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

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The effect of high pressure on the phenyl group motion in amorphous polystyrene (PS-d_5) has been studied using ^{2}H n.m.r. quadrupole echo spectroscopy. The spectra are superpositions of two contributions from phenyl groups performing relatively slow and fast 180° flipping motion, respectively. The motion of the phenyl groups is characterized by a distribution of correlation times. The mean correlation times of the slowly flipping groups vary from milliseconds to microseconds and are in good agreement with data from other relaxation techniques. The effect of pressure on the molecular motion is strong in the glassy state. The reorientational activation volume is of the same order as the volume required for the rotation of a phenyl group. Above the glass transition temperature the effect of pressure is much weaker. We have no evidence that the phenyl group motion is dependent on the main chain motion.

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

INTRODUCTION

In the preceding paper[1] we reported on a deuteron n.m.r. study of the effect of high pressure on the chain motion in polystyrene (PS) near the glass transition temperature (T_g). It was established that the main chain performs small angle reorientational diffusive motion.

In this paper we focus on the analysis of the effect of high pressure on the reorientation of the phenyl groups in PS. The motion of the phenyl ring is responsible for the β-relaxation process[2–4] which in contrast to the α-process (the motion of the main chain) persists also in the glassy state. Therefore, it is interesting to examine the side group motion both below and above T_g and to investigate to what extent the side group motion is coupled to the main chain motion.

In earlier n.m.r. investigations of phenyl group reorientations, Schaefer *et al.*[5] used ^{13}C n.m.r. in determining the relaxation times T_1 and $T_{1\rho}$ and line shapes under magic angle spinning at room temperature. From the ^{13}C T_1 it was concluded that ~7% of the phenyl rings are involved in flips in the megahertz region. The phenyl groups perform 180° flips since the chemical shift tensor of the aromatic carbon appears to be unchanged by the motion as detected with the line shape studies. From T_1, $T_{1\rho}$ and the ratios of dipolar sideband intensities of the measured line shapes it is concluded that the flipping of the other rings is restricted to an average angular displacement of 30–40°. Moreover, $T_{1\rho}$ and the dipolar sideband patterns of the main chain aliphatic CH group show an effect of molecular motion. Two classes of motion have been proposed. The first involves rotations about the ring C_2 axes in co-operation with main chain reorientations. The second class is a co-operative main chain motion in which the rings undergo limited translations but no rotations.

Spiess[6] reported ^{2}H continuous wave wide line spectra of PS deuterated in the phenyl ring (PS-d_5). The spectrum measured at room temperature is equivalent to that of the rigid solid. In the line shape at 383 K two weak extra peaks are present in the middle. A further increase in temperature to 433 K results in a Lorentzian line. It is clear from the recorded spectra that the motion of the phenyl group is restricted since the line shape characteristic for free rotation of the phenyl group (the width would then be reduced to 0.25 of the rigid solid spectrum) is not observed. Rössler[7] and Spiess[8] measured spectra with pulsed ^{2}H n.m.r. Their results indicate motional heterogeneity of the phenyl groups involving the presence of fast and slowly reorienting phenyl groups. The line shape analysis shows that at 373 K ~20% of the phenyl groups take part in the fast motion. The fast flipping phenyl group motion can be frozen by lowering the temperature to 170 K[7].

EXPERIMENTAL

Deuteron n.m.r. spectra. The ^{2}H n.m.r. experiments were carried out at a frequency of 41.43 MHz in the spectrometer and high pressure n.m.r. probe described in the preceding paper[1], using the same methods. Molecular motion on the time-scale of the reciprocal quadrupole coupling constant was determined by recording and analysis of the quadrupole echo spectrum measured with a sequence ($\pi/4$-t_1-$\pi/4$-t_1-acq.) where the limitation is the relaxation time T_2^*. The pulses were separated by a time interval t_1 having values between 25 μs and 100 μs. Ultra-slow motion was investigated using spin alignment

