Molecular Motion of Isolated Polyethylene Chains in the Solid State

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ABSTRACT: In organic inclusion compounds the strong and restrictive polymer–polymer intermolecular interactions of the bulk polymer crystal are replaced with the less limiting geometrical constraints of the channel walls. This facilitates the study of isolated polymer molecules in the solid state. In this report we present the results of a deuterium NMR analysis of the motions of fully extended polyethylene chains confined to the 5 Å diameter channels of the inclusion compound formed with perhydrotriphenylene. Line shape analysis and relaxation data demonstrate that the most important motion is that of the high-frequency libration of the carbon–carbon bonds about the *trans* conformational arrangement. This bond libration effects a low-energy twisting motion that provides a complete reorientation of the C–D bonds about the long axis of the molecule on the nanosecond time scale. A broad distribution of frequencies is associated with this motion.

Introduction

Perhydrotriphenylene (PHTP) rapidly forms inclusion compounds (ICs) with many polymers. The polymer IC can be formed from the corresponding monomer IC by γ-irradiation-initiated polymerization. Alternatively, the IC can be constructed by the cocrystallization of polymer and PHTP from a common solvent or from the melt state. The resultant ICs contain long cylindrical channels in which the isolated polymer chain is fully extended. The ICs have been used for many years to produce linear, stereoregular polymers of high molecular weights. Complete descriptions of the preparation and the nature of both the monomer and polymer ICs have been presented previously.[1–3]

In recent reports we have described the solid-state conformational structures and dynamics of isolated chains of 1,4-*trans*-polyisoprene[4] (TPI) and polyethylene[5] (PE) in the channels of PHTP. As reflected in the ^{13}C NMR data,[4] the isolated polymer chains in the TPI/PHTP-IC adopt a fixed skew-*trans*-skew conformation at the single bonds similar to that of the β-form of the bulk crystalline polymer that is obtained by quenching the polymer from the melt. This conformation has been calculated to be the lowest energy conformation for the isolated polymer chain.[6] In contrast, normal crystallization of TPI leads to the α-form with the slightly higher energy skew-*trans-cis* conformation. The stability of the α-form probably results from its better intermolecular packing compared to the β-form.[7] The measurements of the carbon spin–lattice relaxation times revealed that there is also a similarity in the local chain motions for the TPI molecules in the IC and in the β-crystal structure.[4]

Solid-state ^{13}C NMR data for the PE/PHTP-IC[5] indicate that the isolated chains of PE adopt an *all-trans* planar zigzag conformational arrangement similar to that of the bulk crystalline PE. However, the carbon relaxation data show a substantial difference in the mobility of the polymer chain in these two distinct environments. In the bulk crystalline polymer the chain is very rigid, as reflected in the long (320 s) carbon spin–lattice relaxation time, T_1. In contrast, the T_1 value of 6.4 s for the carbon nuclei of PE in the channels of the IC suggests significant local chain motion. The slope of an Arrhenius plot of the spin–lattice relaxation time corresponds to an energy of only 4.6 kJ/mol. This energy primarily reflects changes with temperature in the amplitude and frequency of the motions associated with spin–lattice relaxation. Significantly, the low energy demonstrates that the motions responsible for this relaxation do not involve *gauche-trans* isomerization, which has an energy barrier of ca. 14.6 kJ/mol.[8] Three possible motions or combinations of these motions for the polymer chain within the channels of the IC would be consistent with all of these ^{13}C NMR data: libration about each carbon–carbon bond, traveling "chain twists", and rigid-rod rotation of the entire molecule about its long axis. Molecular dynamics simulations[9] of the PE/PHTP-IC indicate the presence of low-energy, torsional oscillations that involve only small deviations (±9°) from the *trans* conformation. In order to learn more about the chain motion we have carried out a ^{2}H NMR analysis of perdeuterated polyethylene (PE-d_4) in the channels of PHTP; the results are presented in this report.

