numbers, and mole fractions.[4] The total number of 1-hexene runs per average molecule, N, is given by

$$N = n_1 + n_2 + n_3 + ... + n_x = \sum_{i=1}^{i=x} n_i = (1/2)\text{HE} \qquad (22)$$

$$[\text{N}] = (1/2)[\text{HE}] \qquad (23)$$

$$= [\text{EHE}] + (1/2)[\text{EHH}] = [\text{HEH}] + (1/2)[\text{HEE}] \qquad (24)$$

and leads to the run number, as defined by Harwood:[12]

$$\text{run number} = 100[\text{N}]$$

The mole fractions of each monomer are given by the respective sums of the three like-centered triads and the average sequence lengths for each type of unit are simply

$$\bar{n}_\text{E} = [\text{E}]/[\text{N}] \qquad (25)$$

and

$$\bar{n}_\text{H} = [\text{H}]/[\text{N}] \qquad (26)$$

The tendency of the 1-hexene units to form contiguous series or "clusters" can be described by a term that we will define as the "monomer dispersity", MD (the inverse of the sequence length).

$$\text{MD} = 100[\text{N}]/[\text{H}] \qquad (27)$$

An MD value of 100 would indicate that the 1-hexene units are all "isolated" as ethylene–1-hexene–ethylene sequences. Any value below 100 is indicative of a tendency to "cluster" or form contiguous 1-hexene–1-hexene sequences.

Observed triad distributions, run numbers, comonomer mole fractions, the monomer dispersity, and average sequence lengths are given in Table IIIA for the copolymers used to obtain the assignments. For comparison, the corresponding parameters calculated for perfect Bernoullian distributions with the same overall composition as the copolymers are given in Table IIIB. The copolymer having 1.9 mol % 1-hexene and a monomer dispersity of approximately 97 is clearly a good model for establishing chemical shift assignments associated with EHE, EHEE, and HEEE sequences as shown in Table I. The 17.3 mol % 1-hexene copolymer has a monomer dispersity of only 72, which is considerably less than that predicted for a Bernoullian distribution of the same comonomer composition. The monomer dispersity appears to be a more sensitive indicator of a deviation from the perfectly random distribution than either the run number or an inspection of observed vs. calculated triad distributions. A comparison with Bernoullian distributions is useful because the latter serves as a reference point for the unbiased incorporation of a comonomer.

It should be pointed out that a tetrad distribution can be obtained from the data in Table I if the appropriate necessary relationships are used after carefully selecting the required tetrad ^{13}C NMR resonances. A higher order n-ad distribution would be useful in fitting statistical models as more observations are available for a fixed number of parameters. Aside from statistical considerations, the higher order n-ads are only useful in observing the lower end of the complete sequence distribution. Since it is doubtful that ^{13}C NMR can ever be used to measure sequence lengths of 10–20 contiguous units, it may be better to concentrate on obtaining one very reliable lower n-ad distribution to extract desired quantitative information about the copolymer structure.

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Carbon-13 Spin–Lattice Relaxation in Solid Poly(oxymethylene)

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ABSTRACT: Carbon-13 spin–lattice relaxation parameters of solid poly(oxymethylene) (Delrin) have been measured by means of high-resolution solid-state carbon-13 NMR. Carbon-13 spectra and relaxation parameters clearly show two different types of carbon-13 nuclei. They are assigned to carbons in "amorphous" regions and to carbons in "crystalline" regions, respectively, in accord with the accepted two-phase model of semicrystalline poly(oxymethylene). The data indicate that molecular motions do take place in the crystalline regions as well as in the amorphous regions. Our data are compared with results of dielectric and mechanical relaxation data, as well as other (proton) NMR studies, in order to gain insight into the nature of the motions as well as their correlation frequencies. It is argued that the motions in the amorphous and crystalline regions differ in their amplitudes rather than in their correlation frequencies.

