

Supporting Information

Highly Coloured and Electrophoretically Active Polymer Microparticles via Staggered Dispersion Polymerisation in Supercritical Carbon Dioxide and Dodecane

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Experimental Section

Materials

Methyl methacrylate (MMA, 99 %) was obtained from Acros Organics. 2,2'-Azobis(butyronitrile) (AIBN), methacrylic acid (MAA), ethylene glycol dimethacrylate and SPAN-85 were purchased from Sigma-Aldrich. Dimethylaminoethyl methacrylate (DMAEMA) was purchased from Merck Chemicals Ltd. Methacrylate terminated poly(dimethyl siloxane) (PDMS-MA) ($M_n \sim 10$ KDa) was purchased from ABCR GmbH & Co. Dodecane (99+ %) was purchased from Alfa Aesar. The dyes MM12, MC10, MY13 and MK6 were donated, courtesy of Merck Chemicals Ltd. SFC grade 4.0 CO₂ (≥ 99.99 %) was purchased from BOC Special Gases.

Particle Synthesis

One-stage dispersion polymerisation in scCO₂

For the initial studies a simple, one-step polymerisation was adopted, using 1 wt. % AIBN with respect to monomer for all reactions. In a typical reaction MMA (10 mL, 93.5 mmol) and an

AIBN/PDMS-MA (0.094 g, 0.57 mmol AIBN and 0.468 g, 0.05 mmol PDMS-MA for 5 wt. %) mixture were flushed with argon separately to remove oxygen for 30 minutes. These were then mixed and added directly to the autoclave *via* syringe against a positive pressure of CO₂ to prevent the ingress of air. The autoclave was then sealed and pressurised to 5.5 MPa before heating to 65 °C. The start of the reaction was taken as the moment at which this temperature was reached. The pressure was then increased to 20.7 MPa and the vessel heated for 4 hours before being allowed to cool naturally to <25 °C, vented and emptied. In this and all high pressure reactions the yield was obtained gravimetrically, typically >75 %.

Two-stage dispersion polymerisation in scCO₂

In this process, the reaction is conducted as above in the *one-stage dispersion polymerisation in scCO₂*, with the exception that the initial charge of MMA is reduced (5 mL, 46.7 mmol). After 1 hour a further charge of MMA (2.5 mL, 23.4 mmol) was injected into the autoclave *via* HPLC pump at a rate of 0.2 mL min⁻¹. Where specified, this further charge of monomer may also include a comonomer. This would cause a pressure increase of c.a. 0.7 MPa. The vessel was heated for a further 4 hours from the start of this injection before being allowed to cool naturally to <25 °C before venting to ambient pressure and removing the product.

Three-stage dispersion polymerisation in scCO₂

The three-stage process is an extension of the two-stage version and follows the same procedure initially. However, in this case only MMA (2.5 mL, 23.4 mmol) was injected after one hour. At 5 hours from the start of the reaction a second injection of monomer, typically DMAEMA (up to 5 mL, 29.7 mmol), was made *via* HPLC pump at 0.2 mL min⁻¹. The reaction was maintained at 65 °C for 16 hours following the start of the second injection, before cooling naturally and venting to ambient pressure to remove product from the autoclave. The pressure typically raised from the initial 20.7 MPa to a final value of c.a. 24.1 MPa over the course of the reaction.

One-stage dispersion polymerisation in dodecane

The basic protocol for the dispersion polymerisation in dodecane followed the procedure given by Richez *et al.*^[9] Reactions were carried out in a two-neck, 250 mL round bottomed flask, in which argon was bubbled through dodecane (91 mL) to remove oxygen before heating the flask to 80 °C. Meanwhile, MMA (10 mL, 93.5 mmol) and an AIBN/PDMS-MA (0.094 g, 0.57 mmol AIBN and 1.404 g, 0.14 mmol PDMS-MA) mixture were flushed with argon separately to remove oxygen for 30 minutes. These were then mixed and immediately added

to the dodecane *via* a syringe. This marked the beginning of the reaction. After four hours the reaction was allowed to cool to ambient temperature before the product was collected.