Experimental Section

Materials. The racemic *trans-anti-trans-anti-trans-anti* isomer of PHTP was synthesized as described elsewhere,[10] precipitated as an inclusion compound with heptane, and purified by sublimation at 10^{-4} Torr and 80 °C. It was analyzed by GLC, NMR, and DSC and found to be >99% pure. The linear PE-d_4 was obtained from Merck & Co. and used as received. PE-d_4/PHTP-IC was prepared by intimately mixing together the two components (with excess of PHTP) in the powder form, melting them together at +200 °C under an inert atmosphere, and then cooling slowly (1 °C/min) to room temperature. Crystallization occurs at +155 °C. The sample is then heated to +170 °C and annealed for 2 h, followed by slow cooling (1 °C/min) to room temperature.

Methods. Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer DSC-4 equipped with a Model 3600 data station. The solid-state ^{2}H NMR data were recorded on a Varian Unity-400 spectrometer operating at a deuterium frequency of 61.4 MHz. The spectra were recorded using the standard quadrupole echo pulse sequence. The $\pi/2$ pulse was 2.8 μs and the delay τ_1 between the $\pi/2$ pulses was normally 20 μs. The delay between accumulations was 2–10 s and chosen to

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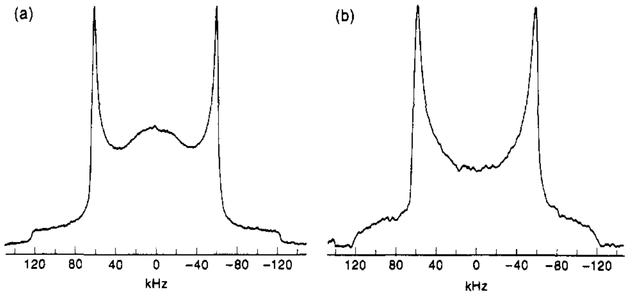

Figure 1. Fully relaxed solid-state ^{2}H NMR spectra at 61.4 MHz for (a) the bulk crystalline PE-d_4 at +20 °C and (b) the PE-d_4/PHTP-IC at −100 °C.

exceed $5T_1$ for each set of conditions. Each spectrum represents between 500 and 1500 accumulations. For comparisons of absolute signal intensities recorded at different temperatures, corrections were made for changes in signal strength due to factors other than molecular dynamics (i.e., Boltzmann distribution of nuclear spin states, Q of coil circuit, etc.). The correction factors were obtained by measuring the integrated intensity for the powder pattern of malonic acid, a rigid crystalline material that undergoes no significant change in molecular dynamics in the −100 to +100 °C range.

Results

Thermal Analysis. The initial DSC trace for the PE-d_4/PHTP-IC sample shows endotherms at 126.6 °C (25.8 J/g) and at 176.4 °C (64.4 J/g). Following a cooling run of 5–10 °C/min, the second heating exhibits endotherms at 125.2 °C (22.6 J/g) and at 174.3 °C (61.3 J/g). The first endotherm corresponds to melting of pure PHTP (in excess) and the second to melting of the PE-d_4/PHTP-IC. The thermal data show no evidence of free crystalline PE in the bulk. Based on the enthalpy of the first transition and the melting enthalpy of pure PHTP of 71.1 J/g, it is determined that the IC sample contains 36% excess PHTP. Therefore the strength of the second endotherm indicates a melting enthalpy for the PE-d_4/PHTP-IC of 100.6 J/g. This compares well with the published value[11] of 107–112 J/g for PE/PHTP-IC and demonstrates that there is little if any free PE-d_4 outside of the channels of the IC.

^{2}H NMR Spectra. The homogeneous environment afforded the PE molecules by the channels of the inclusion compound is evident from comparison of the deuterium NMR spectra shown in Figure 1 for a bulk crystalline PE-d_4 sample at +20 °C and the PE-d_4/PHTP-IC at −100 °C. Typical for the bulk polymer, the Pake powder spectrum at room temperature exhibits a peak separation of 125 kHz emanating from the rigid, crystalline deuterons. The signal intensity at the center of the spectrum is the partially averaged pattern that is produced by the mobile deuterons of the amorphous phase in this semicrystalline material. At +20 °C the motional averaging in the amorphous region is incomplete and only at higher temperatures (ca. +100 °C) is a sharp peak observed.

