^{2}H n.m.r. study of high pressure effects on the molecular dynamics in polystyrene: 3. Spin relaxation studies

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The effect of high pressure on ^{2}H n.m.r. spin relaxation in polystyrene is studied. Deuteron spin-lattice relaxation behaves non-exponentially both in chain- and ring-deuterated polystyrene at temperatures up to 20 K above the glass transition. The non-exponentiality is caused by the broad distribution of correlation times and the slowness of the spin diffusion process. The fast flipping phenyl rings are an effective relaxation mechanism both for the chain and for the phenyl deuterons. The distribution of correlation times is either due to a heterogeneity of local environments or to a change in time-scale of the motion over long time intervals. Denser packing of the polymer caused by high pressure results in a decrease in the spin-lattice relaxation time. The apparent transverse relaxation time can be used as a monitor of the glass transition.

(Keywords: deuteron spin relaxation; ^{2}H n.m.r.; polystyrene)

INTRODUCTION

In the two preceding papers[1,2] we have shown that detailed information about molecular motion in polystyrene (PS) in the vicinity of the glass transition temperature (T_g) can be obtained from deuteron n.m.r. quadrupole echo and spin alignment spectra. Our spin alignment investigations in chain-deuterated PS (PS-d_3) have demonstrated that the main chain is arrested in the structure below T_g. Above T_g, small angle reorientational diffusive motion was determined to be the type of motion occurring. The time-scale varies from hundreds of seconds at T_g to milliseconds just 15 K above T_g. The motional processes cannot be described by a single correlation time but are characterized by a distribution of correlation times. We have observed that the width of this distribution decreases from five decades at T_g to three decades at 388 K. Another motional process taking place in PS consists of 180° reorientations of the phenyl ring as we have determined by quadruople echo experiments in ring-deuterated PS (PS-d_5). In contrast with the main chain motion, phenyl flips proceed also in the glassy state. Analysis of the spectra yields that the line shapes are superpositions of roughly two contributions from phenyl groups performing relatively slow and fast flipping motion, respectively. The molecular dynamics of the slow phenyls is also described by a distribution of correlation times. The mean correlation times vary from milliseconds to microseconds. The motion of the fast flipping phenyl groups is so fast that it averages the electric field gradient (EFG) tensor to a tensor with a quadrupole coupling constant reduced by 0.625 and an asymmetry parameter of 0.6. The correlation times corresponding to this motion are of the order of 10^{-8} s or shorter. The contribution of the fast flipping phenyls was estimated to be $\sim 10\%$.

This paper reports the last part of our deuteron n.m.r. study of the effect of high pressure on the molecular dynamics in PS. Here we focus on the spin relaxation time measurements. The spin-lattice relaxation time (T_1) probes the spectral density of the molecular dynamics in the vicinity of the Larmor frequency ($\omega_L = 2 \times \pi \times 41.43$ MHz). Thus, from these measurements we expect to obtain information about fast motion present in PS-d_3 and PS-d_5. Another motivation of our study is that we expect to use changes in the relaxation times as an indicator of the occurrence of T_g as a function of pressure.

Earlier n.m.r. relaxation studies of PS were reported in papers by Connor[3] and Lindner *et al.*[4]. In the former paper, proton T_1 and $T_{1\rho}$ of PS over a wide range of molecular weight in a wide range of temperature (90–500 K) are reported. The relaxation minimum observed at high temperature is attributed to the α-process. Detailed information about phenyl rotations in the glass is not obtained since at the frequencies used the α and β processes merge into one αβ process. The data were analysed assuming a distribution of correlation times. The best fit was obtained when a Fuoss–Kirkwood distribution with a width of five decades was used. The latter paper reports on proton T_1 and $T_{1\rho}$ of deuterated polystyrenes. It was found that in the glass the T_1 values are strongly influenced by spin diffusion leading to essentially equal T_1 values for different PSs, while the $T_{1\rho}$ values are different for PS-d_3 and PS-d_5. The authors conclude that the phenyl group motion is the dominant proton spin relaxation process in the glass. Again, above T_g, the T_1 values are analysed assuming a Fuoss–Kirkwood distribution of correlation times. It was found that the

