A proton magnetic relaxation study of the mechanism and solvent dependence of the molecular motion of polystyrene in dilute solution

F. Heatley and B. Wood
Chemistry Department, University of Manchester, Manchester M13 9PL, UK
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^{1}H spin–lattice relaxation in polystyrene has been studied as a function of molecular weight, solvent and temperature. The relaxation times are reported for the aliphatic CH and CH_2 and the aromatic *ortho* and (*meta* + *para*) signals. In addition the aliphatic relaxation times under the influence of strong irradiation at the aromatic peaks have been measured. The results have been interpreted in terms of three-bond conformational jumps combined with a rotational diffusional process, and show that the conformational jump correlation time is about an order of magnitude shorter than the diffusional correlation time. The solvent dependence of the relaxation times has been correlated by means of a reduced temperature scale and activation energies are reported.

INTRODUCTION

Polystyrene is a popular subject of studies of polymer dynamics in solution, largely because narrow molecular weight fractions are readily available. N.m.r. studies have not been lacking, and both ^{1}H[1–3] and ^{13}C[3–8] relaxation have been investigated. ^{2}H relaxation[9] has also been employed as well as e.s.r.[10,11], fluorescence depolarization[12], Rayleigh scattering depolarization[13] and acoustic absorption[14,15]. The general conclusion of this work is that magnetic relaxation in polystyrene is dominated by a local segmental process whose correlation time is independent of the molecular weight above a critical value of ~20 000. Moreover, ^{13}C spin–lattice relaxation measurements[3,6,7] have shown that the phenyl ring is capable of undergoing restricted rotation relative to the backbone at a rate comparable to the segmental motion[1,6]. The variation of ring rotation with temperature appears to be discontinuous, judging from changes in slope of ^{1}H linewidth[1] and ^{13}C T_1 values[7] with temperature, and a conformational transition has been suggested[1]. It has been known for some time that polymer segmental motions are neither isotropic nor diffusional, resulting in non-exponential correlation functions. Empirically, the motion can be interpreted in terms of a distribution of isotropic correlation times[5,6,9]. However, a more elegant model[16–18] based on three-bond conformational transitions of a chain on a tetrahedral lattice which also leads to a non-exponential autocorrelation function, has been applied successfully to the interpretation of ^{13}C spin–lattice relaxation times[3,6] and nuclear Overhauser enhancements[6] ^{1}H spin–lattice relaxation times[3] and fluorescence depolarization experiments[12]. A modified version[19] of this model has been applied to ^{19}F relaxation in poly(*p*-fluorostyrene) and poly(*m*-fluorostyrene)[20].

In this paper we report the results of a proton spin–lattice relaxation study of polystyrene in solution, as a function of molecular weight, temperature and solvent with the aim of promoting a more accurate description of the polymer motion. There are two novel features. Firstly, in addition to the well-known unperturbed relaxation times obtained from inversion recovery curves with a non-selective inverting pulse, we have also measured the relaxation times of both types of aliphatic protons under the influence of strong saturating irradiation at the aromatic protons. This technique was introduced in earlier studies of poly(vinyl acetate)[21,22], and effectively measures the rate of spin population transfer (spin diffusion) between observed and irradiated spins i.e. transitions of the type $\alpha\beta \leftrightarrow \beta\alpha$. These occur at frequencies of the order of chemical shifts, so are controlled by low frequency motions, in contrast to the normal spin–lattice relaxation transitions which are controlled by high frequencies of the order of MHz. Secondly, we have made measurements on a random copolymer of styrene and perdeuterostyrene, the mole fraction of the former being 0.05. In these samples, the protons are shielded not only from intermolecular relaxation sources but also from intramolecular interactions between monomer units some distance apart in the chain but which are brought into proximity from time to time by chain coiling. The only significant interactions are those within a single monomer unit and the relaxation times therefore truly reflect the chain motion.

THEORY

Coupled spin–lattice relaxation

There are five distinct types of proton in polystyrene, the aliphatic methine (denoted by A) and methylene (X) and the aromatic ortho (O), meta (M) and para (P) protons. Assuming that only intramolecular ^{1}H–^{1}H dipole–dipole relaxation mechanisms operate, spin–lattice relaxation

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Table 1 Values of N_{ij} for use in equations (2) and (3)
(a) Fully protonated polystyrene

	j				
i	*A*	*X*	*O*	*M*	*P*
A	2	4	2	2	1
X	2	1	4	4	2
O	1	4	1	2	1
M	1	4	2	1	1
P	1	4	2	2	0

(b) Copolymer (random) of 95% styrene-d_8/5% styrene

	j				
i	*A*	*X*	*O*	*M*	*P*
A	0	2	2	2	1
X	1	1	2	2	1
O	1	2	1	2	1
M	1	2	2	1	1
P	1	2	2	2	0

ignoring cross-correlation effects, is governed by five coupled differential equations of the form:

$$\frac{\mathrm{d}S_i}{\mathrm{d}t} = \sum_j \frac{(S_j - S_j{}^0)}{T_{ij}} \tag{1}$$

S_i is the longitudinal magnetization of spins $i(i = A, X, O, M, P)$, and S_i^0 is its value at thermal equilibrium. The diagonal relaxation coefficients can be expressed as:

$$\frac{1}{T_{ii}} = KN_{ii}\left\{\frac{3J(\omega_i) + 12J(2\omega_i)}{R^6}\right\}_{ii} +$$

$$K\sum_{j \neq i} N_{ij}\left\{\frac{J(\omega_i - \omega_j) + 3J(\omega_i) + 6J(\omega_i + \omega_j)}{R^6}\right\}_{ij} \tag{2}$$

and the cross-relaxation (off-diagonal) coefficients by:

$$\frac{1}{T_{ij}} = KN_{ji}\left\{\frac{6J(\omega_i + \omega_j) - J(\omega_i - \omega_j)}{R^6}\right\}_{ij} \tag{3}$$

where

$$K = (\mu_0/4\pi)^2\gamma_H{}^4\hbar^2/10$$

The subscript on each bracket applies to each $J(\omega)$ and R within. N_{ij} is the number of nuclei of type j with which a nucleus of type i interacts; the values are given in matrix form in *Table 1*. R_{ij} is an effective distance for the interaction of nucleii i and j, ω_i is the resonance frequency of nucleus i, and $J_{ij}(\omega)$ is the spectral density of the normalized autocorrelation function of the dipole–dipole interaction between i and j at the frequency ω. The evaluation of the distances and spectral densities depends on the nuclei involved, and can be divided into three sections.

