Local and Cooperative Motions at the Glass Transition of Polystyrene: Information from One- and Two-Dimensional NMR As Compared with Other Techniques[†]

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ABSTRACT: ^{2}H NMR results from 2D exchange, solid echo, and wide-line absorption spectra as well as spin-lattice relaxation times are analyzed in terms of different reorientation models applied to the C-^{2}H bond directions of chain-deuterated polystyrene. The dominant mechanism is rotational diffusion by small angular steps where the mean rotational correlation time agrees with relaxation times from dynamic mechanical experiments over a dynamic range of 10 decades. However, the width of the correlation time distribution extracted from the NMR results varies from about 5 decades at T_g to not more than 1 decade at $T \gtrsim T_g + 40$ K, whereas other relaxation techniques yield constant correlation time distributions. The results of the different methods employed for the study of chain motion are compared. It is shown that the motions of well-defined C-H bond directions which are probed by NMR are tightly coupled to the cooperative motion of the α-process. Moreover, they also monitor the separation of the fast β-process from the slow α-process when approaching T_g by cooling down from the melt.

Introduction

Relaxation and molecular motion in polystyrene (PS) have been discussed extensively, and many new experimental techniques have been applied. In the early mechanical and dielectric relaxation experiments it was common to work at constant frequency and to assign various processes (α, β, γ, etc.) by the intensity maxima observed on lowering the temperature. Relaxation times $\tau \approx \omega_{\max}^{-1}$ and apparent activation energies E_A for these processes were obtained by varying the frequency and noting the temperature shift of the maxima. The frequency dependence at constant temperature was analyzed in terms of distributions of relaxation times or nonexponential relaxation functions. The early ^{1}H NMR experiments provided similar information since correlation times could be determined from the inverse width of the wide-line NMR spectrum at the temperature where motional narrowing was observed and from the inverse Larmor frequency at the minimum of the spin-lattice relaxation time T_1.[2] The early NMR literature on PS is reviewed in the paper by Connor,[3] who has investigated T_1 and the rotating-frame relaxation time $T_{1\rho}$ in a series of monodisperse polystyrenes over a wide range of molecular weights.

Our own work was motivated by the hope that more detailed information on the various modes of molecular motion in PS could be obtained by combining ^{1}H and ^{2}H NMR techniques and by studying chain-deuterated (PS-d_3) and phenyl group deuterated (PS-d_5) polystyrenes where separate information on main-chain and side-group motion is available.[4-14] We discovered that ~25% of the phenyl groups perform fast 180° flip motions around the axis to the chain[6,7] and that this motion must be coupled to chain oscillations seen in the ^{1}H-$T_{1\rho}$ data of PS-d_5.[5] The phenyl flips do not change the dipole moment or the polarizability tensor of the phenyl group and are thus not directly observable in dielectric relaxation or dynamic light scattering.[15,16] However, they give rise to a particular motionally narrowed line shape of the ^{2}H NMR spectrum which is observable down to ~-80 °C in PS-d_5.[9,12] Thus, our studies of ^{1}H and ^{2}H NMR in PS-d_3 and PS-d_5 have provided details of local motions in PS that were inaccessible by other techniques. However, there remained some puzzling problems. In particular, we found that the correlation time distributions extracted from spin-lattice or other relaxation time data extended over more than 2 decades, whereas the line-shape data were incompatible with τ-distributions broader than 1 decade.[6] Recent results[14] from applications of two-dimensional ^{2}H NMR that can monitor ultraslow motions and a reanalysis of solid echo spectra and T_1 data have now provided an explanation of this apparent discrepancy and have led to new insights into the relation of local and cooperative molecular motions in PS at and above the glass transition temperature T_g. It is the purpose of this paper to present these results and relate them to information from other relaxation experiments.

