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]

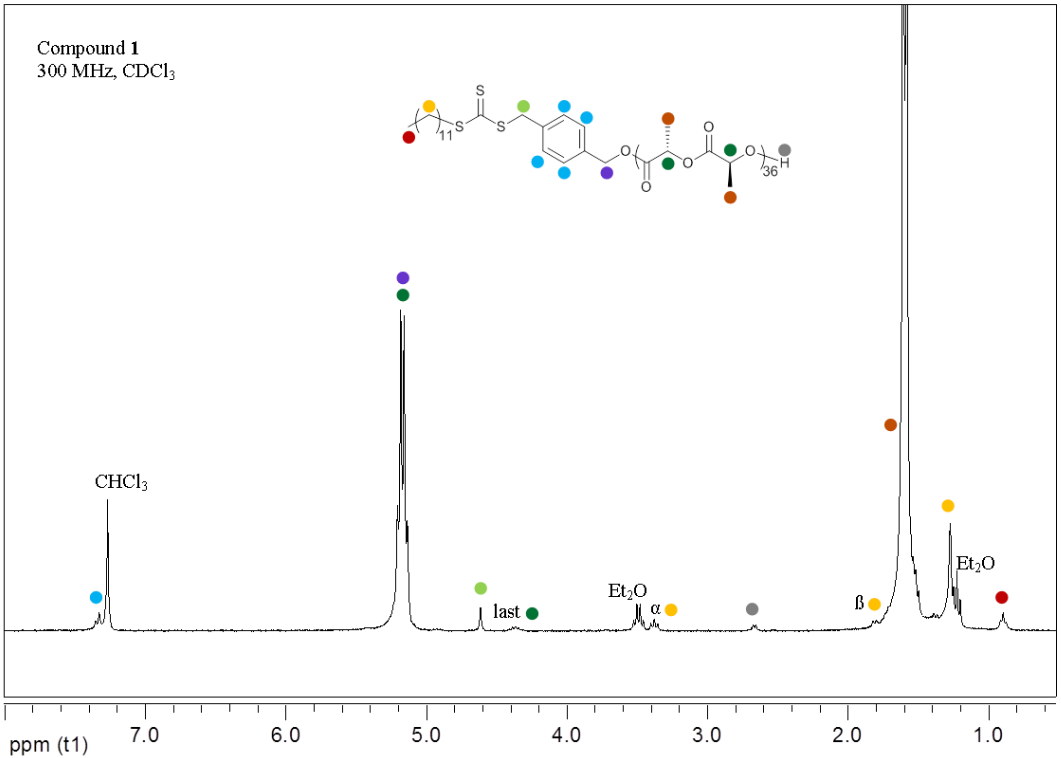


Figure S1. ^{1}H NMR spectrum of P*L*LA$_{36}$ (**1**) (400 MHz, CDCl$_3$).

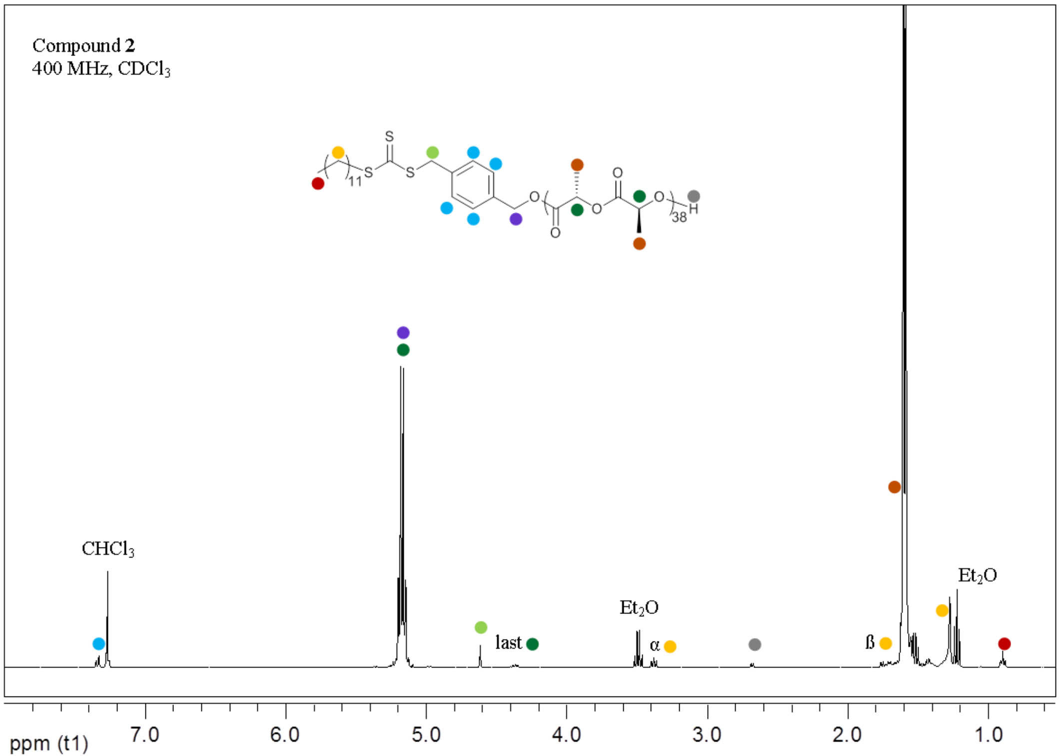


Figure S2. ^{1}H NMR spectrum of P*L*LA$_{38}$ (**2**) (300 MHz, CDCl$_3$).

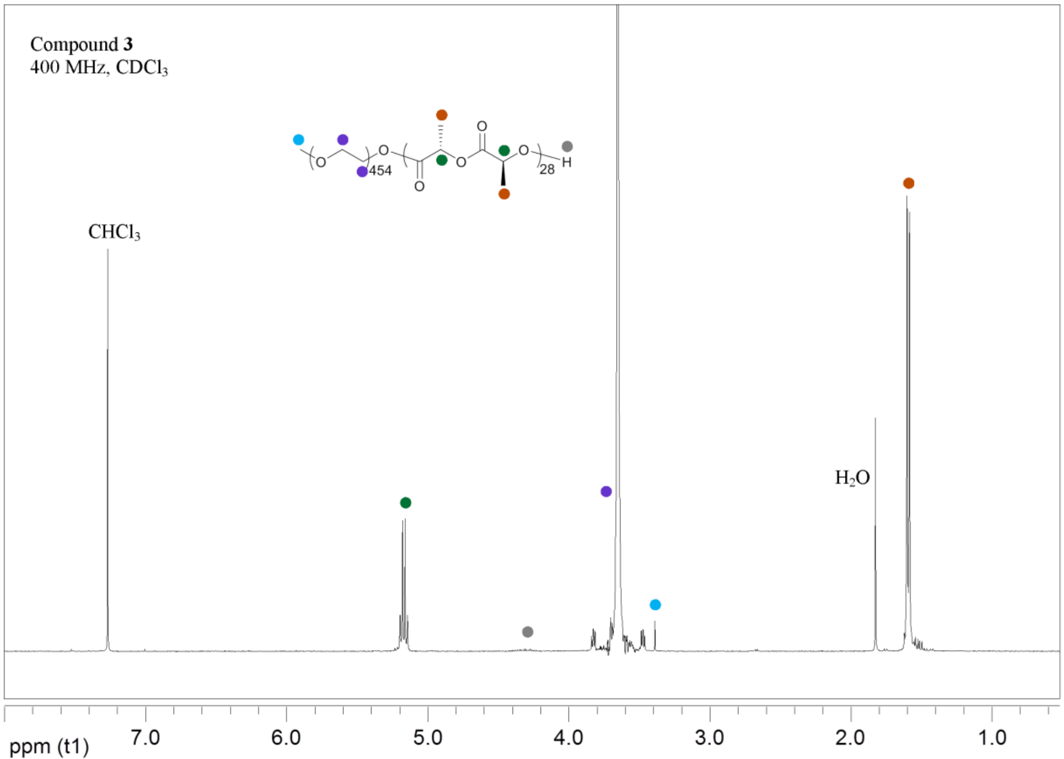


Figure S3. ^{1}H NMR spectrum of PEO$_{454}$-*b*-P*L*LA$_{28}$ (**3**) (400 MHz, CDCl$_3$).