Aliphatic protons. These were treated in the same way as in a previous study of poly(vinyl acetate)[21]. R_{AA}, R_{AX} and R_{XX} incorporate all significant interactions between protons in the backbone and the values used were (pm):

$$R_{AA} = 273; R_{AX} = 242; R_{XX} = 166$$

In the deuterated polymer, only geminal and vicinal interactions are present) the distances being (pm):

$$R_{AA} = \infty; R_{AX} = 272; R_{XX} = 176$$

For the spectral density, we have employed the expression[3] arising from the jump model of Valeur *et al.*[16,17], modified by an empirical exponential factor[18]:

It is written as a function of frequency and two correlation times:

$$J(\omega) = F(\omega, \tau_D, \tau_0)$$

$$= \frac{\tau_0\tau_D(\tau_0 - \tau_D)}{(\tau_0 - \tau_D)^2 + \omega^2\tau_0^2\tau_D^2}\left\{\left(\frac{\tau_0}{2\tau_D}\right)^{1/2}\right.$$

$$\times\left[\frac{(1 + \omega^2\tau_0^2)^{1/2} + 1}{1 + \omega^2\tau_0^2}\right]^{1/2} + \left(\frac{\tau_0}{2\tau_D}\right)^{1/2}$$

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

τ_D is the correlation time characterizing conformational jumps and τ_0 represents either additional isotropic relaxation processes, or deviations from ideal lattice conditions.

Aromatic protons. The spectral density for interactions between aromatic protons depends on a correlation time for ring jumps, τ_J, as well as τ_D and τ_0. Potential energy calculations[23] clearly indicate a two-fold barrier to ring rotation, and we therefore derived the autocorrelation function for 180° jumps by a slight modification of Woessner's treatment[24] of a threefold barrier. However, during the course of this work, Jones[25] independently published an identical account, and the reader is referred to that paper for details. $J(\omega)$ becomes:

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

$$+ 3\sin^2 2\Delta F(\omega, \tau_D, \tau_R)\} \tag{5}$$

where the functions F are given by equation (4) Δ is the angle between the internuclear vector and the internal rotation axis, and τ_R is given by:

$$\frac{1}{\tau_R} = \frac{1}{\tau_0} + \frac{1}{\tau_J}$$

τ_J is the average time between phenyl ring jumps. It was assumed that the phenyl ring is a regular hexagon with C–C and C–H bond lengths of 139.5 and 108.4 pm respectively. In the most favoured conformations of both isotactic and syndiotactic sequences, interactions between protons in different rings are negligible. The appropriate distances (except for R_{OM}) are (pm):

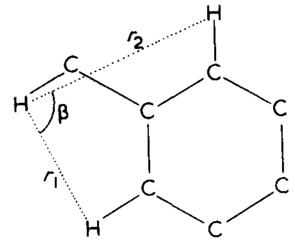

Figure 1 Showing the two *O–A* interactions which interconvert on rotation of the phenyl ring by 180°

$$R_{OO} = R_{OP} = R_{MM} = 429; \qquad R_{MP} = 248$$

For *O–O* and *M–M* interactions $\Delta = 90°$, for *P–M* $\Delta = 60°$, and for *O–P* $\Delta = 30°$. There are two types of *O–M* interaction, one *ortho* with $\Delta = 0°$ and separation $r_o = 248$ pm, and the other *para* with $\Delta = 60°$ and separation $r_p = 496$ pm. On averaging these interactions, the expression for the quotient $J(\omega)/R^6_{OM}$ to be substituted in equations (2) and (3) is:

$$\frac{J(\omega)}{R^6_{OM}} = \frac{1}{2}\left\{\frac{1}{r_o^6} + \frac{7}{16r_p^6}\right\} F(\omega,\tau_D,\tau_0) + \frac{9}{32r_p^6} F(\omega,\tau_D,\tau_R) \tag{6}$$

Interactions between aliphatic and aromatic protons. Only interactions within the unit CH_2–CH(Ph)–CH_2 were included.

Since the *P* proton lies on the ring rotation axis, interactions involving *P* do not vary as the ring rotates, and equation (4) was used for $J(\omega)$. The effective distances were calculated to be:

$$R_{AP} = 585 \text{ pm}; R_{XP} = 614 \text{ pm}$$

(R_{XP} was averaged over *trans* and *gauche* conformations of backbone bonds).

For interactions involving the *O* or *M* protons, the internuclear distance as well as the orientation changes when the phenyl ring rotates, as illustrated in *Figure 1* for the *O–A* interaction. Rowan *et al.*[26] have analysed the spectral density function for such a case when the rotating unit is a methyl group experiencing a three fold potential. We have followed their treatment for the present case of a twofold potential, finding that the effective value of $J(\omega)/R^6_{ij}$ is given by:

$$\frac{J(\omega)}{R^6_{ij}} = D_+F(\omega,\tau_D,\tau_0) + D_-F(\omega,\tau_D,\tau_R)$$

where

$$D_\pm = \tfrac{1}{4}(1/r_1^6 + 1/r_2^6) \pm (3\cos^2\beta - 1)/(4r_1^3r_2^3) \tag{7}$$

r_1 and r_2 are the two values of the internuclear distance and β the angle between then. The calculated values of r_1, r_2 and β for the *O, M, A* and *X* protons are given in *Table 2*. It was assumed[23] that in the potential energy minima, the plane of the phenyl ring bisects the C_α–C_β–C_α bond angle. The values for *X–O* and *X–M* interactions are effective averages over *trans* and *gauche* conformations of backbone bonds.

