

Deuteron n.m.r. in relation to the glass transition in polymers

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^2H n.m.r. is introduced as a tool for investigating slow molecular motion in the glass transition region of amorphous polymers. In particular, we compare ^2H spin alignment echo spectra of chain deuterated polystyrene with models for restricted rotational Brownian motion. Molecular motion in the polystyrene-toluene system has been investigated by analysing ^2H n.m.r. of partially deuterated polystyrene and toluene, respectively. The diluent mobility in the mixed glass has been decomposed into 'solid' and 'liquid' components where the respective average correlation times differ by more than 5 decades.

(Keywords: ^2H -n.m.r.; molecular motion; relaxation; glass transition; polymers; polystyrene)

INTRODUCTION

Previous n.m.r. investigations of the glass transition in polymers¹ have provided information on relatively rapid motions with correlation times below $\sim 10^{-4}$ s at temperatures well above the static glass transition temperature T_g . Recent advances in ^2H n.m.r. have extended the dynamical range to slower motions, and in addition, they yield specific information upon the type of the molecular reorientation processes involved²⁻⁶. In two component glasses, there is the further opportunity of investigating separately the molecular dynamics of both components by applying selective deuteration. Atactic polystyrene has for decades played the role of a 'typical example' for the glass transition in amorphous polymers. Thus, we are also studying ^2H n.m.r. in polystyrene samples deuterated at the chain (PS- d_3) and at the phenyl rings (PS- d_5), respectively⁶. PS and toluene (TOL) form a mixed glass over the whole concentration range which has already been investigated⁷ by ^1H n.m.r., dielectric relaxation, and thermal methods (d.s.c., d.t.a.). It is apparent from this work that the TOL molecules are highly mobile at temperatures well below T_g of the mixture. A ^2H n.m.r. study where either toluene (TOL- d_3 , TOL- d_5) or polystyrene (PS- d_3 , PS- d_5) are deuterated should provide many details of the motion in the glass transition region.

In the following sections we first give an introduction to the relation of ^2H n.m.r. observables with molecular reorientation, for details we refer to a recent review². Furthermore, we attempt to show the extent of new information that can be gained from ^2H n.m.r. with respect to the glass transition, taking PS as a typical example, and we give some details of the polystyrene-toluene system^{6,8}.

^2H n.m.r.

In a rigid solid, the coupling of the deuteron quadrupole moment with the axially symmetric field gradient

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of a C- ^2H bond gives rise to a splitting $2\omega_Q$ of the ^2H Larmor frequency where

$$\omega_Q = \frac{3e^2Qq}{8\hbar}(3\cos^2\theta - 1) \quad (1)$$

and θ is the angle of the C-H bond with respect to the external magnetic field. The weighted superposition of these doublets due to the random orientations in the glass yields the characteristic Pake line shape of the ^2H spectrum having a width of ~ 250 kHz for C- ^2H bonds². Reorientation of the C-H bond can be described by a stochastic process

$$\Omega(t) = \cos\theta(t) \quad (2)$$

which can be modelled by assuming rate equations⁹

$$\frac{d}{dt}P(\Omega_i/\Omega_j, t) = \sum_k P(\Omega_i/\Omega_k, t)\pi_{kj} \quad (3)$$

where the $P(\Omega_i/\Omega_j, t)$ are conditional probabilities and the π_{ij} are rates of the transitions $\Omega_i \rightarrow \Omega_j$. The latter can be chosen in accordance with particular assumptions upon the reorientation process. It can be shown⁹ that the line shape of the n.m.r. spectrum is given by the Fourier transform of the free induction decay (FID) which can be expressed as

$$S_0(t) = \left\langle \exp i \int_0^t \omega_Q(t') dt' \right\rangle \quad (4)$$

where the average can be evaluated by solving a rate equation similar to equation (3) containing the same transition rates π_{ij} of the model for reorientation. Equation (4) applies in the whole 'slow motion' region from the rigid Pake spectrum to the rapid motion limit. Detectable

