Moreover, further investigations of the **q** dependence of the scattered intensity in the intermediate **q** range should confirm this spatial crossover.

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Proton spin–lattice and spin–spin relaxation in vinyl polymers in dilute solution: poly(methyl acrylate)

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Introduction

^{1}H nuclear magnetic relaxation studies of poly(vinyl acetate)[1,2], polystyrene[3,4] and syndiotactic[5] and isotactic[6] poly(methyl methacrylate) have been reported previously, using a variety of techniques to probe molecular motions at widely different frequencies. The techniques included spin–lattice relaxation experiments using non-selective[1–6] and selective[4,6] inversion, spin–lattice relaxation with decoupling[1–3] and spin–spin relaxation[5,6]. Measurements have also been made at different resonance frequencies[2,4–6]. This paper describes an investigation of the spin–lattice and spin–spin relaxation of the backbone protons of poly(methyl acrylate) in dilute solution in $[^2H]_8$–toluene. The study was carried out with two objectives, firstly to extend the range of vinyl polymer structures studied in detail using ^{1}H relaxation, and secondly to examine the application to $[AX_2]_n$ spin systems of spin–spin relaxation measurements previously confined to $[A_2]_n^5$ or $[AX]_n^6$ systems.

Experimental

Relaxation measurements were performed at 300 MHz using a Varian Associates SC-300 spectrometer and at 80 MHz using a Bruker Spectrospin WP-80 spectrometer. Spin–lattice relaxation times were measured using the (π–τ–π/2) sequence and spin–spin relaxation times using the Carr–Purcell–Meiboom–Gill spin–echo sequence as described for syndiotactic poly(methyl methacrylate)[5] with a π pulse spacing of 1 ms. Experimental errors are approximately $\pm 5\%$.

The poly(methyl acrylate) was a sample with $M_w \sim 170000$ and $M_w/M_n \sim 2.2$, supplied by the Aldrich Chemical Company, Gillingham, UK. The n.m.r. spectrum showed it to be essentially atactic. The polymer was purified by precipitation from chloroform solution using diethyl ether and drying under vacuum. Measurements were made on a 1% (w/w) solution in $[^2H]_8$–toluene, degassed and sealed *in vacuo*.

Results

^{1}H chemical shifts of atactic (free-radical initiated) poly(methyl acrylate) in benzene solution have been determined[7] using partly deuterated polymers. The backbone methine proton (labelled A) resonates at 2.61δ. The backbone methylene protons (labelled X) in isotactic dyads are non-equivalent, resonating at 2.12 and 1.63δ, while the equivalent methylene protons in syndiotactic dyads resonate at 1.84δ. In the protonated polymers reported here, the peaks are broadened by spin–spin coupling which prevented resolution of the isotactic and syndiotactic X resonances at 80 MHz but not at 300 MHz. There was little dependence of the relaxation times on stereochemistry, and the X relaxation data reported here are an average over the two dyad types. Because of the overall width of the X resonance (150 Hz), it was impossible to saturate this signal without seriously perturbing the A signal. It was not practicable, therefore, to study A relaxation with X decoupling. However, the A signal was much narrower, so X relaxation with A saturated could be monitored.

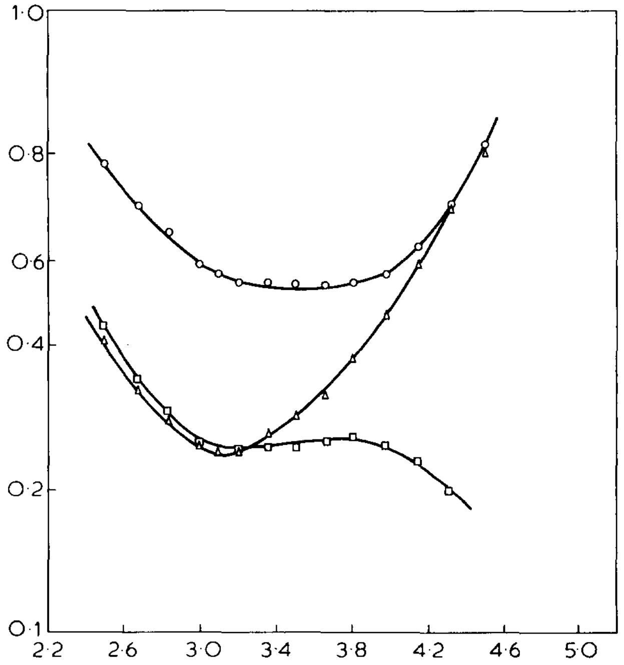

Figure 1 ^{1}H spin–lattice relaxation times at 300 MHz for a 1% (w/w) solution of poly(methyl acrylate) in $[^2H]_8$–toluene. ○, T_{1A}; △, T_{1X}; □, T_{XX}