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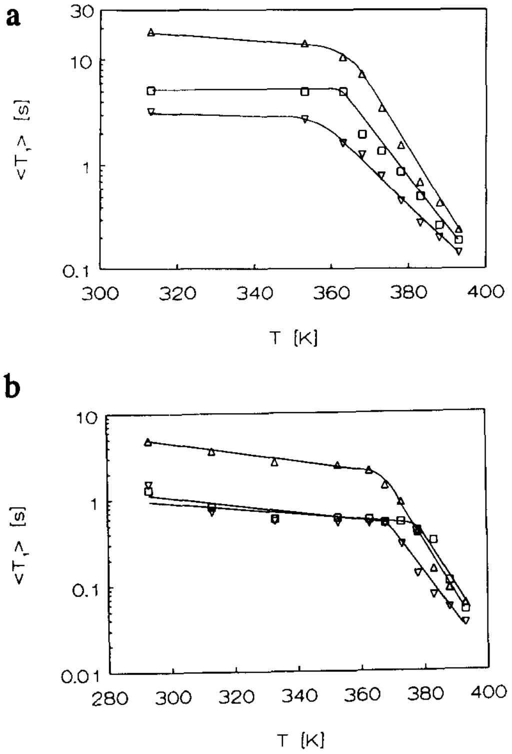

Figure 1 ^{2}H $\langle T_1\rangle$ as a function of temperature at different hydrostatic pressures for (a) PS-d$_3$ and (b) PS-d$_5$: (△) 1 bar; (▽) 1250 bar; (□) 2250 bar

average correlation times for the chain protons are about three times larger than for the phenyl protons.

EXPERIMENTAL

Material. Atactic PS deuterated in the chain, PS-d$_3$, $M_w = 226\,000$, $M_w/M_n = 1.16$ and deuterated in the phenyl ring, PS-d$_5$, $M_w = 225\,000$, $M_w/M_n = 1.20$ were provided by Dr F. Fujara (University of Mainz). Cylindrical samples (length 9 mm, diameter 6.5 mm) were prepared from powdered material.

T_1 and T_2^* measurements. The ^{2}H n.m.r. experiments in the temperature range between 293 K and 403 K were carried out at a frequency of 41.43 MHz in the spectrometer and high pressure n.m.r. probe described elsewhere[1]. The spin-lattice relaxation process was investigated using a saturation pulse sequence consisting of ten $\pi/2$ pulses which, after a variable time delay (up to 200 s), was followed by a quadrupole echo sequence (with a time interval $t_1 = 25\,\mu$s). The recovery of the longitudinal magnetization was monitored by measuring the amplitude of the quadrupole echo as a function of the delay. The recovery was followed to at least 0.86 of the equilibrium value of the magnetization. The length of a $\pi/2$ pulse was $\sim 4.5\,\mu$s. A phase cycling scheme in which the phase of the first pulse is alternated was used to minimize artifacts[5]. The 'apparent' transverse relaxation time T_2^* was obtained from the decay of the quadrupole echo amplitude as a function of the t_1 between the pulses.

RESULTS AND DISCUSSION

Spin-lattice relaxation

Well above T_g the ^{2}H spin-lattice relaxation can be described by a single exponential, both in PS-d$_3$ and in PS-d$_5$. However, in the vicinity of T_g and in the glass the relaxation becomes strongly non-exponential.

In order to present a quantitative description of the relaxation curves, we have used a Kohlrausch–Williams–Watts (KWW) function[6,7]:

$$\Phi(t)=\frac{M_\infty - M(t)}{M_\infty}=\exp\left[-\left(\frac{t}{\Xi}\right)^{\beta}\right] \qquad (1)$$

where Ξ is a measure of the time constants involved in the decay and $(1-\beta)$ is a measure of the non-exponentiality. The KWW function can be thought of as a superposition of exponential contributions as given by:

$$\Phi(t)=\int_0^\infty \rho(T_1)\exp\left(-\frac{t}{T_1}\right)\mathrm{d}T_1 \qquad (2)$$

where $\rho(T_1)$ is a distribution of relaxation times. It is then possible to calculate an average relaxation time[8]:

$$\langle T_1\rangle=\int_0^\infty \mathrm{d}T_1\rho(T_1)T_1=\frac{\Xi}{\beta}\Gamma(\beta^{-1}) \qquad (3)$$

where Γ is the gamma function.

Average deuteron spin-lattice relaxation times $\langle T_1\rangle$ as a function of temperature at different pressures in PS-d$_3$ and PS-d$_5$ are shown in *Figure 1*. In the temperature region below T_g the average spin-lattice relaxation time shows only a weak temperature dependence. The values of $\langle T_1\rangle$ are smaller for PS-d$_5$ than for PS-d$_3$. Above T_g the values of $\langle T_1\rangle$ become strongly temperature dependent. We have observed that the exponent β has a value of ~ 0.6 in the glass at low temperatures and increases slowly on increasing the temperature as can be seen, for example, from *Figure 2*. In the temperature range T_g to $T_g + 20$ K, β changes more rapidly to $\beta = 1$, corresponding to fully exponential relaxation. This effect was observed both in PS-d$_3$ and in PS-d$_5$.

