Orientational distribution of polymer chains studied by ^{2}H n.m.r. line shapes

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The orientational distribution of macromolecular chains in partially ordered polymers can be determined from the line shapes of ^{2}H n.m.r. spectra. Two simple methods for computing magnetic resonance line shapes by superposition of a relatively small number of subspectra, which can in turn be calculated analytically, are described. These methods are particularly suitable for studying moderate and high order, respectively, in drawn fibres. As experimental examples the orientational distributions of the polyethylene chains in the crystalline parts of so called single crystal mats and a drawn ($\lambda \approx 9$) sample of linear polyethylene-d_4 have been determined. In both cases the orientational distribution function was shown to be essentially Gaussian with full width at half height 28° ± 3° and 6.6° ± 0.5°, respectively.

INTRODUCTION

The determination of the orientational distribution of molecules in partially ordered systems is of particular interest. This holds in particular for drawn polymers[1], liquid crystalline systems[2], and membranes[3]. A number of different experimental techniques can be used for determining the molecular order with different accuracy[1]. As far as n.m.r. is concerned earlier wide line work was restricted to a moment analysis[1,4] where the moments of the orientational distribution[5] were obtained from the moments of the spectral line shape being determined by the dipole–dipole interaction, which is a multi spin interaction with both *intra-* and *inter*molecular contributions. N.m.r. line shapes which are dominated by single spin *intra*molecular couplings only, however, can be fully analysed to yield the complete orientational distribution function; clearly only the even constituents of that function can be determined, since the spectra are governed by second rank tensor interactions.

Although a number of different nuclei can be used as spin probes in this context deuterons have recently proved to be especially suited[6–9]. The ^{2}H spectra are dominated by the quadrupole interaction of the $I = 1$ spin with the electric field gradient tensor at the deuteron site. For aliphatic deuterons the field gradient is found to be approximately axially symmetric about the C–D bond direction, which eases the analysis of the data. ^{2}H n.m.r. thus monitors the directions of the C–D bonds in the sample. The large spectral width of ^{2}H spectra, being of the order of 250 kHz in rigid solids, causes experimental difficulties. Therefore most of the earlier work was performed on liquid crystalline systems, where the quadrupole coupling is partially averaged, leading to narrower spectra. By use of superconducting magnets and advanced pulse techniques, however, undistorted ^{2}H spectra covering the full width of 250 kHz can now be obtained by Fourier transform methods[9,10]. A general analysis of n.m.r. and e.s.r. line shapes, by use of an expansion of the orientational distribution function in terms of Wigner rotation matrices[5], has been published elsewhere[11]. Here we give a simpler treatment, applicable to special cases often met in practice, in particular to the case of axial symmetry of both the coupling tensor and the orientational distribution function. It is shown that for both highly and only moderately ordered systems the n.m.r. line shape can conveniently be calculated as a superposition of a relatively small number of subspectra, which are different for high and low order parameters, respectively, but can be calculated easily analytically. Our analysis is particularly suited for determining the orientational distribution of aliphatic chains. This is demonstrated experimentally on the crystalline part of linear polyethylene, where the so called single crystal mats[12] and a melt crystallized drawn ($\lambda \cong 9$) sample served as convenient examples of relatively low and high degree of order, respectively.

LINE SHAPE CALCULATION

The information about partial order contained in the n.m.r. line shape is provided through the anisotropic coupling of the nuclei to their surroundings. Therefore analysis of the line shape yields primarily the distribution of the principal axes of the coupling tensor relative to an external magnetic field. Usually, however, one is interested in the orientational distribution of some structural element of the macromolecule relative to unique directions of the ordered sample. In general, therefore, four different coordinate systems are relevant for the analysis of magnetic resonance line shapes as described in detail in Reference 11:

(1) the principal axes system (x_k, y_k, z_k),
(2) the laboratory system (X_0, Y_0, Z_0),
(3) the sample system (X, Y, Z),
(4) the molecular system (x, y, z).

