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High-Resolution Carbon-13 Nuclear Magnetic Resonance of Solid Poly(oxymethylene)

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ABSTRACT: ^{13}C spectra and relaxation times were determined for poly(oxymethylene) at 45 MHz with proton-decoupled magic-angle-spinning NMR with and without cross-polarization. The results indicate the coexistence of two phases: a crystalline phase with short $T_{1\rho}$ and long T_1 and an amorphous phase with a longer $T_{1\rho}$ and a shorter T_1. These results are consistent with crystallinity measurements on the same samples by X-ray diffraction. The crystalline $T_{1\rho}$, which is not thought to be a pure spin–lattice relaxation parameter but is also determined by spin–spin interaction, depends on the spinning frequency. At high spinning frequency ($>\sim 5$ kHz), the line width (at magic-angle-spinning conditions) increases with an increase in the spinning frequency.

By combining heteronuclear decoupling and cross-polarization techniques[1] with magic-angle spinning, Schaefer and Stejskal[2] have clearly demonstrated that high-resolution NMR of solids is possible. Since then they obtained high-resolution ^{13}C spectra of a number of polymers and showed that one can measure ^{13}C spin–relaxation parameters for every ^{13}C spin which gives a resolved NMR line.[3,4] These relaxation parameters include the spin–lattice relaxation time T_1, the rotating frame spin–lattice relaxation time $T_{1\rho}$, and the ^1H–^{13}C cross-polarization time T_{CH}.

This study concerns a simple polymer, poly(oxymethylene), which under magic-angle-spinning conditions gives one, rather narrow, line. $T_{1\rho}$ measurements, however, reveal clearly that this line consists of two components with very different relaxation behavior. These components are attributed to crystalline and amorphous regions in the material. While this information can also be obtained from a nonspinning sample in this particular simple case, for polymers with chemically different carbons this is not possible due to overlapping powder line shapes. Thus for more complicated polymers, $T_{1\rho}$ (or any other relaxation parameter, of course) measurements under magic-angle-spinning conditions can be performed in order to determine the crystallinity of the polymers.

The ^{13}C $T_{1\rho}$ is measured via the decay of the rotating frame ^{13}C magnetization in a resonant radiofrequency field H_1. Although the notation $T_{1\rho}$ suggests spin–lattice relaxation, spin–spin processes can contribute significantly to this $T_{1\rho}$, especially when H_1 is not at least an order of magnitude larger than the local field.[4,5] While it is interesting to determine the relative contributions of spin–spin and spin–lattice relaxation to $T_{1\rho}$, we do not make such an attempt here.

Experimental Section

The NMR spectrometer is home built around a wide-bore (110 mm) 4.2 T superconducting magnet (Oxford Instruments). The ^{13}C H_1 field used has a rotating component amplitude corresponding to a frequency of 25 kHz. The spinner for magic-angle spinning is of a new design;[6] it has a cylindrical shape (diameter 10 mm) and is supported by two air bearings. Spinning frequencies between 500 and 5600 Hz can be maintained with excellent long-term stability (i.e., routine weekend operation). For the study reported here, the spinner was machined from Delrin, but for other polymers hollow KEL-F spinners have been used.

The $T_{1\rho}$ measurements were completely automatized such that the hold time τ (Figure 1) was varied after each FID. In most cases, 16 τ values were selected, and the corresponding 16 FID's were accumulated separately. This has the advantage that any slow drift of any experimental parameter does not affect the $T_{1\rho}$ plots. With regard to the $T_{1\rho}$ plots, it should be noted that the first point is taken after 100 μs, and under these conditions no $T_{1\rho}$ dispersion is found as reported by Schaefer et al.[3] except for the biexponential decay reported below.

^{13}C spectra and ^{13}C $T_{1\rho}$'s are determined both with and without cross-polarization. In the latter case, ^{13}C magnetization was prepared by a 90° pulse. The two pulse sequences for the $T_{1\rho}$ measurements are shown in Figure 1.

