Dynamics of macromolecular chains. ^{13}C spin relaxation study of short-chain polystyrenes in deutero–chloroform solution

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The results of T_1, T_2 and nuclear Overhauser effect (*NOE*) measurements on molecular weights 510–110 000 at weight fractions 0.05–0.60 in the title system suggest that previously neglected entanglement effects are highly significant for the reorientational processes in polymer chains and that previous T_2 estimates from bandwidths may be too low. T_2 is usually equal to T_1, and deviates only at high concentrations in these systems. The data can be represented by a double exponential reorientational correlation function of the form

$$G(\tau) = A\ \exp(-\tau/\tau_A) + B(-\tau/\tau_B),$$

where $A + B = 1$. The correlation times τ_A and τ_B are typically 1.5×10^{-10} and 1.5×10^{-9} s, respectively. B increases with increasing concentration and molecular weight. The terminal phenyl group rotation is quite free in contrast to the backbone phenyls, and a spinning ratio above 15 has been estimated in a 60% solution for this group. Signal assignments and relaxation times (T_1) are given for 15 different ^{13}C signals of these polymers at high concentrations.

INTRODUCTION

Measurements of ^{13}C spin relaxation rates[1] have shown that (unlike small molecules) the reorientation of individual proton–carbon bonds in a polymer, like, for example, polystyrene in solution, cannot be described by a single exponential correlation function. The 'effective correlation times', evaluated from T_1 and T_2 measurements disagree*, and the nuclear Overhauser effect (*NOE*) is lower than the value expected for such T_1 and T_2 values. As further discussed below, this means that the spectrum of reorientational frequencies is not 'white' in the range zero to the nuclear magnetic resonance region (typically 0–200 MHz). The underlying theory for spin relaxation in polymer systems and its relation to a polymer physics picture of the chain dynamics has recently been summarized in an authoritative and comprehensive review by Heatley[1]. The nuclear spin relaxation characteristics of proton-bearing ^{13}C nuclei under complete ^{1}H decoupling is given by equations of the form (1)–(3):

$$\frac{1}{T_1} = 2c\{J(\omega_H - \omega_c) + 3J(\omega_c) + 6J(\omega_H + \omega_c)\} \qquad (1)$$

$$\frac{1}{T_2} = c\{4J(0) + J(\omega_H - \omega_c) + 3J(\omega_c) + 6J(\omega_H) + 6J(\omega_H + \omega_c)\} \qquad (2)$$

$$\eta = NOE - 1 = \frac{\gamma_H}{\gamma_c} \cdot \frac{6J(\omega_H + \omega_c) - J(\omega_H - \omega_c)}{J(\omega_H - \omega_c) + 3J(\omega_c) + 6J(\omega_H + \omega_c)} \qquad (3)$$

where $J(\omega)$ is the spectral density of the magnetic field fluctuations (arising from reorientation of the ^{13}C–^{1}H internuclear vector in the magnetic field) at various fixed angular frequencies depending on the magnetic field strength of the experiment. The theory of spin relaxation is thus well established. It would appear that the correlation function for the reorientational process $[G(\tau)]$ is available from a study of T_1, *NOE* and T_2, since $G(\tau)$ is the Fourier transform of $J(\omega)$. This is unfortunately not possible, since unless a form for $J(\omega)$ is *assumed*, there are three observables (T_1, T_2 and *NOE*) and five unknowns in these relations. Any attempt to extract information about the functional form of $J(\omega)$ by changing the field strength merely introduces more unknowns. A variable temperature study changes $J(\omega)$ and is therefore not of any value in this context either.

There are also several well-founded polymer physics aspects of the reorientational problem, which must be included in any attempt to explain experimental relaxation behaviour[1]. Constraints, introduced by potential energy minima for local reorientation around C–C bonds should, for example, produce a reorientational model similar to a random walk on a diamond lattice, a physically appealing picture (which leads to a non-exponential correlation function). Numerous other types of local† and small-scale cooperative motions of, for

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* Previous studies of ^{13}C T_2 appear to have been made exclusively through bandwidth measurements. Our data below suggest that T_2 and T_1 usually are equal within experimental error and that previous estimates of T_2 could be too low and should be reinvestigated by the transient methods which have recently become available (see Experimental).

