^{2}H n.m.r. study of high pressure effects on the molecular dynamics in polystyrene: 1. Main chain motion

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The effect of high pressure on the main chain motion near the glass transition temperature (T_g) in amorphous chain-deuterated polystyrene is studied using deuteron n.m.r. spin alignment echo and quadrupole echo spectra. Comparison with simulated spectra yields information on the time-scale and the type of motion. In the vicinity of T_g the main chain performs ultra-slow small angle diffusive motion. The temperature dependence of the mean correlation time shows a strongly non-Arrhenius behaviour, typical for the so-called α-process. The width of the correlation time distribution rapidly increases on approaching T_g. The effect of pressure on the motion is found to be much weaker than could be expected from equation-of-state data.

(Keywords: deuteron n.m.r.; polystyrene; glass transition)

INTRODUCTION

When an amorphous polymer is cooled down from high temperature it enters the glassy state[1]. In the glass the chains are essentially fixed and arrested in the structure. Polymer glasses have many properties of solids, but the spatial order is lacking in contrast with polymers in the crystalline state. Although at the glass transition temperature (T_g) anomalies in the specific heat, the thermal expansion coefficient and other thermodynamic quantities are observed, it cannot be considered to be a phase transition. The location of the transition in the phase diagram strongly depends on the cooling rate, therefore, T_g is not well defined experimentally.

At temperatures just above the glass transition a drastic slowing down of the dynamics occurs, finally resulting in the arrest of the motion of the polymer chains at T_g. As an example, an enormous increase in the viscosity is observed on approaching the glassy state from higher temperatures[2]. The large change in the mechanical properties is related to this change in the dynamics. Whereas the diffusional motion and the structural changes become highly restricted and slow, the relaxation of the vibrational and librational degrees of freedom remain relatively fast. The complex dynamic behaviour is characterized by a distribution of correlation times. The mean correlation time of the slow chain motion shows a very strong temperature dependence, very different from the Arrhenius-like temperature dependence of an activated process[3–5]. Presumably, this is due to the collective nature of the dynamics. Average structural relaxation times are of the order of minutes or hours.

Because of the slow rate of molecular motion in solid polymers, particularly in the vicinity of the glass transition, only a few experimental methods can provide information about the motion. The measurement of the relaxation properties of amorphous polymers by using various mechanical and dielectric techniques yields information about the time-scale of the molecular motion[6]. A typical relaxation spectrum of an amorphous polymer consists of a large α-peak at low frequencies and a smaller β-peak recorded at higher frequencies. The α-peak corresponds to the process of motion of the main chain units and appears near T_g. The β-peak, however, persists also in the glassy state below T_g and is commonly attributed to the process of side group motion. The mean correlation times of both processes merge above T_g.

Dielectric and mechanical relaxation probe fluctuations in macroscopic volumes and, therefore, they provide only macroscopic information. In contrast with these methods n.m.r. probes molecular dynamics on a microscopic scale since the local interactions are effective on the order of a few ångströms. N.m.r. is currently the only experimental method yielding detailed information about molecular order and about the type of molecular motion on the time-scale appropriate for solid polymers. This information is reflected in n.m.r. spectra[7] and relaxation rates[8].

Information on molecular order and the dynamics of polymer systems in ^{2}H n.m.r. originates from the anisotropy of the quadrupole interaction tensor. The local interactions of deuterons with spin quantum number $I = 1$ are dominated by the coupling between the nuclear quadrupole moment (eQ) and the electric field gradient (EFG) which exists at the site of the nucleus. The n.m.r. frequency is given by[8]:

$$\omega = \omega_0 \pm \delta(3\cos^2\vartheta - 1 + \eta\sin^2\vartheta\cos 2\varphi) = \omega_0 \pm \omega_Q(\vartheta, \varphi) \qquad (1)$$

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where $\omega_0 = \gamma B_0$ is the Zeeman frequency; $\delta = 3e^2qQ/8\hbar$, the quantity $e^2qQ/\hbar$ is the quadrupole coupling constant, eq and η are the largest component and the asymmetry parameter of the EFG tensor, respectively. The polar angles ϑ, φ specify the orientation of the magnetic field vector B_0 in the principal axes system of the EFG tensor.

