NMR study of chain dynamics in the hexagonal high-pressure phase of polyethylene

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Abstract

At high pressure ($>$3300 bar) polyethylene shows a hexagonal phase between the orthorhombic phase and the liquid phase. This first NMR investigation of polyethylene in its hexagonal phase shows that the mobility of the molecular chains is very high. Deuteron quadrupole echo spectra have been used to determine the character and rate of local reorientations of the molecular chains. The chains perform rapid axial reorientations, similar to those observed in the rotator phases occurring in the long normal alkanes. From proton rotating frame relaxation data we derive a high rate of translational diffusion in the chain direction. These observations contribute to the understanding of the important role of the hexagonal phase in the growth of chain-extended polyethylene crystals. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

On crystallizing polyethylene (PE) from the melt at ambient pressure, the resulting crystallites consist of lamellae of folded chains. In 1962, Wunderlich and Arakawa [1] found that crystallization of the melt at high pressure ($>$3300 bar) produces crystallites having an extended chain morphology. In 1974, Bassett and Turner [2,3] found that at high pressure polyethylene shows a transition to a new phase below the melting transition. Later they determined that in this phase the crystalline parts of the material have a hexagonal crystal structure [4].

Since these discoveries, many studies of PE have been followed, in attempts to answer some of the many questions surrounding the phenomenon that crystallization through the hexagonal phase results in extended chain morphology. As a result, the evidence existing today concerning the hexagonal phase leads to the following view [5].

All crystallization, both above and below the triple point pressure, takes place in the hexagonal phase. After the first crystallization front the crystals thicken quickly. Below the triple point pressure the hexagonal structure is only stable for small crystallites. When a crystallite grows beyond a certain critical size, the hexagonal structure for that crystallite becomes metastable and it may after some time transform into the orthorhombic structure after which all growth stops. Above the triple point (3300 bar, 488 K) the hexagonal structure remains the stable one for all crystallites, regardless of the size. Therefore, all crystallites can thicken until full chain extension is achieved.

The above picture requires that, in the hexagonal phase, the molecular chains have a high mobility in the chain direction. If this is not the case, then the chains would not be able to rearrange themselves on the time scale of the crystallization process, and as a result full chain extension would not be achieved. Such chain mobility therefore has been assumed, since both full chain extension and rapid thickening have been observed. However, the fast chain motion itself has, to our knowledge, never been observed directly. In the present study, we have for the first time been able apply NMR at the required conditions of temperature and pressure. We have used NMR to benefit from its great sensitivity to molecular motion on the widely varying time scales that usually occur in polymer systems.

This paper is the third in a series of a high pressure NMR study on polyethylene. In the first paper [6] we presented results on the determination of the phase diagram. In the second paper [7] we discussed the NMR data obtained in the orthorhombic phase. In this paper we will focus our attention to the hexagonal phase of PE, and demonstrate how the results from our NMR experiments give information on both

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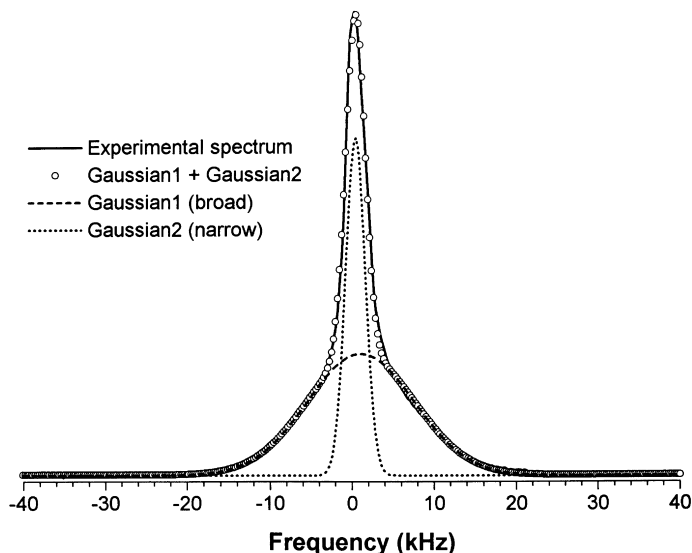*E-mail address:* langen@phys.uva.nl (M. de Langen).

Fig. 1. Characteristic proton NMR spectrum recorded in the hexagonal phase at 486 K and 3550 bar.

the nature and the rate of motion. In addition, these results will be compared to behaviour in the similar rotator phases which occur in the shorter alkanes.

2. Results and discussion

The phase diagram of PE, resulting from our NMR experiments, is shown in the first paper (Fig. 6; [6]). It shows the regions where the orthorhombic, hexagonal and liquid phases are stable, and the positions of the transitions between these phases. The hexagonal phase is found to occur at pressure values exceeding 3300 bar and temperature values above 488 K. In that study we determined proton and deuteron NMR spectra and spin–lattice relaxation rates. A description of the NMR apparatus and the materials used are given in the first article [6] of this series.

2.1. Proton NMR spectra

In the hexagonal phase ^{1}H NMR spectra have shapes that are similar to the ones in the orthorhombic phase. Such a spectrum consists of a broad crystalline component and a narrower component originating from the amorphous regions that are present simultaneously with the hexagonal crystalline material. Both components of the proton NMR spectrum in the hexagonal phase are narrower than the equivalent components observed in the orthorhombic phase. Fig. 1 shows a spectrum that is characteristic for the hexagonal phase. The figure also shows a simple approximation to the recorded spectrum using a superposition of two gaussian functions. The integrated intensity of the broad (crystalline) component is about 75% of the total signal. Since some liquid material may contribute to the narrow component, the true crystallinity (the fraction of crystalline material in the total *solid* material) may well be higher than 75%.

