Supplementary Materials for

Immobilized $^{13}$C-labeled polyether chain ends confined to the crystallite surface detected by advanced NMR

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This PDF file includes:

Sections S1 and S2
Table S1
Figs. S1 to S9
References
1. Quasi-static $^1$H Double Quantum (DQ) Filtering with $^{13}$C Detection

1.1. Theory and Pulse Sequence
The pulse sequence as applied to the $^{13}$C-Ac$_2$-POM sample is shown in Fig. S5a. The evolution of magnetization of a pair of $^1$H spins, $I$ and $J$, under the homonuclear dipolar coupling can be sketched in terms of the relevant product-operator terms selected by phase cycling:

$$I_y + J_y \xrightarrow{90^\circ} (I_x I_z + I_y I_z)g(\tau) \xrightarrow{90^\circ} (I_z I_y + I_y I_z)g(\tau) \xrightarrow{90^\circ} (I_y I_z + I_z I_y)g(\tau)$$

(S1)

where $g(\tau) = \sin(\omega_B \tau)$. For DQ filtering to be quasi-static, the time $\tau$ should be as short as possible compared to the rotation period $\tau_r$. A time of $\tau = 6$ $\mu$s at $\tau_r = 250$ $\mu$s (with only $9^\circ$ rotation of the rotor) efficiently selects DQ coherence between $^1$H spin in rigid CH$_2$ groups, whereas the motionally averaged dipolar coupling in mobile regions are too weak to generate double-quantum coherence in this short time. Phase cycling as listed in Table S1 must be applied to selectively obtain the terms in Eq.(S1). At the end of the reconversion period, cross-polarization (CP) was applied to transfer the single-quantum $^1$H magnetization to $^{13}$C for detection with high spectral resolution.

1.2. Pulse Sequence for $^{13}$C-Detected $^1$H Spin Diffusion after Quasi-static DQ Filtering
The pulse program discussed in the preceding section can be extended by adding a $^1$H $z$-filter between DQ filter and CP, which employs the $^1$H magnetization in the rigid segments as the source for spin diffusion. Figures S5b and S5c demonstrate the effect of 100 ms of spin diffusion after the DQ filtering on the CH$_2$ peak of branched PE and the OCH$_2$ peak of PCL, respectively. The amorphous peaks are seen to gradually build up and the crystalline peak dropped significantly with increasing mixing time, indicating the magnetization gradually transfers to the mobile component as expected.

2. Simulations of $^1$H and $^{13}$C Spin Exchange

2.1. Simulation of Spin Exchange Using the Exchange-Matrix Formalism
The magnetization levels of a $M$-spin system form an $M$-component vector $M(t)$. $M(t)$ fulfills the rate equation

$$\frac{dM(t)}{dt} = \Sigma_{nm} \Pi_{nm} M_n(t) = \bar{\Pi} M(t)$$

(S2)

where $\Pi_{nm}$ is the rate constant of spin exchange between spin $m$ and spin $n$. It can also be considered as an element in the rate-constant matrix ($\bar{\Pi}$) whose columns sum to zero (i.e. $\Sigma_n \Pi_{nm} = 0$). The solution to Eq (S2) is:

$$M(t) = \exp(\bar{\Pi} t) M(0)$$

(S3)

where $M(0)$ is the vector of initial magnetization levels.

From the rate-constant matrix $\bar{\Pi}$, we can calculate the exchange matrix

$$\bar{E} (t_m) = \exp(\bar{\Pi} t_m)$$

(S4)