It is the purpose of this work to make an extensive study of the effect of high pressure on the molecular dynamics in polystyrene (PS) in the vicinity of the glass transition. Atactic PS is a simple synthetic amorphous polymer which has been used as a model polymer in the investigation of the glass transition. Moreover, the properties of PS are of high interest because of its simple chemical structure and wide technical applications. Just above the glass transition ($T_g \sim 373$ K) at a frequency of 0.16 Hz a large α-peak in the mechanical loss curve appears which is centred at 383 K[9]. The β-process, which is attributed to phenyl ring reorientations, shows up as a broad maximum in the mechanical loss curve at 300 K for 0.16 Hz. Other authors[10], using dielectric methods, report this peak at 350 K at a frequency of 10 kHz. At lower temperatures two additional peaks, usually called γ and δ, have been reported[10]. We make use of the selectivity of the ^{2}H n.m.r. methods by studying PS deuterated in the chain (PS-d_3) and in the phenyl ring (PS-d_5). In this paper we investigate how changes in pressure and temperature affect the motion of the main chain in the glass transition range in PS-d_3. The results of the studies of the side group motion in PS-d_5 and spin relaxation studies of PS-d_3 and PS-d_5 will be presented in the next two papers[11,12].

The application of high pressure has distinct effects on the properties of polymers in the solid phase. First, by variation of the pressure it is possible to investigate the phase diagram of solid polymers. Although the glass transition in amorphous polymers is not a thermodynamic phase transition, phase diagrams have been established. Generally, it has been shown that T_g shifts to higher temperatures on applying pressure. Until now, the effect of high pressure in the vicinity of T_g was studied only in thermodynamic experiments like the establishment of the equation of state and differential thermal analysis. For examples on PS we refer the reader to references 13 and 14. Secondly, since the compressibility is large, the application of pressure leads to a considerable reduction of the free volume available for the motion of the main chains and of the side groups. This results in a strong influence on type and time-scale of the molecular motion. Usually, investigations of the molecular motion are carried out at ambient pressure with temperature as the principle variable. However, the effect of pressure is also of interest in studying factors controlling motion. The application of pressure allows the investigation of the motion along isotherms and also along isochores. Therefore, it is possible to distinguish between the effects of temperature and of density on the motion.

In order to analyse the slow motions typical for the main chain in the vicinity of T_g, Spiess and co-workers[3,4,15] used the two-dimensional exchange ^{2}H n.m.r. technique in a study of chain-deuterated PS. In the two-dimensional spectrum the signal along the diagonal appears to be considerably broadened into the second dimension. The intensity is spread over the entire two-dimensional plane, however, one does not observe the elliptical ridges which are typical for molecular motion consisting of discrete angular jumps. This observation leads to the conclusion that the main chain segments perform small angle reorientational diffusive motion. Spectra calculated based on this assumption give good agreement with the experimental ones. The data are fitted assuming a broad distribution of correlation times. The mean correlation time shows non-Arrhenius behaviour and increases according to the Williams–Landel–Ferry (WLF) function[16] on approaching T_g from the melt. The changes in the correlation time are found to be enormous, from 100 s at T_g to only 12 ms just 18 K above T_g.

EXPERIMENTAL

Apparatus. ^{2}H n.m.r. spectra have been obtained at 41.43 MHz using a home-built spectrometer. The high pressure n.m.r. probe is described elsewhere[17]. The experiments were performed in the temperature range from 373 to 388 K. The radio-frequency feed-through into the probe was made out of Vespel-SP21 (Du Pont). The pressurizing medium used for the polymer sample in this study is nitrogen. Hydrostatic pressure was made up to 2250 bar (1 bar $= 10^5$ Pa). The pressure was measured to within an accuracy of ±5 bar, using a manometer calibrated against a pressure balance, the absolute accuracy of which is better than 1:10 000. The probe was placed in a cryostat, which is also described in reference 17. The temperature was controlled to within ±0.01 K in the whole temperature region using a home-built PI unit.

Material. Atactic PS deuterated in the chain, PS-d_3, $M_w = 226\,000$, $M_w/M_n = 1.16$ was provided by Dr F. Fujara (University of Mainz). A cylindrical sample (length 9 mm, diameter 6.5 mm) was prepared from powdered material.