Since the broader gaussian function appears to be a

reasonable approximation for the signal of the hexagonal crystalline material, it has been used as a measure for the second moment of the line shape of hexagonal polyethylene. The second moment thus obtained is 2.527×10^9 rad^2 s^{-2}. Starting from the expressions in Abragam [8], we can calculate the second moment for a rigid crystal using known crystal parameters for hexagonal PE [4] ($a = 8.46$ Å, $b = 4.88$ Å and $c = 2.45$ Å). Separate values have been obtained for the contributions to the second moment from the dipolar interactions between the proton spins on the same chain and on neighbouring chains. It should be noted here that in first instance effects of both motion and conformational disorder have been neglected. The model crystal used for the calculations is therefore not really hexagonal, but rather an orthorhombic crystal with a point lattice that coincides with the point lattice of the hexagonal phase crystal, while having two inequivalent chains per unit cell. Both types of chains are assumed to be in the all-*trans* conformation like in the true orthorhombic phase. This simplification shows up in the results of the calculations through the presence of *two* inequivalent types of proton positions, leading to *two* different values of the calculated second moment. The intra-chain second moment is unaffected by the presence of the two inequivalent proton sites and is equal to 1.33×10^{10} rad^2 s^{-2}. The two different inter-chain second moments calculated for this "rigid hexagonal" crystal are 3.35×10^9 rad^2 s^{-2} and 4.61×10^9 rad^2 s^{-2}, respectively. Together this would give total second moments of 1.67×10^{10} rad^2 s^{-2} and 1.79×10^{10} rad^2 s^{-2}. These values are both far off the observed value of M_2. This is an important indication that in the hexagonal phase molecular motions are so fast that they cause considerable line narrowing.

As will be shown later, it follows from the ^{2}H NMR spectra in the hexagonal phase that the CH$_2$-groups perform a reorientational motion about the chain axis at a rate of at
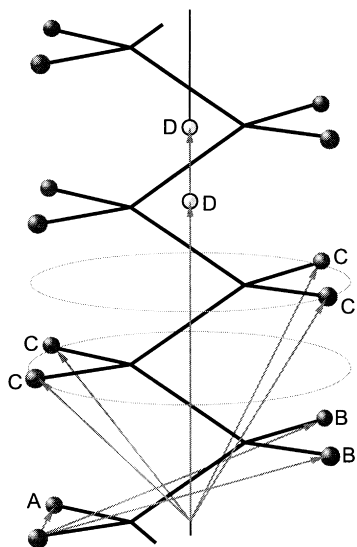
Fig. 2. Model used to calculate the average proton dipole–dipole coupling in a PE molecule in the hexgonal phase.

least 10^7 Hz. This motion will result in partial averaging of both the intra-chain dipolar couplings and the inter-chain dipolar couplings. In order to obtain a good estimate of the effect on the ^{1}H NMR line shape, we use a simplified model of the motion. This model is justified, because we are only interested in the *average* dipolar couplings regardless of the precise details of the motion. A schematic drawing of this model for one PE chain is given in Fig. 2. In the model the assumption is made that the motion of the protons on the same (A) and the first neighbouring carbon atoms (B) in the same chain, is a rigid rotation about the chain axis. In the calculations, the second order Legendre polynomial $(1-3\cos^2 \Theta_{ij})$ used in the expression for the second moment of the line shape (see Ref. [8]; Eq. IV-38), is

replaced by its average over the motion:

$$\overline{(1 - 3\cos^2 \Theta_{ij})} = \frac{1}{2}(3\cos^2 \Theta_B - 1)(1 - 3\cos^2 \Theta'_{ij}). \quad (1)$$

Here the Θ_{ij} are the angles between the interproton vectors and the external magnetic field, Θ_B is the angle between the reorientation axis and the magnetic field, and Θ'_{ij} are the angles of the interproton vectors with the reorientation axis. One should note, here and in the following, that it is well known [8] that, strictly speaking, the line shape second moment is invariant with respect to molecular reorientations in a solid. In spite of this, averaging as in expression (1) results in a significant change of the apparent second moment of the line shape. The powder average over all possible directions of the magnetic field $\vec{B}_0$ averages the factor $(3\cos^2 \Theta_B - 1)^2$ to 4/5. The angle Θ'_{ij} for coupling with the proton on the same CH$_2$ unit is 90°. The protons on the nearest neighbouring carbons require $\Theta'_{ij} = 65.9$ and 59.8°, respectively. To allow for disorderly conformations and motions, the protons on the next nearest carbons are assumed to rotate independently. To deal with this, the central proton is placed on its average position (i.e. the rotation axis), while the protons on the next nearest neighbours and next-next nearest neighbours (C) rotate at appropriate distances about the chain axis. The protons on more distant carbons (D) are set on the center axis of the chain at the appropriate distance. The inter-chain contributions to the second moment are approximated by setting the protons on the centers of their respective chains.

The result of the calculations using this model is that the intra-chain contribution to the second moment is 2.636×10^9 rad^2 s^{-2}, and that the inter-chain contribution to the second moment is 0.986×10^9 rad^2 s^{-2}. When diffusion of the molecular chains in the chain direction is fast enough, the inter-chain dipolar interactions will not
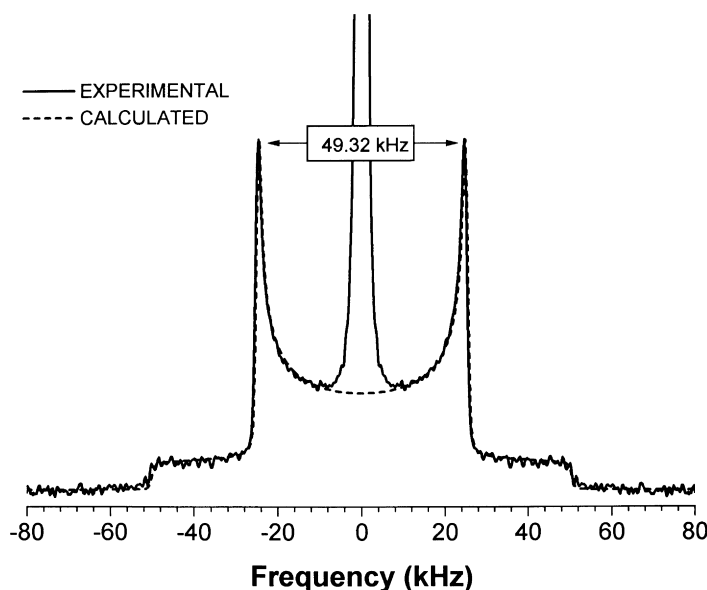

