Molecular motions in low molecular weight melts of polystyrene studied by n.m.r. relaxation

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The proton spin-lattice relaxation times of polystyrene were determined selectively for the phenyl and chain protons at 88 MHz in the temperature range of the α-process using a usual *FT*-inversion-recovery experimental procedure. The temperature and molecular weight dependence of the relaxation times are discussed qualitatively from a phenomenological point of view. The phenyl ring and main chain are coupled and have cooperative character.

(Keywords: ^{1}H-spin-lattice relaxation; polystyrene melts; temperature and molecular weight dependence of chain and ring motions)

INTRODUCTION

Previous papers on nuclear magnetic relaxation (n.m.r.) in polystyrene (PS) have dealt predominantly with the molecular motion in this polymer[1–7]. $T_1(^1H)$ and $T_{1\rho}(^1H)$ measurements were discussed in terms of the four known relaxation processes[8,9].

Recently Kimmich *et al.*[10] reported the frequency and molecular weight dependence of T_1 and interpreted their results on the basis of a three-component model of molecular dynamics in polymer melts including parameters of the reptation model of De Gennes[11].

More recent papers reported on ^{2}H-n.m.r.[12] and ^{13}C-n.m.r.[13] using specific experimental techniques. In particular, Sillescu *et al.*[12] concluded from their ^{2}H experiments that chain motion in the glass transition region of PS can be described by a relatively rapid rotational diffusion process restricted to an angular range of approximately ±10° close to T_g, in agreement with previous results of Spiess[14].

Other features reported by Schaefer *et al.*[13] were based on their results of $T_1(^{13}C)$ and $T_{1\rho}(^{13}C)$ experiments in glassy PS at room temperature. They discussed large-amplitude high-frequency and low-frequency ring motions and main-chain motions. The latter were interpreted in terms of the presence of at least two classes of motions: (i) rotations about the ring C_2 axes in cooperation with main-chain motions, and (ii) cooperative main-chain motions in which the rings undergo limited translations but no rotation.

The aim of this work is to report some experimental results of high-frequency $T_1(^1H)$ relaxation experiments, at 88 MHz, in a series of narrow PS fractions at temperatures above the glass transition temperature $T_g(M_w)$. Direct measurements were made of the nonexponential longitudinal relaxation decays, which were separated into two exponentials related to the ring and chain protons. For temperatures much higher than T_g and for molecular weights smaller than the critical M_c, strong modulations appeared in the nuclear signals (FID) and two separated lines are obtained by Fourier transformation (*FT*). Then the usual ^{1}H-*FT*-inversion-recovery experiment was done to study selectively ring and chain relaxation in the temperature range of the α-process in PS.

EXPERIMENTAL

The measurements of $T_1(^1H)$ were done on a Bruker SXP 4-100 pulse spectrometer at 88 MHz using the inversion-recovery pulse sequence (π)–τ–$(\pi/2)$ directly and with Fourier transformation. The temperature range was 413–523 K. The samples were narrow fractions of atactic PS analogous to those described in ref. 16. Molecular weights 2100, 4000 and 12 000 were chosen for the selective experiments with Fourier transformation (*Table 1*). The samples were evacuated at about 10^{-2} Pa for two days and sealed *in vacuo*.

The homogeneity of the laboratory magnetic field was controlled by a reference water probe which has a T_2 value greater than 5 ms. The accuracy of the experimental relaxation times T_1 was estimated to be better than ±15%. The fitting parameters have comparable accuracy.

RESULTS

As mentioned above, the total longitudinal relaxation decay could be separated into two exponential components (*Figure 1*) for the different molecular weights. The molecular weight dependence of the short and long component of T_1 is shown in *Figure 2a*. From the relative intensities of these components for molecular weights smaller than the critical value, M_c ($M_c = 31\,200$, ref. 15), and from the selective *FT* measurements it is concluded that the short component corresponds to the chain and the long to the phenyl ring protons.