Relaxation mechanism in PS-d$_5$

From the quadrupole echo experiments in PS-d$_5$ we know that $\sim 10\%$ of the phenyl groups perform fast reorientations on a time-scale in the vicinity of the reciprocal ω_L. Therefore, the motion of the fast phenyl groups can be expected to be an effective relaxation mechanism. Such a fast motion with a correlation time $\tau_c \sim \omega_L^{-1}$ contributes to spectral densities which can be measured through the spin-lattice relaxation rate.

The general formalism for the spin-lattice relaxation by quadrupole coupling has been presented by Abragam[9] and

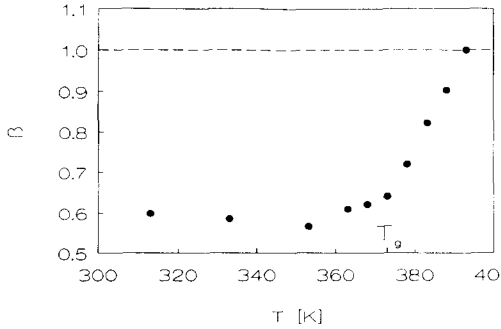

Figure 2 Stretched exponent parameter β as obtained from fits to the experimental relaxation curves of PS-d$_5$ at 1 bar

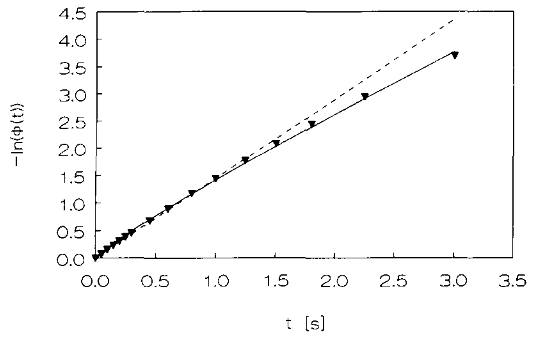

Figure 3 Calculated magnetization recovery curve for the case of 180° flips of the phenyl ring in polystyrene for a single correlation time $\tau_c = 1\,\mu s$ at a Larmor frequency of $\omega_L = 2 \times \pi \times 41.43$ MHz. The full curve represents the fit with a KWW function. The dotted line is an exponential fit

Spiess[10]. Because the quadrupole coupling Hamiltonian depends on the variables of single spins, the deuteron spins relax independently from each other, apart from the effect of spin diffusion, which will be discussed in the next section. Generally, the relaxation rate is orientation dependent, which leads to non-exponential relaxation in a sample containing all orientations. For isotropic motion in a system of spins with $I = 1$ an exponential recovery of the longitudinal magnetization is expected. The orientation dependence of T_1 for a number of types of anisotropic motion has been analysed by Torchia and Szabo[11]. The case of restricted 180° reorientations of a phenyl ring is an example of their two-site jump model. The C-^{2}H bonds flip over 180°, maintaining an angle of 60° with the flip axis. The spin-lattice relaxation rate can be obtained from reference 11 [equation (36) and Table 2]:

$$\frac{1}{T_1} = \frac{27}{512}\left(\frac{e^2qQ}{\hbar}\right)^2 \left\{ \frac{\tau_c}{1+\omega^2\tau_c^2} \times [\cos^2\vartheta + \cos^2 2\vartheta - \cos 2\varphi(3\sin^2\vartheta\cos^2\vartheta - \sin^4\vartheta)] + \frac{4\tau_c \sin^2\vartheta}{1+4\omega^2\tau_c^2}(1+\cos^2\vartheta - \sin^2\vartheta\cos 2\varphi) \right\} \quad (4)$$

where $e^2qQ/\hbar$ is the quadrupole coupling constant (which has the value 177 kHz for the ring deuterons of PS) and the polar angles ϑ and φ describe the orientation of the external magnetic field in a crystal fixed axis system.

Since a decrease of the T_1 values with increasing temperature is observed we conclude that our measurements were carried out in the slow motion limit, where equation (4) for $\omega\tau_c \gg 1$ becomes:

$$\frac{1}{T_1} = \frac{27}{16}\left(\frac{e^2qQ}{\hbar}\right)^2 \frac{1}{\omega^2\tau_c}(1 - 3\cos^2\varphi\cos^2\vartheta\sin^2\vartheta) \quad (5)$$