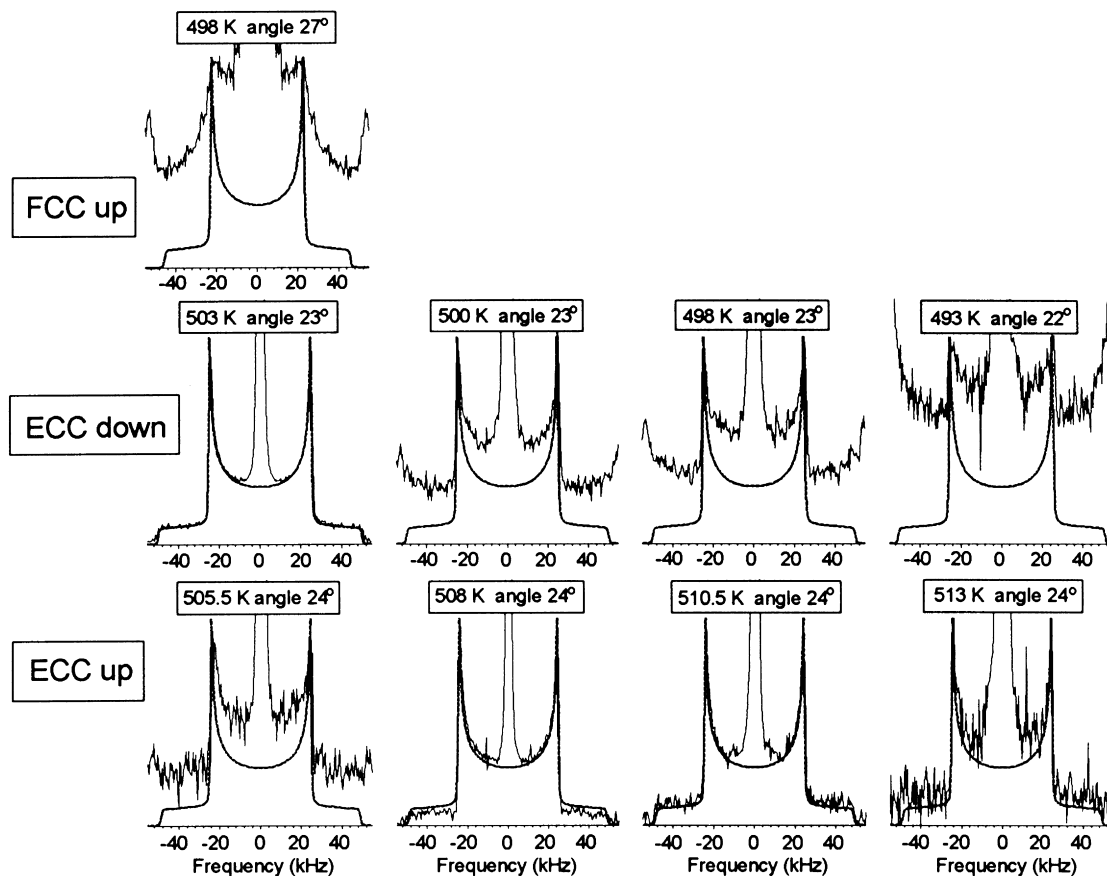Fig. 3. A deuteron NMR spectrum obtained in the hexagonal phase.

Fig. 4. Several spectra obtained in the hexagonal phase approximated by spectra that have been calculated using the double reorientation model.

contribute to the line width. This averaging of inter-chain contributions to the second moment due to chain diffusion occurs when $M_{2\text{inter}} \cdot \tau_D^2 \ll 1$. From the inter-chain M_2 stated above it is seen that the diffusion jump time τ_D should be much smaller than 3×10^{-5} s for this to occur. It will be shown in the subsequent subsections of this section that rates of motion in the hexagonal phase are indeed fast enough for this condition to be satisfied. Supporting evidence is found in the work of Schmidt-Rohr et al. [9], who obtained results showing that at the highest temperatures in the orthorhombic phase, chain diffusion occurs at a rate with $\tau_D = 2.5 \times 10^{-5}$ s, which is almost fast enough. Since motion in the hexagonal phase is expected to be much faster than in the orthorhombic phase it is very reasonable to discard any inter-chain contribution to the second moment. By itself the intra-chain contribution to the second moment calculated from the simple dynamical model discussed above is in good agreement with the experimentally obtained value. Later in this paper it will be shown that chain diffusion is the main $T_{1\rho}^H$ mechanism in the hexagonal phase.

2.2. Deuteron NMR spectra

In Fig. 3, a characteristic ^{2}H NMR spectrum is shown that has been obtained in the hexagonal phase. The observed spectrum consists of a Pake doublet originating from the crystalline material and a narrow line due to the amorphous parts of the sample. The crystallinity of the deuterated material is somewhat smaller than that of the non-deuterated material. The spectrum shows no signs of asymmetry in the EFG tensor. This means that the deuterons in the hexagonal phase experience an axially symmetric EFG tensor just as in the orthorhombic phase. However, the distance between the peaks of the Pake doublet in this spectrum is only about 49 kHz, which is much smaller than the distance in the spectrum found for the rigid orthorhombic crystal. This means that the original EFG tensor is partly averaged by a motion which is fast compared to the width of the original spectrum. The exact nature of such a motion can not be directly deduced from this. It can be a simple reorientation about an axis, but it can also be a more complicated superposition of motions which together result in an axially symmetric EFG tensor.