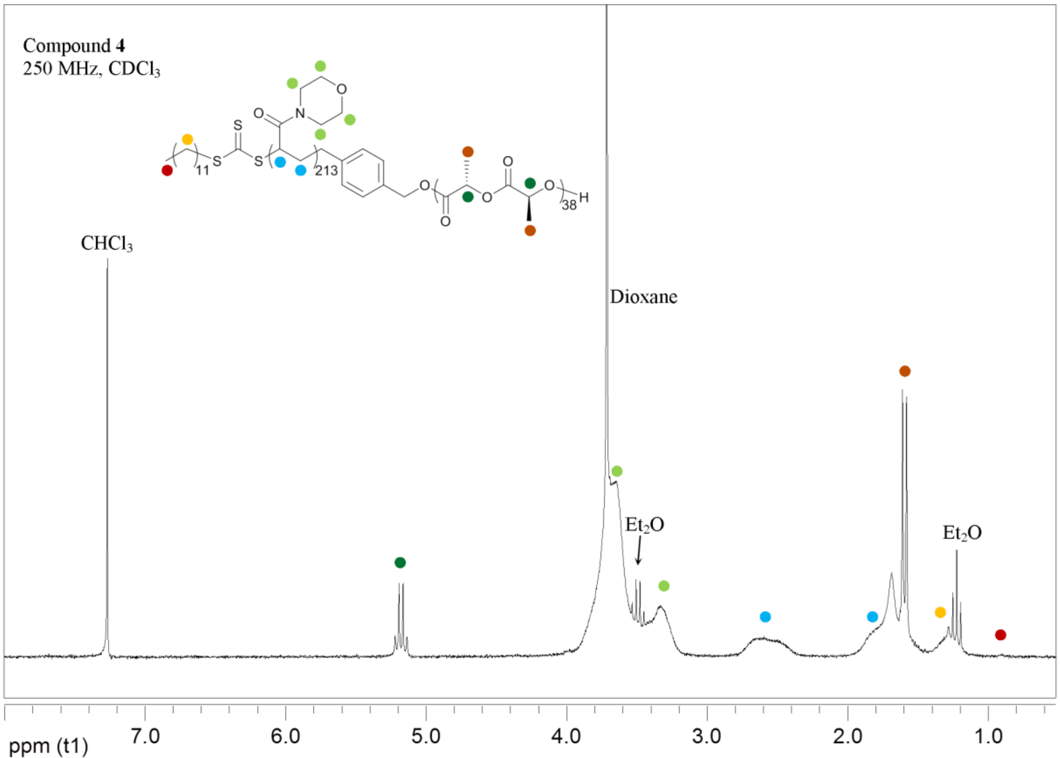


Figure S4. ^{1}H NMR spectrum of P4AM$_{213}$-*b*-P*L*LA$_{38}$ (**4**) (250 MHz, CDCl$_3$).

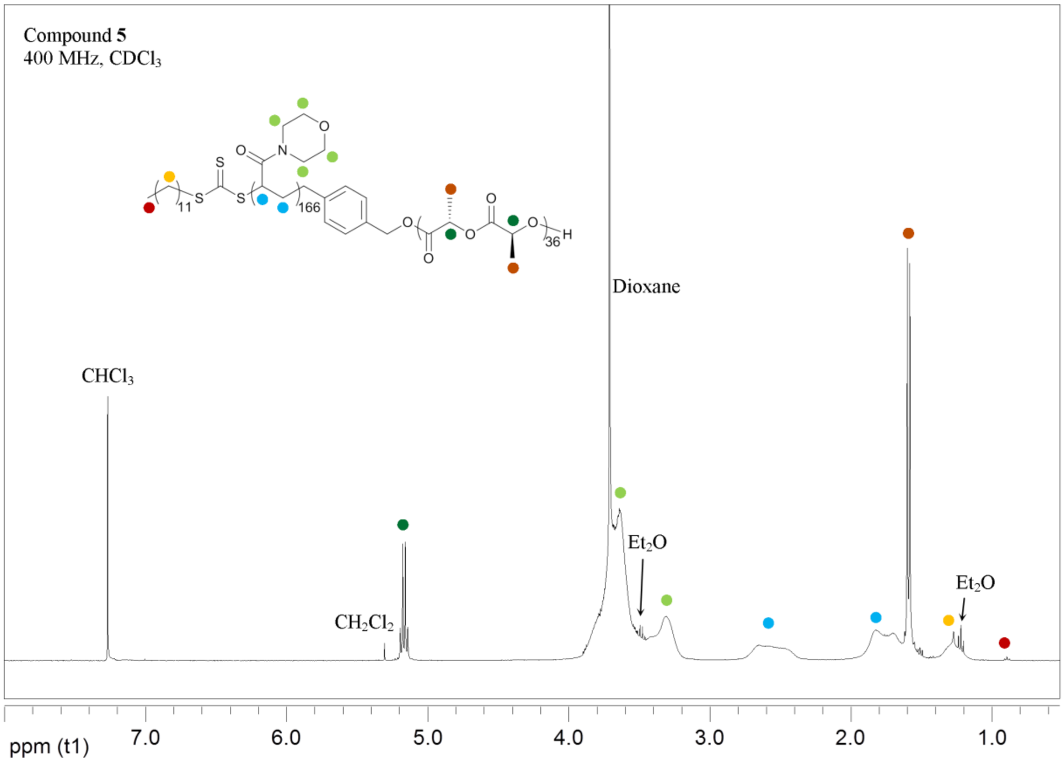


Figure S5. ^{1}H NMR spectrum of P4AM$_{166}$-*b*-P*L*LA$_{36}$ (**5**) (400 MHz, CDCl$_3$).

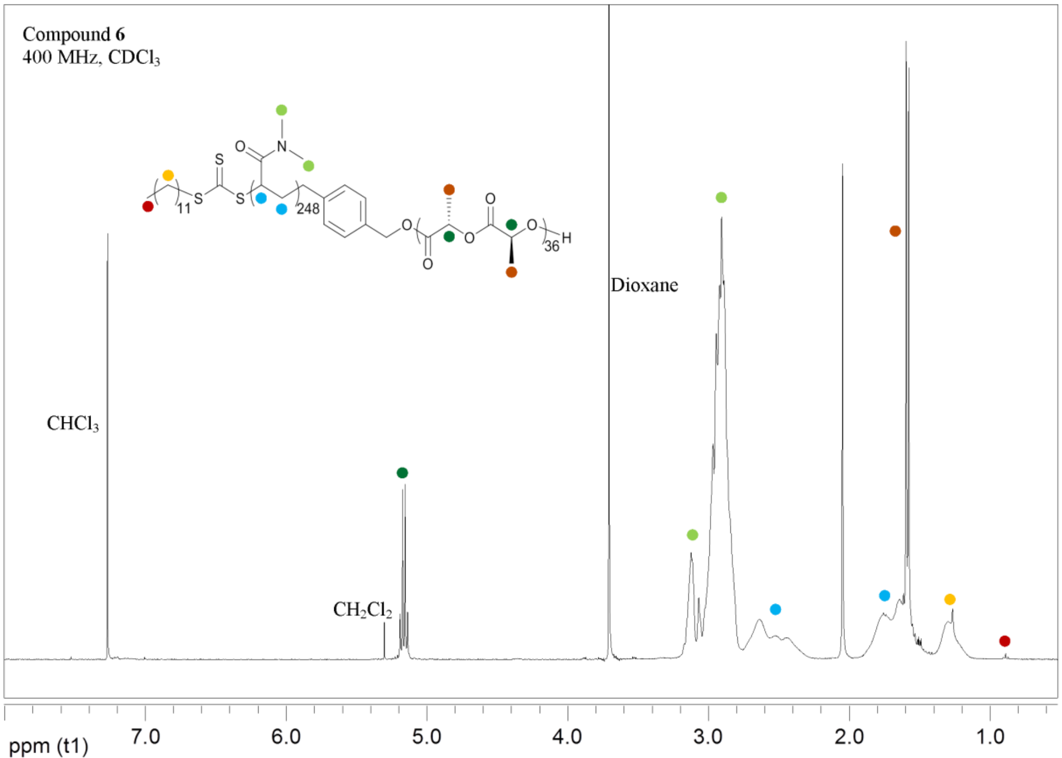


Figure S6. ^{1}H NMR spectrum of PDMA$_{248}$-*b*-P*L*LA$_{36}$ (**6**) (400 MHz, CDCl$_3$).

