A ^{1}H nuclear magnetic relaxation study of the mechanism and solvent dependence of the motion of predominantly syndiotactic poly(methyl methacrylate) in dilute solution

Frank Heatley and Michael K. Cox*
Chemistry Department, University of Manchester, Manchester M13 9PL, UK
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^{1}H spin–lattice and spin–spin relaxation times have been measured for individual groups of nuclei in predominantly syndiotactic poly(methyl methacrylate) in dilute solution. The rate of backbone motion is affected by the viscosity and thermodynamic quality of the solvent, whereas the rate of α-methyl internal rotation is less affected by solvent. The relaxation times have been analysed in terms of backbone conformational transitions and methyl rotation.

INTRODUCTION

Several reports of ^{1}H relaxation data[1–4] for syndiotactic poly(methyl methacrylate) (s-PMMA) in solution have been published, but few measurements have been made over an extended range of such experimental variables as temperature, solvent or resonance frequency. Such measurements are imperative for a full understanding of chain dynamics. Gotlib *et al.*[1] have reported composite ^{1}H spin–lattice and spin–spin relaxation times (T_1 and T_2, respectively) for s-PMMA in $CDCl_3$, CCl_4 and toluene-d_8 over wide ranges of temperature, concentration and molecular weight. At concentrations below 10%, T_1 and T_2 were independent of molecular weight above 3×10^4 and independent of concentration, thus establishing the dominance of segmental motions as the origin of magnetic relaxation. The segmental mobility was lower in CCl_4 than in $CDCl_3$ or toluene-d_8 but the extent of hindrance was greater than expected simply on the grounds of the greater viscosity of CCl_4. The enhanced restriction to movement was attributed to the poorer solvent quality of CCl_4. In order to examine further the roles of thermodynamic and viscosity factors, we have studied ^{1}H relaxation of s-PMMA in solution in four good solvents of widely different viscosities (acetone-d_6, $CDCl_3$, toluene-d_8 and nitrobenzene-d_5) and in the poor solvent acetonitrile-d_3 which is of similar viscosity to acetone-d_6. High resolution Fourier Transform techniques have been used to study motions of individual groups of nuclei.

We have also investigated the mechanism of chain motion. In previous papers[5–8], we have shown how the application of a variety of relaxation experiments to a coupled spin system can be used to clarify this problem by probing spectral densities at different frequencies. The techniques used previously such as relaxation under double irradiation[5–7] and selective inversion[8] rely on a significant degree of cross-relaxation between different proton populations, and are therefore not suitable for s-PMMA where the protons are located in three substantially self-relaxing groups. As an alternative we have measured both T_1 and T_2 values for individual signals.

CALCULATION OF RELAXATION TIMES

It has been shown[3] by means of relaxation measurements on selectively deuterated PMMA samples that relaxation contributions from the interactions between the methoxy protons and the methylene and α-methyl protons are small. For the present purposes, it is sufficient to focus attention on the relaxation properties of the methylene/α-methyl spin system.

Spin–lattice relaxation

Denoting the methylene protons by S and the α-methyl protons by X, longitudinal magnetization of the combined system is represented by the equations:

$$\frac{dS_S}{dt} = -\frac{S_S}{T_{SS}} - \frac{S_X}{T_{SX}} \tag{1a}$$

$$\frac{dS_X}{dt} = -\frac{S_X}{T_{XX}} - \frac{S_S}{T_{XS}} \tag{1b}$$

where S_S and S_X represent the deviations of the longitudinal magnetizations from thermal equilibrium. The relaxation coefficients T_{SS}, T_{SX}, T_{XX} and T_{XS} are given by:

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* Present address: ICI Plastics Division, Welwyn Garden City, Herts., UK

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$$\frac{1}{T_{SS}} = 3K[J(\omega_S) + 4J(2\omega_S)]R_{SS}^{-6} + 6K[J^m(\omega_S - \omega_X) + 3J^m(\omega_S) + 6J^m(\omega_S + \omega_X)] \tag{2a}$$

$$\frac{1}{T_{SX}} = 4K[6J^m(\omega_S + \omega_X) - J^m(\omega_S - \omega_X)] \tag{2b}$$

$$\frac{1}{T_{XX}} = 6K[J^r(\omega_X) + 4J^r(2\omega_X)]R_{XX}^{-6} + 4K[J^m(\omega_S - \omega_X) + 3J^m(\omega_X) + 6J^m(\omega_S + \omega_X)] \tag{2c}$$

$$\frac{1}{T_{XS}} = \frac{3}{2T_{SX}} \tag{2d}$$

where:

$$K = (\mu^0/4\pi)^2\gamma_H^4\hbar^2/10$$

μ^0 is the magnetic permeability of free space ($4\pi \times 10^{-7}$ H m^{-1}) and γ_H is the proton magnetogyric ratio. R_{SS} and R_{XX} are effective internuclear distances (see below). The symbols $J(\omega)$, $J^m(\omega)$ and $J^r(\omega)$ stand for spectral density functions expressing the time dependence of S–S interactions, S–X interactions and X–X interactions, respectively. S–S interactions are modulated by backbone motions only, whereas S–X and X–X interactions are also affected by internal rotation of the α-methyl groups. For backbone motions, we use the autocorrelation function:

$$G(\tau) = \exp(-\tau/\tau_0)\exp(\tau/\tau_D)\,\mathrm{erfc}\,(\tau/\tau_D)^{1/2} \tag{3}$$

derived from a theoretical analysis[9–11] of probable three- and four-bond conformational transitions of an infinitely long polymer chain on a diamond lattice. The correlation time τ_D characterizes three-bond transitions, and the correlation time τ_0 characterizes four-bond motions[10] and other processes[11]. The spectral density $J(\omega)$ resulting from (3) is given by:

$$J(\omega) = {}^1\!/_2 \int_{-\infty}^{+\infty} G(\tau)e^{i\omega\tau}d\tau$$

$$= \frac{\tau_0\tau_D(\tau_0 - \tau_D)}{(\tau_0 - \tau_D)^2 + \omega^2\tau_0^2\tau_D^2}\left\{\left(\frac{\tau_0}{2\tau_D}\right)^{1/2}\left[\frac{(1 + \omega^2\tau_0^2)^{1/2} + 1}{1 + \omega^2\tau_0^2}\right]^{1/2} + \left(\frac{\tau_0}{2\tau_D}\right)^{1/2}\frac{\omega\tau_0\tau_D}{(\tau_0 - \tau_D)}\left[\frac{(1 + \omega^2\tau_0^2)^{1/2} - 1}{1 + \omega^2\tau_0^2}\right]^{1/2} - 1\right\} \tag{4}$$

This function has been used successfully to interpret the temperature and frequency dependence of ^{1}H relaxation in poly(vinyl acetate)[5,6] and polystyrene[7,8,12] and ^{13}C relaxation in polystyrene[12]. A closely related function[13] has been used to analyse ^{1}H relaxation in poly(isobutylene)[14].

The effective internuclear distance for S–S interactions, R_{SS}, incorporates not only the geminal interaction, but also interactions between remote S nuclei[5]. In certain conformations, non-geminal S nuclei are brought into close proximity. The quantity R_{SS}^{-6} was therefore evaluated as a weighted sum of reciprocal sixth powers of S–S distances using the geometrical and conformational structure described by Sundararajan and Flory[15]. R_{SS} was calculated to be 166.3 ± 8 pm, a value supported by determination of the contributions to ^{1}H relaxation in s-PMMA using selectively deuterated polymers[3] (see Discussion).

The spectral density $J^r(\omega)$ appropriate to X–X interactions incorporates a correlation time for α-methyl internal rotation, τ_G, as well as the backbone correlation times τ_0 and τ_D. Jones *et al.*[14] have given the autocorrelation function for internuclear interactions within a freely rotating methyl group attached to a polymer chain undergoing motion according to the limited coupling model of Jones and Stockmayer[13]. However, we suggest that α-methyl rotation in s-PMMA is better represented by random jumps through 120° between three equivalent states, since the barrier to rotation for a methyl group attached to an sp^3 hybridized carbon atom is[16] of the order of 12 kJ mol^{-1}. Making use of the expression given by Woessner *et al.*[17] for the autocorrelation function for methyl rotation by this jump process, and combining this result with equation (4) for backbone motion, following Jones *et al.*[14], we obtain:

$$J^r(\omega) = 1/4[(3\cos^2\Delta - 1)^2F(\omega, \tau_0, \tau_D) + 3(\sin^2 2\Delta + \sin^4\Delta)F(\omega, \tau_J, \tau_D)] \tag{5}$$

where $F(\omega, \tau_0, \tau_D)$ is identical to the function $J(\omega)$ in equation (4) and $F(\omega, \tau_J, \tau_D)$ is equation (4) with τ_J replacing τ_0 and:

$$\tau_J^{-1} = \tau_0^{-1} + \tau_G^{-1}$$

Δ is the angle between the internuclear vector and the axis of internal rotation. Thus for the H–H interaction in a methyl group, $\Delta = 90°$. Equation (5) applies only to intramethyl interactions, but conformational structure calculations show that interactions between protons in different α-methyl groups comprise only approximately 5% of the total X self-relaxation rate. An approximate correction for intermethyl interactions was therefore applied by using a value of 178 pm for R_{XX}, as opposed to the value of 180 pm calculated for the intramethyl H–H distance from the geometry used by Sundararajan and Flory[15].

Interactions between S and X nuclei also involve the three correlation times τ_0, τ_D and τ_G, but a complicating factor is that the internuclear distance between the nuclei varies during the α-methyl rotation. Rowan *et al.*[18] have treated relaxation of this type where a framework proton (S) is equidistant from two methyl protons (X). To analyse relaxation in s-PMMA, we have extended Rowan *et al.*'s theory to the case where the S proton is at different distances from all three methyl protons. Consider first one S proton and one methyl group in a particular chain conformation. Let r_1, r_2 and r_3 be the distances between S and the X protons. Define θ_{ij} as the angle between r_i and r_j.

