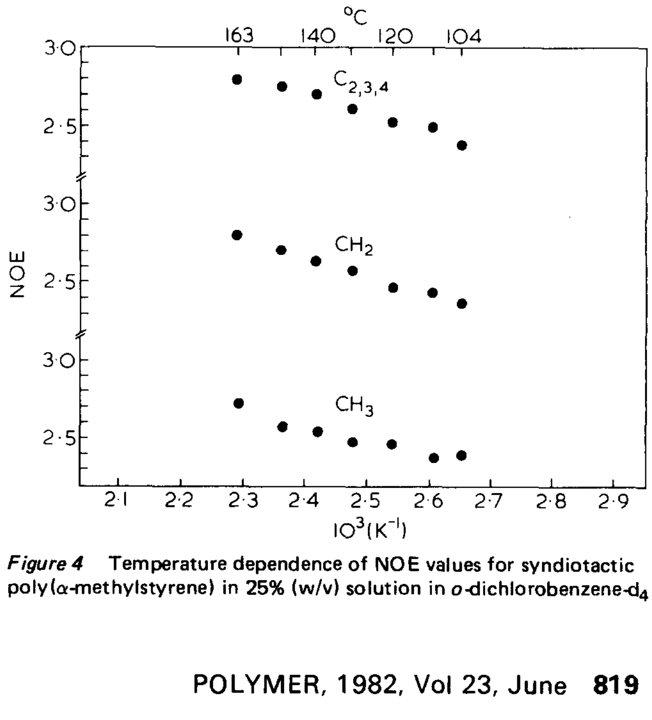

Figure 4 Temperature dependence of NOE values for syndiotactic poly(α-methylstyrene) in 25% (w/v) solution in *o*-dichlorobenzene-d_4

Table 1 Experimental ^{13}C relaxation parameters, T_1 and NOE, model parameters and relaxation parameters predicted from them, and activation energies for methylene carbon of syndiotactic poly(α-methylstyrene) in toluene-d_8

Temperature (°C)	Experimental		Cole–Cole distribution				log-χ^2 distribution*			
	$2T_1$ (ms)	NOE	τ_0 (ns)	γ	$2T_1$ (ms)	NOE	τ_0 (ns)	p	$2T_1$ (ms)	NOE
40	82.0	1.98	1.05	0.57	82.0	1.94	1.26	10	82.1	1.94
50	94.2	2.06	0.603	0.57	94.1	2.04	0.692	10	94.7	2.03
60	111.4	2.08	0.355	0.57	111.2	2.12	0.398	10	111.8	2.10
70	121.2	2.13	0.275	0.57	121.9	2.16	0.316	10	120.9	2.13
80	140.2	2.27	0.200	0.61	140.7	2.27	0.209	12	140.0	2.23
90	162.2	2.36	0.158	0.65	162.5	2.37	0.158	15	161.6	2.34
100	181.4	2.41	0.135	0.67	181.5	2.42	0.132	17	182.1	2.41
Activation energy (kJ mol^{-1})			33				36			

Temperature (°C)	Conformational jump model					Single correlation time model
	ρ (ns)	ρ/θ	θ (ns)	$2T_1$ (ms)	NOE	τ (ns)
40	0.631	0.10	6.31	82.6	1.96	0.661
50	0.398	0.07	5.69	95.1	2.04	0.550
60	0.240	0.04	6.00	111.9	2.08	0.451
70	0.200	0.04	3.61	140.9	2.26	0.347
80	0.145	0.04	3.61	140.9	2.26	0.347
90	0.110	0.04	2.74	163.3	2.38	0.297
100	0.0912	0.04	2.28	181.6	2.46	0.263
Activation energy (kJ mol^{-1})	32		24			15

* Log base (parameter *b* in Schaefer's equation[7]) assumed to be 1000

Table 2 Experimental ^{13}C relaxation parameters, T_1 and NOE, model parameters and relaxation parameters predicted from them, and activation energies for methylene carbon of syndiotactic poly(α-methylstyrene) in *o*-dichlorobenzene-d_4