The entries in the exchange matrix $\bar{E} (t_m)$ are directly the cross- and diagonal-peak intensities in a hypothetical 2D exchange spectrum in which all sites are resolved. This can be verified by multiplying $\bar{E} (t_m)$ with $e_n = (0, 0, ..., 0, 1, 0, ..., 0, 0)$, which corresponds to selective excitation of magnetization in site $n$ followed by a mixing time $t_m$. The $n^{th}$ column of the exchange matrix is the vector

$$M(t_m) = \bar{E} (t_m) e_n = \bar{E} e_n(t_m)$$

(S5)
e.g. exciting peak \( n = 4 \), the vector–matrix equation reads (with irrelevant columns in the matrix shown blank for clarity):

\[
\begin{pmatrix}
M_1(t_m) \\
M_2(t_m) \\
M_3(t_m) \\
M_4(t_m) \\
M_5(t_m) \\
M_6(t_m) \\
M_7(t_m) \\
M_8(t_m) \\
M_9(t_m) \\
M_{10}(t_m)
\end{pmatrix}
= 
\begin{pmatrix}
\varepsilon_{14} \\
\varepsilon_{24} \\
\varepsilon_{34} \\
\varepsilon_{44} \\
\varepsilon_{54} \\
\varepsilon_{64} \\
\varepsilon_{74} \\
\varepsilon_{84} \\
\varepsilon_{94} \\
\varepsilon_{10,4}
\end{pmatrix}
= 
\begin{pmatrix}
\varepsilon_{14} & 0 \\
\varepsilon_{24} & 0 \\
\varepsilon_{34} & 0 \\
\varepsilon_{44} & 1 \\
\varepsilon_{54} & 0 \\
\varepsilon_{64} & 0 \\
\varepsilon_{74} & 0 \\
\varepsilon_{84} & 0 \\
\varepsilon_{94} & 0 \\
\varepsilon_{10,4} & 0
\end{pmatrix}
\]

It contains the intensity \( M_n(t_m) \) of the diagonal peak \( \varepsilon_{n,n}(t_m) \) at \( (\omega_{1}^{(n)}, \omega_{2}^{(n)}) \) and the intensities \( M_{n'\neq n}(t_m) = \varepsilon_{n',n}(t_m) \) of the cross peaks in a horizontal slice at \( \omega_1 = \omega_{1}^{(n)} \) in the 2D spectrum.

A conventional evaluation of \( \mathbf{E}(t) = \exp(\mathbf{\Pi}t) \) as a function of time would require repeated calculation of an exponential of a matrix, which would be time-consuming. This can be avoided making use of the simple “recursive” relation

\[
\mathbf{E}(t') = \exp(\mathbf{\Pi} t') = \exp(\mathbf{\Pi} \Delta t) \exp(\mathbf{\Pi} t)
\]

with \( t' = t + \Delta t \), which enables calculation of \( \exp(\mathbf{\Pi} t) \) at any time \( t = N \Delta t \) by successive multiplications using a single matrix \( \exp(\mathbf{\Pi} \Delta t) \).

2.2. \(^1\text{H} \) Spin Diffusion after \( T_{2\text{H}} \) Filtering

The rate-constant matrix. A non-equilibrium magnetization distribution that is subject to spin diffusion can be generated by a \( T_{2\text{H}} \) filter that suppresses the \(^1\text{H} \) magnetization in the solid-like crystallites while selecting the proton magnetization in the mobile amorphous components. The resulting gradual repolarization of the crystalline layer can be modeled as 1D spin diffusion with nearest-neighbor dipolar spin exchange. 34 spins were placed on a one-dimensional lattice with a spacing of 0.125 nm between adjacent spins. The thickness of the domains was determined based on the long period from SAXS (Fig. S1) and the crystallinity. The non-zero elements of the \( \mathbf{\Pi} \) matrix are as follows:

\[
\begin{align*}
\Pi_{m,m\pm 1} &= \Pi_{1,34} = \Pi_{34,1} = k \\
\Pi_{m,m} &= \Pi_{1,1} = \Pi_{34,34} = -2k \\
(2 \leq m \leq 33)
\end{align*}
\]

This can be approximated by the one-dimensional spin diffusion equation

\[
\frac{\partial \mathbf{M}(x,t)}{\partial t} = k(a^2 \frac{\partial^2 \mathbf{M}}{\partial x^2}) = D \frac{\partial^2 \mathbf{M}}{\partial x^2}
\]

with the spin diffusion coefficient \( D = k a^2 \) \( (a = 0.125 \text{ nm is the special resolution}) \). A spin diffusion coefficient of 0.14 nm\(^2\)/ms and a time step of 10 \( \mu \text{s} \) were adopted in the simulation. The diffusion analysis shows that the cross peak initially increases proportional to \( \sqrt{t} \). Fig. 5b shows the best fitting results for both COO and OCH\(_2\) groups, which was achieved by assigning 7, 2, and 25 spins to amorphous, interfacial and crystalline components, respectively. This indicates that the terminating COO groups are concentrated at the crystallite surface, in a layer of \( \sim 0.25 \text{ nm thickness} \).
2.3. CODEX Simulations