The spectral density function $J^m(\omega)$ for the interaction between S and one of the X protons is given by:

$$J^m(\omega) = {}^1\!/_2[\alpha F(\omega, \tau_0, \tau_D) + \beta F(\omega, \tau_J, \tau_D)] \tag{6}$$

where the functions $F(\omega, \tau_0, \tau_D)$ and $F(\omega, \tau_J, \tau_D)$ are defined as in equation (5), and the quantities α and β are given by:

$$\alpha = 2/9 \left[\sum_{i=1}^{3} r_i^{-6} + \sum_{i=1}^{2} \sum_{j>i} (3\cos^2\theta_{ij} - 1) r_i^{-3} r_j^{-3} \right] \quad (7a)$$

$$\beta = 2/9 \left[2\sum_{i=1}^{3} r_i^{-6} - \sum_{i=1}^{2} \sum_{j>i} (3\cos^2\theta_{ij} - 1) r_i^{-3} r_j^{-3} \right] \quad (7b)$$

To take account of the chain flexibility, α and β were averaged over all significant conformations, giving values:

$$\alpha = 1.327 \times 10^{-15}\ \mathrm{pm}^{-6}$$

$$\beta = 7.176 \times 10^{-16}\ \mathrm{pm}^{-6}$$

As in previous papers[5–8], effective spin–lattice relaxation times, T_{1S} and T_{1X}, were defined by a least-squares fit to an exponential function of the initial 75% of the recovery curves for S_S and S_X calculated from the solution of the coupled differential equations (1a) and (1b).

Spin–spin relaxation

In a spin-coupled system, all groups of nuclei relax with the same average spin–spin relaxation time when the π pulse repetition frequency in the Carr–Purcell experiment is much greater than the chemical shift[19]. The averaging arises because sufficiently rapid repetition of the π pulses suppresses differential precession in the rotating frame, thus rendering all nuclei effectively equivalent. However, spin coupling between S and X protons in s-PMMA is negligible, and the S and X spin–spin relaxation times, T_{2S} and T_{2X} are distinct (see Results below). Individual values of T_{2S} and T_{2X} were calculated using the following expressions:

$$\frac{1}{T_{2S}} = \frac{3}{2} K[3J(0) + 5(\omega_S) + 2J(2\omega_S)] R_{SS}^{-6} + 9K[3J^m(0) + 5J^m(\omega_S) + 2J^m(2\omega_S)] \quad (8a)$$

$$\frac{1}{T_{2X}} = 3K[3J^r(0) + 5J^r(\omega_X) + 2J^r(2\omega_X)] R_{XX}^{-6} + 6K[3J^m(0) + 5J^m(\omega_X) + 2J^m(2\omega_X)] \quad (8b)$$

EXPERIMENTAL

The sample of s-PMMA was supplied by the Rubber and Allied Products Research Association, Shrewsbury, UK. M_w was 140 000 and M_w/M_n was 2.1. Its structure was predominantly syndiotactic, the dyad placements obeying Bernoullian statistics with a *meso* dyad placement probability, P_m, of ~0.2. Deuterated solvents were supplied by Fluorochem Ltd, Glossop, UK (acetone, chloroform and toluene), Aldrich Chemical Company Ltd, Gillingham, UK (nitrobenzene) and Nuclear Magnetic Resonance Ltd, High Wycombe, UK (acetonitrile). All solutions were degassed and sealed *in vacuo*. 1% solutions were used to minimize intermolecular interactions.

Relaxation times were obtained at 300 MHz on a Varian Associates SC-300 spectrometer and at 80 MHz on a Bruker Spectrospin WP-80 spectrometer. T_1 was measured using the inversion recovery sequence. T_2 was measured using the Meiboom–Gill modification[20] of the Carr–Purcell spin–echo sequence[21] $[\pi/2–(t - \pi - t)_n–\text{echo}]$. The decay of the transverse magnetization of individual groups was followed by varying the number of π pulses, n, with a fixed value for t of 0.5 ms, and Fourier transforming the second half of the spin–echo[22]. Repetition of a few measurements with t = 0.15 ms gave unchanged values of T_2. Short samples of length 1 cm or less were used to minimize temperature gradients and to maximize B_1 field homogeneity. The reliability of the T_2 measurements was verified by demonstrating that in the mobile system poly(ethylene oxide) where the extreme narrowing condition is fulfilled, T_1 and T_2 were equal within experimental error. Experimental errors in T_1 and T_2 were less than 5%.

RESULTS

The high-field ^{1}H spectrum of predominantly syndiotactic PMMA similar to the sample used in this work has been reported elsewhere[23]. Even at low temperatures, it was possible to resolve tetrads in the methylene region, and triads in the α-methyl region. The data reported here for S and X peaks are for the *rrr* tetrad in the methylene region and for the *rr* triad in the α-methyl region.

Figure 1 shows spin–lattice and spin–spin relaxation times for the S, X and methoxyl signals for a 1% solution of s-PMMA in toluene-d_8 at 300 MHz as a function of temperature. All T_1 curves pass through a minimum. There is no evidence of equalization of spin–lattice relaxation times at low temperatures due to appreciable cross-relaxation. The methoxyl T_1 is much larger than T_{1S} or T_{1X} because of the greater rotational mobility about C–O bonds. The fact that at the higher temperatures T_{1X} is slightly greater than T_{1S}, and that the minimum in T_{1X} occurs at a slightly lower temperature than the minimum for T_{1S} indicates a modest degree of internal rotation of the α-methyl group.

