

Supporting Information for:

“Industrially-Relevant Polymerization-Induced Self-Assembly Formulations in Non-Polar Solvents: RAFT Dispersion Polymerization of Benzyl Methacrylate”

Matthew J. Derry, Lee A. Fielding, and Steven P. Armes

Table S1. Summary of monomer conversions, mean degrees of polymerization and GPC molecular weights for four PLMA macro-CTAs prepared by RAFT solution polymerization of LMA in toluene at 70 °C using AIBN and CBD. Conditions: total solids concentration = 40% w/w, [CDB]/[AIBN] molar ratio = 5.0.

Target DP	¹ H NMR Conversion %	Actual DP by ¹ H NMR	THF GPC		
			M _n / g mol ⁻¹	M _w / g mol ⁻¹	M _w /M _n
PLMA ₁₀	79	16	4,900	5,800	1.19
PLMA ₁₀	71	18	4,800	5,800	1.20
PLMA ₅₀	81	47	11,600	14,400	1.24

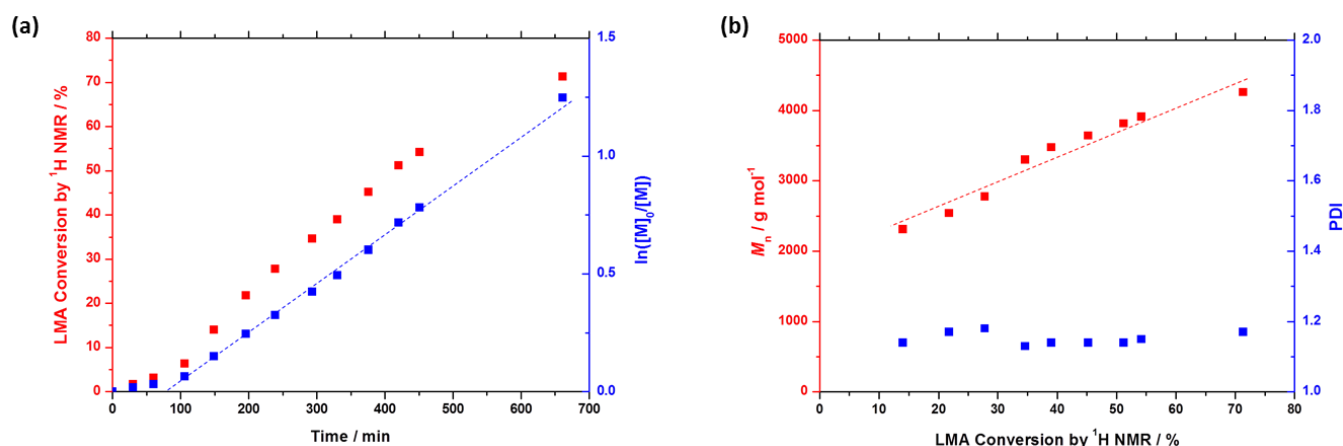


Figure S1. (a) LMA conversion vs. time and (b) M_n and M_w/M_n vs. conversion for the RAFT solution polymerization of LMA in toluene at 70 °C using AIBN and CBD, for a target DP of 10. Conditions: total solids concentration = 40% w/w, [CDB]/[AIBN] molar ratio = 5.0.