Introduction

Nuclear magnetic resonance has been extensively used in the study of structural and physical properties of polymers in solution as well as in the solid state.[1] Wide-line proton NMR studies of linear semicrystalline polymers such as polyethylene and poly(oxymethylene) generally show NMR signals arising from more or less mobile components, giving rise to a (partially) narrowed NMR line,

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and from more rigid components, giving rise to a broad resonance line. A single proton spin-lattice relaxation time, however, is usually observed over a wide range of temperatures due to rapid proton spin diffusion, thus hampering the extraction of more detailed information about molecular motions in the mobile, or "amorphous", regions, and the motions in the rigid, or "crystalline", regions. Moreover, only one T_1 minimum has been observed in solid poly(oxymethylene)[2-4] over a wide temperature range. Therefore proton NMR studies on solid poly(oxymethylene) suggest that either molecular motions take place in the mobile, or amorphous, regions only and that the rigid component is rigid indeed or that complex motional processes, involving both crystalline and amorphous regions, occur. The latter possibility can give rise to a single T_1 minimum over a wide temperature range if the correlation frequencies of the motions in the amorphous and crystalline regions are of the same order of magnitude. Dielectric and mechanical relaxation measurements at room temperature indicate that fast molecular motions (correlation frequency $\sim 10^8$–10^9 Hz) occur in solid poly(oxymethylene) as well as very slow "motions" (correlation frequency >1 Hz) but they do not give direct information on where these motions occur. Most of the pertinent data on poly(oxymethylene) have been compiled by Crist and Peterlin[2] and Trappeniers et al.[3] and the reader is referred to their papers for further details and references.

Since spin diffusion between carbon-13 nuclei in natural abundance is not expected to occur, it is worthwhile to investigate solid polymers by means of carbon-13 NMR. Axelson and Mandelkern[5] investigated many semicrystalline polymers using standard FT carbon-13 NMR techniques, i.e., with proton noise decoupling during acquisition. In these experiments, however, only carbons in mobile regions can be detected. Long carbon-13 spin-lattice relaxation times and large static dipolar interactions between the protons and the carbon-13 nuclei, resulting in broad resonance lines, make the detection of carbons in crystalline regions by means of standard carbon-13 FT NMR virtually impossible.

By combining cross polarization with proton dipolar decoupling, detailed carbon-13 NMR spectra of solids can be obtained,[6] in principle allowing the measurement of individual carbon-13 spin-lattice relaxation times. Carbon-13 NMR spectra of powders obtained this way, however, are still difficult to interpret due to the presence of overlapping chemical shift anisotropy patterns. High-resolution solid-state carbon-13 NMR spectra of powders and solid polymers can be obtained by combining cross polarization and proton dipolar decoupling with magic-angle spinning,[7] as shown successfully by Schaefer and Stejskal.[8] These high-resolution techniques can be, and have been used to obtain a wealth of experimental data on solid polymers. A variety of relaxation times can be measured of individual carbons, including spin-lattice relaxation times in the laboratory frame and spin-lattice relaxation times in the rotating frame ($T_{1\rho}$). The latter are of particular interest since they are expected to yield information about motions in the midkilohertz range.[9] Carbon-13 rotating-frame relaxation times of solid poly(oxymethylene) have been measured by Veeman et al.[10] and Stejskal et al.[11] Interpretation of $T_{1\rho}$ measurements in terms of molecular motions is hampered, however, since both spin-lattice processes and spin-spin processes can contribute to the relaxation, the latter arising from "thermal contact" between the carbon-13 rotating-frame Zeeman reservoir and the proton dipolar reservoir.[11-13] Carbon-13 spin-lattice relaxation in the laboratory frame has received comparatively little attention. Schaefer et al.[14] reported some results on solid glassy polymers. Of the semicrystalline polymers only polyethylene spin-lattice relaxation times in the laboratory frame have been studied extensively.[15,16] We have now measured carbon-13 spin-lattice relaxation times in the laboratory frame and Overhauser enhancements of solid poly(oxymethylene), using high-resolution solid-state carbon-13 NMR. In accord with expectations two different carbon-13 signals are seen, with different spin-lattice relaxation times arising from amorphous and crystalline regions, respectively. The laboratory-frame carbon-13 spin-lattice relaxation times T_1 can be directly related with spin-lattice processes, i.e., molecular motions, since spin diffusion and spin-spin interactions are not expected to contribute to the carbon-13 relaxation. A variety of experiments, including measurements with and without magic-angle spinning, will be presented as well as a discussion of possible molecular motions responsible for the observed relaxation parameters.