Temperature (°C)	Experimental		Cole–Cole distribution				log-χ^2 distribution*			
	$2T_1$ (ms)	NOE	τ_0 (ns)	γ	$2T_1$ (ms)	NOE	τ_0 (ns)	p	$2T_1$ (ms)	NOE
104	129.4	2.35	0.263	0.68	128.2	2.35	0.251	20	131.0	2.36
110	138.8	2.43	0.240	0.72	138.4	2.44	0.229	22	138.9	2.41
120	157.4	2.46	0.195	0.73	157.8	2.48	0.182	22	158.6	2.46
130	186.0	2.56	0.166	0.77	184.3	2.57	0.145	25	188.2	2.55
140	197.6	2.63	0.158	0.80	199.4	2.63	0.138	27	198.1	2.59
150	239.2	2.70	0.132	0.83	241.4	2.70	0.115	32	238.1	2.69
163	288.4	2.79	0.118	0.87	288.4	2.78	0.100	40	286.6	2.79
Activation energy (kJ mol^{-1})			19				22			

Temperature (°C)	Conformational jump model					Single correlation time model
	ρ (ns)	ρ/θ	θ (ns)	$2T_1$ (ms)	NOE	τ (ns)
104	0.209	0.08	2.61	130.5	2.36	0.380
110	0.195	0.08	2.43	139.3	2.40	0.352
120	0.145	0.07	2.07	156.2	2.47	0.307
130	0.110	0.07	1.57	185.7	2.60	0.257
140	0.100	0.07	1.43	197.6	2.65	0.241
150	0.0797	0.07	1.13	237.5	2.72	0.198
163	0.0603	0.07	0.861	289.0	2.82	0.163
Activation energy (kJ mol^{-1})	30		26			19

* Log base (parameter *b* in Schaefer's equation[7]) assumed to be 1000

approaching those expected from single correlation time model, but the absolute values of width parameters even at the highest temperature (163°C in *o*-dichlorobenzene-d_4, $\gamma = 0.87$, $p = 40$) are still significantly smaller than the values expected for single correlation time model ($\gamma = 1$, $p > 100$). The correlation times ρ and θ for the conformational jump models also decrease gradually with temperature. The ratios ρ/θ are less than unity, which is reasonable since it is expected that the correlation time for small-scale, limited local motions will be less than that for larger scale reorientation[17].

In the lower temperature range up to 70°C in toluene-d_8, the width parameters for the Cole–Cole and log-χ^2 distribution models are constant ($\gamma = 0.57$ and $p = 10$, respectively) and the average correlation times decrease gradually with increasing temperature. The values of width parameters show that the distributions of correlation times are relatively wide and the long-range cooperative motions are important at lower temperature.

Comparing these parameters with those obtained for related polymers, Heatley and Begum[17] analysed ^{13}C T_1 and NOE values for atactic polystyrene ($M_w = 110\,000$) in pentachloroethane and predominantly syndiotactic poly(methylmethacrylate) ($M_n = 90\,000$) in *o*-dichlorobenzene. The width parameters (γ,p) at 30° and 50°C reported by them are as follows: polystyrene at polymer concentrations 100 and 400 mg ml^{-1}, (γ, p) = (0.72, 20): poly(methylmethacrylate) at polymer concentration 100 mg ml^{-1}, (γ, p) = (0.57, 8–10) and at 400 mg ml^{-1}, (γ, p) = (0.55, 8). Thus the width parameters for syndiotactic PMS are in reasonable agreement with the values for syndiotactic poly(methylmethacrylate) rather than those for atactic polystyrene. Similar trends can also be found in model parameters of the conformational jump model. The values of ratio ρ/θ for syndiotactic PMS range from 0.04 to 0.10 over a temperature range between 40° and 163°C and are very close to those for syndiotactic poly(methylmethacrylate) which range from 0.025 to 0.10 depending on the temperature (30°–162°C) and the polymer concentration[17]. The corresponding values for atactic polystyrene (from 0.1 to 1.5 depending on the temperature 30°–127°C, polymer concentration and polymer molecular weight[17]) are significantly higher than those for PMS and poly(methylmethacrylate). All parameters show that the characteristic of segmental motion of syndiotactic PMS resembles poly(methylmethacrylate) rather than polystyrene. The relaxation parameters of polymers depend on the solvents, temperature and concentrations employed, hence distribution parameters obtained in different conditions cannot be compared directly. However, distribution parameters estimated for the same or closely related polymers in a variety of solvents and concentrations reported by several authors are in general agreement[1].

