RECENT ADVANCES OF ^{2}H NMR FOR STUDYING MOLECULAR MOTION IN SOLID POLYMERS

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Abstract - Recent developments of ^{2}H NMR spectroscopy are discussed, in
particular, the relation of ^{2}H line shapes, solid echoes, spin alignment,
and relaxation times with molecular motion in solid polymers. The potential
of ^{2}H NMR for studying macromolecular motion is discussed in the light of
some examples of current investigations.

INTRODUCTION

NMR spectroscopy in solid polymers was dominated in the past by wide line spectra and spin-lattice relaxation times of the proton (1,2). More recently, ^{13}C spectra have become possible by the techniques of high power proton decoupling and cross polarization (3,4). Three obstacles had to be overcome in order to make ^{2}H NMR an attractive method: (1) the low natural abundance (1.56 x 10^{-2} %) of ^{2}H, (2) the low magnetic moment of ^{2}H, smaller by a factor of 6.51 in comparison with ^{1}H, and (3) the quadrupole broadening resulting in a spectral width of $\sim$ 250 kHz for ^{2}H spectra in solid polymers. The necessity of isotope enrichment is probably the most severe restriction although a considerable number of deuterated polymers is already available since deuteration is also required for applications of neutron scattering in polymer science. The low ^{2}H magnetic moment is no problem if superconducting magnets are available, and ^{2}H NMR frequencies above 50 MHz can be used. The large width of the quadrupole broadened spectra limits the applicability of conventional wide line spectroscopy since accumulation times of many hours are needed for spectra with reasonable signal to noise ratio (5,6). However the effective signal intensity can be increased by about 2 orders of magnitude if the solid echo Fourier transform technique (7,8) is applied. In view of the short ^{2}H spin-lattice relaxation times ($\lesssim$ 1 s in most polymers) one obtains spectra with excellent signal to noise ratio in typically about 10 minutes (9). In order to obtain undistorted line shapes one should, however, observe several precautions discussed below (9,10,11). In the following section, we shall discuss the relation of observables determined by ^{2}H NMR methods with quantities relevant to polymer science. Some examples of current investigations are given in the final section.

^{2}H NMR METHODS

Line shapes

The theory of ^{2}H NMR spectra is very similar to that of ^{1}H NMR for a proton proton pair. The dipolar interaction between 2 equal spins 1/2 can be treated as an effective I = 1 problem that is identical in form with that of the quadrupolar interaction of a single ^{2}H nucleus (I = 1) with an axially symmetric field gradient tensor (FGT). In C - ^{2}H bonds of polymers the FGT is axially symmetric around the bond direction with good approximation. In both I = 1

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problems, one obtains $0 \longleftrightarrow \pm 1$ transitions that correspond to 2 NMR lines shifted by

$$\Delta\omega = \pm \delta(3\cos^2\theta - 1) \tag{1}$$

with respect to the Larmor frequency ω_0. For an H-H pair, $\delta_{dip} = (3/4)\gamma^2 \hbar/r^3$ is the dipolar coupling constant, γ is the ^{1}H gyromagnetic ratio, r is the H-H distance, and θ the angle of the H-H direction with respect to the external magnetic field $\underset{\sim}{B}_0$. For the distance of r = 0.179 nm in a CH_2 group, $\delta_{dip}/2\pi = 15.7$ kHz for protons. For the quadrupole coupling of a ^{2}H nucleus, we have $\delta_{quadr} = (3/8)e^2Qq/\hbar$ where eQ is the quadrupole moment of the ^{2}H nucleus, eq is the principal component of the axially symmetric FGT (see Note a), and θ is now the angle of the C - ^{2}H bond with respect to the field direction $\underset{\sim}{B}_0$. In solid deuterated polyethylene (5), $\delta_{quadr}/2\pi = 61.5$ kHz. The NMR line shape in polycrystalline material or a polymer glass can be considered as a weighted superposition of the doublets defined in Eq.(1) for all possible values of θ. In an isotropic sample, the resulting shape is the well known Pake spectrum shown in Fig. 1 (see Note b) as a superposition of contributions from the $0 \longleftrightarrow \pm 1$ transitions. It should be noted that the shape due to only one of the transitions agrees with the shape for an $I = \frac{1}{2}$ spin subject to an axially symmetric chemical shift anisotropy (13).