Both T_{2S} and T_{2X} vary monotonically with temperature, with similar activation energies. On the high temperature side of the T_1 minima, the T_2 curves approach the corresponding T_1 curves, indicating that high-frequency motions average dipolar interactions almost completely. Measurements on a 5% (w/v) solution in toluene-d_8 gave identical results to the 1% solution.

Figure 2 shows the solvent dependence of T_{1S} and T_{1X}. Four of these solvents, acetone, chloroform, toluene and nitrobenzene, are 'good' in the sense that the exponent of molecular weight in the intrinsic viscosity–molecular weight relationship lies in the region of 0.7 to 0.8[24]. The fifth solvent, acetonitrile, is a θ-solvent for s-PMMA at 30°C [24]. The viscosities at 20°C are (mPa s)[25]: acetone, 0.327; acetonitrile, 0.360; chloroform, 0.580; toluene, 0.590; nitrobenzene, 2.03.

The graphs of T_{1S} for all five solvents are similar in shape but they are displaced laterally along the temperature axis. It is significant that the minimum value of T_{1S} is the same for all solvents; this indicates that the nature of the motion is essentially unaffected by the solvent, since the depth of the T_1 minimum is a sensitive indicator of the distribution

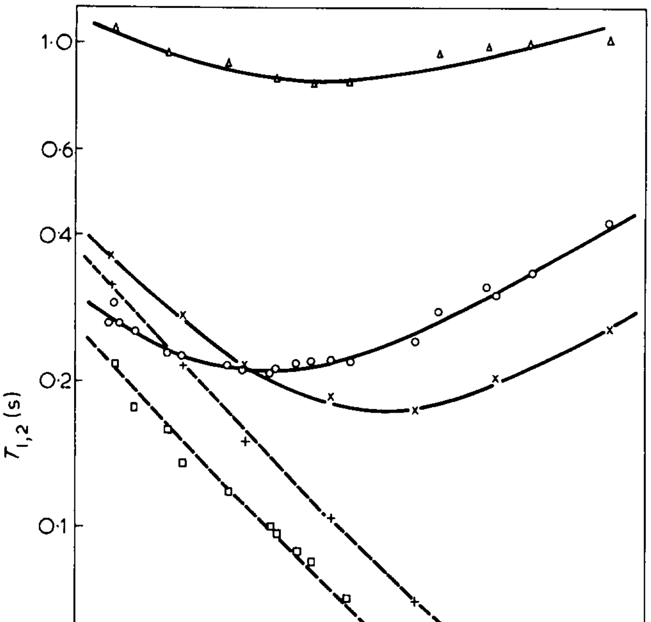

Figure 1 ^{1}H relaxation times at 300 MHz for a 1% solution of s-PMMA in toluene-d_8. △, methoxyl T_1; ○, T_{1S}; □, T_{2S}; x, T_{1X}; +, T_{2X}

of motional processes between high and low frequency modes[5]. Within the range of good solvents employed, the backbone mobility as monitored by T_{1S} appears to be controlled by solvent viscosity, since the graphs are displaced to higher temperatures in order of increasing viscosity. The curve for acetonitrile is anomalous in that the relaxation times correspond to those expected for a good solvent of higher viscosity. Presumably the hindrance to segmental transitions is increased by a more compact coil conformation adopted in a poorer solvent. Similar behaviour has been observed for the solvent dependence of ^{1}H relaxation times in polystyrene[7].

The solvent dependence of T_{1X} (*Figure 2b*) shows a pattern similar to that of T_{1S}, but with two significant differences. Firstly, the shift in temperature of the minimum in T_{1X} with increase in solvent viscosity is not as great as for T_{1S}. In acetone-d_6, the minima in T_{1S} and T_{1X} lie at 65° and 45°C, respectively, a difference of 20°, whereas in nitrobenzene-d_5, the minima in T_{1S} and T_{1X} lie at 130° and 70°C, respectively, a difference of 60°C. Secondly, the minimum value of T_{1X} increases measurably with increasing solvent viscosity. A reasonable explanation of these observations is that T_{1X} is determined by two processes, solvent-dependent backbone motions and solvent-independent α-methyl internal rotation. The two processes are not sufficiently different in frequency to produce two distinct minima in T_{1X}, but the location of the composite minimum does depend on the extent of overlap. The variation of T_{2S} and T_{2X} with solvent is similar to that of T_{1S} and T_{1X}.

In order to express the rate of molecular motion quantitatively in terms of correlation times, we have followed the procedure used in previous papers[5,7]. The correlation time τ_D and the ratios τ_D/τ_0 and τ_G/τ_D were chosen as variables, and calculations of T_{1S}, T_{1X}, T_{2S} and T_{2X} were made as described above for a wide range of these parameters. For particular values of the ratios of correlation times, that value of τ_D which reproduced the value of T_{1S} at 300 MHz at each temperature and solvent was obtained, and used together with the specified ratios to calculate the remaining relaxation times, which were compared with the experimental values. The ability of the assumed motional model to simulate the frequency dependence of relaxation times was checked by including in this comparison values of T_{1S} at 80 MHz for the solution in toluene-d_8. The comparison of calculated and experimental data for the toluene-d_8 solution is shown in *Figures 3–6*.