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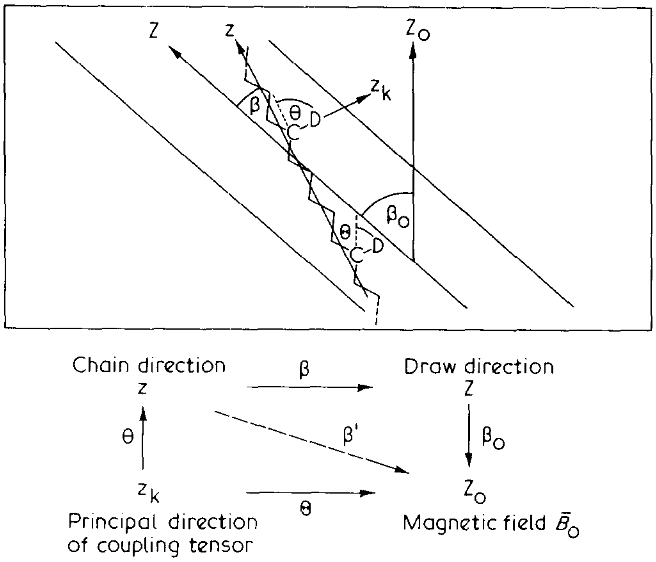

Figure 1 Selected macromolecular chain in a partially ordered polymer and notation for the four unique directions used in the line shape calculations. Notice that the four z-axes need not be in a single plane. The notation is in accord with the more general treatment given in Reference 11

For the analysis of ^{2}H spectra of polymer chains we restrict ourselves to the case often met in practice that axial symmetry exists about each of the relevant four directions (*Figure 1*).

The axial symmetry of the coupling tensor about the C–D bond is a good approximation as revealed by the experimental ^{2}H spectra of isotropic samples[9,13]. The laboratory system is completely specified by the direction of the magnetic field, if the field strength is sufficiently high[11]. For a drawn fibre the sample system can be specified by a single direction—if the molecules are distributed uniformly around the direction of order and finally it suffices to characterize the molecular system by a single direction, if the C–D bonds in the sample are uniformly distributed about a molecular axis—the chain direction (transverse isotropy[14]).

Under these conditions the orientational distribution function $P(\beta)\mathrm{d}\cos\beta$ is defined as the fraction of chain axes forming an angle between β and $\beta+\mathrm{d}\beta$ with respect to the direction of order. The frequency of a single n.m.r. transition of a given deuteron, however, depends on the angle between the corresponding C–D bond and the magnetic field:

$$\omega=\delta\cdot(3\cos^2\Theta-1) \tag{1}$$

with

$$\delta=\frac{3}{8}\frac{e^2qQ}{\hbar} \tag{2}$$

The ^{2}H n.m.r. line shape, therefore, can be calculated by weighting the spectra corresponding to a given value of Θ by the probability to find that value for a given orientational distribution. We will calculate the line shapes for a single n.m.r. transition only. To compare the results with experimental ^{2}H spectra one has to take into account that two transitions are allowed for the $I=1$ spin system, leading to a composite spectrum symmetric about the Larmor frequency. Thus the calculated line shape for a single transition and its mirror image with respect to $\omega=0$ have to be superimposed.

Numerous ways have been described for calculating magnetic resonance line shapes for partially ordered systems, some of the more recent papers are listed below[7,11,15–16]. Here we describe two ways offering particularly easy and straightforward computation of spectra for the special case described above:

Expansion of orientational distribution function

The first method has been described in detail previously[11]. The orientational distribution is expanded in terms of Legendre polynominals:

$$P(\beta)=\sum_l P_{l00}P_l(\cos\beta), \tag{3}$$

where the P_{l00} are the moments of the orientational distribution as defined in Ref 5. In particular $P_{000}=1/8\pi^2$ corresponds to the isotropic part of $P(\beta)$ and higher values of $l=2, 4, \ldots$ describe an increasing degree of order. Rapid convergence of the expansion (3) can be expected for moderately ordered samples only, *vide infra*. Within its range of applicability, however, the n.m.r. line shape can conveniently be calculated using this expansion by realizing that the spectrum can likewise be written as a superposition of subspectra $S_l(\omega)$:

