Application of wide line nuclear magnetic resonance to the determination of the crystallinities of isotropic polyethylenes

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The validity of methods of decomposition of wide line n.m.r. spectra of polymers into constituent lines associated with distinct phases of polymer material of different molecular mobilities is discussed, and it is pointed out that the assumption of more lines than are clearly resolved in a spectrum can lead to an unrealistic decomposition of the line. In general the spectra of isotropic specimens at temperatures above the glass transition show two partly resolved lines. It is shown here that the line shape of the rigid material at 6K and the broad component of the composite line at room temperature is closely approximated by a Gaussian doublet for which the ratio of the square of the second moment to the fourth moment agrees well with the corresponding theoretical value calculated for an isotropic assembly of polyethylene crystals. The decomposition of the experimental lines by this method leads to values of crystallinities in good agreement with those from density measurements for a wide range of crystallinities.

INTRODUCTION

The application of broad line nuclear magnetic resonance measurements to the determination of the fractions of crystalline and non-crystalline phases present in polymer samples has been developed by a number of workers[1–13] since attention was first drawn to the possibility in 1953 by Wilson and Pake[1], who observed that the spectra of polyethylene and polytetrafluorethylene each showed two components at temperatures just above 0°C. The spectra were each decomposed into two components in a rather arbitrary manner, the broad and narrow components being associated with the nuclei in the crystalline and non-crystalline regions, respectively. The justification for this distinction is based on the motional narrowing which occurs for nuclei in sufficiently rapid motion to reduce considerably the average broadening effect of the magnetic dipole interactions between the nuclei. The decompositions of Wilson and Pake[1] led to estimates of the crystallinity of the polymers which were in general agreement with estimates from other sources.

In 1959 Hyndman and Origlio[14] reported the observation of three component lines in the n.m.r. spectra of fibres of polyethylene and polypropylene. They referred to the additional line observed as being intermediate in width between the two lines observed by Wilson and Pake[1], although a comparison of the results of the two workers shows that the drawing process leads to the emergence of a narrow line arising from a small fraction of the non-crystalline material, the bulk of which is responsible for the intermediate line which is slightly broadened on drawing. It is assumed that the broadest line is due to crystalline material with a line shape corresponding to practically immobile hydrogen nuclei while the narrow line is attributed to material of liquid-like mobility. The intermediate line is then considered to arise from the non-crystalline material with limited mobility such as hindered rotation of the methylene protons about C–C bonds. A similar three component line structure was observed by Fischer and Peterlin[15] in assemblies of solution-crystallized single crystals of low density polyethylene swollen by tetrachloroethylene.

Bergmann and Nawotki[3] proposed that the spectra of unoriented linear polyethylenes in general also consisted of three superimposed lines of different width although the narrow and intermediate lines were not separately resolved in observed spectra. In order to analyse them they chose particular forms for the individual line shapes, as follows. For the immobile (crystalline) material they measured the spectrum of a specimen of linear polyethylene of 96% crystallinity at −100°C and corrected the observed shape for the increased lattice spacing at room temperature. For the intermediate line the shape function of Gutowsky and Pake[16] calculated for an isotropic assembly of proton pairs undergoing hindered rotation about the line joining them and broadened by convolution with a Gaussian function, was assumed. The narrowest component was taken to be of Lorentzian shape. Bergmann and Nawotki[3,5,8,9] have developed and discussed their method extensively in a number of papers, considering the effect of overmodulation and the use of a Gaussian–Lorentzian line shape for the intermediate line. A recent paper by Kitamaru, Horii and Hyon[13] has also made use of the same technique.

Another attempt to decompose the three-line spectrum of oriented polyethylenes was that of Loboda–Čačkovič *et al.*[4] who used a somewhat arbitrary method similar to that of Wilson and Pake[1]. The broadest component was first estimated and deducted from the spectrum and the remainder was then decomposed into intermediate and narrow lines. This work produced the rather implausible result that the derivative spectrum of the crystalline component fell to zero

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at about 5 gauss from the centre of the composite line and remained at zero to the corresponding position 5 gauss on the other side of the centre. This work was further extended to the use of four lines by the same group of workers[10]. A four line decomposition of the spectrum of oriented polyethylene was also carried out by Fischer *et al.*[7] using the more justifiable method of Bergmann and Nawotki[5].