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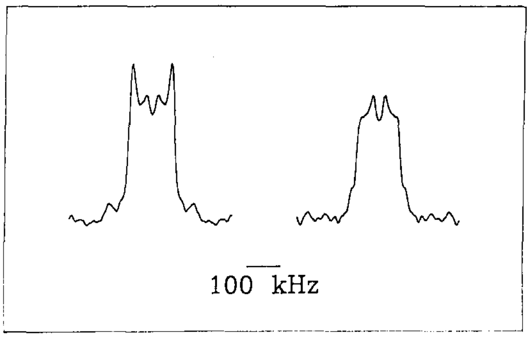

Figure 1 Motional heterogeneity of the phenyl group motion in polystyrene as observed in quadrupole echo spectra at 373 K. Left: fully relaxed; right: partially relaxed

spectra[9]. In the spin alignment echo sequence ($\pi/4$-t_1-$\pi/4$-t_m-$\pi/4$-t_1-acq.) the evolution time t_1 was varied between 20 μs and 50 μs with the mixing time t_m up to 70 ms.

Material. Atactic PS-d_5, $M_w = 225\,000$, $M_w/M_n = 1.2$, was obtained from Dr F. Fujara (University of Mainz). A cylindrical sample (length 9 mm, diameter 6.5 mm) was prepared from powdered material.

RESULTS AND DISCUSSION

Quadrupole echo spectra

Figure 1 shows ^{2}H quadrupole echo spectra of PS-d_5 at 373 K. On the left is a spectrum of a fully relaxed sample recorded with a repetition time of 3 s. T_1 at this temperature is 1 s[10]. On the right is a spectrum of a partially relaxed sample recorded with a repetition time of 100 ms. The spectrum on the left consists of a superposition of more than one component present in the sample ranging from rigid phenyl groups, the motion of which is arrested in the structure, to fast flipping ones. The motional heterogeneity also results in different values of T_1, allowing the separation of the components[10]. The spectrum corresponding to the fast flipping rings is shown in the right part. It corresponds to a spectrum for the averaged electric field gradient (EFG) tensor with a quadrupole coupling constant reduced by 0.625 and an asymmetry parameter of 0.6.

^{2}H quadrupole echo spectra of fully relaxed PS-d_5 measured as a function of temperature and pressure are presented in *Figure 2*. As mentioned above, the spectra at 353 and 383 K are due to fast flipping phenyl groups and to phenyl groups flipping in the slow and intermediate range of the quadrupole echo experiment. At 353 K and 1 bar ($=10^5$ Pa) the shape of the spectra changes as a function of t_1 indicating motion on this time-scale. On applying a pressure of 1250 bar the spectral shape remains unchanged as a function of t_1; only the overall intensity drops. At 383 K the line shapes change as a function of t_1, however, the changes are larger at ambient pressure. The effect of pressure in slowing down the motion is roughly similar to that of lowering the temperature.

Precise information about the time-scale and the type of the motion can be obtained by comparing experimental spectra with spectra calculated from a model of the motion. A phenyl ring attached to the main chain is expected to perform flips over ~180°. In the simulations of the spectra we have assumed that the C-^{2}H bond reorients over 180° on a cone about the flip axis. The opening angle of the cone is the angle between the z-axis of the EFG tensor and the flip axis, which is 60°. In the simulations we have ignored the presence of the *para* deuterons, which do not take part in the reorientations; we come back to this point later.

Lines shapes were calculated[11] using as a parameter the correlation time. Molecular processes in polymers in the glass and in the vicinity of T_g cannot be described by a single correlation time. Therefore, a log-Gaussian distribution of correlation times is assumed[12]:

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

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 16 values of the mean correlation time spanning the whole width of the distribution. A spectrum for a given mean correlation time and distribution width was obtained by summing 16 spectra weighted by the log-Gaussian distribution [equation (1)].

