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Chain Folding and Diffusion in Monodisperse Long *n*-Alkanes by Solid-State NMR

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ABSTRACT: The size of the folded segment of the alkane chain in the integer-folded F2 form of $C_{246}H_{494}$ has been measured directly by NMR and shown to contain an average of 8 ± 2 carbon atoms at 293 K. This tight fold is in contrast to the looser fold obtained indirectly for similar samples in earlier NMR work but in good agreement with the picture provided by SAXS and LAM Raman spectroscopy studies. The recovery after saturation of the carbon-13 magnetization associated with the all-trans carbon-13 peak has also been measured for recovery times as long as 4000 s. The behavior as a function of recovery time has been compared with simple simulations which model the combined effects of chain diffusion and spin−lattice relaxation. These results suggest that at short times the mechanism for the magnetization recovery involves the alkane chain diffusing around the fold with the methyl groups constrained from entering the crystal through the opposite surface of the lamella. Hence, only small fluctuations in the length of the fold segment occur, and the two linked stems move in a loosely co-operative fashion. Despite the tight fold, the rate of magnetization recovery is compatible with a frequency for the underlying chain jump process similar to that responsible for the α-relaxation in polyethylene.

1. Introduction

Kinetic factors drive flexible polymers to crystallize as lamellae separated by disordered interlayers comprising folded chains. However, changes in crystallization conditions result in significant variations in the morphology of the interlayer, even for the simplest polymers, such as polyethylene. For example, samples which have been crystallized from solution exhibit tight chain folds with re-entry at an adjacent position in the crystalline lamella.[1] On the other hand, materials quenched from the melt involve looser folds with random re-entry, forming a so-called "switchboard" structure.[2] The morphology of the interlayer has a significant impact on the molecular motion of the disordered segments of the polymer chain and hence on the mechanical properties of the material.

In addition to local motions in the folds, the polymer chains in semicrystalline polymers diffuse between the crystalline lamella and the disordered interlayer. This phenomenon was shown to be responsible for the recovery of carbon-13 magnetization in solid-state NMR studies[3,4] of polyethylene. Transport over relatively long distances allows large segments of each polymer chain to sample the mobile interlayer environment where relaxation processes are efficient. The local motion underlying the chain diffusion was identified with the jump process responsible for the α-relaxation[5] which consists of a translation of the crystalline stem by one methylene unit combined with a 180° flip. Recently, Yao et al.[6,7] have elucidated the correlation between segmental motions in the mobile interlayer and the rate of chain diffusion. The rapid and isotropic fluctuations expected for loose folds in melt-crystallized polyethylene samples do not necessarily promote translational motion of the crystalline stem. In fact, the more restricted dynamics observed in the tight folds of solution-crystallized materials may enhance chain diffusion by lowering the entropy cost associated with moving from the disordered interlayer into the crystalline lamella.

Studies of crystallization and morphology in semicrystalline polymers are often complicated by polydispersity, and for this reason monodisperse normal alkanes have often been used as models for polyethylene.[8] This extrapolation is valid because the orthorhombic subcell adopted by most crystalline alkanes is identical to the unit cell of polyethylene. Monodisperse *n*-alkanes which were long enough to exhibit chain folding were first synthesized in 1985.[9,10] For mature crystals of these, grown from supercooled melts or solution, the lamella thickness is an integer fraction of the chain length, indicating the formation of so-called "integer-folded" structures.[11] For example, in the once-folded or "F2" form of such alkanes small-angle X-ray scattering (SAXS) and longitudinal acoustic mode (LAM) Raman spectroscopy measurements show a lamella thickness of one-half of the extended chain length. This suggests that each alkane molecule contributes two crystalline stems which are linked by a fold at one surface of the lamella. For a given alkane the number of folds observed rises as the amount of supercooling increases with up to four folds (the "F5" form) obtained for longest alkanes.

In this paper we describe the use of solid-state NMR to study some of the longest monodisperse *n*-alkanes synthesized to date[12] in order to establish morphological details, such as the size and conformation of the chain fold. Chain diffusion in long *n*-alkanes has been studied previously by Klein and Driver,[13] who measured the recovery of carbon-13 magnetization at 333 K in samples prepared by a rapid quench from the melt. However, as mentioned above, the rate and extent of supercooling are known to be of importance in determining the number of folds, and careful control of these parameters is required to produce uniformly folded crystals. Hence, an uncontrolled quench is likely to produce a mixture of randomly folded and noninteger folded forms. It should be noted that careful attention to sample preparation distinguishes the present work from that of Klein

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and Driver and that there are significant differences between their results and those described here.