Type of Local Motions

In Figure 1 we give an example of the recently developed technique of two-dimensional Fourier transform (2D-FT) ^{2}H NMR[13,17-19] as applied to ultraslow motion in PS-d_3.[13,14] Here, one can determine the probability that the orientation of a (chain) C-^{2}H vector has changed by an angle Θ during a "mixing time" t_m that can be varied by the experimentalist in the range between ~1 ms and the ^{2}H spin-lattice relaxation time T_1, which varies from 200 ms at 393 K to ~10 s at T_g = 373 K in PS-d_3. As shown below, this translates into an even larger dynamic range of correlation times. For a simplified description of the 2D NMR technique and its application to the study of the chain motion in polymers, see ref 17. In the 2D spectrum,

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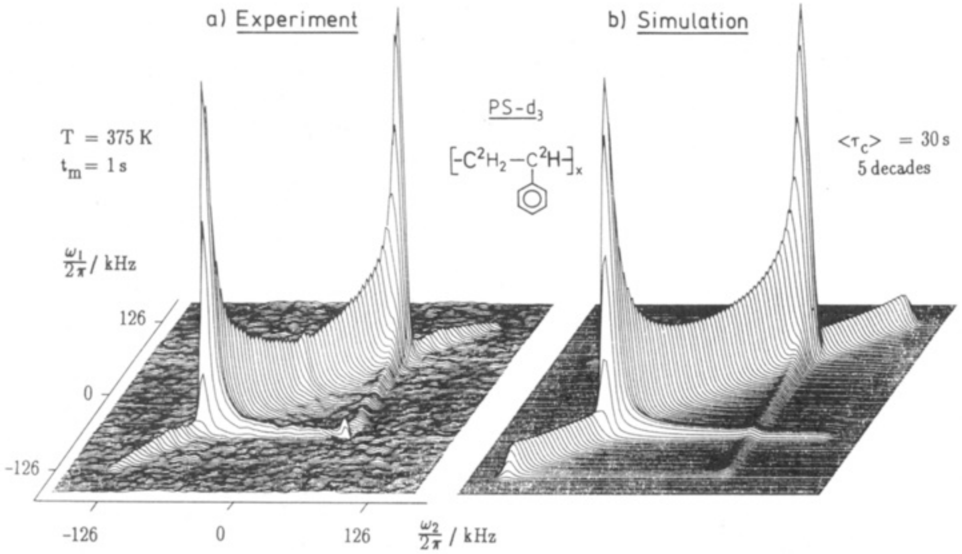

Figure 1. (a) Experimental 2D exchange ^{2}H NMR spectrum of linear-chain deuterated polystyrene PS-d_3 at 375 K for a mixing time t_m = 1 s. (b) Simulated spectrum on the basis of isotropic rotational diffusion assuming a log-Gaussian distribution of correlation times with a width of Δ = 5 decades (see eq 2) and centered around 30 s. For experimental details as well as details of the simulation, see ref 14.

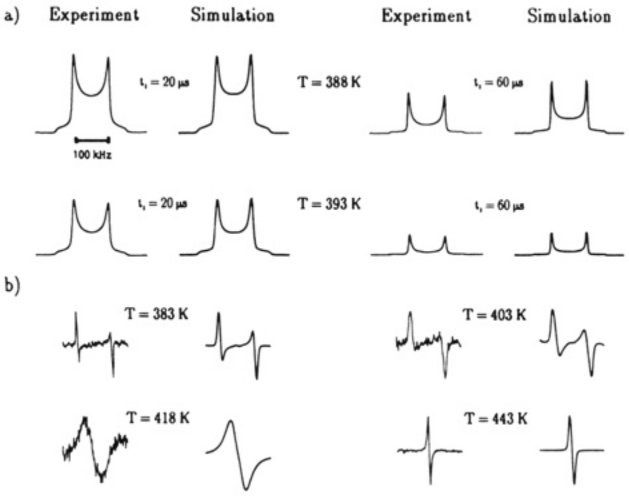

Figure 2. ^{2}H solid echo[9,10] and wide-line[7,11] spectra of linear-chain deuterated PS-d_3 at various temperatures. The simulated solid echo line shapes were corrected for the finite pulse width of 3 μs. The wide-line spectra were recorded in the derivative mode with a modulation amplitude of 1.06 mT $\cong$ 6.9 kHz except for the temperature range 403–423 K, where the broad line shapes required a doubling of the modulation amplitude. The parameters of the simulations are discussed in the text.