A recent paper by Smith, Manuel and Ward[11] considered the decomposition of the spectra of highly oriented polyethylene for which it was not possible to obtain a standard spectrum of known high crystallinity for the shape of the broad component. An approximate theoretical calculation of the line shape showed evidence of a resolved doublet structure for the spectrum of oriented material and such a line shape was used in the analysis to determine the orientation distribution of the non-crystalline phase of ultra-highly oriented polyethylene samples. No attempt was made to decompose the parts of the spectra arising from the non-crystalline material into its narrow and intermediate components, as the contribution of the former was very small and made an insignificant contribution to the second moment which was used to determine the anisotropy of the non-crystalline material. It was also felt that no sound basis existed for assuming a particular line shape amenable to computation, since the non-crystalline material is of great complexity and must contain material with many different forms and degrees of motion and conformations, and consequently the line shape is built up of a continuous distribution of lines of various widths with no clearly definable shape. This is indicated by the changes which take place in the shape of the intermediate and narrow lines on annealing or drawing but which are less noticeable for the broad line arising from the better-defined crystalline phase. It should be pointed out that the usual presentation of derivative n.m.r. spectra on an arbitrary vertical scale can be misleading for the comparison of spectra. This is illustrated by the normalized spectra shown in ref 11, particularly in *Figure 3*.

The assumption that the n.m.r. spectrum of a polymer may be represented by 3 or 4 lines with the corresponding use of at least 5 or 7 adjustable parameters, respectively, can lead to better reproduction of the experimentally observed line, but if the number of lines assumed are not clearly resolved the parameters obtained from the decompositon are not susceptible to satisfactory interpretation. The unsatisfactory nature of the use of three lines to fit experimental curves when only two are clearly resolved is illustrated by the work of Kitamaru, Horii and Hyon[13] on isotropic polyethylene. They studied 15 specimens with molecular weights varying from $\bar{M}_\eta = 618$ for n-$C_{44}H_{90}$ to a sample with $\bar{M}_\eta = 3.4 \times 10^6$. In the five samples of lowest molecular weight up to $\bar{M}_\eta = 31\,800$, a narrow line is clearly visible in the derivative spectrum and the three line fitting procedure leads to a mass fraction of between 0.001 and 0.002, corresponding to the narrow line. The remaining 10 samples do not show an observable narrow line in the experimental derivative spectra but the results of three line fitting give estimated mass fractions of the material corresponding to the narrow line varying from 0.016 for $\bar{M}_\eta = 44\,900$ to 0.187 for $\bar{M}_\eta = 3.4 \times 10^6$. The sudden increase of the apparent mass fraction from 0.002 to 0.016 on going from $\bar{M}_\eta = 31\,800$ to 44 900 is clearly due to the inappropriate use of three lines to fit the curves when only two are clearly visible, and the high mass fractions of highly mobile material assumed for these specimens must be doubtful. The mass fractions of 0.001 to 0.002 derived for specimens for which a narrow line is clearly visible in the n.m.r. spectrum may be attributed to highly mobile hydrogen nuclei such as those in the methyl groups at chain ends. For example, the methyl groups at the ends of a chain of molecular weight 31 800 account for a fraction 0.0013 of the hydrogen nuclei in the chain. The bulk of the material consists of the traditional crystalline and amorphous fractions, of which the crystalline material may be regarded as a fairly well-defined phase whereas the amorphous material contains a wide range of environments for the hydrogen nuclei with a corresponding wide range of mobilities and contributions to the n.m.r. line. The contribution of the crystalline material to the n.m.r. line shape may be assumed to be fairly well-defined. However, the range and distributions of the environments of the hydrogen nuclei in the non-crystalline fraction is likely to be strongly dependent on the nature of the starting material and its preparation and treatment with the consequence that there is no consistent line shape function for amorphous material, applicable to all samples. For this reason we do not feel that there is any justification for assuming a particular line shape function for the part of the spectrum due to non-crystalline material, for example, the separation of this part of the spectrum into a Lorentzian line and a Gaussian broadened doublet. In particular the assumption of a Lorentzian shape for the narrowest component leads to values of line width of the order of 0.5 gauss which is much greater than would be expected on the basis of lifetime broadening for which a Lorentzian line would be appropriate, and being of the same order of magnitude as the amplitude of magnetic field modulation used experimentally is not likely to be a representation of the true line shape.