Molecular motions give rise to reorientation of the C - ^{2}H bond whereby the angle θ of Eq.(1) becomes a function of time. The NMR line shape can be calculated by standard techniques (13) for any well defined reorientation process that can be described by rate equations of the form

$$\frac{d}{dt} P(\theta_i|\theta_j,t) = \sum_k P(\theta_i|\theta_k,t)\pi_{kj} \tag{2}$$

where $P(\theta_i|\theta_j,t)$ is the conditional probability of a C - ^{2}H bond having θ_i at t = 0 to be found in θ_j at time t, and π_{kj} is the rate of transitions $k \longrightarrow j$. The essential features of the resulting NMR line shapes can be summarized as follows:

(a) No line shape change occurs if $\pi_{ij} \ll \omega_{ij} = |\Delta\omega(\theta_i) - \Delta\omega(\theta_j)|$ for all i and j.

(b) The line shape is a function of the transition rates π_{ij} in the "slow motion region" where π_{ij} is of the order of ω_{ij} for some or all possible pairs i and j. Since the π_{ij} are defined through a particular model for reorientation, one can discriminate between different models, and one can determine the π_{ij} (or correlation times π_{ij}^{-1}) by performing line shape studies.

(c) In the fast motion limit, $\pi_{ij} \gg \omega_{ij}$, one obtains a limiting line shape that is independent of the π_{ij}, and is determined by the time averaged FGT. The motional process may lead to an averaged FGT that is no longer axially symmetric, and has principal axes different from the C - ^{2}H direction. However, the line shape is always of the form shown in Fig. 1 where the special cases $\eta = 0$ or 1 correspond to particular motional processes (see below). For isotropic reorientation, e.g., tetrahedral jumps between 4 sites of equal weight (14), the limiting line shape is a δ-function at the Larmor frequency ω_0. For comparison with experimental NMR spectra the theoretical line shapes should be convoluted with a broadening function which is,

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Note a. If the FGT has no axial symmetry, Eq.(1) should be replaced by $\Delta\omega = \pm \delta(3\cos^2\theta - 1 - \eta \sin^2\theta \cos 2\phi)$ where $\eta = (q_{yy} - q_{xx})/q_{zz}$ is the asymmetry parameter of the FGT, $|q| = |q_{zz}| \geq |q_{xx}| \geq |q_{yy}|$, and ϕ is the polar angle of the field direction $\underset{\sim}{B}_0$ in the principal axis system x, y, z of the FGT.

Note b. In oriented (drawn) polymers, the NMR line shape is a function of the orientational distribution which can thus be determined (12).

however, a small perturbation since broadening due to ^{2}H dipolar coupling is only of the order of 1 kHz (6).

