PHYSICAL REVIEW E **76**, 060801(R) (2007)

Morphological differences in semicrystalline polymers: Implications for local dynamics and chain diffusion

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(Received 15 August 2007; published 26 December 2007)

Morphological differences in semicrystalline polymers due to different crystallization conditions have implications for the chain motion. The local dynamics in the noncrystalline regions of solution-crystallized linear polyethylene is lower than in a melt-crystallized sample, but the opposite is observed for chain diffusion between noncrystalline and crystalline regions. The activation enthalpy for chain diffusion, however, is the same, indicating that entropic differences in the noncrystalline regions strongly influence the chain diffusion of the same polymer in different morphologies.

DOI: 10.1103/PhysRevE.76.060801 PACS number(s): 61.41.+e, 61.18.Fs, 66.30.−h

Unlike many organic and inorganic materials, polymers are at best semicrystalline, consisting of thin crystalline lamellae separated by noncrystalline regions (NCRs) [1,2]. In crystalline regions (CRs) polymer chains usually have a well-defined conformation, whereas chains in NCRs are conformationally disordered. The conformational freedom of polymer chains in NCRs is crucial for their mechanical properties and may be influenced by the morphology, which varies with the molar mass and crystallization conditions of the sample [3,4]. Recently, it was shown that differences in the conformational freedom in NCRs have implications for crystal melting, leading to different melt states [5,6]. For a polymer such as linear polyethylene (PE) the crystallization conditions from the melt are far from equilibrium, since the long chains must disentangle from the melt, adopt the required all-*trans* conformation, and align parallel to the other chains of the crystallite. In fact, polymer crystallization is an active and controversial field of research [7]. When the polymer is crystallized from dilute solution (thus from an almost disentangled state), the crystallization is facilitated and the NCRs obtained consist predominantly of chain folds. Thus, the packing of the polymer chains in NCRs of solution-crystallized (SC) samples will be more homogeneous than those in melt-crystallized (MC) samples, which should manifest itself in the dynamic behavior of the polymer chains, e.g., the segmental mobility in NCRs. More interesting, however, is to what extent the medium-range translational motion of the chains between CRs and NCRs (chain diffusion), which limits the long-time stability of the material, depends on the conformational distribution in NCRs. Here we show that both questions can be tackled by ^{13}C solid-state NMR, where linear PE is chosen as the simplest case of a semicrystalline polymer. First, we consider the local dynamics in NCRs followed by a study of the chain diffusion on a nanometer length scale. Then the temperature dependence of the chain diffusion for SC and MC samples is compared and related to thermodynamic quantities. Finally, the chain diffusion is related to the local dynamics in CRs themselves.

To enhance the conformational differences in NCRs of samples crystallized from melt and from solution, ultrahigh-molecular-weight linear polyethylene (UHMWPE) of average molar mass $M_W \sim 4600$ kg/mol is chosen. SC films are prepared following the method described earlier [4]. The MC samples are prepared on cooling the melt of as-prepared SC films at a rate of 10 K/min. All solid-state NMR measurements have been performed with a Bruker DSX spectrometer operating at 500 MHz ^{1}H frequency. NMR techniques correlating isotropic chemical shifts observed under the magic angle spinning (MAS) condition with motional-averaged anisotropic NMR interactions, i.e., ^{1}H-^{13}C dipole-dipole coupling (DDC) [8] and ^{13}C chemical shift anisotropy (CSA) [9], have been used to study the local chain dynamics. The chain translational motion between NCRs and CRs is studied via ^{13}C exchange experiments [10,11].