Two-stage dispersion polymerisation in dodecane

This procedure followed that outlined above in the *one-stage dispersion polymerisation in dodecane*, except that here only 5 mL (46.7 mmol) of MMA was added to the initial reaction mixture. After 1 hour, a further 2.5 mL MMA (2.5 mL, 23.4 mmol) was injected at 0.2 mL min⁻¹ using a syringe pump. To prevent the build-up of pressure, argon was again flowed through the reaction flask during this stage. The reaction was allowed to proceed for another 4 hours before being removed from the oil-bath and cooling to room temperature.

Three-stage dispersion polymerisation in dodecane

The three-stage dispersion polymerisation in dodecane follows the procedure outlined in the two-stage dispersion method and is identical for the first 5 hours. However, rather than terminating the reaction at this point, an aliquot of DMAEMA (up to 5 mL, 29.7 mmol) was injected at 0.2 mL min⁻¹ by syringe pump. This was then left for 16 hours before being allowed to cool to room temperature and the product collected.

Characterisation

Scanning electron microscopy (SEM) was carried out on a Philips XL30 microscope. All samples were washed three times by centrifugation in dodecane to remove residual stabiliser before being dropped onto a glass slide, dried and coated with platinum.

Particle sizes are presented as the number average diameter (d_n) of 100 particles as described by Richez *et al.* (**Equation S1**).^[9]

$$d_n = \frac{\sum d_i n_i}{\sum n_i} \quad (\text{S1})$$

where d_i is the particle diameter and n_i is the number of particles. The volume average diameter (d_v) is also calculated and the particle size distribution (PSD) is taken as the ratio of these (**Equation S2** and **S3** respectively).

$$d_v = \frac{\sum d_i^4 n_i}{\sum d_i^3 n_i} \quad (\text{S2})$$

$$PSD = \frac{d_v}{d_n} \quad (\text{S3})$$

Transmission electron microscopy (TEM) was performed with an FEI Technai BioTwin-12. Samples were first washed with hexane to remove residual stabiliser and then set in Agar 100 resin. The resin blocks were then sectioned using an RMC Powertome ultramicrotome set to 100 nm. Samples incorporating DMAEMA were stained with iodine, whilst samples containing conjugated dyes were stained with RuO_4 . In the case of iodine, this was achieved by placing the samples in a sealed container with 2-3 iodine crystals. RuO_4 was made *in-situ* by dissolving KIO_4 (12 mg) in DI water (3 mL) and cooling the solution. This was then added to RuCl_3 (36 mg) and immediately placed in a sealed container with the samples. Samples generally required 2-4 hours to show sufficient contrast.

Proton nuclear magnetic resonance (^1H NMR) was undertaken using a Bruker DPX 300 MHz NMR spectrometer using CDCl_3 . An example spectrum can be seen below (**SI Figure S 3**).

Dynamic mechanical analysis (DMA) was performed on a Triton Technologies DMA (now Mettler Toledo DMA1). Samples were measured at 1 and 10 Hz using the powder pocket accessory, which allows analysis of powder samples in single cantilever geometry. Measurements were carried out between 25 – 250 °C or -50 – 250 °C depending on the region of interest.

The electrophoretic behaviour of the particles in dodecane was qualitatively assessed by observing in-plane movement. The test cell for this consists of two glass slides which flank two sets of interdigitated electrodes (SI Figure S 1). The depth of the cell is 13 μm and the gap between the electrodes is 500 μm . The samples were dispersed in a mixture of dodecane and 3 wt. % SPAN-85. When placed in the cell, movement of the particles due to the electric field generated by the electrodes can be observed under a microscope.

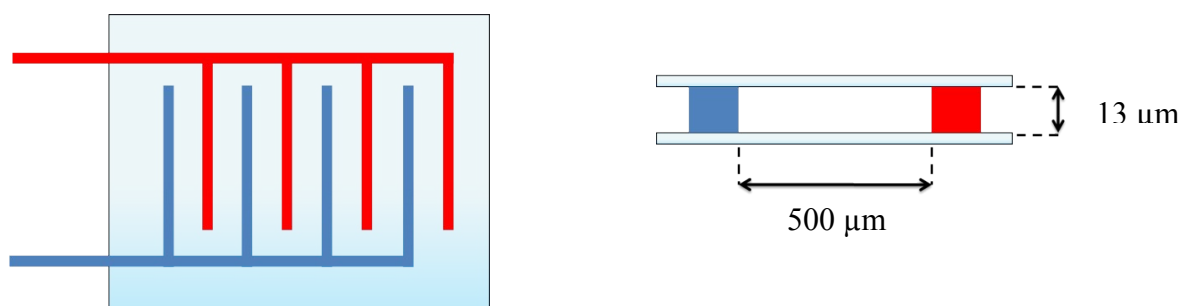


Figure S 1: Plan view (left) and cross-section (right) of in-plane electrophoresis cell with electrodes shown in red and blue.