† Howarth[2] recently pointed out that internal libration motions can explain the relaxation behaviour of short chains. This paper appeared after the publication of ref 1.

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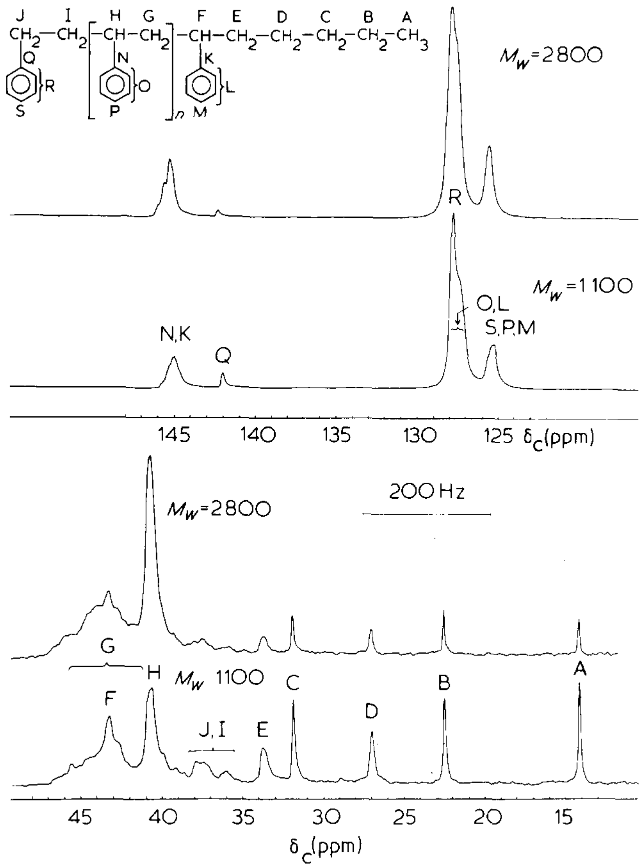

Figure 1 25.05 MHz ^{13}C spectra of short-chain polystyrenes in $CDCl_3$ at 25°C

example, the crankshaft type also contribute, and it is therefore not unreasonable to assume a *distribution* of various reorientational processes and thus a distribution of correlation functions for molecular reorientation. Since the spectral density function $J(\omega)$ and the (effective) correlation function are merely Fourier transforms of each other, this is equivalent to assuming a form for $J(\omega)$. It is therefore not surprising to find (see results reviewed in ref 1) that these 'improved' models lead to a better agreement between observed T_1, T_2 and *NOE* data. In the present authors' opinions this is essentially an effect of the adjustable parameters introduced in the equations. What is clear is that T_2 is (sometimes) less than T_1 and that *NOE* is always less than *NOE*(max); according to (1)–(3), $J(\omega)$ therefore decreases significantly with increasing (ω) in the range 0–200 × 2π × 10^6 rad s^{-1}. A decrease with ω will be true for any distribution of exponential functions‡ since a sum of exponentials leads to a superimposed set of Lorentzians after Fourier transformation§, which decreases monotonically with ω. If at least one of these exponential decays is slower than the inverse n.m.r. frequency this leads to a significantly low frequency peaked form of $J(\omega)$.

During studies of end-group mobility in fairly concentrated solutions of short-chain polystyrenes (*Figure 1*) by ^{13}C relaxation methods we noted some interesting concentration effects which were investigated in some detail. The results indicate large motional effects from previously neglected *inter*molecular contributions (chain entanglements) to the reorientational behaviour. The rotational characteristics of the terminal phenyl ring have also been investigated and ^{13}C chemical shift assignments have been made.

Here, we demonstrate that there appears to be no justification for neglecting entanglement effects when interpreting nuclear spin relaxation data of polymers in solution. Thus the reorientational behaviour of polymers in solution must be far more complex than suggested by the apparent success of the diamond lattice reorientational models for example in interpreting spin relaxation data.