2. Materials and Methods

2.1. Long-Chain *n*-Alkanes. The monodisperse *n*-alkane $C_{246}H_{494}$ (~100 mg) was obtained from Dr. G. Brooke (Durham) and had been synthesized according to the procedures outlined in ref 12. Before NMR measurements this alkane was prepared by Prof. G. Ungar (Sheffield) in either the fully extended (E) and the once-folded (F2) form, as described previously.[11] For the F2 form the samples were cooled from the melt to 363 K at a rate of 3 K min^{-1}, annealed for 8 h, and subsequently cooled to room temperature at a rate of 1 K min^{-1}. The E form was obtained in the same fashion, except that the initial cooling rate was 0.2 K min^{-1} and the sample was annealed for 8 h at 393 K. The nature of the samples was confirmed before and after solid-state NMR measurements by DSC and X-ray scattering.

2.2. Solid-State NMR Measurements. Carbon-13 magic angle spinning (MAS) spectra were recorded at a Larmor frequency of 75.47 MHz and a spinning rate of 3−4 kHz using a saturation recovery method. In this experiment the carbon-13 magnetization was presaturated using 20 $\pi/2$ pulses spaced by 3 ms intervals. During the following delay τ longitudinal carbon-13 magnetization recovers by a combination of chain diffusion and spin−lattice relaxation. Subsequently, the carbon-13 FID was acquired as normal using a $\pi/2$ pulse of 4 μs for excitation and a proton decoupling field of 70 kHz. A relaxation delay of 15 s between experiments ensured that carbon-13 magnetization enhancements due to a transient proton Overhauser effect were eliminated. The duration of the delay τ was varied between 0 and 4000 s in order that the recovery of carbon-13 magnetization could be studied. The number of scans was reduced from 2048 to 12 as the relaxation delay was increased above 20 s in order to avoid experiment times in excess of 12 h for a single spectrum. Experiments were carried out at the ambient temperature of 293 K and at an elevated temperature of 333 K.

Intensities for the individual peaks were obtained by fitting the spectra to several mixed Gaussian and Lorentzian lines and scaling according to the number of scans. The resonance arising from the two methyl carbons at the chain ends was observed with reasonable signal-to-noise in spectra recorded with more than 512 scans. The average intensity of this peak for all spectra recorded with a recovery delay greater than 3 s and more than 512 scans was used to normalize the other peaks in the spectrum. This allows the carbon-13 intensities to be quantified directly without resorting to a fully relaxed carbon spectrum or a separate measurement of the crystallinity for normalization.

2.3. Simulations. Simulations of carbon-13 magnetization recovery were carried out using a simple Monte Carlo approach[3] in which a collection of chain stems diffuse within a crystal lamella. Connectivity between the carbon atoms of a given chain is preserved, and there is no preferential direction for the diffusion of a particular stem. Individual stems undergo random translations to adjacent positions, while the connected fold segments or chain ends increase or decrease commensurately, subject to constraints describing their minimum allowable length. Carbon-13 spin−lattice relaxation is taken into account in a semiempirical fashion with individual nuclei undergoing a relaxation event during each diffusion step with a probability related to the corresponding T_1 value. For carbon-13 nuclei in disordered segments T_1 was set to the experimental value obtained from saturation recovery measurements, while slow spin−lattice relaxation intrinsic to the crystalline regions was also included were appropriate, usually with T_1 in excess of 10 000 s.

Note that these simple simulations do not include any details of the mechanism of chain diffusion which is thought to be associated with the passage of a localized defect along the crystalline stem. Currently, the nature of the defects involved is a matter of some debate, with possibilities ranging from interstitial-like conformational defects[14] to smooth soliton-like “twistons”.[15] In the former the required 180° turn is induced by the presence of several gauche conformers over a segment comprising some 6 or 7 carbon atoms, while in the latter it involves a gradual variation across some 20 successive approximately trans sites along the chain. Zubova et al.[16] have recently described molecular dynamics simulations which model the diffusion of interstitial-like conformational defects and soliton-like “twistons” through a polyethylene crystal. These authors conclude that the defect lifetimes measured in terms of the time taken for the defect to cross the lamella, translating and rotating the crystalline stems as it goes, is less than 2×10^{-6} s. Hence, on the time resolution of our simulations defect passage through the lamella is expected to be instantaneous.

The simulations were tested against saturation recovery data recorded as described above for a sample of ultrahigh molecular weight polyethylene (UHMWPE) at 333 K with a crystallinity of 57% measured using wide-line proton NMR.[4] In this case a single polyethylene chain containing 25 000 all-trans carbon atoms and sufficient disordered folds to account for the measured crystallinity was allowed to diffuse and relax. Setting the smallest allowable fold to an average value of 130 carbons and the frequency of diffusion events to 95 s^{-1} gave a simulated carbon-13 recovery curve in good agreement with the polyethylene data. The value of the smallest allowable fold indicates that in the polyethylene case the chain diffusion is constrained by entanglements in the disordered interlayer, while the frequency obtained corresponds to that expected for the α-process at this temperature.[3] Hence, the simulations can provide quantitative information about the frequency of the chain jumps responsible for diffusion as well as an alternative estimate of the length of the fold segment in integer-folded alkanes. For the F2 form of $C_{246}H_{494}$ 100 alkane chains each containing two crystalline stems linked by a disordered fold were allowed to diffuse and relax. The minimum fold length was constrained to be not less than six carbon atoms, but there was no limit on its maximum value. Other constraints were incorporated into the simulations where appropriate, as described below.