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Table 1 Characteristic data of the atactic low molecular weight PS fractions chosen for the selective T_1 relaxation measurements

Sample	M_w	M_w/M_n	P[a]	T_g^b (K)	T_g^c (K)
2100	2100	1.06	20	329	326
4000	4000	1.10	38	350	349
12000	12200	1.10	115	360	360

[a] Number of monomeric units, degree of polymerization
[b] T_g measured with a Perkin–Elmer DSC-1B calorimeter
[c] T_g calculated from the empirical relation due to Fox and Flory[14]

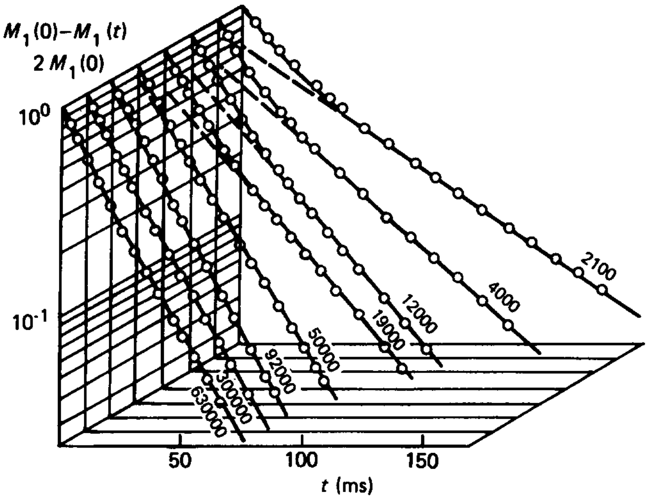

Figure 1 Semilogarithmic plots of the two-component longitudinal relaxation in narrow PS fractions at 508 K and 88 MHz

In the molecular weight dependence of *Figure 2a* two steps are seen above and below M_c. This behaviour was also observed by Kimmich *et al.*[10] at 473 K and 90 MHz, but they predicted only a single averaged exponential relaxation function and indicated only one step near $M_w \approx 8000$. According to their interpretation, based on a three-component model of molecular dynamics in polymer melts with component A (anisotropic segment reorientation by diffusing defects), B (reptative displacement around tube bends) and C (tube renewal), the present results are assumed to reflect the transition from case IVb to case IVa for $M_w > M_c$ and from case IVa to case III for $M_w < M_c$. The last two cases are dominated by component B, while in case IVb, component A becomes important. The approximated slopes of the molecular weight dependence of T_1 in *Figure 2a* are in agreement with this concept.

It can be also seen that the high frequency T_1 data for chain and phenyl-ring relaxation are not influenced by M_c. The relative intensities of the two components (*Figure 2b*) are nearly constant up to M_c and correspond exactly to the initial proton-spin magnetizations related to time $t=0$ of the ring and chain protons in PS. Above M_c the intensity of the long component (ring protons) increases to a value of 0.85 for the highest M_w. This effect is associated with the more effective relaxation of the phenyl groups acting as relaxation sinks for the chain protons. It can be affected by sufficiently large dipolar interactions between both proton groups, indicated by a visible overlapping of the n.m.r. absorption lines (*Figure 3b*) above $M_w = 19\,000$ at 508 K. The averaging processes depend also on temperature, and a broadening of the n.m.r. lines occurs with decreasing temperature. From this it follows that the measurements of a separated relaxation can be realized only at sufficiently high temperatures. For temperatures higher than 420 K strong modulations were observed in the FID, which are caused by the chemical shift between ring and chain protons and by sufficient averaging of the dipolar interactions due to rapid rearrangements of phenyl rings and chain segments as mentioned above (*Figure 3a*).

After Fourier transformation of the FID two distinct lines were observed for the samples with $M_w < M_c$, separated by about 400 Hz and with a width of about 150 Hz (*Figure 3b*). The relative intensities of both these lines correspond to the amounts of the chain (0.375) and ring (0.625) protons as marked in *Figure 3b*. Consequently it was possible to carry out a usual *FT*-inversion-recovery T_1 measurement without additional experimental techniques for the selective relaxation studies in the low molecular weight samples.

Table 2 shows the good agreement between the results of the direct and the *FT*-inversion-recovery T_1 measurements. In *Figures 4a–c* the results of the temperature dependence of T_1 are presented for both proton groups along with the averaged values T_1^e (decay of the inital magnetization M_0 extrapolated to time $t=0$ to the value of M_0/e).