one obtains the rigid powder (Pake) line shape along the diagonal in the limit $t_m \rightarrow 0$. For small t_m, one finds some intensity close to the diagonal if reorientation occurs by small angular step rotational diffusion. This "broadening" is somewhat difficult so see in Figure 1, but it shows up clearly at higher temperatures; cf. Figure 7 of ref 14. It *proves* reorientation by small angles indicative of rotational diffusion. However, there is also some intensity far away from the diagonal originating from C–^{2}H vectors that have already reoriented by a large angle within the short period of t_m = 1 s. As already discussed in ref 13, these features cannot result from small angular step rotational diffusion described by a *single correlation time* but are due to C–^{2}H vectors that have reoriented by the same motional process, yet with a larger rotational diffusion coefficient. In order to account for the reorientation by small and large angles within the period of t_m, the simulated 2D spectrum shown in Figure 1b was generated as a superposition of the line shapes for the different correlation times, as described in detail elsewhere.[13] As before,[13] we assumed a log–Gaussian distribution of correlation times[20,21]

$$g(\ln \tau) = (2\pi\sigma^2)^{-1/2} \exp[-(\ln \tau - \ln \tau_0)^2/2\sigma^2] \qquad (1)$$

and have adjusted its width

$$\Delta = \log \exp(2\sigma) \qquad (2)$$

The agreement between experimental and simulated 2D line shapes both normalized to the same height in the plot is highly satisfactory. The lower intensities in the outer wings along the diagonal of the experimental spectrum result from incomplete excitation of the spectrum due to finite pulse widths. The resulting difference between experimental and simulated spectra, however, does not affect the conclusions presented below, which are based not only on the single example presented here but also on our extensive line-shape analysis published elsewhere.[14] We have also considered reorientation by approximately tetrahedral jumps that could arise from conformational trans–gauche or kink[22] transitions. In addition to large jumps, small angles from a trans–gauche–trans sequence can result from two almost tetrahedral jumps adding up to a small angle.[11] However, this and other models of simultaneous small- and large-angle reorientations could not be fitted to a whole series of 2D spectra recorded at different t_m values with the same model parameters.[14] We cannot exclude the occurrence of medium-size or rare large-angle jumps due to the limited sensitivity and resolution of the spectra; however, we can safely rule out the possibility that trans–gauche transitions play a dominant role close to the glass transition of PS. This is quite remarkable since the barrier of ~15 kJ/mol for trans–gauche transitions is much smaller than the apparent activation energy of ~600 kJ/mol found for the mean rotational correlation time at T_g (see Figure 3).

Solid echo spectra[23] have been studied in PS-d_3 at temperatures of ~380–400 K where the line shape changes due to C–H reorientation on the time scale ~10 μs up to several milliseconds. The spectra can be simulated with the same rotational diffusion model used for fitting the 2D spectra. Examples are shown in Figure 2a, where the line shapes and intensities at t_1 of 20 and 60 μs are fitted with the same τ_0 and σ (cf. eq 1). The fact that large spectral changes are observed already at temperatures