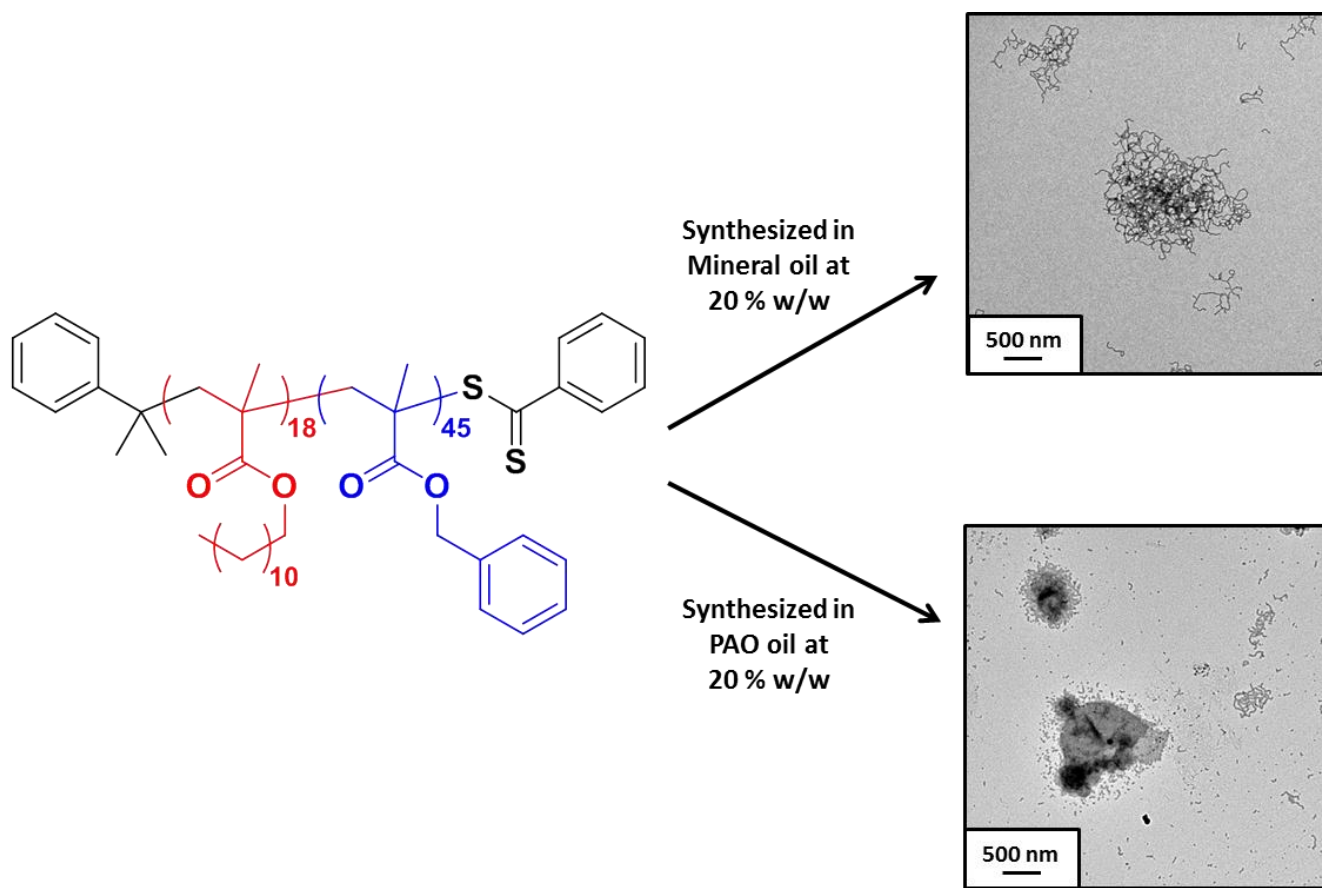


Figure S2. Synthesis of PLMA₁₈-PBzMA₃₅ diblock copolymer spheres in either mineral or PAO oil at 20 % w/w solids. In the former case a pure worm phase is obtained, whereas in the latter case a mixed phase of spheres, worms and vesicles is obtained.

