THE JOURNAL OF PHYSICAL CHEMISTRY B

Addition/Correction

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Correction to "Determination of Chain Flip Rates in Poly(ethylene) Crystallites by Solid-State Low-Field ^{1}H NMR for Two Different Sample Morphologies"

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J. Phys. Chem. B **2012**, *116* (43), 13089−13097. DOI: 10.1021/jp3061625

In our previous publication,[1] we used a log-normal distribution of correlation times

$$p(\ln \tau_c, \mu, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} \exp\{-(\ln \tau_c - \mu)^2/(2\sigma^2)\} \quad (1)$$

where

$$\mu = \langle \ln \tau_c \rangle \quad (2)$$

to describe the monomer jump motion within poly(ethylene) crystallites. This local process mediates the well-known, mechanically active large-scale intracrystalline chain transport. We performed ^{1}H NMR magic-sandwich echo decay experiments for the crystalline signal as obtained by decomposition of the free-induction decay (FID) and fitted the data taken as a function of pulse sequence time t_{seq} via a numerical integral over eq 1 multiplied by a theoretical expression $S_{MSE}(t_{seq}, \Delta M_2^{dyn}, \tau_c)$

$$S_{MSE}^{distr} = \int_0^\infty p(\ln \tau_c, \mu, \sigma) S_{MSE}(t_{seq}, \Delta M_2^{dyn}, \tau_c)\, d \ln \tau_c \quad (3)$$

Equations 1 and 3 correct eqs 6 and 7 of our paper in that an integration on an $\ln \tau_c$ scale is strongly advised. Our implementation of the corresponding integral (linear in τ_c but with increasing interval length in order to cover large τ_c) was subject to numerical inaccuracies related to the upper τ_c limit. Here, we correct the associated, in fact not too large, errors, implementing the integral by a summation over 50 values of $\ln \tau_c$ ranging from −3 to 3 standard deviations σ. The latter roughly corresponds to the overall distribution width in decades.

Much more importantly, we have relied upon a mathematically correct but physically unreasonable quantity for the average correlation time, i.e., the arithmetic average (mean) of the log-normal distribution on a linear τ_c scale, $\langle \tau_c \rangle = \exp\{\mu + \sigma^2/2\}$. This value is highly unsuitable, as it is heavily biased toward the high-τ_c end of the distribution if σ is significantly larger than 1, corresponding to >1 decade wide distributions. A more feasible average is taken on a logarithmic scale

$$\overline{\tau}_c = \exp\{\langle \ln \tau_c \rangle\} = \exp\{\mu\} \quad (4)$$

which corresponds to the *median* of the distribution rather than the mean and corrects eq 8 of the paper. This suitable definition of an average has been common practice in several, but certainly not all, NMR studies of polymers[2] or small molecules[3,4] approaching the glass transition, where wide distributions are common. It better reflects the behavior of the majority of ensemble members.

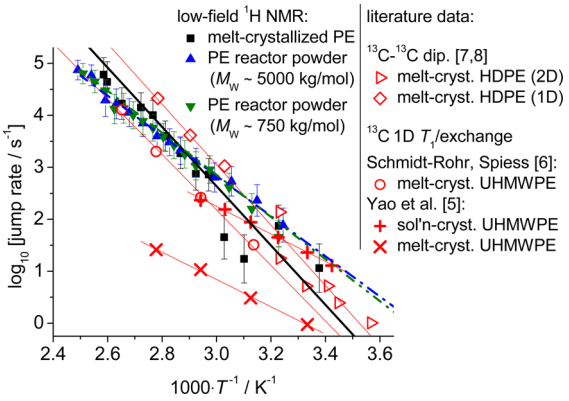

Figure 1. Corrected Arrhenius plot of the jump rates $\overline{k} = 1/(2\overline{\tau}_c)$ for the different PE samples in comparison with literature data. The thick lines visualize the results from the variable-temperature fitting.

Our second and more reliable approach to data treatment consisted of simultaneous fitting of temperature-dependent data, which is implemented by combination of eq 3 with the Arrhenius law

$$\mu(T) = \ln \tau_c^0 + \frac{E_a}{RT} \quad (5)$$

The overall fitting quality of raw data by the two approaches, Figures 6 and 9 of the paper, respectively, does not change visibly, so we refrain from showing updated plots. Some of the fitted parameters, however, change appreciably, so Figure 1 and Table 1 show corrected versions of Figure 8 and Table 1 of the paper, respectively. In Figure 1, we now also include lines corresponding to the activation parameters obtained from fitting data at variable T (second approach), which were only listed in the table and not visualized in the paper. They provide a better comparison of the two approaches than just the tabulated values.

We observe that the major conclusions of the paper do not change, mainly because the distribution widths σ found for most samples are not too different, varying between about 1 and 1.5 decades. Nevertheless, the results now demonstrate that the reactor powder samples show, in the lower temperature range, a trend toward somewhat faster monomer flips in the crystallites. This is in fact more in line with the previous observations by Yao et al.,[5] who observed significantly (a factor >10) faster long-range intracrystalline chain diffusion in an adjacent-reentry dominated solution-grown UHMWPE sample

Published: October 20, 2014

Table 1. Corrected Comparison of Results from Different Methods of Data Analysis

	melt-cryst. PE	PE reactor powder, $M_w \sim 750$ kg/mol	PE reactor powder, $M_w \sim 5000$ kg/mol
		Analysis of $I_c(t_{seq})\|_{T=const}$	
ΔM_2^{dyn} (kHz^2)	6700	6700 ± 800	6700
σ (kHz^2)	1.57	1.57 ± 0.23	1.57
E_a (kJ·mol^{-1})	97 ± 45	80 ± 17	73 ± 19
$\log[\tau_c^0(s)]$	−18.1 ± 6.4	−15.5 ± 2.3	−14.5 ± 2.8
		Analysis of $I_c(T)\|_{t_{seq}=const}$	
ΔM_2^{dyn} (kHz^2)	5720 ± 590	6010 ± 360	6610 ± 430
σ (kHz^2)	1.13 ± 0.22	1.31 ± 0.10	1.51 ± 0.10
E_a (kJ·mol^{-1})	114 ± 7	77.5 ± 2.2	73.5 ± 2.2
$\log[\tau_c^0(s)]$	−20.7 ± 1.0	−15.32 ± 0.32	−14.73 ± 0.32

as compared to a melt-crystallized counterpart. The reactor powders are likely less ideal and therefore do not exhibit a correspondingly accelerated jump process. We note, however, that the comparison with literature data in Figure 1 reveals that it is the melt-crystallized sample of Yao et al. which deviates significantly downward from all other shown literature examples of melt-crystallized (UHMW)PE samples.[6−8]

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