

Supplementary Information

Monitoring Morphology Evolution within Block Copolymer Microparticles during Dispersion Polymerisation in Supercritical Carbon Dioxide: A High Pressure SAXS Study

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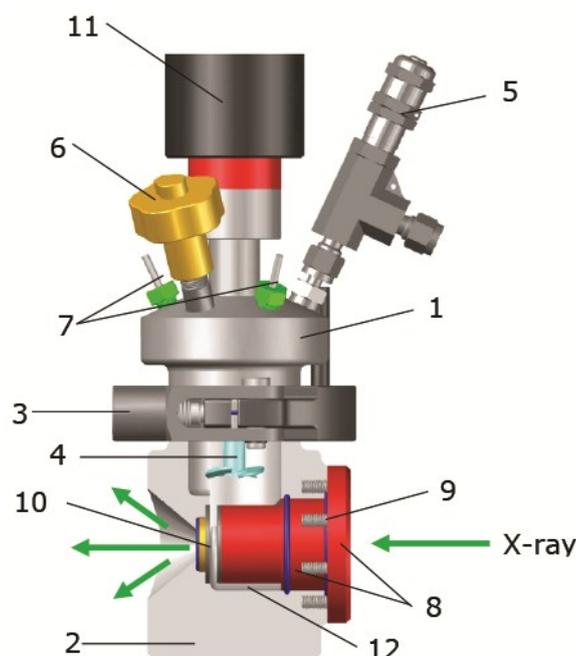


Figure S1. Technical illustration of the high pressure X-ray autoclave used for online SAXS monitoring of the polymerisations described here. The numbers in the diagram correspond with the following components: (1) head, (2) body, (3) clamp, (4) stirrer blade, (5) spring loaded pressure relief valve, (6) torque thumbwheel, (7) inlet and outlet pipes, (8) o-rings, (9) screws to secure the window holder into the cell body, (10) diamond windows, (11) magnetically coupled overhead stirrer, (12) window mount.

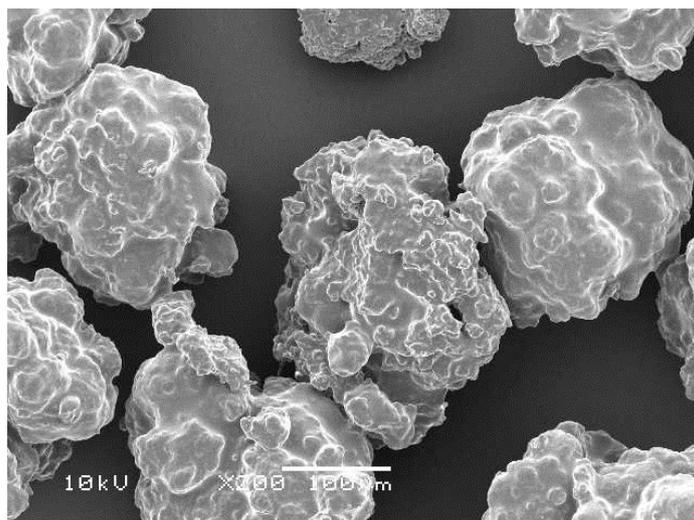


Figure S2. Typical block copolymer product appearance when chain extending PMMA macroCTA microparticles without including any additional PDMS-MA stabiliser.