The deuterium NMR spectrum of the PE-d_4 chains in the channels of the IC also shows a peak separation of 125 kHz, indicating, as in the bulk crystalline phase, that there is no significant reorientation of the C–D bonds on the time scale of the inverse line width, i.e., a few microseconds. Note that, in contrast to the spectrum for the bulk sample, the spectrum for the IC does not contain additional intensity at the center of the powder pattern. This supports the conclusion from the thermal data, namely that all of the polyethylene is within the channels of the inclusion compound.

As seen in Figure 2 the deuterium line shape of the PE-d_4/PHTP-IC changes dramatically upon heating. The changes in the line shapes reflect changes in the rates of the molecular dynamics. Beginning at −30 °C a partial averaging of the powder pattern is apparent. At 0 °C the local chain motions affecting the rate of reorientation of the C–D bonds become intermediate on this NMR time scale (correlation time, $\tau_c \sim 10^{-5}$–10^{-6} s). Above +20 °C the separation of the peaks remains at 50 kHz but the pattern continues to exhibit improved resolution with increasing temperature. This change demonstrates an increase in the frequency of the reorientation of the C–D bonds (fast exchange regime with $\tau_c \leq 10^{-7}$ s), but the reorientation of the bonds relative to the external magnetic field remains anisotropic. From these deuterium NMR data and the carbon NMR data of our earlier study[5] we know the motions of the PE chains in the IC to be anisotropic and associated with a small amount of energy.

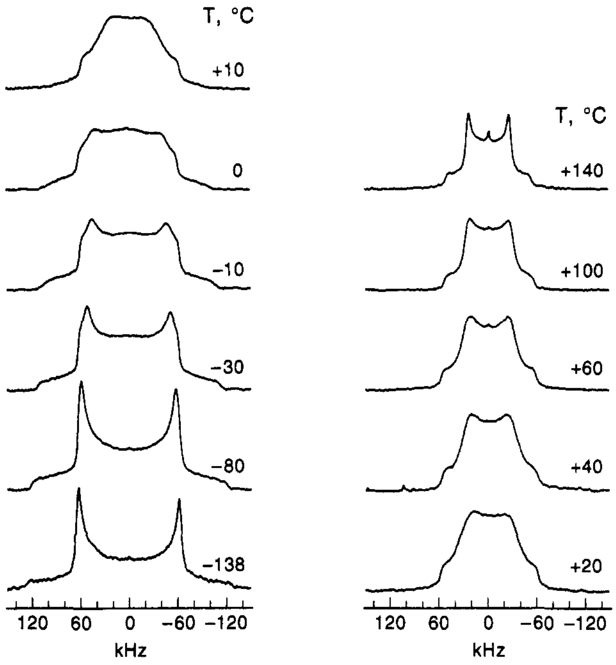

Figure 2. Fully relaxed solid-state ^{2}H NMR spectrum at 61.4 MHz for the PE-d_4/PHTP-IC at the indicated temperatures.

Deuterium NMR spectra can also provide information about the distribution of correlation times associated with local motions. As has been demonstrated by Spiess et al.,[12,13] distortions in the NMR line shapes are to be expected at the intermediate frequency regime where T_2^*, the transverse relaxation, becomes comparable to the delay τ_1 in the echo experiment. As a consequence the magnetization will not be refocused by the second rf pulse and the intensity and shape of the echo spectrum may differ from that of the absorption spectrum. Since T_2^* varies with the orientation of the C–D bond, severe distortion of the pattern can result. In particular, a substantial (ca. 80–90%) loss in intensity should be observed in this intermediate exchange regime if the motion can be described with a single correlation time.[13,14]

The deuterium quadrupole echo spectra for the PE-d_4/PHTP-IC recorded at four temperatures for different values of the echo delay τ_1 are presented in Figure 3. The total integrated intensity is given below each spectrum. The spectra at −100, +5, +20, and +100 °C represent the slow, intermediate, onset of fast, and fast exchange regimes, respectively. A comparison of the data for a τ_1 of 15 μs reveals a signal reduction of only 24% at the intermediate exchange frequency (+5 °C) and thus indicates the chain motion of the PE within the channels of the IC includes a broad distribution of correlation times.