3. Results and Discussion

3.1. Size and Morphology of Folds in Integer-Folded *n*-Alkanes. The carbon-13 NMR spectra at 293 K of (a) the E and (b) the F2 forms of $C_{246}H_{494}$ are shown in Figure 1. These were recorded using the saturation recovery pulse sequence described above with a recovery delay τ of 15 s. The dominant feature in both spectra is a relatively narrow peak at δ = 33.5 ppm which results from carbon atoms in the crystalline lamellae in which the alkane chains adopt an all-trans conformation. In addition, there is a broader peak at approximately δ = 31.5 ppm which can be assigned to carbon atoms in segments of the alkane chains which are disordered, containing a significant population of gauche conformers. The lower δ value observed is an example of the well-known “γ-gauche effect”[17] which arises when a carbon atom experiences a gauche bond at the γ position. Finally, peaks due to the three terminal carbon atoms are also observed, and these can be assigned as follows. The methyl carbon at the end of the alkane chain appears at δ = 15.4 ppm, while the adjacent methylene carbon is observed at δ = 25.3 ppm. The next methylene carbon away from the terminal methyl contributes a shoulder on the downfield side of the main all-trans peak at δ = 34.8 ppm. For these terminal carbon atoms the main contribution to δ arises from their position in the chain end rather than the conformation of neighboring bonds. The observed values are in good agreement with the carbon-13 chemical shifts reported

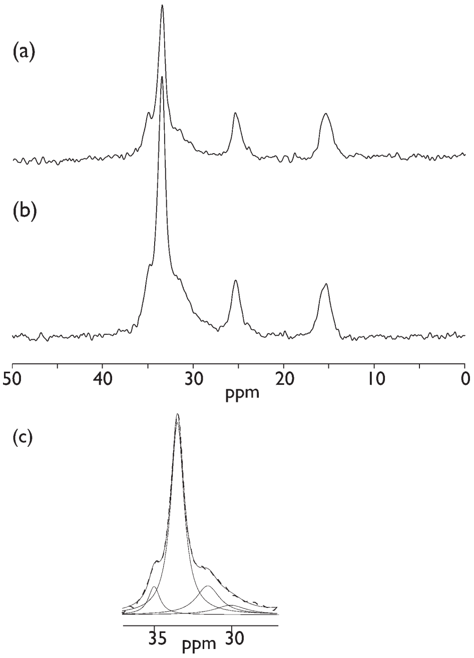

Figure 1. Carbon-13 MAS spectra of (a) the E form and (b) the F2 form of $C_{246}H_{494}$ recorded at 293 K using the saturation recovery experiment described in the text with a recovery delay τ of 15 s. The narrow peak at $\delta = 33.5$ ppm results from segments of the alkane chains which adopt an all-trans conformation. In addition, there is a broader peak at approximately $\delta = 31.5$ ppm which can be assigned to carbon atoms in disordered segments of the alkane chains which contain a significant population of gauche conformers. Normalizing with respect to the methyl carbon which appears at $\delta = 15.4$ ppm allows the quantification of the number of carbon atoms in disordered environments as well as the recovery of the all-trans carbon-13 magnetization. An expansion of the region between 27 and 37 ppm from the spectrum of the F2 form is shown in (c) (wide dashed line), along with the four mixed Lorentzian and Gaussian lines which fit the spectrum in this region and their sum (thin solid lines). Note the good agreement with experiment. The broad peak at 31.5 ppm fits to two lines, suggesting the presence of a range of different conformations in the disordered segments of the chain.

previously by Moller et al.[18] for shorter *n*-alkanes. It should be noted that those authors observed an additional methyl resonance at 16.1 ppm for highly crystalline extended $C_{168}H_{338}$ which they assigned to a fraction of "crystalline" methyl groups fixed in an all-trans conformation. There is no distinct peak with a similarly increased δ value in the carbon-13 MAS spectrum for either form of $C_{246}H_{494}$, suggesting that the bulk of the chain ends are in conformationally disordered environments. This implies that a significant degree of premelting occurs at the lamella surface and that the majority of the methyl end groups do not enter the crystal lamella.

