Configuration dependence of carbon-13 spin-lattice relaxation times of poly(α-methylstyrene)

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Carbon-13 n.m.r. spin-lattice relaxation times have been measured for atactic poly(α-methylstyrene) in 25% (w/v) solution in *o*-dichlorobenzene-d_4 as a function of temperature from 100° to 163°C and the results were compared with those for a syndiotactic poly(α-methylstyrene). It was concluded that the carbon-13 spin-lattice relaxation time is dependent on the stereochemical configuration over a relatively short range, but is not sensitive to longer range effects.

Keywords Poly(α-methylstyrene); configuration; carbon-13 nuclear magnetic resonance; spin-lattice relaxation time; tacticity

INTRODUCTION

Recently the chain dynamics of a variety of macromolecules have been examined by ^{13}C n.m.r. relaxation measurements[1]. In a previous paper we reported on the ^{13}C relaxation parameters of syndiotactic poly(α-methylstyrene) (PMS) in solution over the temperature range 40° to 163°C and we found that the characteristics of segmental motion of syndiotactic PMS resembles those of syndiotactic poly(methyl methacrylate) (PMMA) rather than those of atactic polystyrene (PS)[2]. Both PMMA and PMS have two geminally substituted bulky pendant groups on the backbone carbon. Since distinct dependences of the ^{1}H and ^{13}C spin-lattice relaxation times (T_1) on stereochemical configuration have been found in PMMA[3-9], it is interesting to investigate the configuration dependence of the ^{13}C T_1 of PMS. In this report we will investigate the ^{13}C T_1 values of atactic PMS and compare these values with those of syndiotactic PMS.

EXPERIMENTAL

The atactic PMS used here was prepared with the sodium salt of an α-methylstyrene tetramer dianion as an initiator in tetrahydrofuran at −78°C, and its number- and weight-average molecular weight were $\bar{M}_n = 6.24 \times 10^4$ and $\bar{M}_w = 9.04 \times 10^4$, respectively. The triad tacticity determined from 100 MHz methyl proton resonance was 43% syndiotactic, 48% heterotactic, and 9% isotactic. The characterization of syndiotactic PMS (triad tacticity: 88% syndiotactic, 12% heterotactic, and practically 0% isotactic) and the details of the ^{13}C T_1 measurements were shown in the previous paper[2].

RESULTS AND DISCUSSION

In *Figure 1* the temperature dependences of the ^{13}C T_1 values for the various carbons of atactic PMS over the temperature range 100° to 163°C in 25% (w/v) solution in *o*-dichlorobenzene-d_4 measured at frequency of 25.1 MHz are shown. The assignments of syndiotactic(rr), heterotactic(mr), and isotactic(mm) triads of the aromatic C-4 carbon resonance have been reported[10]. The T_1 value for the C-4 carbon in the isotactic triad sequence could not be measured accurately due to low signal to noise ratio and is therefore not included in *Figure 1*. Since the

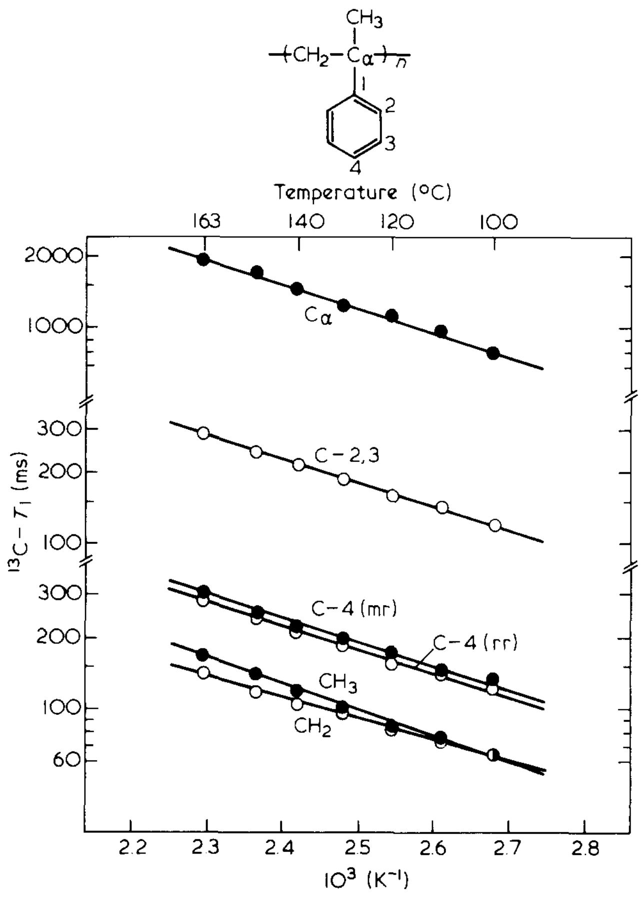

Figure 1 Temperature dependence of ^{13}C T_1 values for atactic poly(α-methylstyrene) in 25% (w/v) solution in *o*-dichlorobenzene-d_4 at 25.1 MHz