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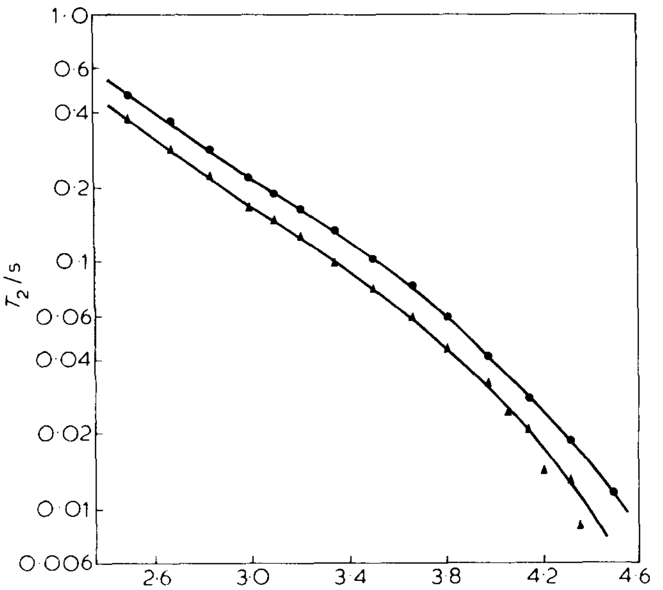

Figure 2 ^{1}H transverse relaxation times at 300 MHz for a 1% (w/w) solution of poly(methyl acrylate) in [^{2}H]$_8$–toluene. ●, T_{2A}; ▲, T_{2X}

Spin–lattice relaxation times are shown in *Figure 1*. T_{1A} and T_{1X} are the time constants characterizing the closely exponential recovery of the A and X signals following complete inversion of all signals, while T_{XX} is the spin–lattice relaxation time of the X protons when the A protons are continuously saturated. A fuller description of these parameters is given in ref 1. Both T_{1A} and T_{1X} pass through a minimum, T_{1A} at ~0°C and T_{1X} at 45°C. At temperatures above the T_1 minima, T_{1A} and T_{1X} differ by a factor of approximately 2.5, whereas at lower temperatures T_{1A} and T_{1X} become equal. This behaviour is due to the fact that at temperatures above the T_1 minima, cross-relaxation between A and X spins ('spin diffusion') is inefficient compared with spin–lattice relaxation processes, and the difference between T_{1A} and T_{1X} reflects the difference in dipolar interactions experienced by the two groups. At temperatures below the T_1 minima, however, cross-relaxation is much more efficient than spin–lattice relaxation and hence the A and X signals relax with a common averaged time constant. The efficient cross-relaxation process also explains the low values of T_{XX} compared with T_{1X} at low temperatures. Irradiation of the A nuclei couples them very efficiently to the lattice, so X relaxation proceeds effectively by cross-relaxation to the A spins.

The transverse relaxation times T_{2A} and T_{2X} decrease monotonically with temperature (*Figure 2*). At the highest temperatures reached, T_{2X} is only slightly less than T_{1X}, indicating that the extreme narrowing condition is almost fulfilled. A significant feature of the T_2 data is that T_{2A} is ~40% greater than T_{2X} throughout the whole temperature range. This behaviour is in agreement with that expected from discussions of transverse relaxation in coupled spin systems by Vold and Vold[8,9]. A simple argument[8] suggests that when the π pulse repetition rate in the Carr–Purcell spin–echo sequence is much greater than the difference in resonance frequency (as was true in this work), effects due to differential precession are suppressed and the strong coupling renders all nuclei effectively equivalent. The transverse magnetization of all peaks should thus decay with the same averaged relaxation time. Subsequent quantitative analysis[9] showed that the averaging extends over transitions of the same symmetry. The small observed difference between T_{2A} and T_{2X} thus presumably arises from a difference between the averaged T_2, s for symmetric and antisymmetric transitions.