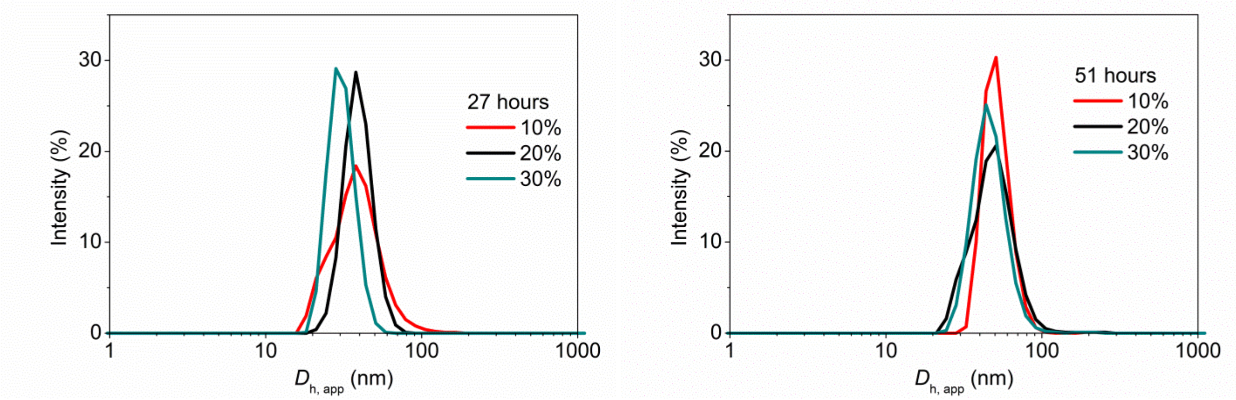


Figure S7. Dynamic light scattering data for the self-assembly of P4AM$_{213}$-*b*-P*L*LA$_{38}$ (**4**) at different THF contents (10-30%) and heating times (27 hours: left, 51 hours: right).

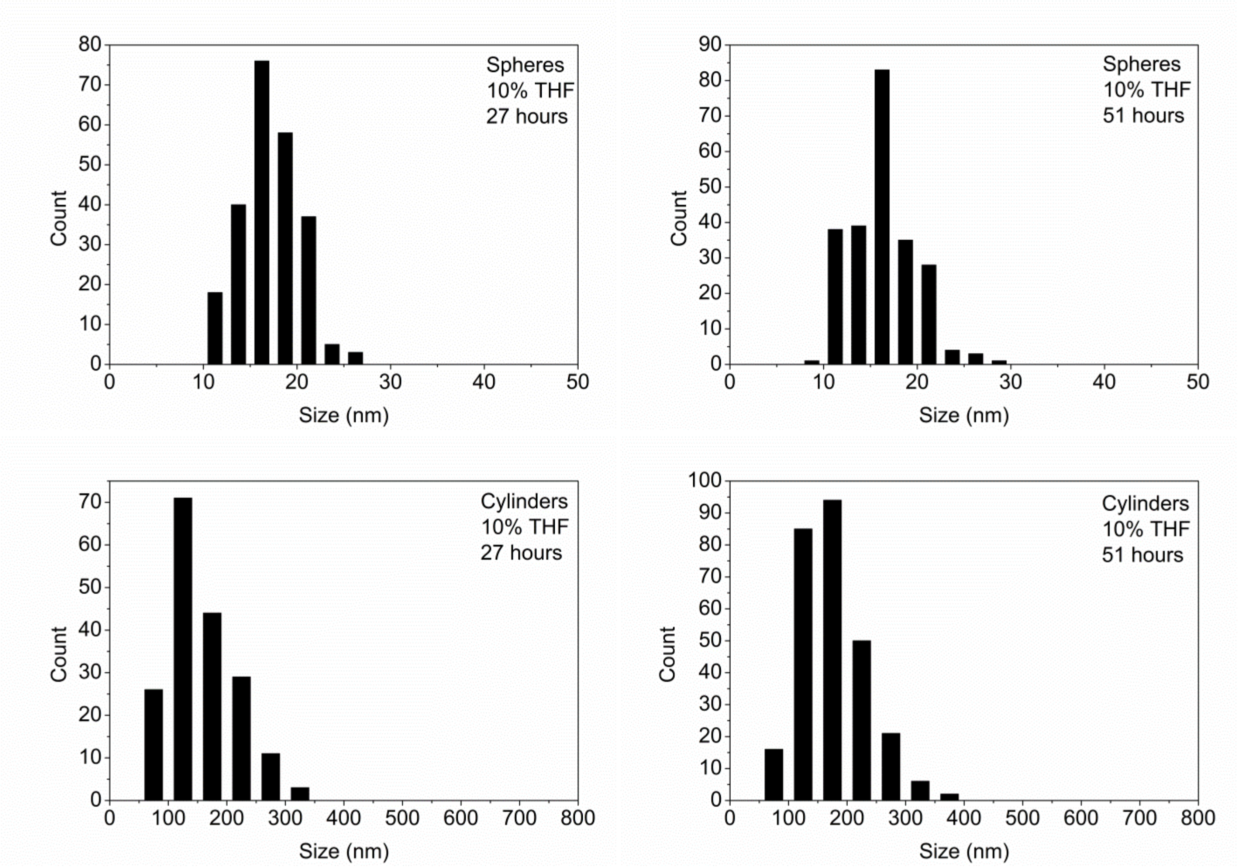


Figure S8. Histograms of the spheres (top) and cylinders (bottom) length produced from the self-assembly of P4AM$_{213}$-*b*-P*L*LA$_{38}$ (**4**) at 20 mg × mL^{-1} in 10% THF with fast water addition after 27 hours (bottom left, L_n = 159 ± 58 nm) and 51 hours (bottom right, L_n = 173 ± 56 nm). A mixed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