The rate-constant matrix. The CODEX intensity for a given model exchange process can be characterized by a rate-constant matrix $\mathbf{\Pi}$ (previously known as the exchange matrix), with elements

$$\Pi_{nm} = 0.5\pi [2\pi \times 7.5 \text{ kHz} \times 10^{-3} \text{ nm}^3 / r_{nm}^3] \left( (P_2(\cos \theta))^2 \right) F(0) \ (n \neq m)$$

$$\Pi_{nn} = -\sum_{n \neq m} \Pi_{nm} \quad (S8)$$

The matrix element $\Pi_{nm}$ reflects the coupling between $^{13}\text{C}$ spins $n$ and $m$. The value of $F(0)$ typically ranges from 0.01-0.04 (42). The pointed brackets of $\left( (P_2(\cos \theta))^2 \right)$ indicate the time-averaging, due to magic-angle spinning, of the orientation dependence of the dipolar interaction, in terms of the instantaneous angle $\theta$ between the $C_n-C_m$ internuclear vector and the external $B_0$ field. This average depends on the angle $\beta$ between the internuclear vector and the rotor axis. Rather than using only the $\beta$-averaged value (0.2) of $\left( (P_2(\cos \theta))^2 \right)$, we evaluated $\left( (P_2(\cos \theta))^2 \right)$ as a function of $\cos \beta$ numerically and took the variation of $\left( (P_2(\cos \theta))^2 \right)$ into account by selecting a random value of $\cos \beta$ between −1 and 1 for each internuclear vector $r_{nm}$ and using the corresponding value of $\left( (P_2(\cos \theta))^2 \right)$ in the calculated value of $\Pi_{nm}$ according to the equation above. This approach provides the same variation of the squared coupling frequencies as full powder averaging and reproduces the observed nonexponential decays better than simulations with a fixed value of $\left( (P_2(\cos \theta))^2 \right)$.

Diagonal-fraction selection. For CODEX with long $N_t$ ($\delta N_t > 12\pi$), to a good approximation dephasing of non-diagonal signals is complete and only diagonal signals contribute to the observed stimulated-echo signal. So, we need to calculate $\mathbf{\tilde{E}}(t) = \exp(\mathbf{\tilde{\Pi}}t)$ and add the “actual diagonal” signals: Many sites in our model have the same frequency and any exchange among them does not contribute to CODEX dephasing. In other words, for our CODEX analysis, we need the diagonal fraction in the actual spectrum. Therefore, in $\mathbf{\tilde{E}}(t_m) = \exp(\mathbf{\tilde{\Pi}}t_m)$, we need to find the unresolved cross peaks ($A \rightarrow A'$ etc.) and add them to the diagonal peaks. To this end, we make a vector marking all $A$ sites, e.g. $(1, 0, 0, 1, 0, 0, 0, 1, 0, 1)$, and multiply it with its transpose to make a matrix of “$A \rightarrow A$” peaks, in our example

$$\mathbf{\tilde{D}}_A = \begin{pmatrix}
1 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 1 \\
0 & 1 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 1 \\
\end{pmatrix} = 
\begin{pmatrix}
1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{pmatrix}$$