The calculations showed that T_{1S} and T_{2S} are essentially independent of the ratio τ_G/τ_D except at temperatures below ~30°C for 300 MHz data and below 15°C for 80 MHz data. For the simulations of T_{2S} at 300 MHz (*Figure 3*) and T_{1S} at 80 MHz (*Figure 4*), τ_G/τ_D was therefore held constant at the value 1.0; these Figures show that the optimum value of the ratio τ_D/τ_0 is ~0.7 at all temperatures. T_{1X} and T_{2X} at 300 MHz were simulated by holding τ_D/τ_0 constant at 0.7 and allowing τ_G/τ_D to vary. *Figures 5* and *6* show that the optimum value of τ_G/τ_D is ~0.4 The same treatment of data for other solutions produced simulations of similar quality. The best-fit parameters for solutions in acetone-d_6, toluene-d_8, nitrobenzene-d_5 and acetonitrile-d_3 are given at various temperatures in *Table 1*. The correlation times in $CDCl_3$ are essentially the same as those in toluene-d_8. Activation energies are given in *Table 2*.

Uncertainties in the derived correlation times arise from two sources, random experimental errors and systematic uncertainties in the internuclear distances. The random

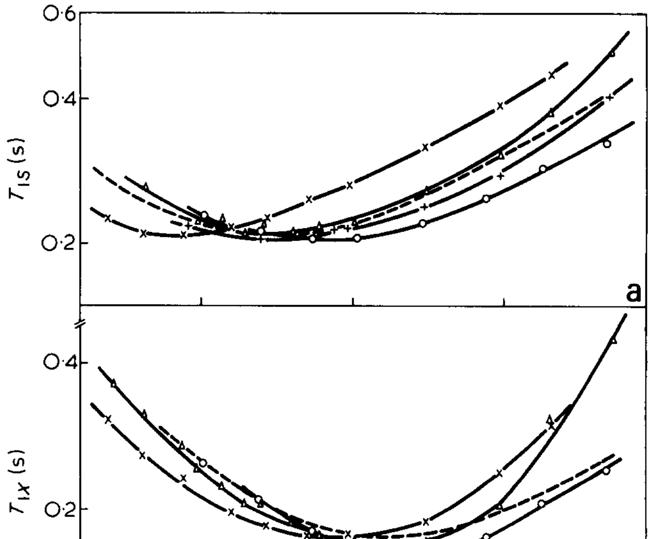

Figure 2 Solvent dependence of (a) T_{1S} and (b) T_{1X} at 300 MHz for 1% solutions of s-PMMA. ○, Acetone-d_6; +, $CDCl_3$; △, CD_3CN; x, nitrobenzene-d_5; — — — — —, toluene-d_8 (from *Figure 1*)

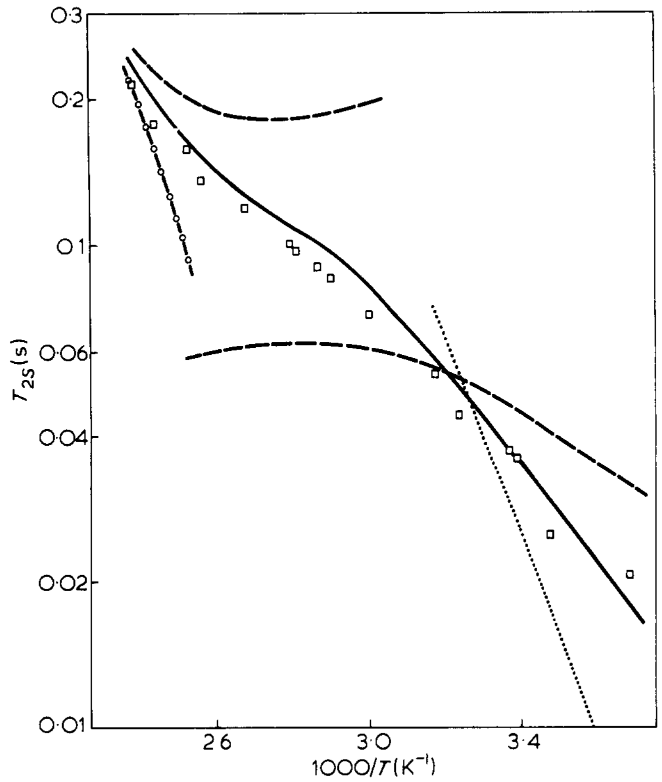

Figure 3 Simulation of T_{2S} at 300 MHz in toluene-d_8 as described in text. The lines are predicted for the following values of τ_D/τ_0: — — — — —, τ_D/τ_0 = 10; ———, τ_D/τ_0 = 0.7; — ○ — ○ —, τ_D/τ_0 = 0.3; . . . . . ., τ_D/τ_0 = 0.1. τ_G/τ_D is 1.0 for all curves. The symbols are experimental values