It is estimated that the distances quoted are accurate to within 5%, giving calculated relaxation times to within 30%.

Treatment of experimental and calculated relaxation curves.

All polystyrene samples used were atactic, giving spectra very similar to that at 60 MHz[27]. The *A*, *X* and *O* protons produce separate broad single peaks at 2.0, 1.6 and 6.5 δ respectively, while the *M* and *P* protons overlap in an unresolved peak at 7.0 δ. Experimentally, one can determine the relaxation curves for the total *A*, *X*, *O* and (*M* + *P*) magnetizations. Although in principle the curves are non-exponential because of coupled relaxation, in practice the recovery following inversion of all protons is exponential within errors of 2–3%. We therefore make use as before of the concept of an effective relaxation time T^i_1 where i = *A, X, O MP*, which is obtained by a least-squares fit of a single exponential to the recovery curve from the initial perturbation to the time when the deviation from equilibrium falls to 25% of its initial value. Calculations of T^i_1 for ranges of correlation times were carried out by numerical solution of the system of five equations (1) which can be written in matrix form:

$$\frac{dS'}{dt} = -RS' \tag{8}$$

where **R** is the 5 x 5 matrix with $R_{ij} = 1/T_{ij}$ and **S**′ is the column vector with $S'_i = S_i - S^0_i$. Solution of equation (8) gives:

$$S' = \exp(-\mathbf{R}t)S'_0$$

where S'_0 contains the initial deviations. For complete inversion, $S'_{i0} = -S^0_i$. After numerical evaluation of the matrix exponential, S'_M and S'_P were added to produce a composite curve.

The *A* and *X* signals were too close in relation to their width to allow *A*– {*X*} or *X*– {*A*} double resonance relaxation measurements of the type described for poly(vinyl acetate)[21]. Instead advantage was taken of the fact that significant relaxation coupling occurs between *O* aromatic and aliphatic protons. Aliphatic relaxation times were therefore also measured with all aromatic protons saturated by a strong decoupling field. The relaxation curves were analysed as described above, producing effective relaxation times which will be denoted by T^A_1 {ar} and T^X_1 {ar}. Under conditions of aromatic saturation, the *A* and *X* relaxation is described by the equations:

$$\frac{dS_A}{dt} = -\frac{(S_A - S^0_A)}{T_{AA}} - \frac{(S_X - S^0_X)}{T_{AX}} + \frac{S^0_O}{T_{AO}} + \frac{S^0_M}{T_{AM}} + \frac{S^0_P}{T_{AP}}$$

$$\frac{dS_X}{dt} = -\frac{(S_X - S^0_X)}{T_{XX}} - \frac{(S_A - S^0_A)}{T_{XA}} + \frac{S^0_O}{T_{XO}} + \frac{S^0_M}{T_{XM}} + \frac{S^0_P}{T_{XP}}$$

which are solvable analytically for S_A and S_X.

EXPERIMENTAL

Fractions of polystyrene were obtained from Pressure Chemical Company, Pittsburgh, Pa, USA. Studies of the solvent

Table 2 Structural data for aromatic–aliphatic dipolar interactions for use in equation (7)

Interaction	r_1/pm	r_2/pm	β
O–A	377	234	86°
M–A	552	466	49°
O–X	251	492	65.2°
M–X	468	691	49°

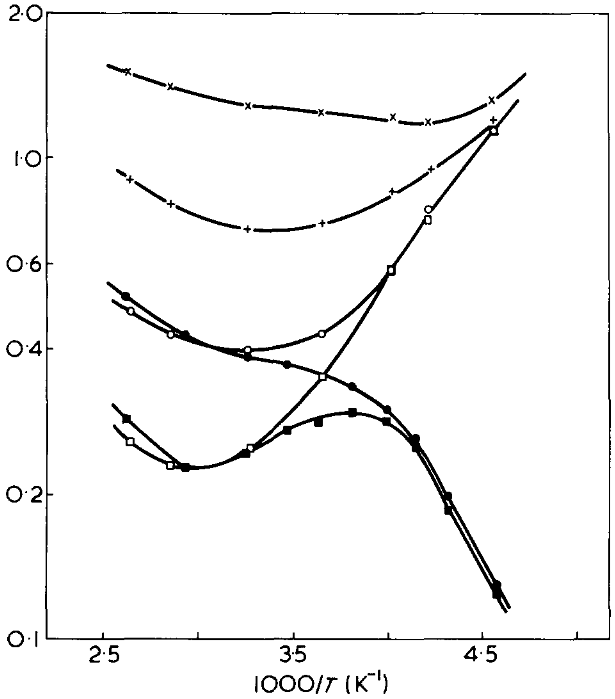

Figure 2 Variation of unperturbed and decoupled relaxation times with temperature for 5% (w/v) polystyrene (M_w = 1.1 x 10^5) in CDCl$_3$: x, T_1^{MP}; +, T_1^{O}; ○, T_1^{A}; ●, T_1^{A} {ar}; □, T_1^{X}; ■, T_1^{X} {ar}

dependence were made on 5% (w/v) solutions of a sample with M_n = 1.1 x 10^5 and M_w/M_n = 1.06 in CDCl$_3$, CCl$_4$, hexachlorobutadiene (HCB) and 90/10 by volume mixture of cyclohexane-d_{12} and toluene-d_8 (CH/T). This last solvent is a θ solvent at 15°C. The molecular weight dependence in CDCl$_3$ solution was investigated using further samples with M_n values of 2.1 x 10^3, 1.0 x 10^4 and 6.7 x 10^5, all with M_w/M_n values of $\leqslant$ 1.1.

