Crystallization Driven Sphere-to-rod Transition of Poly(lactide)-*b*-PAA Diblock Copolymers: Mechanism and Kinetics

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The supporting information provides additional information on the synthesis and self assembly of the polymers and includes images to back up and further develop the work discussed in the main article.

| | M_w/M_n | M _n ^{SEC} | $M_n^{\ NMR}$ | DP | DP | DP |
|------------------|-----------|-------------------------------|---------------|-------|--------|-------|
| | | (kDa) | (kDa) | (PLA) | (THPA) | (PAA) |
| P(L-LA) | 1.09 | 10.3 | 5.8 | 38 | - | - |
| P(DL-LA) | 1.06 | 8.4 | 4.6 | 33 | - | - |
| P(L-LA)-b-PTHPA | 1.11 | 45.3 | 58.1 | 38 | 333 | - |
| P(DL-LA)-b-PTHPA | 1.31 | 34.4 | 43.3 | 33 | 240 | - |
| P(L-LA)-b-PAA | - | - | | 38 | - | 333 |
| P(DL-LA)-b-PAA | - | - | | 33 | - | 240 |

Table S1 Characterization data for polymers prepared by a combination of ROP and RAFT.



Figure S1 SEC traces of the $poly(L-LA)_{38}$, macro–CTA before chain extension (blue trace) and $poly(L-LA_{38})$ -*b*-PTHPA₃₃₃, diblock copolymer after chain extension (red trace) (THF eluent and RI detection).



Figure S2 ¹H NMR spectra of the poly(L-LA₃₈)-b-PTHPA₃₃₃, before the THPA hydrolysis (top spectrum); 1 hour after the reaction commenced (middle spectrum); 2 hours after the reaction commenced (bottom spectrum). All spectra in d₆-DMSO, (400 MHz, 293 K).



Figure S3 IR spectrum of the poly(L-LA₃₈)-b-PTHPA₃₃₃, showing the carbonyl group stretch region.



Figure S4 IR spectrum of the poly(L-LA₃₈)-b-PAA₃₃₃, showing the carbonyl group stretch region.



Figure S5 On the left: representative TEM unstained image on graphene oxide of the spherical micelles, $poly(L-LA_{38})$ -*b*-PAA_{333,} 2 hours after starting the THPA hydrolysis reaction. On the right: DLS trace (number, intensity and volume distributions) of the micelle solution, 2 hours after starting the THPA hydrolysis reaction.



Figure S6 On the left: representative TEM image of the micelle solution produced from the self assembly at 20 g/L assembled in 5% THF with PTA staining (Scale bar = 200 nm). On the right: histogram of the cylinders length produced from the same solution.



Figure S7 On the left: representative TEM image of the micelle solution produced from the self assembly at 20 g/L assembled in 10% THF with PTA staining (Scale bar = 200 nm). On the right: histogram of the cylinders length produced from the same solution.



Figure S8 On the left: representative TEM image of the micelle solution produced from the self assembly at 20 g/L assembled in 20% THF with PTA staining (Scale bar = 200 nm). On the right histogram of the cylinders length produced from the same solution.



Figure S9 On the left representative TEM image of the micelle solution produced from the self assembly at 20 g/L assembled in 40% THF with PTA staining (Scale bar = 200 nm). On the right: histogram of the cylinders length produced from the same solution.



Figure S10 On the left: representative TEM image on graphene oxide of the micelle solution produced from the self assembly of $poly(L-LA_{38})$ -*b*-PAA₃₃₃ at 0.5 g/L in 20%THF at 65 °C. On the right: WAXD spectrum of the sample.



Figure S11 On the left: representative TEM image of the micelle solution produced from the self assembly of poly(*DL*-LA)-PAA at 20 g/L 20 hours after starting the THPA hydrolysis reaction (with PTA staining). On the right: representative TEM image of the same sample on a GO support without staining (Scale bars = 100 nm).



Figure S12 DLS results (number, intensity and volume distributions) of the micelle solution produced from the self assembly of $poly(DL-LA)_{33}$ -PAA₂₄₀ at 20 g/L with 20% THF, 20 hours after starting the THPA hydrolysis reaction.



Figure S13 WAXD results of the micelle solution produced from the self assembly of poly(*DL*-LA)-PAA at 20 g/L with 20% THF, 20 hours after starting the THPA hydrolysis reaction.