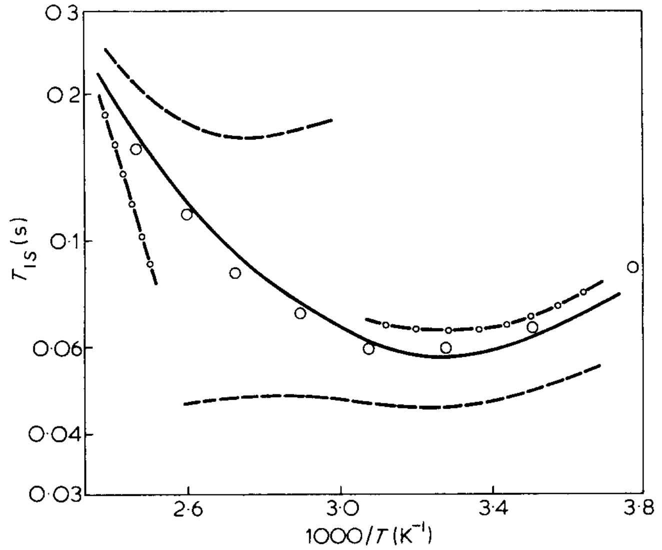

Figure 4 Simulation of T_{1S} at 80 MHz in toluene-d_8. Legend as for *Figure 3*

experimental errors are relatively small, and result in errors of approximately 20% in the correlation times. The uncertainties in estimating effective internuclear distances are more important, although the effect is mitigated by the fact that the major relaxation contributions are between geminal nuclei whose separation is known quite accurately. It is estimated that after taking reasonable uncertainties in the internuclear distances of 1% in the geminal separations and 7% in the non-geminal separations, the acceptable range for the ratio τ_D/τ_0 for all solutions is 0.5 to 2 at the lower temperatures and 0.4 to 1.5 at the higher temperatures. Uncertainties in τ_D amount to ~+50%, –30%. The acceptable range of τ_G/τ_D varies with solvent. For acetone-d_6, it is estimated to be 0.5 to 1.5, for toluene-d_8, $CDCl_3$ and CD_3CN 0.2 to 0.7, and for nitrobenzene-d_5 0.1 to 0.3. We stress that the wide uncertainty range for the correlation time arises from *systematic* uncertainties in the internuclear distances. It is significant therefore that the limits of the ratio τ_D/τ_0 are essentially independent of solvent (though τ_D and τ_0 themselves vary) whereas the limits of the range for τ_G/τ_D decrease with increasing solvent vis-

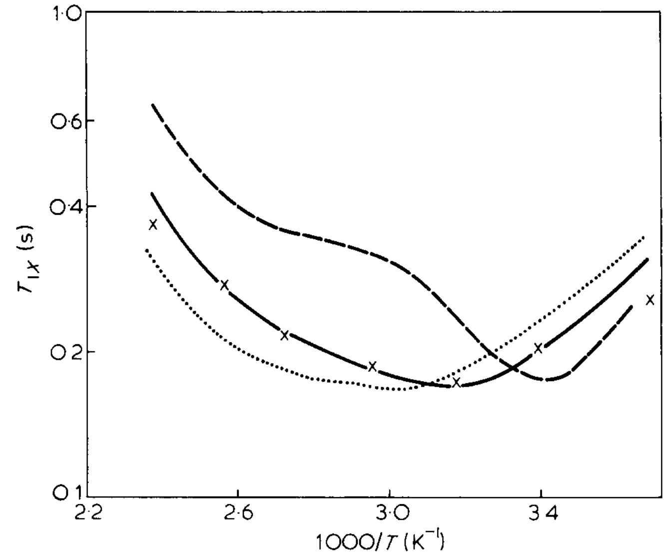

Figure 5 Simulation of T_{1X} at 300 MHz in toluene-d_8 as described in the text. The lines are predictions for the following values of τ_G/τ_D: — — — —, τ_G/τ_D = 1.0; ———, τ_G/τ_D = 0.4; . . . . . ., τ_G/τ_D = 0.1. τ_D/τ_0 is 0.7 for all curves. The symbols are experimental values

