^{1}H nuclear magnetic relaxation in isotactic poly(methyl methacrylate) in dilute solution

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^{1}H spin–lattice and spin–spin relaxation times have been measured for individual groups of nuclei in isotactic poly(methyl methacrylate) in dilute solution in toluene-d_8. The relaxation times have been analysed in terms of backbone conformational transitions and methyl rotation.

INTRODUCTION

Existing studies of ^{1}H [1-3] and ^{13}C [3-7] relaxation in stereoregular samples of poly(methyl methacrylate) in dilute solution have established that the backbone of isotactic polymer (iso-PMMA) is almost three-fold more mobile than the syndiotactic polymer (syn-PMMA). However, no detailed interpretation of magnetic relaxation times has been undertaken, with the exception of Lyerla *et al.*[7] who analysed ^{13}C T_1, T_2 and nuclear Overhauser enhancement (*NOE*) data at 38°C in terms of a distribution of correlation times. The data for iso-PMMA yielded a shorter average correlation time and narrower distribution width than syn-PMMA.

In this paper, ^{1}H relaxation data are reported for a dilute solution of iso-PMMA in toluene-d_8 as a function of temperature. Several relaxation experiments have been performed to probe motional processes at different frequencies. T_1 and T_2 measurements have been made at 300 MHz and T_1 measurements at 80 MHz. Also, cross-relaxation between the non-equivalent methylene protons has been studied by means of transient nuclear Overhauser enhancements following selective inversion of one peak[8].

The results are analysed in terms of the diamond-lattice model of polymer segmental motion[9-11] and the results compared with a recently published similar study of syn-PMMA[12].

CALCULATION OF RELAXATION TIMES

Relaxation theory for iso-PMMA is similar to that for syn-PMMA described previously[12], and full details will not be repeated here. Briefly, the polymer motion is described by three correlation times, two of them (τ_D and τ_0) characterizing backbone motion and the third (τ_G) characterizing internal rotation of the α-methyl group. The methylene and α-methyl protons form a coupled system whose spin–lattice relaxation is described by the set of different equations:

$$\frac{dS_A}{dt} = -\frac{S_A}{T_{AA}} - \frac{S_M}{T_{AM}} - \frac{S_X}{T_{AX}} \quad (1a)$$

$$\frac{dS_M}{dt} = -\frac{S_A}{T_{MA}} - \frac{S_M}{T_{MM}} - \frac{S_X}{T_{MX}} \quad (1b)$$

$$\frac{dS_X}{dt} = -\frac{S_A}{T_{XA}} - \frac{S_M}{T_{XM}} - \frac{S_X}{T_{XX}} \quad (1c)$$

where A denotes the erythro methylene proton, M the threo methylene proton and X the α-methyl protons. S_i represents the deviation of the longitudinal magnetization of proton i from equilibrium. The relaxation coefficients are given by:

$$T_{AA}^{-1} = 6K[J(\omega_A) + 4J(2\omega_A)]R_{AA}^{-6} + K[J(\omega_A - \omega_M) + 3J(\omega_A) + 6J(\omega_A + \omega_M)]R_{AM}^{-6} + 6K[J_A^m(\omega_A - \omega_X) + 3J_A^m(\omega_A) + 6J_A^m(\omega_A + \omega_X)]$$

$$T_{AM}^{-1} = K[6J(\omega_A + \omega_M) - J(\omega_A - \omega_M)]R_{AM}^{-6}$$

$$T_{AX}^{-1} = 2K[6J_A^m(\omega_A + \omega_A) - J_A^m(\omega_A - \omega_X)]$$

$$T_{XX}^{-1} = 6K[J^r(\omega_X) + 4J^r(2\omega_X)]R_{XX}^{-6} + 2K[J_A^m(\omega_A - \omega_X) + J_A^m(\omega_X) + J_A^m(\omega_A + \omega_X)] + 2K[J_M^m(\omega_M - \omega_X) + J_M^m(\omega_X) + J_M^m(\omega_M + \omega_X)]$$

$$T_{XA} = 2T_{AX}/3$$

where

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

The coefficients T_{MM}, T_{MA}, T_{MX} and T_{XM} are given by the equations for T_{AA}, T_{AM}, T_{AX} and T_{XA}, respectively, with the index A changed to M throughout. The symbols $J(\omega)$, $J_A^m(\omega)$, $J_M^m(\omega)$ and $J^r(\omega)$ represent spectral density functions which have been defined in terms of the correlation times τ_0, τ_D and τ_G in the previously published study of syn-PMMA[12]. As in that paper, the effective internuclear distances R_{AA}, R_{AM}, R_{MM} and R_{XX}, and also the structural parameters α_A, β_A, α_M and β_M in the definition of $J_A^m(\omega)$ and $J_M^m(\omega)$ [12], were evaluated as averages over accessible conformations[13]. The values used were:

$R_{AA} = 250.8$ pm; $R_{AM} = 172.5$ pm;

$R_{MM} = 245.8$ pm; $R_{XX} = 178$ pm;

$\alpha_A = 1.43 \times 10^{-15}$ pm^{-6}; $\beta_A = 2.10 \times 10^{-15}$ pm^{-6};

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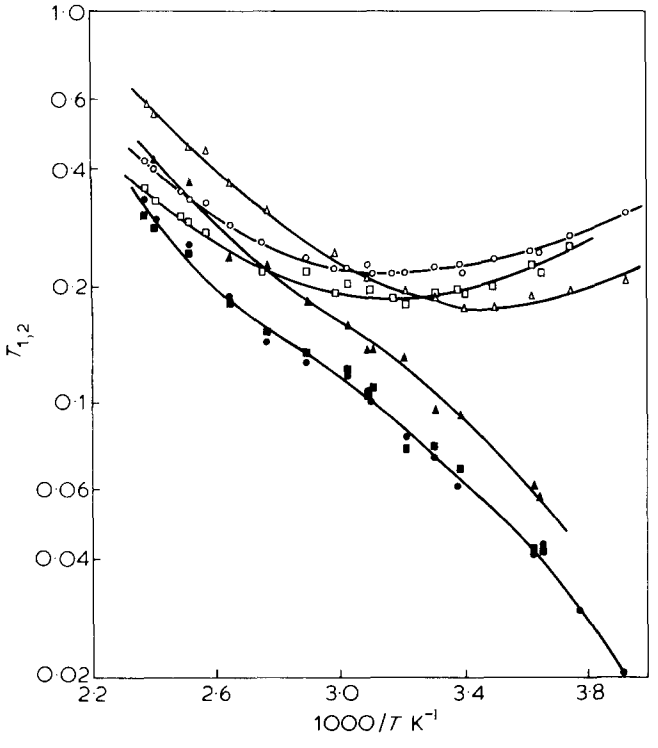

Figure 1 ^{1}H relaxation times at 300 MHz for a 1% solution of iso-PMMA in toluene-d_8. ○, T_{1A}; □, T_{1M}; △, T_{1X}; ●, T_{2A}; ■, T_{2M}; ▲, T_{2X}

$$\alpha_M = 3.10 \times 10^{-15}\ \text{pm}^{-6}; \qquad \beta_M = 3.42 \times 10^{-15}\ \text{pm}^{-6}.$$

Effective spin–lattice relaxation times and transient nuclear Overhauser enhancements were calculated by numerical solution of equations (1) with appropriate initial conditions.

Because the A and M protons are spin-coupled, the rapid pulse repetition rate in the Carr–Purcell pulse sequence used to measure T_2 results in an averaging of the T_2 values of the A and M protons[14]. The averaged value of T_{2A} and T_{2M}, denoted $\overline{T_{2AM}}$, and the value of T_{2X} were obtained from:

$$\overline{T}_{2AM}^{-1} = \tfrac{3}{2}K[3J(0) + 5(\omega_{AM}) + 2J(2\omega_{AM})][R_{AM}^{-6} + R_{AA}^{-6} + R_{MM}^{-6}]$$
$$+ \tfrac{9}{2}K[3J_A^m(0) + 5J_A^m(\omega_{AM}) + 2J_A^m(2\omega_{AM})]$$
$$+ \tfrac{9}{2}K[3J_M^m(0) + 5J_M^m(\omega_{AM}) + 2J_M^m(2\omega_{AM})]$$

