

Synthesis of Core-Shell Polymer Particles in Supercritical Carbon Dioxide via Iterative Monomer Addition

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Experimental Section.

Materials.

Styrene (99 %) was purchased from Sigma-Aldrich. Methyl methacrylate (MMA, 99 %) was obtained from Mitsubishi Chemical. 2,2'-Azobis(isobutyronitrile) (AIBN, 98 %) was purchased from Molekula. Monomethacrylate terminated polydimethylsiloxane (PDMS-MA, 150-200 cSt, 10 000 g/mol) was obtained from Fluorochem. Carbon dioxide (CO₂, SCF grade 5.5, 99.9995 %) was obtained from Air Products and Chemicals Inc. All chemicals were used as received.

Characterisation.

Number-average molar mass and dispersity was determined by gel permeation chromatography (GPC). GPC was performed with THF (HPLC grade, Fisher Scientific, stabiliser free) as the eluent at 30 °C using two Agilent PL-gel mixed-D columns in series with a flow rate of 1 mL min⁻¹. Sample detection was achieved using a multiangle light scattering detector and differential refractometer. The system was calibrated using low dispersity PMMA standards, covering a peak molar mass (M_p) range of 1,090 to 538,500 g mol⁻¹.

¹H NMR was used to identify monomer to polymer conversion. Samples were dissolved in a suitable deuterated solvent (CDCl₃) and analysed using a Bruker DPX 400 MHz spectrometer. Chemical shifts were assigned in parts per million (ppm) and referenced to the residual solvent.¹ All spectra were obtained at ambient temperature (22 ± 1 °C). MestReNova 14.0.1 copyright 2019 (Mestrelab Research S.L.) was used for analysing all spectra.

¹H-¹³C CP-MAS experiments were performed at 100 K on a Bruker Avance III HD spectrometer operating at a ¹H Larmor frequency, $\nu_{OH} = 600$ MHz (14.1 T), equipped with a double resonance low-temperature 3.2 mm CP-MAS probe. Cross polarization was achieved using a 90 to 100 % ramp on the ¹H channel for 2 ms and ¹H decoupling was applied during acquisition using a SWf-TPPM sequence. Spinning frequencies were 9 kHz. Between 8 and 256 scans were accumulated for each sample. For comparison, spectra were scaled according to the number of scans.

Scanning electron microscopy (SEM) was performed on a FEI Phillips XL30 SEM. For analysis samples were mounted on aluminium SEM stubs using carbon tape or redispersed in hexane and deposited on a glass slide prior to mounting on carbon tape. A platinum coating was applied to the samples prior to SEM imaging. The image analysis software Fiji (ImageJ) was used to analyse product morphology and feature size from obtained images. Particle size distributions are presented as sizes determined from 100 randomly selected particles.

Differential scanning calorimetry (DSC) was performed using a TA Instruments Q2000, at a heating rate of 20 °C/min in the temperature range of -20 to 200 °C. Hermetic pans and lids (TA Instruments, Brussels, Belgium) were used for the analysis of the samples, using empty pans as the reference. The DSC cell was constantly purged with nitrogen gas at a flow rate of 50 mL/min.

Dynamic light scattering (DLS) was performed using a Malvern Zetasizer Helix at 25 °C using a 633 nm (4 mW) wavelength laser. The scattered light was detected at an angle of 173°. Particles were suspended in heptane at a concentration of 0.25 mg/mL. The mixtures were homogenised by sonication prior to analysis.

Dynamic mechanical analysis (DMA) was performed using a Triton Technologies dynamic mechanical analyser (now Mettler Toledo DMA1, Columbus, OH, USA) using the powder pocket accessory. The use of this attachment allowed for direct measurement of the synthesised powder with no further sample preparation required. A sample (~40 mg) was packed into a powder pocket and mounted in single cantilever bending geometry. Samples were analysed at a relevant temperature range between –100 and 250 °C, at 1 and 10 Hz frequency, at a heating rate of 3 °C/min. The T_g was recorded as the peak temperature of the $\tan \delta$ trace obtained at 10 Hz or the change maximum of the storage stiffness (S') when the $\tan \delta$ peak was not sufficiently clear.

Transmission electron microscopy (TEM) images were captured using a FEI Tecnai G2 12 Biotwin at an accelerating voltage of 100 kV. Samples were prepared by embedding particles in an epoxy resin (Agar 100) at 50 °C for 48 h prior to slicing 100 nm thick sections using an RMC Powertome microtome equipped with a Diatome diamond knife. Sections were captured on a 400-mesh copper grid and stained for 2-4 h with ruthenium vapour to induce image contrast. Ruthenium tetroxide (RuO_4) vapour was generated in a sealed container by combining RuCl_3 (12.4 mg) with NaIO_4 in H_2O (4.2 mg in 1 mL). After staining, the solution is quenched with an excess of corn oil.

SAXS patterns were recorded at a synchrotron source (Diamond Light Source, station I22, Didcot, UK; Experiment ID SM33098) using monochromatic X-ray radiation (X-ray wavelength $\lambda = 1.00 \text{ \AA}$, with scattering vector q ranging from 0.0017 to 0.17 \AA^{-1} , where $q = 4\pi \sin \theta / \lambda$ and θ is one-half of the scattering angle) and a 2D Pilatus 2M pixel detector (Dectris, Switzerland). Static SAXS measurements were performed on either 0.25 mg mL^{-1} or 1.0% w/w dispersions in 2.0 mm glass capillaries. Scattering data were reduced and normalized, with glassy carbon being used for the absolute intensity calibration utilising standard routines available at the beamline^{2, 3} and further analysed (background subtraction and data modelling) using Irena SAS macros for Igor Pro.⁴

Synthesis.