EXPERIMENTAL

All experiments were performed at 25°C on a JEOL FX-100 spectrometer operating at 25.05 MHz for ^{13}C nuclei. Samples were prepared by weighing in 8 mm thin-walled tubes which were then inserted and centred with Teflon spacers in 10 mm tubes containing D_2O for lock purposes. All transient experiments were carried out under the control of the autostacking mode of the JEOL FG/BG programme package. During T_1 measurements (inversion–recovery sequence) and T_2 measurements (Carr–Purcell–Meiboom–Gill, CPMG, sequence, 180°-pulse interval 2–3 ms) a wait period of at least $5T_1$ was introduced between experiments.

For *NOE*-measurements (by the gated decoupler technique) a wait period of at least $10T_1$ was used.

T_2 measurements are not yet common in *FT* relaxation studies, and some pitfalls regarding ^{13}C T_2 under broadband proton decoupling conditions should be pointed out. As noted by Ernst[3] during pioneering experiments, 'insufficient decoupling power' causes a broadening of the ^{13}C lines, i.e. a *contribution* to the apparent $1/T_2$. Later Freeman and Hill[4,5] noted rotating-frame resonance effects during CPMG experiments, also leading to artificially low T_2 values. It appears from the spectra given[3–5] that these effects will completely dominate the T_2 relaxation for ^{13}C nuclei which otherwise should have long T_2 values. A measured carbon T_2 value will thus depend on the irradiation power, the magnitude of proton couplings to that carbon, noise bandwidth and the irradiation frequency setting; in addition, CPMG-based T_2 values will depend on the pulse interval between 180° pulses. The presence of these $1/T_2$ contributions is detectable from experimental T_2 determinations on small molecules which should have $T_2 = T_1$, because $1/T_1$ is free from such artifacts. Tests indicate that $1/T_2$ values above 1 s^{-1} are essentially free from these unavoidable effects under the measurement conditions used in our experiments, and since the polymer carbons have relaxation rates in the 2–25 s^{-1} range, the effect is unimportant in the present work. In particular it should be noted that most T_2 values are equal to T_1 within error limits and that the crucial observations of $T_2 < T_1$ at higher concentrations are the least affected by the potential artifacts.

The short-chain atactic polystyrenes were obtained from Polymer Laboratories Ltd, UK and had $\bar{M}_w/\bar{M}_n$ specifications below 1.11. The polystyrene sample, $M = 110000$ ($\bar{M}_w/\bar{M}_n \leqslant 1.06$) was obtained from Pressure Chemical Co., USA. Deuterochemicals were purchased from CIBA AG, Switzerland.

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‡ It is instructive to consider the data in *Table 2* below and the underlying functional description of $G(\tau)$.

§ See the mathematically analogous evaluation of the free induction decay in the pulsed n.m.r. experiment.

Table 1 ^{13}C shifts and observed spin–lattice relaxation times in $CDCl_3$ at 25°C

Signal[a]	δ_C	T_1 (M = 1100)/s[b]	T_1 (M = 2800)/s[c]
A	14.1	1.20	1.55
B	22.5	0.53	0.86
C	31.8	0.26	0.43
D	26.9	0.14	0.21
E	33.7	0.093	–
F	43.1	0.11	~0.1
G	40–46	0.033	~0.03
H	40.7	0.062	0.069
I, J	36–38	~0.05	–
K, N	145	~0.8	~0.8
L, O	127.6	0.077	0.089
M, P	125.4	0.075	0.081
Q	141.9	1.8	–
R	127.8	~0.45	~0.55
S	125.4	(<0.15)	–