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

where

$$\omega_{AM} = \tfrac{1}{2}(\omega_A + \omega_M)$$

It is noteworthy that the calculated magnitudes of A–X and M–X interactions are different, reflecting the structural non-equivalence of the erythro and threo protons. The preferred dyad conformation of iso-PMMA is tt [13], in which the threo proton (M) is *gauche* to the α-methyl and the erythro proton (A) is *trans*. Thus it is expected that $\alpha_M > \alpha_A$ and $\beta_M > \beta_A$. (We point out here that the initial calculations gave values of α_A and β_A which were 28% lower, and values of α_M and β_M which were 16% higher than those quoted above. Those initial estimates gave calculated values of T_{1A} and T_{1M} differing by 30%, compared with experimental differences of ~15%. However, the calculated total contribution to methylene relaxation arising from interaction with the methyl groups (A–X plus M–X) was in good agreement with experimental data on relaxation in selectively deuterated polymers[2] (see Discussion). Hence in order to reproduce the observed ratio of T_{1A} and T_{1M}, while maintaining the combined methylene–methyl interaction constant, the initial values of α_A and β_A were increased and the values of α_M and β_M decreased appropriately. This adjustment is taken into account when estimating the reliability of the correlation times resulting from analysing the experimental data).

EXPERIMENTAL

A high molecular weight sample of iso-PMMA was prepared by polymerization in toluene at 0°C using phenyl magnesium bromide initiation[15]. The viscosity-average molecular weight was 6.0×10^5. The n.m.r. spectrum showed the sample to be ~95% isotactic. A 1% solution in toluene-d_8 (Fluorochem Ltd, Glossop, UK) was degassed and sealed *in vacuo*.

Relaxation measurements were made at 300 MHz on a Varian Associates SC-300 spectrometer and at 80 MHz on a Bruker Spectrospin WP-80 spectrometer, using the same techniques as for syn-PMMA[12]. Selective inversion of the M peak was achieved by pulsing the homonuclear decoupler at a power low enough to avoid serious perturbation of neighbouring peaks. The pulse width required for selective inversion was 10 to 15 ms.

RESULTS

Doublets at 2.36 and 1.66 δ have been assigned to the erythro (A) and threo (M) methylene protons respectively[16]. The α-methyl signal (X) occurs at 1.35 δ.

T_1 and T_2 measurements at 300 MHz are shown as a function of temperature in *Figure 1*. The A and M protons have different T_1 values, as expected due to different interactions with the X protons mentioned above. The M proton relaxes more rapidly than the A proton, consistent with its closer approach (on average) to the α-methyl group. At low temperatures, it is expected that T_{1A} and T_{1M} become equal due to rapid spin-diffusion, but this condition is not quite reached in this work.

Both T_{1A} and T_{1M} pass through a minimum at 40°C, about 45° lower than the temperature of the methylene T_1 minimum for syn-PMMA in the same solvent and at the same frequency[12]. T_{1X} also passes through a minimum, at ~30°C lower than the minima in T_{1A} and T_{1M}, indicating a moderate degree of internal mobility of the α-methyl group. In syn-PMMA in the same solvent, the minimum in T_{1X} lies about 35°C lower than the minimum in the methylene T_1 [12]. Thus the rate of α-methyl internal rotation relative to the backbone frequency is comparable in the two stereoisomers.

T_{2A}, T_{2M} and T_{2X} all decrease monotonically with frequency, as expected. On average, T_{2A} and T_{2M} are equal because the rapid repetition rate of the pulse sequences in the Carr–Purcell spin–echo sequence suppresses differential precession of A and M in the rotating frame[14], and the strong spin coupling between A and M renders the two