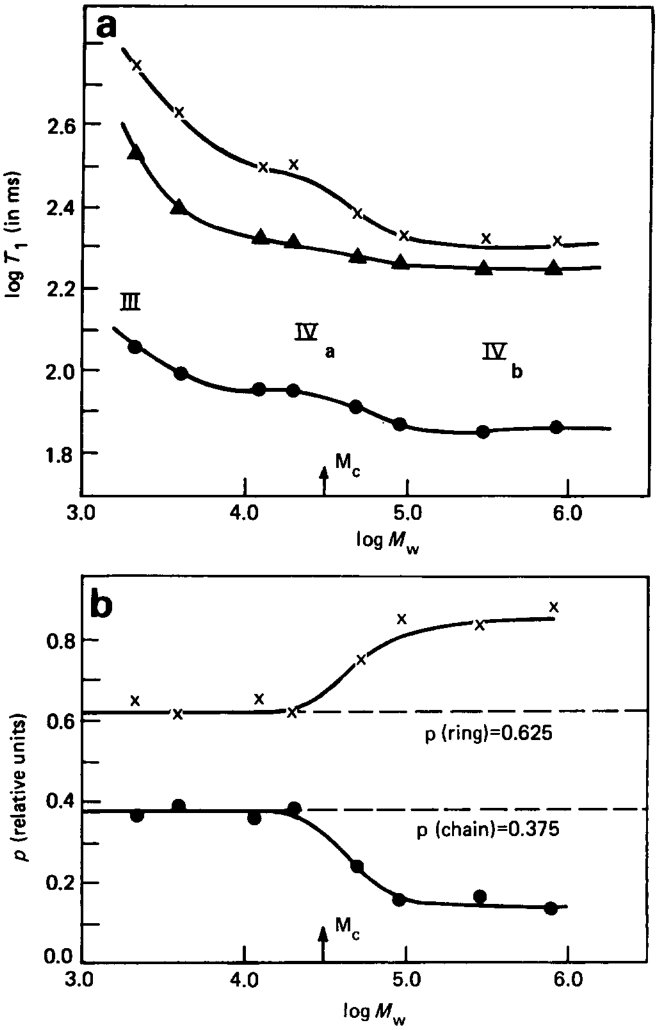

Figure 2 (a) Spin-lattice relaxation times T_1 in atactic PS in relation to M_w at 235°C and 88 MHz. (●), T_{1s} (short component, chain protons); (×), T_{1l} (long component, ring protons); (▲), T_1^e (averaged relaxation times. (b) Relative intensities of the long (p_l) (×) and short (p_s) (●) components of the longitudinal relaxation function *versus* log M_w

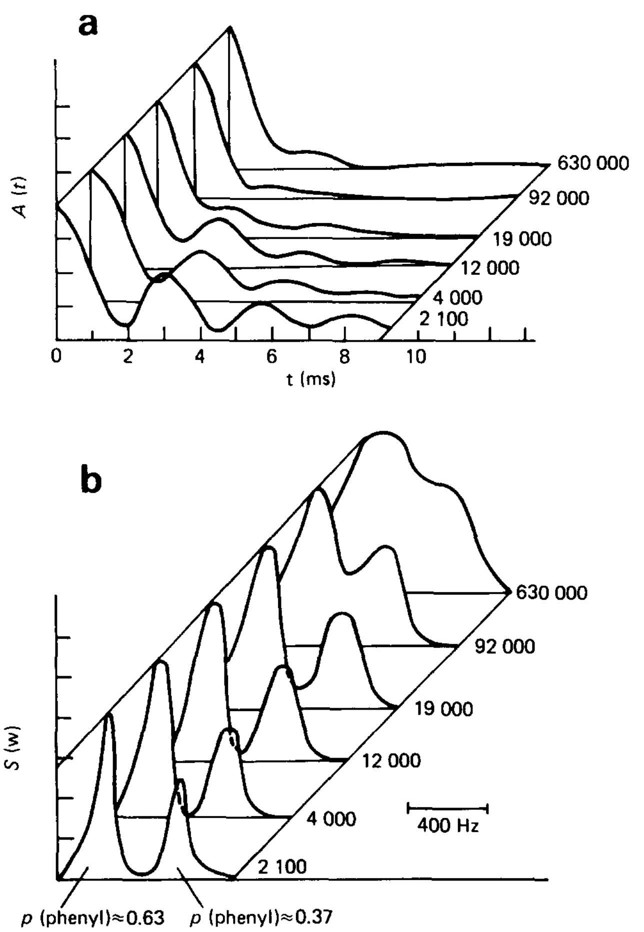

Figure 3 (a) Nuclear signals (FID) for different molecular weights of atactic PS at 200°C and 88 MHz. (b) *FT*-FID of the samples as in (a) with off-resonance $\nu_{\mathrm{off}} = 5$ kHz