Radical dispersion polymerisation of styrene

The reaction was conducted with styrene (12.72 g), PDMS-MA stabiliser (20 wt% relative to styrene) and AIBN initiator (2 wt% relative to styrene) in a 60 mL high pressure autoclave. Styrene, PDMS-MA, and AIBN were degassed by bubbling with argon in a vial kept on ice for 30 minutes. During this time, the autoclave was flushed with CO_2 at 2-3 bar, venting through the keyhole. After 30 minutes, the mixture was injected into the autoclave through the keyhole against a positive flow of CO_2 . The key was then inserted into the autoclave, sealing it off from the atmosphere. At this point CO_2 was added, pressurising the system to 50 bar. Heat was then applied through the heating jacket, bringing the temperature to 65 °C. CO_2 was then added until the system pressure reached 245 bar. The moment the reaction temperature was reached was chosen as the starting point of the reaction. The heating was turned off after 24 h and the system temperature was allowed to fall below 30 °C. At this point the stirring was stopped, and the pressure was released slowly, returning to atmospheric conditions, and yielding a fine white powdered product (11.7 g, 92 %).

Redispersion of PS particles in scCO_2

PS particles were added to the autoclave base prior to reactor assembly. CO_2 was added to the sealed vessel, up to 30 bar, before slowly releasing CO_2 down to a reactor pressure of 10 bar. This pressure cycle was repeated 5 times, to remove oxygen present in the vessel without dispersing the PS powder. After this, CO_2 was added, pressurising the system to 50 bar, and the stirring was engaged at 400 RPM. Heat was then applied through the heating jacket, bringing the temperature to 35 °C. CO_2 and heat were then added incrementally until the desired reaction conditions of 65 °C and 245 bar were reached. After at least 15 hours, the PS particles form a stable dispersion in scCO_2 .

Preparation of PS:PMMA core-shell particles in scCO₂

PS particles were redispersed following the above procedure. A stock solution of MMA, with 1 wt% AIBN relative to MMA, was degassed by bubbling with argon for 30 minutes. Prior to connecting the HPLC pump to the autoclave, the pipe system was rinsed by pumping acetone through to the autoclave connection. Following this, the degassed MMA with AIBN stock solution was pumped through, pushing out the acetone. With the piping filled with the stock solution, the pipe was connected to the HPLC inlet tap of the autoclave. With the autoclave HPLC inlet tap closed, pressure was built up by pumping in stock solution at a slow rate. The pressure of the HPLC pump was brought up to the reactor pressure (245 bar), meaning that opening the HPLC inlet tap would not cause any liquid movement. The flow rate of the HPLC pump was set to 0.1 mL/min, the HPLC inlet tap was opened, and the pump was engaged. The desired amount of MMA was added (assuring that the added mass of MMA remained below the cumulative mass of polymer in the reactor), at which point the pump was stopped and the HPLC inlet tap was closed. HPLC pressure was released through the internal purge system, before disconnecting the pipe from the HPLC inlet.

The entire HPLC system is then flushed with 60 mL of acetone. 240 minutes after HPLC injection, when MMA conversion is $\geq 90\%$, a further injection of MMA with AIBN can be conducted following the same procedure, again assuring that the added mass of MMA remains below the mass of polymer in the reactor (this procedure is repeated the required number of times, see Table S1 below). 240 minutes after the final MMA injection, the reaction time needed to reach $>95\%$ conversion of MMA, the heating was turned off and the system temperature was allowed to fall below 30 °C. At this point the stirring was stopped, and the pressure was released slowly, returning to atmospheric conditions, and yielding a fine white powdered product.

Table S1: Reagent addition methodology for synthesis of core-shell particles

Targeted core-shell mass ratio	PS mass (g)	mass of MMA aliquots (g)				MMA Cumulative mass (g)	Isolated mass (g)	Yield (%)
		1 st addition	2 nd addition	3 rd addition	4 th addition			
1:1	5	5	—	—	—	5	7.5	75
1:2	3	2	4	—	—	6	6.7	75
1:4	1.5	1.5	2	2.5	—	6	5.3	71
1:8	0.75	0.75	1.25	2	2	7	5.2	78

Physical Blends of PS and PMMA

To act as a comparison to the core-shell systems, physical, unprocessed blends of PS and PMMA were prepared in the same mass ratios (1:1, 1:2, 1:4, 1:8) and analysed via DMA. The PS used was that used as the starting material for the core-shell syntheses. The PMMA used was synthesised separately as described below.

Synthesis of PMMA

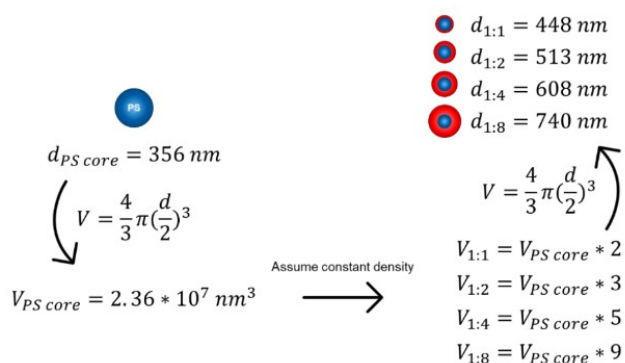
MMA (9.40 g, 93.89 mmol), AIBN (1 wt % wrt MMA, 0.0936 g, 0.570 mmol), and PDMS-MA (5 wt% wrt MMA, 0.47 g, 0.0533mmol) was deoxygenated by flushing with argon for 30 minutes.

