Correction to Local Flips and Chain Motion in Polyethylene Crystallites: A Comparison of Melt-Crystallized Samples, Reactor Powders, and Nanocrystals

Ruth Bärenwald, Sylvia Goerlitz, Reinhold Godehardt, Anna Osichow, Qiong Tong, Marina Krumova, Stefan Mecking, and Kay Saalwächter*

In our recent publication,[1] we have compared the local (monomer) and larger-scale intracrystalline chain dynamics in different poly(ethylene) samples, as assessed by specific novel ^{1}H and established ^{13}C NMR methods, respectively. The comparison of intracrystalline chain diffusion coefficients obtained by the two methods did not afford immediately conclusive results, which prompted us to conclude that samples dominated by adjacent reentry (in our case represented by PE nanodisks) do not generally exhibit the fastest diffusion. This opposed an earlier claim based upon comparing the ^{13}C-detected chain diffusion in solution-grown UHMWPE crystals with a melt-crystallized counterpart.[2]

In the meantime, we have realized that our earlier methodological account of the novel ^{1}H NMR method[3] suffered from an inconsistency related to an unsuitable definition of the average jump correlation time τ_c. A description of the associated problem is published in an erratum.[4] In short, the used arithmetic average (mean) of the assumed log-normal distribution is highly unsuitable, as it is heavily biased toward the high-τ_c end of a wide distribution. A more feasible average is taken on a logarithmic scale

$$\overline{\tau}_c = \exp\{\langle \ln \tau_c \rangle\} \tag{1}$$

which corresponds to the *median* of the distribution rather than the mean. This more suitable definition of an average has been common practice in several, but certainly not all, NMR studies of polymers[5] or small molecules[6,7] approaching the glass transition, where wide distributions are common. It better reflects the behavior of the majority of ensemble members.

The problem arises, and has particularly serious consequences for our recent work,[1] when the width of the correlation time distribution, given by a standard deviation σ in logarithmic units, significantly exceeds about 1 decade. This was the case for the studied reactor powders as well as, in particular, the nanocrystals. Thus, we here report the results of revised analyses of our data and are able to draw new, better substantiated conclusions.

Figure 1 shows a visualization of the temperature-dependent median jump correlation times $\overline{\tau}_c(T)$ in their more suitable definition, as calculated from the fitted activation parameters listed in Table 1. They correct Figure 6b and Table 2 of ref 1. We note that the quality of the fits to the raw data did not change visibly, so we refrain from reporting further details. Because of the significant differences of the fitted distribution widths σ for the different samples, the order of the results for the melt-crystallized samples (HDPEm, PErp5000m), the reactor powders (PErp750, PErp5000), and the nanodisks
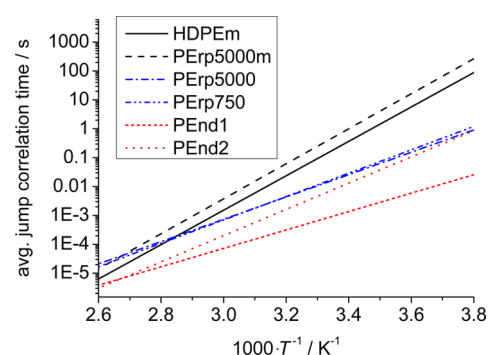

Figure 1. Revised Arrhenius plot of the average jump correlation times $\overline{\tau}_c$ as calculated from the activation parameters given in Table 1.

(PEnd1, PEnd2) has changed qualitatively. It is now seen that $\overline{\tau}_c$ at a given temperature decreases in the order melt-crystallized, reactor powders, and nanodisks. This now provides a local-scale proof and support of the earlier claim of Yao et al.,[2] drawn from ^{13}C-based larger-scale chain diffusivity estimations, and is in line with the notion that more perfect adjacent-reentry structures lead to the largest mobility enhancement.