[a] With reference to *Figure 1*

[b] A 60% w/w solution

[c] A 50% w/w solution

RESULTS AND DISCUSSION

Signal assignments and end-group reorientation

The signal assignments are given in *Figure 1*. They have been made through standard additive substituent rules, considerations of relaxation times, relative intensity changes between different molecular weights and also through coherent ^{13}C–{^{1}H} off-resonance decoupling techniques, which were particularly useful for the assignment of signal F. This small peak on top of the CH_2 band definitely splits into a doublet in off-resonance spectra and therefore must arise from a CH group. Signal R was assigned to the *o,m*-carbons of the terminal phenyl group. Through signal integration of expanded-scale spectra of the aromatic carbons under suppressed *NOE* conditions (with the decoupler on only during acquisition and a long delay ($>10T_1$) between pulses) it was confirmed that the sharp peak on top of the L,O-signal arises from the *o,m* signals of *one* phenyl group. The sharpness of the peak reflects slow relaxation conditions (as do the narrow widths of lines A–E) and thus also a rapid reorientation rate. It is interesting to note that no corresponding sharp peak is found in the *para* band and that the J signal is quite broad. This means that only this phenyl ring rotates 'rapidly' around the J–Q bond. (More correctly, phenyl group rotation is an important process for the reorientation of these *ortho* and *meta* proton–carbon vectors.) Relaxation times (T_1) were determined for all carbons in the molecule and are summarized in *Table 1*. At these high concentrations the reorientational mobility is insensitive to the molecular weight. The relaxation of the L,O,R and M,P,S bands was studied in some detail, to rule out the presence of 'hidden' signals from mobile carbons. A typical collection of spectra from an inversion–recovery experiment with intentionally long pulse intervals and high *S/N* is shown in *Figure 2*. Difference spectra were prepared through data manipulation where for example the 0.4 s spectrum was subtracted from the 0.6–6 s spectra through available software routines. These spectra only revealed the 'R band' and no hidden *para* signal in the M,P,S region. The relaxation of the R-signals in the difference spectra can be analysed with an exponential function of the functional form $A(1-e^{-(t-t_{ref})/T_1})$ if the last part of the relaxation is assumed to be monoexponential; this provides a method for determining the relaxation time of the slowly relaxing signal, without contributions from the main signal (which has completely relaxed at t_{ref}). An alternative procedure is curve-fitting of the raw data to a double exponential. This was also applied for the channel indicated with an arrow in *Figure 2*. These two relaxation time determinations agreed to a satisfactory extent ($\pm 10\%$). T_1 data for the L,O signals in *Table 1* and in *Figures 3a–3c* are corrected for the presence of the sharp L signal.

In conclusion these data reveal that only for the Q,R,S ring is there a large contribution from phenyl group rotation to the total reorientation rate for the *ortho* and *meta* CH bonds. (Phenyl group rotation does not contribute to the *para* CH bond reorientation process.) It is also possible to estimate a numerical value for the Q,R,S phenyl rotation rate in the form of a spinning ratio (ρ) for the phenyl group, from the ratio of T_1 values for the R and J or R and S signals (e.g. ref 9, pp 132–133). For the 60% solution of the $M = 1100$ polymer these data suggest that ρ is above 15.

Several studies of phenyl group rotation in the inner parts of the chain have been undertaken[1] and the results have suggested that these phenyl rotations are of minor importance for the total reorientational rate of this side-group, probably due to severe steric hindrance between adjacent phenyl rings. This effect has evidently much less influence on the terminal phenyl group, although the rotation of the K,L,M group is still quite hindered, despite having only one phenyl neighbour. The terminal alkyl chain exhibits the typical monotonic decrease in mobility along the chain which is found for derivatives of n-alkanes (e.g. ref 10, pp 117–121). At the high concentrations necessary for a study of these signals, no motional dependence on M was found.

Spin relaxation measurements

The results of more detailed measurements on the aromatic carbons are summarized in *Figures 3a–3c* and are given in logarithmic form to give an equal error presentation (relative errors of measured relaxation rates are approximately constant)*. We note that there is a distinct dependence of the relaxation behaviour on both polymer concentration and molecular weight.

A convenient and general parameter for the characterization of polymer solutions is c^*, the crossover concentration from dilute to semidilute solutions (i.e. where incipient chain overlap starts to become significant). According to Simha *et al.*[7,8], c^* can be estimated from the relation $c^* = 1.1/[\eta]$ values, which for short chains are independent of solvent were estiamted to be 2.3, 3.0, 5.2, 10 and 20 $\mathrm{cm^3\,g^{-1}}$ for molecular weights 510, 1100, 3300, 9500 and 110 000, respectively[9]. The significance of c^* is somewhat dubious for the shortest chains, although we still believe that it is a useful first estimate of the concentration region where intermolecular entanglements start to become significant. In *Figures 3a–3c*, c^* values for the different molecular weights have been indicated with arrows.