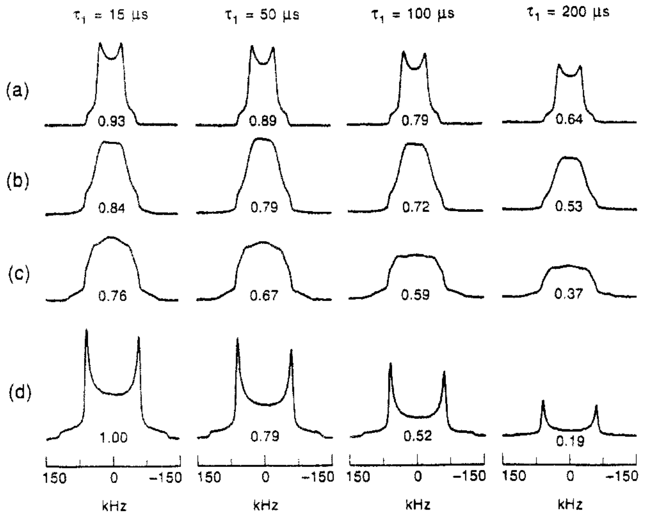

Figure 3. 61.4 MHz ^2H solid echo NMR spectra of the PE-d_4/PHTP-IC recorded at (a) +100, (b) +20, (c) +5, and (d) −100 °C for four values of the echo delay, τ_1. The number under each spectrum is the total integrated intensity referenced to the spectrum recorded at −100 °C with a τ_1 of 15 μs. Integral values were corrected for changes due to factors other than molecular dynamics (see Experimental Section).

The spin–spin relaxation time T_2^* was measured at each temperature by fitting the intensity of the echo spectrum as a function of τ_1 (Figure 3) to a single exponential relaxation. The integrated intensities have been normalized by assigning a value of 1.0 to the integral of the spectrum recorded at −100 °C with a τ_1 of 15 μs. T_2^* is ca. 100 μs at −100 °C and increases to ca. 500 μs at +100 °C. The short T_2^* observed at −100 °C reflects large amplitude kilohertz motions and suggests that the spectral density of the local motions producing the reorientation of the C–D bonds has a significant component in the 10 kHz region at −100 °C and that this component is reduced with increasing temperature.

Discussion

Before considering local chain motions that would be consistent with all of the NMR data, it is helpful to compare the results from the study of the PE-d_4/PHTP-IC to those reported previously for the 1,4-*trans*-polybutadiene-*1,1,4,4*-d_4/PHTP-IC (TPBD-d_4/PHTP-IC).[15] The deuterium NMR data for both polymers at several temperatures are presented in Figure 4. In the analysis of the TPBD-d_4/PHTP-IC we demonstrated that the deuterium pattern reflected a rapid reorientation of the C–D bond of the TPBD about the long axis of the molecule with the bond at an angle of 70–80° to this axis.[15] Further we established that the reorientation of the C–D bond was produced by conformational averaging about the CH–CD_2 bonds.

$$\mathrm{CH{-}CD_2{-}CD_2{-}CH{=}}$$

In contrast the CD_2–CD_2 single bond remains fixed in the *trans* conformation.[11]

As shown in Figure 4 there is a strong similarity in the data of these two polymer ICs, both in the peak separation of 50 kHz and the changes in line shape that occur as the temperature is reduced. (The weak peak at zero frequency in the PE-d_4/PHTP-IC spectrum recorded at +140 °C represents a small amount of free, amorphous PE produced from a slow degradation of the IC at this high temperature.) The strong similarity in the data for the two polymers in the IC suggests that in both polymer chains the C–D bond is undergoing the same type of anisotropic reorientation. However, it does not necessarily follow that the same local chain motion is responsible for the bond reorientation in the two ICs. In fact, the offset of the PE data to higher temperature indicates that the energies associated with the motion in PE are higher than the those associated with the motion in the TPBD chain. In addition, the carbon chemical shift data[5] for the PE/PHTP-IC show that conformational averaging is not occurring in the PE chain. Therefore, despite a similarity in the C–D bond reorientation in the two polymers, the motions driving the reorientations are clearly quite different. This comparison illustrates, as has been reported by Hirschinger and English,[16] that analysis of fully relaxed deuterium spectra alone does not always provide unambiguous identification of chain motion.