Examination of conformational structures of polymers provides a reasonable explanation of the observations, since the chain flexibility is strongly affected by the chemical structure. Poly(α-methylstyrene) and poly(methylmethacrylate) are geminal di-substituted vinyl polymers with bulky ester or phenyl and methyl as pendant groups, whereas polystyrene is mono-substituted polymer with relatively high chain flexibility and possessing stable conformations experiencing weak nonbonded forces among three polymers. According to the results of conformational analysis[18–22], the conformational maps for meso and racemic dyads of poly(α-methylstyrene) and for those of poly(methylmethacrylate) have a striking resemblance, but they are clearly different from those for meso and racemic dyads of polystyrene. Polystyrene possesses many accessible conformations in which energy barriers to overcome for conformational transformation are very low, whereas all conformations acceptable to poly(α-methylstyrene) and poly(methylmethacrylate) have some steric severeness to induce a segmental rotation. The higher barriers to segmental motion may lead to a greater extent of cooperative motions of segment and hence a wider distribution of correlation times.

Logarithmic plots of correlation times (average correlation time τ_0 for Cole–Cole and log-χ^2 distribution models, ρ and θ for jump model, and τ for single correlation model) against reciprocal temperature were observed to be essentially linear, and they yielded the values of apparent activation energy ΔE. The results are also shown in *Tables 1* and *2*. The ΔE values, except for average τ_0 for distribution models in *o*-dichlorobenzene-d_4, are comparable in magnitude with those of structurally related polymers such as polystyrene and poly(methylmethacrylate)[1,17]. The reason for the exceptionally low ΔE values for distribution models in *o*-dichlorobenzene-d_4 is not clear at present. The ΔE values for ρ, θ, and τ in *o*-dichlorobenzene-d_4 compare well with those in toluene-d_8.

Phenyl group motion. ^{13}C T_1 values of C_2, C_3, and C_4 are equal to one another and approximately twice those for backbone methylene carbon, within experimental error, over the full temperature range examined. Although the *para* carbon C_4 is located in the phenyl ring, its relaxation time is unaffected by the internal rotation of phenyl group since the C_4–H bond is collinear with the rotation axis C_α–C_1. Thus the agreement of the NT_1 values for the backbone methylene and C_4 carbons is consistent, if the backbone and C_4 carbons have the same autocorrelation function. The equality of the T_1 values of C_2, C_3, and C_4 means that the internal rotation of the phenyl ring around C_α–C_1 axis does not contribute to the relaxation of C_2 and C_3 carbons even at higher temperature. According to Woessner's formula[23] for the spin–lattice relaxation time of a group which is undergoing internal rotation while attached to a molecule with isotropic rotational reorientation, an internal rotation of phenyl ring occurs with correlation time which is larger than about three times the correlation time for segmental reorientation, but does not contribute to the relaxation of C_2 and C_3. The values of correlation time for backbone methylene carbon of PMS are in the range of 10^{-10}–10^{-9} s. The correlation time for the internal motion of phenyl ring should be larger than 10^{-9} s, which is approximately one order larger than those of polystyrene[2] and poly(2-vinylpyridine)[3]. The crowded backbone of PMS with bulky side chains results in severe steric hindrance to the internal motion of phenyl ring and the contribution from the internal motion to the relaxation of phenyl carbons may be overshadowed by the backbone segmental reorientation.