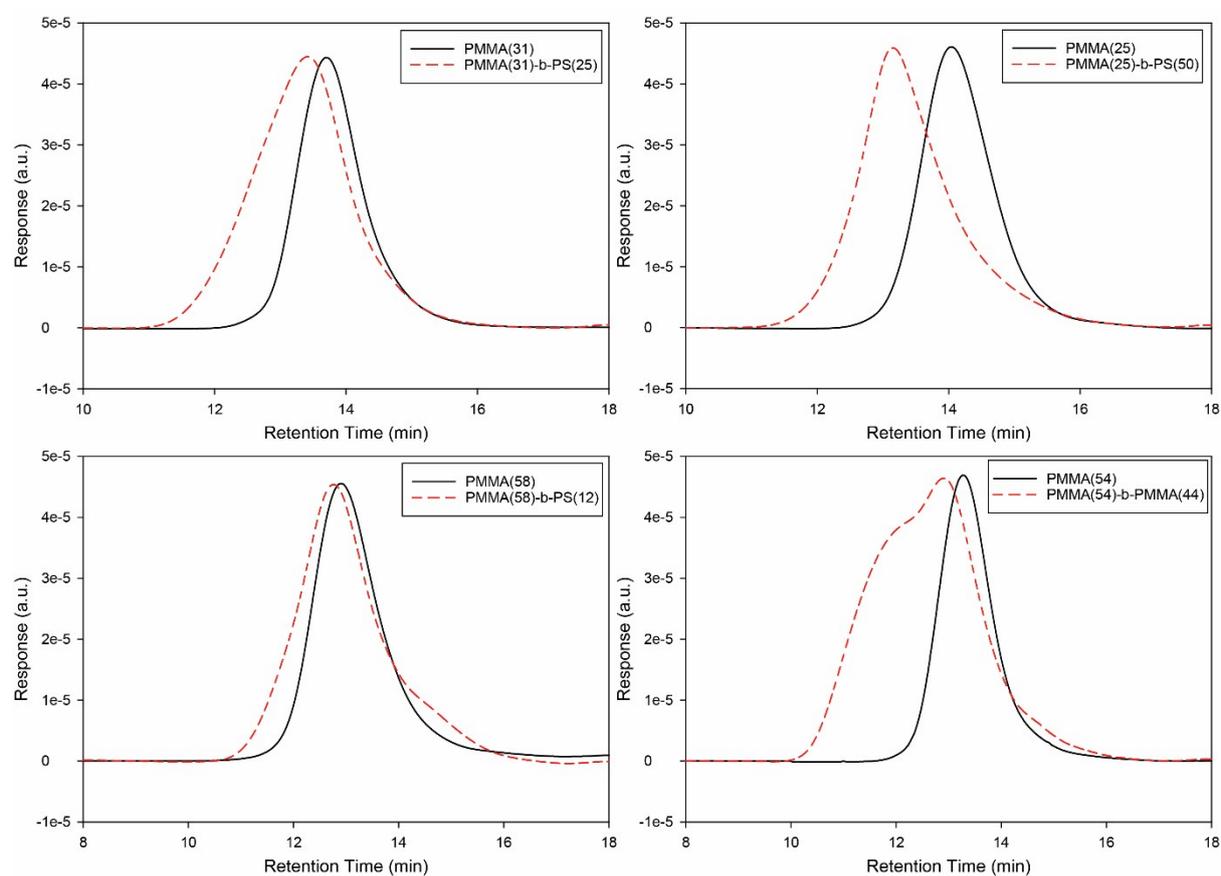


Figure S3. GPC traces of the initial PMMA seed particles and the final block copolymer products collected following their synthesis and in situ monitoring at the synchrotron.