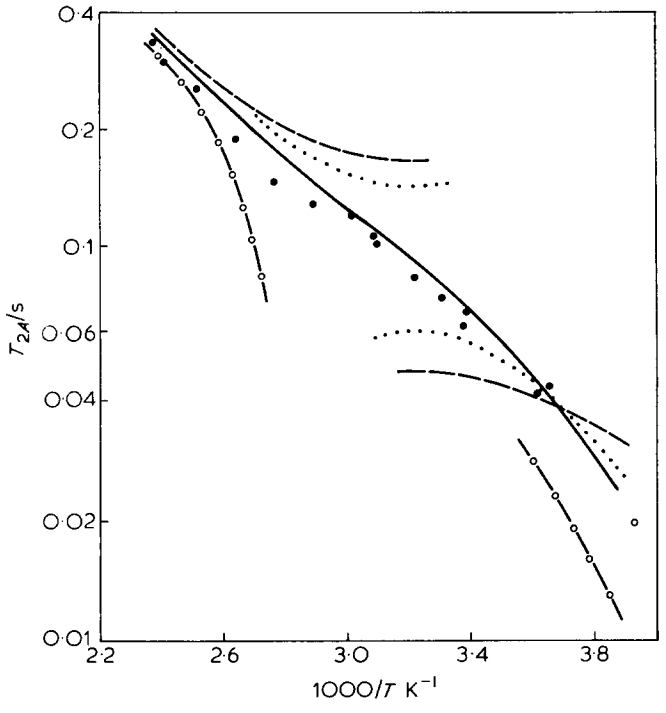

Figure 2 Simulation of T_{2A} at 300 MHz as described in the text. The lines are predicted for the following values of τ_D/τ_0: – – – –, τ_D/τ_0 = 10; · · · · ·, τ_D/τ_0 = 1.0; ——, τ_D/τ_0 = 0.5; —O—O—O—, τ_D/τ_0 = 0.1. τ_G/τ_D is 1.0 for all curves except the τ_D/τ_0 = 0.5 curve for which τ_G/τ_D = 0.6. The symbols are experimental points

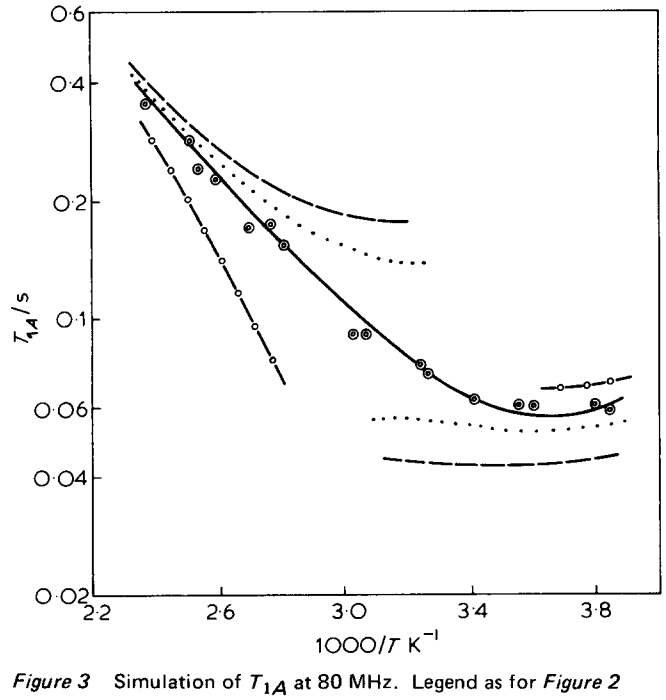

Figure 3 Simulation of T_{1A} at 80 MHz. Legend as for *Figure 2*

protons equivalent. However, transverse relaxation of the X protons is not averaged with that of A and M because of the absence of methyl–methylene spin-coupling.

The interpretation of the experimental data in terms of correlation times was undertaken according to the same procedure as for syn-PMMA[12]. 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_{1i} and T_{2i} ($i = A, M, X$) were made as described above for a wide range of these parameters. The motional parameters were obtained as follows. For particular values of the ratios τ_D/τ_0 and τ_G/τ_D, that value of τ_D reproducing the value of T_{1A} at 300 MHz at each temperature was obtained, and used together with the specified ratios to calculate the remaining relaxation times which were compared graphically with the experimental values. The results are shown in *Figures 2–6*.

T_{1A} and T_{2A} are essentially independent of the ratio τ_G/τ_D over the temperature range employed in this work. For the simulations of T_{2A} at 300 MHz (*Figure 2*) and T_{1A} at 80 MHz (*Figure 3*), τ_G/τ_D was therefore held constant at 1.0. *Figures 2* and *3* show that the optimum value of the ratio τ_D/τ_0 is ~0.5. For the simulation of T_{1X} and T_{2X} at 300 MHz, τ_D/τ_0 was then held constant at 0.5. *Figures 4* and *5* show that the optimum value of τ_G/τ_D is ~0.6. The best-fit