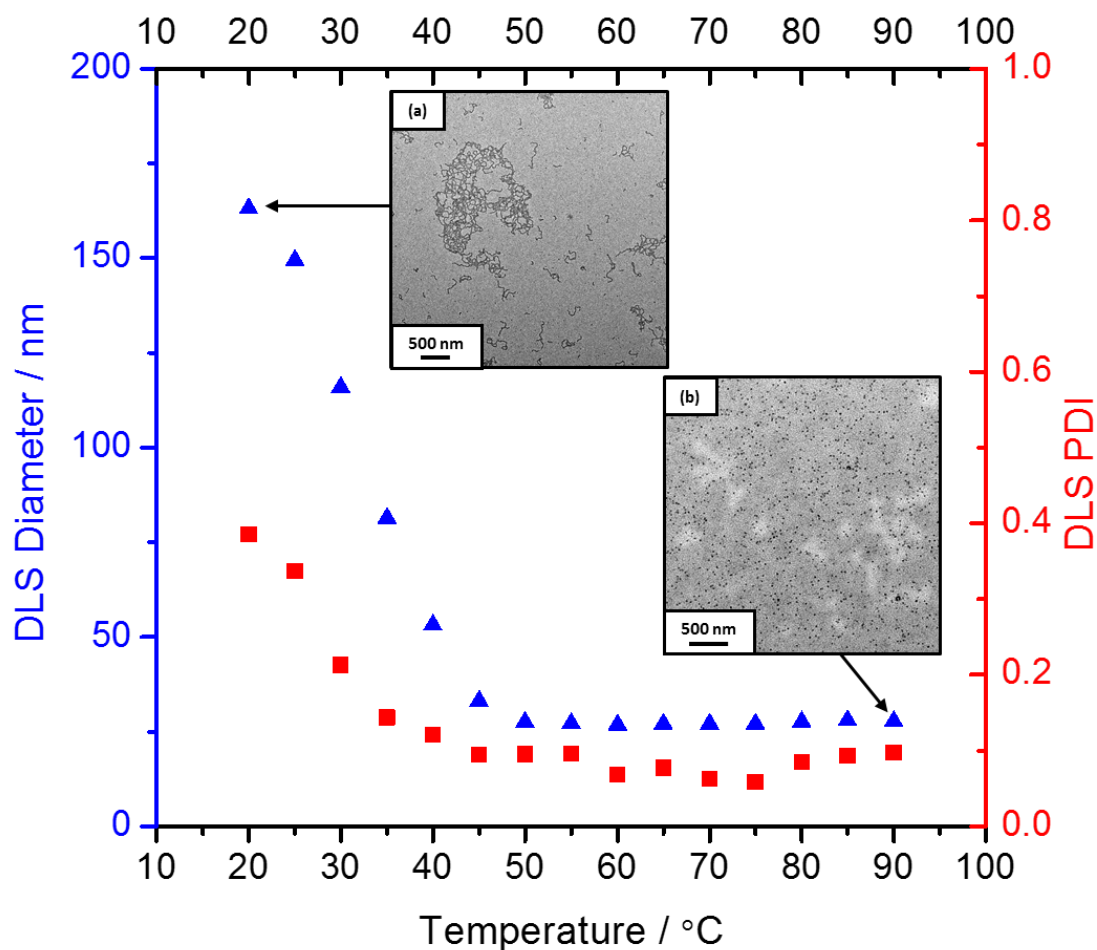


Figure S3. Variable-temperature dynamic light scattering (DLS) studies showing the variation of hydrodynamic diameter (blue symbols) and polydispersity (red symbols) for a 0.10 % w/w PLMA₁₈-PBzMA₄₀ dispersion on heating from 20 °C to 90 °C. Representative transmission electron microscopy (TEM) images obtained show worm-like nanoparticles at 20 °C (a), and spherical nanoparticles at 90 °C (b).