In ^{13}C (cross polarization) CPMAS spectra of the two samples [Figs. 1(a) and 1(b)] the signal of the all-*trans* conformation in CRs of the samples [12], is observed at ~33 ppm with identical linewidth. In contrast, chain segments in NCRs yield broad peaks at ~31 ppm, differing in width for the two samples. The width of these signals reflects the range of conformations in the NCRs, where conformational transitions lead to motional narrowing, if the exchange between the accessible conformations becomes fast on the NMR time scale at about 40–50 K above the static glass transition temperature [13]. The NMR signals of these units thus depend on the conformational statistics in NCRs as well as the exchange rate between different conformations [12,14]. The spectrum of the SC sample shows a broad noncrystalline peak ($\Delta_{\mathrm{FWHM}}=2.36$ ppm) at 31.1 ppm, whereas the noncrystalline signal of the MC sample exhibits a relatively sharp peak ($\Delta_{\mathrm{FWHM}}=0.76$ ppm) at 30.7 ppm due to motional narrowing (FWHM indicates full width at half maximum). Thus, the conformational statistics as well as the dynamic behavior of the chain units in these regions depends on the crystallization procedure and thus on the resultant morphology.

More detailed information on the local chain dynamics in NCRs of PE can be obtained from motional-averaged anisotropic NMR interactions, such as ^{1}H-^{13}C dipole-dipole couplings and ^{13}C chemical shift anisotropy. Rotor-encoded rotational echo double resonance (REREDOR) measurements [8] of the ^{1}H-^{13}C DDC yield sideband patterns, which are analyzed to determine the averaged DDC constants, which in turn can be viewed as dynamic local order parameters [15].

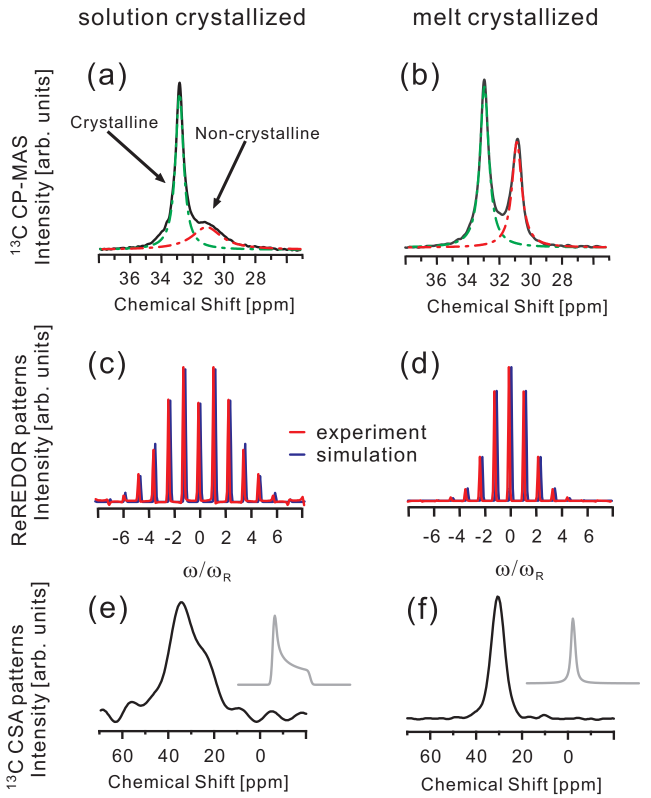

FIG. 1. (Color) NMR spectra of PE samples at $T=340$ K: (a),(b) ^{13}C CPMAS spectra (6 kHz MAS, 2 ms CP contact); (c),(d) REREDOR pattern [8] (25 kHz MAS, 3 τ_R recoupling); (e),(f) ^{13}C CSA powder line shape (CSA recoupling [9], 3 kHz MAS) together with line shape simulations (in gray).

At $T=340$ K the residual DDC of the SC sample is 8.9 kHz as opposed to 5.6 kHz for the MC sample [see Figs. 1(c) and 1(d)]. These values correspond to dynamic local order parameters of 0.42 and 0.26, respectively. Further information on the geometry of the dynamics is obtained from the ^{13}C powder line shape of the noncrystalline signal, which can be extracted from a correlation experiment using CSA recoupling [9], displayed in Figs. 1(e) and 1(f). The ^{13}C NMR powder line shape of NCRs of SC UHMWPE exhibits features characteristic of axially symmetric CSA tensors, in contrast to that of the MC sample, which reflects a more isotropically averaged CSA pattern. Since the CSA of the CH_2 units in the crystalline state is the same, the CSA powder line shape in the NCRs also indicates significantly different motional averaging in the two samples, essentially isotropic in the MC sample vs more restricted in the SC sample. These findings are consistent with the lower crystallinity of the MC sample, which leads to a longer average chain length between the crystallites. This allows a more isotropic motion of the individual chain segments compared to the more restricted chain segments in the NCRs of the SC sample.