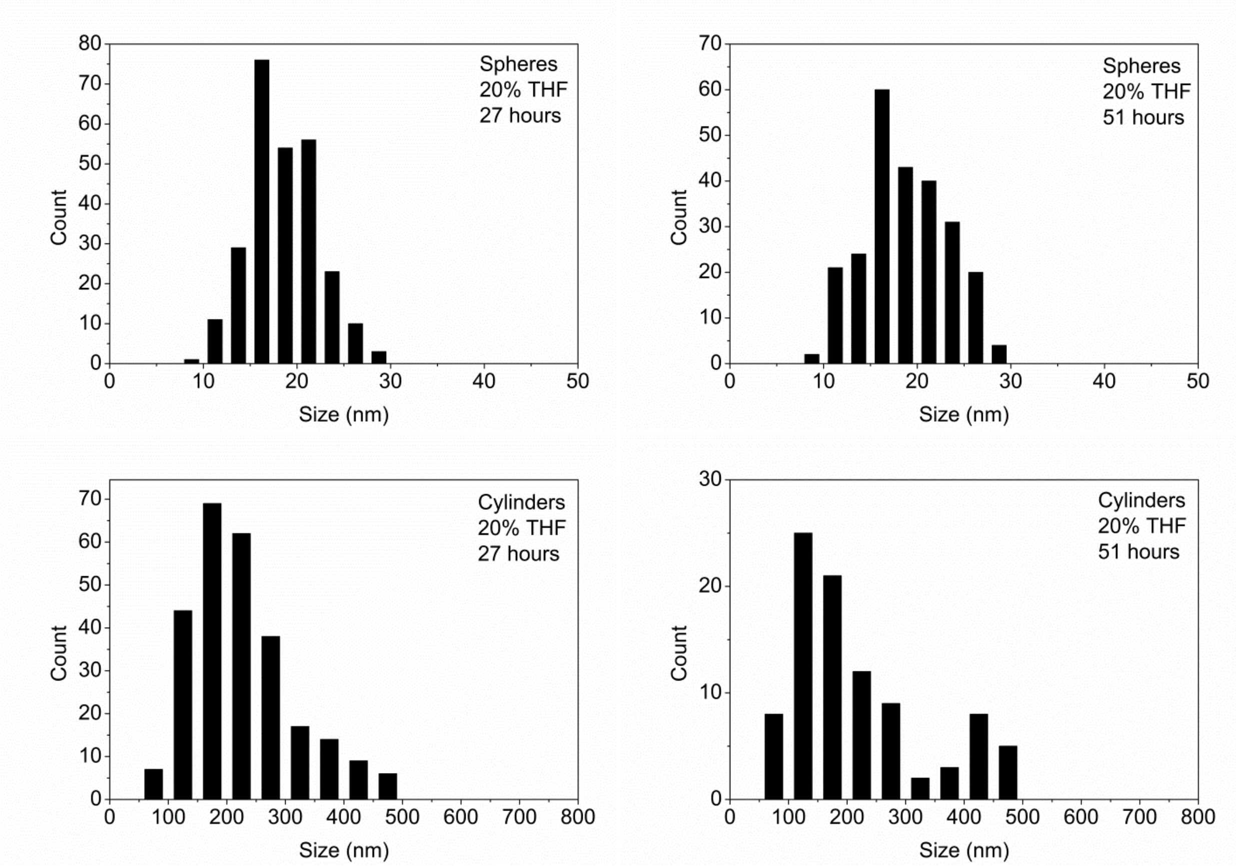


Figure S9. Histograms of the spheres (top) and cylinders (bottom) length produced from the self-assembly of P4AM$_{213}$-*b*-P*L*LA$_{38}$ (**4**) at 20 mg × mL^{-1} in 20% THF with fast water addition after 27 hours (bottom left, L_n = 224 ± 89 nm) and 51 hours (bottom right, L_n = 213 ± 114 nm). A mixed phase was obtained.

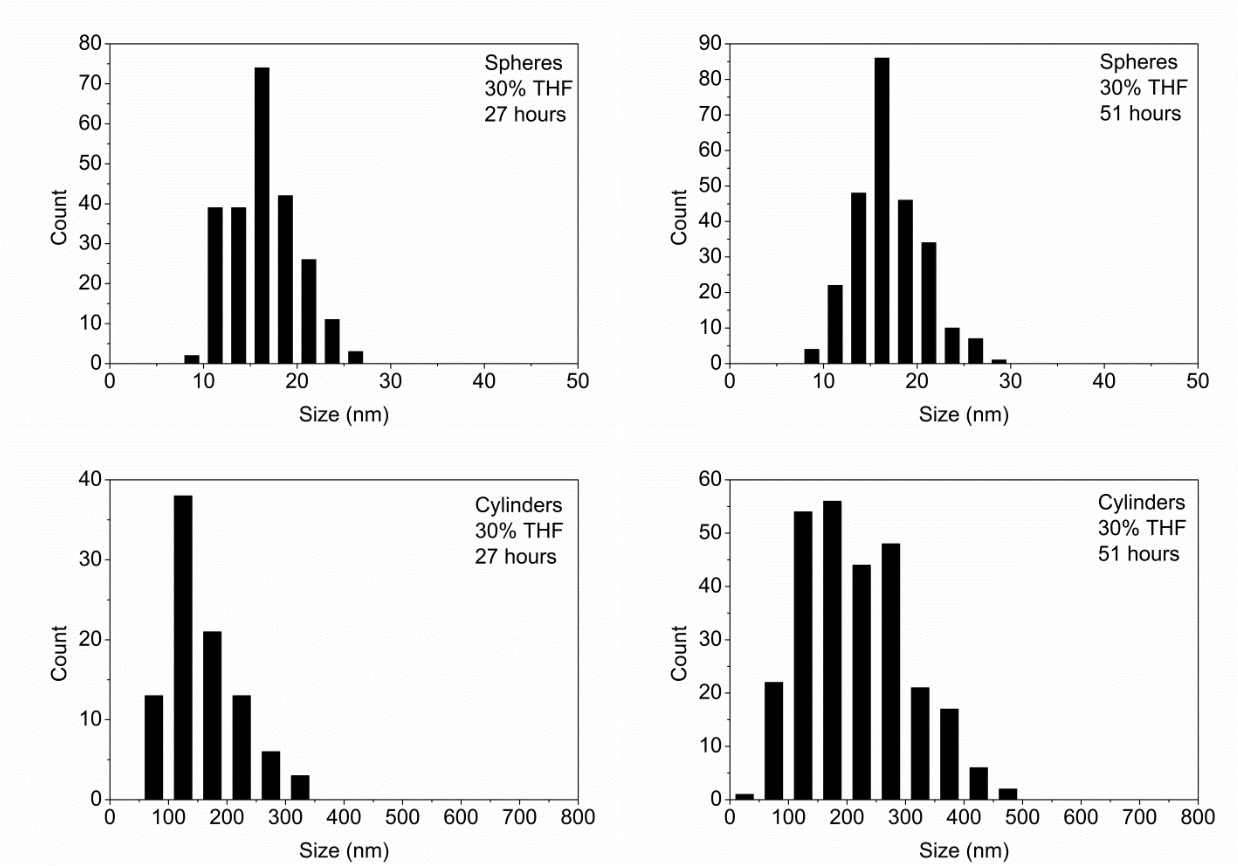


Figure S10. Histograms of the spheres (top) and cylinders (bottom) length produced from the self-assembly of P4AM$_{213}$-*b*-P*L*LA$_{38}$ (**4**) at 20 mg × mL^{-1} in 30% THF after 27 hours (bottom left, L_n = 157 ± 62 nm) and 51 hours (bottom right, L_n = 212 ± 90 nm). A mixed phase was obtained.

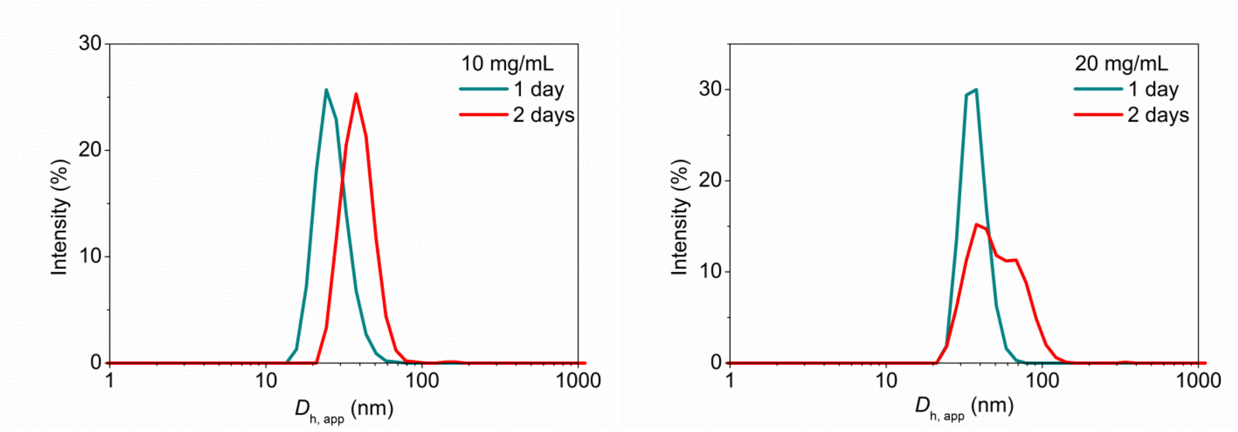


Figure S11. Dynamic light scattering data for the self-assembly of P4AM$_{166}$-*b*-P*L*LA$_{36}$ (**5**) at different times (1-2 days) and polymer concentrations (10 mg × mL^{-1}: left, 20 mg × mL^{-1}: right).