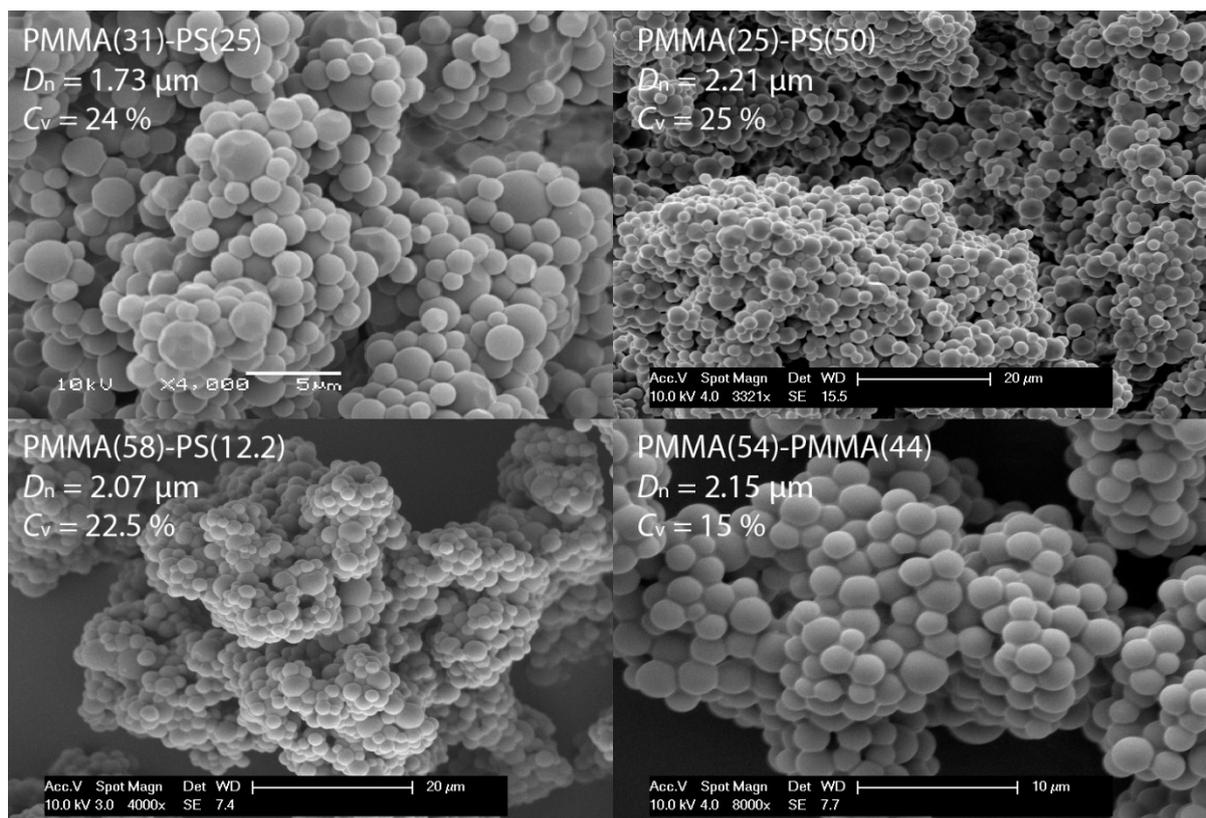


Figure S4. SEM images of the four PMMA microparticle samples used as macroCTAs for chain extension with styrene at the synchrotron.

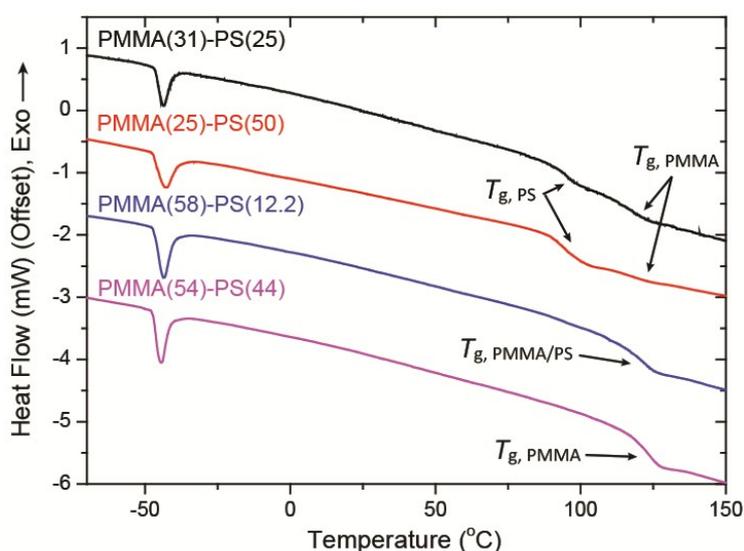


Figure S5. DSC traces of each block copolymer sample. The transition at $-43\text{ }^{\circ}\text{C}$ is the T_g of the PDMS-MA steric stabiliser.

PMMA chain extension kinetics

Prior to the experiments undertaken at the beamline, the polymerisation kinetics for experiments 5 and 6 were investigated in a standard 60 mL sampling autoclave. The reactions were allowed to proceed for 65 and 84 hours, respectively, and aliquots were collected at several time intervals via a needle valve on the base of the vessel.¹ A summary of the molecular weight growth throughout these two reactions determined by GPC and corroborated by ^1H NMR is shown below (Figure S4).