The contribution of the crystalline fraction to the n.m.r. absorption spectrum should, however, have the same shape irrespective of the history of the specimen because of the well-defined nature of the crystalline phase. The simplest approach to an approximation to this line shape is to look upon the hydrogen nuclei as an assembly of methylene pairs of protons. The intra-pair dipolar interaction of these methylene protons is much larger than the individual interactions of a proton on one pair with the protons on the other pairs so that the line shape contribution of a pair of methylene protons may be considered as a doublet broadened by the inter-pair dipolar interactions. This supposition is supported by the approximate theoretical calculation of Smith, Manuel and Ward for highly oriented polyethylene already cited (ref 11).

Polycrystalline material consists of a randomly oriented assembly of crystallites contributing overlapping pairs of broadened doublets and the random nature of the distribution of broadening and overlapping of the individual doublets suggests the use of a Gaussian broadened doublet to represent the composite spectrum of polycrystalline material.

In this paper we show that by fitting the outer part of the n.m.r. spectrum arising from the rigid fraction of the material to a Gaussian broadened doublet, taking account of the fact that the fitted curve should have second and fourth moments corresponding to the theoretical values which may be calculated from the crystal structure of polyethylene, values of crystallinity in close agreement with those derived from density measurements are obtained. In practice we use the ratio of the square of the second moment (M_2^2) to the fourth moment (M_4) calculated from the crystal structure of polyethylene using the theory of Van Vleck[17]. Since the second moment calculation involves the sixth powers of the interproton separations and the fourth moment calculation products with sums of exponents