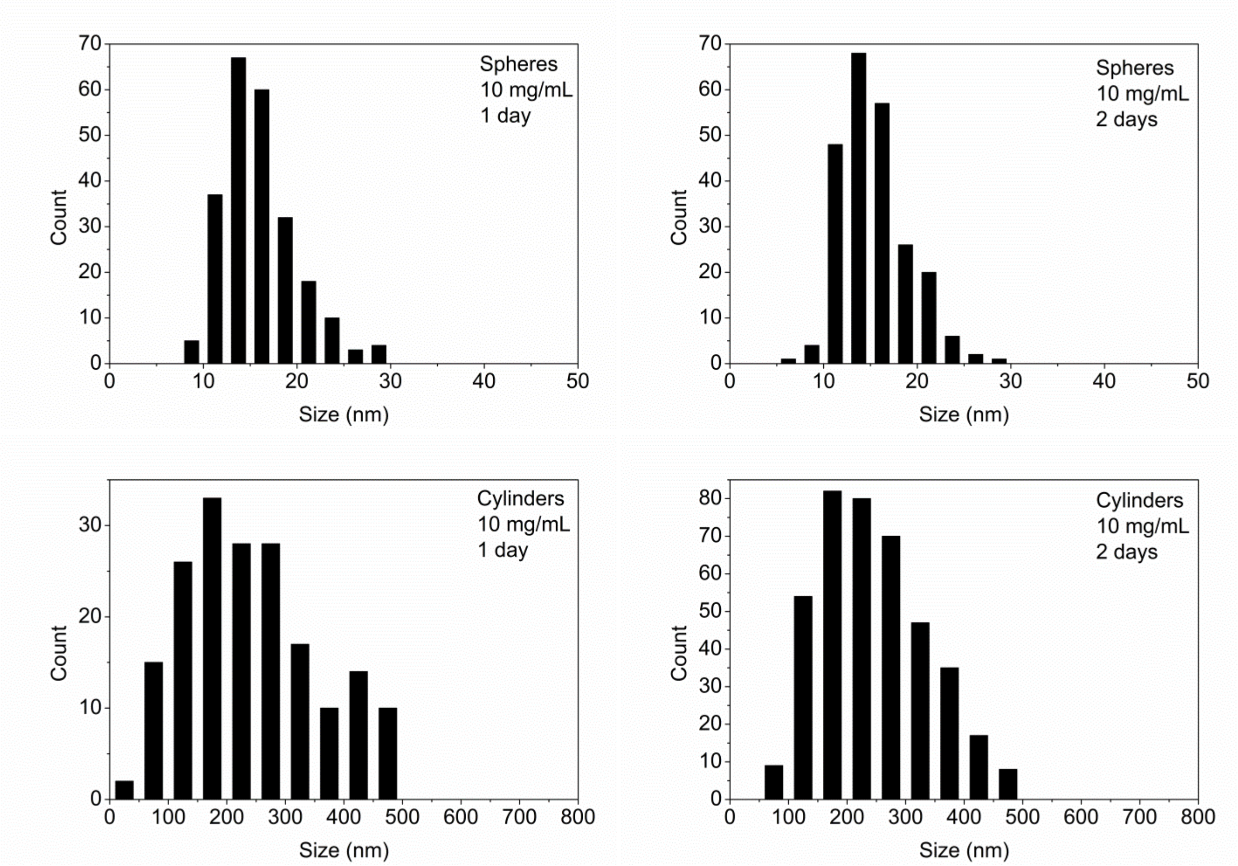


Figure S12. Histograms of the spheres (top) and cylinders (bottom) length produced from the self-assembly of P4AM$_{166}$-*b*-P*L*LA$_{36}$ (**5**) at 10 mg × mL^{-1} in 20% THF with fast water addition after 1 day (bottom left, L_n = 243 ± 112 nm) and 2 days (bottom right, L_n = 246 ± 92 nm). A mixed phase was obtained.

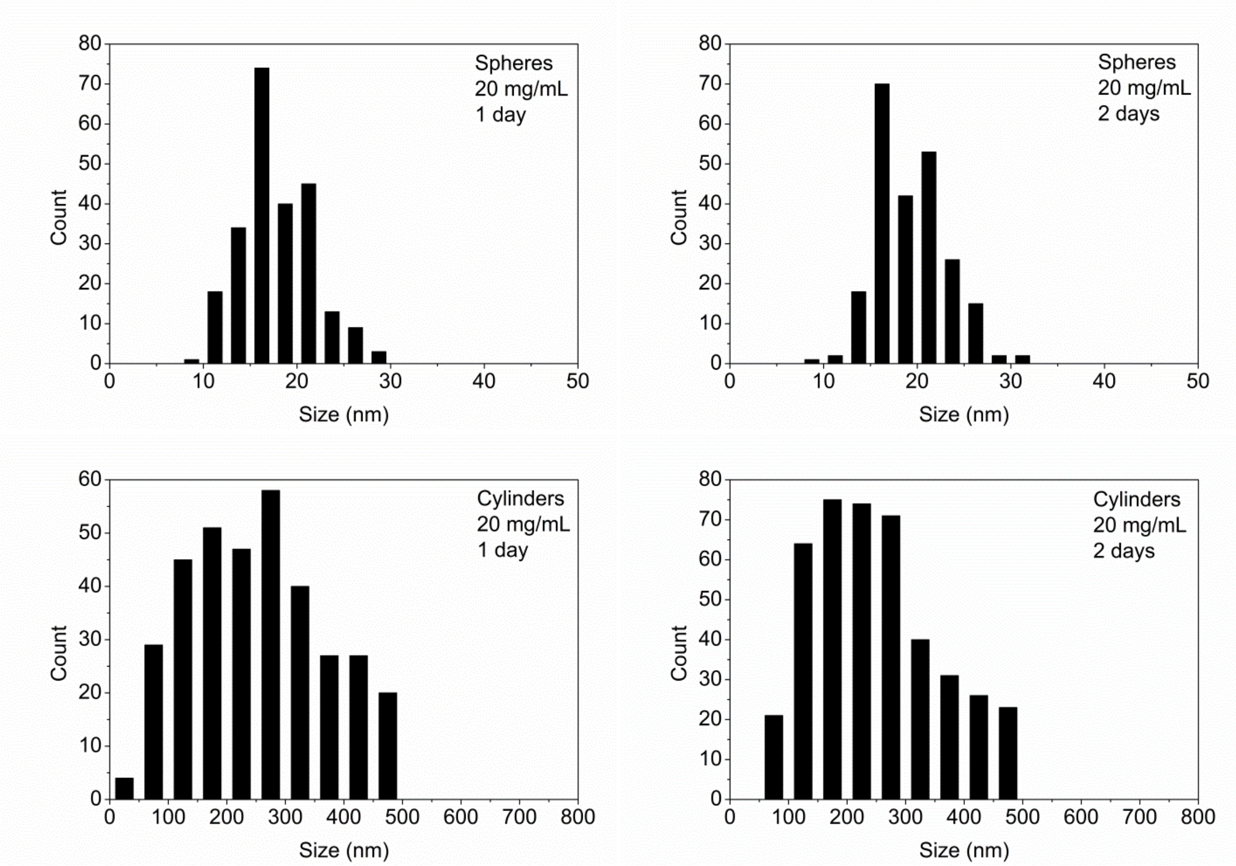


Figure S13. Histograms of the spheres (top) and cylinders (bottom) length produced from the self-assembly of P4AM$_{166}$-*b*-P*L*LA$_{36}$ (**5**) at 20 mgmL^{-1} in 20% THF with fast water addition after 1 day (bottom left, L_n = 291 ± 155 nm) and 2 days (bottom right, L_n = 264 ± 124 nm). A mixed phase was obtained.

