Chain Diffusion between Crystalline and Amorphous Regions in Polyethylene Detected by 2D Exchange ^{13}C NMR

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ABSTRACT: Solid-state chain diffusion between crystalline and amorphous regions in linear polyethylene (PE), at temperatures down to 100 K below T_m, is detected by means of two-dimensional (2D) and one-dimensional (1D) exchange ^{13}C NMR experiments under high-resolution magic-angle-spinning (MAS) conditions. The jump rates and the activation energy of 105 kJ/mol extracted from the data agree well with previously reported values for the underlying chain jump motion, i.e., the dynamic α process. The root-mean-square displacement amounts to more than 10 nm within 100 s near 360 K and is affected by entanglements. The measured effective diffusivities range between 10^{-17} and 10^{-21} m^2/s. Chain diffusion also explains the nuclear Overhauser enhancement factor and the nonexponential ^{13}C longitudinal (T_1) relaxation in the crystallites of PE, as well as the dependence of T_1 on the crystallite thickness reported by other authors.

Introduction

Chain diffusion is an important dynamic process in polymer melts, determining, e.g., their viscoelastic and transport properties.[1] In glassy polymers below the glass transition temperature, T_g, diffusion is strongly quenched. In semicrystalline systems then the interesting question arises as to whether chain diffusion can take place at temperatures above T_g of the amorphous fraction but below T_m of the crystalline regions. Chain diffusion in semicrystalline polymers was occasionally postulated but has not become a generally accepted concept. In fact, to our knowledge it has not yet been proven experimentally.

Solid polyethylene (PE) is a typical example of a semicrystalline polymer. Its bulk structure is known[2,3] to be made up of chain-folded crystalline lamellae that are typically 5–40 nm thick and separated by layers of noncrystalline material. For simplicity, these will be referred to as the amorphous fraction, although they may exhibit some residual order. The degree of crystallinity can range from 20 to 95%, depending on, e.g., side-branch content and annealing conditions.[2] Crystallinity decreases with increasing temperature. Small-angle X-ray scattering strongly indicates, however, that during this process the average crystallite thickness remains virtually unchanged.[4,5]

Dynamic spectroscopic methods, including dielectric and mechanical measurements as well as NMR, reveal three major motional processes in PE, termed α, β, and γ relaxations.[6] The question as to whether the β or the γ relaxation represents the glass transition has been a point of discussion for many years.[7,8] The γ relaxation is found by NMR[9] to be related to strong motions in the amorphous domains, with a corresponding glass transition temperature of approximately 150 K. The origin of the rather weak β relaxation is not completely certain.

The α process is of particular interest with respect to possible solid-state chain diffusion.[10] It is assigned to 180° jumps of the chain stems in the crystallites,[11,12] like the helical jumps in other semicrystalline polymers proved recently by 2D[13,14] and 3D[15] exchange NMR. The motion effectively involves a rotation and a translation by one repeat unit, as shown schematically in Figure 1a,b, such that the portion of the chain in the crystallites is in its energetically most favorable position in the lattice before and after the jump. The rate of this process in PE exceeds 10 000/s at temperatures between 340 and 380 K,[6] depending on crystallite thickness. In the samples investigated in this paper, the rate of 10 000/s is expected near 365 K. In the most naive model of free diffusion, this jump rate would amount to a root-mean-square displacement of the chains within, e.g., 10 s by as much as $(2 \times 10 \times 10\,000)^{1/2} \approx 450$ repeat units, i.e., more than one crystallite thickness. So far it has been an open question as to whether the diffusion is not strongly hindered or virtually quenched by entanglements, tight reentries, and similar constraints of the chain loops in the amorphous domains. It is the purpose of this publication to demonstrate that even in high molecular weight polyethylenes the chain jump process does indeed result in large-scale chain diffusion, which is nevertheless significantly hindered by constraints in the amorphous regions. For shorter linear n-alkanes it is known that molecular motion[16,17] results in micrometer diffusional translation within days.[18] In cycloalkanes and certain phases of some polymers, high mobility involving translation has been established by NMR.[19]