Table 2 T_1 values and relative intensities p of the long (index l) and short (index s) components of the low molecular PS fractions

M_w	2100	4000	12000
T_{1l}^{d} (ms)	547	426	321
T_{1s}^{d} (ms)	116	97	92
p_s^{d}	0.36	0.39	0.35
T_{1l}^{FT} (ms)	517	415	325
T_{1s}^{FT} (ms)	122	108	102
p_s^{FT}	0.33	0.36	0.33

T_1^{d} indicates direct measurement without *FT*, T_1^{FT} indicates *FT*-T_1-inversion-recovery measurements; $p_s + p_l = 1$

The following features are of interest:

(i) The broad minima for both spin-lattice relaxation times indicate broad distributions of correlation times.

(ii) The different temperatures at which the T_1 minima of chain and ring protons appear, the latter at lower temperatures, are related to the higher molecular mobility of the phenyl rings. The shift of the minima to higher temperatures with increasing molecular weight reflects the decreasing free volume.

(iii) The T_1 values at the minima are different for the chain and ring protons corresponding to the smaller value of the second moment M_2 of the phenyl group in comparison with M_2 of the chain segment (monomeric unit), independently of the molecular weight. The small differences between the T_1 values at the minima of the three different molecular weights for ring and chain relaxation are within the limits of accuracy and are not significant.

(iv) The averaging of the dipolar interactions between the chain and ring protons required for carrying out the selective T_1 measurements is possible only at temperatures above $T_g(M_w) + 75$ K.