The question then arises as to how the different local dynamics in NCRs affects the cooperative medium-range chain translational motion. In the melt, translational motions on even longer length scales are readily studied by field gradient NMR [16]. However, in solid PE chain diffusion involves moving a stem just a few nanometers from CRs to NCRs, accompanied by a change in conformation. A simple ^{13}C exchange NMR experiment can be used to monitor this process, because the different conformers indicative of the different regions can be identified by different chemical shifts [Figs. 1(a) and 1(b)] [10]. Chain diffusion can thus directly be monitored by the changes in ^{13}C frequency of the CH_2 groups involved, from that characteristic of the all-*trans* conformation in CRs and the gauche-containing conformers in NCRs. Due to the very long ^{13}C T_1 relaxation times in CRs [17] and the short ^{13}C T_1 relaxation time in NCRs of PE (~0.6 s), the translational motion from CRs to NCRs dominates the polarization decay in the crystallites. This can be checked by the time dependence of the polarization decay. The loss of polarization due to T_1 relaxation would follow an exponential law, whereas a loss due to the diffusive translation motion of the polymer chain follows a power law, i.e., a $t^{1/2}$ dependence for short times.

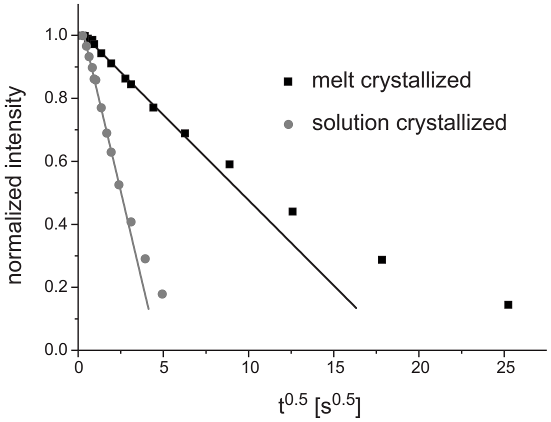

FIG. 2. Decay of crystalline NMR signal plotted versus the square root of time t (6 kHz MAS, $T=340$ K, $t=0.1$ s for normalization).

In Fig. 2 the decay of the crystalline signal in both samples at $T=340$ K is plotted versus $t^{1/2}$. For short times, the signal intensity clearly decays proportionally to $t^{1/2}$, indicating that diffusive translation motion of the polymer chain (chain diffusion) is predominant. For quantitative analysis the length of the all-*trans* stems has to be known, which was determined by longitudinal acoustic mode (LAM) Raman spectroscopy as 11.9 nm for the SC sample [4]. Only minor variations are observed for different crystallization conditions of the MC samples. From the linear region of the decay curves in Fig. 2 and this value, the chain diffusion coefficient $D=3.7\pm0.4\times10^{-18}$ m^2 s^{-1} for the SC sample, and $D=1.8\pm0.2\times10^{-19}$ m^2 s^{-1} for the MC sample is obtained. The latter is ~20 times smaller than the former. At first sight this appears to be counterintuitive in view of the highly restricted local chain dynamics in NCRs of the SC sample. The bending of the decay curve at longer times can only partly be attributed to curvilinear diffusion of the polymer chain [18] and might be due to hindrance in the NCRs caused by, e.g., entanglements.