In the plots of the values of spin–lattice relaxation time, NOE, and line width for the aromatic carbons of syndiotactic PMS against temperature, any transitional change such as found in those of polystyrene[2] and poly(2-vinylpyridine)[3] does not appear. The transitional changes in slope of the plots for both polystyrene and poly(2-vinylpyridine) were attributed to the modal change in internal rotation of the aromatic group: the internal rotation is restricted within narrow range below specific temperature, while above this, more free rotation is allowed. In the case of PMS steric hindrance brought about by the interaction with bulky methyl and phenyl groups should be too high for the phenyl ring to rotate freely even at higher temperature. The non-linear temperature dependences of ^{13}C spin lattice relaxation time was observed for α-methylstyrene hexane and -decane copolymers[10]. In these copolymers the steric hindrance to the internal rotation of phenyl group may be lowered by the introduction of alkane chain into the polymer backbone.

Our observation of linear temperature dependences of ^{13}C relaxation parameters contrasts with the results obtained by ^{1}H n.m.r. spectra. The line width of phenyl

Table 3 ^{13}C NT_1 of syndiotactic poly(α-methylstyrene) in toluene-d_8 and *o*-dichlorobenzene-d_4 solutions

	Toluene-d_8			*o*-Dichlorobenzene-d_4		
Temperature (°C)	$2T_1$ (CH_2) (ms)	$3T_1$ (CH_3) (ms)	Ratio*	$2T_1$ (CH_2) (ms)	$3T_1$ (CH_3) (ms)	Ratio*
80	140.2	168.0	1.20	–	–	–
90	162.2	198.9	1.23	–	–	–
100	181.4	221.7	1.22	–	–	–
104	–	–	–	129.5	187.5	1.44
110	–	–	–	138.8	204.3	1.47
120	–	–	–	157.4	237.6	1.51
130	–	–	–	186.0	285.9	1.53

* [$3T_1$ (CH_3)]/[$2T_1$ (CH_2)]

proton resonances of PMS was reported to change rapidly within the relatively narrow temperature range of 70°–100°C[24]. This was, however, based on the artificially decomposed aromatic proton resonances observed at 60 MHz which are unresolved and broad due to the overlapping of unequivalent *ortho*, *meta*, and *para* proton resonances with small chemical shift separation and with splitting due to spin–spin coupling and stereoirregular structure[25]. Thus, the result of proton resonance is doubtful.

Methyl group motion. From *Figures 1* and *2* it can be seen that the slope of the temperature dependence of ^{13}C T_1 for the methyl carbon is slightly larger than that for the methylene carbon and T_1 values for the former are always larger than two-thirds of those for the latter, showing the evidence of rapid internal rotation of the methyl group which effectively lengthens the spin–lattice relaxation times. *Table 3* lists several NT_1 values of methylene and methyl carbons observed in toluene-d_8 and *o*-dichlorobenzene-d_4 solutions. The NT_1 values of both methylene and methyl carbons observed in toluene-d_8 are markedly larger than those in *o*-dichlorobenzene-d_4 at comparable temperature (100°C in toluene-d_8 and 104°C in *o*-dichlorobenzene-d_4). These differences are attributable to those in solvent viscosity[26].

It is of great interest to note the ratio of NT_1 value for the side chain methyl carbon relative to that for the backbond methylene carbon. The values of ratio are also shown in *Table 3*, which clearly shows the dependence of NT_1 values on the nature of solvent other than viscosity. Although the NT_1 values of methylene carbon in toluene-d_8 at 80°, 90°, and 100°C are nearly equal to those in *o*-dichlorobenzene-d_4 at 104°, 120°, and 130°C, respectively, the ratios in *o*-dichlorobenzene-d_4 are about 1.5 and are always larger than those in toluene-d_8 (about 1.22). This implies that the intramolecular steric barrier for the internal rotation responsible for carbon-13 relaxation is larger in toluene-d_8 than in *o*-dichlorobenzene-d_4. The difference in relative mobility of methyl group suggests that the conformation of the syndiotactic PMS in toluene-d_8 is different from that in *o*-dichlorobenzene-d_4. It is reasonable to assume that the different type of solvent stabilizes different sets of polymer conformation. The solvent dependences of the conformations have also been suggested for poly(methylmethacrylate) and polystyrene from the measurement of ^{13}C T_1 value[27,28]. However, many other experimental studies are required before firm conclusions can be drawn.

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