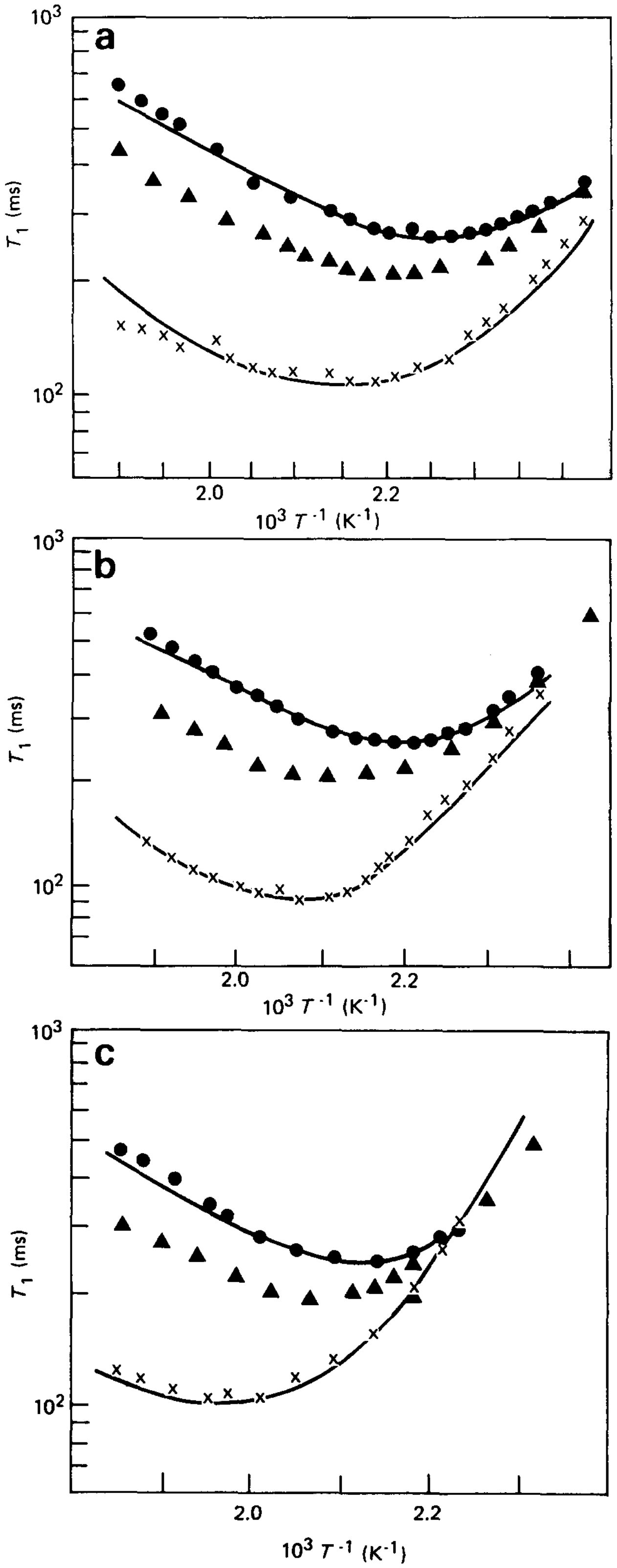

Figure 4 Temperature dependence of spin-lattice relaxation times T_1 at 88 MHz in low molecular weight PS: (×), chain protons; (●), ring protons; (▲), averaged values. (a) $M_w = 2100$; (b) $M_w = 4000$; (c) $M_w = 12\,000$. Solid lines are calculated with fitting parameters described in text

Additionally, in *Figure 5* the temperature dependence of T_1 is shown for three molecular weights (2100, 12 000 and 694 000) and for different frequencies (10, 22, 45 and 88 MHz). Only the averaged values are shown because the separation into two exponentials was too inaccurate for low frequencies and high molecular weights. The curves in *Figure 5* are similar to the previous results of Connor[2], who performed T_1 measurements at 30 MHz. In accordance with the present results he found that the position of the high temperature minimum (α-process) depends on the chain length, while its intensity does not depend on the molecular weight.

DISCUSSION

A first qualitative description of these results is based on the model of the isotropic rotational reorientations of the spin groups[18], taking into consideration some different distribution functions for the thermal correlation times τ[19] and two different equations for the temperature dependence of τ[9]:

Arrhenius equation

$$\tau = \tau_\infty \exp(E_a/RT) \qquad (1)$$

where E_a is the activation energy.

Williams–Landel–Ferry (WLF) equation[20,21]

$$\log(\tau_0/\tau) = C_1(T - T_0)/(C_2 + T - T_0)$$
or
$$(T - T_\infty)\log(\tau/\tau_\infty) = (T_0 - T_\infty)\log(\tau_0/\tau_\infty) \qquad (2)$$

where $C_1 = \log(\tau_0/\tau_\infty)$, $C_2 = T_0 - T_\infty$ and (ν_0, T_0) is a reference point on the WLF curve, near glass transition T_g, for $\nu_0 \approx 10^{-2}$ Hz.

The fitting calculations gave the following results (see also *Table 3* and solid lines in *Figure 4*):

(i) The fitted T_1 data agree with the experimental T_1 data within $\pm 15\%$ in the region of the T_1 minima. The type of the intuitively predicted distribution functions of the correlation times do not markedly influence the temperature dependence of T_1.

(ii) Applying the Arrhenius equation for the temperature dependence of the correlation times the apparent activation energies E_a lie, independently of the molecular weight, in the range from 120 kJ mol^{-1} to 130 kJ mol^{-1} for both relaxation processes, analogously to ref. 5, where E_a is given as 120 kJ mol^{-1} for temperatures above 468 K. The values of $\tau_\infty(\tau_\infty(\text{ring}) \sim (0.9-2.0) \times 10^{-23}$ s, $\tau_\infty(\text{chain}) \sim (1.0\text{–}4.0) \times 10^{-23}$ s) are above the upper frequency limit $\nu_\infty(\nu_\infty = (2\pi\tau_\infty)^{-1})$ for molecular rearrangements of order of magnitude 10^{12}–10^{14} Hz. But the values of the second moments M_2 are reasonable in comparison with ref. 4, yielding M_2 (chain) $\sim (1.1-1.9) \times 10^{10}\,\text{s}^{-2}$ and M_2 (ring) $\sim (5.0\text{–}6.9) \times 10^{9}\,\text{s}^{-2}$ for the two proton groups.

(iii) Calculations applying the WLF equation for the temperature dependence of the correlation times overcome the disadvantage of the small τ_∞ values and give good fitting values for width parameters of distribution functions of correlation times, second moments, reference temperature T_0 and temperature T_∞ for different molecular weights. The latter temperature, T_∞, clearly shows expected molecular weight dependence[22]. T_0 values correspond to conventional T_g which were measured by d.s.c. (*Table 1*) within the accuracy of the fitting calculations.