The copolymer of styrene and styrene-d_8 was prepared by bulk polymerization of a 95/5 mixture of styrene-d_8 and styrene at 60°C for 11 h using benzoyl peroxide as initiator. The polymer was purified by precipitation from toluene solution by addition to methanol followed by filtration and drying. From g.p.c. M_w was found to be 4.2 x 10^5 and $M_w/M_n \sim 2$. Studies were made on a 5% (w/v) solution in CDCl$_3$. All solutions were degassed and sealed *in vacuo.*

N.m.r. measurements were made on a Varian Associates SC-300 spectrometer operating at 300.246 MHz. Spin–lattice relaxation curves were obtained using the (π–τ–$\pi/2$) inversion recovery sequence.

In the double resonance experiments, quite high decoupling fields were necessary to saturate all aromatic protons. In spite of the large offset, the decoupling field itself had a small but noticeable effect on the relaxation rate of the aliphatic protons, as shown by the fact that when the decoupling field was set at the same offset to high field of the aliphatic groups, the aliphatic relaxation times were about 10% shorter than when the decoupler was off. A correction of this magnitude was therefore applied to the double resonance relaxation times actually measured. Reproducibility was better than 5%.

RESULTS

Experimental data

Figure 2 shows the unperturbed and decoupled relaxation times for polystyrene in a 5% solution in CDCl$_3$ as a function of temperature. The unperturbed relaxation times all pass through a minimum, becoming equal at low temperatures because of rapid spin diffusion. As the temperature falls, the increasing effectiveness of aromatic relaxation via spin–diffusion to the aliphatic protons explains the relative flatness of the curves for T_1^O and T_1^{MP}. The decoupled relaxation times continue to decrease with decreasing temperature, again because of the increasing efficiency of spin diffusion. The most significant quantitative feature of the data shown is the value of T_1^X at its minimum, 240 msec. For isotropic rotational diffusion ($\tau_D \gg \tau_0$), the calculated value of $T_{1\,\mathrm{min}}^X$ is 160 msec, and the value rises as the ratio τ_D/τ_0 decreases[21]. It is clear that the jump process must play a substantial, if not dominant, role in PS magnetic relaxation.

The molecular weight dependence of T_1^X is shown in *Figure 3*. T_1^X alone is shown, because it is dominated by the geminal backbone methylene interaction and therefore must accurately reflects the backbone motion. The other relaxation times vary with molecular weight in the same way as T_1^X. It is seen that for molecular weights above ~2 x 10^4, the relaxation times are practically independent of molecular weight, in agreement with ^{1}H T_2 measurements[3], ^{13}C T_1 measurements[4] and e.s.r. linewidths[10]. Above this molecular weight, relaxation is controlled by local segmental processes, whereas below it, end-over-end tumbling of the whole molecule plays an important role[3,10]. This interpretation is consistent with the observa-

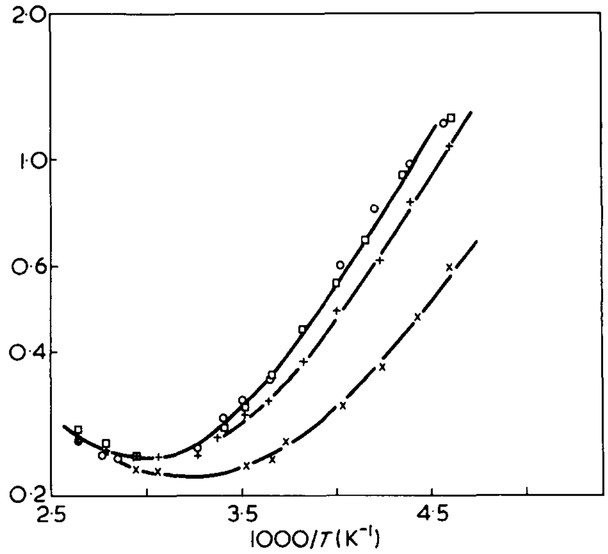

Figure 3 Variation of T_1^X with temperature for 5% (w/v) CDCl$_3$ solutions of polystyrene of different molecular weights. x, 2100; +, 10^4; ○ 1.1 x 10^5; □, 6.7 x 10^5

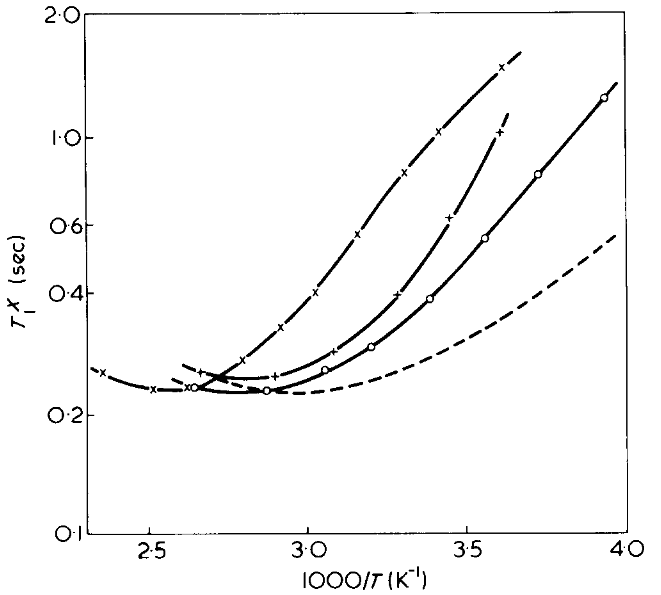

Figure 4 Variation of T_1^X with temperature for 5% w/v solutions of polystyrene, M_w = 1.1 x 10^5: *x*, HCB; +, CH/T; ○, CCl_4; – – – –, $CDCl_3$ (from *Figure 2*)

tion that $T_{1\,\mathrm{min}}^X$ for M_w = 2100 is 10% lower than for the other three samples, indicating a higher value of the ratio τ_D/τ_0.