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Table 1 ^{13}C Spin-lattice relaxation times T_1 of atactic and syndiotactic poly(α-methylstyrene) samples in 25% (w/v) solution in *o*-dichlorobenzene-d_4 at 25.1 MHz

Temperature (°C)	Spin-lattice relaxation times (ms)						
	Aromatic C-4			Methylene		Methyl	
	Syndio	Atactic		Syndio	Atactic	Syndio	Atactic
		rr	mr				
100	–	121	135	–	64	–	64
104	129	–	–	65	–	63	–
110	137	140	148	69	76	68	74
120	155	156	172	79	83	79	84
130	178	184	198	93	95	95	102
140	212	207	223	99	104	112	119
150	233	240	257	120	118	134	141
163	281	284	309	144	141	162	166

aromatic C-2 and C-3 carbons and the backbone methylene carbons show resonances with complicated structures in a relatively narrow range of chemical shifts[10,11] and the methyl and the backbone quaternary C_α carbons show less well-resolved broad resonances[10], the total intensity was used for the determination of the T_1 values for these carbons. Thus T_1 values for these carbons are the average values of nuclei in various configurationally different sequences. Although the aromatic C-1 carbon resonance is split into clearly resolved signals[10], T_1 values for this carbon are not shown because the signals are too weak to enable the T_1 values to be measured accurately. ^{13}C T_1 values for all carbons increase linearly with increasing temperature.

The exact ^{13}C T_1 values for atactic PMS are given in *Table 1*. Those of syndiotactic PMS are also shown for comparison. Over the temperature range investigated here, the methylene carbon in the atactic PMS has a T_1 value which is in close agreement with the T_1 value for a methylene in syndiotactic PMS measured at the same temperature. That is to say the configurationally averaged T_1 value of the backbone methylene carbon of PMS is not sensitive to the polymer tacticity. The T_1 values for the aromatic C-2 and C-3 and the backbone C_α carbons in atactic PMS are also in reasonable agreement with the corresponding values for syndiotactic PMS.

Configuration dependences are found for the side chain aromatic C-4 carbon which shows well-resolved triad splitting with high signal to noise ratio in its ^{13}C spectrum. In atactic PMS, the aromatic C-4 carbon in a heterotactic triad sequence(mr) always has longer T_1 values than T_1 values for the C-4 carbon in a syndiotactic sequence(rr), although the differences are comparable with a probable experimental error of $\pm 10\%$ in T_1 values. These differences are not as large as those found in the α-methyl carbon of atactic PMMA in heterotactic and syndiotactic sequences[6], the trend is evident from the data shown in *Figure 1* and *Table 1*. The difference in T_1 values for the α-methyl carbon in the syndiotactic and heterotactic sequences of PMMA was found to be 63%.[3,6] The T_1 value of the C-4 carbon is unaffected by the internal rotation of the phenyl ring around C_α–C-1 bond since the C-4–H bond is colinear with the rotation axis. Thus the configuration dependence of the C-4 carbon's T_1 value may reflect that of the backbone C_α carbon's T_1 value.

The configuration dependence of ^{13}C T_1 values for PMS may be the same as that for PMMA[6,8], polypropylene[12], and poly(vinyl chloride)[13], i.e., ^{13}C T_1 values increase in the order of syndiotactic, heterotactic, and isotactic sequences. The most interesting result is that T_1 values for the C-4 carbon in the syndiotactic sequence of atactic PMS are closer than that for the C-4 carbon in the heterotactic sequence to that for the C-4 carbon of syndiotactic PMS at every temperature. So far as atactic PMS and syndiotactic-rich PMS are concerned, we can conclude that ^{13}C T_1 value is dependent on the stereochemical configuration over a relatively short range, but is not sensitive to long range effects. Thus, whereas heterotactic and syndiotactic triads have different T_1 values for the aromatic C-4 carbon in atactic chains, syndiotactic triads in both atactic and syndiotactic chains have similar T_1 values.

The methyl carbon in atactic PMS also has slightly longer T_1 values than T_1 values for the methyl carbon in syndiotactic PMS over the full temperature range, although the differences are negligible.

If a PMS with high isotacticity is obtainable, a larger difference in ^{13}C T_1 values of carbons in the isotactic and syndiotactic sequences might be observed. Polymerization conditions for obtaining a PMS having a high isotacticity have not yet been found.

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