Unfortunately the polymerisation conversion during the sampling process cannot be reliably quantified due to monomer evaporation, but based on our previous reports and the linear growth of M_n with time they are expected to proceed with pseudo-first-order kinetics.^{2,3}

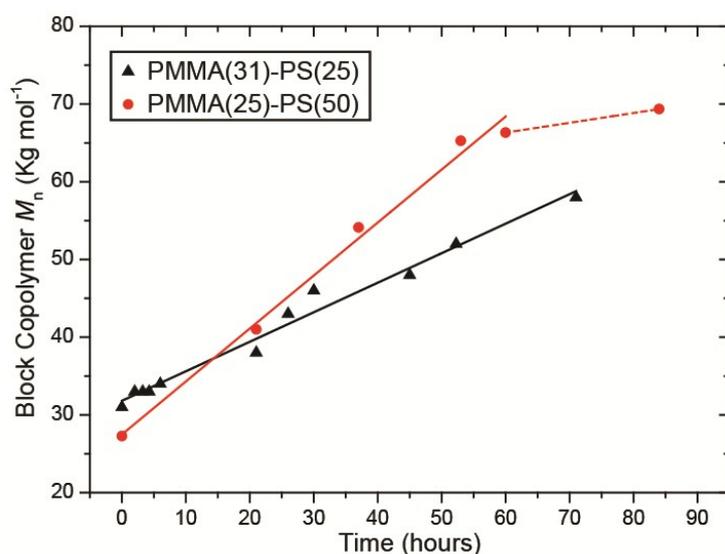


Figure S6. Evolution of block copolymer molecular weight as a function of polymerisation time during the offline synthesis of PMMA(31)-PS(25) and PMMA(25)-PS(50).

^1H NMR analysis conducted on the final products of the kinetic tests of experiments 5 and 6 immediately following their completion enabled conversion values of 85 % and 93 %, respectively, to be estimated, highlighting the slow rate of styrene propagation under these conditions. These results revealed that the polymerisation ideally requires around 72 hrs to achieve the high conversions (> 90 %) required to ensure that the monomer content of the final product is present at low enough levels to minimise surface dissolution upon venting the autoclave. However, due to time restrictions at the beamline, in each case conversions of approximately 80 % were achieved, thus causing the final products to be obtained partially as tacky solids rather than completely free-flowing powders. Although this would not have impacted the results obtained during the time resolved SAXS measurements *in situ*, it is the reason that the experimental M_n values for each product synthesised at the beamline are lower than those calculated from theory. This is also an indication that exposing the reaction mixture to synchrotron radiation for an extended period of time does not appear to have a significant effect on the kinetics of the reaction, a phenomenon which has been reported previously.⁴ This is probably because the volume of the X-ray autoclave employed here (60 mL) is extremely large when compared with the 0.125 mL glass capillary used by Derry and coworkers,⁴ thus considerably reducing the radiation exposure time of the reactants throughout the course of the polymerisation.

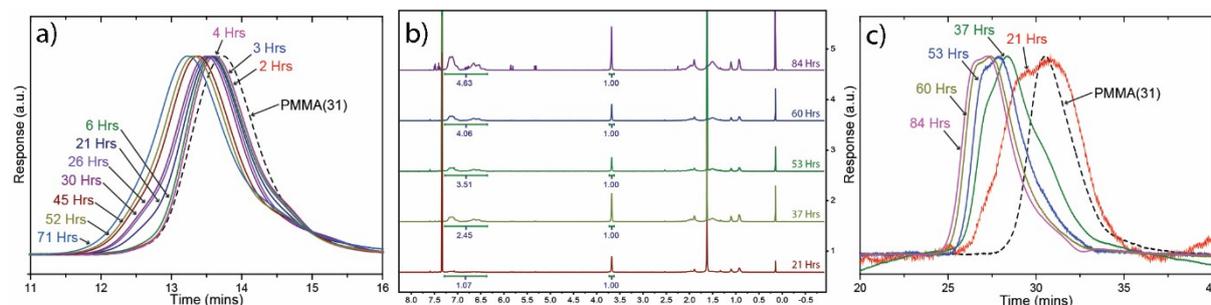


Figure S7. a) GPC data from the aliquots collected during the offline synthesis of PMMA(31)-PS(25), the precursor PMMA(31) (black dashed curve) is shown as a reference. b) ^1H NMR spectra recorded from the aliquots collected throughout the offline synthesis of PMMA(25)-PS(50), highlighting the increasing

fraction of PS. c) GPC data for the aliquots collected during the offline synthesis of PMMA(25)-PS(50), the precursor PMMA(25) (black dashed curve) is shown as a reference.