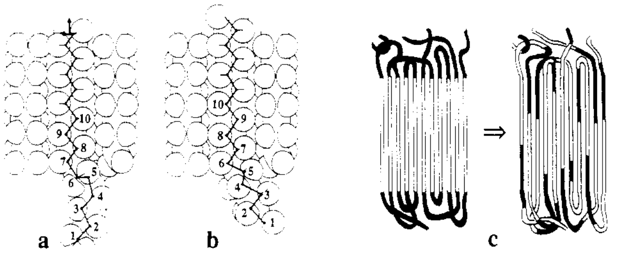

Figure 1. (a) Schematic view of PE chains in a crystallite, near the interface to an amorphous region. The repeat units of one chain extending into the amorphous region are marked by numbers. (b) Same as a, after one elementary step of the dynamic α process motion of the selected chain. Note the translation and the 180° rotation of the chain. (c) Schematic visualization of chain diffusion in PE. At one point in time, all chain units outside of the crystallites are marked. Through many jumps of the type depicted in a and b the marked segments diffuse far into the crystallites. It will be shown below that in our samples displacements of this magnitude occur within 1 min at 370 K or within a few days at room temperature.

Two-dimensional (2D) exchange NMR[20,21] is a powerful means to investigate slow dynamic processes occurring on a time scale up to several seconds. This type of spectroscopy correlates NMR frequencies before and after a long waiting period, the so-called mixing time. In the spectral plane with its two frequency axes, frequency changes in the mixing time give rise to off-diagonal intensities, the cross peaks. The method has been successfully used to detect chemical exchange in solu-

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tion[20,21] and in the solid state.[22-24] In nonrotating solids, especially in solid polymers, it can provide unique information about the geometry of rotational motions, probing the orientation of molecules by localized anisotropic NMR interactions.[13,14] In this paper, however, we use the technique with magic angle spinning to detect chain translations between the different phases of polyethylene.

High-resolution solid-state ^{13}C NMR with magic angle sample spinning (MAS), cross polarization (CP), and dipolar decoupling of protons[25,26] yields, because of the γ-gauche effect,[27] fairly separated signals from the amorphous and crystalline fractions of PE,[28] at approximately 30.5 and 32.5 ppm relative to TMS, respectively. This makes it possible to detect exchange between crystalline and amorphous domains in the 2D exchange spectrum in the form of cross peaks. They are generated by those CH$_2$ groups that have been in the amorphous regions during the evolution but in the crystalline regions during the detection period, or vice versa.

Experimental Section

Ultrahigh molecular weight polyethylene (UHMWPE, $M_w > 4 \times 10^6$, Polystone M) was machined into a cylinder of 5.5-mm diameter to fit into a MAS rotor. From one-pulse ^{13}C MAS spectra the crystallinity by weight was determined to be 58 ± 5% at 340 K, decreasing to 45 ± 4% at 377 K. These relatively low crystallinity values are in accordance with values reported on other UHMWPE samples.[29] High-density polyethylene (Lupolen 5260 Z) oriented by drawing at 390 K (oHDPE) was measured in the form of sheets. The degree of crystallinity was found to be 86 ± 5% at 320 K, decreasing only slightly to 77 ± 5% at 377 K. Sheets of the same material were partially cross-linked via irradiation with a dose of 200 kGy of 4-MeV electrons. According to the literature,[18] this should lead to approximately 75% of cross-linked macromolecules. In none of the samples could side groups or chain ends be detected in the ^{13}C NMR spectra.

Spectra were taken with a Bruker MSL 300 spectrometer at MAS rotation frequencies between 3 and 4 kHz. As the broadening of the ^{13}C spectra by chemical shift anisotropy at a field of 7.05 T amounts to only 3 kHz, spinning side bands were always negligible. The temperature of the bearing gas was varied for measurements from room temperature up to 377 K. 90° pulse lengths ranged between 3.5 and 3.9 μs, corresponding to B_1 fields of approximately $2\pi\gamma^{-1}70$ kHz. The 2D spectra were taken with 30–64 t_1 increments of 800 μs. Measuring times ranged between 5 and 30 h. For the one-pulse 1D exchange spectra, between 4 and 128 scans were averaged.

Results and Discussion

Standard 2D Exchange Experiment. Figure 2 shows a 2D exchange spectrum of a sample of UHMWPE at 350 K, with a mixing time of 1 s. As expected, cross peaks between the signals from crystalline and amorphous domains are detected. However, their intensities amount only to approximately 5% of the intensities of the diagonal peaks. This is in part due to loss of signal during the mixing time occurring via longitudinal relaxation of the magnetization with time constant T_1. While in the crystallites ^{13}C T_1 values exceed 100 s,[29] the T_1 of the amorphous fraction, i.e., of all signal except for the all-trans line at 32.5 ppm, is only between 0.4 and 1.2 s because of their high mobility, rising slightly with temperature.[30] For the example presented in Figure 2a, this longitudinal relaxation has reduced the intensity of the diagonal peak of the amorphous fraction (a) by a factor of 4. The cross peaks are also affected by the fast relaxation in the amorphous domains, as the magnetization showing up in these peaks is due to methylene groups that must have resided in the amorphous domains for some time, during which relaxation is, of course, effective.

