Studies of Polymers by Nuclear Magnetic Resonance at Magic Angle Rotation. I. Analysis of the Amorphous Phase of Polyethylene

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ABSTRACT: It is shown that by measurement of nmr spectra at "magic angle" rotation it is possible to determine the composition of amorphous phases in solid polymers without the knowledge of the shapes of the bands corresponding to various phases in the static (broad line) nmr spectrum. The method is illustrated on the example of several commercial samples of polyethylene. For the interpretation of the spectra of polyethylene, the existence of two distinct amorphous phases has to be assumed. In the measured samples, the relative content of the rigid (crystalline) and of both amorphous components has been determined.

Bands in the nmr spectra of crystalline compounds are broadened by magnetic dipole–dipole interactions, reaching, *e.g.*, in proton spectra, the width of 10–20 G. It follows from theoretical considerations that these dipole–dipole interactions can generally be removed by macroscopic rotation of the sample about an axis inclined with respect to the static magnetic field at the so called "magic angle" $\alpha = 54.7°$, at spinning frequencies $\nu_r = \omega_r/2\pi$, comparable with the static line width on a frequency scale.[1,2] This condition can be relatively easily fulfilled in fluorine and phosphorus resonances, where the method has been successfully applied.[3,4] In spectra measured at magic angle rotation there appears a narrowed central line at the resonance frequency ω_0, flanked by a system of side bands at frequencies differing from the resonance frequency by integral multiples of the spinning frequency, *i.e.*, at $\omega_0 \pm p\omega_r$, where the p's are integers.[5] In cases where the sample can be described as a system of mutually noninteracting rigid nuclear pairs, the side-band intensity distribution can be calculated by the perturbation method.[6] The side-band intensities are given by products of Bessel functions with a modulation index proportional to the ratio C/ω_r, where $2C$ is the spacing of the nuclear pair doublet; at small values of the ratio C/ω_r, side-band intensities decrease rapidly with increasing p.

In cases where the sample cannot be described as a system of mutually weakly interacting nuclear pairs, *i.e.*, where all spin interactions are of comparable order, the spectrum is better described by the stochastic theory.[7,8] According to the stochastic theory, the shape of the absorption line is given by the Fourier transform of the relaxation function of magnetization; for a Gaussian local field distribution, this function has the form

$$G(t) = \exp\left(-\omega_2{}^2\int_0^t (t-\tau)g_\omega(\tau)\mathrm{d}\tau\right) \tag{1}$$

where $\omega_2{}^2$ is the second moment of the resonance line (on a circular frequency scale) and $g_\omega(\tau)$ is the local field correlation function, which depends on the correlation time of internal motion in the nuclear system and, in case macroscopic rotation is present, also on the value of the macroscopic rotation frequency, ω_r. At magic angle rotation, the Fourier transform of (1) again has the form of a narrowed central line and a system of side bands, similarly as in the nuclear pair approximation. In this case, the side-band intensity distribution depends on the ratio ω_2/ω_r. In the rigid nuclear pair approximation, the residual width of the central line, narrowed by magic angle rotation, should be zero or very near to zero[9] at exact magic angle setting; in the stochastic description for $\omega_r\tau \gg 1$, it is given by the expression[8]

$$\delta\omega_r \sim \left(\frac{\omega_{2s}}{\omega_r}\right)^2\left(\frac{1}{\tau}\right) \tag{2}$$

where $\omega_{2s}{}^2$ is the second moment of the nmr signal in a static sample and τ is the correlation time describing the time dependence of spin–spin interaction in the crystal in question.

In this paper we wish to indicate the possibility of utilizing the relation between the second moment of the static absorption line and the side-band intensity distribution at magic angle rotation, as well as the relation between the residual line width and the correlation frequency of internal motion for the determination of phases characterized by different types of internal motion in polymers. The method is illustrated by the example of a series of samples of solid polyethylene.