Analysis of relaxation times

Spin–lattice relaxation was treated in the same way as described previously for poly(vinyl acetate)[1], and details will not be repeated. However, slightly different effective internuclear distances resulted from conformational averaging according to the isomeric state statistical weights calculated for poly(methyl acrylate) by Yoon *et al.*[10]. The effective distances used were:

$$R_{AA}=245.8 \text{ pm};\ R_{AX}=251.6 \text{ pm};\ R_{XX}=168.4 \text{ pm}.$$

Although the non-equivalence of T_{2A} and T_{2X} mentioned above indicates that transverse relaxation of the backbone protons can be fully described only by subtle quantum-mechanical theory, T_{2X} has been interpreted dynamically using an extension of the simple theory[11] for two identical nuclei. T_{2X} is expressed in terms of spectral density functions $J(\omega)$ defined in ref 1 by:

$$1/T_{2X}=(\mu_o/4\pi)^2(\gamma_H^4\hbar^2/20)[\{9J(0)+15J(\omega_X)$$
$$+6J(2\omega_X)\}\times\{R_{XX}^{-6}+2R_{AX}^{-6}\}]$$

γ_H is the ^{1}H magnetogyric ratio and ω_X the X resonance frequency. It is likely that this equation is not greatly in error, since X relaxation is dominated by the geminal interaction. The X nuclei can be regarded to a first approximation as isolated pairs of identical spins for which the above expression is correct. Other interactions constitute only a small perturbation.

As in previous studies[1–6], the relaxation times have been interpreted in terms of the diamond-lattice model of polymer dynamics developed by Valeur *et al.*[12–14]. The correlation function is written as:

$$G(\tau)=\exp(-|\tau|/\tau_o)\exp(|\tau|/\tau_D)\mathrm{erfc}\{(|\tau|/\tau_D)^{1/2}\}$$

The correlation time τ_D characterizes three-bond conformational jumps[12,13], while the correlation time τ_o characterizes four-bond jumps[12,13] and other processes[14]. It is convenient to use the quantities τ_D and the ratio τ_D/τ_o as variables. The procedure to obtain the best-fit dynamic parameters was to select a value for the ratio τ_D/τ_o and determine numerically the value of τ_D reproducing the experimental value of T_{1X} at 300 MHz at each temperature. The remaining relaxation times for those particular ratios and τ_D values were then calculated and the process repeated for a different value of the ratio. The comparisons of predicted and experimental values of T_{2X} and T_{XX} at 300 MHz and T_{1X} at 80 MHz are shown in *Figures 3–5*. There is satisfactory consistency between the three simulations in that the experimental data is reproduced best by a value for τ_D/τ_o of the order of 0.4 over the whole temperature range. The simulation of T_{2X} appears to favour a slightly higher value of the ratio at lower

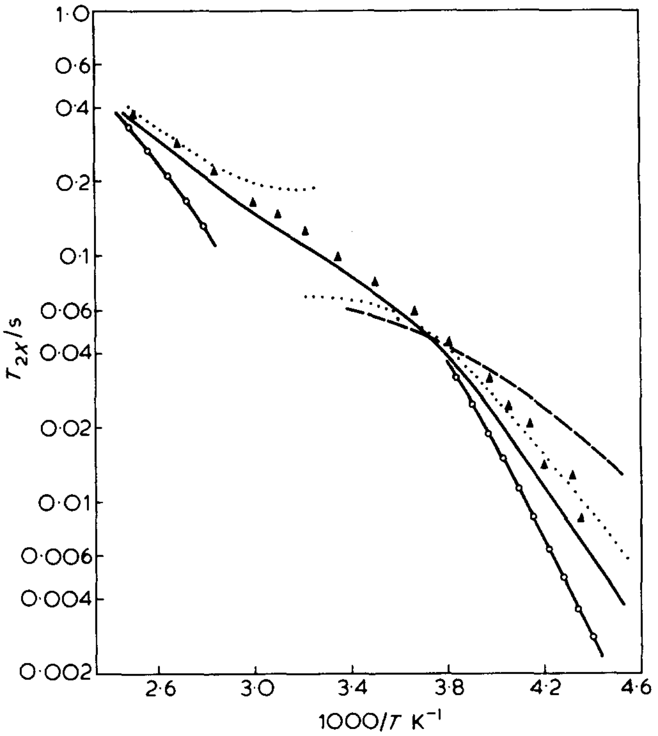

Figure 3 Simulation of T_{2X} at 300 MHz as described in the text. The lines are predicted for the following values of τ_D/τ_0; — — —, τ_D/τ_0 = 10; . . . . , τ_D/τ_0 = 1.0; ——, τ_D/τ_0 = 0.4; –O–O–O–, τ_D/τ_0 = 0.1. The symbols are experimental points