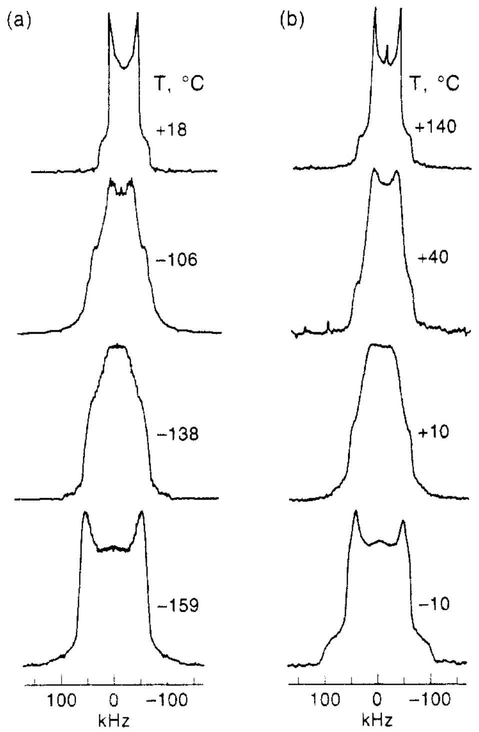

Figure 4. Comparison of the solid-state ^2H NMR spectra for the (a) TPBD-d_4/PHTP-IC and (b) PE-d_4/PHTP-IC at the indicated temperatures.

Line Shape Analysis and Chain Motions. Below −30 °C the deuterium NMR line shape for PE-d_4/PHTP-IC is a Pake doublet with a peak-to-peak width of 125 kHz (Figure 2). This is only consistent with the absence of large-amplitude fast ($>10^8$ Hz) motion. Above +20 °C the line shape remains that of a Pake doublet but with a peak separation of only 50 kHz. The narrowing of the spectral pattern is due to molecular motion.

As a first consideration, simple rotation of the PE chain about the channel axis would reduce the line width significantly. Although this motion is associated with a very high activation energy in the bulk crystal,[17] in the isolation of the channels of the IC it is quite feasible. If such motion were the sole source of reorientation of the C–D bonds, it would reduce the Pake doublet peak splitting to 62.5 kHz, one-half its rigid-lattice value. This is because the C–D bonds are perpendicular to the chain axis when the chain is in the *all-trans* state. The fact that the peak separation is reduced to 40% of the rigid-lattice value indicates that the PE chain is undergoing more than just simple rigid-body rotation about the channel axis; there must also be internal motion. Since the polymer chain is highly constrained in the channel, the only internal motion possible is small-angle torsion of the carbon backbone.

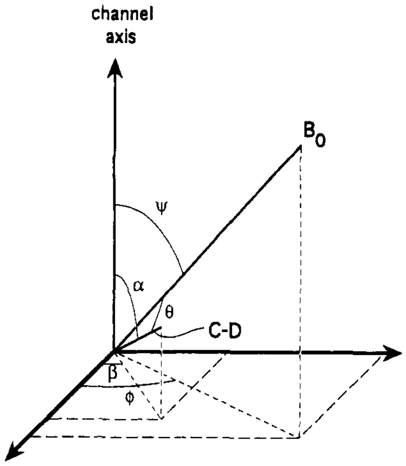

Figure 5. Rectilinear coordinate system with the third axis along the channel axis. The polar and azimuthal angles of the C–D bond are α and β, and for the magnetic field, ψ and ϕ. The angle between the C–D bond and the magnetic field B_0 is θ.

The absence of conformational isomerization has been previously established.[5] Small-angle torsional oscillations about the *trans* position within the low-energy well will reorient the C–D bonds and reduce the deuterium spectral line width.