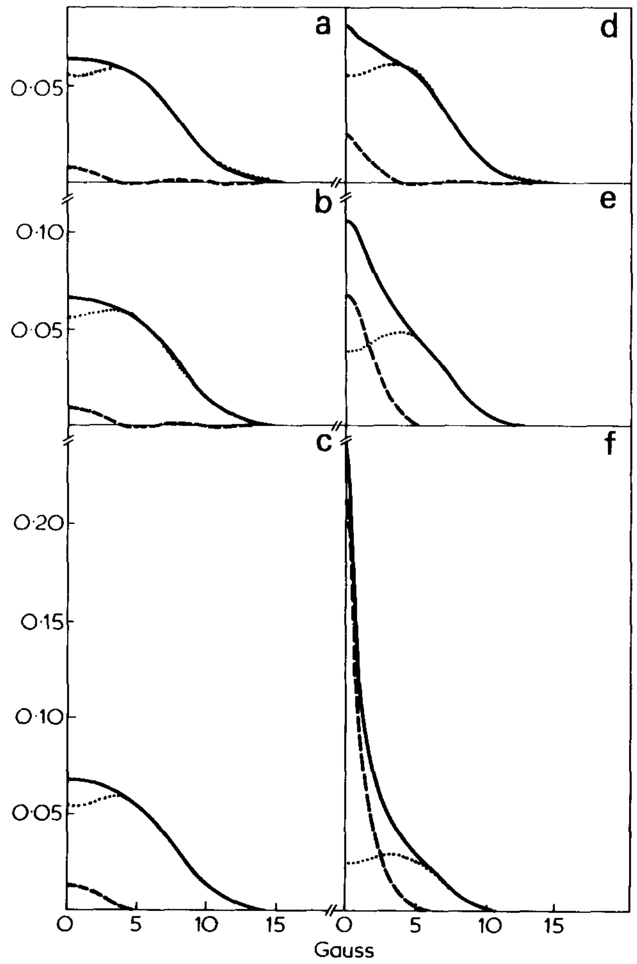

Figure 1 Nuclear magnetic resonance absorption lines and their decomposition into crystalline and amorphous components assuming a Gaussian doublet form for the crystalline component. ———, Experimental spectrum; ········, Gaussian doublet corresponding to crystalline fraction; — — — — —, residual line due to amorphous material. (a), (b), (c) at 6K: (a) R 075-60 crystallized under high pressure; (b) R50; (c) WNF 15. (d), (e), (f) at 293K: (d) R 075-60; (e) R 50; (f) WNF 15. The experimental curves are all normalized to unit integrated intensity. Only half the symmetrical spectra are shown

amounting to the twelfth powers they are both highly sensitive to the bond lengths assumed in the polyethylene structure. The ratio M_2^2/M_4, however, is much less sensitive to the assumed bond lengths since the interproton distances occurring in the ratio are raised to the same overall power. This criterion provides the best theoretical justification for the assumed line shape in the absence of a solution to the problem of the calculation of the exact line shape.

EXPERIMENTAL

N.m.r. measurements

Three specimens of widely differing degrees of crystallinity were chosen:

(1) ICI low density polyethylene grade WNF15 with a low crystallinity of about 0.50 due to its branched character;

(2) BP Chemicals high density polyethylene grade Rigidex 50 prepared by quenching from 160°C into water at room temperature, to obtain a crystallinity of about 0.70 as shown by earlier work in this department[18];

(3) BP Chemicals high density polyethylene grade Rigidex 075-60 crystallized by cooling slowly from the melting point (251°C) at a pressure of 5.2 kbar to give the highest crystallinity.

Measurements were made on all three specimens at 6K and 30 MHz using the Q-meter spectrometer and cryostat described by Davenport and Manuel[19], and at 293K (20°C) using a similar Q-meter spectrometer operating at 60 MHz. A magnetic field modulation amplitude of 0.5 gauss was chosen after a study of the effect of modulation amplitude on the broadening of a Gaussian doublet spectrum by computing the derivative line shapes to be expected for different modulation amplitudes using the theoretical expression

$$f(h) = A \sum_{k=0}^{\infty} \frac{h_m^{2k+1}}{2^{2k}k!(k+1)!} \frac{\mathrm{d}^{2k+1}g(h)}{\mathrm{d}h^{2k+1}} \qquad (1)$$

derived by Andrew[20], in which $f(h)$ is the observed derivative of the true absorption curve $g(h)$ after phase-sensitive detection. h_m is the modulation amplitude and A is a constant. For lines of the widths observed by us a modulation amplitude of 0.5 gauss produced negligible distortion. Radio frequency power levels were chosen to be well below those producing saturation by making preliminary measurements at different power levels at all temperatures.

In the early experiments on Rigidex 50 the derivative n.m.r. signals were coded in digital form onto punched paper tape for computer manipulation. Each spectrum was recorded several times and the results compared for consistency, and then computer averaged. For the remaining measurements a signal averager became available. Using the signal averager the signals from either 32 or 64 sweeps were added and the average spectrum input to the main computer store. This was repeated 3 or 4 times to compare the averaged spectra for consistency before adding them together in the main computer to give the final results. The computer processing produced normalized absorption curves as shown in *Figure 1*.

The magnetic field sweep was calibrated using the sidebands produced by low frequency modulation of the spectrometer oscillator with the narrow line from liquid glycerine using narrow modulation. The signals were recorded digitally onto paper tape in the same way as for the polymer spectra and the field interval between recorded points computed. The average field interval at which the signal height was recorded was about 0.05 gauss. The modulation amplitude was also calibrated by measuring the separation of the maximum and minimum of the derivative signal of the overmodulated line of a glycerine sample.