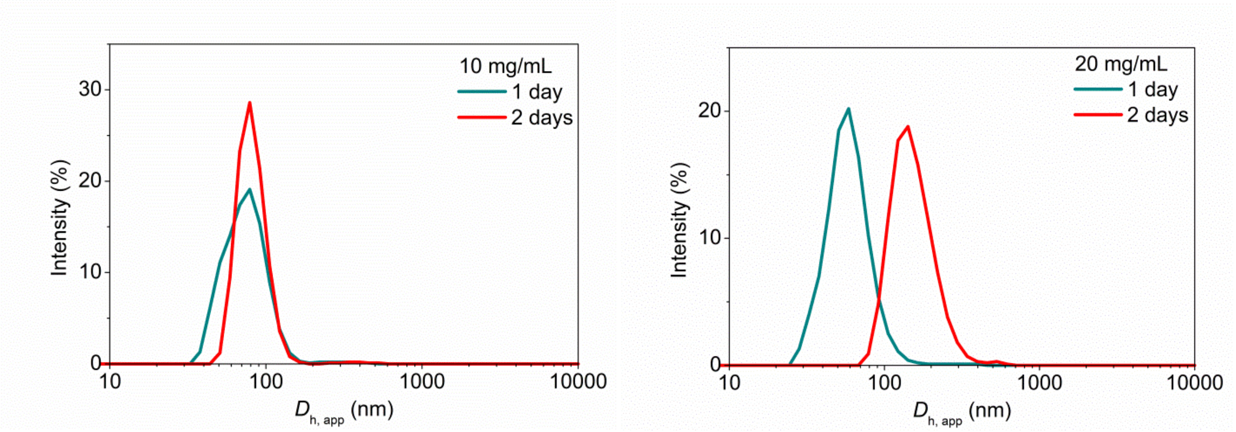


Figure S14. Dynamic light scattering data for the self-assembly of PDMA$_{248}$-*b*-P*L*LA$_{36}$ (**6**) at different times (1-2 days) and polymer concentrations (10 mg × mL^{-1}: left, 20 mg × mL^{-1}: right).

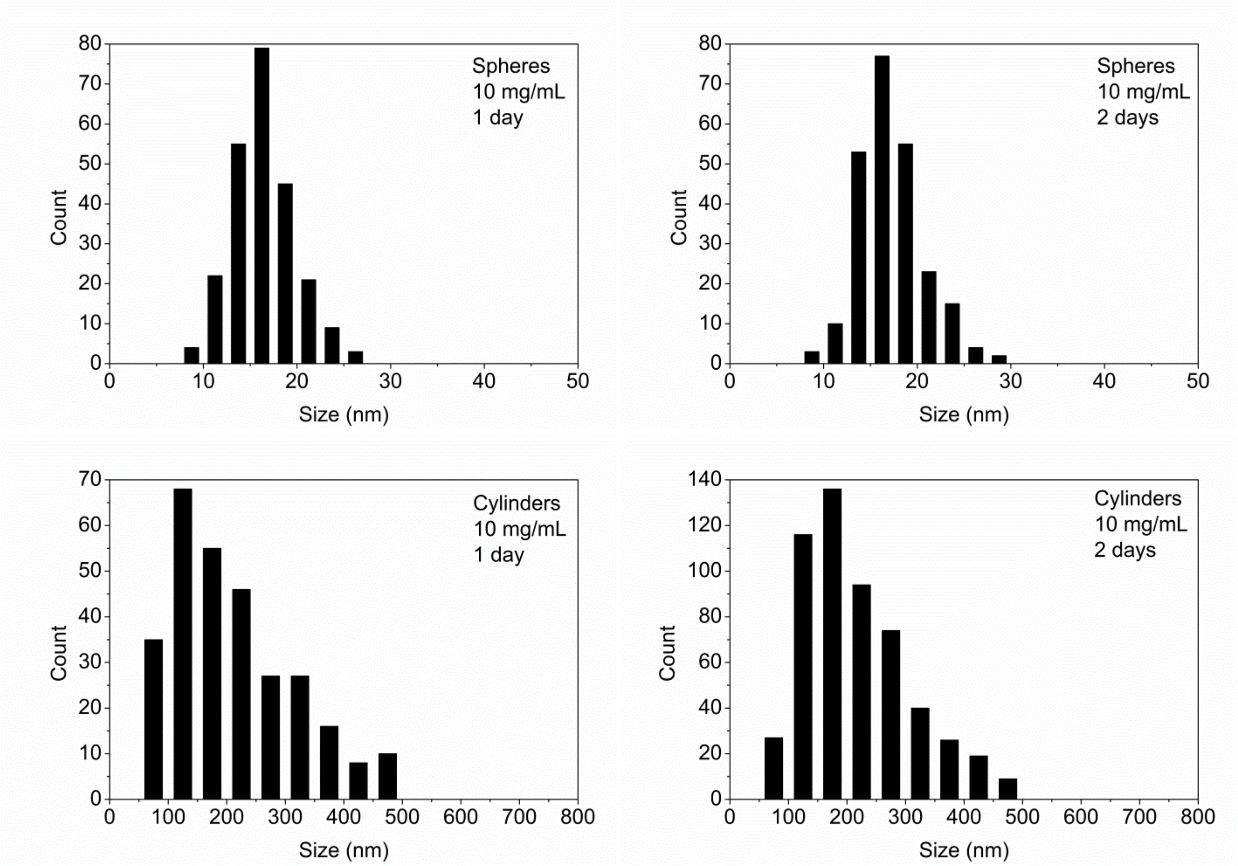


Figure S15. Histograms of the spheres (top) and cylinders (bottom) length produced from the self-assembly of PDMA$_{248}$-*b*-P*L*LA$_{36}$ (**6**) at 10 mg × mL^{-1} in 20% THF with fast water addition after 1 day (bottom left, L_n = 236 ± 135 nm) and 2 days (bottom right, L_n = 216 ± 90 nm). A mixed phase was obtained.