Experimental Section

Carbon-13 NMR spectra and spin-lattice relaxation times of solid poly(oxymethylene) have been measured at 45 MHz on a double-resonance spectrometer, home-built around a 4.2-T superconducting magnet from Oxford Instruments. The amplitudes of the rotating components of the B_1 fields used in our earlier report of ^{13}C $T_{1\rho}$ measurements[10] amount to 25 kHz. Measurements were performed on cylindrical rotors machined from commercially available Delrin (Du Pont). The probe used for magic-angle spinning experiments and the spinners themselves have been described elsewhere.[17] Additionally, some experiments were performed at 15 MHz. Carbon-13 spin-lattice relaxation times were measured by using a cross-polarization version of the inversion-recovery method.[18] Pulse sequences were generated by a programmable digital pulse programmer described elsewhere.[19]

Results

Carbon-13 NMR spectra of solid poly(oxymethylene) at 45 MHz have been reported earlier.[10] The carbon-13 cross-polarization spectrum was shown to be a superposition of a rather narrow component arising from spins with a short T_1 ($\ll$1 s) and a relatively long $T_{1\rho}$ ($\sim$17.5 ms) and a broad component arising from spins with a long T_1 ($\gg$1 s) and a short $T_{1\rho}$ ($\sim$3 ms). The broad component has a line shape characteristic for carbon-13 NMR spectra dominated by anisotropy in the chemical shift and is therefore assigned to rigid ("crystalline") components. The narrow component suggests considerable motional averaging and is therefore assigned to mobile ("amorphous") regions. Under magic-angle spinning conditions the spectrum collapses to a single narrow line ($\sim$3 ppm wide). $T_{1\rho}$ measurements showed, however, that this single line is actually a superposition of two lines, one arising from the amorphous component and the other from the crystalline component.

Here we report quantitative measurements of carbon-13 spin-lattice relaxation times (T_1) of poly(oxymethylene). Both nonspinning samples and samples spinning at the magic angle were investigated. Carbon-13 T_1's were measured by using the cross-polarization version of the inversion-recovery technique.[18] Experiments were carried out with, as well as without, proton saturation during the recovery of the carbon-13 magnetization in order to establish the role played by proton-carbon dipolar couplings in the relaxation behavior of the carbon-13 nuclei. Differential equations describing the relaxation behavior of coupled spin systems under various conditions have been given by Noggle and Schirmer,[20] to which the reader is

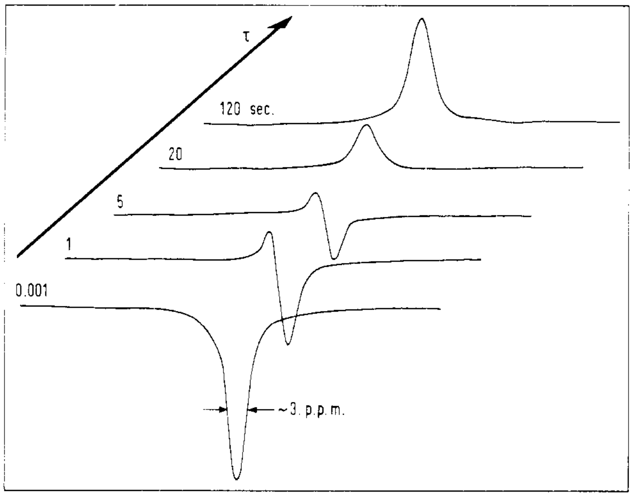

Figure 1. Representative magic-angle cross-polarization ^{13}C NMR spectra as a function of the recovery time τ in a carbon-13 spin–lattice relaxation experiment.

referred for details. We merely note that in general the recovery of the carbon-13 magnetization in the experiment with proton saturation is expected to be exponential, whereas a sum of exponentials is expected to describe the recovery of the carbon-13 magnetization in the experiment without proton saturation. This statement should be considered with reservation if we are dealing with solids. Due to anisotropic motion, the relaxation in solids in an experiment with proton saturation may still be nonexponential. However, since the measured relaxation time represents an average relaxation time from different oriented carbon atoms, it may approach a single exponential, for all practical purposes, as is indeed the case in our experiments. Furthermore, the carbon-13 magnetization in the experiment with proton saturation is expected to relax toward an enhanced equilibrium value (steady-state Overhauser enhancement) whereas it will relax to its "normal" (Boltzmann) equilibrium value in the experiment without proton saturation.