From earlier ^{2}H investigations of PS deuterated in the chain (PS-d_3) below T_g it is known that the motion of the main chain[1,13] is frozen in the glass. Therefore, in our simulations we have assumed that the flip axis is static. An increase of the temperature above T_g results in motion of the main chain. It was found that above T_g the chain performs small angle rotational diffusive motion resulting in motion of the flip axis. The motion of the chain can also be detected in the quadrupole echo spectrum. It is not possible to fit the spectra, obtained above T_g, with a model containing a static flip axis. A simple model which can take the chain motion into account is the 'wobbling' model[11], which consists of the

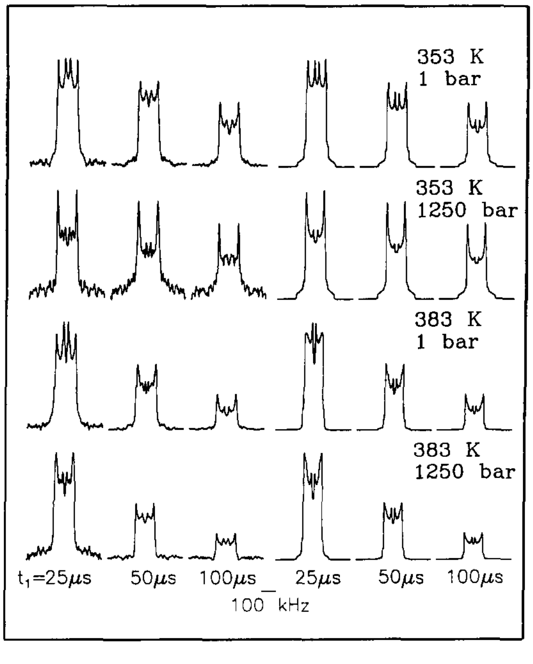

Figure 2 Experimental and calculated quadrupole echo spectra of ring-deuterated polystyrene as a function of pressure at 353 K and 383 K for different pulse distances t_1

Table 1 Correlation times (τ_c) and distribution widths (Δ) used in the comparison of simulated and experimental quadrupole echo spectra

T (K)	*p* (bar)	τ_c (ms)	Δ (decades)
353	1	1	5
	1250	100	5
383	1	0.002	3
	1250	0.02	3

superposition of two motions. In our simulation this is achieved by allowing the flip axis to perform quasi-isotropic motion by diffusion over a cone with an angle of 25° with seven sites on it. Since it is known from the studies of the main chain motion that the mean correlation time at 383 K (the temperature of our measurements) is ~200 ms we have chosen the time between the jumps on the cone to be 10 ms.

The modelling of the main chain diffusion as described above is somewhat arbitrary, however, it has the advantage of taking a relatively short computation time while a further extension of this model is not critical for the resulting line shape. The motion of the flip axis results in an incomplete refocusing of the isochromats in a quadrupole echo at slow exchange rates. This results in a loss of intensity in the middle of the spectrum and in a much better fit than obtained using a static flip axis.

In our simulations we have also taken into account the motional heterogeneity which manifests itself in the rings which are in the fast motion limit of the quadrupole echo experiment. For phenyl jumps with $\tau_c < 20$ ns the quadrupole echo line shape and its intensity are insensitive to changes of τ_c and t_1. We have assumed that the contribution of the fast rings will be represented by a spectrum calculated for a correlation time $\tau_c = 1$ ns and a distribution width of three decades. We note here that for exchange rates with $\tau_c < 20$ ns the quadrupole echo line shape becomes independent of the rate and the pulse spacing since the EFG tensor is averaged by the motion and the spectrum represents the averaged values of its elements.

In addition to the 180° jumps the phenyl rings perform small angle fluctuations about the flip axis. These librations are expected to affect the line shape in the slow motion limit of the 180° jumps. In simulations of this effect for libration angles up to 25° we did not observe major changes from the rigid Pake shape within the accuracy of our experiments. Similarly, small deviations up to 10° from 180° in phenyl ring flips remain essentially unobservable. Therefore, these two effects are not included explicitly in our simulations.