From the temperature dependence of the chain diffusion coefficient as shown in Fig. 3, the activation enthalpy (AE)

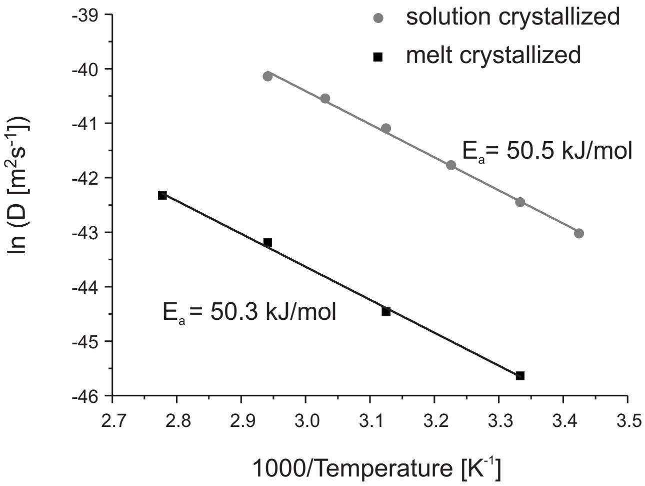

FIG. 3. Arrhenius plots of the chain diffusion coefficients D determined from exchange NMR experiments for the two PE samples.

for this process can be determined. Remarkably, both samples show the same AE (~50±5 kJ/mol). The AE, however, reflects only the energetic aspect of a transition state. The differences in the observed chain diffusion coefficients are then attributed to differences in the entropic barrier the chains have to overcome in order to diffuse between the CRs and the NCRs of SC and MC samples. This difference is estimated as $\Delta S=27$ J/K from the y-axis intercept in Fig. 3, where the entropic barrier is lower for the SC sample. This is consistent with the fact that the entropy difference between NCR and CR in the SC sample is lower than that in the MC sample, as shown by the order parameters determined from the residual DDCs specifying the conformational degrees of freedom.

Chain diffusion of course also requires mobility in CRs themselves. Therefore, we now consider the relation between local chain motions in the crystallites and chain diffusion. Neutron scattering on alkanes [19] as well as advanced solid state NMR studies on MC samples [20,21] have established 180° jumps as the main motional process in the crystal. If the stem in a PE crystal behaves as a rigid body, such 180° jumps must be coupled to translational motion along the chain direction; see also [2]. However, the AE derived from the chain diffusion coefficient differs significantly from the values reported for the chain hopping motion in crystalline PE [10,20,21], namely, ~110 kJ/mol. For direct comparison the chain diffusion coefficient D obtained from ^{13}C exchange NMR can be used to calculate the effective jump rate of CH_2 groups in PE crystals, which leads to translational motion. This can be written as the product of the squared lattice constant a (half the crystallographic c constant 2.534 Å [1]), the hopping rate υ, and a geometry factor g' of about 1. In Fig. 4 local jump rates of CH_2 groups in crystallites of MC PE measured by ^{13}C-^{13}C DDCs [20] and double quantum MAS exchange NMR [21] are compared with the effective CH_2 jump rates obtained from our chain diffusion experiments.

At a given temperature the local jump rates taken from the literature are always higher than the effective jump rates derived from chain diffusion. This indicates that local motions of CH_2 groups in PE crystallites do not always lead to translation of the whole polymer chain. Since the PE samples studied in the literature [20,21] may have slightly different molecular weight, degree of chain branching, or crystallinity, comparison of the absolute values for the jump rates should not be overemphasized. However, the different temperature dependence for the local and effective jump rates, where the former exhibits an increasing apparent AE with increasing temperature [22], whereas the latter shows a simple Arrhenius behavior (Fig. 4), cannot be attributed to possible minor differences in the chemical properties of the samples. In fact, the increasing difference between the effective jump rate determined here and the local jump rates indicates that with increasing temperature the local jump motions observed via anisotropic NMR interactions and by mechanical relaxation [23] become more and more ineffective for the translational motion of the chain.