Figure 6 shows the calculated WLF temperature behaviour of the correlation frequency over a wide temperature range for low molecular weight PS with the fitting parameters from *Table 3*, as well as the γ-relaxation in PS corresponding to ref. 2 extrapolated to high temperatures. The fitting results with the Arrhenius equation from *Table 3* do not give reasonable frequencies for molecular motions. Therefore, both relaxation processes imply phenyl and chain α-relaxations in the regions of the high temperature T_1 minima.

Sufficient separation of the n.m.r. lines could be achieved only for temperatures above $T_g + 75$ K, as mentioned above. If the fractional free volume f is determined from the equation $f = f_g + \Delta\alpha(T - T_g(M_w))$(ref. 22) with the data $f_g = 0.025$ and $\Delta\alpha = 3 \times 10^{-4}\,\text{K}^{-1}$ from ref. 16, then $f \approx 0.05$. Therefore we assume that this kind of selective relaxation measurement is only possible if sufficient free volume ($f > 2f_g$) exists and the entanglement restraints are inefficient.

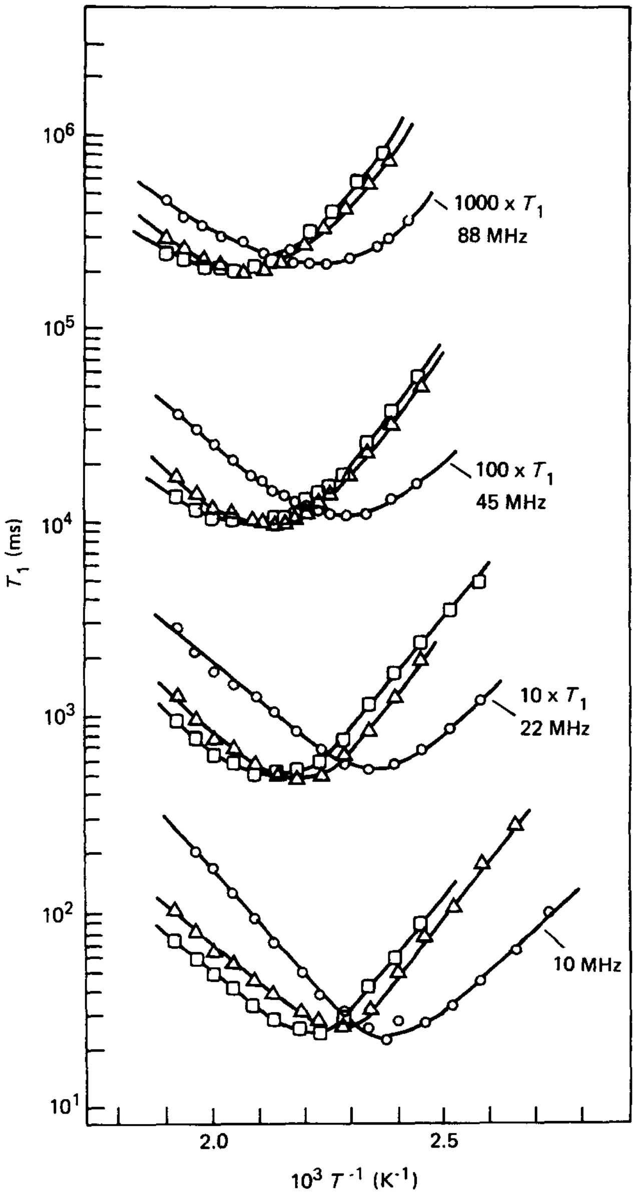

Figure 5 Temperature dependence of averaged spin-lattice relaxation times on different molecular weights: (○), $M_w = 2100$; (△), $M_w = 12\,200$; (□), $M_w = 69\,400$; for various measurement frequencies

Table 3 Some results of fitting calculations from the temperature dependence of the spin-lattice relaxations times of aliphatic (chain) and aromatic phenyl-ring) protons