Deuteron n.m.r. spectra were obtained using the quadrupole echo and spin alignment echo techniques, which have been discussed extensively in references 18 and 19. Quadrupole echoes[20] were obtained using the standard sequence consisting of two radio-frequency pulses with a phase difference $\pi/2$. The pulses were separated by a time interval t_1 with values of 30 and 60 μs. Spin alignment echoes were recorded with the three pulse sequence ($\pi/2$-t_1-$\pi/4$-t_m-$\pi/4$-t_1-acq.) for two values of t_1, namely 30 and 50 μs. The mixing time t_m was varied up to 100 ms. Quadrupole echo spectra and spin alignment echo spectra were obtained by Fourier transformation of the time domain signals.

In our instrument the maximum radio-frequency power that can be applied is limited by the breakdown voltage of the feed-through into the pressure probe. The length of a $\pi/2$ pulse cannot be reduced below $\sim$4.5 μs. We have used $\pi/4$ pulses instead of $\pi/2$ pulses, since a $\pi/2$ pulse of 4.5 μs would lead to considerable distortion of the line shape because of insufficient excitation bandwidth[21].

The quadrupole and spin alignment echo signals were obtained using quadrature detection. They were digitized in 2 × 128 data points with a spectral width of 500 kHz. The acquisition in the time domain was started before reaching the maximum value of the echo signal. Prior to the Fourier transformation resulting in the spectrum, the digitized points were shifted so that the first data point was the echo maximum, using spline functions[22]. In addition, exponential weighting corresponding to a line broadening of 2 kHz was applied. A phase cycling scheme in which the phase of the first pulse is alternated was used to suppress artifacts[22,23].

RESULTS AND DISCUSSION

Spin alignment echo spectra

Figures 1 and *2* show spin alignment spectra recorded at 373 K and 388 K as a function of pressure together with the best fit obtained from the model calculations. At 373 K the line shapes obtained for $t_1 = 30\,\mu s$ correspond to rigid solid behaviour; in the spectra measured for $t_1 = 50\,\mu s$ the intensity in the middle of the spectrum is considerably reduced with respect to the spectra obtained for $t_1 = 30\,\mu s$. In the spectra recorded at 388 K for $t_1 = 30\,\mu s$ the change of the line shape as compared with the spectra at 373 K is insignificant. However, the loss of overall intensity is larger and, in addition, these changes happen on a 10 times shorter time-scale. Line shapes recorded for $t_1 = 50\,\mu s$ significantly deviate from the ones measured at $t_1 = 30\,\mu s$. Apparently, molecular motion occurs. The strong t_1 dependence of the spectra indicates that changes of the orientation of the C-^{2}H bond occur due to small angle reorientations. The spin alignment spectra recorded in our experiment are similar to those obtained by Rössler *et al.*[24,25].

Detailed information about the type and time-scale of the motion is obtained by comparing experimental and simulated spectra. The simulation of the spectra was performed using a program developed at the Max-Planck-Institut für Polymerforschung, Mainz for a model of small rotational angle diffusive motion and has been used before in the analysis of a two-dimensional experiment. The program was made available by Dr D. Schaefer. A full description of the theory involved in simulations can be found in a series of papers published recently[3,15,26]. A somewhat simplified discussion is presented in the following.

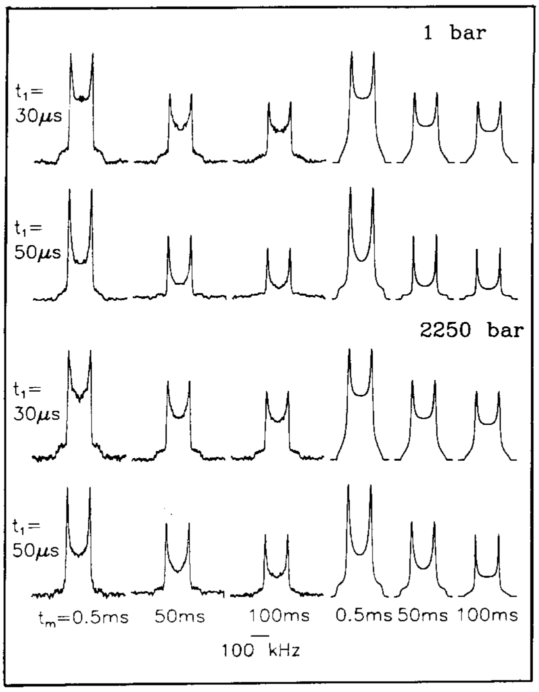

Figure 1 Experimental and calculated spin alignment echo spectra of chain-deuterated polystyrene measured at 373 K for different evolution and mixing times, t_1 and t_m, respectively