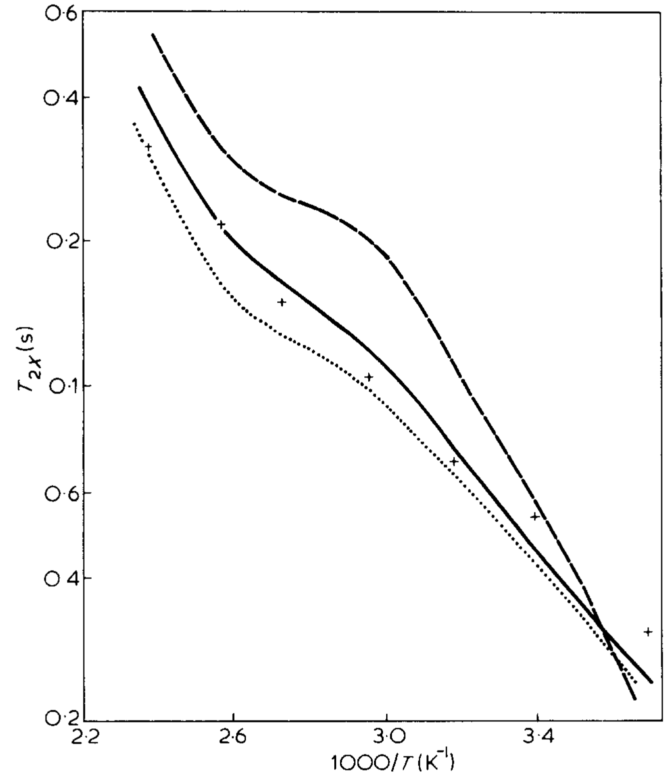

Figure 6 Simulation of T_{2X} at 300 MHz in toluene-d_8. Legend as in *Figure 5*

Table 1 Correlation times from simulation of ^{1}H relaxation times

	Temperature/°C	τ_D /ns	τ_D/τ_0	τ_G/τ_D
(a) acetone-d_6	110	0.26	0.6	0.6
	97	0.37	0.8	0.5
	69	0.56	0.9	0.7
	50	0.87	0.9	0.7
	30	1.5	1.0	0.7
	13	2.7	1.0	0.7
	–1	4.2	1.0	0.7
(b) toluene-d_8	112	0.37	0.7	0.3
	85	0.53	0.8	0.4
	60	0.87	0.8	0.3
	40	1.5	0.7	0.4
	21	3.0	0.7	0.4
	5	6.1	0.8	0.3
(c) nitrobenzene-d_5	151	0.30	0.7	0.4
	122	0.53	0.8	0.3
	97	0.87	0.8	0.3
	72	1.5	0.8	0.2
	50	2.7	0.8	0.2
	30	5.3	0.8	0.2
	21	7.5	0.8	0.2
(d) acetonitrile-d_3	127	0.19	0.4	0.7
	112	0.32	0.6	0.5
	87	0.49	0.7	0.5
	60	1.15	0.9	0.5
	40	1.92	0.9	0.5

cosity. Thus the quantitative analysis of the relaxation times supports the qualitative interpretation of the solvent dependence of T_{1S} and T_{1X} described above in terms of solvent-dependent *rates* of backbone motion, but a solvent-independent *mechanism* of backbone motion and a solvent-independent *rate* of α-methyl internal rotation.

DISCUSSION

Four reports of ^{1}H relaxation in s-PMMA have been published previously[1–4], but only a limited comparison with the present data can be made. The dependence of relaxation behaviour on solvent viscosity and thermodynamic quality reported here is fully consistent with that reported by Gotlib *et al.*[1] for a more limited range of solvents. However, no quantitative comparison of relaxation times can be made because of the fact that these authors reported a composite T_1 value for all protons at 18.6 MHz, including the methoxyl protons. The methoxyl group T_1 is frequency dependent (see below), but no theoretical analysis of its frequency dependence has been made so we are unable to attempt to simulate the composite T_1 temperature dependence. However, the temperature of minimum T_1 produces a useful point of comparison. For a 5 monomer mol % solution in toluene-d_8, Gotlib *et al.* observed a minimum in the composite T_1 at –15°C. In this solvent, we observe a minimum in T_{1S} at ~85°C and a minimum in T_{1X} at 45°C. Assuming an activation energy of ~23 kJ mol^{-1} (*Table 2*), we anticipate at 18.6 MHz a minimum in T_{1S} at –10°C and in T_{1X} at –30°C. The minimum in the composite T_1 arises from the backbone motions and α-methyl internal rotation[1], and is dominated by the shorter methylene relaxation. Thus there is a satisfactory consistency on this particular feature of the relaxation time curves between the two sets of data.

Hatada *et al.*[2] have reported values of 123 ms for T_{1S} and 185 ms for T_{1X} at 100 MHz for a 5 monomer mol% solution in toluene-d_8 at 110°C. Using the correlation times in *Table 1* for this solvent, we calculate values of 112 ms for T_{1S} and 174 ms for T_{1X}, in satisfactory agreement with the experimental data. It is interesting to note that Hatada *et al.*[2] report a methoxyl T_1 value of 500 ms at 100 MHz, compared with our result of ~1000 ms at 300 MHz. The magnitude of these T_1 values is so large, and the linewidth of the methoxyl signal so small, that one would have expected the extreme narrowing condition to be met, and therefore T_1 to be independent of frequency. It appears that although the methoxyl group has great freedom of motion by internal rotation about three bonds in the ester side-group, its motion is not entirely decoupled from the relatively slow backbone motion. Similar behaviour has been observed in ^{13}C relaxation in poly(n-alkyl methacrylates)[26].

In an ingenious study making use of specifically deuterated polymers, Hatada *et al.*[3] have measured the magnitude of the intra- and intergroup contributions to relaxation in s-PMMA. For relaxation of the CH_2 group, 45% arises from the geminal interaction, 35% from interaction between non-geminal CH_2 protons, 14% from interaction with the methyl groups and 6% from interaction with the methoxyl protons. From our structural calculations, the corresponding Figures are ~60, 30, 10 and 0%. The proportional contributions are similar, but the calculations reported here appear to underestimate the non-geminal contributions. If these were enhanced, the calculated relaxation times would be decreased. A match of calculated and experimental T_1 and T_2 values would then be achieved with values of the ratio τ_D/τ_0 towards the smaller end of the ranges quoted in the previous section.