Solid echoes and spin alignment

In conventional FT-NMR spectroscopy, the Fourier transform of the free induction decay (FID) following a 90° pulse is calculated, and yields the NMR spectrum. This method is limited in solids by "dead time" effects due to pulse length, recovery times, etc. that prohibit the detection of the FID at short times. In order to circumvent these problems, the solid echo technique (15) has been devised where two 90° pulses separated by a time distance τ_1 and shifted in phase by 90° are applied that give rise to an echo at $2\tau_1$ (see Fig. 2). For an I = 1 spin the echo decay is identical with the FID provided the coupling Hamiltonian is time
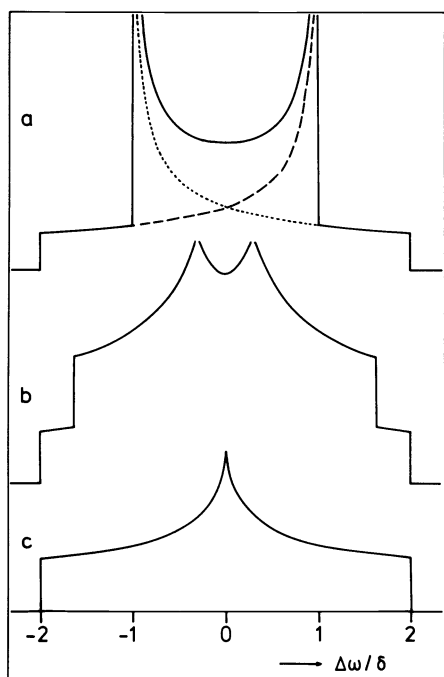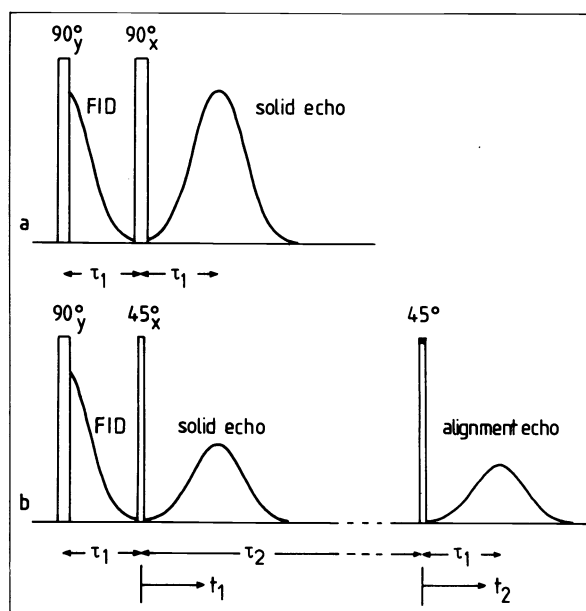

Fig.1

Fig.2

Fig. 1. Theoretical ^{2}H NMR line shapes for a solid glass. (a) Pake spectrum, $\eta = 0$. The dashed and dotted lines correspond to the $0 \leftrightarrow 1$ and $0 \leftrightarrow -1$ transitions, respectively. (b) Spectrum for $\eta = 2/3$. (c) Spectrum for $\eta = 1$.

Fig. 2. (a) Solid echo. (b) Jeener-Broekaert pulse sequence generating a solid echo and an alignment echo.

independent. In practice, it is difficult to generate 90° pulses in a system that is sufficiently broadband for uniform excitation of the ^{2}H spectrum in solids. Undistorted line shapes have been obtained (10) by a superposition of the signals after the 2nd and 3rd 45° pulse of the pulse sequence (16) shown in Fig. 2b.

In the slow motion region, see above, the solid echo becomes a function of the transition rates π_{ij} and the pulse distance τ_1, and may differ considerably from the FID (11). Thus, the

solid echo may be affected in deuterated polymers by motions with correlation times $\tau_c \lesssim 100$ μs whereas the slow motion region of the FID ranges between about 1 and 10 μs. For isotropic reorientation the solid echoes have drastically reduced intensities for $\tau_1 \gtrsim \tau_c$ in a region where $\tau_c \lesssim 10$ μs for typical deuterated compounds [11].

Very slow motions can be investigated by the spin alignment technique developed by Spiess [10]. One applies the 90^0 - τ_1 - 45^0 - τ_2 - 45^0 pulse sequence (Fig. 2b) of Jeener and Broekaert [16] where the first 45^0 pulse creates (besides a solid echo) a state of quadrupolar order, called " spin alignment", that can persist for long times unless the quadrupole coupling is changed by molecular reorientation. A second 45^0 pulse transforms the spin alignment back into magnetization, and gives rise to an alignment echo proportional to (see Note c)

$$F(\tau_1,\tau_2) = \langle \sin[\Delta\omega(0)\tau_1] \, \sin[\Delta\omega(\tau_2)t_2] \rangle \quad . \tag{3}$$