Normalization with respect to the methyl intensity which arises from exactly 2 out of the 246 carbon atoms in each alkane chain allows a quantitative analysis of the carbon-13 magnetization. For this relatively short recovery delay the observed intensity of the saturated all-trans peak at $\delta = 33.5$ ppm represents just 2% and 5% of the carbon sites in the E and F2 forms of $C_{246}H_{494}$, respectively. On the other hand, the conformationally disordered peak at $\delta = 31.5$ ppm is fully relaxed for recovery delays greater than 3 s. Because the jump process is slow compared to the NMR time scale, the normalized average intensity of this peak when fully relaxed is a quantitative measure of the number of carbon atoms in disordered segments of the alkane chain. At 293 K for the E form this was found to correspond to 2.2 ± 0.3 carbon atoms per alkane chain, suggesting that a disordered interlayer containing on average the terminal 4 carbon atoms in the alkane chains is present at the surface of the crystalline lamellae. For the F2 form the corresponding average value was 10 ± 2 carbon atoms per alkane chain, suggesting that on average there are 8 ± 2 carbon atoms in conformationally disordered environments in the fold at 293 K. Similar measurements at 333 K showed that the thickness of the interlayer in the E form does not increase significantly. However, the number of extra carbon atoms in disordered environments in the F2 form rises to 18 ± 3 carbon atoms. As an indication of the quality of the line shape fits, Figure 1c shows an expanded region (wide dashed lines) from the spectrum of the F2 form. Four mixed Lorentzian and Gaussian lines (thin solid lines) are required to fit the spectrum in this region, and their sum (thin solid line) is in good agreement with the data. It should be noted that the broad peak at 31.5 ppm fits to two lines, suggesting the presence of a range of different conformations in the disordered segments of the chain.

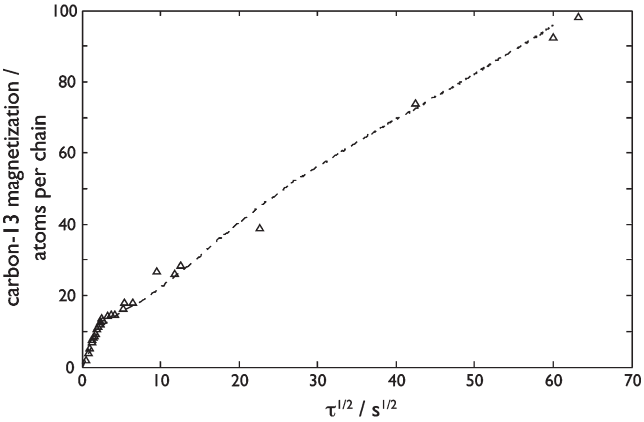

Figure 2. Recovery after saturation of the carbon-13 magnetization (open triangles) associated with the all-trans peak at $\delta = 33.5$ ppm for the F2 form of $C_{246}H_{494}$ at 293 K. The vertical scale measures the recovery of carbon-13 magnetization in terms of the number of carbon atoms per alkane chain after normalization with respect to the methyl group intensity, as described in the text. Also, the result of a simulation (dashed line) which combines chain diffusion of the two crystalline stems around the fold in a loosely co-operative fashion with spin−lattice relaxation. The rate of the chain jump process was set to 25 s^{-1}, and an average fold segment contained 13 carbon atoms. The spin−lattice relaxation times were 0.4 and 12 000 s for sites in the disordered fold and the interior of the crystalline lamella, respectively. A mobile interphase containing 18% of the all-trans carbon atoms was also included, and the corresponding spin−lattice relaxation time was 300 s.

To our knowledge this is the first time that the size of the chain fold in either polyethylene or a model *n*-alkane has been directly quantified by NMR. These results show that $C_{246}H_{494}$ chains form tight folds which comprise a surprisingly small segment of the alkane chain, an observation which agrees with data obtained from other experimental techniques. For example, SAXS measurements of the electron density profile normal to the lamella surface[19] show that the width of the disordered interlayer increases only slightly between the E and F2 forms of $C_{246}H_{494}$. Similarly, infrared spectra of $C_{198}H_{398}$ recorded at 110 K[20] suggest a tight fold containing a significant proportion of *gtg* defects. Finally, the measured number of carbon atoms with gauche bonds in the F2 $C_{246}H_{494}$ fold is similar to that observed in calculated structures of *gtggg*g** folds on the {110} surface of orthorhombic polyethylene crystals.[21]

3.2. Chain Diffusion in Long *n*-Alkanes. Figure 2 shows the recovery after saturation of the carbon-13 magnetization (triangles) associated with the all-trans peak at $\delta = 33.5$ ppm