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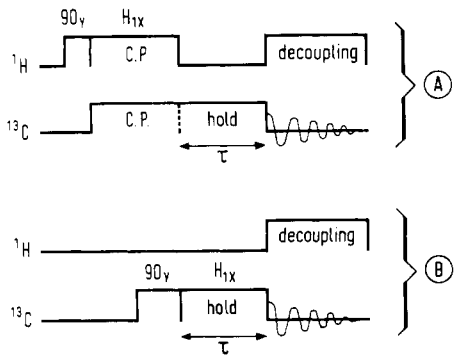

Figure 1. Pulse sequences for ^{13}C $T_{1\rho}$ measurements with (sequence A) and without (sequence B) cross-polarization.

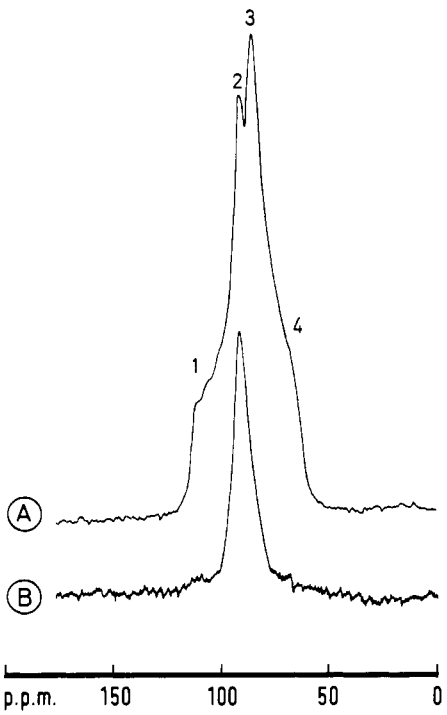

Figure 2. Proton-decoupled ^{13}C spectra of a nonspinning poly(oxymethylene) (Delrin) sample. Spectrum A results from 10 ms cross-polarization, while for spectrum B the carbon magnetization is prepared via a 90° pulse.

Results

A number of different NMR experiments have been performed on poly(oxymethylene), and considered as a whole, a clear and consistent picture of some of the properties of poly(oxymethylene) (Delrin) is obtained. Each experiment alone, however, emphasizes only certain aspects of this picture, and therefore we present in this section all of the experimental results and postpone a more detailed discussion of these results to the next section.

We describe the results of three types of experiments: high-resolution ^{13}C NMR spectra, ^{13}C relaxation measurements ($T_{1\rho}$, T_1), and the dependence of $T_{1\rho}$ and line width on the spinning frequency in a MAS (magic-angle-spinning) experiment.

^{13}C Spectra. Poly(oxymethylene) is a relatively simple, linear polymer with all carbons chemically equivalent. The MAS experiment indeed shows one resonance line at 89-ppm downfield from the ^{13}C resonance of Me_4Si with a line width of ~3 ppm.

Much more information in this case, however, is obtained from the spectrum of the nonspinning sample. Figure 2 shows two proton-decoupled ^{13}C spectra A and B. Spectrum A was obtained using the cross-polarization technique,[1] while for spectrum B a straightforward proton-decoupled FT experiment was used, i.e., ^{13}C 90° pulses with a repetition rate of 1 s^{-1} instead of cross-polarization. The relative narrow line of spectrum 2B coincides with peak 2 of spectrum 2A.

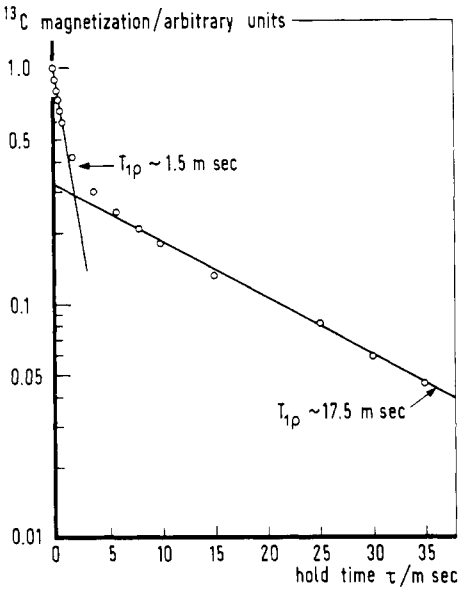

Figure 3. $T_{1\rho}$ measurement for a sample spinning at the magic angle with a frequency of 2.1 kHz. The carbon magnetization is prepared via cross-polarization; i.e., pulse sequence A of Figure 1 is used.