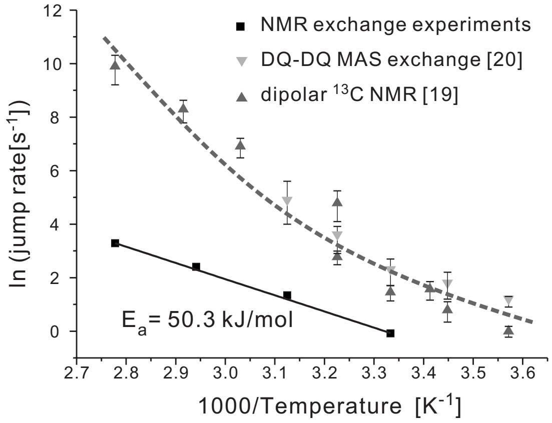

FIG. 4. Arrhenius plots of local and effective jump rates in melt-crystallized PE samples.

In the literature, defect-driven mechanisms have been proposed to explain the translation of an extended all-*trans* chain through a PE crystallite [2,19]. In this scenario, a defect is created, e.g., at one side of the crystal, and the translational motion is accomplished when the defect has moved to the other side and left the crystallite. If, however, the defect only travels inside the crystallite and is reflected back or annihilated, it will not lead to translational motion of the stem, but will still cause local reorientation of the CH_2 units. Thus, local jump rates may differ from the effective jump rate responsible for chain diffusion. Moreover, it should be noted that the defects have to leave the crystallites and thus must pass through the interphase between the crystallite and the noncrystalline region, in order to generate an overall translation of the extended all-*trans* chain stems. Therefore, the conformations in the interphase and their dynamics become essential for the chain translation. In order to further check this scenario, it would be illuminating to compare the local and the effective jump rates in the same SC and MC samples. Unfortunately, however, such data are not available, as doubly ^{13}C labeled samples are required.

Based on the defect model, the nonlinear behavior of local jump rates in the Arrhenius plot of Fig. 4 can readily be understood. As the lattice of the PE crystallites expands with increasing temperature, the number of defects increases [22]. Apparently, however, the likelihood of defects which are not effective for chain diffusion also increases. It should be noted that at lower temperatures the temperature dependence of local and effective jump rates is very similar, indicating that the relative amount of effective jumps is almost constant in this regime. Dynamic mechanical relaxation in PEs show a similar temperature dependence of the AE [23]. Our findings on a molecular level thus provide a microscopic picture of the macroscopic behavior of the material.

In summary, fast, almost isotropic, local molecular fluctuations in NCRs of a semicrystalline polymer are not necessarily favorable for the overall translation motion of the polymer chain. Instead, if the morphology of the sample imposes spatial restriction on the local dynamics in NCRs, the cooperative translation motion of the polymer may be facilitated, provided the fewer conformations do not interfere with the chain diffusion. Our experiments show that this is indeed the case in NCRs of SC PE. Absence of this morphological structure in the MC sample obtained from chemically identical polymers results in almost isotropic local molecular dynamics in NCRs, but greatly reduced chain translation motion. The different behavior of SC and MC samples can be quantified in terms of the conformational entropy difference in the NCRs of the two morphologies. Local jump rates determined from direct observation of CH_2 dynamics in the crystal and effective jump rates determined from the chain diffusion exhibit different temperature dependences. This can be attributed to an increasing number of defects at elevated temperature. The dependence of chain diffusion on morphology has important consequences for phenomena such as crystal thickening [4], long-term stability, and mechanical deformation [24].

Our findings have much more general implications. Follow-up studies of molecular weight dependence show that the reported phenomena are independent of molecular weight down to relatively low molecular weights of ~100 kg/mol; thus chain diffusion occurs on intermediate scales and is not driven by the chain ends. Moreover, a similar behavior is expected for other polymers, which exhibit helical jumps in the crystalline state, like, e.g., polypropylene or polyoxymethylene [25], and thus will be essential for the understanding of the macroscopic behavior of semicrystalline polymers in general. Beyond polymer science, the coupling between local molecular dynamics and mesoscopic transport phenomena is of interest for the understanding of functional materials, such as proton, ion, or photoconductors.

The authors gratefully acknowledge stimulating discussions with B. Ewen, T.C.B. McLeish and G. Strobl.

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