The simplest motion that could account for the observed spectrum is a simple reorientation about an axis. The average EFG tensor resulting from such motion again has an axial character but the coupling constant is reduced by a factor $(1/2)(3 \cos^2 \Theta - 1)$, where Θ is the angle the C–D bond makes with the axis of the reorientation. The reduction

Rates of diffusion
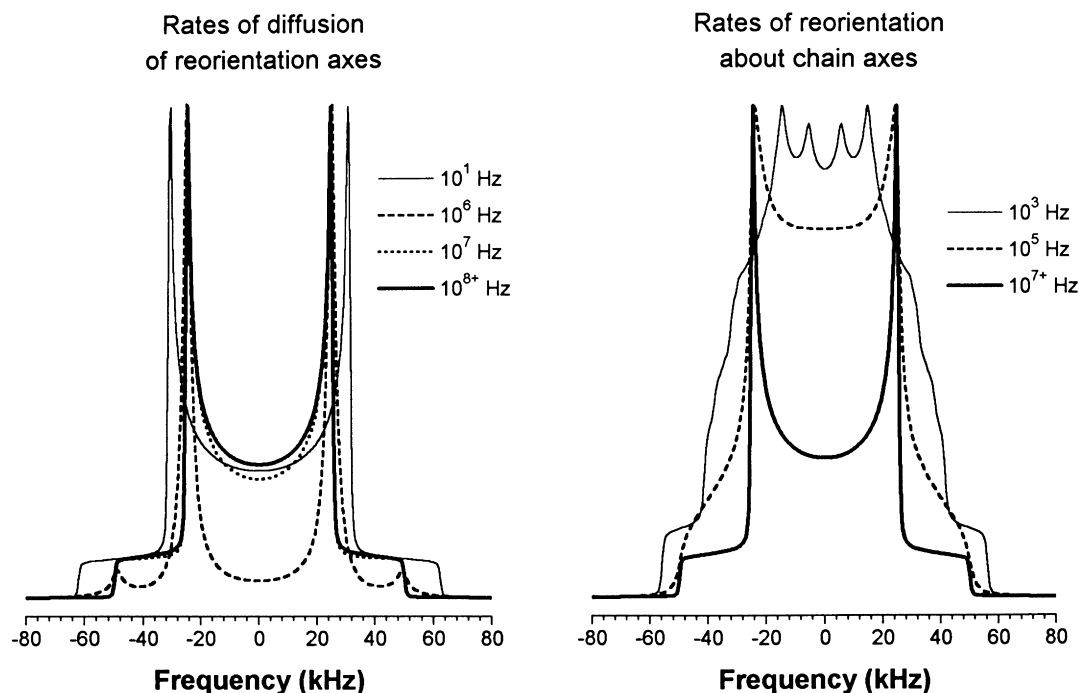of reorientation axes

Rates of reorientation
about chain axes

Fig. 5. Analysis of the rates of motion for the double reorientation model.

factor measured equals 0.403, giving possible angles of 75.3° or 39.1°. It is difficult to interpret these angles when looking at the polyethylene chains. Especially the angle of 39.1° seems very difficult to explain; additional evidence from relaxation measurements presented later in this paper show that this angle may be rejected. The angle of 75.3° may be more acceptable since it is close to the 70.5° angle a C–D

bond would make with the reorientation axis in a so called crankshaft defect.

Since the above single reorientation model is not really satisfactory, we have chosen an other model that is more compatible with intuition about PE chains. The simplest motion a PE chain can perform is perhaps that of fast reorientation about its *c*-axis. In an all-trans chain this would
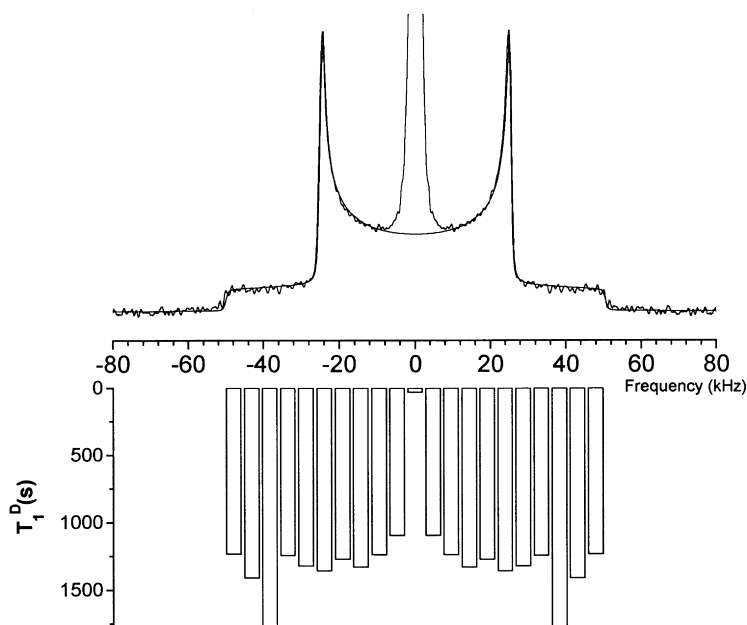

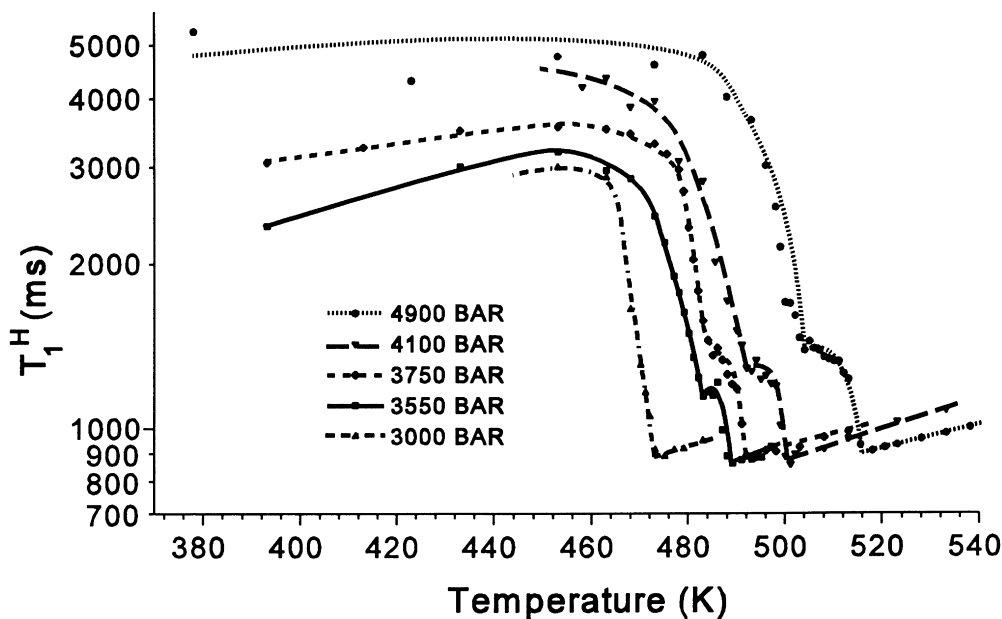Fig. 6. The dependence of T_1^D on the frequency in the spectrum.