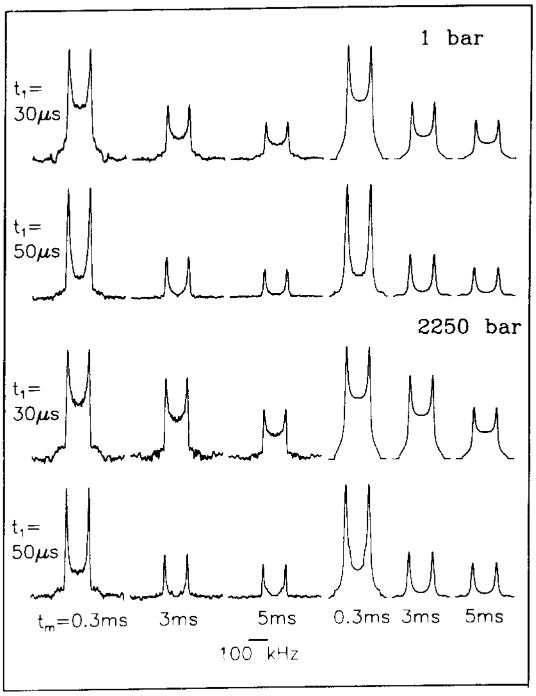

Figure 2 Experimental and calculated spin alignment echo spectra of chain-deuterated polystyrene measured at 388 K for different evolution and mixing times, t_1 and t_m, respectively

It has been shown[27], that the amplitude of the transverse magnetization of the spin alignment directly measures a single particle time correlation function:

$$F(t_1, t_2, t_m) = \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \sin(\omega_1 t_1) \sin(\omega_2 t_2) \Gamma(\omega_1, \omega_2, t_m) \quad (2)$$

where $\Gamma(\omega_1, \omega_2, t_m)$ is the joint probability density that spins having frequency ω_1 during t_1 have frequency ω_2 after t_m. Moreover, $\Gamma(\omega_1, \omega_2, t_m)$ is equal to the pure absorption mode two-dimensional spectrum[26].

In a model where it is assumed that all C-^{2}H vectors perform isotropic rotational diffusion, $\Gamma(\omega_1, \omega_2, t_m)$ in equation (2) takes the form:

$$\Gamma(\omega_1, \omega_2, t_m) = \frac{\sin \omega_1 t_1}{2} \frac{\sin \omega_2 t_2}{2} \times \sum_{\nu=0}^{\infty} (2\nu + 1) P_\nu(\omega_1 t_1) P_\nu(\omega_2 t_2) \exp\left[-\frac{\nu(\nu+1) t_m}{6\tau_d} \right] \quad (3)$$

where τ_d is the correlation time for rotational diffusion and P_ν is the Legendre polynomial of order ν.

Above the glass transition molecular processes cannot be described by a single correlation time. Therefore, in the simulations a log-Gaussian distribution of correlation times is assumed:

$$\rho(\ln \tau) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(\ln \tau - \ln \tau_c)^2}{2\sigma^2} \right] \quad (4)$$

where $\ln \tau_c$ is the mean logarithm of the correlation time. The width of the distribution on a logarithmic scale in base 10 is given by $\Delta = 2\sigma \log e$. In practice the continuous distribution was replaced by a discrete one by calculating spectra for 15 values of the correlation time spanning the whole width of the distribution. A spectrum for a given mean correlation time and distribution width was obtained by summing 15 spectra weighted by the log-Gaussian distribution [equation (4)]. So far, absence of molecular motion is assumed in the evolution and detection period. However, the distributions of the correlation times are very broad and the short time part lies in the region of correlation times which cause changes already in the quadrupole echo. Therefore, the assumption about the slow motion limit was dropped and corrections were introduced in the simulations as discussed in detail by Kaufmann *et al.*[3]. It should be noted that changes in the quadrupole echo spectra were small, as discussed below, however, a severe loss of the quadrupole echo amplitude was observed, which suggests isotropic reorientations of the C-^{2}H bond[18].

