Supporting Information

For

Expanding the scope of the crystallization-driven self-assembly of polylactide-containing polymers

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Self-assembly procedure for the fast water addition:
50 mg of polymer were dissolved in THF in a 20 mL scintillation vial and the solution was stirred. Nanopure water was dropwise to the vial. The vial was closed and a needle was put through the cap to allow the slow evaporation of THF. The vial was then heated at 65 °C with stirring.

Self-assembly procedure for the slow water addition:
50 mg of polymer were dissolved in THF (0.5 mL) in a 20 mL scintillation vial and the solution was stirred. Nanopure water (2 mL) was added to the vial via a peristaltic pump so that the addition takes place over around 90 min. The vial was closed and a needle was put through the cap to allow the slow evaporation of THF. The vial was then heated at 65 °C with stirring.

Procedure for collect and analysis of the samples:
Vial was removed from the heating system and opened. A sample was collected (up to 200 μL), allowed to cool down and then freeze-dried. The vial was closed again and the needle put through the cap. The powder resulting from the freeze-drying process was dissolved in nanopure water to a concentration of 0.5 mg × mL⁻¹ and stirred overnight to obtain a homogeneous solution. DLS and TEM were performed on this dilute solution. Our group has previously demonstrated that this procedure allows for a view of the original sample in the vial.[1]
Figure S1. $^1$H NMR spectrum of PŁA$_{36}$ (1) (400 MHz, CDCl$_3$).

Figure S2. $^1$H NMR spectrum of PŁA$_{38}$ (2) (300 MHz, CDCl$_3$).
Figure S3. $^1$H NMR spectrum of PEO$_{454}$-b-PLA$_{28}$ (3) (400 MHz, CDCl$_3$).

Figure S4. $^1$H NMR spectrum of P4AM$_{213}$-b-PLA$_{38}$ (4) (250 MHz, CDCl$_3$).
Figure S5. $^1$H NMR spectrum of P4AM$_{166}$-$b$-P$_{36}$LA (5) (400 MHz, CDCl$_3$).

Figure S6. $^1$H NMR spectrum of PDMA$_{248}$-$b$-P$_{36}$LA (6) (400 MHz, CDCl$_3$).
**Figure S7.** Dynamic light scattering data for the self-assembly of P4AM$_{213}$-b-PLL$_{38}$ (4) at different THF contents (10-30%) and heating times (27 hours: left, 51 hours: right).

**Figure S8.** Histograms of the spheres (top) and cylinders (bottom) length produced from the self-assembly of P4AM$_{213}$-b-PLL$_{38}$ (4) at 20 mg × mL$^{-1}$ in 10% THF with fast water addition after 27 hours (bottom left, $L_n = 159 \pm 58$ nm) and 51 hours (bottom right, $L_n = 173 \pm 56$ nm). A mixed phase was obtained.
Figure S9. Histograms of the spheres (top) and cylinders (bottom) length produced from the self-assembly of P4AM$_{213}$-b-P$_{7}$LA$_{38}$ (4) at 20 mg × mL$^{-1}$ in 20% THF with fast water addition after 27 hours (bottom left, $L_n = 224 \pm 89$ nm) and 51 hours (bottom right, $L_n = 213 \pm 114$ nm). A mixed phase was obtained.
**Figure S10.** Histograms of the spheres (top) and cylinders (bottom) length produced from the self-assembly of P4AM$_{213}$-b-P$_{L}$LA$_{38}$ (4) at 20 mg × mL$^{-1}$ in 30% THF after 27 hours (bottom left, $L_n = 157 \pm 62$ nm) and 51 hours (bottom right, $L_n = 212 \pm 90$ nm). A mixed phase was obtained.

**Figure S11.** Dynamic light scattering data for the self-assembly of P4AM$_{166}$-b-P$_{L}$LA$_{36}$ (5) at different times (1-2 days) and polymer concentrations (10 mg × mL$^{-1}$: left, 20 mg × mL$^{-1}$: right).
Figure S12. Histograms of the spheres (top) and cylinders (bottom) length produced from the self-assembly of P4AM$_{166}$-b-P$_{36}$LA (5) at 10 mg × mL$^{-1}$ in 20% THF with fast water addition after 1 day (bottom left, $L_n = 243 \pm 112$ nm) and 2 days (bottom right, $L_n = 246 \pm 92$ nm). A mixed phase was obtained.
Figure S13. Histograms of the spheres (top) and cylinders (bottom) length produced from the self-assembly of P4AM_{166}-b-PzLA_{36} (5) at 20 mgmL\(^{-1}\) in 20% THF with fast water addition after 1 day (bottom left, \(L_n = 291 \pm 155\) nm) and 2 days (bottom right, \(L_n = 264 \pm 124\) nm). A mixed phase was obtained.