$$S(\omega)=8\pi^2\sum_{l=2,4\ldots}a_lS_l(\omega) \tag{4}$$

where the weighting factors a_l are given by:

$$a_l=P_{l00}\cdot P_l(\cos\theta)\cdot P_l(\cos\beta_0) \tag{4a}$$

and the subspectra $S_l(\omega)$ can be written in analytical form:

$$S_l(\omega)=\frac{P_l[\chi(\omega)]}{6\delta\chi(\omega)} \tag{4b}$$

with

$$\chi(\omega)=\frac{1}{\sqrt{3}}\sqrt{\frac{\omega}{\delta}+1}\ , \quad -1<\frac{\omega}{\delta}\leqslant+2\ .$$

Subspectra for l-values up to $l=8$ are drawn in *Figure 2* for the convenience of the reader.

The experimental line shape can then be fitted to a calculated one by varying the a_l, from which in turn the moments P_{l00} of the orientational distribution can be determined. The two Legendre Polynomials in the expression of a_l have fixed values for a given sample in a fixed orientation to the field, the angle θ depends on the molecular geometry while β_0 can be changed experimentally (*Figure 1*). By proper choice of β_0 the contribution of leading terms in the expansion of $P(\beta)$ to the ^{2}H n.m.r. line shape can be elimineted, offering the possibility to determine higher moments rather accurately.

Expansion in terms of planar distributions

Consider an ensemble of parallel chains. The C–D bonds are perpendicular to the chain direction ($\theta=\pi/2$) and are isotropically distributed within the plane (transverse isotropy). In our context such an ensemble corresponds to a completely ordered sample. The line shape of this ensemble is a function of the angle β' between

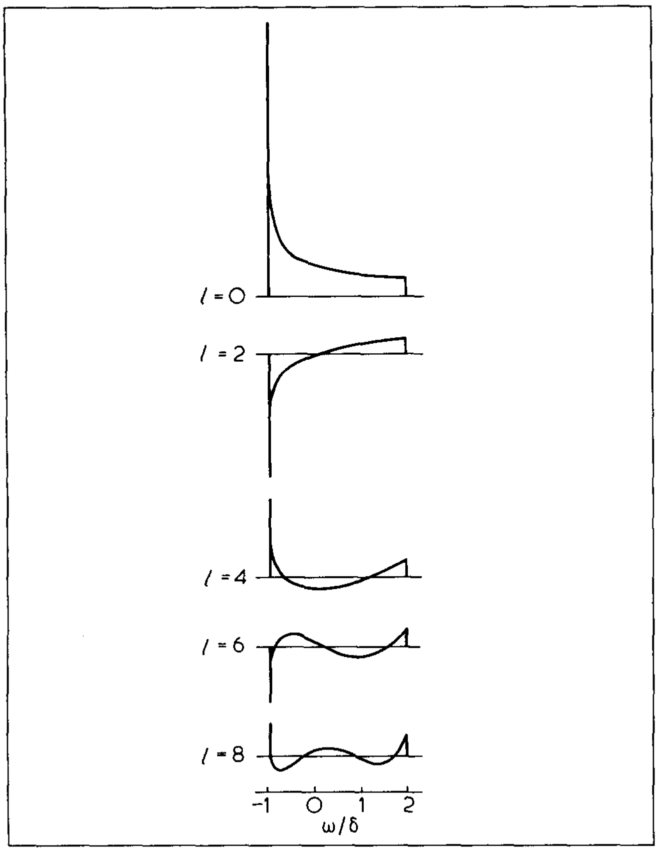

Figure 2 Subspectra $S_l(\omega)$ for composing line shapes according to Equation (4)

the chain axis and the external field (*Figure 1*) and can accordingly be written as $S_{\beta'}(\omega)$. As shown in the Appendix it has the form

$$S_{\beta'}(\omega)=\frac{1}{\pi\delta}\cdot\frac{1}{\sqrt{\left(\frac{\omega}{\delta}+1\right)\left(3\sin^2\beta'-1-\frac{\omega}{\delta}\right)}}\ , \qquad (5)$$