Spevacek and Schneider[4] have measured ^{1}H and ^{13}C T_1 values for s-PMMA in $CDCl_3$ and CD_3CN at the single temperature of 27°C. The frequencies were 60 MHz for ^{1}H and 15 MHz for ^{13}C, and the concentration was 10% w/v. T_{1S} values of 26 ms in $CDCl_3$ and 62 ms in CD_3CN were reported. This marked difference of T_{1S} between $CDCl_3$ and CD_3CN is in contrast to the solvent-independent results obtained here for 1% solutions at 300 MHz. Spevacek and Schneider also quoted T_1 values for the CH_2 ^{13}C resonance of 40 ms in $CDCl_3$ and 20 ms in CD_3CN for the same sample conditions. The reversal in order of the ^{13}C and ^{1}H T_1 values was attributed to changes in local conformational structure. The present results suggest that this is unlikely. A more probable explanation is a fortuitous choice of temperature which lies on the low temperature side of the minimum in T_{1S} at 60 MHz, but on the high temperature side of the CH_2 ^{13}C T_1 minimum at 15 MHz. A decrease in polymer mobility on changing from $CDCl_3$ to CD_3CN would then produce an increase in T_{1S}, but a decrease in the ^{13}C T_1. A decrease in chain mobility for 10% solutions where none is observed for 1% solutions could perhaps be accounted for by increasing polymer–polymer contacts at the higher concentration in the poorer solvent. However, the ^{13}C T_1 measurements we have made for 5% solutions at 75 MHz show only insignificant differences between $CDCl_3$ and CD_3CN

Table 2 Activation energies (kJ mol^{-1}). Uncertainties are ±5 kJ mol^{-1}

Solvent	E_D	E_0	E_G
Acetone-d_6	22	19	22
Toluene-d_8	24	20	23
Nitrobenzene-d_5	25	25	22
Acetonitrile-d_3	29	19	28

solvents. It is clear that at present there is insufficient data to resolve this conflict, and an extensive study of both concentration *and* temperature dependences of relaxation is required.

Dynamic studies of s-PMMA in solution have also been made using dielectric relaxation[27] and e.s.r. spin-labelling[28] However, in both these techniques, the relaxing entity is located in a side-chain subject to both internal rotations and backbone motions which the relaxation measurements are unable to separate. Correlation times obtained from e.s.r. spin labels[28] for solutions of s-PMMA in chloroform, benzene and dimethylformamide at 25°C are more than an order of magnitude shorter than those reported here. The difference is presumably due to facile internal rotation about bonds linking the spin-label to the polymer chain. The dielectric relaxation technique[27] yields relaxation times of similar magnitude to those observed in this work. At 30°C, the frequency of maximum dielectric loss in toluene is 47 MHz, corresponding to a correlation time of 3.4×10^{-9} s which is comparable with the value we obtain for τ_D of 2.1×10^{-9} s under the same conditions. The larger value for the dielectric correlation time is due to some extent to the fact that dielectric relaxation depends on loss of correlation of first-order spherical harmonic functions whereas n.m.r. relaxation depends on loss of correlation of second-order spherical harmonics, which decay more rapidly. The activation energy for the dielectric process, 25 kJ mol^{-1}, is close to the activation energy for τ_D recorded in *Table 2*. The trend of dielectric relaxation time with solvent follows an identical pattern to that described here. Dielectric relaxation was studied[27] in the 'good' solvents toluene and dioxane (viscosities 0.59 and 1.25 mPa s at 20°C, respectively) and in the poor solvent carbon tetrachloride (θ solvent at 30°C[29]; viscosity 0.97 mPa s at 20°C). The dielectric relaxation times were observed to be 3.4×10^{-9}, 5.1×10^{-9} and 6.9×10^{-9} s in toluene, dioxane and CCl_4, respectively, at 30°C. The absence of a monotonic relationship between relaxation time and viscosity led Mashimo *et al.*[27] to the conclusion that the active process in dielectric relaxation in s-PMMA is independent of solvent, but no allowance was made for the variation in thermodynamic quality which is clearly important. It is interesting to note that if one estimates a value for τ_D in dioxane by correcting the dielectric relaxation time above by the ratio between τ_D and the dielectric relaxation time in toluene, one obtains a value of 3.2×10^{-9} s at 30°C. This value, together with the values of τ_D in the three good solvents in *Table 1*, gives a reasonable straight line when plotted against solvent viscosity. A similar relation has been observed[29] for relaxation of poly(ethylene oxide) in solution.

Heatley and Begum[30] have measured ^{13}C T_1 and nuclear Overhauser enhancements for s-PMMA in *ortho*-dichlorobenzene as a function of temperature, and have analysed the results in terms of the diamond-lattice model. For a 10% (w/v) solution, the analysis yielded values of the ratio τ_D/τ_0 in the region 0.04 to 0.1, considerably lower than the values given here. A similar conflict has been noted between ^1H and ^{13}C data for polystyrene[12] and attributed to differences in correlation functions for H–H and C–H interactions. It is intended to clarify this discrepancy in a future study of the frequency dependence of ^{13}C relaxation parameters. It is noteworthy that there is consistency between the ^{13}C and ^1H analyses for the values of τ_G and for activation energies for both backbone motions and methyl rotation.

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