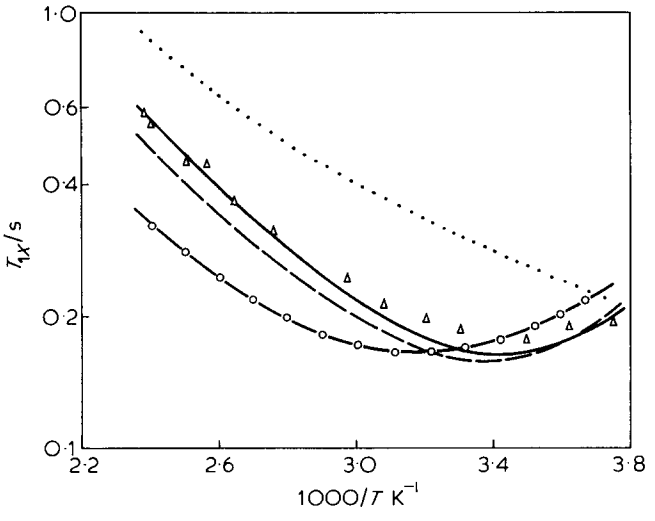

Figure 4 Simulation of T_1X at 300 MHz as described in the text. The lines are predicted for the following values of τ_G/τ_D: · · · · · · , τ_G/τ_D = 0.1; ——, τ_G/τ_D = 0.6; – – – –, τ_G/τ_D = 1.0; —O—O—O—, τ_G/τ_D = 10.0. τ_D/τ_0 is 0.5 for all curves. The symbols are experimental points