The autoclave was purged with CO₂ for 30 minutes at 2-3 bar to remove oxygen. The MMA/AIBN/PDMS-MA mixture was injected into the autoclave using a syringe against a positive pressure of CO₂ to avoid the ingress of air. The autoclave was sealed and stirring commenced (450 rpm) before heating alongside the addition of CO₂ until desired conditions were reached (65 °C, 241.3 bar).

After 24 hours the heating was discontinued, and the autoclave allowed to cool to < 25 °C before being slowly returned to ambient pressure by the release of CO₂. The product was then collected from the autoclave, giving PMMA (7.72 g, 82 % yield, 97 % conversion) as a free-flowing white powder.

Prediction of particle diameter

Particle sizes were predicted based upon assumption of spherical geometry and consistent density throughout the particles, using standard geometric rationale as per Scheme S1 below.



Scheme S1: Prediction method of particle diameter of core-shell particles, assuming perfectly spherical particles with a uniform density (where V = particle volume, and d = particle diameter).

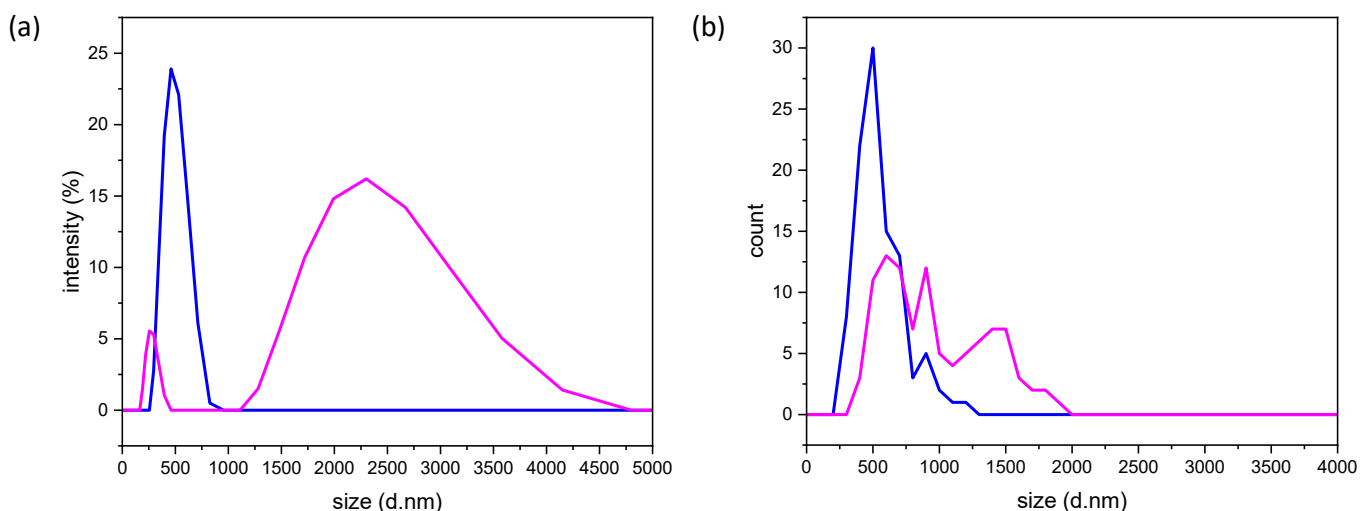
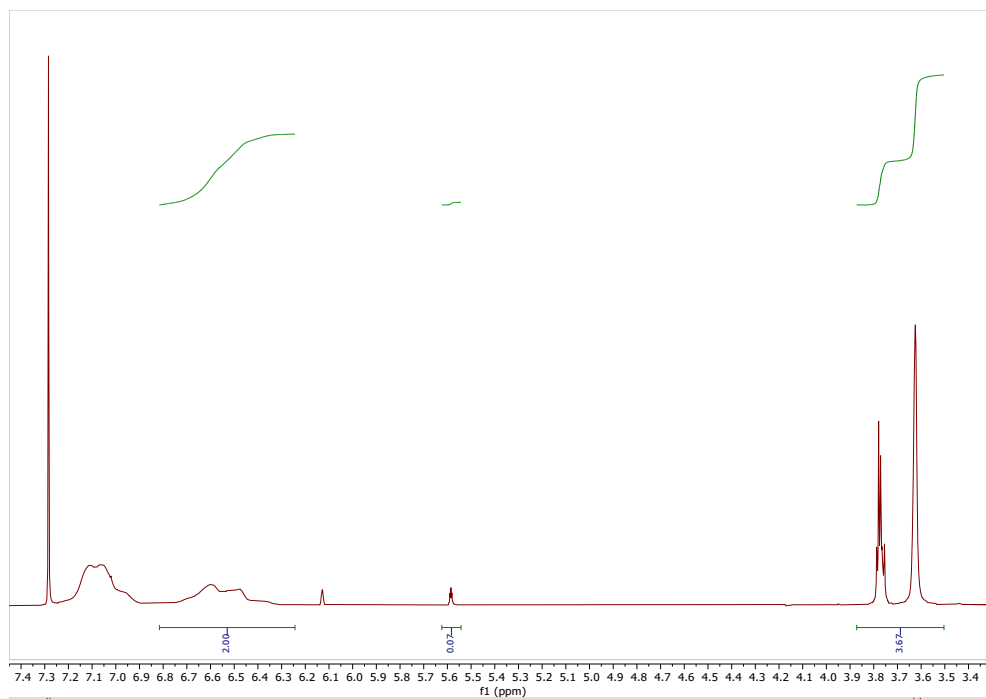
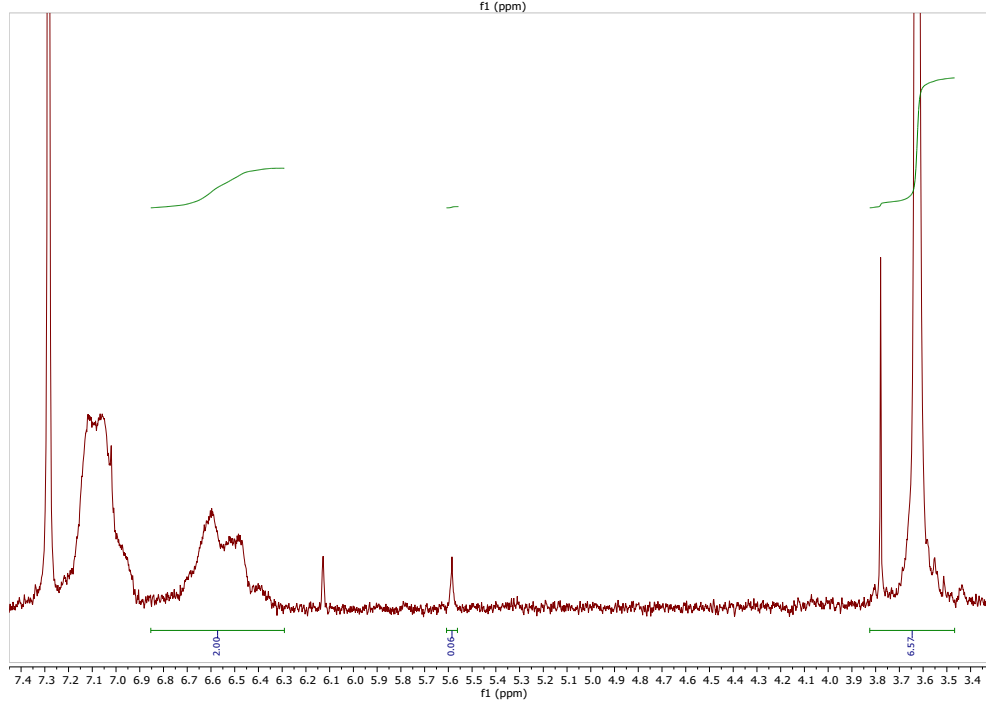