We note that in our simulations we have assumed that the EFG tensor at the deuteron sites in the phenyl groups is slightly asymmetric, as reported before by Henrichs *et al.*[14]. We have used the following principal elements of the quadrupole coupling tensor: 68.6, 63.4 and 176 kHz, which correspond to an asymmetry parameter of 0.04. This asymmetry results in a small change of the line shape in the slow motion limit.

Altogether our fit has three parameters: the mean jump rate, the distribution width and the contribution of the fast phenyl groups. The best fit is obtained when one set of parameters results in a fit at all values of t_1. Such a fit can be obtained in all cases, except for 383 K and 1250 bar where only the fits made at 50 and 100 μs had the same parameters.

As can be seen in *Figure 2*, at 353 K and 1 bar we observe a change in the middle of the spectrum as a function of t_1. We have found that 10% of all rings are in the fast motion limit while the rest performs reorientations with $\tau_c = 1$ ms. At a pressure of 1250 bar no changes on the time-scale of the quadrupole echo are observed and the best fit can be obtained without the contribution of the fast phenyl groups. The best fit was obtained for $\tau_c = 100$ ms. The width of the distribution at this temperature is five decades at both values of the pressure.

At 383 K and ambient pressure the spectra are approximated by assuming that 90% of the phenyl rings show 180° flip motion with $\tau_c = 2\,\mu$s while the rest is assumed to be in the fast motion limit. A pressure increase of 1250 bar results in slowing down the motion. Here the contribution of the fast flippers is also 10%. Spectra at 50 and 100 μs were fitted with $\tau_c = 3.3\,\mu$s, while the best fit for the spectrum at 25 μs was obtained for $\tau_c = 20\,\mu$s. The distribution width at this temperature was found to be three decades at both pressure values. The results are summarized in *Table 1*.

The reorientational diffusion of the main chain is also expected to influence the orientation of the *para* C-^{2}H bonds. This effect could also be simulated, in principle, with the wobbling model, though the *para* C-^{2}H bond diffuses over smaller angles than the main chain, because of the length of the phenyl group. However, we expect the effect of the flipping motion of the phenyl groups on the *para* C-^{2}H bond direction to be much more important. After each jump the phenyl ring is left in a somewhat different orientation as a result of a slight rearrangement of its environment. This means that the *para* C–^{2}H bonds perform small angle reorientational diffusion, as a result of the flips, and with the same correlation frequencies, i.e. between 0.01 kHz and 500 kHz (*Table 1*). Therefore, and because the analysis would have become very complicated otherwise, we have assumed that the contributions of the *para* deuterons to the quadrupole echo decay very fast as a function of t_1, so that they can be ignored. This assumption, of course, could be checked in an experiment on PS selectively deuterated in the *para* position.

Spin alignment echo spectra

It is possible to detect motions which are in the slow limit of the quadrupole echo experiment by applying the spin alignment technique[9]. Whereas the limitation on the time-scale of the quadrupole echo experiment is determined by the relatively short transverse relaxation time T_2^*, the limit on the time-scale of the spin alignment echo experiment is the much longer relaxation time of spin alignment T_{1Q}, which is of the order of T_1[9].

Figures 3 and *4* show spin alignment echo spectra recorded as a function of temperature for two different pressure values. As in the quadrupole echo spectra we observed motional heterogeneity on the time-scale of spin alignment. The spectrum consists of more than one component due to a distribution ranging from fast flipping phenyl groups to rigid ones. Precise information about the time-scale and the type of motion can be obtained from spin alignment spectra if a comparison