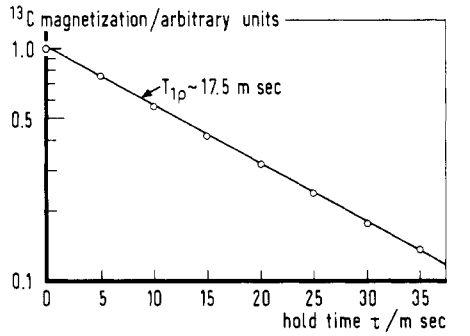

Figure 4. $T_{1\rho}$ measurement for a sample spinning at the magic angle with frequency of 2.1 kHz; 90° pulses are used to prepare the carbon magnetization, i.e., with pulse sequence B of Figure 1.

By decreasing the repetition rate in the 90° pulse experiment almost two orders of magnitude, the resulting spectrum is similar to spectrum 2A. Apparently, spectrum 2A consists of at least two components with very different ^{13}C T_1, the narrow component having a short T_1 (≤1 s) and the other component(s) a much larger T_1.

Also, the relative intensities in spectrum 2A were observed to depend on the length of the cross-polarization time. For spectrum 2A, this time was 10 ms, and a shorter cross-polarization results in a decrease of the narrow component 2, thus the cross-polarization is not as efficient for the narrow component as it is for the other component(s) making up spectrum 2A.

With MAS, the narrowed ^{13}C line is found at almost the same frequency (1 ppm toward higher field) as that for the narrow component of spectrum 2B, where the sample is nonspinning.

$T_{1\rho}$ Measurements. $T_{1\rho}$ measurements have been made for poly(oxymethylene) samples spinning at the magic angle with frequencies between 0 and 5600 Hz. Both pulse sequences shown in Figure 1 have been used, and

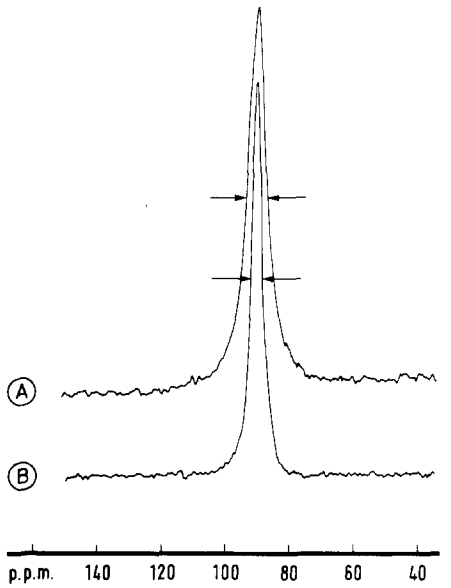

Figure 5. Increase of ^{13}C line width with increasing MAS frequency. Spectrum A shows the line with 5.6 kHz spinning (line width 5.7 ppm), while spectrum B is obtained with 3.1 kHz spinning, and then a line width of 3.7 ppm is found. At lower MAS frequencies (>1 kHz), the line width hardly changes with spinning frequency.

typical examples of $T_{1\rho}$ decay curves are given in Figure 3 for pulse sequence A and in Figure 4 for pulse sequence B with a repetition rate of 1 s^{-1}. Here again, a difference is observed between the cross-polarization experiment and the 90° pulse experiment: the cross-polarization pulse sequence A yields, for all spinning frequencies, a well-resolved biexponential $T_{1\rho}$ decay (for 2.1 kHz spinning the two values of $T_{1\rho}$ are ~1.5 and ~17.5 ms), while a $T_{1\rho}$ measurement with pulse sequence B and repetition rate 1 s^{-1} gives a single exponential with a $T_{1\rho}$ of 17.5 ms. When pulse sequence B with a much longer repolarization time (>30 s) is used, again a double exponential is found. Therefore, we conclude that the narrow component 2 of spectrum 2A (i.e., the line in spectrum 2B) has a $T_{1\rho}$ of ~17.5 ms and that all other components have a much shorter $T_{1\rho}$.

Dependence of ^{13}C Line Width and $T_{1\rho}$ on MAS Frequency. For poly(oxymethylene), the ^{13}C chemical shift anisotropy is rather small, and even with a relative low MAS frequency of 1 kHz, the spinning side bands are weak.