Analysis of the Effects of Magic Angle Rotation upon Nmr Spectra of Polymers

In proton nmr spectra of crystalline compounds the static line width (on a frequency scale) is usually of the order of 40–60 kcps. In turbines propelled by nitrogen, the highest attainable spinning frequencies are about 10 kcps, and it is therefore practically impossible to reach spinning frequencies comparable with line width. Therefore, in proton nmr spectra, magic angle rotation can be expected to be successful only in substances in which the line width for a static sample (further denoted as "static line width") is narrowed with respect to the line width of the rigid crystalline lattice, *e.g.*, by

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internal molecular motion. For isotropic internal motion, the static line width is approximately given by the relation[10]

$$(\Delta\nu)^2 = A^2 \frac{2}{\pi} \arctan\,(\Delta\nu/\nu_c) \tag{3}$$

where A is the line width in the rigid (crystalline) sample and ν_c is the correlation frequency of the isotropic internal motion. In this case, magic angle rotation can lead to line narrowing only at spinning frequencies higher than ν_c. In all proton nmr spectra where the static line width is narrowed by isotropic internal motion, the correlation frequency is higher than technically attainable values of ν_r ($\sim$10 kcps). From this it would follow that magic angle rotation cannot bring measurable effects in proton resonance.

In spite of this, already from our first experiments with magic angle rotation it was evident[11] that in a number of polymers line narrowing and side-band appearance take place at relatively low spinning frequencies. This fact we explained by the assumption that the internal motion in these polymers is anisotropic. In such cases, the line width in the static sample can be described by the Gutowsky equation[12]

$$(\Delta\nu)^2 \cong B^2 + C^2 \frac{2}{\pi} \arctan\left(\frac{\alpha\Delta\nu}{\nu_c}\right) \tag{4}$$

where α is a factor of order unity, B is the static line width at sufficiently high correlation frequency ν_c, and C is defined by the relation $A^2 = B^2 + C^2$, where A again corresponds to static line width in a quite rigid sample. As the correlation frequency of internal motion ν_c is generally larger than the spinning frequency ν_r, the component of the line defined by the second member of eq 4 remains unaffected by magic angle rotation, whereas the component corresponding to the first member of this equation is affected similarly as spectra of completely rigid systems.

The effects of magic angle rotation upon nmr spectra already partially narrowed by certain types of internal motion, *e.g.*, reorientations of complex anions in ionic crystals of the type $K(AsF_6)$, have been theoretically analyzed by Andrew and Jasinski.[4,13] For the width of the line narrowed by magic angle rotation (further denoted as "residual line width"), they have derived the relation

$$\delta\omega_r \sim \omega_{2a}{}^2\tau_a + \left(\frac{\omega_{2b}}{\omega_r}\right)^2 \tau_b{}^{-1} \tag{5}$$

where $\omega_{2b}{}^2$ is the second moment of the line in the static sample, $\omega_{2c}{}^2$ is the second moment of the line in a completely rigid sample, and ω_{2a} is defined similarly as in eq 4 by the relation

$$\omega_{2c}{}^2 = \omega_{2a}{}^2 + \omega_{2b}{}^2 \tag{6}$$

τ_a is the correlation time of the rapid internal motion which has caused the narrowing of the static line width with respect to the line width of a completely rigid sample and τ_b is the correlation time describing the time dependence of dipolar interactions which have not been averaged by the specialized internal motion. In polymers the anisotropy of internal motion cannot be described so simply as in the ionic crystals discussed by Andrew and Jasinski; nevertheless, the fact that magic angle rotation leads to line narrowing and appearance of a system of side bands indicates that the internal motions in these polymers are anisotropic and that, at least formally, they may be described by a similar equation. In all the polymers which we measured (poly(methyl methacrylate), polystyrene, polyamide, polyethylene, polyisobutylene), the residual line width was independent of the spinning frequency. According to eq 5, in these polymers the residual line width must therefore be given by the correlation time of the rapid internal motion, and it should be possible to determine this correlation time from the residual line width according to eq 5.

In the stochastic approach, for compounds with a static line width partially narrowed by internal motion and subject to further narrowing and side-band generation at magic angle rotation, eq 1 has to be transformed in the sense of eq 6 to the form

$$G(t) = \exp\left(-\omega_{2a}{}^2\int_0^t (t-\tau)g_a(\tau)\mathrm{d}\tau\right) \times \exp\left(-\omega_{2b}{}^2\int_0^t (t-\tau)g_b(\tau)\mathrm{d}\tau\right) = G_a(t)G_b(t) \tag{7}$$

where $g_a(\tau)$ is the correlation function of the local field modified by the microscopic motions.