	Phenyl-ring relaxation data: Cole–Cole distribution with									
	Arrhenius equation				WLF equation					
M_w	τ_∞ (10^{-23} s)	M_2 (10^9 s^{-2})	β_{CC}	E_a (kJ mol^{-1})	τ_∞ (10^{-14} s)	M_2 (10^9 s^{-2})	β_{CC}	ν_0 (10^{-2} Hz)	T_0 (K)	T_∞ (K)
2100	1.01	6.3	0.41	120	0.62	4.9	0.53	4.9	321	254
4000	1.64	6.0	0.43	122	0.97	5.4	0.48	1.7	347	292
12000	2.37	6.3	0.43	124	1.11	5.8	0.47	2.2	365	310
	Chain relaxation data: Cole–Cole distribution with									
	Arrhenius equation				WLF equation					
M_w	τ_∞ (10^{-23} s)	M_2 (10^{10} s^{-2})	β_{CC}	E_a (kJ mol^{-1})	τ_∞ (10^{-14} s)	M_2 (10^{10} s^{-2})	β_{CC}	ν_0 (10^{-2} Hz)	T_0 (K)	T_∞ (K)
2100	2.14	1.1	0.56	121	5.00	1.2	0.53	0.96	327	265
4000	3.82	2.1	0.52	125	5.25	1.9	0.46	2.5	351	287
12000	4.00	1.7	0.56	128	4.23	1.3	0.49	2.2	369	306

M_2, second moment; β_{CC}, width parameter of Cole–Cole distribution; other parameters see equations (1) and (2)

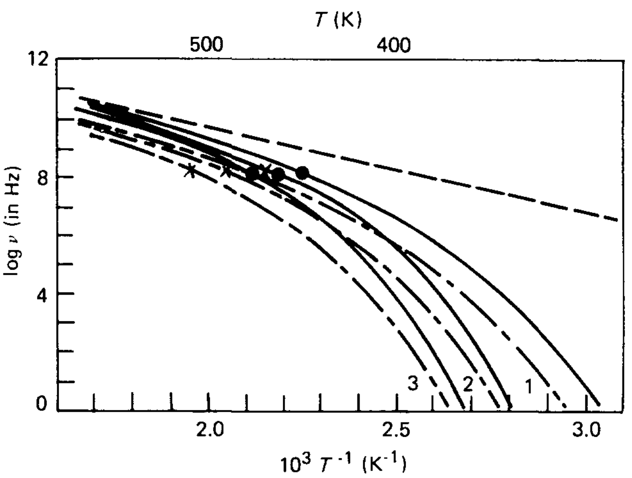

Figure 6 WLF curves calculated with parameters from *Table 3* for ring (———) and chain (–·–·–) relaxation. Temperatures are indicated of the T_1-minima of the selective measurements for ring (●) and chain (×) relaxation, respectively. (–––), γ-process presented in refs. 2 and 6 (extrapolated). (1), $M_w = 2100$; (2), $M_w = 4000$; (3) $M_w = 12000$

The estimation of the mean molecular weight M_e between the entanglements based on the relation $M_c \approx 2M_e$ from ref. 9 and the value of $M_c = 31200$ from ref. 15 gives for PS $M_e \approx 16000$. In this molecular weight region the beginning of the overlapping of the chain and ring ^{1}H-n.m.r. lines was observed.

A similar effect was discussed by Charlesby *et al.*[23], who studied network properties in different molecular weight PS by analysis of the proton transverse relaxation. For their sample with $M_w = 3000$ they stated that the entanglement density is insufficient to form any network at temperatures higher than 400 K as opposed to the high molecular weight samples ($M_w > M_c$).

The applicability of the WLF equation for the description of the high frequency ring and chain spin-lattice relaxation suggests that both types of molecular motion processes in the glass transition zone are cooperatively coupled. This corresponds to results of T_1(^{13}C) and $T_{1\rho}$(^{13}C) experiments discussed by Schaefer *et al.*[13].