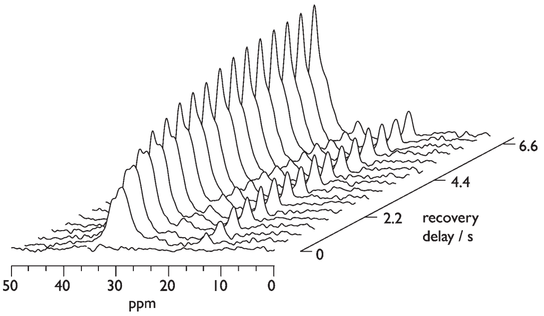

Figure 3. Carbon-13 MAS spectra of the F2 form of $C_{246}H_{494}$ recorded at 293 K using the saturation recovery experiment described in the text with recovery delays τ between 0 and 7.04 s.

for the F2 form of $C_{246}H_{494}$ at 293 K. The vertical scale measures the recovery of carbon-13 magnetization in terms of the number of carbon atoms per alkane chain after normalization with respect to the methyl group intensity as described above. Two magnetization recovery regimes can be clearly discerned with a rapid initial growth which involves fewer than 15 of the all-trans carbon atoms superimposed on a more moderate recovery of the bulk. The latter is so inefficient that even for a recovery delay as long as 4000 s less than 50% of the all-trans carbon atoms in the alkane chain relax. In contrast, magnetization at δ = 31.5 ppm which arises from the 10 carbon atoms in conformationally disordered environments (see above) recovers rapidly according to a single exponential with a time constant of 0.4 s. In order to further demonstrate this efficient relaxation, Figure 3 shows a series of carbon-13 NMR spectra of the F2 form at 20 °C recorded with recovery delays τ of between 0 and 7.04 s. The chain ends and the broad peak at 31.5 ppm which arises from the remainder of the disordered interlayer are fully relaxed after ~2 s. This efficient spin−lattice relaxation arises from the enhanced mobility in the disordered regions and suggests that there is a significant degree of conformational flexibility in the fold despite its tightness. By analogy with polyethylene, the whole of the observed all-trans magnetization recovery might be ascribed to chain diffusion which constantly transports segments of the alkane chain into the mobile fold region where spin−lattice relaxation is efficient. This hypothesis is supported by the linear recovery with respect to $\tau^{1/2}$, while the observation of two regimes suggests the chain diffusion becomes constrained as the folds become progressively tighter. This is essentially the conclusion of Klein and Driver[13] from carbon-13 magnetization recovery measurements on samples of long *n*-alkanes prepared by a rapid quench from the melt.

To obtain a clearer picture of the processes underlying the carbon-13 magnetization recovery, it is necessary to compare data recorded for both forms of $C_{246}H_{494}$ and at different temperatures. Figure 4 shows an expansion of Figure 2 for τ up to about 200 s (open up triangles) together with similar magnetization recovery data for the E form (filled up triangles) at 293 K. The initial regime of rapid recovery observed for the F2 sample is absent for the E form which even at short times exhibits only a slow linear growth reminiscent of the behavior observed at long times in Figure 2. Figure 4 also shows magnetization recovery data recorded at an elevated temperature of 333 K for both the F2 sample (open down triangles) and the E form (filled down triangles). A comparison with the 293 K data suggests that both the rate and extent of the initial F2 recovery increase as the temperature is raised, while the behavior of the E from is apparently unaffected. This suggests that the initial recovery is a property of the fold segment itself and that the underlying process is an activated one, as expected for chain diffusion. However, the slow growth common to both forms observed at longer times is essentially independent of temperature.

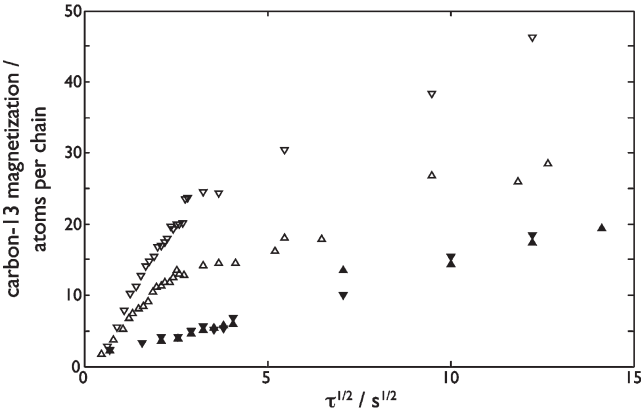

Figure 4. An expansion of the data in Figure 2 (open up triangles), together with similar magnetization recovery data for the same F2 sample at an elevated temperature of 333 K (open down triangles), the E form at 293 K (filled up triangles), and the E form at 333 K (filled down triangles).