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* The relaxation of the *para* signal reflects the same reorientational processes as experienced by the backbone carbons, but is easier to study. Since phenyl rotation is slow the same is true for the *ortho* and *meta* carbons. Thereby the relaxation can be studied at a higher signal-to-noise ratio and the results become more accurate than for the broad backbone signals.

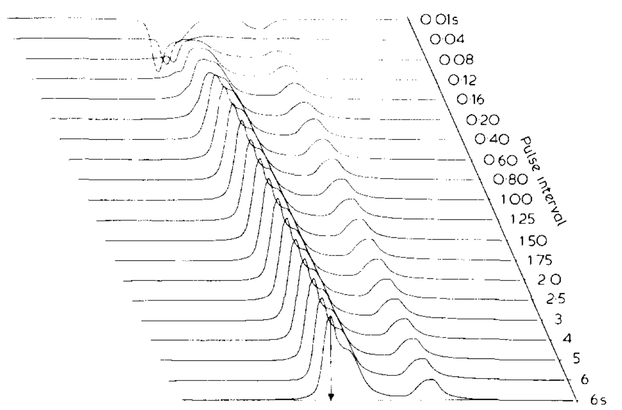

Figure 2 Inversion–recovery experiment on the aromatic carbons of polystyrene (M = 1100) for the detection of slowly relaxing signals (see text)

As seen in the Figures, there are several correlations between c^* and the relaxation behaviour: (a) T_2 is *equal* to T_1 within experimental error up to c^*, but then T_2 diverges to a significant extent; (b) the *NOE* for each molecular weight is constant with concentration up to c^* and then decreases; (c) at c^* the relaxation rates are equal for all molecular weights, despite the differences in polymer concentration. These combined observations can hardly be the result of coincidences. Although this does not lead to a form for $J(\omega)$ it does definitely point to a major *cause* for low-frequency motions, which seems to have been neglected or deemed unimportant — namely that intermolecular entanglements evidently hinder local or small-scale reorientation processes for long fractions of time. The effect appears to be so large that it obscures most other low frequency reorientational processes. It should be noted that virtually all previous studies of chain dynamics[1] have been made on relatively high molecular weight polymers, well above their c^* (which occur at low concentrations) and therefore the interpretations of the results are affected by the conclusions of the present paper. The introduction of intermolecular effects into local and small-scale chain reorientation models is probably not an appealing task, however.

Overall rotation of the polymer coils is a possible reorientational process, especially for the lowest molecular weights and the low concentration $M = 510$ polymer data are probably strongly affected by this. These coils should approximately be of the size of a cholesterol molecule, which typically has $R_1 \sim 2\ s^{-1}$ for CH carbons in non-viscous solution. According to spin relaxation theory and crude hydrodynamic approximations applied to molecular systems, R_1 should increase approximately proportionally to the molecular radius cubed, were it the only reorientational process (i.e. for a rigid molecule). This is not in agreement with the experimental data, and therefore overall reorientation is probably a process of minor importance already at $M = 1010$. Lauprêtre *et al.*[11] have also considered this particular problem and calculated the overall rotational diffusion coefficients for $M = 600$ and 2100 from a hydrodynamic equation and the solution viscosity. They also reached similar conclusions through comparisons with experimental data. It does appear likely that the steeper slopes of the $M = 510$ relaxation data in *Figures 3a–3b* are the result of significant overall rotational contributions at low concentrations.