Assessment of the particles for use in electrophoretic displays was performed in out-of-plane test cells. A cell consists of two transparent indium tin oxide (ITO) electrodes which are held apart at a distance of 50 μm (SI Figure S 2). A dispersion of each sample was made containing 8 wt. % colour particles, 22 wt. % TiO_2 (white particles), 3 wt. % SPAN-85 and 1 wt. % AOT.

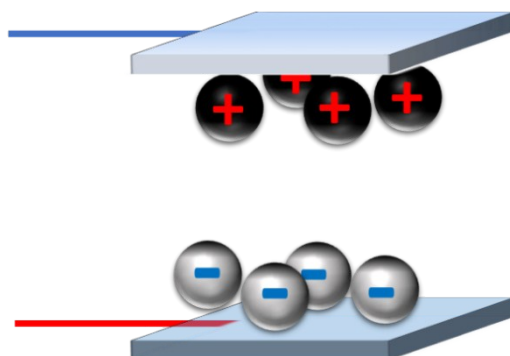


Figure S 2: Schematic of an out-of-plane test cell. The cell will appear the colour of the particles which are attracted to the top electrode when viewed from above.

This mixture was placed between the two electrodes which were held at a potential difference of 20 V, which could be reversed in order to switch between coloured and white states.

The colour of the dyed particles was analysed using an X-Rite Color i5 spectrophotometer. A dispersion of each sample was made containing 8 wt. % colour particles, 22 wt. % TiO₂ (white particles), 3 wt. % SPAN-85 and 1 wt. % AOT. The colour of the white and coloured states after switching was assessed directly by reflectance spectrometry using the out-of-plane test cells described above. The colour of the polymer particles without mixing with TiO₂ was measured separately using the in-plane test cell. The L*a*b* colour space data obtained are included below in the additional data section.

The colour change between the colour and white states is quantified using the conventional ΔE as determined by Pythagoras' theorem (**Equation S4**):

$$\Delta E = \sqrt{(L_c^* - L_w^*)^2 + (a_c^* - a_w^*)^2 + (b_c^* - b_w^*)^2} \quad (\text{S4})$$

Where subscript *c* and *w* indicate colour and white states respectively.

