

## Supporting info

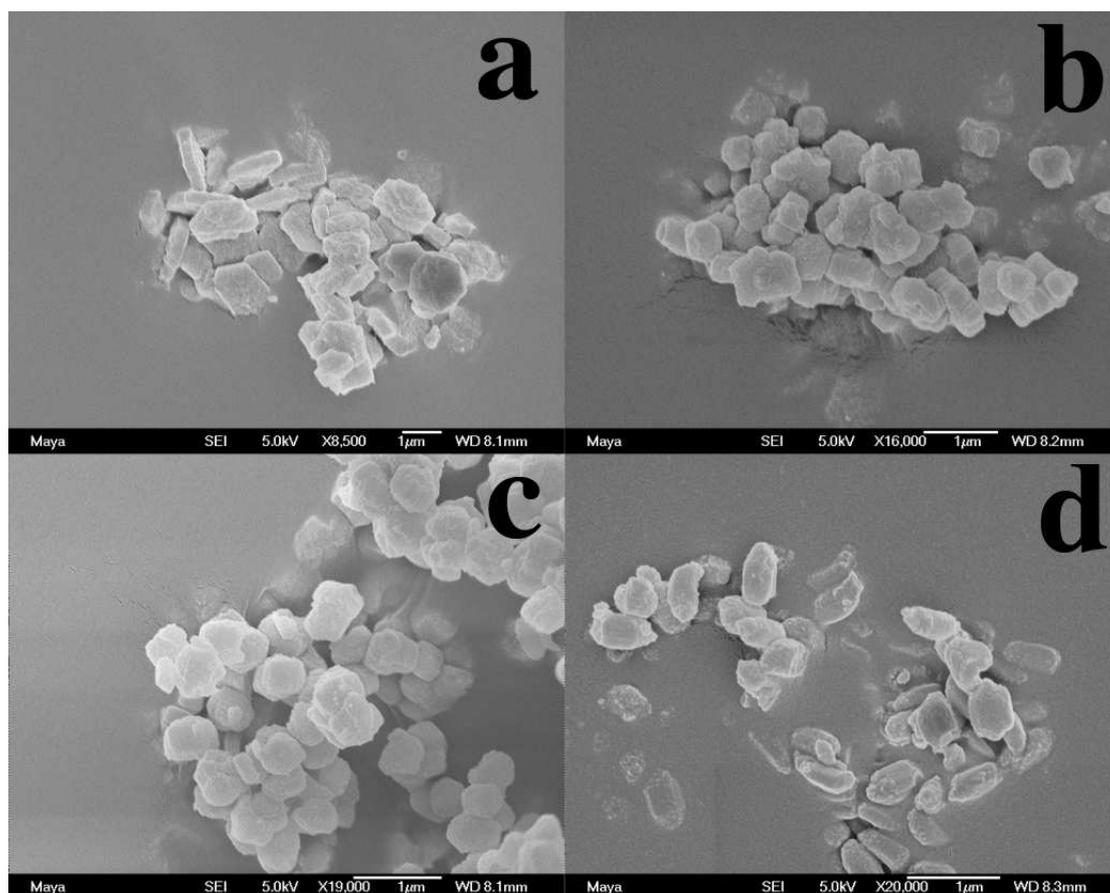


Figure 1. Scanning electron micrographs on the samples made during the time resolved in-situ SAXS measurements. The pumping of the reaction solution does not appear to have any significant impact on the final morphology as these compare well with observations on samples made in a simple closed vessel.