The times τ_1, τ_2, and t_2 are defined in Fig. 2b. $\Delta\omega(0)$ is the frequency defined in Eq.(1) for a C - ^{2}H bond having an angle $\theta(0)$ at $\tau_2 = 0$, and $\Delta\omega(\tau_2)$ is the same quantity at time τ_2. It is assumed that $\Delta\omega$ remains constant during the time τ_1, and that τ_1 is smaller than the inverse homogeneous width T_2 (see below). Furthermore, it is assumed that τ_2 is much smaller than the spin-lattice relaxation time T_1. The average in Eq.(3) is over a probability function that corresponds to Eq.(2). Thus $F(\tau_1, \tau_2)$ represents a correlation function that can be used for discriminating between different motional models, and for determining the respective correlation times. Roughly, it is a measure of how many molecules have reoriented substantially during the time τ_2. Since τ_2 is only limited from above by T_1, motional processes with correlation times up to about 1 s can be investigated by the spin alignment technique.

Relaxation times

The width of the NMR spectrum can be related with a <u>spin relaxation time T_2'</u> defined in some arbitrary way by the inverse of the half width or the square root of the 2nd moment [1,2,17]. In a solid powder or glass, the NMR spectrum can be considered as a superposition of "single crystal" spectra, say, the doublets defined in Eq.(1). The lines of these doublets have a finite width due to static (dipolar) couplings or dynamic processes, e.g., at the onset of the slow motion region. This "homogeneous" width is related with a <u>spin relaxation time T_2</u> that can be measured by determining the amplitude of the solid echo maximum as a function of the pulse distance τ_1 [18]. For isotropic reorientation T_2 becomes very short in the slow motion region, and the solid echo vanishes for $\tau_1 \gg \tau_c$. However, there may remain a residual coupling if the reorientation process is not completely isotropic. For example, about 1% of the static coupling remains in entangled polymer melts for about 100 μs, and gives rise to a "pseudo-solid echo" [19].

The theory of the ^{2}H <u>spin-lattice relaxation time T_1</u> is essentially the same as for ^{1}H NMR [1,2,17], and yields information upon rapid motions reorienting C - ^{2}H vectors in polymers. It should be noted that the influence of spin diffusion [2,17] is largely reduced in ^{2}H as compared with ^{1}H relaxation. By comparing ^{2}H with ^{1}H dipolar coupling [20] one obtains a ratio of roughly 1/5 for the diffusion distances traveled in equal times by the spin energy in a deuterated and a protonated solid, respectively. Since $T_1(^2$H) is usually much smaller than $T_1(^1$H) for the same motional process, the effective spin diffusion times are smaller for deuterated systems. As a rule, spin diffusion effects should only become important in deuterated

Note c. In solids $\Delta\omega(\tau_2) = \Delta\omega(0) = \Delta\omega$, and Eq.(3) can be written as 2 $F(\tau_1,\tau_2) =$ $\langle \cos \Delta\omega \cdot (t_2 - \tau_1) \rangle - \langle \cos \Delta\omega \cdot (t_2 + \tau_1) \rangle$ which is a superposition of a solid echo at $t_2 = \tau_1$ and a virtual FID that seems to have started at $t_2 = -\tau_1$ (cf. Ref. 10).

polymers for $T_1 \gtrsim 1$ s. Thus one can study separately molecular motions in the crystalline and amorphous regions of semicrystalline polymers by determining the T_1 values that may differ by more than a factor of 50 in the different regions (18,21).