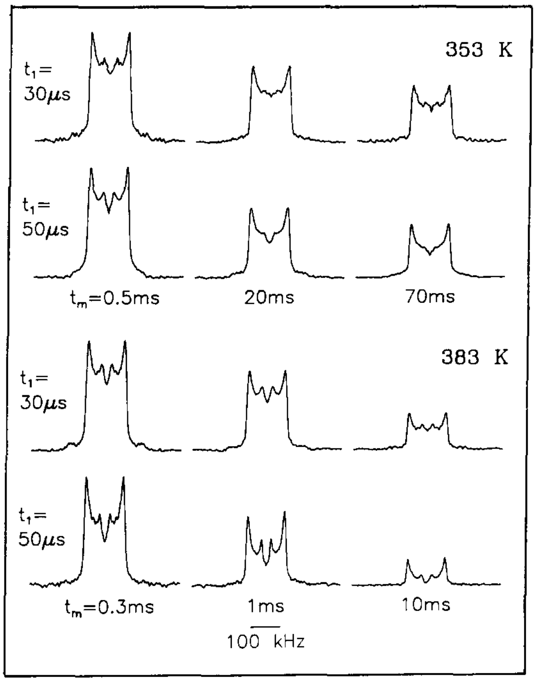

Figure 3 Experimental spin alignment echo spectra of ring-deuterated polystyrene measured at ambient pressure at 353 K and 383 K for different evolution and mixing times, t_1 and t_m, respectively

with model calculations is performed. We only draw some general conclusions.

It is of interest to check whether spin alignment can prove the existence below T_g of local domains where motion of the main chain occurs at positions near fast flipping phenyl groups, as proposed by Schaefer *et al.*[5]. We assumed that the possible type of motion would be the same as above T_g, i.e. small angle rotational diffusive motion. As was already pointed out, spin alignment is a measure of a single particle correlation function[15] and it is possible to distinguish between different geometries of the motion. This is visible in the t_1 dependence since random jumps by large angles lead to a weak and small angle reorientations to a strong t_1 dependence. As was found in the spin alignment spectra of PS-d_3, small angle rotational diffusive motion manifests itself in the fast loss of the overall signal and in the loss of intensity in the middle of the spectrum. Therefore, in our recorded spectra we are looking for such changes.

At 353 K and 1 bar we have recorded spectra for two values of t_1, namely 30 and 50 μs, as a function of t_m up to 70 ms, while at 1250 bar the t_1 values were 20 and 30 μs. We observe no major changes in the spectra as a function of t_1. This leads to the conclusion that small angle reorientations are not observable in our spectra and we cannot prove the existence of the domains mentioned above using spin alignment. We are aware of the two limitations of this experiment. First, the time-scale, since spin alignment was measured only to 70 ms and motions of the main chain with mean correlation times of the order of tens of seconds are not visible[1]. Secondly, the number of fast flipping rings is only 10% as found in the quadrupole echo experiments. Therefore, the eventual signal from the domains is lost.

The changes in the spectra as a function of pressure are very weak. The 180° ring reorientations give a very weak exchange signal in the two-dimensional exchange experiments[16], thus, spin alignment echo spectra are not sufficiently sensitive to detect them. As a general feature we see that the contribution of the fast flipping groups decreases as a function of t_m. This effect is probably due to the faster decay of the signal from the rapid 180° phenyl flips.

At 383 K and 1 bar we have measured spin alignment spectra for two t_1 values, namely 30 and 50 μs, with a t_m up to 10 ms. Comparison of the spectra measured at $t_1 = 30$ μs and 50 μs yields that the latter has a different shape showing reduced intensity in the middle. Presumably, this is an effect of the diffusive small angle reorientations of the flip axis as mentioned above. Since unrestricted diffusion of the phenyl group can be excluded[6], we believe that this is due to the motion of the main chain. This is consistent with the observation from one- and two-dimensional ^{2}H n.m.r. on PS-d_3 that the main chain performs small angle rotational diffusive motion with a mean correlation time of 200 ms at 383 K.

After increasing the pressure to 1250 bar we have recorded spectra for t_1 values of 20 and 30 μs. The spectra measured for $t_1 = 30$ μs show no major changes as compared with those measured at ambient pressure. In the line shapes recorded for $t_1 = 20$ μs we observe a component in the middle of the spectrum. Its shape suggests that it originates from the fast phenyl groups. We observe a faster loss of the intensity of the central pattern than of the outer wings.

From the spin alignment echo spectra it follows that at 353 K no influence of the small angle rotational diffusive motion of the main chain on the phenyl ring motion is observable. At 383 K, the effect of the main chain motion manifests itself as an intensity loss in the middle of the spectrum.