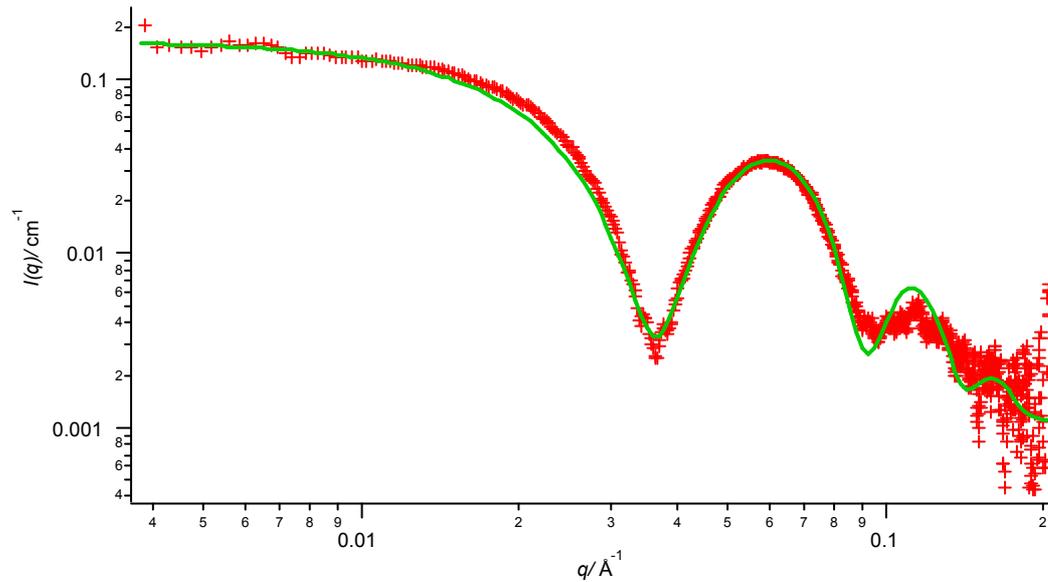


Figure 2. SAXS data for P104 solution (red markers) at 65°C before TMOS addition is well described by non-interacting polydisperse a spherical (green curve) core-shell object. The radius of the core equals 55Å, the shell thickness equals 24Å and the radial core polydispersity equals 0.08 (core polydispersity is defined as the standard deviation of Schultz distribution divided by the radius). The scattering length density for the core was set to 9.24e-6 Å<sup>2</sup>, the solvent to 9.57e-6 Å<sup>2</sup> and the shell to 9.99e-6 Å<sup>2</sup>.

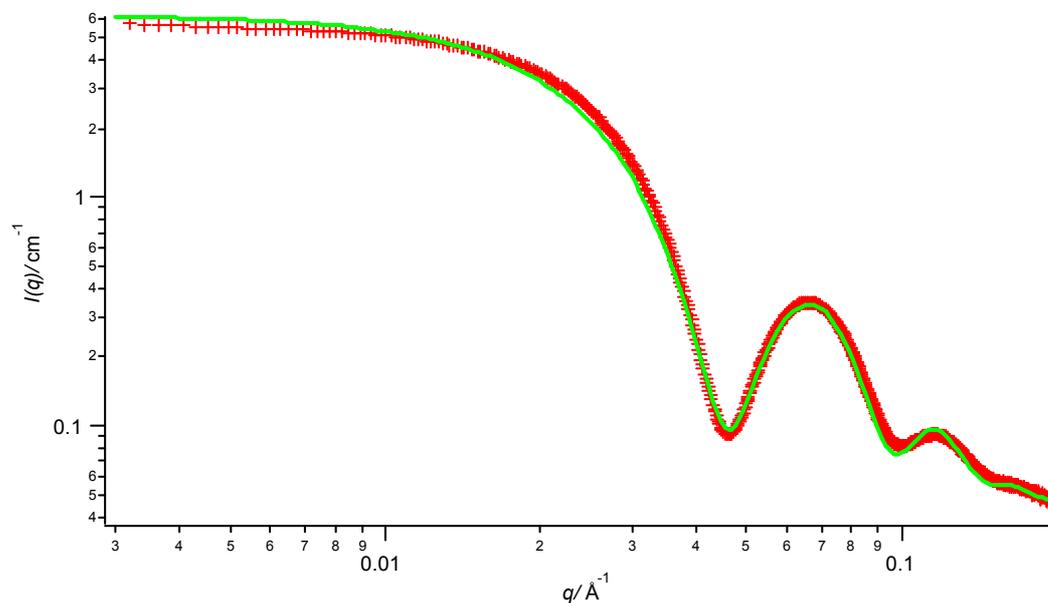


Figure 3. SAXS data for P104 and TMOS solution (red markers) at 50°C and 12 minutes after the start of the synthesis is well described by non-interacting polydisperse a spherical core-shell micelles (green curve). The radius of the core equals 51Å, the shell thickness equals 24Å and the radial core polydispersity equals 0.11 (core polydispersity is defined as the standard deviation of Schultz distribution divided by the radius). The scattering length density for the core was set to 9.24e-6 Å<sup>2</sup>, the solvent to 9.57e-6 Å<sup>2</sup> and the shell to 1.13e-5 Å<sup>2</sup>.