Evidently, as the criterion for a good fit of simulated to experimental spectra we want the same set of parameters to fit all spectra measured at a given temperature and pressure. The quality of the fits has been judged by visual inspection by plotting the experimental and calculated spectra onto each other, scaled to the same intensity. The ratio of the intensity in the middle and the intensity of the Pake singularities appears to be very sensitive to the value of τ_c. Using this as a criterion we obtain a relative inaccuracy of $\sim 5\%$ in τ_c. The width of the distribution is less accurate, the inaccuracy is $\sim 20\%$. The calculated spectra resulting in the best fits are also shown in *Figures 1* and *2*. The fit between calculated and experimental spectra is quite satisfactory. In the following we present the quantitative results obtained.

At 373 K, 1 bar the best fit was obtained assuming a value of τ_c of 130 s with a width Δ of the distribution of five decades. An increase of pressure of 2250 bar results in all experimental spectra recorded at $t_1 = 30\,\mu$s having the same shape and differing only in the intensity of the signal. Very small changes of the line shapes as a function of t_m can be detected for an evolution time $t_1 = 50\,\mu$s. We have obtained a good fit for $\tau_c = 250$ s and a distribution width of five decades. We note that the longer correlation times obtained from our analysis could be inaccurate since molecular motion takes place on the time-scale of hundreds of seconds while our spectra have been measured up to 100 ms. This is caused by experimental problems: it was very difficult to obtain spectra with a sufficient signal-to-noise ratio for $t_m > 100$ ms.

At 388 K, just 15 K above T_g, the change in the detected correlation times is remarkably small. At 1 bar, simulated spectra with $\tau_c = 12.5$ ms and a distribution width of three decades give the best fit to the experimental ones. A pressure increase of 2250 bar results only in small changes in the spectra. The motion slows down slightly; the simulated line shapes have been obtained for $\tau_c = 20$ ms and a distribution width of three decades.

The results of the analysis are summarized in *Figure 3*.

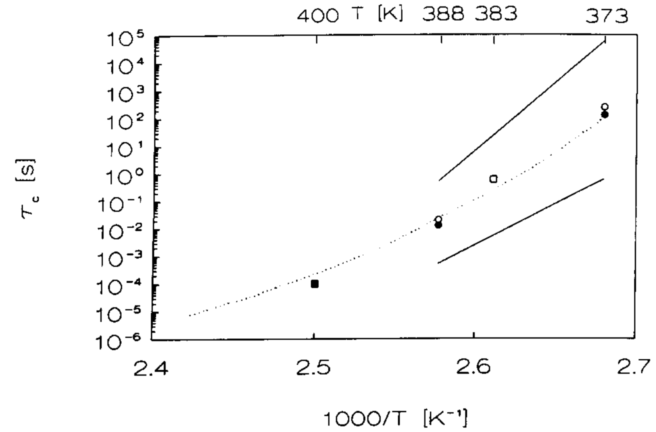

Figure 3 Mean correlation times for the motion of the main chain in polystyrene obtained from the comparison of experimental and calculated spectra: (●) 1 bar; (○) 2250 bar. The dotted line shows the WLF fit of reference 4. (□) and (■) show the results of references 9 and 10, measured with mechanical and dielectric techniques, respectively. The solid lines show the width of the distribution of correlation times

Quadrupole echo spectra

We have also recorded quadrupole echo spectra at temperatures of 373 K and 388 K, which are presented in *Figure 4*. The line shapes measured at 373 K seem to be unaffected by pressure and by the spacing between the pulses. At 388 K considerable changes in the line shape are observed as a function of the pulse spacing, resulting in the loss of intensity in the middle of the spectrum. At 1 bar these changes are somewhat more pronounced than at 2250 bar.