Effect of density changes

At 353 K we have found that the correlation times are in the slow motion limit of the quadrupole echo

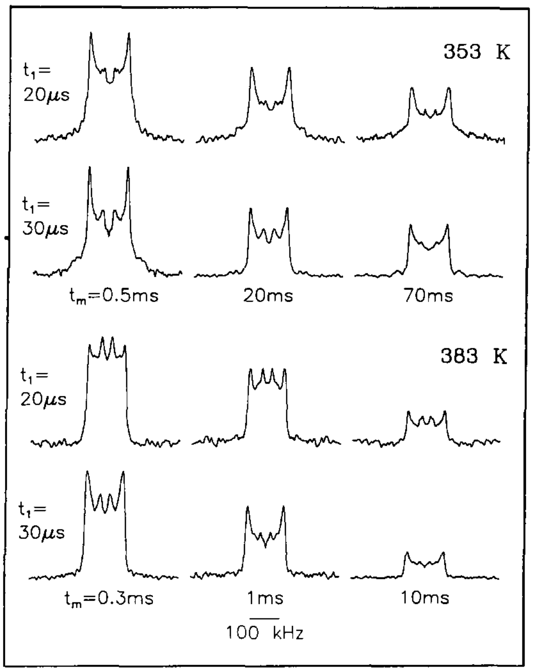

Figure 4 Experimental spin alignment echo spectra of ring-deuterated polystyrene measured at 1250 bar at 353 K and 383 K for different evolution and mixing times, t_1 and t_m, respectively

Table 2 Activation volume (ΔV) and activation enthalpy (ΔH) for phenyl group reorientations in PS-d_5

T (K)	ΔV ($cm^3 mol^{-1}$)	p (bar)	ΔH ($kJ mol^{-1}$)
353	108	1	233
383	59	1250	318

experiment. At 1 bar we estimate the contribution of the fast flipping groups to be 10%. The application of hydrostatic pressure of 1250 bar results in complete suppression of the fast flippers. From the equation of state[17] we know that the density changes from 1.03 to 1.06 g cm^{-3} at 1250 bar. In the glass the main chain is arrested in the structure. A limited volume is available for motion of the phenyl groups. The spectra show heterogeneity in the motion. Locally, domains exist where enough space is available for virtually unrestricted phenyl rotations. The application of pressure results in a much denser packing of the chains and to a reduction of the interchain distances by 1.48%. Therefore, the molecular motion is more constrained. The density at 353 K and 1250 bar is the same as at 1 bar and 197 K. Thus, the density change corresponds to an enormous change of the temperature. We are aware that effects of density and temperature changes on molecular motion can be different. However, we believe that the mean correlation time of the fast flipping rings at 1250 bar shifts to the region which lies within the distribution of higher correlation times found in the line shape analysis.

For comparison, in studies of different polycarbonates[14,18] it was found that an increase of density also slows down the motion. However, the motion of the fast flipping phenylene groups in polycarbonate is not so sensitive to the changes of the density as the motion of phenyl groups in PS. This is due to the fact that in polycarbonate the phenylene group is a part of the main chain while in PS the phenyl group is a side group.

At 383 K, 10 K above T_g, the correlation times are in the intermediate range of the quadrupole echo. We still observe motional heterogeneity, however, the application of pressure has no effect on the contribution of the fast flipping groups. In both cases it is estimated to be ~10%. Presumably, the increase of free space is significant due to co-operative motion of the large chain units above T_g. Apparently the effect of density changes at this temperature is limited to only slowing down the motion.