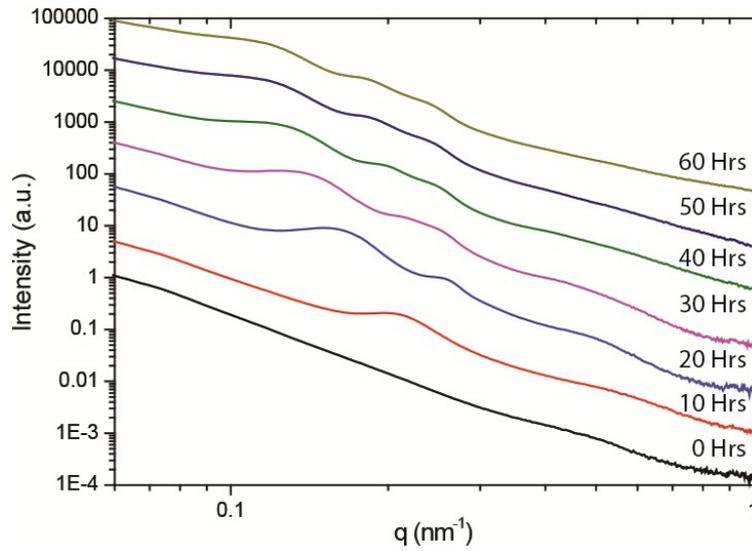


Figure S8. Stacked SAXS profiles collected in situ at 10 hour intervals during the polymerisation of PMMA(31)-PS(25).

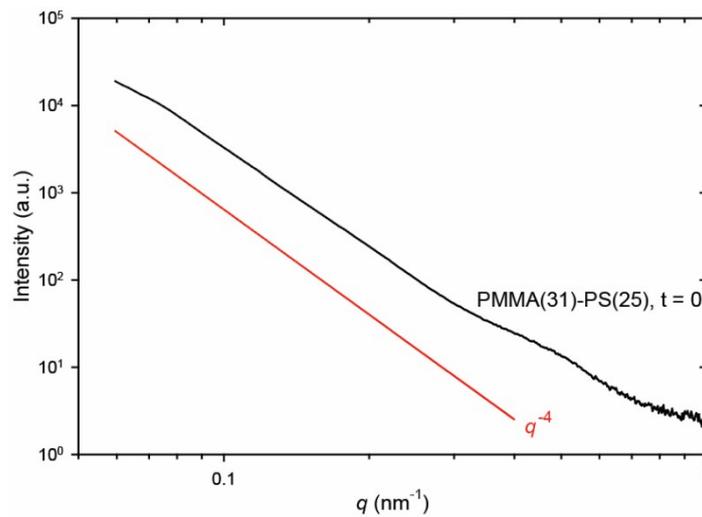


Figure S9. SAXS profile of PMMA(31) recorded during the beginning of the chain extension (at $t = 0$) with styrene, plotted alongside a q^{-4} decay function to confirm the presence of Porod scattering.

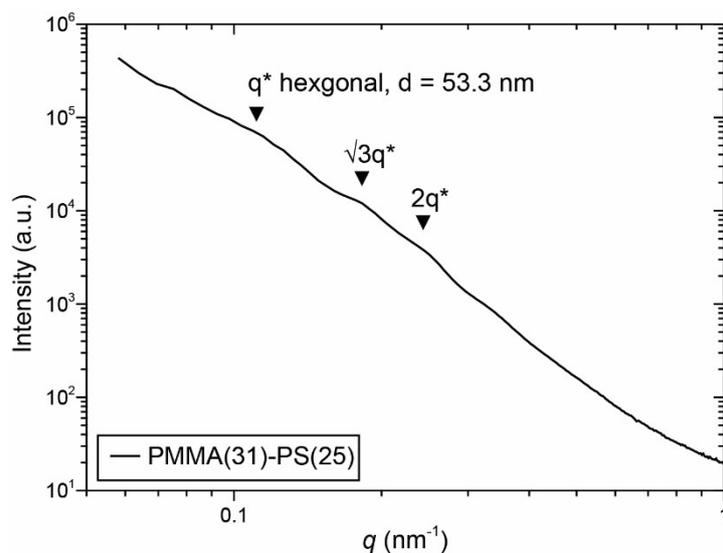


Figure S10. SAXS profile obtained from the PMMA(31)-PS(25) powder product collected after terminating the polymerisation and venting the autoclave.