For $\tau_a\omega_r \ll 1$, the function $G_a(t)$ has the form[13]

$$G_a(t) = \exp(-\omega_{2a}{}^2\tau_a{}^2(\exp(-t/\tau_a) - 1 + t/\tau_a)) \tag{8}$$

from which it follows, in accord with eq 5, that $G_a(t)$ does not depend on the macroscopic spinning frequency.

The relaxation function $G_b(t)$ describes the behavior of that component of the system which is affected by macroscopic rotation. Its internal motion is characterized by the correlation time τ_b, and the corresponding correlation function of the local field can be described by the relation[8]

$$g_b(\tau) = \exp(-t/\tau_b)[(1/4)(3\cos^2\alpha - 1)^2 + (3/4)\sin^4\alpha\cos 2\omega_r\tau_b + (3/4)\sin^2 2\alpha\cos\omega_r\tau_b] \tag{9}$$

Introducing this expression into eq 1, we obtain a general relation for correlation times τ_b of arbitrary length. For $\tau_b \rightarrow \infty$ at magic angle rotation, the relaxation function assumes the relatively simple form

$$G_b(t) = \exp\left\{-\frac{\omega_{2b}{}^2}{\omega_r{}^2}\left[\frac{2}{3}(1 - \cos\omega_r t) + \frac{1}{12}(1 - \cos 2\omega_r t)\right]\right\} \tag{10}$$

the Fourier transform of which corresponds to the absorption spectrum obtained in a magic angle rotation experiment. The side-band intensity distribution is in this case a function of only ω_r and ω_{2b}, so that at a known spinning frequency, the second moment of the static nmr spectrum can be determined from it.

For $\tau_b \neq \infty$, the full eq 1 and 9 must be used. In this case, the side-band intensity distribution is a function not only of ω_r and ω_{2b}, but also of τ_b. Side-band intensities calculated for various spinning frequencies, agreeing with the experimental ones well within experimental error, can in this case be obtained with a whole series of combinations of ω_{2b} and τ_b. We can therefore always describe mathematically the side-band intensity distribution in the experimental spectrum by selecting some value of τ_b, most simply by selecting $\tau_b = \infty$; as long as the actual value of τ_b is unknown, however, the true second moment of the static nmr spectrum cannot be determined.

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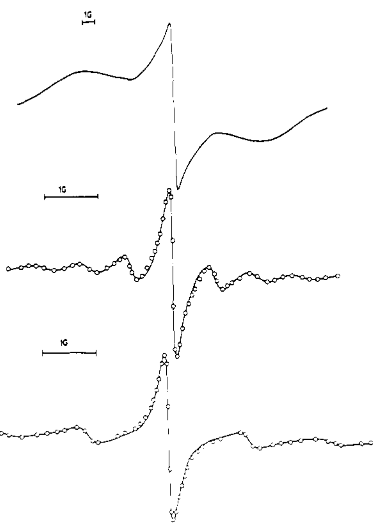

Figure 1. Nmr spectrum of polyethylene, sample 6041D: (a) static sample; (b, c) sample rotated at the magic angle, (b) ν_r = 3650 cps, (c) ν_r = 6800 cps; (———) experimental, (○) calculated.

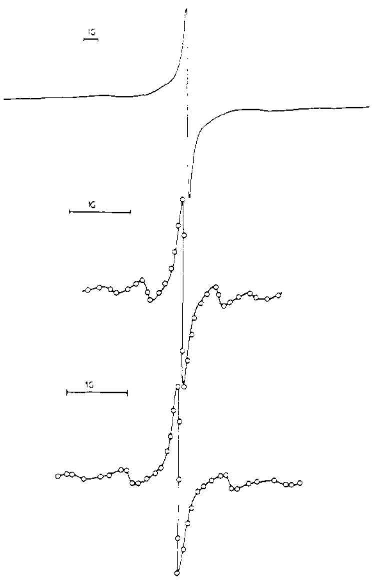

Figure 2. Nmr spectrum of polyethylene, sample 3020D: (a) static sample; (b, c) sample rotated at the magic angle, (b) ν_r = 2800 cps, (c) ν_r = 3800 cps; (———) experimental, (○) calculated.