Figure S14. Dynamic light scattering data for the self-assembly of PDMA_{248}-b-PzLA_{36} (6) at different times (1-2 days) and polymer concentrations (10 mg \times mL^{-1}: left, 20 mg \times mL^{-1}: right).
Figure S15. Histograms of the spheres (top) and cylinders (bottom) length produced from the self-assembly of PDMA\textsubscript{248-}b-P\textsubscript{L}LA\textsubscript{36} (6) at 10 mg × mL\textsuperscript{-1} in 20\% THF with fast water addition after 1 day (bottom left, $L_n = 236 \pm 135$ nm) and 2 days (bottom right, $L_n = 216 \pm 90$ nm). A mixed phase was obtained.
Figure S16. Histograms of the spheres (top) and cylinders (bottom) length produced from the self-assembly of PDMA<sub>248</sub>-b-P<sub>L</sub>LA<sub>36</sub> (6) at 20 mg × mL<sup>-1</sup> in 20% THF with fast water addition after 1 day (bottom left, $L_n = 179 \pm 88$ nm) and 2 days (bottom right, $L_n = 257 \pm 103$ nm). A mixed phase was obtained.

Figure S17. TEM images of the self-assembly of P4AM<sub>166</sub>-b-P<sub>L</sub>LA<sub>36</sub> (5) with a slow water addition at 20 mg × mL<sup>-1</sup> and 20% THF at different times (1-3 days).
Figure S18. Dynamic light scattering data for the self-assembly of PEO\textsubscript{454}-b-P\textsubscript{L}LA\textsubscript{28} (3) with a slow water addition at the initial starting point (left) and after 1 hour of heating (right).

![Graph showing dynamic light scattering data]

Figure S19. Histogram of the cylinders length observed by TEM for the self-assembly of PEO\textsubscript{454}-b-P\textsubscript{L}LA\textsubscript{28} (3) at 20 mg × mL\textsuperscript{-1} in 20% THF with a slow water addition at different times (1-3 days). Note that the size of the few spheres did not significantly change during assembly.

<table>
<thead>
<tr>
<th>Time</th>
<th>Count</th>
</tr>
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<tbody>
<tr>
<td>1 day</td>
<td>146 ± 62</td>
</tr>
<tr>
<td>2 days</td>
<td>160 ± 51</td>
</tr>
<tr>
<td>3 days</td>
<td>105 ± 55</td>
</tr>
</tbody>
</table>

![Histogram showing cylinder lengths]

Figure S20. Dynamic light scattering data for the self-assembly of PDMA\textsubscript{248}-b-P\textsubscript{L}LA\textsubscript{36} (6) with the slow addition of water at different times.

![Graph showing dynamic light scattering data]
Figure S21. Histogram of the spheres (top) and cylinders (bottom) length observed by TEM for the self-assembly of PDMA$_{248}$-$b$-P$_{76}$LA$_{36}$ (6) at 20 mg × mL$^{-1}$ in 20% THF with slow water addition at different times (1-3 days).

<table>
<thead>
<tr>
<th></th>
<th>$L_a$ ± std dev (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 day</td>
<td>71 ± 26</td>
</tr>
<tr>
<td>2 days</td>
<td>108 ± 42</td>
</tr>
<tr>
<td>3 days</td>
<td>127 ± 48</td>
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Figure S22. SAXS profiles and fittings of the self-assembly process of diblocks PEO\textsubscript{454-}b-P\textsubscript{LA}\textsubscript{28} (3), P4AM\textsubscript{166-}b-P\textsubscript{LA}\textsubscript{36} (5) and PDMA\textsubscript{248-}b-P\textsubscript{LA}\textsubscript{36} (6) at 20 mg × mL\textsuperscript{-1} in 20% THF with slow addition of water at 3 days.

Figure S23. Hydrophilic character of the polymers PDMA, P4AM and PEO determined by prediction of logP according to the degree of polymerization.

References