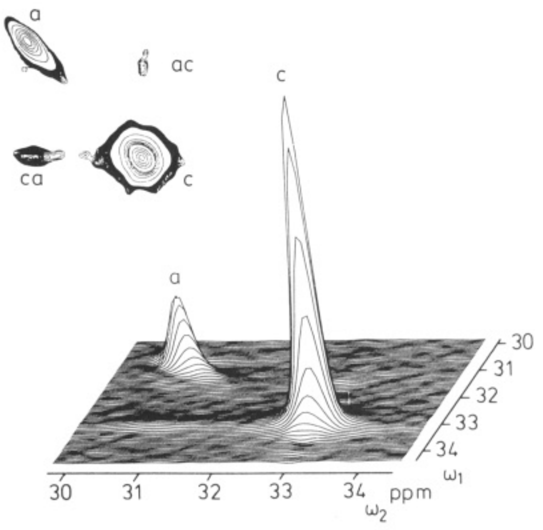

Figure 2. CP-MAS 2D exchange spectrum of UHMWPE at 363 K, with a mixing time of 1 s. ^{13}C $T_{1,\text{amorph}} = 0.7$ s. Slight resolution enhancement has been applied to suppress the long wings of the original Lorentzian line shape. The intensity of the cross peak (ca) is 2.5% of that of the diagonal peak (c), while the (ac) peak intensity makes up 6% of that in the diagonal peak (a). The former ratio is more decreased by T_1 relaxation, so the effect due to exchange amounts to roughly 5%.

Generation of more intense exchange peaks turns out to be difficult. Shorter mixing times, with a lesser decrease in magnetization by T_1 relaxation, reduce the exchange intensity. At higher temperatures, where exchange should be enhanced, the crystalline peak broadens significantly, with a corresponding loss in height. Experimentally it was determined that the line broadening decreases strongly with the increasing strength of the decoupling field. This fact and the observed Gaussian envelope of the broadened line indicate that the broadening is due to partial failure of proton decoupling brought about by the chain motions in the kilohertz range themselves.[31] This can be viewed as being similar to the breakdown of homonuclear dipolar decoupling[32] when the rate of the motion approaches the cycle time of the decoupling sequence. Actually, it can be shown that under high-power decoupling the average Hamiltonian[32] of the interchain heteronuclear dipolar interactions increases gradually while the jump rate approaches the frequency equivalent of the decoupling field strength, thereby diminishing the decoupling efficiency. In principle, the broadening could be reduced by using decoupling fields beyond our maximum value of $B_1 = 2\pi\gamma^{-1}70$ kHz, but this leads to intolerable arcing in the probehead.

For a reliable analysis of the exchange process, the intensity of the off-diagonal peaks has to be enhanced in relation to the diagonal signals. A way of achieving this will become clear as we present additional ^{13}C MAS NMR experiments on PE that strongly indicate that magnetization transfer through chain diffusion between crystalline and amorphous regions does occur on the time scale of many seconds.

1D Exchange Experiments. As an alternative to two-dimensional exchange NMR, one can perform selective 1D experiments. In this case, after selective excitation of the magnetization of one component, exchange is detected as the intensity in the resonance(s) of the other component(s) after a mixing time. In PE, a simple selective experiment can easily be performed on the basis of the huge differences in ^{13}C T_1 relaxation times (see above). As shown in Figure 3a, the amorphous parts are quite selectively magnetized over several seconds after saturation