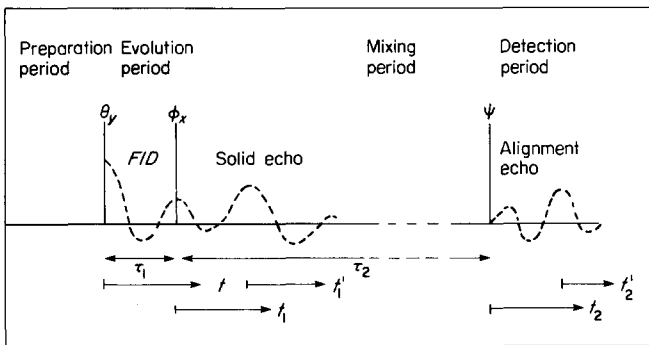


Figure 1 Notation for the solid echo, and the generalized Jeener–Broekaert 3 pulse sequence. θ_y , ϕ_x , and ψ are the flip angles of the respective high frequency pulses

line shape changes of ^2H spectra occur in a correlation time range of $\sim 1\text{--}20 \mu\text{s}$. This time scale can be extended to $\sim 200 \mu\text{s}$ by investigating the solid echo spectrum which can be formulated⁴ as the Fourier transform of

$$S_1(t_1, \tau_1) = \left\langle \exp \left\{ i \int_0^{\tau_1} \omega_Q(t') dt' - i \int_0^{2\tau_1} \omega_Q(t') dt' - \int_{2\tau_1}^{t_1} \omega_Q(t') dt' \right\} \right\rangle \quad (5)$$

τ_1 is the distance between the two pulses of the solid echo sequence and t_1 is the time starting from the echo maximum at $2\tau_1$ (see *Figure 1*). Equation (5) can be evaluated⁴ from the same rate equation that is used for solving equation (4). As a matter of fact, S_1 and S_0 become equal in the rigid solid limit since the contributions of the first two integrals of equation (5) cancel in this case. However, for correlation times $\tau_c \lesssim \tau_1$ no cancellation occurs, and S_1 may differ considerably⁴ from S_0 . The dynamical range of the solid echo technique is limited by the transverse relaxation time T_2 since no solid echo is detectable for $\tau_1 \gg T_2$. In most solid polymers $T_2 \sim 200\text{--}500 \mu\text{s}$ for ^2H spectra. It should be noted that T_2 is related with the reciprocal homogeneous width that would be seen in a single crystal, c.f. equation (1). Ultra slow motions with correlation times up to $\sim 1\text{ s}$ can be investigated by application of the Jeener–Broekaert pulse sequence (*Figure 1*) that yields a spin alignment echo after the third pulse³. Alignment echo spectra are obtained as the Fourier transform of^{3,5}

$$S_2(t_2', \tau_1, \tau_2) = \left\langle \sin[\omega_Q(0)\tau_1] \sin[\omega_Q(\tau_2)(\tau_1 + t_2')] \right\rangle \quad (6)$$

$$= \frac{1}{2} \left\langle \cos\{\omega_Q(\tau_2)t_2' + [\omega_Q(0) - \omega_Q(\tau_2)]\tau_1\} \right\rangle - \langle FID \rangle$$

The term⁵ $\langle FID \rangle$ is of minor importance in the context of the present paper. It is assumed that the mixing period τ_2 is much longer than the evolution and detection periods, respectively, and that Ω changes only on the time scale of τ_2 . Thus, $\tau_2 \gg \tau_1, t_2'$ and only the constant orientations $\Omega(0)$ and $\Omega(\tau_2)$ enter in equation (6) where products of the form $\omega_Q t$ have replaced the integrals $\int_0^t \omega_Q(t') dt'$ of equations (4) and (5). In the rigid solid limit, the alignment echo $S_2(t_2', \tau_1, \tau_2)$ is a trivial superposition³ of a solid echo and the term $\langle FID \rangle$. Molecular motion is seen through the difference

$$\Delta\omega_Q = \omega_Q(0) - \omega_Q(\tau_2) = (9e^2Qq/8\hbar)(\cos^2\theta_0 - \cos^2\theta) \quad (7)$$

It is remarkable that reorientation by small step rotational Brownian motion causes dramatic changes in the alignment echo spectrum provided τ_2 is of the order of the time τ_s between 2 angular steps and $\Delta\omega_Q\tau_1 \sim \pi$. Since τ_s is much smaller than the rotational correlation time τ_c , the alignment echo method provides a unique opportunity for distinguishing random small angular step reorientation from large angular jump motion where τ_s and τ_c are of the same order of magnitude. It should be noted that the average $\langle \dots \rangle$ of equation (6) can be evaluated from numerical solutions of equation (3) where small step rotational Brownian motion is described by a finite approximation of the diffusion equation.