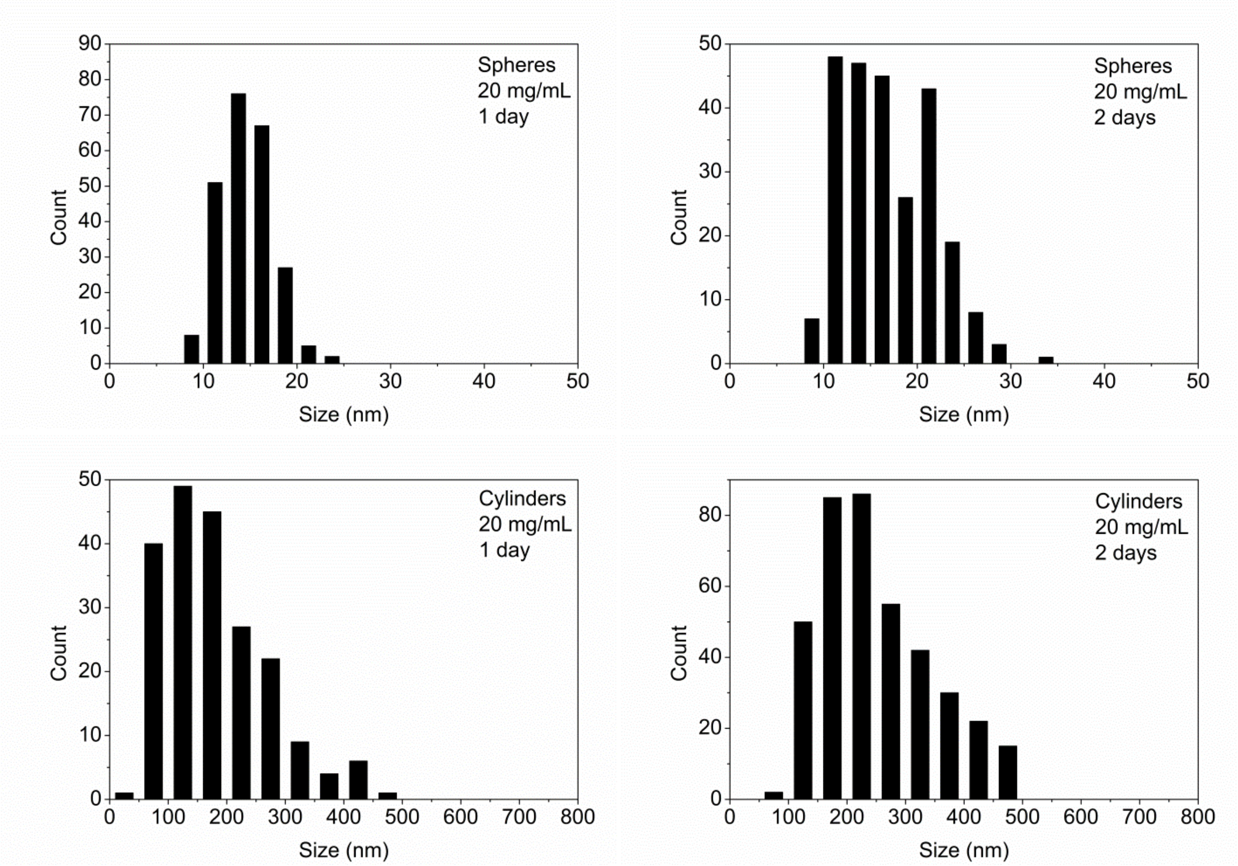


Figure S16. Histograms of the spheres (top) and cylinders (bottom) length produced from the self-assembly of PDMA$_{248}$-*b*-P*L*LA$_{36}$ (**6**) at 20 mg × mL^{-1} in 20% THF with fast water addition after 1 day (bottom left, L_n = 179 ± 88 nm) and 2 days (bottom right, L_n = 257 ± 103 nm). A mixed phase was obtained.

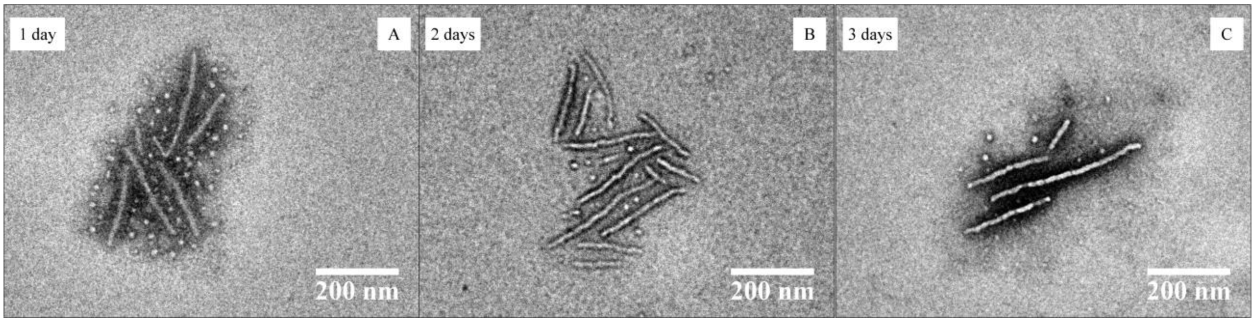


Figure S17. TEM images of the self-assembly of P4AM$_{166}$-*b*-P*L*LA$_{36}$ (**5**) with a slow water addition at 20 mg × mL^{-1} and 20% THF at different times (1-3 days).

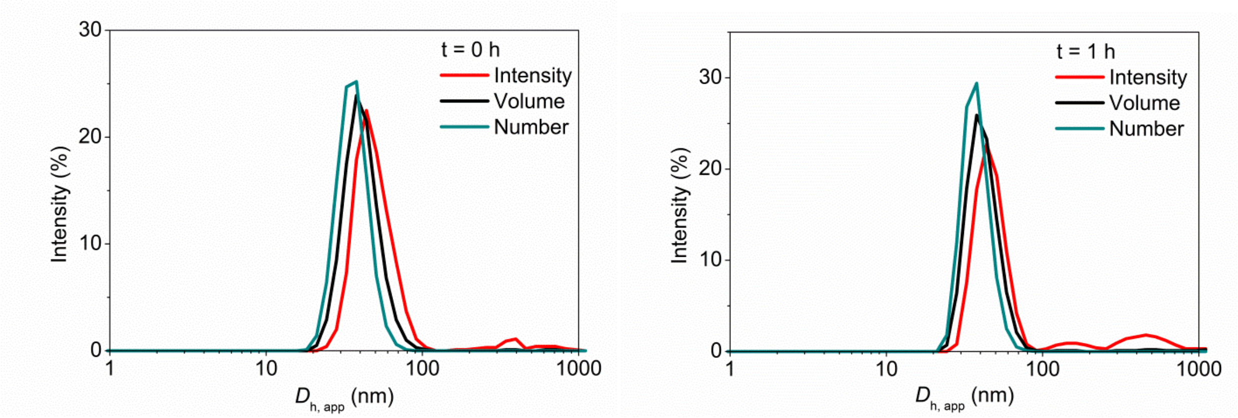
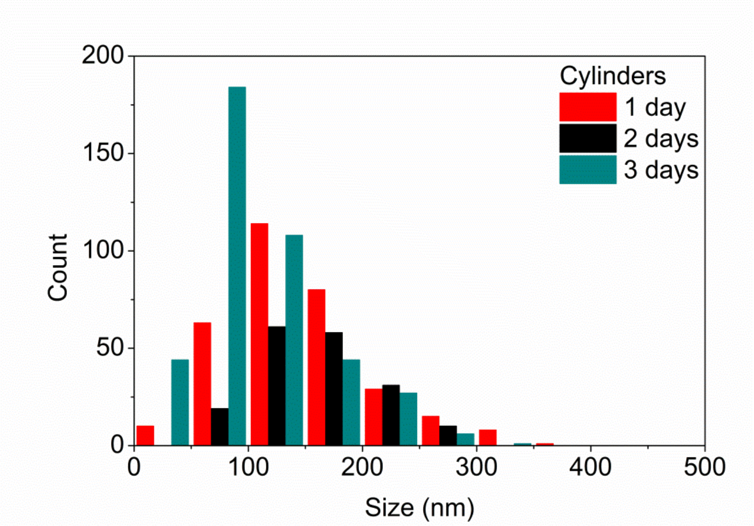


Figure S18. Dynamic light scattering data for the self-assembly of PEO$_{454}$-*b*-P*L*LA$_{28}$ (**3**) with a slow water addition at the initial starting point (left) and after 1 hour of heating (right).



	L_n ± std dev (nm)
1 day	146 ± 62
2 days	160 ± 51
3 days	105 ± 55

Figure S19. Histogram of the cylinders length observed by TEM for the self-assembly of PEO$_{454}$-*b*-P*L*LA$_{28}$ (**3**) at 20 mg × mL^{-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.