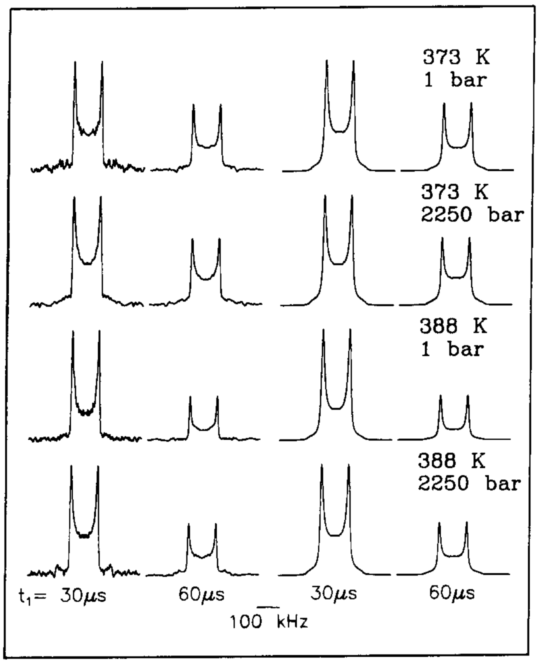

Figure 4 Experimental and calculated quadrupole echo spectra of chain-deuterated polystyrene as a function of pressure at 373 K and 388 K for different pulse distances t_1

The experimental quadrupole echo spectra have been compared with simulations based on the analysis of the effect of motion on the shape of the quadrupole echo, presented by Spiess and Sillescu[18]. In the calculations we have attempted to simulate the small angle rotational diffusion model which we used in fitting the spin alignment line shapes. Since, to our knowledge, no program for simulation of the effect of isotropic diffusion on quadrupole echo spectra has been developed, we have used the program, developed for jump motion by Greenfield *et al.*[28]. We have approximated the isotropic motion by jumps of the C-^{2}H bonds to nearest neighbour orientations, characterized by 20 equally spaced sites on a cone with an opening angle rather arbitrarily chosen to be 54.7°. The spectra calculated using the values of τ_c and Δ found from the spin alignment experiments should match the experimental quadrupole echo spectra. The simulated spectra are also shown in *Figure 4*. At 373 K the spectra are equivalent to those of the rigid solid. At 388 K a change in the line shape is observed on the time-scale of the experiment (microseconds), although the mean correlation times are of the order of milliseconds. As has been pointed out[18], changes in the quadrupole echo line shape due to rotational diffusion or small angle reorientations occur already even when the correlation times are still much longer than the pulse spacing t_1. In contrast, molecular motion involving large angular jumps causes changes in the line shape only when the correlation time is of the order of the pulse spacing.

Temperature dependence of the chain motion

Figure 3 shows the drastic slowing down of the chain motion on approaching T_g from the melt. The temperature dependence of the correlation times found in our measurements at 1 bar is in reasonably good agreement with the one obtained in a two-dimensional n.m.r. study of PS by Pschorn *et al.*[4], as is also shown in *Figure 3*. The dotted line in this figure follows the WLF equation:

$$\log[\tau_c(T_g)/\tau_c(T)] = \frac{C_1(T-T_g)}{C_2+(T-T_g)} \qquad (5)$$

with parameters $C_1 = 15.9$, $C_2 = 49.0$ K and $\tau_c = 100$ s at $T_g = 373$ K.

The motion of the main chain results in some distortion of the lattice. Molecular motion influences the speed and ease of electric polarization changes in an alternating electric field. Therefore, the motion is mechanically and dielectrically active. The results from mechanical and dielectric relaxation measurements are close to the n.m.r. findings, as can be seen in *Figure 3*.

Effect of density changes

At 373 K, the glass transition temperature, we have found that the application of pressure results in small changes of the line shape. It causes only a small effect on the rate of the motion; the mean correlation time increases by a factor of about two. From the equation of state[13] we know that the density changes from 1.025 g cm^{-3} at 1 bar to 1.08 g cm^{-3} at 2250 bar. This results in a denser packing of the chains; the interchain distances are reduced at least by 1.78%. We believe that the insensitivity of the motion to this change in density is caused by the fact that at temperatures near T_g the chain motion is almost completely arrested. A much larger effect of density changes is expected on the motion of the phenyl group, because it sticks out of the main chain. For comparison, we have shown in our study of phenyl group motion in PS[11] that a reduction of the interchain distance of ~1.1% increases the mean correlation time of the phenyl rings by a factor of 100.