Figure 4 shows the solvent dependence of T_1^X. It is clear that the solvent has an enormous influence on the segmental motion. The curves for $CDCl_3$, CCl_4 and HCB are similar in shape but are displaced successively to higher temperatures in that order. These three are all good solvents for PS, with similar chemical structure. They differ chiefly in viscosity, the values at 20°C being: $CDCl_3$ 0.58 cp; CCl_4 0.97 cp; HCB 3.30 cp. This is probably the controlling dynamic factor. The CH/T solvent has a viscosity close to CCl_4, and the relaxation times are comparable above ~50°C but as the temperature approaches the θ temperature, the CH/T values display a much higher activation energy, due presumably to higher barriers in a tightly coiled polymer. These observations are in full agreement with e.s.r. data[11] for toluene, cyclohexane and α-chloronaphthalene solutions and ^2H n.m.r. data[9] for benzene and diethylmalonate solutions.

Scaling of solvent dependence

Because of the similarity in shape between the T_1^X *versus* temperature plots for all four solvents, attempts were made to develop a master curve on some form of reduced temperature scale. The following procedure proved satisfactory. Suppose that a correlation time (either τ_D or τ_0) in solvents a and b behaves in each according to the Arrhenius equation but with different activation energies (E) and frequency factors (τ^0)

$$\tau_a = \tau_a^0 \exp(E_a/RT)$$

$$\tau_b = \tau_b^0 \exp(E_b/RT)$$

The temperatures T_a and T_b at which τ_a and τ_b are equal are related by

$$\frac{1}{T_a} = \frac{E_b}{E_a}\,\frac{1}{T_b} + \frac{R}{E_b}\ln(\tau_b^0/\tau_a^0) \qquad (9)$$

Choosing solvent a as a standard, a reduced temperature T^* can therefore be defined for another solvent b by:

$$\frac{1000}{T^*} = p_b \cdot \frac{1000}{T} + q_b \qquad (10)$$

where p_b and q_b are constants for solvent b and are given by:

$$p_b = E_b/E_a$$

$$q_b = \frac{R}{E_a}\ \ln\frac{\tau_b^0}{\tau_a^0}$$

$CDCl_3$ was chosen as the standard solvent, and p_b and q_b for the other three were determined from equation (9) using the temperatures at which T_1^X achieved its minimum value, and the value of 1 sec. *Table 3* gives the results obtained, while *Figures 5–7* show all the relaxation data for all four solvents plotted against the resultant reduced temperature. All four solvents lie on the same master curve within experimental error. This result shows that there is no qualitative difference between polymer motion in the four solvents, only a shift along the temperature scale arising from differences in thermal activation parameters.

Determination of correlation times

Because of the correlation of relaxation time solvent dependence in the preceding section, only the relaxation times

Table 3 Temperature scaling parameters and activation energies for 5% (w/v) solutions of polystyrene, M_w = 1.1 x 10^5

Solvent	p_s	q_s (K^{-1})	(kJ/mol) E_D	E_η	E_{int}
$CDCl_3$	(1)	(0)	19 ± 3	8	11 ± 3
CCl_4	1.29 ± 0.1	–0.60 ± 0.2	25 ± 4	11	14 ± 4
HCB	1.52 ± 0.1	–0.84 ± 0.3	29 ± 4	13	16 ± 4
CH/T	1.67 ± 0.2	–1.62 ± 0.4	32 ± 5	13	19 ± 5

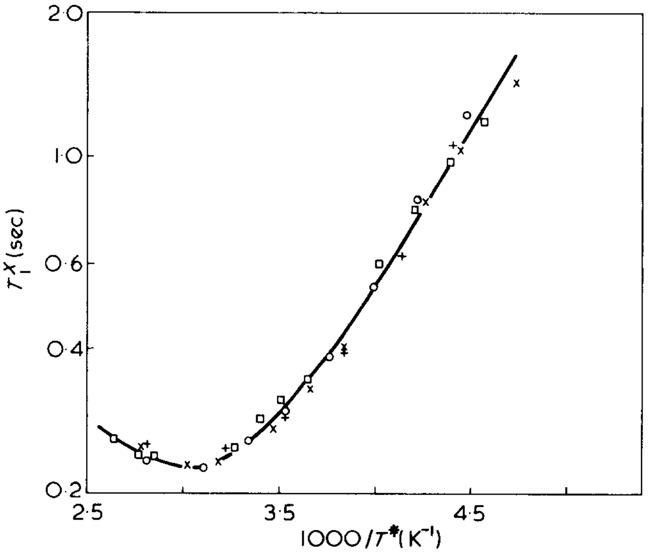

Figure 5 Variation of T_1^X with reduced temperature T^* calculated from equation (10) using the shift parameters p_b and q_b given in *Table 3*. M_w = 1.1 x 10^5. x. HCB; +, CH/T; ○, CCl_4; □, $CDCl_3$

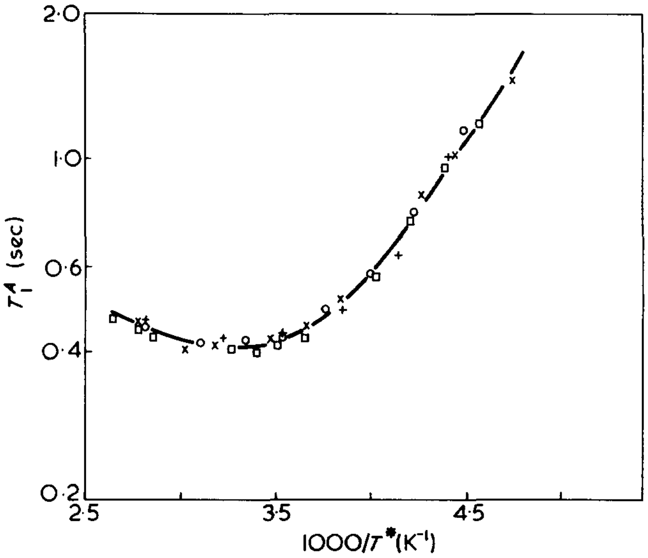

Figure 6 Variation of T_1^A with reduced temperature T^*. (Details in caption to *Figure 5*)

