Structure of amorphous polyethylene from n.m.r. line shape analysis and MAR-n.m.r.

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Based on results of proton nuclear magnetic resonance measurements with magic angle rotation (*MAR* n.m.r.), the line of amorphous polyethylene in conventionally measured proton n.m.r. spectra is described as a convolution of a basic narrow line-shape function $S(\nu)$ with an orientation-dependent dipolar broadening function $G(\nu)$. With this approach it is possible to describe the broadline n.m.r. spectrum of polyethylene as a superposition of the crystalline component and of a single amorphous phase. The fit of experimental and computed spectra, and the parameters obtained by this type of line-shape analysis are discussed for a series of polyethylene samples of different crystallinity.

INTRODUCTION

The problem of structure and dynamics in the crystalline and amorphous phases of linear polyethylene (PE) has been the subject of much discussion in papers on nuclear magnetic resonance (n.m.r.) spectra of solid polymers[1-8], but the picture obtained so far is by no means final. One of the basic and as yet unsolved problems is the question of the relation between the line shape in n.m.r. spectra of solid PE and the structure and dynamics of the spin system in the solid phase. Analysis of the temperature dependence of this line shape indicated the presence of two amorphous phases: one, corresponding to the narrow n.m.r. line component, with internal motion of microBrownian character, and the other, corresponding to the intermediate n.m.r. line component, with internal motion characterized roughly as hindered rotation of CH_2-groups. A structural distinction between these two amorphous phases remains unclear.

Several years ago we found[9] that the line component corresponding to amorphous polymer in broadline (*BL*) n.m.r. spectra of PE undergoes narrowing by magic angle spinning (*MAR* n.m.r.). This proved the presence of essentially static ($\tau_c > 10^{-3}$ s) residual dipolar interactions in the amorphous phase of PE. As in the measured *MAR* n.m.r. spectra the residual width of the central line was smaller than that of the sidebands, line-shape analysis by means of stochastic theory seemed to confirm previous assumptions about the presence of at least two distinct phases in amorphous PE.

In recent communications from this laboratory[10,11] it has been shown that in most systems with proton n.m.r. lines much narrower than the rigid lattice line width, in which further line narrowing can be achieved by magic angle spinning, the interpretation of line shapes in conventionally measured n.m.r. spectra must involve an orientation-dependent residual dipolar broadening function leading to the appearance of a more or less pronounced 'super-Lorentzian' (*SL*) line form. In the present paper we have attempted to analyse the proton n.m.r. line component corresponding to amorphous PE in terms of this model.

EXPERIMENTAL

All studied samples (Lupolen BASF) as well as the measurement of their *BL* and *MAR* n.m.r. spectra were described in our previous communication[9]. The basic characteristics of the studied samples are summarized in *Table 1*. For line-shape fitting, the *BL* n.m.r. spectra were remeasured on the Varian WL–109 spectrometer at 35 MHz (*Figure 1*) with modulation amplitudes 0.2 G (samples 3020D, 3010S, 5261Z) and 0.3G (sample 6011L). The degree of branching was estimated from the relative areas of the CH_3 and CH_2 peaks in high-resolution (*HR*) ^1H n.m.r. spectra at 100 MHz (PS-100 Jeol) and characterized as the number of CH_3 groups per 100 CH_2 groups.

METHOD OF LINE-SHAPE ANALYSIS

In n.m.r. spectra *SL* line shapes, characterized by very sharp peaks and very broad wings, are exhibited by systems undergoing rapid internal motions which are subjected to space restrictions[12]. If for the interacting spin system there exists a direction in which the dipolar interactions are not averaged to zero by rapid internal motions, and if these directions in the sample are randomly distributed in space, then the line-shape function can be described[10] as a convolution of a basic Lorentzian function S related to the rapid internal motions with a dipolar broadening function G:

$$L(\nu - \nu_0) = \int_0^{1+\infty} \int_{-\infty}^{+\infty} \left[S(\nu - \nu_1) G \left(\frac{(\nu_1 - \nu_0)}{|3\cos^2\theta - 1|} \right) \right]$$

$$|3\cos^2\theta - 1| \, d\nu_1 \, d\cos\theta \qquad (1)$$

where θ is the angle between the specified direction and the direction of the static magnetic field H_0. The shape of the G function is generally unknown. It has been shown in our

previous paper[10] that the line-shape function L differs little for Gaussian or Lorentzian shape of the function G, and the difference can only be detected in the wings. For Lorentzian shape of the function G, a simple explicit expression has been derived for L:

$$L(\nu - \nu_0) = \int_0^1 \frac{A\,|3\cos^2\theta - 1| + B}{\pi[(\nu - \nu_0)^2 + (A\,|3\cos^2\theta - 1| + B)^2]}\, d\cos\theta$$

(2)

where $2B$ is the width at medium height of the limiting line shape at $\theta = 54.7°$ (pure function S at the magic angle condition), and $2A$ is the width at medium height of the dipolar broadening function G for $\theta = 90°$. In the sense of a model introduced independently by Gotlib *et al.* (ref 13, *Figure 2*) it is assumed that the value of the parameter B is related to the effective correlation time of rapid segmental motions responsible for the major line narrowing from the rigid lattice width to the value observed in the conventionally measured n.m.r. spectrum, and that the parameter A is a measure of the correlation between the direction of the interproton vector and the specified direction, and therefore it is a measure of space restrictions upon segmental motion.