Due to the angular dependence of the T_1 values, the recovery of the magnetization can be expressed as a superposition of differently oriented local units relaxing with different T_1 values. The relaxation function describing the recovery of the magnetization is given by:

$$\Phi(t) = 1 - \sum_{i=1}^{n}\sum_{j=1}^{m} \mathrm{p}(\vartheta_i, \varphi_j)\left\{1 - \exp\left[-\frac{t}{T_1(\vartheta_i, \varphi_j)}\right]\right\} \quad (6)$$

where $\mathrm{p}(\vartheta_i, \varphi_j)$ represents the weight of the element of solid angle with its centre at (ϑ_i, φ_j). The summation over i, j is not trivial since the sum goes over the elements of the sphere. Therefore, the surface of the sphere is divided into elements of equal surface[12]. Each of the elements contributes an exponential term with relaxation time $T_1(\vartheta_i, \varphi_j)$. In order to calculate $\Phi(t)$, we have calculated T_1 for the values of ϑ, φ corresponding to the centre of the element. In our calculation the sphere was divided into 10000 elements which ensures proper and smooth summation. We have found that the recovery of the magnetization is non-exponential. A typical recovery of the magnetization calculated for $\tau_c = 1\,\mu s$ is shown in *Figure 3*. The deviation from exponential recovery is small. Assuming that the magnetization can recover to 0.86 of the equilibrium value the best fit was obtained for the parameter $\beta = 0.94$. The value of $\beta = 0.94$ is much larger than the value of $\beta \sim 0.6$ found in our experiment. Therefore, we believe that other processes cause the strong non-exponentiality.

We note that the formula for T_1 is based on the differential equation for the density matrix[9]. This master equation is valid if $|H_Q\tau_c|^2 \ll 1$, where $\hbar H_Q$ is the quadrupole coupling Hamiltonian. This condition requires that τ_c is $\ll 1\,\mu s$ which corresponds to a value of T_1 of ~ 400 ms. As can be seen from *Figure 1*, this condition is fulfilled only for temperatures above T_g. Actually, the condition $|H_Q\tau_c|^2 \ll 1$ only starts to be valid in the region of our measurements.

As has been mentioned above, the non-exponentiality in the recovery of the magnetization, as observed in our T_1 experiments in PS-d$_5$ (*Figure 2*), is much stronger than can be understood from the anisotropy of the phenyl group motion. This leads to the conclusion that it is due to the wide distribution of correlation times present in the material. As was shown in the quadrupole echo studies, the width of the distribution of the correlation times at 20 K below the T_g was estimated to be five decades. In the simplest model for the origin of the correlation time distribution it is the result of the existence of local regions which vary significantly in correlation times. The dependence of T_1 on τ_c causes the local regions to show different T_1 values. Therefore, a broad distribution of correlation times will result in a broad distribution of relaxation times, which leads to non-exponential recovery of the magnetization. On increasing the temperature the width of the distribution of the correlation times decreases leading finally to exponential recovery. Even at 383 K the recovery is still non-exponential, which is consistent with the width of the distribution of about three decades, as obtained from our quadrupole echo experiment. At 398 K we observe exponential behaviour: the distribution becomes sufficientiently narrow (1.5 to 2 decades) that spin diffusion is able to obscure the remaining differences in the local relaxation times. We return to the question of the origin of the correlation time distribution in the section on ergodicity.

We have made an attempt to obtain information on the short time tail of the correlation time distribution. As has been shown in reference 8, a distribution of relaxation times $\rho(T_1)$ can be obtained from equations (1) and (2). By neglecting the effect of spin diffusion, which will be discussed later, $\rho(T_1)$ can be transformed into a distribution of correlation times $\rho_{T_1}(\tau)$ using equation (5). Examples of the results of this analysis are shown in *Figure 4* at 353 K and 1 bar and at 383 K and 1250 bar. In this figure the distribution $\rho_{T_1}(\tau)$ is also compared with the distribution of the correlation times $\rho_{QE}(\tau)$, obtained from our analysis of

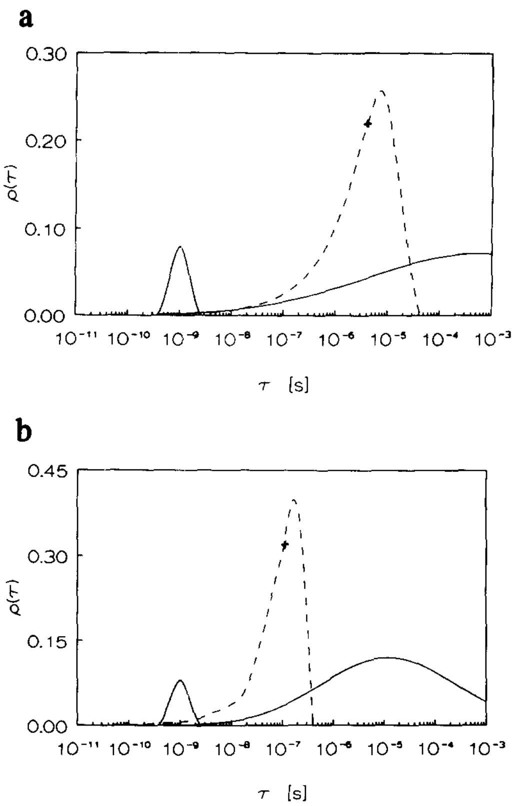

Figure 4 Distribution of correlation times $\rho_{QE}(\tau)$ obtained from the analysis of the quadrupole echo (——) together with the distribution of correlation times $\rho_{T_1}(\tau)$ obtained from relaxation time measurements (– – –): (a) at 353 K and 1 bar; (b) at 383 K and 1250 bar. + indicates the value of $\rho_{T_1}(\tau)$ at the mean correlation time