BULK POLYSTYRENE

Our extensive study of partially deuterated PS- d_3 and PS- d_5 has already provided a wealth of information upon molecular motions above and below T_g part of which has been summarized in previous reviews^{2,10}. In this section, we wish to concentrate on the nature of chain motion in the glass transition region where new aspects have evolved from an analysis of alignment echo spectra. Model calculations⁶ show that the spin alignment echo spectrum changes appreciably for times $\tau_2 \ll \tau_c$, where the $\text{C-}^2\text{H}$ bonds can only reorient within a small angular range of a few degrees. Such small angle reorientations in particular change the n.m.r. frequencies in the centre of the spectrum. As a result the central portion loses intensity much faster with increasing τ_2 than the singularities, (cf. *Figure 1*). The corresponding n.m.r. signals in the time domain, equation (6), however, do not show the behaviour predicted for complete rotational diffusion. The alignment echo decays highly non-exponential, where the initial decay becomes more rapid and more efficient with increasing τ_1 . The long time behaviour, on the other hand, is largely independent of τ_1 . The decay of the alignment echo is not yet fully clarified, however, we suggest tentatively that only a fraction of the C–H bonds can fully reorient, most likely through conformational changes on a time scale of $\sim 1\text{ s}$ and this fraction decreases rapidly below T_g . At higher temperatures $T \gtrsim 400\text{ K}$, we know from the ^2H c.w. absorption spectra^{2,10} that full reorientation of the C–H bonds occurs by essentially a single process where any ‘distribution of correlation times’ must be restricted to less than one decade. Now, it turns out that the correlation times determined from the slow motion line shapes are at least an order of magnitude larger than those obtained from spin lattice relaxation times T_1 in this temperature range^{6,8}. Apparently, the latter are determined by the fast restricted rotational diffusion discussed above. Thus, we conclude that chain motion in the glass transition region can be described by a rapid rotational diffusion process which is restricted by an angular range of approximately $\pm 10^\circ$ at T_g and decreases at lower temperatures. Full reorientation of the C–H bonds occurs by a slower process. It should be noted that ^2H n.m.r. is presently the only experimental method for detecting the reorientation of a single bond vector in the glass transition region. Photon correlation spectra as well as dielectric and mechanical relaxation are related with fluctuations of larger volume elements where the cooperativity caused by free volume redistributions may be the reason for finding broad distributions of correlation times^{10–12}.

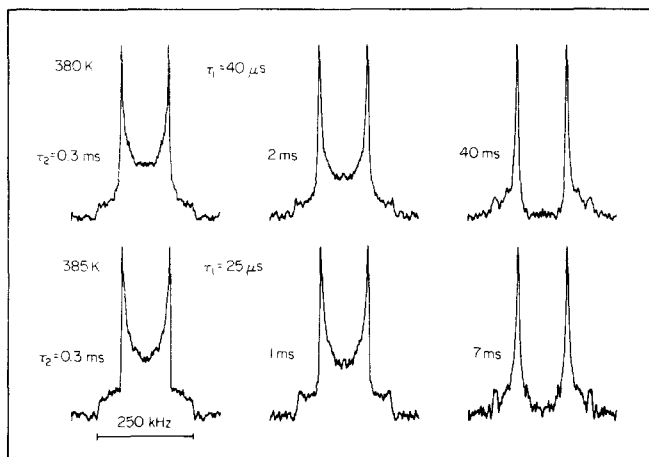


Figure 2 Experimental ^2H alignment echo spectra of chain deuterated polystyrene above T_g