Fig. 7. Temperature dependence of T_1^H at several values of pressure in and near the hexagonal phase. The experiments shown were obtained in runs with decreasing temperature.

mean that the C–D bond rotates with an angle of 90° with respect to the reorientation axis, leading to a reduction factor of 0.5. Because this reduction is still not enough to account for the experimental spectra, an other axial motion is superimposed on this. The reorientation axis itself is in turn assumed to be (locally) performing a diffusive motion within a solid angle. The opening angle has to be about 23° to result in the required reduction factor in the width of the Pake doublet. The results of fits using this model—which we will call the double reorientation model—are shown in Fig. 4. One can see that the average angle does not differ much with temperature within the small temperature interval investigated, and also there is not much difference between paths of increasing and decreasing temperature. The NMR spectrum obtained at the point where the hexagonal phase first emerges from the orthorhombic phase in the folded chain conformation appears to be the only one consistent with an angle of 27°. This could be a result of lower crystal perfection of chain folded material.

For the double reorientation model some rate limits have been determined using the simulation program. The results of this analysis are shown in Fig. 5. The experimental spectrum is best approximated when both components of the motion are in the fast motion regime. The left figure shows deviations of the calculated spectrum when the rate of diffusion of the reorientation axis is changed while keeping the reorientation rate about this axis in the fast motion regime. The right figure shows what happens when the reorientation rate is changed while keeping the rate of diffusion of the axes in the fast motion regime. From these figures it can be concluded that the minimum rate of both components of the motion should be at least 10^7 Hz.

2.3. Deuteron spin–lattice relaxation

In the deuteron NMR spectrum (shown in Fig. 3), the contributions of the hexagonal crystalline component and of the amorphous component can be clearly distinguished. Deuteron spin–lattice relaxation curves also show two distinct components [7]. From a spectral analysis of the relaxation (see Fig. 6), the fast relaxing component with a T_1^D value of about 45 ms has been attributed to the amorphous part. In the same analysis the slow relaxing part of the relaxation curve has been proved to originate from the crystalline part of the sample. The T_1^D of this part is about 1300 ms.

To test models explaining these values, we start with the general expression for T_1^D. As shown in Abragam [8; Chapter VIII, Eq. 138] the spin–lattice relaxation process for a deuteron (spin $I = 1$) is exponential, with time constant T_1^D. For a deuteron in an axial electric field gradient, that is reorienting isotropically with correlation time τ_2, the following expression is obtained:

$$\frac{1}{T_1^D} = \frac{3}{40}\left(\frac{e^2qQ}{\hbar}\right)^2\left[\frac{\tau_2}{1 + \omega_D^2\tau_2^2} + \frac{4\tau_2}{1 + 4\omega_D^2\tau_2^2}\right]. \qquad (2)$$

In the amorphous part of the sample quasi-isotropic motion of the C–D bonds is an acceptable model. By inserting the proper values for the quadrupole coupling constant and the deuteron Zeeman frequency, we find a minimum value of T_1^D of 1.5 ms for a τ_2 of 3.5×10^{-9} s. The experimental T_1^D value of the amorphous part is consistent with τ_2 equalling either 2.4×10^{-7} s or 5.4×10^{-11} s, depending on whether τ_2 is on the low temperature side or high
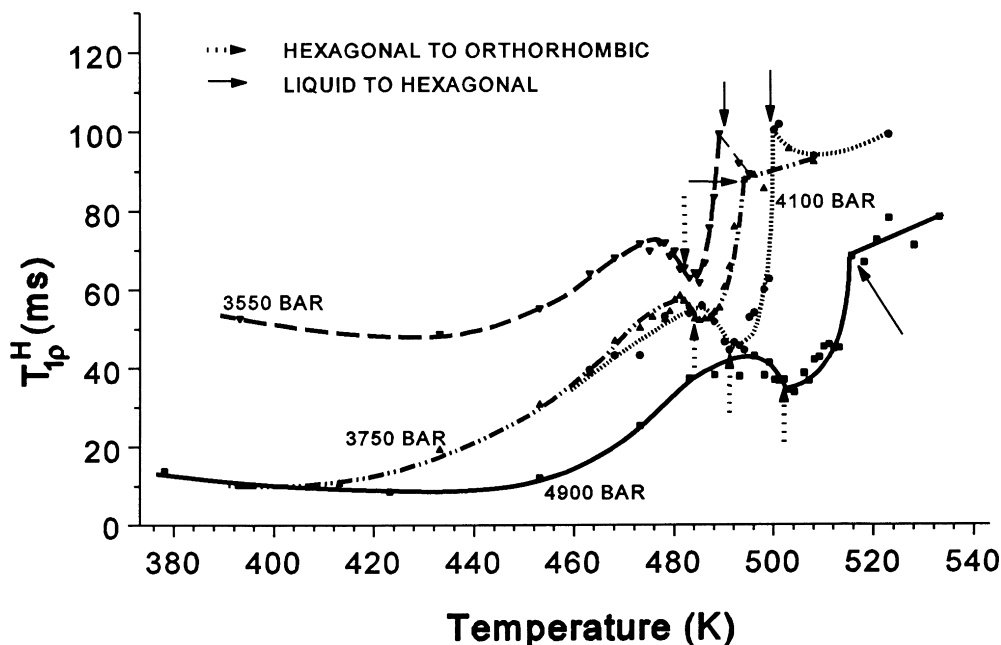
Fig. 8. Temperature dependence of $T_{1\rho}^{H}$ at several pressure values in the hexagonal phase. The experiments shown were obtained in runs with decreasing temperature.

temperature side of the minimum. As the first value is not consistent with the observed line width, we conclude that $\tau_2 = 5.4 \times 10^{-11}$ s.