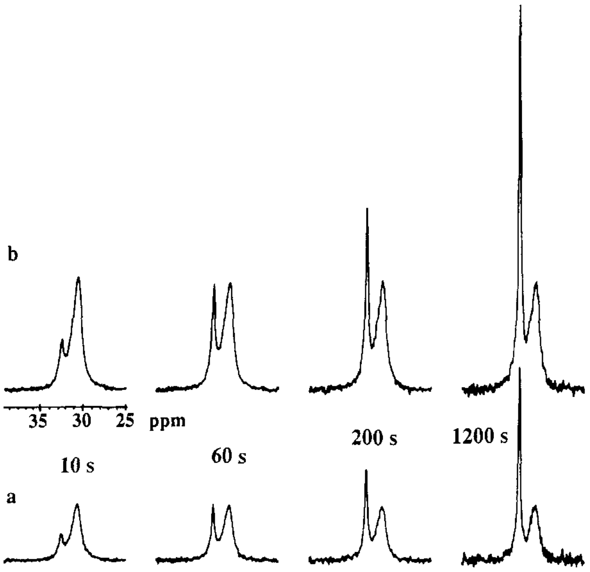

Figure 3. (a) Series of one-pulse MAS spectra of UHMWPE at 305 K. The recyle delays are given above the spectra. (b) Same as a but with pulsed saturation of protons during the recycle delay. ^{1}H 180° pulses were applied with a repetition delay of 500 ms. The NOEF of 2 is exactly equal for both peaks, in spite of the 3 orders of magnitude difference in the ^{13}C T_1 values. This indicates that the magnetization in the crystalline resonance actually originates from the amorphous regions.

by one or several 90° pulses. The signal at the crystalline resonance near 32.5 ppm appears only after longer recycle delays. This could be due to (i) ^{13}C T_1 relaxation in the crystallites, (ii) ^{13}C spin diffusion, or (iii) magnetization transported into the crystallites by the diffusing chains.

In the following, experiments will be discussed that show that the first two explanations can be ruled out, while transfer of magnetization via chain diffusion is favored. Note that, for cases ii and iii, the portion of the recycle delay after the reappearance of magnetization in the amorphous components is equivalent to a mixing time in a 1D exchange experiment and will be treated as such in the following.

The crystalline signal grows with the recycle delay in a clearly nonexponential fashion, see below, and is heterogeneous; i.e., components that appear early also relax away within a short time. This is impossible for intrinsic relaxation within homogeneous crystals, and explanations in terms of interfacial effects would require "quasi-crystalline" interfacial layers with enormous thicknesses of more than 5 nm. The strong dependence of T_1 on crystallite thickness reported by Axelson et al.[29] is another effect that is not readily understood in terms of intrinsic T_1 relaxation in the crystals.

One way to check whether the magnetization giving rise to the sharp signal at the crystalline resonance originates from the amorphous regions via a diffusion process is provided by the measurement of the heteronuclear Overhauser effect (NOE).[33,34] When the ^{1}H absorption is saturated, the intensity of the ^{13}C signal can be increased by an enhancement factor NOEF = $1 + \eta$, which has a maximum of 2.988 for isotropic motion in the extreme narrowing condition if the ^{13}C magnetization relaxes by dipolar couplings to the protons only. If motions are slow compared to the Larmor frequency, a value of the NOEF of only 1.15 is expected. In our PE samples, an NOEF of 2 can be generated in the amorphous parts, see Figure 3, indicating their mobility with rates exceeding the Larmor frequency.[33] Exactly the same large value of the NOEF is also found for the crystalline magnetization in all measured cases, even at ambient temperature (Figure 3b). There, the (apparent) ^{13}C T_1 of the crystalline resonance of more than 400 s indicates that, if there are any NOE-driving motions in the crystallites, their rates would have to exceed 10 THz, and if these were responsible for T_1 relaxation, T_1 should rise with temperature, in contrast to the experimental results shown below. These findings indicate that the ^{13}C magnetization detected in the crystalline regions is not generated by ^{13}C T_1 relaxation in the crystallites but has instead been transported in from the amorphous domains.

As has been pointed out to us by one of the reviewers, the NOE of the crystalline resonance is strongly anisotropic in drawn samples of PE. When the order axis is parallel to the $\mathbf{B}_0$ field, the NOEF reaches a value of 3.4 at 300 K but drops to 2.6 at 373 K, while it stays close to 1.7 in this temperature range if the draw direction and $\mathbf{B}_0$ are orthogonal. If the anisotropy were due to motions within the crystallites, the anisotropic NOE should also manifest itself strongly in a powder spectrum. This, however, is not the case. In isotropic samples the NOEF varies with the angular-dependent frequency between 2.6 and 2.0 at the most. Chain diffusion, in fact, can quite easily account for this dependence of the NOEF on sample ordering and temperature, as it is found that in drawn samples the NOEF for parts of the amorphous phase is also anisotropic. In a sample with the draw direction parallel to $\mathbf{B}_0$, chain units outside of the crystallites that move anisotropically are detected via their resonance frequencies that are located between the isotropic chemical shift and the crystalline resonance (note that the samples does not rotate in this special experiment). These oriented amorphous components exhibits NOEF's of up to 3.5 at room temperature. The corresponding chain segments are expected to be located near the interface to the crystallites, where the motion of chains cannot be isotropic for steric reasons. All chain units that move from the amorphous domains into the crystallites due to chain diffusion necessarily pass through this oriented interfacial region and acquire its orientation-dependent NOE, as their residence time in this interphase is on the order of the T_1 there. In an isotropic sample, only weak ordering effects on the interphase are generated by the crystallites, and therefore the anisotropy of the NOE is reduced.