We still observe qualitative differences as compared to this earlier study in that the fitted activation energies decrease in the order melt-crystallized, reactor powders, and nanodisks, in contrast to an apparently constant E_a reported by Yao et al.[2] As discussed in our previous work,[3] we attributed the apparent constancy to uncertainties related to analyzing the initial signal decay in the ^{13}C experiments (see also below). The [1]H-based result for E_a, which is in fact robust with regards to the definition of the distribution average of $\overline{\tau}_c$, rather indicated the growing importance of cooperative processes in the amorphous phase. The revised data in Figure 1 now support this notion even better in that all samples are similar in the high-temperature region, above which they likely run parallel. Lowering the temperature leads to a more pronounced slowdown in the melt-crystallized samples. If we assume that the defects mediating the jump process (and ultimately the chain diffusion) originate in the amorphous region of these samples, we can straightforwardly attribute the increased E_a and also the unphysically low front factors ($\tau_{c,0} \sim 10^{-21}$ s, see Table 1) to a Vogel−Fulcher behavior describing the amorphous-phase glass transition.[1]

In contrast, the samples rich in adjacent-reentry structures may well retain some degree of fast (yet strongly anisotropic)

Table 1. Revised Results from the Fits to ^{1}H Low-Field and ^{13}C−^{1}H High-Field NMR Data Characterizing the Motions in PE Crystallites

	local flip process[a]				chain diffusion
	ΔM_2^{dyn} (kHz^2)	σ	$\log[\tau_{c,0}/s]$	E_a (kJ mol^{-1})	E_a^{diff} (kJ mol^{-1})
HDPEm	5720 ± 970	1.13 ± 0.45	−20.7 ± 2.6	114 ± 20	43.4 ± 1.2
PErp5000m	8500 ± 2200	1.16 ± 0.43	−20.6 ± 1.4	116 ± 11	65.5 ± 2.0
PErp5000	6610 ± 1800	1.51 ± 0.35	−14.7 ± 1.5	74 ± 10	64.0 ± 3.5
					66.4 ± 2.0[b]
PErp750	6010 ± 760	1.31 ± 0.17	−15.3 ± 1.5	78 ± 10	61.7 ± 2.1
PEnd1	7400 ± 1300	2.25 ± 0.12	−13.7 ± 2.0	61 ± 12	30.6 ± 1.0
PEnd2	7820 ± 520	2.25 ± 0.05	−17.3 ± 2.3	87 ± 16	

[a]The error intervals, which are larger than the ones reported in refs 3 and 4, also include the additional uncertainty related to the correction due to the apparent decay time $T_{2,app}^{dd}$. [b]Annealed (2 days, 363 K).

local mobility in the fold surface. If we assume this dynamics to not be subject to a cooperative T_g-related slowdown, reminding that the amorphous regions of the PEnd samples consist only of constrained interphase material (see Figure 4 of ref 1), the trend toward lower E_a and overall faster jump dynamics could be explained. A proof of this hypothesis would of course require more information on the time scale of fast local motions in the interphase, as e.g. revealed by a comparison of the associated ^{13}C T_1 or $T_{1\rho}$ relaxation times. It is noted that higher apparent E_a values (which roughly parallel the amorphous-phase contents and thus the presence of constrained loop structures and tie chains) are also exhibited by all other literature examples of intracrystalline dynamics in melt-crystallized PE samples.[3,4]

This brings us to a more realistic, revised comparison of derived values for the intracrystalline monomer/chain diffusion coefficient D shown in Figure 2, replacing Figure 8b of ref 1. The range of unphysically larger D values derived from ^{13}C (large-scale) vs ^{1}H (local-scale) observables is now limited to a narrow temperature range for the melt-crystallized samples, and possible origins have been discussed,[1] stressing the qualitative nature of the initial decay analysis of the ^{13}C data. One major

problem appears to be that at high temperatures and correspondingly larger stem displacements the initial-rise analysis should be replaced by a more realistic data treatment taking into account the constraints posed by the amorphous phase, as originally done by Schmidt-Rohr and Spiess,[8] who obtained a significantly larger apparent E_a value that is in line with what we derive from the local jumps in similar samples. This may also explain why our data converge to low D values at high temperatures, while much higher upper-limit D values are derived from the local jumps. Notably, the large difference between the differently determined D values in the low-temperature region suggests a larger relevance of inactive back-and-forth jumps in more tightly folded adjacent-reentry samples. Reassuringly, the order of the different samples is now roughly conserved for both methods, with the fastest diffusion always being observed for the nanodisks.