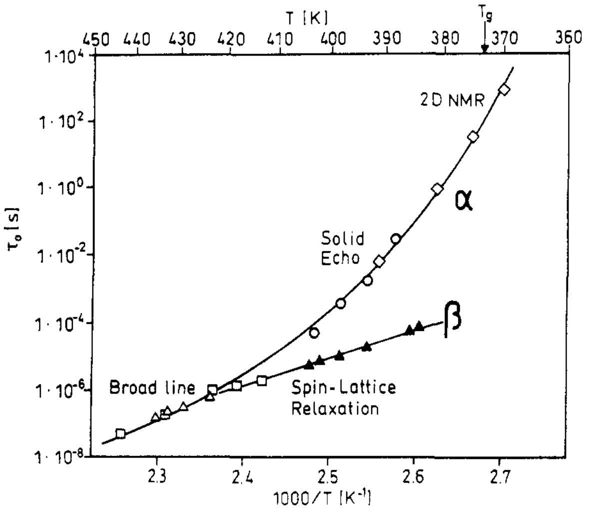

Figure 3. Mean correlation times τ_0 for the chain motion in polystyrene obtained from the various NMR experiments: (◇) 2D exchange NMR; (○) solid echo spectroscopy; (□) wide-line NMR; (△, ▲) spin–lattice relaxation (only the open triangles, however, were included in the WLF fit, yielding the curved solid line).

where the time t_1 between the two rf pulses applied for solid echo generation is much smaller than the rotational correlation time (Figure 3) is consistent with the assumption of reorientation by small angular steps. Large angular jumps only affect the spectral shape if t_1 is of the order of the time between jumps.[23] At temperatures above 400 K, the solid echo intensity is almost lost since the spin relaxation time T_2 becomes shorter than the minimum pulse distance t_1 achievable with present NMR instrumentation where the "dead time" of the receiver limits the time scale of spin–echo spectroscopy. In this temperature range we have recorded NMR line shapes by using a conventional CW wide-line spectrometer[11] where the derivative of the absorption spectrum is recorded. Examples are shown in Figure 2b along with simulations, again using the small-step rotational diffusion model. Although the line shape depends upon the type of molecular reorientation in the "slow-motion" regime, the line shapes are not sensitive enough for drawing definite conclusions. However, all attempts to fit the line shapes at 410–430 K with a correlation time distribution broader than 1 decade were unsuccessful: Under those circumstances the simulated spectra display characteristics from those in the slow-motion and/or fast-motion limit, which are not observed. This important result will be discussed further in the following section along with the T_1 results, which provide no direct information upon the type of molecular motion.

Mean Correlation Times and Cooperative Motions

In Figure 3 we have plotted the mean rotational correlation times τ_c obtained for the chain C–H bond directions from the various different ^{2}H NMR experiments in PS-d_3. The curved solid line is a fit of the WLF equation[25]

$$\log\,[\tau_c(T_g)/\tau_c/(T)] = \frac{C_{1g}(T - T_g)}{C_{2g} + T - T_g} \qquad (3)$$

with the parameters $C_{1g} = 15.9$, $C_{2g} = 49.0$ K, and $\tau_c = 100$ s at $T_g = 373$ K. These values are rather close to results from mechanical relaxation. For example, one obtains $\tau = 50$ s from $\omega\tau = 1$ at the maximum of the loss modulus $G''(\omega)$ and 60 s from the maximum of the relaxation spectrum $H(\tau)$ (Figures 2–4 and 3–3 of ref 25). One can also estimate a rotational correlation time from the monomeric friction coefficient Å$_0$ that can be determined from mechanical relaxation[25] or polymer self-diffusion of short (Rouse) chains.[26] By combining the Stokes–Einstein and Debye equations, one obtains $\tau_c = 2\zeta_0 r^2/9kT$, where r can be assumed as the sphere radius of the monomer volume in bulk PS. The different methods for determining ζ_0 yield values within 0.1 and 10 N s/m for PS at T_g, resulting in τ_c between 0.5 and 50 s if $r = 0.35$ nm is assumed. The large uncertainty of $\zeta_0(T_g)$ is partly due to extrapolating $\zeta_0(T)$ values obtained at $T - T_g \sim 50$ K, where errors of the WLF parameters are proportional to log ζ_0. Dielectric relaxation times in PS are 0.5 s at T_g[27,28] but may be influenced by the more rapid phenyl group motion since values of the order of 100 s are reported in other glass formers at T_g.[21] The τ_c values obtained from photon correlation spectroscopy[15,16] are at ~50–100 s very close to the mechanical relaxation and NMR data. Thus, we conclude that the mean rotational correlation times obtained from ^{2}H NMR for the local motion of chain C–H vectors agree with relaxation times for cooperative motion of the α-process determined by techniques sensitive to relaxation in larger volumes.