$$-1<\frac{\omega}{\delta}<(3\sin^2\beta'-1)$$

The most prominent features of the line shapes, plotted in *Figure 3* for different values of β', are the two symmetric singularities at $\omega/\delta=-1$ and $\omega/\delta=3\sin^2\beta'-1$, respectively. The line shape of the partially ordered polymer is now obtained by a superposition of the line shapes $S_{\beta'}(\omega)$ for the planar distributions defined above:

$$S(\omega)=2\pi\int_{-1}^{+1}Q_{\beta_0}(\beta')\cdot S_{\beta'}(\omega)d\cos\beta' \quad , \qquad (6)$$

where the weighting factor $Q_{\beta_0}(\beta')d\cos\beta'$ is the fraction of chain axes forming an angle between β' and $\beta'+\mathrm{d}\beta'$ with respect to the external field. It depends parametrically on β_0 and can be calculated from $P(\beta)$ according to

$$\varrho_{\beta_0}(\beta')=\int_{-\pi}^{+\pi}P(\beta)\mathrm{d}\gamma' \qquad (7)$$

where β is related to β', β_0 and γ' according to

$$\cos\beta=\sin\beta_0\sin\beta'\cos\lambda'+\cos\beta_0\cos\beta' \quad . \qquad (8)$$

The numerical calculation of $S(\omega)$ according to equations (6)–(8) is straightforward and can by done for any $P(\beta)$. Typically we will choose a suitable functional form for $P(\beta)$ and fit the experimental line shape to the calculated one by varying the parameters defining that function. This method is generally applicable, we found it to be especially useful for calculating the line shapes of highly oriented samples.

EXPERIMENTAL

Samples

Two samples of partially oriented linear polyethylene-d_4 ($M_w\approx100\,000$, Merck, Darmstadt) were studied. The single crystal mats were prepared as described by Olf and Peterlin[12], using C_2Cl_4 as a solvent. The temperature of crystallization was 313 K. The drawn sample was prepared by A. Ziegeldorf, University of Marburg, from a melt crystallized foil, cold drawn at 351 K to $\lambda\approx9$.

N.m.r. spectra

Fourier transform ^{2}H spectra using quadrature phase detection were obtained at 55 MHz with a Bruker SXP spectrometer, a homebuilt probehead and a superconducting magnet (Oxford Instruments, 8.5 T). Details of the measurements have been published elsewhere[9]. The pulse length was 1.7 μs in our broad band probe with a bandwidth of more than 1 MHz, corresponding to a tilt angle of 54°; solid echoes and spin alignment echoes were added as described in Ref 10. The spectra were corrected for the finite pulse length[9,17]. As shown by Davis *et al.*[17] the distortions are less severe, if tilt angles below 90° are used. Moreover, essentially no distortion is contained in the contribution to the signal generated from the spin alignment echo[18].

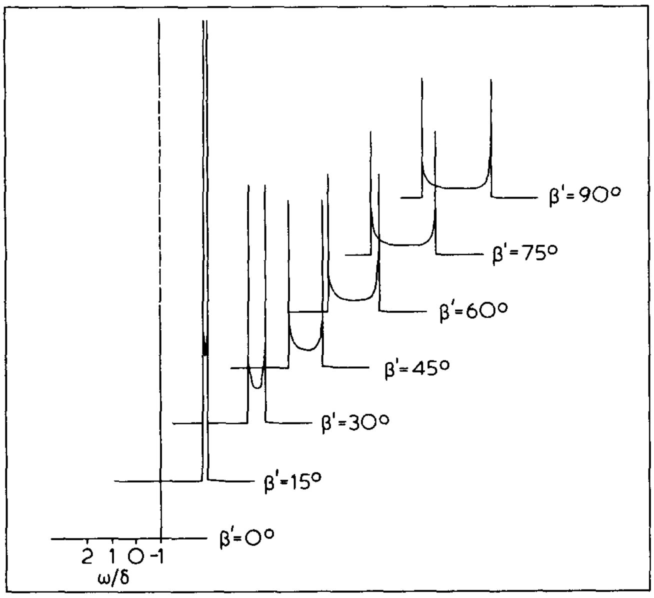

Figure 3 Subspectra $S_{\beta'}(\omega)$ of planar distributions of C—D bonds for composing line shapes according to Equation (6)