(with columns and rows of zeroes shown blank for clarity, except on the diagonal). We generate the corresponding matrix for B sites at $(0, 1, 0, 0, 0, 0, 0, 1, 0, 0)$:
The evolution of (S/S₀)₀ among ¹³C spins in the system as a function of mixing time was calculated using the exchange-matrix theory described above. For samples with both natural abundance and ¹³C-palmitic acid, COO groups on the crystalline lattice were statistically assigned as ¹³C spins based on the fraction of the ¹³C in the sample. The side lengths of the square simulation surface were scaled by \( \sqrt{\frac{1000}{LR}} \) and periodic boundary conditions (in both dimensions) were applied to the simulation square to mimic an infinitely large flat surface. The ¹³C spins were randomly distributed with a probability of LR, and their coordinates were stored in an array to calculate the inter-spin coupling strength using Eq. (S8). Here \( F(0) \) was found to be 0.004, which is much smaller than reported in the literature (42). This can be attributed to truncation of the weak long-range couplings by the strong short-range ¹³C-
$^{13}$C dipolar coupling between magnetically equivalent sites, which do not give rise to fast exchange but still slow down exchange with other $^{13}$C spins.

For the natural abundance palmitic acid (PA-1.1:98.9), spin diffusion among these sparse spin pairs leads to $S/S_0 \sim \sqrt{t}$. A linear regression of the natural-abundance data (Fig. S8a, open circles) to

$$y_1 = 1 - k_1 \sqrt{t}$$

with $k_1 = (0.078 \pm 0.001)/\sqrt{5}$ shows good agreement with the experimental data (red trace). For 100% $^{13}$C-labeled PA (PA-100:0), $S/S_0$ first decays to 50% at $\sim 1$ s, which is followed by a very slow decay within 10 s. The slow further decay seen in Fig. S8a indicates that spin diffusion to naturally abundant $^{13}$CH$_2$ spins takes place during long mixing times. The data after 1 s can be regressed to

$$y_2 = 0.5 \left( 1 - k_2 \sqrt{t} \right)$$

with $k_2 = (0.032 \pm 0.004)/\sqrt{5}$. The reduced exchange rate constant $k_2 < k_1$ is consistent with truncation of the COOH-to-CH$_2$ dipolar couplings by the large $^{13}$COOH-to-$^{13}$COOH dipolar couplings in the $^{13}$C-enriched PA. For partially $^{13}$COO-labeled samples, a correction interpolated between natural-abundance and full labeling was calculated using a linear mixing model:

$$(S/S_0)_{\text{simu.corrected for COO-CH2}} = (S/S_0)_{\text{COO-COO}} \left( (1 - k_1 \sqrt{t}) (1 - \frac{3}{2} LR) \right) + (1 - k_2 \sqrt{t}) \frac{3}{2} LR$$

The simulated curves, shown as solid lines in Fig. S8a, fit well with the experimental data. The same correction was applied in the simulation of CODEX in POM, see Fig. 6, as described in Section 2.3.2.

2.3.2. CODEX Simulations for Two $^{13}$C-Ac$_2$-POM Crystallite Surfaces

Chain tilt is required for spin exchange between chain ends in a flat POM crystallite surface to produce frequency changes and the experimentally observed pronounced CODEX decay, see Figs. S9a and S9b. The CODEX NMR data of $^{13}$COO- terminating groups in $^{13}$C-Ac$_2$-POM shown in Fig. 6a were fitted by simulating the spin exchange between 1000 $^{13}$C spins uniformly distributed on the tilted (2 $\bar{1}$ 14) face of the unit-cell with a width = length $= \sqrt{\frac{1000}{\text{chain-end} \%}}$. Periodic boundary conditions were applied to the simulation square to mimic an infinitely large flat surface. The $\Pi$ matrix can be built according to Eq. (S8) with $F(0) = 0.025$. The chain-end percentages of interest are 100%, 50%, 33%, 25%, 20%, and 10%, which correspond to folding numbers of 0, 1, 2, 3, 4, 5, and 10, respectively. The case of $\sim$33% chain ends is schematically represented in Figs. S9c and S9d. It results if a 5 kg/mol POM chain of $\sim$30 nm contour length makes three passes through the 8.5 nm long period (see Fig. S1), taking into account a chain- and bond-tilt factor of $\sim 1/\cos(30^\circ) = 1.2$. The chain passes through the crystalline-amorphous interface 6 times, out of which two are occupied by the chain ends, which therefore account for $2/6 = 33\%$ of all segments in the crystalline surface. Applying Eq. (S10) with LR = chain-end%, simulated CODEX curves were obtained as displayed in Fig. 6a.