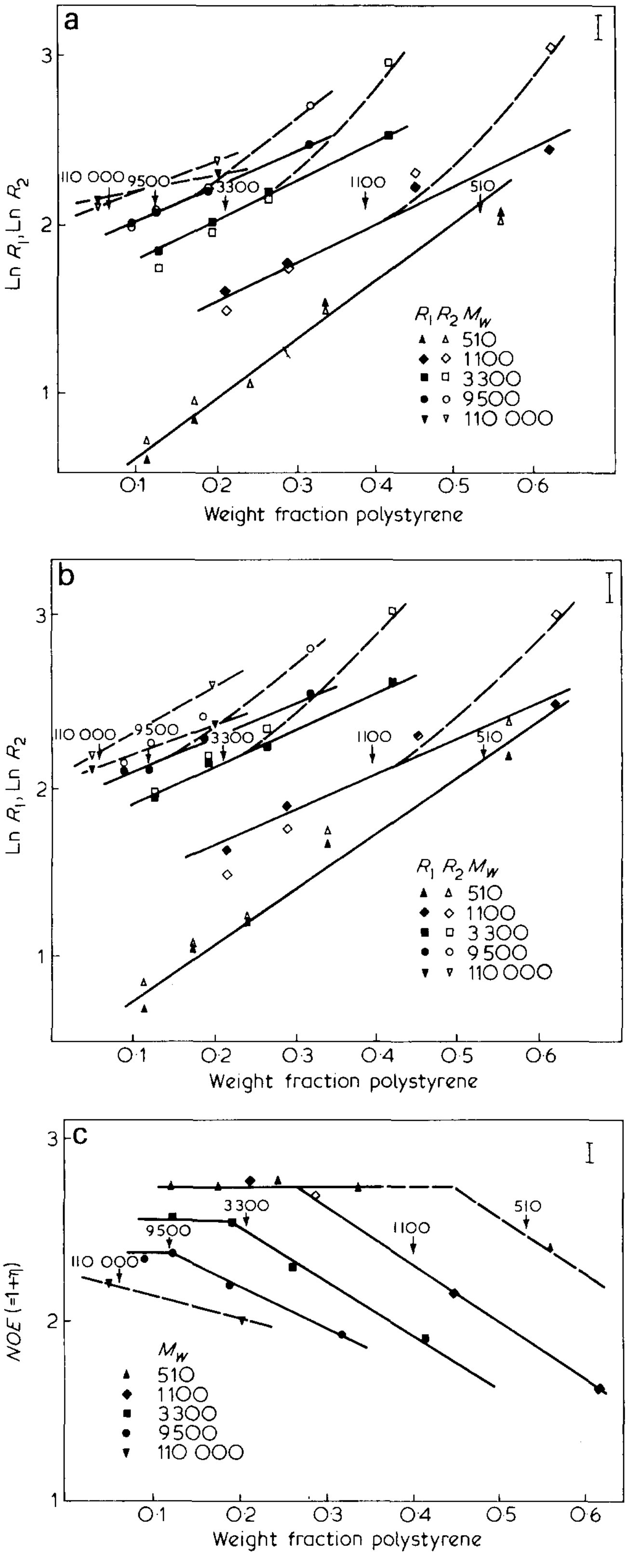

Figure 3 (a) Relaxation rates R_1 (= $1/T_1$) and R_2 (= $1/T_2$) for the *ortho* and *meta* carbons for various molecular weights and polymer concentrations in $CDCl_3$ at 25°C. (b) Corresponding diagram for the *para* carbons. (c) Nuclear Overhauser effects as a function of polymer concentration and molecular weight. Values for the *ortho, meta*, and *para* carbons were similar throughout and therefore an average value has been presented in this diagram. In all three diagrams, the estimated error limits are given in the upper right-hand corner. The arrows indicate the approximate midpoint of the region where intermolecular coil overlap occurs (see text). The solid lines in (a) and (b) are linear least-squares fits to the R_1-values. The broken lines in (a)–(c) are intended to be an aid to the eye and have no other significance

Table 2a Results of an interpretation of the relaxation data in terms of a double exponential correlation function[a]