Density measurements and crystallinity

The mass fraction of crystalline material in a sample of polymer, f_m, may be estimated from a measurement of its density, ρ, knowing the densities ρ_c and ρ_a of fully crystalline and amorphous materials using the expression

$$f_m = \frac{\rho_c}{\rho} \frac{(\rho - \rho_a)}{(\rho_c - \rho_c)} \qquad (2)$$

The accuracy to which f_m can be estimated is highly sensitive to the accuracies with which ρ_c and ρ_a are known, as well as the accuracy to which the specimen density ρ is measured. The greatest uncertainty is in the knowledge of the density of the amorphous material (ρ_a), which has been estimated between 0.855 and 0.870 g cm^{-3} [21]. Since in the expression for f_m the differences $\rho - \rho_a$ and $\rho_c - \rho_a$ occur,

Table 1 Results of Gaussian doublet fitting to broad component of n.m.r. absorption spectra for different specimens of polyethylene at 6K and 293K

Sample	Temperature (K)	Figure No.	a_1	a_2	a_3	M_2	$\frac{M_2^2}{M_4}$	f_m (n.m.r.)	$f_m (\rho)$
R 075-60	6	1a	0.054	4.17	3.59	30.3	0.427	0.97	–
R 50	6	1b	0.055	4.05	3.50	28.6	0.427	0.97	–
WNF 15	6	1c	0.054	4.06	3.47	28.5	0.429	0.94	–
R 075-60	293	1d	0.056	3.81	3.33	25.6	0.424	0.94	0.93–0.94
R 50	293	1e	0.048	3.88	3.06	24.4	0.447	0.74	0.67–0.71
WNF 15	293	1f	0.035	3.42	2.97	20.5	0.426	0.52	0.46–0.52

small errors in ρ_a, ρ_c and ρ lead to much larger errors in f_m, although the errors in the numerator and denominator of equation (2) cancel to some extent. This cancellation is most effective for highly crystalline material, the accuracy of the value of f_m derived from (2) decreasing rapidly as the crystalline fraction decreases.

The value of ρ_c can be obtained from X-ray diffraction measurements of the lattice parameters, but there are significant discrepancies among the work of different authors, partly due to measurements at different temperatures, and it is important to correct the densities calculated from X-ray diffraction to the temperature at which the specimen densities have been measured. For linear polyethylene we have used the lattice parameters of Zugenmaier and Cantow[22] ($a = 7.418 \pm 0.001$ Å, $b = 4.945 \pm 0.001$ Å, $c = 2.545 \pm 0.001$ Å) measured at 25°C. Combining these results with the standard relative atomic masses of H(1.00797) and C(12.01115) based on $^{12}C = 12.00000$ and using the Unified Atomic Mass Unit of 1.66043×10^{-27} kg we find the density of crystalline linear polyethylene at 25°C to be 0.9979 ± 0.0008 g cm^{-3} at 25°C. The density gradient column used in our laboratory is standardized at 23°C for which, using a volume thermal expansion coefficient of 3×10^{-4} °C^{-1} the corresponding crystalline density of linear polyethylene is 0.9985 ± 0.0008 g cm^{-3}. To estimate the crystalline density of the low density (branched) polyethylene WNF 15 we used the data of Cole and Holmes[23] on the increase of the crystalline lattice parameters for branched material made by ICI similar to the WNF 15. This gave a value of 0.9791 g cm^{-3}. Using these values and both the extreme values of the density of amorphous material $\rho_c = 0.855$ and $\rho_c = 0.870$ we have calculated the range of the corresponding values of the crystalline fractions f_m. These are shown in *Table 1*. It is clear that for material of low crystallinity the uncertainty in ρ_a leads to large uncertainties in f_m.

COMPUTATIONAL PROCEDURES

Fitting of the Gaussian broadened doublet

The Gaussian doublet line shape may be defined as:

$$Y(\Delta H) = a_1 \left\{ \exp\left[-\frac{(\Delta H - a_2)^2}{2a_3^2} \right] + \exp\left[-\frac{(\Delta H + a_2)^2}{2a_3^2} \right] \right\} \tag{3}$$