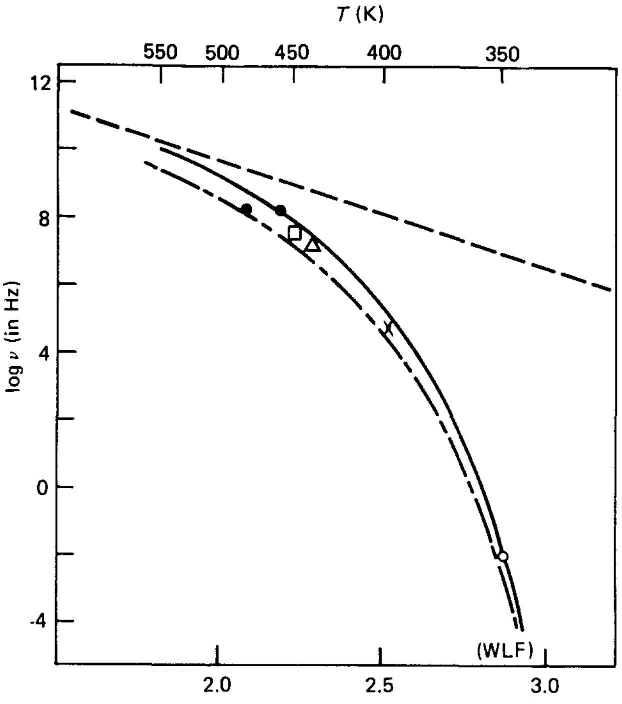

Figure 7 N.m.r. transition map for PS ($M_w = 4000$), calculated by WLF equation with parameters from *Table 3*:(———), ring; (–·–·–), chain. Experimental points: (●), T_1 (88 MHz) selectively, (□), T_1 (22 MHz), (△), T_1 (10 MHz), (×), $T_{1\rho}$ (60 kHz) averaged relaxation, (○), T_g (d.s.c. measurements), (–––), extrapolated γ-relaxation in PS from refs. 2 and 6 ($E = 30$ kJ mol^{-1})

In *Figure 7* the n.m.r. transitions from T_1(^{1}H) and $T_{1\rho}$(^{1}H) measurements are plotted as an example for $M_w = 4000$. The temperatures, which are determined from averaged relaxation behaviour, are arranged between the calculated chain and ring WLF curves based on the fitting parameters in *Table 3*. At low frequencies ($\nu \sim 10^{-2}$ Hz) the calculated curves for both, ring and chain, α-relaxations converge and correspond to T_g measured by d.s.c. The same behaviour as for $M_w = 4000$ is obtained for the other low molecular weight samples.

The detailed interpretation of the phenomena is complex because they can be related to chain element motions and ring reorientations. Some features are related to a newer concept of signal arrangement across the glass transition zone due to Donth and Schneider[24], who propose a general scaling hypothesis and use the following picture.

In principle molecular motions of very different kinds are possible in a polymeric sample, which will be associated with a distribution of molecular modes and, consequently, a distribution of mode lengths. Therefore, any kind of motion is reducible to a characteristic length and its occurrence in the spectrum of molecular motions is defined by this length and discused for PS and poly(vinyl acetate)[24].

In the present case of selective T_1 relaxation in low molecular weight PS the authors believe that these experiments have made possible refined insight into the mode spectrum of the cooperative molecular rearrangements at high frequencies, especially related to ring and chain motions. In consequence, the shorter modes of ring motions should occur at the higher frequencies of the glass transition zone and the longer modes of the chain motions at the lower ones, which is confirmed by the present T_1 measurements in the MHz region. In the limits of high temperatures or low frequencies the two corresponding WLF hyperbolae have the same asymptotic values T_∞ and τ_∞^{-1}, respectively, in agreement with the scaling hypothesis[24].

CONCLUSION

Study of a well defined series of narrow atactic polystyrene fractions by $T_1(^1H)$ high frequency measurements in a temperature range above the glass transition temperature has shown that the non-exponential spin-lattice relaxation in samples can be explained by the separated relaxation of the phenyl-ring and main-chain protons. In particular, selective relaxation measurements with the usual experimental technique were possible for a sufficiently homogeneous laboratory magnetic field and for the conditions $M_w < M_c$ and $T \approx T_g + 75$ K. Both high temperature minima corresponding to the α-process of the ring and chain motions were shifted with change in molecular weight.

A fitting calculation has been done for the temperature dependence of both relaxation processes and for three low molecular weights on the basis of a simple relaxation model including rotational fluctuations, a distribution of correlation times and the WLF equation. The fitting parameters are in accordance with numerous results in the literature.

The different temperatures at which the minima of the ring and chain proton spin-lattice relaxation times appear, and the similar values of the fitted WLF parameters, T_∞ and τ_∞, for similar molecular weights are consistent with a newer concept of signal arrangement across the glass transition zone.

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