THE POLYSTYRENE-TOLUENE SYSTEM

It is well known^{1,3} that the glass transition T_g of a polymer can be considerably reduced by adding relatively small amounts of a low molecular weight diluent. If phase separation occurs due to thermodynamical instability, no further reduction of T_g below the demixing temperature is possible. However, polystyrene and toluene remain miscible over the whole concentration range down to the glass transition of toluene⁷. Our ^2H n.m.r. study of this system has provided information upon molecular motion that may be typical for any glassy mixture of a polymer and a small molecule diluent. In bulk PS- d_5 , we have discovered that about 20% of the phenyl groups perform 180° jumps around their axis to the backbone even at temperatures well below T_g .² By adding toluene, the glass transition can be reduced to low temperatures. We find that the fraction of flipping phenyl groups becomes smaller and more difficult to detect for diluent concentrations where the solid glass regime is shifted to lower temperatures. There is no indication of large amplitude phenyl group libration as was concluded from ^1H wide line n.m.r. by Adachi *et al.*^{7,14}. Thus, we could use PS- d_5 for investigating the chain motion in the PS-TOL system. In *Figure 3*, we have shown the T_2 values of PS- d_5 determined by measuring the echo height as a function of the distance τ_1 between the two pulses of the solid echo sequence. The plot of $\log T_2$ versus $1/T$ is linear at temperatures above the glass transition, and it changes to an almost constant value at a temperature $T_{g,P}$ close to the static T_g as determined from other experimental methods⁷, cf *Figure 6*. In the toluene rich region, T_2 decreases as the temperature is lowered below $T_{g,P}$, attains a minimum, and increases again to the rigid solid value. Thus a second temperature $T'_{g,P}$ can be estimated as is shown in *Figure 3* for a solution of 35.1% PS- d_5 in TOL- d_0 . Apparently, there is a temperature range between $T_{g,P}$ and $T'_{g,P}$ where the chains are not fully immobilized due to the abundance of highly mobile solvent molecules (see below). The solid echo line shapes of PS- d_5 will be discussed in a later publication⁶.

The diluent mobility has been investigated by using TOL- d_3 or TOL- d_5 . No substantial difference between these toluenes was found for the overall TOL motion. However, the rapid methyl group rotation in TOL- d_3

persists even at the lowest temperatures of our experiments, thus reducing the widths of all ^2H spectra to one third of the corresponding TOL- d_5 values. On cooling a TOL- d_3 (or TOL- d_5) solution of PS below the temperature $T_{g,SE}$ shown in *Figures 5* and *6*, a solid echo can be detected on top of the 'liquid' FID. If this signal is Fourier transformed with respect to t'_1 starting at $t=2\tau_1$ (cf. *Figure 1*) we obtain a spectrum as shown in *Figure 4A*. The central portion originates from part of the 'liquid' FID that starts at $t=0$. It should be noted that the second 90° pulse of the solid echo sequence has no influence upon the FID of a liquid since it is shifted in phase by 90° with respect to the first pulse. In *Figure 4B*, τ_1 has been increased to a value where the FID has decayed to zero ($2\tau_1 \gg T_{2,FID}$). The solid echo spectrum of *Figure 4B* has essentially the rigid limit Pake line shape. Thus, the rotational correlation time of the TOL- d_3 molecules that give rise to this spectrum must be larger than $\sim 100 \mu\text{s}$. Since we can detect a spin alignment echo after ~ 50 ms, the correlation times are even above this slow time scale. On the other hand, the TOL- d_3 molecules contributing to the 'liquid' FID have correlation times below $\sim 1 \mu\text{s}$. Though this corresponds to reorientation in a rather viscous liquid the correlation time difference of more than 5 decades provides sufficient evidence for qualitatively different behaviour. We have tried to estimate the intensities of the 'liquid' and 'solid' contributions by extrapolating the FID to $t \rightarrow 0$ and the amplitude of the solid echo to $\tau_1 \rightarrow 0$. Since the solid echo amplitude becomes non-exponential at short times⁶ this estimate is admittedly crude. We should also emphasize that the decomposition implies no statement upon possible correlation time distributions within the 'solid' and 'liquid' components. Nevertheless, it allows for some important conclusions upon diluent motion in the mixed glass. The TOL solid echo becomes observable above $T_{g,P}$ at temperatures where PS- d_5 also gives rise to a solid echo (cf. *Figure 3*). Thus, the mobility of the 'rigid' TOL molecules is linked to that of the PS chains at $T \lesssim T_{g,SE}$. There are even indications that it is slower as will be discussed in ref. 6. On lowering the temperature below $T_{g,P}$, increasing amounts of TOL 'freeze' towards the chains until the whole mixture becomes a solid glass at $T_{g,FID}$. It is apparent from *Figure 5* that the intensities of the 'solid' and 'liquid' components add to an approximately constant total intensity. The latter has been scaled in *Figure 5* by an arbitrary factor appropriate for presentation of the data in one figure, and by the Boltzmann factor determin-