According to the equation of state, a pressure increase of 2250 bar at 388 K should lead to the glassy state. Therefore, the mean correlation time is expected to change by a factor of the order of 10 000 since the mean correlation time at ambient pressure at T_g is 130 s while it is only 12.5 ms at 388 K. Remarkably, the correlation time at 2250 bar is less than two times longer than at ambient pressure at 388 K. In addition, it is by a factor of 6500 shorter than at T_g at 1 bar. We conclude that we did not enter the glassy phase. This discrepancy could be due to the effect of the pressurizing medium, nitrogen gas, on the PS sample. This problem is also encountered in our next paper[12], where we discuss spin relaxation measurements on PS.

Nature of the motion

In our analysis of the data a log-Gaussian distribution of the correlation times has been assumed. This distribution is used because of its mathematical simplicity. As was shown recently in a reduced four-dimensional exchange n.m.r. experiment[29], it is possible to measure the shape of the correlation time distribution in more detail. The result of the experiment is that the distribution of the correlation times corresponds to a time correlation function which has the Kohlrausch–Williams–Watts (KWW)[30,31] stretched exponential form $q(t) = q(0)\exp[-(t/\tau)^\beta]$ with $\beta \in (0;1)$. The KWW correlation function can be expressed as a superposition of exponential functions:

$$q(t) = q(0)\exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] = \int_0^\infty \mathrm{d}\tau\,\rho(\tau)\exp\left(-\frac{t}{\tau}\right) \qquad (6)$$

in which $\rho(\tau)$ is a distribution of correlation times. From the mathematical form of this expression it is possible to calculate the correlation function starting from a distribution of correlation times or to calculate the distribution of correlation times when the correlation function is known[32].

The simplest conceivable origin of a correlation time distribution is the existence of locally different environments. In the discussion of the physical origin of the occurrence of a distribution of correlation times one of the interesting questions is whether the elementary relaxation steps, in spatially distinct regions, are independent (occurring in parallel) as in permanently different environments, or dependent (occurring in series). Both ways finally lead to a non-Arrhenius behaviour. In support of the latter model, it has been shown[33] that co-operative motion, in which faster motion precedes and induces slower motion, generates a wide range of correlation times. Only recently the first results of investigations of the elementary processes which make up the dynamics have become available[29]. We will return to this point and to the question of ergodicity in a paper dealing with deuteron spin-lattice relaxation[12]. Although the correlation times found in our study follow the WLF behaviour, an 'apparent' activation enthalpy (ΔH) for both pressure values can be found from the temperature dependence of the mean correlation times on approaching T_g; the values are 741 and 756 kJ mol^{-1}, respectively. The difference between these values is small, indicating once again the weak density dependence of the molecular motion. The observed steep temperature dependence of the correlation times is typical for processes in which the motion is of a co-operative nature, as for instance in order–disorder phase transitions. This is a strong indication of the co-operative nature of the motion of the main chain on approaching T_g.

Finally, we remark that the 'apparent' ΔH is an order of magnitude larger than the *trans–gauche* barrier (~15 kJ mol^{-1}), which is the usual conformational transition in a polymer chain. The presence of the large angle jumps characteristic for an elementary *trans–gauche* conformation was found neither in our results nor in two-dimensional n.m.r. measurements[3,4,15]. Similar behaviour was found in polypropylene[5]. There, however, *trans–gauche* conformations were determined by ^{13}C magic angle spinning n.m.r.[34]. Recent computer simulations of polyethylene chains[35,36] have shown that conformational changes can also arise from co-operative motion of large chain units with the *trans–gauche* conformation as the elementary process. This is exactly what is believed to be the nature of the main chain motion in PS.

CONCLUSIONS

We have shown that the main chain performs ultra-slow small angle reorientational diffusive motion in the vicinity of T_g. The molecular motion is characterized by a distribution of correlation times. The temperature dependence of the mean correlation time shows a strongly non-Arrhenius behaviour, which is typical for the α-process. We have observed that the width of the distribution of correlation times rapidly increases on approaching T_g from higher temperature. The effect of pressure on the motion is found to be much weaker than could be expected from the equation-of-state data.

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