Major contributions of ^{13}C spin diffusion to the exchange of magnetization between amorphous and crystalline regions can be excluded by the following three arguments. First, according to VanderHart and other authors,[10,29] spin diffusion reaches distances on the order of 1 nm only after 100 s. In our experiments near 370 K, the ^{13}C magnetization has easily crossed distances on the order of one crystallite thickness (30 nm) within 100 s (see the discussion below). In other polymers of similar structure and proton density, like polypropylene or poly(methyl methacrylate), ^{13}C spin diffusion just between the different sites of a repeat unit, i.e., on a 0.3-nm scale, starts to become relevant only at mixing times of 3–10 s when the exchange between the phases of PE, i.e., on a 10-nm scale, can already be considerable. Second, at short mixing times significant effects of spin diffusion could be excluded directly. High-power proton decoupling, which in connection with nonresonant MAS *completely eliminates* carbon spin diffusion,[35] was applied in a 1D experiment during a recycle delay of 0.4 s. If the crystalline peak were generated by spin diffusion, it should disappear under these conditions. However, its relative intensity was not changed by the decoupling. In fact, the whole spectrum was enhanced by the NOEF of 2. Third, the strong increase of the exchange

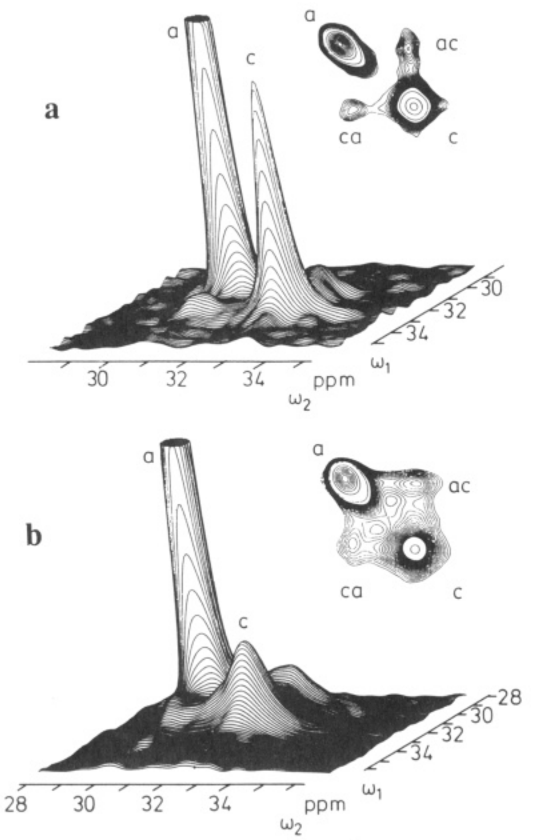

Figure 4. (a) MAS 2D exchange spectrum of UHMWPE at the same conditions as in Figure 2. However, instead of cross polarization, one-pulse excitation was used, with a recycle delay of 4 s. The relative enhancement of the exchange peak (ca), compared with that in Figure 2, is obvious. In the stacked plot, the amorphous diagonal peak was cut at 25% of its maximum. (b) At 373 K and a mixing time of 2 s, the relative strength of the cross peaks is still stronger. Amorphous peak cut at 25% of the maximum.

rate with temperature, see below, also discredits spin diffusion as the decisive step of the magnetization transport.[36]

2D Spectra with Exchange Experiment. In one-pulse experiments with short recycle delays, as described above, the crystalline resonance is saturated. However, the hopping chains transport magnetization from the amorphous domains to the regions in the crystallites that are near the interface. It is obvious that, together with the chains, this magnetization will also diffuse back to the amorphous regions relatively fast. This fact can be utilized to generate large cross peaks, while suppressing the strong crystalline resonance on the diagonal. Such 2D exchange spectra recorded with one-pulse excitation rather than cross polarization and a recycle delay of only 4 s are presented in Figure 4. As expected, under these conditions the diagonal spectrum is dominated by the signal from the amorphous regions (see also Figure 3). The intensity of the cross peak (ca), which indicates exchange of magnetization from the crystalline to the amorphous regions, now amounts to 20% of the crystalline peak on the diagonal (c). In the spectrum of Figure 2 the corresponding fraction was only 2.5%. In that case, ^{13}C magnetization was created homogeneously in the crystallites by cross polarization, and the segments in the core of the crystallites contribute only to the diagonal peak, because they cannot reach the amorphous parts within the mixing time of 1 s.