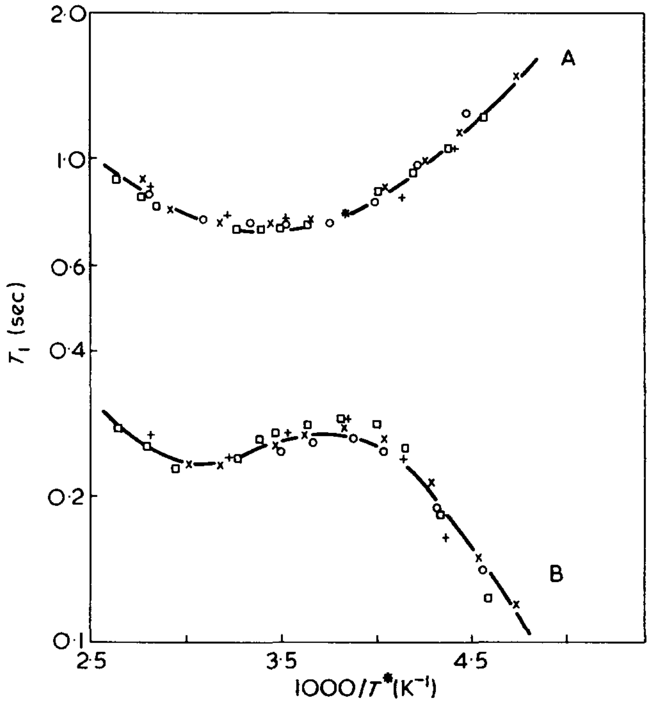

Figure 7 Variation of (A) T_1^O and (B) T_1^X {ar} with reduced temperature T^*. (Details in caption to *Figure 5*)

in $CDCl_3$ were analysed to determine τ_D and τ_0. A number of assumptions were made in this analysis, and these will be discussed before presenting the method and results.

The calculation of effective relaxation times given the correlation times τ_D, τ_0 and τ_J has been outlined in the theory section with the assumption that the only relaxation contributions arise from protons within a sequence of three monomer units. Two other possible sources were ignored. The first, intermolecular interactions, is negligible since dilute solutions in non-protonated solvents were used. The second possibility is interactions between protons in the same molecule but on monomer units separated by some distance along the chain but brought into close proximity by chain coiling. The aromatic *M* and *P* protons are most likely to experience such an effect. However, we shall show later that this mechanism is also negligible with the aid of measurements on the deuterated sample.

The influence of ring rotation on the relaxation times was investigated by carrying out a number of trial calculations for wide ranges of correlation times. These revealed that unlike ^{13}C relaxation times[7], neither aliphatic nor aromatic ^1H relaxation times are strongly affected by τ_J, due to the facts that the *O–M* interaction in the ring has $\Delta = 0°$, and is unaffected by ring rotation, and that the coupling between aromatic and aliphatic protons is weak. It is therefore not possible to derive τ_J from the present data with any degree of accuracy. It has been assumed that $\tau_D = \tau_J$, based on two arguments:

(i) a comparison of the magnitudes of aromatic and aliphatic ^{13}C T_1 values [3,6,7] shows that the phenyl ring is not immobile relative to the backbone, but neither is it rotating much more rapidly. We conclude that τ_J is comparable to whichever correlation time controls the backbone motion i.e. τ_D.

(ii) Potential energy calculations[23] suggest that in the most favoured backbone conformations, the barrier to ring rotation is extremely high, and certainly higher than the observed activation energies[7] of ^{13}C T_1's. It is likely therefore that the ring is free to rotate only when the backbone is in a highly disfavoured conformation[23] or during the backbone jump itself. τ_J will therefore be comparable to τ_D, in both value and activation energy.

τ_D and τ_0 were determined graphically as follows. For a given value of the ratio τ_D/τ_0, the values of τ_D required to obtain the value of T_1^X at each temperature were interpolated from relaxation times calculated for a wide range of τ_D. The remaining five relaxation times expected for that particular τ_D/τ_0 ratio and those τ_D values were calculated and plotted against temperature. The process was repeated for a different τ_D/τ_0 ratio, and finally the experimental values of the remaining relaxation times were superimposed on the predicted plots.

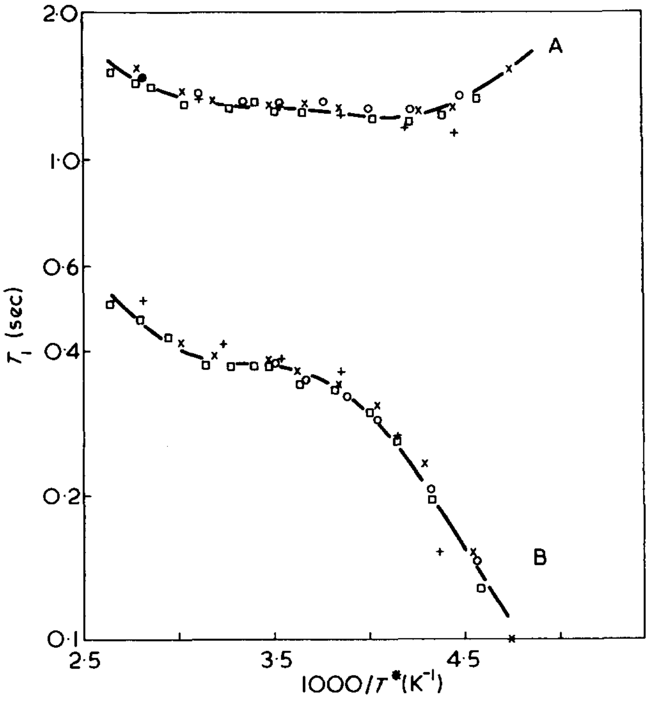

Figure 8 Variation of (A) T_1^{MP} and (B) T_1^A {ar} with reduced temperature T^*. (Details in caption to *Figure 5*)