In the discussion of the deuteron NMR spectra, it was shown that for the hexagonal crystalline part the chain motion is highly anisotropic. Two models were discussed. In the single reorientation model the C–D bonds move on average on a cone with an opening angle of $2 \times 75.3°$. In the double reorientation model, the motion of the C–D bonds is a superposition of two axial motions with an angle of $90°$ and $23°$ respectively.

For a calculation of T_1^D in the single reorientation model we make use of an expression derived by Torchia and Szabo [10], which incorporates diffusive axial motion with diffusion coefficient D. In the extreme narrowing limit their result reduces to

$$\frac{1}{T_1^D} = \frac{1}{8} \left(\frac{3e^2 qQ}{4\hbar} \right)^2 \left[\frac{\sin^2 2\Theta}{\tau_1} (2 + 3\sin^2 \vartheta) \right.$$
$$\left. + \frac{\sin^4 \Theta}{\tau_1} (2 - 3\sin^2 \vartheta) \right].$$
(3)

For this case Θ is the angle between the C–D bond and the axis of the motion and $\tau_1 \equiv D^{-1}$. In this expression the relaxation rate depends on the angle ϑ between the external magnetic field and the axis of the motion, which is the main axis of the average EFG tensor. Therefore T_1^D depends on the frequency in the spectrum. For an angle Θ of $70.5°$ the relaxation is independent of the orientation ϑ. If the angles found for the single reorientation model are used, it is found that for $\Theta = 75.3°$ the variation of the relaxation time over

ϑ is a factor of 1.36. For a value of $\Theta = 39.1°$ the variation is a factor 2.18. The dependence of T_1^D on the frequency in the spectrum of the hexagonal crystal has been tested as is shown in Fig. 6. There appears to be no significant change in T_1^D within experimental error. Because the experimental error is rather large due to low signal to noise ratio in the wings of the powder spectrum a variation with a factor 1.36 can not be ruled out. However, a change by a factor of 2.18 would have been visible so the angle of $39.1°$ can be ruled out as expected. The average value of T_1^D is 1300 ms. From the powder average of expression (3), calculated using $\Theta = 75.3°$, we find a value for the correlation time of the reorientational diffusion τ_1 of 5.5×10^{-12} s.

2.4. Proton spin–lattice relaxation

In the hexagonal phase we have determined the relaxation times T_1^H and $T_{1\rho}^H$ as a function of temperature at pressure values ranging from around the triple point pressure (about 3300 bar) to 5500 bar. Fig. 7 shows some of the results obtained for T_1^H. Note that the phase transitions are very distinctly visible in this figure. Therefore T_1^H can be used as an excellent probe to detect all phase transitions in the phase diagram of PE. This has been shown in detail in the previous papers [6,7]. In the region of the hexagonal phase the T_1^H relaxation curve follows a single exponential, with T_1^H is about 1.5 s. No distinct contributions can be distinguished of the hexagonal crystalline part and the amorphous parts of the sample.

It is expected that fast reorientations of the CH_2 groups about the chain axis as observed in the proton NMR spectrum, deuteron NMR line shapes and T_1^D measurements, also

form a good mechanism for proton spin–lattice relaxation. This reorientational motion affects the magnetic dipolar interactions between a particular proton and protons on the same chain and protons on a number of neighbouring chains. The models of motion introduced earlier do not allow us to calculate the proton spin–lattice relaxation rate, as the various inter-proton vectors all change their directions and lengths in a different way.

In order to obtain a reasonable estimate of T_1^H in the hexagonal crystalline part of the sample, it is best to use an expression [11] that makes use of the reduction of the observable second moment of the ^{1}H NMR line shape:

$$\frac{1}{T_1} = \frac{2}{3} \Delta M_2 \left[\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right]. \qquad (4)$$

For ΔM_2 the difference between the values calculated for a rigid "hexagonal" crystal and a hexagonal crystal with fast motion has been taken. It consists of an intra-chain part $\Delta M_2(\text{intra}) = 1.064 \times 10^{10} \text{ rad}^2 \text{ s}^{-2}$ and of an inter-chain part $\Delta M_2(\text{inter}) = 2.99 \times 10^9 \text{ rad}^2 \text{ s}^{-2}$. For the characteristic time of the motion τ_c, the value $\tau_2 = 5.5 \times 10^{-12}$ s as derived from T_1^D is used. The substitution of these values in (4) results in an estimate for T_1^H of 4.0 s. This differs significantly from the observed T_1^H.

In the amorphous parts of the sample the protons are believed to be moving quasi-isotropically with correlation time 5.4×10^{-11} s, as derived from the value of T_1^D. T_1^H for these parts can be estimated using the standard expression from Abragam [8]. Taking into account nearest neighbour proton pair interactions only, the obtained estimate for T_1^H in the amorphous parts of the sample is 600 ms. We remark here that for the real situation more proton pairs need to be considered, leading to a smaller value, while, on the other hand, a *distribution* of correlation times should be used which will lead to a higher T_1^H value.

From the above we can conclude that the experimentally observed value of T_1^H is explained by assuming that the main relaxation path is the fast relaxation of the protons in the amorphous parts of the sample. The magnetization of the crystalline parts is strongly coupled to this by spin diffusion. This results in the observed single time constant for the relaxation where the Zeeman energy of the protons in the crystalline part acts as a load on the relaxation of the protons in the amorphous regions.

2.5. Proton spin–lattice relaxation in the rotating frame

Experimental values of $T_{1\rho}^H$, obtained at a number of pressure values in the orthorhombic and in the hexagonal phase are shown in Fig. 8. The $T_{1\rho}^H$ experiments have been performed using a spin-locking field equivalent to 100 kHz, for durations up to 150 ms. In the region of the hexagonal phase the relaxation curves are slightly curved, but contributions from the hexagonal crystalline fraction and the non-crystalline fractions cannot be distinguished clearly. Since the crystallinity of the material used in the

proton NMR experiments exceeds 75% in the region of the hexagonal phase, it is reasonable to assume that in a $T_{1\rho}^H$ experiment we mainly observe the crystalline component.