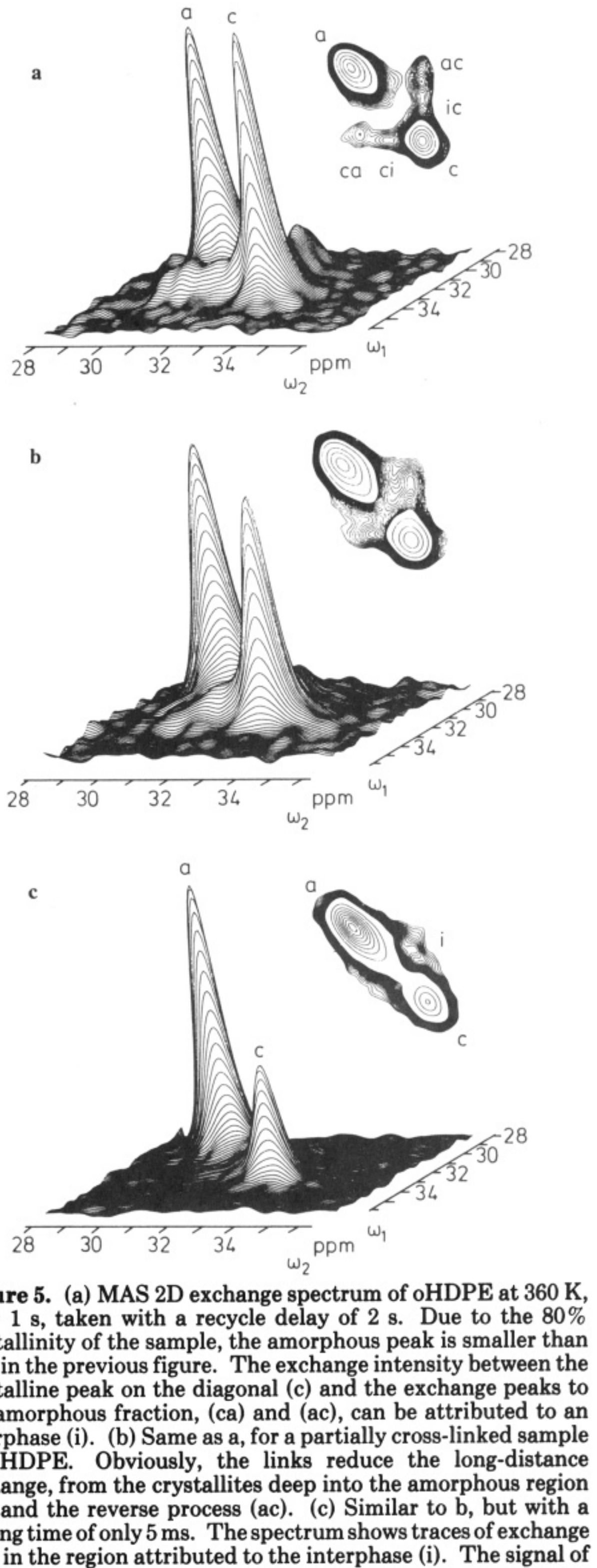

Figure 5. (a) MAS 2D exchange spectrum of oHDPE at 360 K, t_m = 1 s, taken with a recycle delay of 2 s. Due to the 80% crystallinity of the sample, the amorphous peak is smaller than that in the previous figure. The exchange intensity between the crystalline peak on the diagonal (c) and the exchange peaks to the amorphous fraction, (ca) and (ac), can be attributed to an interphase (i). (b) Same as a, for a partially cross-linked sample of oHDPE. Obviously, the links reduce the long-distance exchange, from the crystallites deep into the amorphous region (ca) and the reverse process (ac). (c) Similar to b, but with a mixing time of only 5 ms. The spectrum shows traces of exchange only in the region attributed to the interphase (i). The signal of the amorphous fraction is larger than in a and b, since it is not affected by T_1 relaxation here due to the short mixing time. Low-level (outer) contour lines are drawn at equal levels relative to the crystalline peak height for all three spectra.