It consists of the superposition of two identical Gaussian line shapes whose individual second moments about their centres are a_3^2, separated by a field interval $2a_2$. The variable $\Delta H = H - H_0$ where H_0 is the magnetic field at the centre of the doublet. The area under the curve can easily be shown to be $(8\pi)^{1/2}a_1a_3$ and the second and fourth moments are $\langle \Delta H^2 \rangle = a_2^2 + a_3^2$ and $\langle \Delta H^4 \rangle = a_2^4 + 3a_3^4 + 6a_2^2a_3^2$. This line shape was fitted to the outer part of the experimental lines with a_1, a_2 and a_3 as adjustable parameters, using a least squares procedure with parabolic extrapolation described by Bevington[24] by minimizing the sum:

$$\chi^2 = \sum_i \frac{[A_i - Y(\Delta H_i)]^2}{\sigma_i^2} \tag{4}$$

in which A_i is the experimental value of the absorption at the ith point and $Y(\Delta H_i)$ the corresponding value of the Gaussian doublet function. One can consider χ^2 as a function of the parameters a_1, a_2 and a_3 of the Gaussian doublet function represented by a 3-dimensional hypersurface which must be searched for a minimum. One of the difficulties is that there may be several local minima for χ^2 among which we require the global minimum. To begin the search, initial values of a_1, a_2 and a_3 must be chosen and the minimum found will depend on this initial choice. It was therefore necessary to vary the initial values of a_1, a_2 and a_3 used to find the global minimum in χ^2. The choice of initial values of a_2 and a_3 was made by calculating the value of a_2 appropriate to a pair of protons in a CH$_2$ group and then deriving a_3 from the theoretical second moment for isotropic crystalline polyethylene using $\langle \Delta H^2 \rangle = a_2^2 + a_3^2$. With these two parameters chosen, an initial value of a_1 could then easily be estimated. A range of initial values of the a_n was used to determine the best overall fit of the outer part of the n.m.r. absorption spectrum using different ranges of the outer part of the line. It was found that as the lower limit at which fitting started was increased to 5 gauss the goodness of fit increased but little change occurred on increasing the lower limit above 5 gauss. The Gaussian doublets fitted over the range 5 to 18 gauss are the optima since less information is used if the lower limit is increased above 5 gauss. Confirmation of the satisfactory nature of the fitting procedure was obtained by examining the ratios of the squares of the second moment to the fourth moments for the Gaussian doublets fitted. These are shown in *Table 1* and all are close to the theoretical value of 0.43 calculated below for isotropic samples of crystalline polyethylene.

Calculation of the moments of the n.m.r. absorption line for isotropic samples of crystalline polyethylene

Theoretical calculations of the moments of the n.m.r. absorption lines for polyethylene require a knowledge of the hydrogen positions in the crystalline lattice, which have not been determined directly. They may be calculated from the positions of the carbon atoms in the unit cell measured by X-ray diffraction, together with a knowledge of the bond angles and CH bond lengths on the polyethylene chain. The choice of bond length has a significant effect on the values obtained for the moments since the H–H separation in the methylene pairs is by far the smallest and makes the largest individual contribution to the moment. Values of CH bond length are not known accurately for polyethylene and it is possible to justify values in the range 1.07 to 1.094 Å [25–27]. Using these CH bond lengths and the lattice parameters of Bunn[28] at room temperature the values of second moment for an isotropic crystalline specimen calculated from the Van Vleck formula[17] are 28.1 gauss^2 and 26.5 gauss^2 for CH bond lengths of 1.07 Å and 1.094 Å, respectively, using an H–C–H bond angle of 109°28′. At low temperatures the theoretical second moments are greater due to contraction of the lattice. The lowest temperature at which lattice parameters have been measured is −196°C [29] from which the corresponding calculated second moments are 29.3 gauss^2 and 27.7 gauss^2 for the two CH bond lengths used.

Because of the uncertainty in the calculated second moment it is not by itself a good guide to the validity of our Gaussian doublet fitting procedure. However, the ratio of the square of the second moment to the fourth moment, M_2^2/M_4 will be much less sensitive to the choice of CH bond length since they are dependent on the same powers of the internuclear distances in the specimen. We have calculated the fourth moment for isotropic crystalline polyethylene using Bunn's[28] lattice parameters and a CH bond length of 1.094 giving a value of 1621 gauss^4 and a ratio M_2^2/M_4 = 0.43. For the reason given above, this ratio is not expected to depend significantly on the CH bond length chosen.