Between 1- and 4-kHz spinning, the ^{13}C line width is independent of the spinning frequency, both in the spectra obtained by cross-polarization and by 90° pulses.

At very high spinning rates, however, a noticeable increase in the line width is observed in the cross-polarization spectrum, whereas the line width in spectra obtained by 90° pulses with a repetition rate of 1 s^{-1} remains the same. This is illustrated in Figure 5A, where two ^{13}C cross-polarization spectra are shown for 5.6- and 3.1-kHz spinning, respectively. Apparently, the two (or more) components which constitute the cross-polarization spectrum behave differently under fast magic-angle-spinning conditions. As these two components have different $T_{1\rho}$, at fast magic-angle spinning a change in line width is expected as a function of τ in a cross-polarization $T_{1\rho}$ experiment. This is indeed observed; as expected, a decrease in line width is found with increasing τ. Therefore, we can conclude: the spins with the long $T_{1\rho}$ and short T_1 (which are responsible for the relative narrow line 2 of spectrum A in Figure 2) in the MAS condition give rise to a line whose

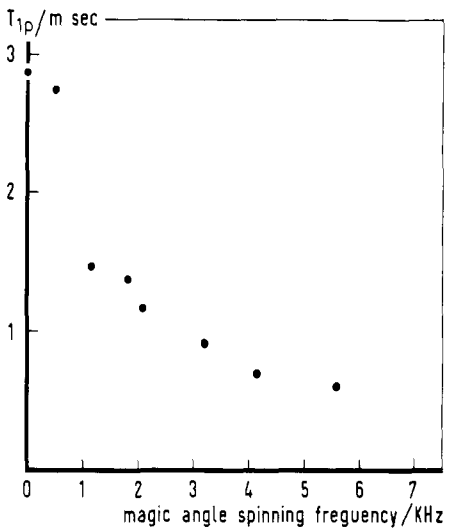

Figure 6. Dependence of the crystalline $T_{1\rho}$ on MAS frequency.

line width is independent of spinning frequency (at least up to 5.6 kHz).

The spinning-dependent line width must be due to the spins with a short $T_{1\rho}$ and long T_1 which yield the broad structure of Figure 2A.

It appears that this short $T_{1\rho}$ is also a function of the spinning frequency, as is shown in Figure 6. The long $T_{1\rho}$ (~17.5 ms), however, is independent of the spinning frequency in these experiments.

Fast spinning therefore changes both the line width and $T_{1\rho}$ of the NMR component with the short $T_{1\rho}$ and the long T_1.

Discussion

Both the ^{13}C spectral data and the $T_{1\rho}$ data strongly point to the existence of two different phases in the polymeric material with different ^{13}C relaxation times T_1 and $T_{1\rho}$. Because it is known that poly(oxymethylene) generally contains both crystalline and amorphous components, it seems justified to assume that the two signals with different relaxation times come from the ^{13}C spins in crystalline and amorphous regions of the material. Then it seems a natural assumption that the narrow line of Figure 2 (line 2) is due to the amorphous material and that the broad structure is a chemical shift anisotropy broadened line from the crystalline regions in the sample. There is so much motion in the amorphous material that the chemical shift anisotropy is largely, but not completely, averaged out. Also, this assignment implies that the amorphous line has the long $T_{1\rho}$ (17.5 ms) and the short T_1 (≤1 s), while the crystalline line has a short spinning-frequency-dependent $T_{1\rho}$ (0.5–3 ms) and a long T_1 (≫10 s).

At first, before we studied in detail the nonspinning spectra, based on the work of Schaefer and Stejskal,[3,4] we assumed that the short $T_{1\rho}$ should correspond to the amorphous phase.[7] However, the nonspinning spectra show that this assumption is not correct; i.e., the amorphous phase has a longer $T_{1\rho}$ than the crystalline phase. As is mentioned in the introduction, the relaxation parameter $T_{1\rho}$, which we measure via the decay of the spin-locked ^{13}C magnetization, by no means has to be a pure spin–lattice relaxation parameter. When the radiofrequency spin-lock field is not much greater than the dipolar field, spin–spin relaxation may contribute significantly to our apparent $T_{1\rho}$. The largest ^{13}C H_1 field we can presently achieve corresponds to a rotating component of 25 kHz, and therefore we must expect that, certainly

for the crystalline spins, the $T_{1\rho}$ may be dominated by spin–spin interactions.[4,5] A more complete study is needed to determine the ratio of spin–lattice and spin–spin relaxation contributions to our $T_{1\rho}$ values, which we plan as soon as our instrument is modified for larger radiofrequency fields.