TABLE I
CHARACTERIZATION OF POLYETHYLENE SAMPLES

No.	Trade-mark	d, g/cm^3	[η]	Melting index, g/10 min	Crystallinity, % d	Ir	Nmr
1	6011L	0.962	1.6	5	78.0	79.8	94.0
2	6041D	0.960		0.2	77.5	75.3	88.5
3	5261Z	0.953	3.8	<0.1	72.5	66.6	87.5
4	3010S	0.930	0.8	20	55.6	43.7	74.0
5	3020D	0.929	1.3	0.2	54.5	43.7	72.7
6	1800S	0.919		20	48.8	24.6	

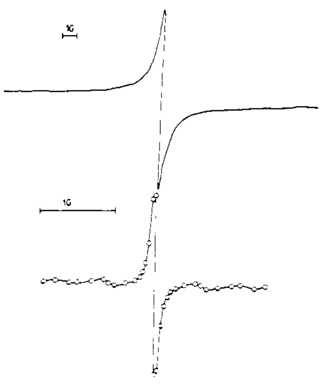

Figure 3. Nmr spectrum of polyethylene, sample 1800S: (a) static sample, (b) sample rotated at the magic angle, ν_r = 2900 cps; (———) experimental, (○) calculated.

Experimental Section

All measured samples of polyethylene were commercial samples of Lupolen (BASF). They were used in the form of blocks without further treatment, and their characteristics are summarized in Table I. Crystallinity from infrared spectra was determined from the pair of bands at 1380 and 1890 cm^{-1} by the method of Tobin and Carrano.[14,15] Crystallinity from densities was calculated by means of the equation[16] $k = (1.165 - d^{-1})/0.160$. Crystallinity from nmr spectra was determined by the method of Wilson and Pake.[17] Samples 1–5, which had sufficient mechanical strength, were machined into the form of turbines of ϕ 6.5 mm. Sample 5 and sample 6, which was too soft, were measured in the form of cylinders of ϕ 3 mm in a hollow Teflon turbine.

All nmr spectra were measured on the high-resolution JNM-3-60 (Jeolco) spectrometer at 60 Mcps, equipped with an attachment for the measurement of broad-line nmr spectra (Jeolco Type ZN) using 35-cps modulation. The measuring probe was of our own construction,[18] adapted for measurement at magic angle rotation both in the derivative and in the absorption mode. The precise magic angle setting was found by mechanical angle adjustment to minimum line width in a spinning experiment. Inside the hollow Teflon turbine, field homogeneity of 3 cps was achieved at the magic angle position. The spinning frequency was measured either by microphone or directly from the spacing of side bands. Polyethylene turbines were measured in the frequency range 2–6 kcps, soft samples in the Teflon turbine in the frequency range 800–2500 cps.

Experimental spectra shown in Figures 1–3 are averaged from several independent runs at the same spinning frequency. Theoretical spectra were calculated on the Minsk 22 computer.

Results and Discussion

Derivative nmr spectra of polyethylene samples measured statically and at magic angle rotation are shown in Figures 1–3. From these figures it is seen that the broad band corresponding to the crystalline form is almost unaffected by rotation. The band corresponding to amorphous polyethylene, on the other hand, generates a narrowed central line and a system of side bands by magic angle rotation. This decomposition is observable in all our samples already at spinning frequencies around 2 kcps. The width of the narrowed central line measured as the peak-to-peak distance in the derivative spectrum was in all samples less than 1 kcps; in the softest samples it reached 400 cps, which is the limit of our derivative apparatus. In all samples the width of the side bands appeared larger than that of the central band, approximately by a factor of 2. In all cases the residual line widths, both

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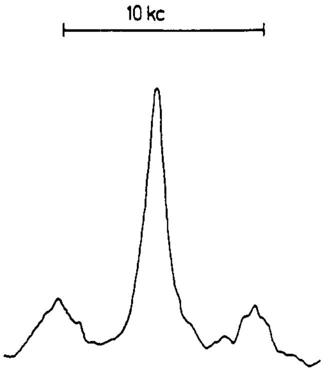

Figure 4. Nmr spectrum of polyethylene, sample 6041D, measured at magic angle rotation in the high-resolution mode, $\nu_r = 5000$ cps.

of the central band and of the side bands, were independent of the spinning frequency. In samples 6041D (Figure 4), 3010S, and 1800S (Figure 5), direct absorption spectra were also measured in the normal high-resolution mode. In sample 6041D phase-sensitive detection (2 kcps modulation) could not be used because of large line width, which explains the poorer quality of the trace in Figure 4. In spite of this, it is evident that the measured line width has been reproduced correctly in the derivative spectra both for the central band and for the side bands, and that all the lines are approximately of Lorentzian shape. In sample 1800S, even the spectrum of the static sample could be measured in the high-resolution (absorption) mode, and the line narrowing by magic angle rotation is demonstrated in Figure 5. From this figure it is also evident that the width of the narrowed line does not depend on the spinning frequency.