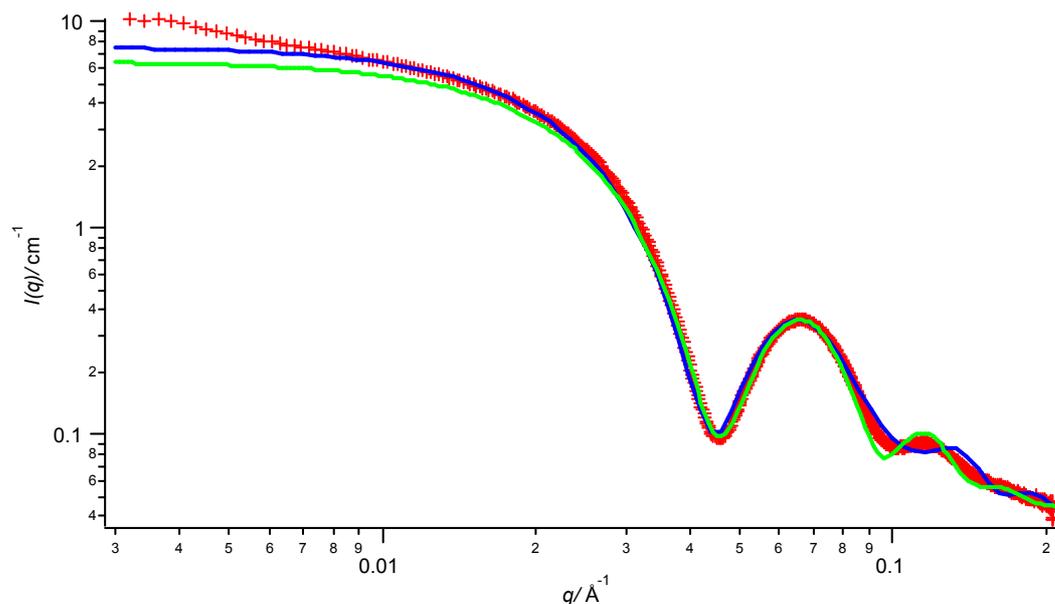


Figure 4. SAXS data for P104 and TMOS solution (red markers) at 55°C and at 8 minutes and 45 seconds after the start of the synthesis can not be satisfactorily fitted either a non-interacting polydisperse spherical (green curve) or cylindrical (blue curve) core-shell object. The curves shown are 'best' fits but there is a significant residual mismatch at small  $q$ . These changes are discussed in the light of USAXS data in the paper.

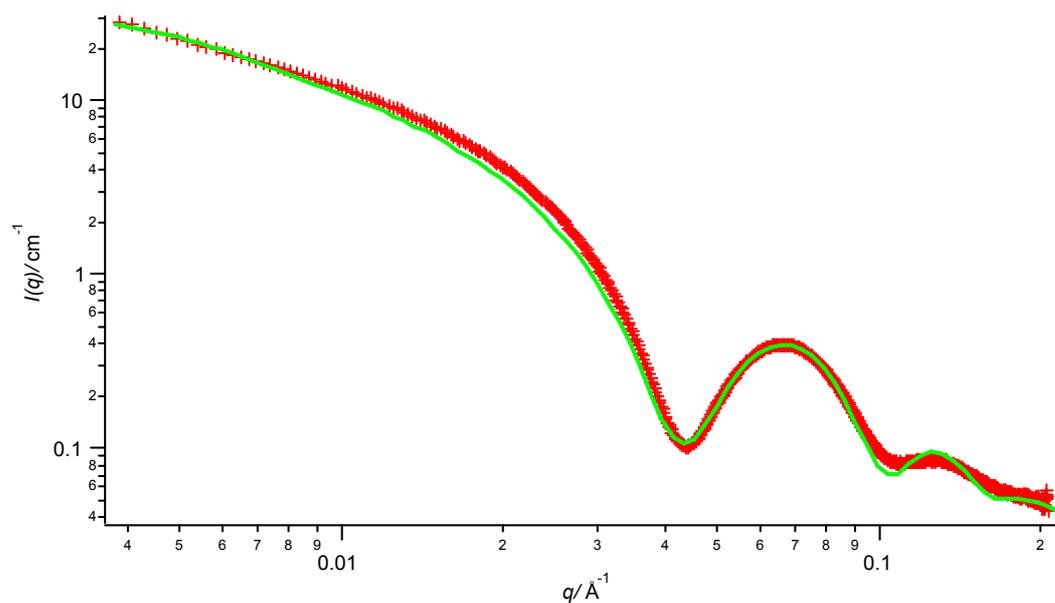


Figure 5. SAXS data for P104 and TMOS solution (red markers) at 65°C and at 6 minutes and 45 seconds after the start of the synthesis is well described by non-interacting polydisperse a cylindrical core-shell object (green curve). The radius of the core equals 41.8Å, the radial shell thickness equals 20Å, the core length equals 800Å and the radial polydispersity equals 0.11 (core polydispersity is the Gaussian distribution of core radii). The scattering length density for the core was set to 9.24e-6 Å<sup>2</sup>, the solvent to 9.57e-6 Å<sup>2</sup> and the shell to 1.185e-5 Å<sup>2</sup>.

Table 1. The scattering length densities of pure PPO, PEO, solvent and SiO<sub>2</sub> were done with NIST scattering length density calculator. <http://www.ncnr.nist.gov/resources/sldcalc.html>

<b>Pure substance</b>	<b>Scattering length density (Å<sup>-2</sup>)</b>
Polypropylene oxide	9.24e-6
Polyethylene oxide	1.04e-5
1.6M hydrochloric acid	9.57e-6
Silicon dioxide (SiO <sub>2</sub> )	2.06e-5

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