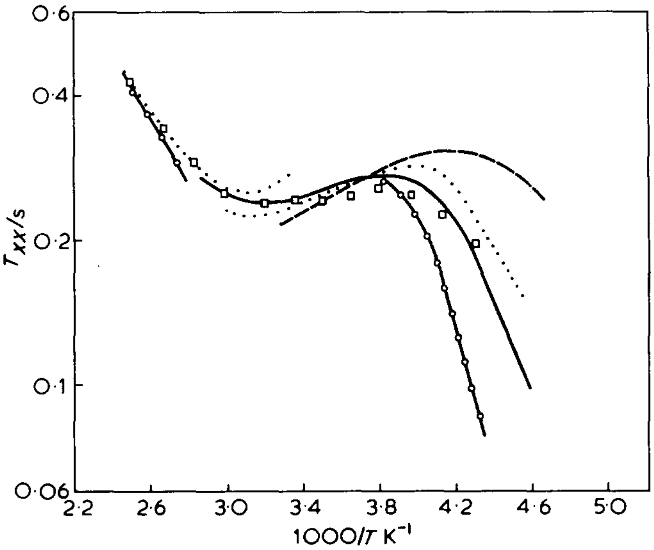

Figure 4 Simulation of T_{XX} at 300 MHz. Legend as for *Figure 3*

temperatures, while the simulation of T_{1X} at 80 MHz favours a slightly lower value at intermediate temperatures. However, since relaxation times depend on the sixth power of internuclear distances, small geometrical uncertainties are greatly magnified in the calculated relaxation times. Taking this factor into account, and also deficiencies in the theoretical expressions for T_1 and T_2, we suggest a reasonable range for τ_D/τ_0 to be ~0.2 to 0.8. As a guide to the magnitude of the correlation times, the values of τ_D appropriate to setting $\tau_D/\tau_0 = 0.4$ are listed in *Table 1*. These values are accurate to no better than a factor of 2 or so. The activation energy is 23±5 kJ mol^{-1}. It is particularly noteworthy that T_{XX} at low temperatures is simulated by approximately the same parameters as T_{2X} and T_{1X} (80 MHz), since in that region T_{XX} is determined by the A–X interaction (i.e. R_{AX}) while T_{1X} and T_{2X} are determined mainly by the geminal X–X interaction (i.e. R_{XX}). Thus the method of estimating the internuclear distances can be regarded with some confidence.

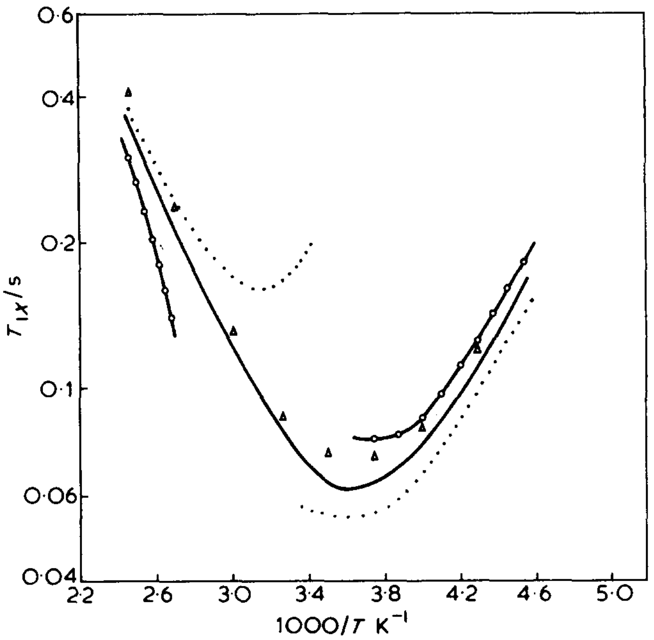

Figure 5 Simulation of T_{1X} at 80 MHz. Legend as for *Figure 3*

Table 1 Values of τ_D reproducing T_{1X} at 300 MHz for a ratio τ_D/τ_0 of 0.4

Temperature/°C	τ_D/ns
128.5	0.069
102	0.10
80	0.14
61	0.22
45	0.32
25	0.63
12.5	0.83
0.5	1.16
−10	1.87
−21	3.0
−31.5	5.3
−41	10
−50.5	17

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