As the wings of the line of the amorphous component in n.m.r. spectra of solid PE are always obscured by the broad line of the crystalline phase, the true shape of the function
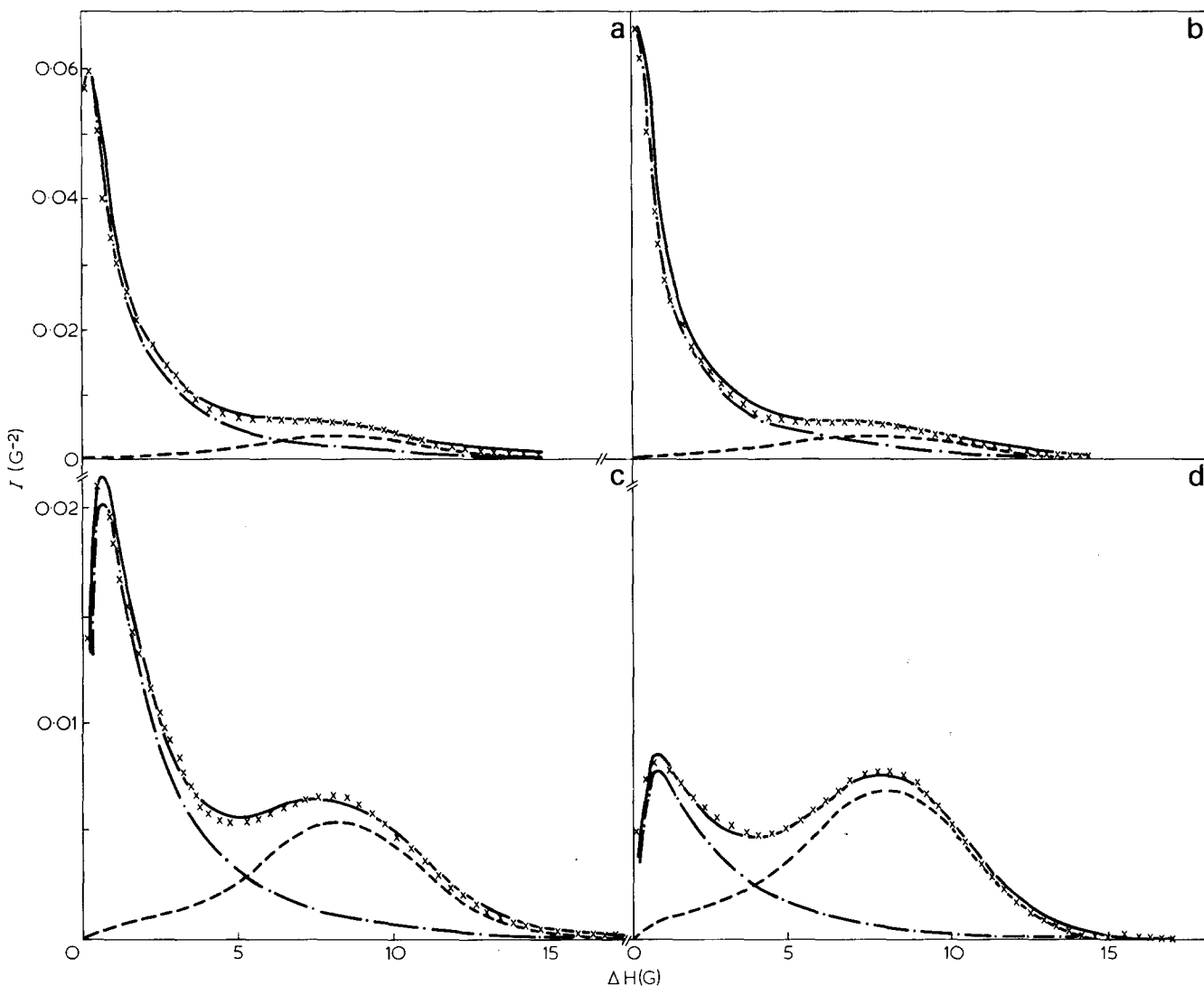
Table 1 Characteristics of polyethylene samples