A spin alignment relaxation time T_Q can be determined by measuring the amplitude of the spin alignment echo maximum as a function of the distance τ_2 between the 2nd and the 3rd pulse of the sequence shown in Fig. 2b. If T_Q is determined by the function $F(\tau_1,\tau_2)$ defined in Eq.(3), it is of the order of a rotational correlation time τ_c. However, there may exist other rapid processes with correlation times τ_c' much shorter than τ_c, e.g., librational motions leaving a time averaged FGT that reorients slowly with τ_c. In this case, the condition $T_1(\tau_c') \lesssim \tau_c$ may apply, and Eq.(3) is no longer valid. It can be shown (10) that T_Q is then of the order of T_1, and can be denoted as T_{1Q}. If $T_1(\tau_c') > \tau_c$, Eq.(3) can simply be multiplied by $\exp(- \tau_2/T_{1Q})$ in order to account for rapid processes that are statistically independent of the slow process.

APPLICATIONS

We have used a sample of perdeuterated linear polyethylene ($M_w \approx 10^5$, $M_w/M_n \approx 10$, Merck, Darmstadt) for a first study of molecular motion by ^{2}H NMR (6,18,21). The sample was isothermally crystallized from the melt at 396K resulting in a crystallinity of 74% as determined by X-rays. The ^{2}H NMR line shapes (Fig. 3) can be considered as a superposition of the Pake spectrum (Fig. 1a) and a motionally narrowed spectrum. Quantitative decomposition (6) yields about 72% of "rigid" deuterons at temperatures below about 370 K thus indicating that all deuterons in the amorphous regions give rise to the motionally narrowed part of the spectrum. Motions in the crystalline regions cause small changes of the Pake spectrum (see spectra above 350 K in Fig. 3) that can be explained by a small asymmetry parameter of the FGT due to chain oscillations around the stem axis. We obtained a variation of the root mean square angle of these oscillations between 5 and 12^0 at temperatures between 313 and 383 K (6). It should be noted that the 180^0 jumps of the α-process in the crystalline regions are not observable in ^{2}H NMR since they do not change the quadrupole coupling tensor. At temperatures close to the melting point the mobile fraction of the ^{2}H spectrum increases and the line width decreases considerably (18) in agreement with other evidence of premelting phenomena in polyethylene (22).