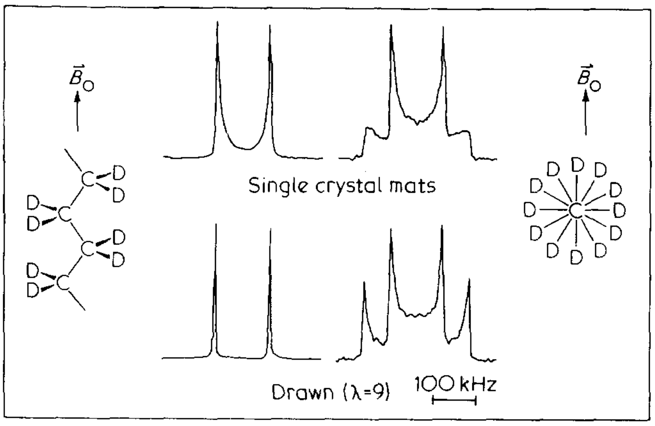

Figure 4 ^{2}H spectra of oriented polyethylene. Left: $\vec{B}_0$ parallel, right: $\vec{B}_0$ perpendicular to the direction of order, respectively. Upper traces: single crystal mats[12], lower traces: drawn sample

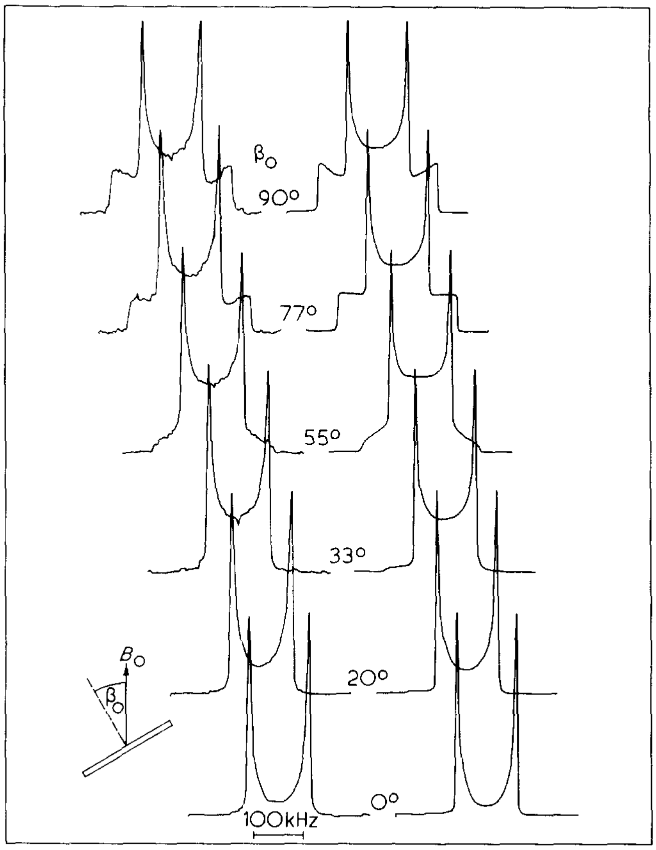

Figure 5 Observed and calculated ^{2}H spectra of the single crystal mats[12] for various angles β_0 between the normal to the mats and $\vec{B}_0$. Experimental conditions: pulse delays[10] τ_1 = 200 μs, τ_2 = 800 μs, repetition time 3 s, 250 runs each. The calculated spectra were convoluted with a Gaussian of variance 0.9 kHz to take into account the dipolar coupling between the deuterons[22]

RESULTS AND DISCUSSION

Two samples of linear polyethylene with significant different degrees of order[1] were chosen for testing the reliability of determining the orientational distribution by ^{2}H n.m.r. In both cases the spectra presented here correspond to the rigid deuterons in the crystalline regions which can be discriminated from the mobile ones in the amorphous regions by their longer transverse relaxation time T_2 (Ref 19).