Using one-pulse excitation, considerable exchange intensity is obtained also in oriented high-density PE (oHDPE) (Figure 5a). Between the true cross peaks and the diagonal peaks, strong ridges are observed, which are also found, though less pronounced, in the spectra of Figure 4. They are attributed to the segments in the interphase between crystalline and amorphous regions. These can be expected to exhibit chain conformations with a higher trans content than the core of the amorphous fraction. The ^{13}C chemical shifts for chains in this interphase are, therefore, expected to lie between those of the crystalline and amorphous chains, and this has been confirmed experimentally.[38] In the interphase, the exchange effect is naturally seen most strongly. Molecules that have been in the interphase before the mixing time are carried away in both directions and are therefore very unlikely to be found in the interphase afterward. This leads to the relatively strong exchange ridges and depletes the diagonal between the crystalline and amorphous peaks.

The chain diffusion between crystalline and amorphous regions should be hindered by cross-linking. Indications of this are indeed found in the 2D exchange spectrum (Figure 5b) of a partially cross-linked sample of oHDPE measured under identical conditions as the spectrum shown in Figure 5a. Here the cross peaks (ca) and (ac) for exchange between crystalline and amorphous domains are somewhat suppressed, while the exchange due to the interphase is retained. Comparison with a nearly diagonal spectrum at short mixing time (Figure 5c) shows the significance of the exchange intensities in Figure 5a,b.

The 2D exchange spectra of Figures 4 and 5 show the interdomain exchange very clearly. However, to investigate the exchange process over longer mixing times, 2D spectroscopy is not well suited. Because of the fast ^{13}C T_1 relaxation of the amorphous component, after mixing times longer than 5 s hardly anything other than the signal from the crystallites on the diagonal is observed. However, ^{13}C T_1 selective 1D experiments open the way to longer mixing times, namely up to values on the order of the T_1 relaxation time of the crystalline component. Some care must be taken to distinguish magnetization transport effects from T_1 relaxation processes in the crystallites. In the case studied here, however, according to the discussion above, the latter are negligible.

Quantitative Analysis and Simulation of Chain Diffusion. The final proof for chain diffusion is provided by the quantitative analysis of the 1D exchange experiments. At different temperatures, the height of the crystalline resonance in one-pulse spectra, as shown in Figure 3 and taken with recycle delays ranging from 1 to 1200 s, was evaluated. To achieve this with sufficient accuracy in spite of spectral overlap of the resonances, the line shape of the crystalline component was taken into account. It was determined by suppression of the signal of the amorphous component in the spectra, based on its short T_1 relaxation time. The peak heights thus found, plotted against the square root of the recycle delay, which has the character of a mixing time in this context, are shown in Figure 6a. Final values (100%) were determined by use of recycle delays up to 1200 s and by comparison with CP spectra, assuming a CP efficiency of 3.5 for the crystalline resonance. The initial slope is fairly linear, as should be expected for a diffusive process.