Motions, which in the amorphous region partly average out the chemical shift anisotropy, can also reduce the C–H cross-polarization efficiency for the amorphous line. This would explain the relative increase of the narrow amorphous line in the cross-polarization spectrum of the nonspinning sample with increasing cross-polarization time.

From the $T_{1\rho}$ measurement, one can estimate the percentage of crystallinity of the polymeric material. The $T_{1\rho}$ plots for every spinning frequency can be very accurately fitted with a function:

$$M(\tau) = A \exp(-\tau/t_1) + B \exp(-\tau/t_2)$$

where $M(\tau)$ is proportional to the ^{13}C signal after being spin locked for τ seconds, t_1 and t_2 represent the two $T_{1\rho}$ values to be determined, and A and B are the relative amounts of crystalline and amorphous material. We find a 70% (±5) crystalline and a 30% (±5) amorphous content. This is quite close to the value determined by X-ray diffraction, 63 and 37%, respectively. Even though our percentages depend somewhat on the length of the cross-polarization, they do provide strong support for the assignment that the long $T_{1\rho}$ is due to the amorphous component. For a more accurate determination of these percentages, one should take into account the difference of cross-polarization efficiencies for the amorphous and crystalline regions. We simply took the average for different spinning rates.

The spinning dependence of the crystalline $T_{1\rho}$ can in principle be explained by several mechanisms. A possible explanation could be, as suggested by Schaefer et al.,[3] that the anisotropy of $T_{1\rho}$ is averaged by the spinning, causing a shorter $T_{1\rho}$. However, preliminary studies on a nonspinning sample do not reveal such anisotropy. Also, the $T_{1\rho}$ plots of slow-spinning samples do not show a $T_{1\rho}$ dispersion except for the double-exponential decay.

Although there always remains the possibility that spinning modulates molecular motions and increases the spectral density at the rotating frame Larmor precession frequency, in our case, it seems likely that the spinning influences the spin–spin contribution to our $T_{1\rho}$. Further studies are in progress to explain this spinning dependence of $T_{1\rho}$.

The increase of the line width of the crystalline line at the highest spinning frequency may be related to the change of $T_{1\rho}$ with spinning. This line broadening might be explained as the result of strain in the material due to spinning forces and would only be observed at the high-spinning rates.

Conclusion

Poly(oxymethylene) (Delrin) consists of at least two components, one amorphous and at least one crystalline, having clearly different $T_{1\rho}$'s and different T_1's. If the difference we find in the $T_{1\rho}$'s of the crystalline and amorphous components of Delrin proves to be generally true for polymers, then such measurements will allow the determination of the degree of crystallinity in polymeric material. Also, this study shows that the T_1 of the crystalline component is very different from the amorphous T_1. Studying T_1, therefore, seems very worthwhile, especially because here spin–spin relaxation does not confuse the picture. T_1 measurements on Delrin will be reported later. Finally, the dependence of $T_{1\rho}$ and spectral width on spinning frequency needs further study.

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Fluorescence Depolarization Study of the Glass–Rubber Relaxation in a Polyisoprene

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ABSTRACT: The glass–rubber relaxation of an anionic poly(*cis*-1,4-isoprene) is investigated in the range of 10^{-7}–10^{-9} s, using a fluorescent label bonded within the chain backbones and several probes of varying size dissolved in the polymer matrix. Fluorescence depolarization allows appropriate models of rotational Brownian motion to be checked and relaxation times to be calculated as a function of temperature. Label and large probes are shown to reflect the glass–rubber relaxation in agreement with the WLF equation. The size dependence of the probe relaxation times is also analyzed. When the label and probe relaxation times are compared, the smallest chain segments involved in the glass–rubber relaxation seem to be composed of about five monomer units.

Fluorescence depolarization is a means of probing molecular rotational processes occurring in the range of 10^{-7}–10^{-10} s.[1-3] Fluorescence decay experiments give the autocorrelation function:[4-6]

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