When analyzing the magnetization recovery curves, it is kept in mind that the initial magnetization is created by cross polarization rather than a simple 180° pulse. Thus a single-exponential recovery curve, obtained in experiments with proton saturation, is represented by

$$M_z(t) = (M_{CP}^0 - M_\infty)e^{-t/T_1} + M_\infty$$

where M_{CP}^0 represents the cross-polarized initial magnetization, M_∞ the equilibrium magnetization, and T_1 the spin–lattice relaxation time. The ratio M_{CP}^0/M_∞ is not constant but depends on the efficiency of the cross-polarization process. Therefore it depends on the length of the cross-polarization time as well as the sample spinning frequency. Experimental T_1 values were determined by a least-squares procedure in which M_{CP}^0, M_∞, and T_1 are treated as adjustable parameters.

Figure 1 shows some representative spectra obtained in a typical T_1 experiment with magic-angle spinning. It is immediately seen that the "single line" is actually a superposition of two lines: a fast relaxing line and a much slower relaxing line at slightly higher field. Deconvolution of the spectra gives two separate magnetization recovery curves, one for the fast relaxing amorphous part and one for the slowly relaxing crystalline part. Such experiments have been carried out at various sample spinning frequencies between 1 and 5 kHz.

Both magnetization recovery curves were found to be single exponential (within experimental error) in experiments with proton saturation. The carbon-13 spin-lattice relaxation times obtained from these experiments are 75 ms for the amorphous part and 15 s for the crystalline part, respectively. These values are independent of the sample spinning frequency, in contrast with earlier reported $T_{1\rho}$ values of the crystalline part, which were shown to be strongly dependent on the sample spinning frequency.[10] The ratio M_{CP}^0/M_∞ for the crystalline part does not change much when the sample spinning frequency is increased from 1 to 5 kHz. The ratio M_{CP}^0/M_∞ for the amorphous part decreases significantly upon an increase in sample spinning frequency, indicating a drastic decrease in cross-polarization efficiency. Oscillations of the ratio M_{CP}^0/M_∞ as a function of a mismatch of the Hartmann–Hahn condition as observed for adamantane[21] are not observed in poly(oxymethylene).

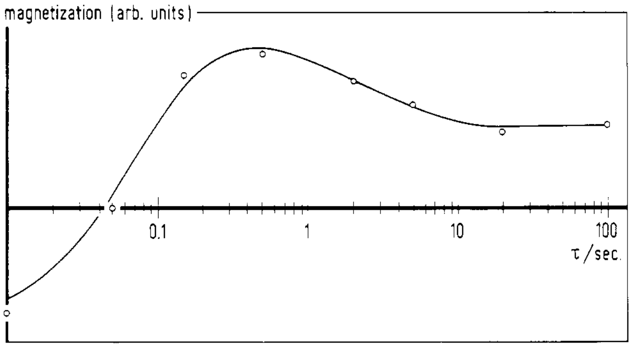

Figure 2. Magnetization recovery of the amorphous carbons in a typical T_1 measurement without proton saturation showing the transient Overhauser effect.

The relaxation behavior of the crystalline part in experiments without proton saturation was, again within experimental error, found to be single exponential as well. Again a value of 15 s was obtained. The equilibrium magnetization reached in this experiment is smaller than the equilibrium value reached in experiments with proton saturation. From the ratio of the respective equilibrium values a (steady state) Overhauser enhancement value of 1.3 ($1 + \eta = 1.3$) is obtained. The relaxation behavior of the amorphous part is no longer simple exponential in experiments without proton saturation. In fact it was found to overshoot its equilibrium value. Figure 2 shows an example of the magnetization recovery of the amorphous part obtained from such an experiment. Again, a larger equilibrium value is reached in experiments with proton saturation than in those without and an Overhauser enhancement of 1.6 is obtained from the ratio of the respective equilibrium magnetizations.

Essentially the same features were observed in experiments without magic-angle spinning. The narrow component, attributed to the amorphous part, has a short T_1 (~75 ms) and the broad pattern, assigned to the crystalline part, a much longer T_1. Again, the amorphous part overshoots its equilibrium value in experiments without proton saturation. Furthermore, steady-state Overhauser enhancements are observed for both the amorphous and the crystalline part. The poor S/N ratio in these experiments does not allow precise measurements of the relaxation times and Overhauser enhancements but is good enough to show that they are of the same order of magnitude as those measured in samples spinning at the magic angle. Measurements on nonspinning samples at higher temperatures (up to 75 °C) do not show significant changes in relaxation times and Overhauser enhancements, for both the amorphous and the crystalline components.