For an easy understanding of the spectra observed let us discuss the spectra of both samples for two unique directions, i.e. with the magnetic field either parallel or perpendicular to the axis of order, as presented in *Figure 4*. In both cases the order consists of a preferred alignment of the polymer chains along a single direction. For the spectra at the left the field also points into that direction. If the order were complete it would be along the chain axis and thus perpendicular to all C–D bonds. The spectrum, therefore, would consist of a single doublet (*Figure 4*). The planar distribution of C–D bonds described above, however, is probed directly, if the field is perpendicular to the direction of order, spectra at the right. It is clear that the different degrees of order of the samples[20,21] lead to drastically different line shapes. By comparing these experimental line shapes with the subspectra discussed above (*Figures 2* and *3*) both spectra may be calculated by a superposition of a small number of subspectra only, if we use $S_l(\omega)$ and $S_{\beta'}(\omega)$ for the upper and lower one, respectively.

To monitor the orientational distribution faithfully through ^{2}H spectra, rotation patterns have to be taken by varying β_0, i.e. the orientation of the direction of order with respect to the magnetic field. The resulting experimental spectra and calculated line shapes for the single crystal mats are presented in *Figure 5*. These spectra can be described by an orientational distribution of the form given in equation (3) with $l \leqslant 8$. The theoretical line shapes were calculated according to equation (4), where the moments P_{l00} were not taken as independent parameters, but were calculated assuming a Gaussian distribution of chain axes about the normal to the foil:

$$P(\beta)=N\cdot\exp\left(-\frac{\sin^2\beta}{2\sin^2\bar{\beta}}\right)=\sum_l P_{l00}P_l(\cos\beta) \qquad (9)$$

The averages $\langle P_l(\cos\beta)\rangle = 8\pi^2 P_{l00}/(2l+1)$ are plotted for various widths of that Gaussian in *Figure 6*. This shows

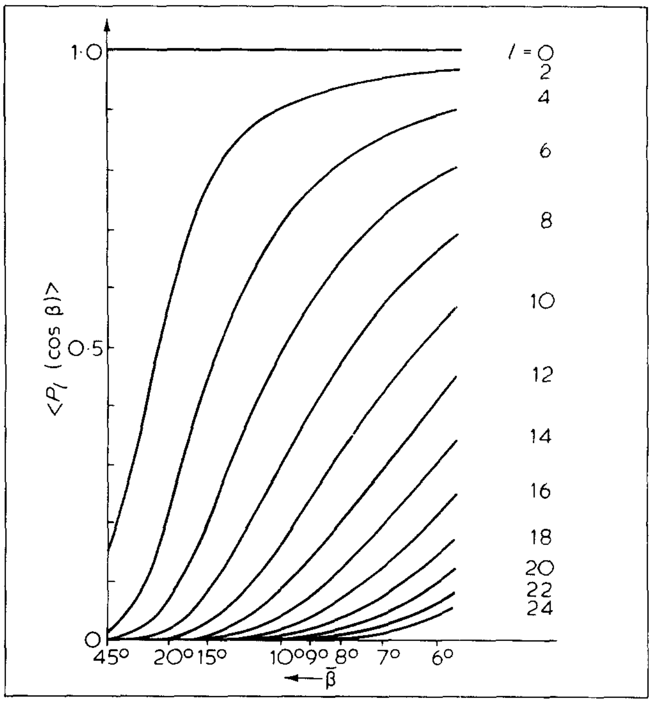

Figure 6 Moments of Gaussian orientational distribution function (Equation (9)) for different widths of the distribution