Contrary to the foregoing, the τ_c values determined from spin–lattice relaxation times T_1 close to T_g[9] are much shorter than those of the α-process and therefore are attributed to a β-process. The analysis of ^{2}H T_1 data in the glass transition regime is rather complex and is presently being investigated thoroughly in supercooled liquids.[29,30] It has been possible to relate T_1 with the β-process as seen by dielectric relaxation in supercooled o-terphenyl[30] where the amplitude of rapid fluctuations could be determined by recent neutron scattering results.[30,31] Since the temperature dependence of these fluctuations is unknown in PS, the τ_c values given for the β-process in Figure 3 must be considered as a rough estimate only, and no activation energy should be extracted. It should be noted that T_1 at T_g is smaller than the correlation time τ_c of the α-process and thus only sensitive to the β-process. This implies that the small angular step reorientation seen in the 2D spectra (see above) cannot be followed over the full angular range of the C–H orientations, and we cannot exclude that rotational diffusion is restricted for the "slow" fraction where only the "broadening" seen in Figure 1 can be observed during the achievable mixing times $t_m \lesssim 2T_1$.

Motional Heterogeneity

At higher temperatures close to the T_1 minimum, the α- and β-processes merge to an αβ-process[1] and both influence the NMR parameters. Previously, we have analyzed our T_1 data at these temperatures by assuming a Fuoss–Kirkwood (FK) distribution of correlation times[21] where a width parameter $\beta_{FK} = 0.49$ was obtained from ^{2}H T_1 of PS-d_3 at the T_1 minimum (490 K),[9,32] which for a log–Gaussian distribution corresponds to a width of 1.5 decades. This is notably broader than the maximum width of 0.5 decade deduced from the absorption line-shape analysis at lower temperatures (410–430 K). However, the T_1 analysis yields narrower correlation time distributions if we take account of the "fast β-process" seen in neutron scattering. In a semiquantitative estimate along the lines of refs 27–29 we assume that the mean square displacement $\langle r^2\rangle$ of the ^{2}H positions in PS-d_3 at the T_1 minimum equals the value (~0.5 Å^2) estimated from neutron scattering at the corresponding T_1 minimum in o-terphenyl. Preliminary incoherent neutron scattering data in PS-d_5[33] indicate that $\langle r^2 \rangle$ of the chain protons in PS at 490 K may be even larger. These small-amplitude fluctuations on a picosecond time scale can be treated as a reduction of the static quadrupole coupling constant in the expression that relates T_1 to the correlation time distribution at the T_1 minimum. (A rather similar approach has been adopted in order to account for rapid fluctuations in the analysis of ^{13}C spin relaxation in molten polymers.[34]) From the estimate based on the $\langle r^2 \rangle$ in *o*-terphenyl, a width of only 1 decade is obtained, in harmony with the line-shape result (β_{FK} increases from 0.49 to 0.6). By analyzing T_1 of the protons in PS-d_5 and mixtures of PS-d_3 with fully deuterated PS-d_8, we obtained β_{FK} values of the Fuoss–Kirkwood correlation time distributions for motions of chain H–H bond directions, phenyl group H–H bond directions, and the connecting lines of protons sitting on phenyl groups of adjacent PS chains, β = 0.44, 0.37, and 0.23, respectively.[5] By applying the same procedure used above for increasing β_{FK} of the C–^{2}H bond directions, we obtain for log–Gaussian distributions widths of 1.3, 1.9, and 3.5 decades, respectively. Clearly, this reflects the motional heterogeneity in PS at length scales of up to about one monomeric unit as contrasted to single bonds. This is partly averaged in other relaxation experiments analyzed in terms of correlation time distributions. The relations between the width parameters characterizing different correlation time distributions have been discussed in our earlier publication.[5] Here, we note that β_{FK} = 0.5 (0.4) of a Fuoss–Kirkwood distribution corresponds to β_{KWW} = 0.43 (0.34) of a Kohlrausch–Williams–Watts (KWW) distribution if compared at the T_1 minimum. Patterson and collaborators have obtained β_{KWW} = 0.40 from depolarized[35] and 0.33 from polarized[15] dynamic light scattering (LS) in PS at temperatures of 373–403 K, and they explain the larger width from polarized LS by the contribution of density fluctuations that do not influence depolarized LS. In principle, the relaxation spectrum $H(\tau)$ determined from dynamic mechanical experiments can also be considered as a correlation time distribution in the vicinity of the α-process maximum. One obtains a width at half-height of about 2 decades (Figure 3-3 of ref 25), in harmony with the LS results. In both experiments, one finds a constant width of the τ distribution in the temperature range above T_g as in many other glass formers where the constant shape of the α-process is considered a prerequisite of the time–temperature superposition principle.[25]