Additionally, preliminary spin–lattice relaxation time measurements have been performed at 15 MHz. The ^{13}C

Table I
Carbon-13 Relaxation Parameters of Solid Poly(oxymethylene) at Room Temperature

	amorphous part	crystalline part
T_1 (at 45 MHz)	75 ms	15 s
NOE (at 45 MHz)	1.6	1.3
T_1 (at 15 MHz)	50 ms[a]	~1.5 s[a]
$T_{1\rho}$ (from ref 10)	17.5 ms	~0.5–3 ms

[a] Estimated errors at least 20%.

spin–lattice relaxation time T_1 of the amorphous component is of the same order of magnitude as that measured at 45 MHz. The carbon-13 spin–lattice relaxation time of the crystalline component appeared to be much shorter, however, and was estimated to be ~1.5 s.

The various spin–lattice relaxation parameters as reported above are summarized in Table I.

Discussion

The observed differences in carbon-13 relaxation behavior in experiments with and without proton saturation during the recovery of the carbon-13 magnetization strongly suggest that proton–carbon dipolar relaxation is the dominant relaxation mechanism. Single-exponential recovery curves to (Overhauser) enhanced equilibrium values are observed under proton saturation conditions for both the crystalline and amorphous components, whereas the carbon-13 magnetizations relax toward their normal equilibrium values in experiments without proton saturation. Moreover, the relaxation of the amorphous part in experiments without proton saturation is no longer exponential. This deviation from simple exponential recovery is expected for coupled spin systems (see, e.g., ref 20) when both spins relax simultaneously. The observed "overshoot" in the carbon-13 magnetization of the amorphous part indicates that the carbon-13 T_1 is shorter than the proton T_1. Direct measurement of the proton T_1 shows that this is indeed the case: a proton T_1 of ~200 ms, was measured against a carbon-13 T_1 of 75 ms for the amorphous part. The expected deviation from single-exponential recovery is not observed for the crystalline part. This is not surprising since the crystalline carbon-13 T_1 is much longer than the proton T_1. In that case the protons reach a steady-state magnetization in a time very short compared with the time needed for the carbon-13 magnetization to relax significantly. We therefore conclude that both amorphous and crystalline carbon-13 relaxation parameters can be discussed in terms of proton–carbon dipolar relaxation. Besides, other relaxation mechanisms are not expected to play any role of importance in solid polymers such as poly(oxymethylene).

Before analyzing our data, we note that other experiments, i.e., dielectric and mechanical relaxation measurements, as well as proton spin–lattice relaxation measurements, at room temperature only show evidence of fast motions (γ relaxation, correlation frequency ~10^8 Hz) in solid poly(oxymethylene).[2,3] These experiments, however, do not tell where these motions take place, i.e., whether these motions occur in the amorphous part only or whether a complex motional process takes place, involving the amorphous as well as the crystalline parts. Another possibility is that the motions in amorphous and crystalline regions differ in, for instance, amplitude but that they have the same, or very similar, correlation times.

Assuming isotropic random reorientation of C–H vectors, the carbon-13 T_1, $T_{1\rho}$, and NOE factor are given, in standard notation, by

$$\frac{1}{T_1} = \frac{1}{10}\gamma_H^2\gamma_C^2\hbar^2\sum r_i^{-6}\left\{\frac{\tau_c}{1+(\omega_H-\omega_C)^2\tau_c^2} + \frac{3\tau_c}{1+\omega_C^2\tau_c^2} + \frac{6\tau_c}{1+(\omega_H+\omega_C)^2\tau_c^2}\right\} \tag{1}$$

$$\frac{1}{T_{1\rho}} = \frac{1}{20}\gamma_H^2\gamma_C^2\hbar^2\sum r_i^{-6}\left\{\frac{4\tau_c}{1+\omega_1^2\tau_c^2} + \frac{\tau_c}{1+(\omega_H-\omega_C)^2\tau_c^2} + \frac{3\tau_c}{1+\omega_C^2\tau_c^2} + \frac{6\tau_c}{1+(\omega_H+\omega_C)^2\tau_c^2} + \frac{6\tau_c}{1+\omega_H^2\tau_c^2}\right\} \tag{2}$$

$$\mathrm{NOE} = 1+\eta = 1+\frac{\gamma_H}{\gamma_C}\left\{\frac{6\tau_c}{1+(\omega_H+\omega_C)^2\tau_c^2} - \frac{\tau_c}{1+(\omega_H-\omega_C)^2\tau_c^2}\right\}\Bigg/\left\{\frac{\tau_c}{1+(\omega_H-\omega_C)^2\tau_c^2} + \frac{3\tau_c}{1+\omega_C^2\tau_c^2} + \frac{6\tau_c}{1+(\omega_H+\omega_C)^2\tau_c^2}\right\} \tag{3}$$