'One-pot' RAFT PISA synthesis
Target composition: PLMA₅₀-PBzMA₁₀₀
DLS diameter = 39 nm
PDI = 0.03

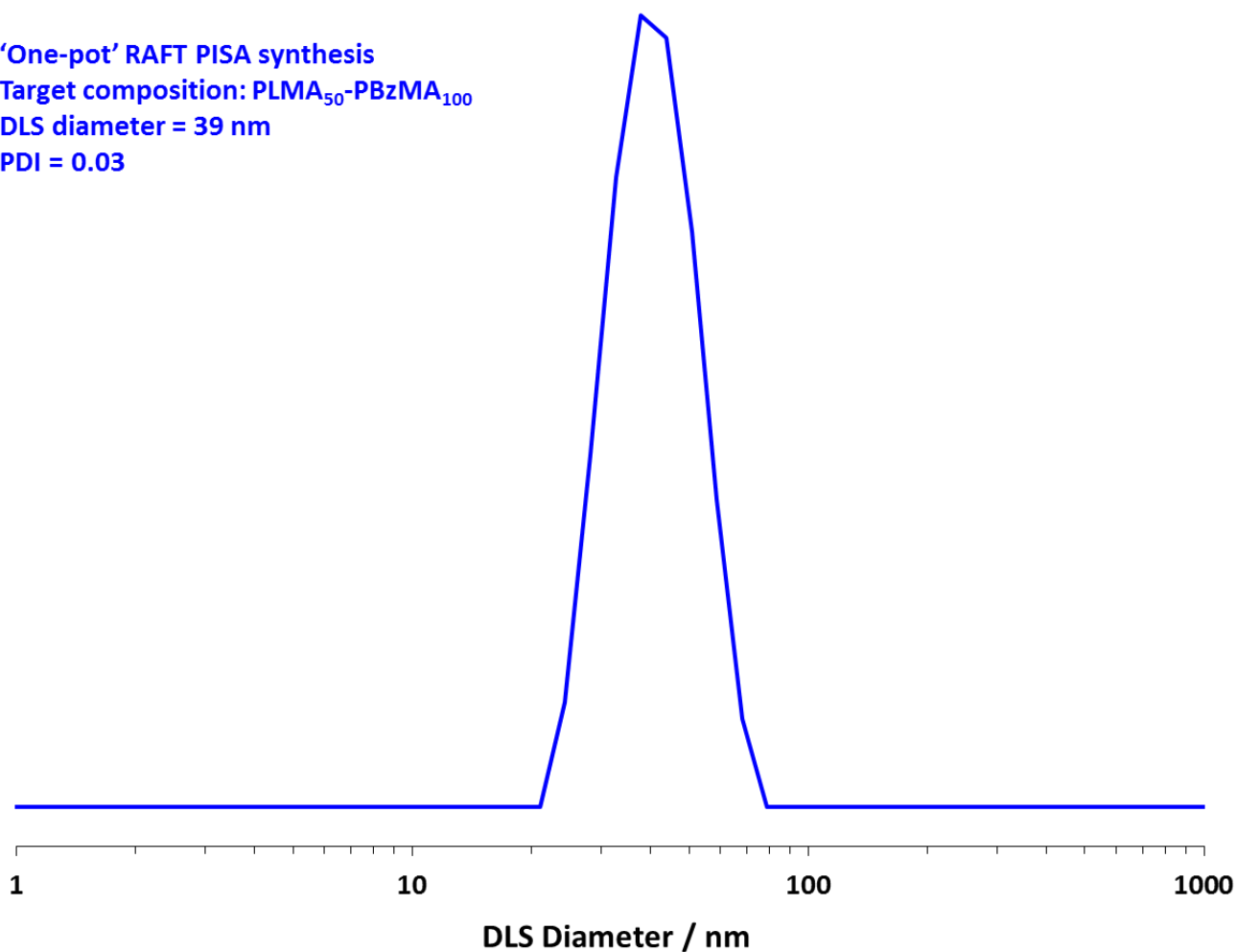


Figure S4. Intensity-average particle size distribution obtained by dynamic light scattering for PLMA₅₀-PBzMA₁₀₀ diblock copolymer spheres targeted via a 'one-pot' protocol at 30 % w/w solids.