M	% w/w	A	τ_A/s	B	τ_B/s	R_1 (obs)	R_1 (calc)	R_2 (obs)	R_2 (calc)	NOE (obs)	NOE (calc)
110 000	5.0	0.58	0.104×10^{-11}	0.42	0.149×10^{-8}	8.40	8.12	8.62	8.89	2.21	2.23
	20.0	0.70	0.226×10^{-9}	0.30	0.320×10^{-8}	10.42	10.42	12.12	12.12	2.02	2.02
9500	9.0	0.67	0.924×10^{-10}	0.33	0.147×10^{-8}	7.77	7.51	7.85	8.09	2.35	2.37
	12.2	0.81	0.232×10^{-9}	0.19	0.226×10^{-8}	8.13	8.13	8.80	8.80	2.38	2.38
	18.8	0.53	0.133×10^{-10}	0.47	0.154×10^{-8}	9.49	9.38	10.18	10.30	2.20	2.21
	31.6	0.66	0.300×10^{-9}	0.34	0.465×10^{-8}	12.55	12.55	16.04	16.04	1.89	1.89
3300	12.5	0.81	0.167×10^{-9}	0.19	0.133×10^{-8}	6.62	6.32	6.36	6.62	2.58	2.61
	19.2	0.68	0.151×10^{-9}	0.32	0.119×10^{-8}	8.00	7.78	7.98	8.19	2.55	2.57
	26.3	0.59	0.880×10^{-10}	0.41	0.150×10^{-8}	9.16	8.95	9.49	9.70	2.30	2.31
	41.6	0.64	0.334×10^{-9}	0.36	0.690×10^{-8}	13.20	13.20	20.29	20.29	1.81	1.81
1100	21.2	0.79	0.109×10^{-9}	0.21	0.722×10^{-9}	4.81	4.56	4.44	4.65	2.78	2.83
	28.7	0.88	0.206×10^{-9}	0.12	0.130×10^{-8}	6.23	5.90	5.81	6.09	2.70	2.74
	44.6	0.52	0.362×10^{-14}	0.48	0.157×10^{-8}	9.73	9.42	10.07	10.37	2.16	2.18
	61.8	0.61	0.212×10^{-9}	0.39	0.780×10^{-8}	11.94	11.94	21.12	21.12	1.63	1.63
510	11.3	0.96	0.587×10^{-10}	0.04	0.142×10^{-8}	1.90	1.98	2.15	2.05	2.74	2.70
	17.4	0.96	0.909×10^{-10}	0.04	0.137×10^{-8}	2.56	2.60	2.72	2.67	2.80	2.78
	24.1	0.96	0.112×10^{-9}	0.04	0.150×10^{-8}	3.08	3.07	3.13	3.14	2.78	2.78
	33.8	0.81	0.117×10^{-9}	0.19	0.951×10^{-9}	4.98	4.91	5.00	5.07	2.73	2.74
	55.9	0.70	0.175×10^{-9}	0.30	0.157×10^{-8}	8.46	8.49	9.12	9.09	2.42	2.42

[a] Results are based on a least-squares fit of the trial correlation function $G(\tau) = A\,\exp(-\tau/\tau_A) + B\,\exp(-\tau/\tau_B)$ to the experimental data $(A + B = 1)$. The quantity $((R_1\,(\mathrm{obs}) - R_1\,(\mathrm{calc}))/R_1\,(\mathrm{obs}))$**2 + $((R_2\,(\mathrm{obs}) - R_2(\mathrm{calc}))/R_2(\mathrm{obs}))$**2 + $((NOE(\mathrm{obs}) - NOE(\mathrm{calc}))/NOE(\mathrm{obs}))$**2 has been minimized for each set of data. Average values for the aromatic carbons have been used since the results were quite similar (see *Figure 3*). The proton–carbon distance has been assumed to be 0.109 nm

Table 2b Corresponding data interpretation in terms of two fixed correlation times, $\tau_A = 1.5 \times 10^{-10}$ s and $\tau_B = 1.5 \times 10^{-9}$ s, in varying proportions