Figure S1: Particle size distributions from (a) DLS and (b) SEM analysis for the unsuccessful 1:2 core-shell synthesis (magenta) using a “one shot” monomer addition and the successful 1:2 core-shell synthesis using iterative monomer addition (blue). Note, the bimodal populations from both DLS and SEM analysis for the “one shot” monomer addition experiment.

(a)
1:1



(b)
1:2



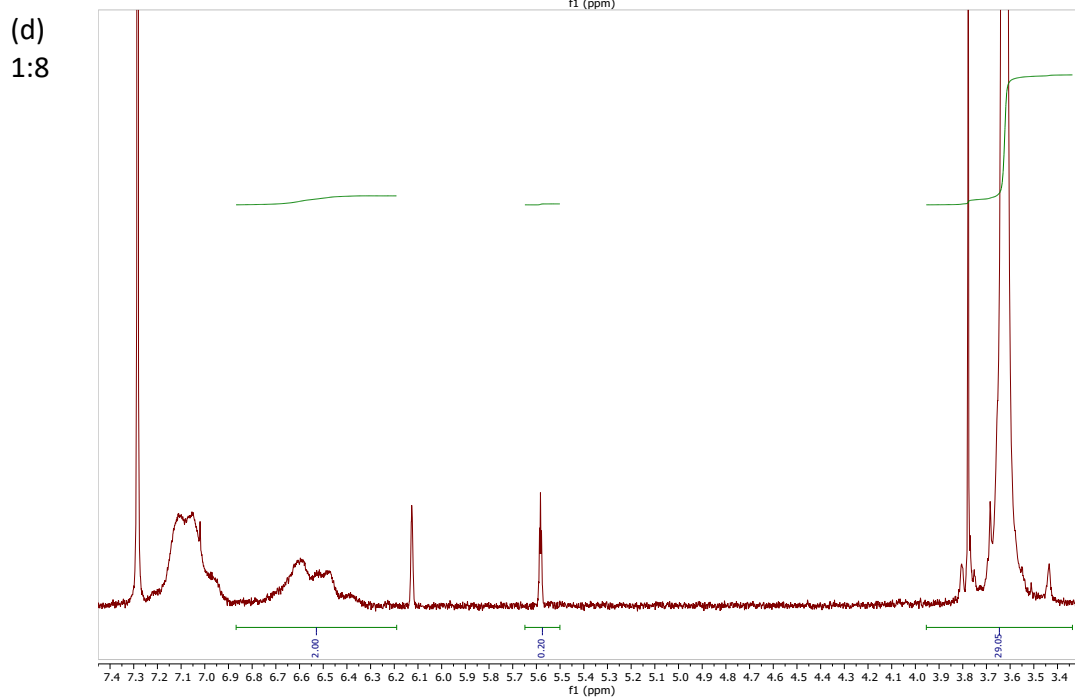
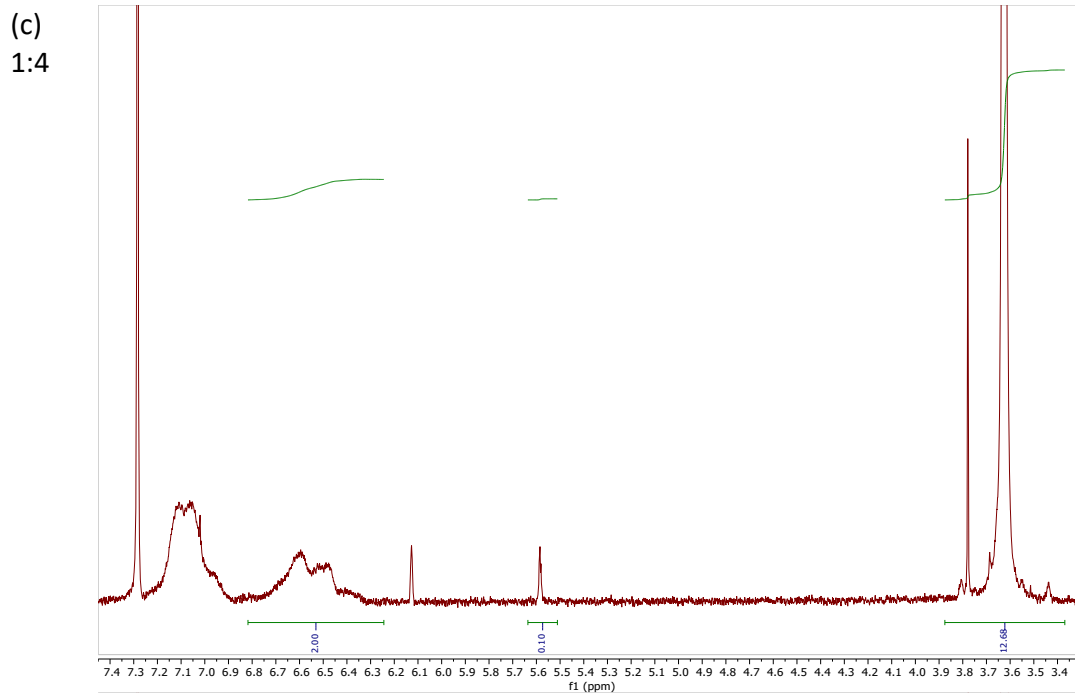