Additional Data

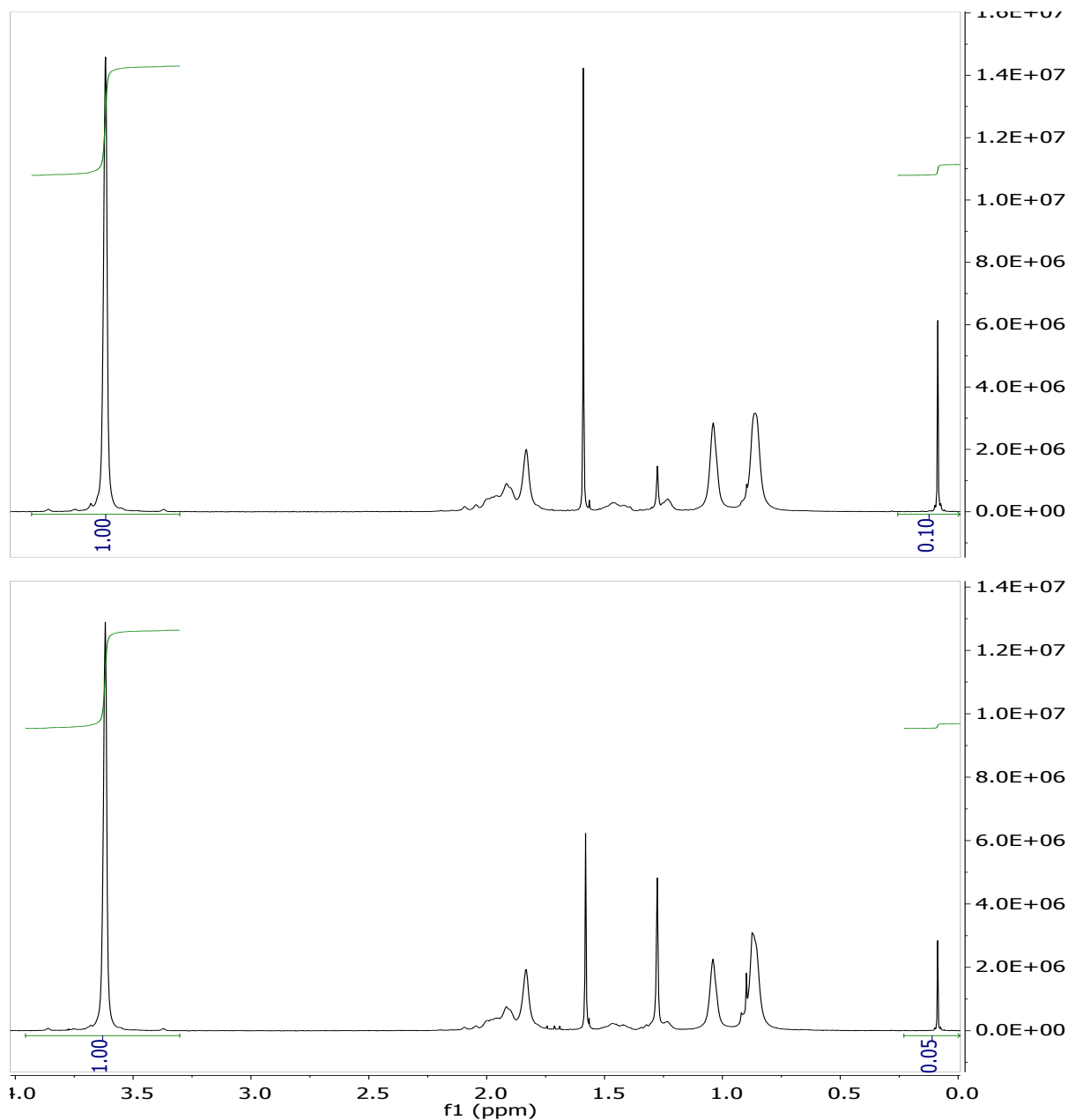


Figure S 3: ^1H NMR spectra of PMMA in CDCl_3 synthesised by one-stage dispersion polymerisation in scCO_2 (top) and dodecane (bottom) after washing with hexane. Comparison of the PDMS peak (δ 0.09) to the pendent methyl group of the PMMA (δ 3.62) shows that the particles synthesised in dodecane contain twice the amount of grafted stabiliser. However, as the stabiliser is seen to accumulate only at the surface of those particles synthesised in scCO_2 , it is likely that these particles have a much larger surface concentration of PDMS.