M	% w/w	A	B	R_1 (obs)	R_1 (calc)	R_2 (obs)	R_2 (calc)	NOE (obs)	NOE (calc)
110 000	5	0.68	0.32	8.40	8.27	8.62	8.86	2.21	2.42
	20	0.52	0.48	10.42	10.90	12.12	11.79	2.02	2.33
9500	9.0	0.73	0.27	7.77	7.57	7.85	8.08	2.35	2.45
	12.2	0.69	0.31	8.13	8.18	8.80	8.76	2.38	2.42
	18.8	0.60	0.40	9.49	9.52	10.18	10.25	2.20	2.37
	31.6	0.35	0.65	12.55	13.63	16.04	14.84	1.89	2.28
3300	12.5	0.81	0.19	6.62	6.27	6.36	6.63	2.58	2.53
	19.2	0.72	0.28	8.00	7.69	7.98	8.21	2.55	2.44
	26.3	0.64	0.36	9.16	9.01	9.49	9.68	2.30	2.39
	41.6	0.25	0.75	13.20	15.23	20.29	16.62	1.81	2.26
1100	21.2	0.92	0.08	4.81	4.50	4.44	4.66	2.78	2.71
	28.7	0.84	0.16	6.23	5.79	5.81	6.10	2.70	2.56
	44.6	0.60	0.40	9.73	9.59	10.07	10.33	2.16	2.37
	61.8	0.30	0.70	11.94	14.36	21.12	15.65	1.63	2.27
510	11.3	1.00	0.00	1.90	3.16	2.15	3.16	2.74	2.97
	17.4	1.00	0.00	2.56	3.16	2.72	3.16	2.80	2.97
	24.1	1.00	0.00	3.08	3.16	3.13	3.16	2.78	2.97
	33.8	0.89	0.11	4.98	4.87	5.00	5.07	2.73	2.66
	55.9	0.67	0.33	8.46	8.48	9.12	9.09	2.42	2.41

Regarding the intermolecular entanglement effects on the chain dynamics it also appears probable that the differences in chain mobility between different molecular weights at low concentrations can be assigned to a result of increased *intra*molecular entanglements, the occurrence of which naturally increases with molecular weight. As discussed above, the polymer 'coils' are too large for overall rotation to be an important process, so the motional effect must be due to local or small-scale processes. It may be argued that differences are due to changes in solution viscosity†. The viscosity coefficient, however, relating frictional force and velocity in a solution, is a macroscopic model parameter with only minor significance for the reorientational behaviour of small molecules as numerous n.m.r. investigations have shown (for some early studies, see ref 10, pp 117 121). This would also be true for small-scale chain reorientational processes. From the large effects of molecular weight on chain mobility it thus appears that the intramolecular entanglement effect could be so important that it may completely obscure any subtle details (e.g. random walks on diamond lattices, librational motions and crankshaft reorientations) of the chain dynamics.

While this work was in progress a ^{13}C T_1 and NOE study of ^{13}C enriched polystyrene appeared ($M = 165\,000$, $\bar{M}_w/\bar{M}_n = 1.63$)[12]. The concentration dependence of the T_1

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† In a way this would be a circular argument: fluid viscosity is, on the microscopic level, related to various kinds of molecular interactions, such as entanglements, hydrogen bonding etc.

values of the enriched α carbon clearly indicated concentration effects above 10% concentrations in toluene-d_8 (which, however, should be far above c^*) and these were also interpreted in terms of intermolecular entanglements. We have not noted any such effects in our study, but the conclusions are similar and raise many arguments against previous interpretations of nuclear spin relaxation data in terms of local and small-scale chain dynamics. It appears to be feasible to suppress entanglement effects only for relatively short chains (say 20–50 monomer units) at relatively low concentrations.

For completeness, an analysis of the experimental data has been made in terms of a doubly exponential reorientational correlation function (*Table 2a*) with the introduction of three parameters [τ_A, τ_B and A ($A+B=1$)] the data can be represented within experimental error throughout the series (sometimes almost exactly) by this simplest possible description of the reorientational process. The parameters are highly covariant, and an error analysis has not been considered meaningful. An overall description of the trends in the data suggests that B (representing the slow process) increases with higher concentration and molecular weight. τ_A and τ_B, respectively, are typically of the orders of 1.5×10^{-10} and 1.5×10^{-9} s. *Table 2b* summarizes an analysis in terms of varying proportions of these two reorientational descriptions. The agreement is mostly within experimental error. These motional parameters could be assigned to average descriptions of local and small-scale reorientational processes.

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