Figure S2:-Expansions of ^1H NMR spectra in CDCl_3 for core-shell systems with targeted PS:PMMA mass ratios of (a) 1:1, (b) 1:2, (c) 1:4, and (d) 1:8. Integrals included are those used to calculate percentage conversion of MMA and the ratio of PS:PMMA present.

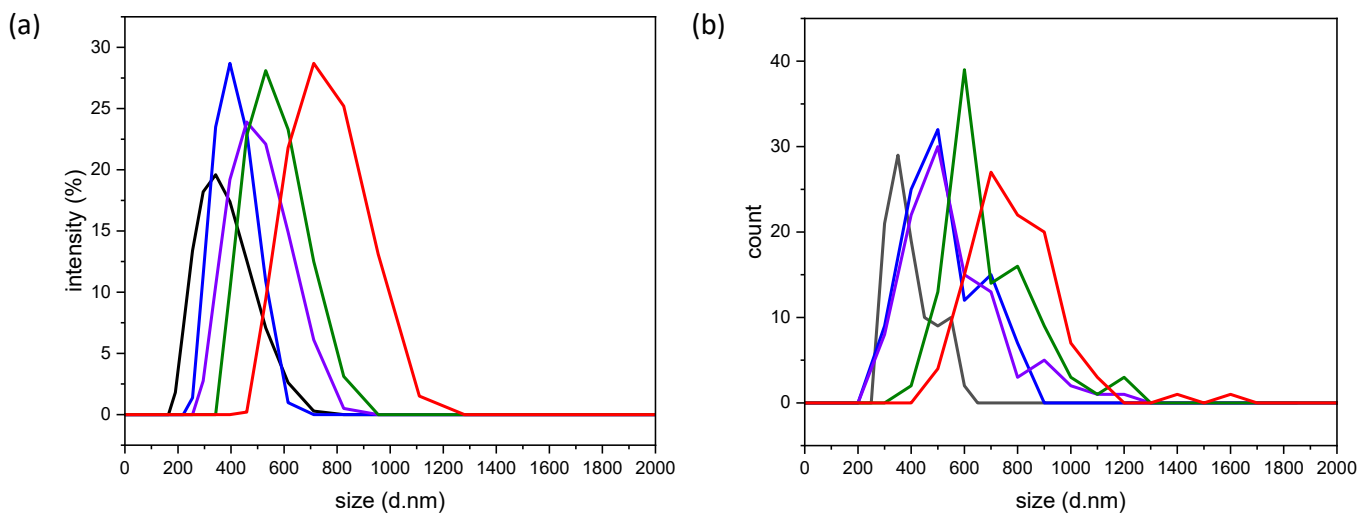


Figure S3: Particle size distributions from (a) DLS and (b) SEM analysis for the PS core (black) and the core-shell particles prepared using iterative monomer addition with targeted PS:PMMA mass ratios of 1:1 (blue), 1:2 (purple), 1:4 (green), and 1:8 (red).