the quadrupole echo presented in the preceding paper[2]. Because of the effect of spin diffusion, one expects $\rho_{T_1}(\tau)$ to be a reasonable representation of the distribution only at short correlation times. The distribution $\rho_{QE}(\tau)$ contains an additional contribution of ~10%, somewhat arbitrarily chosen to be at $\sim 10^{-9}$ s. We note that such a contribution is not present in $\rho_{T_1}(\tau)$ obtained at 353 K and 1 bar. On the other hand, $\rho_{T_1}(\tau)$ at 383 K and 1250 bar has a large contribution at small τ values, which may be consistent with the peak at small τ in $\rho_{QE}(\tau)$. Taking into account the crudeness of this comparison, we have to conclude that we cannot make a definite statement as to the existence of the peak at small τ.

As can be seen in *Figure 1b*, the temperature dependence of $\langle T_1 \rangle$ becomes very weak below ~360 K. This is most likely due to the presence of paramagnetic impurities in low concentration, which act as relaxation centres; in the transport of magnetization to these dilute centres spin diffusion is the rate controlling process, which is only weakly temperature dependent.

Spin diffusion

The spin-lattice relaxation in our experiments on PS-d_3 and PS-d_5 is strongly affected by spin diffusion. In this process, spin magnetization is transported between spatially separated spins, in parallel with the local spin-lattice relaxation processes. When spin diffusion is fast with respect to the local relaxation rates, its effect will be the establishment of a common spin temperature; the complete spin system relaxes to the lattice temperature with some average relaxation time. However, this situation does not occur in the systems of deuteron spins, present in PS-d_3 and PS-d_5. In first order, spin diffusion requires spin flip-flop transitions, caused by the $I_+^i I_-^j + I_-^i I_+^j$ term in the homonuclear dipole–dipole coupling[9]. This process is energy conserving, when the resonance lines of the individual spins show overlap. Because of the dependence of the quadrupole coupling on the orientation of the external magnetic field, the quadrupole splittings of the resonances of neighbouring deuteron spins are unequal. Spin diffusion is quenched to a large extent by this effect. The spin flip-flop process will involve the spectral density of the motion of the C-^{2}H bonds at the frequency corresponding to the difference in the quadrupole coupling of neighbouring deuterons. In PS-d_5 the mean correlation frequencies of the phenyl group motion ranges from 0.01 to 500 kHz, depending on temperature and pressure, therefore the flip-flop process may still be effective between a limited fraction of neighbouring deuterons. This is not so for the C-^{2}H bonds in PS-d_3, where the correlation frequency does not exceed 1 kHz. Apart from this effect one would expect that the deuteron spins relax independently of each other, with different rates due to locally different orientations and correlation times. The orientation dependence of spin diffusion has been studied on deuteron spins in single crystals[13]. By varying the orientation of a crystal in the external magnetic field the quadrupole splittings of neighbouring spins can be made equal, which enables the spin diffusion process to occur. The observed enhancement of deuteron spin-lattice relaxation in slowly rotating samples[14] is due to the same effect: the rotation modulates the quadrupole coupling and leads to overlap of the resonances of neighbouring deuterons during part of the rotation period.

It has been shown, however, that in cases where the difference between the quadrupole splittings of neighbouring spins exceeds the line width, the spin diffusion is not quenched entirely. Three mechanisms for the remaining spin diffusion have been proposed: energy conserving double quantum transitions[15], higher order flip-flop processes involving four spins[13] and dipolar coupling to the dipolar reservoir, formed by the proton spins present in the system[16].

An analysis of these mechanisms in amorphous PS-d_3 and PS-d_5 cannot be made. We restrict ourselves to the following qualitative observations. From the results obtained in reference 13 an order of magnitude estimate of the time constant involved in the equilibration of neighbouring deuterons is 10 s. In a magnetization recovery curve one observes the fast initial recovery of the deuterons with short correlation times. At longer times magnetization is transferred by spin diffusion from the slowly moving deuterons to the fast relaxing deuterons in such a way that on a longer time-scale a common spin temperature is established. The effect of spin diffusion is shown in *Figure 4* as a steep drop in the correlation time distribution for long correlation times. Therefore, the longer correlation times in the distribution, which are known to exist from our line shape studies, cannot be observed in the T_1 experiment.