In deriving 2 we have assumed that the frequency ω_1 of the radiation field H_1 is much smaller than ω_H and ω_C. Substituting in these equations the parameters obtained for the carbon-13 of the amorphous part (see Table I) and assuming that the carbon-13 nuclei are relaxed by two protons at a distance $r = 1.09$ Å, we obtain for the correlation time τ_c 3×10^{-9} s (from T_1), 1.5×10^{-9} s (from NOE), and 1.3×10^{-8} s (from $T_{1\rho}$). The correlation times derived from the measured ^{13}C T_1 and NOE agree quite well. Spin–spin contribution to the measured ^{13}C $T_{1\rho}$ cannot be excluded for the radio-frequency fields used in our earlier studies.[10] Therefore the measured $T_{1\rho}$ should be considered as a lower limit for $T_{1\rho}$ due to molecular motions, and, consequently, the τ_c derived from $T_{1\rho}$ should be seen as an upper limit for the correlation time of the molecular motions. Thus we feel that the results of the experiments above suggest more or less isotropic motions for the carbons in the amorphous part. The observed carbon-13 line width of the amorphous part in nonspinning samples (~15 ppm), however, indicates that the motions are not completely isotropic, since it is expected that isotropic motions with such short correlation times would average out the anisotropy in the chemical shift. We therefore conclude that the motions in the amorphous part have rather large amplitudes, approaching isotropic reorientation. Our calculated correlation times are in good agreement with correlation times found by, e.g., Trappeniers et al.,[3] who calculated a correlation time $\tau_c = 2 \times 10^{-9}$ s at room temperature from proton T_1 measurements, and correlation frequencies of γ relaxation in poly(oxymethylene) as determined by dielectric and mechanical loss experiments.

Analysis of the crystalline carbon-13 data is less straightforward. Before we can attempt to estimate any molecular correlation time, it is necessary to establish whether molecular motions do take place in the crystalline part or whether the crystalline part is rigid. Evidence for the latter is, for instance, the line shape observed for the crystalline part in experiments without magic-angle spinning. A typical powder pattern, characteristic for anisotropy in the chemical shift, was observed, indicating little or no motional narrowing. In other words, molecular motions consistent with this line shape either are very slow, with a correlation frequency smaller than the line width (expressed in frequency units), or are of a highly restricted nature, that is, molecular motions of limited amplitude. These restricted motions are not expected to average the chemical shift powder pattern to a large extent, not even in the case of fast restricted motions, i.e., with correlation frequencies larger than the line width. Dielectric and mechanical loss measurements at room temperature only indicate high-frequency motions (correlation frequency $\sim 10^8$ Hz) in solid poly(oxymethylene). The possibility of motions in the crystalline part with long correlation times, i.e., correlation frequencies smaller than the line width, can therefore be discarded. Therefore the molecular motions in the crystalline part, if there are any, must be of a restricted nature (small amplitude), having correlation times comparable to those of the motions in the amorphous part. Evidence that molecular motions do take place is provided by the observed carbon-13 spin-lattice relaxation time T_1 of 15 s since a much longer T_1 is expected for a rigid lattice. Such long T_1's have been observed for crystalline polyethylene for instance (1000 s or more!). Before concluding from our T_1 measurements that motions take place in the crystalline part, we must consider the possibility that crystalline carbon-13 nuclei, considered as rigid for the moment, are relaxed by mobile protons in the amorphous part. Using the correlation time deduced for the amorphous part ($\tau_c \approx 3 \times 10^{-9}$ s) and inserting a C–H distance of 5 Å in formula 1, we obtain a theoretical T_1 for the crystalline carbons of $\sim$650 s. This value, which is probably a lower limit, indicates that the observed carbon-13 T_1 cannot be explained by the mechanism considered above. In other words, the CH_2 groups in the crystalline parts themselves must be mobile in order to explain the short T_1. Summarizing the arguments above, we conclude that restricted motions take place in the crystalline parts with correlation times comparable to those of the motions in the amorphous part (10^{-8}–10^{-9} s). Several authors investigated molecular motions in poly(oxymethylene) crystals by means of proton NMR line width studies (see, e.g., Shibata and Iwayanagi[22] and references cited therein). Several motional processes were invoked to explain the experimental data, almost invariably involving rotational oscillations around the helical axis of poly(oxymethylene) chains. Estimates of the amplitude of these oscillations range from 9° to 40°. The same helical conformations are expected to occur in crystalline regions of commercial poly(oxymethylene), because of the strong preference of gauche–gauche conformations. Accordingly, similar molecular motions might occur in commerical poly(oxymethylene). Clearly, these motions are of a highly restricted nature. They are not expected to average out chemical shift anisotropy patterns completely, not even in the case of short correlation times. Also, these restricted motions are expected to give rise to longer spin–lattice relaxation times than more or less isotropic motions with comparable correlation times. Preliminary calculations show, for instance, that C–H vectors restricted to motions inside a cone, with a top angle of 16°, give rise to average relaxation times that are 200 times as long as relaxation times arising from C–H vectors allowed to reorient within a complete sphere with the same correlation time. Hence the difference in the observed carbon-13 spin–lattice relaxation times for the amorphous and crystalline parts (75 ms and 15 s, respectively) might reflect differences in the amplitude of the motions involved (more or less isotropic motions vs. restricted rotational oscillations), rather than greatly different correlation times of the respective motions.