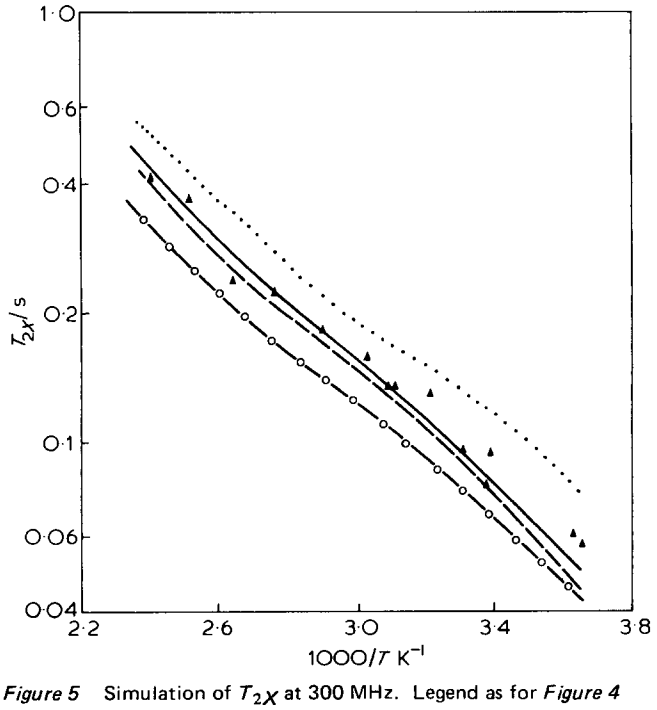

Figure 5 Simulation of T_2X at 300 MHz. Legend as for *Figure 4*

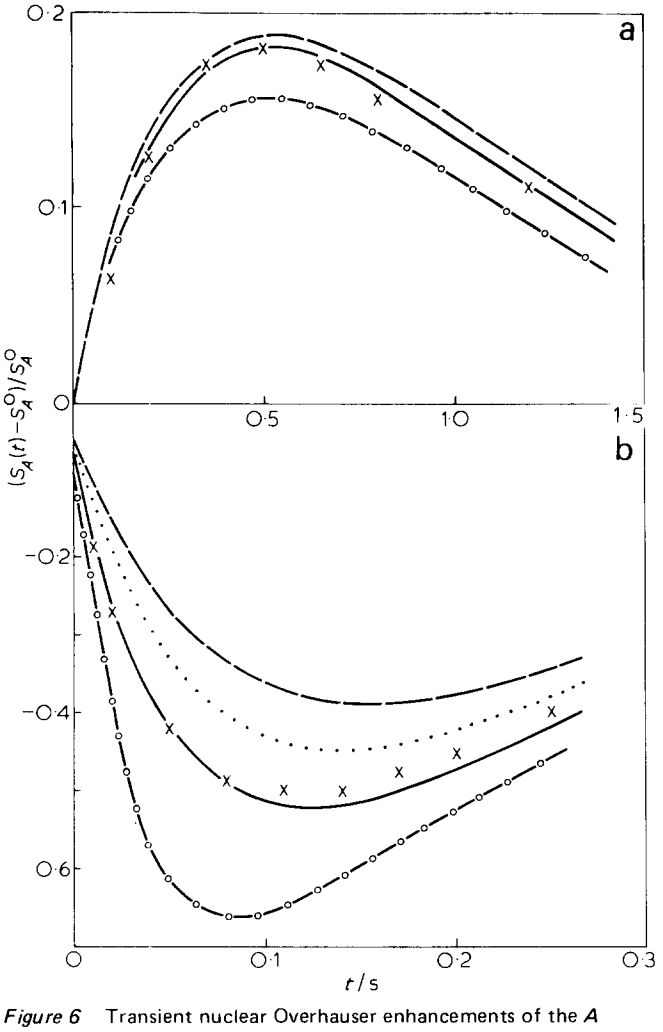

Figure 6 Transient nuclear Overhauser enhancements of the *A* resonance following selective inversion of the *M* resonance. (a) 140°C. The initial fractional deviations from equilibrium were: H_A, 0.0; H_M, −1.72; H_X, −0.22. (b) −19°C. The initial fractional deviations from equilibrium were: H_A, −0.05; H_M, −1.60; H_X, −1.29. In both (a) and (b), the curves are designated as in the legend to *Figure 2*

values of τ_D and the ratios τ_D/τ_0 and τ_G/τ_D are given in *Table 1*. An Arrhenius plot of τ_D gives an activation energy of 20 ± 5 kJ mol^{-1}.

As a further test of these optimum-fit parameters, the transient nuclear Overhauser enhancement[8] of the *A* signal following selective inversion of the *M* resonance was simulated and compared with experiment at two temperatures one on either side of the T_{1A} minimum. The results are shown in *Figure 6*. There is good agreement between the experimental curves and those calculated using the data in *Table 1*.

These correlation times and optimum ratios are of course subject to some variation due to uncertainties in the internuclear distances. It is estimated that reasonable ranges are 0.25 to 1.0 for τ_D/τ_0 and 0.5 to 2 for τ_G/τ_D. The correlation times τ_D in *Table 1* are reliable to no better than a factor of 2 or so.

DISCUSSION

The values of τ_D in *Table 1* are a factor of ~3 shorter than those for sym-PMMA in the same solvent. A similar ratio has been observed for dielectric relaxation times[1,7]. From ^{13}C relaxation data, Lyerla *et al.*[7] also conclude that iso-

Table 1 Correlation times from simulation of ^{1}H relaxation times of iso-PMMA in toluene-d_8

Temperature/°C	τ_D/ns	τ_D/τ_0	τ_G/τ_D
144	0.075	0.5	0.6
112	0.11	0.5	0.6
85	0.17	0.5	0.6
60	0.24	0.5	0.6
40	0.42	0.5	0.6
21	0.75	0.5	0.6
5	1.3	0.5	0.6
−10	2.4	0.5	0.6

PMMA is more mobile than syn-PMMA, but they find that the average correlation time for iso-PMMA is only about two-fold smaller than that for syn-PMMA. However, in that work, the molecular weight of the syn-PMMA sample was only 6000. This is within the range of molecular weights where overall tumbling contributes to the relaxation process, leading to a reduction in correlation times. The iso-PMMA sample was of molecular weight 28 000, well above the limiting value where overall tumbling ceases to be significant. A quantitative comparison of the correlation times obtained here with those reported elsewhere is precluded by the different models used for the chain motions.

It was reported previously that for syn-PMMA in toluene-d_8, acceptable values for τ_D/τ_0 lie in the range 0.4 to 2, and for τ_G/τ_D in the range 0.2 to 0.7. These limits for τ_D/τ_0 are about a factor of two greater, and for τ_G/τ_D about a factor of two smaller, than the limits for iso-PMMA estimated above. It is likely that uncertainties in the internuclear distances will be of the same sign for both isomers. It is therefore possible that the differences in ratio limits are significant, implying slightly different motional mechanisms. However, there is not sufficient reliable evidence on this point to make a satisfactory judgment.

Finally, we note that Hatada *et al.*[1] have reported values of 206 and 321 ms for T_{1A} and T_{1X}, respectively, for iso-PMMA in toluene-d_8 at 110°C and 100 MHz. The values calculated for these conditions using the correlation times in their *Table 1* are 220 and 350 ms respectively, in satisfactory agreement. From measurements on selectively deuteriated polymers, Hatada *et al.*[2] have determined the contributions of various sources to methylene relaxation in iso-PMMA. The proportions arising from the geminal methylene, methylene–methyl, methylene–methoxyl and intermethylene interactions were reported as 53, 17, 1 and 29%, respectively. The proportions calculated using the geometrical data given above are 58, 20, 0 and 22%, respectively, in good agreement.

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