Comparison with proton T_1 *values*

Our ^{2}H T_1 data in PS-d_5 should be compared with the proton T_1 measurements on PS-d_3 of Lindner *et al.*[4]. They carefully analysed their data in the temperature region above 400 K, while our measurements are taken below and up to 400 K. Therefore, we can only compare the results on the experimental points measured at this temperature. As derived from the ^1H T_1 data, the motion of the phenyl groups is characterized by a distribution of correlation times with an average correlation time of 3 μs. This result, however, has been obtained by assuming that the motion is isotropic. Taking into account that the motion of the phenyl rings is anisotropic would lead to a slightly shorter correlation time. In our ^2H quadrupole echo and T_1 investigations we find the existence of regions with much shorter correlation times (*Figure 4*), which are not observed from the proton T_1 data. It should be realized that the ^1H T_1 results represent a measure of the average τ_c since spin diffusion in protonated systems is very strong. As a result a common spin temperature is established which leads to averaging of the different local relaxation times.

Relaxation mechanism in PS-d$_3$

The deuteron spin-lattice relaxation in PS-d_3 is expected to proceed in a different way. There, in the glassy state the motion of the main chain is frozen. A possible relaxation mechanism proceeds via relaxation centres consisting of deuterons, coupled to the proton spins in those phenyl groups which perform fast flipping motion. We have made a rough estimate of the relaxation rates due to dipolar coupling between deuterons in the chain and protons in the phenyl ring, using nuclear distances obtained from reference 17. The largest contribution to the relaxation rate is expected to be due to the coupling between the two *ortho* protons in the ring and the deuteron on the main chain carbon, to which the ring is attached. The two deuteron–proton vectors of length 2.9 and 4.1 Å, making an angle of 62°, are interchanged by the 180° reorientations of the phenyl rings. We have again used the formalism for two-site jumps developed by Torchia and Szabo[11], in the extreme narrowing limit. Again, T_1 values are orientation dependent, which leads to non-exponential recovery of the magnetization. In our crude estimate of the relaxation rate we have assumed that the internuclear vector has a constant length of 3.5 Å. For a phenyl group flipping rate of 1 GHz the relaxation time of the main chain deuteron, averaged over all orientations, is $\sim$1 s. Thus, it is in the range of the experimental values. On the other hand, in our quadrupole echo study we estimated the number of fast flipping phenyl groups to be only 10%. From this, the following picture emerges: the relaxation centres in PS-d_3 are formed by deuterons coupled to the fast flipping protonated phenyl rings with correlation times of the order of nanoseconds. Since the number of these centres is limited, the magnetization is transported to them by the spin diffusion process, which, as discussed above, is slow. On increasing the temperature the rate of the phenyl ring flips gets larger and the number of relaxation centres increases, leading to smaller values of the relaxation time.

As in PS-d_5, the relaxation rate becomes nearly temperature independent below 360 K. The same explanation applies.

Ergodicity

As has been discussed above, our investigations of line shapes and relaxation times in PS lead to the conclusion that the molecular motion in the vicinity of T_g can be characterized by a distribution of correlation times. The interesting question arises: what is the physical origin of the distribution. Two explanations have been proposed[8,18]. In the first, the distribution of correlation times has its origin in a spatial heterogeneity of local environments while in the second one the nature of the chain motion is collective where the fastest motion constrains the slower ones leading to a distribution of the correlation times.

In the literature a relation has been suggested between motional heterogeneity, showing up as a distribution of correlation times, and non-ergodic behaviour in the system. In statistical mechanics a system is called ergodic when the phase point representing the system will pass in succession through every point in phase space before returning to its original position[19].

Recently Schnauss *et al.*[20] and Schmidt-Rohr and Spiess[21] have discussed the problem of ergodicity in n.m.r. experiments. In the former paper it was proposed that ^2H spin-lattice relaxation could be used as a monitor of ergodicity. It is known that the glass transition can be considered as an example of the transition to a non-ergodic state[22]. As in our experiments, it has been established that in a glassy system the crossover from exponential to non-exponential magnetization recovery occurs at $\sim$20 K above the T_g. In the latter paper some very important results are reported. In a reduced four-dimensional n.m.r. exchange experiment on poly(vinyl acetate) it was shown that the correlation itself is non-exponential and that a given molecular unit originally developing with a long correlation time changes its correlation time to a smaller value, and vice versa. It appears that for times very much longer than the mean correlation time the system starts to become homogeneous. However, on the rather large time-scale of 50 average correlation times a molecular unit still shows residual motional heterogeneity. The authors also introduce a somewhat modified definition of ergodicity, namely, a system is considered to be ergodic when within the longest correlation time all different parts of phase space corresponding to different configurations can be explored.