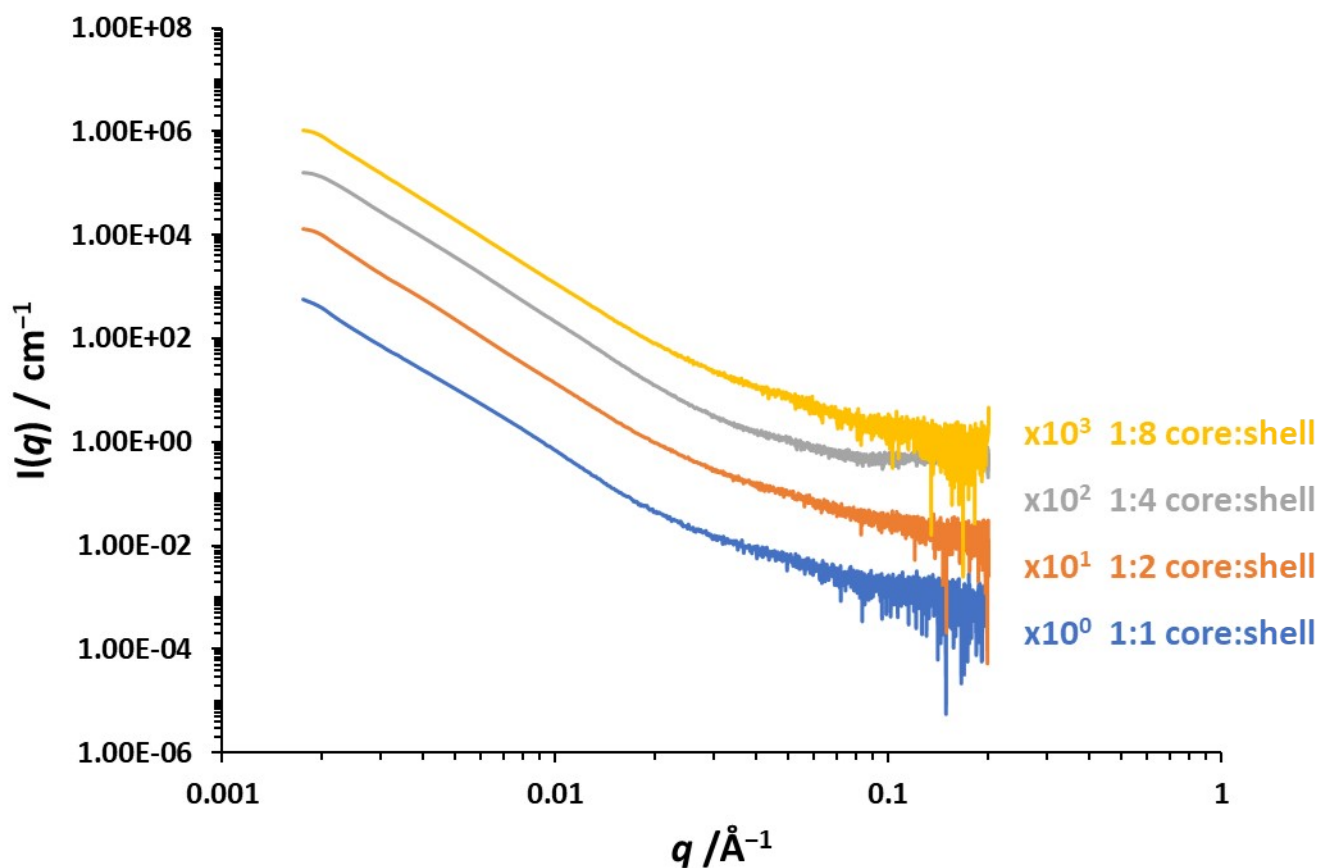


Figure S4: Background-subtracted synchrotron small-angle X-ray scattering (SAXS) data for 1% w/w dispersions of PS-PMMA core-shell polymers with PS:PMMA ratios of 1:1 (blue data), 1:2 (orange data), 1:4 (grey data) and 1:8 (yellow data).