The intensities of side bands in the spectra of polyethylenes measured at magic angle rotation do not conform to intensity distributions calculated by means of the stochastic theory from eq 1 and 9, for arbitrary values of the second moment and τ_b, as long as the presence of only one noncrystalline phase is assumed. Agreement of calculated and experimental spectra can only be obtained if the presence of at least two amorphous phases is considered. Also, the fact that the side bands in all the spectra are about twice as wide as the central line indicates that the noncrystalline phase is composed of at least two components differing by second moments and correlation times. The spectra were therefore interpreted on the assumption that the amorphous phase of polyethylene contains two components: component I, with a narrower line width, both in the spectra of static and in the spectra of rotating samples, and component II, with wider lines.

The content of both components was calculated so that in the approximation with $\tau_b = \infty$, lines of Lorentzian shape with relative intensities obtained from the Fourier transform of the relaxation function of magnetization were composed at frequencies $\omega_0 + p\omega_r$, with line widths estimated from spectra measured at magic angle rotation. The relative contents, second moments, and line widths of both components were varied until satisfactory agreement of experimental and calculated spectra was obtained for all measured spinning frequencies ω_r. The relative contents of both components of the amorphous phase obtained in this way are given in Table II. The simultaneously calculated second moments need not be identical with the real second moments of components I and II. For $\tau_b \neq \infty$, different values of second moments are obtained, but the calculated composition of the amorphous phase is not changed by this.

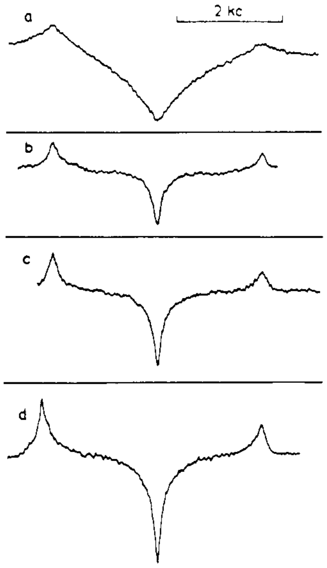

Figure 5. Nmr spectrum of polyethylene, sample 1800S, measured in the high-resolution (absorption) mode: (a) static sample, (b, c, d) sample rotated at the magic angle, (b) $\nu_r = 900$ cps, (c) $\nu_r = 1900$ cps, (d) $\nu_r = 2900$ cps (the outer peaks are 2-kcps modulation side bands from the PSD system).

TABLE II

RESULTS OF ANALYSIS OF NMR SPECTRA OF POLYETHYLENE SAMPLES MEASURED AT MAGIC ANGLE ROTATION

Sample no.	Composition, % Crystal	Amorphous I	Amorphous II	Static line width, $\delta\omega_s$, G I	Static line width, $\delta\omega_s$, G II	Residual line width, $\delta\omega_r$, G I	Residual line width, $\delta\omega_r$, G II
6011L	89.8	3.4	6.8	1.6	4.4	0.35	0.8
6041D	81.4	6.2	12.4	1.6	4.4	0.35	0.8
5261Z	81.4	6.2	12.4	1.6	4.4	0.35	0.8
3020D	68.0	16.8	15.2	0.8	2.4	0.2	0.4
3010S	68.0	16.8	15.2	0.8	2.4	0.2	0.4
1800S		47.5	52.5	0.2	1.5	0.1	0.3

