Supporting Information

New insights into the multilevel structure and phase transitions of synthetic organoclays

Adam Kiersnowski\textsuperscript{ab*}, Krzysztof Kolman\textsuperscript{ab}, Ingo Lieberwirth\textsuperscript{a}, Stoyan Yordanov\textsuperscript{a}, Hans-Jürgen Butt\textsuperscript{a}, Michael Ryan Hansen\textsuperscript{a*} and Spiros H. Anastasiadis\textsuperscript{cd}

\textsuperscript{a}Max Planck Institute for Polymer Research, Ackermannweg 10, 55128, Mainz, Germany
\textsuperscript{b}Polymer Engineering and Technology Div., Wroclaw Univ. Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland
\textsuperscript{c}Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1527, 711 10 Heraklion Crete, Greece
\textsuperscript{d}Department of Chemistry, University of Crete, P.O. Box 2208, 710 03 Heraklion Crete, Greece

Corresponding Authors
Adam Kiersnowski
adam.kiersnowski@mpip-mainz.mpg.de
adam.kiersnowski@pwr.wroc.pl
Tel. +49 6431 379 545, Tel./Fax. +48 71 320 2814
Michael Ryan Hansen
mrh@mpip-mainz.mpg.de
Tel. +49 6431 379 216, Fax. +49 6131 379 100
**Figure S1.** TEM camera calibration check image recorded for an asbestos standard (expected $d_{(002)} = 0.903$ nm)

**Figure S2.** TGA plot of M1C18 complex
Figure S3. DSC thermograms of M1C18 complex. Heating/cooling ramp: 1K/min

Figure S4. DSC thermograms of M1C18 complex. Heating/cooling ramp: 5K/min
**Figure S5.** DSC thermograms of M1C18 complex. Heating/cooling ramp: 10K/min

**Figure S6.** DSC thermograms of M1C18 complex. Heating/cooling ramp: 20K/min
Figure S7. FTIR spectra of M1C18 complex recorded during first heating and cooling cycles. Insets in plots c and d show variation in peak positions upon temperature.
Figure S8. Deconvoluted solid-state $^{13}$C{${}^1$H} CP/MAS NMR spectra of M1C18 recorded at 11.75 T (500.11 MHz for $^1$H) where (a) is before and (b) after the first heating (see Figure 8). Red and blue curves indicate positions of trans and gauche fractions of the methyl and main chain methylene groups for the intercalated 1C18 chains, respectively. Signal positions, linewidths, and corresponding integrals are given in Table S1.

Table S1. Isotropic chemical shifts, linewidths, and integrals from the deconvoluted spectra in Figure S7.\(^a\)

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Before</th>
<th></th>
<th></th>
<th></th>
<th>After</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta_{iso}$ (ppm)</td>
<td>Linewidth (Hz)</td>
<td>Integral (Arb.)</td>
<td>$\delta_{iso}$ (ppm)</td>
<td>Linewidth (Hz)</td>
<td>Integral (Arb.)</td>
<td></td>
<td></td>
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<tr>
<td>CH$_3$, gauche</td>
<td>14.8</td>
<td>69</td>
<td>0.93</td>
<td>14.9</td>
<td>80</td>
<td>0.65</td>
<td></td>
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<tr>
<td>CH$_3$, trans</td>
<td>15.2</td>
<td>208</td>
<td>6.76</td>
<td>15.3</td>
<td>167</td>
<td>2.28</td>
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<tr>
<td>CH$_2$, end</td>
<td>24.6</td>
<td>300</td>
<td>9.39</td>
<td>24.5</td>
<td>283</td>
<td>5.19</td>
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<tr>
<td>CH$_2$, gauche</td>
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<td>674</td>
<td>43.4</td>
<td>30.3</td>
<td>673</td>
<td>37.5</td>
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<tr>
<td>CH$_2$, trans</td>
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<td>238</td>
<td>85.9</td>
<td>33.3</td>
<td>323</td>
<td>64.8</td>
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<td>CH$_2$, head</td>
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<td>268</td>
<td>6.42</td>
<td>41.2</td>
<td>300</td>
<td>3.80</td>
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</tr>
</tbody>
</table>

\(^a\)Assignment “head” and “end” refers to the methylene position with respect to the NH$_3^+$-head group.