Because the values of T_1^H for the crystalline and amorphous parts in the region of the hexagonal phase as estimated in the previous section for reorientational mechanisms are in the extreme narrowing limit, they should also be good estimates for $T_{1\rho}^H$. However, the experimental values of $T_{1\rho}^H$ in the hexagonal phase, as shown in Fig. 8, vary between 30 and 60 ms, while T_1^H is about 1500 ms. Apparently another relaxation process involving lower frequencies must exist, that acts as a more effective relaxation mechanism in the rotating frame. The only plausible process for this is chain diffusion. It has been mentioned that fast chain diffusion narrows the ^{1}H NMR line shape of hexagonal crystalline PE. We define the correlation time τ_c^d of the inter-chain dipolar coupling of the protons somewhat loosely as the average time between a relative jump of two neighbouring PE-chains over one carbon–carbon distance l, that is half the mean time τ between diffusion jumps of a single chain. The rate of chain diffusion should be fast enough to average out the inter-chain contributions to the line shape second moment which is $9.86 \times 10^9 \text{ rad}^2 \text{ s}^{-2}$. From this requirement it follows that τ_c^d should be much smaller than 3.0×10^{-5} s. An estimate of $T_{1\rho}^H$ caused by the chain diffusion process can be made by inserting the value of the inter-chain contribution to the line shape second moment M_2 in

$$\frac{1}{T_{1\rho}^H} = \frac{M_2^{\text{inter}}}{\omega_1} \left[\frac{\omega_1 \tau_c^d}{1 + 4\omega_1^2 \tau_c^{d2}} \right]. \qquad (5)$$

A minimum value of $T_{1\rho}^H = 2.4$ ms is obtained from this expression, for $\tau_c^d = 8 \cdot 10^{-7}$ s. The average experimental value $T_{1\rho}^H = 40$ ms corresponds to a value of τ_c^d of 2.1×10^{-8} s at the high temperature side of the minimum. The value on the low temperature side of the minimum $(3.5 \times 10^{-5}$ s) can be excluded because it is so long that it is only on the verge of narrowing and therefore also outside the validity range of (5). As can be seen from Fig. 8, $T_{1\rho}^H$ in the hexagonal crystal increases rapidly with increasing temperature, indicating a fast increase in the rate of chain diffusion. Diffusion gets slower on increasing pressure. Note that the rate of chain diffusion in the hexagonal phase is rather high. The observed range of $T_{1\rho}^H$ values from 30 to 60 ms corresponds to a variation of the mean time between jumps τ from 3×10^{-8} to 6×10^{-8} s. The coefficient $D = l^2/(2\tau)$ for one dimensional diffusion varies between 1.5×10^{-9} and $3.5 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. For example: it takes about 2.5 min for a PE-chain to travel over 10 μm.

As has been shown in a two-dimensional ^{13}C NMR exchange experiment [9] and and in a ^{13}C spin–lattice relaxation experiment [12], longitudinal chain diffusion also occurs in the orthorhombic phase. The mean time between longitudinal jumps τ becomes shorter than 10^{-4} s above about 10 K below the melting point. Chain diffusion

there becomes a mechanism for $T_{1\rho}^{H}$. At high pressure similar rates of diffusion may be expected to occur just below the phase transitions. The effect can be observed in Fig. 8 and Fig. 5 of the first paper [6]. Whereas $T_{1\rho}^{H}$ due to the torsional reorientations is expected to increase with temperature, a decrease is observed just below the transition to the hexagonal phase. This presumably is the onset of the effect of chain diffusion on $T_{1\rho}^{H}$, which becomes the main mechanism in the hexagonal phase. Since the rate of this process for $T_{1\rho}^{H}$ is on the low temperature side of the minimum in the orthorhombic phase while being on the high temperature side in the hexagonal phase, we conclude that chain diffusion in the latter must be much faster.

Chain diffusion is assumed to be a much slower process in the amorphous parts of the sample. Presumably the mechanism for $T_{1\rho}^{H}$ in the amorphous regions is the quasi-isotropic motion of the protons in the extreme narrowing limit, discussed in the previous section. Therefore $T_{1\rho}^{H}$ is expected to be of the order of 600 ms. Such a value is outside the range of our measurements, because it would require very long locking pulses. However, the slight curvature of the relaxation curves observed in our data may very well be due to the contribution of the amorphous regions.

3. Comparison with computer md simulations and with the behaviour in *n*-alkanes

To our knowledge, the most complete MD simulation [13,14] of the chain dynamics in an orthorhombic PE crystal has been made in a model consisting of up to 37 PE chains (each consisting of 100 CH_2 groups), initially placed in their all-trans conformation in an orthorhombic arrangement with fixed cell parameters. The model contains appropriate potential functions for the intra-chain and inter-chain atom–atom interactions. The CH_2 groups are simplified to single particles of mass 14. At a number of temperature values, the trajectories of all particles are followed for a duration of 30×10^{-12} s, starting from the initial configuration. In these simulations it appears that the number of *gauche* defects in the chains is very low. Deviations of the precise all-trans conformations are observed as twists of the chains. However, in more than 90% of the cases the rotation of successive C–C bonds remains within $16°$. Locally, these twists result in large angle reorientation of chain segments about the chain axes. In the simulations this motion already occurs at low temperature (80 K), while at high temperature (430 K) its time scale is about 10^{-12} s.

As it was shown in the previous paper [7], this is certainly not the case in the real crystal. In the orthorhombic phase the angles of reorientation of the C–D bonds can be derived from the ^{2}H NMR spectra. Even at much higher temperature (393 K) the average reorientation angle is only about $20°$. In addition, the fast and large reorientations occurring in the simulations would be an efficient mechanism for proton and deuteron spin–lattice relaxation, which is not observed.