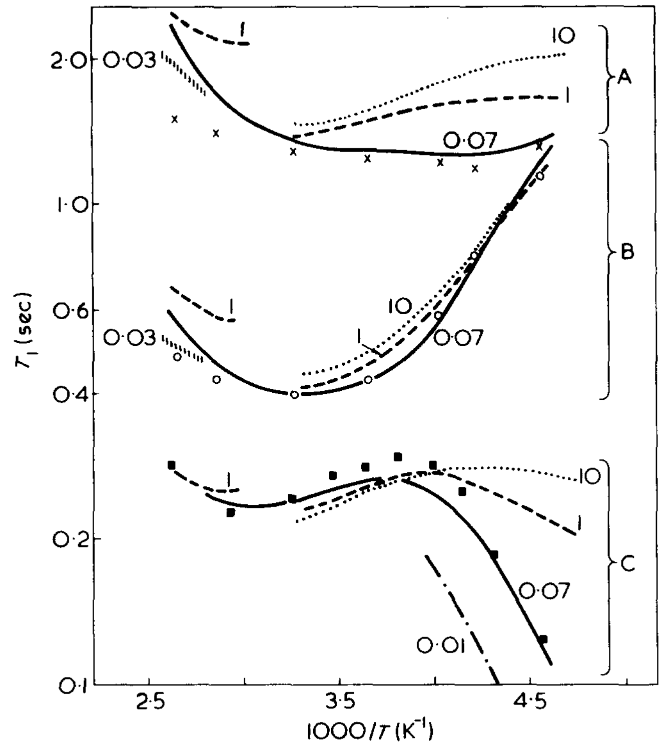

Figure 9 Comparison of experimental and calculated values of (a) T_1^{MP}, (b) T_1^A, and (c) T_1^X {ar}. The symbols are the experimental points and the lines are those predicted for the ratio τ_D/τ_0 given on each curve and the value of τ_D reproducing the experimental value of T_1^X

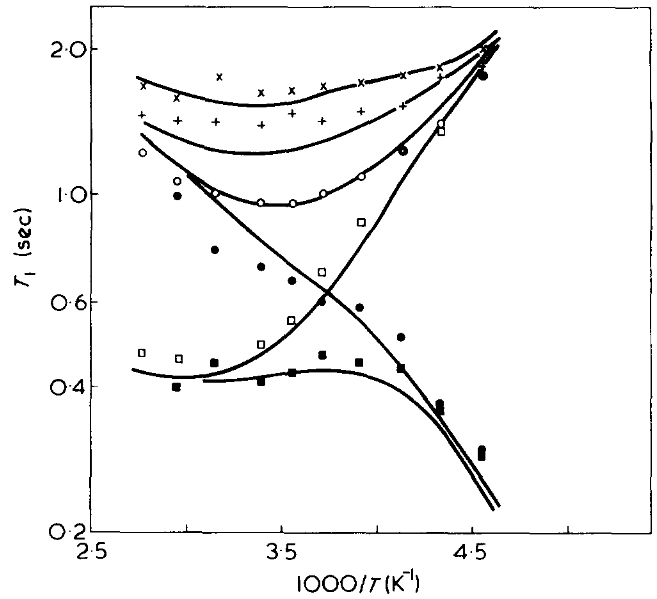

Figure 10 Comparison of experimental (symbols) and calculated (lines) relaxation times for the copolymer of 95% styrene-d_8/5% styrene, 5% w/v in $CDCl_3$. τ_D/τ_0 = 0.1 at all temperatures, and τ_D varies with temperature as in *Figure 11*. x, T_1^{MP}; +, T_1^O; ○, T_1^A; ●, T_1^A {ar}; □, T_1^X; ■, T_1^X {ar}

Results for the $CDCl_3$ solution are shown in *Figure 9*. At low temperatures, the predicted decoupled relaxation times are strongly dependent on the ratio τ_D/τ_0 selected, and the comparison with experimental values unequivocally identifies the value of $\tau_D/\tau_0 \sim 0.07$ as giving the best agreement. At other temperatures, the sensitivity is not so clear but the curves for $\tau_D/\tau_0 \sim 0.1$ seem to give the most convenient fit. This is certainly true at the minimum in T_1^X. As mentioned in the description of the experimental results earlier the minimum value of T_1^X is quite strongly dependent on τ_D/τ_0, and the value observed, 240 msec, corresponds to that predicted for $\tau_D/\tau_0 \sim 0.1$. The same also applies to the minimum in T_1^A. When uncertainties in the internuclear distances and experimental errors are taken into account, the most probable range of τ_D/τ_0 is 0.06–0.3 at the higher temperatures and 0.05 to 0.15 at the lower temperatures. This conclusion applies to all solvents and also to molecular weights greater than ~15 000.

The test of our assumption that only local intramolecular relaxation occurred was carried out by comparing experimental measurements on the deuterated polystyrene in $CDCl_3$ with the values calculated for the correlation times derived for the fully protonated polymer in $CDCl_3$. The result is shown in *Figure 10*. Although in places there are discrepancies of up to 15%, it must be remembered that this can result from distances which are incorrect by less than 3%. The overall agreement is sufficiently good to justify both the neglect of intermolecular interactions and the model used for the chain motion.

An Arrhenius plot of the variation of τ_D with temperature in the $CDCl_3$ solution is shown in *Figure 11*. The activation energy, together with those derived for the other solvents from the temperature shift factors p_b are listed in *Table 3*.