The range of motion of the C–D bonds can be estimated from the deuterium NMR line shape and from that estimate the amplitude of the torsional motion of the carbon backbone. In order to interpret the high-temperature deuterium line shape data, it is convenient to construct a model probability distribution for the C–D bond orientation in the frame of reference of the channel. A simple probability function for the C–D bond directions is

$$P(\alpha,\beta) = \frac{1}{(2\pi)^{3/2}\sin\epsilon}\exp\left(-\frac{\cos^2\alpha}{2\sin^2\epsilon}\right) \qquad \sin\epsilon \ll 1 \qquad (1)$$

where α and β are the polar and azimuthal angles of the C–D bond with respect to the channel axis (see Figure 5) and ϵ is the root-mean-square deviation of α from 90°. These deviations are due to internal motion. The Gaussian character to the α-dependence of this function is not necessarily physical; the functional form was chosen out of convenience. The important points are that the probability distribution be sharply peaked about $\alpha = 90°$ and be axially symmetric about the channel axis to reflect the symmetry of the channel. To be precise, it should be noted that the channel has 3-fold symmetry. Rapid motion within such a channel will have the same averaging effect on interactions with character of second rank spherical tensor elements as rapid motion within a cylindrically-symmetric well. For this reason any dependence of the probability distribution on the azimuthal angle can be justly ignored.

The secular component of the quadrupolar Hamiltonian for the deuterons in a strong field is

$$\mathcal{H}_{Q,\mathrm{sec}} = \frac{eQV_{\mathrm{CD}}}{4I(2I-1)\hbar}\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)(3I_z^2 - I(I+1)) \qquad (2)$$

where θ is the angle between the C–D bond and the magnetic field (see Figure 5). e is the proton charge, Q is the nuclear quadrupole moment, and V_{CD} is the electric field gradient along the C–D bond at the position of the deuterium nucleus. In the fast motion limit, the line shape is dictated by the time-averaged Hamiltonian

$$\mathcal{H}_{Q,\mathrm{sec}} = \frac{eQV_{\mathrm{CD}}}{4I(2I-1)\hbar}\overline{\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)}(3I_z^2 - I(I+1)) \qquad (3)$$

where the bar denotes a time average. By the addition theorem for spherical harmonics, the geometric term can be rewritten in terms of spherical harmonics with arguments pertaining to the channel orientation in the magnetic field and spherical harmonics with arguments pertaining to the C–D bond orientation in the channel reference frame:

$$\overline{\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)} = \sum_{m=-2}^{2} Y_{2,m}(\psi,\phi)\,\overline{Y_{2,-m}(\alpha,\beta)} \qquad (4)$$

where ψ and ϕ are the polar and azimuthal angles of the magnetic field with respect to the channel axis and α and β are angles of the C–D bond with respect to the channel axis as defined above and shown in Figure 5. From the probability distribution of eq 1, the averages of the spherical harmonics are

$$\overline{Y_{2,m}(\alpha,\beta)} = \left(\frac{5}{4\pi}\right)^{1/2}\left(\frac{3}{2}\sin^2\epsilon - \frac{1}{2}\right)\delta_{m,0} \qquad (5)$$

where $\delta_{m,0}$ is the Kronecker delta. This gives the time-averaged Hamiltonian:

$$\mathcal{H}_{Q,\mathrm{sec}} = \left(\frac{3}{2}\sin^2\epsilon - \frac{1}{2}\right)\frac{eQV_{\mathrm{CD}}}{4I(2I-1)\hbar}\left(\frac{3}{2}\cos^2\psi - \frac{1}{2}\right)\times (3I_z^2 - I(I+1)) \qquad (6)$$

Since the channel axes are isotropically arranged, the line shape resulting from the motionally-averaged quadrupolar Hamiltonian will be a Pake doublet with a peak-to-peak splitting of

$$\Delta\nu = \frac{\Delta\nu_0}{2}|1 - 3\sin^2\epsilon| \qquad \epsilon \ll 1 \qquad (7)$$

where $\Delta\nu_0$ is the rigid-lattice peak-to-peak splitting (125 kHz). The observed splitting above +20 °C is 50 kHz. From eq 7 this corresponds to a value for ϵ of 15°.