Sample	Density (g/cm³)	Branches[a]	Crystallinity (%)		MAR[d]
			C_d[b]	IR[c]	$\delta H_{lim}(G)$
3020D	0.929	4.5	49.0	43.7	0.21
3010S	0.930	4	49.8	43.7	0.22
5261Z	0.953	<2	67.1	66.6	0.23
6011L	0.962	<2	73.7	79.8	0.29

a Number of CH_3 groups per 100 of CH_2 groups, from ^1H n.m.r. spectra

b $C_d = 100(V_a - d^{-1})/(V_a - V_c)$, with V_a = 1.15 and V_c = 1.00; d is density; V_a and V_c are the specific volumes of amorphous and crystalline phase, respectively.

c Determined from the pair of infrared bands at 1300 and 1890 cm⁻¹ according to ref 16

d One half of width at medium height, measured for sidebands in MAR n.m.r.

Figure 1   35 MHz broadline n.m.r. spectra of polyethylene samples at room temperature. (a) 3020D; (b) 3010S; (c) 5261Z; (d) 6011L; xxx, experimental; ———, calculated total line shape; — — —, crystalline component; —·—·—·—·—·, amorphous component. The scales of the spectra have been normalized to unit total band intensity (after double integration of both halves of the derivative curves)

Table 2 Results of line-shape analysis of polyethylene samples*

Sample	Bergmann[2,a]				Preidel *et al.*[14,b]			
	$A(G)$	$B(G)$	$C(\%)^c$	$\Delta^d \times 10^4 (G^{-2})$	$A(G)$	$B(G)$	$C(\%)^c$	$\Delta^d \times 10^4 (G^{-2})$
3020D	3.32	0.298	34.1	4.25	3.18	0.298	35.6	4.53
3010S	3.56	0.249	34.7	4.03	3.38	0.249	36.6	4.18
5261Z	3.26	0.572	58.0	2.68	2.84	0.576	61.7	3.12
6011L	3.87	0.752	75.2	1.98	2.68	0.752	81.7	2.15

* Improved by multiplying the width of the Bergmann shape by 1.022 and the Preidel shape by 1.052
a Width of the crystalline component multiplied by the factor 1.022
b Width of the crystalline component multiplied by the factor 1.052
c Contents of immobile ('crystalline') component
d $\Delta = [(\Sigma\delta^2)/n]^{1/2}$

G could not be found experimentally. For the sake of simplicity, equation (2) was applied as first approximation in the following line-shape analysis. Based on this equation, a programme was devised which for given values of the parameters A and B of equation (2) and for a given shape of the n.m.r. band of the crystalline component permits calculation, by least squares adjustment to experimental line shape, of the relative amounts of the crystalline and amorphous phases and of the sum of square deviations of intensities, $\Sigma\delta^2$. By stepwise variation of A and B, values of the parameters A and B and of crystallinity corresponding to the minimum of $\Sigma\delta^2$ are found. The calculation was performed in n steps of 0.2 G; the δ values are based on intensity units as defined in *Figure 1*.

RESULTS

Our first attempts at line-shape fitting with the crystalline component approximated by Gaussian shape of width at medium height 14.2 G and by a doublet of Gaussians (spacing 7.33 G, width at medium height 8.08 G) gave a rather poor fit. Much better fits were obtained with the shapes proposed by Bergmann[2] and by Preidel *et al.*[14]; these could be further improved by a very small adjustment of the width scale, and the results of this analysis are summarized in *Table 2*. The fit of experimental line shapes with those calculated by the described procedure using the Bergmann shape of the crystalline component is demonstrated in *Figure 1*. Small discrepancies occur only in the vicinity of the peaks where the true line shape is likely to be distorted by the measuring technique, and far in the wings where the overall shape is strongly affected by the choice of the shape of the crystalline component. The general agreement for all studied samples is very good, indicating that the Lorentzian approximation of the dipolar broadening function G is adequate for the case studied. The obtained values of the parameter A remain roughly constant in the measured series. The contents of the immobile phase resulting from our line-shape adjustment procedure are included in *Table 2* and are seen to fall reasonably in line with crystallinity values obtained by other independent methods.

An important result emerges from the success of the line-shape fitting procedure based on equations (1) and (2): It can be concluded that by introducing an orientation-dependent residual dipolar broadening function, it is possible to describe the n.m.r. line shapes of PE samples in a broad crystallinity range with the assumption of the presence of only a single amorphous phase.

DISCUSSION

In the described n.m.r. line-shape analysis, two basic assumptions have been made without actual experimental verification: one of these concerns the shape of the dipolar broadening function G, the other the shape of the n.m.r. line of the crystalline component. Minor modifications of the function G are likely to affect somewhat the resulting parameters (A, B and % of immobile phase) particularly in samples of low crystalline contents. Modifications of the crystalline line shape should be more perceptible in the more highly crystalline samples, and this is clearly demonstrated in *Table 2*.