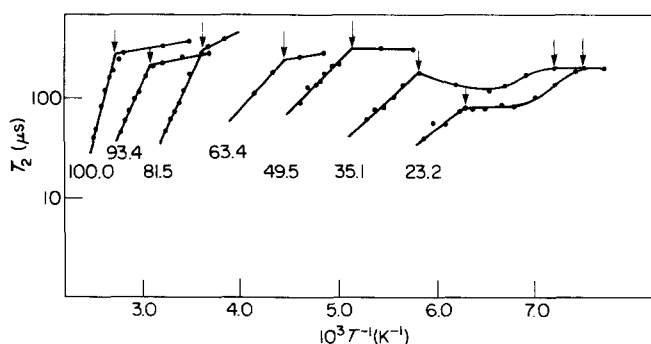


Figure 3 Spin relaxation times T_2 of PS- d_5 in PS-TOL mixed glasses. Numbers in the Figure denote wt.% PS- d_5 . The arrows indicate glass transition temperatures $T_{g,P}$ and $T'_{g,P}$ (see text)

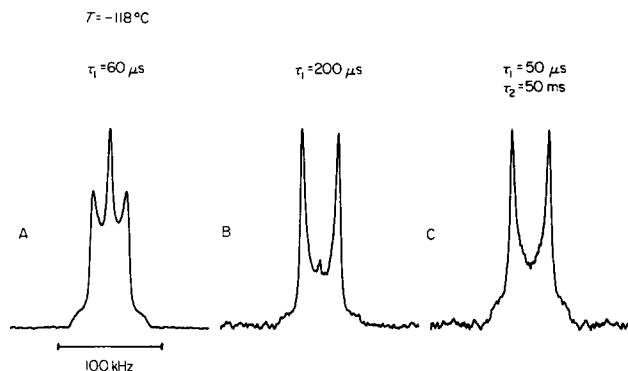


Figure 4 ^2H solid echo (A,B) and alignment echo (C) spectra of TOL- d_3 in a mixed glass with 28.7% PS

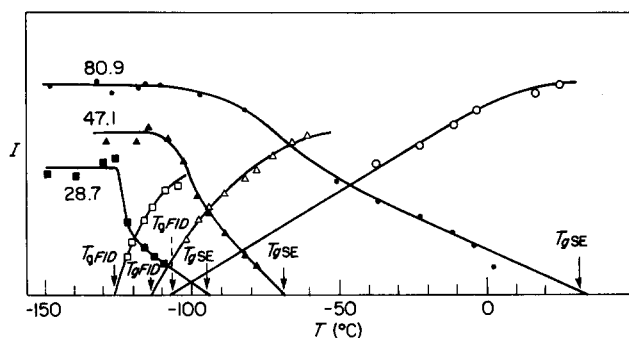


Figure 5 ^2H intensities (I in arbitrary units, see text) of TOL- d_3 and TOL- d_5 (\circ , \bullet ; \square , \blacksquare) in mixed glass with PS. Numbers in the Figure denote wt. % PS. Open and full symbols denote 'liquid' and 'solid' components, respectively (see text)