In order to focus on the initial recovery, Figure 5 shows plots of the difference between the recovered carbon-13 magnetization for the F2 form and that for the E form at both 293 K (up triangles) and 333 K (down triangles). Superimposed are the results of simulations of chain diffusion and spin−lattice relaxation carried out as described above. For these simulations diffusion was constrained so that the methyl groups were prevented from entering the crystal, since this produces an energetically unfavorable defect in the lamellae surface. The freedom of the alkane chain to slide around the fold is therefore fairly restricted, and the two crystalline stems are forced to move in a loosely co-operative fashion in order to simultaneously maintain the minimum fold length and a constant overall fraction of disordered sites. Inefficient spin−lattice relaxation intrinsic to the crystalline regions was not included in this simulation. Hence, the simulated curves rise to a plateau which is a measure of the number of all-trans carbon atoms which can sample the mobile fold segment while this limited diffusion occurs. For the 293 K simulation (solid line), the rate of the chain jump process was set to 25 s^{-1} and the average length of the fold segment was 13 carbon atoms, while at 333 K these parameters were 30 s^{-1} and 20, respectively. The good agreement between the data and the simulations suggests that limited chain diffusion around the fold with the methyl groups prevented from entering the crystal at the opposite surface of the lamella is responsible for the initial carbon-13 magnetization recovery in the F2 sample. We note that the average length of the folded segment is slightly larger than the number of carbons in disordered environments measured directly from the carbon-13 MAS spectrum, but this discrepancy might be explained by the presence in the fold itself of some carbon atoms in all-trans environments.

The simulations suggest that both the frequency and activation energy of the chain jumps are lower than those for the α-process in melt-crystallized polyethylene.[5] However, this is also observed in atypical polyethylene samples which contain a similarly small fraction of disordered segments, such as fibers or single crystals.[22] Zubova et al.[16] have associated chain diffusion in these atypical samples with conformational defects, rather than soliton-like twistons, on the grounds of the lower activation energy calculated for the injection of the former into the crystal. The formation

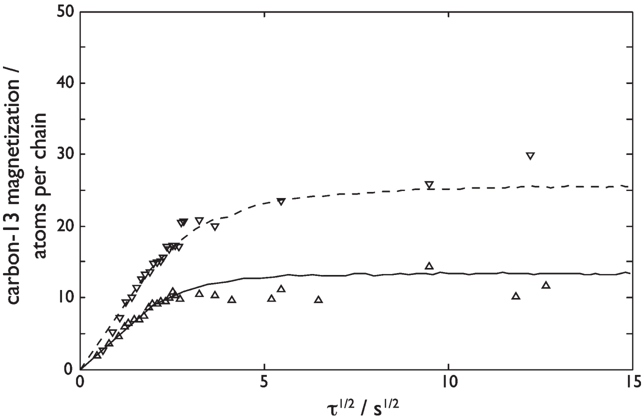

Figure 5. Difference between the recovered all-trans carbon-13 magnetization for the F2 form of $C_{246}H_{494}$ and that for the E form, recorded at 293 K (open up triangles) and at 333 K (open down triangles). Also the results of Monte Carlo simulations which combine chain diffusion of the two crystalline stems around the fold in a loosely co-operative fashion with spin−lattice relaxation in the disordered fold segments only. For the 293 K simulation (solid line) the rate of the chain jump process was set to 25 s^{-1} and an average fold segment contained 13 carbon atoms, while at 333 K (dashed line) these parameters were 30 s^{-1} and 20, respectively.

of the correct sequence of conformations in the tight fold to create such a defect might be expected to be so rare as to suppress diffusion altogether, as suggested by Klein and Driver.[13] However, the rapid recovery of the carbon-13 magnetization associated with the fold itself as demonstrated in Figure 3 suggests a large degree of conformational exchange. In addition, as mentioned above, Yao et al.[6,7] have recently demonstrated that tight folds in solution-crystallized polyethylene enhance chain diffusion by lowering the entropy cost associated with entering the crystalline lamella. Their conclusions are supported by our results which suggest that even the short fold segment in the F2 form of $C_{246}H_{494}$ can apparently promote diffusion at a rate which corresponds to an appreciable chain jump frequency.

With a tight fold and the chain ends constrained at the lamella surface only a small fraction of the alkane chain can sample the mobile interlayer environment by sliding around the fold in this way. While this mechanism can explain the rapid initial regime observed for the F2 form, it cannot be responsible for the slow magnetization recovery common to both forms which dominates at long times. The linear recovery with $\tau^{1/2}$ observed for the latter strongly suggests the presence of a second diffusive process. This operates at a significantly slower rate but nevertheless ensures that in time a substantial fraction of the alkane chain samples the mobile environment of the interlayer. Many possibilities for this process can be envisioned. For example, it has been shown[23] that short *n*-alkanes initially from separate macroscopic crystals can intermix completely on a time scale of days, even at temperatures well below the melting point. Hence, a further mechanism is the diffusion of alkane chains into neighboring lamellae via defects in the surface. Note that this would result in an all-trans methyl resonance at $\delta = 16.1$ ppm in the carbon-13 MAS spectrum of Figure 1b which is not observed. However, only a small proportion of alkane molecules need to be involved in order to significantly increase the extent of magnetization recovery because the whole chain samples the mobile environment of the disordered interlayer while swapping between lamellae. For the F2 form of $C_{246}H_{494}$ a similar effect can be achieved by a cyclic arrangement of the molecule with a fold at each surface produced when one chain end enters the lamella though a defect generated by the prior entry of the other end.

