Supplementary Information

Novel synthesis of polyurea nanoparticles via spontaneous nanoprecipitation.

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Figure ESI 1: Wide-angle X-ray scattered intensity vs. scattering angle, θ, obtained for L40, C40 and A40 samples. WAXS experiments were performed using a Philips X’Pert-APD (PW3011/10) camera equipped with a Cu (Kα’ 0.154 nm) anode X-Ray tube, operating at 40 mA and 45 kV. The detector used was a PW3011/10 (Miniprop. small window) sealed Xe proportional detector. The experiments were carried out at room temperature using an angular range of 10 to 50 °, and a scanning step of 0.05 °.
**Figure ESI 2:** DSC graphs obtained at 10 °C min$^{-1}$ for L-MDI, C-MDI, A-MDI and Mono-MDI reference compounds.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Experimental values</th>
<th>Theoretical values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C%</td>
<td>N%</td>
</tr>
<tr>
<td>L-MDI</td>
<td>79.6%</td>
<td>10.7%</td>
</tr>
<tr>
<td>C-MDI</td>
<td>83.8%</td>
<td>8.8%</td>
</tr>
<tr>
<td>A-MDI</td>
<td>88.4%</td>
<td>4.8%</td>
</tr>
<tr>
<td>Mono-MDI</td>
<td>77.6%</td>
<td>0.7%</td>
</tr>
<tr>
<td>L-40</td>
<td>74%</td>
<td>2.3%</td>
</tr>
<tr>
<td>C-40</td>
<td>73.2%</td>
<td>4.7%</td>
</tr>
<tr>
<td>A-40</td>
<td>75.5%</td>
<td>0.4%</td>
</tr>
</tbody>
</table>

**Table ESI 1:** Measured (by XPS) and theoretical (from known bulk compositions) elemental composition of reference compounds and PNP samples.
<table>
<thead>
<tr>
<th>Samples</th>
<th>( \text{C-C/C-H} )</th>
<th>( \text{C=\text{C}} )</th>
<th>( \text{C-N} )</th>
<th>( \text{C-O} )</th>
<th>( \text{N-(C=O)-N} )</th>
<th>( \text{C-O} )</th>
<th>( \text{N-(C=O)-N} )</th>
<th>( \text{Shake-up} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-MDI</td>
<td>17.1%</td>
<td>47.4%</td>
<td>19.9%</td>
<td>8.8%</td>
<td>6.8%</td>
<td>38.4%</td>
<td>61.6%</td>
<td></td>
</tr>
<tr>
<td><strong>Theoretical values</strong></td>
<td>4.8%</td>
<td>57.2%</td>
<td>19%</td>
<td>9.5%</td>
<td>9.5%</td>
<td>33.3%</td>
<td>66.7%</td>
<td></td>
</tr>
<tr>
<td>C-MDI</td>
<td>49.9%</td>
<td>29.5%</td>
<td>14.9%</td>
<td>-</td>
<td>5.7%</td>
<td>-</td>
<td>9.1%</td>
<td>90.9%</td>
</tr>
<tr>
<td><strong>Theoretical values</strong></td>
<td>33.3%</td>
<td>44.4%</td>
<td>14.8%</td>
<td>-</td>
<td>7.5%</td>
<td>-</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>A-MDI</td>
<td>32.1%</td>
<td>62.1%</td>
<td>3.5%</td>
<td>-</td>
<td>2.3%</td>
<td>-</td>
<td>9.1%</td>
<td>90.9%</td>
</tr>
<tr>
<td><strong>Theoretical values</strong></td>
<td>16.3%</td>
<td>69.8%</td>
<td>9.3%</td>
<td>-</td>
<td>4.6%</td>
<td>-</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>Mono-MDI</td>
<td>41.6%</td>
<td>-</td>
<td>57.2%</td>
<td>1.2%</td>
<td>98.4%</td>
<td>-</td>
<td>1.6%</td>
<td></td>
</tr>
<tr>
<td><strong>Theoretical values</strong></td>
<td>40.5%</td>
<td>8.1%</td>
<td>50%</td>
<td>1.4%</td>
<td>97.2%</td>
<td>-</td>
<td>2.8%</td>
<td></td>
</tr>
</tbody>
</table>

**Table ESI 2**: Measured (from fitting of C 1s and O 1s spectra) and theoretical (from known sample bulk compositions) molar composition of the different species contributing to the C 1s and O 1s spectra of the reference compounds (see text for more details)
Table ESI 3: Binding energies obtained from the fitting analysis of the C 1s and O 1s spectra of the PNP samples (values in italics indicate fixed peak positions used to calibrate the binding energy scale of the spectra).

<table>
<thead>
<tr>
<th>Samples</th>
<th>C-C/C-H</th>
<th>C=C</th>
<th>C=N_C-O</th>
<th>N-(C=O)-N</th>
<th>C-O</th>
<th>N-(C=O)-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-MDI</td>
<td>285.0</td>
<td>284.5</td>
<td>286.5</td>
<td>288.8</td>
<td>532.6</td>
<td>531.5</td>
</tr>
<tr>
<td>C-MDI</td>
<td>285.0</td>
<td>284.4</td>
<td>286.7</td>
<td>288.8</td>
<td>532.7</td>
<td>531.6</td>
</tr>
<tr>
<td>A-MDI</td>
<td>285.0</td>
<td>284.4</td>
<td>286.6</td>
<td>288.8</td>
<td>532.7</td>
<td>531.4</td>
</tr>
</tbody>
</table>

Table ESI 4: $T_g$s and associated $\Delta C_p$s obtained for the reference compounds. (See figure ESI 2 for corresponding DSC curves.)

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$(°C)</th>
<th>$\Delta C_p$ J(g°C)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-MDI</td>
<td>102.6±0.2</td>
<td>0.14±0.03</td>
</tr>
<tr>
<td>C-MDI</td>
<td>194.6±0.6</td>
<td>0.18±0.01</td>
</tr>
<tr>
<td>A-MDI</td>
<td>204.7±0.5</td>
<td>0.27±0.01</td>
</tr>
<tr>
<td>Mono-MDI</td>
<td>-67.0±0.2</td>
<td>0.703±0.002</td>
</tr>
</tbody>
</table>