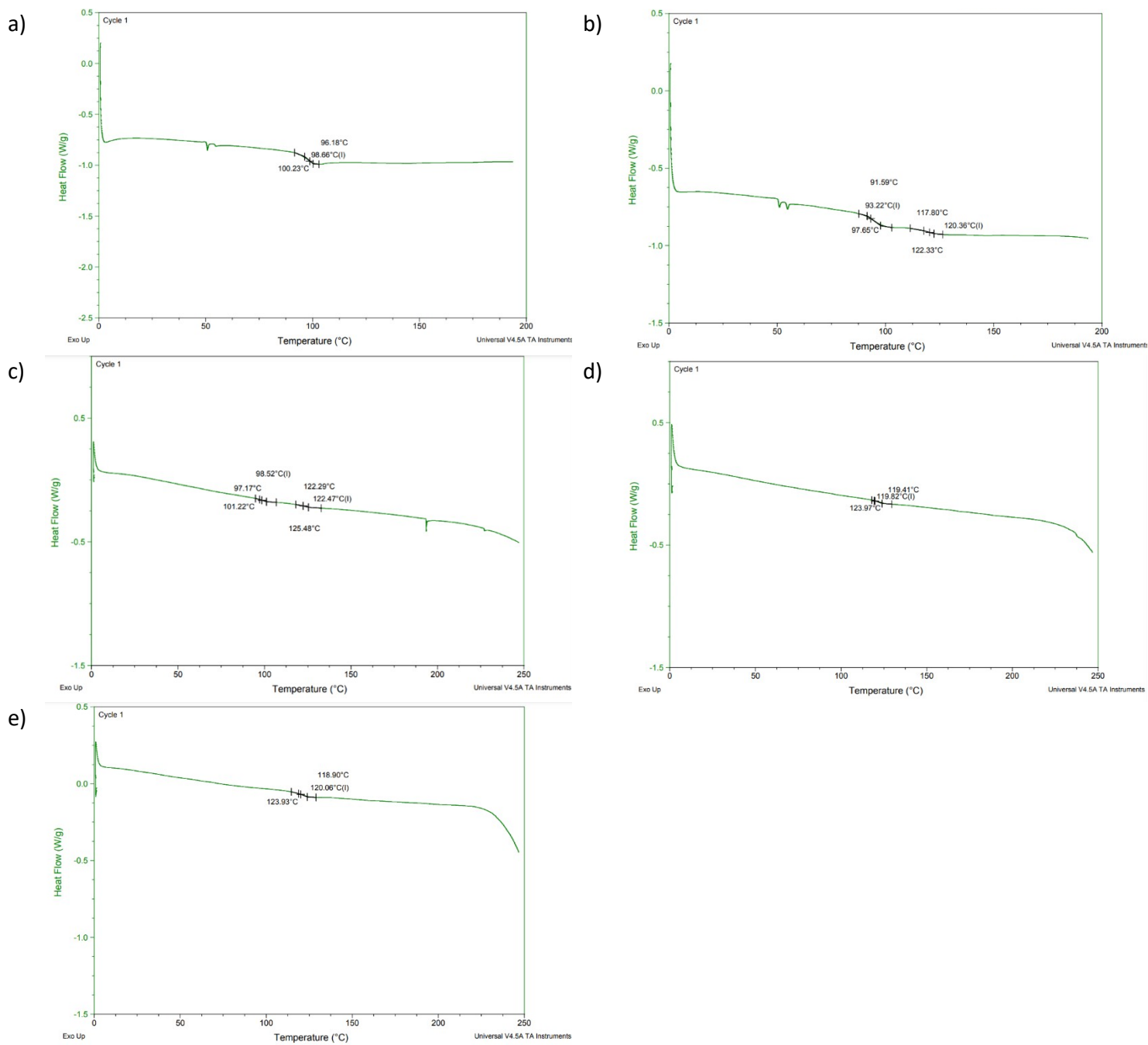


Figure S5: DSC curves of (a) PS particles (core), and PS-PMMA core-shell particles with targeted mass ratios of (b) 1:1, (c) 1:2, (d) 1:4 and (e) 1:8.