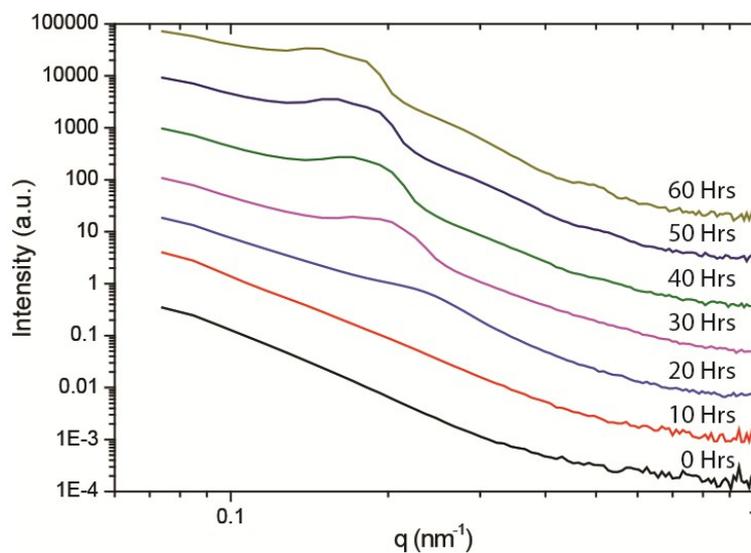


Figure S11. Stacked SAXS profiles collected in situ at 10 hour intervals during the polymerisation of PMMA(25)-PS(50).

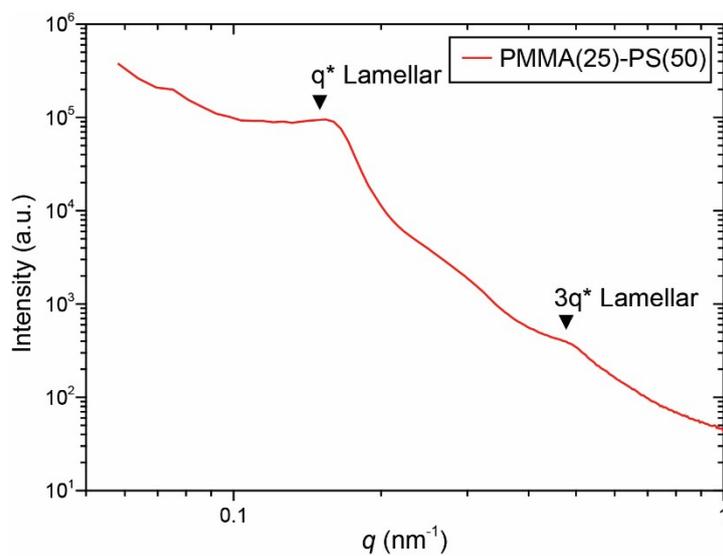


Figure S12. SAXS profile obtained from the PMMA(25)-PS(50) powder product collected after terminating the polymerisation and venting the autoclave.

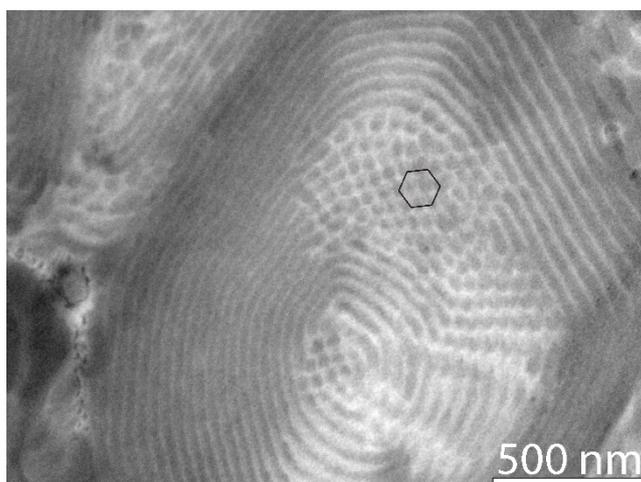


Figure S13. TEM image taken from the kinetic aliquot of the offline chain extension of PMMA(25) with PS(50) at 53 hours highlighting the presence of a hexagonally packed cylinder morphology throughout the microparticle interior.