Another possibility is a contribution to the magnetization recovery from spin−lattice relaxation intrinsic to sites in the crystalline lamella, assuming a distribution of T_1 values in order to reproduce the linear $\tau^{1/2}$ increase in magnetization. Figure 2 shows a simulation (dashed line) which includes a layer of more mobile all-trans carbon environments on the surface of the crystalline lamellae. For this simulation the mobile region contained 18% of the all-trans carbon atoms and the associated spin−lattice relaxation constant was 300 s, while the intrinsic T_1 for the interior of the lamella was 12 000 s. Hence, a contribution to the recovery at long times from T_1 relaxation intrinsic to the crystalline regions cannot be discounted. Many studies of polyethylene give evidence for an interphase occurring just below the lamella surface which separates the rigid crystalline regions from the disordered interlayer.[24−26] This region contains chains in the all-trans conformation expected for the crystalline regions, but with enhanced mobility which in turn results in a substantially shorter T_1 value. A similar situation might arise if a proportion of the defects responsible for chain diffusion do not cross the lamella but are annihilated after a short distance. In this case the local motions associated with defect passage might cause more efficient T_1 relaxation at sites closer to the lamella surface.

Note that in common with the conclusions of earlier workers[13] our experimental data do not allow the separation of contributions from spin−lattice relaxation intrinsic to the crystalline regions and chain diffusion at long times. While the linear recovery with $\tau^{1/2}$ suggests an underlying diffusive process, a distribution of crystalline T_1 values can also describe the data in the slow recovery regime. It is likely that both effects contribute to the magnetization recovery at long times.

3.3. Comparison with Previous NMR Studies of Folded *n*-Alkanes. As mentioned above, our carbon-13 NMR results differ significantly from those described previously by Klein and Driver[13] for quenched samples of $C_{246}H_{494}$. Superficially, the data presented by these authors for the recovery of carbon-13 magnetization in the E and F2 forms of $C_{246}H_{494}$ resemble those shown in Figures 2 and 4 of the current work. For example, in the F2 form two diffusion regimes are observed with an initial rapid rise in the magnetization occurring for recovery times τ less than ~16 s. However, there are significant differences in the extent of the recovery which in ref 13 reaches over 33% for folded $C_{246}H_{494}$ at a recovery time of 160 s, while the corresponding value taken from Figure 4 is only 20% even at 333 K. These differences are presumably related to the nature of the folded samples under investigation. The samples of Klein and Driver were prepared by a rapid and uncontrolled quench from the melt, a procedure which is likely to produce a mixture of randomly folded and noninteger folded forms. Such randomly folded materials would exhibit lower crystallinity than the uniformly F2 samples prepared for our work. Indeed, the crystallinity measured by proton NMR in ref 13 for quenched $C_{246}H_{494}$ is only 80%, while for our uniformly folded F2 samples the corresponding value is 94 ± 1% at ambient temperature, falling to 90 ± 2% at 333 K. Hence, it seems likely that Klein and Driver's quenched $C_{246}H_{494}$ contains significant disordered chain segments which are outside the fold. Finally, the progressive saturation pulse sequence they use to measure the magnetization recovery can result in nuclear Overhauser enhancements which preclude quantification of the carbon-13 signals.

Given these differences, it is not surprising that some of our conclusions contrast with those of Klein and Driver. These authors consider that the folds themselves represent a significant obstacle to chain diffusion, in contrast to the results of Yao et al. for solution-crystallized polyethylene mentioned above.[6,7] Klein and Driver analyze the magnetization recovery in terms of a “dual reptation” model which produces two diffusion coefficients. In their picture the larger coefficient is associated with the independent and unconstrained chain diffusion possible for two crystalline stems linked by a fairly loose fold, while the smaller coefficient is ascribed to a more constrained diffusion regime which dominates at longer times. In this regime the two connected stems move in and out of the lamella in a co-operative fashion causing fluctuations in the length of the fold. The conclusions of Klein and Driver are incompatible with our results, since significant growth in individual folds is precluded by the need to maintain an average length of only eight carbon atoms. In addition, our tight fold does not allow for an initial regime of unconstrained chain diffusion. Instead, our simulations suggest that the initial rapid recovery can be explained by the alkane chains sliding around the fold, a possibility which Klein and Driver discount on the basis of a comparison with branched alkanes.