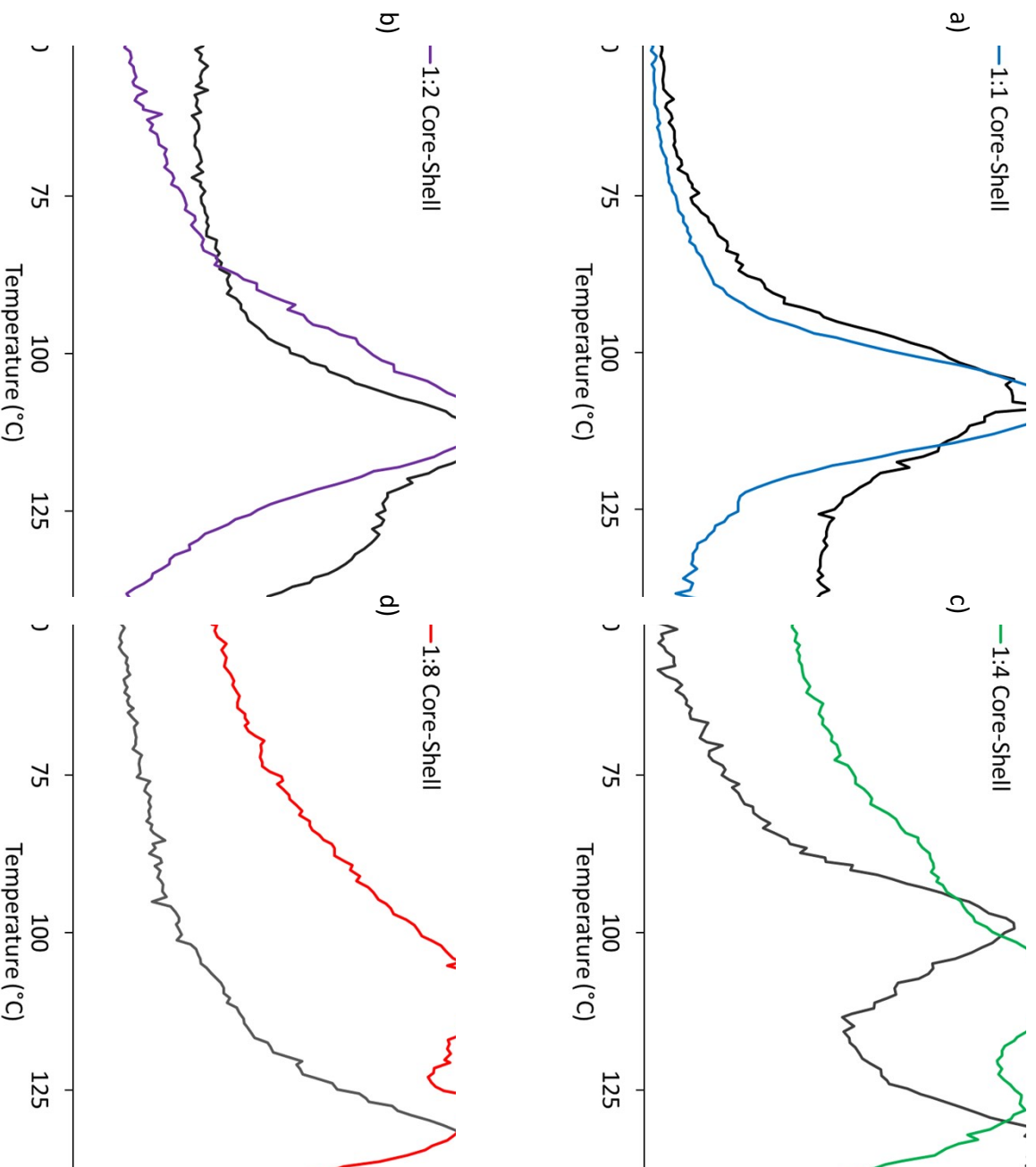


Figure S6: Normalise $\tan \delta$ plots for core-shell PS-PMMA particles (coloured lines) and physical blends (black lines) with PS:PMMA mass ratios of (a) 1:1, (b) 1:2, (c) 1:4, and (d) 1:8.

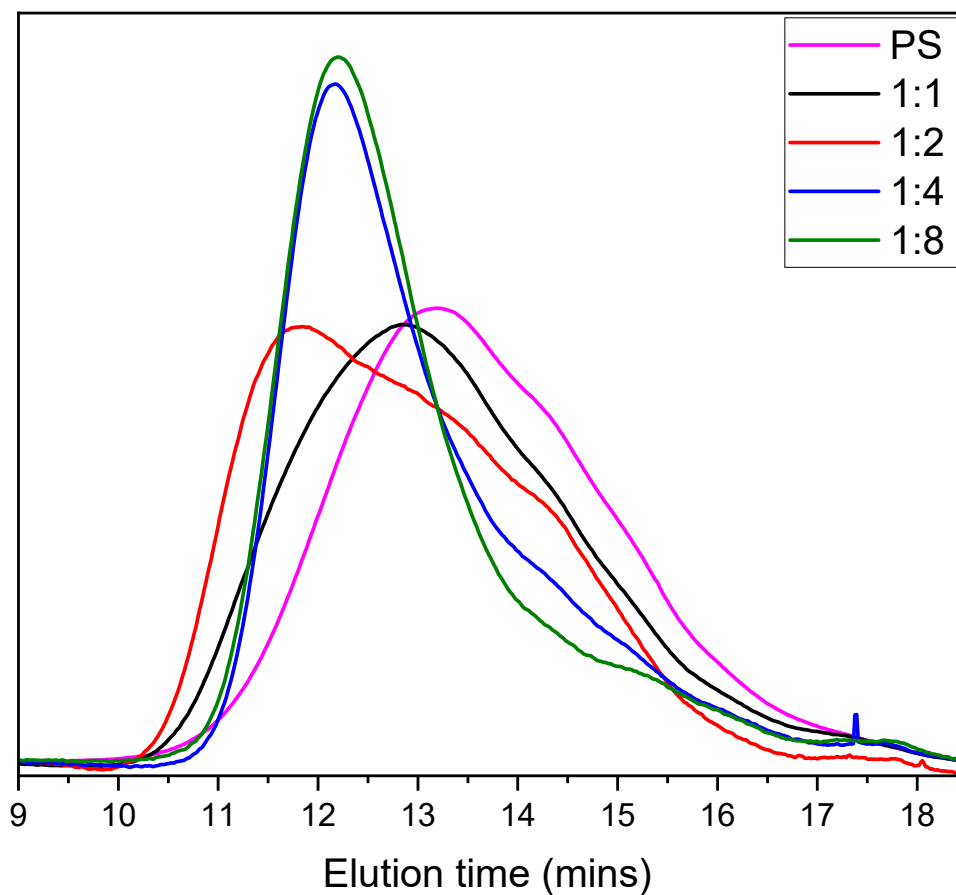


Figure S7: Peak area normalised GPC traces for polystyrene (PS) core starting material (magenta) and core-shell systems with mass ratios of 1:1 (black), 1:2 (red), 1:4 (blue), and 1:8 (green).

1. H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512-7515.
2. J. Filik, A. W. Ashton, P. C. Y. Chang, P. A. Chater, S. J. Day, M. Drakopoulos, M. W. Gerring, M. L. Hart, O. V. Magdysyuk, S. Michalik, A. Smith, C. C. Tang, N. J. Terrill, M. T. Wharmby and H. Wilhelm, *J. Appl. Crystallogr.*, 2017, **50**, 959-966.
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