Therefore, it may be concluded that these simulations do not represent the strongly ordered orthorhombic phase of PE. Rather, these MD simulations show a highly mobile, conformationally disordered state of PE in which chain positions and orientations are preserved. This shows more resemblance to the behaviour of real PE chains in the hexagonal phase.

Whereas no MD simulations are available on the chain dynamics in the hexagonal phase of PE, a number of computer simulations, using the Monte Carlo (MC) and Molecular Dynamics (MD) methods, have been made on the normal alkanes. In the *n*-alkanes a number of so-called rotator phases has been observed [15–18] below the melting transition which differ in structure and order of occurrence depending on the exact length of the paraffin molecule. Due to the fast reorientation, phase II in paraffin crystals is called pseudo-hexagonal, and exhibits some similarities with hexagonal PE. However, in contrast to PE, these phases only occur at low pressure and vanish at high pressure [19]. A ^{2}H NMR study [20] on motion in $C_{19}H_{40}$ has shown that the molecules reorient fast about their *c*-axes between two sites. The importance of the comparison with the lower alkanes lies in the fact that computer simulations that are supposed to simulate PE, only use chains with lengths up to about 100 CH_2 groups. Therefore, differences of the results of such simulations with the observed behaviour of real PE should be attributed to the too short chain lengths when these results do agree with the behaviour of the paraffin crystals under the simulated conditions.

Most of the studies on the alkanes [21–24] are concerned with simulations of rigid and flexible long normal alkanes (up to $C_{23}H_{48}$), in particular with the aim of understanding the structure and the dynamic properties of the orthorhombic and hexagonal rotator phases. In another MD study [14,25] a crystal consisting of flexible chains of $C_{50}H_{102}$ has been used as a model for a polyethylene crystal. In this study, at zero pressure, it appears that orthorhombic, monoclinic and hexagonal initial arrangements (with lattice parameters corresponding to experimental values) all quickly transform to the same, hexagonal, structure. Therefore, also this study essentially simulates the hexagonal rotator phase of a long *n*-alkane.

Some of the conclusions of these investigations are the following. In the rotator phases the chains mainly maintain their all-*trans* conformation. Except at the chain ends, only a very small fraction of gauche defects develops. Even in the rotator phases the chains tend to parallel their zig-zag planes in dynamic domains. In the orthorhombic rotator phases, the distribution of orientational angles of the chains with respect to the crystal *a*-axis has four maxima at $\pm 41 \pm 180°$, whereas in the hexagonal phases the angle distribution has peaks at multiples of $60°$. The whole chain shows reorientations between these preferred angles. In different simulations the mean time between these reorientations varies between about 10^{-13} and 10^{-11} s. Apart from the few gauche defects, the disorder within a chain mainly consists of soft

twists [14,25,26]. Locally, these twists also result in the reorientation of chain segments, on a time scale of about 10^{-12} s.

The chain reorientations in an orthorhombic rotator phase have been observed in a ^{2}H NMR experiment [27] on selectively deuterated samples of *n*-nonadecane ($C_{19}H_{40}$). The reorientational motion results in a non-axial average EFG tensor, consistent with reorientational jump angles of $82 \pm 180°$, in agreement with the angle distribution found in the MD results.

In hexagonal PE the long chains may be expected to develop twists and kinks and crankshaft defects, allowing reorientational motion motion of long chain segments in a similar way as in the long *n*-alkanes with two free end groups. Therefore the observations, made in simulations of the hexagonal rotator phases of the long alkanes may be expected to also provide a qualitatively correct representation of the behaviour in the hexagonal phase of polyethylene. As we have seen earlier, the motional averaging of the EFG tensor at the deuteron position in a C–D bond results in an *axial* average tensor, as is to be expected for chain reorientations over the six-fold symmetric angle distribution found in the MD simulations of a hexagonal rotator phase. Whereas purely axial motion would reduce the average coupling constant by a factor 2 the experimentally observed coupling constant is further reduced by the changes in the direction of the local orientation axis, caused by the dynamic chain twists. This direction is time dependent on the time scale of the life time of a chain twist, which, in the simulations, is of the order of picoseconds. This justifies the use of the double reorientation model to account for the ^{2}H NMR spectra in the hexagonal phase. The MD results do not contain data on the time dependence of the orientations of the bonds of each carbon atom. However, from the pictorial presentation of the evolution of a single chain, given in Ref. [14], it appears that the assumption of a motion of the local axis of reorientation in a solid angle of about 23°, as derived from the ^{2}H NMR spectra, is entirely acceptable. We also like to note here, that the reorientational correlation time, as derived from the deuteron spin–lattice relaxation rate in the hexagonal crystal, is about 5.5×10^{-12} s. This value is in the range of values of the mean time between chain reorientations, obtained in the MD simulations of the hexagonal rotator phases of the long *n*-alkanes.

4. Conclusions

The hexagonal phase of PE has been investigated by NMR for the first time. Proton spin–lattice relaxation times recorded along isobaric paths at several pressure values, were found to be an excellent probe to detect the transitions to this phase. The values of T_1^H can be explained by fast ($\tau_c = 5.4 \times 10^{-11}$ s) quasi-isotropic motion of the protons in the amorphous parts of the sample. Relaxation in the crystalline parts is coupled to this by spin diffusion.

Proton NMR line shapes can be accounted for, provided that fast chain diffusion is assumed. That this is indeed the case has been demonstrated from $T_{1\rho}^H$ data that can only be explained by assuming fast chain diffusion. The chain diffusion in the hexagonal phase as determined from proton NMR line shapes and $T_{1\rho}^H$ occurs with an average diffusion jump time τ_c^d between 3×10^{-8} and 6×10^{-8} s. The onset of the speeding-up of the rate of chain diffusion is already seen in the orthorhombic phase just below the transition to the hexagonal phase.

From deuteron NMR spectra and relaxation times we find that the PE chains in the hexagonal crystals perform rapid axial reorientations. A model explaining the experimental results is one where the CH_2 units reorient fast (>10 MHz) about the chain axes, while the directions of these reorientation axes diffuse fast (>10 MHz) within a solid angle with an opening angle of about 23°.

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