There are other ways of separating the contributions of rigid and mobile deuterons to the ^{2}H spectrum since the relaxation times T_1 and T_2 (see above) are much shorter in the latter. If the pulse distance τ_1 of the solid echo sequence (Fig. 2) is chosen larger than T_2 of the mobile deuterons, their contribution to the solid echo is effectively suppressed, and only the rigid deuterons are seen in the spectrum (12). On the other hand, the contribution of the rigid deuterons is suppressed if the total magnetization is saturated first by a series of 90^0 pulses, and then the solid echo is created after a waiting period of the order of T_1 of the mobile deuterons. This technique has been applied in order to obtain the spectrum of mobile deuterons at low temperatures (21). Thus the spectrum at 143 K shown in Fig. 4 is due to mobile deuterons at the onset of the γ-process where the transition rates are small in comparison with the quadrupole splitting (case (a), see above). The 2 small central peaks are due to rotating methyl groups whose contribution to the spectrum is exaggerated by a factor of about 10 since the signal of the chain deuterons is attenuated by incomplete recovery from saturation. The spectrum at 193 K is an example of the τ_1 dependence of the solid echo line shape in the slow motion region (11). Spectra with a similar intensity loss in the central region have been calculated for jumps of the C - ^{2}H bonds between only 2 possible orientations
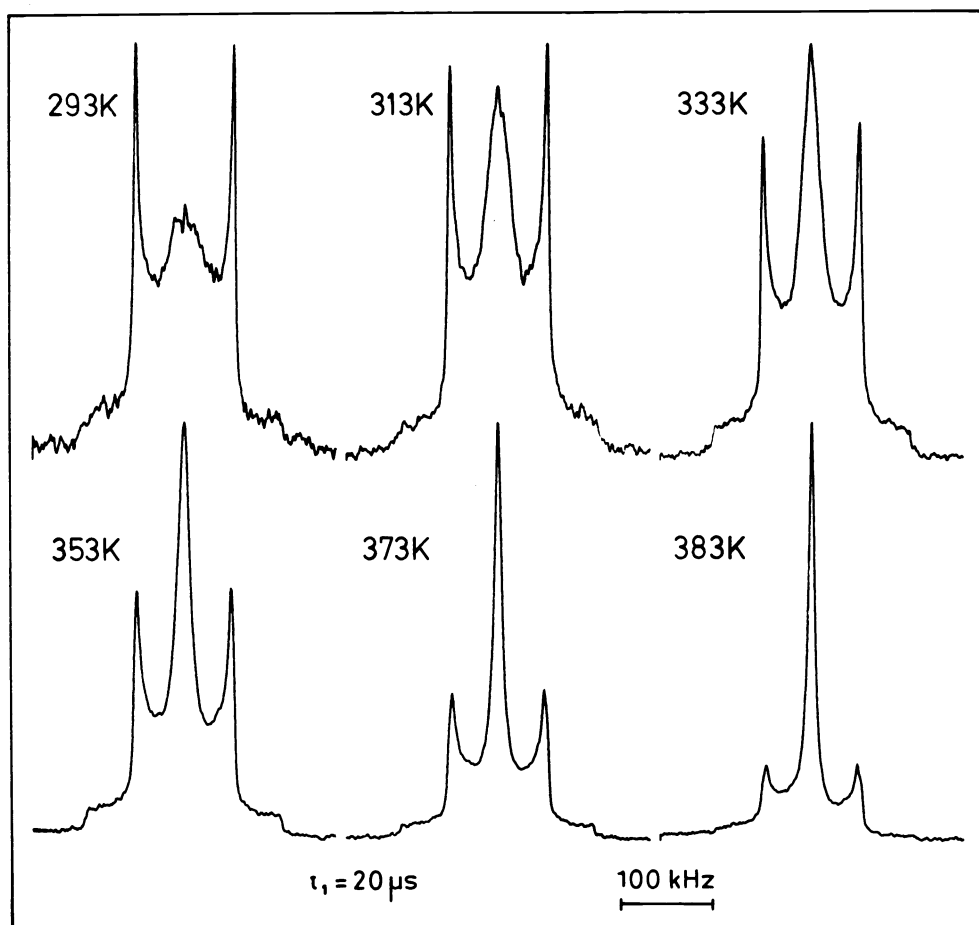
Fig. 3. ^{2}H NMR spectra of deuterated polyethylene.

with a correlation time τ_c of the order of τ_1 which is 50 µs in Fig. 4. The line shape at 213 and 233 K can also be understood as originating from this process, but for τ_c values of $\sim 10^{-6}$ and $\lesssim 10^{-7}$ s, respectively. The spectrum at 233 K can be explained by a superposition of a $\eta = 1$ and a $\eta = 0$ spectrum (Fig. 1) where the latter is reduced in width by a factor of 3 compared with the rigid solid spectrum. The $\eta = 1$ spectrum is consistent with the rapid motion limit of the jump process considered above. This is in harmony with previous publications (23) relating the γ-process with three bond motions (Boyer crankshaft, kink diffusion). The $\eta = 0$ spectrum can be explained by assuming a five bond crankshaft motion (14,24). The motionally narrowed spectra shown in Fig. 3 can be compared with model calculations (14) where the total chain in the amorphous regions is divided in subchains of variable length that perform rapid conformational transitions. The time averaged FGT obtained for each deuteron of the model chain yields line shapes of the types shown in Fig. 1. The weighted superpositions of the spectra of all different deuterons are then compared with the experimental spectra (Fig. 3). We conclude that in our polyethylene sample the average length of flexible chains increases from 3-5 bonds at room temperature to 10-15 bonds at
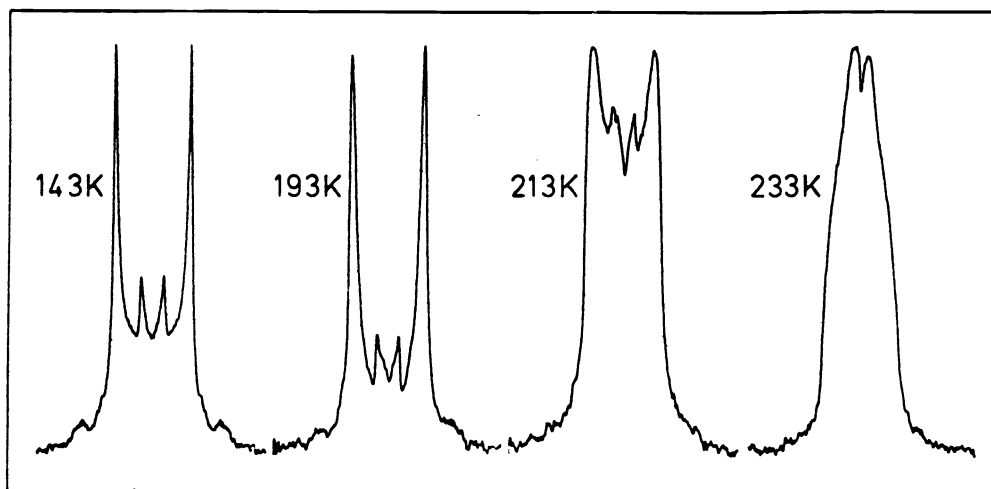
Fig. 4. ^{2}H solid echo NMR spectra of mobile deuterons in polyethylene.