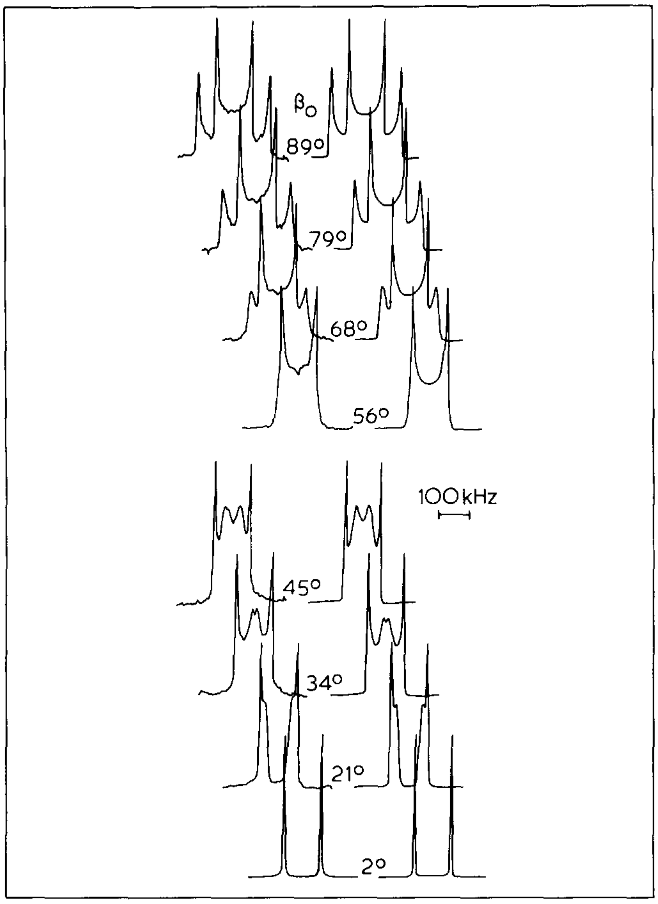

Figure 7 Observed and calculated ^2H spectra of the drawn ($\lambda \approx 9$) sample for various angles β_0 between the draw direction and $\bar{B}_0$. Experimental conditions: pulse delays[10] $\tau_1 = 200\ \mu s$, $\tau_2 = 800\ \mu s$, repetition time 20 s, 40 runs each. The calculated spectra were convoluted with a Gaussian of variance 0.9 kHz to take into account the dipolar coupling between the deuterons[22]

that the moment expansion converges sufficiently rapid for $\bar{\beta} > 10°$ only and that for $10° < \bar{\beta} \lesssim 20°$ higher moments $l = 4, 6, \ldots$ are significant. The fitted line shapes shown on the right of *Figure 5* were obtained with $\bar{\beta} = 12° \pm 1°$, taking into account the even moments P_{l00} up to $l = 8$ in accordance with equation (9), and an additional isotropic contribution corresponding to 20% of the total intensity. The close agreement between observed and calculated line shapes clearly justifies the assumption of an essentially Gaussian orientational distribution function. In fact, no significant better agreement could be obtained by using P_{l00} calculated from the Gaussian as starting values and fitting each one separately.

The rotation pattern for the drawn sample is presented in *Figure 7*. The line shape shows a much more marked dependence on the angle β_0. The theoretical spectra shown on the right were calculated using the line shapes of the planar distributions as described above. The spectra for $\beta_0 = 34°$ and 45° are most sensitive to the width of the orientational distribution. The spectra can again be fitted assuming a Gaussian for $P(\beta)$, equation (9), with $\bar{\beta} = 2.8 \pm 0.25°$. The agreement between observed and calculated line shapes is remarkable, again justifying the assumption of a Gaussian. Other forms of $P(\beta)$, e.g. a square function or a superposition of two Gaussians of significantly different widths, were also checked but could not be fitted as well. The axial symmetry of the orientational distribution function was also checked experimentally, by taking another rotation pattern with the draw direction as the rotation axis. No systematic angular dependence outside experimental error could be detected. This highly oriented sample, however, showed that one of the assumptions tacitly applied in our calculation had to be slightly modified. We were unable to fit the spectra shown in *Figure 7* with a single value of the quadrupole coupling constant δ, (equation (1)). Instead we had to assume that δ itself can be described by a Gaussian distribution with mean value $\bar{\delta} = (390 \pm 5).10^3$ rad s^{-1} and variance 1.2%. The spread in frequency introduced by this distribution is of the same order as the natural widths of the ^2H lines due to their dipolar coupling[22] but introduces a different angular dependence[18].