DISCUSSION

Figures 5–9 show that the conformational jump model gives a satisfactory interpretation of all the experimental data, and presumably has a reasonably realistic basis. Our conclusions that τ_D is significantly smaller than τ_0, and that τ_D/τ_0 is independent of temperature are in agreement with an earlier ^{13}C T_1 and *NOE* study[6] of PS in pentachloroethane though the value of τ_D/τ_0 reported there of ~0.4 is slightly higher than the range 0.06 to 0.3 found in the present work. Laupretre *et al.*[3] reported τ_D/τ_0 values of ~0.75 from ^1H T_1 data and ~0.035 from ^{13}C T_1, T_2 and *NOE*

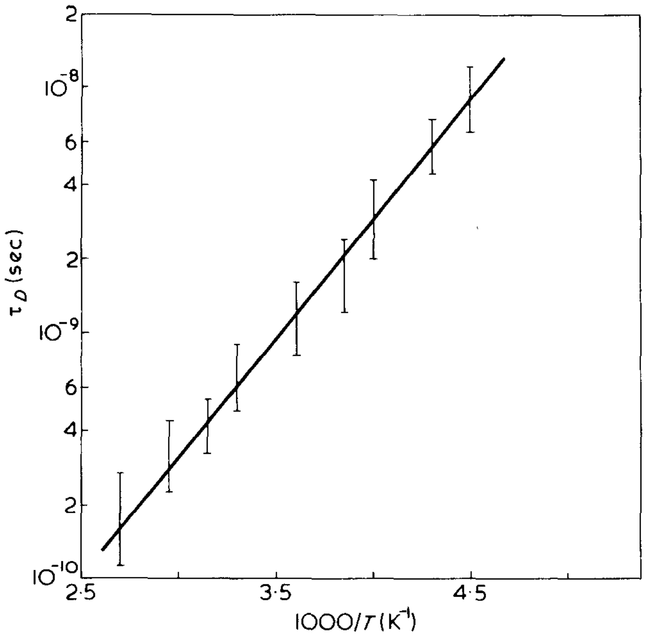

Figure 11 Variation of τ_D with temperature for 5% w/v polystyrene (M_w = 1.1 x 10^5) in $CDCl_3$

measurements on PS in HCB (10% w/v), explaining the discrepancy in terms of differences between the correlation functions for $^{13}C-^{1}H$ and $^{1}H-^{1}H$ internuclear vectors. However, part of it may be due to the fact that coupled relaxation within the proton system was not considered. Valeur and Monnerie[12] have given a τ_D/τ_0 ratio of 0.33 for PS in $CDCl_3$ at 23°C from fluorescence polarization experiments, and Matsuo *et al.*[20] have given a value of 0.083 from ^{19}F relaxation in poly(*m*-fluorostyrene) and poly(*p*-fluorostyrene) in chloroform and benzene solution.

There has recently been some discussion[18,19] of the physical interpretation of the diffusional correlation time τ_0. Valeur *et al.*[18] incorporated an exponential term $e^{-\tau/\theta}$ into the correlation function for three-bond jumps as an allowance for either unspecified isotropic diffusional modes or departure from ideal lattice conditions. A possible isotropic diffusional mode is overall molecular tumbling i.e. the first Rouse–Zimm mode, but this process cannot be significant for the present samples since we find that both τ_D and τ_0 are independent of molecular weight. Moreover, calculations[3,12] of the relaxation time of the first Rouse–Zimm mode show that it is much longer than the measured values of τ_0. Since we have shown that τ_D/τ_0 for PS is independent of molecular weight, solvent and temperature, then the processes contributing to τ_0 must be related to the jumps characterized by τ_D. A possible explanation of the relationship is that τ_0 represents conformational transitions which oblige the whole chain to move, for example when a single bond undergoes a *trans* ↔ *gauche* transition. Such transitions are less probable than those considered by Valeur *et al.*[16] in which the transition is such that the remainder of the polymer chain is undisturbed. Moreover, they will be strongly modified by the large viscous drag exerted on the polymer 'tails' as they attempt to respond to the transition, and it is possible that this viscous damping will produce a small step diffusional correlation function for segments remote from the site of the transition. It is interesting that fluorescence depolarization measurements[12] appear to show that τ_D/τ_0 increases as the solvent viscosity increases, though no values were given. The solution viscosities in that work ranged up to 7.5 cp, considerably higher than in the present work, where experimental uncertainties may obscure a small effect.

Jones and Stockmayer[19] have provided an alternative explanation of τ_0. They have shown that if one assumes Valeur *et al.*'s jump model but with limited coupling between bonds, then a correlation function results which is almost identical to Valeur *et al.*'s exponentially modified expression[18].

If coupling is limited to seven bond units, the correlation function is almost equivalent to Valeur *et al.*'s expression[18] with $\tau_D/\tau_0 = 0.083$, a value which is very close to the ratio obtained from our results. However, until experiments are devised which are sufficiently precise to distinguish the very small differences between the correlation functions, the meaning of τ_0 remains open. It is perhaps significant that it has been found that in poly(vinyl acetate)[21,22], the ratio τ_D/τ_0 rises dramatically as the temperature falls and the τ_0 processes become dominant in strong contrast to polystyrene. The difference may be associated with the difference in polarity of the side-group, which would lead to stronger conformational correlations in poly(vinyl acetate) than in polystyrene. According to Jones and Stockmayer however, stronger coupling leads to *lower* values of τ_D/τ_0. We feel the explanation of this behaviour is still unclear, and further studies of other polymers are in progress in order to obtain sufficient data for a sensible correlation of τ_D/τ_0 with structure.

The activation energies E_D in *Table 3* have been analysed according to Bullock *et al.*[11], using Kramers' theory[30] for diffusion of a particle over a potential barrier. E_D can be written as the sum of activation energies for the solvent viscosity (E_η) and the height of the internal potential barrier (E_{int}):

$$E_D = E_\eta + E_{int}$$

Values of E_η and E_{int} are also listed in *Table 3*. The values for E_{int} are rather higher than the range 8 to 12.5 kJ/mol for the internal barrier quoted in the literature from e.s.r.[11] and other techniques[31,32]. The abnormally high value for CH/T is in agreement with e.s.r. data[11], and presumably arises from greater steric hindrance in a more tightly coiled conformation adopted in poor solvents. The higher values observed here for the good solvents probably reflects the use of a non-exponential autocorrelation function. This is equivalent to a distribution of correlation times which has the effect of decreasing the apparent activation energy of relaxation times.

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