The roll-milling induced four-point SAXS diffraction pattern suggests a tilt angle of 30° upon deformation. If the (2 $\bar{1}$ 14) plane is the crystallite surface, as demonstrated in Fig. S9c, the plane containing the stem-axis and surface-normal directions is parallel to the (1 0 0) face of the unit-cell.
An alternative crystallite surface with a tilt angle of $\phi = 30^\circ$ would be (1 0 14). The plane spanned by the surface-normal and chain-axis direction is parallel to the (1 1 0) face of the unit-cell. The CODEX simulations of the surface (1 0 14) of the unit cell resulted in the decay curves shown in Fig. S8b. Compared with simulated decays in Fig. 6a with corresponding chain-end%, the simulated decays for (1 0 14) are significantly slower. The consistently reduced slope of the initial decay indicates a slower spin-exchanging rate, which can be attributed to a reduction of dipolar coupling resulting from larger $^{13}\text{C}^{13}\text{C}$ pair distances in the (1 0 14) plane. Indeed, the averaged shortest carbon-carbon distance in (2 1 1 14) face and (1 0 14) face of unit cell are ca. 3.9 Å and 4.1 Å, respectively. However, the (1 0 14) crystal plane provides an acceptable fit only at a high chain-end surface fraction close to 50%. This would require the chains to be folded only once, which given the known crystallite thickness and chain length would result in a ~14 nm loose amorphous loop formed by the center of the chains and an estimated crystallinity of only ~60%. Such a scenario is inconsistent with the observed high crystallinity and can thus be ruled out.

Table S1. Pulse phases for quasi-static $^1\text{H}$ DQ filtering using the pulse sequence in Fig. S5a.

| First $^1\text{H}$ 90° pulse | Second $^1\text{H}$ 90° pulse | Third $^1\text{H}$ 90° pulse | (Optional) Z-storage | (Optional) Z-read | $^1\text{H}$ CP-contact | $^{13}\text{C}$ CP-contact | Receiver |
|-------------------------------|-------------------------------|-------------------------------|---------------------|-------------------|-------------------------|--------------------------|---------|
| +x                            | +x                            | +x                            | +x                  | -x                | -y                      | +x                       | +x      |
| +x                            | +x                            | +y                            | +y                  | -y                | +x                      | +x                       | -x      |
| +x                            | +x                            | -x                            | +x                  | -x                | -y                      | +x                       | +x      |
| +x                            | +x                            | -y                            | +y                  | -y                | +x                      | +x                       | -x      |
| -x                            | +x                            | +x                            | +x                  | -x                | -y                      | +x                       | +x      |
| -x                            | +x                            | -x                            | +x                  | -x                | -y                      | +x                       | +x      |
| -x                            | +x                            | -x                            | +x                  | -x                | -y                      | +x                       | +x      |
| +y                            | +y                            | +y                            | +y                  | -y                | +x                      | +x                       | +x      |
| +y                            | +y                            | -x                            | -x                  | +x                | +y                      | +x                       | -x      |
| +y                            | +y                            | -y                            | +y                  | -y                | +x                      | +x                       | +x      |
| +y                            | +y                            | +x                            | -x                  | +x                | +y                      | +x                       | -x      |
| -y                            | +y                            | +y                            | +y                  | -y                | +x                      | +x                       | +x      |
| -y                            | +y                            | -x                            | -x                  | +x                | +y                      | +x                       | -x      |
| -y                            | +y                            | -x                            | +x                  | +y                | +x                      | +x                       | -x      |
Fig. S1. Small angle X-ray scattering profile of Ac₂-POM. The first-order peak at $q = 0.075 \, \text{Å}^{-1}$ corresponds to a long period of 8.5 nm. The intensity was averaged for 5 minutes.