380 K. It is obvious that other motional models can also explain the experimental line shapes. However, in any model the ^{2}H line shapes provide a measure of the number of conformations that are accessible to rapid motion for a given segment.

The constraints described in our model calculation by the lengths of flexible subchains are related with the structure of the amorphous regions, and they depend upon the crystallinity and morphology of the sample (25,26). We can prove that they consist for long times by application of the solid echo and spin alignment techniques (21). The fact that solid echoes can be obtained from the mobile deuterons after $\tau_1 \sim 100$ μs proves that the time averaged FGT exists at least over this period which is of the order of T_2. The spin alignment technique is not limited by T_2 and provides information whether the constraints persist after a duration of the order of T_1 which is about 50 ms for the mobile deuterons in polyethylene. We find between room temperature and the melting point that the shape of the spin alignment spectrum remains invariant for times up to $\tau_2 \sim T_1$ (21). Thus the time averaged FGT determined by the structure of the constraints remains constant over this period. At lower temperatures, our spin alignment results reveal a distribution of correlation times for the rapid three bond motion (21), but also yield long lived constraints. In conclusion, we have shown that the constraints limiting the rapid motion in the amorphous regions persist for at least 50 ms in the whole temperature region below the melting point. On melting, the solid echoes and the alignment echoes vanish leaving only the "pseudosolid" echoes mentioned above (19) showing that constraints caused by chain entanglement in molten polyethylene persist for only about 100 μs.

The constrained motion in the amorphous regions of semicrystalline polymers should be contrasted with the motion in amorphous polymers above the glass transition temperature T_g. Our first results (27,28) of ^{2}H NMR spectroscopy applied to chain deuterated polystyrene (PS-d_3) show that long lived constraints are absent above $T_g = 373$ K. The spin alignment time T_Q (see above) decreases rapidly with increasing temperature, and is of the order of the rota-

tional correlation time of the C - ^{2}H bonds. Thus, neither spin alignment nor solid echoes are observable above 400 K, and we have to use conventional wide line spectroscopy in order to investigate the line shape in the slow motion region. The change from the solid like Pake spectrum to the motionally narrowed Lorentzian occurs in a small temperature region between 400 and 430 K, and can be described by isotropic reorientation of the C - ^{2}H bonds with essentially a single correlation time. By comparison, the ^{2}H spectrum changes in a temperature region between 140 K and the melting point in semicrystalline polyethylene, and the line shape is determined throughout by constrained anisotropic motions.

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