In order to physically characterize the detected two components of the amorphous phase, it is necessary to know their second moments or the shapes of their lines in the spectrum of the static sample. These data can be obtained from the spectrum of the static sample, if its shape is analyzed with the knowledge of the relative contents of the two amorphous components. According to the stochastic theory, the shape of the static spectra of noncrystalline phases ($\omega_r \rightarrow 0$) can have any form between the purely Gaussian for $\tau_b \rightarrow \infty$ and purely Lorentzian for large correlation frequencies. In all our samples, the shape of the static spectrum is best described as a superposition of a nearer to Gaussian line of component II and a nearer to Lorentzian line of component I. It is therefore possible to estimate the width of the line of component II in the static spectrum from the second moment determined from the intensity distribution of side bands for $\tau_b = \infty$. The width of the line of component I can be better estimated directly from the peak-to-peak distance in the derivative spectrum of the static sample. Line widths of both components of the amorphous phase in the spectra of static samples determined in this way are given in Table II. By subtracting the bands of both amorphous components from the total spectrum of the static sample, the shape of the line of the rigid (crystalline) phase can be obtained, and the overall composition of the polymer determined. For the measured samples, this is also given in Table II. Values given in this table correspond to spectra shown in Figures 1–3a.

In Table II are also given residual line widths, $\delta\omega_r$, in spectra measured at magic angle rotation. From these residual line widths it is possible to estimate the correlation frequency of the anisotropic motion causing partial narrowing of the line of the corresponding phase in the static spectrum from the relation

$$\delta\omega_r \cong \omega_a^2\tau_a \qquad (11)$$

In our samples, the value τ_a calculated in this way changes gradually from 10^{-6} sec for component II in the sample with highest crystallinity to 10^{-7} sec for component I in the softest sample. Correlation times calculated in this way are in all cases shorter, by half an order of magnitude, than the correlation times calculated from the static line width with the assumption of isotropic internal motion.

Conclusion

The finding that the amorphous phase of polyethylene is composed at least of two components is not surprising. Such a composition of the amorphous phase has already been proposed by Bergmann and Nawotki[16] and later by Piesczek and Fischer.[19] In these papers, different assumptions about the molecular structure of the polymer chain and type of motions have been made, and theoretical line shapes of various phases have been calculated on the basis of these assumptions; these theoretical shapes were then used for the determination of the overall composition of the polymer. The results of the two cited papers differ to some extent. Contrary to the previous procedures, the method of magic angle rotation makes it possible to determine the presence and relative amounts of both components of the amorphous phase experimentally without any assumptions about molecular structure and type of motion. It should therefore be possible to use this method also for the analysis of polymers more complicated than polyethylene, where theoretical calculations of line shapes would be extremely difficult.

The method of magic angle rotation is also able to yield basic information about the type of molecular motion: it makes it possible to differentiate whether the partial narrowing of the band in the spectrum of the static sample has been caused by slower isotropic molecular motion or by more rapid anisotropic motion. In all previous papers, it has been assumed that the most narrow band in nmr spectra of polyethylene corresponds to a phase characterized by isotropic micro-Brownian motion. It follows from our measurements that even the most narrow band in the softest of our samples (1800S) is still further narrowed by magic angle rotation, and that it must therefore correspond to a phase characterized by partially anisotropic internal motion.

From Tables I and II it is seen that by considering two components of the amorphous phase we obtain a somewhat lower content of the rigid (crystalline) phase compared, *e.g.*, to the determination according to Wilson and Pake;[17] crystallinity values from nmr spectra thus get nearer to values from densities or infrared spectra, but still remain higher. This is caused by the fact that by each of these methods the content of the crystalline phase is determined according to different criteria: the infrared method is based on the determination of the relative contents of tt and tg conformational forms, and crystallinity determinations from densities are influenced by chain branching. The nmr method in general determines the content of the rigid phase, irrespective of the existence or nonexistence of actually crystalline order in it. In the method of magic angle rotation, forms defined as rigid are those for which the residual line width is larger than the spinning frequency. For our experimental conditions, these are forms of polyethylene with a correlation time of the anisotropic internal motion $\tau_a > 2 \times 10^{-6}$ sec.

The two amorphous phases detected by the above-described procedure need not be sharply defined, *i.e.*, each of them may correspond to a certain distribution of motions and correlation times. A more precise characterization of this distribution would require further more detailed investigations. The aim of the present paper was mainly to demonstrate the possibility of the analysis of amorphous phases in polymers from nmr spectra measured at magic angle rotation.

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