This value of ϵ is consistent with the results of a molecular dynamics simulation of the chain motion in the PE/PHTP-IC reported by Zahn and Mattice.[9] Their simulation for a temperature of 300 K indicated that the C–H vectors of the polymer chain reorient about the channel axis rapidly and fluctuate on the order of ~13° about the plane perpendicular to the channel axis.

High-frequency libration about a large number of consecutive bonds is quite unusual for a crystalline material. In general, librating bonds in crystalline polymers are isolated by neighboring bonds with fixed conformations. This is the situation found in the TPBD/PHTP-IC where the librations at the three single bonds of each monomer repeat are isolated from bond librations of neighboring units by the rigid *trans* double bond. Therefore, the reorientation of the C—D bond about the long axis of this molecule cannot result from the bond librations alone because the longest sequence of motionally labile bonds is limited to three. Rather the large changes in bond orientation are the consequence of coupled conformational transitions at pairs of CH—CD$_2$ bonds across the trans CH═CH and CH$_2$—CH$_2$ bonds.[11,15,18]

In contrast, the large scale reorientation of the C–D bond of PE included in PHTP is achieved by the cumulative effect of small torsions of many main-chain carbon–carbon bonds. This concept is apparent in the paradigm of the chain twist.[17] As the result of small-angle librations at each of many bonds, a partial or localized twisting will be imparted to the polymer chain. This motional picture is consistent with all of the NMR data. The small torsions of the carbon bonds would (1) effect no change in the carbon chemical shift, (2) provide an effective carbon spin–lattice relaxation mechanism, (3) not involve significant energies, and (4) yield a deuterium spectrum with a peak separation below 62 kHz.

The variable-τ relaxation data (Figure 3) contain information about the distribution of frequencies associated with the small torsions of the carbon bonds. Spiess[13] has demonstrated that the intensity of the deuterium spectrum as a function of τ_1 provides information about the width of the distribution function for the motion of the C–D bond. As the breadth of the distribution of motional frequencies increases, the motional component that matches the time scale of the inverse line width is reduced. Therefore the loss in intensity in the intermediate exchange regime is also reduced. At the same time, the broad distribution of motional frequencies means that even at very low or very high temperatures there will always be a motional component that matches the NMR time scale and provides some relaxation during the solid echo time τ_1, thereby reducing the spectral intensity in the slow and fast exchange regimes compared to a system with a narrow distribution of motional frequencies. The small change in intensity with temperature and the minimal changes in line shape at different values of τ (Figure 3) are attributed to a very broad distribution of correlation times or amplitudes for the motion that is reorienting the C–D bonds of the PE chain in the IC.

The ^{2}H NMR results are consistent with the findings of the published molecular dynamics simulation for the PE/PHTP-IC.[9] The simulation indicated that the C–H bond orientation was nearly randomized on the time scale of 1 ns at 300 K, and an energy of less than 4.2 kJ/mol was associated with this reorientation. Furthermore, this reorientation was to a significant degree the result of the librations about the *trans* conformation at each carbon–carbon bond. The simulation also considered twisting of the polymer chain and demonstrated that over a length of 12 bonds short twists of −100 to +100° occurred frequently within a period of 1 ns but that twists of greater than 125° did not occur. Twisting of the chain over a greater number of bonds was not considered. The range of α found in the reported simulation was from about 77 to 103°.

Conclusions

The deuterium NMR data for the PE-d_4/PHTP-IC demonstrate that high-frequency librations about the carbon–carbon bonds are the principal motions of the polymer chain. Librations at a number of consecutive bonds introduce large amplitude reorientations of the C–D bond by introducing localized twisting of the polymer chain. Chain twists not only reorient the C–D bonds about the long axis of the inclusion channel but also cause the bonds to fluctuate slightly above and below the plane perpendicular to the axis. The root-mean-square angle of deviation of these fluctuations is ca. 15°. The spin–spin relaxation behavior indicates that a very broad distribution of frequencies and amplitudes is associated with the librational motions of the polymer chain.

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