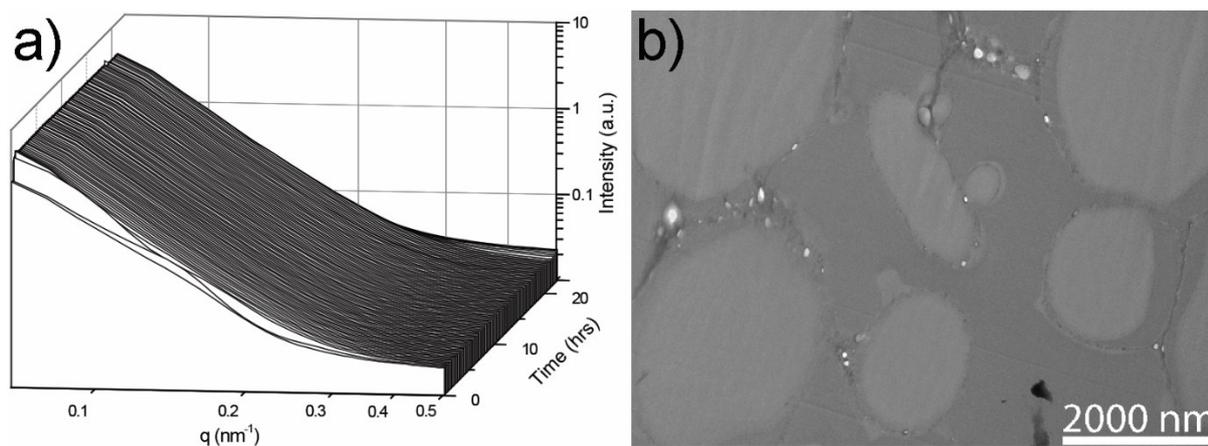


Figure S14. a) Time-resolved in situ SAXS data collected during the chain extension of PMMA(54) to form PMMA(54)-PMMA(44) via dispersion polymerisation in $scCO_2$. b) TEM images taken of the final product.

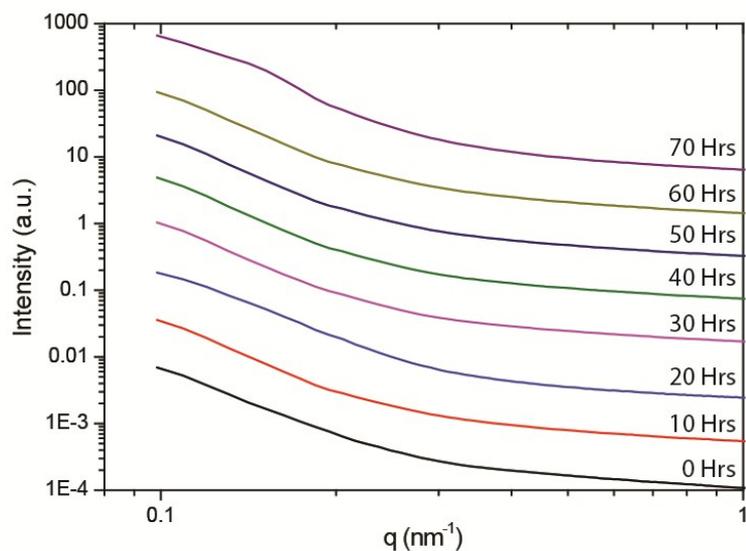


Figure S15. Stacked SAXS profiles collected in situ at 10 hour intervals during the polymerisation of PMMA(58)-PS(12).

References

1. Thurecht, K. J.; Heise, A.; deGeus, M.; Villarroya, S.; Zhou, J.; Wyatt, M. F.; Howdle, S. M. *Macromolecules* **2006**, *39*, 7967-7972.
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3. Zong, M.; Thurecht, K. J.; Howdle, S. M. *Chem. Commun. (Cambridge, U. K.)* **2008**, 5942-5944.
4. Derry, M. J.; Fielding, L. A.; Warren, N. J.; Mable, C. J.; Smith, A. J.; Mykhaylyk, O. O.; Armes, S. P. *Chem. Sci.* **2016**, *7*, 5078-5090.