Activated processes

In contrast with the α-relaxation process, the β-relaxation process shows Arrhenius behaviour. Molecular motion can be treated as an activated process having a free enthalpy of activation (ΔG), so that the correlation time is given by:

$$\tau_c = \tau' \exp(\Delta G/RT) \tag{2}$$

where $\Delta G = \Delta E + p\Delta V - T\Delta S$, and ΔE, ΔV and ΔS are the energy, volume and entropy of activation, respectively. In analogy with the analysis of vacancy diffusion[19], we assume that ΔE is the energy barrier for the reorientation of a phenyl group. The activation volume (ΔV) consists of the expansion of the system at the saddle-point configuration and of the volume increase involved in the creation of the volume, necessary for that type of motion. Using the results obtained from the line shape analysis of the quadrupole echo, we have calculated ΔV and the activation enthalpy (ΔH) according to:

$$\Delta V = RT\left(\frac{\partial \ln \tau_c}{\partial P}\right)_T \qquad \Delta H = R\left(\frac{\partial \ln \tau_c}{\partial T^{-1}}\right)_p \tag{3}$$

The calculated values of activation volume and enthalpy are given in *Table 2*. The values of ΔV can be compared with the volume (92.4 cm^3 mol^{-1}) of the molecular repeat unit $(\text{-}CH_2\text{-}CHC_6H_5\text{-})_n$, as determined from X-ray diffraction data[20] of isotactic PS and with the volume required for a 180° rigid reorientation of a phenyl group which can be calculated to be ~50 cm^3 mol^{-1}. The value of ΔV is very roughly equal to both volumes. It is reasonable to assume that ΔV is related to the volume required for phenyl flips. In the glass at 353 K the chains are arrested in the structure. In contrast, above the glass transition at 383 K, the molecular motion in PS is not limited to the side group but also co-operative motion of the main chains takes place. As a result the phenyl group motion is less restricted which manifests itself in a value of ΔV which is smaller than in the glass.

The calculation of the ΔH values is somewhat uncertain. This is due to the glass transition which occurs between 353 K and 383 K. The derivation of ΔH is valid when the changes in ΔS with temperature and pressure can be neglected. We also observe that the ΔH value calculated at 1250 bar is >40% larger than at ambient pressure. The main contribution to ΔH is the energy barrier ΔE, since the term $p\Delta V$ is small compared with the ΔH values. We believe that the phenyl rings experience a stronger steric hindrance than at ambient pressure, due to the decrease of the interchain distances on application of pressure. This results in a higher energy barrier.

Comparison of our results with mechanical and dielectric data

A conclusion from the line shape analysis is that part of the phenyl rings is involved in jumps with short correlation time. In dielectric studies[3] a weak peak is observed at 180 K for a correlation time of 100 μs. This so-called γ-relaxation process is attributed to reorientating phenyl groups. Experimentally, the activation energy for this process was found to be 38 kJ mol^{-1}. From these numbers we have estimated the correlation time for this process in the region of our measurements to be ~250 ps. Since in our simulations we have assumed that fast flipping motion occurs with a mean correlation time of 1 ns we can identify the high frequency jumps observed in our spectra with the γ-process, indicating that the character of this component of the motion remains unchanged between 180 K and the region of our measurements.

For the β-process the activation energy values found[3,4] in dynamic mechanical and dielectric measurements vary between 125 kJ mol^{-1} and 146 kJ mol^{-1}. Our n.m.r. results yield a value of 233 kJ mol^{-1} for ΔH at ambient pressure. Since the contribution of the $p\Delta V$ term at 1 bar can be neglected, it follows that ΔH is approximately equal to ΔE. The difference between the results of n.m.r. and of dielectric and mechanical measurements is rather large. It should be remembered that our value was obtained in the glass transition region, while the mechanical and dielectric measurements were performed