ing the trivial temperature dependence of the spin populations. Thus, the intensities given in Figure 5 are a measure of the 'solid' and 'liquid' fractions in the temperature region $T_{g,FID} \leq T \leq T_{g,SE}$. This region becomes very broad for large PS concentrations. Furthermore, the solid echo line shapes of the 'solid' TOL fraction become motionally narrowed for PS concentrations above $\sim 80\%$ indicating the abundance of 'free volume' between the rigid PS chains⁶. It is clearly visible in Figure 6 that the static glass transition T_g (dotted line) is close to $T_{g,P}$ in the PS rich regime indicating that the solid glass behaviour is governed by the polymer. However, the TOL glass transition takes over in the TOL rich regime with less than $\sim 50\%$ PS. Here, the static T_g is close to $T'_{g,P}$ and $T_{g,FID}$, and some chain mobility persists in the temperature region $T_{g,P} \geq T \geq T'_{g,P}$.⁶ The temperatures $T_{g,P}$ and $T'_{g,P}$ converge at very high TOL concentrations where the TOL glass transition could be determined from T_2 measurements in TOL- d_3 having a similar temperature dependence as shown in Figure 3 for PS- d_5 .⁶

Finally, we wish to point out that different mobilities in PS have also been found for the 'dual mode sorption' of ammonia as investigated by ^1H n.m.r.¹⁵ and for di-n-alkyl-phthalates where dielectric relaxation data were interpreted in terms of three different α processes¹⁶.

CONCLUSIONS

We can conclude from a comparison of ^2H spin alignment echo spectra with model calculations that chain motion in the glass transition region of PS can be described by a

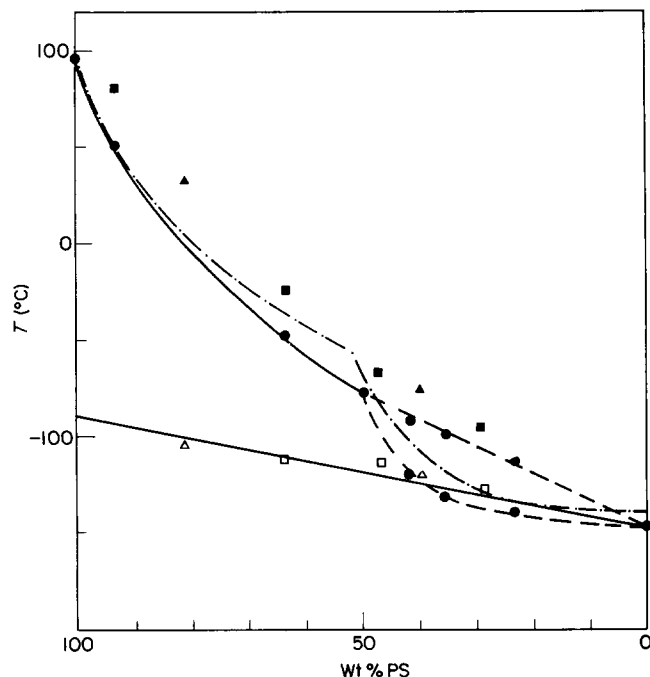


Figure 6 Glass transition temperatures in the PS-TOL system. Abscissa: wt% PS. Full line, open symbols: $T_{g,FID}$. Full and dashed lines, full circles: $T_{g,P}$ and $T'_{g,P}$ (see text). Full squares (PS- d_3) and triangles (PS- d_5): $T_{g,SE}$. Dotted line: T_g as determined by dielectric relaxation and thermal methods (ref. 7)

relatively rapid rotational diffusion process which is restricted to an angular range of approximately $\pm 10^\circ$ close to T_g . Full reorientation by a slower process tends to become motionally heterogeneous as the glass transition is approached from above.

^2H n.m.r. spectra of deuterated toluene in the PS-TOL glass can be interpreted in terms of a two component decomposition. The motion of the 'solid' component is linked to that of the PS chains at temperatures below a temperature $T_{g,SE}$ where a solid echo becomes observable. On lowering the temperature, the fraction of 'solid' TOL increases until the whole mixture becomes a solid glass at a temperature $T_{g,FID}$. There is a range $T_{g,FID} \leq T \leq T_{g,SE}$ where a 'liquid' fraction of highly mobile TOL molecules exists at temperatures below the 'static' glass transition temperature T_g as determined by dielectric relaxation or thermal methods⁷. T_g is close to $T_{g,SE}$ in PS rich systems and close to $T_{g,FID}$ in systems with PS concentrations below 50% (see Figure 6). In the TOL rich regime we can determine a temperature $T_{g,P} > T_g$ where the chain motion becomes highly restricted and a 'solid' TOL fraction is observable.

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