Therefore, it is very striking that our combined ^{2}H NMR experiments in PS-d_3 exhibit a large increase of the width Δ (see eq 2) on approaching T_g from higher temperatures. Thus, from the T_1 minimum at 490 K we find $\Delta \approx 1$ decade. The adsorption line shapes at temperatures 410–430 K are best described with $\Delta \lesssim 0.5$ decade, and the solid echo spectra indicate an increase of the width parameter Δ from 1.5 decades at 400 K to 3 decades at 388 K, in harmony with the analysis of the 2D spectra, which show a further increase of Δ from 3 decades at 391 K to 5 decades at T_g = 373 K. It is plausible to relate this broadening of the τ distribution with the separation of the α- and β-processes due to their different temperature dependences. However, why is it then that the mean correlation times shown in Figure 3 agree with those found for the α-process in the other relaxation experiments? Here, one should realize that the correlation times determined from relaxation maxima using $\omega\tau_0 = 1$ always refer to the logarithmic average $\tau_0 = \exp\langle \ln \tau \rangle$ if the distribution is symmetric on a logarithmic time scale.[36] In Figure 3, we also have displayed τ_0, which is independent of the width parameter β_{FK} and thus remains invariant if the width becomes temperature dependent. The fact that τ_0 follows the WLF equation indicates that once the information about the time scale and the amplitude of the motion is separated as in the line shape, solid echo, and 2D NMR techniques discussed here, the slow α-process can be monitored directly whereas the spin–lattice relaxation, sensitive to higher frequency motions, follows the β-process on approaching T_g (see Figure 3). The different τ averages seen in different experiments have been discussed previously,[37] and temperature-dependent width parameters have been found in other glass formers.[38]

Conclusions

From our combined ^{2}H NMR experiments in chain-deuterated polystyrene, PS-d_3, we conclude that at temperatures close to the glass transition the reorientation of chain C–H bond directions occurs predominantly by small angular step rotational diffusion. Trans–gauche conformational transitions, which predominate in polymer solutions and in the bulk well above T_g,[39] must play a minor role close to T_g since they are not detected as a separate motional mechanism in the 2D exchange spectra. The mean rotational correlation times follow the WLF temperature dependence of the α-process, and they agree in magnitude with those found in dynamic mechanical and dynamic light scattering experiments. A similar behavior was found[17] for the chain motion of atactic polypropylene above T_g. The NMR results in PS-d_3 can be fitted to a correlation time distribution having a width of less than 1 decade at $T \gtrsim 410$ K, increasing to about 5 decades on approaching T_g = 373 K. This increase is attributed to the separation of the α- and β-processes occurring in this range due to the different temperature dependence. The fact that the mean correlation time seen in the large dynamic range of our NMR experiments follows the WLF equation indicates a strong coupling of the motion of individual chain C–H bond directions with the cooperative motions responsible for the strong temperature dependence of the α-process.

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