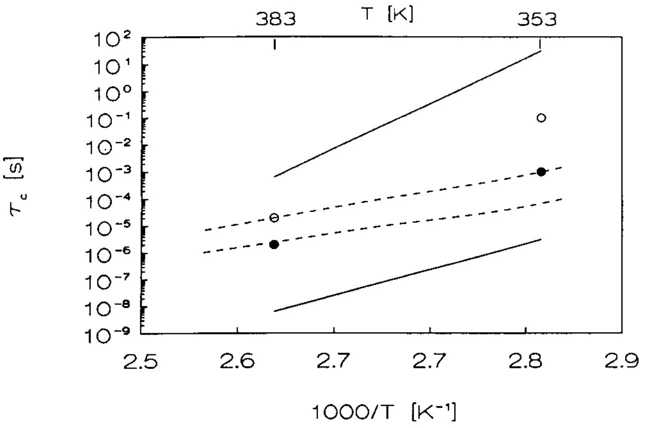

Figure 5 Temperature dependence of the mean correlation time for the motion of the phenyl ring in polystyrene, obtained from the comparison of experimental and calculated spectra: (●) 1 bar; (○) 1250 bar. The solid lines show the width of the distribution of correlation times. The upper and lower dotted lines show the results of references 3 and 4, respectively, measured with dielectric and mechanical techniques

in the glass. We note that on crossing the glass transition ΔS can change. This will introduce an error in our results. In addition, in our analysis we have found a wide distribution of correlation times and ΔE has been calculated from the mean values. Similarly, the peaks in the dielectric and mechanical data as a function of temperature are very broad. This may also result in a difference in ΔE derived from both types of methods. The correlation times of the β-process found in our experiment (1 ms) match very well with the results of different techniques as can be seen in *Figure 5*. Yano and Wada found a peak at 100 μs, centred at 350 K. Seefried and Koleske[4] reported a motion of 6.25 s at 300 K. Thus, at 353 K the correlation time is about $6.25 \times \exp(-146000/8.31) \times (353^{-1} - 300^{-1}) = 1$ ms.

Nature of the motion

In our line shape analysis we have assumed the existence of two types of environments with different phenyl mobility. In the first type the phenyl groups perform nearly unrestricted motion while the motion in the second type is hindered by local interactions. In our analysis we first have attempted to fit the calculated line shapes to the experimental ones using only a single log-Gaussian distribution of correlation times. However, the fit was unsatisfactory, therefore, a second distribution was introduced. Together, the distributions result in an acceptable agreement between experimental and calculated spectra. Our results do not provide convincing evidence for the existence of two mobile regions since the contribution of the fast phenyl groups is estimated to be only 10%. Actually, the problem is whether a distinct region of fast flipping motion really exists or that it is simply a part of a very broad distribution of correlation times. We are also aware of the fact that the log-Gaussian shape of the correlation time distribution is only an approximation of the real distribution with the advantage of being mathematically simple. We come back to this point in our next paper[10].

We note that the results of dielectric and dynamic mechanical measurements are also consistent with the assumption of two types of regions with different mobility. As has been mentioned above, extrapolation of the correlation times of the γ-process from low temperatures to the temperature region of the measured spectra results in correlation times leading to the line shape corresponding to the average EFG tensor. Also the correlation times of the β-process obtained from other techniques agree with the mean correlation time obtained in the line shape analysis (*Figure 5*). The existence of such a large inhomogeneity in the mobility has been demonstrated recently in a Monte Carlo simulation of the two-dimensional kinetic Ising model[21]. The simulation was performed in order to show dynamic processes in the glassy state. It was assumed that the flipping of the spins depends on strong local kinetic constraints, such as that a spin cannot flip unless its neighbours have already flipped. It is shown that in this model large spatial inhomogeneities of flip states exist. In particular, after millions of simulation steps domains exist in which the spins do not change orientation. On the other hand, also domains of high flip rates are found whose size and shape remain unchanged over millions of time steps. Slow changes in the domains with slower spins are caused by the existence of spin clusters which are able to propagate their influence through the system.

CONCLUSIONS

We have shown that the phenyl group in PS performs 180° flips. The 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 is characterized by a distribution of correlation times. The mean correlation times of the slowly flipping groups vary from milliseconds to microseconds and coincide with data from other relaxation techniques. The motion of the fast flipping phenyls is so fast that it averages the EFG tensor. The effect of pressure on the molecular motion is strong in the glassy state and the reorientational activation volume is of the same order as the volume required for a phenyl group reorientation. The effect of pressure is much weaker above T_g. We have no evidence that the phenyl group motion is dependent on the main chain motion.

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