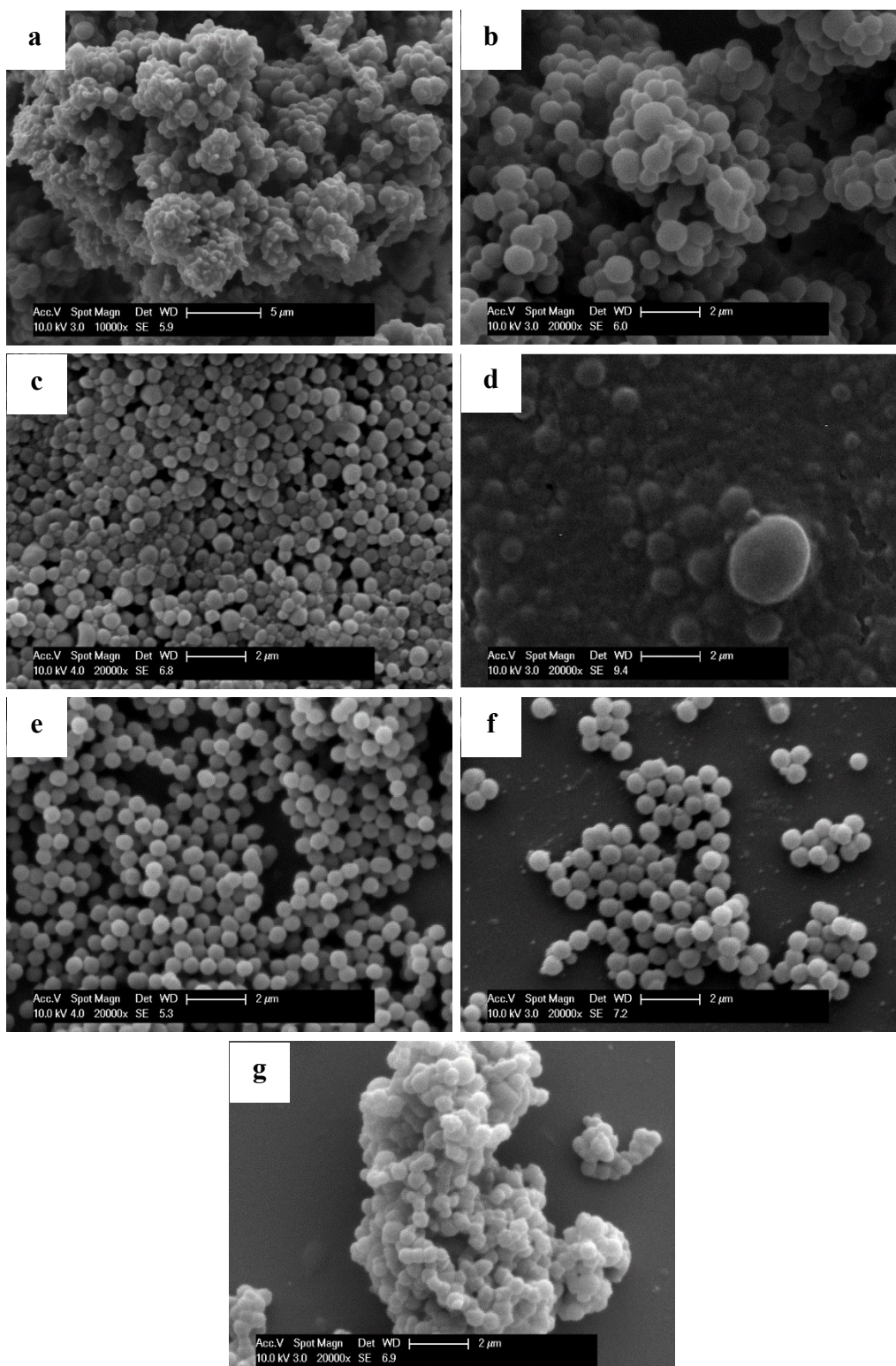


Figure S 4: SEM images of PMMA particles synthesised using the three-stage method in $scCO_2$ containing a) 20, b) 37 and c) 44 wt. % DMAEMA. d) The product of the corresponding one-stage polymerisation in $scCO_2$ containing 35 wt. % DMAEMA is given for comparison. Also shown are the particles synthesised by three-stage method in dodecane containing e) 5, f) 10 and g) 16 wt. % DMAEMA. These correspond to **Table 2, Entry 1, 2, 4, 5, 6, 8 and 9**, respectively. Note that the three-stage method is essential to achieve good particle morphology with high DMAEMA incorporation in $scCO_2$. It is also seen that syntheses in $scCO_2$ produced higher DMAEMA incorporation than the analogous reactions in dodecane.

Table S1: L^ a^* b^* colour space data for the coloured and white states of the out-of-plane electrophoretic test cells. The solvent in which the particles were synthesised are denoted in brackets.*

Sample	Coloured State			White State			ΔE
	L^*	a^*	b^*	L^*	a^*	b^*	
Magenta (scCO ₂)	44.9	34.5	-3.2	72.6	0.2	1.3	44.3
Magenta (dodecane)	33.6	53.4	2.7	65.0	9.7	-1.8	54.0
Cyan (dodecane)	46.2	-14.8	-25.0	69.7	-3.1	0.3	36.5
Yellow (dodecane)	73.0	-13.0	51.9	74.3	-2.4	3.3	49.8
Black (dodecane)	47.7	-1.6	-7.0	74.4	-2.8	0.3	27.7