Fig. S2. $T_{1C}$ relaxation of the O-CH₂-O (filled circles) and COO (filled squares) carbons in $^{13}$C-Ac₂-POM. Open triangles: Data points of commercial POM (Delrin) shown for reference. The data show that $T_{1C}$ relaxation is essentially complete within 125 s.
Fig. S3. Deconvolution of O-CH$_2$-O peaks in selective and in quantitative $^{13}$C spectra. The position and the width of the amorphous O-CH$_2$-O peak were determined from amorphous-rich spectra obtained with (a) 0.5 s DP (see Fig. 2) and (b) $T_{2H}$ filtered CP and were held fixed. (c) Deconvolution of the quantitative DP spectrum with 125 s recycle delay (see Fig. 2); (d) CP spectrum, showing the two-peak character of the crystalline signal clearly; (e) CP spectrum after a quasi-static $^1$H DQ filter, which reduces the amorphous signal by 41%.
Fig. S4. Contour plots of 2D SUPER spectra of (a) PCL and (b) $^{13}$C-Ac$_2$-POM. The CSA patterns of rigid (blue) and mobile (red) COOs presented in Fig. 2 were extracted at the chemical shifts indicated by the horizontal dashed lines.
Fig. S5. **Quasi-static $^1$H DQ filtered CP experiment at a MAS frequency of 4 kHz.** (a) Pulse sequence extended with a mixing time. After the short $^1$H DQ filter, $^1$H spin diffusion out of the crystallites for 0.01 ms (thin red line) and 100 ms (thick purple line) is detected in the $^{13}$C spectrum, in (b) branched PE and (c) PCL. After long spin diffusion, the crystalline peak reduces to the equilibrium level seen in the CP spectra (blue traces, matching the amorphous peaks). The fractional intensity of the crystalline peak at long vs. short spin-diffusion time equals the crystallinity of the sample.
**Fig. S6.** $^1$H NMR spectra of $^{13}$C-Ac$_2$-POM. Spectra were recorded at magic-angle spinning frequencies of (a) 5 kHz, (b) 10 kHz, and (c) 14 kHz. Pulse-length-doubling probe-head background suppression was applied. The spectra show broad signals from immobilized crystalline and narrow peaks of mobile noncrystalline segments.

**Fig. S7.** Normalized CODEX signal $S/S_0$ of $^{13}$COO end groups in $^{13}$C-Ac$_2$-POM at different spinning frequencies. The same CSA recoupling of 0.8 ms was used at all three spinning frequencies. An increase in the MAS frequency induces a clear slow-down of the CODEX decay, indicating that the molecular motions are not the dominant reason for the observed decay. (34)
Fig. S8. Analysis of chain end clustering in 1-\(^{13}\)C-palmitic acid (PA) and \(^{13}\)C-Ac\(_2\)-POM by simulation of CODEX \(^{13}\)C NMR intensity decays. (a) Normalized CODEX signal S/S\(_0\) and corresponding simulations for the COOH peak in 1-\(^{13}\)C-palmitic acid (PA). The \(^{13}\)COO:\(^{12}\)COO ratios of 100:0 (filled pentagons), 50:50 (diamonds), 25:75 (inverted triangles), 10:90 (regular triangles) and 1.1:98.9 (circles) were used in the simulations. The solid traces with corresponding color code are simulations for the COOH groups in the crystal lattice (43). (b) Simulation of spin diffusion among \(^{13}\)COO chain ends randomly distributed on the surface of the (1 0 1 4) plane in the POM crystal structure.
**Fig. S9. Schematic illustrations of chain ends at the crystallite surface in the POM crystal structure.** (a) Schematic showing that in the absence of chain tilt, all ester groups in acetyl chain ends at the crystallite surface (highlighted in red) have the same orientation and orientation-dependent chemical-shift frequency, so $^{13}$C spin exchange would result in no frequency change and therefore no CODEX decay. (b) With chain tilt relative to the crystallite surface normal, many neighboring ester groups (highlighted in red, green, and blue) have different orientations and frequencies, resulting in frequency changes and CODEX decay when $^{13}$C spin exchange occurs. (c) Typical side view of the crystallite surface as the (2 1 14) plane and (d) typical top view of the carbons at the surface. The chain-end $^{13}$C spins are all highlighted in red (i.e. the color scheme is simplified relative to part b). The chain-end percentage is calculated as the ratio of red carbons: all carbons, which is ~ 31% here.
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