4. Conclusion

The size of the folded segment of the alkane chain in the F2 form of integer-folded $C_{246}H_{494}$ has been measured directly by NMR and shown to contain an average of 8 ± 2 carbon atoms at 293 K. To our knowledge this is the first time that the length of the chain fold in either polyethylene or a model *n*-alkane has been directly quantified by NMR. The tight fold is in good agreement with previous SAXS and LAM Raman spectroscopy studies. The recovery of the carbon-13 magnetization associated with the all-trans peak has also been measured to times as long as 4000 s and compared with simulations that model the combined effects of chain diffusion and spin−lattice relaxation. These suggest that at short times the mechanism for the magnetization recovery in the F2 form involves the alkane chain sliding around the fold, while the methyl groups are constrained at the opposite lamella surface. Hence, only small fluctuations in the length of the fold segment occur, forcing the two linked stems to move in a loosely co-operative fashion. Despite the tight fold, the rate of magnetization recovery is compatible with a frequency for the underlying chain jump process similar to that responsible for the α-relaxation in polyethylene. This result is in line with the surprising conclusions of Yao et al.,[6,7] who demonstrated recently that tight folds in solution-crystallized polyethylene enhance chain diffusion. This is thought to be caused by a reduction in the entropy cost associated with entering the crystalline lamella relative to that for longer, more disordered folds.

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References and Notes

(1) Keller, A. *Philos. Mag.* **1957**, *2*, 1171.
(2) Flory, P. J. *J. Am. Chem. Soc.* **1962**, *84*, 2857.
(3) Schmidt-Rohr, K.; Spiess, H. W. *Macromolecules* **1991**, *24*, 5288.
(4) Robertson, M. B.; Ward, I. M.; Klein, P. G.; Packer, K. J. *Macromolecules* **1997**, *30*, 6893.
(5) McCrum, N. G.; Read, B. E.; Williams, G. In *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley: New York, 1967.
(6) Yao, Y.-F.; Graf, R.; Spiess, H. W.; Rastogi, S. *Macromolecules* **2008**, *41*, 2514.
(7) Yao, Y.-F.; Graf, R.; Spiess, H. W.; Lippits, D. R.; Rastogi, S. *Phys. Rev. E* **2007**, *76*, 060801(R).
(8) Ungar, G.; Zeng, X. *Chem. Rev.* **2001**, *101*, 4157.
(9) Bidd, I.; Whiting, M. C. *J. Chem. Soc., Chem. Commun.* **1985**, 543.
(10) Lee, K. S.; Wegner, G. *Makromol. Chem. Rapid Commun.* **1985**, *6*, 203.
(11) Ungar, G.; Stejny, J.; Keller, A.; Bidd, I.; Whiting, M. C. *Science* **1985**, *229*, 386.
(12) Brooke, G. M.; Burnett, S.; Mohammed, S.; Proctor, D.; Whiting, M. C. *J. Chem. Soc., Perkin Trans.* **1996**, 1635.
(13) Klein, P. G.; Driver, M. A. N. *Macromolecules* **2002**, *35*, 6598.
(14) Reneker, D. H.; Fanconi, B. M.; Mazur, J. *J. Appl. Phys.* **1977**, *48*, 4032.
(15) Mansfield, M.; Boyd, R. H. *J. Polym. Sci., Part B: Polym. Phys.* **1978**, *16*, 1227.
(16) Zubova, E. A.; Balabaev, N. K.; Manevitch, L. I. *Polymer* **2007**, *48*, 1802.
(17) Tonelli, A. *NMR Spectroscopy and Polymer Microstructure*; VCH: New York, 1989.
(18) Moller, M.; Cantow, H.; Drotloff, H.; Emeis, D. *Makromol. Chem.* **1986**, *187*, 1237.
(19) Ungar, G. In *Characterization of Solid Polymers*; Chapman and Hall: London, 1994.
(20) Ungar, G.; Organ, S. J. *Polym. Commun.* **1987**, *28*, 232.
(21) Petraccone, V.; Corradini, P.; Allegra, L. *Macromolecules* **1971**, *4*, 770.
(22) Kuwabara, K.; Kaji, H.; Tsuji, M.; Horii, F. *Macromolecules* **2000**, *33*, 7093.
(23) Ungar, G.; Keller, A. *Colloid Polym. Sci.* **1979**, *257*, 90.
(24) Kitamarau, R.; Horii, F. *Adv. Polym. Sci.* **1978**, *26*, 137.
(25) Cheng, J.; Fone, M.; Reddy, V. N.; Schwartz, K. B.; Fisher, H. P.; Wunderlich, B. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 2683.
(26) Stribeck, N.; Alamo, R. G.; Mandelkern, L.; Zachmann, H. G. *Macromolecules* **1995**, *28*, 5029.