It is well-known that molecular motions in polymers are generally better described by distributions of correlation times than by a single correlation time.[4,23,24] These distributions result in rather shallow minima in T_1 vs. $1/T$ plots. In particular, it raises the T_1 values at the minimum and lowers the T_1 values away from the minimum. Therefore, the observed, essentially temperature-independent, relaxation times (for both the amorphous and crystalline parts) in the range studied (20–75 °C) might reflect a distribution of correlation times rather than a single correlation time. At the same time a distribution of correlation times can better explain the observed field dependence of the carbon-13 T_1 of the crystalline part. Such a field dependence is not expected for a single correlation time of the order of 10^{-8}–10^{-9} s but can be expected for distributions of correlation times centered around average correlation times of that order of magnitude. This can be seen from the following argument. The position of the T_1 minimum, which for a single correlation time τ_c is given by $\omega\tau_c \approx 1$, is in the case of a distribution given by $\omega\bar{\tau}_c \approx 1$, where $\bar{\tau}_c$ is the average correlation time. For a single correlation time τ_c the theoretical T_1 curves for different magnetic fields coincide for short correlation times ($\tau_c < \omega^{-1}$). A field-dependent T_1 is predicted for long correlation times ($\tau_c > \omega^{-1}$). A slightly different situation is met with in the case of a distribution of correlation times. Then field-independent T_1's are predicted only for very short average correlation times ($\bar{\tau}_c \ll \omega^{-1}$) while average correlation times $\bar{\tau}_c$ of the order of magnitude $\bar{\tau}_c \approx \omega^{-1}$ will not result in field-dependent T_1's. This, of course, results from the presence of relatively long correlation times in the distribution, i.e., correlation times longer than the average $\bar{\tau}_c$. Thus the observed field dependence of the carbon-13 T_1 of the crystalline part is not inconsistent with restricted motions characterized by average correlation times of the order of magnitude $\bar{\tau}_c \approx \omega^{-1}$, i.e., of the order of magnitude 10^{-8}–10^{-9} s.

Other evidence for molecular motions in the crystalline part with short average correlation times is provided by the observed NOE (1.3), which is well above its minimum (theoretical) value of 1.1. Using the single correlation time model, we calculate $\tau_c = 3 \times 10^{-9}$ s, from the NOE. The extraction of information from the NOE alone, however, must be considered with care, since, in principle, protons not directly bonded to the carbon under study can contribute to the NOE. This may become particularly important when the directly bonded protons do not dominate the relaxation behavior. This, however, is not likely in our case.