In the present work, two crystalline line shapes were taken from the literature[2,14] and only their width scales were adjusted to optimum fit of overall line shape. However, the present results suggest that it should be possible to adjust also the shape of the line of the crystalline phase so as to yield crystallinity values nearer to those obtained by other methods. The question remains, which are the 'ideal crystallinity values' to be used in such a procedure. It has to be kept in mind that changes of crystallinity in the studied series are a consequence of different chemical composition of the samples: 3020D and 3010S are typical high pressure PE samples, which are known to contain several ethyl and butyl branches per 100 carbon atoms, whereas sample 6011L is a typical low pressure PE, in which the number of branches is lower by an order of magnitude and, as indicated by ^{13}C n.m.r., mainly methyl branches are present[15]. In comparing the obtained 'crystallinity' values with the results of other methods, the specificities of each method have to be kept in mind. Thus values obtained by the infrared spectral method[16] are indicative of the contents of long sequences of units in trans conformation; this should correspond to the contents of crystallizable matter, but it is conceivable that the content of actually immobilized matter which is indicated by n.m.r. may be slightly lower. Crystallinity values calculated from density are extremely sensitive to the limiting crystalline and amorphous densities used in the calculation. As it is known from recent studies[17] that the ethyl and butyl branches of high pressure PE do not enter the crystalline regions, the density of the crystalline phase may be assumed to be constant in the series studied. However, the density of the amorphous phase might vary considerably, and this could be the reason of the differences between crystallinity values determined from density and those determined by the spectroscopic methods. As a precise determination of crystallinity has not been the primary objective of this work,

the crystalline line-shape adjustment procedure has not been attempted at the present stage.

Previous n.m.r. line-shape analyses working with the concept of a single amorphous phase (e.g. ref 1) yielded for low density PE samples ($d \sim 0.93$) crystallinity values around 72%. The success of the procedures based on the concept of two amorphous phases demonstrated the fact that the n.m.r. line component corresponding to amorphous PE cannot be described by a single line of Lorentzian or Gaussian shape, and the introduction of two lines widely differing in shape was the simplest approach to a fit of experimental data, even though the corresponding theoretical interpretation was not quite straightforward. The application of the orientation-dependent dipolar broadening function used in this paper is a necessary consequence of the experimentally observed line-narrowing effect of *MAR* n.m.r. measurements, and it is seen to lead to a very simple interpretation of the n.m.r. line shape, without any assumptions about the existence of several distinct amorphous phases in solid PE.

The necessity of considering two distinct amorphous phases in our previous analysis of *MAR* n.m.r. spectra of solid PE[9] was caused by neglecting the very pronounced contribution even of small amounts of branches to the shape of the central line in *MAR* n.m.r. spectra. Therefore in this paper, *MAR* n.m.r. residual line widths were determined from sidebands and can be regarded as characteristic of the polymer chain itself. From its definition, the value of the parameter *B* should be near to the limiting line width measured in a *MAR* n.m.r. spectrum. The values of the parameter *B* in *Table 2* are in all cases much higher than the *MAR* n.m.r. line width, and this is evidently mainly due to shape distortions in the line peak caused by the high modulation amplitudes necessary for adequate S/N values. In this situation it would be futile to attach any physical meaning to parameters *B* obtained by line-shape adjustment, and it is better to use the *MAR* n.m.r. values for characterization of segmental motions. From the δH *(MAR)* values in *Table 1* it is evident that the effective correlation time of rapid segmental motions in the amorphous phase of PE is only weakly affected by changes of crystallinity.

The values of the parameter *A* should not be greatly affected by distortion of the limiting line shape *S* and are supposed to be physically significant. The optimum fit *A* values (calculated with the Bergmann[2] shape) in *Table 2* may be regarded as practically constant in the measured series. From

this analysis it may therefore be concluded that the character of the amorphous phase of PE is largely independent of the degree of crystallinity. The small change of the *MAR* n.m.r. line width may reflect a small change in the distribution of correlation times of rapid segmental motions, whereas the space restrictions upon these motions remain practically unchanged. It seems that these restrictions are not connected with the size and distribution of crystalline domains, but rather that they are inherent to the solid amorphous phase itself.

Our interpretation does not exclude the existence of a certain distribution of geometric and dynamic characteristics of the amorphous phase. It is assumed that such a distribution, if present, is reflected in the form of the function *G*. A detailed investigation of this problem, together with a more precise determination of the line shape of the crystalline component for PE samples of controlled chemical structure and crystallinity, will be the subject of our further studies.

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