In our opinion, precise information about the ergodic or non-ergodic motional behaviour can be obtained only in a multidimensional n.m.r. experiment. The use of ^2H T_1 as a monitor of ergodicity is somewhat doubtful. Locally, the recovery of the magnetization behaves exponentially, independent of the precise time dependence of the correlation function of the coupling causing the relaxation. Presumably, the crossover from non-exponential to exponential magnetization recovery in a T_1 measurement is connected with the decrease of the width of the correlation time distribution. We note that, similar to the results in reference 17, we have found that in the region of the crossover from exponential to non-exponential recovery of the magnetization the relaxation time T_1 becomes larger than the mean correlation time of the α-process, which is attributed to the motion of the main chain. We do not have a proper explanation for this observation.

Pressure dependence of T_l

As can be seen in *Figure 1*, in PS-d_3 the T_1 values first decrease considerably on increasing the pressure to 1250 bar. A further pressure increase to 2250 bar results in an increase of the T_1 values, although even at this pressure the T_1 values are smaller than at ambient pressure. This behaviour occurs both below and above

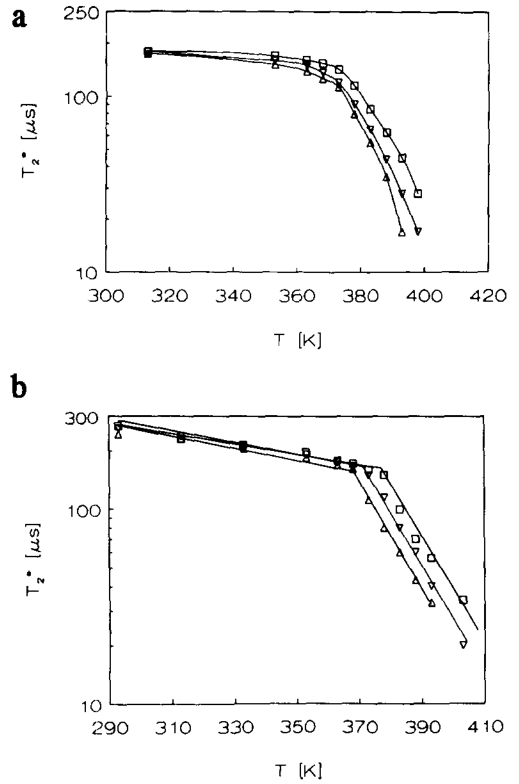

Figure 5 ^2H T_2^* as a function of temperature at different hydrostatic pressures for (a) PS-d_3 and (b) PS-d_5: (△) 1 bar; (▽) 1250 bar; (□) 2250 bar

T_g. In PS-d_5, the effect of increasing the pressure to 1250 bar is similar to that in PS-d_3. A further pressure increase to 2250 bar has only a small effect in the glass whereas the effect is large above T_g, where T_1 becomes longer than at 1 bar. These effects are contrary to our expectation that the T_1 values would always increase with pressure, since a higher density should lead to more constraints on the motion, and thus to longer correlation times.

Since N_2 gas was used as the pressurizing medium, it could be assumed that the observed effect of pressure on T_1 is due to N_2 dissolving in the polymer and having the effect of increasing the mobility. However, such an effect is not observed in our study of the effect of pressure on the quadrupole echo and spin alignment spectra. In addition, no such effect was seen in our high pressure n.m.r. experiments on polycarbonate[23]. In particular, in ring-deuterated polycarbonate (PC-d_4) a marked increase of the ^2H T_1 values with pressure is observed. There, no correlation between an increase of N_2 gas pressure and an enhancement of the molecular dynamics is observed. To our knowledge, no plasticization effects of N_2 in glassy polymers are reported, like the ones due to CO_2 as recently observed by Smith and Moll[24] in the molecular dynamics in the glassy polymers PS-d_8, PC-d_8, polyestercarbonate-d_4 and poly(methyl methacrylate)-d_8. The application of CO_2 pressure (only up to 50 bar) enhances the molecular dynamics, resulting in a large variation of the ^2H T_1 values as a function of pressure. Two alternative explanations are given for these results. In the first, the diffusion of CO_2 is directly related to the polymer dynamics as measured with n.m.r. In the second, the specific frequencies involved in the CO_2 diffusion are assumed not to be dominant in n.m.r.; then the n.m.r. results and the diffusion can depend on plasticization or polymer swelling.