Summarizing, the observed carbon-13 T_1's and NOE factor for the crystalline part can be accounted for if one assumes restricted motions with relatively short average correlation times. The arguments used are based upon the assumption that the carbon-13 relaxation is of proton–carbon dipolar origin and not, for instance, caused by paramagnetic impurities. It is well-known that commercial polymers may contain paramagnetic impurities, like oxygen, and the question may be raised whether such impurities may account for the observed carbon-13 relaxation behavior. Our samples, however, did not show any detectable paramagnetism. Moreover, since spin diffusion between carbon-13 nuclei at natural abundance is very slow, these paramagnetic centers can only contribute to the relaxation of a few nearby carbon-13 spins and therefore not to the observed relaxation time. In fact, as recently shown by Ganapathy et al.,[25] deliberately doping samples with paramagnetic impurities has very little effect on the carbon-13 T_1 of a wide variety of compounds (although it does affect the observed proton T_1 because of rapid proton spin diffusion). We therefore feel that the possible effect of paramagnetic impurities upon the carbon-13 relaxation in solid poly(oxymethylene) can be ignored. Moreover, the observed carbon-13 relaxation (in particular, the effect of proton saturation) is typically as expected for proton–carbon dipolar relaxation.

Finally, we note that the observed $T_{1\rho}$ of the crystalline part ($\sim$2 ms) is shorter than the $T_{1\rho}$ of the amorphous part ($\sim$17.5 ms). This is not consistent with restricted molecular motions in the crystalline part, having correlation times comparable to the more isotropic motions occurring in the amorphous part. Instead, a longer $T_{1\rho}$ would be expected. This discrepancy results from the fact that the $T_{1\rho}$ of the crystalline carbons is determined by spin–spin interactions.[11,13] This is confirmed by proton $T_{1\rho}$ measurements in poly(oxymethylene)[26] in experiments where amorphous proton–crystalline proton spin diffusion has been reduced. The crystalline proton $T_{1\rho}$ then is 150 ms and the amorphous proton $T_{1\rho}$ is 30 ms; i.e., a longer (proton) $T_{1\rho}$ is observed for the crystalline part than for the amorphous part.

In conclusion, we feel that our data, combined with data from other experiments, suggest that molecular motions in solid poly(oxymethylene) take place in both amorphous and crystalline components and that these motions, possibly involving rotational oscillations of CH_2 units around the helical axis, can be characterized by (average) correlation times of the same order of magnitude. The amplitudes of these motions, however, are quite different, small-amplitude oscillations taking place in the crystalline component and larger amplitude motions in the amorphous components.

Obviously, measurement of carbon-13 spectra and relaxation parameters alone do not provide enough information to derive a clear model of the complex motions taking place in solid semicrystalline polymers. They do provide, however, useful complementary data, in particular, about the sites (or regions) where motions take place. In particular, carbon-13 line shapes and spin–lattice relaxation times in the laboratory frame seem to be useful parameters in the study of molecular motions in solid polymers.

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Simulation Results for the End-to-End Vector Distribution Function of Short Polymethylene Chains

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ABSTRACT: Numerical results are obtained by means of simulation methods for the end-to-end vector distribution function of short polymethylene molecules represented by rotational isomeric chains and slightly different models. These results are used to test the accuracy of those previously obtained through quasi-analytical (i.e., nonsimulation) algorithms. Thus a procedure recently developed by Fixman et al. is confirmed to yield reasonably good values. The simulation results reveal orientational preferences in the region corresponding to small values of the end-to-end distance where intramolecular kinetic processes may occur when reactive groups are present. This region cannot be conveniently explored by current quasi-analytical methods.

I. Introduction

Correlations between the end repeating units of a polymer chain or, in general, between the terminal units of a sequence of N bonds along the polymer backbone have a fundamental role in the theory of dilute polymer solutions since they determine many macroscopic properties. These correlations are described by means of the end-to-end vector, $\mathbf{R}$, i.e., the vector joining the end units referred to a frame embedded in the sequence of bonds considered.[1] In many instances (polarized light scattering intensities, hydrodynamic properties, etc.) the macroscopic magnitudes depend mainly on the radial correlations[2] so that they can be conveniently related to the end-to-end distance, $R \equiv |\mathbf{R}|$. Some other properties (depolarized light scattering intensities,[3] change transfer between the ends of short chains,[4,5] etc.) depend on or may depend more strongly on the angular correlations. Thereby the end-to-end vector distribution function, $F(\mathbf{R})$, is a very interesting conformational characteristic of flexible-chain molecules.

For very long chains or sequences, i.e., for high values of N, $F(\mathbf{R})$ tends to be spherically symmetric and the

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