RESULTS AND DISCUSSION

The results are summarized in *Figure 1* and *Table 1*. The low temperature (6K) results for the three widely different samples shown in *a*, *b* and *c* of *Figure 1* are remarkably similar. At this temperature little molecular motion is to be expected and the Gaussian doublet curves fit the spectra well, accounting for 97% of the hydrogen nuclei in the high density materials and 94% in the low density material. The difference between the two types of material is to be expected since the low density material contains many more hydrogen nuclei in methyl groups which for an isotropic assembly gives a triplet n.m.r. line (Andrew and Bersohn[30]) with a strong central component. Furthermore, there is the possibility of methyl group rotational motion, even at this low temperature, leading to a narrowing of the methyl group triplet. For WNF 15 polyethylene there are estimated to be 32 CH_3 groups per 1000 carbon atoms corresponding to 4.8% of the hydrogen nuclei and hence 4.8% of the intensity of the n.m.r. absorption signal.

The values of M_2^2/M_4 for the fitted curve are in good agreement with the calculated value for isotropic crystalline polyethylene. The average value of the second moment of the fitted curves is 29.1 gauss^2 with a mean deviation of 0.8 gauss^2 over the three samples. This is within the range of values from 27.7 to 29.3 gauss^2 calculated for a temperature of 77K. At 6K this range is expected to move to slightly higher values due to further contraction of the lattice, leading to even better agreement between the theoretical and experimental results.

Turning to the results at 20°C the spectra in *Figures 1d* to *1f* show clearly the different mobile fractions for the three different specimens. The Gaussian doublet fittings to the outer part of the lines are still good and the comparison of the parameters in *Table 1* describing the shape of the Gaussian doublet for each line are what would be expected both in their similarities and their differences. From the parameters a_1 and a_3, the rigid fraction of the material at room temperature, which may be associated with the mass fraction of crystalline material, may be calculated. These mass fractions are shown in column 9 of *Table 1*. They compare very well with the range of crystallinities estimated from density measurements shown in column 10 of the Table using the accepted range of densities for amorphous material, 0.855 to 0.870.

The second moments of the Gaussian doublets for the linear polyethylenes are about 4 to 5 gauss^2 less than at 6K, of which about 2 gauss^2 can be accounted for by the difference in lattice parameters, the small remainder possibly being due to some limited hindered molecular rotation in the crystalline regions. The values of a_2 corresponding to the Gaussian doublet separation are the same for these two specimens and only slightly smaller than the 6K values, confirming this possibility. Gutowsky and Pake[16] have discussed the effect of such hindered rotation of a proton pair appropriate to this case. The parameter a_3 which describes the Gaussian broadening is also slightly smaller than at 6K. This Gaussian broadening arises from intermolecular interactions and is reduced by thermal expansion of the lattice and relative intermolecular motion, both of which could contribute to the observed difference between 6K and 20°C results.

The differences between the parameters of the Gaussian doublet for the low density polyethylene and high density polyethylene are what might be expected from our knowledge of the physical properties of the materials. The low density material contains branches which reduce the perfection of the crystal structure and cause an expansion of the crystalline lattice. These two effects both lead to a reduction of the second moment due to: (i) reduced intermolecular contribution; and (ii) the favourable conditions for limited molecular motions in the crystal. The reduced value of a_2 corresponds to narrowing of the doublet due to hindered rotation and that of a_3 to increased lattice parameters and intermolecular motion. The reductions in a_2 and a_3 both contribute to the reduction in the second moment by about 4 gauss^2 below those of the high density materials.

Overall then we can say that the 6K results for widely differing types of sample justify the use of a Gaussian broadened doublet with a value of M_2^2/M_4 equal to the theoretical value calculated from the crystal structure of polyethylene, to represent the n.m.r. spectrum of the crystalline material. The application of this to the three specimens at room temperature gives values of crystallinity in good agreement with those of density measurements and the small differences in the parameters defining the doublet vary in the right sense and order of magnitude between the samples.

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