Our experimental examples show that ^2H line shapes can be analysed fully to yield the complete orientational distribution of partially ordered polymer chains. It is important to realize that all the spectra of the rotation patterns (*Figures 5* and *7*) were fitted with only two adjustable parameters, respectively. The crystalline part of linear polyethylene was chosen to test our method, because the orientational distribution can also be determined by X-ray methods[1]. In fact, our deuterated samples were also investigated by X-ray wide angle scattering[20,21]. In both cases the orientational distribution was also found to be essentially Gaussian with widths $\bar{\beta} = 15° \pm 2°$ and $3.4° \pm 0.5°$, respectively. These values are slightly higher than ours, but the deviations are within experimental error and the agreement justifies the application of ^2H n.m.r. line shape analysis to study the orientational distribution of amorphous systems, where reliable information about the complete orientational distribution function is difficult to obtain otherwise. In fact, preliminary ^2H spectra of the mobile deuterons in the amorphous regions of our drawn sample show that the order there is significantly lower, a detailed study is now underway[23].

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Note added in proof

The line shape calculations described here have recently been generalized[26] for non-axially symmetric coupling tensors as well as expansion of the orientational distribution function in terms of conical distributions.

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APPENDIX

We want to calculate the subspectra $S_{\beta'}(\omega)$ for a planar distribution of coupling tensors. This can be done[18] using the general formalism of Ref 11. For our present purpose it suffices, however, to treat $S_{\beta'}(\omega)$ in analogy to calculating the n.m.r. line shape of a powder sample described in detail elsewhere[24,25]. We first note that for $\theta=\pi/2$ the angular dependence of the frequency for the various principal directions within the planar distributions can be written:

$$\omega(\varphi)=\frac{\delta}{2}[3\sin^2\beta'-2+3\sin^2\beta'\cos 2(\varphi-\varphi_0)] \qquad \text{(A1)}$$

which reduces to:

$$\omega(\varphi)=\delta[3\cos^2(\varphi-\varphi_0)-1] \qquad \text{(A1a)}$$

for $\beta'=\pi/2$. Here φ is an angle characterizing the orientation of a given principal axis within the plane of the distribution relative to a fixed orientation φ_0. If the principal directions are uniformly distributed within the plane, the spectral intensity for a frequency interval $\omega_a\leqslant\omega\leqslant\omega_b$ can easily be calculated[24,25]

$$\int_{\omega_a}^{\omega_b} S_{\beta'}(\omega)\mathrm{d}\omega=\frac{1}{2\pi}\int_{\varphi_a}^{\varphi_b}\mathrm{d}\varphi, \qquad \text{(A2)}$$

$$-1\leqslant\omega_a<\omega_b\leqslant 3\sin^2\beta'-1$$

By taking the derivative $\mathrm{d}\omega/\mathrm{d}\varphi$ and eliminating the terms depending on $(\varphi-\varphi_0)$ through (A1) we obtain:

$$\begin{aligned}\frac{\mathrm{d}\omega}{\mathrm{d}\varphi}&=-3\delta\sin^2\beta'\sin 2(\varphi-\varphi_0)\\&=-\delta\sqrt{\left(\frac{\omega}{\delta}+1\right)\left(3\sin^2\beta'-1-\frac{\omega}{\delta}\right)}\end{aligned} \qquad \text{(A3)}$$

and

$$\int_{\omega_a}^{\omega_b} S_{\beta'}(\omega)\mathrm{d}\omega=\frac{1}{\pi}\int_{\omega_a}^{\omega_b}\frac{\mathrm{d}\omega}{\delta\sqrt{\left(\frac{\omega}{\delta}+1\right)\left(3\sin^2\beta'-1-\frac{\omega}{\delta}\right)}} \qquad \text{(A4)}$$

yielding equation (5).