We finally stress again that in a direct comparison of the relevant data (e.g., apparent D values or jump rates)[3,4] it is the melt-crystallized sample of Yao et al.[2] which deviates downward from the main trend of all other melt-crystallized samples investigated by us as well as others.[8−10] This highlights the importance of yet unclear morphological differences between the different melt-crystallized samples and deserves further studies.

Figure 2. Arrhenius plot of the ^{13}C NMR-based chain diffusion coefficients determined for different samples (symbols) with linear fits (thin lines) used to determine the apparent activation energies listed in Table 1. The hatched area for the annealed PErp5000 sample (crossed triangles) exemplarily marks the uncertainty range as arising from uncertainties in the stem length. The thick lines are revised diffusion coefficients calculated from the local jump correlation times measured by ^{1}H NMR (Table 1).

■ **REFERENCES**

(1) Bärenwald, R.; Goerlitz, S.; Godehardt, R.; Osichow, A.; Tong, Q.; Krumova, M.; Mecking, S.; Saalwächter, K. *Macromolecules* **2014**, *47*, 5163−5173.

(2) Yao, Y. F.; Graf, R.; Spiess, H. W.; Lippits, D. R.; Rastogi, S. *Phys. Rev. E* **2007**, *76*, 060801(R).

(3) Bärenwald, R.; Champouret, Y.; Saalwächter, K.; Schäler, K. *J. Phys. Chem. B* **2012**, *116*, 13089−13097.

(4) Bärenwald, R.; Champouret, Y.; Saalwächter, K.; Schäler, K. *J. Phys. Chem. B*, DOI: 10.1021/jp5100796.

(5) Schaefer, D.; Spiess, H. W. *J. Chem. Phys.* **1992**, *97*, 7944−7954.

(6) Vogel, M.; Brinkmann, C.; Eckert, H.; Heuer, A. *Phys. Chem. Chem. Phys.* **2002**, *4*, 3237−3245.

(7) Sauer, D.; Schuster, B.; Rosenstihl, M.; Schneider, S.; Talluto, V.; Walther, T.; Blochowicz, T.; Stün, B.; Vogel, M. *J. Chem. Phys.* **2014**, *140*, 114503.

(8) Schmidt-Rohr, K.; Spiess, H. W. *Macromolecules* **1991**, *24*, 5288−5293.

(9) Hu, W.-G.; Boeffel, C.; Schmidt-Rohr, K. *Macromolecules* **1999**, *32*, 1611−1619.

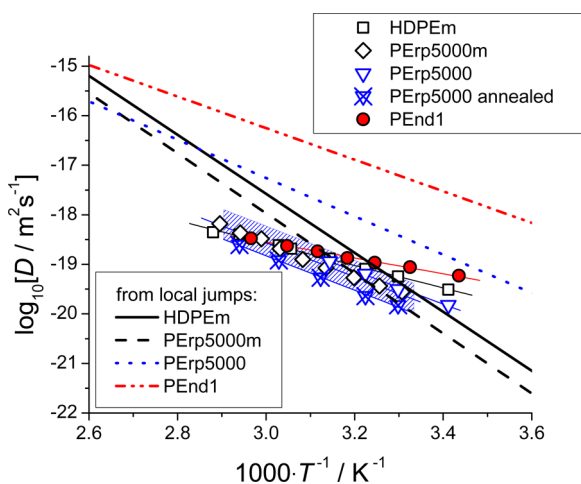(10) Hu, W.-G.; Boeffel, C.; Schmidt-Rohr, K. *Macromolecules* **1999**, *32*, 1714.