Dependence of T_2^* *on temperature and pressure*

The apparent transverse relaxation time T_2^* is a measure of the time constant involved in the decay of the quadrupole echo as a function of the t_1 between the pulses. In the present experiments, the decay appears to be exponential. In *Figure 5* T_2^* values as a function of temperature at different pressures are shown in PS-d_3 and PS-d_5. We observe that at temperatures below 370 K T_2^* increases only slightly on lowering the temperature. At temperatures above 370 K, i.e. above T_g, a strong decrease of T_2^* with increasing temperature is observed. In the slow motion limit of the quadrupole echo experiment, where the reciprocal correlation times are much smaller than the quadrupole coupling, the formation of the echo is undisturbed and T_2^* is governed by the dipole–dipole interaction between deuterons and deuterons and protons. In the intermediate region of the quadrupole echo experiment molecular motion occurs with correlation times of the order of the reciprocal quadrupole coupling constant. Molecular motion disturbs the formation of the echo and the decay of the echo amplitude is not caused by dipole–dipole coupling anymore but also depends on a reduction parameter[25] determined by the type and rate of molecular motion and by t_1. The drop in the T_2^* values is observed in PS-d_3 as well as in PS-d_5, suggesting that it is caused by one process namely the loss of constraints on the molecular motion at the glass transition. Therefore, T_2^* can be used as an indicator of the glass transition[26]. We note here that the quadrupole echo line shapes are much less sensitive to the changes occurring at T_g than T_2^*. In PS-d_3 slight changes in the spectra are observed only at 388 K, 15 K above the T_g, while in PS-d_5 the spectra change gradually in the intermediate region of the quadrupole echo.

The glass transition in a pressure–temperature diagram

From the behaviour of T_2^* we have constructed a transition line representing the glass transition in a pressure–temperature (p–T) diagram. For the values of the transition temperature at each value of the pressure we have taken the point of maximum curvature in the T_2^* *versus* temperature plot for PS-d_3. The results together with those from equation of state ($M_w = 20\,396$)[27] and differential thermal analysis (d.t.a.) ($M_w = 244\,961$)[28] measurements are shown in *Figure 6*. The changes in T_g with pressure, obtained with these different methods,

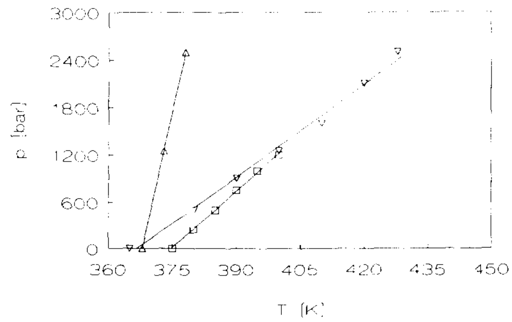

Figure 6 Glass transition temperature in polystyrene as a function of pressure as obtained by d.t.a. (□), equation of state (▽) and n.m.r. (△) measurements

are found to be remarkably different. From T_2^* we have determined a dp/dT value of $\sim$200 bar K^{-1} while from the equation of state and d.t.a. results dp/dT values of $\sim$40 bar K^{-1} are obtained. We note here that DiMarzio[29] in his equilibrium theory of glasses predicts a value of 29 bar K^{-1}. This result should be taken with some reservation since it is based on a theory where the glass transition is considered to be an equilibrium phenomenon while recent theories suggest a kinetic nature for the glass transition[30].

The thermal analysis experiments are non-equilibrium methods and the temperature scan rate can influence the measured T_g value[31]. This is due to the very slow motion of the polymer chains. Sufficient time must be given to reach thermal equilibrium at each temperature as the temperature is varied. In contrast, the n.m.r. experiments do not require a temperature scan. This could explain the fact that the values of T_g at 1 bar are slightly lower for the n.m.r. and the equation of state experiments. The small difference in T_g at ambient pressure obtained with the equation of state and the n.m.r. techniques is probably due to the different molecular weight of the samples. However, we have no explanation for the large difference in the dp/dT values.

CONCLUSIONS

In our investigations we have found that the deuteron spin-lattice relaxation both in PS-d$_3$ and PS-d$_5$ behaves non-exponentially at temperatures up to 20 K above the glass transition. It is concluded that the non-exponentiality is not due to the anisotropy of the motion but that it is caused by the broad distribution of correlation times and the slowness of the spin diffusion process. We have established that the fast flipping phenyl rings are an effective relaxation mechanism both for the chain deuterons and for the phenyl deuterons. In the former case, the mechanism is provided by the time dependence of the dipole coupling between the chain deuterons and the protons in the phenyl groups; in the latter case it is caused by the time dependence of the quadrupole coupling of the deuterons in the phenyl groups. The distribution of correlation times is either due to permanent spatial heterogeneity of local environments of the molecular units or it is due to the change in time-scale of the motion of the molecular units over long time intervals. It is observed that a denser packing of the polymer caused by high pressure results in a decrease of T_1. We have shown that T_2^* can be used as a monitor of the glass transition. We have determined the variation of T_g as a function of pressure. An increase of T_g with pressure was found which is about five times smaller than in earlier measurements.

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