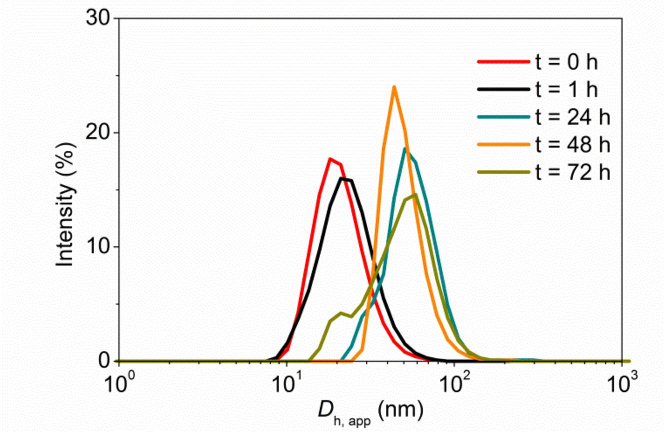
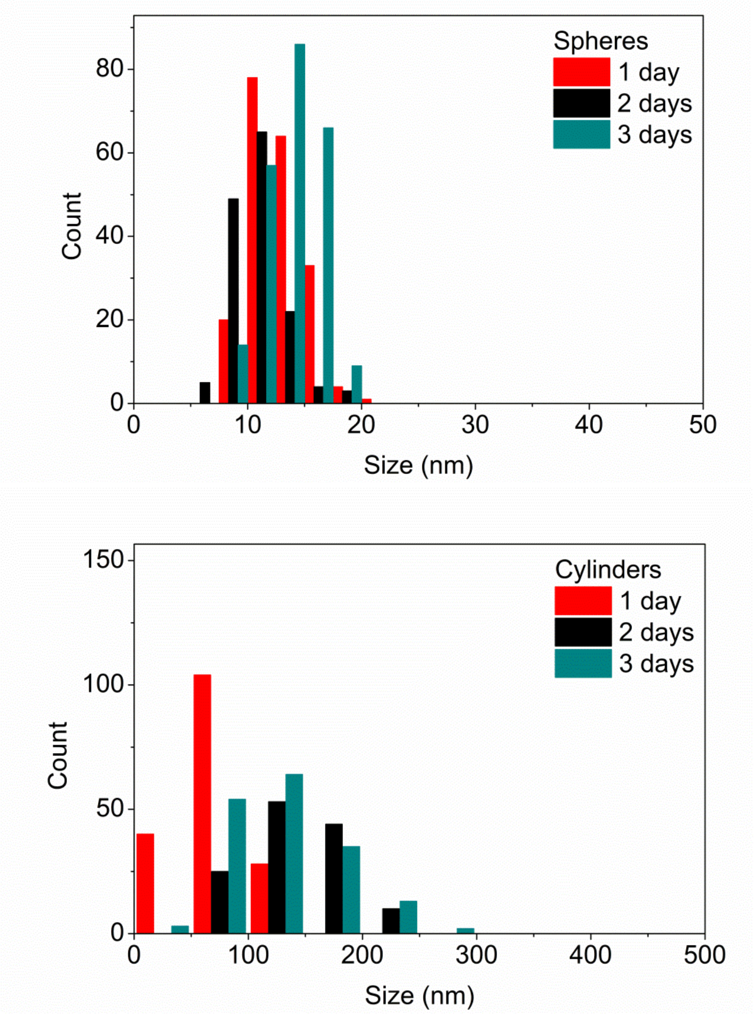


Figure S20. Dynamic light scattering data for the self-assembly of PDMA$_{248}$-*b*-P*L*LA$_{36}$ (**6**) with the slow addition of water at different times.



	L_n ± std dev (nm)
1 day	71 ± 26
2 days	108 ± 42
3 days	127 ± 48

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

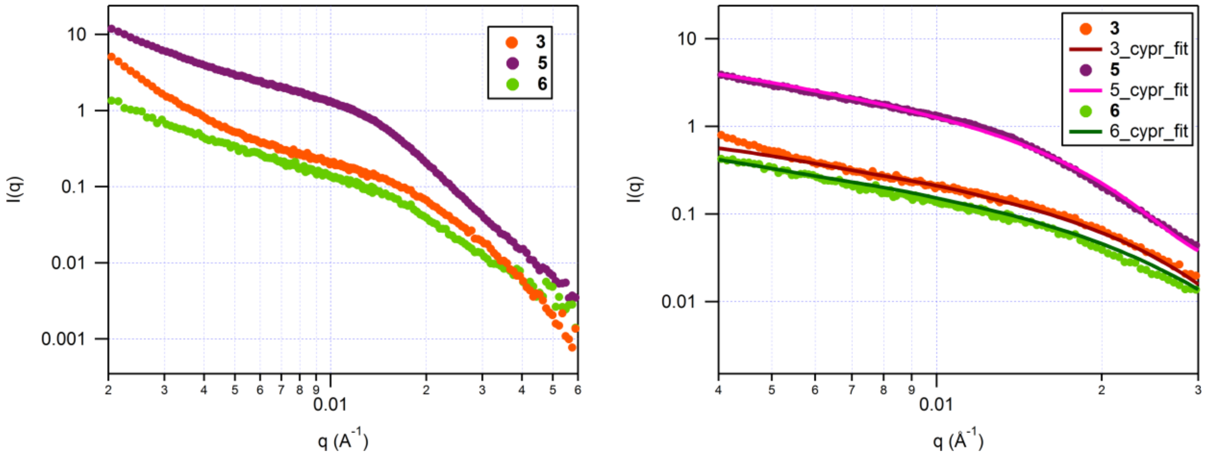


Figure S22. SAXS profiles and fittings of the self-assembly process of diblocks PEO$_{454}$-*b*-P*L*LA$_{28}$ (**3**), P4AM$_{166}$-*b*-P*L*LA$_{36}$ (**5**) and PDMA$_{248}$-*b*-P*L*LA$_{36}$ (**6**) at 20 mg × mL^{-1} in 20% THF with slow addition of water at 3 days.

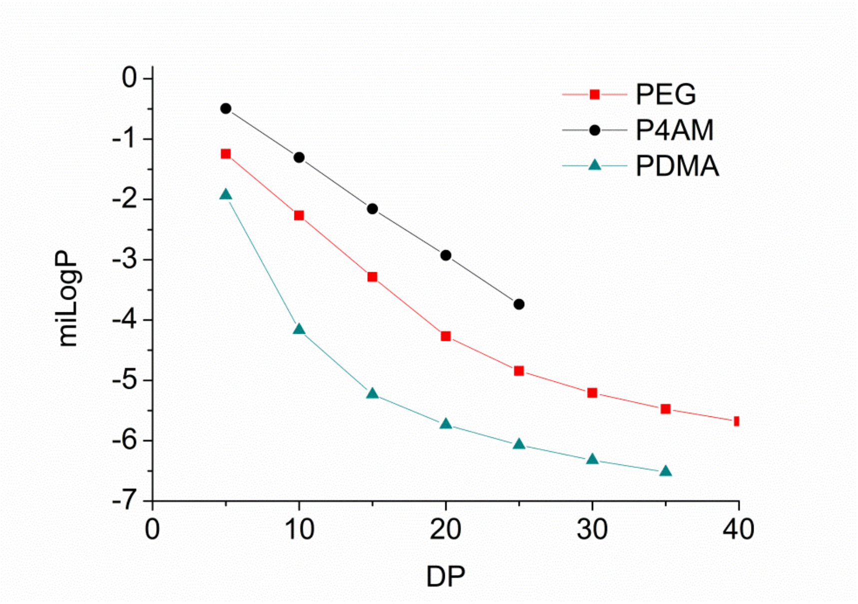


Figure S23. Hydrophilic character of the polymers PDMA, P4AM and PEO determined by prediction of logP according to the degree of polymerization.

References

[1] N. Petzetakis, A. P. Dove, R. K. O'Reilly, *Soft Matter*, **2012**, *8*, 7408-7414.