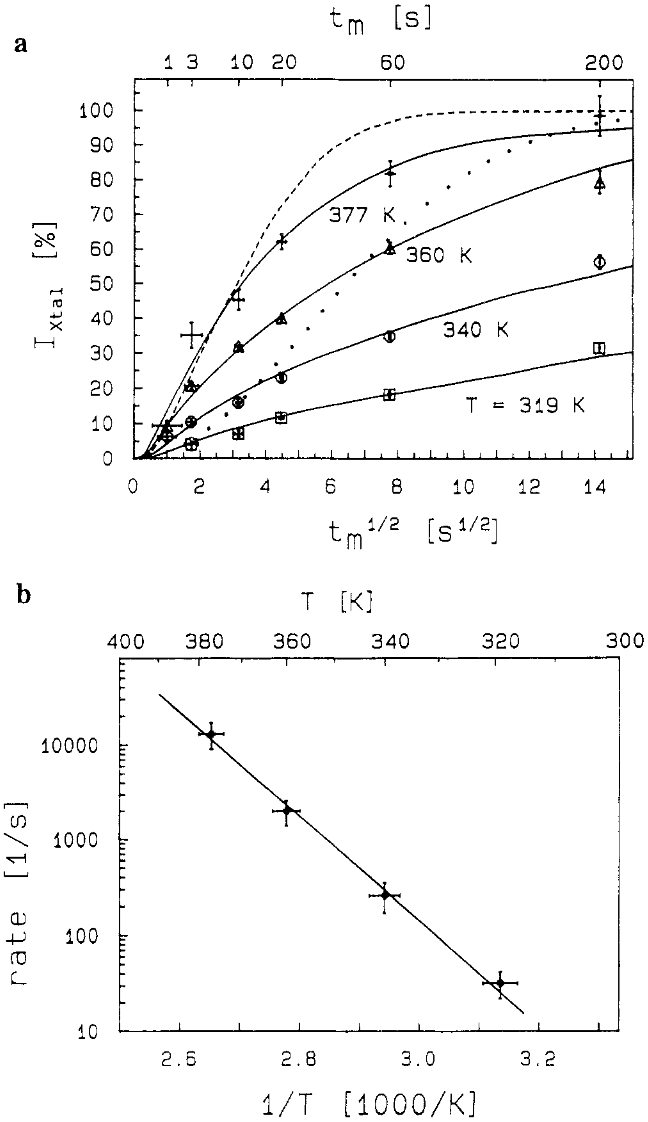

Figure 6. (a) Intensity of the crystalline resonance of UHMWPE at different temperatures, plotted against the square-root of the recycle delay. The dashed curve represents free diffusion behavior with a rate of 1000 jumps/s. The solid curves are fit based on Monte Carlo chain hopping simulations with entanglement effects, for details see text. For reference, the dotted curve indicates the shape of monoexponential relaxation in this plot. (b) Arrhenius plot of the jump rates derived from the fit curves in a. The value of E_a = 105 ± 10 kJ/mol agrees well with literature values[6] of 104–116 kJ/mol for the α relaxation in PE.

Fits to the curves in Figure 6a were produced by means of a Monte Carlo simulation of the diffusion of a sample chain in a lamellar crystal. This model chain consists of 100 crystalline stems, each 250 repeat units long, and 99 amorphous loops (plus two chain ends) whose length was adjusted to match the crystallinity. With every jump of a crystalline stem, the lengths of the two adjacent loops are increased and decreased, respectively, by one repeat unit. As a result of successive diffusion steps, all parts of the chain slowly move away from their initial positions, while the loop lengths fluctuate. The dashed curve in Figure 6a is obtained under the assumption of free diffusion of the chains with a rate of 1000 jumps/s. Obviously, after some time the experimental points start to lag behind the free diffusion curve, indicating restrictions to diffusion at larger displacements. This is not too surprising since free diffusion would demand quite unrealistic fluctuations of loop lengths in the amorphous regions. In the further simulations, therefore, each individual loop length was constrained not to become shorter than the starting value by more than a certain number n_f of repeat units. This yields the curvature required by the experimental data. The solid curves in Figure 6a are fits obtained with an average n_f of 20 ± 5 repeat units. This relatively small value indicates significant obstacles to loop length variations in the amorphous domains, like topological constraints, entanglements, or nonadjacent reentry. No additional assumptions on the details of loop length distributions, reentry statistics, etc., were necessary. The diffusion process is slowed down by these obstacles, but it nevertheless moves repeat units of the chain over large distances. For instance, at 360 K their root-mean-square displacement after 100 s of diffusion exceeds 10 nm. This corresponds to an effective diffusivity of about 10^{-18} m^2/s. Virtually complete exchange between the phases is reached after sufficiently long times, even though the ends of the model chain were not allowed to diffuse through the crystallites. In the simulations, the time required for magnetization buildup by ^{13}C T_1 relaxation in the amorphous domains was also taken into account. In particular, this gives rise to the curvature of the fits at very short recycle delays.

Figure 6b presents an Arrhenius plot of the jump rates in the chain diffusion process obtained from the fits shown in Figure 6a. The activation energy of 105 ± 10 kJ/mol as well as the absolute values of the rate are in good agreement with data obtained for the α process in PE by other methods.[6] The corresponding diffusion constants range between 10^{-17} and 10^{-21} m^2/s. Note that the strong increase of the magnetization transport rate with temperature further supports the supposition that the exchange cannot be due to spin diffusion. The spin diffusion rate should not rise but instead drop with increasing temperature, as average domain sizes grow[4,5] and dipolar couplings are reduced more and more by molecular motion and MAS.

The characteristic time constant of the diffusion process is proportional to the square of the crystallite thickness. Thus, the chain diffusion model can qualitatively explain the strong dependence of the apparent crystalline ^{13}C T_1 relaxation times on lamellar widths in polyethylenes, which has been experimentally established by Axelson et al.[29]

Concluding Remarks

The 2D and 1D exchange NMR experiments prove long-distance solid-state chain diffusion in polyethylenes, for temperatures down to ambient temperature. These remarkable long-range dynamic effects can be explained quantitatively on the basis of the rates and the mechanism of the α process in PE. The concept of α process related chain diffusion may lead to some interesting consequences for theories on chain ordering, phase structure, and dynamics in semicrystalline polymers, as well as in systems where polymer chains are adsorbed on surfaces or subject to other confinements.

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